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Method 624.1 – Purgeables by GC/MS

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METHOD 624.1 – PURGEABLES BY GC/MS

1. Scope and Application

1.1 This method is for determination of purgeable organic pollutants in industrial discharges and other environmental samples by gas chromatography combined with mass spectrometry (GC/MS), as provided under 40 CFR 136.1. This revision is based on previous protocols (References 1 - 3), on the revision promulgated October 26, 1984 (49 FR 43234), and on an interlaboratory method validation study (Reference 4). Although this method was validated through an interlaboratory study conducted more than 29 years ago, the fundamental chemistry principles used in this method remain sound and continue to apply.

1.2 The analytes that may be qualitatively and quantitatively determined using this method and their CAS Registry numbers are listed in Table 1. The method may be extended to determine the analytes listed in Table 2; however, poor purging efficiency or gas chromatography of some of these analytes may make quantitative determination difficult. For example, an elevated temperature may be required to purge some analytes from water. If an elevated temperature is used, calibration and all quality control (QC) tests must be performed at the elevated temperature. EPA encourages the use of this method to determine additional compounds amenable to purge-and-trap GC/MS.

1.3 The large number of analytes in Tables 1 and 2 of this method makes testing difficult if all analytes are determined simultaneously. Therefore, it is necessary to determine and perform QC tests for "analytes of interest" only. Analytes of interest are those required to be determined by a regulatory/control authority or in a permit, or by a client. If a list of analytes is not specified, the analytes in Table 1 must be determined, at a minimum, and QC testing must be performed for these analytes. The analytes in Table 1 and some of the analytes in Table 2 have been identified as Toxic Pollutants (40 CFR 401.15), expanded to a list of Priority Pollutants (40 CFR 423, appendix A).

1.4 Method detection limits (MDLs; Reference 5) for the analytes in Table 1 are listed in that table. These MDLs were determined in reagent water (Reference 6). Advances in analytical technology, particularly the use of capillary (open-tubular) columns, allowed laboratories to routinely achieve MDLs for the analytes in this method that are 2 - 10 times lower than those in the version promulgated in 1984 (40 FR 43234). The MDL for a specific wastewater may differ from those listed, depending on the nature of interferences in the sample matrix.

1.4.1 EPA has promulgated this method at 40 CFR Part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described in Section 13.2 are focused on such monitoring needs and may not be relevant to other uses of the method.

1.4.2 This method includes "reporting limits" based on EPA's "minimum level" (ML) concept (see the glossary in Section 20). Table 1 contains MDL values and ML values for many of the analytes. The MDL for an analyte in a specific wastewater may differ from that listed in Table 1, depending upon the nature of interferences in the sample matrix.

1.5 This method is performance-based. It may be modified to improve performance (e.g., to overcome interferences or improve the accuracy of results) provided all performance requirements are met.

1.5.1 Examples of allowed method modifications are described at 40 CFR 136.6. Other examples of allowed modifications specific to this method are described in Section 8.1.2.

1.5.2 Any modification beyond those expressly allowed at 40 CFR 136.6 or in Section 8.1.2 of this method shall be considered a major modification that is subject to application and approval of an alternate test procedure under 40 CFR 136.4 and 136.5.

1.5.3 For regulatory compliance, any modification must be demonstrated to produce results equivalent or superior to results produced by this method when applied to relevant wastewaters (Section 8.3).

1.6 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge-and-trap system and a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure in Section 8.2.

1.7 Terms and units of measure used in this method are given in the glossary at the end of the method.

2. Summary of Method

2.1 A gas is bubbled through a measured volume of water in a specially-designed purging chamber (Figure 1). The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped (Figure 2). After purging is completed, the trap is heated and backflushed with the gas to desorb the purgeables onto a gas chromatographic column (Figures 3 and 4). The column is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

2.2 Different sample sizes in the range of 5 - 25 mL are allowed in order to meet differing sensitivity requirements. Calibration and QC samples must have the same volume as field samples.

3. Interferences

3.1 Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory 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 analyzing blanks as described in Section 8.5. Fluoropolymer tubing, fittings, and thread sealant should be used to avoid contamination.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. Protect samples from sources of volatiles during collection, shipment, and storage. A reagent water field blank carried through sampling and analysis can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are analyzed sequentially. To reduce the potential for carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a blank to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required. Screening samples at high dilution may prevent introduction of contaminants into the system.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDSs, OSHA, 29 CFR 1910.1200[g]) should also be made available to all personnel involved in sample handling and chemical analysis. Additional references to laboratory safety are available and have been identified (References 7 - 9) for the information of the analyst.

4.2. The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene; carbon tetrachloride; chloroform; 1,4-dichlorobenzene; 1,2-dichloroethane; 1,2-dichloropropane; methylene chloride; tetrachloroethylene; trichloroethylene; and vinyl chloride. Primary standards of these toxic compounds should be prepared in a chemical fume hood, and a NIOSH/MESA approved toxic gas respirator should be worn when handling high concentrations of these compounds.

4.3 This method allows the use of hydrogen as a carrier gas in place of helium (Section 5.3.1.2). The laboratory should take the necessary precautions in dealing with hydrogen, and should limit hydrogen flow at the source to prevent buildup of an explosive mixture of hydrogen in air.

5. Apparatus and Materials

Note: *Brand names, suppliers, and part numbers are cited for illustration purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here. Demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory. Suppliers for equipment and materials in this method may be found through an on-line search.*

5.1 Sampling equipment for discrete sampling.

5.1.1 Vial – 25 or 40 mL capacity, or larger, with screw cap with a hole in the center (Pierce #13075 or equivalent). Unless pre-cleaned, detergent wash, rinse with tap and reagent water, and dry at 105°C before use.

5.1.2 Septum – Fluoropolymer-faced silicone (Pierce #12722 or equivalent). Unless pre-cleaned, detergent wash, rinse with tap and reagent water, and dry at 105 ± 5°C for one hour before use.

5.2 Purge-and-trap system – The purge-and-trap system consists of three separate pieces of equipment: A purging device, trap, and desorber. Several complete systems are commercially available. Any system that meets the performance requirements in this method may be used.

5.2.1 The purging device should accept 5- to 25-mL samples with a water column at least 3 cm deep. The purge gas must pass though the water column as finely divided bubbles. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging device illustrated in Figure 1 meets these design criteria. Purge devices of a different volume may be used so long as the performance requirements in this method are met.

5.2.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap should be packed to contain the following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 6.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 6.3.1), and 8 cm of silica gel (Section 6.3.3). The minimum specifications for the trap are illustrated in Figure 2. A trap with different dimensions and packing materials is acceptable so long as the performance requirements in this method are met.

5.2.3 The desorber should be capable of rapidly heating the trap to the temperature necessary to desorb the analytes of interest, and of maintaining this temperature during desorption. The trap should not be heated higher than the maximum temperature recommended by the manufacturer. The desorber illustrated in Figure 2 meets these design criteria.

5.2.4 The purge-and-trap system may be assembled as a separate unit or coupled to a gas chromatograph as illustrated in Figures 3 and 4.

5.3 GC/MS system

5.3.1 Gas chromatograph (GC) – An analytical system complete with a temperature programmable gas chromatograph and all required accessories, including syringes and analytical columns. Autosamplers designed for purge-and-trap analysis of volatiles also may be used.

5.3.1.1 Injection port – Volatiles interface, split, splitless, temperature programmable split/splitless (PTV), large volume, on-column, backflushed, or other.

5.3.1.2 Carrier gas – Data in the tables in this method were obtained using helium carrier gas. If another carrier gas is used, analytical conditions may need to be adjusted for optimum performance, and calibration and all QC tests must be performed with the alternate carrier gas. See Section 4.3 for precautions regarding the use of hydrogen as a carrier gas.

5.3.2 GC column – See the footnote to Table 3. Other columns or column systems may be used provided all requirements in this method are met.

5.3.3 Mass spectrometer – Capable of repetitively scanning from 35-260 Daltons (amu) every 2 seconds or less, utilizing a 70 eV (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all criteria in Table 4 when 50 ng or less of 4-bromofluorobenzene (BFB) is injected through the GC inlet. If acrolein, acrylonitrile, chloromethane, and vinyl chloride are to be determined, it may be necessary to scan from below 25 Daltons to measure the peaks in the 26 - 35 Dalton range for reliable identification.

5.3.4 GC/MS interface – Any GC to MS interface that meets all performance requirements in this method may be used.

5.3.5 Data system – A computer system must be interfaced to the mass spectrometer that allows continuous acquisition and storage of mass spectra throughout the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z's (masses) and plotting m/z 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 abundance at any EICP between specified time or scan number limits.

5.4 Syringes – Graduated, 5 - 25 mL, glass hypodermic with Luerlok tip, compatible with the purging device.

5.5 Micro syringes – Graduated, 25 - 1000 µL, with 0.006 in. ID needle.

5.6 Syringe valve – Two-way, with Luer ends

5.7 Syringe – 5 mL, gas-tight with shut-off valve.

5.8 Bottle – 15 mL, screw-cap, with Teflon cap liner.

5.9 Balance – Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water – Reagent water is defined as water in which the analytes of interest and interfering compounds are not detected at the MDLs of the analytes of interest. It may be generated by passing deionized water, distilled water, or tap water through a carbon bed, passing the water through a water purifier, or heating the water to between 90 and 100°C while bubbling contaminant free gas through it for approximately 1 hour. While still hot, transfer the water to screw-cap bottles and seal with a fluoropolymer-lined cap.

6.2 Sodium thiosulfate – (ACS) Granular.

6.3 Trap materials

6.3.1 2,6-Diphenylene oxide polymer – Tenax, 60/80 mesh, chromatographic grade, or equivalent.

6.3.2 Methyl silicone packing – 3% OV-1 on Chromosorb-W, 60/80 mesh, or equivalent.

6.3.3 Silica gel – 35/60 mesh, Davison, Grade-15 or equivalent.

Other trap materials are acceptable if performance requirements in this method are met.

6.4 Methanol – Demonstrated to be free from the target analytes and potentially interfering compounds.

6.5 Stock standard solutions – Stock standard solutions may be prepared from pure materials, or purchased as certified solutions. Traceability must be to the National Institute of Standards and Technology (NIST) or other national standard. Stock solution concentrations alternate to those below may be used. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because some of the compounds in this method are known to be toxic, primary dilutions should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations of neat materials are handled. The following procedure may be used to prepare standards from neat materials:

6.5.1 Place about 9.8 mL of methanol in a 10-mL 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 0.1 mg.

6.5.2 Add the assayed reference material.

6.5.2.1 Liquids – Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask. Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight.

6.5.2.2 Gases – To prepare standards for any of compounds that boil below 30°C, fill a 5-mL valved gas-tight syringe with reference standard vapor to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the vapor above the surface of the liquid (the vapor will rapidly dissolve in the methanol). Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight.

6.5.3 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.

6.5.4 Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. All standards should be replaced after one month, or sooner if the concentration of an analyte changes by more than 10 percent.

Note: *2-Chloroethylvinyl ether has been shown to be stable for as long as one month if prepared as a separate standard, and the other analytes have been shown to be stable for as long as 2 months if stored at less than -10°C with minimal headspace in sealed, miniature inert-valved vials.*

6.6 Secondary dilution standards – Using stock solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed. Secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 7.3.2 will bracket the working range of the analytical system.

6.7 Surrogate standard spiking solution – Select a minimum of three surrogate compounds from Table 5. The surrogates selected should match the purging characteristics of the analytes of interest as closely as possible. Prepare a stock standard solution for each surrogate in methanol as described in Section 6.5, and prepare a solution for spiking the surrogates into all blanks, LCSs, and MS/MSDs. The spiking solution should be prepared such that spiking a small volume will result in surrogate concentrations near the mid-point of the calibration range. For example, adding 10 µL of a spiking solution containing the surrogates at a concentration of 15 µg/mL in methanol to a 5-mL aliquot of water would result in a concentration of 30 µg/L for each surrogate. Other surrogate concentrations may be used.

6.8 BFB standard – Prepare a solution of BFB in methanol as described in Sections 6.5 and 6.6. The solution should be prepared such that an injection or purging from water will result in introduction of ≤ 50 ng into the GC. BFB may be included in a mixture with the internal standards and/or surrogates.

6.9 Quality control check sample concentrate – See Section 8.2.1.

6.10 Storage – When not being used, store standard solutions (Sections 6.5 - 6.9) at -10 to -20°C, protected from light, in fluoropolymer-sealed glass containers with minimal headspace.

7. Calibration

7.1 Assemble a purge-and-trap system that meets the specifications in Section 5.2. Prior to first use, condition the trap overnight at 180°C by backflushing with gas at a flow rate of at least 20 mL/min. Condition the trap daily prior to use.

7.2 Connect the purge-and-trap system to the gas chromatograph. The gas chromatograph should be operated using temperature and flow rate conditions equivalent to those given in the footnotes to Table 3. Alternative temperature and flow rate conditions may be used provided that performance requirements in this method are met.

7.3 Internal standard calibration

7.3.1 Internal standards

7.3.1.1 Select three or more internal standards similar in chromatographic behavior to the compounds of interest. Suggested internal standards are listed in Table 5. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are found at the base peak, use one of the next two most intense m/z's for quantitation. Demonstrate that measurement of the internal standards are not affected by method or matrix interferences.

7.3.1.2 To assure accurate analyte identification, particularly when selected ion monitoring (SIM) is used, it may be advantageous to include more internal standards than those suggested in Section 7.3.1.1. An analyte will be located most accurately if its retention time relative to an internal standard is in the range of 0.8 to 1.2.

7.3.1.3 Prepare a stock standard solution for each internal standard surrogate in methanol as described in Section 6.5, and prepare a solution for spiking the internal standards into all blanks, LCSs, and MS/MSDs. The spiking solution should be prepared such that spiking a small volume will result in internal standard concentrations near the mid-point of the calibration range. For example, adding 10 µL of a spiking solution containing the internal standards at a concentration of 15 µg/mL in methanol to a 5-mL aliquot of water would result in a concentration of 30 µg/L for each internal standard. Other concentrations may be used. The internal standard solution and the surrogate standard spiking solution (Section 6.7) may be combined, if desired. Store the solution at ≤6°C in fluoropolymer-sealed glass containers with a minimum of headspace. Replace the solution after 1 month, or more frequently if comparison with QC standards indicates a problem.

7.3.2 Calibration

7.3.2.1 Calibration standards

7.3.2.1.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding appropriate volumes of one or more stock standards to a fixed volume (e.g., 40 mL) of reagent water in volumetric glassware. Fewer levels may be necessary for some analytes based on the sensitivity of the MS. The concentration of the lowest calibration standard for an analyte should

be at or near the ML value in Table 1 for an analyte listed in that table. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML value~~s~~ listed in Table 1 for those analytes which list ML values. Alternatively, the laboratory may establish the ML for each analyte based on the concentration of the lowest calibration standard in a series of standards obtained from a commercial vendor, again, provided that the ML values do~~es~~ not exceed the MLs in Table 1, and provided that the resulting calibration meets the acceptance criteria in Section 7.3.4, based on the RSD, RSE, or R^2.

The concentrations of the higher standards should correspond to the expected range of concentrations found in real samples, or should define the working range of the GC/MS system for full-scan and/or SIM operation, as appropriate. A minimum of six concentration levels is required for a second order, non-linear (e.g., quadratic; $ax^2 + bx + c$) calibration. Calibrations higher than second order are not allowed.

7.3.2.1.2 To each calibration standard or standard mixture, add a known constant volume of the internal standard spiking solution (Section 7.3.1.3) and surrogate standard spiking solution (Section 6.7) or the combined internal standard solution and surrogate spiking solution (Section 7.3.1.3). Aqueous standards may be stored up to 24 hours, if held in sealed vials with zero headspace as described in Section 9.1. If not so stored, they must be discarded after one hour.

7.3.2.2 Prior to analysis of the calibration standards, analyze the BFB standard (Section 6.8) and adjust the scan rate of the MS to produce a minimum of 5 mass spectra across the BFB GC peak, but do not exceed 2 seconds per scan. Adjust instrument conditions until the BFB criteria in Table 4 are met.

Note: *The BFB spectrum may be evaluated by summing the intensities of the m/z's across the GC peak, subtracting the background at each m/z in a region of the chromatogram within 20 scans of but not including any part of the BFB peak. The BFB spectrum may also be evaluated by fitting a Gaussian to each m/z and using the intensity at the maximum for each Gaussian, or by integrating the area at each m/z and using the integrated areas. Other means may be used for evaluation of the BFB spectrum so long as the spectrum is not distorted to meet the criteria in Table 4.*

7.3.2.3 Analyze the mid-point standard and enter or review the retention time, relative retention time, mass spectrum, and quantitation m/z in the data system for each analyte of interest, surrogate, and internal standard. If additional analytes (Table 2) are to be quantified, include these analytes in the standard. The mass spectrum for each analyte must be comprised of a minimum of 2 m/z's; 3 to 5 m/z's assure more reliable analyte identification. Suggested quantitation m/z's are shown in Table 6 as the primary m/z. For analytes in Table 6 that do not have a secondary m/z, acquire a mass spectrum and enter one or more secondary m/z's for more reliable identification. If an interference occurs at the primary m/z, use one of the secondary m/z's or an alternate m/z. A single m/z only is required for quantitation.

7.3.2.4 For SIM operation, determine the analytes in each descriptor, the quantitation m/z for each analyte (the quantitation m/z can be the same as for full-scan operation; Section 7.3.2.3), the dwell time on each m/z for each analyte, and the beginning and ending retention time for each descriptor. Analyze the verification standard in scan mode to verify m/z's and establish retention times for the analytes. There must be a minimum of two m/z's for each analyte to assure analyte identification. To maintain sensitivity, the number of m/z's in a descriptor should be limited. For example, for a descriptor with 10 m/z's and a chromatographic peak width of 5 sec, a dwell time of 100 ms at each m/z would result in a scan time of 1 second and provide 5 scans across the GC peak. The quantitation m/z will usually be the most intense peak in the mass spectrum. The quantitation m/z and dwell time may be optimized for each analyte. However, if a GC peak spans two (or more) descriptors, the dwell time and cycle time (scans/sec) should be set to the same value in both segments in order to maintain equivalent response. The acquisition table used for SIM must take into account the mass defect (usually less than 0.2 Dalton) that can occur at each m/z monitored.

7.3.2.5 For combined scan and SIM operation, set up the scan segments and descriptors to meet requirements in Sections 7.3.2.2 - 7.3.2.4.

7.3.3 Analyze each calibration standard according to Section 10 and tabulate the area at the quantitation m/z against concentration for each analyte of interest, surrogate, and internal standard. Calculate the response factor (RF) for each compound at each concentration using Equation 1.

Equation 1

$$RF = \frac{(A_s x C_{is})}{(A_{is} x C_s)}$$

where:

A_s = Area of the characteristic m/z for the analyte to be measured.
A_{is} = Area of the characteristic m/z for the internal standard.
C_{is} = Concentration of the internal standard (µg/L).
C_s = Concentration of the analyte to be measured (µg/L).

7.3.4 Calculate the mean (average) and relative standard deviation (RSD) of the response factors. If the RSD is less than 35%, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to fit a linear or quadratic regression of response ratios, A_s/A_{is}, vs. concentration ratios C_s/C_{is}. If used, the regression must be weighted inversely proportional to concentration (1/C). The coefficient of determination (R^2) of the weighted regression must be greater than 0.920 (this value roughly corresponds to the RSD limit of 35%). Alternatively, the relative standard error (Reference 10) may be used as an acceptance criterion. As with the RSD, the RSE must be less than 35%. If an RSE less than 35% cannot be achieved for a quadratic regression, system performance is unacceptable, and the system must be adjusted and re-calibrated.

Note: *Using capillary columns and current instrumentation, it is quite likely that a laboratory can calibrate the target analytes in this method and achieve a linearity metric (either RSD or RSE) well below 35%. Therefore, laboratories are permitted to use more stringent acceptance criteria for calibration than described here, for example, to harmonize their application of this method with those from other sources.*

7.4 Calibration verification – Because the analytical system is calibrated by purge of the analytes from water, calibration verification is performed using the laboratory control sample (LCS). See Section 8.4 for requirements for calibration verification using the LCS, and the Glossary for further definition.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analysis of spiked samples and blanks to evaluate and document data quality (40 CFR 136.7). The laboratory must maintain records to document the quality of data generated. Results of ongoing performance tests are compared with established QC acceptance criteria to determine if the results of analyses meet performance requirements of this method. When results of spiked samples do not meet the QC acceptance criteria in this method, a quality control check sample (laboratory control sample; LCS) must be analyzed to confirm that the measurements were performed in an in-control mode of operation. A laboratory may develop its own performance criteria (as QC acceptance criteria), provided such criteria are as or more restrictive than the criteria in this method.

8.1.1 The laboratory must make an initial demonstration of capability (DOC) to generate acceptable precision and recovery with this method. This demonstration is detailed in Section 8.2.

8.1.2 In recognition of advances that are occurring in analytical technology, and to overcome matrix interferences, the laboratory is permitted certain options (Section 1.5 and 40 CFR 136.6(b)) to improve separations or lower the costs of measurements. These options may include an alternate purge-and-trap device, and changes in both column and type of mass spectrometer (see 40 CFR 136.6(b)(4)(xvi)). Alternate determinative techniques, such as substitution of spectroscopic or immunoassay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than GC/MS is used, that technique must have a specificity equal to or greater than the specificity of GC/MS for the analytes of interest. The laboratory is also encouraged to participate in inter-comparison and performance evaluation studies (see Section 8.9).

8.1.2.1 Each time a modification is made to this method, the laboratory is required to repeat the procedure in Section 8.2. If the detection limit of the method will be affected by the change, the laboratory must demonstrate that the MDLs (40 CFR Part 136, Appendix B) are lower than one-third the regulatory compliance limit, or at least as low as the MDLs listed in this method, whichever are greater. If calibration will be affected by the change, the instrument must be recalibrated per Section 7. Once the modification is demonstrated to produce results equivalent or superior to results produced by this method, that modification may be used routinely thereafter, so long as the other requirements in this method are met (e.g., matrix spike/matrix spike duplicate recovery and relative percent difference).

8.1.2.1.1 If a modification is to be applied to a specific discharge, the laboratory must prepare and analyze matrix spike/matrix spike duplicate (MS/MSD) samples (Section 8.3) and LCS samples (Section 8.4). The laboratory must include internal standards and surrogates (Section 8.7) in each of the samples. The MS/MSD and LCS samples must be fortified with the analytes of interest (Section

1.3.) If the modification is for nationwide use, MS/MSD samples must be prepared from a minimum of nine different discharges (See Section 8.1.2.1.2), and all QC acceptance criteria in this method must be met. This evaluation only needs to be performed once, other than for the routine QC required by this method (for example it could be performed by the vendor of the alternate materials) but any laboratory using that specific material must have the results of the study available. This includes a full data package with the raw data that will allow an independent reviewer to verify each determination and calculation performed by the laboratory (see Section 8.1.2.2.5, items a-l).

8.1.2.1.2 Sample matrices on which MS/MSD tests must be performed for nationwide use of an allowed modification:

(a) Effluent from a POTW
(b) ASTM D5905 *Standard Specification for Substitute Wastewater*
(c) Sewage sludge, if sewage sludge will be in the permit
(d) ASTM D1141 *Standard Specification for Substitute Ocean Water*, if ocean water will be in the permit
(e) Untreated and treated wastewaters up to a total of nine matrix types (see http:water.epa.gov/scitech/wastetech/guide/industry.cfm) for a list of industrial categories with existing effluent guidelines).

At least one of the above wastewater matrix types must have at least one of the following characteristics:
(i) Total suspended solids greater than 40 mg/L
(ii) Total dissolved solids greater than 100 mg/L
(iii) Oil and grease greater than 20 mg/L
(iv) NaCl greater than 120 mg/L
(v) $CaCO_3$ greater than 140 mg/L

The interim acceptance criteria for MS, MSD recoveries that do not have recovery limits specified in Table 7, and recoveries for surrogates that do not have recovery limits specified in Table 7, must be no wider than 60 -140 %, and the relative percent difference (RPD) of the concentrations in the MS and MSD that do not have RPD limits specified in Table 7 must be less than 30%. Alternatively, the laboratory may use the laboratory's in-house limits if they are tighter.

(f) A proficiency testing (PT) sample from a recognized provider, in addition to tests of the nine matrices (Section 8.1.2.1.1).

8.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

8.1.2.2.1 The names, titles, street addresses, telephone numbers, and e-mail addresses of the analyst(s) that performed the analyses and modification, and of the quality control officer that witnessed and will verify the analyses and modifications.

8.1.2.2.2 A list of analytes, by name and CAS Registry Number.

8.1.2.2.3 A narrative stating reason(s) for the modifications.

8.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

a) Calibration (Section 7).
b) Calibration verification/LCS (Section 8.4).
c) Initial demonstration of capability (Section 8.2).
d) Analysis of blanks (Section 8.5).
e) Matrix spike/matrix spike duplicate analysis (Section 8.3).
f) Laboratory control sample analysis (Section 8.4).

8.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

a) Sample numbers and other identifiers.
b) Analysis dates and times.
c) Analysis sequence/run chronology.
d) Sample volume (Section 10).
e) Sample dilution (Section 13.2).
f) Instrument and operating conditions.
g) Column (dimensions, material, etc).
h) Operating conditions (temperature program, flow rate, etc).
i) Detector (type, operating conditions, etc).
j) Chromatograms, mass spectra, and other recordings of raw data.
k) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.
l) A written Standard Operating Procedure (SOP).

8.1.2.2.6 The individual laboratory wishing to use a given modification must perform the start-up tests in Section 8.1.2 (e.g., DOC, MDL), with the modification as an integral part of this method prior to applying the modification to specific discharges. Results of the DOC must meet the QC acceptance criteria in Table 7 for the analytes of interest (Section 1.3), and the MDLs must be equal to or lower than the MDLs in Table3 for the analytes of interest

8.1.3 Before analyzing samples, the laboratory must analyze a blank to demonstrate that interferences from the analytical system, labware, and reagents are under control. Each time a batch of samples is analyzed or reagents are changed, a blank must be analyzed as a safeguard against laboratory contamination. Requirements for the blank are given in Section 8.5.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of one sample, in duplicate, with the batch of samples run during a given 12-hour shift (see the note at Section 8.4). The laboratory must also spike and analyze, in duplicate, a minimum of 5% of all samples from a given site or discharge to monitor and evaluate method and laboratory performance on the sample matrix. The batch and site/discharge samples may be the same. The procedure for spiking and analysis is given in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through analysis of a quality control check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) that the measurement system is in control. This procedure is given in Section 8.4.

8.1.6 The laboratory should maintain performance records to document the quality of data that is generated. This procedure is given in Section 8.8.

8.1.7 The large number of analytes tested in performance tests in this method present a substantial probability that one or more will fail acceptance criteria when many analytes are tested simultaneously, and a re-test is allowed if this situation should occur. If, however, continued re-testing results in further repeated failures, the laboratory should document the failures (e.g., as qualifiers on results) and either avoid reporting results for analytes that failed or report the problem and failures with the data. Failure to report does not relieve a discharger or permittee of reporting timely results. Results for regulatory compliance must be accompanied by QC results that meet all acceptance criteria.

8.2 Initial demonstration of capability (DOC) – To establish the ability to generate acceptable recovery and precision, the laboratory must perform the DOC in Sections 8.2.1 through 8.2.6 for the analytes of interest. The laboratory must also establish MDLs for the analytes of interest using the MDL procedure at 40 CFR 136, Appendix B. The laboratory's MDLs must be equal to or lower than those listed in Table 1 for those analytes which list MDL values, or lower than one-third the regulatory compliance limit, whichever is greater. For MDLs not listed in Table 1, the laboratory must determine the MDLs using the MDL procedure at 40 CFR 136, Appendix B under the same conditions used to determine the MDLs for the analytes listed in Table 1. All procedures used in the analysis must be included in the DOC.

8.2.1 For the DOC, a QC check sample concentrate containing each analyte of interest (Section 1.3) is prepared in methanol. The QC check sample concentrate must be prepared independently from those used for calibration, but may be from the same source as the second-source standard used for calibration verification/LCS (Sections 7.4 and 8.4). The concentrate should produce concentrations of the analytes of interest in water at the mid-point of the calibration range, and may be at the same concentration as the LCS (Section 8.4).

Note: *QC check sample concentrates are no longer available from EPA.*

8.2.2 Using a pipet or micro-syringe, prepare four LCSs by adding an appropriate volume of the concentrate to each of four aliquots of reagent water. The volume of reagent water must be the same as the volume that will be used for the sample, blank (Section 8.5), and MS/MSD (Section 8.3). A volume of 5 mL and a concentration of 20 µg/L were used to develop the QC acceptance criteria in Table 7. An alternative volume and sample concentration may be used, provided that all QC tests are performed and all QC acceptance criteria in this method are met. Also add an aliquot of the surrogate spiking solution (Section 6.7) and internal standard spiking solution (Section 7.3.1.3) to the reagent-water aliquots.

8.2.3 Analyze the four LCSs according to the method beginning in Section 10.

8.2.4 Calculate the average percent recovery ($\overline{X}$) and the standard deviation of the percent recovery (s) for each analyte using the four results.

8.2.5 For each analyte, compare s and $\overline{X}$ with the corresponding acceptance criteria for precision and recovery in Table 7. For analytes in Tables 1 and 2 not listed in Table 7, DOC QC

acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 11 and 12). If s and $\overline{X}$ for all analytes of interest meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If any individual s exceeds the precision limit or any individual $\overline{X}$ falls outside the range for recovery, system performance is unacceptable for that analyte.

Note: *The large number of analytes in Tables 1 and 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when many or all analytes are determined simultaneously. Therefore, the analyst is permitted to conduct a "re-test" as described in Sec. 8.2.6.*

8.2.6 When one or more of the analytes tested fail at least one of the acceptance criteria, repeat the test for only the analytes that failed. If results for these analytes pass, system performance is acceptable and analysis of samples and blanks may proceed. If one or more of the analytes again fail, system performance is unacceptable for the analytes that failed the acceptance criteria. Correct the problem and repeat the test (Section 8.2). See Section 8.1.7 for disposition of repeated failures.

Note: *To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between this pair of tests.*

8.3 Matrix spike and matrix spike duplicate (MS/MSD) – The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored in duplicate to assess accuracy (recovery and precision). The data user should identify the sample and the analytes of interest (Section 1.3) to be spiked. If direction cannot be obtained, the laboratory must spike at least one sample per batch of samples analyzed on a given 12-hour shift with the analytes in Table 1. Spiked sample results should be reported only to the data user whose sample was spiked, or as requested or required by a regulatory/control authority, or in a permit.

8.3.1 If, as in compliance monitoring, the concentration of a specific analyte will be checked against a regulatory concentration limit, the concentration of the spike should be at that limit; otherwise, the concentration of the spike should be one to five times higher than the background concentration determined in Section 8.3.2, at or near the midpoint of the calibration range, or at the concentration in the LCS (Section 8.4) whichever concentration would be larger.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of the each analyte of interest. If necessary, prepare a new check sample concentrate (Section 8.2.1) appropriate for the background concentration. Spike and analyze two additional sample aliquots, and determine the concentration after spiking (A_1 and A_2) of each analyte. Calculate the percent recoveries (P_1 and P_2) as 100 (A_1 - B) / T and 100 (A_2 - B) / T, where T is the known true value of the spike. Also calculate the relative percent difference (RPD) between the concentrations (A_1 and A_2) as 200 $|A_1 - A_2| / (A_1 + A_2)$. If necessary, adjust the concentrations used to calculate the RPD to account for differences in the volumes of the spiked aliquots.

8.3.3 Compare the percent recoveries (P_1 and P_2) and the RPD for each analyte in the MS/MSD aliquots with the corresponding QC acceptance criteria in Table 7. A laboratory may develop and apply QC acceptance criteria more restrictive than the criteria in Table 6, if desired.

8.3.3.1 If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is suspect and may not be reported or used for permitting or regulatory compliance purposes. See Section 8.1.7 for disposition of failures.

8.3.3.2 The acceptance criteria in Table 7 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 spike to background ratio approaches 5:1 (Reference 13). If spiking is performed at a concentration lower than 20 µg/L, the laboratory must use either the QC acceptance criteria in Table 7, or optional QC acceptance criteria calculated for the specific spike concentration. To use the optional acceptance criteria: (1) Calculate recovery (X') using the equation in Table 8, substituting the spike concentration (T) for C; (2) Calculate overall precision (S') using the equation in Table 8, substituting X' for $\overline{X}$; (3) Calculate the range for recovery at the spike concentration as (100 X'/T) ± 2.44(100 S'/T)% (Reference 4). For analytes of interest in Tables 1 and 2 not listed in Table 7, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 11 and 12).

8.3.4 After analysis of a minimum of 20 MS/MSD samples for each target analyte and surrogate, the laboratory must calculate and apply in-house QC limits for recovery and RPD of future MS/MSD samples (Section 8.3). The QC limits for recovery are calculated as the mean observed recovery ± 3 standard deviations, and the upper QC limit for RPD is calculated as the mean RPD plus 3 standard deviations of the RPDs . The in-house QC limits must be updated at least every two years and re-established after any major change in the analytical instrumentation or process. At least 80% of the analytes tested in the MS/MSD must have in-house QC acceptance criteria that are tighter than those in Table 7. If an in-house QC limit for the RPD is greater than the limit in Table 7, then the limit in Table 7 must be used. Similarly, if an in-house lower limit for recovery is below the lower limit in Table 7, then the lower limit in Table 7 must be used, and if an in-house upper limit for recovery is above the upper limit in Table 7, then the upper limit in Table 7 must be used. The laboratory must evaluate surrogate recovery data in each sample against its in-house surrogate recovery limits. The laboratory may use 60 -140% as interim acceptance criteria for surrogate recoveries until in-house limits are developed.

8.4 Calibration verification/laboratory control sample (LCS) – The working calibration curve or RF must be verified at the beginning of each 12-hour shift by the measurement of an LCS.

Note: *The 12-hour shift begins after analysis of the blank that follows the LCS and ends 12 hours later. The blank is outside of the 12-hour shift. The MS and MSD are treated as samples and are analyzed within the 12-hour shift.*

8.4.1 Prepare the LCS by adding QC check sample concentrate (Section 8.2.1) to reagent water. Include all analytes of interest (Section 1.3) in the LCS. The LCS may be the same sample prepared for the DOC (Section 8.2.1). The volume of reagent water must be the same as the volume used for the sample, blank (Section 8.5), and MS/MSD (Section 8.3). Also add an aliquot of the surrogate solution (Section 6.7) and internal standard solution (Section 7.3.1.3). The concentration of the analytes in reagent water should be the same as the concentration in the DOC (Section 8.2.2).

8.4.2 Analyze the LCS prior to analysis of field samples in the batch of samples analyzed during the 12-hour shift (see the Note at Section 8.4). Determine the concentration (A) of each analyte. Calculate the percent recovery (Q) as 100 (A/T) %, where T is the true value of the concentration in the LCS.

8.4.3 Compare the percent recovery (Q) for each analyte with its corresponding QC acceptance criterion in Table 7. For analytes of interest in Tables 1 and 2 not listed in Table 7, use the QC acceptance criteria developed for the MS/MSD (Section 8.3.3.2). If the recoveries for all analytes of interest fall within their respective QC acceptance criteria, analysis of blanks and field samples may proceed. If any individual Q falls outside the range, proceed according to Section 8.4.4.

Note: *The large number of analytes in Tables 1 - 2 present a substantial probability that one or more will fail the acceptance criteria when all analytes are tested simultaneously. Because a re-test is allowed in event of failure (Sections 8.1.7 and 8.4.3), it may be prudent to analyze two LCSs together and evaluate results of the second analysis against the QC acceptance criteria only if an analyte fails the first test.*

8.4.4 Repeat the test only for those analytes that failed to meet the acceptance criteria (Q). If these analytes now pass, system performance is acceptable and analysis of blanks and samples may proceed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, repeat the test using a fresh LCS (Section 8.2.2) or an LCS prepared with a fresh QC check sample concentrate (Section 8.2.1), or perform and document system repair. Subsequent to repair, repeat the calibration verification/LCS test (Section 8.4). If the acceptance criteria for Q cannot be met, re-calibrate the instrument (Section 7). If failure of the LCS indicates a systemic problem with samples analyzed during the 12-hour shift, re-analyze the samples analyzed during that 12-hour shift. See Section 8.1.7 for disposition of repeated failures.

Note: *To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between this pair of tests.*

8.4.5 After analysis of 20 LCS samples, the laboratory must calculate and apply in-house QC limits for recovery to future LCS samples (Section 8.4). Limits for recovery in the LCS are calculated as the mean recovery ±3 standard deviations. A minimum of 80% of the analytes tested for in the LCS must have QC acceptance criteria tighter than those in Table 7. Many of the analytes and surrogates may not contain recommended acceptance criteria. The laboratory should use 60 -140% as interim acceptance criteria for recoveries of spiked analytes and surrogates that do not have recovery limits specified in Table 7, until in-house LCS and surrogate limits are developed. If an in-house lower limit for recovery is lower than the lower limit in Table 7, the lower limit in Table 7 must be used, and if an in-house upper limit for recovery is higher than the upper limit in Table 7, the upper limit in Table 7 must be used.

8.5 Blank – A blank must be analyzed at the beginning of each 12-hour shift to demonstrate freedom from contamination. A blank must also be analyzed after a sample containing a high concentration of an analyte or potentially interfering compound to demonstrate freedom from carry-over.

8.5.1 Spike the internal standards and surrogates into the blank. Analyze the blank immediately after analysis of the LCS (Section 8.4) and prior to analysis of the MS/MSD and samples to demonstrate freedom from contamination.

8.5.2 If any analyte of interest is found in the blank: 1) at a concentration greater than the MDL for the analyte, 2) at a concentration greater than one-third the regulatory compliance limit, or 3) at a concentration greater than one-tenth the concentration in a sample analyzed during the 12-hour shift (Section 8.4), whichever is greater; analysis of samples must be halted and samples affected by the blank must be re-analyzed. Samples must be associated with an uncontaminated blank before they may be reported or used for permitting or regulatory compliance purposes.

8.6 Surrogate recoveries – Spike the surrogates into all samples, blanks, LCSs, and MS/MSDs. Compare surrogate recoveries against the QC acceptance criteria in Table 7. For surrogates in Table 5 without QC acceptance criteria in Table 7, and for other surrogates that may be used by the laboratory, limits must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 11 and 12). If any recovery fails its criteria, attempt to find and correct the cause of the failure. Surrogate recoveries from the blank and LCS may be used as pass/fail criteria by the laboratory or as required by a regulatory authority, or may be used to diagnose problems with the analytical system.

8.7 Internal standard responses

8.7.1 Calibration verification/LCS – The responses (GC peak heights or areas) of the internal standards in the calibration verification/LCS must be within 50% to 200% (1/2 to 2x) of their respective responses in the mid-point calibration standard. If they are not, repeat the LCS test using a fresh QC check sample (Section 8.4.1) or perform and document system repair. Subsequent to repair, repeat the calibration verification/LCS test (Section 8.4). If the responses are still not within 50% to 200%, re-calibrate the instrument (Section 7) and repeat the calibration verification/LCS test.

8.7.2 Samples, blanks, and MS/MSDs – The responses (GC peak heights or areas) of the internal standards in each sample, blank, and MS/MSD must be within 50% to 200% (1/2 to 2x) of its respective response in the most recent LCS. If, as a group, all internal standard are not within this range, perform and document system repair, repeat the calibration verification/ LCS test (Section 8.4), and re-analyze the affected samples. If a single internal standard is not within the 50% to 200% range, use an alternate internal standard for quantitation of the analyte referenced to the affected internal standard.

8.8 As part of the QC program for the laboratory, control charts or statements of accuracy for wastewater samples must be assessed and records maintained periodically (see 40 CFR 136.7(c)(1)(viii)). After analysis of five or more spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\overline{X}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from $\overline{X}$ -2s_p to $\overline{X}$ +2s_p. For example, if $\overline{X}$ = 90% and s_p = 10%, the accuracy interval is expressed as 70 - 110%. Update the accuracy assessment for each analyte on a regular basis (e.g., after each 5 - 10 new accuracy measurements).

8.9 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 environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Collect the sample as a grab sample in a glass container having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If needed, collect additional sample(s) for the MS/MSD (Section 8.3).

9.2 Ice or refrigerate samples at <6 °C from the time of collection until analysis, but do not freeze. If residual chlorine is present, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottle just prior to shipping to the sampling site. Any method suitable for field use may be employed to test for residual chlorine (Reference 14). Field test kits are also available for this purpose. If sodium thiosulfate interferes in the determination of the analytes, an alternate preservative (e.g., ascorbic acid or sodium sulfite) may be used. If preservative has been added, shake the sample vigorously for one minute. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 If acrolein is to be determined, analyze the sample within 3 days. To extend the holding time to 14 days, acidify a separate sample to pH 4 - 5 with HCl using the procedure in Section 9.7.

9.4 Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions (Reference 3). Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. To extend the holding time for aromatic compounds to 14 days, acidify the sample to approximately pH 2 using the procedure in Section 9.7.

9.5 If halocarbons are to be determined, either use the acidified aromatics sample in Section 9.4 or acidify a separate sample to a pH of about 2 using the procedure in Section 9.7. Aqueous samples should not be preserved with acid if the ethers in Table 2, or the alcohols that they would form upon hydrolysis, are of analytes of interest.

9.6 The ethers listed in Table 2 are prone to hydrolysis at pH 2 when a heated purge is used. Aqueous samples should not be acid preserved if these ethers are of interest, or if the alcohols they would form upon hydrolysis are of interest and the ethers are anticipated to present.

9.7 Sample acidification – Collect about 500 mL of sample in a clean container and adjust the pH of the sample to 4 - 5 for acrolein (Section 9.3), or to about 2 for the aromatic compounds (Section 9.4) by adding 1+1 HCl while swirling or stirring. Check the pH with narrow range pH paper. Fill a sample container as described in Section 9.1. Alternatively, fill a precleaned vial (Section 5.1.1) that contains approximately 0.25 mL of 1+1 HCl with sample as in Section 9.1. If preserved using this alternative procedure, the pH of the sample can be verified to be <2 after some of the sample is removed for analysis. Acidification will destroy 2-chloroethylvinyl ether; therefore, determine 2-chloroethylvinyl ether from the unacidified sample.

9.8 All samples must be analyzed within 14 days of collection (Reference 3), unless specified otherwise in Sections 9.3 - 9.7.

10. Sample Purging and Gas Chromatography

10.1 The footnote to Table 3 gives the suggested GC column and operating conditions. Included in Table 3 are retention times and MDLs that can be achieved under these conditions. Sections 10.2 through 10.7 suggest procedures that may be used with a manual purge-and-trap system. Auto-

samplers and other columns or chromatographic conditions may be used if requirements in this method are met.

10.2 Attach the trap inlet to the purging device, and set the purge-and-trap system to purge (Figure 3). Open the syringe valve located on the purging device sample introduction needle.

10.3 Allow the sample to come to ambient temperature prior to pouring an aliquot into the syringe. Remove the plunger from a syringe and attach a closed syringe valve. Open the sample bottle (or standard) 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. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add the surrogate spiking solution (Section 6.7) and internal standard spiking solution (Section 7.3.1.3) through the valve bore, then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Autosamplers designed for purge-and-trap analysis of volatiles also may be used.

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

10.5 Close both valves and purge the sample at a temperature, flow rate, and duration sufficient to purge the less-volatile analytes onto the trap, yet short enough to prevent blowing the more-volatile analytes through the trap. The temperature, flow rate, and time should be determined by test. The same purge temperature, flow rate, and purge time must be used for all calibration, QC, and field samples.

10.6 After the purge, set the purge-and-trap system to the desorb mode (Figure 4), and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to the desorb temperature while backflushing the trap with carrier gas at the flow rate and for the time necessary to desorb the analytes of interest. The optimum temperature, flow rate, and time should be determined by test. The same temperature, desorb time, and flow rate must be used for all calibration, QC, and field samples. If heating of the trap does not result in sharp peaks for the early eluting analytes, the GC column may be used as a secondary trap by cooling to an ambient or subambient temperature. To avoid carry-over and interferences, maintain the trap at the desorb temperature and flow rate until the analytes, interfering compounds, and excess water are desorbed. The optimum conditions should be determined by test.

10.7 Start MS data acquisition at the start of the desorb cycle and stop data collection when the analytes of interest, potentially interfering compounds, and water have eluted (see the footnote to Table 3 for conditions).

10.8 Cool the trap to the purge temperature and return the trap to the purge mode (Figure 3). When the trap is cool, the next sample can be analyzed.

11. Performance Tests

11.1 At the beginning of each 12-hour shift during which analyses are to be performed, GC/MS performance must be verified before blanks or samples may be analyzed (Section 8.4). Use the instrument operating conditions in the footnotes to Table 3 for these performance tests. Alternate conditions may be used so as long as all QC requirements are met.

11.2 BFB – Inject 50 ng of BFB solution directly on the column. Alternatively, add BFB to reagent water or an aqueous standard such that 50 ng or less of BFB will be introduced into the GC. Analyze according to Section 10. Confirm that all criteria in Section 7.3.2.2 and Table 4 are met. If all criteria are not met, perform system repair, retune the mass spectrometer, and repeat the test until all criteria are met.

11.3 GC resolution – There must be a valley between 1,2-dibromoethane and chlorobenzene, and the height of the valley must not exceed 25 percent of the shorter of the two peaks. For an alternate GC column, apply this valley height criterion to two representative GC peaks separated by no more than 7 seconds.

11.4 Verify calibration with the LCS (Section 8.4) after the criteria for BFB are met (Reference 15) and prior to analysis of a blank or sample. After verification, analyze a blank (Section 8.5) to demonstrate freedom from contamination and carry-over at the MDL.

12. Qualitative Identification

12.1 Target analytes are identified by comparison of results from analysis of a sample or blank with data stored in the GC/MS data system (Section 7.3.2.3). Identification of an analyte is confirmed per Sections 12.1.1 through 12.1.4.

12.1.1 The signals for all characteristic m/z's stored in the data system (Section 7.3.2.3) for each analyte of interest must be present and must maximize within the same two consecutive scans.

12.1.2 Based on the relative retention time (RRT), the RRT for the analyte must be within ± 0.06 of the RRT of the analyte in the LCS run at the beginning of the shift (Section 8.4). Relative retention time is used to establish the identification window because it compensates for small changes in the GC temperature program whereas the absolute retention time does not (see Section 7.3.1.2).

Note: *RRT is a unitless quantity (see Sec. 20.2), although some procedures refer to "RRT units" in providing the specification for the agreement between the RRT values in the sample and the LCS or other standard.*

12.1.3 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum, must agree within 50% to 200% (1/2 to 2 times) for all m/z's in the reference mass spectrum stored in the data system (Section 7.3.2.3), or from a reference library. For example, if a peak has an intensity of 20% relative to the base peak, the analyte is identified if the intensity of the peak in the sample is in the range of 10% to 40% of the base peak.

12.1.4 The m/z's present in the acquired mass spectrum for the sample that are not present in the reference mass spectrum must be accounted for by contaminant or background m/z's. A reference library may be helpful to identify and account for background or contaminant m/z's. If the acquired mass spectrum is contaminated, or if identification is ambiguous, an experienced spectrometrist (Section 1.6) must determine the presence or absence of the compound.

12.2 Structural isomers that have very similar mass spectra can be identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the

baseline to valley height between the isomers is less than 50% of the height of the shorter of the two peaks. Otherwise, structural isomers are identified as isomeric pairs.

13. Calculations

13.1 When an analyte has been identified, quantitation of that analyte is based on the integrated abundance from the EICP of the primary characteristic m/z in Table 5 or 6. Calculate the concentration using the response factor (RF) determined in Section 7.3.3 and Equation 2. If a calibration curve was used, calculate the concentration using the regression equation for the curve. If the concentration of an analyte exceeds the calibration range, dilute the sample by the minimum amount to bring the concentration into the calibration range, and re-analyze. Determine a dilution factor (DF) from the amount of the dilution. For example, if the extract is diluted by a factor of 2, DF = 2.

Equation 2

$$C_s\ (\mu g/L) = \frac{A_s \times C_{is} \times DF}{A_{is} \times RF}$$

where:

C_s = Concentration of the analyte in the sample, and the other terms are as defined in Section 7.3.3.

13.2 Reporting of results

As noted in Section 1.4.1, EPA has promulgated this method at 40 CFR Part 136 for use in wastewater compliance monitoring under the National Pollutant Discharge Elimination System (NPDES). The data reporting practices described here are focused on such monitoring needs and may not be relevant to other uses of the method.

13.2.1 Report results for wastewater samples in µg/L without correction for recovery. (Other units may be used if required by in a permit.) Report all QC data with the sample results.

13.2.2 Reporting level

Unless otherwise specified in by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria are reported down to the concentration of the ML established by the laboratory through calibration of the instrument (see Section 7.3.2 and the glossary for the derivation of the ML). EPA considers the terms "reporting limit," "quantitation limit," and "minimum level" to be synonymous.

13.2.2.1 Report a result for each analyte in each sample, blank, or standard at or above the ML to 3 significant figures. Report a result for each analyte found in each sample below the ML as "<ML," or as required by the regulatory authority or permit. Results are reported without blank subtraction unless requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

13.2.2.2 In addition to reporting results for samples and blanks separately, the concentration of each analyte in a blank associated with the sample may be subtracted from the result for that sample, but only if requested or required by a regulatory authority or in a permit. In this case, both the sample result and the blank results must be reported together.

13.2.2.3 Report a result for an analyte found in a sample that has been diluted at the least dilute level at which the area at the quantitation m/z is within the calibration range (i.e., above the ML for the analyte) and the MS/MSD recovery and RPD are within their respective QC acceptance criteria (Table 7). This may require reporting results for some analytes from different analyses.

13.2.3 Results from tests performed with an analytical system that is not in control (i.e., that does not meet acceptance criteria for all of QC tests in this method) must not be reported or otherwise used for permitting or regulatory compliance purposes, but do not relieve a discharger or permittee of reporting timely results. If the holding time would be exceeded for a re-analysis of the sample, the regulatory/control authority should be consulted for disposition.

14. Method Performance

14.1 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5 - 600 µg/L (References 4 and 16). 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 8.

14.2 As noted in Sec. 1.1, this method was validated through an interlaboratory study conducted more than 29 years ago. However, the fundamental chemistry principles used in this method remain sound and continue to apply.

15. Pollution Prevention

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

15.2 The analytes in this method are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

15.3 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872-4477.

16. Waste Management

16.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits

and regulations. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).

16.2 Samples at pH <2, or pH >12, are hazardous and must be neutralized before being poured down a drain, or must be handled and disposed of as hazardous waste.

16.3 Many analytes in this method decompose above 500 ºC. Low-level waste such as absorbent paper, tissues, and plastic gloves may be burned in an appropriate incinerator. Gross quantities of neat or highly concentrated solutions of toxic or hazardous chemicals should be packaged securely and disposed of through commercial or governmental channels that are capable of handling these types of wastes.

16.4 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better-Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036, 202/872-4477.

17. References

1. Bellar, T.A. and Lichtenberg, J.J. "Determining Volatile Organics at Microgram-per-Litre Levels by Gas Chromatography," *Journal American Water Works Association, 66,* 739 (1974).

2. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977.

3. Bellar, T.A. and Lichtenberg, J.J. "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," Measurement of Organic Pollutants in Water and Wastewater, C.E. Van Hall, editor, American Society for Testing and Materials, Philadelphia, PA. Special Technical Publication 686, 1978.

4. "EPA Method Study 29 EPA Method 624-Purgeables," EPA 600/4-84-054, National Technical Information Service, PB84-209915, Springfield, Virginia 22161, June 1984.

5. 40 Code of Federal Regulations 136, Appendix B

6. "Method Detection Limit for Methods 624 and 625," Olynyk, P., Budde, W.L., and Eichelberger, J.W. Unpublished report, May 14, 1980.

7. "Carcinogens-Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

8. "OSHA Safety and Health Standards, General Industry," (29 CFR Part 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

9. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 7th Edition, 2003.

10. 40 Code of Federal Regulations 136.6(b)(5)(*x*)

11. 40 Code of Federal Regulations 136.6(b)(2)(*i*)

12. Protocol *for EPA Approval of New Methods for Organic and Inorganic Analytes in Wastewater and Drinking Water* (EPA-821-B-98-003) March 1999

13. Provost, L.P. and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory, 15,* 58-63 (1983).

14. 40 CFR 136.3(a), Table IB, Chlorine - Total residual

15. Budde, W.L. and Eichelberger, J.W. "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-80-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April 1980.

16. "Method Performance Data for Method 624," Memorandum from R. Slater and T. Pressley, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, January 17, 1984.

18. Tables

Table 1 – Purgeables[1]			
Analyte	**CAS Registry No.**	**MDL (µg/L)[2]**	**ML (µg/L)[3]**
Acrolein	107-02-8		
Acrylonitrile	107-13-1		
Benzene	71-43-2	4.4	13.2
Bromodichloromethane	75-27-4	2.2	6.6
Bromoform	75-25-2	4.7	14.1
Bromomethane	74-83-9		
Carbon tetrachloride	56-23-5	2.8	8.4
Chlorobenzene	108-90-7	6.0	18.0
Chloroethane	75-00-3		
2-Chloroethylvinyl ether	110-75-8		
Chloroform	67-66-3	1.6	4.8
Chloromethane	74-87-3		
Dibromochloromethane	124-48-1	3.1	9.3
1,2-Dichlorobenzene	95-50-1		
1,3-Dichlorobenzene	541-73-1		
1,4-Dichlorobenzene	106-46-7		
1,1-Dichloroethane	75-34-3	4.7	14.1
1,2-Dichloroethane	107-06-2	2.8	8.4
1,1-Dichloroethene	75-35-4	2.8	8.4
trans-1,2-Dichloroethene	156-60-5	1.6	4.8
1,2-Dichloropropane	78-87-5	6.0	18.0
cis-1,3-Dichloropropene	10061-01-5	5.0	15.0
trans-1,3-Dichloropropene	10061-02-6		
Ethyl benzene	100-41-4	7.2	21.6
Methylene chloride	75-09-2	2.8	8.4
1,1,2,2-Tetrachloroethane	79-34-5	6.9	20.7
Tetrachloroethene	127-18-4	4.1	12.3
Toluene	108-88-3	6.0	18.0
1,1,1-Trichloroethane	71-55-6	3.8	11.4
1,1,2-Trichloroethane	79-00-5	5.0	15.0
Trichloroethene	79-01-6	1.9	5.7
Vinyl chloride	75-01-4		

[1] All the analytes in this table are Priority Pollutants (40 CFR 423, Appendix A)
[2] MDL values from the 1984 promulgated version of Method 624
[3] ML = Minimum Level – see Glossary for definition and derivation

Table 2 – Additional Purgeables	
Analyte	**CAS Registry**
Acetone [1]	67-64-1
Acetonitrile [2]	75-05-8
Allyl alcohol [1]	107-18-6
Allyl chloride	107-05-1
t-Amyl ethyl ether (TAEE)	919-94-8
t-Amyl methyl ether (TAME)	994-058
Benzyl chloride	100-44-7
Bromoacetone [2]	598-31-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
1,3-Butadiene	106-99-0
n-Butanol [1]	71-36-3
2-Butanone (MEK) [1,2]	78-93-3
t-Butyl alcohol (TBA)	75-65-0
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
t-Butylbenzene	98-06-6
t-Butyl ethyl ether (ETBE)	637-92-3
Carbon disulfide	75-15-0
Chloral hydrate [2]	302-17-0
Chloroacetonitrile [1]	107-14-2
1-Chlorobutane	109-69-3
Chlorodifluoromethane	75-45-6
2-Chloroethanol [2]	107-07-3
bis (2-Chloroethyl) sulfide [2]	505-60-2
1-Chlorohexanone	20261-68-1
Chloroprene (2-chloro-1,3-butadiene)	126-99-8
3-Chloropropene	107-05-1
3-Chloropropionitrile	542-76-7
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Crotonaldehyde [1,2]	123-73-9
Cyclohexanone	108-94-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
cis-1,4-Dichloro-2-butene	1476-11-5
trans-1,4-Dichloro-2-butene	110-57-6
cis-1,2-Dichloroethene	156-59-2
Dichlorodifluoromethane	75-71-8

Table 2 – Additional Purgeables	
Analyte	**CAS Registry**
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,3-Dichloro-2-propanol [2]	96-23-1
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene	10061-01-5
1:2,3:4-Diepoxybutane	1464-53-5
Diethyl ether	60-29-7
Diisopropyl ether (DIPE)	108-20-3
1,4-Dioxane [2]	123-91-1
Epichlorohydrin [2]	106-89-8
Ethanol [2]	64-17-5
Ethyl acetate [2]	141-78-6
Ethyl methacrylate	97-63-2
Ethylene oxide [2]	75-21-8
Hexachlorobutadiene	87-63-3
Hexachloroethane	67-72-1
2-Hexanone [2]	591-78-6
Iodomethane	74-88-4
Isobutyl alcohol [1]	78-83-1
Isopropylbenzene	98-82-8
p-Isopropyltoluene	99-87-6
Methacrylonitrile [2]	126-98-7
Methanol [2]	67-56-1
Malonitrile [2]	109-77-3
Methyl acetate	79-20-9
Methyl acrylate	96-33-3
Methyl cyclohexane	108-87-2
Methyl iodide	74-88-4
Methyl methacrylate	78-83-1
4-Methyl-2-pentanone (MIBK) [2]	108-10-1
Methyl-*t*-butyl ether (MTBE)	1634-04-4
Naphthalene	91-20-3
Nitrobenzene	98-95-3
N-Nitroso-di-*n*-butylamine [2]	924-16-3
2-Nitropropane	79-46-9
Paraldehyde [2]	123-63-7
Pentachloroethane [2]	76-01-7
Pentafluorobenzene	363-72-4
2-Pentanone [2]	107-19-7
2-Picoline [2]	109-06-8

Table 2 – Additional Purgeables	
Analyte	**CAS Registry**
1-Propanol [1]	71-23-8
2-Propanol [1]	67-63-0
Propargyl alcohol [2]	107-19-7
beta-Propiolactone [2]	57-58-8
Propionitrile (ethyl cyanide) [1]	107-12-0
n-Propylamine	107-10-8
n-Propylbenzene	103-65-1
Pyridine [2]	110-86-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
Tetrahydrofuran	109-99-9
o-Toluidine [2]	95-53-4
1,2,3-Trichlorobenzene	87-61-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,3-Trimethylbenzene	526-73-8
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl acetate	108-05-4
m-Xylene [3]	108-38-3
o-Xylene [3]	95-47-6
p-Xylene [3]	106-42-3
m+*o*- Xylene [3]	179601-22-0
m+*p*- Xylene [3]	179601-23-1
o+*p*- Xylene [3]	136777-61-2

[1] Determined at a purge temperature of 80°C

[2] May be detectable at a purge temperature of 80°C

[3] Determined in combination separated by GC column. Most GC columns will resolve *o*-xylene from *m*+*p*-xylene. Report using the CAS number for the individual xylene or the combination, as determined.

Table 3 – Example Retention Times	
Analyte	**Retention time (min)**
Chloromethane	3.68
Vinyl chloride	3.92
Bromomethane	4.50
Chloroethane	4.65
Trichlorofluoromethane	5.25
Diethyl ether	5.88
Acrolein	6.12
1,1-Dichloroethene	6.30
Acetone	6.40
Iodomethane	6.58
Carbon disulfide	6.72
3-Chloropropene	6.98
Methylene chloride	7.22
Acrylonitrile	7.63
trans-1,2-Dichloroethene	7.73
1,1-Dichloroethane	8.45
Vinyl acetate	8.55
Allyl alcohol	8.58
2-Chloro-1,3-butadiene	8.65
Methyl ethyl ketone	9.50
cis-1,2-Dichloroethene	9.50
Ethyl cyanide	9,57
Methacrylonitrile	9.83
Chloroform	10.05
1,1,1-Trichloroethane	10.37
Carbon tetrachloride	10.70
Isobutanol	10.77
Benzene	10.98
1,2-Dichloroethane	11.00
Crotonaldehyde	11.45
Trichloroethene	12.08
1,2-Dichloropropane	12.37
Methyl methacrylate	12.55
p-Dioxane	12.63
Dibromomethane	12.65
Bromodichloromethane	12.95
Chloroacetonitrile	13.27
2-Chloroethylvinyl ether	13.45
cis-1,3-Dichloropropene	13.65
4-Methyl-2-pentanone	13.83

Table 3 – Example Retention Times	
Analyte	**Retention time (min)**
Toluene	14.18
trans-1,3-Dichloropropene	14.57
Ethyl methacrylate	14.70
1,1,2-Trichloroethane	14.93
1,3-Dichloropropane	15.18
Tetrachloroethene	15.22
2-Hexanone	15.30
Dibromochloromethane	15.68
1,2-Dibromoethane	15.90
Chlorobenzene	16.78
Ethylbenzene	16.82
1,1,1,2-Tetrachloroethane	16.87
m+*p*-Xylene	17.08
o-Xylene	17.82
Bromoform	18.27
Bromofluorobenzene	18.80
1,1,2,2-Tetrachloroethane	18.98
1,2,3-Trichloropropane	19.08
trans-1,4-Dichloro-2-butene	19.12

Column: 75 m x 0.53 mm ID x 3.0 μm wide-bore DB-624

Conditions: 40°C for 4 min, 9°C/min to 200°C, 20°C/min (or higher) to 250°C, hold for 20 min at 250°C to remove water

Carrier gas flow rate: 6 - 7 mL/min at 40°C
Inlet split ratio: 3:1
Interface split ratio: 7:2

Table 4 – BFB Key m/z Abundance Criteria [1]	
m/z	**Abundance criteria**
50	15 - 40% of m/z 95.
75	30 - 60% of m/z 95.
95	Base Peak, 100% Relative Abundance.
96	5 - 9% of m/z 95.
173	<2% of m/z 174.
174	>50% of m/z 95.
175	5 - 9% of m/z 174.
176	>95% but <101% of m/z 174.
177	5 - 9% of m/z 176.

[1] Abundance criteria are for a quadrupole mass spectrometer; contact the manufacturer for criteria for other types of mass spectrometers

Table 5 – Suggested Surrogate and Internal Standards			
Analyte	**Retention time (min)[1]**	**Primary m/z**	**Secondary m/z's**
Benzene-d_6	10.95	84	
4-Bromofluorobenzene	18.80	95	174, 176
Bromochloromethane	9.88	128	49, 130, 51
2-Bromo-1-chloropropane	14.80	77	79, 156
2-Butanone-d_5	9.33	77	
Chloroethane-d_5	4.63	71	
Chloroform-^{13}C	10.00	86	
1,2-Dichlorobenzene-d_4		152	
1,4-Dichlorobutane	18.57	55	90, 92
1,2-Dichloroethane-d_4	10.88	102	
1,1-Dichloroethene-d_2	6.30	65	
1,2-Dichloropropane-d_6	12.27	67	
trans-1,3-Dichloropropene-d_4	14.50	79	
1,4-Difluorobenzene		114	63, 88
Ethylbenzene-d_{10}	16.77	98	
Fluorobenzene		96	70
2-Hexanone-d_5	15.30	63	
Pentafluorobenzene		168	
1,1,2,2-Tetrachloroethane-d_2	18.93	84	
Toluene-d_8	14.13	100	
Vinyl chloride-d_3	3.87	65	

[1] For chromatographic conditions, see the footnote to Table 3.

Table 6 – Characteristic m/z's for Purgeable Organics		
Analyte	**Primary m/z**	**Secondary m/z's**
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51, and 86
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61 and 98
1,1-Dichloroethane	63	65, 83, 85, 98, and 100
trans-1,2-Dichloroethene	96	61 and 98
Chloroform	83	85
1,2-Dichloroethane	98	62, 64, and 100
1,1,1-Trichloroethane	97	99, 117, and 119
Carbon tetrachloride	117	119 and 121
Bromodichloromethane	83	127, 85, and 129
1,2-Dichloropropane	63	112, 65, and 114
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, and 132
Benzene	78	
Dibromochloromethane	127	129, 208, and 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, and 134
cis-1,3-Dichloropropene	75	77
2-Chloroethylvinyl ether	106	63 and 65
Bromoform	173	171, 175, 250, 252, 254, and 256
1,1,2,2-Tetrachloroethane	168	83, 85, 131, 133, and 166
Tetrachloroethene	164	129, 131, and 166
Toluene	92	91
Chlorobenzene	112	114
Ethyl benzene	106	91
1,3-Dichlorobenzene	146	148 and 111
1,2-Dichlorobenzene	146	148 and 111
1,4-Dichlorobenzene	146	148 and 111

Table 7 – LCS (Q), DOC (s and $\overline{X}$), and MS/MSD (P and RPD) Acceptance Criteria [1]					
Analyte	**Range for Q (%)**	**Limit for s (%)**	**Range for $\overline{X}$ (%)**	**Range for P (%)**	**Limit for RPD**
Benzene	65-135	33	75-125	37-151	61
Benzene-d_6				70-130	
Bromodichloromethane	65-135	34	50-140	35-155	56
Bromoform	70-130	25	57-156	45-169	42
Bromomethane	15-185	90	D-206	D-242	61
2-Butanone-d_5				60-140	
Carbon tetrachloride	70-130	26	65-125	70-140	41
Chlorobenzene	65-135	29	82-137	37-160	53
Chloroethane	40-160	47	42-202	14-230	78
Chloroethane-d_5				60-140	
2-Chloroethylvinyl ether	D-225	130	D-252	D-305	71
Chloroform	70-135	32	68-121	51-138	54
Chloroform-^{13}C				70-130	
Chloromethane	D-205	472	D-230	D-273	60
Dibromochloromethane	70-135	30	69-133	53-149	50
1,2-Dichlorobenzene	65-135	31	59-174	18-190	57
1,2-Dichlorobenzene-d_4				70-130	
1,3-Dichlorobenzene	70-130	24	75-144	59-156	43
1,4-Dichlorobenzene	65-135	31	59-174	18-190	57
1,1-Dichloroethane	70-130	24	71-143	59-155	40
1,2-Dichloroethane	70-130	29	72-137	49-155	49
1,2-Dichloroethane-d_4				70-130	
1,1-Dichloroethene	50-150	40	19-212	D-234	32
1,1-Dichloroethene-d_2				70-130	
trans-1,2-Dichloroethene	70-130	27	68-143	54-156	45
1,2-Dichloropropane	35-165	69	19-181	D-210	55
1,2-Dichloropropane-d_6				60-140	
cis-1,3-Dichloropropene	25-175	79	5-195	D-227	58
trans-1,3-Dichloropropene	50-150	52	38-162	17-183	86
trans-1,3-Dichloropropene-d_4				70-130	
Ethyl benzene	60-140	34	75-134	37-162	63
2-Hexanone-d_5				60-140	
Methylene chloride	60-140	192	D-205	D-221	28
1,1,2,2-Tetrachloroethane	60-140	36	68-136	46-157	61
1,1,2,2-Tetrachloroethane-d_2				70-130	
Tetrachloroethene	70-130	23	65-133	64-148	39
Toluene	70-130	22	75-134	47-150	41
Toluene-d_8				70-130	
1,1,1-Trichloroethane	70-130	21	69-151	52-162	36
1,1,2-Trichloroethane	70-130	27	75-136	52-150	45
Trichloroethene	65-135	29	75-138	70-157	48
Trichlorofluoromethane	50-150	50	45-158	17-181	84
Vinyl chloride	5-195	100	D-218	D-251	66
Vinyl chloride-d_3				70-130	

[1] Criteria were calculated using an LCS concentration of 20 µg/L

Q = Percent recovery in calibration verification/LCS (Section 8.4)

s = Standard deviation of percent recovery for four recovery measurements (Section 8.2.4)

$\overline{X}$ = Average percent recovery for four recovery measurements (Section 8.2.4)

P = Percent recovery for the MS or MSD (Section 8.3.3)

D = Detected; result must be greater than zero

Notes:

1. Criteria for pollutants are based upon the method performance data in Reference 4. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.
2. Criteria for surrogates are from EPA CLP SOM01.2D

Table 8 – Recovery and Precision as Functions of Concentration			
Analyte	**Recovery, X' (µg/L)**	**Single analyst precision, s_r' (µg/L)**	**Overall precision, S' (µg/L)**
Benzene	0.93C+2.00	20.26 $\overline{X}$ -1.74	0.25 $\overline{X}$ -1.33
Bromodichloromethane	1.03C-1.58	0.15 $\overline{X}$ +0.59	0.20 $\overline{X}$ +1.13
Bromoform	1.18C-2.35	0.12 $\overline{X}$ +0.36	0.17 $\overline{X}$ +1.38
Bromomethane[a]	1.00C	0.43 $\overline{X}$	0.58 $\overline{X}$
Carbon tetrachloride	1.10C-1.68	0.12 $\overline{X}$ +0.25	0.11 $\overline{X}$ +0.37
Chlorobenzene	0.98C+2.28	0.16 $\overline{X}$ -0.09	0.26 $\overline{X}$ -1.92
Chloroethane	1.18C+0.81	0.14 $\overline{X}$ +2.78	0.29 $\overline{X}$ +1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62 $\overline{X}$	0.84 $\overline{X}$
Chloroform	0.93C+0.33	0.16 $\overline{X}$ +0.22	0.18 $\overline{X}$ +0.16
Chloromethane	1.03C+0.81	0.37 $\overline{X}$ +2.14	0.58 $\overline{X}$ +0.43
Dibromochloromethane	1.01C-0.03	0.17 $\overline{X}$ -0.18	0.17 $\overline{X}$ +0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22 $\overline{X}$ -1.45	0.30 $\overline{X}$ -1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14 $\overline{X}$ -0.48	0.18 $\overline{X}$ -0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22 $\overline{X}$ -1.45	0.30 $\overline{X}$ -1.20
1,1-Dichloroethane	1.05C+0.36	0.13 $\overline{X}$ -0.05	0.16 $\overline{X}$ +0.47
1,2-Dichloroethane	1.02C+0.45	0.17 $\overline{X}$ -0.32	0.21 $\overline{X}$ -0.38
1,1-Dichloroethene	1.12C+0.61	0.17 $\overline{X}$ +1.06	0.43 $\overline{X}$ -0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14 $\overline{X}$ +0.09	0.19 $\overline{X}$ +0.17
1,2-Dichloropropane[a]	1.00C	0.33 $\overline{X}$	0.45 $\overline{X}$
cis-1,3-Dichloropropene[a]	1.00C	0.38 $\overline{X}$	0.52 $\overline{X}$
trans-1,3-Dichloropropene[a]	1.00C	0.25 $\overline{X}$	0.34 $\overline{X}$
Ethyl benzene	0.98C+2.48	0.14 $\overline{X}$ +1.00	0.26 $\overline{X}$ -1.72
Methylene chloride	0.87C+1.88	0.15 $\overline{X}$ +1.07	0.32 $\overline{X}$ +4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16 $\overline{X}$ +0.69	0.20 $\overline{X}$ +0.41
Tetrachloroethene	1.06C+0.60	0.13 $\overline{X}$ -0.18	0.16 $\overline{X}$ -0.45
Toluene	0.98C+2.03	0.15 $\overline{X}$ -0.71	0.22 $\overline{X}$ -1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12 $\overline{X}$ -0.15	0.21 $\overline{X}$ -0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14 $\overline{X}$ +0.02	0.18 $\overline{X}$ +0.00
Trichloroethene	1.04C+2.27	0.13 $\overline{X}$ +0.36	0.12 $\overline{X}$ +0.59
Trichlorofluoromethane	0.99C+0.39	0.33 $\overline{X}$ -1.48	0.34 $\overline{X}$ -0.39
Vinyl chloride	1.00C	0.48 $\overline{X}$	0.65 $\overline{X}$

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 found of $\overline{X}$, in µg/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\overline{X}$, in µg/L.
C = True value for the concentration, in µg/L.
$\overline{X}$ = 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 (References 4 and 16).
[b] Due to coelutions, performance statements for these isomers are based upon the sums of their concentrations.

19. Figures

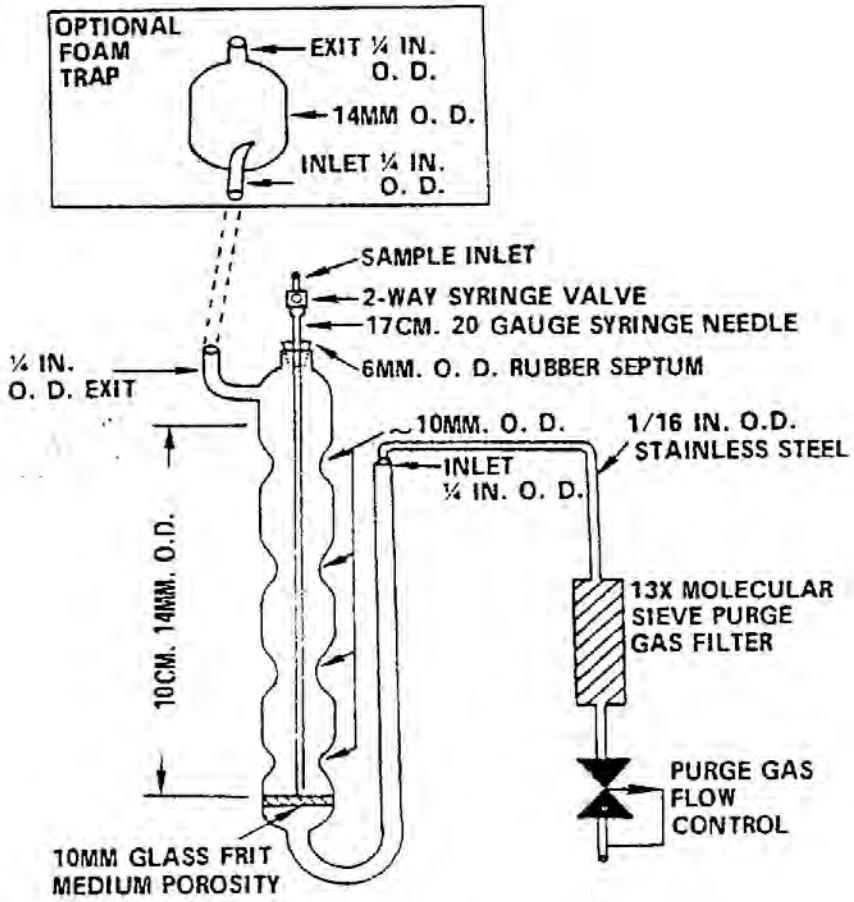

Figure 1. Purging device.

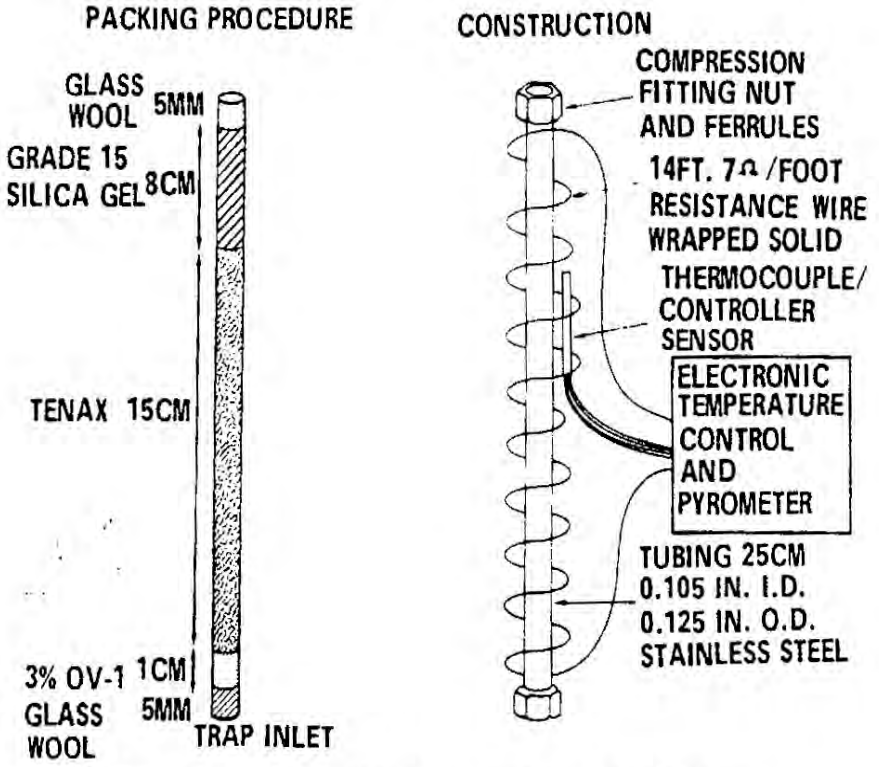

Figure 2. Trap packings and construction to include desorb capability.

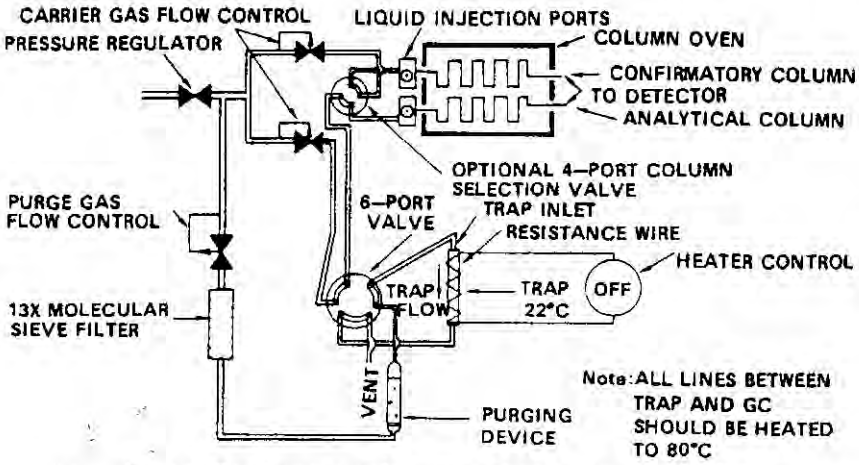

Figure 3. Purge and trap system - purge mode.

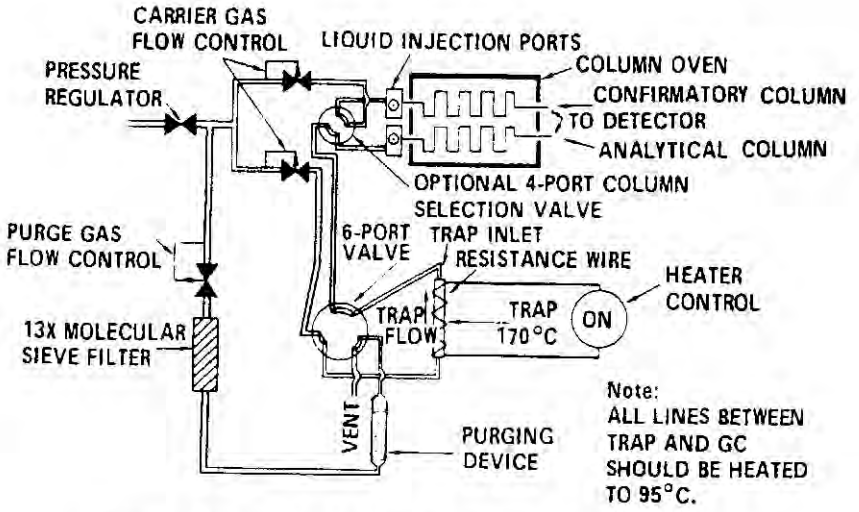

Figure 4. Purge and trap system - desorb mode.

20. Glossary

These definitions and purposes are specific to this method, but have been conformed to common usage to the extent possible.

20.1 Units of weight and measure and their abbreviations

20.1.1 Symbols

ºC	degrees Celsius
µg	microgram
µL	microliter
<	less than
>	greater than
%	percent

20.1.2 Abbreviations (in alphabetical order)

cm	centimeter
g	gram
h	hour
ID	inside diameter
in.	inch
L	liter
M	Molecular ion
m	mass
mg	milligram
min	minute
mL	milliliter
mm	millimeter
ms	millisecond
m/z	mass-to-charge ratio
N	normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per liter of solution
ng	nanogram
pg	picogram
ppb	part-per-billion
ppm	part-per-million
ppt	part-per-trillion
psig	pounds-per-square inch gauge
v/v	volume per unit volume
w/v	weight per unit volume

20.2 Definitions and acronyms (in alphabetical order)

Analyte – A compound tested for by this method. The analytes are listed in Tables 1 and 2.

Analyte of interest – An analyte of interest is an analyte required to be determined by a regulatory/control authority or in a permit, or by a client.

Analytical batch – The set of samples analyzed on a given instrument during a 12-hour period that begins and ends with analysis of a calibration verification/LCS. See Section 8.4.

Blank – An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus. See Section 8.5.

Calibration – The process of determining the relationship between the output or response of a measuring instrument and the value of an input standard. Historically, EPA has referred to a multi-point calibration as the "initial calibration," to differentiate it from a single-point calibration verification.

Calibration standard – A solution prepared from stock solutions and/or a secondary standards and containing the analytes of interest, surrogates, and internal standards. The calibration standard is used to calibrate the response of the GC/MS instrument against analyte concentration.

Calibration verification standard – The laboratory control sample (LCS) used to verify calibration. See Section 8.4.

Descriptor – In SIM, the beginning and ending retention times for the RT window, the m/z's sampled in the RT window, and the dwell time at each m/z.

Extracted ion current profile (EICP) – The line described by the signal at a given m/z.

Field duplicates – Two samples collected at the same time and place under identical conditions, and treated identically throughout field and laboratory procedures. Results of analyses of field duplicates provide an estimate of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Field blank – An aliquot of reagent water or other reference matrix that is placed in a sample container in the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC – Gas chromatograph or gas chromatography

Internal standard – A compound added to a sample in a known amount and used as a reference for quantitation of the analytes of interest and surrogates. Internal standards are listed in Table 5. Also see Internal standard quantitation.

Internal standard quantitation – A means of determining the concentration of an analyte of interest (Tables 1 and 2) by reference to a compound added to a sample and not expected to be found in the sample.

DOC – Initial demonstration of capability (DOC; Section 8.2); four aliquots of reagent water spiked with the analytes of interest and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. A DOC is performed prior to the first time this method is used and any time the method or instrumentation is modified.

Laboratory control sample (LCS; laboratory fortified blank (LFB); on-going precision and recovery sample; OPR) – An aliquot of reagent water spiked with known quantities of the analytes of interest and surrogates. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery. In this method, the LCS is synonymous with a calibration verification sample (See Sections 7.4 and 8.4).

Laboratory fortified sample matrix – See Matrix spike

Laboratory reagent blank – See Blank

Matrix spike (MS) and matrix spike duplicate (MSD) (laboratory fortified sample matrix and duplicate) – Two aliquots of an environmental sample to which known quantities of the analytes of interest and surrogates are added in the laboratory. The MS/MSD are prepared and analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations.

May – This action, activity, or procedural step is neither required nor prohibited.

May not – This action, activity, or procedural step is prohibited.

Method blank (laboratory reagent blank) – See Blank.

Method detection limit (MDL) – A detection limit determined by the procedure at 40 CFR 136, Appendix B. The MDLs determined by EPA in the original version of the method are listed in Table 1. As noted in Sec. 1.4, use the MDLs in Table 1 in conjunction with current MDL data from the laboratory actually analyzing samples to assess the sensitivity of this procedure relative to project objectives and regulatory requirements (where applicable)

Minimum level (ML) – The term "minimum level" refers to either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. Minimum levels may be obtained in several ways: They may be published in a method; they may be based on the lowest acceptable calibration point used by a laboratory; or they may be calculated by multiplying the MDL in a method, or the MDL determined by a laboratory, by a factor of 3. For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: "quantitation limit," "reporting limit," and "minimum level."

MS – Mass spectrometer or mass spectrometry

Must – This action, activity, or procedural step is required.

m/z – The ratio of the mass of an ion (m) detected in the mass spectrometer to the charge (z) of that ion.

Quality control sample (QCS) – A sample containing analytes of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards.

The purpose is to check laboratory performance using test materials that have been prepared independent of the normal preparation process.

Reagent water – Water demonstrated to be free from the analytes of interest and potentially interfering substances at the MDLs for the analytes in this method.

Regulatory compliance limit (or regulatory concentration limit) – A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory/control authority.

Relative retention time (RRT) – The ratio of the retention time of an analyte to the retention time of its associated internal standard. RRT compensates for small changes in the GC temperature program that can affect the absolute retention times of the analyte and internal standard. RRT is a unitless quantity.

Relative standard deviation (RSD) – The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

RF – Response factor. See Section 7.3.3.

RSD – See relative standard deviation

Safety Data Sheet (SDS) – Written information on a chemical's toxicity, health hazards, physical properties, fire, and reactivity, including storage, spill, and handling precautions that meet the requirements of OSHA, 29 CFR 1910.1200(g) and Appendix D. United Nations Globally Harmonized System of Classification and Labelling of Chemicals (GHS), third revised edition, United Nations, 2009.

Selected Ion Monitoring (SIM) – An MS technique in which a few m/z's are monitored. When used with gas chromatography, the m/z's monitored are usually changed periodically throughout the chromatographic run to correlate with the characteristic m/z's for the analytes, surrogates, and internal standards as they elute from the chromatographic column. The technique is often used to increase sensitivity and minimize interferences.

Signal-to-noise ratio (S/N) – The height of the signal as measured from the mean (average) of the noise to the peak maximum divided by the width of the noise.

SIM – See Selection Ion Monitoring

Should – This action, activity, or procedural step is suggested but not required.

Stock solution – A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Surrogate – A compound unlikely to be found in a sample, and which is spiked into sample in a known amount before purge-and-trap. The surrogate is quantitated with the same procedures used to quantitate the analytes of interest. The purpose of the surrogate is to monitor method performance with each sample.