METHOD 8261

VOLATILE ORGANIC COMPOUNDS BY VACUUM DISTILLATION IN COMBINATION WITH GAS CHROMATOGRAPHY/MASS SPECTROMETRY (VD/GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8261 is used to determine the concentrations of volatile organic compounds, and some low-boiling semivolatile organic compounds, in a variety of liquid, solid, and oily waste matrices, as well as animal tissues. This method is applicable to nearly all types of matrices regardless of water, soil, sediment, sludge, oil, and biota content. Method 8261 is useful in the determination of the following compounds:

Compound	CAS Registry No.
Acetone	67-64-1
Acetonitrile	75-05-8
Acetophenone	98-86-2
Acrolein	107-02-8
Acrylonitrile	107-13-1
Allyl Chloride	107-05-1
Aniline	62-53-3
Benzene	71-43-2
Bromochloromethane	75-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone	78-93-3
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chlorodibromomethane	124-48-1
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
1,2-Dibromo-3-chloropropane	96-12-8

Compound	CAS Registry No.
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
cis-1,4-Dichloro-2-butene	764-41-0
trans-1,4-Dichloro-2-butene	110-57-6
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-35-4
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-3
trans-1,2-Dichloroethene	156-60-5
cis-1,2-Dichloroethene	156-59-2
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	594-20-7
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Diethyl ether	60-29-7
1,4-Dioxane	128-91-1
Ethyl acetate	141-78-6
Ethylbenzene	100-41-4
Ethyl methacrylate	97-63-2
Hexachlorobutadiene	87-68-3
2-Hexanone	591-78-6
Iodomethane	74-88-4
Isobutyl alcohol	78-83-1
Isopropylbenzene	98-82-8
p-Isopropyltoluene	99-87-6
Methacrylonitrile	126-98-7
Methylene chloride	75-09-2
Methyl methacrylate	80-62-6
1-Methylnaphthalene	90-12-0
2-Methylnaphthalene	91-57-6
4-Methyl-2-pentanone	108-10-1
Naphthalene	91-20-3

Compound	CAS Registry No.
N-Nitrosodibutylamine	924-16-3
N-Nitrosodiethylamine	55-18-5
N-Nitrosodimethylamine	62-75-9
N-Nitrosodi-*n*-propylamine	621-64-7
N-Nitrosomethylethylamine	10595-95-6
Pentachloroethane	76-01-7
2-Picoline	109-06-8
Propionitrile	107-12-0
n-Propylbenzene	103-65-1
Pyridine	110-86-1
Styrene	100-42-5
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Tetrahydrofuran	109-99-9
Toluene	108-88-3
o-Toluidine	95-53-4
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-00-3
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

1.2 This method can be used to quantitate most volatile organic compounds that have a boiling point below 245°C and a partition coefficient below 15,000, which includes compounds that are miscible with water. Note that this range includes compounds not normally considered to be volatile analytes (e.g., nitrosamines, aniline, and pyridine).

1.3 Method detection limits (MDLs) are provided in Table 8. These values are provided for guidance in developing appropriate quantitation limits. Each laboratory should develop its own matrix-specific quantitation limits using the guidance found in Chapter One. Samples that require dilution will have proportionately higher detection limits.

1.4 Method 8261 is based on a vacuum distillation and cryogenic trapping procedure (Method 5032) followed by gas chromatography/mass spectrometry (GC/MS). The method incorporates surrogate-based matrix correction, where the analysis of multiple samples is used to predict matrix effects by employing specific surrogates. As a result, the calculations involved are specific to Method 8261, and may not be used with data generated by another method. This method includes all of the necessary steps from sample preparation through instrumental analysis.

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 3500, 3600, 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, Sec. 2.1, 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 This method is restricted to use by, or under the supervision of, experienced personnel who are familiar with the techniques of vacuum distillation and experienced in the use of gas chromatography and mass spectrometry. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 An aliquot of a liquid, solid, or tissue sample is transferred to a sample flask, which is then attached to the vacuum distillation apparatus (see Figure 1). Nominal sample sizes are 5 mL for water, 5 g for soil, 5 g for tissue, and 0.2 to 1 g for oil. The sample sizes may be varied, depending on analytical requirements, while using the same calibration curve. The surrogate corrections will compensate for variations in sample size. A total of 5 mL of reagent water is added to the aliquot of soil, tissue, or oil.

2.2 The sample chamber pressure is reduced using a vacuum pump and remains at approximately 10 torr (the vapor pressure of water) as water is removed from the sample. The vapor is passed over a condenser coil chilled to 5°C, which results in the condensation of water vapor. The uncondensed distillate is cryogenically trapped in a section of stainless steel tubing chilled to the temperature of liquid nitrogen (-196°C).

2.3 After an appropriate distillation period, which may vary due to matrix or analyte group, the condensate contained in the cryotrap is thermally desorbed and transferred to the gas chromatograph using helium as a carrier gas.

2.4 Analytes eluted from the gas chromatographic 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).

2.5 Quantitation is accomplished in three specific steps.

2.5.1 The first step is the determination of the response of each analyte at the mass spectrometer using external standard means. The amount (mass) of analyte introduced into the mass spectrometer is determined by comparing the response (area) of the quantitation ion for the analyte from a sample analyses to the quantitation ion response generated during the initial calibration.

2.5.2 The second step is the determination of surrogate recovery. The recommended surrogates are listed in Table 3. The recovery of each analyte can be predicted using the recovery-properties relationship solutions (see Sec. 12.8).

2.5.3 Finally, using the predicted recovery, sample size, and quantity of analyte detected at the mass spectrometer, the concentration of analyte is calculated.

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

2.7 It must be emphasized that the vacuum distillation conditions are optimized to remove analyte from the sample matrix and to isolate water from the distillate. The conditions may be varied to optimize the method for a given analyte or group of analytes. The length of time required for distillation may vary due to matrix effects or the analyte group of interest. Operating parameters may be varied to achieve optimum analyte recovery.

3.0 DEFINITIONS

Many of the terms used in this method are defined in Chapter One. Other terms specific to this procedure are listed in the glossary at the end of the method.

4.0 INTERFERENCES

4.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baseline in the chromatograms.

4.1.1 Interferences distilled from the sample will vary from source to source, depending on the particular sample or matrix. The analytical system should be checked to insure freedom from interferences by analyzing method blanks utilizing the identical analytical conditions used for samples.

4.1.2 The apparatus can be decontaminated with a ten-minute evacuation of the distillation apparatus while the condenser coils are heated to 45°C or higher.

4.2 The laboratory where the analysis is to be performed should be completely free of solvents. 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 a clean environment to eliminate the potential for contamination from ambient sources.

4.3 Samples may be contaminated during shipment. Field and trip blanks should be analyzed to insure integrity of the transported sample. It is recommended that wherever possible, sample aliquots and surrogates are transferred directly to sample flasks in the field, weighed and sealed using Viton® (or equivalent) O-ring connections.

4.4 Impurities in purge gas and from organic compounds out-gassing from plumbing account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by including laboratory reagent blanks. All gas lines should be equipped with traps to remove hydrocarbons and oxygen.

5.0 SAFETY

5.1 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 specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 The following analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, trichloroethene, vinyl chloride, 1,1,2-trichloroethane, *N*-Nitrosodibutylamine, *N*-Nitrosodiethylamine, *N*-Nitrosodimethylamine, *N*-Nitrosodi-*n*-propylamine, and *N*-Nitrosomethylethylamine. Pure standard materials and stock standard solutions containing these compounds should be handled in a hood and a NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentration solutions of these compounds.

5.3 This method employs liquid nitrogen as a cryogenic coolant. Liquid nitrogen can cause burns to exposed skin, and should be handled with care. Employ insulated gloves or tongs when using this material.

6.0 EQUIPMENT AND SUPPLIES

6.1 Microsyringes - 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1000-µL. Each of these syringes should be equipped with a 20-gauge (0.006 in ID) needle.

6.2 Syringe - 5-mL and 10-mL gas-tight, with Luer Lock tip and needles.

6.3 Balances

6.3.1 Analytical balance capable of accurately weighing 0.0001 g.

6.3.2 Top-loading balance capable of weighing 0.1 g.

6.4 Balance weights - Stainless steel S-class weights ranging from 5 mg to 100 g.

6.5 Sample flask - 100-mL borosilicate bulb joined to a 15-mm ID borosilicate O-ring connector, or equivalent. The flask must be capable of being evacuated to a pressure of 10 millitorr without implosion. The flask is sealed for sample storage with an O-ring capable of maintaining the vacuum in the chamber, a 15-mm ID O-ring connector cap, and a pinch clamp.

6.6 Vacuum distillation apparatus (See Figure 1) - The basic apparatus consists of a sample chamber connected to a condenser which is attached to a heated six-port valve (V4) and is available from Cincinnati Analytical Instruments, Cincinnati, OH. The sampling valve is connected to the following;

1) condenser (by way of vacuum pump valve - V3)
2) vacuum pump
3) cryotrap
4) gas chromatograph/mass spectrometer

The six-port sampling valve (V4) should be heated to at least 120°C to prevent condensation and potential carryover.

6.6.1 The condenser is operated at two different temperatures. The lower temperature is between -5 and 10°C, and the upper temperature is greater than 45°C. The lower temperature is used to condense water and should be a consistent temperature throughout the interior surface. The condenser is heated to the upper temperature to remove water and potential contaminants. The initial apparatus described in Reference 9 used circulating fluids (see Fig 1) but other means of controlling temperatures may be used.

6.6.2 The apparatus is heated to a temperature sufficient to prevent condensation of analytes onto condenser walls, valves, and connections. The transfer line from the sampling valve to the gas chromatograph should be heated to a temperature between 150°C and the upper temperature utilized by the GC program.

6.6.3 Pirani gauges are recommended at the vacuum pump for monitoring the distillation (Edwards Pirani gauge model 1001 with Pirani gauge head model PRH10K, or equivalent).

6.6.4 The original apparatus used a cryoloop consisting of an 8-in length of 1/8-in OD stainless steel tubing without any packing. These dimensions are not critical, but the loop must be of dimensions sufficient to trap the analytes of concern. Shorter loops will trap the most volatile analytes less effectively. Revised performance criteria should be determined whenever the dimensions of the cryoloop are changed significantly.

6.6.5 The dimensions of the initial apparatus have been published in Reference 5. These dimensions are not critical and can be varied without altering the results (i.e., 6-

port valves versus combinations of other valves, different condenser sizes, vacuum pump capacity). Any apparatus used must demonstrate appropriate performance for the intended application (see Tables 6-9).

6.7 Gas chromatograph/mass spectrometer system

6.7.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

6.7.2 Column - 60 m x 0.53-mm ID, 3.0-µm film thickness VOCOL fused-silica capillary column (Supelco, Bellefonte, PA), or equivalent. Laboratories may use other columns provided that they document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.7.3 Mass spectrometer - Capable of scanning from 35-350 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets the criteria listed in Table 1 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.

6.7.4 Gas chromatograph/mass spectrometer heated jet separator interface - A heated glass jet separator interface capable of removing from 10 to 40 mL/min of helium from the exit end of the wide-bore capillary column. The interface should have the ability to be heated through a range of 100 to 220°C.

6.8 Containers for liquid nitrogen - Dewars or other containers suitable for holding the liquid nitrogen used to cool the cryogenic trap and sample loop.

7.0 REAGENTS AND SUPPLIES

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

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. Store away from other solvents.

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

7.4.1 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 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.4.2 Add the assayed reference material, as described below.

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

7.4.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side-arm relief valve and direct a gentle stream of gas onto the methanol meniscus.

7.4.3 Reweigh, dilute to volume, stopper, and mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (µg/µL) 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.

7.4.4 Transfer the stock standard solution into a PTFE-sealed screw cap bottle. Store, with minimal headspace, at -10 to -20°C and protect from light.

7.4.5 Prepare fresh gas standards every two months. Reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently. All other standards should be replaced after six months, or sooner if comparison with check standards indicates a problem.

7.5 Secondary dilution standards - Using stock standard solutions, prepare in methanol secondary dilution standards 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.

7.6 Surrogate standards

This method incorporates surrogates that are added to each sample prior to analysis and are used to monitor and correct for matrix effects such as gas-liquid partitioning and condensation. Additional surrogates are used to monitor the effectiveness of the surrogate corrections. The specific surrogates used are described in the following sections. Additional information is provided in the glossary. A stock solution containing all of the surrogates should be prepared in methanol at the concentrations listed in Table 3 (15-150 ng/mL). Each sample should be spiked with 5 µL of the surrogate spiking solution prior to analysis.

7.6.1 Gas-liquid partitioning surrogates (α-surrogates) - The following compounds are recommended for use as α-surrogates:

Hexafluorobenzene
Pentafluorobenzene
Fluorobenzene
1,4-Difluorobenzene
o-Xylene-d_{10}
Chlorobenzene-d_5 (may also be used as a β-surrogate)
1,2-Dichloroethane-d_4
1,2-Dibromoethane-d_4
Ethyl acetate-$^{13}C_2$
Acetone-d_6
1,4-Dioxane-d_8
Pyridine-d_5

7.6.2 Condensation surrogates (boiling point or β-surrogates) - The following compounds are recommended for use as β-surrogates:

Toluene-d_8
Chlorobenzene-d_5 (may also be used as an α-surrogate)
Bromobenzene-d_5
Decafluorobiphenyl
1,2,4-Trichlorobenzene-d_3
1,2-Dichlorobenzene-d_4
1-Methylnaphthalene-d_{10}

7.6.3 Additional surrogates

Additional surrogates (check surrogates) should be analyzed to monitor the effectiveness of the matrix corrections. The recommended check surrogates are listed below, along with the aspects of the vacuum distillation process that they may be used to evaluate.

7.6.3.1 Benzene-d_6, 1,1,2-trichloroethane-d_3, and 1,2-dichloropropane-d_6 are low-boiling, volatile analytes. Their recoveries represent the adequacy of the relative volatility-recovery relationship for most analytes.

7.6.3.2 Methylene chloride-d_2 is similar to benzene-d_6 and 1,2-dichloropropane-d_6 (see Sec. 7.6.3.1), but is more sensitive to the presence of excessive methanol. Low recovery of this analyte may indicate a large amount of polar solvents in a sample.

7.6.3.3 Diethyl ether-d_{10} is a volatile low-boiling surrogate that coelutes with methanol. This compound is used to identify when the concentration of methanol begins to affect the GC/MS determination step.

7.6.3.4 4-Bromo-1-fluorobenzene and naphthalene-d_8 are higher-boiling analytes and their recoveries are an indication of the adequacy of corrections for their boiling-point range.

7.6.3.5 Acetophenone-d_5 and nitrobenzene-d_5 are higher-boiling and less volatile analytes and their recoveries are an indication of the adequacy of matrix corrections for the less volatile analytes.

7.6.3.6 Acetone-d_6 is used to check the adequacy of the surrogate corrections for the less volatile analytes.

7.6.3.7 Ethyl acetate-$^{13}C_2$ is a less volatile analyte that has been observed to degrade in some media and is also affected by the presence of methanol. Its recovery should be considered with the recovery of other surrogates.

7.6.3.8 Pyridine-d_5 is the least volatile of the surrogates and its recovery is an excellent indication of the limits of the method. It is very sensitive to matrix variations and can be poorly (or excessively) recovered when all other surrogates (and analytes) are recovered adequately.

7.7 4-Bromofluorobenzene (BFB) standard - A solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

7.8 Calibration standards

Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Sections 7.1 and 7.2). Prepare these solutions in reagent water or purge-and-trap grade methanol. 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. Store for one week or less at -10 to -20°C in a vial with minimal headspace.

7.8.1 It is the intent of EPA that all target analytes for a particular analysis be included in the calibration standard(s). These target analytes may not include the entire list of analytes (see 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).

7.8.2 The calibration standards must also contain the surrogates chosen for the analysis.

7.9 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards by stored at -10 to -20°C in screw-cap or crimp-top amber bottles with PTFE liners.

7.10 Liquid nitrogen - For use in cooling the cryogenic trap (see Figure 1) and the condenser described in Reference 9, if employed.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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 other samples.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One and Method 8000 for specific quality control procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

9.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows and calibration verification. In addition, the initial calibration and calibration verification data must be evaluated as described below.

9.2.1 The GC/MS must be tuned to meet the BFB criteria in Table 1, each 12-hour period during which analyses are performed.

9.2.2 The GC/MS must undergo an initial calibration, as described in Sec. 10.3.

9.2.3 A system performance check should be made before the initial calibration data are used. The surrogates chlorobenzene-d_5, 1,2-dichlorobenzene-d_4, and tetrahydrofuran-d_8 are used as reference compounds against which other analytes are evaluated as relative responses. This provides assurance that the system is sufficiently sensitive to determine the analytes presented in Table 2. There are four classes of compounds that are determined using this method. Class I compounds include those compounds with boiling points generally below 160 °C and α-values (or K-values) below 50 (i.e., the permanent gases and volatiles). Class II compounds are those with boiling points greater than 160 °C (i.e., the neutral semivolatiles). Class III compounds are those with α-values greater than 50 (i.e., the water soluble volatiles). Class IV compounds are the basic compounds that are susceptible to degradation and have a low detector response (i.e., the basic semivolatiles).

9.2.3.1 Class I compounds are monitored using four compounds (the System Performance Check Compounds, or SPCCs for Class I) that are checked for a minimum average response relative to chlorobenzene-d_5. These compounds are chloromethane, 1,1-dichloroethane, bromoform, and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

9.2.3.1.1 Chloromethane is an analyte likely to be lost if the cryotrap is not properly cooled or if there is a significant air leak in the system.

9.2.3.1.2 Bromoform is a compound that can be poorly recovered if the system is under a required vacuum or there are significant cold spots.

9.2.3.1.3 1,1,2,2-Tetrachloroethane and 1,1-dichloroethane may be degraded in the apparatus or by system contamination.

9.2.3.1.4 The minimum mean relative responses for the various Class I SPCCs are as follows:

Chloromethane	0.05
1,1-Dichloroethane	0.10
Bromoform	0.10
1,1,2,2-Tetrachloroethane	0.30

9.2.3.2 Class II compounds are monitored using two compounds (SPCCs for Class II) that are checked for a minimum average response relative to 1,2-dichlorobenzene-d_4. These compounds are hexachlorobutadiene, and 2-methyl- naphthalene.

9.2.3.2.1 Hexachlorobutadiene is likely to be lost if there is a cold spot or degradation due to system contamination.

9.2.3.2.2 2-Methyl naphthalene is very sensitive to cold spots and contamination.

9.2.3.2.3 The minimum mean relative responses for the Class II SPCCs are as follows:

Hexachlorobutadiene	0.30
2-Methylnaphthalene	0.30

9.2.3.3 Class III compounds are monitored using two compounds (SPCCs for Class III) that are checked for a minimum average response to tetrahydrofuran-d_8. These compounds are 1,4-dioxane and pyridine.

9.2.3.3.1 1,4-Dioxane can be lost due to a poor system vacuum. The compound may also have a low response due to poor chromatography.

9.2.3.3.2 Pyridine can be lost due to poor system vacuum and system contamination. Too much water in the cryoloop will also depress the relative response.

9.2.3.3.3 The minimum mean relative responses for the Class III SPCCs are as follows:

1,4-Dioxane	0.10
Pyridine	0.10

9.2.3.4 Class IV compounds are monitored using two compounds (SPCCs for Class IV) and are checked for a minimum average response relative to tetrahydrofuran-d_8. These compounds are aniline, *N*-nitrosodimethylamine and *N*-nitrosodiethylamine.

9.2.3.4.1 Each of the SPCCs for Class IV is easily lost if there is a poor vacuum, system contamination, or active sites. The SPCC compounds may also have low responses due to poor chromatography.

9.2.3.4.2 The minimum mean relative responses for the Class III SPCCs are as follows:

Aniline	0.010
N-Nitrosodimethylamine	0.005
N-Nitrosodiethylamine	0.010

9.2.4 The Calibration Check Compound (CCC) data must be evaluated before the initial calibration data are employed. As with the SPCC criteria, the CCC criteria are based on four classes of compounds (I-IV). The CCCs are evaluated on the basis of the relative standard deviation (RSD) of the calibration factors of each compound determined by an external standard calibration procedure. Calculate the standard deviation and relative standard deviation (RSD) of the calibration factors for each compound in the initial calibration, as described in Sec. 12.4.

9.2.4.1 The CCCs for the Class I compounds are:

Vinyl chloride
Chloroform
Toluene
Ethylbenzene
1,2-Dichloroethane
Bromobenzene

In practice, the calculated RSD for each Class I CCC should be $\leq$ 20%, and it must be $\leq$ 35%.

9.2.4.2 The CCCs for the Class II compounds are:

1,3-Dichlorobenzene
1,2,3-Trichlorobenzene
Naphthalene

In practice, the calculated RSD for each Class II CCC should be $\leq$ 25 % and it must be $\leq$ 35%.

9.2.4.3 The CCCs for the Class III compounds are:

4-Methyl-2 pentanone
Methacrylonitrile
1,4-Dioxane

In practice, the calculated RSD for each Class III CCC should be $\leq$ 30% and it must be $\leq$ 40%.

9.2.4.4 The CCCs for the Class IV compounds are:

N-Nitrosomethylethylamine
N-Nitrosodi-n-propylamine

In practice, the calculated RSD for each Class IV CCC should be ≤ 35% and it must be ≤ 45%.

9.2.4.5 If any CCC fails the criteria listed in Secs. 9.2.4.1 - 9.2.4.4, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

9.2.5 Initial calibration linearity

9.2.5.1 If the RSD of the calibration factors for any compound is 20% or less, then the instrument response is assumed to be constant over the calibration range, and the average calibration factor may be used for quantitation (Secs. 12.3 and 12.8.5).

9.2.5.2 If the RSD of the calibration factors for any compound is greater than 20%, see Sec. 7.0 in Method 8000 for options on dealing with non-linear calibrations. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

9.2.5.3 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.

NOTE: The RSD is used as a measure of linearity of each compound's response irrespective of the CCC criteria in Sec. 9.2.4. If the CCC criteria are met, then the results from the initial calibration may be used to calculate subsequent sample results. However, the calculations for each analyte must take into account the linearity of the calibration factors for that analyte in determining which of the calibration approaches described in Method 8000 are to be employed.

9.2.6 GC/MS calibration verification

A calibration verification must be performed for all samples analyzed after the 12-hour analytical shift during which the initial calibration was performed.

9.2.6.1 Prior to the analysis of samples, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system using the same introduction method as is used for samples. The resultant mass spectra for the BFB must meet the criteria given in Table 1 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

9.2.6.2 The initial calibration curve (Sec. 9.2.2) for each compound of interest must be verified once every 12 hours during analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS and by checking the SPCCs and CCCs, as described in Sec. 10.5.

NOTE: A method blank should be analyzed prior to the calibration standard to ensure that the total system (introduction device, transfer lines, and GC/MS system) is free of contaminants.

9.2.6.3 System performance check compounds (SPCCs)

A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Secs. 9.2.3.1 - 9.2.3.4). This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

9.2.6.4 Calibration check compounds (CCCs)

9.2.6.4.1 After the system performance check is met, the CCCs listed in Secs. 9.2.4.1 - 9.2.4.4 are used to check the validity of the initial calibration. Calculate the percent difference as described in Sec. 12.5.

9.2.6.4.2 If the percent difference for each CCC is $\leq$ 35% for the Class I and Class II CCCs, $\leq$ 40% for the Class III CCCs, and $\leq$ 45% for the Class IV CCCs, then the initial calibration is assumed to be valid, and analyses may continue. If the criteria are not met for any one CCC, then corrective action must be taken prior to the analysis of samples.

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

9.2.7 The responses of the surrogates and their retention times must be evaluated immediately after or during data acquisition. If the retention time for any surrogate changes by more than 30 seconds from the last calibration verification (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the surrogates changes by a factor of two (-50% to +l00%) from the previous calibration verification standard, 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 necessary.

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. The laboratory must also repeat the demonstration of proficiency whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

9.4 Sample quality control for preparation and analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection/quantitation limit). At a minimum, this includes the analysis of QC samples including a method blank and a laboratory control sample (LCS) in each analytical batch, the addition of surrogates to each field sample and QC sample, and routine analyses of matrix spike and matrix spike duplicate aliquots.

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

9.4.2 The various surrogates added to the sample are used to document the effect of the sample matrix on the overall analysis. Therefore, the use of matrix spike/matrix spike duplicate samples is not necessary.

9.4.3 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. When the surrogate recoveries in a sample 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.

9.5 Surrogate recoveries

The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on developing and updating surrogate limits. Matrix effects and distillation performance may be monitored separately through the use of surrogates. The effectiveness of using the α- and β-surrogates to correct matrix effects is monitored using the check surrogates identified in Sec. 7.6.3.

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

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

10.0 CALIBRATION AND STANDARDIZATION

10.1 Establish the GC/MS operating conditions, using the following information as guidance. Optimize the conditions for selectivity and sensitivity. Once established, the same operating conditions must be used for all analyses, including calibrations, blanks, and samples.

Recommended GC/MS operating conditions:

Electron energy:	70 volts (nominal)
Mass range:	38-270 amu
Scan time:	To give 8 scans/peak but not to exceed 3 sec/scan
Jet separator temperature:	210°C
Transfer line temperature:	280°C
Injector inlet temperature:	240°C
Inlet pressure:	10 psi
Initial column temperature:	10°C
Initial hold time:	3.0 min
Temperature Program #1:	50°C/min to 40°C
Temperature Program #2:	5°C/min to 120°C
Temperature Program #3:	20°C/min to 220°C
Final column temperature:	220°C
Final hold time:	3.4 min

10.2 Prior to the initial calibration, the GC/MS system must be hardware-tuned to meet the criteria in Table 1 for a 5-50 ng injection of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

10.3 Initial calibration

As with techniques such as purge-and-trap GC/MS, the initial calibration involves carrying the calibration standards through the entire distillation and analysis procedure.

10.3.1 Cool the cryoloop to -150°C (or lower) while the sample loop valve is in the load position (Valve V4 in Figure 1).

10.3.2 Cool the condenser column to the recommended temperature for vacuum distillation operation (-5 to + 5°C).

10.3.3 Close the valve to the sample chamber (Valve V1 in Figure 1).

10.3.4 Add 5 mL of reagent water to the sample flask and spike the water with the appropriate standards and surrogates, and reconnect the flask to the apparatus.

10.3.5 Perform the vacuum distillation and introduce the distillate into the GC/MS, as described in Sec. 11.2.

10.3.6 Repeat the procedure for the remaining calibration standards.

10.4 Calibration factors

Calculate a calibration factor (CF) for each target analyte and surrogate in each of the five initial calibration standards as described in Sec. 12.1, using external standard calibration techniques (see Method 8000). Calculate the relative response (RR) for each SPCC in the calibration standards, as described in Sec. 12.2.

10.5 Calibration verification

The initial calibration must be verified at the beginning of each 12-hour analytical shift during which samples are to be analyzed. The verification involves the analysis of the mid-concentration standard from the initial calibration, using the procedures described in Secs. 10.3.1 to 10.3.5.

10.5.1 Prior to the analysis of standards, blanks, or samples, the GC/MS system must be hardware tuned to meet the criteria in Table 1 for BFB.

10.5.2 For each analyte in the calibration verification standard, calculate the calibration factor, as described in Sec. 12.1. Calculate the relative response for each SPCC in the calibration verification standard, as described in Sec. 12.2.

10.5.3 Evaluate the SPCCs and CCCs as described in Secs. 9.2.6.3 and 9.2.6.4. The analysis of samples should not proceed until the calibration has been verified.

11.0 PROCEDURE

11.1 Sample preparation

Other sample volumes or weights may be employed, provided that the sensitivity of the method is adequate for project needs. Given the inherent recovery correction, changes in sample size do <u>not</u> necessitate recalibration of the instrument.

11.1.1 Aqueous samples

Quickly transfer a 5-mL aliquot of the sample to the distillation flask, taking care not to introduce air bubbles or agitate the sample during the transfer. Add 10 µL of the surrogate spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

11.1.2 Solid and soil samples

Solid and soil samples should be rapidly withdrawn from their sample container and weighed while still cold. Weigh out a 5-g aliquot and then rapidly transfer it to the sample chamber. Add 10 µL of the surrogate spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

11.1.2.1 Determination of percent dry weight - When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed at the same time as the portion used for analytical determination.

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

Immediately after weighing the sample for extraction, weigh 5 - 10 g of the sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as described in Sec. 12.6.

11.1.2.2 It is highly recommended that the sample aliquot for dry weight determination not be withdrawn from the sample container until it is certain that no analytical samples will be needed for high concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere.

11.1.3 Tissue samples

Tissue samples which are fleshy may have to be minced into small pieces to get them through the neck of the sample chamber. This is best accomplished by freezing the sample in liquid nitrogen before any additional processing takes place. Biota containing leaves and other softer samples may be minced using clean scissors. Weigh out a 5-g aliquot and then rapidly transfer it to the sample chamber. Add 10 µL of the surrogate spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

11.1.4 Oil samples

Weigh out 0.2 to 1.0 g of oil, and then rapidly transfer it to the sample chamber. Add 10 µL of the surrogate spiking solution to the sample in the flask, and attach the flask to the vacuum distillation apparatus.

11.2 Analysis

11.2.1 Turn the coolant/heat valve (V2 in Fig. 1) to circulate coolant through the condenser coils. Be sure all connections are complete and sealed properly. Open the sample chamber valve to begin the distillation. Continue distillation for 5-10 minutes.

NOTE: IF PIRANI GAUGES ARE USED, after five minutes of distillation, the Pirani gauge at the vacuum pump should indicate $\leq$ 0.1 torr. If this pressure is not attained, a leak may be present and the distillation may not be successful. Distillation performance surrogates should be evaluated for acceptability of distillation.

11.2.2 Setup the data system for acquisition of the data file. This may be done prior to 11.2.1. While distillation times may vary depending on sample matrix, the data system should be ready and the GC oven should be at equilibrium by the time the distillation is complete.

11.2.3 GC/MS analyses may be performed once the distillation is complete. Turn the sampling valve handle to the inject position while maintaining the cryoloop at -150°C or lower. Begin heating the cryoloop and desorb the sample in the loop. Commence GC/MS data acquisition.

11.2.4 Once acquisition has begun, the sample chamber valve may be closed and the sample flask removed.

11.2.5 The distillation apparatus can now be readied for the next analyses. This is accomplished by switching the vacuum pump valve (V3 in Fig. 1) to the vacuum pump position which disconnects the vacuum stream to the sampling valve (V4 in Fig. 1). The condenser is heated to the decontamination temperature recommended by the manufacturer. Evacuate the distillation apparatus for 10 minutes.

12.0 DATA ANALYSIS AND CALCULATIONS

The quantitation routine employed in Method 8261 differs significantly from that used in Method 8260 (using the Method 5032 sample preparation). Where Method 8260 uses one internal standard to correct injection/preparation variations for a given analyte, Method 8261 uses a series of surrogates to define the relationships of compound recoveries to their physical properties. Those relationships are used to extrapolate target analyte recoveries. Each target analyte and surrogate is calibrated using an external standard calibration procedure. The concentration of the analyte in the sample is determined using the predicted analyte recovery, sample size, and amount of analyte detected by the mass spectrometer. The relationships are solved using multiple surrogates and the errors associated with these relationships can be calculated and can be used as indicators of data accuracy for the analyses. The quantitation limits for those analytes that are not detected are also corrected to reflect matrix effects.

The quantitation algorithms and sequence presented here have been demonstrated to be acceptable and can be accomplished easily in a spreadsheet format (Reference 7). The quantitation routine presented is a stepwise procedure that initially estimates the α-effects on the β-surrogates, calculates the boiling point effects, and then calculates the relative volatility effects. After the analyte recoveries are calculated, the amount of analyte detected by the mass spectrometer is corrected by the recovery and sample size to provide the analyte concentration. Table 3 lists the α- and β-surrogates. Additional surrogates can be used to improve the solution of the matrix effects-recovery relationship.

Other surrogate correction approaches may be employed when they have been demonstrated to improve the assessment of matrix effects. Large samples of biota (10 g or more) may require that the analyst address the partitioning of analytes between air and the organic phase. Such an approach is described in References 8 and 9.

12.1 Calculation of calibration factors

The response of the mass spectrometer to a given concentration of a surrogate or target analyte is used to calculate a calibration factor (CF) in a fashion analogous to the external calibration procedures used in GC methods.

The following equation is used to calculate the calibration factor for each target analyte and surrogate.

$$\text{Calibration factor} = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Amount of the Compound Injected (in nanograms)}}$$

12.2 Calculation of relative response for SPCCs

The relative response (RR) is simply the ratio of the response of an SPCC to the response of the surrogate compound used as a reference (see Table 3), calculated as shown below:

$$\text{Relative response} = \frac{\text{CF of SPCC}}{\text{CF of the surrogate compound}}$$

12.3 Calculate the mean RR for each SPCC using the five RR values from the initial (5-point) calibration curve in Sec. 12.2, as follows:

$$\text{mean RR} = \frac{\sum_{i=1}^{n} RR_i}{n}$$

Calculate the mean calibration factor for each target analyte (including the SPCCs), as follows:

$$\text{mean CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

12.4 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the calibration factors for each compound from the initial calibration, as follows:

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

where:

CF_i = CF for each of the calibration standards
$\overline{CF}$ = Mean CF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

12.5 Calculate the percent difference (%D) of the calibration factor determined during the calibration verification and the mean calibration factor from the most recent initial calibration, using the equation below:

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

where:

$\overline{CF}$ = Mean CF from the initial calibration
CF_v = CF from the calibration verification standard

12.6 Where appropriate, calculate the percent dry weight of a solid sample using the equation below and the weights determined in Sec. 11.1.2.

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

12.7 Qualitative analysis

The qualitative identification of compounds 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.

12.7.1 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.

12.7.2 The retention time (RT) of the sample component is within ± 30 seconds of the RT of the standard component.

12.7.3 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%.)

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

12.7.5 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.

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

12.7.7 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.

12.8 Quantitative analysis

Quantitative of target analytes requires four distinct steps: calculation of the α-effects on the β-surrogates, calculations of the boiling point effects, calculation of the relative volatility effects on recovery, and finally, recovery correction of the quantity of analyte measured by the mass spectrometer to reflect these three effects. An explanation of these effects and the use of the following equations are given in greater detail in References 5 and 6.

12.8.1 Calculation of α-effects on the β-surrogates

The initial approximation of the α-effect on the β-surrogates is accomplished by using the α-surrogates, fluorobenzene and 1,2-dichloroethane-d_4 (boiling points of 85 and 84°C, respectively), with the assumption that β-effects are minimal at 85°C. The equation used is:

$$\ln(R_\alpha) = e^{(c_1 \times \alpha_K)} + c_2$$

where:

R_α = The surrogate's relative recovery corresponding to its α_K-value
α_K = Relative volatility of the surrogate (describes the α-effect versus recovery relationship).
c_1, c_2 = Empirically-derived constants

The relative recoveries of the β-surrogates (toluene-d_8, chlorobenzene-d_5, bromobenzene-d_5 and 1,2-dichlorobenzene-d_4) are adjusted for their α-effects (R_β = measured recovery/R_α). The resulting relative recovery represents the component of the relative recovery related to β-effects. Similarly, the α-surrogates (1,2-dichloroethane-d_4 and 1,4-dioxane-d_8) are used to interpolate R_β for the β-surrogate 1-methylnaphthalene-d_{10}.

12.8.2 Calculation of boiling point effects

Using the β-surrogate R_β values, the R_β-boiling point relationship is described using the equation:

$$R_\beta = (c_3 \times [bp - bp_0]) + c_4$$

where:

R_β = The β-surrogate's relative recovery corresponding to the boiling point
bp = The analyte's boiling point
bp_0 = The lowest boiling point of the β-surrogate used in the solution
c_3, c_4 = Empirically-derived constants

The impact of a single β-surrogate relative-recovery measurement error is minimized by calculating three solutions to the equation above for each analyte. The β-surrogate pairs used to solve this equation for groups of analytes by boiling point are identified in Table 5. The average and standard deviation of the three R_β values (only two solutions for the 80 to 111°C and 220 to 250 °C ranges) generates the predicted analyte relative recovery range, $\overline{R}_\beta \pm r_\beta$, corresponding to β-effects. The resultant $\overline{R}_\beta$ for each α-surrogate is used to correct their measured relative responses (R_α = measured recovery/$\overline{R}_\beta$) to isolate the relative recoveries related to α-effects.

12.8.3 Calculation of the relative volatility effects on recovery

The α-surrogate corrections are performed by grouping analytes with similar α_K-values. The α-effects exhibited by those compounds at the limits of a group are the best data to describe the α-effects for those analytes within these groups and therefore pairs of α-surrogates are selected to represent the extremes of each group's range of α_K-values (i.e., the surrogates hexafluorobenzene and fluorobenzene represent the lower and upper ends of the grouping of α-values between 0.07 and 3).

One lower-value α-surrogate and one higher-value α-surrogate are selected to calculate the relationship of relative recovery to α_K-values within the group. Using the four possible combinations of surrogates to solve the equation in 12.8.1, each analyte will have four α-effect measurements. The equation used is:

$$\ln(R_\alpha) = e^{(c_1 \times \alpha_x)} + c_2$$

where:

R_α = The surrogate's relative recovery corresponding to its α_K-value
α_x = Relative volatility of compound X (describes the α-effect versus recovery relationship).
c_1, c_2 = Empirically-derived constants

12.8.4 The predicted relative recovery relating to α-effects for an analyte is $\overline{R}_\alpha \pm r_\alpha$. The predicted total relative recovery that includes α- and β-effects is:

$$R_T = \overline{R}_\alpha \times \overline{R}_\beta$$

where:

$\overline{R}_\alpha$ = Average relative recovery using the equation in 12.8.3.
$\overline{R}_\beta$ = Average relative recovery using the equation in 12.8.2 for the combinations of β-surrogates in the analytes boiling point grouping.
R_T = Predicted total relative recovery

The associated variance term is:

$$r_T^2 = r_\alpha^2 + r_\beta^2$$

where the r values are the standard deviations of the corresponding relative recoveries.

12.8.5 Calculation of sample concentration

The calculation of the concentration in a sample is a three-step process.

12.8.5.1 The amount (mass in ng) of the analyte detected by the mass spectrometer is calculated using an external standard approach, such that:

$$\text{Amount (ng)} = \frac{(A_s)(D)}{(\overline{CF})}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.
$\overline{CF}$ = Mean calibration factor from the initial calibration (area per ng).

12.8.5.2 The relative recovery (R_T) is predicted from the equations in Secs. 12.8.1 - 12.8.4.

12.8.5.3 The third step is to perform the recovery correction on the amount of analyte detected and to relate that amount to the size of the actual sample, as described below:

$$\text{Concentration} = \frac{(\text{ng analyte detected})}{R_T \times (\text{sample size})}$$

For aqueous samples, the sample size is expressed in mL, leading to a concentration in ng/mL, which is equivalent to µg/L. For solid samples, oil samples, and tissues, the sample size is expressed in g, leading to a concentration in ng/g, which is equivalent to µg/kg.

Using the variance term in Sec. 12.8.4, a concentration range can be calculated for each analyte.

12.9 Calculation of check surrogate recovery

The check surrogates are used to monitor the overall performance of the analytical system. The recovery of each check surrogate is calculated in a fashion similar to the analyte concentrations, correcting the mass spectrometer response for the recoveries of the other surrogates and the sample size, such that:

$$\text{Recovery} = \frac{(\text{ng check surrogate detected})}{R_T \times (\text{ng of check surrogate spiked})}$$

12.10 Reporting matrix corrections

A graphical representation of the effect of the sample matrix on the recovery of the analytes may prove useful in evaluating method performance. Although not required, Figure 2 provides an example of one form of such documentation.

13.0 METHOD PERFORMANCE

13.1 The recovery of the target analytes spiked into three soils is summarized in Table 6, along with the relative error of replicate recovery measurements and the precision of the surrogate recoveries in these spiked samples.

13.2 Similar recovery data from an oil sample spiked with the target analytes are presented in Table 7.

13.3 The MDL is defined in Chapter One. **The MDLs for water, soil, oil, and waste oil matrices are presented in Table 8 and are provided for illustrative purposes only.** These MDLs were based on the analysis of 21 replicate samples of each spiked matrix, which is not the same procedure described in either Chapter One or 40 CFR 136. The MDL values presented in Table 8 are corrected for the recoveries of the surrogates. Each laboratory should develop its own matrix-specific MDLs, if necessary, using the guidance found in Chapter One.

13.4 The target analytes were spiked into water containing salt, soap, and glycerine, as a test of the effects of ionic strength, surfactants, etc., on the VD/GC/MS procedure. The recovery data from these analyses are provided in Table 9.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of a waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. 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 feasibley 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. NW, Washington, D.C. 20036, (202) 872-4477.

14.3 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards that will require disposal.

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 pages to follow contain Tables 1 through 11, Figures 1 and 2, a flow diagram of the method procedure, and a glossary of terms specific to this method.

TABLE 1

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]Alternative tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

TABLE 2

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	41, 40, 39
Acetophenone	105	-
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl chloride	76	76, 41, 39, 78
Aniline	66	93
Benzene	78	-
Bromobenzene	156	158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
2-Butanone	72	43, 72
n-Butylbenzene	134	91, 92
sec-Butylbenzene	134	105
tert-Butylbenzene	134	91, 119
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chlorobenzene	112	77, 114
Chlorodibromomethane	129	208, 206
Chloroethane	64	66
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	126	91
4-Chlorotoluene	126	91
1,2-Dibromo-3-chloropropane	157	75, 155
Dibromomethane	174	93, 95
1,2-Dibromomethane	107	109
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148

TABLE 2
(continued)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	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
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
Diethyl ether	74	45, 59
1,4-Dioxane	88	88, 58, 43, 57
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethyl methacrylate	69	69, 41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
2-Hexanone	58	100
Iodomethane	142	127, 141
Isobutyl alcohol	74	43, 41, 42
Isopropylbenzene	120	105
p-Isopropyltoluene	134	91, 119
Methacrylonitrile	67	41, 39, 52, 66
Methylene chloride	84	86, 49
Methyl methacrylate	69	69, 41, 100, 39
1-Methylnaphathalene	142	141
2-Methylnaphathalene	142	141
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	127

TABLE 2
(continued)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Nitrobenzene	123	-
N-Nitrosodibutylamine	84	158
N-Nitrosodiethylamine	102	57
N-Nitrosodimethylamine	74	42
N-Nitrosodi-*n*-propylamine	130	70
N-Nitrosomethylethylamine	88	56, 42
Pentachloroethane	167	167, 130, 132, 165, 169
2-Picoline	93	93, 66, 92, 78
Propionitrile	54	54, 52, 55, 40
n-Propylbenzene	120	91
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
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	166	129, 131, 164
Toluene	92	91
o-Toluidine	106	107
1,2,3-Trichlorobenzene	180	182
1,2,4,-Trichlorobenzene	180	182
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	97	83, 85
Trichloroethene	130	95, 97, 132
Trichlorofluoromethane	101	151, 153
1,2,3-Trichloropropane	110	75, 77
1,2,4-Trimethylbenzene	120	105
1,3,5-Trimethylbenzene	120	105
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91

TABLE 2
(continued)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Surrogates		
Acetone-d_6	64	46
Acetophenone-d_5	110	82
Benzene-d_6	84	83
Bromobenzene-d_5	82	162
4-Bromofluorobenzene	174	95, 176
Chlorobenzene-d_5	117	119
Decafluorobiphenyl	256	234
1,2-Dibromomethane-d_4	111	113
1,2-Dichlorobenzene-d_4	152	115, 150
Dichloroethane-d_4	65	102
1,2-Dichloropropane-d_6	67	69
Diethyl ether-d_{10}	84	66, 50
1,4-Difluorobenzene	114	63
1,4-Dioxane-d_8	96	64
Ethyl acetate-$^{13}C_2$	71	62
Fluorobenzene	96	77
Hexafluorobenzene	186	117
Methylene chloride-d_2	88	90
Methylnaphthalene-d_{10}	152	150
Naphthalene-d_8	136	108
Nitrobenzene-d_5	128	82
Nitromethane-d_3	64	46
Pentafluorobenzene	168	-
Pyridine-d_5	84	56
Tetrahydrofuran-d_8	78	80
1,2,4-Trichlorobenzene-d_3	183	185
1,1,2-Trichloroethane-d_3	100	-
Toluene-d_8	98	-
o-Xylene-d_{10}	98	116

TABLE 2
(continued)

The ions listed above are those recommended, but not required, for use in this method. In general, the ions listed as the primary characteristic ion provide a better response or suffer from fewer interferences. However, either the primary ion or one of the secondary ions listed here may be used for quantitation of the analytes, provided that the same ions are used for both calibrations and sample analyses. In some instances, sample-specific interferences may occur that complicate the use of the characteristic ion that was used for the calibration. If such interferences occur, the use of a secondary ion for quantitation must be clearly documented and supported by multi-point calibration factors derived from the same ion.

TABLE 3
RELATIVE VOLATILITY VALUES (α_K)

Compound	Surrogate Type[a]	b.p.[b] (°C)	Conc.[c] (ppb)	K[d]	α_k-value Avg.[e]	α_k-value SD[f]
Permanent gases (Class I)						
Dichlorodifluoromethane		-30	80		0.07	0.02
Trichlorofluoromethane		24	80		0.20	0.02
Vinyl chloride		-13	80		0.48	0.06
Chloroethane		12	80		1.01	0.02
Chloromethane		-24	80		1.37	0.07
Bromomethane		4	80		1.82	0.12
Volatiles (Class I)						
1,1-Dichloroethene		37	40		0.63	0.07
Carbon tetrachloride		76	40		0.64	0.02
Hexafluorobenzene	α	82	25		0.86	0.06
1,1-Dichloropropene		104	40		0.88	0.03
1,1,1-Trichloroethane		74	40	1.41	1.31	0.04
Allyl chloride		45	100		1.34	0.45
2,2-Dichloropropane		69	40		1.37	0.18
Tetrachloroethene		121	40	1.55	1.43	0.03
Pentafluorobenzene	α	85	9		1.51	0.04
Iodomethane		42	100		2.29	0.43
trans-1,2-Dichloroethene		48	40		2.3	0.46
Trichloroethene		87	40		2.34	0.09
Isopropylbenzene		152	40	2.20	2.75	0.05
Fluorobenzene	α	85	9		3.5	0.21
Benzene		80	40	4.36	3.55	0.27
Ethylbenzene		136	40	3.28	3.6	0.12
1,4-Difluorobenzene	α	88	9		3.83	0.07
Toluene		111	40	3.93	3.88	0.12
m+*p*-Xylenes		138	40		3.91	0.11
Benzene-d_6	c	79	26	4.4	3.92	0.27
1,1-Dichloroethane		57	40		4.12	0.08
Toluene-d_8	β	111	25		4.28	0.09
n-Propylbenzene		159	40	2.49	2.43	0.04
cis-1,2-Dichloroethene		60	40		5.34	0.07
o-Xylene		144	40	5.11	5.54	0.09
o-Xylene-d_{10}	α	143	25	5.1	6.14	0.2
Chlorobenzene-d_5	α + β	131	25		6.27	0.17

TABLE 3
(continued)

Compound	Surrogate Type[a]	b.p.[b] (°C)	Conc.[c] (ppb)	K^{d}	α_k-value Avg.[e]	α_k-value SD[f]
Volatiles (continued)						
Chloroform		62	40	5.85	6.39	0.09
Styrene		145	40		6.87	0.36
Chlorobenzene		132	40		6.07	0.24
Bromobenzene		156	40		7.89	0.73
Bromobenzene-d_5	β	155	25		7.93	0.59
4-Bromo-1-fluorobenzene	c	152	25		8.05	0.7
Methylene chloride		40	40	9.33	10.1	1.6
Methylene chloride-d_2	c	40	24		11.1	1.9
1,2-Dichloropropane		96	40		10.9	0.2
1,2-Dichloropropane-d_6	c	95	21		11	0.1
1,1,1,2-Tetrachloroethane		130	40		11.6	0.6
Bromodichloromethane		90	40		12.3	0.6
trans-1,3-Dichloropropene		112	40		14.1	0.7
Bromochloromethane		68	40		15.4	0.4
1,2-Dichloroethane		84	40	20.23	18.7	0.9
Dibromochloromethane		120	40		19.2	1.4
cis-1,3-Dichloropropene		104	40		19.6	1.4
1,2-Dichloroethane-d_4	α	84	25		20.0	20.0
Bromoform		150	40		23.4	2.4
Dibromomethane		97	40		23.9	1.7
1,3-Dichloropropane		120	40		24.9	1.9
1,2-Dibromoethane-d_4	α	131	26		26.0	1.7
1,1,2-Trichloroethane		114	40		26.2	2.4
1,1,2-Trichloroethane-d_3	c	112	20		26.6	0.7
1,2-Dibromoethane		132	40		26.7	2.0
1,1,2,2-Tetrachloroethane		146	40		30.3	2.8
cis-1,4-Dichloro-2-butene		152	100		33.3	8.1
1,2,3-Trichloropropane		157	40		33.6	2.9
trans-1,4-Dichloro-2-butene		156	100		33.8	7.4
Neutral semivolatiles (Class II)						
n-Butylbenzene		183	40	1.65	1.88	0.08
sec-Butylbenzene		173	40		1.91	0.04
Hexachlorobutadiene		215	40		2.08	0.06
p-Isopropyltoluene		183	40	2.25	2.5	0.07
tert-Butylbenzene		169	40		2.72	0.05

TABLE 3
(continued)

Compound	Surrogate Type[a]	b.p.[b] (°C)	Conc.[c] (ppb)	K[d]	α_k-value Avg.[e]	α_k-value SD[f]
Neutral semivolatiles (continued)						
Decafluorobiphenyl	β	206	25		3.03	0.06
1,3,5-Trimethylbenzene		165	40	3.52	3.75	0.18
2-Chlorotoluene		159	40		4.04	0.17
1,2,4-Trimethylbenzene		169	40		4.5	0.4
4-Chlorotoluene		162	40		4.78	0.43
1,3-Dichlorobenzene		173	40		5.72	0.73
1,4-Dichlorobenzene		174	40		6.14	0.84
1,2,4-Trichlorobenzene		214	40		7.73	1.22
1,2-Dichlorobenzene		180	40		7.86	1.19
1,2,4-Trichlorobenzene-d_3	β	213	25		7.88	1.19
1,2-Dichlorobenzene-d_4	β	181	24		8.03	1.23
1,2,3-Trichlorobenzene		218	40		11.3	1.6
Pentachloroethane		162	100		13.2	3.3
Naphthalene		218	40		16.7	2.2
Naphthalene-d_8	c	217	25		18	3.7
1,2-Dibromo-3-chloropropane		196	40		38.9	4.9
1-Methylnaphthalene-d_{10}	β	241	100			67
2-Methylnaphthalene		245	500		67	17
Soluble volatiles (Class III)						
Diethyl ether		35	80		34.9	5.7
Ethyl methacrylate		117	100		48.4	2.8
Methyl methacrylate		101	100		71.4	4.1
Methacrylonitrile		90	100		102.9	2.4
Acrolein		53	200	180	116.8	1
4-Methyl-2-pentanone		117	100		119.9	8.4
2-Hexanone		128	100		131.1	2.1
Ethyl acetate-$^{13}C_2$	α	77	250	150		150
Acrylonitrile		78	100		161	32.0
Acetophenone-d_5	c	202	100		161	20.0
Isobutyl alcohol		108	100		1750	156.0
Tetrahydrofuran		66	N/A		456	67.0
Acetonitrile		82	100	1200	545	103.0
Acetone		56	100	580	600	32.0
Acetone-d_6	α	57	490	600	600	
2-Butanone		80	100	380	770	110

TABLE 3
(continued)

Compound	Surrogate Type[a]	b.p.[b] (°C)	Conc.[c] (ppb)	K^d	α_k-value Avg.[e]	SD[f]
Soluble volatiles (continued)						
Propionitrile		97	100		1420	320
1,4-Dioxane-d_8	α	101	240	5800	5800	
1,4-Dioxane		101	100	5750	6200	700
2-Picoline		129	100		6800	5200
Pyridine		116	100		13100	600
Pyridine-d_5	α	115	100	15000	15000	
Basic semivolatiles (Class IV)						
N-Nitrosodimethylamine		154	500		129	37.3
N-Nitrosomethylethylamine		165	500		1900	800
N-Nitrosodi-*n*-propylamine		206	500		2400	2000
N-Nitrosodiethylamine		177	500		4900	2200
Aniline		184	500		13700	2300
o-Toluidine		200	500		15200	2100
N-Nitrosodibutylamine		240	500		21000	5000

[a]Surrogate Type: α = α-surrogate
β = β-surrogate
c = check surrogate

[b]Boiling point of analyte

[c]Concentration of analyte in solutions used to determine α-values

[d]Partition coefficient of analyte between headspace and water at 20 °C

[e]Average of 3 to 4 replicates

[f]One standard deviation

TABLE 4

RELATIVE VOLATILITY RANGES OF THE GAS-LIQUID PARTITIONING (α-) SURROGATES

Relative Volatility Range	Surrogate Pairs	
0.07 to 3.0	Hexafluorobenzene	Fluorobenzene
	Hexafluorobenzene	1,4-Difluorobenzene
	Pentafluorobenzene	Fluorobenzene
	Pentafluorobenzene	1,4-Difluorobenzene
3.0 to 6.3	Fluorobenzene	*o*-Xylene-d_{10}
	Fluorobenzene	Chlorobenzene-d_5
	1,4-Difluorobenzene	*o*-Xylene-d_{10}
	1,4-Difluorobenzene	Chlorobenzene-d_5
6.3 to 20	*o*-Xylene-d_{10}	1,2-Dichloroethane-d_4
	o-Xylene-d_{10}	1,2-Dibromoethane-d_4
	Chlorobenzene-d_5	1,2-Dichloroethane-d_4
	Chlorobenzene-d_5	1,2-Dibromoethane-d_4
20 to 600	1,2-Dichloroethane-d_4	Tetrahydrofuran-d_8
	1,2-Dichloroethane-d_4	1,4-Dioxane-d_8
	1,2-Dibromoethane-d_4	Tetrahydrofuran-d_8
	1,2-Dibromoethane-d_4	1,4-Dioxane-d_8
600 to 6000	Tetrahydrofuran-d_8	1,4-Dioxane-d_8
	Nitromethane-d_3	1,4-Dioxane-d_8

TABLE 5

BOILING POINT RANGES OF THE BOILING POINT (β-) SURROGATES

Boiling Point Range (°C)	Surrogate Pairs	
80 to 111	Toluene-d_8	80 °C[a]
	Chlorobenzene-d_5	80 °C[a]
111 to 131	Toluene-d_8	Chlorobenzene-d_5
	Toluene-d_8	Bromobenzene-d_5
	Chlorobenzene-d_5	80 °C[a]
131 to 155	Toluene-d_8	Bromobenzene-d_5
	Chlorobenzene-d_5	Bromobenzene-d_5
	Chlorobenzene-d_5	1,2-Dichlorobenzene-d_4
155 to 181	Chlorobenzene-d_5	1,2-Dichlorobenzene-d_4
	Bromobenzene-d_5	1,2-Dichlorobenzene-d_4
	Bromobenzene-d_5	Decafluorobiphenyl
181 to 206	Bromobenzene-d_5	Decafluorobiphenyl
	1,2-Dichlorobenzene-d_4	Decafluorobiphenyl
	1,2-Dichlorobenzene-d_4	1,2,4-Trichlorobenzene-d_3
206 to 220	1,2-Dichlorobenzene-d_4	1,2,4-Trichlorobenzene-d_3
	Decafluorobiphenyl	1,2,4-Trichlorobenzene-d_3
	Decafluorobiphenyl	1-Methylnaphthalene-d_{10}
220 to 250	Decafluorobiphenyl	1-Methylnaphthalene-d_{10}
	Decafluorobiphenyl	1-Methylnaphthalene-d_{10}

[a] The boiling point effects relating to an analyte with a boiling point of ≤ 80°C are assumed to be negligible.

TABLE 6

RECOVERY OF ANALYTES SPIKED INTO THREE SOILS AND ANALYZED BY VACUUM DISTILLATION GC/MS

	Soil #1[a]			Soil #2[b]			Soil #3[c]		
Compound	% Rec[d]	Rel Error[e]	Sur Pref[f]	% Rec[d]	Rel Error[e]	Sur Pref[f]	% Rec[d]	Rel Error[e]	Sur Pref[f]
Dichlorodifluoromethane	128	28	0	122	30	92	22	4	4
Chloromethane	116	9	0	109	13	74	71	6	12
Vinyl chloride	114	14	0	118	18	87	94	7	15
Bromomethane	106	12	0	101	12	62	24	1	2
Chloroethane	109	11	0	110	11	75	15	0	2
Trichlorofluoromethane	111	11	0	125	14	98	12	0	2
Diethyl ether	20	8	1	18	8	6	10	1	1
Acetone	112	3	6	102	4	75	139	21	60
1,1-Dichloroethene	110	4	0	120	17	91	68	7	10
Iodomethane	106	6	0	96	15	56	94	3	6
Allyl chloride	116	8	0	111	12	77	88	4	10
Methylene chloride-d_6	105	6	2	96	6	60	101	3	2
Methylene chloride	104	5	2	94	4	57	94	4	2
Acrylonitrile	106	5	7	93	4	60	135	9	62
trans-1,2-Dichloroethene	99	8	0	93	9	53	85	5	6
1,1-Dichloroethane	109	5	1	103	2	66	179	0	0
Methacrylonitrile	106	3	6	69	7	35	152	2	11
2-Butanone	112	11	6	102	4	77	152	9	64
Propionitrile	122	4	6	109	2	83	167	6	64
2,2-Dichloropropane	105	1	0	115	7	83	89	1	10
cis-1,2-Dichloroethene	101	2	2	97	0	59	101	1	2
Chloroform	99	2	3	98	2	62	103	0	2
Isobutyl alcohol	103	9	6	105	6	75	NA	NA	NA
Bromochloromethane	98	0	2	93	2	59	105	1	2
1,1,1-Trichloroethane	99	1	0	112	6	78	85	1	10
1,1-Dichloropropene	102	2	2	120	7	87	83	1	12
Carbon tetrachloride	93	3	0	112	8	78	83	1	12
Benzene-d_6	102	1	1	99	1	60	102	1	1
1,2-Dichloroethane	99	1	2	94	0	108	108	1	3
Benzene	101	1	1	98	1	101	101	1	1
Trichloroethene	90	2	1	94	1	95	95	2	6
1,2-Dichloropropane-d_6	102	1	2	101	1	103	103	1	2
1,2-Dichloropropane	102	2	3	101	1	102	102	1	2
Methyl methacrylate	152	2	9	149	11	145	145	4	13
Bromodichloromethane	94	2	2	95	1	103	103	1	2
1,4-Dioxane	110	1	5	103	1	123	123	2	29

TABLE 6
(continued)

Compound	Soil #1[a] % Rec[d]	Soil #1[a] Rel Error[e]	Soil #1[a] Sur Pre[f]	Soil #2[b] % Rec[d]	Soil #2[b] Rel Error[e]	Soil #2[b] Sur Pre[f]	Soil #3[c] % Rec[d]	Soil #3[c] Rel Error[e]	Soil #3[c] Sur Pre[f]
Dibromomethane	93	2	5	93	1	105	105	1	9
4-Methyl-2-pentanone	125	2	8	112	6	147	147	4	13
trans-1,3-Dichloropropene	99	1	3	99	0	101	101	1	2
Toluene	99	0	3	99	1	96	96	1	1
Pyridine	95	5	8	119	1	71	71	3	43
cis-1,3-Dichloropropene	91	2	2	93	1	102	102	1	3
N-Nitrosodimethylamine	68	5	4	54	11	20	20	1	2
1,1,2-Trichloroethane-d_3	95	3	5	100	4	102	102	1	8
2-Hexanone	125	6	6	110	4	145	145	8	13
1,1,2-Trichloroethane	93	2	5	96	2	103	103	1	9
Tetrachloroethene	98	7	2	105	2	123	123	8	14
1,3-Dichloropropane	99	1	6	101	1	103	103	1	9
Dibromochloromethane	92	2	3	95	0	103	103	1	3
2-Picoline	71	5	3	66	20	62	62	8	15
1,2-Dibromoethane	104	1	5	108	1	108	109	0	9
Chlorobenzene	96	1	4	97	1	109	104	1	2
1,1,1,2-Tetrachloroethane	96	1	3	97	1	98	98	1	2
Ethylbenzene	102	0	2	99	1	52	96	1	1
N-Nitrosomethylethylamine	84	6	4	92	13	46	29	1	10
m+*p*-Xylenes	101	1	2	99	1	52	94	1	1
Styrene	97	1	3	96	1	49	96	0	3
o-Xylene	102	1	2	100	1	53	97	1	2
Isopropylbenzene	101	2	1	98	1	49	87	1	4
Bromoform	94	0	5	103	2	64	101	1	8
cis-1,4-Dichloro-2-butene	106	5	6	115	1	79	116	1	9
N-Nitrosodiethylamine	104	13	4	128	16	84	45	1	11
1,1,2,2-Tetrachloroethane	93	2	5	100	1	61	101	2	8
4-Bromo-1-fluorobenzene	94	2	3	93	1	45	99	0	2
1,2,3-Trichloropropane	111	6	6	120	1	86	115	1	9
n-Propylbenzene	100	3	1	95	0	45	85	1	5
trans-1,4-Dichloro-2-butene	103	4	5	114	3	76	119	1	10
1,3,5-Trimethylbenzene	103	1	1	93	2	42	91	1	2
Bromobenzene	97	1	3	98	0	50	102	0	2
2-Chlorotoluene	98	1	1	90	2	41	94	1	1
4-Chlorotoluene	98	3	2	93	1	43	95	1	2
Pentachloroethane	88	2	2	86	3	39	72	4	2
tert-Butylbenzene	103	2	2	99	1	47	83	1	4
1,2,4-Trimethylbenzene	104	1	2	96	2	44	91	1	2

TABLE 6
(continued)

Compound	Soil #1[a]			Soil #2[b]			Soil #3[c]		
	% Rec[d]	Rel Error[e]	Sur Pre[f]	% Rec[d]	Rel Error[e]	Sur Pre[f]	% Rec[d]	Rel Error[e]	Sur Pre[f]
sec-Butylbenzene	99	4	2	93	3	43	83	1	8
Aniline	106	16	10	143	29	106	15	1	10
p-Isopropyltoluene	104	2	3	101	3	48	87	2	7
1,3-Dichlorobenzene	94	3	3	88	1	38	100	1	4
1,4-Dichlorobenzene	94	2	4	90	1	41	100	1	4
n-Butylbenzene	97	5	3	89	4	38	83	1	8
1,2-Dichlorobenzene	95	2	4	93	0	42	103	1	5
Benzyl alcohol	98	6	8	128	30	82	22	1	9
N-Nitrosodi-*n*-propylamine	120	16	9	185	27	168	108	3	38
Acetophenone-d_5	104	10	9	167	11	136	270	7	124
o-Toluidine	118	21	12	172	45	149	19	1	14
1,2-Dibromo-3-chloro propane	104	7	8	143	10	106	185	3	24
Hexachlorobutadiene	88	3	14	81	12	58	75	2	8
1,2,4-Trichlorobenzene	88	2	13	81	1	38	104	1	8
Naphthalene-d_8	88	5	17	109	5	69	141	2	12
Naphthalene	88	4	18	109	2	70	132	2	12
1,2,3-Trichlorobenzene	83	0	18	77	2	40	111	1	10
N-Nitrosodibutylamine	133	30	44	152	51	149	11	1	11
2-Methylnaphthalene	60	5	20	60	0	36	62	3	29

[a]Garden soil with 37% moisture and 21% organic matter. Three replicates were analyzed.
[b]Garden soil with 15% moisture and 16% organic matter. Three replicates were analyzed.
[c]Desert soil with 3% moisture and 1% organic matter. Seven replicates were analyzed.
[d]% Rec = Average of replicate accuracy results using surrogate corrections.
[e]Rel Error = Relative standard deviation of replicate analyses.
[f]Surr Prec = Average variation between the predicted analyte recoveries of the surrogate pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.
NA = Analyte not significantly present in vacuum distillate.

TABLE 7

RECOVERY OF ANALYTES SPIKED INTO OIL
AND ANALYZED BY VACUUM DISTILLATION GC/MS

Compound	% Rec[a]	Relative Error[b]	Surrogate Precision[c]
Dichlorodifluoromethane	3	0	0
Chloromethane	141	18	2
Vinyl chloride	137	11	2
Bromomethane	120	29	0
Chloroethane	128	44	2
Trichlorofluoromethane	313	176	0
Diethyl ether	103	5	3
Acetone-d_6	70	8	12
Acrolein	526	166	28
Acetone	323	125	42
1,1-Dichloroethene	116	4	1
Iodomethane	105	6	1
Allyl chloride	119	16	1
Acetonitrile	24	4	4
Methylene chloride-d_6	104	7	2
Methylene chloride	106	10	2
Acrylonitrile	88	7	14
trans-1,2-Dichloroethene	116	4	0
1,1-Dichloroethane	103	2	1
Methacrylonitrile	94	4	4
2-Butanone	92	9	13
Propionitrile	85	4	13
Ethyl acetate-$^{13}C_2$	84	5	3
2,2-Dichloropropane	97	2	1
cis-1,2-Dichloroethene	105	2	1
Chloroform	97	2	2

TABLE 7
(continued)

Compound	% Rec[a]	Relative Error[b]	Surrogate Precision[c]
Isobutyl alcohol	115	11	20
Bromochloromethane	98	3	2
1,1,1-Trichloroethane	97	3	1
1,1-Dichloropropene	120	4	3
Carbon tetrachloride	93	2	1
Benzene-d_6	100	2	1
1,2-Dichloroethane	101	3	3
Benzene	238	40	0
Trichloroethene	92	3	1
1,2-Dichloropropane-d_6	71	13	2
1,2-Dichloropropane	128	7	3
Methyl methacrylate	101	3	4
Bromodichloromethane	92	1	2
1,4-Dioxane	88	13	14
Dibromomethane	95	4	4
4-Methyl-2-pentanone	95	5	4
trans-1,3-Dichloropropene	103	2	4
Toluene	164	16	5
Pyridine	58	42	19
cis-1,3-Dichloropropene	94	1	4
Ethyl methacrylate	109	2	5
N-Nitrosodimethylamine	189	50	7
1,1,2-Trichloroethane-d_3	88	2	4
2-Hexanone	106	6	3
1,1,2-Trichloroethane	89	2	4
Tetrachloroethene	68	1	1
1,3-Dichloropropane	99	3	4
Dibromochloromethane	85	1	3

TABLE 7
(continued)

Compound	% Rec[a]	Relative Error[b]	Surrogate Precision[c]
2-Picoline	33	24	8
1,2-Dibromoethane	106	2	3
Chlorobenzene	101	1	2
1,1,1,2-Tetrachloroethane	83	2	1
Ethylbenzene	114	3	1
N-Nitrosomethylethylamine	192	48	0
m+*p*-Xylenes	122	3	1
Styrene	102	1	2
o-Xylene	115	3	1
Isopropylbenzene	109	5	1
Bromoform	88	2	3
cis-1,4-Dichloro-2-butene	103	3	4
N-Nitrosodiethylamine	222	44	30
1,1,2,2-Tetrachloroethane	83	5	3
4-Bromo-1-fluorobenzene	93	2	2
1,2,3-Trichloropropane	103	4	4
n-Propylbenzene	122	4	1
trans-1,4-Dichloro-2-butene	95	3	4
1,3,5-Trimethylbenzene	93	9	2
Bromobenzene	98	2	2
2-Chlorotoluene	78	2	1
4-Chlorotoluene	93	2	2
Pentachloroethane	81	4	2
tert-Butylbenzene	120	55	3
1,2,4-Trimethylbenzene	127	8	3
sec-Butylbenzene	89	10	3
Aniline	NA	NA	NA[d]
p-Isopropyltoluene	NA	NA	NA

TABLE 7
(continued)

Compound	% Rec[a]	Relative Error[b]	Surrogate Precision[c]
1,3-Dichlorobenzene	70	2	2
1,4-Dichlorobenzene	87	3	4
n-Butylbenzene	105	4	6
1,2-Dichlorobenzene	119	14	7
Benzyl alcohol	NA	NA	NA
n-Nitroso-di-*n*-propylamine	270	58	51
Acetophenone-d_5	175	31	34
o-Toluidine	108	69	36
1,2-Dibromo-3-chloropropane	84	14	6
Hexachlorobutadiene	119	6	20
1,2,4-Trichlorobenzene	94	5	14
Naphthalene-d_8	132	16	29
Naphthalene	123	15	32
1,2,3-Trichlorobenzene	80	3	21
n-Nitrosodibutylamine	2000	3600	3200
2-Methylnaphthalene	667	1644	4900

[a]Average of seven replicate analyses of 1 g of cod liver oil.

[b]Relative standard deviation of replicate analyses.

[c]Average variation between the predicted analyte recoveries of the surrogate pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.

[d]NA = Compound could not be accurately measured due to spectral interferences.

TABLE 8

METHOD DETECTION LIMITS[a]

	MDL (ppb)			
Compound	Water[b]	Soil[c]	Oil[d]	Waste Oil[e]
Dichlorodifluoromethane	2.1	5.2	17	56
Chloromethane	1.5	1.6	15	44
Vinyl chloride	1.7	1.7	15	45
Bromomethane	1.5	0.8	9.7	31
Chloroethane	0.9	0.6	6.9	54
Trichlorofluoromethane	0.5	1.0	66	270
Diethyl ether	0.4	2.4	2.4	9.2
Acrolein	12	75	int[f]	int
Acetone	3.0	2.7	23	97
1,1-Dichloroethene	0.3	1.4	2.7	8.2
Iodomethane	0.4	0.5	4.6	14
Allyl chloride	1.0	2.0	20	66
Acetonitrile	1.2	1.2	int	int
Methylene chloride	0.3	0.6	4.0	19
Acrylonitrile	1.0	1.4	4.3	91
trans-1,2-Dichloroethene	0.5	0.6	1.9	6.5
1,1-Dichloroethane	0.6	0.2	1.5	5.5
Methacrylonitrile	0.6	0.5	6.2	47
2-Butanone	41	5.9	35	190
Propionitrile	0.7	0.9	7.1	140
2,2-Dichloropropane	0.2	0.1	1.1	6.1
cis-1,2-Dichloroethene	0.1	0.1	1.5	5.6
Chloroform	0.2	0.3	2.0	27
Isobutyl alcohol	8.3	3.5	int	int
Bromochloromethane	0.2	0.1	1.0	3.6
1,1,1-Trichloroethane	0.4	0.2	1.5	4.9

TABLE 8
(continued)

	MDL (ppb)			
Compound	Water[b]	Soil[c]	Oil[d]	Waste Oil[e]
1,1-Dichloropropene	0.3	0.3	2.4	6.8
Carbon tetrachloride	0.2	0.2	1.1	6.0
1,2-Dichloroethane	0.2	0.1	0.3	1.3
Benzene	0.5	0.1	9.8	22
Trichloroethene	0.2	0.1	1.1	6.3
1,2-Dichloropropane	0.2	0.1	9.2	5.3
Methyl methacrylate	0.6	0.7	3.8	16
Bromodichloromethane	0.1	0.1	1.0	3.1
1,4-Dioxane	1.1	0.5	5.1	32
Dibromomethane	0.2	0.1	0.7	6.3
4-Methyl-2-pentanone	1.1	0.7	12	59
trans-1,3-Dichloropropene	0.2	0.4	2.8	8.1
Toluene	0.9	0.2	0.2	0.7
Pyridine	2.8	2.6	36	130
cis-1,3-Dichloropropene	0.3	0.3	2.1	6.2
Ethyl methacrylate	0.4	1.1	7.8	10
N-Nitrosodimethylamine	33	27	410	730
2-Hexanone	1.4	1.4	14	66
1,1,2-Trichloroethane	0.2	0.1	1.7	3.9
Tetrachloroethene	0.6	0.7	1.7	4.4
1,3-Dichloropropane	0.2	0.1	1.2	5.1
Dibromochloromethane	0.2	0.2	2.1	7.1
2-Picoline	NA[g]	100	NA	NA
1,2-Dibromoethane	0.2	0.1	0.9	3.1
Chlorobenzene	0.3	0.2	2.0	16
1,1,1,2-Tetrachloroethane	0.2	0.1	2.0	6.6
Ethylbenzene	0.3	0.2	3.2	2.4
N-Nitrosomethylethylamine	28	16	450	57

TABLE 8
(continued)

Compound	MDL (ppb)			
	Water[b]	Soil[c]	Oil[d]	Waste Oil[e]
m+*p*-Xylenes	0.6	0.2	5.8	6.4
Styrene	0.1	0.1	1.2	3.5
o-Xylene	0.5	0.2	5.0	7.3
Isopropylbenzene	0.3	0.2	1.4	4.7
Bromoform	0.5	0.2	2.0	9.3
cis-1,4-Dichloro-2-butene	0.7	0.5	2.5	17
N-Nitrosodiethylamine	22	11	420	860
1,1,2,2-Tetrachloroethane	0.4	0.2	2.9	19
4-Bromo-1-fluorobenzene	0.0	0.0	0.4	2.1
1,2,3-Trichloropropane	1.0	0.9	14	25
n-Propylbenzene	0.3	0.2	4.6	10
trans-1,4-Dichloro-2-butene	0.8	0.6	9.0	17
1,3,5-Trimethylbenzene	0.4	0.3	22	38
Bromobenzene	0.2	0.1	0.7	3.5
2-Chlorotoluene	0.2	0.2	1.7	7.9
4-Chlorotoluene	0.2	0.2	1.0	8.4
Pentachloroethane	1.1	1.2	6.6	24
tert-Butylbenzene	0.2	0.3	26	58
1,2,4-Trimethylbenzene	0.5	0.2	30	180
sec-Butylbenzene	0.2	0.3	4.0	55
Aniline	23	13.2	int	int
p-Isopropyltoluene	0.2	0.3	16	62
1,3-Dichlorobenzene	0.1	0.1	1.3	5.9
1,4-Dichlorobenzene	0.2	0.1	1.0	6.8
n-Butylbenzene	0.4	0.4	4.5	13
1,2-Dichlorobenzene	0.3	0.2	10	33
Benzyl alcohol	20	11.8	int	int
N-Nitro-di-*n*-propylamine	26	14	290	1300

TABLE 8
(continued)

	MDL (ppb)			
Compound	Water[b]	Soil[c]	Oil[d]	Waste Oil[e]
o-Toluidine	26	12	530	2100
1,2-Dibromo-3-chloropropane	0.7	0.3	2.7	15
Hexachlorobutadiene	0.4	0.4	3.1	14
1,2,4-Trichlorobenzene	0.3	0.3	3.2	7.4
Naphthalene	0.6	0.3	5.4	9.3
1,2,3-Trichlorobenzene	0.4	0.3	5.6	19.5
N-Nitrosodibutylamine	36	14	NA	NA
2-Methylnaphthalene	1.8	1.0	NA	NA

[a] Method detection limits reported here are equal to 3 times the average standard deviation of 3 sets of 7 replicate analyses performed on three nonconsecutive days and are for illustrative purposes only. (Note: This is similar to, but not the same as, the procedures described in either Chapter One or 40 CFR 136). Units for water are µg/L, and µg/kg for all other matrices.

[b] Results are for 5-mL water samples.

[c] Results are for 5-g soil samples.

[d] Results are for 1-g samples.

[e] Results are for 0.2-g samples of cod liver oil.

[f] Int = Spectral interferences prevented accurate integrations.

[g] NA = Compound not significantly present in vacuum distillate.

TABLE 9

RECOVERY OF ANALYTES SPIKED INTO WATER SOLUTIONS AND ANALYZED BY VACUUM DISTILLATION GC/MS

	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
Compound	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
Dichlorodifluoromethane	76	9	1	84	8	1	85	6	1	56	7	1
Chloromethane	81	6	1	86	8	1	83	10	1	77	3	1
Vinyl chloride	78	5	1	81	3	1	74	4	1	81	4	1
Bromomethane	101	5	1	103	2	0	116	47	1	102	4	1
Chloroethane	95	5	1	96	2	1	112	52	1	95	5	1
Trichlorofluoromethane	122	52	1	98	1	1	120	58	1	96	3	1
Diethyl ether	106	17	2	98	12	1	14	8	0	17	14	1
Acrolein	111	16	3	114	5	1	20	10	2	49	6	2
Acetone	114	17	5	286	41	16	88	5	20	71	10	3
1,1-Dichloroethene	102	10	1	98	6	1	20	12	0	93	9	1
Iodomethane	103	7	1	104	7	0	98	4	1	103	2	0
Allyl chloride	102	10	1	101	6	1	95	4	1	101	3	1
Acetonitrile	122	21	6	189	2	7	82	11	17	99	8	4
Methylene chloride-d_2	103	7	1	104	9	0	99	7	1	102	6	2
Methylene chloride	99	9	1	101	10	0	95	10	1	98	8	2
Acrylonitrile	97	1	7	95	3	7	112	21	27	93	3	4
trans-1,2-Dichloroethane	100	4	1	100	5	0	94	8	1	93	6	1
1,1-Dichloroethane	102	5	1	102	5	0	101	4	0	101	1	1
Methacrylonitrile	101	3	2	101	1	1	108	7	7.	104	2	4
2-Butanone	68	43	7	106	31	10	105	27	25	97	2	4

TABLE 9
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
Propionitrile	100	6	6	109	9	14	111	31	22	103	3	4
2,2-Dichloropropane	100	1	1	99	1	1	100	1	1	102	1	1
cis-1,2-Dichloroethene	100	1	1	100	1	0	97	2	0	103	0	1
Chloroform	100	1	1	100	2	1	100	2	0	103	1	2
Isobutyl alcohol	86	7	5	137	17	5	116	21	30	76	10	3
Bromochloromethane	102	1	1	102	1	0	100	0	1	102	1	1
1,1,1-Trichloroethane	100	1	1	99	1	1	98	3	1	99	1	1
1,1-Dichloropropene	95	3	1	96	3	1	94	3	1	99	3	1
Carbon tetrachloride	100	0	1	100	2	1	100	2	1	88	2	1
Benzene-d_6	99	1	1	99	1	1	99	1	0	100	1	1
1,2-Dichloroethane	101	1	1	101	1	1	99	1	1	100	1	2
Benzene	99	0	1	100	1	1	99	2	0	99	1	1
Trichloroethene	100	1	1	99	1	0	98	1	1	109	1	0
1,2-Dichloropropane-d_6	99	2	1	99	2	0	99	2	1	101	2	2
1,2-Dichloropropane	100	1	1	100	1	0	99	1	1	101	1	2
Methyl methacrylate	106	7	2	128	10	1	114	4	5	106	2	5
Bromodichloromethane	102	1	1	100	1	0	102	2	1	101	1	2
1,4-Dioxane	101	8	8	156	15	83	96	18	16	102	3	14
Dibromomethane	102	1	2	101	1	1	99	1	3	100	1	5
4-Methyl-2-pentanone	102	5	3	102	3	1	116	1	9	110	2	5
trans-1,3-Dichloropropene	99	1	1	100	0	1	99	2	1	103	1	1

TABLE 9
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
Toluene	98	2	1	99	1	1	97	3	1	97	1	1
Pyridine	61	20	16	NA	NA	NA	104	24	37	128	7	36
cis-1,3-Dichloropropene	99	1	1	99	1	1	97	2	1	100	1	2
Ethyl methacrylate	109	9	2	156	17	1	109	25	3	105	2	4
N-Nitrosodimethylamine	75	8	2	97	8	1	105	32	10	69	9	4
1,1,2-Trichloroethane-d_3	100	1	2	100	2	1	101	2	3	99	1	5
2-Hexanone	102	9	3	99	4	1	118	4	11	112	3	5
1,1,2-Trichloroethane	100	2	2	100	1	1	101	1	2	101	1	5
Tetrachloroethene	98	11	1	98	14	1	106	34	1	200	36	0
1,3-Dichloropropane	98	1	2	99	1	1	98	2	3	98	1	5
Dibromochloromethane	102	1	1	101	2	1	104	1	1	102	1	2
2-Picoline	NA	NA	NA	NA	NA	NA	169	69	26	217	28	33
1,2-Dibromoethane	100	1	2	100	1	1	101	1	2	104	1	5
Chlorobenzene	100	1	1	100	1	1	99	1	1	102	0	2
1,1,1,2-Tetrachloroethane	101	1	1	100	1	0	102	1	1	100	1	2
Ethylbenzene	97	2	1	99	2	1	98	1	0	97	2	1
N-Nitrosomethylethylamine	70	9	4	111	10	20	130	35	25	79	1	4
m+*p*-Xylenes	98	2	1	99	1	1	97	1	0	101	1	1
Styrene	98	0	1	99	1	1	97	3	1	102	0	3
o-Xylene	98	1	1	99	1	1	98	1	1	106	1	2
Isopropylbenzene	97	2	1	99	2	1	95	3	1	84	2	2

TABLE 9
(continued)

Compound	Water[a] % Rec[e]	Water[a] Rel Error[f]	Water[a] Surr Prec[g]	Water/Glycerin[b] % Rec[e]	Water/Glycerin[b] Rel Error[f]	Water/Glycerin[b] Surr Prec[g]	Water/Salt[c] % Rec[e]	Water/Salt[c] Rel Error[f]	Water/Salt[c] Surr Prec[g]	Water/Soap[d] % Rec[e]	Water/Soap[d] Rel Error[f]	Water/Soap[d] Surr Prec[g]
Bromoform	103	2	2	101	2	1	109	1	2	108	2	6
cis-1,4-Dichloro-2-butene	102	4	2	102	2	1	110	2	1	114	4	6
N-Nitrosodiethylamine	78	9	6	133	11	60	128	31	18	78	2	9
1,1,2,2-Tetrachloroethane	101	2	2	100	3	1	111	2	2	82	3	4
4-Bromo-1-fluorobenzene	101	1	1	101	1	1	101	1	1	102	1	3
1,2,3-Trichloropropane	97	6	2	99	3	1	105	6	2	112	3	6
n-Propylbenzene	97	2	1	98	2	1	94	3	1	81	3	2
trans-1,4-Dichloro-2-butene	101	4	2	102	2	1	111	2	2	115	4	7
1,3,5-Trimethylbenzene	98	3	1	99	2	1	96	3	1	83	1	1
Bromobenzene	101	0	1	101	0	1	100	1	1	104	1	3
2-Chlorotoluene	96	4	1	99	3	1	95	3	1	88	2	2
4-Chlorotoluene	101	2	1	100	2	1	98	1	1	94	2	2
Pentachloroethane	103	10	1	100	9	1	94	18	1	29	8	1
tert-Butylbenzene	99	3	1	100	3	1	95	5	1	66	2	1
1,2,4-Trimethylbenzene	98	2	1	99	2	1	96	2	1	88	2	2
sec-Butylbenzene	98	3	1	99	2	1	93	3	2	74	2	2
Aniline	119	40	18	74	15	65	79	37	30	97	9	29
p-Isopropyltoluene	97	0	2	98	4	2	93	3	2	81	2	4
1,3-Dichlorobenzene	101	1	1	100	1	1	99	1	1	98	1	3
1,4-Dichlorobenzene	101	1	1	101	1	1	100	2	1	105	1	3
n-Butylbenzene	97	2	2	98	3	2	91	2	2	74	2	3

TABLE 9
(continued)

Compound	Water[a]			Water/Glycerin[b]			Water/Salt[c]			Water/Soap[d]		
	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]	% Rec[e]	Rel Error[f]	Surr Prec[g]
1,2-Dichlorobenzene	100	1	1	100	1	1	100	1	2	102	1	5
Benzyl alcohol	128	28	19	167	14	125	65	35	15	93	5	23
N-Nitroso-di-*n*-propylamine	68	14	5	108	9	25	56	15	29	112	5	15
Acetophenone-d_5	71	20	7	81	7	7	99	66	23	156	7	17
o-Toluidine	127	42	21	66	20	61	97	49	41	115	15	37
1,2-Dibromo-3-chloropropane	101	9	3	99	5	3	111	25	4	156	7	15
Hexachlorobutadiene	101	2	2	102	4	3	92	3	3	74	2	4
1,2,4-Trichlorobenzene	101	1	2	100	1	3	102	1	3	104	1	5
Naphthalene-d_8	102	5	2	100	2	4	112	5	5	127	3	10
Naphthalene	101	4	2	101	2	4	110	2	5	125	3	9
1,2,3-Trichlorobenzene	100	2	2	100	1	4	100	3	5	93	3	8
N-Nitrosodibutylamine	208	109	43	400	32	384	90	69	67	98	21	43
2-Methylnaphthalene	84	6	8	91	10	12	98	27	24	55	3	11

[a]5-mL water samples
[b]1 g of glycerin added to 5 mL of water
[c]1 g of salt added to 5 mL of water
[d]0.2 g of concentrated soap added to 5 mL of water
[e]Average of four replicate analyses
[f]Relative standard deviation of replicate analyses
[g]Average variation between the predicted analyte recoveries of the surrogate pairs for the replicate analyses. This precision value provides a measure of the inherent error in the overall measurement.
[h]NA = compound not significantly present in vacuum distillate.

TABLE 10

METHOD PERFORMANCE IN FISH TISSUE

			Using water standards[a]			Using tuna standards[b]				
Compound	Surrogate Type	Spike (ppb)[c]	Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	MDL vs. Water Std[g]	MDL vs. Tuna Std
Dichlorodifluoromethane		1000	109	22	24	116	17	16	5	6
Chloromethane		1000	105	16	16	102	13	10	5	5
Vinyl chloride		1000	105	20	21	115	15	14	4	5
Bromomethane		1000	90	19	11	89	18	7	7	8
Chloroethane		1000	102	21	18	110	17	12	5	5
Trichlorofluoromethane		1000	97	24	21	125	18	16	5	5
Diethyl ether-d_{10}	Check	250	113	9	4	108	9	3	ND	ND
Ether		500	104	10	4	106	10	3	17	18
Acetone-d_6	Check	2500	41	27	0	149	20	1	ND	ND
Acetone		Cont	--	--	--	--	--	--	67	60
1,1-Dichloroethene		500	44	54	8	134	31	15	8	7
Iodomethane		500	10	101	1	57	129	3	9	13
Allyl chloride		500	55	75	9	96	79	9	14	3
Acetonitrile		Int	--	--	--	--	--	--	ND	ND
Methylene chloride-d_6	Check	250	94	18	3	109	19	2	ND	ND
Methylene chloride		500	74	24	2	91	22	2	2	1
Acrylonitrile		500	65	25	0	75	28	0	21	15
trans-1,2-Dichloroethene		500	77	29	7	84	32	5	2	2
Nitromethane-d_3	Check	250	121	42	3	133	41	2	ND	ND
1,1-Dichloroethane		500	89	74	1	53	40	0	6	4
Hexafluorobenzene	Alpha	250	--	--	--	--	--	--	ND	ND
Tetrahydrofuran-d_8	Alpha	250	--	--	--	--	--	--	ND	ND
Methacrylonitrile		500	103	17	5	100	17	5	8	8
2-Butanone		500	122	11	2	149	10	1	9	6

TABLE 10
(continued)

Compound	Surrogate Type	Spike (ppb)[c]	Using water standards[a] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Using tuna standards[b] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	MDL vs. Water Std[g]	MDL vs. Tuna Std
Propionitrile		500	113	8	5	120	8	3	3	3
Ethyl acetate-^{13}C	Check	2500	76	18	1	95	18	0	ND	ND
2,2-Dichloropropane		500	94	16	14	108	13	10	3	2
cis-1,2-Dichloroethene		500	102	6	3	100	7	2	2	2
Chloroform		500	101	6	4	100	7	3	2	2
Pentafluorobenzene	Alpha	250	--	--	--	--	--	--	ND	ND
Bromochloromethane		500	100	5	2	99	5	2	1	1
1,1,1-Trichloroethane		500	91	18	14	113	13	10	2	2
1,1-Dichloropropene		500	99	21	18	128	15	15	3	3
Carbon tetrachloride		500	80	22	15	122	17	14	3	5
Benzene-d_6	Alpha	500	--	--	--	--	--	--	ND	ND
1,2-Dichloroethane-d_4	Alpha	250	--	--	--	--	--	--	ND	ND
1,2-Dichloroethane		500	100	3	2	99	3	2	1	1
Benzene		500	102	3	1	101	3	1	1	1
Fluorobenzene	Alpha	250	--	--	--	--	--	--	ND	ND
1,4-Difluorobenzene	Alpha	250	--	--	--	--	--	--	ND	ND
Trichloroethene		500	71	10	6	86	8	5	2	2
1,2-Dichloropropane-d_6	Check	250	93	2	3	94	2	2	ND	ND
1,2-Dichloropropane		500	93	3	3	93	2	2	1	1
Methyl methacrylate		500	102	13	5	99	13	4	2	2
1,4-Dioxane-d_8	Alpha	2500	--	--	--	--	--	--	ND	ND
Bromodichloromethane		500	75	10	2	86	11	2	3	4
1,4-Dioxane		500	115	3	22	108	3	11	3	2
Dibromomethane		500	92	4	4	99	4	3	1	1
4-Methyl-2-pentanone		1000	128	20	8	108	21	6	3	2
trans-1,3-Dichloropropene		500	61	36	2	61	36	2	1	2

TABLE 10
(continued)

Compound	Surrogate Type	Spike (ppb)[c]	Using water standards[a] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Using tuna standards[b] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	MDL vs. Water Std[g]	MDL vs. Tuna Std
Toluene-d_8	Beta	250	--	--	--	--	--	--	ND	ND
Toluene		500	101	4	4	98	4	2	2	1
Pyridine-d_5	Check/Alpha	2500	51	25	25	72	16	21	ND	ND
Pyridine		500	62	21	27	81	13	20	6	6
cis-1,3-Dichloropropene		500	61	27	2	66	27	2	1	2
Ethyl methacrylate		500	100	12	5	95	12	4	1	1
N-Nitrosodimethylamine		3350	657	28	39	160	30	10	208	100
1,1,2-Trichloroethane-d_3	Check	250	80	6	4	93	6	3	ND	ND
2-Hexanone		500	141	23	9	114	23	7	1	1
1,1,2-Trichloroethane		500	82	5	4	93	5	3	1	1
Tetrachloroethene		500	73	16	11	106	12	10	2	2
1,3-Dichloropropane		500	99	2	5	97	2	3	1	1
Dibromochloromethane		500	61	11	3	90	19	3	6	8
1,2-Dibromoethane-d_4		250	--	--	--	--	--	--	ND	ND
2-Picoline		500	163	16	38	131	11	16	7	7
1,2-Dibromoethane		500	99	4	6	99	4	4	1	1
Chlorobenzene-d_5	Beta	250	--	--	--	--	--	--	ND	ND
Chlorobenzene		500	95	3	6	99	3	4	1	1
1,1,1,2-Tetrachloroethane		500	88	4	5	95	5	3	1	1
Ethylbenzene		500	111	7	4	110	7	2	1	1
N-Nitrosomethylethylamine		3350	516	31	31	182	27	7	71	33
m+*p*-Xylenes		500	107	6	4	107	6	2	1	1
Styrene		500	94	3	4	95.7	3	3	2	1
o-Xylene-d_{10}		250	--	--	--	--	--	--	ND	ND
o-Xylene		500	102	4	4	101	4	3	1	1
Isopropylbenzene		500	116	16	8	124	15	6	1	1

TABLE 10
(continued)

Compound	Surrogate Type	Spike (ppb)[c]	Using water standards[a] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Using tuna standards[b] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	MDL vs. Water Std[g]	MDL vs. Tuna Std
Bromoform		500	53	30	2	118	38	4	55	163
cis-1,4-Dichloro-2-butene		500	5	134	0	5	134	0	45	238
N-Nitrosodiethylamine		3350	356	31	62	168	28	18	24	10
1,1,2,2-Tetrachloroethane		500	37	62	2	144	72	5	103	664
4-Bromofluorobenzene	Check	250	92	4	4	97	3	4	1	2
1,2,3-Dichloropropane		500	103	10	5	98	11	4	4	4
Propylbenzene		500	113	17	10	125	16	8	2	1
trans-1,4-Dichloro-2-butene		500	0	0	0	0	0	0	20	37
1,3,5-Trimethylbenzene		500	115	9	4	113	10	3	1	1
Bromobenzene-d_5	Beta	250	--	--	--	--	--	--	ND	ND
Bromobenzene		500	96	4	5	97	3	4	2	2
2-Chlorotoluene		500	105	4	3	107	4	3	2	2
4-Chlorotoluene		500	101	4	3	104	5	3	2	2
Pentachloroethane		500	28	54	1	135	75	5	0	0
tert-Butylbenzene		500	118	19	10	126	19	8	2	1
1,2,4-Trimethylbenzene		500	112	9	5	107	10	4	1	1
sec-Butylbenzene		500	114	24	15	134	22	13	2	1
Aniline		500	80	36	37	57	38	15	9	14
p-Isopropyltoluene		500	124	21	16	127	20	12	2	1
1,3-Dichlorobenzene		500	94	5	7	98	4	5	1	1
1,4-Dichlorobenzene		500	93	6	7	96	5	6	1	1
n-Butylbenzene		500	109	22	17	128	20	15	2	1
1,2-Dichlorobenzene-d_4	Beta	250	--	--	--	--	--	--	ND	ND
1,2-Dichlorobenzene		500	91	10	10	96	9	7	2	2
Decafluorobiphenyl	Beta	250	--	--	--	--	--	--	ND	ND
N-Nitrosodi-*n*-propylamine		3350	288	51	47	179	50	21	35	20

TABLE 10
(continued)

Compound	Surrogate Type	Spike (ppb)[c]	Using water standards[a] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	Using tuna standards[b] Mean Compound Recovery[d]	RSD[e]	Mean Surrogate Recovery[f]	MDL vs. Water Std[g]	MDL vs. Tuna Std
Nitrobenzene-d_5	Check	250	374	105	283	176	58	40	ND	ND
Acetophenone-d_5	Check	1000	216	47	29	187	47	19	ND	ND
o-Toluidine		3350	67	39	34	58	41	18	62	103
1,2-Dibromo-3-chloropropane		500	97	39	12	107	40	10	31	42
Hexachlorobutadiene		500	108	27	20	122	28	18	4	3
1,2,4-Trichlorobenzene-d_3	Beta	250	--	--	--	--	--	--	ND	ND
1,2,4-Trichlorobenzene		500	94	12	14	94	9	11	4	6
Naphthalene-d_8	Check	500	85	14	18	93	12	14	ND	ND
Naphthalene		1000	95	11	22	95	9	16	5	3
1,2,3-Trichlorobenzene		500	88	8	23	96	9	18	10	13
N-Nitrosodibutylamine		3350	25	99	19	25	115	12	79	15
2-Methylnaphthalene		3350	194	21	74	96	23	26	159	50
1-Methylnaphthalene-d_{10}	Beta	1000	--	--	--	--	--	--	ND	ND

[a]Calibration standards were prepared using 5 mL of water as the matrix.
[b]Calibration standards were prepared using 1 g of tuna as the matrix.
[c]1-g samples were spiked, mixed ultrasonicly, and allowed to equilibrate overnight (>1000 min) prior to analysis.
[d]Average percent recovery of seven replicate analyses of fish tissue taken from canned, water-packed tuna.
[e]Relative standard deviation
[f]Method detection limits reported here were calculated as three times the standard deviation of four replicate analyses.
ND = Not determined
Int = Spectral interferences prevented accurate integrations.
Cont = The spike could not be distinguished from the background levels.

TABLE 11A
EXAMPLE SURROGATE DATA

First Pass Relative Volatility vs. Recovery (Used to Estimate Relative Volatility Effects on BP Surrogates)			
Compound	Boiling Point	Relative Volatility	Recovery (%)
Fluorobenzene	40	3.5	99.1
1,2-Dichloroethane-d_4	37	20.0	101.2
Recovery vs. Boiling Point (First-Pass Relative Volatility Corrections)			
Compound	Boiling Point	Relative Volatility	Recovery (%)
Toluene-d_8	111	4.28	102.0
Chlorobenzene-d_5	131	6.27	101.3
Bromobenzene-d_5	155	7.93	102.8
1,2-Dichlorobenzene-d_4	181	8.03	103.2
Decafluorobiphenyl	206	3.03	103.3
1,2,4-Trichlorobenzene-d_3	213	7.88	102.8
1-Methylnapthalene-d_{10}	241	67.00	94.0
Slope (% per degree)	0.000143		
Recovery at 140°C	102.2%		
Correction coefficient	0.758352		
Recovery (BP corrected) vs. Relative Volatility			
Compound	Boiling Point	Relative Volatility	Recovery (%)
Hexafluorobenzene	82	0.86	99.7
Pentafluorobenzene	85	1.51	99.2
Fluorobenzene	85	3.50	98.8
1,4-Difluorobenzene	89	3.83	98.7
o-Xylene-d_{10}	143	6.14	100.0
Chlorobenzene-d_5	131	6.27	99.5
1,2-Dichloroethane-d_4	84	20.00	100.9
1,2-Dibromoethane-d_4	131	26.00	101.6
Tetrahydrofuran-d_{10}	66	355.00	103.7
1,4-Dioxane-d_8	101	5800.00	97.0
Pyridine-d_5	101	15000.00	76.2
Slope (% per ln[rel. vol.])	-0.01363		
Recovery at 140°C	98.2%		
Correction coefficient	0.370579		

TABLE 11B

EXAMPLE OF THE ACCURACY OF THE CHECK SURROGATES

				Accuracy of Check Surrogates					
				Predicted		Measured/Predicted		Predicted/Measured	
Compound	Boiling Point	Relative Volatility	Measured Recovery (%)	Recovery	SD	Recovery	SD	Accuracy	SD
Purgeable volatiles									
Benzene-d_6	79	3.92	100.2	98.8	0.1	101.4	0.1	98.6	0.1
Methylene chloride	40	11.10	101.7	100.2	0.2	101.5	0.2	98.5	0.2
1,2-Dichloropropane-d_6	95	11.00	101.1	100.9	0.4	100.2	0.3	99.8	0.3
1,1,2-Trichloroethane-d_3	112	26.60	103.4	102.9	0.7	100.4	0.6	99.6	0.6
4-Bromofluorobenzene	152	8.05	102.9	102.4	0.4	100.6	0.3	99.4	0.3
	Mean ± 1 sigma		101.9 ± 1.2	101.0	1.5	100.8	0.5	99.2	0.5
Semivolatiles									
Naphthalene-d_8	217	18.00	104.6	102.7	1.1	101.8	1.1	98.2	1.0
Nitrobenzene-d_5	210	87.50	107.1	104.7	2.7	102.3	2.6	97.7	2.5
Acetophenone-d_5	202	161.00	103.1	107.3	0.2	96.1	0.2	104.0	0.2
	Mean ± 1 sigma		104.9 ± 1.6	104.9	8.3	100.1	3.2	100.0	2.9
Non-purgeable volatiles									
Ethyl acetate-$^{13}C_2$	77	150.00	106.0	104.0	0.1	101.9	0.1	98.1	0.1
Acetone-d_6	57	600.00	106.5	103.2	0.1	103.2	0.1	96.9	0.1
Pyridine-d_5	115	15000.00	77.6	82.7	5.3	93.9	6.0	106.5	6.8
	Mean ± 1 sigma		96.7 ± 13.5	96.7	7.0	99.6	2.9	100.5	4.3

FIGURE 1

DIAGRAM OF VACUUM DISTILLATION APPARATUS

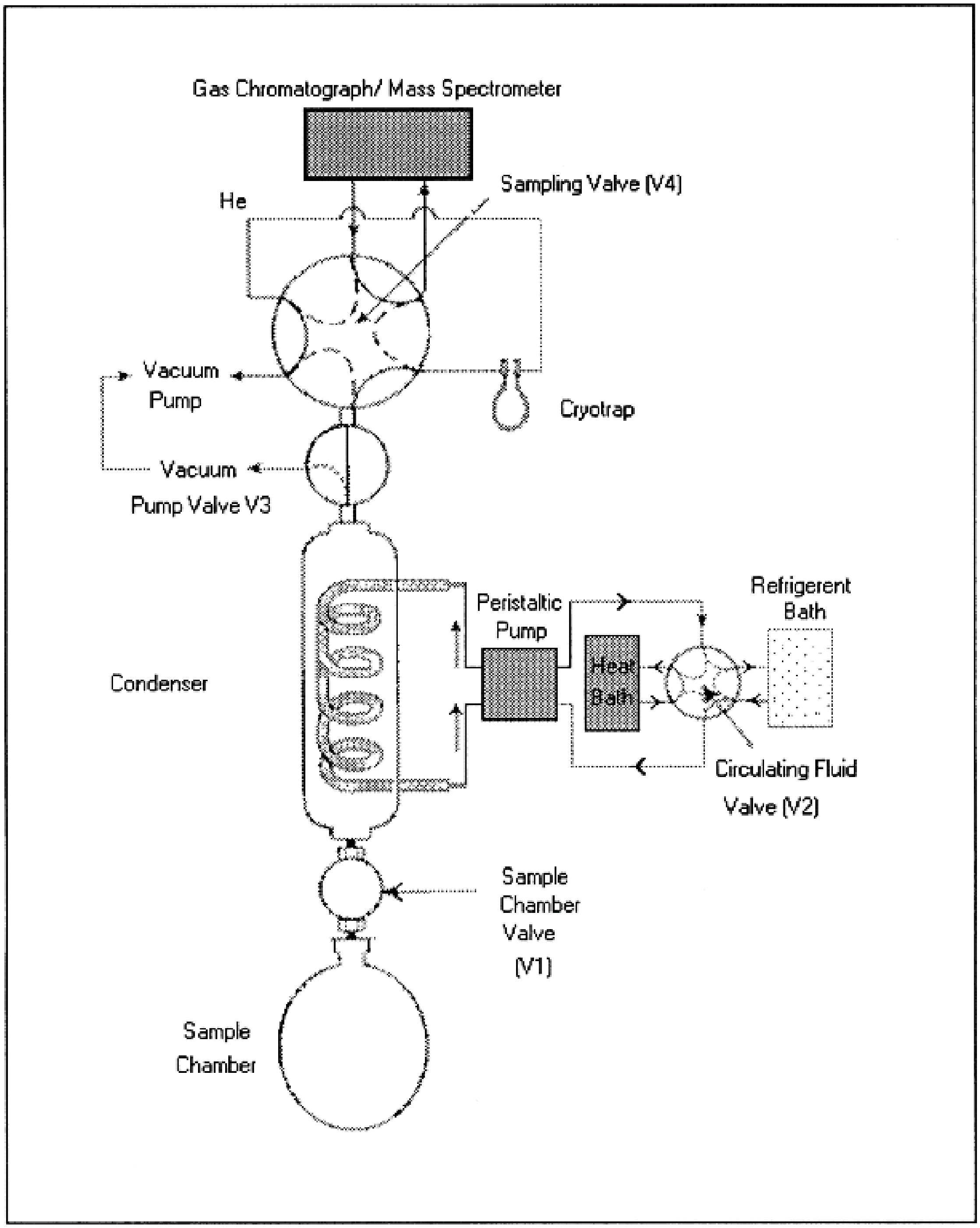
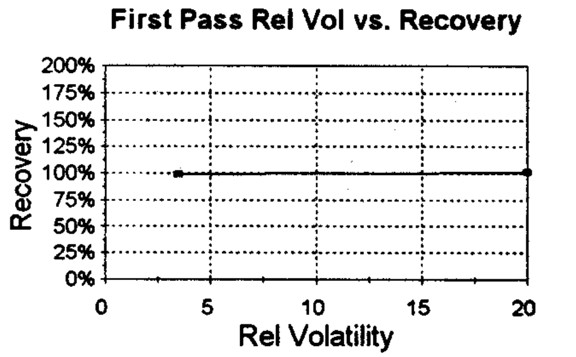
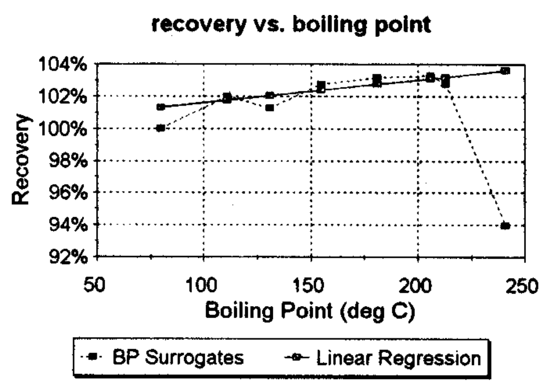
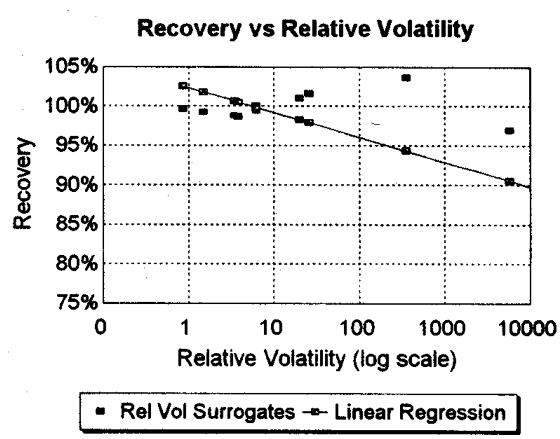


FIGURE 2

EXAMPLE SURROGATE RECOVERY CORRECTION GRAPHS



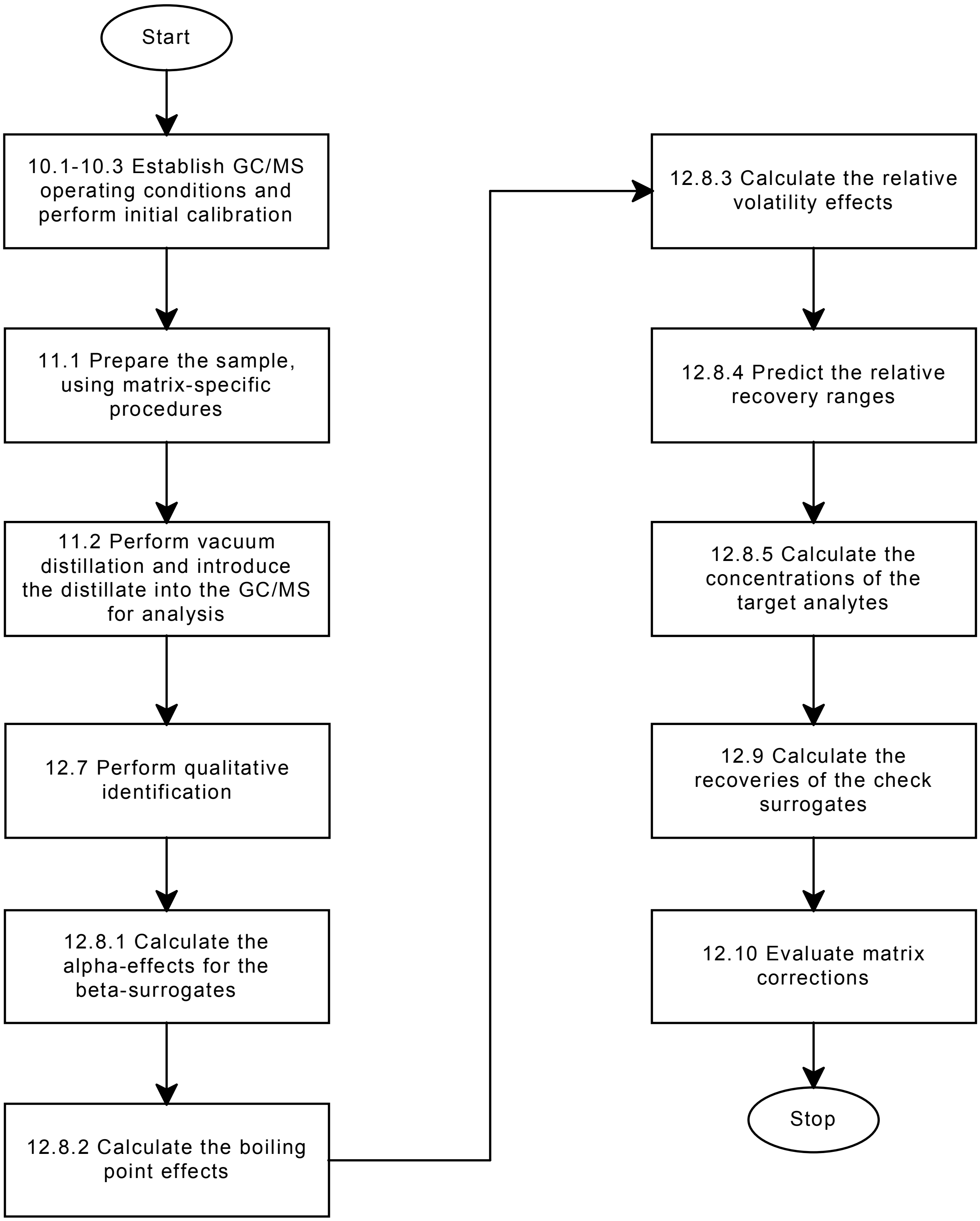




These graphs illustrate the effects of recovery corrections based on relative volatility and boiling point on the results for the target analytes from a 5-mL water sample. Such graphs, in conjunction with the check surrogate data themselves, may provide a means to identify matrix effects, including those related to specific analytes. See Tables 11A and 11B for examples of the surrogate data.

METHOD 8261

VOLATILE ORGANIC COMPOUNDS BY VACUUM DISTILLATION GC/MS



GLOSSARY

α-effect - The effect of the matrix on the relative volatility of a compound.

α-surrogate - see Gas-liquid partitioning surrogate.

β-effect - The effect of the matrix on recovery as a function of boiling point of a compound. Also known as boiling point effects.

β-surrogates - See condensation surrogates.

Class I compounds - Those compounds with boiling points generally below 160°C and α-values (or K-values) below 50. Class I compounds include the permanent gases and most volatiles.

Class II compounds - Those with boiling points greater than 160 °C. Class II compounds include the neutral semivolatiles.

Class III compounds - Those with α-values greater than 50. Class III compounds include the water-soluble volatiles.

Class IV compounds - The basic compounds that are susceptible to degradation and have a low detector response. Class IV compounds include the basic semivolatiles.

Condensation surrogates (boiling point or β-surrogates) - The β-surrogates are added to the sample to measure the recovery of analytes relative to how the compounds condense on apparatus and sample surfaces during a vacuum distillation. The β-surrogates are presented in Table 3.

Distillation performance surrogates - See gas-liquid partitioning surrogates.

Gas-liquid partitioning surrogates (α-surrogates) - The α-surrogates are added to the sample to measure the recovery of analytes relative to how the compound partitions between gas and liquid (partition coefficient K). Compounds that are going to be used as α-surrogates that have boiling points above 40°C must first be evaluated for potential losses due to condensation and a correction made to their recoveries when condensation is evident. α-surrogates are also known as distillation performance surrogates.

Relative volatility (α) - The property of an analyte that determines its presence in the vapor phase above an aqueous sample. The relative volatility is proportional to the gas-liquid partition coefficient (K) of the compound. Either α- or K-values can be used to describe this effect and Table 3 lists α-values for the compounds in Table 1 that are equivalent to K (Reference 7).