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

1.0 SCOPE AND APPLICATION

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Technique	
Analyte	CAS No.[b]	Purge-and-Trap	Direct Injection
Acetone	67-64-1	pp	a
Acetonitrile	75-05-8	pp	a
Acrolein (Propenal)	107-02-8	pp	a
Acrylonitrile	107-13-1	pp	a
Allyl alcohol	107-18-6	pp	a
Allyl chloride	107-05-1	a	a
Benzene	71-43-2	a	a
Benzyl chloride	100-44-7	pp	a
Bromoacetone	598-31-2	pp	a
Bromochloromethane (I.S.)	74-97-5	a	a
Bromodichloromethane	75-27-4	a	a
4-Bromofluorobenzene (surr.)	460-00-4	a	a
Bromoform	75-25-2	a	a
Bromomethane	74-83-9	a	a
2-Butanone (MEK)	78-93-3	pp	a
Carbon disulfide	75-15-0	pp	a
Carbon tetrachloride	56-23-5	a	a
Chloral hydrate	302-17-0	pp	a
Chlorobenzene	108-90-7	a	a
Chlorobenzene-d_5 (I.S.)	3114-55-4	a	a
Chlorodibromomethane	124-48-1	a	a
Chloroethane	75-00-3	a	a
2-Chloroethanol	107-07-3	pp	a
bis-(2-Chloroethyl) sulfide	505-60-2	pp	a
2-Chloroethyl vinyl ether	110-75-8	a	a
Chloroform	67-66-3	a	a
Chloromethane	74-87-3	a	a
Chloroprene	126-99-8	a	pc
3-Chloropropionitrile	542-76-7	ND	pc
1,2-Dibromo-3-chloropropane	96-12-8	pp	a
1,2-Dibromoethane	106-93-4	a	a

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
Dibromomethane	74-95-3	a	a
1,4-Dichloro-2-butene	764-41-0	pp	a
Dichlorodifluoromethane	75-71-8	a	a
1,1-Dichloroethane	75-34-3	a	a
1,2-Dichloroethane	107-06-2	a	a
1,2-Dichloroethane-d_4(surr.)	107-06-2	a	a
1,1-Dichloroethene	75-35-4	a	a
trans-1,2-Dichloroethene	156-60-5	a	a
1,2-Dichloropropane	78-87-5	a	a
1,3-Dichloro-2-propanol	96-23-1	pp	a
cis-1,3-Dichloropropene	10061-01-5	a	a
trans-1,3-Dichloropropene	10061-02-6	a	a
1,2,3,4-Diepoxybutane	1464-53-5	a	a
1,4-Difluorobenzene (I.S.)	540-36-3	a	a
1,4-Dioxane	123-91-1	pp	a
Epichlorohydrin	106-89-8	i	a
Ethanol	64-17-5	i	a
Ethylbenzene	100-41-4	a	a
Ethylene oxide	75-21-8	pp	a
Ethyl methacrylate	97-63-2	a	a
2-Hexanone	591-78-6	pp	a
2-Hydroxypropionitrile	78-97-7	ND	pc
Iodomethane	74-88-4	a	a
Isobutyl alcohol	78-83-1	pp	a
Malononitrile	109-77-3	pp	a
Methacrylonitrile	126-98-7	pp	a
Methylene chloride	75-09-2	a	a
Methyl iodide	74-88-4	a	a
Methyl methacrylate	80-62-6	a	a
4-Methyl-2-pentanone	108-10-1	pp	a
Pentachloroethane	76-01-7	i	pc
2-Picoline	109-06-8	pp	a
Propargyl alcohol	107-19-7	pp	a
β-Propiolactone	57-57-8	pp	a
Propionitrile	107-12-0	pp	a
n-Propylamine	107-10-8	a	a
Pyridine	110-86-1	i	a
Styrene	100-42-5	a	a
1,1,1,2-Tetrachloroethane	630-20-6	a	a
1,1,2,2-Tetrachloroethane	79-34-5	a	a
Tetrachloroethene	127-18-4	a	a
Toluene	108-88-3	a	a
Toluene-d_8 (surr.)	2037-26-5	a	a
1,1,1-Trichloroethane	71-55-6	a	a
1,1,2-Trichloroethane	79-00-5	a	a
Trichloroethene	79-01-6	a	a
Trichlorofluoromethane	75-69-4	a	a

Analyte	CAS No.[b]	Appropriate Technique: Purge-and-Trap	Appropriate Technique: Direct Injection
1,2,3-Trichloropropane	96-18-4	a	a
Vinyl acetate	108-05-4	a	a
Vinyl chloride	75-01-4	a	a
Xylene (Total)	1330-20-7	a	a

a Adequate response by this technique.
b Chemical Abstract Services Registry Number.
pp Poor purging efficiency resulting in high EQLs.
i Inappropriate technique for this analyte.
pc Poor chromatographic behavior.
surr Surrogate
I.S. Internal Standard
ND Not determined

1.2 Method 8240 can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Table 1 for a list of compounds, retention times, and their characteristic ions that have been evaluated on a purge-and-trap GC/MS system.

1.3 The estimated quantitation limit (EQL) of Method 8240 for an individual compound is approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 2). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

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

1.5 To increase purging efficiencies of acrylonitrile and acrolein, refer to Methods 5030 and 8030 for proper purge-and-trap conditions.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). The

components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with organic-free reagent water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 The purge-and-trap process - An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences, under the analysis conditions, by analyzing method blanks.

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

3.3 Cross contamination can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of organic-free reagent water to check for cross contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-concentration sample.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3.5 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running calibration and reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL, and 1,000 µL. These syringes should be equipped with a 20 gauge (0.006 in. ID) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

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

4.3 Syringe - 5 mL, gas-tight with shutoff valve.

4.4 Balances - Analytical, 0.0001 g, and top-loading, 0.1 g.

4.5 Glass scintillation vials - 20 mL, with screw caps and Teflon liners or glass culture tubes with a screw cap and Teflon liner.

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

4.7 Vials - 2 mL, for GC autosampler.

4.8 Spatula - Stainless steel.

4.9 Disposable pipets - Pasteur.

4.10 Heater or heated oil bath - Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.11 Purge-and-trap device - The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.11.1 The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be utilized, provided equivalent performance is demonstrated.

4.11.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap should contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone coated packing be inserted at the inlet to extend the life of the trap (see Figure 2). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons

of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning. However, the column must be run through the temperature program prior to analysis of samples.

4.11.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake out mode. The desorber design illustrated in Figure 2 meets these criteria.

4.11.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.11.5 Trap Packing Materials

4.11.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

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

4.11.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.11.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, lot #M-2649, by crushing through 26 mesh screen (or equivalent).

4.12 Gas chromatograph/mass spectrometer system

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

4.12.2 Column - 6 ft x 0.1 in. ID glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.12.3 Mass spectrometer - Capable of scanning from 35-260 amu every 3 seconds or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet.

4.12.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 3) may be used. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

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

5.0 REAGENTS

5.1 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.

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

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

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

5.3.2 Add the assayed reference material, as described below.

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

5.3.2.2 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 Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

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

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

5.3.5 Prepare fresh stock standards for gases weekly or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds a 20% drift.

5.3.6 Optionally, calibration using a certified gaseous mixture can be accomplished daily utilizing commercially available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichlorodifluoromethane and trichlorofluoromethane in nitrogen. These mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.4 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.

5.5 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Sec. 5.3, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 µg/10 mL in methanol. Each water sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis.

5.6 Internal standards - The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other compounds

may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.3 and 5.4. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L.

5.7 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared.

5.8 Calibration standards - Calibration standards at a minimum of five concentrations should be prepared from the secondary dilution of stock standards (see Secs. 5.3 and 5.4). Prepare these solutions in organic-free reagent water. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method. It is EPA's intent that all target analytes for a particular analysis be included in the calibration standard(s). However, these target analytes may not include the entire List of Analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s). Calibration standards must be prepared daily.

5.9 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.10 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards in methanol be stored at -10°C to -20°C in screw cap amber bottles with Teflon liners.

5.11 Methanol, CH_3OH. Pesticide quality or equivalent. Store apart from other solvents.

5.12 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

5.12.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), $C_8H_{18}O_5$. Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

CAUTION: Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper

protective equipment to minimize exposure to liquid and vapor.

Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed in a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and a vacuum is maintained at < 10 mm Hg for at least two hours using a two stage mechanical pump. The vacuum system is equipped with an all glass trap, which is maintained in a dry ice/methanol bath. Cool the tetraglyme to ambient temperature and add 100 mg/L of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw cap bottle in an area that is not contaminated by solvent vapors.

5.12.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, an organic-free reagent water/tetraglyme blank must be analyzed.

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

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

7.0 PROCEDURE

Samples may be introduced into the GC by either direct injection or purge-and-trap procedures. Whichever procedure is used, the instrument calibration and sample introduction must be performed by the same procedure.

Regardless of which sample introduction procedure is employed, establish GC/MS operating conditions using the following recommendations as guidance.

Recommended GC/MS operating conditions:

Electron energy:	70 volts (nominal).
Mass range:	35-260 amu.
Scan time:	To give 5 scans/peak, but not to exceed 1 sec/scan.
Initial column temperature:	45°C.
Initial column holding time:	3 minutes.
Column temperature program:	8°C/minute.
Final column temperature:	220°C.
Final column holding time:	15 minutes.
Injector temperature:	200-225°C.
Source temperature:	According to manufacturer's specifications.
Transfer line temperature:	250-300°C.

Carrier gas: Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.1 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 µg/L); therefore, it is only permitted when concentrations in excess of 10,000 µg/L are expected or for water soluble compounds that do not purge. The system must be calibrated by direct injection using the procedures described in Sec. 7.2,, but bypassing the purge-and-trap device.

7.2 Initial calibration for purge-and-trap procedure

7.2.1 Establish the GC/MS operating conditions, using the recommendations in Sec. 7.0 as guidance.

7.2.2 Each GC/MS system must be hardware tuned to meet the criteria in Table 3 for a 50 ng injection or purging of 4-bromofluorobenzene (2 µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.3 Assemble a purge-and-trap device that meets the specification in Sec. 4.11. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.4 Connect the purge-and-trap device to a gas chromatograph.

7.2.5 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device (use freshly prepared stock solutions when preparing the calibration standards for the initial calibration.) Add 5.0 mL of organic-free reagent water to the purging device. The organic-free reagent water is added to the purging device using a 5 mL glass syringe fitted with a 15 cm, 20 gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14 gauge needle that forms the sample inlet will permit insertion of the 20 gauge needle. Next, using a 10 µL or 25 µL microsyringe equipped with a long needle (Sec. 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (Sec. 5.6). Add the aliquot of calibration solution directly to the organic-free reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the organic-free reagent water. Similarly, add 10 µL of the internal standard solution (Sec. 5.4). Close the 2 way syringe valve at the sample inlet.

7.2.6 Carry out the purge-and-trap analysis procedure as described in Sec. 7.4.1.

7.2.7 Tabulate the area response of the characteristic ions (see Table 1) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Sec. 7.5.2). The RF is calculated as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the compound being measured.

7.2.8 The average RF must be calculated for each compound using the 5 RF values calculated for each compound from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average relative response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (>0.10 for bromoform). These compounds typically have RFs of 0.4-0.6 and are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.2.8.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

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

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

7.2.9 Using the RFs from the initial calibration, calculate and record the percent relative standard deviation (%RSD) for all compounds. The percent RSD is calculated as follows:

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

where:

$\overline{RSD}$ = relative standard deviation.
$\overline{RF}$ = mean of 5 initial RFs for a compound.
SD = standard deviation of average RFs for a compound.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{N - 1}}$$

where:

RF_i = RF for each of the 5 calibration levels
N = Number of RF values (i.e., 5)

The percent relative standard deviation should be less than 15% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) must be less than 30%. Late-eluting compounds usually have much better agreement. The CCCs are:

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

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

7.2.10 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation (Sec. 7.5.2.2).

7.2.10.1 If the %RSD of any compound is greater than 15%, construct calibration curves of area ratio (A/A_{is}) versus concentration using first or higher order regression fit of the five calibration points. The analyst should select the regression order which introduces the least calibration error into the quantitation (Sec. 7.5.2.4). The use of calibration curves is a recommended alternative to average response factor calibration, and a useful diagnostic of standard preparation accuracy and absorption activity in the chromatographic system.

7.2.11 These curves are verified each shift by purging a performance standard. Recalibration is required only if calibration and on-going performance criteria cannot be met.

7.3 Daily GC/MS calibration

7.3.1 Prior to the analysis of samples, inject or purge 50 ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12 hour shift.

7.3.2 The initial calibration curve (Sec. 7.2) for each compound of interest must be checked and verified once every 12 hours of analysis time. 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 checking the SPCC (Sec. 7.3.3) and CCC (Sec. 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum relative response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum relative response factor for volatile SPCCs is 0.300 (>0.10 for Bromoform). Some possible problems are 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.

7.3.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Sec. 7.2.9 are used to check the validity of the initial calibration.

Calculate the percent drift using the following equation:

$$\% \text{ Drift} = \frac{C_I - C_c}{C_I} \times 100$$

where:

C_I = Calibration Check Compound standard concentration.
C_c = Measured concentration using selected quantitation method.

If the percent difference for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% drift), for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins. If the CCCs are

not required analytes by the permit, then all required analytes must meet the 20% drift criterion.

7.3.5 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last calibration check (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 internal standards changes by a factor of two (- 50% to + 100%) from the last daily calibration check 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.

7.4 GC/MS analysis

7.4.1 Water samples

7.4.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be used are: the headspace sampler (Method 3810) using a gas chromatograph (GC) equipped with a photo ionization detector (PID) in series with an electrolytic conductivity detector (HECD); and extraction of the sample with hexadecane and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Sec. 7.2.1.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Sec. 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response (see Sec. 7.2.8).

7.4.1.6 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if

there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.4.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas tight syringe.

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

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

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Sec. 7.4.1.6 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.4.1.7.4 Fill a 5 mL syringe with the diluted sample as in Sec. 7.4.1.6.

7.4.1.8 Add 10.0 µL of surrogate spiking solution (Sec. 5.5) and 10 µL of internal standard spiking solution (Sec. 5.6) through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 µg/L of each surrogate standard.

7.4.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.4.1.10 Close both valves and purge the sample for 11.0 $\pm$ 0.1 minutes at ambient temperature.

7.4.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC/MS data acquisition. Concurrently, introduce the trapped materials to the

gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for 4 minutes. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial program temperature of 45°C.

7.4.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of organic-free reagent water (or methanol followed by organic-free reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.4.1.13 After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.4.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.4.1.15 For matrix spike analysis, add 10 µL of the matrix spike solution (Sec. 5.9) to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.4.1.16 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Secs. 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 Water miscible liquids

7.4.2.1 Water miscible liquids are analyzed as water samples after first diluting them at least 50 fold with organic-free reagent water.

7.4.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100 mL volumetric flask and

diluting to volume with organic-free reagent water. Transfer immediately to a 5 mL gas tight syringe.

7.4.2.3 Alternatively, prepare dilutions directly in a 5 mL syringe filled with organic-free reagent water by adding at least 20 µL, but not more than 100 µL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 Sediment/soil and waste samples - It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may be used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-concentration method (0.005-1 mg/kg) or the high-concentration method (> 1 mg/kg).

7.4.3.1 Low-concentration method - This is designed for samples containing individual purgeable compounds of < 1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples. See Figure 5 for an illustration of a low soils impinger.

7.4.3.1.1 Use a 5 g sample if the expected concentration is < 0.1 mg/kg or a 1 g sample for expected concentrations between 0.1 and 1 mg/kg.

7.4.3.1.2 The GC/MS system should be set up as in Secs. 7.4.1.2-7.4.1.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-concentration method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

7.4.3.1.3 Remove the plunger from a 5 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 µL each of surrogate spiking solution (Sec. 5.5) and internal standard solution (Sec. 5.6) to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) The addition of 10 µL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 µg/kg of each surrogate standard.

7.4.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Sec. 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent dry weight of the soil/sediment sample. This includes waste samples that are amenable to percent dry weight determination. Other wastes should be reported on a wet-weight basis.

7.4.3.1.5.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before re-weighing. Concentrations of individual analytes are reported relative to the dry weight of sample.

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

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

7.4.3.1.6 Add the spiked water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, the procedures in Secs. 7.4.3.1.4 and 7.4.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.4.3.1.7 Heat the sample to 40°C $\pm$ 1°C and purge the sample for 11.0 $\pm$ 0.1 minute.

7.4.3.1.8 Proceed with the analysis as outlined in Secs. 7.4.1.11-7.4.1.16. Use 5 mL of the same organic-free reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1 g sample were analyzed, the high-concentration method must be followed.

7.4.3.1.9 For low-concentration sediment/soils add 10 µL of the matrix spike solution (Sec. 5.9) to the 5 mL of organic-free reagent water (Sec. 7.4.3.1.3). The

concentration for a 5 g sample would be equivalent to 50 µg/kg of each matrix spike standard.

7.4.3.2 High-concentration method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with reagent tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water containing internal standards. This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

7.4.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20 mL vial. Use a top loading balance. Note and record the actual weight to 0.1 gram and determine the percent dry weight of the sample using the procedure in Sec. 7.4.3.1.5. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of solvent into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.4.3.2.2 Quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

NOTE: Secs. 7.4.3.2.1 and 7.4.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.4.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of appropriate solvent to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis. The addition of a 100 µL aliquot of each of these extracts in Sec. 7.4.3.2.6 will give a concentration equivalent to 6,200 µg/kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Secs. 7.4.1.2-7.4.1.4. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.4.3.2.5 Table 4 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed (Method 3810 or 3820), use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100 µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.4.3.2.6 Remove the plunger from a 5.0 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 µL of internal standard solution. Also add the volume of solvent extract determined in Sec. 7.4.3.2.5 and a volume of extraction or dissolution solvent to total 100 µL (excluding methanol in standards).

7.4.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the organic-free reagent water/methanol sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Sec. 7.4.1.11-7.4.1.16. Analyze all reagent blanks on the same instrument as that use for the samples. The standards and blanks should also contain 100 µL of solvent to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the high-concentration sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Sec. 5.5), and 1.0 mL of matrix spike solution (Sec. 5.9) as in Sec. 7.4.3.2.2. This results in a 6,200 µg/kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100 µL aliquot of this extract to 5 mL of organic-free reagent water for purging (as per Sec. 7.4.3.2.6).

7.5 Data interpretation

7.5.1 Qualitative analysis

7.5.1.1 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 should be identified as present when the criteria below are met.

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

7.5.1.1.2 The RRT of the sample component is within $\pm$ 0.06 RRT units of the RRT of the standard component.

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

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

7.5.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. 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 can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.5.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses

being conducted. Guidelines for making tentative identification are:

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

(2) The relative intensities of the major ions should agree within $\pm$ 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.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5.2 Quantitative analysis

7.5.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g. see Table 5).

7.5.2.2 When linearity exists, as per Sec. 7.2.10, calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(\overline{RF})(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
A_{is} = Area of characteristic ion for the internal standard.
$\overline{RF}$ = Mean relative response factor for compound being measured (Sec. 7.2.8).
V_o = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis)

$$\text{concentration } (\mu g/kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, A_{is}, $\overline{RF}$, = Same as for water.
V_t = Volume of total extract (μL) (use 10,000 μL or a factor of this when dilutions are made).
V_i = Volume of extract added (μL) for purging.
W_s = Weight of sample extracted or purged (g).
D = % dry weight of sample/100, or 1 for a wet-weight basis.

7.5.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulae given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.5.2.4 Alternatively, the regression line fitted to the initial calibration (Sec. 7.2.10.1) may be used for determination of analyte concentration.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control reference sample must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 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 extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of sample preparation and measurement.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration 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 useable, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the BFB specifications in Sec. 7.2.2.

8.4.2 There must be an initial calibration of the GC/MS system as specified in Sec. 7.2.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Step 7.3.3 and the CCC criteria in Sec. 7.3.4, each 12 hours.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 mg/L in methanol. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Prepare a QC reference sample to contain 20 µg/L of each analyte by adding 200 µL of QC reference sample concentrate to 100 mL of water.

8.5.3 Four 5-mL aliquots of the well mixed QC reference sample are analyzed according to the method beginning in Sec. 7.4.1.

8.5.4 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte using the four results.

8.5.5 For each analyte compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and x for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual x falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Sec. 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Sec. 8.5.2.

8.5.6.2 Beginning with Sec. 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Sec. 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a method blank and a spiked replicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of spiked replicates. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Sec. 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in a water sample is not being checked against a specific limit, the spike should be at 20 µg/L or 1 to 5 times higher than the background concentration determined in Sec. 8.6.2, whichever concentration would be larger. For other matrices, recommended spiking concentration is 10 times the EQL.

8.6.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Sec. 8.5.1) appropriate for the background

concentration in the sample. Spike a second 5-mL sample aliquot with 10 µL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A-B)%/T, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 µg/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for x; (3) calculate the range for recovery at the spike concentration as (100x'/T) $\pm$ 2.44(100S'/T)%.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Sec. 8.7.

8.7 If any analyte in a water sample fails the acceptance criteria for recovery in Sec. 8.6, a QC reference sample containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC reference sample will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Sec. 8.6, the probability that the analysis of a QC reference sample will be required is high. In this case, the QC reference sample should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC reference sample by adding 10 µL of the QC reference sample concentrate (Sec. 8.5.1 or 8.6.2) to 5 mL of reagent water. The QC reference sample needs only to contain the analytes that failed criteria in the test in Sec. 8.6.

8.7.2 Analyze the QC reference sample to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100(A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Sec. 8.6 need to be compared with these criteria. If

the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Sec. 8.6, calculate the average percent recovery (p) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $p - 2s_p$ to $p + 2s_p$. If p = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g., after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Sec. 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 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. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 This method was tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600 µg/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

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

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TABLE 1.
RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
Ethylene oxide	1.30	44	44, 43, 42
Chloromethane	2.30	50	52, 49
Dichlorodifluoromethane	2.47	85	85, 87, 101, 103
Bromomethane	3.10	94	96, 79
Vinyl chloride	3.80	62	64, 61
Acetonitrile	3.97	41	41, 40, 39
Chloroethane	4.60	64	66, 49
Methyl iodide	5.37	142	142, 127, 141
Methylene chloride	6.40	84	49, 51, 86
Carbon disulfide	7.47	76	76, 78, 44
Trichlorofluoromethane	8.30	101	103, 66
Propionitrile	8.53	54	54, 52, 55, 40
Allyl chloride	8.83	76	76, 41, 39, 78
1,1-Dichloroethene	9.00	96	61, 98
Bromochloromethane (I.S.)	9.30	128	49, 130, 51
Allyl alcohol	9.77	57	57, 58, 39
trans-1,2-Dichloroethene	10.00	96	61, 98
1,2-Dichloroethane	10.10	62	64, 98
Propargyl alcohol	10.77	55	55, 39, 38, 53
Chloroform	11.40	83	85, 47
1,2-Dichloroethane-d_4(surr)	12.10	65	102
2-Butanone	12.20	72	43, 72
Methacrylonitrile	12.37	41	41, 67, 39, 52, 66
Dibromomethane	12.53	93	93, 174, 95, 172, 176
2-Chloroethanol	12.93	49	49, 44, 43, 51, 80
b-Propiolactone	13.00	42	42, 43, 44
Epichlorohydrin	13.10	57	57, 49, 62, 51
1,1,1-Trichloroethane	13.40	97	99, 117
Carbon tetrachloride	13.70	117	119, 121
1,4-Dioxane	13.70	88	88, 58, 43, 57
Isobutyl alcohol	13.80	43	43, 41, 42, 74
Bromodichloromethane	14.30	83	85, 129
Chloroprene	14.77	53	53, 88, 90, 51
1,2:3,4-Diepoxybutane	14.87	55	55, 57, 56
1,2-Dichloropropane	15.70	63	62, 41
Chloral hydrate (b)	15.77	82	44, 84, 86, 111
cis-1,3-Dichloropropene	15.90	75	77, 39
Bromoacetone	16.33	136	43, 136, 138, 93, 95
Trichloroethene	16.50	130	95, 97, 132
Benzene	17.00	78	52, 71
trans-1,3-Dichloropropene	17.20	75	77, 39
1,1,2-Trichloroethane	17.20	97	83, 85, 99
3-Chloropropionitrile	17.37	54	54, 49, 89, 91
1,2-Dibromoethane	18.40	107	107, 109, 93, 188
Pyridine	18.57	79	79, 52, 51, 50

TABLE 1.
(Continued)

Compound	Retention Time (minutes)	Primary Ion	Secondary Ion(s)
2-Chloroethyl vinyl ether	18.60	63	65,106
2-Hydroxypropionitrile	18.97	44	44,43,42,53
1,4-Difluorobenzene (I.S.)	19.60	114	63,88
Malononitrile	19.60	66	66,39,65,38
Methyl methacrylate	19.77	69	69,41,100,39
Bromoform	19.80	173	171,175,252
1,1,1,2-Tetrachloroethane	20.33	131	131,133,117,119,95
1,3-Dichloro-2-propanol	21.83	79	79,43,81,49
1,1,2,2-Tetrachloroethane	22.10	83	85,131,133
Tetrachloroethene	22.20	164	129,131,166
1,2,3-Trichloropropane	22.20	75	75,77,110,112,97
1,4-Dichloro-2-butene	22.73	75	75,53,77,124,89
n-Propylamine	23.00	59	59,41,39
2-Picoline	23.20	93	93,66,92,78
Toluene	23.50	92	91,65
Ethyl methacrylate	23.53	69	69,41,99,86,114
Chlorobenzene	24.60	112	114,77
Pentachloroethane[a]	24.83	167	167,130,132,165,169
Ethylbenzene	26.40	106	91
1,2-Dibromo-3-chloropropane	27.23	157	157,75,155,77
4-Bromofluorobenzene (surr.)	28.30	95	174,176
Benzyl chloride	29.50	91	91,126,65,128
Styren	30.83	104	104,103,78,51,77
bis-(2-Chloroethyl) sulfide(b)	33.53	109	111, 158, 160
Acetone	--	43	58
Acrolein	--	56	55,58
Acrylonitrile	--	53	52,51
Chlorobenzene-d_5 (I.S.)	--	117	82,119
Chlorodibromomethane	--	129	208,206
1,1-Dichloroethane	--	63	65,83
Ethanol	--	31	45,27,46
2-Hexanone	--	43	58,57, 100
Iodomethane	--	142	127,141
4-Methyl-2-pentanone	--	43	58,57,100
Toluene-d_8 (surr.)	--	98	70,100
Vinyl acetate	--	43	86
Xylene (Total)	--	106	91

a The base peak at m/e 117 was not used due to an interference at that mass with a nearly coeluting internal standard, chlorobenzene-d_5.
b Response factor judged to be too low (less than 0.02) for practical use.
(I.S.) = Internal Standard
(surr) = Surrogate

TABLE 2.
ESTIMATED QUANTITATION LIMITS (EQL) FOR VOLATILE ORGANICS

Volatiles	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Acetone	100	100
Acetonitrile	100	100
Allyl chloride	5	5
Benzene	5	5
Benzyl chloride	100	100
Bromodichloromethane	5	5
Bromoform	5	5
Bromomethane	10	10
2-Butanone	100	100
Carbon disulfide	100	100
Carbon tetrachloride	5	5
Chlorobenzene	5	5
Chlorodibromomethane	5	5
Chloroethane	10	10
2-Chloroethyl vinyl ether	10	10
Chloroform	5	5
Chloromethane	10	10
Chloroprene	5	5
1,2-Dibromo-3-chloropropane	100	100
1,2-Dibromoethane	5	5
Dibromomethane	5	5
1,4-Dichloro-2-butene	100	100
Dichlorodifluoromethane	5	5
1,1-Dichloroethane	5	5
1,2-Dichloroethane	5	5
1,1 Dichloroethene	5	5
trans-1,2-Dichloroethene	5	5
1,2-Dichloropropane	5	5
cis-1,3-Dichloropropene	5	5
trans-1,3-Dichloropropene	5	5
Ethylbenzene	5	5
Ethyl methacrylate	5	5
2-Hexanone	50	50
Isobutyl alcohol	100	100
Methacrylonitrile	100	100
Methylene chloride	5	5
Methyl iodide	5	5
Methyl methacrylate	5	50
4-Methyl-2-pentanone	50	50
Pentachloroethane	10	10

TABLE 2.
(Continued)

Volatiles	Estimated Quantitation Limits[a] Ground water µg/L	Low Soil/Sediment[b] µg/kg
Propionitrile	100	100
Styrene	5	5
1,1,1,2-Tetrachloroethane	5	5
1,1,2,2-Tetrachloroethane	5	5
Tetrachloroethene	5	5
Toluene	5	5
1,1,1-Trichloroethane	5	5
1,1,2-Trichloroethane	5	5
Trichloroethene	5	5
1,2,3-Trichloropropane	5	5
Vinyl acetate	50	50
Vinyl chloride	10	10
Xylene (Total)	5	5

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

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

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

[c]EQL = [EQL for low soil/sediment (see Table 2)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet weight basis.

TABLE 3.
BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 4.
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS
OF HIGH-CONCENTRATION SOILS/SEDIMENTS

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

Calculate appropriate dilution factor for concentrations exceeding this table.

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

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

TABLE 5.
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

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

Chlorobenzene-d_5
Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Ethyl methacrylate
2-Hexanone
4-Methyl-2-pentanone
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylene

TABLE 6.
CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (µg/L)	Limit for s (µg/L)	Range for x (µg/L)	Range p, p_s (%)
Benzene	12.8-27.2	6.9	15.2-26.0	37-151
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0	35-155
Bromoform	14.2-25.8	5.4	11.4-31.1	45-169
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
2-Chloroethyl vinyl ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Chloromethane	D-40.8	19.8	D-45.9	D-273
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4	54-156
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethyl benzene	11.8-28.2	7.5	17.4-26.7	37-162
Methylene chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.5-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl chloride	0.8-39.2	20.0	D-43.5	D-251

Q = Concentration measured in QC check sample, in µg/L.
$\underline{s}$ = Standard deviation of four recovery measurements, in µg/L.
x = Average recovery for four recovery measurements, in µg/L.
p, p_s = Percent recovery measured.
D = Detected; result must be greater than zero.

a Criteria from 40 CFR Part 136 for Method 624 and were calculated assuming a QC check sample concentration of 20 µg/L. These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S'(µg/L)
Benzene	0.93C+2.00	0.26x-1.74	0.25x-1.33
Bromodichloromethane	1.03C-1.58	0.15x+0.59	0.20x+1.13
Bromoform	1.18C-2.35	0.12x+0.34	0.17x+1.38
Bromomethane	1.00C	0.43x	0.58x
Carbon tetrachloride	1.10C-1.68	0.12x+0.25	0.11x+0.37
Chlorobenzene	0.98C+2.28	0.16x-0.09	0.26x-1.92
Chloroethane	1.18C+0.81	0.14x+2.78	0.29x+1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62x	0.84x
Chloroform	0.93C+0.33	0.16x+0.22	0.18x+0.16
Chloromethane	1.03C-1.81	0.37x+2.14	0.58x+0.43
Dibromochloromethane	1.01C-0.03	0.17x-0.18	0.17x+0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22x-1.45	0.30x-1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14x-0.48	0.18x-0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22x-1.45	0.30x-1.20
1,1-Dichloroethane	1.05C+0.36	0.13x-0.05	0.16x+0.47
1,2-Dichloroethane	1.02C+0.45	0.17x-0.32	0.21x-0.38
1,1-Dichloroethene	1.12C+0.61	0.17x+1.06	0.43x-0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14x+0.09	0.19x+0.17
1,2-Dichloropropane[a]	1.00C	0.33x	0.45x
cis-1,3-Dichloropropene[a]	1.00C	0.38x	0.52x
trans-1,3-Dichloropropene[a]	1.00C	0.25x	0.34x
Ethyl benzene	0.98C+2.48	0.14x+1.00	0.26x-1.72
Methylene chloride	0.87C+1.88	0.15x+1.07	0.32x+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16x+0.69	0.20x+0.41
Tetrachloroethene	1.06C+0.60	0.13x-0.18	0.16x-0.45
Toluene	0.98C+2.03	0.15x-0.71	0.22x-1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12x-0.15	0.21x-0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14x+0.02	0.18x+0.00
Trichloroethene	1.04C+2.27	0.13x+0.36	0.12x+0.59
Trichlorofluoromethane	0.99C+0.39	0.33x-1.48	0.34x-0.39
Vinyl chloride	1.00C	0.48x	0.65x

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.
s_r' = Expected single analyst standard deviation of measurements at an average concentration of x, in µg/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in µg/L.
C = True value for the concentration, in µg/L.
x = Average recovery found for measurements of samples containing a concentration of C, in µg/L.
a Estimates based upon the performance in a single laboratory.
b Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

TABLE 8.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117

FIGURE 1.
PURGING CHAMBER

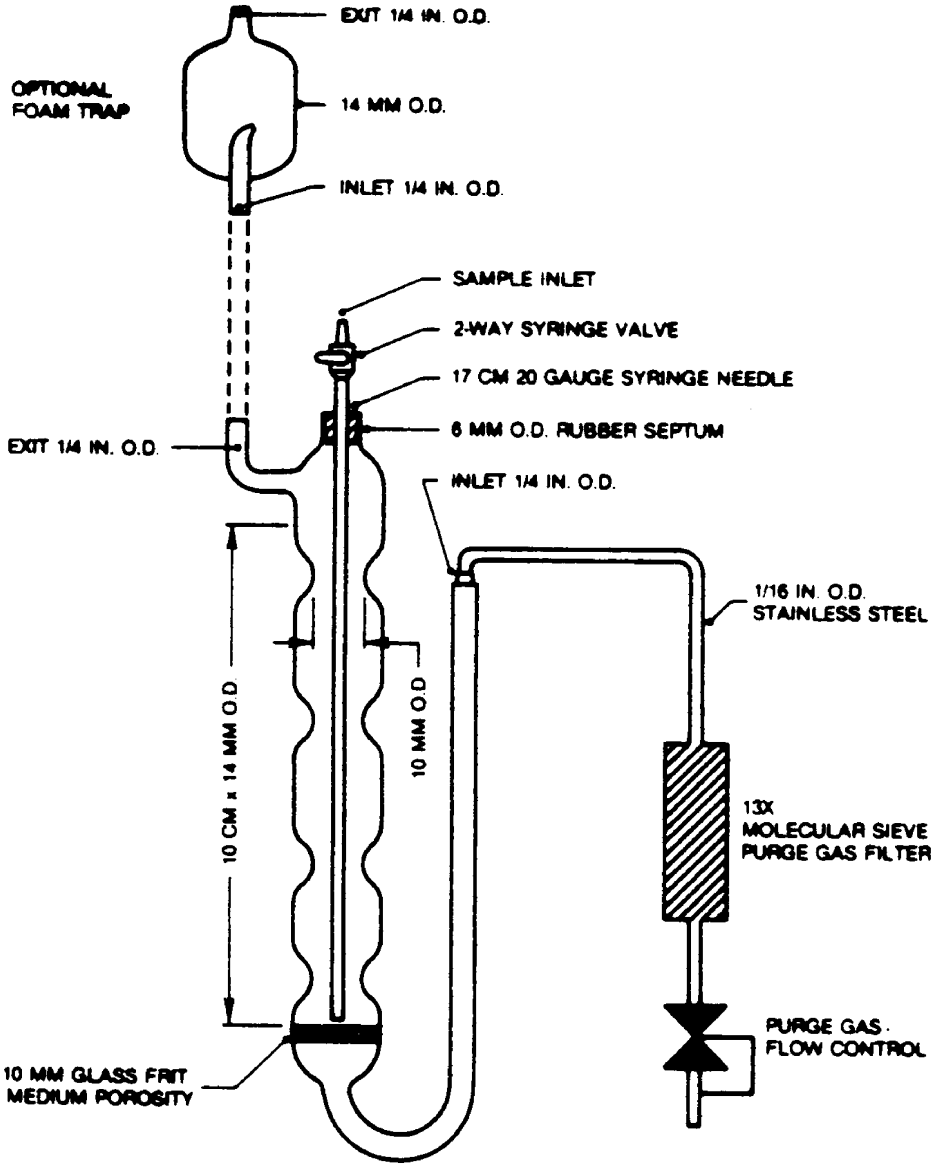


FIGURE 2.
TRAP PACKINGS AND CONSTRUCTION TO INCLUDE
DESORB CAPABILITY FOR METHOD 8240B

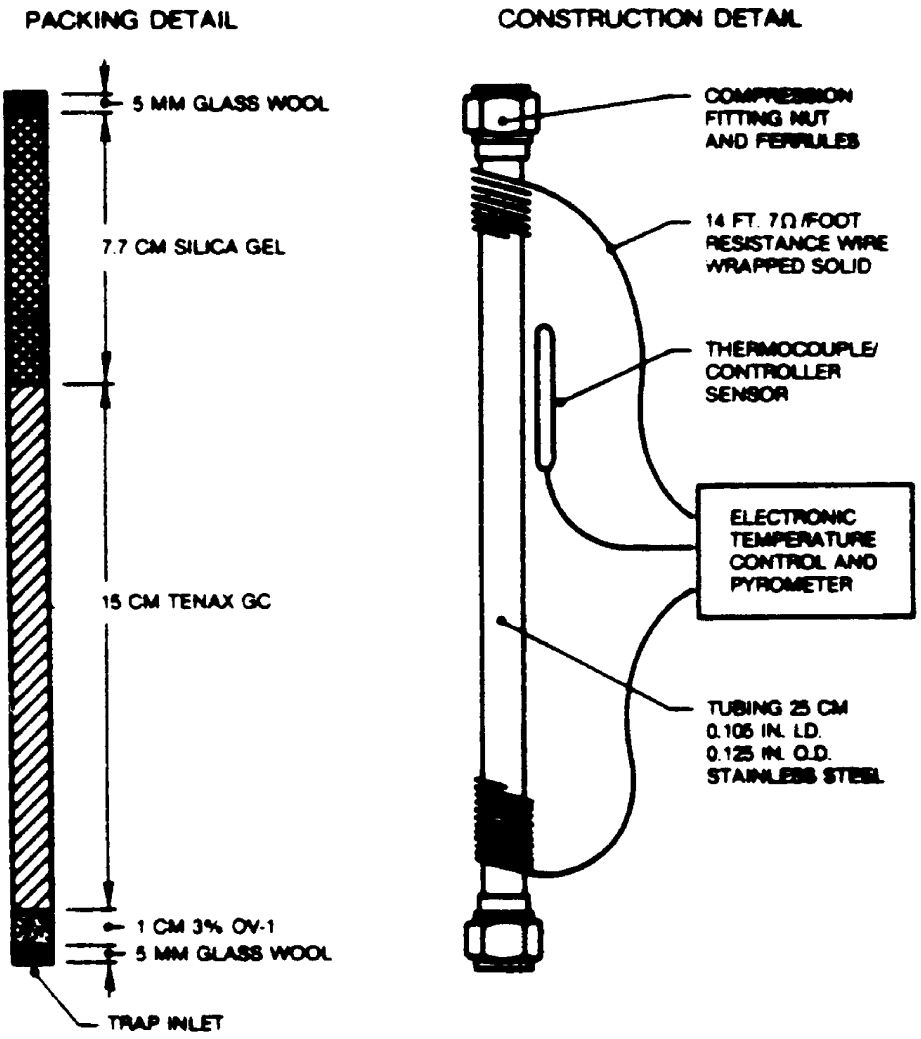


FIGURE 3.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - PURGE MODE FOR METHOD 8240B

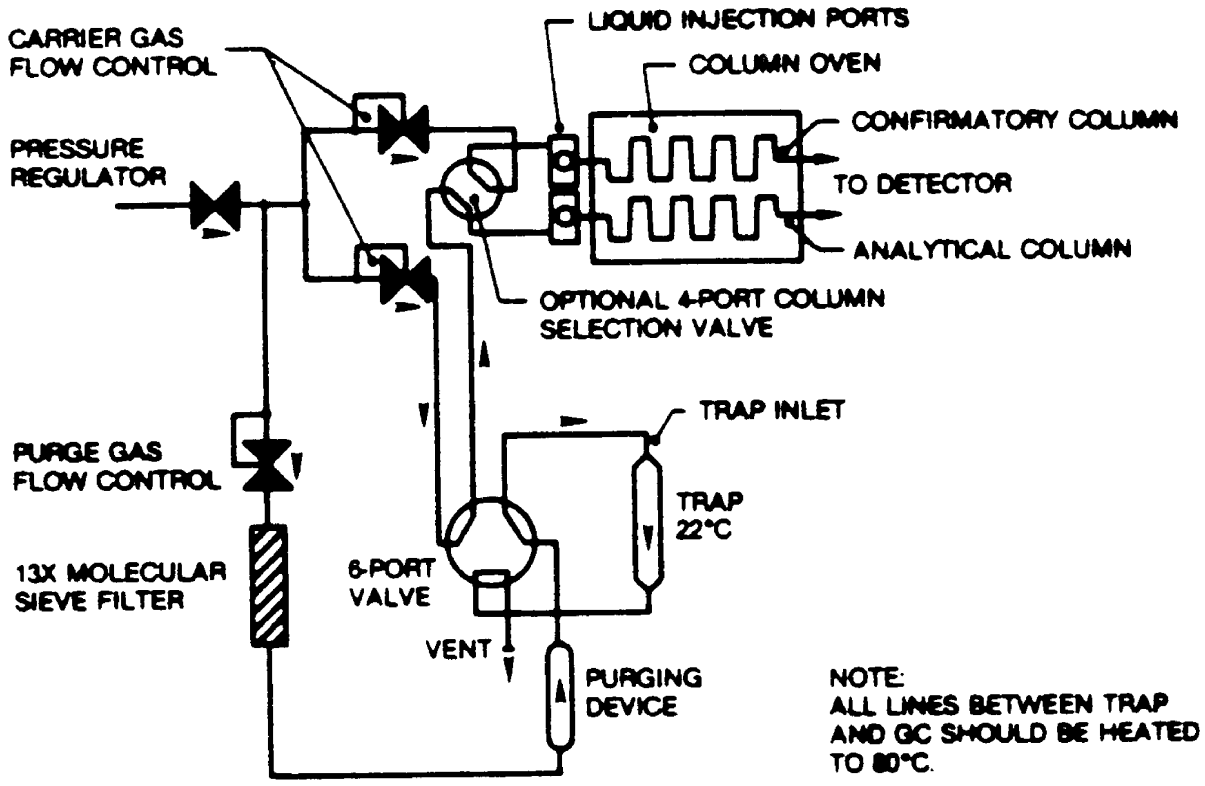


FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE FOR METHOD 8240B

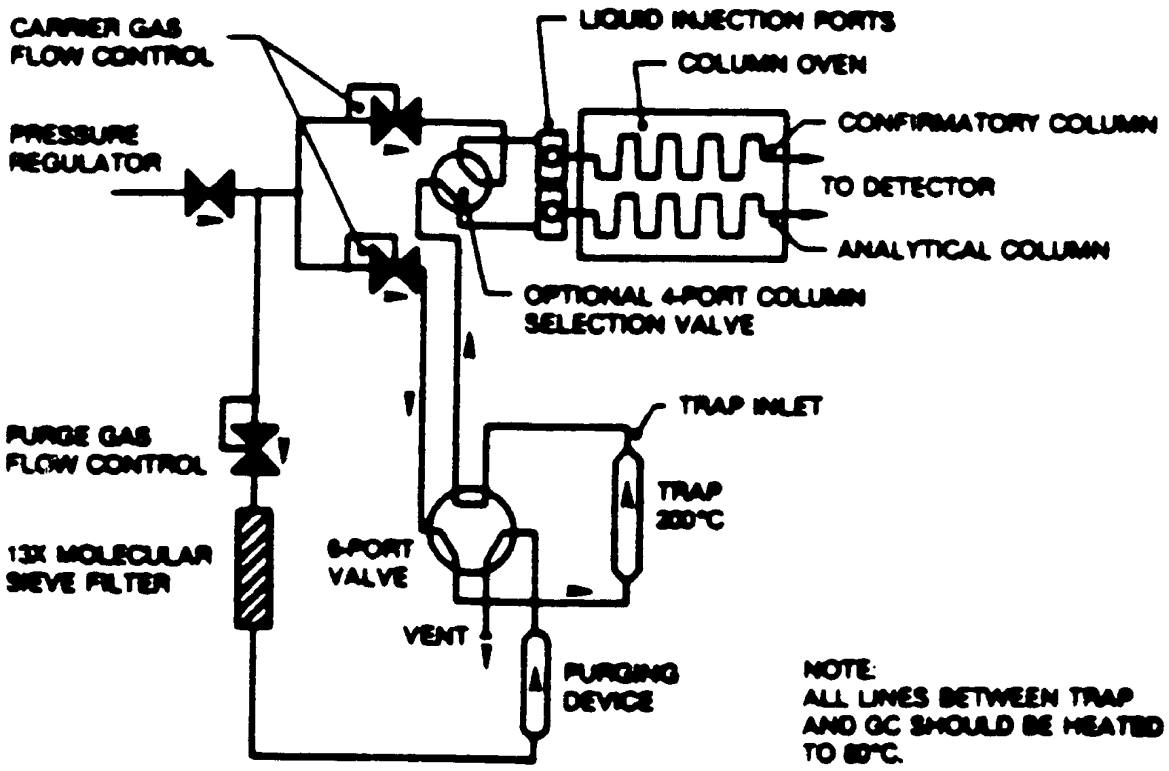
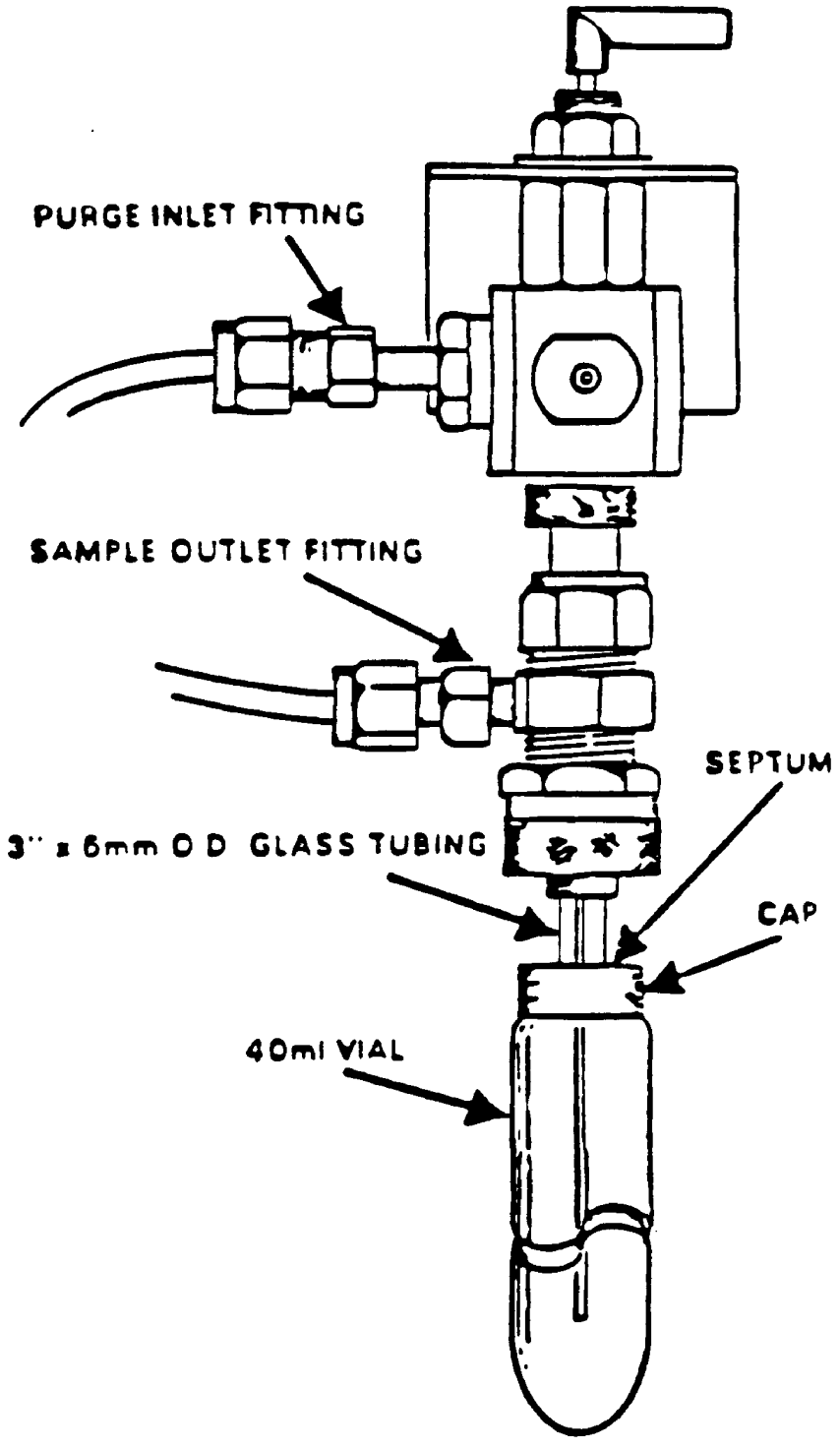
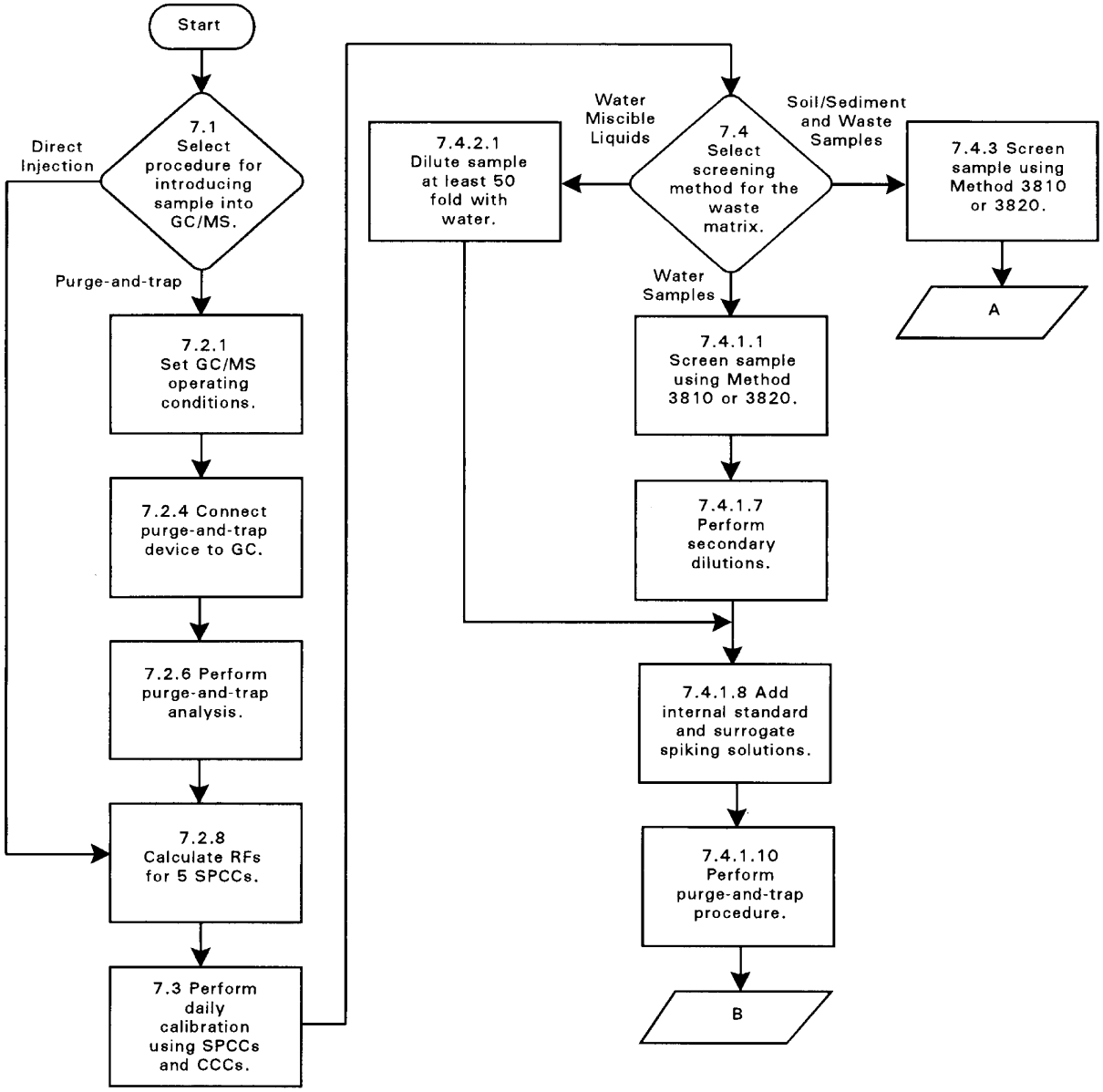
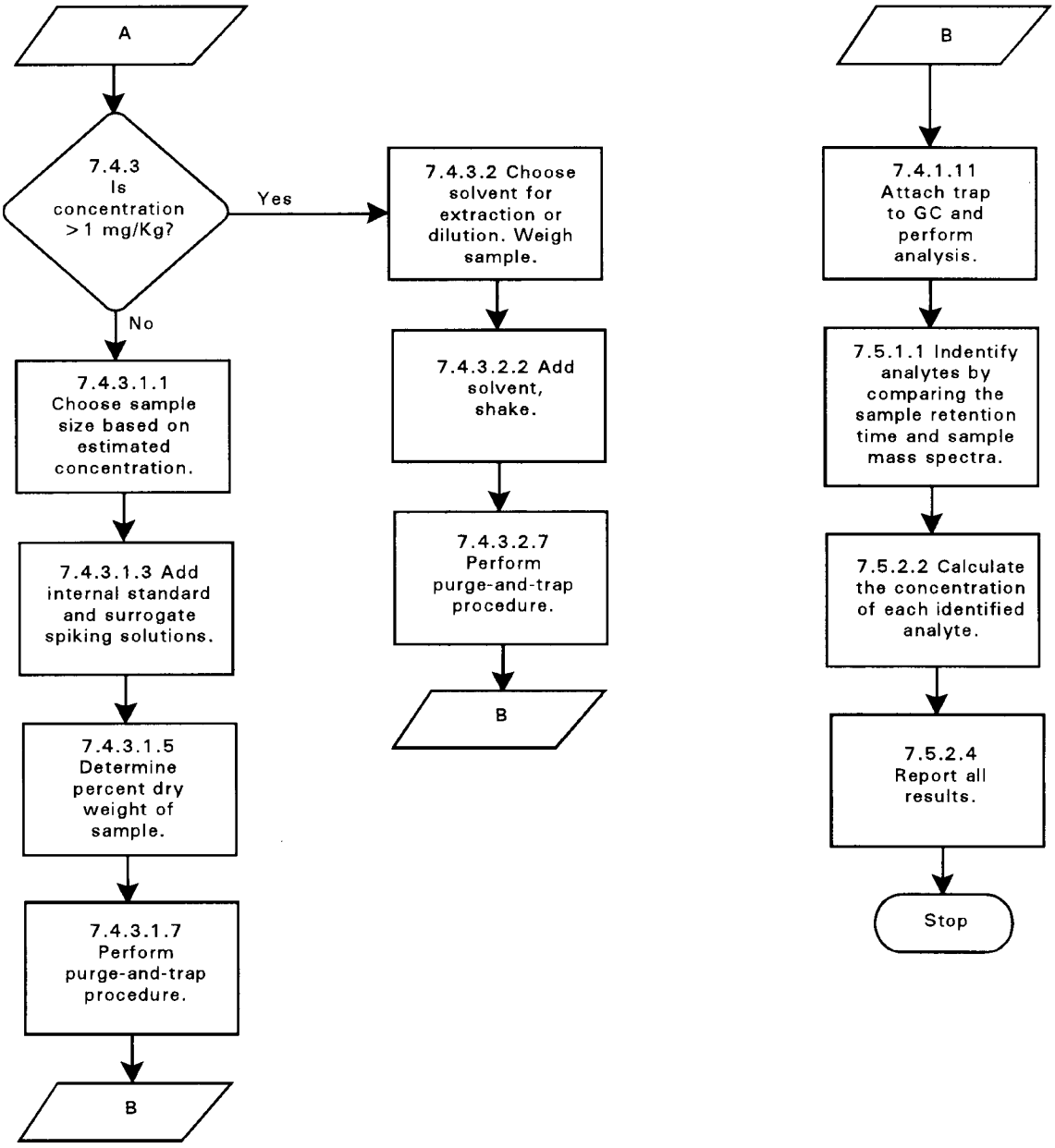


FIGURE 5.
LOW SOILS IMPINGER




Start
7.1 Select procedure for introducing sample into GC/MS.
Direct Injection
Purge-and-trap
7.2.1 Set GC/MS operating conditions.
7.2.4 Connect purge-and-trap device to GC.
7.2.6 Perform purge-and-trap analysis.
7.2.8 Calculate RFs for 5 SPCCs.
7.3 Perform daily calibration using SPCCs and CCCs.
7.4 Select screening method for the waste matrix.
Water Miscible Liquids
Soil/Sediment and Waste Samples
Water Samples
7.4.2.1 Dilute sample at least 50 fold with water.
7.4.3 Screen sample using Method 3810 or 3820.
A
7.4.1.1 Screen sample using Method 3810 or 3820.
7.4.1.7 Perform secondary dilutions.
7.4.1.8 Add internal standard and surrogate spiking solutions.
7.4.1.10 Perform purge-and-trap procedure.
B


A
7.4.3 Is concentration > 1 mg/Kg?
Yes
No
7.4.3.2 Choose solvent for extraction or dilution. Weigh sample.
7.4.3.2.2 Add solvent, shake.
7.4.3.2.7 Perform purge-and-trap procedure.
B
7.4.3.1.1 Choose sample size based on estimated concentration.
7.4.3.1.3 Add internal standard and surrogate spiking solutions.
7.4.3.1.5 Determine percent dry weight of sample.
7.4.3.1.7 Perform purge-and-trap procedure.
B
B
7.4.1.11 Attach trap to GC and perform analysis.
7.5.1.1 Indentify analytes by comparing the sample retention time and sample mass spectra.
7.5.2.2 Calculate the concentration of each identified analyte.
7.5.2.4 Report all results.
Stop