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

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

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

1.0 SCOPE AND APPLICATION

1.1 This method 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 RCRA analytes have been determined by this method:

		Appropriate Preparation Technique[a]					
Compound	CAS No.[b]	5030/ 5035	5031	5032	5021	5041	Direct Inject.
Acetone	67-64-1	ht	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
t-Amyl ethyl ether (TAEE)	919-94-8	c / ht	nd	nd	c	nd	c
t-Amyl methyl ether (TAME)	994-05-8	c / ht	nd	nd	c	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

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
t-Butyl alcohol	75-65-0	ht	c	nd	nd	nd	c
Carbon disulfide	75-15-0	c	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
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	c	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
Diisopropyl ether (DIPE)	108-20-3	c / ht	nd	nd	c	nd	c
1,4-Difluorobenzene (IS)	540-36-3	c	nd	nd	nd	c	nd
1,4-Dioxane	123-91-1	ht	c	c	nd	nd	c
Epichlorohydrin	106-89-8	I	nd	nd	nd	nd	c
Ethanol	64-17-5	I	c	c	nd	nd	c
Ethyl acetate	141-78-6	I	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

Compound	CAS No.[b]	Appropriate Preparation Technique[a]					
		5030/ 5035	5031	5032	5021	5041	Direct Inject.
Fluorobenzene (IS)	462-06-6	c	nd	nd	nd	nd	nd
Ethyl tert-butyl ether (ETBE)	637-92-3	c / ht	nd	nd	c	nd	c
Hexachlorobutadiene	87-68-3	c	nd	nd	c	nd	c
Hexachloroethane	67-72-1	I	nd	nd	nd	nd	c
2-Hexanone	591-78-6	pp	nd	c	nd	nd	c
Iodomethane	74-88-4	c	nd	c	nd	c	c
Isobutyl alcohol	78-83-1	ht / 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	I	nd	nd	nd	c
Methanol	67-56-1	I	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
Methyl tert-butyl ether (MTBE)	1634-04-4	c / ht	nd	nd	c	nd	c
Naphthalene	91-20-3	c	nd	nd	c	nd	c
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	I	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	ht / pp	c	nd	nd	nd	c
2-Propanol	67-63-0	ht / pp	c	nd	nd	nd	c
Propargyl alcohol	107-19-7	pp	I	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	I	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

		Appropriate Preparation Technique[a]					
Compound	CAS No.[b]	5030/ 5035	5031	5032	5021	5041	Direct Inject.
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
I = 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 polytetrafluoroethylene (PTFE) bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 This method 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 lower limits of quantitation 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
Methyl acrylate
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
Hexachloroethane
p-Isopropyltoluene

1-Chlorobutane
1-Chlorohexane
2-Chlorotoluene
4-Chlorotoluene
Cyclohexane
cis-1,2-Dichloroethene
Methylcyclohexane
Pentachloroethane
Pentafluorobenzene
n-Propylbenzene
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

1.4 The lower limits of quantitation for this method when determining an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrupole 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. Somewhat lower limits may be achieved using an ion trap mass spectrometer or other similar instrumentation. However, regardless of which instrument is used, the lower limits of quantitation 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. The lower limits of quantitation listed in the performance data tables are provided for guidance and may not always be achievable.

1.5 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 5000 and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

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

1.6 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

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, or the effluent from the trap is sent to an injection port operating in the split mode for injection to a narrow-bore capillary column. 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 mass spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using an appropriate calibration curve for the intended application.

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

3.0 DEFINITIONS

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

4.0 INTERFERENCES

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

4.2 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The laboratory where the analysis is to be performed should be free of solvents other than water and methanol. Many common solvents, most notably acetone and methylene chloride, are frequently found in laboratory air at low levels. The sample receiving chamber should be loaded in an environment that is clean enough to eliminate the potential for contamination from ambient sources. In addition, the use of non-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. Subtracting blank values from sample results is not permitted. If reporting values for situations where the laboratory feels is a false positive result for a sample, the laboratory should fully explain this in text accompanying the uncorrected data and / or include a data qualifier that is accompanied with an explanation.

4.3 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.

4.4 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 appropriately clean the purging device, 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).

4.5 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.

4.6 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.

4.7 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.

4.8 Use of sensitive mass spectrometers to achieve lower quantitation levels will increase the potential to detect laboratory contaminants as interferences.

4.9 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.

4.10 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.

5.0 SAFETY

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

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

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

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

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

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

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

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

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

6.8 Injection port liners (Agilent 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.

6.9 Gas chromatography/mass spectrometer/data system

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

6.9.1.1 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.

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

6.9.1.3 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.

6.9.1.4 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.

6.9.1.5 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.

6.9.2 Gas chromatographic columns - The following columns have been found to provide good separation of volatile compounds, however they are not listed in preferential order based on performance and the ability to achieve project-specific data quality objectives.

6.9.2.1 Column 1 - 60m x 0.32 mm ID, 1.5-µm column film thickness, (Restek) RTX-Volatiles.

6.9.2.2 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.

6.9.2.3 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.

6.9.2.4 Column 4 - 60m x 0.32 mm ID, capillary column (Agilent-VOC), 1.8-µm film thickness, or equivalent.

6.9.2.5 Column 5 - 20m x 0.18mm ID, 1-µm column film thickness, DB-VRX.

6.9.3 Mass spectrometer

6.9.3.1 Capable of scanning from m/z 35 to 270 every 1 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 the criteria as outlined in Sec. 11.3.1.

6.9.3.2 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 the criteria as outlined in Sec. 11.3.1.

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

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

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

6.9.4.3 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 of BFB) 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.

6.9.5 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.

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

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

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

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

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

6.15 Vials - 2-mL, for GC autosampler.

6.16 Disposable pipets - Pasteur.

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

6.18 Spatula - Stainless steel.

7.0 REAGENTS AND STANDARDS

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

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

7.3 Methanol, CH_3OH - Purge and trap grade or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

7.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method quantitation 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.

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

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

7.7 Stock standard solutions - The 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.

7.7.1 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.

7.7.2 Add the assayed pure standard material, as described below.

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

7.7.2.2 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 pure 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.

7.7.3 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.

7.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at ≤6°C or as recommended by the standard manufacturer. Standards should be returned to the refrigerator or freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

7.7.5 Frequency of Standard Preparation

7.7.5.1 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 may 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 chloromethane 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.

7.7.5.2 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 may need to be replaced after one month for working standards and three months for opened stocks 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.

7.7.6 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).

7.7.6.1 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.

7.7.6.2 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.

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

7.7.6.4 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.

7.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps from Sec. 7.7.6.4 (a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

7.7.6.6 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.

7.7.6.7 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.

7.7.6.8 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.

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

7.7.6.10 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

7.7.6.11 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

7.8 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. Secondary standards for most compounds should be replaced after 2-4 weeks unless the acceptability of the standard can be documented. 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. 7.7.4 and return them to the refrigerator or freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

7.9 Surrogate standards - The recommended surrogates are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. 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 an appropriate concentration in methanol. Each sample undergoing GC/MS analysis must be spiked with the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower quantitation levels, then more dilute surrogate solutions may be required.

7.10 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. 7.7 and 7.8. 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 quantitation 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.

7.11 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 quantitation levels, then a more dilute BFB standard solution may be required.

7.12 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.

7.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 7.7 and 7.8) 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.

7.12.2 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. 7.7 and 7.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 11.4 for guidance on calibration verification.

7.12.3 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).

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

7.13 Matrix spiking and laboratory control sample (LCS) standards - See Method 5000 for instructions on preparing the matrix spike standard. The matrix spike and laboratory control standards should be from the same source as the initial calibration standards to restrict the influence of accuracy on the determination of recovery throughout preparation and analysis. Matrix spiking and LCS 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.

7.13.1 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 an appropriate concentration.

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

7.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards be stored with minimal headspace and protected from light, at $\leq 6^\circ$C or as recommended by the standard manufacturer using screw-cap or crimp-top amber containers equipped with PTFE liners. Standards should be returned to the refrigerator or freezer as soon as the analyst has completed mixing or diluting the standards to prevent the loss of volatile target compounds.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Aqueous samples should be stored with minimal or no headspace to minimize the loss of highly volatile analytes.

8.3 Samples to be analyzed for volatile compounds should be stored separately from standards and from other samples expected to contain significantly different concentrations of volatile compounds, or from samples collected for the analysis of other parameters such as semivolatiles.

NOTE: Storage blanks should be used to monitor potential cross-contamination of samples due to improper storage conditions. The specific of this type of monitoring activity should be outlined in a laboratory standard operating procedure pertaining to volatiles sample storage.

9.0 QUALITY CONTROL

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

9.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, discussions regarding the instrument QC requirements listed below can be found in the referenced sections of this method:

- The GC/MS must be tuned to meet the recommended BFB criteria prior to the initial calibration and for each 12-hr period during which analyses are performed. See Secs. 11.3.1 and 11.4.1 for further details.

- There must be an initial calibration of the GC/MS system as described in Sec. 11.3. In addition, the initial calibration curve should be verified immediately after performing the standard analyses using a second source standard (prepared using standards different from the calibration standards) spiked into organic-free reagent water. The suggested acceptance limits for this initial calibration verification analysis are 70 - 130%. Alternative acceptance limits may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

- The GC/MS system must meet the calibration verification acceptance criteria in Sec. 11.4, each 12 hours.

- The RRT of the sample component must fall within the RRT window of the standard component provided in Sec. 11.6.1.

9.3 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. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish this demonstration of proficiency.

9.4 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences and/or contaminants 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 for the compounds of interest as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

9.5 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 method sensitivity). At a minimum, this should include 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.

9.5.1 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.

9.5.2 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 appropriate. 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. Also note the LCS for water sample matrices is typically prepared in organic-free reagent water similar to the continuing calibration verification standard. In these situations, a single analysis can be used for both the LCS and continuing calibration verification.

9.5.3 See Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.5.4 Method blanks - Before processing any samples, the analyst must demonstrate that all equipment and reagent interferences are under control. Each day a set of samples is extracted or, equipment or reagents are changed, a method blank must be analyzed. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing samples.

9.6 Surrogate recoveries

The laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Suggested surrogate recovery limits are provided in Table 8. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.7 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, a septum is changed), see the guidance in Method 8000 regarding whether recalibration of the system must take place.

9.8 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.

10.0 CALIBRATION AND STANDARDIZATION

See Sec 11.3 for information on calibration and standardization.

11.0 PROCEDURE

11.1 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.

11.1.1 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%.

11.1.2 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.

11.1.2.1 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.

11.1.2.2 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 and soil/solid samples at elevated temperatures (e.g., 80°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

11.1.3 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.

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

11.1.5 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).

11.2 Recommended chromatographic conditions are provided as examples based on an assortment of analyses used to generate performance data for this method. The actual conditions will ultimately be dependent on the compounds of interest, instrument, and column manufacturer's guidelines. The maximum temperatures of operation should always be verified with the specific manufacturer.

11.2.1 General conditions

Injector temperature:	200 - 275°C
Transfer line temperature:	200 - 300°C

11.2.2 Split / splitless injection - Column 1 (example chromatogram is presented in Figure 1). The following are example conditions which may vary depending on the instrument and column manufacturer's recommendations:

Carrier gas (He) flow rate:	1.0 mL/min
Initial temperature:	35°C
Temperature program:	35°C for 1 min, 9°C/min to 250°C, hold for 2.5 min
Final temperature:	250°C, hold until all expected compounds have eluted.

11.2.3 Direct injection - Column 2. The following are example conditions which may vary depending on the instrument and column manufacturer's recommendations:

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

11.2.4 Direct split interface - Column 3. The following are example conditions which may vary depending on the instrument and column manufacturer's recommendations:

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

11.2.5 Split injection - Column 4. The following are example conditions which may vary depending on the instrument and column manufacturer's recommendations:

Carrier gas (He) flow rate:	1 mL/min
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	35 °C to 60 °C at 10 °C/min; 60 °C to 150 °C at 15 °C/min; 150 °C to 230 °C at 6 °C/min, final hold of 0.5 min
Final temperature:	230°C, hold until all expected compounds have eluted
Injector temperature:	250°C
Transfer line temperature:	280°C

11.2.6 Split injection - Column 5 (example chromatogram is presented in Figure 2). The following are example conditions which may vary depending on the instrument and column manufacturer's recommendations:

Carrier gas (He) flow rate:	0.9 mL/min
Initial temperature:	30°C, hold for 3 minutes
Temperature program:	10°C/min to 100°C, 20°C/min to 220°C, hold for 1 min
Final temperature:	220°C, hold until all expected compounds have eluted.
Split ratio:	50:1

11.3 Initial calibration

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

Mass range:	From m/z 35 - 270
Sampling rate:	To result in at least five full mass spectra across the peak but not to exceed 1 second per mass spectrum
Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

11.3.1 The GC/MS system must be hardware-tuned such that injecting 50 ng or less of BFB meets the manufacturer's specified acceptance criteria or as listed in Table 3. The tuning criteria listed in Table 3 were developed using quadrupole mass spectrometer instrumentation and it is recognized that other tuning criteria may be more effective depending on the type of instrumentation, e.g., Time-of-Flight, Ion Trap, etc. In these cases it would be appropriate to follow the manufacturer’s tuning instructions or some other consistent tuning criteria. However no matter which tuning criteria is selected, the system calibration must not begin until the tuning acceptance criteria are met with the sample analyses performed under the same conditions as the calibration standards.

11.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach should be used: 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 acquired within 20 scans of the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the BFB peak or any other discrete peak that does not coelute with BFB.

11.3.1.2 Use the BFB mass intensity criteria in the manufacturer's instructions as primary tuning acceptance criteria or those in Table 3 as default tuning acceptance criteria if the primary tuning criteria are not available. Alternatively, other documented tuning criteria may be used (e.g., CLP or Method 524.2), provided that method performance is not adversely affected. The analyst is always free to choose criteria that are tighter than those included in this method or to use other documented criteria provided they are used consistently throughout the initial calibration, calibration verification, and sample analyses.

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

11.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 11.1). 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. 7.12 and Method 8000). Calibration must be performed using the same sample introduction technique as that being 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.

11.3.2.1 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 underneath the surface of the reagent water. Remove the needle as quickly as possible after injection and dilute to the volume mark with additional reagent water. Mix by inverting the flask sufficiently to achieve the desired dissolution. However, excessive mixing could result in the loss of gaseous standards. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower quantitation 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.

When using an autosampler, prepare the calibration standard in a volumetric flask and transfer it to a vial and seal it. Place the sample vial in the instrument carousel according to the manufacturer's instructions. Without disturbing the hermetic seal on the sample vial, a specific sample volume is withdrawn (usually 5 or 25 mL) and placed into the purging vessel along with the addition of internal standards and surrogate compounds using an automated sampler.

11.3.2.2 The internal standards selected in Sec. 7.10 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 5). If interferences are noted, use the next most intense ion as the quantitation ion.

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

11.3.3 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.

NOTE: Historically the surrogate compounds have been included in the multi-point initial calibration at variable concentrations in order to evaluate the linear response as with any target analyte. However, with improvements in instrumentation and more reliance on the autosampler, an option is available depending on the project-specific data quality requirements for allowing the autosampler (or using a manual technique) to spike the initial calibration standards with surrogates in the same manner as the samples are spiked. With this option the surrogate standards in the initial calibration can be averaged to develop a response factor and an effective one point calibration with the sole purpose to measure the surrogate recovery using the same concentration for each sample analysis. For this calibration option the surrogate linear response is less important, since multiple concentrations of surrogates are not being measured. Instead, the surrogate concentration remains constant throughout and the recovery of this known concentration can easily be attained without demonstrating if the response is linear.

Under a second calibration option, the surrogates can be calibrated in the same manner as the target analytes, however, the laboratory should have the latitude to employ either option given the instrument system limitations and the ability to meet the project's data quality objectives.

11.3.4 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. 11.7.1).

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.

11.3.4.1 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte using the following equations. The RSD should be less than or equal to 20% for each target analyte. It is also recommended that a minimum response factor for the most common target analytes as noted in Table 4, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed by this method, some compounds will fail to meet this criteria. For these occasions, it is acknowledged that the failing compounds may not be critical to the specific project and therefore they may be used as qualified data or estimated values for screening purposes. The analyst should also strive to place more emphasis on meeting the calibration criteria for those compounds that are critical project compounds, rather than meeting the criteria for those less important compounds.

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

$$RSD = \frac{SD}{\overline{RF}} \times 100$$

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

11.3.4.2 If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too imprecise for analysis to begin. Adjust moisture control parameters, replace analytical trap or column, replace moisture trap or adjust desorb time, then repeat the calibration procedure beginning with Sec. 11.3.

11.3.5 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement. The RRT is calculated as follows:

$$\text{RRT} = \frac{\text{Retention time of the analyte}}{\text{Retention time of the internal standard}}$$

11.3.6 Linearity of target analytes - If the RSD of any target analyte is 20% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 11.7).

11.3.6.1 If the RSD of any target analyte is greater than 20%, refer to 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. The average RF should not be used for compounds that have an RSD greater than 20% unless the concentration is reported as estimated.

11.3.6.2 When the RSD exceeds 20%, 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.

11.3.6.3 Due to the large number of compounds that may be analyzed by this method, some compounds may fail to meet either the 20% RSD, minimum correlation coefficient criteria (0.99), or the acceptance criteria for alternative calibration procedures in Method 8000. Any calibration method stipulated in Method 8000 may be used, but it should be used consistently. It is considered inappropriate once the calibration analyses are completed to select an alternative calibration procedure in order to pass the recommended criteria on a case by case basis. If compounds fail to meet these criteria, the associated concentrations may still be determined but they must be reported as estimated. In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit.

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

11.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 50 ng or less of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria as outlined in Sec. 11.3.1 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

11.4.2 The initial calibration curve should be verified immediately after performing the standard analyses using a second source standard (prepared using standards different from the calibration standards) spiked into organic-free reagent water with a concentration preferably at the midpoint of the initial calibration range. The suggested acceptance limits for this initial calibration verification analysis are 70 - 130%. Alternative acceptance limits may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding these results could be used for screening purposes and would be considered estimated values.

11.4.3 The initial calibration (Sec. 11.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard (containing all the compounds for quantitation) at a concentration either near the midpoint concentration for the calibrating range of the GC/MS or near the action level for the project. The results must be compared against the most recent initial calibration curve and should meet the verification acceptance criteria provided in Secs. 11.4.5 through 11.4.7.

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.

11.4.4 A method blank should be analyzed prior to sample analyses in order 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 Method 8000 for method blank performance criteria.

11.4.5 Calibration verification standard criteria

11.4.5.1 Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 4. This criterion is particularly important when the common target analytes are also critical project-required compounds. This is the same check that is applied during the initial calibration.

11.4.5.2 If the minimum response factors are not met, the system should be evaluated, and corrective action should 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, active sites in the analytical column, trap, or chromatographic system, and problems with the moisture control system.

11.4.5.3 All target compounds of interest must be evaluated using a 20% variability criterion. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Method 8000 for guidance on calculating percent difference and drift.

11.4.5.4 If the percent difference or percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, some compounds will fail to meet the criteria. If the criterion is not met (i.e., greater than 20% difference or drift) for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when the failed compound is present, the concentrations must be reported as estimated values.

11.4.5.5 Problems similar to those listed under initial calibration could affect the ability to pass the calibration verification standard analysis. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

11.4.5.6 The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve (See Method 8000 for additional details). It is not necessary to re-analyze a low concentration standard, rather the data system can recalculate the concentrations as if it were an unknown sample. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives and for those situations the minimum quantitation check criteria should be outlined in a laboratory standard operating procedure, or a project-specific Quality Assurance Project Plan. Analytes which do not meet the minimum quantitation calibration re-fitting criteria should be considered "out of control" and corrective action such as redefining the lower limit of quantitation and/or reporting those "out of control" target analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.

11.4.6 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 10 seconds from 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.

11.4.7 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.

11.5 GC/MS analysis of samples

11.5.1 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 screening solid samples for volatile organics (Method 3815), 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 quantitation levels.

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

11.5.3 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.

11.5.4 The process of taking an aliquot destroys the validity of the remaining volume of an aqueous sample for future analysis when target analytes are at low concentration and taking the aliquot leaves significant headspace in the sample vial. Higher concentration samples, for example those which need to be diluted before analysis at a 5-mL purge volume, often show no detectable changes when a small aliquot is removed, the sample vial is immediately recapped, and the same vial reanalyzed at a later time. That said, it is best practice not to analyze a sample vial repeatedly. Therefore, if only one VOA vial of a relatively clean aqueous matrix such as tap water is provided to the laboratory, to protect against possible loss of sample data, the analyst should prepare two aliquots for analysis at this time. A second aliquot in a syringe 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.

11.5.5 Place the sample vial in the instrument carousel according to the manufacturer's instructions. Without disturbing the hermetic seal on the sample vial, a specific sample volume is withdrawn (usually 5 or 25 mL) and placed into the purging vessel along with the addition of internal standards and surrogate compounds using an automated sampler.

Alternatively, 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 invert before compressing the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower quantitation limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

NOTE: For most applications pouring a sample aliquot directly into the syringe is preferred in order to minimize the loss of volatile constituents, however when smaller volumes are necessary to prepare dilutions, drawing the sample directly into the syringe is considered acceptable.

11.5.6 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.

11.5.6.1 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.

11.5.6.2 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.

11.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask underneath the reagent water surface. 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 this procedure for additional dilutions.

11.5.6.4 Fill a 5-mL syringe by pouring with the diluted sample, as described in Sec. 11.5.5. Should smaller sample volumes be necessary to prepare dilutions, drawing the sample directly into the syringe is considered acceptable

11.5.6.5 Systems with autosamplers allow the user to perform automated dilutions. Refer to instrument manufacturer's instructions for more information. In addition, if an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions.

11.5.7 Compositing aqueous samples prior to GC/MS analysis

11.5.7.1 The following compositing options may be considered depending on the sample composition and desired data quality objectives:

11.5.7.1.1 Flask compositing - for this procedure, a 300 to 500 mL round-bottom flask is immersed in an ice bath. The individual VOA grab samples, maintained at <6°C, are slowly poured into the round-bottom flask. The flask is swirled slowly to mix the individual grab samples. After mixing, multiple aliquots of the composited sample are poured into VOA vials and sealed for subsequent analysis. An aliquot can also be poured into a syringe for immediate analysis.

11.5.7.1.2 Purge device compositing - Equal volumes of individual grab samples are added to a purge device to a total volume of 5 or 25 mL. The sample is then analyzed.

11.5.7.1.3 Syringe compositing - In the syringe compositing procedure, equal volumes of individual grab samples are aspirated into a 25 mL syringe while maintaining zero headspace in the syringe. Either the total volume in the syringe or an aliquot is subsequently analyzed. The disadvantage of this technique is that the individual samples must be poured carefully in an attempt to achieve equal volumes of each. An alternate procedure uses multiple 5 mL syringes that are filled with the individual grab samples and then injected sequentially into the 25 mL syringe. 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.

11.5.7.2 Introduce the composited sample into the instrument, using the method of choice. (see Sec. 11.1)

11.5.8 Add appropriate volumes of the surrogate spiking solution and the internal standard spiking solution to each sample either manually or by autosampler to achieve the desired concentrations. The surrogate and internal standards may be mixed and added as a single spiking solution.

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

11.5.9 Add 10 µL of the matrix spike solution (Sec. 7.13) 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.

11.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 9.5 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

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

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

11.5.10.1 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).

11.5.10.2 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.

11.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the upper limit of 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.

11.5.11.1 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. Depending on the extent of the decontamination procedures, recalibration may be necessary.

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

11.5.12 The use of selected ion monitoring (SIM) is acceptable for applications requiring quantitation limits below the normal range of electron impact mass spectrometry. However, SIM may provide a lesser degree of confidence in the compound identification, since less mass spectral information is available. Using the primary ion for quantitation and the secondary ions for confirmation set up the collection groups based on their retention times. The selected ions are nominal ions and most compounds have small mass defect, usually less than 0.2 amu, in their spectra. These mass defects should be used in the acquisition table. The dwell time may be automatically calculated by the laboratory's GC/MS software or manually calculated using the following formula. The total scan time should be less than 1,000 msec and produce at least 5 to 10 scans per chromatographic peak. The start and stop times for the SIM groups are determined from the full scan analysis using the formula below:

$$\text{Dwell Time for the Group} = \frac{\text{Laboratory's Scan Time (msec)}}{\text{Total Ions in the Group}}$$

11.6 Analyte identification

11.6.1 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.

11.6.1.1 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.

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

11.6.1.3 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%.)

11.6.1.4 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 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported.

11.6.1.5 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.

11.6.1.6 Examination of extracted ion current profiles (EICP) 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.

11.6.2 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.

11.7 Quantitation

11.7.1 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.

11.7.1.1 It is highly recommended to use the integration produced by the software if the integration is correct because the software should produce more consistent integrations. However, manual integrations are necessary when the software does not produce proper integrations due to improper baseline selection, the correct peak is missed, a coelution is integrated, a peak is partially integrated, etc. The analyst is responsible for ensuring that the integration is correct whether performed by the software or done manually.

11.7.1.2 Manual integrations should not be substituted for proper maintenance of the instrument or setup of the method (e.g. retention time updates, integration parameter files, etc). The analyst should seek to minimize manual integration by properly maintaining the instrument, updating retention times, and configuring peak integration parameters.

11.7.2 If the RSD of a compound's response factor is 20% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (Sec. 11.3.5). See Method 8000 for the equations describing internal standard calibration and either linear or non-linear calibrations.

11.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 11.6.2) 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. The resulting concentration should be reported indicating that the value is an estimate. Use the nearest internal standard free of interferences.

11.7.4 Structural isomers that produce very similar mass spectra should be quantitated 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 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The resolution should be verified on the mid-point concentration of the initial calibration as well as the laboratory designated continuing calibration verification level if closely eluting isomers are to be reported.

11.7.5 Quantitation of multicomponent parameters such as gasoline range organics (GROs) and total petroleum hydrocarbons (TPH) using the Method 8260 recommended internal standard quantitation technique is beyond the scope of this method. Typically, analyses for these parameters are performed using GC/FID or GC with a MS detector capability that is available with Method 8015.

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.7 for information on data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 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 example lower limits of quantitation are presented in Table 1.

13.3 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. Example lower limits of quantitation were also calculated from these data and are presented in Table 2.

13.4 Initial demonstration of capability data from two EPA Regional laboratories were submitted using purge-and-trap (Method 5030) with water spiked at 20 µg/L and analyzed on a narrow-bore column. The accuracy and precision data for these studies are presented in Tables 8 and 9.

13.5 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 12 and 13 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.

13.6 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 waste landfill, and a surface garden soil. Sample preparation was by Method 5035. Each sample was fortified with the analytes at a concentration of 20 µg/kg. These data are listed in Tables 18, 19, and 20. 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%.

13.6.1 In general, the recoveries of the analytes from the sand matrix are the highest, the hazardous waste landfill 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.

13.6.2 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.

13.7 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 14 to 17.

13.8 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 21 to 25.

13.9 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in a garden soil matrix. Replicate samples were fortified with the analytes at a concentration of 20 µg/kg. These data are listed in Table 28. All data were calculated using the internal standards listed for each analyte in Table 26. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

13.9.1 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 benzene, toluene, and xylenes. This is due to contamination of the soil prior to sample collection.

13.9.2 The example lower limits of quantitation using Method 5021 are listed in Table 27 and 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 lower limits of quantitation were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

13.10 The lower limits of quantitation listed in Table 29 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 lower limit of quantitation 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 lower limit of quantitation for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

13.11 The lower limit of quantitation for samples 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 31). Matrix effects may cause the individual compound quantitation limits to be higher.

13.12 The recommended internal standards with corresponding analytes assigned for quantitation that are appropriate for Method 5041 are listed in Table 30.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

EXAMPLE CHROMATOGRAPHIC RETENTION TIMES AND LOWER LIMITS OF QUANTITATION FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes)			LOQ[d]
	Column 2A[a]	Column 2B[b]	Column 2C[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)			LOQ[d]
	Column 1A[a]	Column 2B[b]	Column 2C[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 1A[a]	 Column 2B[b]	 Column 2C[c]	LOQ[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 2A - 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 2B - 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 2C - 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] Limit of quantitation based on a 25-mL sample volume.

TABLE 2

EXAMPLE CHROMATOGRAPHIC RETENTION TIMES AND LOWER LIMITS OF QUANTITATION FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 4[a]	Lower Limit of Quantitation (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 4[a]	Lower Limit of Quantitation (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] Lower limit of quantitation based on a 25-mL sample volume.

TABLE 3

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] The criteria in this table are intended to be used as default criteria for quadrupole instrumentation if optimized manufacturer's operating conditions are not available. Alternate tuning criteria may be employed (e.g., CLP or Method 524.2), provided that method performance is not adversely affected. See Sec. 11.3.1

TABLE 4

RECOMMENDED MINIMUM RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION

Volatile Compounds	Minimum Response Factor (RF)[a]	Typical Response Factor (RF)[b]
Dichlorodifluoromethane	0.100	0.327
Chloromethane	0.100	0.537
Vinyl chloride	0.100	0.451
Bromomethane	0.100	0.255
Chloroethane	0.100	0.254
Trichlorofluoromethane	0.100	0.426
1,1-Dichloroethene	0.100	0.313
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100	0.302
Acetone	0.100	0.151
Carbon disulfide	0.100	1.163
Methyl Acetate	0.100	0.302
Methylene chloride	0.100	0.380
trans-1,2-Dichloroethene	0.100	0.351
cis-1,2-Dichloroethene	0.100	0.376
Methyl tert-Butyl Ether	0.100	0.847
1,1-Dichloroethane	0.200	0.655
2-Butanone	0.100	0.216
Chloroform	0.200	0.557
1,1,1-Trichloroethane	0.100	0.442
Cyclohexane	0.100	0.579
Carbon tetrachloride	0.100	0.353
Benzene	0.500	1.368
1,2-Dichloroethane	0.100	0.443
Trichloroethene	0.200	0.338
Methylcyclohexane	0.100	0.501
1,2-Dichloropropane	0.100	0.382

Volatile Compounds	Minimum Response Factor (RF)[a]	Typical Response Factor (RF)[b]
Bromodichloromethane	0.200	0.424
cis-1,3-Dichloropropene	0.200	0.537
trans-1,3-Dichloropropene	0.100	0.515
4-Methyl-2-pentanone	0.100	0.363
Toluene	0.400	1.577
1,1,2-Trichloroethane	0.100	0.518
Tetrachloroethene	0.200	0.606
2-Hexanone	0.100	0.536
Dibromochloromethane	0.100	0.652
1,2-Dibromoethane	0.100	0.634
Chlorobenzene	0.500	1.733
Ethylbenzene	0.100	2.827
meta-/para-Xylene	0.100	1.080
ortho-Xylene	0.300	1.073
Styrene	0.300	1.916
Bromoform	0.100	0.413
Isopropylbenzene	0.100	2.271
1,1,2,2-Tetrachloroethane	0.300	0.782
1,3-Dichlorobenzene	0.600	1.408
1,4-Dichlorobenzene	0.500	1.427
1,2-Dichlorobenzene	0.400	1.332
1,2-Dibromo-3-chloropropane	0.050	0.129
1,2,4-Trichlorobenzene	0.200	0.806

[a] The project-specific response factors obtained may be affected by the quantitation ion selected and when using possible alternate ions the actual response factors may be lower than those listed. In addition, lower than the recommended minimum response factors may be acceptable for those compounds that are not considered critical target analytes and the associated data may be used for screening purposes.

[b] Data provided by EPA Region III laboratory.

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 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	101	103
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

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Chloroform-d_1	84	
Dibromofluoromethane	113	
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

US EPA REGION III LABORATORY INITIAL DEMONSTRATION OF CAPABILITY DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Spike Conc. (µg/L)	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Average	%Rec	RSD
Acetone	20	23.78	21.41	21.10	21.95	22.06	110.3	5.4
Benzene	20	19.42	19.31	18.41	20.08	19.31	96.5	3.6
Bromobenzene	20	22.74	19.32	18.61	19.52	20.05	100.2	9.2
Bromochloromethane	20	22.87	19.58	18.91	19.60	20.24	101.2	8.8
Bromodichloromethane	20	18.07	18.10	17.57	18.69	18.11	90.5	2.5
Bromoform	20	18.97	19.39	18.88	19.09	19.08	95.4	1.2
Bromomethane	20	18.93	18.76	17.77	19.86	18.83	94.2	4.5
2-Butanone	20	21.81	20.70	21.61	22.01	21.53	107.7	2.7
n-Butylbenzene	20	22.16	19.14	18.04	19.12	19.62	98.1	9.0
sec-Butylbenzene	20	22.84	19.36	18.15	19.39	19.94	99.7	10.1
tert-Butylbenzene	20	21.87	18.62	17.64	18.62	19.19	95.9	9.6
Carbon disulfide	20	19.01	18.69	17.25	20.23	18.80	94.0	6.5
Carbon tetrachloride	20	19.46	18.74	17.77	20.34	19.08	95.4	5.7
Chlorobenzene	20	19.54	19.39	18.77	20.23	19.48	97.4	3.1
Chloroethane	20	18.86	18.89	17.06	19.95	18.69	93.5	6.4
2-Chloroethylvinyl ether	20	18.26	16.54	16.31	16.51	16.91	84.5	5.4
Chloroform	20	19.47	19.62	18.60	20.14	19.46	97.3	3.3
Chloromethane	20	18.89	18.27	16.78	19.37	18.33	91.6	6.1
2-Chlorotoluene	20	22.82	19.45	18.52	19.69	20.12	100.6	9.3
4-Chlorotoluene	20	22.46	19.08	18.19	19.38	19.78	98.9	9.4
Cyclohexane	20	19.10	18.60	17.46	20.20	18.84	94.2	6.0
1,2-Dibromo-3-chloropropane	20	18.90	18.07	18.54	18.64	18.54	92.7	1.9

TABLE 8 (cont.)

US EPA REGION III LABORATORY INITIAL DEMONSTRATION OF CAPABILITY DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Spike Conc. (µg/L)	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Average	%Rec	RSD
Dibromochloromethane	20	19.70	19.62	19.23	19.83	19.60	98.0	1.3
1,2-Dibromoethane	20	19.95	19.92	19.83	20.39	20.02	100.1	1.2
Dibromomethane	20	22.77	19.72	19.47	20.21	20.54	102.7	7.4
1,2-Dichlorobenzene	20	18.85	18.89	18.29	19.56	18.90	94.5	2.8
1,3-Dichlorobenzene	20	19.27	19.22	18.71	19.91	19.28	96.4	2.6
1,4-Dichlorobenzene	20	19.60	19.49	18.81	20.20	19.53	97.6	2.9
Dichlorodifluoromethane	20	21.07	20.36	18.76	22.20	20.60	103.0	7.0
1,1-Dichloroethane	20	19.23	19.42	18.22	20.15	19.26	96.3	4.1
1,2-Dichloroethane	20	20.15	20.21	19.71	20.67	20.19	100.9	1.9
1,1-Dichloroethene	20	19.36	18.98	17.78	20.59	19.18	95.9	6.0
cis-1,2-Dichloroethene	20	18.56	18.67	17.77	19.40	18.60	93.0	3.6
trans-1,2-Dichloroethene	20	19.26	18.96	17.85	20.04	19.03	95.1	4.8
1,2-Dichloropropane	20	19.73	19.46	18.74	20.18	19.53	97.6	3.1
1,3-Dichloropropane	20	22.23	19.68	19.51	19.59	20.25	101.3	6.5
2,2-Dichloropropane	20	23.16	19.40	17.71	19.08	19.84	99.2	11.8
1,1-Dichloro-1-propene	20	23.24	19.70	18.29	19.97	20.30	101.5	10.3
cis-1,3-Dichloropropene	20	18.96	19.09	18.47	19.54	19.02	95.1	2.3
trans-1,3-Dichloropropene	20	20.19	20.31	19.57	20.36	20.11	100.5	1.8
Ethylbenzene	20	19.55	19.28	18.21	20.21	19.31	96.6	4.3
Hexachlorobutadiene	20	21.14	18.20	17.30	18.34	18.75	93.7	8.9
2-Hexanone	20	23.39	21.20	21.24	22.01	21.96	109.8	4.7
Isopropylbenzene	20	19.13	18.91	17.81	19.84	18.92	94.6	4.4

TABLE 8 (cont.)

US EPA REGION III LABORATORY INITIAL DEMONSTRATION OF CAPABILITY DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Spike Conc. (µg/L)	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Average	%Rec	RSD
p-Isopropyltoluene	20	22.28	18.98	17.93	18.93	19.53	97.7	9.7
Methylene chloride	20	20.03	19.89	20.17	20.56	20.16	100.8	1.4
Methyl acetate	20	20.21	19.73	20.34	20.77	20.26	101.3	2.1
Methyl cyclohexane	20	19.24	18.80	17.75	20.18	18.99	95.0	5.3
4-Methyl-2-pentanone	20	22.00	21.19	21.44	22.00	21.66	108.3	1.9
Methyl tert-butyl ether	20	20.23	20.30	19.82	20.41	20.19	101.0	1.3
Naphthalene	20	20.98	18.60	18.42	18.89	19.22	96.1	6.2
n-Propylbenzene	20	22.56	19.20	18.05	19.31	19.78	98.9	9.8
Styrene	20	16.72	16.46	15.90	16.87	16.49	82.4	2.6
1,1,1,2-Tetrachloroethane	20	22.67	19.12	18.58	19.46	19.96	99.8	9.2
1,1,2,2-Tetrachloroethane	20	20.54	20.21	20.24	20.96	20.49	102.4	1.7
Tetrachloroethene	20	18.88	18.57	17.32	19.67	18.61	93.1	5.2
Toluene	20	20.01	19.59	18.78	20.51	19.72	98.6	3.7
1,2,3-Trichlorobenzene	20	21.68	19.12	18.59	19.20	19.65	98.2	7.0
1,2,4-Trichlorobenzene	20	19.39	18.50	18.13	19.04	18.77	93.8	3.0
1,1,1-Trichloroethane	20	19.06	18.58	17.47	19.95	18.77	93.8	5.5
1,1,2-Trichloroethane	20	19.76	19.91	19.47	20.33	19.87	99.3	1.8
Trichloroethene	20	20.19	19.84	18.42	20.67	19.78	98.9	4.9
Trichlorofluoromethane	20	18.25	17.98	16.79	18.98	18.00	90.0	5.1
1,2,3-Trichloropropane	20	21.83	19.89	19.76	20.32	20.45	102.3	4.6

TABLE 8 (cont.)

US EPA REGION III LABORATORY INITIAL DEMONSTRATION OF CAPABILITY DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Spike Conc. (µg/L)	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Average	%Rec	RSD
1,1,2-Trichloro-1,2,2-trifluoroethane	20	20.33	19.65	18.54	21.18	19.93	99.6	5.6
1,2,4-Trimethylbenzene	20	22.67	19.41	18.47	19.45	20.00	100.0	9.2
1,3,5-Trimethylbenzene	20	22.51	19.13	18.09	19.20	19.73	98.7	9.7
Vinyl acetate	20	22.23	19.92	19.44	19.86	20.36	101.8	6.2
Vinyl chloride	20	19.85	19.72	18.08	21.12	19.69	98.5	6.3
o-Xylene	20	19.78	19.63	18.87	20.46	19.69	98.4	3.3
m & p-Xylene	40	39.08	38.42	36.45	40.21	38.54	96.4	4.1
Surrogates								
1,2-Dichloroethane-d_4	20	20.33	20.33	20.35	20.41	20.36	101.8	0.2
Toluene-d_8	20	20.39	20.24	20.36	20.21	20.30	101.5	0.4
Bromofluorobenzene	20	20.18	20.17	20.12	20.19	20.17	100.8	0.2

TABLE 9

US EPA REGION VI LABORATORY INITIAL DEMONSTRATION OF CAPABILITY DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Spike Conc. (µg/L)	Rep. #1	Rep. #2	Rep. #3	Rep. #4	Rep. #5	Average	%Rec	RSD
Acetone	20	18.69	22.81	19.57	21.73	21.30	20.82	104	8.0
Benzene	20	17.99	19.64	18.25	19.77	20.06	19.14	96	5.0
Bromodichloromethane	20	17.86	20.40	18.39	20.45	20.02	19.42	97	6.2
Bromoform	20	18.47	20.16	18.12	20.83	20.39	19.59	98	6.2
Bromomethane	20	18.53	21.27	19.25	20.66	21.31	20.20	101	6.2
2-Butanone	20	17.20	20.88	18.33	20.86	20.84	19.62	98	8.9
Carbon disulfide	20	18.63	20.86	19.00	20.99	21.50	20.20	101	6.4
Carbon tetrachloride	20	17.82	20.11	18.41	19.79	20.19	19.26	96	5.6
Chlorobenzene	20	18.11	20.65	18.47	20.60	20.63	19.69	98	6.5
Chloroethane	20	21.84	20.31	19.18	20.57	21.70	20.72	104	5.3
Chloroform	20	18.48	21.32	19.10	21.28	20.44	20.12	101	6.4
Chloromethane	20	18.35	20.08	19.11	20.38	19.18	19.42	97	4.2
Cyclohexane	20	18.00	20.07	18.01	19.55	20.35	19.20	96	5.9
1,2-Dibromo-3-chloropropane	20	17.23	20.88	18.03	21.62	20.69	19.69	98	9.8
Dibromochloromethane	20	17.36	20.07	18.23	19.76	20.07	19.10	95	6.5
1,2-Dibromoethane	20	17.97	20.06	18.13	20.01	20.88	19.41	97	6.6
1,2-Dichlorobenzene	20	17.74	19.92	18.11	19.41	20.05	19.05	95	5.6
1,3-Dichlorobenzene	20	17.95	20.10	17.98	19.90	20.25	19.24	96	6.1
1,4-Dichlorobenzene	20	18.05	19.66	18.22	19.47	19.67	19.01	95	4.3
Dichlorodifluoromethane	20	18.81	21.17	19.46	20.98	20.76	20.24	101	5.1
1,1-Dichloroethane	20	18.34	20.86	18.57	20.43	20.69	19.78	99	6.2
1,2-Dichloroethane	20	18.94	21.32	19.35	21.44	20.63	20.34	102	5.6

TABLE 9 (cont.)

US EPA REGION VI LABORATORY INITIAL DEMONSTRATION OF CAPABILITY DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Spike Conc. (µg/L)	Rep. #1	Rep. #2	Rep. #3	Rep. #4	Rep #5	Average	%Rec	RSD
1,1-Dichloroethene	20	17.69	20.18	18.44	21.12	19.81	19.45	97	7.1
cis-1,2-Dichloroethene	20	18.23	20.74	18.49	20.13	19.60	19.44	97	5.5
trans-1,2-Dichloroethene	20	18.29	20.50	18.25	19.89	20.04	19.39	97	5.4
1,2-Dichloropropane	20	17.97	20.35	18.23	19.98	20.44	19.39	97	6.2
cis-1,3-Dichloropropene	20	16.29	17.93	16.14	17.93	17.77	17.21	86	5.3
trans-1,3-Dichloropropene	20	16.83	18.88	16.93	18.46	18.50	17.92	90	5.4
Ethylbenzene	20	17.03	19.05	17.20	18.82	19.04	18.23	91	5.6
2-Hexanone	20	17.00	20.59	18.63	19.59	21.16	19.39	97	8.5
Isopropylbenzene	20	17.22	19.51	17.32	18.75	19.19	18.40	92	5.8
Methylene chloride	20	18.56	20.23	18.76	20.53	20.06	19.63	98	4.6
Methyl acetate	20	18.74	21.20	19.04	21.21	20.57	20.15	101	5.9
Methyl cyclohexane	20	18.36	20.51	18.33	20.50	20.26	19.59	98	5.8
4-Methyl-2-pentanone	20	15.91	19.04	16.86	18.10	18.86	17.75	89	7.6
Methyl tert-butyl ether	20	17.52	20.14	18.03	20.41	19.46	19.11	96	6.7
Styrene	20	17.59	19.93	17.88	19.52	19.87	18.96	95	6.0
1,1,2,2-Tetrachloroethane	20	18.29	21.59	19.00	22.17	21.09	20.43	102	8.3
Tetrachloroethene	20	18.12	20.53	18.80	20.79	20.91	19.83	99	6.5
Toluene	20	18.36	20.57	18.77	20.25	20.85	19.76	99	5.7
1,2,4-Trichlorobenzene	20	16.97	18.95	17.09	18.38	18.86	18.05	90	5.3
1,1,1-Trichloroethane	20	18.30	19.87	18.49	20.37	19.91	19.39	97	4.8
1,1,2-Trichloroethane	20	17.68	19.74	18.02	20.37	19.84	19.13	96	6.3
Trichloroethene	20	17.89	19.49	18.20	19.80	20.06	19.09	95	5.1

TABLE 9 (cont.)

US EPA REGION VI LABORATORY INITIAL DEMONSTRATION OF CAPABILITY DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Spike Conc. (µg/L)	Rep. #1	Rep. #2	Rep. #3	Rep. #4	Rep. #5	Average	%Rec	RSD
Trichlorofluoromethane	20	19.53	21.52	19.86	21.76	21.68	20.87	104	5.2
1,1,2-Trichloro-1,2,2-trifluoroethane	20	19.48	21.10	18.18	21.16	21.46	20.28	101	6.9
Vinyl chloride	20	19.22	21.48	19.35	21.33	20.97	20.47	102	5.4
o-Xylene	20	17.89	19.87	17.58	19.38	20.00	18.94	95	6.0
m & p-Xylene	40	36.15	40.29	36.51	39.44	40.57	38.59	96	5.5
Surrogates									
1,2-Dichloroethane-d_4	50	45.62	45.78	45.94	46.31	45.35	45.80	92	0.8
Toluene-d_8	50	47.00	47.17	47.65	47.24	46.93	47.20	94	0.6
Bromofluorobenzene	50	48.40	49.46	49.32	48.61	49.48	49.05	98	1.0

TABLE 10

EXAMPLE 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 11

RECOMMENDED QUANTITY OF EXTRACT 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 12

DIRECT INJECTION ANALYSIS OF NEW OIL AT VARIOUS CONCENTRATIONS (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 13

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 13 (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 14

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 15

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 16

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 17

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

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

TABLE 18

RECOVERIES IN SAND SAMPLES FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5035)

	Recovery per Replicate (ng)							Mean
Compound	1	2	3	4	5	Mean	RSD	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 19
RECOVERIES IN HAZARDOUS WASTE LANDFILL SOILS FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5035)

	Recovery per Replicate (ng)							Mean
Compound	1	2	3	4	5	Mean	RSD	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 20
RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5035)

	Recovery per Replicate (ng)							Mean
Compound	1	2	3	4	5	Mean	RSD	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 21

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

	Soil/H_2O[b] Recovery		Soil/Oil[c] Recovery		Soil/Oil/H_2O[d] Recovery	
Compound	Mean	RSD	Mean	RSD	Mean	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 21 (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. 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 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 22

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 22 (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 23

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

Compound	5 mL H_2O Recovery Mean	RSD	20 mL H_2O Recovery Mean	RSD	20 mL H_2O/Oil[b] 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	5 mL H_2O[b] Recovery RSD	20 mL H_2O[c] Recovery Mean	20 mL H_2O[c] Recovery RSD	20 mL H_2O/Oil Recovery Mean	20 mL H_2O/Oil Recovery 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

VOLATILE ORGANIC ANALYTE RECOVERY FROM FISH 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 24 (cont.)

Compound	Recovery Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane-d_4	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 oil 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-eluting compounds prevented accurate measurement of analyte.

TABLE 25

EXAMPLE LOWER LIMITS OF QUANTITATION FOR VOLATILE ORGANIC ANALYTES IN FISH OIL (METHOD 5032)[a]

	Lower Limit of Quantitation (ppb)	
Compound	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

TABLE 25 (cont.)

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[a] Method quantitation limits (MQLs) are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MQLs 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. MQLs can be used to establish the lower limit of instrument quantitation, however, since they are statistical approximations of the actual method sensitivity, it is recommended that the lowest calibration concentration be used to establish the minimum quantitation limit.

[b] No analyses.

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

TABLE 26

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 27

EXAMPLE PRECISION AND STATISTICAL MINIMUM QUANTITATION LIMIT (MQL) DETERMINED FOR ANALYSIS OF FORTIFIED SAND[a] (METHOD 5021)

Compound	% RSD	MQL (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 27 (cont.)

Compound	% RSD	MQL (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 28

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

Compound	Recovery per Replicate (ng)			Mean	RSD	Recovery
	Sample 1	Sample 2	Sample 3	(ng)		(%)
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-chloropropane	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 28 (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 29

EXAMPLE MINIMUM QUANTITATION LIMITS (MQL) AND BOILING POINTS FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)[a]

Compound	MQL (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.

TABLE 29 (cont.)

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* The method quantitation limit (MQL) is defined in Chapter One. The quantitation 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. MQLs can be used to establish the lower limit of instrument quantitation, however, since they are statistical approximations of the actual method sensitivity, it is recommeded that the lowest calibration concentration be used to establish the minimum quantitation limit.

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

TABLE 30

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

Bromochloromethane

Acetone
Acrylonitrile
Bromomethane
Carbon disulfide
Chloroethane
Chloroform
Chloromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,2-Dichloroethane-d_4 (surrogate)
1,1-Dichloroethene
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

1,4-Difluorobenzene

Benzene
Bromodichloromethane
Bromoform
Carbon tetrachloride
Chlorodibromomethane
Dibromomethane
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,1,1-Trichloroethane
1,1,2-Trichloroethane

TABLE 31

METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

Compound	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Quantitation 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 quantitation limits.

FIGURE 1
EXAMPLE GAS CHROMATOGRAM OF VOLATILE ORGANICS

(Provided Courtesy APPL, Inc.)

```
File        : M:\MAX\DATA\M050720\0720M07W.D
Operator    : RP
Acquired    : 20 Jul 05   19:50      using AcqMethod PM82602
Instrument  :    Max
Sample Name: Vol Std 07-20-05Z@10ug/L
Misc Info   : Water 10mL w/IS: 07-12-05AQ
Vial Number: 7
```

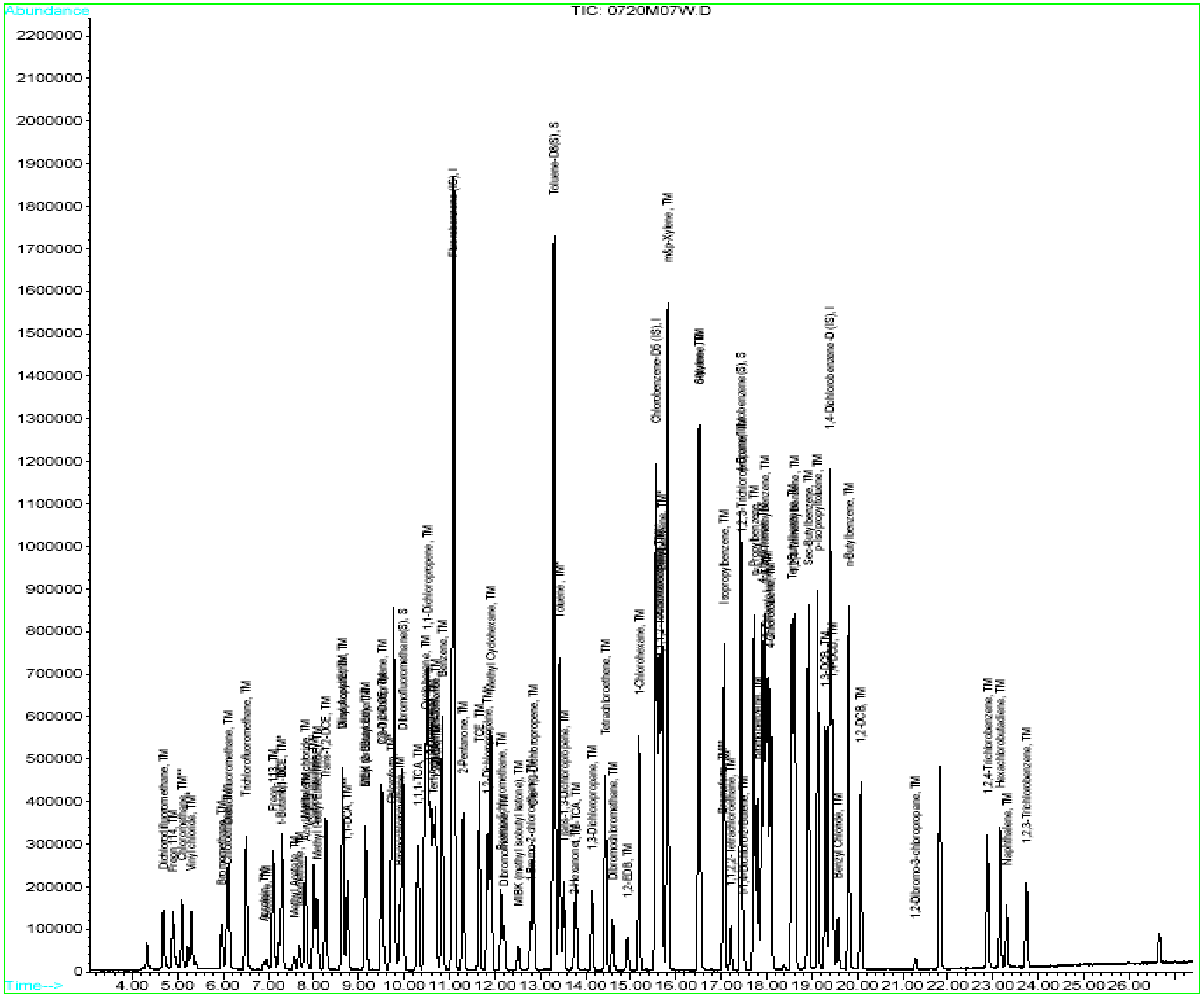

FIGURE 2
EXAMPLE GAS CHROMATOGRAM OF VOLATILE ORGANICS
(Provided Courtesy EPA Region III)