ATTORNEY GENERAL, et al v GELMAN SCIENCES, INC.

(Washtenaw County Circuit Court No. 88-34734-CE)

ATTACHMENT B

United States Environmental Protection Agency

Office of Water

www.epa.gov 1990

Method 1624, Revision C: Volatile Organic Compounds by Isotope Dilution GCMS

Method 1624

Revision C

Volatile Organic Compounds by Isotope Dilution GCMS

Method 1624

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 in 1986); the Comprehensive Environmental Response, Compensation, and Liability Act (as amended in 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 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 1%, 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 to 25°C in a chamber designed for soil or water samples. If the solids content is greater than one, mL of reagent water and the labeled compounds are added to a 5-aliquot of sample and the mixture is purged at 40°C. Compounds that will not purge at 20 to 25°C or at 40°C are purged at 75 to 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 iscalibrated 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.

Table 1. Volatile Organic 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
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

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 [1]	107-18-6
533	Carbon disulfide	75-15-0
534	2-Chloro-1,3-butadiene (Chloroprene)	126-99-8
535	Chloroacetonitrile[1]	107-14-2
536	3-Chloropropene	107-05-1
537	Crotonaldehyde[1]	123-73-9
538	1,2-Dibromoethane (EDB)	106-93-3
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 [1]	107-12-0
544	Ethyl methacrylate	97-63-2
545	2-Hexanone	591-78-6
546	Iodomethane	74-88-4
547	Isobutyl alcohol[1]	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*- and *p*-Xylene	

[1] Determined at a purge temperature of 75–85°C.

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-hour 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 to 125°C. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

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

Table 3. Gas Chromatography of Purgeable Organic Compounds

EGD No.[1]	Compound	Retention Time Mean (sec)	EGD Ref	Relative [2]	Minimum Level [3] (µg/L)	Method Detection Limit [4] Low Solids (µg/kg)	High Solids (µg/kg)
245	Chloromethane-d_3	147	181	0.141–0.270	50		
345	Chloromethane	148	245	0.922–1.210	50	207 [7]	13
246	Bromomenthane-d_3	243	181	0.233–0.423	50		
346	Bromomethane	246	246	0.898–1.195	50	148 [7]	11
288	Vinyl chloride-d_3	301	181	0.286–0.501	50		
388	Vinyl chloride	304	288	0.946–1.023	10	190 [7]	11
216	Chloroethane-d_5	378	181	0.373–0.620	50		
316	Chloroethane	386	216	0.999–1.060	50	789 [7]	24
244	Methylene chloride-d_2	512	181	0.582–0.813	10		
344	Methylene chloride	517	244	0.999–1.017	10	566 [7]	280 [7]
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 [7]	50	3561	322 [7]
202	Acrolein-d_4	564	181	0.641–0.903	-- [5]	50	
302	Acrolein	566	202	0.984–1.018[5]	50	377 [7]	18
203	Acrylonitrile-d_3	606	181	0.735–0.926	50		
303	Acrylonitrile	612	203	0.985–1.030	50	360 [7]	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 [7]	80 [7]
223	Chloroform-$^{13}C_1$	861	181	1.092–1.322	10		
323	Chloroform	861	223	0.961–1.009	10	21	2

EGD No.[1]	Compound	Retention Time Mean (sec)	EGD Ref	Relative [2]	Minimum Level [3] (µg/L)	Method Detection Limit [4] Low Solids (µg/kg)	High Solids (µg/kg)
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 [7]
206	Carbon tetrachloride-$^{13}C_2$	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	Benezene-d_6	1200	182	0.888–0.952	10		
304	Benezene	1212	204	1.002–1.026	10	23	8
251	Chlorodibromomethane-$^{13}C_1$	1222	182	0.915–0.949	10		
351	Chlorodibromomethane	1222	231	0.989–1.030	10	15	2
214	1,1,2-Trichloroethane-$^{13}C_2$	1224	182	0.922–0.953	10		
314	1,1,2-Trichloroethane	1224	214	0.975–1.027	10	26	1
233	trans-1,3-Dichloropropene-d_4	1226	182	0.922–0.959	10		
333	trans-1,3-Dichloropropene	1226	233	0.993–1.016	10	--[6,7]	--[6,7]
019	2-Chloroethyvinyl 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		

EGD No.[1]	Compound	Retention Time Mean (sec)	EGD Ref	Relative [2]	Minimum Level [3] (µg/L)	Method Detection Limit [4] Low Solids (µg/kg)	High Solids (µg/kg)
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 [7]
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*- and *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.

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

Column: 2.4 m (8 ft) × 2 mm I.D. glass, packed with 1% SP-1000 coated on 60/80 Carbopak B.
Carrier gas: Helium at 40 mL/min.
Temperature program: 3 min at 45°C, 8°C/min to 240°C, hold at 240°C for 15 minutes.

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 through 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 a minimum of 1 hour before use.

5.1.2 Septum: Teflon-faced silicone (Pierce 12722, or equivalent), cleaned as above and baked at 100 to 200°C for 1 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.

5.2.1.2 Purging device for solid samples: Designed to accept 5 g 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 to 25°C) and of being controlled at temperatures of 40°C (±2°C) and 80°C (±5°C) while the sample is being purged. The purging device shown in Figure 2 meets these criteria.

5.2.2 Trap: 25 to 30 cm long × 2.5 mm I.D. minimum, containing the following:

5.2.2.1 Methyl silicone packing: 1cm (±0.2cm), 3% OV-1 on 60/80 mesh Chromosorb W, or equivalent.

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

5.2.2.3 Silica gel: 8cm (±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°C (±5°C) in 45 seconds or less. The polymer section of the trap shall not exceed a temperature of 180°C and the remaining sections shall not exceed 220°C during desorb, and no portion of the trap shall exceed 225°C during bakeout. The desorber shown in Figure 3 meets these specifications.

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

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 1% 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 to 3 seconds, and produce a unit resolution (valleys between m/z 174 to 176 less than 10% 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% of m/z 95
75	30 to 60% of m/z 95
95	base peak, 100%
96	5 to 9% of m/z 95
173	less than 2% of m/z 174
174	greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	95 to 101% of m/z 174
177	5 to 9% 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 ongoing 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 µL.

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°C (±5°C).

5.12.2 Dessicator.

5.12.3 Beakers: 50 to 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 between 90 and 100°C and bubble contaminant free inert gas through it for approximately 1 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% or greater, the weight may be used without correction to calculate the concentration of the standard.

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

6.5.1 Place approximately 9.8 mL of methanol in a 10-mL ground-glass-stoppered volumetric flask. Allow the flask to stand unstoppered for approximately 10 minutes or until all methanol wetted surfaces have dried. In each case, weigh the flask, immediately add the compound, then immediately reweigh to prevent evaporation losses from affecting the measurement.

6.5.1.1 Liquids: Using a 100 µL syringe, permit 2 drops of liquid to fall into the methanol without contacting the neck of the flask. Alternatively, inject a known volume of the compound into the methanol in the flask using a micro-syringe.

6.5.1.2 Gases (chloromethane, bromomethane, chloroethane, vinyl chloride): Fill a valved 5-mL gas-tight syringe with the compound. Lower the needle to approximately 5 mm above the methanol meniscus. Slowly introduce the compound above the surface of the meniscus. The gas will dissolve rapidly in the methanol.

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

6.5.3 Transfer the stock solution to a Teflon−sealed screw-cap bottle. Store, with minimal headspace, in the dark at −10 to −20°C.

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

6.6 Labeled compound spiking solution: From stock standard solutions prepared as above, or from mixtures, prepare the spiking solution to contain a concentration such that a 5- to 10- µL 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 µg/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-µL syringe, add 20 µL 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 µg/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 µg/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 µg/L of the labeled and pollutant gases and water soluble compounds, 10 µg/L BFB, and 20 µg/L of all other pollutants, labeled compounds, and internal standards. It may be the nominal 20 µg/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 µg/mL or 500 µg/mL of the gases and water soluble compounds, and 100 µg/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 five most intense mass spectral peaks and all other mass spectral peaks greater than 10% of the base peak. The spectrum may be further edited to remove common interfering masses. If five 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 to 180°C by backflushing with an inert gas at a flow rate of 20 to 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 1 µL of the methanolic standard (Section 6.7.3) to determine compound recovery. The recovery shall be greater than 20% for the water soluble compounds (Section 6.6), and 60 to 110% for all other compounds. This recovery is demonstrated initially for each purge-and-trap GCMS system. The test is repeated only if the

purge-and-trap or GCMS systems are modified in any way that might result in a change in recovery.

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

Table 5. Volatile Organic Compound Characteristic M/Z'S

Compound	labeled Analog	Primary m/z[1]	Reference Compound[2]	Response 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			
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		55			
trans-1,4-Dichloro-2-butene		75	183	0.093	0.014
1,1-Dichloroethane	d_3	63/66			

Compound	labeled Analog	Primary m/z[1]	Reference Compound[2]	Response purge temp. Of: 20 °C	80 °C
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	-
0- and *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 standard's 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.

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 (µg/L) is plotted or computed using a linear regression. An example of a calibration curve for toluene using toluene-d_8 is given in Figure 6. Also shown are the ±10% 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.*)

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:

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

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,
area of mz/Z = 0,
then R = 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:

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

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

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

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% coefficient of variation) over the five 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 five 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:

$$R = \frac{(A_s \times C_{is}),}{(a_{is} \times C_s)}$$

Where:

A = *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* (µg/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 µg/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% coefficient of variation) over the five-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 five-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 ongoing performance (Section 11.5) criteria cannot be met.

7.7 Elevated purge temperature calibration: Samples containing greater than 1% solids are analyzed at a temperature of 40°C (±2°C) (Section 10). For these samples, the analytical system may be calibrated using a purge temperature of 40°C(±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 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 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.

Table 6. Acceptance Criteria for Performance Tests

EGD		Acceptance criteria at 20 µg/L or as noted			
		Labeled and native compound initial precision and accuracy (Sect. 8.2.3)		Labeled compound recovery (Sect. 8.3 and 14.2)	Labeled and native compound ongoing accuracy (Sect. 11.5)
No.[1]	Compound	s (µg/L)	X (µg/L)	P (%)	R (µg/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	bromodichloro-methane	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	dibromochloro-methane	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-dichloro-ethene	7.4	11 - 32	15 - 195	8 - 34
032	1,2-dichloropropane	19.0	d - 47	ns - 343	d - 51
033	trans-1,3-dichloro-propene	15.0	d - 40	ns - 284	d - 44
515	diethyl ether*	44.0	75 - 146	44 - 156	55 - 145

EGD No.[1]	Compound	Acceptance criteria at 20 µg/L or as noted: Labeled and native compound initial precision and accuracy (Sect. 8.2.3) s (µg/L)	X (µg/L)	Labeled compound recovery (Sect. 8.3 and 14.2) P (%)	Labeled and native compound ongoing accuracy (Sect. 11.5) R (µg/L)
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	tetrachloroethane	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 µg/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.

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 µg/L and the standard deviation of the recovery (s) in µg/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 (sp) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from P - 2sp to P + 2sp. For example, if P = 90% and sp = 10%, the accuracy interval is expressed as 70 to 110%. Update the accuracy assessment for each compound on a regular basis (e.g., after each 5 to 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 µg/L of a pollutant of interest (Tables 1 and 2) into a succeeding blank shall be determined by analyzing successively larger concentrations of these compounds. When a sample contains this concentration or more, a blank shall be analyzed immediately following this sample to demonstrate no carry-over at the 5 µg/L level.

8.5.2 With each sample lot (samples analyzed on the same 8-hour 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 µg/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 ongoing (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 to 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 1% 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 to 10 g of sample into a tared beaker.

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

10.1.3 Determine percent solids as follows:

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

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

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

10.4 Samples containing less than 1% 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 mL (±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 1% 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 g (±1 g) of sample into a purging vessel (Figure 2). Record the weight to three significant figures.

10.5.3 Add 5 mL (±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 1% 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 5g (±1 g) of sample into a calibrated 15- to 25-mL centrifuge tube. Record the weight of the sample to three significant figures.

10.6.3 Add 10 mL of methanol to the centrifuge tube. Cap the tube and shake it vigorously for 15 to 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% of the volume of the supernatant methanol using a 15- to 25- µL syringe. This volume will be in the range of 10 to 15 µL.

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 (Section 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 Section 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 minutes (±0.1 minute) at 20 to 25°C for samples containing less than 1% solids. Purge samples containing one percent solids or greater at 40°(±2°). If the compounds in Table 2 that do not purge at 20 to 40°C are to be determined, a purge temperature of 80°C (±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 between 170 and 180°C while backflushing with carrier gas at 20 to 60 mL/min for 4 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 between 170 and 180°C. After approximately 7 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 aminimum of 1 hour in an oven at a temperature greater than 150°C.

11. SYSTEM PERFORMANCE

11.1 At the beginning of each 8 hour 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 to 782 seconds; 2-bromo-1-chloropropane: 1270 to 1369 seconds; 1,4-dichlorobutane: 1510 to 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% of the taller of the two peaks.

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

11.5.1 For each pollutant and labeled compound, compare the concentration with the corresponding limit for ongoing accuracy in Table 6. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue. If any individual value falls outside the range given, system performance is unacceptable for that compound.

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

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

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

11.5.2 Add results which pass the specification in Section 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). 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 (sr). Express the accuracy as a recovery interval from R − 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85 to 105%.

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 2 (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 2 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 µg/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.

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

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:

$$Concentration\ in\ solid\ (\mu g/kg) = \frac{0.005\ L \times aqueous\ conc\ (\mu g/L)}{0.01 \times percent\ solids(g)}$$

where
"percent 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 g 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 through 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 1% solids, the units are µg/L; and for undiluted samples containing 1% solids or greater, units are µg/kg.

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 µg/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 1% solids, or 0.5 g of samples containing 1% 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 µg/L aqueous performance standards (Sections 6.7.2 and 11.1) is shown in Figure 9.

Reference

1. "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," USEPA, EMSL Cincinnati, OH 45268, EPA-600/4-80-025 (April 1980).
2. Bellar, T. A. and Lichtenberg, J. J., "Journal American Water Works Association," 66, 739 (1974).
3. Bellar, T. A. and Lichtenberg, J. J., "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," in *Measurement of Organic Pollutants in Water and Wastewater*, C. E. VanHall, ed., American Society for Testing Materials, Philadelphia, PA, Special Technical Publication 686, (1978).
4. National Standard Reference Data System, "Mass Spectral Tape Format," U.S. National Bureau of Standards (1979 and later attachments).
5. "Working with Carcinogens," DHEW, PHS, NIOSH, Publication 77-206 (1977).
6. "OSHA Safety and Health Standards, General Industry," 29 *CFR* 1910, OSHA 2206, (1976).
7. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety (1979).
8. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL Cincinnati, OH 45268, EPA-4-79-019 (March 1979).
9. "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL Cincinnati, OH 45268, EPA-4-79-020 (March 1979).
10. "Method 624--Purgeables", 40 *CFR* Part 136 (49 *FR* 43234), 26 October 1984.
11. "Narrative for SAS 106: Development of an Isotope Dilution GC/MS Method for Hot Purge and-Trap Volatiles Analysis," S-CUBED Division of Maxwell Laboratories, Inc., Prepared for W. A. Telliard, Industrial Technology Division (WH-552), USEPA, 401 M St. SW, Washington DC 20460 (July 1986).
12. Colby, Bruce N. and Ryan, Philip W., "Initial Evaluation of Methods 1634 and 1635 for the Analysis of Municipal Wastewater Treatment Sludges by Isotope Dilution GCMS," Pacific Analytical Inc., Prepared for W. A. Telliard, Industrial Technology Division (WH-552), USEPA, 401 M St. SW, Washington DC 20460 (July 1986).

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 isoboutyl 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 0- + 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		

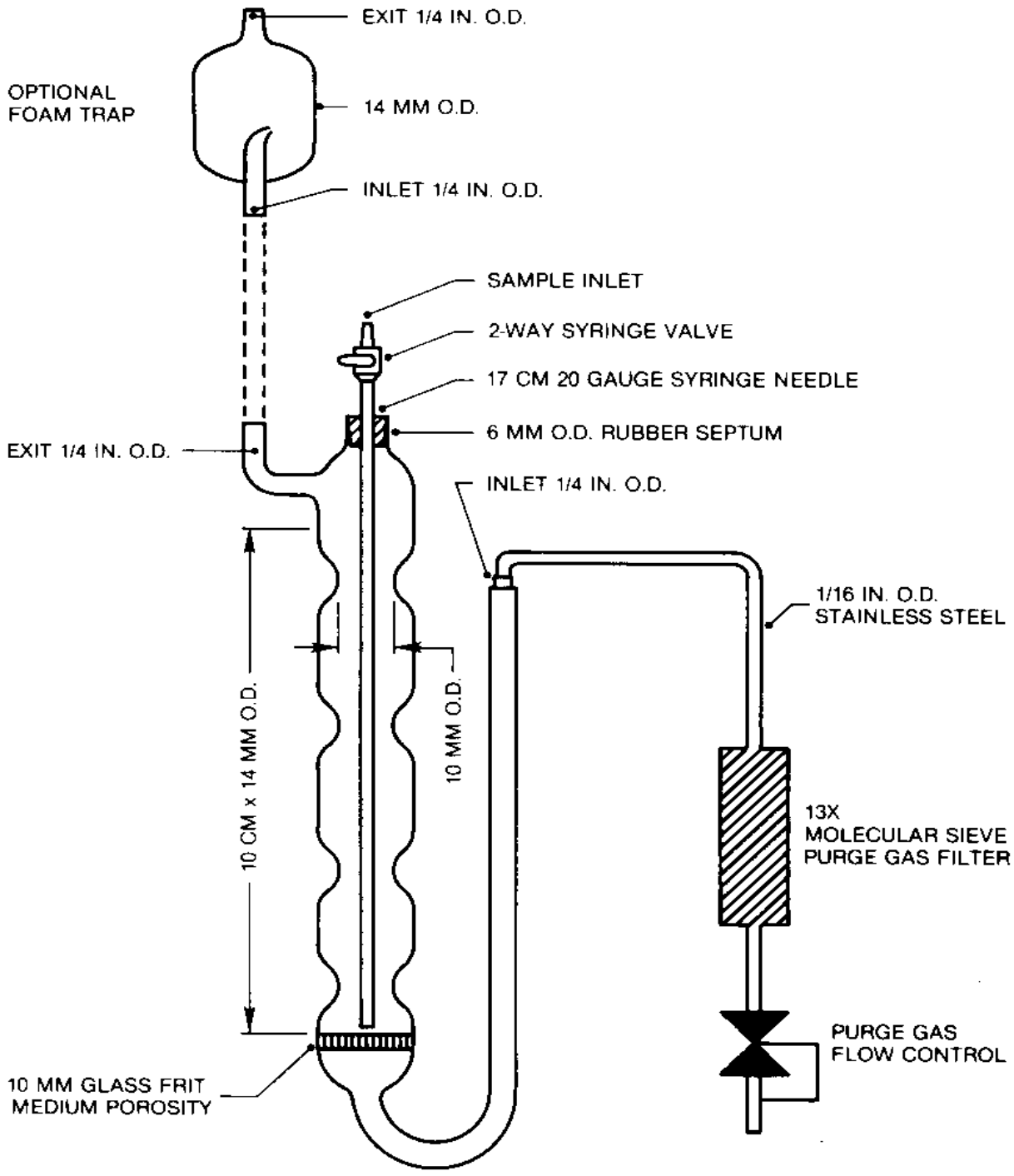


FIGURE 1 Purging Device for Waters

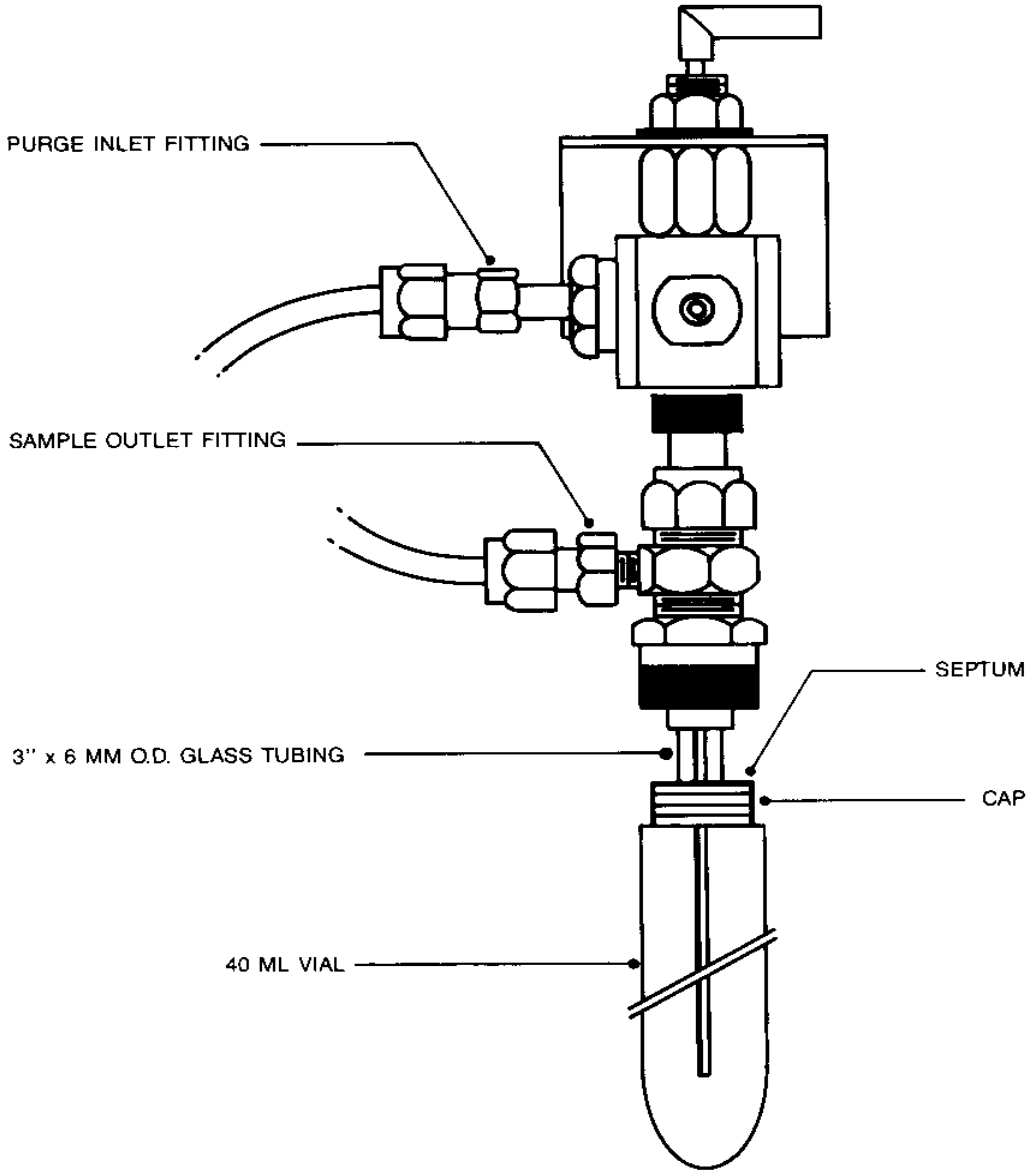


FIGURE 2 Purging Device for Soils or Waters

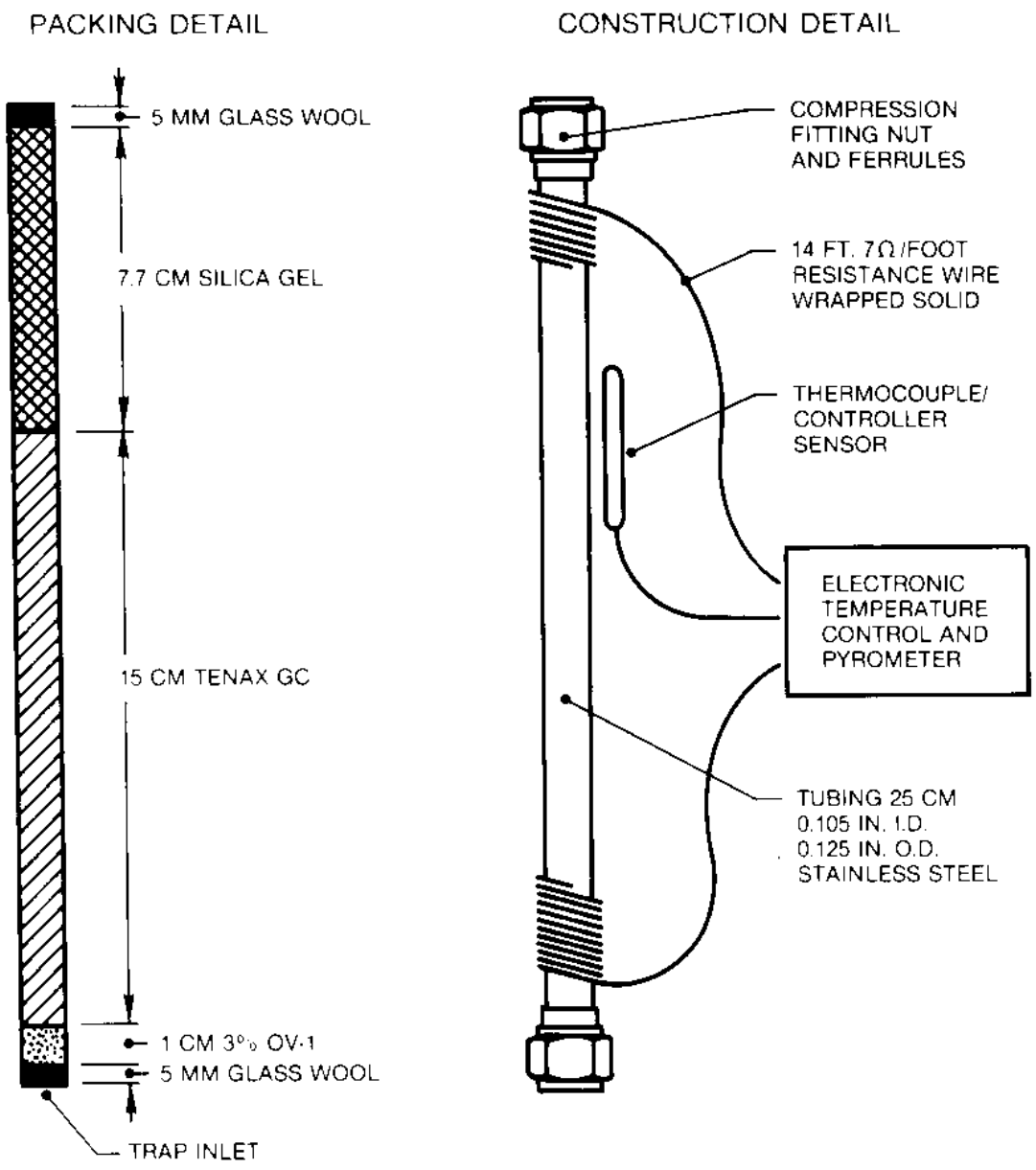


FIGURE 3 Trap Construction and Packings

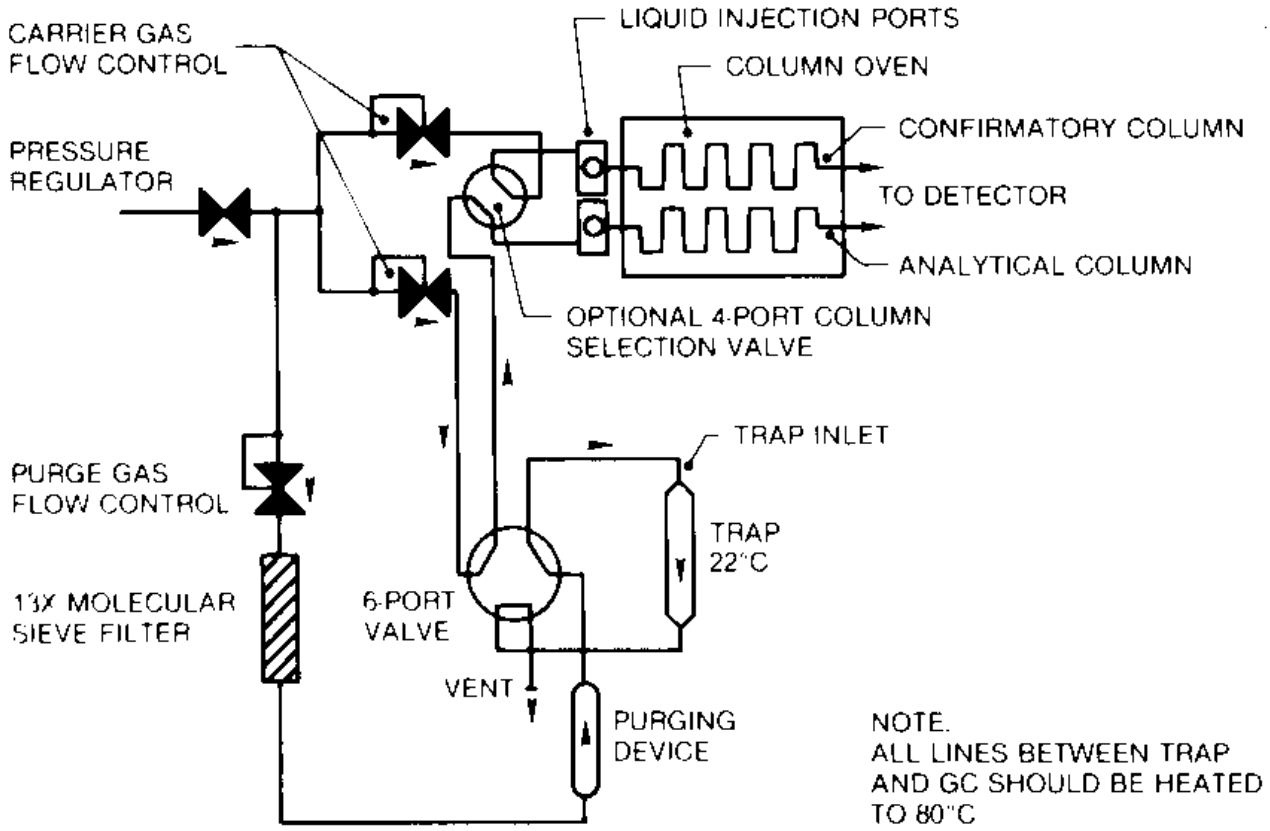


FIGURE 4 Schematic of Purge and Trap Device--Purge Mode

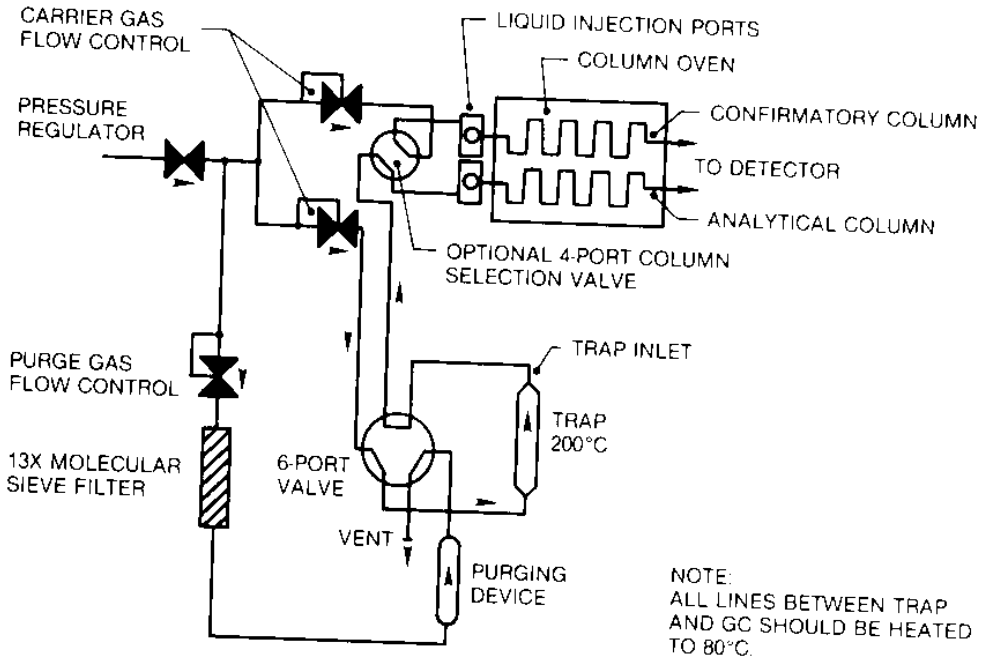


FIGURE 5 Schematic of Purge and Trap Device--Desorb Mode

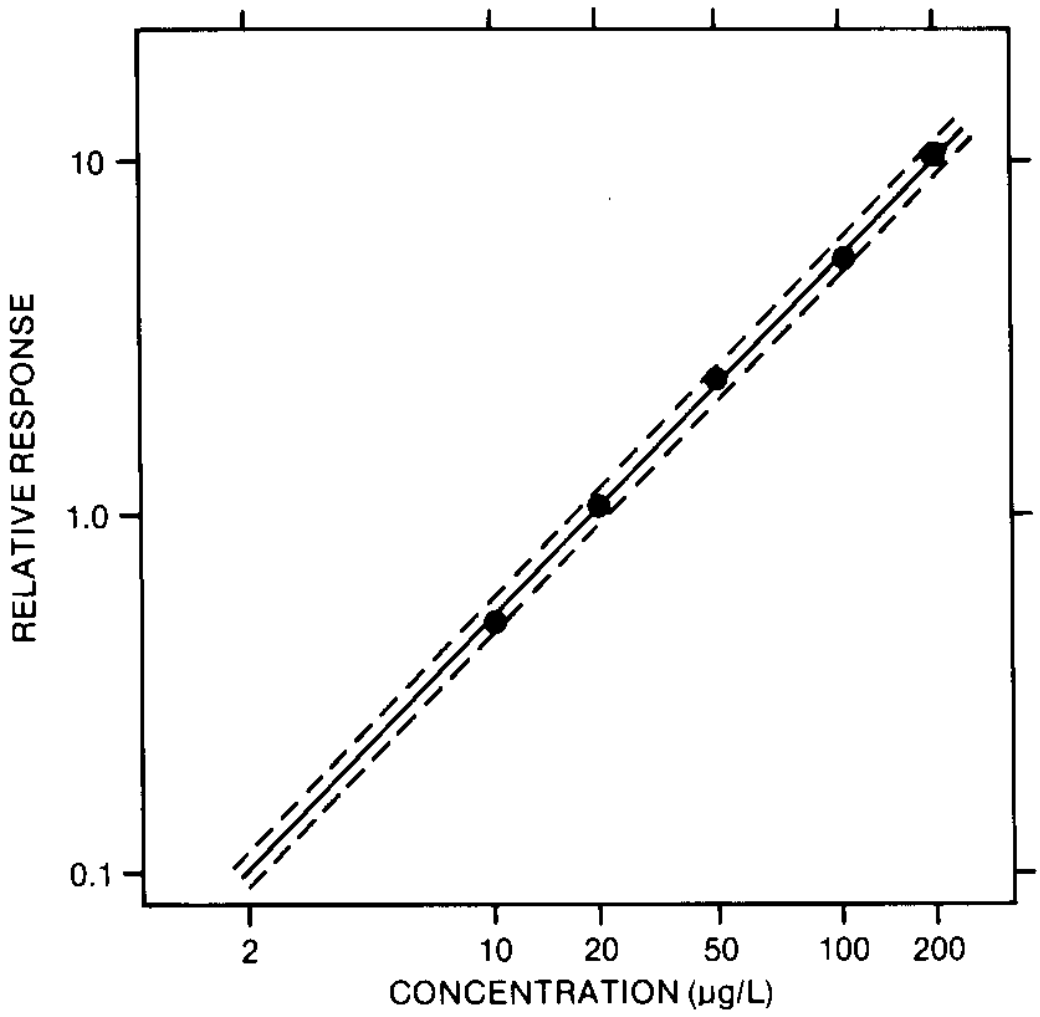


FIGURE 6 Relative Response Calibration Curve for Toluene. The Dotted Lines Enclose a +/- 10 Percent Error Window

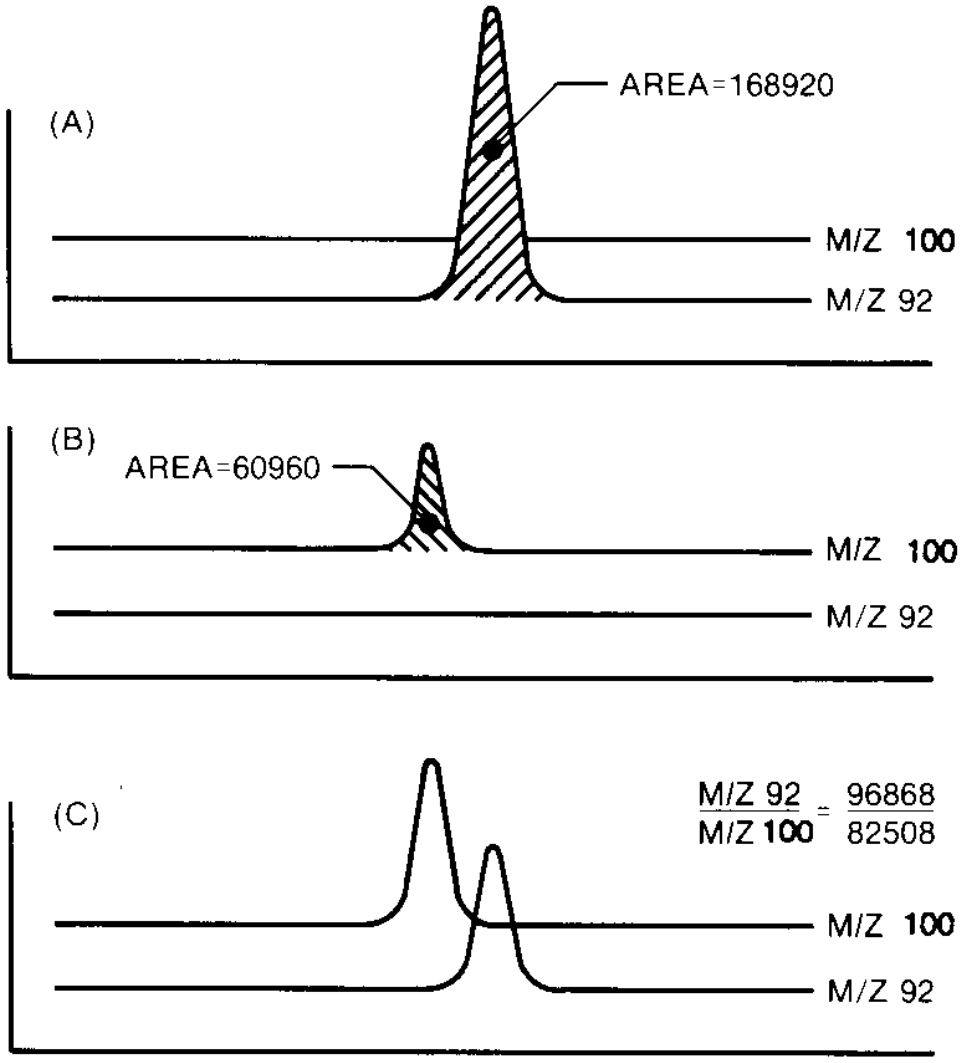


FIGURE 7 Extracted Ion Current Profiles for (A) Toluene, (B) Toluene-d_8, and (C) a Mixture of Toluene and Toluene-d_8

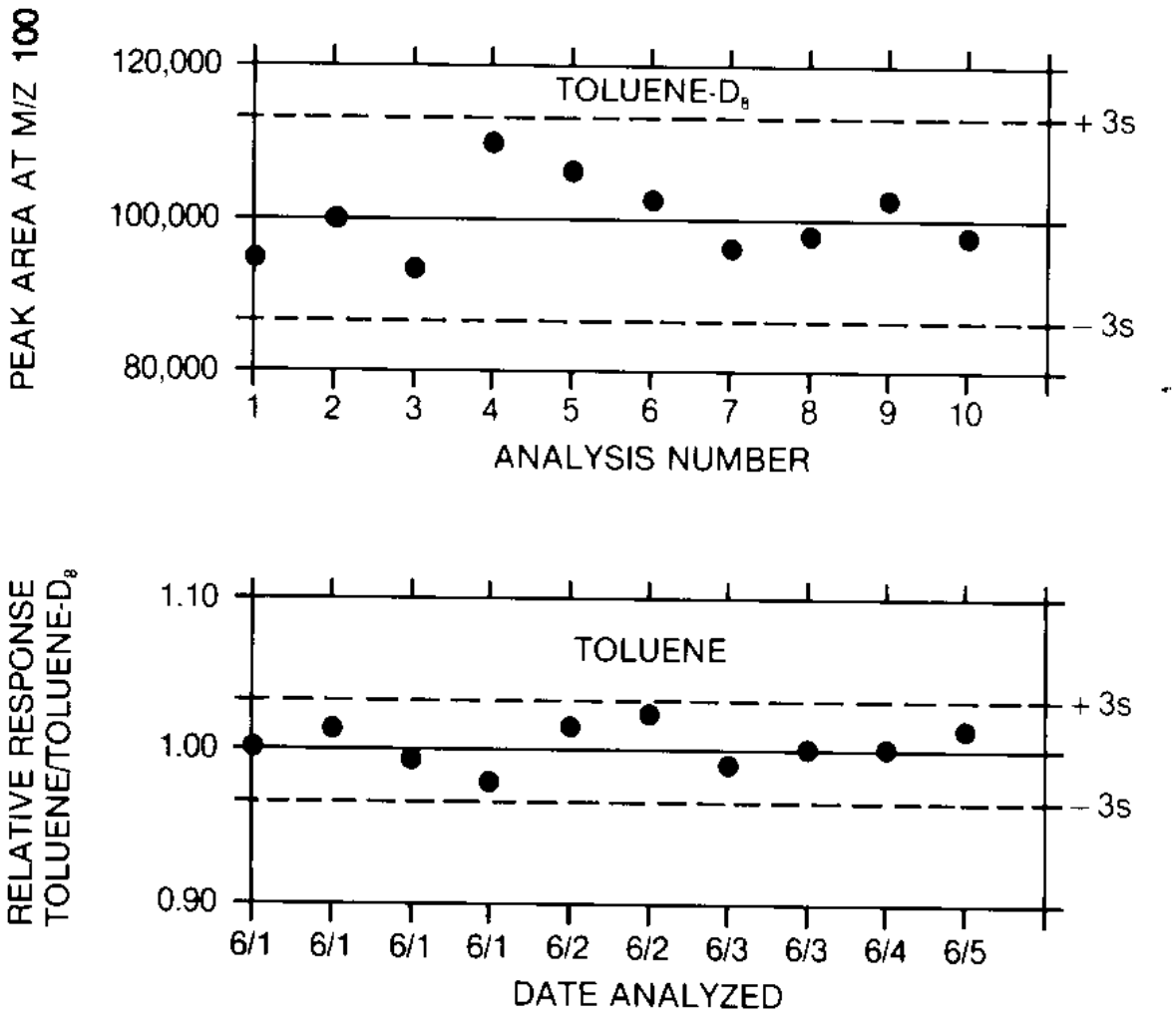


FIGURE 8 Quality Control Charts Showing Area (top graph) and Relative Response of Toluene to Toluene-d8 (lower graph) Plotted as Function of Time or Analysis Number

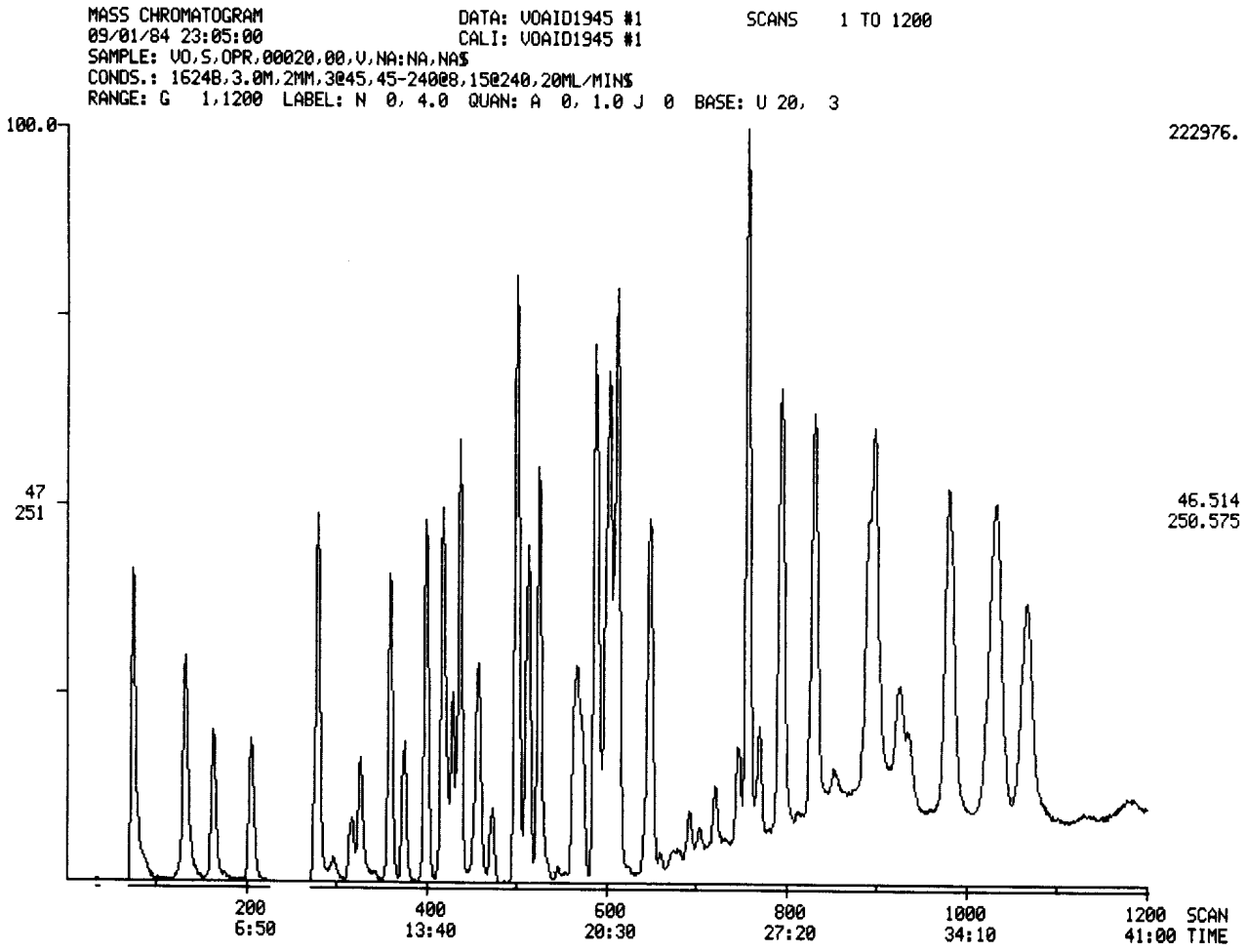


FIGURE 9 Chromatogram of Aqueous Performance Standard

METHOD 8260B
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/
MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Preparation Technique[a]					
Compound	CAS No.[b]	5030/ 5035	5031	5032	5021	5041	Direct Inject.
Acetone	67-64-1	pp	c	c	nd	c	c
Acetonitrile	75-05-8	pp	c	nd	nd	nd	c
Acrolein (Propenal)	107-02-8	pp	c	c	nd	nd	c
Acrylonitrile	107-13-1	pp	c	c	nd	c	c
Allyl alcohol	107-18-6	ht	c	nd	nd	nd	c
Allyl chloride	107-05-1	c	nd	nd	nd	nd	c
Benzene	71-43-2	c	nd	c	c	c	c
Benzyl chloride	100-44-7	c	nd	nd	nd	nd	c
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd	nd	nd	nd	c
Bromoacetone	598-31-2	pp	nd	nd	nd	nd	c
Bromochloromethane	74-97-5	c	nd	c	c	c	c
Bromodichloromethane	75-27-4	c	nd	c	c	c	c
4-Bromofluorobenzene (surr)	460-00-4	c	nd	c	c	c	c
Bromoform	75-25-2	c	nd	c	c	c	c
Bromomethane	74-83-9	c	nd	c	c	c	c
n-Butanol	71-36-3	ht	c	nd	nd	nd	c
2-Butanone (MEK)	78-93-3	pp	c	c	nd	nd	c
t-Butyl alcohol	75-65-0	pp	c	nd	nd	nd	c
Carbon disulfide	75-15-0	pp	nd	c	nd	c	c
Carbon tetrachloride	56-23-5	c	nd	c	c	c	c
Chloral hydrate	302-17-0	pp	nd	nd	nd	nd	c
Chlorobenzene	108-90-7	c	nd	c	c	c	c
Chlorobenzene-d_5 (IS)		c	nd	c	c	c	c
Chlorodibromomethane	124-48-1	c	nd	c	nd	c	c
Chloroethane	75-00-3	c	nd	c	c	c	c
2-Chloroethanol	107-07-3	pp	nd	nd	nd	nd	c
2-Chloroethyl vinyl ether	110-75-8	c	nd	c	nd	nd	c
Chloroform	67-66-3	c	nd	c	c	c	c
Chloromethane	74-87-3	c	nd	c	c	c	c
Chloroprene	126-99-8	c	nd	nd	nd	nd	c
3-Chloropropionitrile	542-76-7	l	nd	nd	nd	nd	pc

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Crotonaldehyde	4170-30-3	pp	c	nd	nd	nd	c
1,2-Dibromo-3-chloropropane	96-12-8	pp	nd	nd	c	nd	c
1,2-Dibromoethane	106-93-4	c	nd	nd	c	nd	c
Dibromomethane	74-95-3	c	nd	c	c	c	c
1,2-Dichlorobenzene	95-50-1	c	nd	nd	c	nd	c
1,3-Dichlorobenzene	541-73-1	c	nd	nd	c	nd	c
1,4-Dichlorobenzene	106-46-7	c	nd	nd	c	nd	c
1,4-Dichlorobenzene-d_4 (IS)		c	nd	nd	c	nd	c
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd	c	nd	nd	c
trans-1,4-Dichloro-2-butene	110-57-6	pp	nd	c	nd	nd	c
Dichlorodifluoromethane	75-71-8	c	nd	c	c	nd	c
1,1-Dichloroethane	75-34-3	c	nd	c	c	c	c
1,2-Dichloroethane	107-06-2	c	nd	c	c	c	c
1,2-Dichloroethane-d_4 (surr)		c	nd	c	c	c	c
1,1-Dichloroethene	75-35-4	c	nd	c	c	c	c
trans-1,2-Dichloroethene	156-60-5	c	nd	c	c	c	c
1,2-Dichloropropane	78-87-5	c	nd	c	c	c	c
1,3-Dichloro-2-propanol	96-23-1	pp	nd	nd	nd	nd	c
cis-1,3-Dichloropropene	10061-01-5	c	nd	c	nd	c	c
trans-1,3-Dichloropropene	10061-02-6	c	nd	c	nd	c	c
1,2,3,4-Diepoxybutane	1464-53-5	c	nd	nd	nd	nd	c
Diethyl ether	60-29-7	c	nd	nd	nd	nd	c
1,4-Difluorobenzene (IS)	540-36-3	nd	nd	nd	nd	c	nd
1,4-Dioxane	123-91-1	pp	c	c	nd	nd	c
Epichlorohydrin	106-89-8	l	nd	nd	nd	nd	c
Ethanol	64-17-5	l	c	c	nd	nd	c
Ethyl acetate	141-78-6	l	c	nd	nd	nd	c
Ethylbenzene	100-41-4	c	nd	c	c	c	c
Ethylene oxide	75-21-8	pp	c	nd	nd	nd	c
Ethyl methacrylate	97-63-2	c	nd	c	nd	nd	c
Fluorobenzene (IS)	462-06-6	c	nd	nd	nd	nd	nd
Hexachlorobutadiene	87-68-3	c	nd	nd	c	nd	c
Hexachloroethane	67-72-1	l	nd	nd	nd	nd	c
2-Hexanone	591-78-6	pp	nd	c	nd	nd	c
2-Hydroxypropionitrile	78-97-7	l	nd	nd	nd	nd	pc
Iodomethane	74-88-4	c	nd	c	nd	c	c
Isobutyl alcohol	78-83-1	pp	c	nd	nd	nd	c
Isopropylbenzene	98-82-8	c	nd	nd	c	nd	c
Malononitrile	109-77-3	pp	nd	nd	nd	nd	c
Methacrylonitrile	126-98-7	pp	l	nd	nd	nd	c
Methanol	67-56-1	l	c	nd	nd	nd	c
Methylene chloride	75-09-2	c	nd	c	c	c	c
Methyl methacrylate	80-62-6	c	nd	nd	nd	nd	c
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	c	c	nd	nd	c
Naphthalene	91-20-3	c	nd	nd	c	nd	c

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Nitrobenzene	98-95-3	c	nd	nd	nd	nd	c
2-Nitropropane	79-46-9	c	nd	nd	nd	nd	c
N-Nitroso-di-n-butylamine	924-16-3	pp	c	nd	nd	nd	c
Paraldehyde	123-63-7	pp	c	nd	nd	nd	c
Pentachloroethane	76-01-7	l	nd	nd	nd	nd	c
2-Pentanone	107-87-9	pp	c	nd	nd	nd	c
2-Picoline	109-06-8	pp	c	nd	nd	nd	c
1-Propanol	71-23-8	pp	c	nd	nd	nd	c
2-Propanol	67-63-0	pp	c	nd	nd	nd	c
Propargyl alcohol	107-19-7	pp	l	nd	nd	nd	c
β-Propiolactone	57-57-8	pp	nd	nd	nd	nd	c
Propionitrile (ethyl cyanide)	107-12-0	ht	c	nd	nd	nd	pc
n-Propylamine	107-10-8	c	nd	nd	nd	nd	c
Pyridine	110-86-1	l	c	nd	nd	nd	c
Styrene	100-42-5	c	nd	c	c	c	c
1,1,1,2-Tetrachloroethane	630-20-6	c	nd	nd	c	c	c
1,1,2,2-Tetrachloroethane	79-34-5	c	nd	c	c	c	c
Tetrachloroethene	127-18-4	c	nd	c	c	c	c
Toluene	108-88-3	c	nd	c	c	c	c
Toluene-d_8 (surr)	2037-26-5	c	nd	c	c	c	c
o-Toluidine	95-53-4	pp	c	nd	nd	nd	c
1,2,4-Trichlorobenzene	120-82-1	c	nd	nd	c	nd	c
1,1,1-Trichloroethane	71-55-6	c	nd	c	c	c	c
1,1,2-Trichloroethane	79-00-5	c	nd	c	c	c	c
Trichloroethene	79-01-6	c	nd	c	c	c	c
Trichlorofluoromethane	75-69-4	c	nd	c	c	c	c
1,2,3-Trichloropropane	96-18-4	c	nd	c	c	c	c
Vinyl acetate	108-05-4	c	nd	c	nd	nd	c
Vinyl chloride	75-01-4	c	nd	c	c	c	c
o-Xylene	95-47-6	c	nd	c	c	c	c
m-Xylene	108-38-3	c	nd	c	c	c	c
p-Xylene	106-42-3	c	nd	c	c	c	c

[a] See Sec. 1.2 for other appropriate sample preparation techniques
[b] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80°C
nd = Not determined
l = Inappropriate technique for this analyte
pc = Poor chromatographic behavior
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
surr = Surrogate
IS = Internal Standard

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Chloroacetonitrile
1-Chlorobutane
1-Chlorohexane
2-Chlorotoluene
4-Chlorotoluene
Dibromofluoromethane
cis-1,2-Dichloroethene
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
p-Isopropyltoluene
Methyl acrylate
Methyl-t-butyl ether
Pentafluorobenzene
n-Propylbenzene
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

1.4 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Sec. 1.2). The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explained this in text accompanying the uncorrected data.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

3.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

3.7 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.8 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

3.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device for aqueous samples - Described in Method 5030.

4.2 Purge-and-trap device for solid samples - Described in Method 5035.

4.3 Automated static headspace device for solid samples - Described in Method 5021.

4.4 Azeotropic distillation apparatus for aqueous and solid samples - Described in Method 5031.

4.5 Vacuum distillation apparatus for aqueous, solid and tissue samples - Described in Method 5032.

4.6 Desorption device for air trapping media for air samples - Described in Method 5041.

4.7 Air sampling loop for sampling from Tedlar® bags for air samples - Described in Method 0040.

4.8 Injection port liners (HP Catalog #18740-80200, or equivalent) - modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven (see illustration below). A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

4.9 Gas chromatography/mass spectrometer/data system

4.9.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.9.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.9.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

4.9.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

4.9.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.9.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.9.2 Gas chromatographic columns

4.9.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5-µm film thickness, or equivalent.

4.9.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

4.9.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt_x-5, SPB-5, or equivalent), 1-µm film thickness.

4.9.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

4.9.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.9.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

4.9.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

4.9.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

4.9.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 8.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.9.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.10 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000-µL.

4.11 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.12 Syringes - 5-, 10-, or 25-mL, gas-tight with shutoff valve.

4.13 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

4.15 Vials - 2-mL, for GC autosampler.

4.16 Disposable pipets - Pasteur.

4.17 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.18 Spatula - Stainless steel.

5.0 REAGENTS

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

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to

5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.7.5 Frequency of Standard Preparation

5.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.7.6 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichloro-difluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100-µL or 500-µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

5.7.6.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.9 The concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
40 µL	20 µg/L
100 µL	50 µg/L
200 µL	100 µg/L
300 µL	150 µg/L
400 µL	200 µg/L

5.7.6.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

5.8 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.9 Surrogate standards - The recommended surrogates are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

5.12 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

5.12.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.4 for guidance on calibration verification.

5.12.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.12.4 The calibration standards must also contain the internal standards chosen for the analysis.

5.13 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.13.1 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.2 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

5.13.3 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

7.1.1 Direct injection - This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

7.1.2 Purge-and-trap - This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

7.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

7.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

7.1.3 Vacuum distillation - this technique may be used for the introduction of volatile organics from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system.

7.1.4 Automated static headspace - this technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

7.1.5 Cartridge desorption - this technique may be for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

7.2 Recommended chromatographic conditions

7.2.1 General conditions

Injector temperature:	200 - 225°C
Transfer line temperature:	250 - 300°C

7.2.2 Column 1 and Column 2 with cryogenic cooling (example chromatograms are presented in Figures 1 and 2)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

7.2.5 Direct injection - Column 2

Carrier gas (He) flow rate:	4 mL/min
Column:	J&W DB-624, 70m x 0.53 mm
Initial temperature:	40°C, hold for 3 minutes
Temperature program:	8°C/min
Final temperature:	260°C, hold until all expected compounds have eluted.
Column Bake out:	75 minutes
Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.6 Direct split interface - Column 4

Carrier gas (He) flow rate:	1.5 mL/min
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	4°C/min to 50°C 10°C/min to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted
Split ratio:	100:1
Injector temperature:	125°C

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

Mass range:	35 - 260 amu
Scan time:	0.6 - 2 sec/scan
Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of

BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

7.3.1.2 Use the BFB mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (see Sec. 5.12 and Method 8000). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

7.3.2.2 The internal standards selected in Sec. 5.10 should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion.

7.3.2.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

7.3.3 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 - 2 µL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

7.3.4 Tabulate the area response of the characteristic ions (see Table 5) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured (Sec. 7.6.2).

The RF is calculated as follows:

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

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard.

7.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

7.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.5.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

7.3.6 Calibration check compounds (CCCs)

7.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of Method 8000.

7.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \overline{RF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

7.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

7.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

7.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.8 Linearity of target analytes

7.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Sec. 7.7.2).

7.3.8.2 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 of Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The 20% RSD criteria in Method 8000 pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000 for method blank performance criteria.

7.4.4 System Performance Check Compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 7.3.5.4). This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration Check Compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Sec. 7.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater

than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low detection levels.

7.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

7.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

7.5.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

7.5.6.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

7.5.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.6.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 7.5.5.

7.5.7 Compositing aqueous samples prior to GC/MS analysis

7.5.7.1 Add 5 mL of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

7.5.7.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

7.5.7.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

7.5.7.4 Once all the aliquots have been combined on the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Sec. 7.1).

7.5.7.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

7.5.8 Add 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution to each sample either manually or by autosampler. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of a non-aqueous sample will yield a concentration of 50 µg/kg of each standard.

If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.9 Add 10 µL of the matrix spike solution (Sec. 5.13) to a 5-mL aliquot of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 8.4 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

7.5.9.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

7.5.10 Analyze the sample following the procedure in the introduction method of choice.

7.5.10.1 For direct injection, inject 1 to 2 µL into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

7.5.10.2 The concentration of the internal standards, surrogates, and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2 µL injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

7.5.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.11.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.12 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library

searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

(1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.7.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.3.6). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8260:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria described in Sec. 7.4.4 and the CCC criteria in Sec. 7.4.5, each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested using purge-and-trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using purge-and-trap (Method 5030) with water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are presented in Tables 10 and 11 for TCLP volatiles in oil. The performance data were developed by spiking and analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, except for the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm, well below the regulatory concentrations. Prior to spiking, the new oil (an SAE 30-weight motor oil) was heated at 80°C overnight to remove volatiles. The used oil (a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of BTEX compounds and isobutanol. These contaminants contributed to the extremely high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

9.5 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand; a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon; and a surface garden soil. Sample preparation was by Method 5035. Each

sample was fortified with the analytes at a concentration of 4 µg/kg. These data are listed in Tables 17, 18, and 19. All data were calculated using fluorobenzene as the internal standard added to the soil sample prior to extraction. This causes some of the results to be greater than 100% recovery because the precision of results is sometimes as great as 28%.

9.5.1 In general, the recoveries of the analytes from the sand matrix are the highest, the C-Horizon soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

9.5.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, are somewhat greater than 100%. This is due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. Also, the garden soil results in Table 19 include some extraordinarily high recoveries for some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection, and to the fact that no background was subtracted.

9.6 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 12 to 16.

9.7 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 20 to 27.

9.8 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in two soil matrices: sand and a surface garden soil. Replicate samples were fortified with the analytes at concentrations of 10 µg/kg. These data are listed in Table 30. All data were calculated using the internal standards listed for each analyte in Table 28. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

9.8.1 If a detector other than an MS is used for analysis, consideration must be given to the choice of internal standards and surrogates. They must not coelute with any other analyte and must have similar properties to the analytes. The recoveries of the analytes are 50% or higher for each matrix studied. The recoveries of the gases or very volatile compounds are greater than 100% in some cases. Also, results include high recoveries of some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection.

9.8.2 The method detection limits using Method 5021 listed in Table 29 were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These MDLs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

9.9 The MDL concentrations listed in Table 31 were determined using Method 5041 in conjunction with Method 8260. They were obtained using cleaned blank VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under the test conditions, the MDLs for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

9.10 The EQL of sample taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 ppm (See Table 33). Matrix effects may cause the individual compound detection limits to be higher.

10.0 REFERENCES

1. Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water Method 524.2, U.S. Environmental Protection Agency, Office of Research Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 1986.

2. Bellar, T.A., Lichtenberg, J.J, J. Amer. Water Works Assoc., 1974, 66(12), 739-744.

3. Bellar, T.A., Lichtenberg, J.J., "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds"; in Van Hall, Ed.; Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.

4. Budde, W.L., Eichelberger, J.W., "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, April 1980; EPA-600/4-79-020.

5. Eichelberger, J.W., Harris, L.E., Budde, W.L., "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems"; Analytical Chemistry 1975, 47, 995-1000.

6. Olynyk, P., Budde, W.L., Eichelberger, J.W., "Method Detection Limit for Methods 624 and 625"; Unpublished report, October 1980.

7. Non Cryogenic Temperatures Program and Chromatogram, Private Communications; M. Stephenson and F. Allen, EPA Region IV Laboratory, Athens, GA.

8. Marsden, P.J., Helms, C.L., Colby, B.N., "Analysis of Volatiles in Waste Oil"; Report for B. Lesnik, OSW/EPA under EPA contract 68-W9-001, 6/92.

9. Methods for the Determination of Organic Compounds in Drinking Water, Supplement II Method 524.2; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1992.

10. Flores, P., Bellar, T., "Determination of Volatile Organic Compounds in Soils Using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, December, 1992.

11. Bruce, M.L., Lee, R.P., Stephens, M.W., "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environmental Science and Technology 1992, 26, 160-163.

12. Cramer, P.H., Wilner, J., Stanley, J.S., "Final Report: Method for Polar, Water Soluble, Nonpurgeable Volatile Organics (VOCs)", For U.S. Environmental Protection Agency, Environmental Monitoring Support Laboratory, EPA Contract No. 68-C8-0041.

13. Hiatt, M.H., "Analysis of Fish and Sediment for Volatile Priority Pollutants", Analytical Chemistry 1981, 53, 1541.

14. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.

15. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes)			MDL[d]
	Column 1[a]	Column 2[b]	Column 2'[c]	(µg/L)
Dichlorodifluoromethane	1.35	0.70	3.13	0.10
Chloromethane	1.49	0.73	3.40	0.13
Vinyl Chloride	1.56	0.79	3.93	0.17
Bromomethane	2.19	0.96	4.80	0.11
Chloroethane	2.21	1.02	--	0.10
Trichlorofluoromethane	2.42	1.19	6.20	0.08
Acrolein	3.19			
Iodomethane	3.56			
Acetonitrile	4.11			
Carbon disulfide	4.11			
Allyl chloride	4.11			
Methylene chloride	4.40	2.06	9.27	0.03
1,1-Dichloroethene	4.57	1.57	7.83	0.12
Acetone	4.57			
trans-1,2-Dichloroethene	4.57	2.36	9.90	0.06
Acrylonitrile	5.00			
1,1-Dichloroethane	6.14	2.93	10.80	0.04
Vinyl acetate	6.43			
2,2-Dichloropropane	8.10	3.80	11.87	0.35
2-Butanone	--			
cis-1,2-Dichloroethene	8.25	3.90	11.93	0.12
Propionitrile	8.51			
Chloroform	9.01	4.80	12.60	0.03
Bromochloromethane	--	4.38	12.37	0.04
Methacrylonitrile	9.19			
1,1,1-Trichloroethane	10.18	4.84	12.83	0.08
Carbon tetrachloride	11.02	5.26	13.17	0.21
1,1-Dichloropropene	--	5.29	13.10	0.10
Benzene	11.50	5.67	13.50	0.04
1,2-Dichloroethane	12.09	5.83	13.63	0.06
Trichloroethene	14.03	7.27	14.80	0.19
1,2-Dichloropropane	14.51	7.66	15.20	0.04
Bromodichloromethane	15.39	8.49	15.80	0.08
Dibromomethane	15.43	7.93	5.43	0.24
Methyl methacrylate	15.50			
1,4-Dioxane	16.17			
2-Chloroethyl vinyl ether	--			
4-Methyl-2-pentanone	17.32			
trans-1,3-Dichloropropene	17.47	--	16.70	--
Toluene	18.29	10.00	17.40	0.11
cis-1,3-Dichloropropene	19.38	--	17.90	--

TABLE 1 (cont.)

Compound	Retention Time (minutes)			MDL[d]
	Column 1[a]	Column 2[b]	Column 2"[c]	(µg/L)
1,1,2-Trichloroethane	19.59	11.05	18.30	0.10
Ethyl methacrylate	20.01			
2-Hexanone	20.30			
Tetrachloroethene	20.26	11.15	18.60	0.14
1,3-Dichloropropane	20.51	11.31	18.70	0.04
Dibromochloromethane	21.19	11.85	19.20	0.05
1,2-Dibromoethane	21.52	11.83	19.40	0.06
1-Chlorohexane	--	13.29	--	0.05
Chlorobenzene	23.17	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	0.05
Ethylbenzene	23.38	13.39	21.00	0.06
p-Xylene	23.54	13.69	21.30	0.13
m-Xylene	23.54	13.68	21.37	0.05
o-Xylene	25.16	14.52	22.27	0.11
Styrene	25.30	14.60	22.40	0.04
Bromoform	26.23	14.88	22.77	0.12
Isopropylbenzene (Cumene)	26.37	15.46	23.30	0.15
cis-1,4-Dichloro-2-butene	27.12			
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	0.04
Bromobenzene	27.46	15.86	24.00	0.03
1,2,3-Trichloropropane	27.55	16.23	24.13	0.32
n-Propylbenzene	27.58	16.41	24.33	0.04
2-Chlorotoluene	28.19	16.42	24.53	0.04
trans-1,4-Dichloro-2-butene	28.26			
1,3,5-Trimethylbenzene	28.31	16.90	24.83	0.05
4-Chlorotoluene	28.33	16.72	24.77	0.06
Pentachloroethane	29.41			
1,2,4-Trimethylbenzene	29.47	17.70	31.50	0.13
sec-Butylbenzene	30.25	18.09	26.13	0.13
tert-Butylbenzene	30.59	17.57	26.60	0.14
p-Isopropyltoluene	30.59	18.52	26.50	0.12
1,3-Dichlorobenzene	30.56	18.14	26.37	0.12
1,4-Dichlorobenzene	31.22	18.39	26.60	0.03
Benzyl chloride	32.00			
n-Butylbenzene	32.23	19.49	27.32	0.11
1,2-Dichlorobenzene	32.31	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	35.30	21.08	--	0.26
1,2,4-Trichlorobenzene	38.19	23.08	31.50	0.04
Hexachlorobutadiene	38.57	23.68	32.07	0.11
Naphthalene	39.05	23.52	32.20	0.04
1,2,3-Trichlorobenzene	40.01	24.18	32.97	0.03

TABLE 1 (cont.)

Compound	Retention Time (minutes) Column 1[a]	Column 2[b]	Column 2"[c]	MDL[d] (µg/L)
INTERNAL STANDARDS/SURROGATES				
1,4-Difluorobenzene	13.26			
Chlorobenzene-d_5	23.10			
1,4-Dichlorobenzene-d_4	31.16			
4-Bromofluorobenzene	27.83	15.71	23.63	
1,2-Dichlorobenzene-d_4	32.30	19.08	27.25	
Dichloroethane-d_4	12.08			
Dibromofluoromethane	--			
Toluene-d_8	18.27			
Pentafluorobenzene	--			
Fluorobenzene	13.00	6.27	14.06	

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.

[c] Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

[d] MDL based on a 25-mL sample volume.

TABLE 2

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06

TABLE 2 (cont.)

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25-mL sample volume.

TABLE 3

ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

Estimated Quantitation Limits		
5-mL Ground Water Purge (µg/L)	25-mL Ground water Purge (µg/L)	Low Soil/Sediment[b] µg/kg
5	1	5

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High concentration soil and sludge	125
Non-water miscible waste	500

[c] EQL = [EQL for low soil sediment (Table 3)] x [Factor].

For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

[a] Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers" instructions), provided that method performance is not adversely affected.

TABLE 5

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64 (49*)	66 (51*)
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50 (49*)	52 (51*)
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
β-Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates:		
Benzene-d_6	84	83
Bromobenzene-d_5	82	162
Bromochloromethane-d_2	51	131
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	115, 150
1,1,2-Trichloroethane-d_3	100	
4-Bromofluorobenzene	95	174, 176
Chloroform-d_1	84	
Dibromofluoromethane	113	

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Dichloroethane-d_4	102	
Toluene-d_8	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

TABLE 6

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3

TABLE 6 (cont.)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a] Recoveries were calculated using internal standard method. The internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data from three concentrations.

TABLE 7

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.5	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3

TABLE 7 (cont.)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8

SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Water	Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117
Dichloroethane-d_4[a]	80-120	80-120

[a] Single laboratory data, for guidance only.

TABLE 9

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

Approximate Concentration Range (µg/kg)	Volume of Extract[a]
500 - 10,000	100 µL
1,000 - 20,000	50 µL
5,000 - 100,000	10 µL
25,000 - 500,000	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10

DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone	91	14.8	1.9	5.0
Benzene	86	21.3	0.1	0.5
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	86	44.7	0.0	0.5
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	81	29.3	0.0	5.0
Chloroform	84	29.3	0.0	6.0
1,4-Dichlorobenzene	98	24.9	0.0	7.5
1,2-Dichloroethane	101	23.1	0.0	0.5
1,1-Dichloroethene	97	45.3	0.0	0.7
Diethyl ether	76	24.3	0.0	5.0
Ethyl acetate	113	27.4	0.0	5.0
Ethylbenzene	83	30.1	0.2	5.0
Hexachloroethane	71	30.3	0.0	3.0
Methylene chloride	98	45.3	0.0	5.0
Methyl ethyl ketone	79	24.6	0.4	5.0
MIBK	93	31.4	0.0	5.0
Nitrobenzene	89	30.3	0.0	2.0
Pyridine	31	35.9	0.0	5.0
Tetrachloroethene	82	27.1	0.0	0.7
Trichlorofluoromethane	76	27.6	0.0	5.0
1,1,2-Trichlorotrifluoroethane	69	29.2	0.0	5.0
Toluene	73	21.9	0.6	5.0
Trichloroethene	66	28.0	0.0	0.5
Vinyl chloride	63	35.2	0.0	0.2
o-Xylene	83	29.5	0.4	5.0
m/p-Xylene	84	29.5	0.6	10.0

* Alternate mass employed
** IS quantitation

Data are taken from Reference 9.

TABLE 11

SINGLE LABORATORY PERFORMANCE
DATA FOR THE DIRECT INJECTION METHOD - USED OIL (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone**	105	54	2.0	5.0
Benzene	3135	44	14	0.5
Benzene-d_6	56	44	2.9	0.5
n-Butanol**	100	71	12	5.0
iso-Butanol*,**	132	27	0	5.0
Carbon tetrachloride	143	68	0	0.5
Carbon tetrachloride-^{13}C	99	44	5.1	0.5
Carbon disulfide**	95	63	0	5.0
Chlorobenzene	148	71	0	5.0
Chlorobenzene-d_5	60	44	3.6	5.0
Chloroform	149	74	0	6.0
Chloroform-d_1	51	44	2.6	6.0
1,4-Dichlorobenzene	142	72	0	7.5
1,4-Dichlorobenzene-d_4	53	44	3.4	7.5
1,2-Dichloroethane**	191	54	0	0.5
1,1-Dichloroethene*	155	51	0	0.7
1,1-Dichloroethene-d_2	68	44	3.4	0.7
Diethyl ether**	95	66	0	5.0
Ethyl acetate*,**	126	39	0	5.0
Ethylbenzene	1298	44	54	5.0
Ethylbenzene-d_{10}	63	44	3.6	5.0
Hexachloroethane	132	72	0	3.0
Hexachloroethane-^{13}C	54	45	3.5	3.0
Methylene chloride**	86	65	0.3	5.0
Methyl ethyl ketone**	107	64	0	5.0
4-Methyl-2-pentanone (MIBK)**	100	74	0.1	5.0
Nitrobenzene	111	80	0	2.0
Nitrobenzene-d_5	65	53	4.0	2.0
Pyridine**	68	85	0	5.0
Pyridine-d_5	ND	--	0	5.0
Tetrachloroethene**	101	73	0	0.7
Trichlorofluoromethane**	91	70	0	5.0
1,1,2-Cl_3F_3ethane**	81	70	0	5.0
Toluene	2881	44	128	5.0
Toluene-d_8	63	44	3.6	5.0
Trichloroethene	152	57	0	0.5
Trichloroethene-d_1	55	44	2.8	0.5

TABLE 11 (cont.)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Vinyl chloride**	100	69	0	0.2
o-Xylene	2292	44	105	5.0
o-Xylene-d_{10}	76	44	4.2	5.0
m-/p-Xylene	2583	44	253	10.0
p-Xylene-d_{10}	67	44	3.7	10.0

* Alternate mass employed
** IS quantitation
ND = Not Detected

Data are based on seven measurements and are taken from Reference 9.

TABLE 12

METHOD DETECTION LIMITS (METHOD 5031)

Compound	MDL (µg/L) Macro[a]	Concentration Factor Macro	Micro
Acetone	31	25-500	-
Acetonitrile	57	25-500	200
Acrolein	-	-	100
Acrylonitrile	16	25-500	100
Allyl Alcohol	7	25-500	-
1-Butanol	-	-	250
Crotonaldehyde	12	25-500	-
1,4-Dioxane	12	25-500	150
Ethyl Acetate	-	-	100
Isobutyl alcohol	7	25-500	-
Methanol	38	25-500	140
Methyl Ethyl Ketone	16	25-500	-
2-Methyl-1-propanol	-	-	250
n-Nitroso-di-n-butylamine	14	25-500	-
Paraldehyde	10	25-500	-
2-Picoline	7	25-500	-
1-Propanol	-	-	240
Propionitrile	11	25-500	200
Pyridine	4	25-500	-
o-Toluidine	13	25-500	-

[a] Produced by analysis of seven aliquots of reagent water spiked at 25 ppb at the listed compounds; calculations based on internal standard technique and use of the following equation:

MDL = 3.134 x Std. Dev. of low concentration spike (ppb).

[b] When a 40-mL sample is used, and the first 100 µL of distillate are collected.

TABLE 13

TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS (METHOD 5031)

Target Compound	Surrogate	Internal Standard
Acetone	d_6-Acetone	d_8-Isopropyl alcohol
Acetonitrile	d_3-Acetonitrile	d_8-Isopropyl alcohol
Acrylonitrile	d_8-Isopropyl alcohol	
Allyl alcohol	d_7-Dimethyl formamide	
Crotonaldehyde	d_8-Isopropyl alcohol	
1,4-Dioxane	d_8-1,4-Dioxane	d_7-Dimethyl formamide
Isobutyl alcohol	d_7-Dimethyl formamide	
Methanol	d_3-Methanol	d_8-Isopropyl alcohol
Methyl ethyl ketone	d_8-Isopropyl alcohol	
N-Nitroso-di-n-butylamine	d_7-Dimethyl formamide	
Paraldehyde	d_7-Dimethyl formamide	
2-Picoline	d_7-Dimethyl formamide	
Propionitrile	d_8-Isopropyl alcohol	
Pyridine	d_5-Pyridine	d_7-Dimethyl formamide
o-Toluidine	d_7-Dimethyl formamide	

TABLE 14

RECOMMENDED CONCENTRATIONS FOR CALIBRATION SOLUTIONS (METHOD 5031)

Compound	Concentration(s) (ng/µL)
Internal Standards	
d_5-benzyl alcohol	10.0
d_{14}-Diglyme	10.0
d_7-Dimethyl formamide	10.0
d_8-Isopropyl alcohol	10.0
Surrogates	
d_6-Acetone	10.0
d_3-Acetonitrile	10.0
d_8-1,4-Dioxane	10.0
d_3-Methanol	10.0
d_5-Pyridine	10.0
Target Compounds	
Acetone	1.0, 5.0, 10.0, 25.0, 100.0
Acetonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Acrylonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Allyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Crotonaldehyde	1.0, 5.0, 10.0, 25.0, 100.0
1,4-Dioxane	1.0, 5.0, 10.0, 25.0, 100.0
Isobutyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Methanol	1.0, 5.0, 10.0, 25.0, 100.0
Methyl ethyl ketone	1.0, 5.0, 10.0, 25.0, 100.0
N-Nitroso-di-n-butylamine	1.0, 5.0, 10.0, 25.0, 100.0
Paraldehyde	1.0, 5.0, 10.0, 25.0, 100.0
2-Picoline	1.0, 5.0, 10.0, 25.0, 100.0
Propionitrile	1.0, 5.0, 10.0, 25.0, 100.0
Pyridine	1.0, 5.0, 10.0, 25.0, 100.0
o-Toluidine	1.0, 5.0, 10.0, 25.0, 100.0

TABLE 15

CHARACTERISTIC IONS AND RETENTION TIMES FOR VOCs (METHOD 5031)

Compound	Quantitation Ion[a]	Secondary Ions	Retention Time (min)[b]
Internal Standards			
d_8-Isopropyl alcohol	49		1.75
d_{14}-Diglyme	66	98,64	9.07
d_7-Dimethyl formamide	50	80	9.20
Surrogates			
d_6-Acetone	46	64,42	1.03
d_3-Methanol	33	35,30	1.75
d_3-Acetonitrile	44	42	2.63
d_8-1,4-Dioxane	96	64,34	3.97
d_5-Pyridine	84	56,79	6.73
d_5-Phenol[c]	99	71	15.43
Target Compounds			
Acetone	43	58	1.05
Methanol	31	29	1.52
Methyl ethyl ketone	43	72,57	1.53
Methacrylonitrile[c]	67	41	2.38
Acrylonitrile	53	52,51	2.53
Acetonitrile	41	40,39	2.73
Methyl isobutyl ketone[c]	85	100,58	2.78
Propionitrile	54	52,55	3.13
Crotonaldehyde	41	70	3.43
1,4-Dioxane	58	88,57	4.00
Paraldehyde	45	89	4.75
Isobutyl alcohol	43	33,42	5.05
Allyl alcohol	57	39	5.63
Pyridine	79	50,52	6.70
2-Picoline	93	66	7.27
N-Nitroso-di-n-butylamine	84	116	12.82
Aniline[c]	93	66,92	13.23
o-Toluidine	106	107	13.68
Phenol[c]	94	66,65	15.43

[a] These ions were used for quantitation in selected ion monitoring.
[b] GC column: DB-Wax, 30 meter x 0.53 mm, 1 µm film thickness.
Oven program: 45°C for 4 min, increased to 220°C at 12°C/min.
[c] Compound removed from target analyte list due to poor accuracy and precision.

TABLE 16

METHOD ACCURACY AND PRECISION BY MEAN PERCENT RECOVERY AND PERCENT RELATIVE STANDARD DEVIATION[a] (METHOD 5031 - MACRODISTILLATION TECHNIQUE)
(Single Laboratory and Single Operator)

Compound	25 ppb Spike		100 ppb Spike		500 ppb Spike	
	Mean %R	%RSD	Mean %R	%RSD	Mean %R	%RSD
d_6-Acetone	66	24	69	14	65	16
d_3-Acetonitrile	89	18	80	18	70	10
d_8-1,4-Dioxane	56	34	58	11	61	18
d_3-Methanol	43	29	48	19	56	14
d_5-Pyridine	83	6.3	84	7.8	85	9.0
Acetone	67	45	63	14	60	14
Acetonitrile	44	35	52	15	56	15
Acrylonitrile	49	42	47	27	45	27
Allyl alcohol	69	13	70	9.7	73	10
Crotonaldehyde	68	22	68	13	69	13
1,4-Dioxane	63	25	55	16	54	13
Isobutyl alcohol	66	14	66	5.7	65	7.9
Methanol	50	36	46	22	49	18
Methyl ethyl ketone	55	37	56	20	52	19
N-Nitroso-di-n-butylamine	57	21	61	15	72	18
Paraldehyde	65	20	66	11	60	8.9
Picoline	81	12	81	6.8	84	8.0
Propionitrile	67	22	69	13	68	13
Pyridine	74	7.4	72	6.7	74	7.3
o-Toluidine	52	31	54	15	58	12

[a] Data from analysis of seven aliquots of reagent water spiked at each concentration, using a quadrapole mass spectrometer in the selected ion monitoring mode.

TABLE 17

RECOVERIES IN SAND SAMPLES FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	8.0	7.5	6.7	5.4	6.6	6.8	13.0	34.2
Trichlorofluoromethane	13.3	16.5	14.9	13.0	10.3	13.6	15.2	68.0
1,1-Dichloroethene	17.1	16.7	15.1	14.8	15.6	15.9	5.7	79.2
Methylene chloride	24.5	22.7	19.7	19.4	20.6	21.4	9.1	107
trans-1,2-Dichloroethene	22.7	23.6	19.4	18.3	20.1	20.8	0.7	104
1,2-Dichloroethane	18.3	18.0	16.7	15.6	15.9	16.9	6.4	84.4
cis-1,2-Dichloroethene	26.1	23.1	22.6	20.3	20.8	22.6	9.0	113
Bromochloromethane	24.5	25.4	20.9	20.1	20.1	22.2	10.2	111
Chloroform	26.5	26.0	22.1	18.9	22.1	23.1	12.2	116
1,1,1-Trichloroethane	21.5	23.0	23.9	16.7	31.2	23.4	21.2	117
Carbon tetrachloride	23.6	24.2	22.6	18.3	23.3	22.4	9.4	112
Benzene	22.4	23.9	20.4	17.4	19.2	20.7	11.2	103
Trichloroethene	21.5	20.5	19.2	14.4	19.1	18.9	12.7	94.6
1,2-Dichloropropane	24.9	26.3	23.1	19.0	23.3	23.3	10.5	117
Dibromomethane	25.4	26.4	21.6	20.4	23.6	23.5	9.6	117
Bromodichloromethane	25.7	26.7	24.1	17.9	23.0	23.5	13.1	117
Toluene	28.3	25.0	24.8	16.3	23.6	23.6	16.9	118
1,1,2-Trichloroethane	25.4	24.5	21.6	17.7	22.1	22.2	12.1	111
1,3-Dichloropropane	25.4	24.2	22.7	17.0	22.2	22.3	12.8	112
Dibromochloromethane	26.3	26.2	23.7	18.2	23.2	23.5	12.5	118
Chlorobenzene	22.9	22.5	19.8	14.6	19.4	19.9	15.0	99.3
1,1,1,2-Tetrachloroethane	22.4	27.7	25.1	19.4	22.6	23.4	12.0	117
Ethylbenzene	25.6	25.0	22.1	14.9	24.0	22.3	17.5	112
p-Xylene	22.5	22.0	19.8	13.9	20.3	19.7	15.7	98.5
o-Xylene	24.2	23.1	21.6	14.0	20.4	20.7	17.3	103
Styrene	23.9	21.5	20.9	14.3	20.5	20.2	15.7	101
Bromoform	26.8	25.6	26.0	20.1	23.5	24.4	9.9	122
iso-Propylbenzene	25.3	25.1	24.2	15.4	24.6	22.9	16.6	114
Bromobenzene	19.9	21.8	20.0	15.5	19.1	19.3	10.7	96.3
1,2,3-Trichloropropane	25.9	23.0	25.6	15.9	21.4	22.2	15.8	111
n-Propylbenzene	26.0	23.8	22.6	13.9	21.9	21.6	19.0	106
2-Chlorotoluene	23.6	23.8	21.3	13.0	21.5	20.6	19.2	103
4-Chlorotoluene	21.0	19.7	18.4	12.1	18.3	17.9	17.1	89.5
1,3,5-Trimethylbenzene	24.0	22.1	22.5	13.8	22.9	21.1	17.6	105
sec-Butylbenzene	25.9	25.3	27.8	16.1	28.6	24.7	18.1	124
1,2,4-Trimethylbenzene	30.6	39.2	22.4	18.0	22.7	26.6	28.2	133
1,3-Dichlorobenzene	20.3	20.6	18.2	13.0	17.6	17.9	15.2	89.7
p-iso-Propyltoluene	21.6	22.1	21.6	16.0	22.8	20.8	11.8	104
1,4-Dichlorobenzene	18.1	21.2	20.0	13.2	17.4	18.0	15.3	90.0
1,2-Dichlorobenzene	18.4	22.5	22.5	15.2	19.9	19.7	13.9	96.6
n-Butylbenzene	13.1	20.3	19.5	10.8	18.7	16.5	23.1	82.4
1,2,4-Trichlorobenzene	14.5	14.9	15.7	8.8	12.3	13.3	18.8	66.2
Hexachlorobutadiene	17.6	22.5	21.6	13.2	21.6	19.3	18.2	96.3
1,2,3-Trichlorobenzene	14.9	15.9	16.5	11.9	13.9	14.6	11.3	73.1

Data in Tables 17, 18, and 19 are from Reference 15.

TABLE 18
RECOVERIES IN C-HORIZON SOILS FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	33.4	31.0	30.9	29.7	28.6	30.8	5.2	154
Trichlorofluoromethane	37.7	20.8	20.0	21.8	20.5	24.1	28.2	121
1,1-Dichloroethene	21.7	33.5	39.8	30.2	32.5	31.6	18.5	158
Methylene chloride	20.9	19.4	18.7	18.3	18.4	19.1	5.1	95.7
trans-1,2-Dichloroethene	21.8	18.9	20.4	17.9	17.8	19.4	7.9	96.8
1,1-Dichloroethane	23.8	21.9	21.3	21.3	20.5	21.8	5.2	109
cis-1,2-Dichloroethene	21.6	18.8	18.5	18.2	18.2	19.0	6.7	95.2
Bromochloromethane	22.3	19.5	19.3	19.0	19.2	20.0	6.0	100
Chloroform	20.5	17.1	17.3	16.5	15.9	17.5	9.2	87.3
1,1,1-Trichloroethane	16.4	11.9	10.7	9.5	9.4	11.6	22.4	57.8
Carbon tetrachloride	13.1	11.3	13.0	11.8	11.2	12.1	6.7	60.5
Benzene	21.1	19.3	18.7	18.2	16.9	18.8	7.4	94.1
Trichloroethene	19.6	16.4	16.5	16.5	15.5	16.9	8.3	84.5
1,2-Dichloropropane	21.8	19.0	18.3	18.8	16.5	18.9	9.0	94.4
Dibromomethane	20.9	17.9	17.9	17.2	18.3	18.4	6.9	92.1
Bromodichloromethane	20.9	18.0	18.9	18.2	17.3	18.6	6.6	93.2
Toluene	22.2	17.3	18.8	17.0	15.9	18.2	12.0	91.2
1,1,2-Trichloroethane	21.0	16.5	17.2	17.2	16.5	17.7	9.6	88.4
1,3-Dichloropropane	21.4	17.3	18.7	18.6	16.7	18.5	8.8	92.6
Dibromochloromethane	20.9	18.1	19.0	18.8	16.6	18.7	7.5	93.3
Chlorobenzene	20.8	18.4	17.6	16.8	14.8	17.7	11.2	88.4
1,1,1,2-Tetrachloroethane	19.5	19.0	17.8	17.2	16.5	18.0	6.2	90.0
Ethylbenzene	21.1	18.3	18.5	16.9	15.3	18.0	10.6	90.0
p-Xylene	20.0	17.4	18.2	16.3	14.4	17.3	10.9	86.3
o-Xylene	20.7	17.2	16.8	16.2	14.8	17.1	11.4	85.7
Styrene	18.3	15.9	16.2	15.3	13.7	15.9	9.3	79.3
Bromoform	20.1	15.9	17.1	17.5	16.1	17.3	8.6	86.7
iso-Propylbenzene	21.0	18.1	19.2	18.4	15.6	18.4	9.6	92.2
Bromobenzene	20.4	16.2	17.2	16.7	15.4	17.2	10.1	85.9
1,1,2,2-Tetrachloroethane	23.3	17.9	21.2	18.8	16.8	19.6	12.1	96.0
1,2,3-Trichloropropane	18.4	14.6	15.6	16.1	15.6	16.1	8.0	80.3
n-Propylbenzene	20.4	18.9	17.9	17.0	14.3	17.7	11.6	88.4
2-Chlorotoluene	19.1	17.3	16.1	16.0	14.4	16.7	9.2	83.6
4-Chlorotoluene	19.0	15.5	16.8	15.9	13.6	16.4	10.6	81.8
1,3,5-Trimethylbenzene	20.8	18.0	17.4	16.1	14.7	17.4	11.7	86.9
sec-Butylbenzene	21.4	18.3	18.9	17.0	14.9	18.1	11.8	90.5
1,2,4-Trimethylbenzene	20.5	18.6	16.8	15.3	13.7	17.0	14.1	85.0
1,3-Dichlorobenzene	17.6	15.9	15.6	14.2	14.4	15.6	7.9	77.8
p-iso-Propyltoluene	20.5	17.0	17.1	15.6	13.4	16.7	13.9	83.6
1,4-Dichlorobenzene	18.5	13.8	14.8	16.7	14.9	15.7	10.5	78.7
1,2-Dichlorobenzene	18.4	15.0	15.4	15.3	13.5	15.5	10.5	77.6
n-Butylbenzene	19.6	15.9	15.9	14.4	18.9	16.9	11.7	84.6
1,2,4-Trichlorobenzene	15.2	17.2	17.4	13.6	12.1	15.1	13.5	75.4
Hexachlorobutadiene	18.7	16.2	15.5	13.8	16.6	16.1	10.0	80.7
Naphthalene	13.9	11.1	10.2	10.8	11.4	11.5	11.0	57.4
1,2,3-Trichlorobenzene	14.9	15.2	16.8	13.7	12.7	14.7	9.5	73.2

TABLE 19
RECOVERIES IN GARDEN SOIL FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	12.7	10.9	9.8	8.1	7.2	9.7	20.2	48.7
Trichlorofluoromethane	33.7	6.4	30.3	27.8	22.9	24.2	39.6	121
1,1-Dichloroethene	27.7	20.5	24.1	15.1	13.2	20.1	26.9	101
Methylene chloride	25.4	23.9	24.7	22.2	24.2	24.1	4.4	120
trans-1,2-Dichloroethene	2.8	3.0	3.3	2.2	2.4	2.7	15.0	13.6
1,1-Dichloroethane	24.1	26.3	27.0	20.5	21.2	23.8	11.0	119
cis-1,2-Dichloroethene	8.3	10.2	8.7	5.8	6.4	7.9	20.1	39.4
Bromochloromethane	11.1	11.8	10.2	8.8	9.0	10.2	11.2	50.9
Chloroform	16.7	16.9	17.0	13.8	15.0	15.9	7.9	79.3
1,1,1-Trichloroethane	24.6	22.8	22.1	16.2	20.9	21.3	13.4	107
Carbon tetrachloride	19.4	20.3	22.2	20.0	20.2	20.4	4.6	102
Benzene	21.4	22.0	22.4	19.6	20.4	21.2	4.9	106
Trichloroethene	12.4	16.5	14.9	9.0	9.9	12.5	22.9	62.7
1,2-Dichloropropane	19.0	18.8	19.7	16.0	17.6	18.2	7.1	91.0
Dibromomethane	7.3	8.0	6.9	5.6	6.8	6.9	11.3	34.6
Bromodichloromethane	14.9	15.9	15.9	12.8	13.9	14.7	8.3	73.3
Toluene	42.6	39.3	45.1	39.9	45.3	42.4	5.9	212
1,1,2-Trichloroethane	13.9	15.2	1.4	21.3	14.9	15.9	17.0	79.6
1,3-Dichloropropane	13.3	16.7	11.3	10.9	9.5	12.3	20.3	61.7
Dibromochloromethane	14.5	13.1	14.5	11.9	14.4	13.7	7.6	68.3
Chlorobenzene	8.4	10.0	8.3	6.9	7.8	8.3	12.1	41.3
1,1,1,2-Tetrachloroethane	16.7	16.7	15.6	15.8	15.7	16.1	3.2	80.4
Ethylbenzene	22.1	21.4	23.1	20.1	22.6	21.9	4.8	109
p-Xylene	41.4	38.4	43.8	38.3	44.0	41.2	6.1	206
o-Xylene	31.7	30.8	34.3	30.4	33.2	32.1	4.6	160
Styrene	0	0	0	0	0	0	0	0
Bromoform	8.6	8.9	9.1	7.0	7.7	8.3	9.4	41.4
iso-Propylbenzene	18.1	18.8	9.7	18.3	19.6	18.9	3.5	94.4
Bromobenzene	5.1	5.4	5.3	4.4	4.0	4.8	11.6	24.1
1,1,2,2-Tetrachloroethane	14.0	13.5	14.7	15.3	17.1	14.9	8.5	74.5
1,2,3-Trichloropropane	11.0	12.7	11.7	11.7	11.9	11.8	4.5	59.0
n-Propylbenzene	13.4	13.3	14.7	12.8	13.9	13.6	4.7	68.1
2-Chlorotoluene	8.3	9.0	11.7	8.7	7.9	9.1	14.8	45.6
4-Chlorotoluene	5.1	5.4	5.5	4.8	4.5	5.0	7.9	25.2
1,3,5-Trimethylbenzene	31.3	27.5	33.0	31.1	33.6	31.3	6.8	157
sec-Butylbenzene	13.5	13.4	16.4	13.8	15.4	14.5	8.3	72.5
1,2,4-Trimethylbenzene	38.7	32.4	40.8	34.1	40.3	37.3	9.1	186
1,3-Dichlorobenzene	3.6	3.6	3.7	3.0	3.2	3.4	8.0	17.2
p-iso-Propyltoluene	14.7	14.1	16.1	13.9	15.1	14.8	5.2	73.8
1,4-Dichlorobenzene	3.0	3.5	3.3	2.6	2.8	3.0	10.2	15.0
1,2-Dichlorobenzene	3.6	4.3	4.0	3.5	3.6	3.8	8.3	19.0
n-Butylbenzene	17.4	13.8	14.0	18.9	24.0	17.6	21.2	88.0
1,2,4-Trichlorobenzene	2.8	2.9	3.3	2.6	3.2	3.0	8.5	15.0
Hexachlorobutadiene	4.8	4.0	6.1	5.6	6.0	5.3	15.1	26.4
Naphthalene	5.5	5.1	5.5	4.7	5.6	5.3	6.2	26.5
1,2,3-Trichlorobenzene	2.2	2.3	2.4	2.2	2.3	2.3	3.5	11.4

Data in Table 19 are from Reference 15.

TABLE 20

VOLATILE ORGANIC ANALYTE RECOVERY FROM SOIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Soil/H_2O[b] Recovery Mean	Soil/H_2O[b] Recovery RSD	Soil/Oil[c] Recovery Mean	Soil/Oil[c] Recovery RSD	Soil/Oil/H_2O Recovery Mean	Soil/Oil/H_2O Recovery RSD
Chloromethane	61	20	40	18	108	68
Bromomethane	58	20	47	13	74	13
Vinyl chloride	54	12	46	11	72	20
Chloroethane	46	10	41	8	52	14
Methylene chloride	60	2	65	8	76	11
Acetone	INT[e]	INT	44	8		
Carbon disulfide	47	13	53	10	47	4
1,1-Dichloroethene	48	9	47	5	58	3
1,1-Dichloroethane	61	6	58	9	61	6
trans-1,2-Trichloroethane	54	7	60	7	56	5
cis-1,2-Dichloroethene	60	4	72	6	63	8
Chloroform	104	11	93	6	114	15
1,2-Dichloroethane	177	50	117	8	151	22
2-Butanone	INT	36	38	INT		
1,1,1-Trichloroethane	124	13	72	16	134	26
Carbon tetrachloride	172	122	INT	INT		
Vinyl acetate	88	11	INT			
Bromodichloromethane	93	4	91	23	104	23
1,1,2,2-Tetrachloroethane	96	13	50	12	104	7
1,2-Dichloropropane	105	8	102	6	111	6
trans-1,3-Dichloropropene	134	10	84	16	107	8
Trichloroethene	98	9	99	10	100	5
Dibromochloromethane	119	8	125	31	142	16
1,1,2-Trichloroethane	126	10	72	16	97	4
Benzene	99	7	CONT[f]	CONT		
cis-1,3-Dichloropropene	123	12	94	13	112	9
Bromoform	131	13	58	18	102	9
2-Hexanone	155	18	164	19	173	29
4-Methyl-2-pentanone	152	20	185	20	169	18
Tetrachloroethene	90	9	123	14	128	7
Toluene	94	3	CONT	CONT		
Chlorobenzene	98	7	93	18	112	5
Ethylbenzene	114	13	CONT	CONT		
Styrene	106	8	93	18	112	5
p-Xylene	97	9	CONT	CONT		
o-Xylene	105	8	112	12	144	13

TABLE 20 (cont.)

Compound	Soil/H_2O[b] Recovery Mean	Soil/H_2O[b] Recovery RSD	Soil/Oil[c] Recovery Mean	Soil/Oil[c] Recovery RSD	Soil/Oil/H_2O Recovery Mean	Soil/Oil/H_2O Recovery RSD
Surrogates						
1,2-Dichloroethane	177	50	117	8	151	22
Toluene-d_8	96	6	79	12	82	6
Bromofluorobenzene	139	13	37	13	62	5

[a] Results are for 10 min. distillations times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision value reflects the propagated errors. Each analyte was spiked at 50 ppb. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may introduce bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Soil samples spiked with 0.2 mL water containing analytes and then 5 mL water added to make slurry.

[c] Soil sample + 1 g cod liver oil, spiked with 0.2 mL water containing analytes.

[d] Soil samples + 1 g cod liver oil, spiked as above with 5 mL of water added to make slurry.

[e] Interference by co-eluting compounds prevented accurate measurement of analyte.

[f] Contamination of sample matrix by analyte prevented assessment of efficiency.

TABLE 21

VACUUM DISTILLATION EFFICIENCIES FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Efficiency Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	CONT[c]	
Acetone	CONT[c]	
Carbon disulfide	79	36
1,1-Dichloroethene	122	39
1,1-Dichloroethane	126	35
trans-1,2-Trichloroethene	109	46
cis-1,2-Dichloroethene	106	22
Chloroform	111	32
1,2-Dichloroethane	117	27
2-Butanone	INT[d]	
1,1,1-Trichloroethane	106	30
Carbon tetrachloride	83	34
Vinyl acetate	INT[d]	
Bromodichloromethane	97	22
1,1,2,2-Tetrachloroethane	67	20
1,2-Dichloropropane	117	23
trans-1,3-Dichloropropene	92	22
Trichloroethene	98	31
Dibromochloromethane	71	19
1,1,2-Trichloroethane	92	20
Benzene	129	35
cis-1,3-Dichloropropene	102	24
Bromoform	58	19
2-Hexanone	INT[d]	
4-Methyl-2-pentanone	113	37
Tetrachloroethene	66	20
Toluene	CONT[c]	
Chlorobenzene	65	19
Ethylbenzene	74	19
Styrene	57	14
p-Xylene	46	13
o-Xylene	83	20

TABLE 21 (cont.)

Compound	Efficiency Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	115	27
Toluene-d_8	88	24
Bromofluorobenzene	52	15

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicate 10-g aliquots of fish spiked at 25 ppb were analyzed using GC/MS external standard quantitation. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards were replicated and results reflect 1 sigma propagated standard deviation.

[b] No analyses.

[c] Contamination of sample matrix by analyte prevented accurate assessment of analyte efficiency.

[d] Interfering by co-eluting compounds prevented accurate measurement of analyte.

TABLE 22

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	7.8	7.3
Bromomethane	9.7	9.8
Vinyl chloride	9.5	9.4
Chloroethane	9.2	10.0
Methylene chloride	CONT[b]	CONT[b]
Acetone	CONT[b]	CONT[b]
Carbon disulfide	5.4	4.9
1,1-Dichloroethene	4.0	5.7
1,1-Dichloroethane	4.0	3.5
trans-1,2-Dichloroethene	4.4	4.0
cis-1,2-Dichloroethene	4.7	4.1
Chloroform	5.6	5.0
1,2-Dichloroethane	3.3	3.2
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	1.1	4.2
Carbon tetrachloride	3.2	3.5
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	3.2	2.8
1,1,2,2-Tetrachloroethane	4.4	3.8
1,2-Dichloropropane	3.8	3.7
trans-1,3-Dichloropropene	3.4	3.0
Trichloroethene	3.1	4.0
Dibromochloromethane	3.5	3.2
1,1,2-Trichloroethane	4.4	3.3
Benzene	3.6	3.2
cis-1,3-Dichloropropene	3.5	3.0
Bromoform	4.9	4.0
2-Hexanone	7.7	8.0
4-Methyl-2-pentanone	7.5	8.0
Tetrachloroethene	4.3	4.0
Toluene	3.0	2.5
Chlorobenzene	3.3	2.8
Ethylbenzene	3.6	3.5
Styrene	3.5	3.3
p-Xylene	3.7	3.5
o-Xylene	3.3	4.7

Footnotes are on the following page.

[a] Values shown are the average MDLs for studies on three non-consecutive days, involving seven replicate analyses of 10 g of fish tissue spiked a 5 ppb. Daily MDLs were calculated as three times the standard deviation. Quantitation was performed by GC/MS Method 8260 and separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] Contamination of sample by analyte prevented determination.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 23

VOLATILE ORGANIC ANALYTES RECOVERY FOR WATER
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Chloromethane	114	27	116	29	176	67
Bromomethane	131	14	121	14	113	21
Vinyl chloride	131	13	120	16	116	23
Chloroethane	110	15	99	8	96	16
Methylene chloride	87	16	105	15	77	6
Acetone	83	22	65	34	119	68
Carbon disulfide	138	17	133	23	99	47
1,1-Dichloroethene	105	11	89	4	96	18
1,1-Dichloroethane	118	10	119	11	103	25
trans-1,2-Dichloroethene	105	11	107	14	96	18
cis-1,2-Dichloroethene	106	7	99	5	104	23
Chloroform	114	6	104	8	107	21
1,2-Dichloroethane	104	6	109	8	144	19
2-Butanone	83	50	106	31	INT[c]	
1,1,1-Trichloroethane	118	9	109	9	113	23
Carbon tetrachloride	102	6	108	12	109	27
Vinyl acetate	90	16	99	7	72	36
Bromodichloromethane	104	3	110	5	99	5
1,1,2,2-Tetrachloroethane	85	17	81	7	111	43
1,2-Dichloropropane	100	6	103	2	104	7
trans-1,3-Dichloropropene	105	8	105	4	92	4
Trichloroethene	98	4	99	2	95	5
Dibromochloroethane	99	8	99	6	90	25
1,1,2-Trichloroethane	98	7	100	4	76	12
Benzene	97	4	100	5	112	10
cis-1,3-Dichloropropene	106	5	105	4	98	3
Bromoform	93	16	94	8	57	21
2-Hexanone	60	17	63	16	78	23
4-Methyl-2-pentanone	79	24	63	14	68	15
Tetrachloroethene	101	3	97	7	77	14
Toluene	100	6	97	8	85	5
Chlorobenzene	98	6	98	4	88	16
Ethylbenzene	100	3	92	8	73	13
Styrene	98	4	97	9	88	16
p-Xylene	96	4	94	8	60	12
o-Xylene	96	7	95	6	72	14

TABLE 23 (cont.)

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	104	6	109	6	144	19
Toluene-d_8	104	5	102	2	76	7
Bromofluorobenzene	106	6	106	9	40	8

[a] Results are for 10 min. distillation times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision values reflect the propagated errors. Concentrations of analytes were 50 ppb for 5-mL samples and 25 ppb for 20-mL samples. Recovery data generated with comparison to analyses of standards without the water matrix.

[b] Sample contained 1 gram cod liver oil and 20 mL water. An emulsion was created by adding 0.2 mL of water saturated with lecithin.

[c] Interference by co-eluting compounds prevented accurate assessment of recovery.

TABLE 24

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
USING VACUUM DISTILLATION (METHOD 5032) (INTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.2	8.0	7.3	N/A[f]
Bromomethane	2.8	4.9	9.8	N/A[f]
Vinyl chloride	3.5	6.0	9.4	N/A[f]
Chloroethane	5.9	6.0	10.0	N/A[f]
Methylene chloride	3.1	4.0	CONT[g]	0.05
Acetone	5.6	CONT[g]	CONT[g]	0.06
Carbon disulfide	2.5	2.0	4.9	0.18
1,1-Dichloroethene	2.9	3.2	5.7	0.18
1,1-Dichloroethane	2.2	2.0	3.5	0.14
trans-1,2-Dichloroethene	2.2	1.4	4.0	0.10
cis-1,2-Dichloroethene	2.0	2.3	4.1	0.07
Chloroform	2.4	1.8	5.0	0.07
1,2-Dichloroethane	1.7	1.5	3.2	0.06
2-Butanone	7.4	INT[h]	INT[h]	INT[h]
1,1,1-Trichloroethane	1.8	1.7	4.2	0.10
Carbon tetrachloride	1.4	1.5	3.5	0.13
Vinyl acetate	11.8	INT[h]	INT[h]	INT[h]
Bromodichloromethane	1.6	1.4	2.8	0.06
1,1,2,2-Tetrachloroethane	2.5	2.1	3.8	0.02
1,2-Dichloropropane	2.2	2.1	3.7	0.15
trans-1,3-Dichloropropene	1.5	1.7	3.0	0.05
Trichloroethene	1.6	1.7	4.0	0.04
Dibromochloromethane	1.7	1.5	3.2	0.07
1,1,2-Trichloroethane	2.1	1.7	3.3	0.05
Benzene	0.5	1.5	3.2	0.05
cis-1,3-Dichloropropene	1.4	1.7	3.0	0.04
Bromoform	1.8	1.5	4.0	0.05
2-Hexanone	4.6	3.6	8.0	INT[h]
4-Methyl-2-pentanone	3.5	4.6	8.0	INT[h]
Tetrachloroethene	1.4	1.6	4.0	0.10
Toluene	1.0	3.3	2.5	0.05
Chlorobenzene	1.4	1.4	2.8	0.06
Ethylbenzene	1.5	2.8	3.5	0.04
Styrene	1.4	1.4	3.3	0.18
p-Xylene	1.5	2.9	3.5	0.20
o-Xylene	1.7	3.4	4.7	0.07

Footnotes are found on the following page.

[a] Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Method detection limits are the average MDLs for studies on three non-consecutive days.

[b] Method detection limits are the average MDLs for studies of three non-consecutive days. Daily studies were seven replicated analyses of 5 mL aliquots of 4 ppb soil. Daily MDLs were three times the standard deviation.

[c] Daily studies were seven replicated analyses of 10 g fish tissue spiked at 5 ppb. Daily MDLs were three times the standard deviation. Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[d] Method detection limits are estimated analyzing 1 g of cod liver oil samples spiked at 250 ppm. Five replicates were analyzed using Method 8260.

[e] No analyses.

[f] Contamination of sample by analyte prevented determination.

[g] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 25

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
(METHOD 5032) (EXTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.1	8.6[f]	7.8	N/A[g]
Bromomethane	2.5	4.9[f]	9.7	N/A[g]
Vinyl chloride	4.0	7.1[f]	9.5	N/A[g]
Chloroethane	6.1	7.5[f]	9.2	N/A[g]
Methylene chloride	3.1	3.3	CONT[h]	0.08
Acetone	33.0[f]	CONT[h]	CONT[h]	0.12
Carbon disulfide	2.5	3.2	5.4	0.19
1,1-Dichloroethene	3.4	3.8	4.0	0.19
1,1-Dichloroethane	2.3	1.7	4.0	0.13
trans-1,2-Dichloroethene	3.0	3.2	4.4	0.09
cis-1,2-Dichloroethene	2.4	2.7	4.7	0.08
Chloroform	2.7	2.6	5.6	0.06
1,2-Dichloroethane	1.6	1.7	3.3	0.06
2-Butanone	57.0[f]	INT[i]	INT[i]	INT[i]
1,1,1-Trichloroethane	1.6	2.4	1.1	0.08
Carbon tetrachloride	1.5	1.7	3.2	0.15
Vinyl acetate	23.0[f]	INT[i]	INT[i]	INT[i]
Bromodichloromethane	2.0	2.3	3.2	0.05
1,1,2,2-Tetrachloroethane	3.6	3.2	4.4	0.09
1,2-Dichloropropane	2.9	3.7	3.8	0.12
trans-1,3-Dichloropropene	2.3	2.4	3.8	0.08
Trichloroethene	2.5	3.0	3.1	0.06
Dibromochloromethane	2.1	2.9	3.5	0.04
1,1,2-Trichloroethane	2.7	2.8	4.4	0.07
Benzene	1.7	2.9	3.6	0.03
cis-1,3-Dichloropropene	2.1	2.5	3.5	0.06
Bromoform	2.3	2.5	4.9	0.10
2-Hexanone	4.6	4.6	7.7	INT[i]
4-Methyl-2-pentanone	3.8	3.9	7.5	INT[i]
Tetrachloroethene	1.8	2.6	4.3	0.12
Toluene	1.8	4.4	3.0	0.09
Chlorobenzene	2.4	2.6	3.3	0.07
Ethylbenzene	2.4	4.1	3.6	0.09
Styrene	2.0	2.5	3.5	0.16
p-Xylene	2.3	3.9	3.7	0.18
o-Xylene	2.4	4.1	3.3	0.08

[a] Method detection limits are the average MDLs for studies on three non-consecutive days. Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb. Daily MDLs were three times the standard deviation.

[b] Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb.

[c] These studies were seven replicate analyses of 5-g aliquots of soil spiked at 4 ppb.

[d] These studies were seven replicate analyses of 10-g aliquots of fish tissue spiked at 5 ppb.

[e] Method detection limits were estimated by analyzing cod liver oil samples spiked at 250 ppb. Five replicates were analyzed using Method 8260.

[f] Method detection limits were estimated by analyzing replicate 50 ppb standards five times over a single day.

[g] No analyses.

[h] Contamination of sample by analyte prevented determination.

[l] Interference by co-eluting compound prevented accurate quantitation.

TABLE 26

VOLATILE ORGANIC ANALYTE RECOVERY FROM OIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Recovery Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	62	32
Acetone	108	55
Carbon disulfide	98	46
1,1-Dichloroethene	97	24
1,1-Dichloroethane	96	22
trans-1,2-Trichloroethene	86	23
cis-1,2-Dichloroethene	99	11
Chloroform	93	14
1,2-Dichloroethane	138	31
2-Butanone	INT[c]	
1,1,1-Trichloroethane	89	14
Carbon tetrachloride	129	23
Vinyl acetate	INT[c]	
Bromodichloromethane	106	14
1,1,2,2-Tetrachloroethane	205	46
1,2-Dichloropropane	107	24
trans-1,3-Dichloropropene	98	13
Trichloroethene	102	8
Dibromochloromethane	168	21
1,1,2-Trichloroethane	95	7
Benzene	146	10
cis-1,3-Dichloropropene	98	11
Bromoform	94	18
2-Hexanone	INT[c]	
4-Methyl-2-pentanone	INT[c]	
Tetrachloroethene	117	22
Toluene	108	8
Chlorobenzene	101	12
Ethylbenzene	96	10
Styrene	120	46
p-Xylene	87	23
o-Xylene	90	10

TABLE 26 (cont.)

Compound	Recovery Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	137	30
Toluene-d_8	84	6
Bromofluorobenzene	48	2

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicates of 10-g fish aliquots spiked at 25 ppb were analyzed. Quantitation was performed with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Standards and samples were replicated and precision value reflects the propagated errors. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Not analyzed.

[c] Interference by co-evaluating compounds prevented accurate measurement of analyte.

TABLE 27

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN OIL (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	N/A[b]	N/A[b]
Bromomethane	N/A[b]	N/A[b]
Vinyl chloride	N/A[b]	N/A[b]
Chloroethane	N/A[b]	N/A[b]
Methylene chloride	80	50
Acetone	120	60
Carbon disulfide	190	180
1,1-Dichloroethene	190	180
1,1-Dichloroethane	130	140
trans-1,2-Dichloroethene	90	100
cis-1,2-Dichloroethene	80	70
Chloroform	60	70
1,2-Dichloroethane	60	60
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	80	100
Carbon tetrachloride	150	130
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	50	60
1,1,2,2-Tetrachloroethane	90	20
1,2-Dichloropropane	120	150
trans-1,3-Dichloropropene	80	50
Trichloroethene	60	40
Dibromochloromethane	40	70
1,1,2-Trichloroethane	70	50
Benzene	30	50
cis-1,3-Dichloropropene	60	40
Bromoform	100	50
2-Hexanone	INT[c]	INT[c]
4-Methyl-2-pentanone	INT[c]	INT[c]
Tetrachloroethene	120	100
Toluene	90	50
Chlorobenzene	70	60
Ethylbenzene	90	40
Styrene	160	180
p-Xylene	180	200
o-Xylene	80	70

[a] Method detection limits are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MDLs were calculated as three times the standard deviation. Quantitation was performed using a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] No analyses.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 28

INTERNAL STANDARDS FOR ANALYTES AND SURROGATES PREPARED USING EQUILIBRIUM HEADSPACE ANALYSIS (METHOD 5021)

Chloroform-d_1	1,1,2-TCA-d_3	Bromobenzene-d_5
Dichlorodifluoromethane	1,1,1-Trichloroethane	Chlorobenzene
Chloromethane	1,1-Dichloropropene	Bromoform
Vinyl chloride	Carbon tetrachloride	Styrene
Bromomethane	Benzene	iso-Propylbenzene
Chloroethane	Dibromomethane	Bromobenzene
Trichlorofluoromethane	1,2-Dichloropropane	n-Propylbenzene
1,1-Dichloroethene	Trichloroethene	2-Chlorotoluene
Methylene chloride	Bromodichloromethane	4-Chlorotoluene
trans-1,2-Dichloroethene	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
1,1-Dichloroethane	trans-1,3-Dichloropropene	tert-Butylbenzene
cis-1,2-Dichloroethene	1,1,2-Trichloroethane	1,2,4-Trimethylbenzene
Bromochloromethane	Toluene	sec-Butylbenzene
Chloroform	1,3-Dichloropropane	1,3-Dichlorobenzene
2,2-Dichloropropane	Dibromochloromethane	1,4-Dichlorobenzene
1,2-Dichloroethane	1,2-Dibromoethane	p-iso-Propyltoluene
	Tetrachloroethene	1,2-Dichlorobenzene
	1,1,2-Trichloroethane	n-Butylbenzene
	Ethylbenzene	1,2-Dibromo-3-chloropropane
	m-Xylene	1,2,4-Trichlorobenzene
	p-Xylene	Naphthalene
	o-Xylene	Hexachlorobutadiene
	1,1,2,2-Tetrachloroethane	1,2,3-Trichlorobenzene
	1,2,3-Trichloropropane	

TABLE 29

PRECISION AND MDL DETERMINED FOR ANALYSIS OF FORTIFIED SAND[a] (METHOD 5021)

Compound	% RSD	MDL (µg/kg)
Benzene	3.0	0.34
Bromochloromethane	3.4	0.27
Bromodichloromethane	2.4	0.21
Bromoform	3.9	0.30
Bromomethane	11.6	1.3
Carbon tetrachloride	3.6	0.32
Chlorobenzene	3.2	0.24
Chloroethane	5.6	0.51
Chloroform	3.1	0.30
Chloromethane	4.1	3.5[b]
1,2-Dibromo-3-chloropropane	5.7	0.40
1,2-Dibromoethane	3.2	0.29
Dibromomethane	2.8	0.20
1,2-Dichlorobenzene	3.3	0.27
1,3-Dichlorobenzene	3.4	0.24
1,4-Dichlorobenzene	3.7	0.30
Dichlorodifluoromethane	3.0	0.28
1,1-Dichloroethane	4.5	0.41
1,2-Dichloroethane	3.0	0.24
1,1-Dichloroethene	3.3	0.28
cis-1,2-Dichloroethene	3.2	0.27
trans-1,2-Dichloroethene	2.6	0.22
1,2-Dichloropropane	2.6	0.21
1,1-Dichloropropene	3.2	0.30
cis-1,3-Dichloropropene	3.4	0.27
Ethylbenzene	4.8	0.47
Hexachlorobutadiene	4.1	0.38
Methylene chloride	8.2	0.62[c]
Naphthalene	16.8	3.4[c]
Styrene	7.9	0.62
1,1,1,2-Tetrachloroethane	3.6	0.27
1,1,2,2-Tetrachloroethane	2.6	0.20
Tetrachloroethene	9.8	1.2[c]
Toluene	3.5	0.38
1,2,4-Trichlorobenzene	4.2	0.44
1,1,1-Trichloroethane	2.7	0.27
1,1,2-Trichloroethane	2.6	0.20
Trichloroethene	2.3	0.19

TABLE 29 (cont.)

Compound	% RSD	MDL (µg/kg)
Trichlorofluoromethane	2.7	0.31
1,2,3-Trichloropropane	1.5	0.11
Vinyl chloride	4.8	0.45
m-Xylene/p-Xylene	3.6	0.37
o-Xylene	3.6	0.33

[a] Most compounds spiked at 2 ng/g (2 µg/kg)
[b] Incorrect ionization due to methanol
[c] Compound detected in unfortified sand at >1 ng

TABLE 30

RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5021)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Benzene	37.6	35.2	38.4	37.1	3.7	185[a]
Bromochloromethane	20.5	19.4	20.0	20.0	2.3	100
Bromodichloromethane	21.1	20.3	22.8	21.4	4.9	107
Bromoform	23.8	23.9	25.1	24.3	2.4	121
Bromomethane	21.4	19.5	19.7	20.2	4.2	101
Carbon tetrachloride	27.5	26.6	28.6	27.6	3.0	138
Chlorobenzene	25.6	25.4	26.4	25.8	1.7	129
Chloroethane	25.0	24.4	25.3	24.9	1.5	125
Chloroform	21.9	20.9	21.7	21.5	2.0	108
Chloromethane	21.0	19.9	21.3	20.7	2.9	104[a]
1,2-Dibromo-3-chloro-propane	20.8	20.8	21.0	20.9	0.5	104
1,2-Dibromoethane	20.1	19.5	20.6	20.1	2.2	100
Dibromomethane	22.2	21.0	22.8	22.0	3.4	110
1,2-Dichlorobenzene	18.0	17.7	17.1	17.6	2.1	88.0
1,3-Dichlorobenzene	21.2	21.0	20.1	20.8	2.3	104
1,4-Dichlorobenzene	20.1	20.9	19.9	20.3	2.1	102
Dichlorodifluoromethane	25.3	24.1	25.4	24.9	2.4	125
1,1-Dichloroethane	23.0	22.0	22.7	22.6	1.9	113
1,2-Dichloroethane	20.6	19.5	19.8	20.0	2.3	100
1,1-Dichloroethene	24.8	23.8	24.4	24.3	1.7	122
cis-1,2-Dichloroethene	21.6	20.0	21.6	21.1	3.6	105
trans-1,2-Dichloroethene	22.4	21.4	22.2	22.0	2.0	110
1,2-Dichloropropane	22.8	22.2	23.4	22.8	2.1	114
1,1-Dichloropropene	26.3	25.7	28.0	26.7	3.7	133
cis-1,3-Dichloropropene	20.3	19.5	21.1	20.3	3.2	102
Ethylbenzene	24.7	24.5	25.5	24.9	1.7	125
Hexachlorobutadiene	23.0	25.3	25.2	24.5	4.3	123
Methylene chloride	26.0	25.7	26.1	25.9	0.7	130[a]
Naphthalene	13.8	12.7	11.8	12.8	6.4	63.8[a]
Styrene	24.2	23.3	23.3	23.6	1.8	118
1,1,1,2-Tetrachloroethane	21.4	20.2	21.3	21.0	2.6	105
1,1,2,2-Tetrachloroethane	18.6	17.8	19.0	18.5	2.7	92.3
Tetrachloroethene	25.2	24.8	26.4	25.5	2.7	127
Toluene	28.6	27.9	30.9	29.1	4.4	146[a]
1,2,4-Trichlorobenzene	15.0	14.4	12.9	14.1	6.3	70.5
1,1,1-Trichloroethane	28.1	27.2	29.9	28.4	4.0	142
1,1,2-Trichloroethane	20.8	19.6	21.7	20.7	4.2	104

TABLE 30 (cont.)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Trichloroethene	26.3	24.9	26.8	26.0	3.1	130
Trichlorofluoromethane	25.9	24.8	26.5	25.7	2.7	129
1,2,3-Trichloropropane	18.8	18.3	19.3	18.8	2.2	94.0
Vinyl chloride	24.8	23.2	23.9	24.0	2.7	120
m-Xylene/p-Xylene	24.3	23.9	25.3	24.5	2.4	123
o-Xylene	23.1	22.3	23.4	22.9	2.0	115

[a] Compound found in unfortified garden soil matrix at >5 ng.

TABLE 31

METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)[a]

Compound	Detection Limit (ng)	Boiling Point (°C)
Chloromethane	58	-24
Bromomethane	26	4
Vinyl chloride	14	-13
Chloroethane	21	13
Methylene chloride	9	40
Acetone	35	56
Carbon disulfide	11	46
1,1-Dichloroethene	14	32
1,1-Dichloroethane	12	57
trans-1,2-Dichloroethene	11	48
Chloroform	11	62
1,2-Dichloroethane	13	83
1,1,1-Trichloroethane	8	74
Carbon tetrachloride	8	77
Bromodichloromethane	11	88
1,1,2,2-Tetrachloroethane**	23	146
1,2-Dichloropropane	12	95
trans-1,3-Dichloropropene	17	112
Trichloroethene	11	87
Dibromochloromethane	21	122
1,1,2-Trichloroethane	26	114
Benzene	26	80
cis-1,3-Dichloropropene	27	112
Bromoform**	26	150
Tetrachloroethene	11	121
Toluene	15	111
Chlorobenzene	15	132
Ethylbenzene**	21	136
Styrene**	46	145
Trichlorofluoromethane	17	24
Iodomethane	9	43
Acrylonitrile	13	78
Dibromomethane	14	97
1,2,3-Trichloropropane**	37	157
total Xylenes**	22	138-144

Footnotes are found on the following page.

* The method detection limit (MDL) is defined in Chapter One. The detection limits cited above were determined according to 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Boiling Point greater than 130°C. Not appropriate for quantitative sampling by Method 0030.

TABLE 32

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (METHOD 5041)

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrylonitrile	Bromodichloromethane
Bromomethane	Bromoform
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	Dibromomethane
Chloromethane	1,2-Dichloropropane
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane	trans-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	1,1,1-Trichloroethane
1,1-Dichloroethene	1,1,2-Trichloroethane
Trichloroethene	
trans-1,2-Dichloroethene	
Iodomethane	
Methylene chloride	
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
4-Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylenes

TABLE 33

METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

Compound	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Detection Limit[a] (ppm)
Dichlorodifluoromethane	-30	Gas	0.20
Vinyl chloride	-19	Gas	0.11
1,3-Butadiene	-4	Gas	0.90
1,2-Dichloro-1,1,2,2-tetrafluoroethane	4	Gas	0.14
Methyl bromide	4	Gas	0.14
Trichlorofluoromethane	24	88	0.18
1,1-Dichloroethene	31	22	0.07
Methylene chloride	40	44	0.05
1,1,2-Trichloro-trifluoroethane	48	37	0.13
Chloroform	61	21	0.04
1,1,1-Trichloroethane	75	13	0.03
Carbon tetrachloride	77	11	0.03
Benzene	80	10	0.16
Trichloroethene	87	8	0.04
1,2-Dichloropropane	96	5	0.05
Toluene	111	3	0.08
Tetrachloroethene	121	2	0.03

[a] Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS

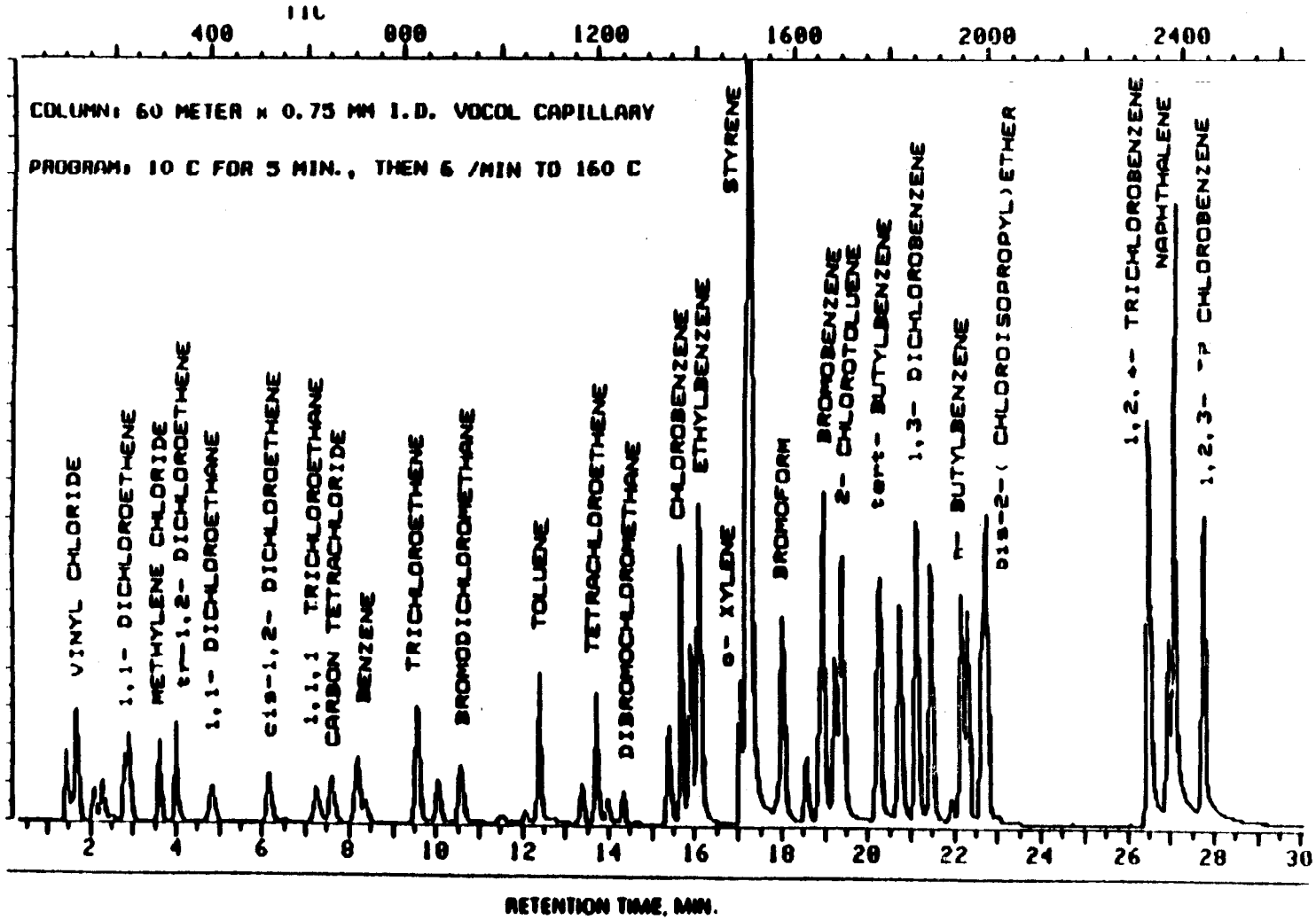


FIGURE 2
GAS CHROMATOGRAM OF VOLATILE ORGANICS

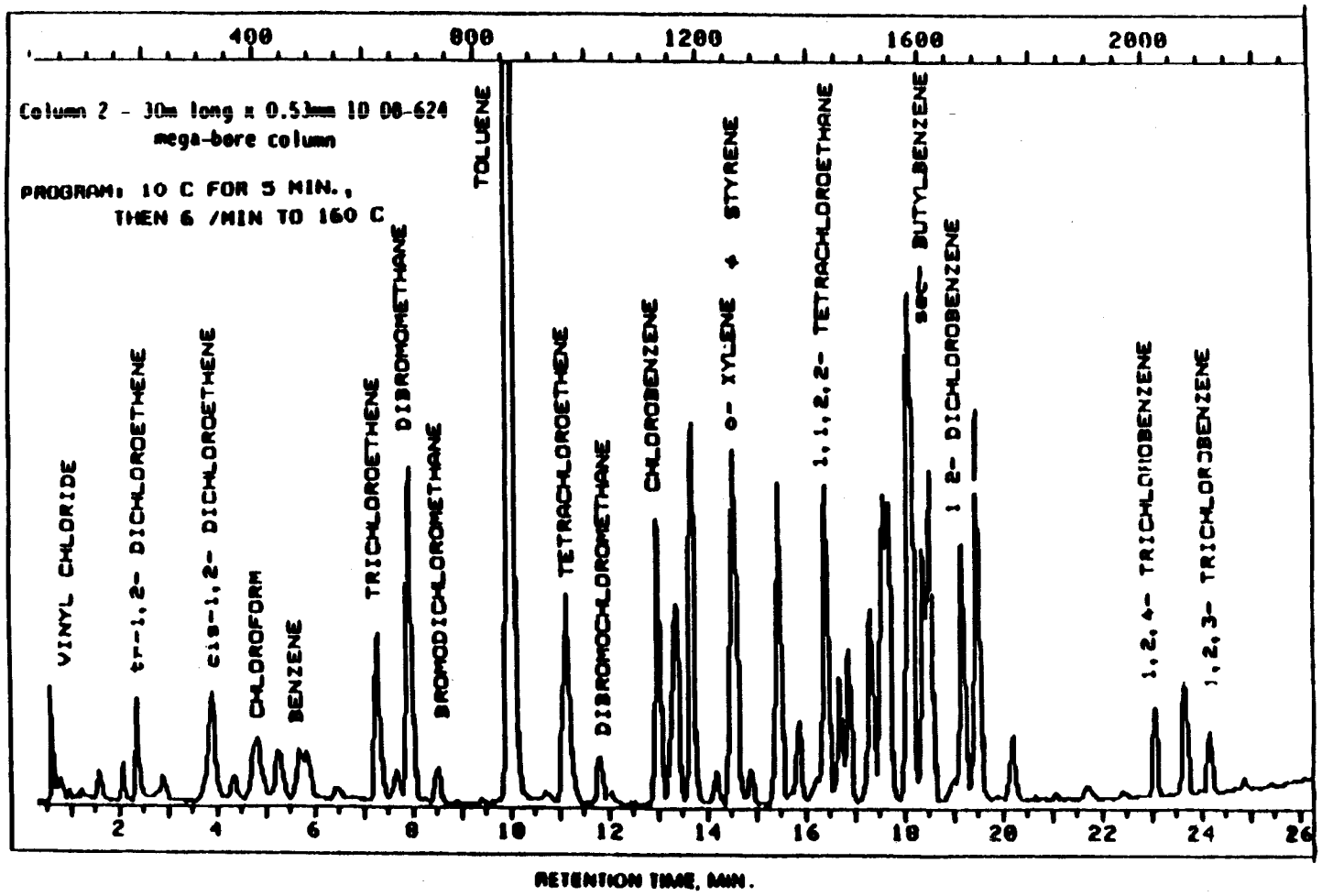


FIGURE 3
GAS CHROMATOGRAM OF VOLATILE ORGANICS

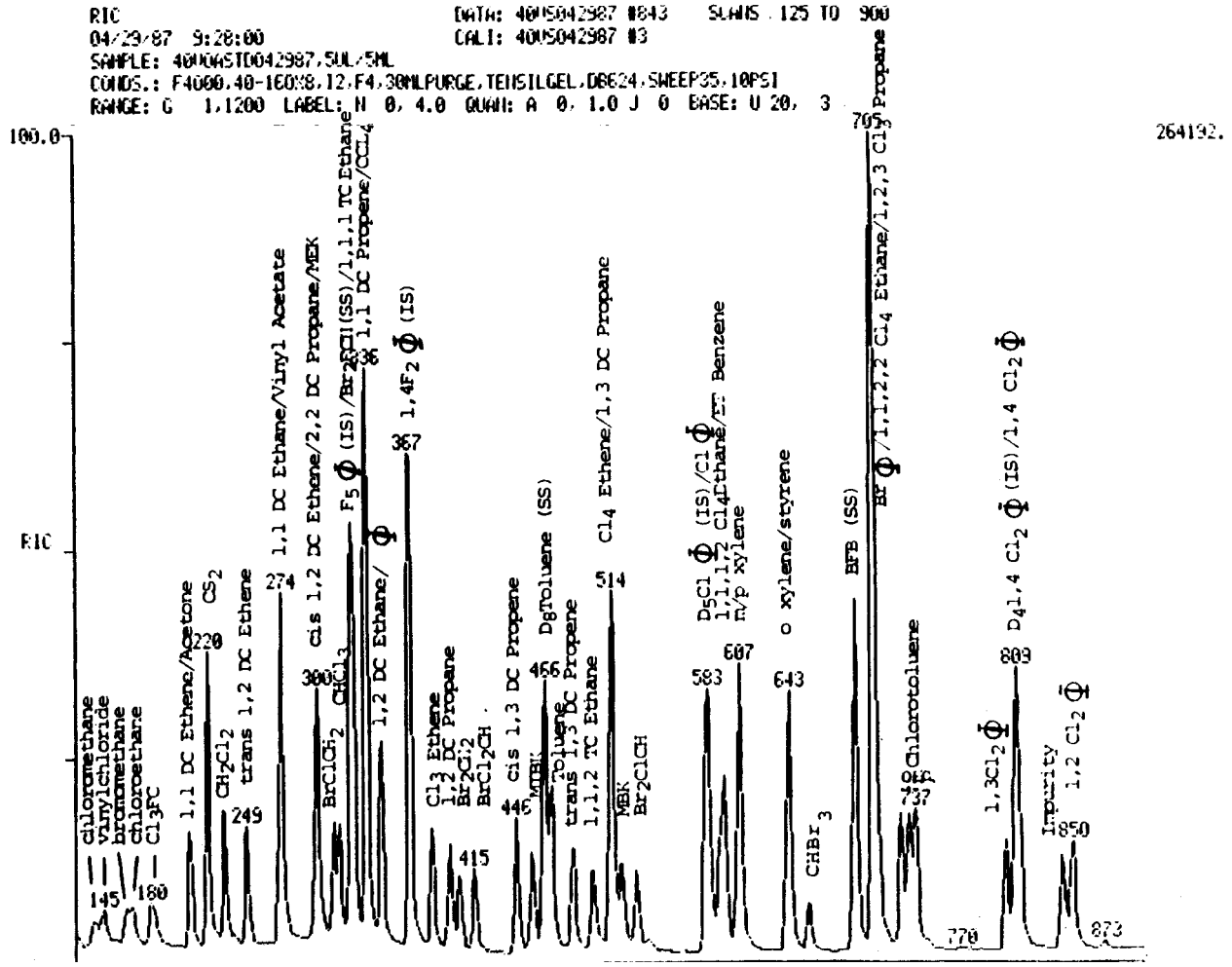
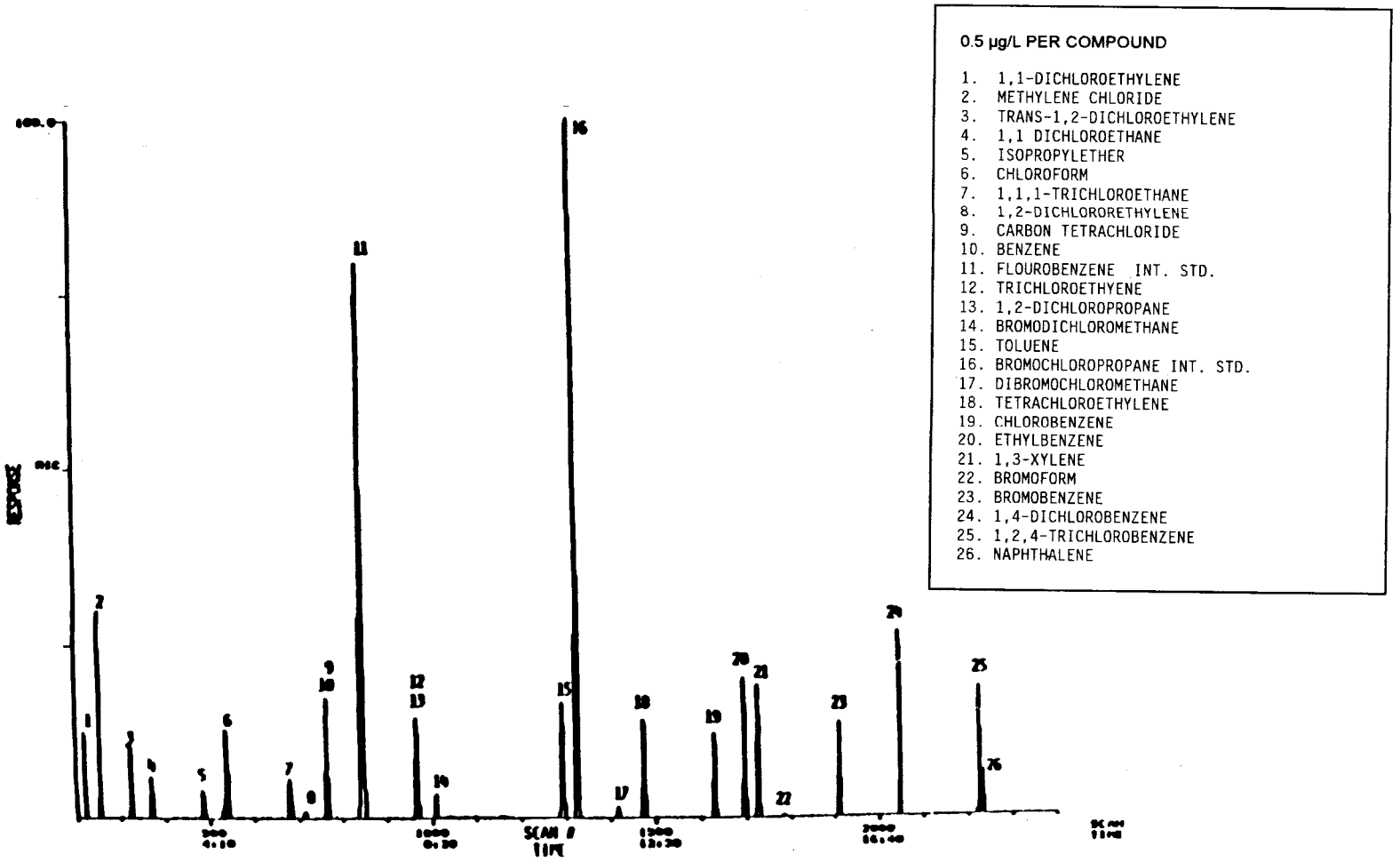
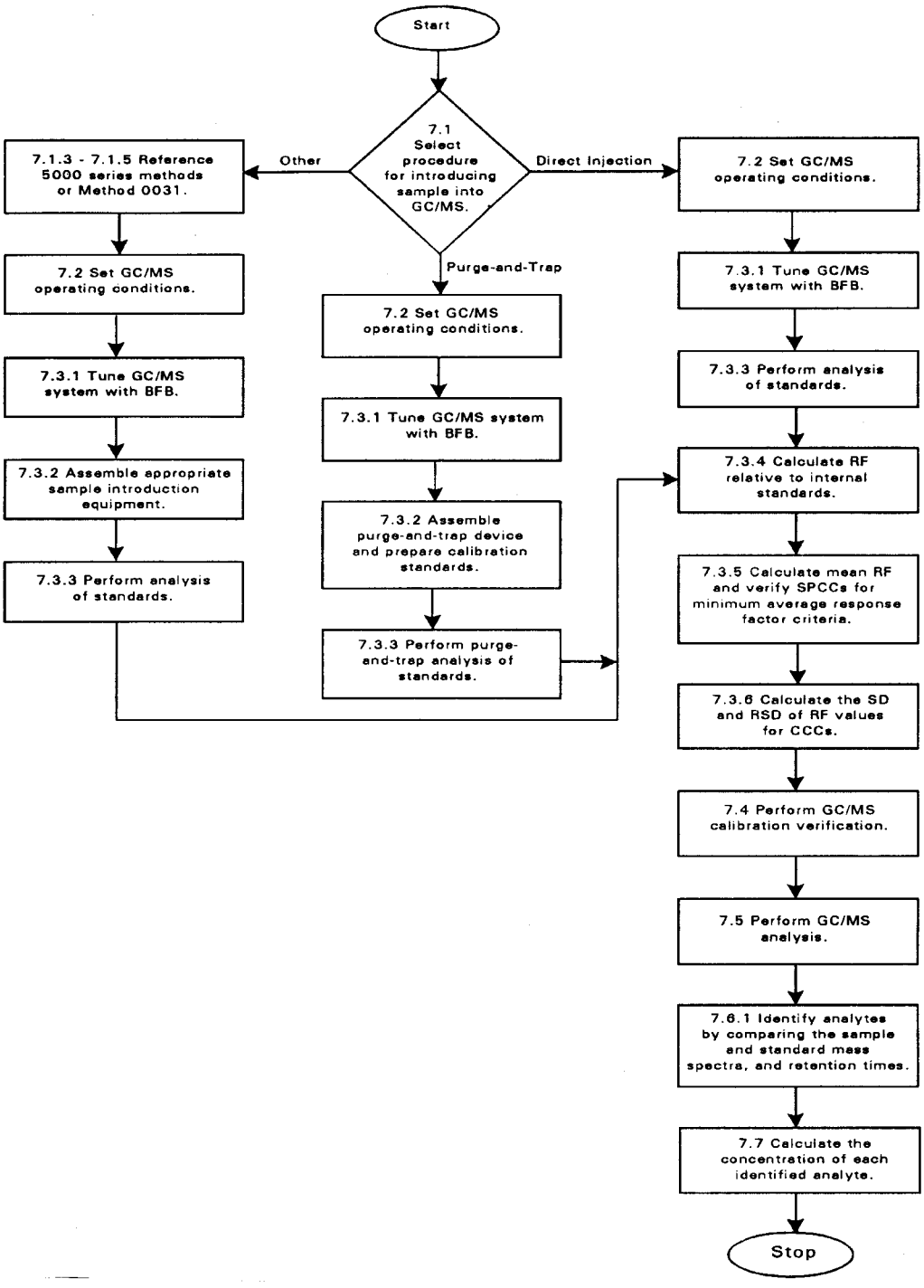


FIGURE 4
GAS CHROMATOGRAM OF TEST MIXTURE




Start
7.1 Select procedure for introducing sample into GC/MS.
Other
Purge-and-Trap
Direct Injection
7.1.3 - 7.1.5 Reference 5000 series methods or Method 0031.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble appropriate sample introduction equipment.
7.3.3 Perform analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble purge-and-trap device and prepare calibration standards.
7.3.3 Perform purge-and-trap analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.3 Perform analysis of standards.
7.3.4 Calculate RF relative to internal standards.
7.3.5 Calculate mean RF and verify SPCCs for minimum average response factor criteria.
7.3.6 Calculate the SD and RSD of RF values for CCCs.
7.4 Perform GC/MS calibration verification.
7.5 Perform GC/MS analysis.
7.6.1 Identify analytes by comparing the sample and standard mass spectra, and retention times.
7.7 Calculate the concentration of each identified analyte.
Stop

METHOD 5035

CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

1.2 The low soil method utilizes a hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 0.5 to 200 µg/kg range.

1.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

1.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030..

1.5 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency.

1.6 Method 5035, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5035 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Method 8021 in series with Method 8015.

1.7 As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.8 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 6.2.2).

1.9 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to and soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains 5 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent.

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol or polyethylene glycol (PEG), a separate aliquot of the sample is spiked with surrogates and diluted in the appropriate solvent. An aliquot of the solution is added to 5 mL of reagent water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) are added to the solution which is then purged using Method 5030 and analyzed by an appropriate determinative method.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other

systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 4.2.2).

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the Disclaimer at the front of this manual for guidance on the use of alternative equipment.

4.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed, it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all the target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocarb 4000), as some degradation has been noted when higher desorption temperatures (especially above 240 - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 The trap used to develop this method was 25 cm long, with an inside diameter of 0.105 inches, and was packed with Carbopack/Carbosieve (Supelco, Inc.).

4.2.2.2 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If

the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

4.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.2.2.2.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.2.2.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.3 Syringe and Syringe Valves

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25-µL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10-, 100-µL.

4.3.5 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

4.4 Miscellaneous

4.4.1 Glass vials

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance - Capable of accurately weighing to 0.01 g.

4.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground-glass stoppers.

4.4.5 2-mL glass vials, for GC autosampler - Used for oily waste samples extracted with methanol or PEG.

4.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

4.5 Field Sampling Equipment

4.5.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.5.2 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.3 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

4.5.4 Portable balance - For field use, capable of weighing to 0.01 g.

4.5.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH_3OH - purge-and-trap quality or equivalent. Store away from other solvents.

5.3 Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$ - free of interferences at the detection limit of the target analytes.

5.4 Low concentration sample preservative

5.4.1 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

5.4.2 The preservative should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

5.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of ≤ 2.

6.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

6.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the

laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

6.1.2 High concentration soil samples collected without a preservative

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60-mL glass vials with septum seals (see Sec. 4.4).

6.1.3 High concentration soil samples collected and preserved in the field

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.3.1 Add 10 mL of methanol to each vial.

6.1.3.2 Seal the vial with the screw-cap and septum seal.

6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

NOTE: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

6.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the sample after it is returned to the laboratory and prior to analysis.

6.1.4 Oily waste samples

When oily waste samples are known to be soluble in methanol or PEG, sample vials may be prepared as described in Sec. 6.1.3, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 6.1.2.

6.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler ™, and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.2.1 Low concentration soil samples

6.2.1.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

NOTE: Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials that do not contain the preservative solution.

6.2.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

6.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60-mL glass vial or a third 40-mL soil sample vial. However, this third vial must *not* contain the sample preservative solution, as an aliquot will be used to determine dry weight. If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

6.2.1.7 If samples are known or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2 g instead of the 5 g collected in Sec. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

6.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 6.2.2).

6.2.2 High concentration soil samples preserved in the field

The collection of soil samples in vials that contain methanol has been suggested by some as a combined preservation and extraction procedure. However, this procedure is not appropriate for use with the low concentration soil procedure described in this method.

NOTE: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of two potential problems. First, the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure (0.5-200 µg/kg). The exact dilution factor will depend on the masses of solvent and sample, but generally exceeds 1000, and may make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes. Because the analytes of interest are volatile, the methanol extract cannot be concentrated to overcome the dilution problem. Thus, for samples of unknown composition, it may still be necessary to collect an aliquot for analysis by this closed-system procedure and another aliquot preserved in methanol and analyzed by other procedures. The second problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste.

6.2.2.1 When samples are known to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

6.2.2.2 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.2.3 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

6.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight, as described in Sec. 6.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

6.2.3 High concentration soil sample not preserved in the field

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

6.2.4 Oily waste samples

The collection procedures for oily samples depend on knowledge of the waste and its solubility in methanol or other solvents.

6.2.4.1 When an oily waste is known to be soluble in methanol or PEG, the sample may be collected in a vial containing such a solvent (see Sec. 6.1.4), using procedures similar to those described in Sec. 6.2.2.

6.2.4.2 When the solubility of the oily waste is not known, the sample should either be collected in a vial without a preservative, as described in Sec. 6.2.3, or the solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in Sec. 6.2.2. Otherwise, collect an unpreserved sample as described in Sec. 6.2.3.

6.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

6.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at -10°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel. See Sec. 6.2.1.2 for additional information.

7.0 PROCEDURE

This section describes procedures for sample screening, the low concentration soil method, the high concentration soil method, and the procedure for oily waste samples. High concentration samples are to be introduced into the GC system using Method 5030. Oily waste samples are to be introduced into the GC system using Method 5030 if they are soluble in a water-miscible solvent, or using Method 3585 if they are not.

7.1 Sample screening

7.1.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system**,** thereby requiring extensive cleanup and instrument maintenance. The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low concentration closed-system direct purge-and-trap method (Sec. 7.2), the high concentration (methanol extraction) method (Sec. 7.3), or the nonaqueous liquid (oily waste) methanol or PEG dilution procedure (Sec. 7.4).

7.1.2 The analyst may employ any appropriate screening technique. Two suggested screening techniques employing SW-846 methods are:

7.1.2.1 Automated headspace (Method 5021) using a gas chromatograph (GC) equipped with a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series, or,

7.1.2.2 Extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC equipped with a FID and/or an ECD.

7.1.3 The analyst may inject a calibration standard containing the analytes of interest at a concentration equivalent to the upper limit of the calibration range of the low concentration soil method. The results from this standard may be used to determine when the screening results approach the upper limit of the low concentration soil method. There are no linearity or other performance criteria associated with the injection of such a standard, and other approaches may be employed to estimate sample concentrations.

7.1.4 Use the low concentration closed-system purge-and-trap method (Sec. 7.2) if the estimated concentration from the screening procedure falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range of the low concentration soil method, then use either the high concentration soil method (Sec. 7.3), or the oily waste method (Sec. 7.4).

7.2 Low concentration soil method (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.2.1 Initial calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.2.1.2 Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing with an inert gas flow of at least 20 mL/minute. If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.3 If the standard trap in Sec. 4.2.2.2 is employed, prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min, or according to the manufacturer's recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.4 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

7.2.1.5 Prepare a minimum of five initial calibration standards containing all the analytes of interest and surrogates, as described in Method 8000, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL added to the vial before shipping it to the field plus the organic-free reagent water added by the instrument). The calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (e.g., ~1 g), as the presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same fashion as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the surrogates using standards at five concentrations, it may be necessary to disable the automatic addition of surrogates to each vial containing a calibration standard (consult the manufacturer's instructions). Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as recommended by the manufacturer.

7.2.1.6 Carry out the purge-and-trap procedure as outlined in Secs. 7.2.3. to 7.2.5.

7.2.1.7 Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.

7.2.1.8 For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.8.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.2.1.8.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.8.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.9 When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross-contamination and memory effects from a high concentration sample or even the standard are a common problem.

Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification

Refer to Method 8000 for details on calibration verification. A single standard near the mid-point of calibration range is used for verification. This standard should also contain approximately 1 g of sodium bisulfate.

7.2.3 Sample purge-and-trap

This method is designed for a 5-g sample size, but smaller sample sizes may be used. Consult the instrument manufacturer's instructions regarding larger sample sizes, in order to avoid clogging of the purging apparatus. The soil vial is hermetically sealed at the sampling site, and MUST remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01 g, even if the sample weight was determined in the field, and record this weight. This second weighing provides a check on the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant discrepancies between the field and laboratory weights.

7.2.3.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

7.2.3.2 Without disturbing the hermetic seal on the sample vial, add 5 mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

7.2.3.3 For the sample selected for matrix spiking, add the matrix spiking solution described in Sec. 5.0 of Method 5000, either manually, or automatically, following the manufacturer's instructions. The concentration of the spiking solution and the amount added should be established as described in Sec. 8.0 of Method 8000.

7.2.3.4 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

7.2.4 Sample Desorption

7.2.4.1 Non-cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow

of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes (1.5 min is normally adequate for analytes in Method 8015). Begin the temperature program of the gas chromatograph and start data acquisition.

7.2.4.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 245°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Methods 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.5 Trap Reconditioning

After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

7.2.6 Data Interpretation

Perform qualitative and quantitative analysis following the guidance given in the determinative method and Method 8000. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. Such reanalyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method. Alternatively, if a sample aliquot of 1-2 g was also collected (see Sec. 6.2.1.7), it may be practical to analyze that aliquot for the analytes that exceeded the instrument calibration range in the 5-g analysis. If results are to be reported on a dry weight basis, proceed to Sec. 7.5

7.3 High concentration method for soil samples with concentrations generally greater than 200 µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free reagent water containing surrogates and, if applicable, internal and matrix spiking standards, purged according to Method 5030, and analyzed by an appropriate determinative method. Wastes that are insoluble in methanol (i.e., petroleum and coke wastes) are diluted with hexadecane (see Sec. 7.3.8).

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were <u>not</u> preserved in the field are prepared using the steps below, beginning at Sec. 7.3.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.3.4.

7.3.1 When the high concentration sample is <u>not</u> preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Whenever practical, mix the contents of the sample container by shaking or other mechanical means without opening the vial. When shaking is not practical, quickly mix the contents of the vial with a narrow metal spatula and immediately reseal the vial.

7.3.2 If the sample is from an unknown source, perform a solubility test before proceeding. Remove several grams of material from the sample container. Quickly reseal the container to minimize the loss of volatiles. Weigh 1-g aliquots of the sample into several test tubes or other suitable containers. Add 10 mL of methanol to the first tube, 10 mL of PEG to the second, and 10 mL of hexadecane to the third. Swirl the sample and determine if it is soluble in the solvent. Once the solubility has been evaluated, discard these test solutions. If the sample is soluble in either methanol or PEG, proceed with Sec. 7.3.3. If the sample is only soluble in hexadecane, proceed with Sec. 7.3.8.

7.3.3 For soil and solid waste samples that are soluble in methanol, add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution to a tared 20-mL vial. Using a top-loading balance, weigh 5 g (wet weight) of sample into the vial. Quickly cap the vial and reweigh the vial. Record the weight to 0.1 g. Shake the vial for 2 min. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0 mL of PEG in place of the methanol. Proceed with Sec. 7.3.5.

NOTE: The steps in Secs. 7.3.1, 7.3.2, and 7.3.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.4 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 6.2.2), weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum, shake for 2 min, as described above, and proceed with Sec. 7.3.5.

7.3.5 Pipet approximately 1 mL of the extract from either Sec. 7.3.3 or 7.3.4 into a GC vial for storage, using a disposable pipet, and seal the vial. The remainder of the extract may be discarded. Add approximately 1 mL of methanol or PEG to a separate GC vial for use as the method blank for each set of samples extracted with the same solvent.

7.3.6 The extracts must be stored at 4°C in the dark, prior to analysis. Add an appropriate aliquot of the extract (see Table 2) to 5.0 mL of organic-free reagent water and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging high concentration samples.

7.3.7 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the procedure in Sec. 7.5, after the sample extract has been transferred to a GC vial and the vial sealed.

7.3.8 For solids that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste) dilute or extract the sample with hexadecane using the procedures in Sec. 7.0 of Method 3585.

7.4 High concentration method for oily waste samples

This procedure for the analysis of oily waste samples involves the dilution of the sample in methanol or PEG. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. A portion of the diluted sample is then added to 5.0 mL of organic-free reagent water, purged according to Method 5030, and analyzed using an appropriate determinative method.

For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with hexadecane using the procedures in Sec. 7.0 of Method 3585.

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.4.1. If methanol preservation was employed in the field, then the preparation begins with Sec. 7.4.3.

7.4.1 If the waste was not preserved in the field and it is soluble in methanol or PEG, weigh 1 g (wet weight) of the sample into a tared 10-mL volumetric flask, a tared scintillation vial, or a tared culture tube. If a vial or tube is used instead of a volumetric flask, it must be calibrated prior to use. This operation must be performed prior to opening the sample vial and weighing out the aliquot for analysis.

7.4.1.1 To calibrate the vessel, pipet 10.0 mL of methanol or PEG into the vial or tube and mark the bottom of the meniscus.

7.4.1.2 Discard this solvent, and proceed with weighing out the 1-g sample aliquot.

7.4.2 Quickly add 1.0 mL of surrogate spiking solution to the flask, vial, or tube, and dilute to 10.0 mL with the appropriate solvent (methanol or PEG). Swirl the vial to mix the contents and then shake vigorously for 2 minutes.

7.4.3 If the sample was collected in the field in a vial containing methanol or PEG, weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum. Swirl the vial to mix the contents and then shake vigorously for 2 minutes and proceed with Sec. 7.4.4.

7.4.4 Regardless of how the sample was collected, the target analytes are extracted into the solvent along with the majority of the oily waste (i.e., some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

7.4.5 Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis, using Method 5030.

7.4.6 Prepare a matrix spike sample by adding 10 - 50 µL of the matrix spike standard dissolved in methanol to a 1-g aliquot of the oily waste. Shake the vial to disperse the matrix spike solution throughout the oil. Then add 10 mL of extraction solvent and proceed with the extraction and analysis, as described in Secs. 7.4.2 - 7.4.5. Calculate the recovery of the spiked analytes as described in Method 8000. If the recovery is not within the acceptance limits for the application, use the hexadecane dilution technique in Sec. 7.0 of Method 3585.

7.5 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample.

NOTE: It is highly recommended that the dry weight determination only be made after the analyst has determined that no sample aliquots will be taken from the 60-mL vial for high

concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the dry weight determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

7.5.1 Weigh 5-10 g of the sample from the 60-mL VOA vial into a tared crucible.

7.5.2 Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

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

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS), and the addition of surrogates to each sample and QC sample.

8.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Single laboratory accuracy and precision data were obtained for the method analytes in three soil matrices, sand, a soil collected 10 feet below the surface of a hazardous landfill, called the

C-Horizon, and a surface garden soil. Each sample was fortified with the analytes at a concentration of 20 ng/5 g, which is equivalent to 4 µg/kg. These data are listed in tables found in Method 8260.

9.2 Single laboratory accuracy and precision data were obtained for certain method analytes when extracting oily liquid using methanol as the extraction solvent. The data are presented in a table in Method 8260. The compounds were spiked into three portions of an oily liquid (taken from a waste site) following the procedure for matrix spiking described in Sec. 7.4. This represents a worst case set of data based on recovery data from many sources of oily liquid.

10.0 REFERENCES

1. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

2. Siegrist, R. L., Jenssen, P. D., “Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils”, Envir Sci Technol, 1990; 24; 1387-92.

3. Hewitt, A. D., Jenkins, T. F., Grant, C. L., “Collection, Handling and Storage: Keys to Improved Data Quality for Volatile Organic Compounds in Soil”, Am Environ Lab, 1995; 7(1); 25-8.

4. Liikala, T. L., Olsen, K. B., Teel, S. S., Lanigan, D. C., “Volatile Organic Compounds: Comparison of Two Sample Collection and Preservation Methods”, Envir Sci Technol, 1996; 30; 3441-7.

5. Lewis, T. E., Crockett, A. B., Siegrist, R. L., Zarrabi, K., “Soil Sampling and Analysis for Volatile Organic Compounds”, Envir Monitoring & Assessment, 1994; 30; 213-46.

6. Hewitt, A. D., “Enhanced Preservation of Volatile Organic Compounds in Soil with Sodium Bisulfate”, SR95-26, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

7. Hewitt, A. D., Lukash, N. J. E., “Sampling for In-Vial Analysis of Volatile Organic Compounds in Soil”, Am Environ Lab, 1996; Aug; 15-9.

8. Hewitt, A. D., Miyares, P. H., Sletten, R. S., “Determination of Two Chlorinated Volatile Organic Compounds in Soil by Headspace Gas Chromatography and Purge-and-Trap Gas Chromatography/Mass Spectrometry”, Hydrocarbon Contaminated Soils, 1993, 3; 135-45, Chelsea, MI, Lewis Publishers.

9. Hewitt, A. D., “Methods of Preparing Soil Samples for Headspace Analysis of Volatile Organic Compounds: Emphasis on Salting Out”, 12th Annual Waste Testing and Quality Assurance Symposium, Washington, DC, 1996, 322-9.

10. Hewitt, A. D., Miyares, P. H., Leggett, D. C., Jenkins, T. F., “Comparison of Analytical Methods for Determination of Volatile Organic Compounds”, Envir Sci Tech, 1992; 26; 1932-8.

TABLE 1

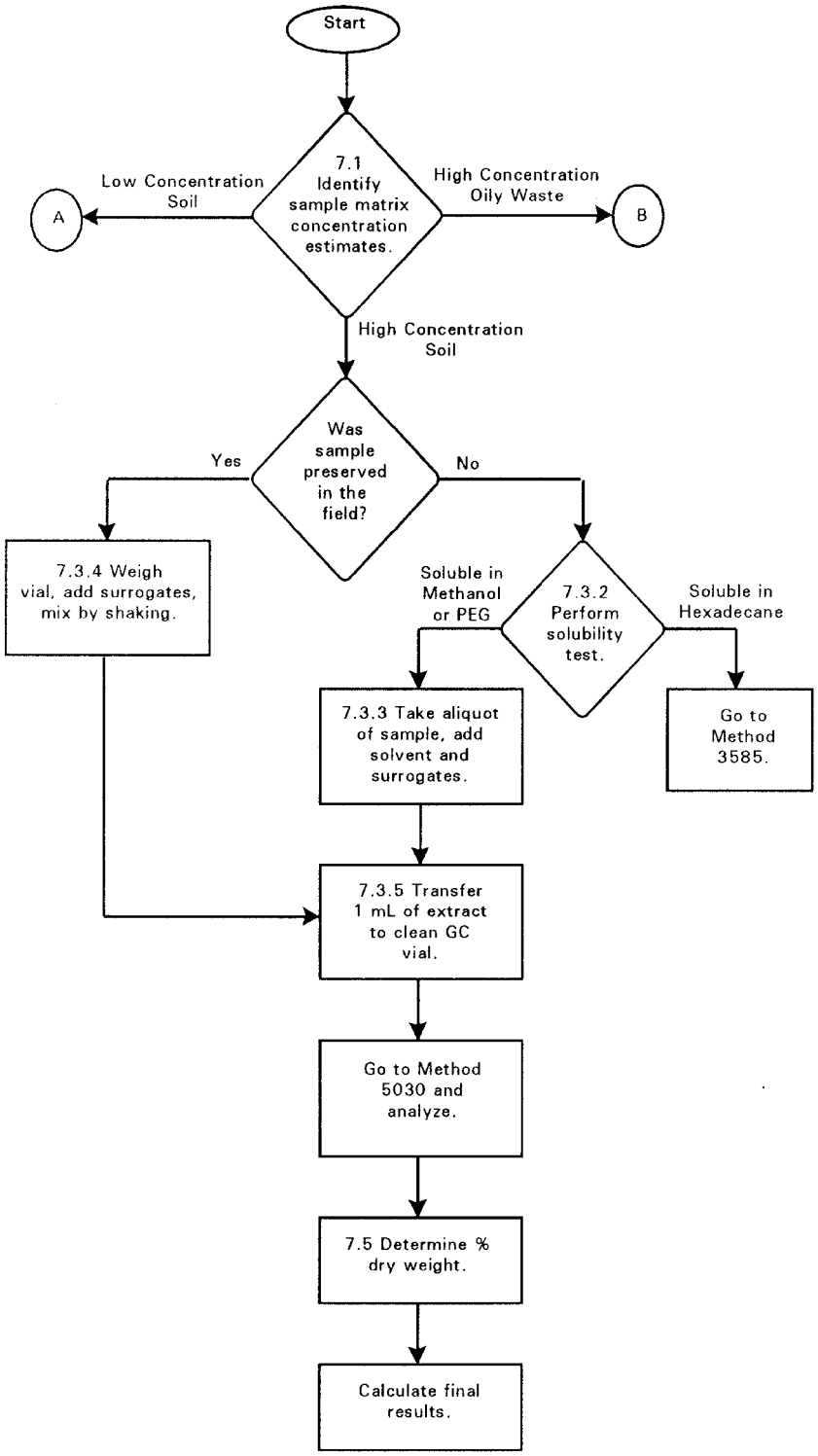
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SOILS/SEDIMENTS

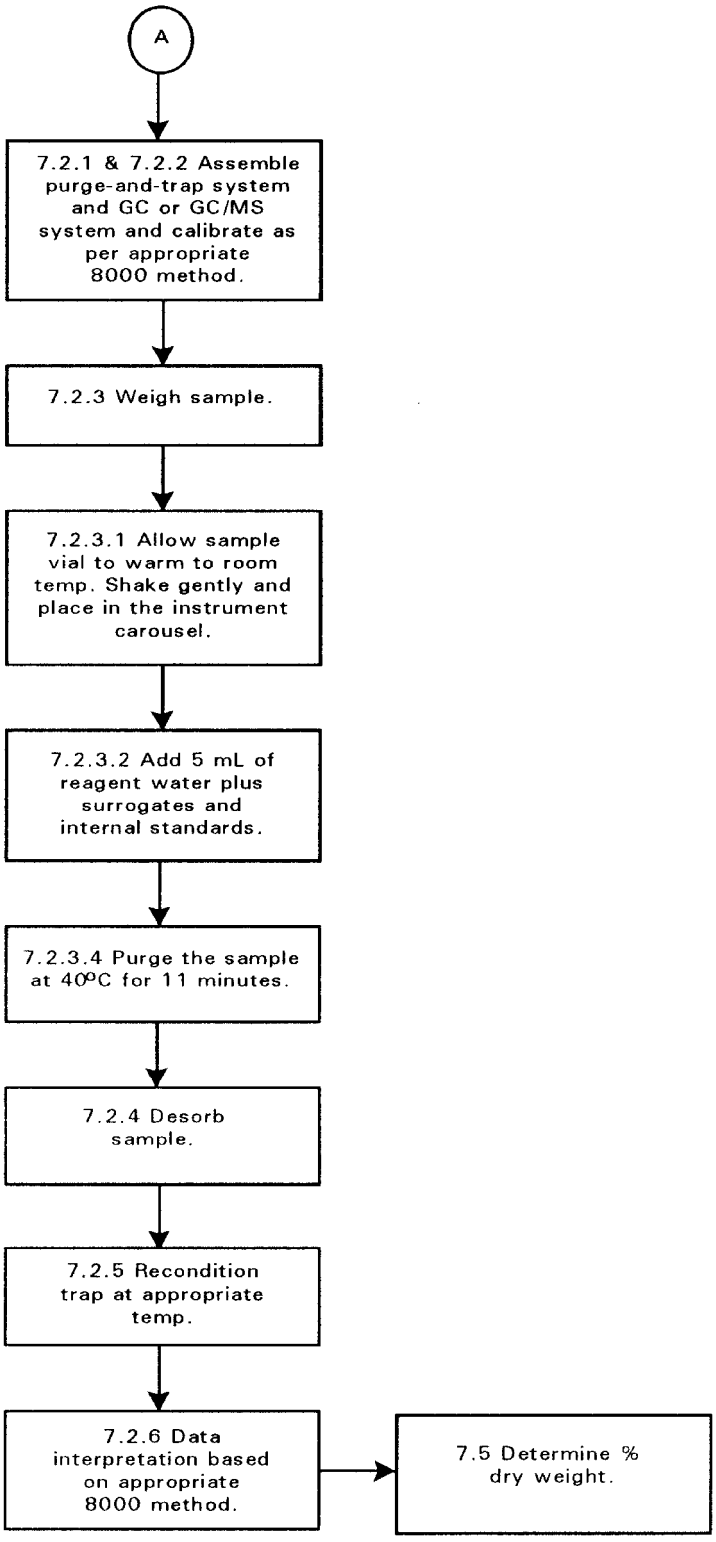
Approximate Concentration Range	Volume of Methanol Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

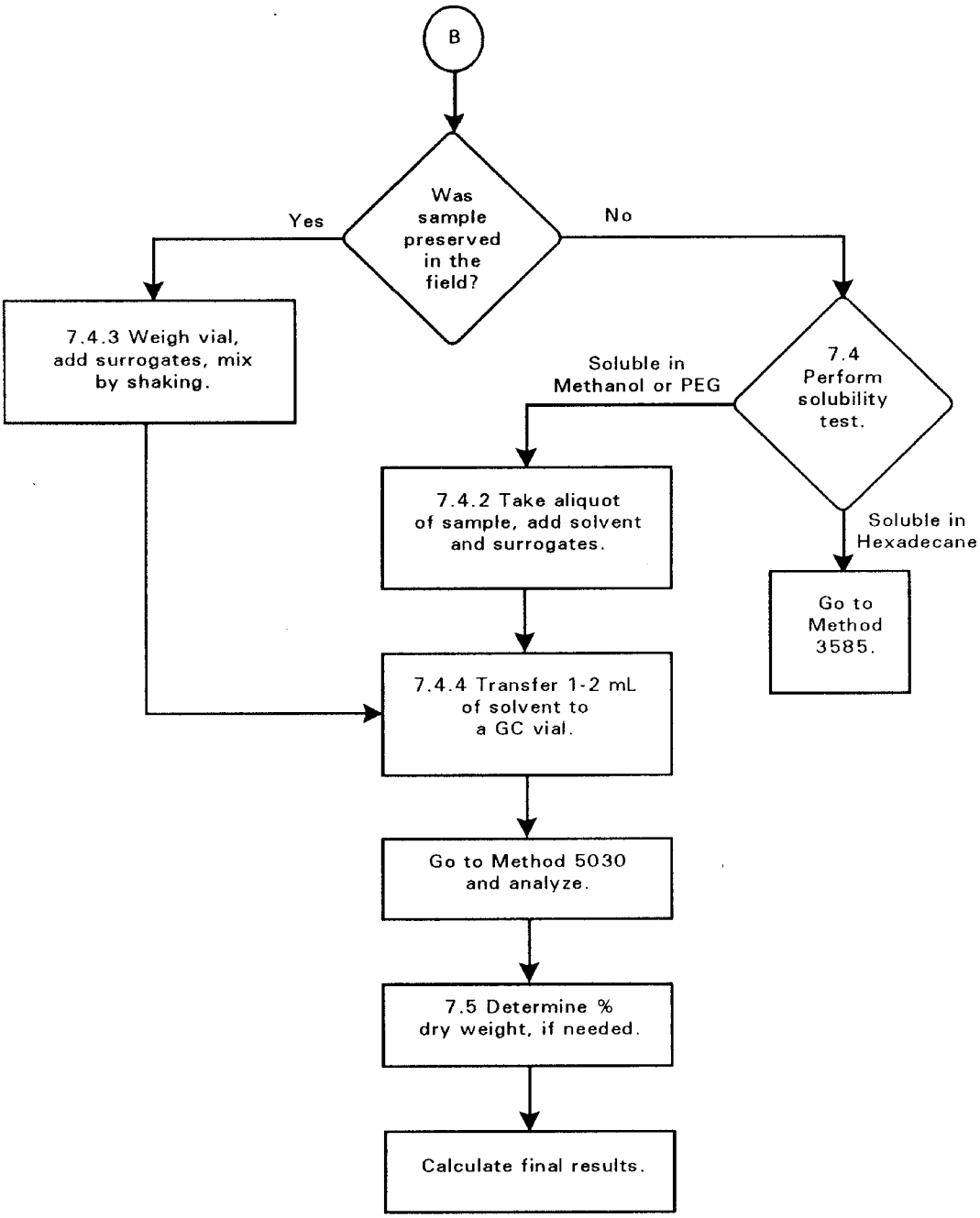
Calculate appropriate dilution factor for concentrations exceeding those in this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100 µL of methanol.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.


Start
7.1 Identify sample matrix concentration estimates.
Low Concentration Soil
A
High Concentration Oily Waste
B
High Concentration Soil
Was sample preserved in the field?
Yes
No
7.3.4 Weigh vial, add surrogates, mix by shaking.
7.3.2 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.3.3 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.3.5 Transfer 1 mL of extract to clean GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight.
Calculate final results.


A
7.2.1 & 7.2.2 Assemble purge-and-trap system and GC or GC/MS system and calibrate as per appropriate 8000 method.
7.2.3 Weigh sample.
7.2.3.1 Allow sample vial to warm to room temp. Shake gently and place in the instrument carousel.
7.2.3.2 Add 5 mL of reagent water plus surrogates and internal standards.
7.2.3.4 Purge the sample at 40°C for 11 minutes.
7.2.4 Desorb sample.
7.2.5 Recondition trap at appropriate temp.
7.2.6 Data interpretation based on appropriate 8000 method.
7.5 Determine % dry weight.


B
Was sample preserved in the field?
Yes
No
7.4.3 Weigh vial, add surrogates, mix by shaking.
7.4 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.4.2 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.4.4 Transfer 1-2 mL of solvent to a GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight, if needed.
Calculate final results.