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Method 625.1 – Base/Neutrals and Acids by GC/MS

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METHOD 625.1 – BASE/NEUTRALS AND ACIDS BY GC/MS

1. Scope and Application

1.1 This method is for determination of semivolatile 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 a previous protocol (Reference 1), on the basic revision promulgated October 26, 1984 (49 FR 43234), and on an interlaboratory method validation study (Reference 2). 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 Tables 1 and 2. The method may be extended to determine the analytes listed in Table 3; however, extraction or gas chromatography of some of these analytes may make quantitative determination difficult. For examples, benzidine is subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction, *alpha*-BHC, *gamma*-BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclo-pentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodiphenylamine and other nitrosoamines may decompose in the gas chromatographic inlet. EPA has provided other methods (e.g., Method 607 – Nitrosamines) for determination of some of these analytes.

1.3 The large number of analytes in Tables 1 - 3 of this method makes testing difficult if all analytes are determined simultaneously. Therefore, it is necessary to determine and perform quality control (QC) tests for the "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 Tables 1 and 2 must be determined, at a minimum, and QC testing must be performed for these analytes. The analytes in Tables 1 and 2, and some of the analytes in Table 3 have been identified as Toxic Pollutants (40 CFR 401.15), expanded to a list of Priority Pollutants (40 CFR 423, Appendix A).

1.4 In this revision to Method 625, the pesticides and polychlorinated biphenyls (PCBs) have been moved from Table 1 to Table 3 (Additional Analytes) to distinguish these analytes from the analytes required in quality control tests (Tables 1 and 2). QC acceptance criteria for pesticides and PCBs have been retained in Table 6 and may continue to be applied if desired, or if requested or required by a regulatory/control authority or in a permit. Method 608 should be used for determination of pesticides and PCBs. Method 1668C may be useful for determination of PCBs as individual chlorinated biphenyl congeners, and Method 1699B may be useful for determination of pesticides. At the time of writing of this revision, Methods 1668C and 1699B had not been approved for use at 40 CFR part 136. The screening procedure for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) contained in the version of Method 625 promulgated October 26, 1984 (49 FR 43234) has been replaced with procedures for selected ion monitoring (SIM), and 2,3,7,8-TCDD may be determined using the SIM procedures. However, EPA Method 613 or 1613B should be used for analyte-specific determination of 2,3,7,8-TCDD because of the focus of these methods on this compound. Methods 613 and 1613B are approved for use at 40 CFR part 136.

1.5 Method detection limits (MDLs; Reference 3) for the analytes in Tables 1, 2, and 3 are listed in those tables. These MDLs were determined in reagent water (Reference 4). 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 an analyte in a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5.1 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 15.2 are focused on such monitoring needs and may not be relevant to other uses of the method.

1.5.2 This method includes "reporting limits" based on EPA's "minimum level" (ML) concept (see the glossary in Section 22). Tables 1, 2, and 3 contain MDL values and ML values for many of the analytes. The MDL for an analyte in a specific wastewater may differ from those listed in Tables 1, 2, and 3, depending upon the nature of interferences in the sample matrix.

1.6 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.

1.6.1 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.

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

1.6.3 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).

1.7 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 8.2.

1.8 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 measured volume of sample, sufficient to meet an MDL or reporting limit, is serially extracted with methylene chloride at pH 11 - 13 and again at a pH less than 2 using a separatory funnel or continuous liquid/liquid extractor.

2.2 The extract is concentrated to a volume necessary to meet the required compliance or detection limit, and analyzed by GC/MS. Qualitative identification of an analyte in the extract is performed using the retention time and the relative abundance of two or more characteristic masses (m/z's). Quantitative analysis is performed using the internal standard technique with a single characteristic m/z.

3. Contamination and Interferences

3.1 Solvents, reagents, glassware, and other sample processing labware may yield artifacts, elevated baselines, or matrix interferences causing misinterpretation of chromatograms and mass spectra. All materials used in the analysis must be demonstrated to be free from contamination and interferences by analyzing blanks initially and with each extraction batch (samples started through the extraction process in a given 12-hour period, to a maximum of 20 samples - see Glossary for detailed definition), as described in Section 8.5. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, labware is cleaned by extraction or solvent rinse, or baking in a kiln or oven.

3.2 Glassware must be scrupulously cleaned (Reference 5). Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and reagent water. The glassware should then be drained dry, and heated at 400 °C for 15 - 30 minutes. Some thermally stable materials, such as PCBs, may require higher temperatures and longer baking times for removal. Solvent rinses with pesticide quality acetone, hexane, or other solvents may be substituted for heating. Volumetric labware should not be heated above 90 °C. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with solvent-rinsed or baked aluminum foil.

3.3 Matrix interferences may be caused by contaminants co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. Interferences extracted from samples high in total organic carbon (TOC) may result in elevated baselines, or by enhancing or suppressing a signal at or near the retention time of an analyte of interest. Analyses of the matrix spike and duplicate (Section 8.3) may be useful in identifying matrix interferences, and gel permeation chromatography (GPC; Section 11.1) and sulfur removal (Section 11.2) may aid in eliminating these interferences. EPA has provided guidance that may aid in overcoming matrix interferences (Reference 6).

3.4 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 4 and 5 give characteristic CI m/z's for many of the analytes covered by this method. The use of CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged, but not required.

4. Safety

4.1 Hazards associated with each reagent used in this method have 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 by whatever means available. 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: benzo(a)anthracene, benzidine, 3,3'-dichloro-benzidine, benzo(a)pyrene, *alpha*-BHC, *beta*-BHC, *delta*-BHC, *gamma*-BHC, Dibenz(a,h)-anthracene, N-nitrosodimethylamine, 4,4'-DDT, and PCBs. Other compounds in Table 3 may also

be toxic. Primary standards of 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 5.6.1.2). 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 for illustration purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here. Demonstrating that the equipment and supplies used in the laboratory achieves the required performance is the responsibility of the laboratory. Suppliers for equipment and materials in this method may be found through an on-line search. Please do not contact EPA for supplier information.*

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle – amber glass bottle large enough to contain the necessary sample volume, fitted with a fluoropolymer-lined screw cap. Foil may be substituted for fluoropolymer if the sample is not corrosive. If amber bottles are not available, protect samples from light. Unless pre-cleaned, the bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional) – the sampler must incorporate a pre-cleaned glass sample container. Samples must be kept refrigerated at <6 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow-proportioned composites.

5.2 Glassware

5.2.1 Separatory funnel – Size appropriate to hold sample volume and extraction solvent volume, and equipped with fluoropolymer stopcock.

5.2.2 Drying column – Chromatographic column, approximately 400 mm long by 19 mm ID, with coarse frit, or equivalent, sufficient to hold 15 g of anhydrous sodium sulfate.

5.2.3 Concentrator tube, Kuderna-Danish – 10 mL, graduated (Kontes 570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish – 500 mL (Kontes 57001-0500 or equivalent). Attach to concentrator tube with springs.

Note: *Use of a solvent recovery system with the K-D or other solvent evaporation apparatus is strongly recommended.*

5.2.5 Snyder column, Kuderna-Danish – Three ball macro (Kontes 503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish – Two-ball micro (Kontes 569001-0219 or equivalent).

5.2.7 Vials – 10-15 mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid-liquid extractor – Equipped with fluoropolymer or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6848-20, or equivalent.)

5.2.9 In addition to the glassware listed above, the laboratory should be equipped with all necessary pipets, volumetric flasks, beakers, and other glassware listed in this method and necessary to perform analyses successfully.

5.3 Boiling chips – Approximately 10/40 mesh, glass, silicon carbide, or equivalent. Heat to 400 °C for 30 minutes, or solvent rinse or Soxhlet extract with methylene chloride.

5.4 Water bath – Heated, with concentric ring cover, capable of temperature control (±2 °C). The bath should be used in a hood.

5.5 Balances

5.5.1 Analytical, capable of accurately weighing 0.1 mg

5.5.2 Top loading, capable of accurately weighing 10 mg

5.6 GC/MS system

5.6.1 Gas chromatograph (GC) – An analytical system complete with a temperature programmable gas chromatograph and all required accessories, including syringes and analytical columns.

5.6.1.1 Injection port – Can be split, splitless, temperature programmable split/splitless (PTV), solvent-purge, large-volume, on-column, backflushed, or other. An autosampler is highly recommended because it injects volumes more precisely than volumes injected manually.

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

5.6.2 GC column – See the footnotes to Tables 4 and 5. Other columns or column systems may be used provided all requirements in this method are met.

5.6.3 Mass spectrometer – Capable of repetitively scanning from 35-450 Daltons (amu) every two seconds or less, utilizing a 70 eV (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9A or 9B when 50 ng or less of decafluorotriphenyl phosphine (DFTPP; CAS 5074-71-5; bis(pentafluorophenyl) phenyl phosphine) is injected into the GC.

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

5.6.5 Data system – A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage of mass spectra acquired 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.

5.7 Automated gel permeation chromatograph (GPC)

5.7.1 GPC column – 150 - 700 mm long x 21 - 25 mm ID, packed with 70 g of SX-3 Biobeads; Bio-Rad Labs, or equivalent

5.7.2 Pump, injection valve, UV detector, and other apparatus necessary to meet the requirements in this method.

5.8 Nitrogen evaporation device – Equipped with a water bath than can be maintained at 30 - 45 °C; N-Evap, Organomation Associates, or equivalent.

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.

6.2 Sodium hydroxide solution (10 N) – Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate – (ACS) granular.

6.4 Sulfuric acid (1+1) – Slowly add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methylene chloride, 2-propanol – High purity pesticide quality, or equivalent, demonstrated to be free of the analytes of interest and interferences (Section 3). Purification of solvents by distillation in all-glass systems may be required.

6.6 Sodium sulfate – (ACS) granular, anhydrous, rinsed or Soxhlet extracted with methylene chloride (20 mL/g), baked at in a shallow tray at 450°C for one hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering.

6.7 Stock standard solutions (1.00 µg/µL) – 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, when available. Stock solution concentrations alternate to those below may be used. Because of the toxicity of some of the compounds, 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.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality methanol or other suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes may be used at the convenience of the laboratory. 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.

6.7.2 Transfer the stock standard solutions to fluoropolymer-sealed screw-cap bottles. Store at <6 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Replace purchased certified stock standard solutions per the expiration date. Replace stock standard solutions prepared by the laboratory or mixed with purchased solutions after one year, or sooner if comparison with QC check samples indicates a problem.

6.8 Surrogate standard spiking solution

6.8.1 Select a minimum of three surrogate compounds from Table 8 that most closely match the recovery of the analytes of interest. For example, if all analytes tested are considered acids, use surrogates that have similar chemical attributes. Other compounds may be used as surrogates so long as they do not interfere in the analysis. The deuterium and carbon-13 labeled compounds in Method 1625 are particularly useful because Method 1625 contains QC acceptance criteria for recovery of these compounds. If only one or two analytes are determined, one or two surrogates may be used.

6.8.2 Prepare a solution containing each selected surrogate such that the concentration in the sample would match the concentration in the mid-point calibration standard. For example, if the midpoint of the calibration is 100 µg/L, prepare the spiking solution at a concentration of 100 µg/mL in methanol. Addition of 1.00 mL of this solution to 1000 mL of sample will produce a concentration of 100 µg/L of the surrogate. Alternate volumes and concentrations appropriate to the response of the GC/MS instrument or for selective ion monitoring (SIM) may be used, if desired.

6.8.3 Store the spiking solution at ≤ 6°C in a fluoropolymer-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after one year, or sooner if comparison with quality control check standards indicates a problem.

6.9 Internal standard spiking solution

6.9.1 Select three or more internal standards similar in chromatographic behavior to the analytes of interest. Internal standards are listed in Table 8. Suggested internal standards are: 1,4-dichlorobenzene-d_4; naphthalene-d_8; acenaphthene-d_{10}; phenanthrene-d_{10}; chrysene-d_{12}; and perylene-d_{12}. The laboratory must demonstrate that measurement of the internal standards is not affected by method or matrix interferences (see also Section 7.3.4).

6.9.2 Prepare the internal standards at a concentration of 10 mg/mL in methylene chloride or other suitable solvent. When 10 µL of this solution is spiked into a 1-mL extract, the concentration of the internal standards will be 100 µg/mL. A lower concentration appropriate to the response of the GC/MS instrument or for SIM may be used, if desired.

6.9.3 To assure accurate analyte identification, particularly when SIM is used, it may be advantageous to include more internal standards than those suggested in Section 6.9.1. 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.

6.10 DFTPP standard – Prepare a solution of DFTPP in methanol or other suitable solvent such that 50 ng or less will be injected (see Section 13.2). An alternate concentration may be used to compensate for specific injection volumes or to assure that the operating range of the instrument is not exceeded, so long as the total injected is 50 ng or less. Include benzidine and pentachlorophenol in this solution such that ≤100 ng of benzidine and ≤50 ng of pentachlorophenol will be injected.

6.11 Quality control check sample concentrate – See Section 8.2.1.

6.12 GPC calibration solution

6.12.1 Prepare a methylene chloride solution to contain corn oil, bis(2-ethylhexyl) phthalate (BEHP), perylene, and sulfur at the concentrations in Section 6.12.2, or at concentrations appropriate to the response of the detector.

Note: Sulfur does not readily dissolve in methylene chloride, but is soluble in warm corn oil. The following procedure is suggested for preparation of the solution:

6.12.2 Weigh 8 mg sulfur and 2.5 g corn oil into a 100-mL volumetric flask and warm to dissolve the sulfur. Separately weigh 100 mg BEHP and 2 mg perylene and add to flask. Bring to volume with methylene chloride and mix thoroughly.

6.12.3 Store the solution in an amber glass bottle with a fluoropolymer-lined screw cap at 0 - 6 ºC. Protect from light. Refrigeration may cause the corn oil to precipitate. Before use, allow the solution to stand at room temperature until the corn oil dissolves, or warm slightly to aid in dissolution. Replace the solution every year, or more frequently if the response of a component changes.

6.13 Sulfur removal – Copper foil or powder (bright, non-oxidized), or tetrabutylammonium sulfite (TBA sulfite).

6.13.1 Copper foil, or powder – Fisher, Alfa Aesar 42455-18, 625 mesh, or equivalent. Cut copper foil into approximately 1-cm squares. Copper must be activated on each day it will be used, as follows:

6.13.1.1 Place the quantity of copper needed for sulfur removal (Section 11.2.1.3) in a ground-glass-stoppered Erlenmeyer flask or bottle. Cover the foil or powder with methanol.

6.13.1.2 Add HCl dropwise (0.5 - 1.0 mL) while swirling, until the copper brightens.

6.13.1.3 Pour off the methanol/HCl and rinse 3 times with reagent water to remove all traces of acid, then 3 times with acetone, then 3 times with hexane.

6.13.1.4 For copper foil, cover with hexane after the final rinse. Store in a stoppered flask under nitrogen until used. For the powder, dry on a rotary evaporator or under a stream of nitrogen. Store in a stoppered flask under nitrogen until used.

6.13.2 Tetrabutylammonium sodium sulfite (TBA sodium sulfite)

6.13.2.1 Tetrabutylammonium hydrogen sulfate, $[CH_3(CH_2)_3]_4NHSO_4$

6.13.2.2 Sodium sulfite, Na_2SO_3

6.13.2.3 Dissolve approximately 3 g tetrabutylammonium hydrogen sulfate in 100 mL of reagent water in an amber bottle with fluoropolymer-lined screw cap. Extract with three 20-mL portions of hexane and discard the hexane extracts.

6.13.2.4 Add 25 g sodium sulfite to produce a saturated solution. Store at room temperature. Replace after 1 month.

7. Calibration

7.1 Establish operating conditions equivalent to those in the footnote to Table 4 or 5 for the base/neutral or acid fraction, respectively. If a combined base/neutral/acid fraction will be analyzed, use the conditions in the footnote to Table 4. Alternative temperature program and flow rate conditions may be used. It is necessary to calibrate the GC/MS for the analytes of interest (Section 1.3) only.

7.2 Internal standard calibration

7.2.1 Prepare calibration standards for the analytes of interest and surrogates at a minimum of five concentration levels by adding appropriate volumes of one or more stock standards to volumetric flasks. One of the calibration standards should be at a concentration near the ML for the analyte in Table 1, 2, or 3. The ML value may be rounded to a whole number that is more convenient for preparing the standard, but must not exceed the ML values listed in Table 1, 2, or 3 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 not exceed the MLs in Tables 1, 2, or 3, and provided that the resulting calibration meets the acceptance criteria in Section 7.2.3, based on the RSD, RSE, or R^2.

The other concentrations 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. To each calibration standard or standard mixture, add a known constant volume of the internal standard solution (Section 6.9), and dilute to volume with methylene chloride.

Note: *The large number of analytes in Tables 1 through 3 may not be soluble or stable in a single solution; multiple solutions may be required if a large number of analytes are to be determined simultaneously.*

7.2.1.1 Prior to analysis of the calibration standards, inject the DFTPP standard (Section 6.10) and adjust the scan rate of the mass spectrometer to produce a minimum of 5 mass spectra across the DFTPP GC peak. Adjust instrument conditions until

the DFTPP criteria in Table 9A or 9B are met. Calculate peak tailing factors for benzidine and pentachlorophenol. Calculation of the tailing factor is illustrated in Figure 1. The tailing factor for benzidine and pentachlorophenol must be <2; otherwise, adjust instrument conditions and either replace the column or break off a short section of the front end of the column, and repeat the test.

Note: *The DFTPP 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 DFTPP peak. The DFTPP 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 DFTPP spectrum so long as the spectrum is not distorted to meet the criteria in Table 9A or 9B.*

7.2.1.2 Analyze the mid-point combined base/neutral and acid calibration 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 3) 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 (Tables 4 and 5); 3 to 5 m/z's assure more reliable analyte identification. Suggested quantitation m/z's are shown in Tables 4 and 5 as the primary m/z. 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.

7.2.1.3 For SIM operation, determine the analytes in each descriptor, the quantitation and qualifier m/z's for each analyte (the m/z's can be the same as for full-scan operation; Section 7.2.1.2), 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 the 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 and capture enough scans (≥5) across each chromatographic peak, there should be no more than 10 m/z's in a descriptor. 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 Daltons) that can occur at each m/z being monitored.

7.2.1.4 For combined scan and SIM operation, set up the scan segments and descriptors to meet requirements in Sections 7.2.1.1 - 7.2.1.3.

7.2.2 Analyze each calibration standard according to Section 12 and tabulate the area at the quantitation m/z against concentration for each analyte of interest, surrogate, and internal standard. If an interference is encountered, use a secondary m/z (Table 4 or 5) for

quantitation. Calculate a response factor (RF) for each analyte of interest 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 of interest or surrogate.
A_{is} = Area of the characteristic m/z for the internal standard.
C_{is} = Concentration of the internal standard (µg/mL).
C_s = Concentration of the analyte of interest or surrogate (µg/mL).

7.2.3 Calculate the mean (average) and relative standard deviation (RSD) of the responses 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. The coefficient of determination (R^2; Reference 10) of the weighted regression must be greater than 0.920. Alternatively, the relative standard error (Reference 11) 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.*

7.3 Calibration verification – The RF or calibration curve must be verified immediately after calibration and at the beginning of each 12-hour shift, by analysis of a mid-point calibration standard (Section 7.2.1). The standard(s) must be obtained from a second manufacturer or a manufacturer's batch prepared independently from the batch used for calibration. Traceability must be to a national standard, when available. The concentration of the standard should be near the mid-point of the calibration. Include the surrogates (Section 6.8) in this solution. It is necessary to verify calibration for the analytes of interest (Section 1.3) only.

Note: *The 12-hour shift begins after the DFTPP (Section 13.1) and DDT/endrin tests (if DDT and endrin are to be determined), and after analysis of the calibration verification standard. The 12-hour shift ends 12 hours later. The DFTPP and DDT/endrin tests are outside of the 12-hour shift.*

7.3.1 Analyze the calibration verification standard(s) beginning in Section 12. Calculate the percent recovery of each analyte. Compare the recoveries for the analytes of interest against the acceptance criteria for recovery (Q) in Table 6, and the recoveries for the surrogates against the acceptance criteria in Table 8. If recovery of the analytes of interest and surrogates meet acceptance criteria, system performance is acceptable and analysis of samples may continue. If any individual recovery is outside its limit, system performance is unacceptable for that analyte.

Note: *The large number of analytes in Tables 6 and 8 present a substantial probability that one or more will fail acceptance criteria when all analytes are tested simultaneously.*

7.3.2 When one or more analytes fail acceptance criteria, analyze a second aliquot of the calibration verification standard and compare only those analytes that failed the first test (Section 7.3.1) with their respective acceptance criteria. If these analytes now pass, system performance is acceptable and analysis of samples may continue. A repeat failure of any analyte that failed the first test, however, will confirm a general problem with the measurement system. If this occurs, repair the system (Section 7.2.1.1) and repeat the test (Section 7.3.1), or prepare a fresh calibration standard and repeat the test. If calibration cannot be verified after maintenance or injection of the fresh calibration standard, re-calibrate the instrument.

Note: *If it is necessary to perform a repeat verification test frequently; i.e., perform two tests in order to pass, it may be prudent to perform two injections in succession and review the results, rather than perform one injection, review the results, then perform the second injection if results from the first injection fail. To maintain the validity of the test and re-test, system maintenance and/or adjustment is not permitted between the injections.*

7.3.3 Many of the analytes in Table 3 do not have QC acceptance criteria in Table 6, and some of the surrogates in Table 8 do not have acceptance criteria. If calibration is to be verified and other QC tests are to be performed for these analytes, acceptance criteria must be developed and applied. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13).

7.3.4 Internal standard responses – Verify that detector sensitivity has not changed by comparing the response of each internal standard in the calibration verification standard (Section 7.3) to the response of the respective internal standard in the midpoint calibration standard (Section 7.2.1). The peak areas or heights of the internal standards in the calibration verification standard must be within 50% to 200% (1/2 to 2x) of their respective peak areas or heights in the mid-point calibration standard. If not, repeat the calibration verification test using a fresh calibration verification standard (7.3), or perform and document system repair. Subsequent to repair, repeat the calibration verification test (Section 7.3.1). If the responses are still not within 50% to 200%, re-calibrate the instrument (Section 7.2.2) and repeat the calibration verification test.

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 1.6 and 40 CFR 136.6(b)) to improve separations or lower the costs of measurements. These options may include alternate extraction, concentration, and cleanup procedures (e.g., solid-phase extraction; rotary-evaporator concentration; column chromatography cleanup), changes in column and type of mass spectrometer (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 8.10).

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 the MDLs 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 SPE, or another allowed method 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 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 SPE materials) but any laboratory using that specific SPE 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-q).

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 6, and recoveries for surrogates that do not have recovery limits specified in Table 8, 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 6 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 (Section 7).
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) Extraction dates.
c) Analysis dates and times.
d) Analysis sequence/run chronology.
e) Sample weight or volume (Section 10).
f) Extract volume prior to each cleanup step (Sections 10 and 11).
g) Extract volume after each cleanup step (Section 11).
h) Final extract volume prior to injection (Sections 10 and 12).
i) Injection volume (Section 12.2.3).
j) Sample or extract dilution (Section 12.2.3.2).
k) Instrument and operating conditions.
l) Column (dimensions, material, etc).
m) Operating conditions (temperature program, flow rate, etc).
n) Detector (type, operating conditions, etc).
o) Chromatograms, mass spectra, and other recordings of raw data.
p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.
(q) A written Standard Operating Procedure (SOP)

8.1.2.2.6 Each 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 6 for the analytes of interest (Section 1.3), and the MDLs must be equal to or lower than the MDLs in Tables 4 and 5 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 extracted or reagents are changed, a blank must be extracted and 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 samples in an extraction batch (Section 3.1). 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 8.9.

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.

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 Tables 1, 2, or 3 or lower than one third the regulatory compliance limit, whichever is greater. For MDLs not listed in Tables 4 and 5, 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 Tables 1, 2, and 3. All procedures used in the analysis, including cleanup procedures, 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 a water-miscible solvent. 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 (Section 7.3). 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). Multiple solutions may be required.

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 1-L aliquots of reagent water, and mix well. 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 concentration of 100 µg/L was used to develop the QC acceptance criteria in Table 6. Also add an aliquot of the surrogate spiking solution (Section 6.8). Also add an aliquot of the surrogate spiking solution (Section 6.8) to the reagent-water aliquots.

8.2.3 Extract and 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 6. For analytes in Table 3 not listed in Table 6, DOC QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13). 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 - 3 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 extraction batch of up to 20 samples with the analytes in Tables 1 and 2. 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.

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 6. 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 6 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 14). If spiking is

performed at a concentration lower than 100 µg/L, the laboratory must use either the QC acceptance criteria in Table 6, 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 7, substituting the spike concentration (T) for C; (2) Calculate overall precision (S') using the equation in Table 7, 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 14). For analytes in Table 3 not listed in Table 6, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 12 and 13).

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 6. If an in-house QC limit for the RPD is greater than the limit in Table 6, then the limit in Table 6 must be used. Similarly, if an in-house lower limit for recovery is below the lower limit in Table 6, then the lower limit in Table 6 must be used, and if an in-house upper limit for recovery is above the upper limit in Table 6, then the upper limit in Table 6 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 Laboratory control sample (LCS) – A QC check sample (laboratory control sample, LCS; on-going precision and recovery sample, OPR) containing each analyte of interest (Section 1.3) and surrogate must be prepared and analyzed with each extraction batch of up to 20 samples to demonstrate acceptable recovery of the analytes of interest from a clean sample matrix.

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 spiking solution (Section 6.8). 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 extraction batch. Determine the concentration (A) of each analyte. Calculate the percent recovery (P_S) as 100 (A/T)%, where T is the true value of the concentration in the LCS.

8.4.3 Compare the percent recovery (P_S) for each analyte with its corresponding QC acceptance criterion in Table 6. For analytes of interest in Table 3 not listed in Table 6, 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 P_S falls outside the range, proceed according to Section 8.4.4.

Note: *The large number of analytes in Tables 1 - 3 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 extract and 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 (P_S). 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 LCS test (Section 8.4). If failure of the LCS indicates a systemic problem with samples in the batch, re-extract and re-analyze the samples in the batch. 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 the 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 6. 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 8, 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 6, the lower limit in Table 6 must be used, and if an in-house upper limit for recovery is higher than the upper limit in Table 6, the upper limit in Table 6 must be used.

8.5 Blank – A blank must be extracted and analyzed with each extraction batch to demonstrate that the reagents and equipment used for preparation and analysis are free from contamination.

8.5.1 Spike the surrogates into the blank. Extract and concentrate the blank using the same procedures and reagents used for the samples, LCS, and MS/MSD in the batch. 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 in the extraction batch, whichever is greater, analysis of samples must be halted and samples affected by the blank must be re-extracted and the extracts 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 Internal standards responses

8.6.1 Calibration verification – The responses (GC peak heights or areas) of the internal standards in the calibration verification 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 calibration verification (Section 7.4) test or perform and document system repair. Subsequent to repair, repeat the calibration verification. If the responses are still not within

50% to 200%, re-calibrate the instrument (Section 7) and repeat the calibration verification/LCS test.

8.6.2 Samples, blanks, LCSs, 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 standards 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.

8.7 Surrogate recoveries – Spike the surrogates into all samples, blanks, LCSs, and MS/MSDs. Compare surrogate recoveries against the QC acceptance criteria in Table 8 and/or those developed in Section 7.3.3. 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.

8.8 DDT and endrin decomposition (breakdown) – If DDT and/or endrin are to be analyzed using this method, a DDT/endrin decomposition test must be performed to reliably quantify these two pesticides. The DDT/endrin decomposition test to be used is in EPA Method 608A or 1656.

8.9 As part of the QC program for the laboratory, control charts or statements of accuracy for wastewater samples must be assessed and records maintained (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).

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of 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 samples as grab samples in glass bottles or in refrigerated bottles using automatic sampling equipment. Collect 1-L of ambient waters, effluents, and other aqueous samples. If the sensitivity of the analytical system is sufficient, a smaller volume (e.g., 250 mL), but no less than 100 mL, may be used. Conventional sampling practices (Reference 15) should be followed, except that the bottle must not be pre-rinsed with sample before collection. Automatic sampling equipment must be as free as possible of polyvinyl chloride or other tubing or other potential sources of contamination. 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 extraction, but do not freeze. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. Any method suitable for field use may be employed to test for residual chlorine (Reference 16). Do not add excess sodium thiosulfate. If sodium thiosulfate interferes in the determination of the analytes, an alternate preservative (e.g., ascorbic acid or sodium sulfite) may be used.

9.3 All samples must be extracted within 7 days of collection and sample extracts must be analyzed within 40 days of extraction.

10. Extraction

10.1 This section contains procedures for separatory funnel liquid-liquid extraction (SFLLE) and continuous liquid-liquid extraction (CLLE). SFLLE is faster, but may not be as effective as CLLE for recovery of polar analytes such as phenol. SFLLE is labor intensive and may result in formation of emulsions that are difficult to break. CLLE is less labor intensive, avoids emulsion formation, but requires more time (18-24 hours) and more hood space, and may require more solvent. The procedures assume base-neutral extraction followed by acid extraction. For some matrices and analytes of interest, improved results may be obtained by acid-neutral extraction followed by base extraction. A single acid or base extraction may also be performed. If an extraction scheme alternate to base-neutral followed by acid extraction is used, all QC tests must be performed and all QC acceptance criteria must be met with that extraction scheme as an integral part of this method.

10.2 Separatory funnel liquid-liquid extraction (SFLLE) and extract concentration

10.2.1 The SFLLE procedure below assumes a sample volume of 1 L. When a different sample volume is extracted, adjust the volume of methylene chloride accordingly.

10.2.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into the separatory funnel. Pipet the surrogate standard spiking solution (Section 6.8) into the separatory funnel. If the sample will be used for the LCS or MS or MSD, pipet the appropriate check sample concentrate (Section 8.2.1 or 8.3.2) into the separatory funnel. Mix well. Check the pH of the sample with wide-range pH paper and adjust to pH 11 - 13 with sodium hydroxide solution.

10.2.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for approximately 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a flask. If the emulsion cannot be broken (recovery of <80% of the methylene chloride), transfer the sample, solvent, and emulsion into a continuous extractor and proceed as described in Section 10.3.

10.2.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.2.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60 mL aliquots of methylene chloride. Collect and combine the extracts in a flask in the same manner as the base/neutral extracts.

Note: *Base/neutral and acid extracts may be combined for concentration and analysis provided all QC tests are performed and all QC acceptance criteria met for the*

analytes of interest with the combined extract as an integral part of this method, and provided that the analytes of interest are as reliably identified and quantified as when the extracts are analyzed separately. If doubt exists as to whether identification and quantitation will be affected by use of a combined extract, the fractions must be analyzed separately.

10.2.6 For each fraction or the combined fractions, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator so long as the requirements in Section 8.2 are met.

10.2.7 For each fraction or the combined fractions, pour the extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20-30 mL of methylene chloride to complete the quantitative transfer.

10.2.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction (Section 10.2.7). Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL or other determined amount, remove the K-D apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 - 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. If the sample will be cleaned up, reserve the K-D apparatus for concentration of the cleaned up extract. Adjust the volume to 5 mL with methylene chloride and proceed to Section 11 for cleanup; otherwise, further concentrate the extract for GC/MS analysis per Section 10.2.9 or 10.2.10.

10.2.9 Micro Kuderna-Danish concentration – add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 1 mL or other determined amount, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of or methylene chloride. Adjust the final volume to 1.0 mL or a volume appropriate to the sensitivity desired (e.g., to meet lower MDLs or for selected ion monitoring). Record the volume, stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to fluoropolymer-lined screw-cap vials and labeled base/neutral or acid fraction as appropriate. Mark the level of the extract on the vial so that solvent loss can be detected.

10.2.10 Nitrogen evaporation and solvent exchange – Extracts may be concentrated for analysis using nitrogen evaporation in place of micro K-D concentration (Section 10.2.9). Extracts

that have been cleaned up using sulfur removal (Section 12.2) and are ready for analysis are exchanged into methylene chloride.

10.2.10.1 Transfer the vial containing the sample extract to the nitrogen evaporation (blowdown) device (Section 5.8). Lower the vial into the water bath and begin concentrating. If the more volatile analytes (Section 1.2) are to be concentrated, use room temperature for concentration; otherwise, a slightly elevated (e.g., 30 - 45 °C) may be used. During the solvent evaporation process, keep the solvent level below the water level of the bath and do not allow the extract to become dry. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed. A large vortex in the solvent may cause analyte loss.

10.2.10.2 Extracts to be solvent exchanged – When the volume of the liquid is approximately 200 µL, add 2 to 3 mL of methylene chloride and continue concentrating to approximately 100 µL. Repeat the addition of solvent and concentrate once more. Adjust the final extract volume to be consistent with the volume extracted and the sensitivity desired.

10.2.10.3 For extracts that have been cleaned up by GPC and that are to be concentrated to a nominal volume of 1 mL, adjust the final volume to compensate the GPC loss. For a 50% GPC loss, concentrate the extract to 1/2000 of the volume extracted. For example, if the volume extracted is 950 mL, adjust the final volume to 0.48 mL. For extracts that have not been cleaned up by GPC and are to be concentrated to a nominal volume of 1.0 mL, adjust the final extract volume to 1/1000 of the volume extracted. For example, if the volume extracted is 950 mL, adjust the final extract volume to 0.95 mL.

Note: *The difference in the volume fraction for an extract cleaned up by GPC accounts for the loss in GPC cleanup. Also, by preserving the ratio between the volume extracted and the final extract volume, the concentrations and detection limits do not need to be adjusted for differences in the volume extracted and the extract volume.*

10.2.11 Transfer the concentrated extract to a vial with fluoropolymer-lined cap. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for GC analysis. If GC analysis will not be performed on the same day, store the vial in the dark at ≤6 °C. Analyze the extract by GC/MS per the procedure in Section 12.

10.2.12 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. For sample volumes on the order of 1000 mL, record the sample volume to the nearest 10 mL; for sample volumes on the order of 100 mL, record the volume to the nearest 1 mL. Sample volumes may also be determined by weighing the container before and after filling to the mark with water.

10.3 Continuous liquid/liquid extraction (CLLE)

Note: *With CLLE, phenol, 2,4-dimethyl phenol, and some other analytes may be preferentially extracted into the base-neutral fraction. Determine an analyte in the fraction in which it is identified and quantified most reliably. Also, the short-chain phthalate esters (e.g., dimethyl phthalate, diethyl phthalate) and some other compounds may hydrolyze during prolonged exposure to basic conditions required for continuous extraction, resulting in low*

recovery of these analytes. When these analytes are of interest, their recovery may be improved by performing the acid extraction first.

10.3.1 Use CLLE when experience with a sample from a given source indicates an emulsion problem, or when an emulsion is encountered during SFLLE. CLLE may be used for all samples, if desired.

10.3.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH 11-13 with sodium hydroxide solution. Transfer the sample to the continuous extractor. Pipet surrogate standard spiking solution (Section 6.8) into the sample. If the sample will be used for the LCS or MS or MSD, pipet the appropriate check sample concentrate (Section 8.2.1 or 8.3.2) into the extractor. Mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor.

10.3.3 Repeat the sample bottle rinse with an additional 50-100 mL portion of methylene chloride and add the rinse to the extractor.

10.3.4 Add a suitable volume of methylene chloride to the distilling flask (generally 200 - 500 mL), add sufficient reagent water to ensure proper operation, and extract for 18 - 24 hours. A shorter or longer extraction time may be used if all QC acceptance criteria are met. Test and, if necessary, adjust the pH of the water during the second or third hour of the extraction. After extraction, allow the apparatus to cool, then detach the distilling flask. Dry, concentrate, and seal the extract per Sections 10.2.6 through 10.2.11. See the note at Section 10.2.5 regarding combining extracts of the base/neutral and acid fractions.

10.3.5 Charge the distilling flask with methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 18 - 24 hours. A shorter or longer extraction time may be used if all QC acceptance criteria are met. Test and, if necessary, adjust the pH of the water during the second or third hour of the extraction. After extraction, allow the apparatus to cool, then detach the distilling flask. Dry, concentrate, and seal the extract per Sections 10.2.6 through 10.2.11. Determine the sample volume per Section 10.2.12.

11. Extract Cleanup

Note Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the laboratory may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the laboratory must demonstrate that the requirements of Section 8.1.2 can be met using the cleanup procedure as an integral part of this method.

11.1 Gel permeation chromatography (GPC)

11.1.1 Calibration

11.1.1.1 Load the calibration solution (Section 6.12) into the sample loop

11.1.1.2 Inject the calibration solution and record the signal from the detector. The elution pattern will be corn oil, bis(2-ethylhexyl) phthalate, pentachlorophenol, perylene, and sulfur.

11.1.1.3 Set the "dump time" to allow >85% removal of the corn oil and >85% collection of the phthalate.

11.1.1.4 Set the "collect time" to the peak minimum between perylene and sulfur.

11.1.1.5 Verify calibration with the calibration solution after every 20 or fewer extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85%. If calibration is not verified, recalibrate using the calibration solution, and re-extract and clean up the preceding extracts using the calibrated GPC system.

11.1.2 Extract cleanup – GPC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 0.5 g of high molecular weight material in a 5-mL extract. If the extract is known or expected to contain more than 0.5 g, the extract is split into fractions for GPC and the fractions are combined after elution from the column. The solids content of the extract may be obtained gravimetrically by evaporating the solvent from a 50-µL aliquot.

11.1.2.1 Filter the extract or load through the filter holder to remove particulates. Load the extract into the sample loop. The maximum capacity of the column is 0.5 - 1.0 g. If necessary, split the extract into multiple aliquots to prevent column overload.

11.1.2.2 Elute the extract using the calibration data determined in Section 11.1.1. Collect the eluate in the K-D apparatus reserved in Section 10.2.8.

11.1.3 Concentrate the cleaned up extract per Sections 10.2.8 and 10.2.9 or 10.2.10.

11.1.4 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.

11.1.5 If a particularly dirty extract is encountered, run a methylene chloride blank through the system to check for carry-over.

11.2 Sulfur removal

Note: *Separate procedures using copper or TBA sulfite are provided in this section for sulfur removal. They may be used separately or in combination, if desired.*

11.2.1 Removal with copper (Reference 17)

Note: *If (1) an additional compound (Table 3) is to be determined; (2) sulfur is to be removed; (3) copper will be used for sulfur removal; and (4) a sulfur matrix is known or suspected to be present, the laboratory must demonstrate that the additional compound can be successfully extracted and treated with copper in the sulfur matrix. Some of the additional compounds (Table 3) are known not to be amenable to sulfur removal with copper (e.g. Atrazine and Diazinon).*

11.2.1.1 Quantitatively transfer the extract from Section 10.2.8 to a 40- to 50-mL flask or bottle. If there is evidence of water in the concentrator tube after the transfer, rinse the tube with small portions of hexane:acetone (40:60) and add to the flask or bottle. Mark and set aside the concentrator tube for use in re-concentrating the extract.

11.2.1.2 Add 10 - 20 g of granular anhydrous sodium sulfate to the flask. Swirl to dry the extract.

11.2.1.3 Add activated copper (Section 6.13.1.4) and allow to stand for 30 - 60 minutes, swirling occasionally. If the copper does not remain bright, add more and swirl occasionally for another 30 - 60 minutes.

11.2.1.4 After drying and sulfur removal, quantitatively transfer the extract to a nitrogen-evaporation vial or tube and proceed to Section 10.2.10 for nitrogen evaporation and solvent exchange, taking care to leave the sodium sulfate and copper in the flask.

11.2.2 Removal with TBA sulfite

11.2.2.1 Using small volumes of hexane, quantitatively transfer the extract to a 40- to 50-mL centrifuge tube with fluoropolymer-lined screw cap.

11.2.2.2 Add 1 - 2 mL of TBA sulfite reagent (Section 6.13.2.4), 2 - 3 mL of 2-propanol, and approximately 0.7 g of sodium sulfite (Section 6.13.2.2) crystals to the tube. Cap and shake for 1 - 2 minutes. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 0.5 g portions until a solid residue remains after repeated shaking.

11.2.2.3 Add 5 - 10 mL of reagent water and shake for 1 - 2 minutes. Centrifuge to settle the solids.

11.2.2.4 Quantitatively transfer the hexane (top) layer through a small funnel containing a few grams of granular anhydrous sodium sulfate to a nitrogen-evaporation vial or tube and proceed to Section 10.2.10 for nitrogen evaporation and solvent exchange.

12. Gas Chromatography/Mass Spectrometry

12.1 Establish the operating conditions in Table 4 or 5 for analysis of a base/neutral or acid extract, respectively. For analysis of a combined extract (Section 10.2.5, note), use the operating conditions in Table 4. Included in these tables are retention times and MDLs that can be achieved under these conditions. Examples of the separations achieved are shown in Figure 2 for the combined extract. Alternative columns or chromatographic conditions may be used if the requirements of Section 8.2 are met. Verify system performance per Section 13.

12.2 Analysis of a standard or extract

12.2.1 Bring the standard or concentrated extract (Section 10.2.9 or 10.2.11) to room temperature and verify that any precipitate has redissolved. Verify the level on the extract and bring to the mark with solvent if required.

12.2.2 Add the internal standard solution (Section 6.9) to the extract. Mix thoroughly.

12.2.3 Inject an appropriate volume of the sample extract or standard solution using split, splitless, solvent purge, large-volume, or on-column injection. If the sample is injected manually the solvent-flush technique should be used. The injection volume depends upon the technique used and the ability to meet MDLs or reporting limits for regulatory compliance. Injected volumes must be the same for standards and sample extracts. Record the volume injected to two significant figures.

12.2.3.1 Start the GC column oven program upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after benzo(ghi)perylene elutes for the base/neutral or combined fractions, or after pentachlorophenol elutes for the acid fraction. Return the column to the initial temperature for analysis of the next standard solution or extract.

12.2.3.2 If the concentration of any analyte of interest exceeds the calibration range, either extract and analyze a smaller sample volume, or dilute and analyze the diluted extract after bringing the concentrations of the internal standards to the levels in the undiluted extract.

12.2.4 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When standards and extracts are not being used for analyses, store them refrigerated at ≤6°C protected from light in screw-cap vials equipped with un-pierced fluoropolymer-lined septa.

13. Performance tests

13.1 At the beginning of each 12-hour shift during which standards or extracts will be analyzed, perform the tests in Sections 13.2 - 13.7 to verify system performance. If DDT and/or endrin are to be determined, perform the decomposition test in Section 13.8. If an extract is concentrated for greater sensitivity (e.g., by SIM), all tests must be performed at levels consistent with the reduced extract volume.

13.2 DFTPP – Inject the DFTPP standard (Section 6.10) and verify that the criteria for DFTPP in Section 7.2.1.1 and Table 9A (Reference 18) for a quadrupole MS, or Table 9B (Reference 19) for a time-of-flight MS, are met. It is not necessary to meet DFTPP criteria for SIM operation.

13.3 GC resolution – There must be a valley between benzo(b)fluoranthene and benzo(k)fluoranthene at m/z 252, and the height of the valley must not exceed 25 percent of the shorter of the two peaks.

13.4 Calibration verification – Verify calibration per Sections 7.3 and Table 6.

13.5 Peak tailing – Verify the tailing factor specifications are met per Section 7.2.1.1.

13.6 Laboratory control sample and blank – Analyze the extracts of the LCS and blank at the beginning of analyses of samples in the extraction batch (Section 3.1). The LCS must meet the requirements in Section 8.4, and the blank must meet the requirements in Section 8.5 before sample extracts may be analyzed.

13.7 Matrix spike/matrix spike duplicate – Analyze the background sample for the MS/MSD and the MS and MSD after the blank (Section 8.3.2). Results for the MS/MSD must meet the requirements in Section 8.3 before a result for an analyte in any unspiked sample in the batch may be reported or used for permitting or regulatory compliance purposes.

13.8 DDT/endrin decomposition test – If DDT and/or endrin analytes of interest, the DDT/endrin test (Section 8.8) must be performed and the QC acceptance criteria must be met before analyzing samples for DDT and/or endrin.

14. Qualitative Identification

14.1 Identification is accomplished by comparison of data from analysis of a sample or blank with data stored in the GC/MS data system (Sections 5.6.5 and 7.2.1.2, and Tables 4 and 5). Identification of an analyte is confirmed per Sections 14.1.1 through 14.1.4.

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

14.1.2 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 calibration verification run at the beginning of the shift (Section 7.3 or 13.4). 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 6.9.3).

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 calibration verification or other standard.*

14.1.3 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 7.2.1.2), 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.

14.1.4 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 1.7) must determine the presence or absence of the compound.

14.2 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.

15. Calculations

15.1 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 4 or 5. Calculate the concentration in the extract using the response factor (RF) determined in Section 7.2.2 and Equation 2. If the concentration of an analyte exceeds the calibration range, dilute the extract by the minimum amount to bring the concentration into the calibration range, and re-analyze the extract. 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

$$C_{ex}\ (\mu g/mL) = \frac{A_s \times I_{is}}{A_{is} \times RF}$$

where:
C_{ex} = Concentration of the analyte in the extract, in µg/mL, and the other terms are as defined in Equation 1

Calculate the concentration of the analyte in the sample using the concentration in the extract, the extract volume, the sample volume, and the dilution factor, per Equation 3:

Equation 3

$$C_s\ (\mu g/L) = \frac{C_{ex} \times V_{ex} \times DF}{V_s}$$

where:
C_s = Concentration of the analyte in the sample
C_{ex} = Concentration of the analyte in the extract, in µg/mL
V_{ex} = Volume of extract (mL)
V_s = Volume of sample (L)
DF = Dilution factor

15.2 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.

15.2.1 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.

15.2.2 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.

15.2.2.1 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.

15.2.2.2 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.

15.2.2.3 Report a result for an analyte found in a sample or extract 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 6). This may require reporting results for some analytes from different analyses.

15.2.3 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.

16. Method Performance

16.1 The basic version of this method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1300 µg/L (Reference 2). Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

16.2 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.

16.3 A chromatogram of the combined acid/base/neutral calibration standard is shown in Figure 2.

17. Pollution Prevention

17.1 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.

17.2 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. This method

utilizes significant quantities of methylene chloride. Laboratories are encouraged to recover and recycle this and other solvents during extract concentration.

17.3 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.

18. Waste Management

18.1 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).

18.2 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.

18.3 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.

18.4 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.

19. References

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5. Annual Book of ASTM Standards, Volume 11.02, D3694-96, "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.

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

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11. 40 Code of Federal Regulations 136.6(b)(4)(*x*)

12. 40 Code of Federal Regulations 136.6(b)(2)(*i*)

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14. Provost, L.P. and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory,* 15, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)

15. ASTM Annual Book of Standards, Part 31, D3370-76. "Standard Practices for Sampling Water," American Society for Testing and Materials, Philadelphia.

16. 40 Code of Federal Regulations 136.3(a), Table IB, Chlorine – Total Residual

17. "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples," EPA-600/8-80-038, U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina.

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19. Letter of approval of acceptance criteria for DFTPP for time-of-flight mass spectrometers from William A. Telliard and Herb Brass of EPA to Jack Cochran of LECO Corporation, February 9, 2005.

20. Tables

Table 1 – Non Pesticide/PCB Base/Neutral Extractables[1]			
Analyte	**CAS Registry**	**MDL[4]**	**ML[5]**
Acenaphthene	83-32-9	1.9	5.7
Acenaphthylene	208-96-8	3.5	10.5
Anthracene	120-12-7	1.9	5.7
Benzidine [2]	92-87-5	44	132
Benzo(a)anthracene	56-55-3	7.8	23.4
Benzo(a)pyrene	50-32-8	2.5	7.5
Benzo(b)fluoranthene	205-99-2	4.8	14.4
Benzo(k)fluoranthene	207-08-9	2.5	7.5
Benzo(ghi)perylene	191-24-2	4.1	12.3
Benzyl butyl phthalate	85-68-7	2.5	7.5
bis(2-Chloroethoxy)methane	111-91-1	5.3	15.9
bis(2-Ethylhexyl)phthalate	117-81-7	2.5	7.5
bis(2-Chloroisopropyl) ether (2,2'-Oxybis(1-chloropropane))	108-60-1	5.7	17.1
4-Bromophenyl phenyl ether	101-55-3	1.9	5.7
2-Chloronaphthalene	91-58-7	1.9	5.7
4-Chlorophenyl phenyl ether	7005-72-3	4.2	12.6
Chrysene	218-01-9	2.5	7.5
Dibenz(a,h)anthracene	53-70-3	2.5	7.5
Di-*n*-butylphthalate	84-74-2	2.5	7.5
3,3'-Dichlorobenzidine	91-94-1	16.5	49.5
Diethyl phthalate	84-66-2	1.9	5.7
Dimethyl phthalate	131-11-3	1.6	4.8
2,4-Dinitrotoluene	121-14-2	5.7	17.1
2,6-Dinitrotoluene	606-20-2	1.9	5.7
Di-*n*-octylphthalate	117-84-0	2.5	7.5
Fluoranthene	206-44-0	2.2	6.6
Fluorene	86-73-7	1.9	5.7
Hexachlorobenzene	118-74-1	1.9	5.7
Hexachlorobutadiene	87-68-3	0.9	2.7
Hexachloroethane	67-72-1	1.6	4.8
Indeno(1,2,3-cd)pyrene	193-39-5	3.7	11.1
Isophorone	78-59-1	2.2	6.6
Naphthalene	91-20-3	1.6	4.8
Nitrobenzene	98-95-3	1.9	5.7
N-Nitrosodi-*n*-propylamine [3]	621-64-7	--	--
Phenanthrene	85-01-8	5.4	16.2
Pyrene	129-00-0	1.9	5.7
1,2,4-Trichlorobenzene	120-82-1	1.9	5.7

[1] All analytes in this table are Priority Pollutants (40 CFR 423, Appendix A)
[2] Included for tailing factor testing
[3] See Section 1.2
[4] MDL values from the 1984 promulgated version of Method 624
[5] ML = Minimum Level – see Glossary for definition and derivation

Table 2--Acid Extractables[1]			
Analyte	**CAS Registry**	**MDL[3]**	**ML[4]**
4-Chloro-3-methylphenol	59-50-7	3.0	9.0
2-Chlorophenol	95-57-8	3.3	9.9
2,4-Dichlorophenol	120-83-2	2.7	8.1
2,4-Dimethylphenol	105-67-9	2.7	8.1
2,4-Dinitrophenol	51-28-5	42	126
2-Methyl-4,6-dinitrophenol	534-52-1	24	72
2-Nitrophenol	88-75-5	3.6	10.8
4-Nitrophenol	100-02-7	2.4	7.2
Pentachlorophenol [2]	87-86-5	3.6	10.8
Phenol	108-95-2	1.5	4.5
2,4,6-Trichlorophenol	88-06-2	2.7	8.1

[1] All analytes in this table are Priority Pollutants (40 CFR 423, Appendix A)
[2] See Section 1.2; included for tailing factor testing
[3] MDL values from the 1984 promulgated version of Method 624
[4] ML = Minimum Level – see Glossary for definition and derivation

Table 3 – Additional Extractable Analytes[1, 2]			
Analyte	**CAS Registry**	**MDL[6]**	**ML[7]**
Acetophenone	98-86-2		
2-Acetylaminofluorene	53-96-3		
1-Acetyl-2-thiourea	591-08-2		
Alachlor	15972-60-8		
Aldrin [3]	309-00-2	1.9	5.7
Ametryn	834-12-8		
2-Aminoanthraquinone	117-79-3		
Aminoazobenzene	60-09-3		
4-Aminobiphenyl	92-67-1		
3-Amino-9-ethylcarbazole	132-32-1		
Anilazine	101-05-3		
Aniline	62-53-3		
o-Anisidine	90-04-0		
Aramite	140-57-8		
Atraton	1610-17-9		
Atrazine	1912-24-9		
Azinphos-methyl	86-50-0		
Barban	101-27-9		
Benzanthrone	82-05-3		
Benzenethiol	108-98-5		
Benzidine [3,4]	92-87-5	44	132
Benzoic acid	65-85-0		
2,3-Benzofluorene	243-17-4		
p-Benzoquinone	106-51-4		
Benzyl alcohol	100-51-6		
alpha-BHC [3,4]	319-84-6		
beta-BHC [3]	319-85-7	3.1	9.3
gamma-BHC (Lindane) [3,4]	58-89-8	4.2	12.6
delta-BHC [3]	319-86-8		
Biphenyl	92-52-4		
Bromacil	314-40-9		
2-Bromochlorobenzene	694-80-4		
3-Bromochlorobenzene	108-39-2		
Bromoxynil	1689-84-5		
Butachlor	2318-4669		
Butylate	2008-41-5		
n-C10 (*n*-decane)	124-18-5		
n-C12 (*n*-undecane)	112-40-2		
n-C14 (*n*-tetradecane)	629-59-4		
n-C16 (*n*-hexadecane)	544-76-3		
n-C18 (*n*-octadecane)	593-45-3		
n-C20 (*n*-eicosane)	112-95-8		
n-C22 (*n*-docosane)	629-97-0		
n-C24 (*n*-tetracosane)	646-31-1		
n-C26 (*n*-hexacosane)	630-01-3		
n-C28 (*n*-octacosane)	630-02-4		
n-C30 (*n*-triacontane)	638-68-6		
Captafol	2425-06-1		

Table 3 – Additional Extractable Analytes[1, 2]			
Analyte	**CAS Registry**	**MDL[6]**	**ML[7]**
Captan	133-06-2		
Carbaryl	63-25-2		
Carbazole	86-74-8		
Carbofuran	1563-66-2		
Carboxin	5234-68-4		
Carbophenothion	786-19-6		
Chlordane [3,5]	57-74-9		
bis(2-Chloroethyl) ether [3,4]	111-44-4	5.7	17.1
Chloroneb	2675-77-6		
4-Chloroaniline	106-47-8		
Chlorobenzilate	510-15-6		
Chlorfenvinphos	470-90-6		
4-Chloro-2-methylaniline	95-69-2		
3-(Chloromethyl)pyridine hydrochloride	6959-48-4		
4-Chloro-2-nitroaniline	89-63-4		
Chlorpropham	101-21-3		
Chlorothalonil	1897-45-6		
1-Chloronaphthalene	90-13-1		
3-Chloronitribenzene	121-73-3		
4-Chloro-1,2-phenylenediamine	95-83-0		
4-Chloro-1,3-phenylenediamine	5131-60-2		
2-Chlorobiphenyl	2051-60-7		
Chlorpyrifos	2921-88-2		
Coumaphos	56-72-4		
m+*p*-Cresol	65794-96-9		
o-Cresol	95-48-7		
p-Cresidine	120-71-8		
Crotoxyphos	7700-17-6		
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5		
Cyanazine	21725-46-2		
Cycloate	1134-23-2		
p-Cymene	99-87-6		
Dacthal (DCPA)	1861-32-1		
4,4'-DDD [3]	72-54-8	2.8	8.4
4,4'-DDE [3]	72-55-9	5.6	16.8
4,4'-DDT [3]	50-29-3	4.7	14.1
Demeton-O	298-03-3		
Demeton-S	126-75-0		
Diallate (*cis* or *trans*)	2303-16-4		
2,4-Diaminotoluene	95-80-7		
Diazinon	333-41-5		
Dibenz(a,j)acridine	224-42-0		
Dibenzofuran	132-64-9		
Dibenzo(a,e)pyrene	192-65-4		
Dibenzothiophene	132-65-0		
1,2-Dibromo-3-chloropropane	96-12-8		
3,5-Dibromo-4-hydroxybenzonitrile	1689-84-5		
2,6-Di-*tert*-butyl-*p*-benzoquinone	719-22-2		

Table 3 – Additional Extractable Analytes[1, 2]			
Analyte	**CAS Registry**	**MDL[6]**	**ML[7]**
Dichlone	117-80-6		
2,3-Dichloroaniline	608-27-5		
2,3-Dichlorobiphenyl	16605-91-7		
2,6-Dichloro-4-nitroaniline	99-30-9		
2,3-Dichloronitrobenzene	3209-22-1		
1,3-Dichloro-2-propanol	96-23-1		
2,6-Dichlorophenol	120-83-2		
Dichlorvos	62-73-7		
Dicrotophos	141-66-2		
Dieldrin [3]	60-57-1	2.5	7.5
1,2:3,4-Diepoxybutane	1464-53-5		
Di(2-ethylhexyl) adipate	103-23-1		
Diethylstilbestrol	56-53-1		
Diethyl sulfate	64-67-5		
Dilantin (5,5-Diphenylhydantoin)	57-41-0		
Dimethoate	60-51-5		
3,3'-Dimethoxybenzidine	119-90-4		
Dimethylaminoazobenzene	60-11-7		
7,12-Dimethylbenz(a)anthracene	57-97-6		
3,3'-Dimethylbenzidine	119-93-7		
N,N-Dimethylformamide	68-12-2		
3,6-Dimethylphenathrene	1576-67-6		
alpha, *alpha*-Dimethylphenethylamine	122-09-8		
Dimethyl sulfone	67-71-0		
1,2-Dinitrobenzene	528-29-0		
1,3-Dinitrobenzene	99-65-0		
1,4-Dinitrobenzene	100-25-4		
Dinocap	39300-45-3		
Dinoseb	88-85-7		
Diphenylamine	122-39-4		
Diphenyl ether	101-84-8		
1,2-Diphenylhydrazine	122-66-7		
Diphenamid	957-51-7		
Diphenyldisulfide	882-33-7		
Disulfoton	298-04-4		
Disulfoton sulfoxide	2497-07-6		
Disulfoton sulfone	2497-06-5		
Endosulfan I [3,4]	959-98-8		
Endosulfan II [3,4]	33213-65-9		
Endosulfan sulfate [3]	1031-07-8	5.6	16.8
Endrin [3,4]	72-20-8		
Endrin aldehyde [3,4]	7421-93-4		
Endrin ketone [3,4]	53494-70-5		
EPN	2104-64-5		
EPTC	759-94-4		
Ethion	563-12-2		
Ethoprop	13194-48-4		
Ethyl carbamate	51-79-6		

Table 3 – Additional Extractable Analytes[1, 2]			
Analyte	**CAS Registry**	**MDL[6]**	**ML[7]**
Ethyl methanesulfonate	65-50-0		
Ethylenethiourea	96-45-7		
Etridiazole	2593-15-9		
Ethynylestradiol-3-methyl ether	72-33-3		
Famphur	52-85-7		
Fenamiphos	22224-92-6		
Fenarimol	60168-88-9		
Fensulfothion	115-90-2		
Fenthion	55-38-9		
Fluchloralin	33245-39-5		
Fluridone	59756-60-4		
Heptachlor [3]	76-44-8	1.9	5.7
Heptachlor epoxide [3]	1024-57-3	2.2	6.6
2,2',3,3',4,4',6-Heptachlorobiphenyl	52663-71-5		
2,2',4,4',5',6-Hexachlorobiphenyl	60145-22-4		
Hexachlorocyclopentadiene [3,4]	77-47-4		
Hexachlorophene	70-30-4		
Hexachloropropene	1888-71-7		
Hexamethylphosphoramide	680-31-9		
Hexanoic acid	142-62-1		
Hexazinone	51235-04-2		
Hydroquinone	123-31-9		
Isodrin	465-73-6		
2-Isopropylnapthalene	2027-17-0		
Isosafrole	120-58-1		
Kepone	143-50-0		
Leptophos	21609-90-5		
Longifolene	475-20-7		
Malachite green	569-64-2		
Malathion	121-75-5		
Maleic anhydride	108-31-6		
Merphos	150-50-5		
Mestranol	72-33-3		
Methapyrilene	91-80-5		
Methoxychlor	72-43-5		
2-Methylbenzothioazole	120-75-2		
3-Methylcholanthrene	56-49-5		
4,4'-Methylenebis(2-chloroaniline)	101-14-4		
4,4'-Methylenebis(N,N-dimethylaniline)	101-61-1		
4,5-Methylenephenanthrene	203-64-5		
1-Methylfluorene	1730-37-6		
Methyl methanesulfonate	66-27-3		
2-Methylnaphthalene	91-57-6		
Methylparaoxon	950-35-6		
Methyl parathion	298-00-0		
1-Methylphenanthrene	832-69-9		
2-(Methylthio)benzothiazole	615-22-5		
Metolachlor	5218-45-2		

Table 3 – Additional Extractable Analytes[1, 2]			
Analyte	**CAS Registry**	**MDL[6]**	**ML[7]**
Metribuzin	21087-64-9		
Mevinphos	7786-34-7		
Mexacarbate	315-18-4		
MGK 264	113-48-4		
Mirex	2385-85-5		
Molinate	2212-67-1		
Monocrotophos	6923-22-4		
Naled	300-76-5		
Napropamide	15299-99-7		
1,4-Naphthoquinone	130-15-4		
1-Naphthylamine	134-32-7		
2-Naphthylamine	91-59-8		
1,5-Naphthalenediamine	2243-62-1		
Nicotine	54-11-5		
5-Nitroacenaphthene	602-87-9		
2-Nitroaniline	88-74-4		
3-Nitroaniline	99-09-2		
4-Nitroaniline	100-01-6		
5-Nitro-*o*-anisidine	99-59-2		
4-Nitrobiphenyl	92-93-3		
Nitrofen	1836-75-5		
5-Nitro-*o*-toluidine	99-55-8		
Nitroquinoline-1-oxide	56-57-5		
N-Nitrosodi-*n*-butylamine [4]	924-16-3		
N-Nitrosodiethylamine [4]	55-18-5		
N-Nitrosodimethylamine [3,4]	62-75-9		
N-Nitrosodiphenylamine [3,4]	86-30-6		
N-Nitrosomethylethylamine [4]	10595-95-6		
N-Nitrosomethylphenylamine [4]	614-00-6		
N-Nitrosomorpholine [4]	59-89-2		
N-Nitrosopiperidine [4]	100-75-5		
N-Nitrosopyrrolidine [4]	930-55-2		
trans-Nonachlor	39765-80-5		
Norflurazon	27314-13-2		
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	40186-71-8		
Octamethyl pyrophosphoramide	152-16-9		
4,4'-Oxydianiline	101-80-4		
Parathion	56-38-2		
PCB-1016 [3,5]	12674-11-2		
PCB-1221 [3,5]	11104-28-2	30	90
PCB-1232 [3,5]	11141-16-5		
PCB-1242 [3,5]	53469-21-9		
PCB-1248 [3,5]	12672-29-6		
PCB-1254 [3,5]	11097-69-1	36	108
PCB-1260 [3,5]	11098-82-5		
PCB-1268 [3,5]	11100-14-4		
Pebulate	1114-71-2		
Pentachlorobenzene	608-93-5		

Table 3 – Additional Extractable Analytes[1, 2]			
Analyte	**CAS Registry**	**MDL[6]**	**ML[7]**
Pentachloronitrobenzene	82-68-8		
2,2',3,4',6-Pentachlorobiphenyl	68194-05-8		
Pentachloroethane	76-01-7		
Pentamethylbenzene	700-12-9		
Perylene	198-55-0		
Phenacetin	62-44-2		
cis-Permethrin	61949-76-6		
trans-Permethrin	61949-77-7		
Phenobarbital	50-06-6		
Phenothiazene	92-84-2		
1,4-Phenylenediamine	624-18-0		
1-Phenylnaphthalene	605-02-7		
2-Phenylnaphthalene	612-94-2		
Phorate	298-02-2		
Phosalone	2310-18-0		
Phosmet	732-11-6		
Phosphamidon	13171-21-6		
Phthalic anhydride	85-44-9		
alpha-Picoline (2-Methylpyridine)	109-06-8		
Piperonyl sulfoxide	120-62-7		
Prometon	1610-18-0		
Prometryn	7287-19-6		
Pronamide	23950-58-5		
Propachlor	1918-16-7		
Propazine	139-40-2		
Propylthiouracil	51-52-5		
Pyridine	110-86-1		
Resorcinol (1,3-Benzenediol)	108-46-3		
Safrole	94-59-7		
Simazine	122-34-9		
Simetryn	1014-70-6		
Squalene	7683-64-9		
Stirofos	22248-79-9		
Strychnine	57-24-9		
Styrene	100-42-5		
Sulfallate	95-06-7		
Tebuthiuron	34014-18-1		
Terbacil	5902-51-2		
Terbufos	13071-79-9		
Terbutryn	886-50-0		
alpha-Terpineol	98-55-5		
1,2,4,5-Tetrachlorobenzene	95-94-3		
2,2',4,4'-Tetrachlorobiphenyl	2437-79-8		
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	1746-01-6		
2,3,4,6-Tetrachlorophenol	58-90-2		
Tetrachlorvinphos	22248-79-9		
Tetraethyl dithiopyrophosphate	3689-24-5		
Tetraethyl pyrophosphate	107-49-3		

Table 3 – Additional Extractable Analytes[1, 2]			
Analyte	**CAS Registry**	**MDL[6]**	**ML[7]**
Thianaphthene (2,3-Benzothiophene)	95-15-8		
Thioacetamide	62-55-5		
Thionazin	297-97-2		
Thiophenol (Benzenethiol)	108-98-5		
Thioxanthone	492-22-8		
Toluene-1,3-diisocyanate	26471-62-5		
Toluene-2,4-diisocyanate	584-84-9		
o-Toluidine	95-53-4		
Toxaphene [3,5]	8001-35-2		
Triadimefon	43121-43-3		
1,2,3-Trichlorobenzene	87-61-6		
2,4,5-Trichlorobiphenyl	15862-07-4		
2,3,6-Trichlorophenol	933-75-5		
2,4,5-Trichlorophenol	95-95-4		
Tricyclazole	41814-78-2		
Trifluralin	1582-09-8		
1,2,3-Trimethoxybenzene	634-36-6		
2,4,5-Trimethylaniline	137-17-7		
Trimethyl phosphate	512-56-1		
Triphenylene	217-59-4		
Tripropyleneglycolmethyl ether	20324-33-8		
1,3,5-Trinitrobenzene	99-35-4		
Tris(2,3-dibromopropyl) phosphate	126-72-7		
Tri-p-tolyl phosphate	78-32-0		
O,O,O-Triethyl phosphorothioate	126-68-1		
Trithiane	291-29-4		
Vernolate	1929-77-7		

[1] Compounds that have been demonstrated amenable to extraction and gas chromatography
[2] Determine each analyte in the fraction that gives the most accurate result
[3] Priority Pollutant (40 CFR 423, Appendix A)
[4] See Section 1.2
[5] These compounds are mixtures of various isomers
[6] MDL values from the 1984 promulgated version of Method 624
[7] ML = Minimum Level – see Glossary for definition and derivation

Table 4 – Chromatographic Conditions and Characteristic m/z's for Base/Neutral Extractables							
	Retention Time (sec) [1]	Characteristic m/z's					
		Electron impact ionization			Chemical ionization		
Analyte		Primary	Second	Second	Methane		
N-Nitrosodimethylamine	385	42	74	44	…	…	…
bis(2-Chloroethyl) ether	704	93	63	95	63	107	109
bis(2-Chloroisopropyl) ether	799	45	77	79	77	135	137
Hexachloroethane	823	117	201	199	199	201	203
N-Nitrosodi-*n*-propylamine	830	130	42	101	…	…	…
Nitrobenzene	849	77	123	65	124	152	164
Isophorone	889	82	95	138	139	167	178
bis(2-Chloroethoxy) methane	939	93	95	123	65	107	137
1,2,4-Trichlorobenzene	958	180	182	145	181	183	209
Naphthalene	967	128	129	127	129	157	169
Hexachlorobutadiene	1006	225	223	227	223	225	227
Hexachlorocyclopentadiene	1142	237	235	272	235	237	239
2-Chloronaphthalene	1200	162	164	127	163	191	203
Acenaphthylene	1247	152	151	153	152	153	181
Dimethyl phthalate	1273	163	194	164	151	163	164
2,6-Dinitrotoluene	1300	165	89	121	183	211	223
Acenaphthene	1304	154	153	152	154	155	183
2,4-Dinitrotoluene	1364	165	63	182	183	211	223
Fluorene	1401	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	1409	204	206	141	…	…	…
Diethyl phthalate	1414	149	177	150	177	223	251
N-Nitrosodiphenylamine	1464	169	168	167	169	170	198
4-Bromophenyl phenyl ether	1498	248	250	141	249	251	277
alpha-BHC	1514	183	181	109	…	…	…
Hexachlorobenzene	1522	284	142	249	284	286	288
beta-BHC	1544	183	181	109	…	…	…
gamma-BHC	1557	181	183	109	…	…	…
Phenanthrene	1583	178	179	176	178	179	207
Anthracene	1592	178	179	176	178	179	207
delta-BHC	1599	183	109	181	…	…	…
Heptachlor	1683	100	272	274	…	…	…
Di-*n*-butyl phthalate	1723	149	150	104	149	205	279
Aldrin	1753	66	263	220			
Fluoranthene	1817	202	101	100	203	231	243
Heptachlor epoxide	1820	353	355	351	…	…	…
gamma-Chlordane	1834	373	375	377	…	…	…
Pyrene	1852	202	101	100	203	231	243
Benzidine [2]	1853	184	92	185	185	213	225
alpha-Chlordane	1854	373	375	377	…	…	…
Endosulfan I	1855	237	339	341	…	…	…
4,4'-DDE	1892	246	248	176	…	…	…
Dieldrin	1907	79	263	279	…	…	…
Endrin	1935	81	263	82	…	…	…
Endosulfan II	2014	237	339	341	…	…	…
4,4'-DDD	2019	235	237	165	…	…	…
Endrin aldehyde	2031	67	345	250	…	…	…

Table 4 – Chromatographic Conditions and Characteristic m/z's for Base/Neutral Extractables							
	Retention Time (sec) [1]	Characteristic m/z's					
		Electron impact ionization			Chemical ionization		
Analyte		Primary	Second	Second	Methane		
Butyl benzyl phthalate	2060	149	91	206	149	299	327
Endosulfan sulfate	2068	272	387	422	…	…	…
4,4'-DDT	2073	235	237	165	…	…	…
Chrysene	2083	228	226	229	228	229	257
3,3'-Dichlorobenzidine	2086	252	254	126	…	…	…
Benzo(a)anthracene	2090	228	229	226	228	229	257
bis(2-Ethylhexyl) phthalate	2124	149	167	279	149	…	…
Di-*n*-octyl phthalate	2240	149	43	57	…	…	…
Benzo(b)fluoranthene	2286	252	253	125	252	253	281
Benzo(k)fluoranthene	2293	252	253	125	252	253	281
Benzo(a)pyrene	2350	252	253	125	252	253	281
Indeno(1,2,3-cd) pyrene	2650	276	138	277	276	277	305
Dibenz(a,h)anthracene	2660	278	139	279	278	279	307
Benzo(ghi)perylene	2750	276	138	277	276	277	305
Toxaphene	…	159	231	233	…	…	…
PCB 1016	…	224	260	294	…	…	…
PCB 1221	…	190	224	260	…	…	…
PCB 1232	…	190	224	260	…	…	…
PCB 1242	…	224	260	294	…	…	…
PCB 1248	…	294	330	262	…	…	…
PCB 1254	…	294	330	362	…	…	…
PCB 1260	…	330	362	394	…	…	…

[1] Column: 30 m x 0.25 mm ID; 94% methyl, 5% phenyl, 1% vinyl bonded phase fused silica capillary
Conditions: 5 min at 30°C; 30 - 280 at 8°C per min; isothermal at 280°C until benzo(ghi)perylene elutes
Gas velocity: 30 cm/sec at 30°C (at constant pressure).

[2] See Section 1.2; included for tailing factor testing

Table 5 – Chromatographic Conditions and Characteristic m/z's for Acid Extractables							
		Characteristic m/z's					
		Electron impact ionization			Chemical ionization		
Analyte	Retention Time (sec) [1]	Prime	Second	Second	Methane		
2-Chlorophenol	705	128	64	130	129	131	157
Phenol	700	94	65	66	95	123	135
2-Nitrophenol	900	139	65	109	140	168	122
2,4-Dimethylphenol	924	122	107	121	123	151	163
2,4-Dichlorophenol	947	162	164	98	163	165	167
4-Chloro-3-methylphenol	1091	142	107	144	143	171	183
2,4,6-Trichlorophenol	1165	196	198	200	197	199	201
2,4-Dinitrophenol	1325	184	63	154	185	213	225
4-Nitrophenol	1354	65	139	109	140	168	122
2-Methyl-4,6-dinitrophenol	1435	198	182	77	199	227	239
Pentachlorophenol	1561	266	264	268	267	265	269

Column: 30 m x 0.25 mm ID; 94% methyl, 5% phenyl, 1% vinyl bonded phase fused silica capillary
Conditions: 5 min at 30°C; 30 - 250 at 8°C per min; isothermal at 280°C until pentachlorophenol elutes
Gas velocity: 30 cm/sec at 30°C (at constant pressure)

Table 6 – QC Acceptance Criteria – Method 625 [1]					
Analyte	**Range for Q (%) [2]**	**Limit for s (%) [3]**	**Range for $\overline{X}$ (%) [3]**	**Range for P, P_s (%) [3]**	**Limit for RPD (%)**
Acenaphthene	70-130	29	60-132	47-145	48
Acenaphthylene	60-130	45	54-126	33-145	74
Aldrin	7-152	39	7-152	D-166	81
Anthracene	58-130	40	43-120	27-133	66
Benzo(a)anthracene	42-133	32	42-133	33-143	53
Benzo(b)fluoranthene	42-140	43	42-140	24-159	71
Benzo(k)fluoranthene	25-146	38	25-146	11-162	63
Benzo(a)pyrene	32-148	43	32-148	17-163	72
Benzo(ghi)perylene	13-195	61	D-195	D-219	97
Benzyl butyl phthalate	43-140	36	D-140	D-152	60
beta-BHC	42-131	37	42-131	24-149	61
delta-BHC	D-130	77	D-120	D-120	129
bis(2-Chloroethyl)ether	52-130	65	43-126	12-158	108
bis(2-Chloroethoxy)methane	52-164	32	49-165	33-184	54
bis(2-Chloroisopropyl) ether	63-139	46	63-139	36-166	76
bis(2-Ethylhexyl) phthalate	43-137	50	29-137	8-158	82
4-Bromophenyl phenyl ether	70-130	26	65-120	53-127	43
2-Chloronaphthalene	70-130	15	65-120	60-120	24
4-Chlorophenyl phenyl ether	57-145	36	38-145	25-158	61
Chrysene	44-140	53	44-140	17-168	87
4,4'-DDD	D-135	56	D-135	D-145	93
4,4'-DDE	19-130	46	19-120	4-136	77
4,4'-DDT	D-171	81	D-171	D-203	135
Dibenz(a,h)anthracene	13-200	75	D-200	D-227	126
Di-*n*-butyl phthalate	52-130	28	8-120	1-120	47
3,3'-Dichlorobenzidine	18-213	65	8-213	D-262	108
Dieldrin	70-130	38	44-119	29-136	62
Diethyl phthalate	47-130	60	D-120	D-120	100
Dimethyl phthalate	50-130	110	D-120	D-120	183
2,4-Dinitrotoluene	53-130	25	48-127	39-139	42
2,6-Dinitrotoluene	68-137	29	68-137	50-158	48
Di-*n*-octyl phthalate	21-132	42	19-132	4-146	69
Endosulfan sulfate	D-130	42	D-120	D-120	70
Endrin aldehyde	D-189	45	D-189	D-209	75
Fluoranthene	47-130	40	43-121	26-137	66
Fluorene	70-130	23	70-120	59-121	38
Heptachlor	D-172	44	D-172	D-192	74
Heptachlor epoxide	70-130	61	71-120	26-155	101
Hexachlorobenzene	38-142	33	8-142	D-152	55
Hexachlorobutadiene	68-130	38	38-120	24-120	62
Hexachloroethane	55-130	32	55-120	40-120	52
Indeno(1,2,3-cd)pyrene	13-151	60	D-151	D-171	99
Isophorone	52-180	56	47-180	21-196	93
Naphthalene	70-130	39	36-120	21-133	65
Nitrobenzene	54-158	37	54-158	35-180	62
N-Nitrosodi-*n*-propylamine	59-170	52	14-198	D-230	87

Table 6 – QC Acceptance Criteria – Method 625 [1]					
Analyte	**Range for Q (%) [2]**	**Limit for s (%) [3]**	**Range for $\overline{X}$ (%) [3]**	**Range for P, P_s (%) [3]**	**Limit for RPD (%)**
PCB-1260	19-130	77	19-130	D-164	128
Phenanthrene	67-130	24	65-120	54-120	39
Pyrene	70-130	30	70-120	52-120	49
1,2,4-Trichlorobenzene	61-130	30	57-130	44-142	50
4-Chloro-3-methylphenol	68-130	44	41-128	22-147	73
2-Chlorophenol	55-130	37	36-120	23-134	61
2,4-Dichlorophenol	64-130	30	53-122	39-135	50
2,4-Dimethylphenol	58-130	35	42-120	32-120	58
2,4-Dinitrophenol	39-173	79	D-173	D-191	132
2-Methyl-4,6-dinitrophenol	56-130	122	53-130	D-181	203
2-Nitrophenol	61-163	33	45-167	29-182	55
4-Nitrophenol	35-130	79	13-129	D-132	131
Pentachlorophenol	42-152	52	38-152	14-176	86
Phenol	48-130	39	17-120	5-120	64
2,4,6-Trichlorophenol	69-130	35	52-129	37-144	58

[1] Acceptance criteria are based upon method performance data in Table 7 and from EPA Method 1625. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.
[2] Test concentration = 100 µg/mL
[3] Test concentration = 100 µg/L

Q = Calibration verification (Sections 7.3.1 and 13.4)
s = Standard deviation for four recovery measurements in the DOC test (Section 8.2.4).
$\overline{X}$ = Average recovery for four recovery measurements in the DOC test (Section 8.2.4).
P, P_s = MS/MSD recovery (Section 8.3.2, Section 8.4.2).
RPD = MS/MSD relative percent difference (RPD; Section 8.3.3).
D = Detected; result must be greater than zero.

Table 7 – Precision and Recovery as Functions of Concentration – Method 625 [1]			
Analyte	**Recovery, X' (µg/L)**	**Single analyst precision, s_r' (µg/L)**	**Overall precision, S' (µg/L)**
Acenaphthene	0.96C+0.19	0.15 $\overline{X}$ -0.12	0.21 $\overline{X}$ -0.67
Acenaphthylene	0.89C+0.74	0.24 $\overline{X}$ -1.06	0.26 $\overline{X}$ -0.54
Aldrin	0.78C+1.66	0.27 $\overline{X}$ -1.28	0.43 $\overline{X}$ +1.13
Anthracene	0.80C+0.68	0.21 $\overline{X}$ -0.32	0.27 $\overline{X}$ -0.64
Benzo(a)anthracene	0.88C-0.60	0.15 $\overline{X}$ +0.93	0.26 $\overline{X}$ -0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22 $\overline{X}$ +0.43	0.29 $\overline{X}$ +0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19 $\overline{X}$ +1.03	0.35 $\overline{X}$ +0.40
Benzo(a)pyrene	0.90C-0.13	0.22 $\overline{X}$ +0.48	0.32 $\overline{X}$ +1.35
Benzo(ghi)perylene	0.98C-0.86	0.29 $\overline{X}$ +2.40	0.51 $\overline{X}$ -0.44
Benzyl butyl phthalate	0.66C-1.68	0.18 $\overline{X}$ +0.94	0.53 $\overline{X}$ +0.92
beta-BHC	0.87C-0.94	0.20 $\overline{X}$ -0.58	0.30 $\overline{X}$ -1.94
delta-BHC	0.29C-1.09	0.34 $\overline{X}$ +0.86	0.93 $\overline{X}$ -0.17
bis(2-Chloroethyl)ether	0.86C-1.54	0.35 $\overline{X}$ -0.99	0.35 $\overline{X}$ +0.10
bis(2-Chloroethoxy)methane	1.12C-5.04	0.16 $\overline{X}$ +1.34	0.26 $\overline{X}$ +2.01
bis(2-Chloroisopropyl)ether	1.03C-2.31	0.24 $\overline{X}$ +0.28	0.25 $\overline{X}$ +1.04
bis(2-Ethylhexyl)phthalate	0.84C-1.18	0.26 $\overline{X}$ +0.73	0.36 $\overline{X}$ +0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13 $\overline{X}$ +0.66	0.16 $\overline{X}$ +0.66
2-Chloronaphthalene	0.89C+0.01	0.07 $\overline{X}$ +0.52	0.13 $\overline{X}$ +0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20 $\overline{X}$ -0.94	0.30 $\overline{X}$ -0.46
Chrysene	0.93C-1.00	0.28 $\overline{X}$ +0.13	0.33 $\overline{X}$ -0.09
4,4'-DDD	0.56C-0.40	0.29 $\overline{X}$ -0.32	0.66 $\overline{X}$ -0.96
4,4'-DDE	0.70C-0.54	0.26 $\overline{X}$ -1.17	0.39 $\overline{X}$ -1.04
4,4'-DDT	0.79C-3.28	0.42 $\overline{X}$ +0.19	0.65 $\overline{X}$ -0.58
Dibenz(a,h)anthracene	0.88C+4.72	0.30 $\overline{X}$ +8.51	0.59 $\overline{X}$ +0.25
Di-*n*-butyl phthalate	0.59C+0.71	0.13 $\overline{X}$ +1.16	0.39 $\overline{X}$ +0.60
3,3'-Dichlorobenzidine	1.23C-12.65	0.28 $\overline{X}$ +7.33	0.47 $\overline{X}$ +3.45
Dieldrin	0.82C-0.16	0.20 $\overline{X}$ -0.16	0.26 $\overline{X}$ -0.07
Diethyl phthalate	0.43C+1.00	0.28 $\overline{X}$ +1.44	0.52 $\overline{X}$ +0.22
Dimethyl phthalate	0.20C+1.03	0.54 $\overline{X}$ +0.19	1.05 $\overline{X}$ -0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12 $\overline{X}$ +1.06	0.21 $\overline{X}$ +1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14 $\overline{X}$ +1.26	0.19 $\overline{X}$ +0.35
Di-*n*-octyl phthalate	0.76C-0.79	0.21 $\overline{X}$ +1.19	0.37 $\overline{X}$ +1.19
Endosulfan sulfate	0.39C+0.41	0.12 $\overline{X}$ +2.47	0.63 $\overline{X}$ -1.03
Endrin aldehyde	0.76C-3.86	0.18 $\overline{X}$ +3.91	0.73 $\overline{X}$ -0.62
Fluoranthene	0.81C+1.10	0.22 $\overline{X}$ +0.73	0.28 $\overline{X}$ -0.60
Fluorene	0.90C-0.00	0.12 $\overline{X}$ +0.26	0.13 $\overline{X}$ +0.61
Heptachlor	0.87C-2.97	0.24 $\overline{X}$ -0.56	0.50 $\overline{X}$ -0.23
Heptachlor epoxide	0.92C-1.87	0.33 $\overline{X}$ -0.46	0.28 $\overline{X}$ +0.64
Hexachlorobenzene	0.74C+0.66	0.18 $\overline{X}$ -0.10	0.43 $\overline{X}$ -0.52
Hexachlorobutadiene	0.71C-1.01	0.19 $\overline{X}$ +0.92	0.26 $\overline{X}$ +0.49
Hexachloroethane	0.73C-0.83	0.17 $\overline{X}$ +0.67	0.17 $\overline{X}$ +0.80

Table 7 – Precision and Recovery as Functions of Concentration – Method 625 [1]			
Analyte	**Recovery, X' (µg/L)**	**Single analyst precision, s_r' (µg/L)**	**Overall precision, S' (µg/L)**
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29 $\overline{X}$ +1.46	0.50 $\overline{X}$ +0.44
Isophorone	1.12C+1.41	0.27 $\overline{X}$ +0.77	0.33 $\overline{X}$ +0.26
Naphthalene	0.76C+1.58	0.21 $\overline{X}$ -0.41	0.30 $\overline{X}$ -0.68
Nitrobenzene	1.09C-3.05	0.19 $\overline{X}$ +0.92	0.27 $\overline{X}$ +0.21
N-Nitrosodi-*n*-propylamine	1.12C-6.22	0.27 $\overline{X}$ +0.68	0.44 $\overline{X}$ +0.47
PCB-1260	0.81C-10.86	0.35 $\overline{X}$ +3.61	0.43 $\overline{X}$ +1.82
Phenanthrene	0.87C-0.06	0.12 $\overline{X}$ +0.57	0.15 $\overline{X}$ +0.25
Pyrene	0.84C-0.16	0.16 $\overline{X}$ +0.06	0.15 $\overline{X}$ +0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15 $\overline{X}$ +0.85	0.21 $\overline{X}$ +0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23 $\overline{X}$ +0.75	0.29 $\overline{X}$ +1.31
2-Chlorophenol	0.78C+0.29	0.18 $\overline{X}$ +1.46	0.28 $\overline{X}$ +0.97
2,4-Dichlorophenol	0.87C+0.13	0.15 $\overline{X}$ +1.25	0.21 $\overline{X}$ +1.28
2,4-Dimethylphenol	0.71C+4.41	0.16 $\overline{X}$ +1.21	0.22 $\overline{X}$ +1.31
2,4-Dinitrophenol	0.81C-18.04	0.38 $\overline{X}$ +2.36	0.42 $\overline{X}$ +26.29
2-Methyl-4,6-Dinitrophenol	1.04C-28.04	0.05 $\overline{X}$ +42.29	0.26 $\overline{X}$ +23.10
2-Nitrophenol	1.07C-1.15	0.16 $\overline{X}$ +1.94	0.27 $\overline{X}$ +2.60
4-Nitrophenol	0.61C-1.22	0.38 $\overline{X}$ +2.57	0.44 $\overline{X}$ +3.24
Pentachlorophenol	0.93C+1.99	0.24 $\overline{X}$ +3.03	0.30 $\overline{X}$ +4.33
Phenol	0.43C+1.26	0.26 $\overline{X}$ +0.73	0.35 $\overline{X}$ +0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16 $\overline{X}$ +2.22	0.22 $\overline{X}$ +1.81

[1] Regressions based on data from Reference 2

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.

Table 8 – Suggested Internal and Surrogate Standards		
	Range for Surrogate Recovery (%) [1]	
Base/neutral fraction	**Calibration verification**	**Recovery from samples**
Acenaphthalene-d_8	66 - 152	33 - 168
Acenaphthene-d_{10}	71 - 141	30 - 180
Aniline-d_5		
Anthracene-d_{10}	58 - 171	23 - 142
Benzo(a)anthracene-d_{12}	28 - 357	22 - 329
Benzo(a)pyrene-d_{12}	32 - 194	32 - 194
4-Chloroaniline-d_4	1 - 145	1 - 145
bis(2-Chloroethyl) ether-d_8	52 - 194	25 - 222
Chrysene-d_{12}	23 - 290	23 - 290
Decafluorobiphenyl		
4,4'-Dibromobiphenyl		
4,4'-Dibromooctafluorobiphenyl		
1,4-Dichlorobenzene-d_4	65 - 153	11 - 245
2,2'-Difluorobiphenyl		
Dimethyl phthalate-d_6	47 - 211	1 - 500
Fluoranthene-d_{10}	47 - 215	30 - 187
Fluorene-d_{10}	61 - 164	38 - 172
4-Fluoroaniline		
1-Fluoronaphthalene		
2-Fluoronaphthalene		
2-Methylnaphthalene-d_{10}	50 - 150	50 - 150
Naphthalene-d_8	71 - 141	22 - 192
Nitrobenzene-d_5	46 - 219	15 - 314
2,3,4,5,6-Pentafluorobiphenyl		
Perylene-d_{12}		
Phenanthrene-d_{10}	67 - 149	34 - 168
Pyrene-d_{10}	48 - 210	28 - 196
Pyridine-d_5		
Acid fraction		
2-Chlorophenol-d_4	55 - 180	33 - 180
2,4-Dichlorophenol-d_3	64 - 157	34 - 182
4,6-Dinitro-2-methylphenol-d_2	56 - 177	22 - 307
2-Fluorophenol		
4-Methylphenol-d_8	25 - 111	25 - 111
2-Nitrophenol-d_4	61 - 163	37 - 163
4-Nitrophenol-d_4	35 - 287	6 - 500
Pentafluorophenol		
2-Perfluoromethylphenol		
Phenol-d_5	48 - 208	8 - 424

[1] Recovery from samples is the wider of the criteria in the CLP SOW for organics or in Method 1625

Table 9A – DFTPP Key m/z's and Abundance Criteria for Quadrupole Instruments [1]	
m/z	**Abundance criteria**
51	30 - 60 percent of m/z 198
68	Less than 2 percent of m/z 69
70	Less than 2 percent of m/z 69
127	40 - 60 percent of base peak m/z 198
197	Less than 1 percent of m/z 198
198	Base peak, 100 percent relative abundance
199	5 - 9 percent of m/z 198
275	10 - 30 percent of m/z 198
365	Greater than 1 percent of m/z 198
441	Present but less than m/z 443
442	40 - 100 percent of m/z 198
443	17 - 23 percent of m/z 442

[1] Criteria in these tables are for quadrupole and time-of-flight instruments. Alternative tuning criteria may be used for other instruments, provided method performance is not adversely affected.

Table 9B – DFTPP Key m/z's and Abundance Criteria for Time-of-flight Instruments [1]	
m/z	**Abundance criteria**
51	10 - 85 percent of the base peak
68	Less than 2 percent of m/z 69
70	Less than 2 percent of m/z 69
127	10 - 80 percent of the base peak
197	Less than 2 percent of Mass 198
198	Base peak, or greater than 50% of m/z 442
199	5 - 9 percent of m/z 198
275	10 - 60 percent of the base peak
365	Greater than 0.5 percent of m/z 198
441	Less than 150 percent of m/z 443
442	Base peak or greater than 30 percent of m/z 198
443	15 - 24 percent of m/z 442

[1] Criteria in these tables are for quadrupole and time-of-flight instruments. Alternative tuning criteria may be used for other instruments, provided method performance is not adversely affected.

21. Figures

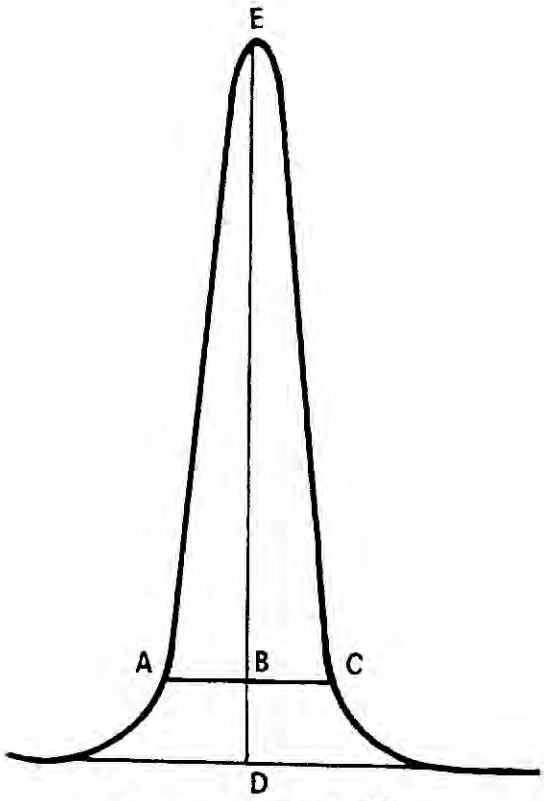

Figure 1 Tailing factor calculation

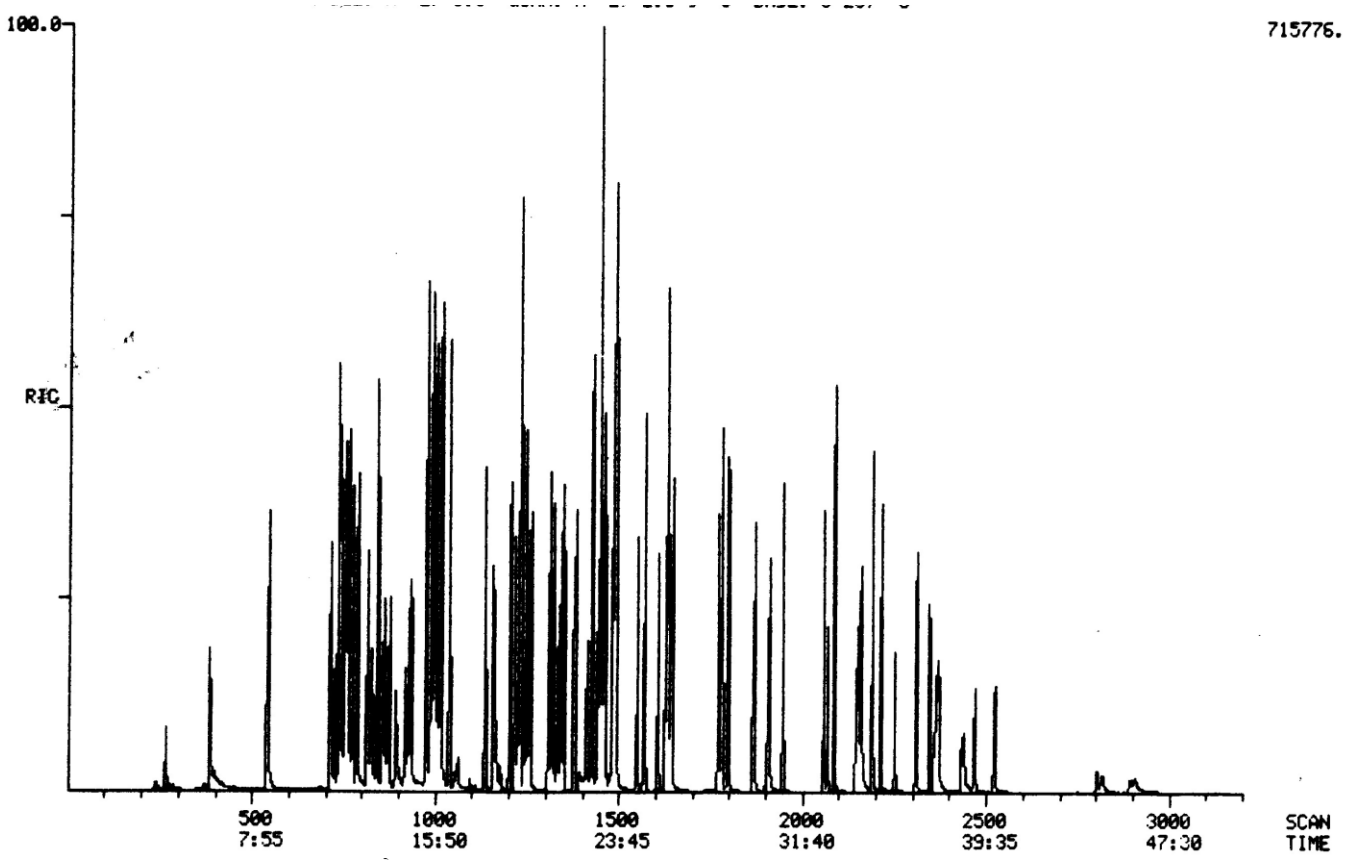

Figure 2 Chromatogram of combined acid/base/neutral standard

22. Glossary

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

22.1 Units of weight and measure and their abbreviations

22.1.1 Symbols

ºC	degrees Celsius
µg	microgram
µL	microliter
<	less than
>	greater than
≤	less than or equal to
%	percent

22.1.2 Abbreviations (in alphabetical order)

cm	centimeter
g	gram
h	hour
ID	inside diameter
in.	inch
L	liter
M	Molecular ion
m	mass or meter
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

22.2 Definitions and acronyms (in alphabetical order)

Analyte – A compound or mixture of compounds (e.g., PCBs) tested for by this method. The analytes are listed in Tables 1 - 3.

Batch – See Extraction

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.

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 mid-point calibration standard used to verify calibration. See Sections 7.3 and 13.4.

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.

Extraction Batch – A set of up to 20 field samples (not including QC samples) started through the extraction process on a given 12-hour shift (Section 3.1). Each extraction batch must be accompanied by a blank (Section 8.5), a laboratory control sample (LCS, Section 8.4), and a matrix spike and duplicate (MS/MSD; Section 8.3), resulting in a minimum of five analyses (1 sample, 1 blank, 1 LCS, 1 MS, and 1 MSD) and a maximum of 24 analyses (20 field samples, 1 blank, 1 LCS, 1 MS, and 1 MSD) for the batch. If greater than 20 samples are to be extracted in a 12-hour shift, the samples must be separated into extraction batches of 20 or fewer samples.

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 the 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 an extract or standard solution in a known amount and used as a reference for quantitation of the analytes of interest and surrogates. In this method the internal standards are stable isotopically labeled analogs of selected method analytes (Table 8). Also see Internal standard quantitation.

Internal standard quantitation – A means of determining the concentration of an analyte of interest (Tables 1 - 3) by reference to a compound not expected to be found in a sample.

DOC – Initial demonstration of capability (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. An 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; Section 8.4) – 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.

Laboratory fortified sample matrix – See Matrix spike

Laboratory reagent blank – A blank run on laboratory reagents; e.g., methylene chloride (Section 11.1.5).

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 – 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 Tables 1, 2 and 3. As noted in Sec. 1.5, use the MDLs in Tables 1, 2, and 3 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, or matrix spike (a QC sample type)

MSD – Matrix spike duplicate (a QC sample type)

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

Preparation blank – See blank

Quality control check sample (QCS) – See Laboratory Control Sample

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 7.2.2.

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 of 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.

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

SPE – Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous solution by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

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, authenticity, and concentration of the standard.

Surrogate – A compound unlikely to be found in a sample, and which is spiked into sample in a known amount before extraction or other processing, and is quantitated with the same procedures used to quantify other sample components. The purpose of the surrogate is to monitor method performance with each sample.