APPENDIX D-15
Analytical Procedure for Trichloroethylene: Method 8021B

AROMATIC AND HALOGENATED VOLATILES BY GAS CHROMATOGRAPHY USING PHOTOIONIZATION AND/OR ELECTROLYTIC CONDUCTIVITY DETECTORS

1.0 SCOPE AND APPLICATION

1.1 Method 8021 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:

Analyte	CAS No.[a]	Appropriate Technique			
		Purge-and -Trap	Direct Injection	Vac Distln	Head Space
Allyl chloride	107-05-1	b	b	nd	nd
Benzene	71-43-2	b	b	b	b
Benzyl chloride	100-44-7	pp	b	nd	nd
Bis(2-chloroisopropyl) ether	108-60-1	b	b	nd	nd
Bromoacetone	598-31-2	pp	b	nd	nd
Bromobenzene	108-86-1	b	nd	nd	nd
Bromochloromethane	74-97-5	b	b	nd	b
Bromodichloromethane	75-27-4	b	b	b	b
Bromoform	75-25-2	b	b	b	b
Bromomethane	74-83-9	b	b	b	b
Carbon tetrachloride	56-23-5	b	b	b	b
Chlorobenzene	108-90-7	b	b	b	b
Chlorodibromomethane	124-48-1	b	b	b	b
Chloroethane	75-00-3	b	b	b	b
2-Chloroethanol	107-07-03	pp	b	nd	nd
2-Chloroethyl vinyl ether	110-75-8	b	b	b	nd
Chloroform	67-66-3	b	b	b	b
Chloromethyl methyl ether	107-30-2	pp	pc	nd	nd
Chloroprene	126-99-8	b	nd	nd	nd
Chloromethane	74-87-3	b	b	b	b
4-Chlorotoluene	106-43-4	b	b	nd	nd
1,2-Dibromo-3-chloropropane	96-12-8	pp	b	nd	b
1,2-Dibromoethane	106-93-4	b	nd	nd	b
Dibromomethane	74-95-3	b	b	b	b
1,2-Dichlorobenzene	95-50-1	b	nd	nd	b
1,3-Dichlorobenzene	541-73-1	b	nd	nd	b
1,4-Dichlorobenzene	106-46-7	b	nd	nd	b
Dichlorodifluoromethane	75-71-8	b	b	b	b
1,1-Dichloroethane	75-34-3	b	b	b	b
1,2-Dichloroethane	107-06-2	b	b	b	b

Analyte	CAS No.[a]	Appropriate Technique			
		Purge-and -Trap	Direct Injection	Vac Distln	Head Space
1,1-Dichloroethene	75-35-4	b	b	b	b
cis-1,2-Dichloroethene	156-59-2	b	nd	nd	nd
trans-1,2-Dichloroethene	156-60-5	b	b	b	b
1,2-Dichloropropane	78-87-5	b	nd	b	b
1,3-Dichloro-2-propanol	96-23-1	pp	b	nd	nd
cis-1,3-dichloropropene	10061-01-5	b	b	b	nd
trans-1,3-dichloropropene	10061-02-6	b	b	b	nd
Epichlorhydrin	106-89-8	pp	b	nd	nd
Ethylbenzene	100-41-4	b	b	b	b
Hexachlorobutadiene	87-68-3	b	nd	nd	b
Methylene chloride	75-09-2	b	b	b	b
Naphthalene	91-20-3	b	nd	nd	b
Styrene	100-42-5	b	b	b	b
1,1,1,2-Tetrachloroethane	630-20-6	b	nd	nd	b
1,1,2,2-Tetrachloroethane	79-34-5	b	b	b	b
Tetrachloroethene	127-18-4	b	b	b	b
Toluene	108-88-3	b	b	b	b
1,2,4-Trichlorobenzene	120-82-1	b	nd	nd	b
1,1,1-Trichloroethane	71-55-6	b	b	b	b
1,1,2-Trichloroethane	79-00-5	b	b	b	b
Trichloroethene	79-01-6	b	b	b	b
Trichlorofluoromethane	75-69-4	b	b	b	b
1,2,3-Trichloropropane	96-18-4	b	b	b	b
Vinyl chloride	75-01-4	b	b	b	b
o-Xylene	95-47-6	b	b	b	b
m-Xylene	108-38-3	b	b	b	b
p-Xylene	106-42-3	b	b	b	b

[a] Chemical Abstract Service Registry Number.
b Adequate response by this technique.
i Inappropriate technique for this analyte.
nd Not Determined
pc Poor chromatographic behavior.
pp Poor purging efficiency resulting in high EQLs. May require heated purge (e.g., 40°C) or a more appropriate sample preparation technique, e.g., azeotropic distillation, equilibrium headspace or vacuum distillation, for good method performance.

1.2 Method detection limits (MDLs) are compound dependent and vary with purging efficiency and concentration. The MDLs for selected analytes are presented in Table 1. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts. Determination of some structural isomers (i.e., xylenes) may be hampered by coelution.

1.3 The estimated quantitation limit (EQL) of Method 8021A for an individual compound is approximately 1 µg/kg (wet weight) for soil/sediment samples, 0.1 mg/kg (wet weight) for wastes, and 1 µg/L for ground water (see Table 3). 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 for use by, or under the supervision of, analysts experienced in the use of gas chromatographs for measurement of purgeable organics at low µg/L concentrations and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst (References 4 and 6).

1.6 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

1.7 Other non-RCRA compounds which are amenable to analysis by Method 8021 include:

Analyte	CAS No.[a]
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
2-Chlorotoluene	95-49-8
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	594-20-7
1,1-Dichloropropene	563-58-6
Isopropylbenzene	98-82-8
p-Isopropyltoluene	99-87-6
n-Propylbenzene	103-65-1
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8

[a] Chemical Abstract Service Registry Number

2.0 SUMMARY OF METHOD

2.1 Method 8021 provides gas chromatographic conditions for the detection of halogenated and aromatic volatile organic compounds. Samples can be analyzed using direct injection (Method 3585 for oily matrices) or purge-and-trap (Method 5030/5035), headspace (Method 5021), or vacuum distillation (Method 5032). Groundwater samples may be analyzed using Method 5030, Method

5021, or Method 5032. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series. The GC system may also be set up to use a single detector when an analyst is looking for only halogenated compounds (HECD) or aromatic compounds (PID).

2.2 Tentative identifications are obtained by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Confirmatory information can be gained by comparing the relative response from the two detectors. Concentrations of the identified components are measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard.

3.0 INTERFERENCES

3.1 Refer to the appropriate 5000 Series method and Method 8000.

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

3.3 Sulfur dioxide is a potential interferant in the analysis for vinyl chloride.

4.0 APPARATUS AND MATERIALS

4.1 Sample introduction apparatus - Refer to Sec. 4.0 of the appropriate 5000 Series method for a listing of the equipment for each sample introduction technique.

4.2 Gas Chromatograph - capable of temperature programming; equipped with variable-constant differential flow controllers, subambient oven controller, photoionization and electrolytic conductivity detectors connected with a short piece of uncoated capillary tubing, 0.32-0.5 mm ID, and data system.

4.2.1 Primary Column - 60-m x 0.75 mm ID VOCOL wide-bore capillary column with 1.5-µm film thickness (Supelco) or equivalent.

4.2.2 Confirmation column - 60-m x 0.53 ID SPB-624 wide-bore capillary column with 3.0-µm film thickness (Supelco) has been suggested as one possible option. Other columns that will provide appropriate resolution of the target compoundsmay also be employed for confirmation, or confirmation may be performed using GC/MS.

4.2.3 Photoionization detector (PID) (Tracor Model 703, or equivalent).

4.2.4 Electrolytic conductivity detector (HECD) (Tracor Hall Model 700-A, or equivalent).

4.3 Syringes - 5 mL glass hypodermic with Luer-Lok tips.

4.4 Syringe valves - 2-way with Luer ends [polytetrafluoroethylene (PTFE) or Kel-F].

4.5 Microsyringe - 25-µL with a 2-in. x 0.006-in. ID, 22° bevel needle (Hamilton #702N or equivalent).

4.6 Microsyringes - 10-, 100-µL.

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

4.8 Bottles - 15-mL, PTFE-lined with screw-cap or crimp top.

4.9 Analytical balance - 0.0001 g.

4.10 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

5.0 REAGENTS

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

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

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

5.4 Vinyl chloride, (99.9% pure), CH_2=CHCl. Vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey, as well as from other sources. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

5.5 Stock standards - Stock solutions may either be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials of the toxicity should be prepared in a hood.

NOTE: If direct injection is used, the solvent system of standards must match that of the sample. It is not necessary to prepare high concentration aqueous mixed standards when using direct injection.

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

5.5.2 Add the assayed reference material, as described below.

5.5.2.1 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.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, 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 rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.5.3 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.

5.5.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap or crimp top. Store, with minimal headspace, at -10°C to -20°C and protect from light. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.5.5 Frequency of Standard Preparation

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

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

5.6 Prepare secondary dilution standards, using stock standard solutions, in methanol, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sec. 5.8 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.5.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

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

5.7.1 Initial calibration standards should be prepared at a minimum of five concentrations from the secondary dilution of stock standards (see Secs. 5.5 and 5.6) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve. See Sec. 7.0 of Method 8000 for guidance on initial calibration.

5.7.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.5 and 5.6) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.0 of Method 8000 for guidance on calibration verification.

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

5.7.4 The calibration standards should also contain the internal standards chosen for the analysis if internal standard calibration is used.

5.8 In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

NOTE: Prepare calibration solutions for use with direct injection analyses in water at the concentrations required.

5.8.1 Do not inject more than 20 µL of alcoholic standards into 100 mL of water.

5.8.2 Use a 25-µL Hamilton 702N micro syringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.8.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.8.4 Mix aqueous standards by inverting the flask three times.

5.8.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.8.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.8.7 Standards should be stored and handled according to guidance in Secs. 5.5.4 and 5.5.5.

5.9 Internal standards - It is recommended that a spiking solution containing fluorobenzene and 2-bromo-1-chloropropane in methanol be prepared, using the procedures described in Secs. 5.5

and 5.6. It is further recommended that the secondary dilution standard be prepared at a concentration of 5 mg/L of each internal standard compound. The addition of 10 µL of such a standard to 5.0 mL of sample calibration standard would be equivalent to 10 µg/L. External standard quantitation may also be used.

5.10 Surrogate standards -The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with two or more surrogate compounds. A combination of 1,4-dichlorobutane and bromochlorobenzene is recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Sec. 5.5, add a volume to give 750 µg of each surrogate to 45 mL of organic-free reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Sec. 5.9).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection (Method 3585 for oily matrices) or purge-and-trap (Methods 5030/5035), headspace (Method 5021), or by vacuum distillation (Method 5032). Methods 5030, 5021, or 5032 may be used directly on groundwater samples. Methods 5035, 5021, or 5032 may be used for low-concentration contaminated soils and sediments. For high-concentration soils or sediments (>200 µg/kg), methanolic extraction, as described in Method 5035, may be necessary prior to purge-and-trap analysis. For guidance on the dilution of oily waste samples for direct injection refer to Method 3585.

7.2 Gas chromatography conditions (Recommended)

7.2.1 Set up the gas chromatograph system so that the photoionization detector (PID) is in series with the electrolytic conductivity detector (HECD). It may be helpful to contact the manufacturer of the GC for guidance on the proper installation of dual detector systems.

NOTE: Use of the dual detector system is not a requirement of the method. The GC system may also be set up to use a single detector when the analyst is looking for just halogenated compounds (using the HECD) or for just aromatic compounds (using the PID).

7.2.2 Oven settings:

Carrier gas (Helium) Flow rate:	6 mL/min.
Temperature program	
Initial temperature:	10°C, hold for 8 minutes at
Program:	10°C to 180°C at 4°C/min
Final temperature:	180°C, hold until all expected compounds have eluted.

7.2.3 The carrier gas flow is augmented with an additional 24 mL of helium flow before entering the photoionization detector. This make-up gas is necessary to ensure optimal response from both detectors.

7.2.4 These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step. A Tracor Hall Model 700-A detector was used to gather the single laboratory accuracy and precision data presented in Table 2. The operating conditions used to collect these data are:

Reactor tube:	Nickel, 1/16 in OD
Reactor temperature:	810°C
Reactor base temperature:	250°C
Electrolyte:	100% n-Propyl alcohol
Electrolyte flow rate:	0.8 mL/min
Reaction gas:	Hydrogen at 40 mL/min
Carrier gas plus make-up gas:	Helium at 30 mL/min

7.2.5 A sample chromatogram obtained with this column is presented in Figure 1. This column was used to develop the method performance statements in Sec. 9.0. Estimated retention times and MDLs that can be achieved under these conditions are given in Table 1. Other columns or element specific detectors may be used if the requirements of Sec. 8.0 are met.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Sec. 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Methods 5030/5035 (purge-and-trap method) or the direct injection method (see Sec. 7.4.1.1), by Method 5021 (headspace) or by Method 5032 (vacuum distillation). If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g., aqueous process wastes) direct injection of the sample into the GC system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L), therefore, it is only permitted where 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 (bypassing the purge-and-trap device).

7.4.1.2 Refer to Method 3585 for guidance on the dilution and direct injection of waste oil samples.

7.4.1.3 Samples may be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature and acceptable method performance is demonstrated.

7.4.2 Follow Sec. 7.0 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, identification criteria, and calibration verification. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two detectors for a number of organic compounds analyzable using this method.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 Second column confirmation

A 60-m x 0.53 ID SPB-624 wide-bore capillary column with 3.0-µm film thickness (Supelco) has been suggested as one possible option for confirming compound identifications. Other columns that will provide appropriate resolution of the target compoundsmay also be employed for confirmation, or confirmation may be performed using GC/MS.

7.4.7 If the response for a peak is off-scale, i.e., beyond the calibration range of the standards, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

7.4.8 For target compounds that boil below 30°C at 1 atm pressure (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, and vinyl chloride), analysts may use a calibration verification acceptance criteria of within ± 20% difference from the initial calibration response.

8.0 QUALITY CONTROL

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

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and includes evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

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

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy,

and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

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

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

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

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

8.6 Calibration verification acceptance criteria - For target compounds that boil below 30°C at 1 atm pressure (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, and vinyl chloride), analysts may use a calibration verification acceptance criteria of within ± 20% difference from the initial calibration response.

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

9.0 METHOD PERFORMANCE

9.1 Method detection limits for these analytes have been calculated from data collected by spiking organic-free reagent water at 0.1 µg/L. These data are presented in Table 1.

9.2 This method was tested in a single laboratory using organic-free reagent water spiked at 10 µg/L. Single laboratory precision and accuracy data for each detector are presented for the method analytes in Table 2.

10.0 REFERENCES

1. "Volatile Organic Compounds in Water by Purge-and-Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series",

Method 502.2, Rev. 2.0 (1989); Methods for the Determination of Organic Compounds in Drinking Water", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, EPA/600/4-88/039, December, 1988.

2. "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method", Method 502.1; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH 45268, September, 1986.

3. "Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography", Method 503.1; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH, September, 1986.

4. Glaser, J.A., Forest, D.L., McKee, G.D., Quave, S.A., Budde, W.L. "Trace Analyses for Wastewaters", Environ. Sci. Technol., 1981, 15, 1426.

5. Bellar, T.A., Lichtenberg, J.J. "The Determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 45268.

TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS WITH PHOTOIONIZATION DETECTION (PID) AND HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

Analyte	PID Ret. Time[a] minute	HECD Ret. Time minute	PID MDL µg/L	HECD MDL µg/L
Dichlorodifluoromethane	-[b]	8.47		0.05
Chloromethane	-	9.47		0.03
Vinyl Chloride	9.88	9.93	0.02	0.04
Bromomethane	-	11.95		1.1
Chloroethane	-	12.37		0.1
Trichlorofluoromethane	-	13.49		0.03
1,1-Dichloroethene	16.14	16.18	ND[c]	0.07
Methylene Chloride	-	18.39		0.02
trans-1,2-Dichloroethene	19.30	19.33	0.05	0.06
1,1-Dichloroethane	-	20.99		0.07
2,2-Dichloropropane	-	22.88		0.05
cis-1,2-Dichloroethane	23.11	23.14	0.02	0.01
Chloroform	-	23.64		0.02
Bromochloromethane	-	24.16		0.01
1,1,1-Trichloroethane	-	24.77		0.03
1,1-Dichloropropene	25.21	25.24	0.02	0.02
Carbon Tetrachloride	-	25.47		0.01
Benzene	26.10	-	0.009	
1,2-Dichloroethane	-	26.27		0.03
Trichloroethene	27.99	28.02	0.02	0.01
1,2-Dichloropropane	-	29.66		0.006
Bromodichloromethane	-	29.43		0.02
Dibromomethane	-	29.59		2.2
Toluene	31.95	-	0.01	
1,1,2-Trichloroethane	-	33.21		ND
Tetrachloroethene	33.88	33.90	0.05	0.04
1,3-Dichloropropane	-	34.00		0.03
Dibromochloromethane	-	34.73		0.03
1,2-Dibromoethane	-	35.34		0.8
Chlorobenzene	36.56	36.59	0.003	0.01
Ethylbenzene	36.72	-	0.005	
1,1,1,2-Tetrachloroethane	-	36.80		0.005
m-Xylene	36.98	-	0.01	
p-Xylene	36.98	-	0.01	
o-Xylene	38.39	-	0.02	
Styrene	38.57	-	0.01	
Isopropylbenzene	39.58	-	0.05	
Bromoform	-	39.75		1.6
1,1,2,2-Tetrachloroethane	-	40.35		0.01
1,2,3-Trichloropropane	-	40.81		0.4

TABLE 1(cont.)

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS WITH PHOTOIONIZATION DETECTION (PID) AND HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

Analyte	PID Ret. Time[a] minute	HECD Ret. Time minute	PID MDL µg/L	HECD MDL µg/L
n-Propylbenzene	40.87	-	0.004	
Bromobenzene	40.99	41.03	0.006	0.03
1,3,5-Trimethylbenzene	41.41	-	0.004	
2-Chlorotoluene	41.41	41.45	ND	0.01
4-Chlorotoluene	41.60	41.63	0.02	0.01
tert-Butylbenzene	42.92	-	0.06	
1,2,4-Trimethylbenzene	42.71	-	0.05	
sec-Butylbenzene	43.31	-	0.02	
p-Isopropyltoluene	43.81	-	0.01	
1,3-Dichlorobenzene	44.08	44.11	0.02	0.02
1,4-Dichlorobenzene	44.43	44.47	0.007	0.01
n-Butylbenzene	45.20	-	0.02	
1,2-Dichlorobenzene	45.71	45.74	0.05	0.02
1,2-Dibromo-3-Chloropropane		48.57		3.0
1,2,4-Trichlorobenzene	51.43	51.46	0.02	0.03
Hexachlorobutadiene	51.92	51.96	0.06	0.02
Naphthalene	52.38	-	0.06	
1,2,3-Trichlorobenzene	53.34	53.37	ND	0.03
Internal Standards				
Fluorobenzene	26.84	-		
2-Bromo-1-chloropropane	-	33.08		

[a] Retention times determined on 60 m x 0.75 mm ID VOCOL capillary column. Program: Hold at 10°C for 8 minutes, then program at 4°C/min to 180°C, and hold until all expected compounds have eluted.

[b] Dash (-) indicates detector does not respond.

[c] ND = Not determined

TABLE 2

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN WATER[d]

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Standard Recovery,[a] %	Deviation of Recovery	Standard Recovery,[a] %	Deviation of Recovery
Benzene	99	1.2	-[b]	-
Bromobenzene	99	1.7	97	2.7
Bromochloromethane	-	-	96	3.0
Bromodichloromethane	-	-	97	2.9
Bromoform	-	-	106	5.5
Bromomethane	-	-	97	3.7
n-Butylbenzene	100	4.4	-	-
sec-Butylbenzene	97	2.6	-	-
tert-Butylbenzene	98	2.3	-	-
Carbon tetrachloride	-	-	92	3.3
Chlorobenzene	100	1.0	103	3.7
Chloroethane	-	-	96	3.8
Chloroform	-	-	98	2.5
Chloromethane	-	-	96	8.9
2-Chlorotoluene	ND[c]	ND	97	2.6
4-Chlorotoluene	101	1.0	97	3.1
1,2-Dibromo-3-chloropropane	-	-	86	9.9
Dibromochloromethane	-	-	102	3.3
1,2-Dibromoethane	-	-	97	2.7
Dibromomethane	-	-	109	7.4
1,2-Dichlorobenzene	102	2.1	100	1.5
1,3-Dichlorobenzene	104	1.7	106	4.3
1,4-Dichlorobenzene	103	2.2	98	2.3
Dichlorodifluoromethane	-	-	89	5.9
1,1-Dichloroethane	-	-	100	5.7
1,2-Dichloroethane	-	-	100	3.8
1,1-Dichloroethene	100	2.4	103	2.9
cis-1,2 Dichloroethene	ND	ND	105	3.5
trans-1,2-Dichloroethene	93	3.7	99	3.7
1,2-Dichloropropane	-	-	103	3.8
1,3-Dichloropropane	-	-	100	3.4
2,2-Dichloropropane	-	-	105	3.6
1,1-Dichloropropene	103	3.6	103	3.4
Ethylbenzene	101	1.4	-	-
Hexachlorobutadiene	99	9.5	98	8.3
Isopropylbenzene	98	0.9	-	-
p-Isopropyltoluene	98	2.4	-	-

TABLE 2 (cont.)

SINGLE LABORATORY ACCURACY AND PRECISION DATA
FOR VOLATILE ORGANIC COMPOUNDS IN WATER[d]

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Standard Recovery,[a] %	Deviation of Recovery	Standard Recovery,[a] %	Deviation of Recovery
Methylene chloride	-	-	97	2.8
Naphthalene	102	6.3	-	-
n-Propylbenzene	103	2.0	-	-
Styrene	104	1.4	-	-
1,1,1,2-Tetrachloroethane	-	-	99	2.3
1,1,2,2-Tetrachloroethane	-	-	99	6.8
Tetrachloroethene	101	1.8	97	2.4
Toluene	99	0.8	-	-
1,2,3-Trichlorobenzene	106	1.9	98	3.1
1,2,4-Trichlorobenzene	104	2.2	102	2.1
1,1,1-Trichloroethane	-	-	104	3.4
1,1,2-Trichloroethane	-	-	109	6.2
Trichloroethene	100	0.78	96	3.5
Trichlorofluoromethane	-	-	96	3.4
1,2,3-Trichloropropane	-	-	99	2.3
1,2,4-Trimethylbenzene	99	1.2	-	-
1,3,5-Trimethylbenzene	101	1.4	-	-
Vinyl chloride	109	5.4	95	5.6
o-Xylene	99	0.8	-	
m-Xylene	100	1.4	-	-
p-Xylene	99	0.9	-	-

[a] Recoveries and standard deviations were determined from seven samples and spiked at 10 µg/L of each analyte. Recoveries were determined by internal standard method using a purge-and-trap. Internal standards were: Fluorobenzene for PID, 2-Bromo-1-chloropropane for HECD.

[b] Detector does not respond

[c] ND = Not determined

[d] This method was tested in a single laboratory using water spiked at 10 µg/L (see Reference 8).

TABLE 3

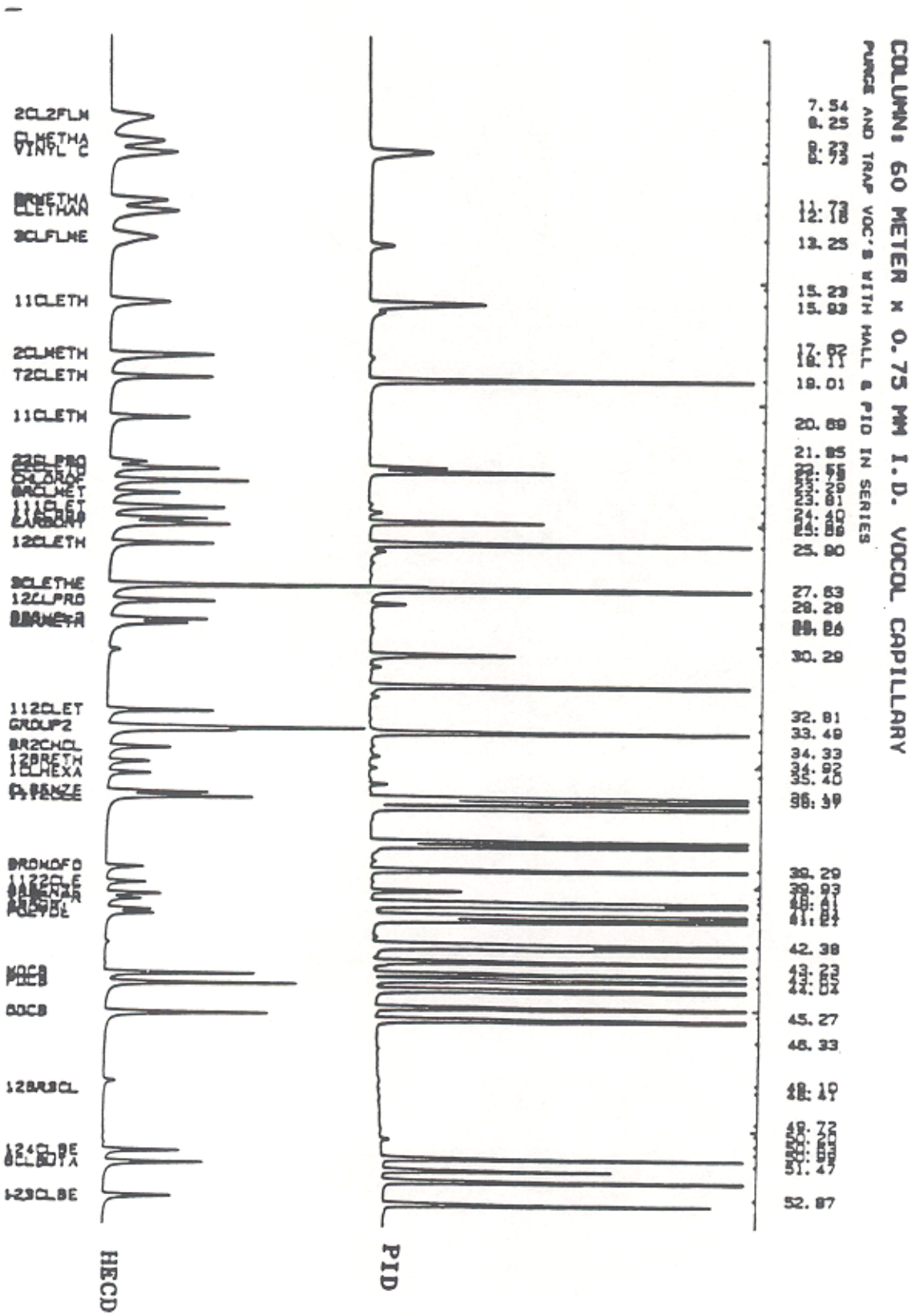
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES[a]

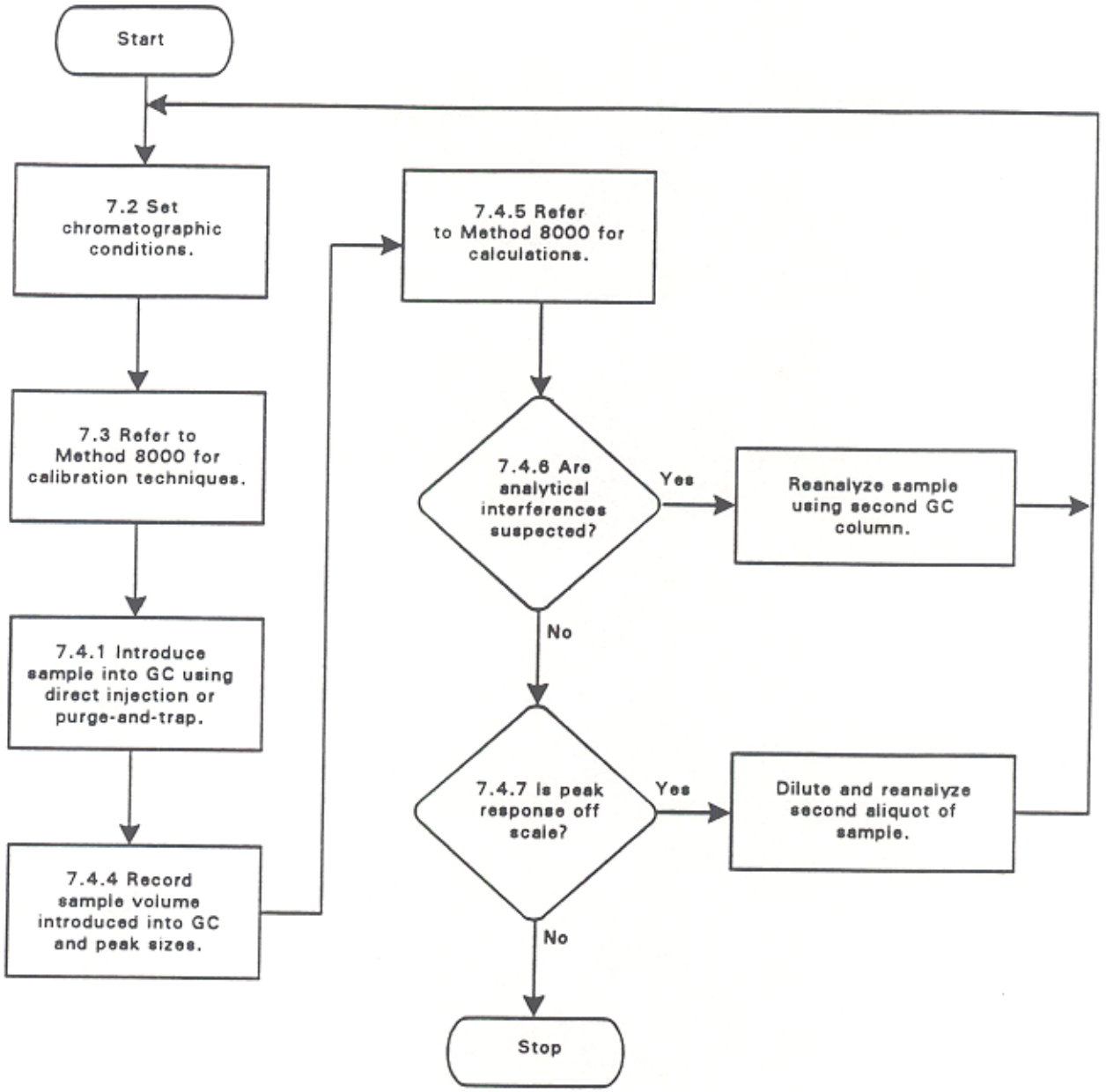
Matrix	Factor[b]
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

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

[b] EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS




Start
7.2 Set chromatographic conditions.
7.3 Refer to Method 8000 for calibration techniques.
7.4.1 Introduce sample into GC using direct injection or purge-and-trap.
7.4.4 Record sample volume introduced into GC and peak sizes.
7.4.5 Refer to Method 8000 for calculations.
7.4.6 Are analytical interferences suspected?
Yes
Reanalyze sample using second GC column.
No
7.4.7 Is peak response off scale?
Yes
Dilute and reanalyze second aliquot of sample.
No
Stop