METHOD 608, REVISION A—ORGANOCHLORINE PESTICIDES AND PCBS BY GC/HSD

Method 608A, June 6, 2013

1. Scope and Application

1.1 This method is for determination of organochlorine pesticides and polychlorinated biphenyls (PCBs) in industrial discharges and other environmental samples by gas chromatography (GC) combined with a halogen-specific detector (HSD; e.g., electron capture, electrolytic conductivity), as provided under 40 CFR 136.1. This revision is based on a previous protocol (Reference 1), on the revision promulgated October 26, 1984 (49 FR 43234), on an interlaboratory method validation study (Reference 2), and on EPA Method 1656. The analytes that may be qualitatively and quantitatively determined using this method and their CAS Registry numbers are listed in Table 1.

1.2 This method may be extended to determine the analytes listed in Table 2. However, extraction or gas chromatography of some of these analytes may make quantitative determination difficult.

1.3 When this method is used to analyze unfamiliar samples for an analyte listed in Table 1 or 2, analyte identification must be supported by at least one additional qualitative and quantitative technique. This method gives analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for the analytes listed in Tables 1 and 2 using the extract produced by this method.

Comment [BR1]: Clarify.

1.4 The large number of analytes in Tables 1 and 2 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 Table 1 must be determined, at a minimum, and QC testing must be performed for these analytes. The analytes in Table 1 and some of the analytes in Table 2 have been identified as Toxic Pollutants (40 CFR 401.15), expanded to a list of Priority Pollutants (40 CFR 423, appendix A).

1.5 In this revision to Method 608, Chlordane has been listed as the alpha- and gamma-isomers. Reporting may be by the individual isomers, or as the sum of the concentrations of these isomers, as requested or required by a regulatory/control authority or in a permit. Toxaphene and the PCBs have been moved from Table 1 to Table 2 (Additional Analytes) to distinguish these analytes from the analytes required in quality control tests

Comment [BR2]: Specify in Table 1 also.

(Table 1). QC acceptance criteria for Toxaphene and the PCBs have been retained in Table 5 and may continue to be applied if desired, or if requested or required by a regulatory/control authority or in a permit. Method 1668C may be useful for determination of PCBs as individual chlorinated biphenyl congeners, and Method 1699B may be useful for determination of the pesticides listed in this method. At the time of writing of this revision, Methods 1668C and 1699B had not been approved for use at 40 CFR part 136.

1.6 Method detection limits (MDLs; 40 CFR 136 appendix B) for the analytes in Table 1, and some of the analytes in Table 2, are listed in Table 3. These MDLs were determined in reagent water (Reference 3). The MDL for an analyte in a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

Comment [BR3]: Cover letter re general detection and quantitation issues.

Comment [BR4]: Take the MDLs out; some are not believable.

1.7 The sample extraction and concentration steps in this method are essentially the same as in Methods 606, 609, 611, and 612. Thus, a single sample may be extracted to measure the analytes included in the scope of each of these methods.

1.8 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. Method modifications that are permitted are described at 40 CFR 136.6 and in Section 8.1.2 of this method. Any modification beyond those expressly permitted shall be considered a major modification subject to application and approval of an alternate test procedure under 40 CFR 136.4 and 136.5. For regulatory compliance, the modification must be demonstrated to produce results equivalent or superior to results produced by this method when applied to relevant wastewaters (Section 8.3).

1.9 This method is restricted to use by or under the supervision of analysts experienced in the use of GC/HSD. The laboratory must demonstrate the ability to generate acceptable results with this method using the procedure in Section 8.2.

1.10 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, the amount required to meet an MDL or reporting limit (~~typically 1 L~~Typically between 40mL and 1L, based on extraction technique), is extracted with methylene chloride using a separatory funnel or continuous liquid/liquid extractor. The extract is dried and concentrated ~~to~~ for cleanup, if required. After cleanup, or if cleanup is not required, the extract is concentrated to the volume necessary to meet the required compliance or detection limit, and analyzed by GC/HSD.

2.2 Qualitative identification of an analyte in the extract is performed using the retention times and determined concentrations on dissimilar GC columns. Quantitative analysis is

performed using the peak areas for the analyte on the dissimilar columns and the external or internal standard technique.

2.3 Gel permeation chromatography (GPC), Florisil, alumina, solid-phase extraction (SPE), and an elemental sulfur cleanup procedure are provided to aid in elimination of interferences that may be encountered.

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. All materials used in the analysis must be demonstrated free from contamination and interferences by running blanks initially and with each extraction batch (samples started through the extraction process in a given 24-hour period, to a maximum of 20 samples). 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. All materials used must be routinely demonstrated to be free from interferences under the conditions of the analysis by running blanks as described in Section 8.5.

3.2 Glassware must be scrupulously cleaned (Reference 4). 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 excessively or for long periods of time. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.3 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. The phthalate esters generally appear in the chromatogram as large late eluting peaks, especially in the 15 and 50% fractions from Florisil. Common flexible plastics contain varying amounts of phthalates that may be extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding use of non-fluoropolymer plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination (References 5 and 6). Interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

Comment [BR5]: Allow height?

Comment [BR6]: Need to add acid cleanup for PCBs (add in Section 11).

Comment [BR7]: Higher temperatures cause active sites; recommend removing this line (check with laboratory for specifics).

3.4 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 the cleanup procedures in Section 11 may aid in eliminating these interferences. EPA has provided guidance that may aid in overcoming matrix interferences (Reference 7); however, unique samples may require additional cleanup approaches to achieve the MDLs listed in Table 3.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level 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) should also be made available to all personnel involved in sampling handling and chemical analysis. Additional references to laboratory safety are available and have been identified (References 8 - 10) 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: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic analytes should be prepared in a chemical fume hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

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 achieve 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 ~~(generally 1 L or 1 quart),~~ 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 use a glass or fluoropolymer container and tubing for sample collection. 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 sample contamination. An integrating flow meter is required to collect flow proportional composites. The sample container must be kept refrigerated at <6 °C and protected from light during compositing.

5.2. Labware

5.2.1 Extraction

5.2.1.1 pH measurement

5.2.1.1.1 pH meter, with combination glass electrode

5.2.1.1.2 pH paper, wide range (Hydrion Papers, or equivalent)

5.2.1.2 Separatory funnel—Size appropriate to hold the sample and extraction solvent volumes, equipped with fluoropolymer stopcock.

5.2.1.3 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 6841-10 or equivalent.)

5.2.1.3.1 Round-bottom flask, ~~500 mL~~, with heating mantle

5.2.1.3.2 Condenser, Graham, to fit extractor

5.2.2 Filtration

5.2.2.1 Glass powder funnel, 125- to 250-mL

5.2.2.2 Filter paper for above, Whatman 41, or equivalent

5.2.3 Drying column

5.2.3.1 Chromatographic column—approximately 400 mm long x 15 mm ID, with fluoropolymer stopcock and coarse frit filter disc (Kontes 42054 or equivalent).

5.2.3.2 Glass wool—Pyrex, extracted with methylene chloride or baked at 450 °C for 1 hour minimum

5.2.4 Column for Florisil or alumina cleanup—approximately 300 mm long x 10 mm ID, with fluoropolymer stopcock. Cartridges packed with florisil are a commercially available alternative

5.2.5 Concentration/evaporation

5.2.5.1 Kuderna-Danish concentrator

5.2.5.1.1 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes 570050-1025 or equivalent). Calibration must be checked at the volumes employed for extract volume measurement. A ground-glass stopper is used to prevent evaporation of extracts.

5.2.5.1.2 Evaporative flask, Kuderna-Danish—500-mL (Kontes 570001-0500 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.

5.2.5.1.3 Snyder column, Kuderna/Danish—Three-ball macro (Kontes 503000-0121, or equivalent)

5.2.5.1.4 Snyder column—Two-ball micro (Kontes 569001-0219, or equivalent)

5.2.5.1.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2 °C), installed in a hood.

5.2.5.1.6 Nitrogen evaporation device—Equipped with heated bath that can be maintained at 35 to 40 °C (N-Evap, Organomation Associates, Inc., Turbovap, Biotage or equivalent)

5.2.5.2 Rotary evaporator – Buchi/Brinkman-American Scientific No. E5045-10, or equivalent, equipped with a variable temperature

water bath, vacuum source with shutoff valve at the evaporator, and vacuum gauge. A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

5.2.5.2.1 Round-bottom flask – 100-mL and 500-mL or larger, with ground-glass fitting compatible with the rotary evaporator

5.2.5.3 Boiling chips—Glass, silicon carbide, or equivalent, approximately 10/40 mesh. Heat at 400 °C for 30 minutes, or solvent rinse or Soxhlet extract with methylene chloride.

5.3 Vials

5.3.1 Extract storage—10- to 15-mL, amber glass, with fluoropolymer-lined screw cap

5.3.2 GC autosampler—1- to 5-mL, amber glass, with fluoropolymer-lined screw- or crimp-cap, to fit GC autosampler

5.4 Balances

5.4.1 Analytical—capable of accurately weighing 0.1 mg

5.4.2 Top loading—capable of weighing 10 mg

5.5 Sample cleanup

Comment [BR8]: Add acid cleanup for PCBs here.

5.5.1 Automated gel permeation chromatograph—~~Analytical Biochemical Labs, Inc. GPC Autoprep 1002, or equivalent~~

Comment [BR9]: No longer in business.

5.5.1.1 Column—600 to 700 mm long x 25 mm ID, packed with 70 - 75 g of SX-3 biobeads (Analytical Biochem, or equivalent)

5.5.1.2 Syringe—10-mL, with Luer fitting

5.5.1.3 Syringe-filter holder—stainless steel, and glass fiber or fluoropolymer filters (Gelman Acrodisc, 1 to 5 µ, or equivalent).

5.5.1.4 UV detector—254-nm, preparative or semi-prep flow cell: (Isco, Inc., Type 6; Schmadzu, 5 mm path length; Beckman_Altex 152W, 8 µL micro-prep flow cell, 2 mm path; Pharmacia UV-1, 3 mm flow cell; LDC Milton-Roy UV-3, monitor #1203; or equivalent).

Comment [BR10]: Remove all vendors.

5.5.2 Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature (± 5 °C) in the range of 105-250 °C.

5.5.3 Vacuum system and cartridges for solid-phase extraction (SPE).

5.5.3.1 Vacuum system—Capable of achieving 0.1 bar (house vacuum, vacuum pump, or water aspirator), with vacuum gauge.

5.5.3.2 VacElute Manifold (Analytichem International, or equivalent).

5.5.3.3 Vacuum trap—Made from 500-mL sidearm flask fitted with single-hole rubber stopper and glass tubing.

5.5.3.4 Rack for holding 50-mL volumetric flasks in the manifold.

5.5.3.5 Column—Mega Bond Elut, Non-polar, C18 Octadecyl, 10 g/60 mL (Analytichem International Cat. No. 607H060, or equivalent)

5.5.4 Sulfur removal tube—40- to 50-mL bottle, test tube, or Erlenmeyer flask with fluoropolymer-lined screw cap

5.6 Centrifuge apparatus

5.6.1 Centrifuge—Capable of rotating 500-mL centrifuge bottles or 15-mL centrifuge tubes at 5,000 rpm minimum

5.6.2 Centrifuge bottle—500-mL, with screw cap, to fit centrifuge

5.6.3 Centrifuge tube—15-mL, with screw cap, to fit centrifuge

5.7 Miscellaneous labware—graduated cylinders, pipettes, beakers, volumetric flasks, vials, syringes, and other labware necessary to support the operations in this method

5.8 Gas chromatograph—Dual column with simultaneous split/splitless, temperature programmable split/splitless (PTV), or on-column injection; temperature program with isothermal holds, and all required accessories including syringes, analytical columns, gases, and detectors. An autosampler is highly recommended because it injects volumes more reproducibly than volumes injected manually.

5.8.1 Columns and operating conditions—See Footnote 2 to Table 3. Other columns may be used provided performance requirements in this method are met.

Comment [BR11]: Don't believe they are still in business.

Comment [mw12]: As we discussed, some laboratories may use single column with follow-up confirmation on another GC with a different column.

5.8.1.1 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.

5.8.2 Detector—Halide specific detector (electron capture (ECD), electrolytic conductivity (ELCD), or equivalent). The ECD has proven effective in the analysis of wastewaters for the analytes listed in Tables 1 and 2, and was used to develop the method performance in Section 17 and Tables 5 and 6. Section 12.1 contains a statement concerning use of alternate detectors.

5.8.3 Data system—A computer system must be interfaced to the GC that allows continuous acquisition and storage of data from the detectors throughout the chromatographic program. The computer must have software that allows searching GC data for specific analytes, and for plotting responses versus time. Software must also be available that allows integrating peak areas in selected retention time windows and calculating concentrations of the analytes.

6. Reagents and Standards

6.1 pH adjustment

6.1.1 Sodium hydroxide solutions

6.1.1.1 Concentrated (10 M)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.1.1.2 Dilute (1 M)—Dissolve 40 g NaOH in 1 L of reagent water.

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

6.1.3 Hydrochloric acid—Reagent grade, 6N

6.2 Sodium thiosulfate—(ACS) granular.

6.3 Sodium sulfate—Sodium sulfate, reagent grade, granular anhydrous ~~(Baker 3375, or equivalent)~~, rinsed with methylene chloride (20 mL/g), baked in a shallow tray at 450 °C for 1 hr minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw cap which prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate suitable for use.

6.4 Reagent water—Reagent water is defined as a water in which the analytes of interest and interfering compounds are not observed at the MDLs of the analytes in this method.

6.5 Solvents—methylene chloride, acetone, methanol, hexane, acetonitrile, and isooctane, high purity pesticide quality, or equivalent, demonstrated to be free of the analytes and interferences (Section 3). Purification of solvents by distillation in all-glass systems may be required.

6.6 Ethyl ether—Nanograde, redistilled in glass if necessary

Comment [BR13]: Recommend ether not needed for this test.

6.6.1 Ethyl ether must be shown to be free of peroxides before use, as indicated by EM Laboratories Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, add 20 mL of ethyl alcohol preservative to each liter of ether.

6.7 Materials for sample cleanup

6.7.1 Florisil—PR grade (60/100 mesh), activated at 650 - 700 °C, stored in the dark in a glass container with fluoropolymer-lined screw cap. Activate each batch immediately prior to use for 16 hours minimum at 130 °C in a foil-covered glass container and allow to cool. Alternatively, 500 mg cartridges ~~(J.T. Baker, or equivalent)~~ may be used.

6.7.2 Solutions for ~~solid-phase extraction~~cleanup columns.

6.7.2.1 SPE cartridge calibration solution—2,4,6-trichlorophenol, 0.1 µg/mL in acetone.

6.7.2.2 SPE elution solvent—methylene chloride:acetonitrile:hexane (50:3:47).

Comment [BR14]: Recommend hexane/acetone or manufacturer instructions.

6.7.3 Alumina, neutral, Brockman Activity I, 80-200 mesh (Fisher Scientific certified, or equivalent). Heat in a glass bottle for 16 hours at 400 to 450 °C. Seal and cool to room temperature. Add 7% (w/w) reagent water and mix for 10 to 12 hours. Keep bottle tightly sealed.

6.7.4 Sulfur removal

6.7.4.1 Copper foil or powder—Fisher, Alfa Aesar, or equivalent. Cut copper foil into approximately 1-cm squares. Copper must be activated on each day it will be used, as described below.

6.7.4.1.1 Place the quantity of copper needed for sulfur removal (Section 11.6.1.3) in a ground-glass-stoppered Erlenmeyer flask or bottle. Cover the foil or powder with methanol.

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

6.7.4.1.3 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.

6.7.4.1.4 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. Store in a stoppered flask under nitrogen until used.

6.7.4.2 Tetrabutylammonium sulfite (TBA sulfite)

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

6.7.4.2.2 Sodium sulfite, Na_2SO_3

6.7.4.2.3 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.

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

6.8 GPC calibration solution

6.8.1 Prepare a solution in methylene chloride containing 25 mg/mL corn oil, 1.0 mg/mL bis(2-ethylhexyl) phthalate (BEHP), 0.02 mg/mL perylene, and 0.08 mg/mL sulfur, 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:

6.8.2 Weigh 8.0 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 2.0 mg perylene and add to flask. Bring to volume with methylene chloride and mix thoroughly.

6.8.3 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.

6.9 Standard solutions—Purchase as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepare from materials of known purity and composition. If compound purity is 96% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, store in the dark at 20 to -10 °C in screw-cap vials with fluoropolymer-lined caps. ~~Place a mark on the vial at the level of the solution so that solvent evaporation loss can be detected.~~ Bring the vial to room temperature prior to use to redissolve any precipitate. ~~Add solvent if loss has occurred.~~

Comment [BR15]: Should not put solutions in the freezer; use vendor instructions.

6.9.1 Stock standard solutions—Standard solutions may be prepared from pure standard materials or purchased as certified solutions. Traceability must be to a national standard, when available. Prepare in isooctane. Observe the safety precautions in Section 4. The following procedure may be used to prepare standards from neat materials. Replace stock solutions after 12 months or as recommended by a standards vendor or sooner if comparison with quality control check standards indicates a change in concentration.

6.9.1.1 Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 10 mg of aldrin in a 10-mL ground-glass-stoppered volumetric flask and fill to the mark with isooctane. Larger volumes may be used at the convenience of the laboratory. After the aldrin is completely dissolved, transfer the solution to a 15-mL vial with fluoropolymer-lined cap.

6.9.1.2 Check for signs of degradation prior to preparation of calibration or performance-test standards.

6.9.1.3 ~~Replace stock solutions after 12 months, or sooner if comparison with quality control check standards indicates a change in concentration.~~

6.9.2 Calibration solutions—It is necessary to prepare calibration solutions for the analytes of interest (Section 1.4) only. Other analytes may be included as desired.

6.9.2.1 Prepare calibration standards for the analytes of interest and surrogates at a minimum of ~~three~~ five concentration levels ~~(5 is suggested)~~ by adding appropriate volumes of one or more stock standards to volumetric flasks. One of the calibration standards should be at a concentration at or below the quantitation limit~~near the MDL~~ and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC system. A minimum of six concentration levels is required for a non-linear (e.g., quadratic) calibration (Section 7.5.2 or 7.6.2). Suggested calibration solution concentrations and calibrations groups are listed in Table 4. Other concentrations and groups may be used provided all QC requirements in this method are met.

Comment [BR16]: Allow single point for Aroclors other than 1016/1260?

Comment [BR17]: Remove concentrations from Table 4.

Comment [BR18]: Suggest removing Table 4 altogether since these are not the compounds normally analyzed by Method 608.

6.9.2.1.1 Analytes with calibration data in Table 4—The analytes in each calibration group in Table 4 were chosen so that each analyte would be separated from the others by approximately 1 minute on the primary column. The concentrations were chosen to bracket the working range of the ECD. Because the response of the ELCD is less for some analytes than that of the ECD, it may be necessary to prepare solutions at different concentrations than those in Table 4, or to inject a larger volume of the calibration solutions when the ELCD is used. ~~Add an aliquot of the surrogate standard(s) (Section 6.9.4) to each solution.~~ If the internal standard method is used, add an aliquot of the internal standard(s) solution (Section 6.9.3) to each solution.

Comment [BR19]: Remove Table 4 and everything related.

6.9.2.1.2 Analytes without calibration data in Table 4—Prepare calibration standards at a minimum of ~~3~~ 5 concentration levels ~~(5 is suggested)~~ in as many solutions as necessary to assure that all analytes can be determined separately. Add ~~surrogate(s) and~~ internal standard(s) (if used) per Section 6.9.2.1.1.

6.9.2.1.3 Combined QC standard—To preclude periodic analysis of all of the individual calibration standards, prepare a ~~combined QC standard~~CCV containing all single component analytes of interest at the same level as the mid-point calibration standard.

Comment [BR20]: Should be called a CCV.

Add a second source ICV

6.9.3 Internal standard solution—If the internal standard calibration technique is to be used, prepare pentachloronitrobenzene (PCNB) at a concentration of 10 µg/mL in ethyl acetate. Alternate and multiple internal standards; e.g., tetrachloro-m-xylene, 4,4'-dibromobiphenyl, and/or decachlorobiphenyl may be used provided that the laboratory performs all QC tests and meets all QC acceptance criteria with the alternate or additional internal standard(s) as an integral part of this method.

6.9.4 Surrogate solution—Prepare dibutyl chlorendate (DBC) at a concentration of 2 µg/mL in acetone. Alternate and multiple surrogates; e.g., tetrachloro-m-xylene, 4,4'-dibromobiphenyl, or decachlorobiphenyl may be used provided that the laboratory performs all QC tests and meets all QC acceptance criteria with the alternate surrogate(s) as an integral part of this method. If the internal standard calibration technique is used, make sure the surrogate is not the same as the internal standard.

Comment [BR21]: Suggest TCMX and DCB as recommended surrogates; DBC is in the middle of the chromatogram.

6.9.5 DDT and endrin decomposition (breakdown) solution—Prepare a solution containing endrin at a concentration of 1 µg/mL and 4,4'-DDT at a concentration of 2 µg/mL, in isooctane.

6.9.6 ~~Quality control check sample~~ (~~laboratory~~ Laboratory control sample; LCS) concentrate—See Sections 8.2.1 and 8.4.

6.9.7 ~~Stability of solutions—Analyze all standard solutions (Sections 6.9.1 through 6.9.6) within 48 hours of preparation, and on a monthly basis thereafter, for signs of degradation. Standards will remain acceptable if the concentration remains within ±15% of the concentration determined in the initial analysis of the standard.~~

Comment [BR22]: Because the instrument is less stable than the solutions.

Add ICV section

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those in Footnote 2 to Table 3. Alternative temperature program and flow rate conditions may be used. The system may be calibrated using the external standard technique (Section 7.5) or the internal standard technique (Section 7.6). It is necessary to calibrate the system for the analytes of interest (Section 1.4) only.

7.2 Separately inject the mid-level calibration standard for each calibration mixture. Store the retention time on each GC column.

7.3 Demonstrate that each column/detector system meets the MDLs (Table 3) and the DDT/endrin decomposition test (Section 13.6).

Comment [BR23]: This does not belong in the calibration section.

Comment [mw24]: What were MDLs listed based on other than following Appendix B to Part 136; why list?

7.4 Injection of calibration solutions—Inject a constant volume ~~in the range of 0.5 to 2.0 µL~~ of each calibration solution into the GC column/detector pairs, beginning with the lowest level mixture and proceeding to the highest. For each analyte, compute, record, and store, as a function of the concentration injected, the retention time and peak area on each column/detector system (primary and confirmatory). If multi-component analytes (PCBs, toxaphene) are to be analyzed, store the retention time and peak area for the five largest peaks.

7.4.1 Retention time—Because of adsorption on the GC columns, the polar nature of some analytes may cause the retention time to decrease as the quantity injected increases. To compensate this effect, and to assure rigorous identification, it may be desirable to correlate the retention time with the analyte level.

Comment [BR25]: Have not observed this problem for OCPs ; delete the section.

7.4.1.1 If the difference between the maximum and minimum retention times for any analyte is less than 5 seconds over the calibration range, the retention time for that analyte can be considered constant and an average retention time may be used for analyte identification (Section 14.2.1).

Comment [mw26]: 5 seconds seems excessive (typical RT window is 0.03 minutes).

7.4.1.2 Retention time calibration line or curve (retention time vs. amount)—If the retention time for an analyte in the lowest level standard is more than 5 seconds greater than the retention time for the analyte in the highest level standard, a retention time calibration line or curve may assist in identification of that analyte (Section 14.2.2).

Comment [BR27]: Does anyone do this?

7.5 External standard calibration

7.5.1 From the calibration data (Section 7.4), calculate the calibration factor (CF) for each analyte at each concentration according to the following equation:

$$CF = C_s / A_s$$

where

C_s = Concentration of the analyte in the standard (ng/mL)
A_s = Peak height or area

7.5.2 Calculate the mean (average) and relative standard deviation (RSD) of the calibration factors. If the RSD is less than ~~35%~~25%, linearity through the origin can be assumed and the average CF can be used for calculations. Alternatively, the results can be used to prepare a calibration curve for the analyte. A minimum of six concentration levels is required for a non-linear (e.g., quadratic) regression. If used, the regression must be weighted inversely proportional to concentration, and the correlation coefficient (coefficient of determination) of the weighted

Comment [BR28]: For consistency with internal standard below.

regression must be greater than ~~0.9200~~0.990. The relative standard error (Reference 11) may also be used as an acceptance criterion. As with the RSD, the RSE must be less than ~~35~~25%. If an RSE less than ~~35~~25% cannot be achieved for a quadratic regression, system performance is unacceptable and the system must be adjusted and re-calibrated.

Note: Regression calculations are not included in this method because the calculations are cumbersome and because ~~GC/MS~~ data systems allow selection of weighted regression for calibration and calculation of analyte concentrations.

Comment [BR29]: GC and GC/MS.

7.6 Internal standard calibration

7.6.1 From the calibration data (Section 7.4), calculate the response factor (RF) for each analyte at each concentration according to the following equation:

$$RF = (A_s \times C_{is}) / (C_s \times A_{is})$$

where:

A_s = Response for the analyte to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard (ng/mL)
C_s = Concentration of the analyte to be measured (ng/mL).

7.6.2 Calculate the mean (average) and relative standard deviation (RSD) of the response factors. If the RSD is less than 25%, linearity through the origin can be assumed and the average RF can be used for calculations. Alternatively, the results can be used to prepare a calibration curve of response ratios, A_s/A_{is}, vs. concentration ratios, C_s/C_{is}, for the analyte. A minimum of six concentration levels is required for a non-linear (e.g., quadratic) regression. If used, the regression must be weighted inversely proportional to concentration, and the correlation coefficient (coefficient of determination) of the weighted regression must be greater ~~than 0.939~~than 0.990. The relative standard error (Reference 11) may also be used as an acceptance criterion. As with the RSD, the RSE must be less than 25%. If an RSE less than 25% cannot be achieved for a quadratic regression, system performance is unacceptable and the system must be adjusted and re-calibrated.

Comment [BR30]: Not sure why internal is 25% and external 35% ; suggest 25% for both.

7.7 Combined QC standard—To preclude periodic analysis of all of the individual calibration groups of analytes (Table 4), the GC systems are calibrated with the combined QC standard (Section 6.9.2.1.3) as a final step. Not all of the analytes in this standard will be separated by the GC columns used in this method.

Comment [BR31]: Need to add a second source ICV (see Method 625 language); suggest same criteria as CCV.

Comment [mw32]: As in Section 6, CCV.

Comment [BR33]: Remove Table 4; rewrite use of the CCV.

7.7.1 Analyze the combined QC standard on each column/detector pair.

Comment [BR34]: Search and replace Combined QC standard with CCV.

7.7.1.1 For those analytes that exhibit a single, resolved GC peak for an analyte, the retention time must be within ±10 seconds of the retention time of the peak in the medium level calibration standard (Section 7.4), and the calibration or response factor using the primary column must be within ±30% of its respective factor in the medium level standard (Section 7.5 or 7.6).

Comment [BR35]: Do not agree with this; RT in the CCV should be allowed to vary from the initial calibration to allow for some column clipping.

Comment [BR36]: Non standard; suggest that the calibration drift should be within 30%.

7.7.1.2 For a peak containing two or more analytes, compute and store the retention time at the peak maxima on both columns (primary and confirmatory), and also compute and store the calibration or response factors on both columns. These results will be used for calibration verification (Section 13.5) and LCS (Section 13.7).

7.8 The working calibration curve, CF, or RF must be verified at the beginning and end of each 24-hour shift by the analysis of the ~~combined QC~~ CCV standard (Section 6.9.2.1.3). Requirements for calibration verification are given in Section 13.5 and Table 5.

Comment [BR37]: Add a note that more frequent analysis of the CCV may be useful to avoid reanalysis of so many samples if one fails. Set a maximum of 20 samples as well.

Note: The 24-hour shift begins after analysis of the combined QC standard and ends 24 hours later. The ending calibration verification standard is run immediately after the last sample run during the 24-hour shift, so the beginning and ending calibration verifications are outside of the 24-hour shift.

7.9 Florisil calibration—The cleanup procedure in Section 11.4 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, use of the lauric acid value (Reference 12) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

Comment [BR38]: Remove and replace with a florisil batch check that evaluates recovery of the analytes of interest (possibly CLP language?).

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. The laboratory must maintain records to document the quality of data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet performance requirements of this method. When results of spiked samples indicate atypical method performance, a quality control check standard (LCS, Section 8.4) 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 the 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 1.8 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), and changes in GC columns (40 CFR 136.6(b)(4)(xvi)). Alternate determinative techniques, such as the substitution of spectroscopic or immunoassay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or greater than the specificity of the techniques in this method for the analytes of interest. The laboratory is also encouraged to participate in inter-comparison and performance evaluation studies (see Section 8.9).

8.1.2.1 Each time a modification is made to this method, the laboratory is required to repeat the procedure in Section 8.2. If the detection limit of the method will be affected by the change, the laboratory is required to 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 as written, 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).

Comment [BR39]: Should remove the MDLs in the method and replace with a statement that the MDLs must support the needs of the project.

8.1.2.2 The laboratory must 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 13.5).
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 (Sections 12.3 and 13.2).
j) Sample or extract dilution (Section 15.4).
k) Instrument and operating conditions.
l) Column (dimensions, material, etc).
m) Operating conditions (temperatures, flow rates, etc).
n) Detector (type, operating conditions, etc).
o) Chromatograms and other recordings of raw data.
p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

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 5% of all samples in a batch (Section 3.1) or from a given site or discharge, in duplicate, to monitor and evaluate method and laboratory performance on the sample matrix. This procedure is described in Section 8.3.

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Comment [BR40]: Why complicate by putting the requirements for the blank in a different section than the requirement to have a blank? Put both in the same section. Same goes for duplicates, LCS, etc.

Comment [mw41]: Duplicate plus MS/MSD? 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 described 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 8.7.

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 all 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 and either avoid reporting results for the analytes that failed or report the problem and failures with the data. A QC failure does not relieve a discharger or permittee of reporting timely results.

8.2 Initial demonstration of capability (IDC)—To establish the ability to generate acceptable recovery and precision, the laboratory must perform the DOC in Sections 8.2.1 through 8.2.6 for the analytes of interest. The laboratory must also establish MDLs for the analytes of interest using the MDL procedure at 40 CFR 136, appendix B. The laboratory's MDLs ~~must be equal to or lower than those listed in Table 3 or lower than the regulatory compliance limit, whichever is greater.~~ Must support a quantitation limit of 50 ng/L for the analytes in table 1, or the regulatory compliance limit, whichever is greater. MDLs in the range or 2-3 times lower than the quantitation limit are adequate. For analytes in Table 2, the laboratory MDL is used. ~~For MDLs not listed in Table 3, the laboratory's MDLs should be used.~~ All procedures used in the analysis, including cleanup procedures, must be included in the DOC.

Comment [BR42]: Suggest further discussion on whether it is good to include a specific number.

8.2.1 For the DOC, a QC check sample concentrate containing each analyte of interest (Section 1.4) is prepared in a water-miscible solvent. The QC check sample concentrate must be prepared independently from those used for calibration, but may be the same as the combined QC standard (Sections 6.9.2.1.3 and 7.7). The concentrate should produce concentrations of the analytes of interest in water at or below the mid-point of the calibration range. Multiple solutions may be required.

Comment [BR43]: Call this an LCS.

Comment [BR44]: Should be same source as calibration; ICV should be only standard that is different source.

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

8.2.2 Using a pipet or syringe, prepare four QC check samples by adding an appropriate volume of the concentrate and of the surrogate(s) to each of four ~~1 L~~ aliquots of reagent water. Swirl or stir to mix.

8.2.3 Extract and analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average percent recovery ($\bar{X}$) 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 $\bar{X}$ with the corresponding acceptance criteria for precision and recovery in Table 5. For analytes in Table 2 not listed in Table 5, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 13 and 14). If s and $\bar{X}$ for all analytes of interest meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for recovery, system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Tables 1 and 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when many or all analytes are determined simultaneously.

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.

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 1.4) to be spiked. If direction cannot be obtained, the laboratory must spike at least one sample per extraction batch of up to 20 samples (Section 3.1) with the analytes in Table 1. Spiked sample results should be reported only to the data user whose sample was spiked, or as requested or required by a regulatory/control authority.

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 to meet the requirement in Section 8.3.1, prepare a new check sample concentrate (Section 8.2.1) appropriate for the

Comment [BR45]: Do we need new acceptance criteria? Yes; suggest using limits from NELAC PT vendors.

Comment [mw46]: Statistically developed by laboratory.

Comment [BR47]: Section needs to be rethought as it is not really appropriate for an extraction method; check Method 625 language. It may be OK since this is the IDOC section.

Comment [BR48]: Check Method 625 language for this and the rest of Section 8.3.

background concentration. Spike and analyze two additional sample aliquots, and determine the concentrations 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 $|A_1 - A_2| / (A_1 + A_2)$.

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 for recovery (P) and RPD in Table 5.

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 or, if reported, must be flagged as an estimated value or identified to the data user as not meeting acceptance criteria.

8.3.3.2 The acceptance criteria in Table 5 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 15). If spiking was performed at a concentration lower than the test concentrations in Table 5, the analyst must use either the QC acceptance criteria in Table 5, 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 6, substituting the spike concentration (T) for C; (2) Calculate overall precision (S') using the equation in Table 6, substituting X' for $\bar{X}$; (3) Calculate the range for recovery at the spike concentration as (100 X'/T) ±2.44(100 S'/T)% (Reference 15). For analytes in Table 2 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 13 and 14).

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 1.4) must be prepared and analyzed with each extraction batch of up to 20 samples (Section 3.1) 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 1.4) in the LCS. The volume of reagent water must be the same as the volume used for the sample, the

Comment [BR49]: What about multipeak analytes? For Aroclors the 1016/1260 mixture suffices for the LCS. For toxaphene and technical chlordane at least one LCS per 5 batches or once per week, whichever is more frequent.

IDC (Section 8.2), the blank (Section 8.5), and the MS/MSD (Section 8.3). Also add a volume of the surrogate solution (Section 6.9.4).

8.4.2 Analyze the LCS prior to analysis of samples in the extraction batch (Section 3.1). 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 For each analyte, compare the percent recovery (P) with its corresponding QC acceptance criterion in Table 5. For analytes of interest in Table 2 not listed in Table 5, 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 the designated ranges, analysis of blanks and field samples may proceed. If any individual recovery falls outside the range, proceed according to Section 8.4.4.

Comment [BR50]: Suggest PT data instead.

Note: The large number of analytes in Tables 1 and 2 present a substantial probability that one or more will fail the acceptance criteria when all analytes are tested simultaneously. Because a re-test is allowed in event of failure (Sections 8.1.7 and 8.4.4), 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.

Comment [BR51]: Not good; review Method 625.

8.4.4 Repeat the test only for those analytes that failed to meet the acceptance criteria (P). 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 8.2.1) 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). See Section 8.1.7 for disposition of repeated failures.

Comment [BR52]: Look at Mrthod 625 language and add language describing what to do with the associated samples—reprep batch.

8.5 Blank—Extract and analyze a blank with each extraction batch (Section 3.1) 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 and materials 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 at a concentration greater than the MDL for the analyte, at a concentration greater than one-third the regulatory compliance limit, or at a concentration greater than one-tenth the concentration in a sample in the batch (Section 3.1), whichever is greater, analysis of samples must

Comment [BR53]: No; use at least 2X MDL or preferably RL or ½ RL.

Comment [mw54]: Agree RL should be used.

be halted and samples in the batch must be re-extracted and the extracts re-analyzed. Samples in a batch must be associated with an uncontaminated blank before the results for those samples may be reported or used for permitting or regulatory compliance purposes. If re-testing of blanks results in repeated failures, the laboratory should document the failures and report the problem and failures with the data.

8.6 Surrogate recovery—As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution (Section 6.9.4) per Section 10.2.2 or 10.4.2, analyze the samples, and calculate the percent recovery of each surrogate. QC acceptance criteria for surrogates must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 13 and 14). If any recovery fails its criterion, attempt to find and correct the cause of the failure. Surrogate recoveries from the blank and LCS may be used as pass/fail criteria by the laboratory or as required by a regulatory authority, or may be used to diagnose problems with the analytical system.

8.7 As part of the QC program for the laboratory, it is suggested but not required that method accuracy for wastewater samples be assessed and records maintained. After analysis of five or more spiked wastewater samples as in Section 8.4, 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 to ensure process control (e.g., after each 5 - 10 new accuracy measurements).

8.8 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. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. 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 high concentrations of the analytes of interest are expected (e.g., for untreated effluents or in-process waters), collect a smaller volume (e.g., 250 mL), but no less than 100 mL, in addition to the 1-L sample. Follow conventional sampling practices (Reference 16), except do not pre-rinse the bottle with sample before collection. Automatic sampling equipment must be as free as possible of polyvinyl chloride or other tubing or other

Comment [BR55]: Quite severe, especially given that there probably is not more sample available. Look for language in Method 625 or 8081.

Comment [BR56]: Need more clarity? Corrective action criteria for failures (for samples).

Comment [BR57]: Normally use 3 standard deviations (or expect failure in every sample).

Comment [BR58]: Much too frequent!! Change to once per year.

Comment [BR59]: Rewrite; appropriate volume for RLs but >= 100mL (or 40mL to allow microextraction?

See Method 625.

potential sources of contamination. If needed, collect additional sample(s) for the MS/MSD (Section 8.3).

9.2 Ice or refrigerate the sample at <6°C from the time of collection until extraction, but do not freeze. If the sample will not be extracted within 72 hours of collection, adjust the sample pH to range of 5.0 - 9.0 with sodium hydroxide solution or sulfuric acid. Record the volume of acid or base used. If aldrin is to be determined and residual chlorine is present, add 80 mg/L of sodium thiosulfate but do not add excess. Any method suitable for field use may be employed to test for residual chlorine (Reference 17). If sodium thiosulfate interferes in the determination of the analytes, an alternate preservative (e.g., ascorbic acid or sodium sulfite) may be used.

Comment [BR60]: Is this necessary? Suggest removing.

9.3 Extract all samples within seven days of collection and completely analyze within 40 days of extraction (Reference 1).

10. Sample 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. 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. If an extraction scheme alternate to the extraction schemes detailed in this method 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.

Comment [BR61]: Allows microextraction or SPE?

Comment [mw62R61]: Agree that microextraction and SPE should be allowed as options.

10.2 Separatory funnel liquid-liquid extraction (SFLLE)

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 6.9.4) into the separatory funnel. ~~If the sample will be used for~~For the LCS ~~or~~ and MS or MSD, pipet the appropriate ~~check sample concentrate~~spiking solution (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 5.0 - 9.0 with sodium hydroxide or sulfuric acid solution.

Comment [BR63]: Is this necessary?

10.2.3 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 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 an emulsion forms and the emulsion interface between the layers is more than one-third the volume of the solvent layer, 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 less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Section 10.4.

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 flask. Perform a third extraction in the same manner. Proceed to macro-concentration (Section 10.3).

10.2.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. Record the sample volume to the nearest 5 mL. Sample volumes may also be determined by weighing the container before and after extraction or filling to the mark with water.

Comment [BR64]: Allow other volume measurement techniques if demonstrated accurate.

10.3 Concentration

10.3.1 Macro concentration

Comment [BR65]: Other evaporation/ concentration techniques can be used.

10.3.1.1 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 of Section 8.2 are met.

10.3.1.2 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 flask and column with 20-30 mL of methylene chloride to complete the quantitative transfer.

10.3.1.3 Add one or two clean boiling chips and attach a three-ball Snyder column to the K-D evaporative flask. 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 evaporation 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 it to drain and cool for at least 10 minutes. If the sample will be cleaned up, reserve the K-D apparatus for concentration of the cleaned up extract.

10.3.1.4 If the extract is to be cleaned up using GPC or removal of sulfur, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Adjust the final volume to 10 mL and proceed to GPC cleanup (Section 11.2) or sulfur removal (Section 11.6). If the extract is to cleaned up using one of the other cleanup procedures or is to be injected into the GC, proceed to Kuderna-Danish micro-concentration (Section 10.3.2) or nitrogen evaporation and solvent exchange (Section 10.3.3).

10.3.2 Kuderna-Danish micro concentration

10.3.2.1 Add another one or two clean boiling chips to the concentrator tube 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 approximately 1 mL or other required 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 methylene chloride, and proceed to Section 10.3.3 for nitrogen evaporation and solvent exchange.

10.3.3 Nitrogen evaporation and solvent exchange—Extracts to be cleaned up using solid-phase extraction (SPE) are exchanged into 1.0 mL of the SPE elution solvent (Section 6.7.2.2). Extracts to be cleaned up using Florisil or alumina are exchanged into hexane. Extracts that have been cleaned up and are ready for analysis are exchanged into hexane.

Comment [BR66]: Loading.

10.3.3.1 Transfer the vial containing the sample extract to the nitrogen evaporation (blowdown) device (Section 5.2.5.1.6). Lower the vial into a 45 °C water bath and begin concentrating. 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.

10.3.3.2 Extracts to be solvent exchanged

10.3.3.2.1 When the volume of the liquid is approximately 200 µL, add 2 to 3 mL of the desired solvent (SPE elution solvent for SPE, hexane for Florisil, alumina, or for injection into the GC) and continue concentrating to approximately 100 µL. Repeat the addition of solvent and concentrate once more.

Comment [BR67]: Solvent exchange is normally done on a larger scale, in the KD or turbovap. Evaporating to 200uL risks losing analyte.

10.3.3.3.2 Adjust the volume of an extract to be cleaned up by SPE, Florisil, or alumina to 1.0 mL. Proceed to extract cleanup (Section 11).

10.3.3.3 Extracts that have been cleaned up and are ready for analysis—Adjust the final extract volume to be consistent ~~with the volume extracted and~~ with the sensitivity desired.

10.3.3.3.1 ~~For extracts that have been cleaned up using GPC and that are to be concentrated to a nominal volume of 10 mL, adjust the final extract volume to 1/200 of the volume extracted. For example, if the volume extracted is 950 mL, adjust the final extract volume to 4.8 mL. For extracts that have not been cleaned up by GPC and are to be concentrated to a nominal volume of 10 mL, adjust the final extract volume to 1/100 of the volume extracted. For example, if the volume extracted is 950 mL, adjust the final extract volume to 9.5 mL.~~

Comment [BR68]: Delete this, as per Method 625.

10.3.3.3.2 ~~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 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 volume fractions (1/200 for a nominal 10-mL final volume or 1/2000 for a nominal 1.0-mL final volume) accounts for the 50% 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.*~~

10.3.4 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 ~~< 10~~4 °C. Analyze the extract by GC per the procedure in Section 12.

10.4 Continuous Liquid/Liquid Extraction (CLLE)

10.4.1 Use CLLE when experience with a sample from a given source indicates an emulsion problem, or when an emulsion is encountered using SFLLE. CLLE may be used for all samples, if desired. Directions are for 1L samples – the quantity of solvent may need to be reduced when extracting smaller sample sizes.

10.4.2 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 5.0 - 9.0 with sodium hydroxide or sulfuric acid solution. Transfer the sample to the continuous extractor and, using a pipet, add surrogate standard spiking solution. 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. 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.

10.4.3 Repeat the sample bottle rinse with two additional 50-100 mL portions of methylene chloride and add the rinses to the extractor.

10.4.4 Add a suitable volume of methylene chloride to the distilling flask (generally 200 - 500 mL) and sufficient reagent water to ensure proper operation of the extractor, and extract the sample 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, solvent exchange, and seal the extract per Section 10.3.

Comment [BR69]: Delete this, as per Method 625.

Comment [BR70]: Change to refrigerated storage; it is not good to put samples in the freezer.

Formatted: French (Canada)

Comment [BR71]: Is this necessary?

10.4.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to an appropriately sized graduated cylinder. Record the sample volume to the nearest 5 mL. Sample volumes may also be determined by weighing the container before and after extraction or filling to the mark with water.

Comment [BR72]: Alternative ways to determine volume.

11. Extract Cleanup

Comment [mw73]: Add sulfuric acid for PCBs to this section?

11.1 Cleanup may not be necessary for a relatively clean sample matrix. 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. However, the laboratory must first repeat the tests in Sections 8.2 and 8.3 to demonstrate that the requirements of Section 8.2 can be met using the cleanup procedure(s) as an integral part of this method.

11.1.1 Gel permeation chromatography (Section 11.2) removes many high molecular weight interferents that cause GC column performance to degrade. It is used for water extracts that are expected to contain high molecular weight organic substances (e.g., polymeric materials, humic acids).

11.1.2 The solid-phase extraction cartridge (Section 11.3) removes polar organic compounds such as phenols.

11.1.3 The Florisil column (Section 11.4) allows for selected fractionation of the organo chlorine analytes and will also eliminate polar interferences.

11.1.4 Alumina column cleanup (Section 11.5) also removes polar materials.

11.1.5 Elemental sulfur, which interferes with the electron capture gas chromatography of some of the pesticides, is removed using GPC, activated copper, or TBA sodium sulfite. Sulfur removal (Section 11.6) is required when sulfur is known or suspected to be present.

11.2 Gel permeation chromatography (GPC).

Comment [BR74]: The details of the GPC procedure are outdated; instead use vendor recommendations.

11.2.1 Column packing.

11.2.1.1 Place 70 to 75 g of SX-3 Bio-beads (Section 5.5.1.1) in a 400- to 500-mL beaker.

11.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (12 hours minimum).

11.2.1.3 Transfer the swelled beads to the column and pump solvent through the column, from bottom to top, at 4.5 to 5.5 mL/min prior to connecting the column to the detector.

11.2.1.4 After purging the column with solvent for one to two hours, adjust the column head pressure to 7 to 10 psig, and purge for 4 to 5 hours to remove air. Maintain a head pressure of 7 to 10 psig. Connect the column to the detector.

11.2.2 Column calibration.

11.2.2.1 Load 5 mL of the calibration solution (Section 6.8) into the sample loop.

11.2.2.2 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.

11.2.2.3 Set the "dump time" to allow greater than 85% removal of the corn oil and greater than 85% collection of the phthalate.

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

11.2.2.5 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.

11.2.3 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.

11.2.3.1 Filter the extract or load through the filter holder to remove particulates. Load 5.0 mL of the extract onto the column.

11.2.3.2 Elute the extract using the calibration data determined in Section 11.2.2. Collect the eluate in the K-D apparatus reserved in Section 10.3.1.3.

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

11.2.3.4 If a particularly dirty extract is encountered, run a 5.0-mL methylene chloride blank through the system to check for carry-over.

11.2.3.5 Concentrate the extract and exchange into hexane per Section 10.3.

11.3 Solid-phase ~~extraction~~ cleanup ~~(SPE)~~

Comment [BR75]: Assume this is SPE for cleanup? The whole section needs to be rewritten.

11.3.1 Setup

11.3.1.1 Attach the Vac-elute Manifold (Section 5.5.3.2) to a water aspirator or vacuum pump with the trap and gauge installed between the manifold and vacuum source.

11.3.1.2 Place the SPE cartridges in the manifold, turn on the vacuum source, and adjust the vacuum to 5 to 10 psi.

11.3.2 Cartridge washing—Pre-elute each cartridge prior to use sequentially with 10-mL portions each of hexane, methanol, and water using vacuum for 30 seconds after each eluant. Follow this pre-elution with 1 mL methylene chloride and three 10-mL portions of the elution solvent (Section 6.7.2.2) using vacuum for 5 minutes after each eluant. Tap the cartridge lightly while under vacuum to dry between eluants. The three portions of elution solvent may be collected and used as a blank if desired. Finally, elute the cartridge with 10 mL each of methanol and water, using the vacuum for 30 seconds after each eluant.

Comment [BR76]: Need to either add cartridge type or delete details; prefer deleting details.

11.3.3 Cartridge certification—Each cartridge lot must be certified to ensure recovery of the analytes of interest and removal of 2,4,6-trichlorophenol.

Comment [BR77]: May make sense if the cartridge type is to remove polar compounds, otherwise it does not.

11.3.3.1 To make the test mixture, add the trichlorophenol solution (Section 6.7.2.1) to the combined QC standard (Section 7.7). Transfer the mixture to the column and dry the column. Pre-elute with three 10-mL portions of elution solvent, drying the column between elutions. Elute the cartridge with 10 mL each of methanol and water, as in Section 11.3.2.

11.3.3.2 Concentrate the eluant to per Section 10.3.3 and inject 1.0 µL of the concentrated eluant into the GC using the procedure in Section 12. The recovery of all analytes (including the unresolved GC peaks) shall be within the ranges for calibration verification (Section 13.5 and Table 5), and the peak for trichlorophenol shall not be detectable; otherwise the SPE cartridge is not performing properly and the cartridge lot shall be rejected.

11.3.4 Extract cleanup.

11.3.4.1 After cartridge washing (Section 11.3.2), release the vacuum and place the rack containing the 50-mL volumetric flasks (Section 5.5.3.4) in the vacuum manifold. Re-establish the vacuum at 5 to 10 psi.

11.3.4.2 Using a pipette or a 1-mL syringe, transfer 1.0 mL of extract to the SPE cartridge. Apply vacuum for five minutes to dry the cartridge. Tap gently to aid in drying.

11.3.4.3 Elute each cartridge into its volumetric flask sequentially with three 10-mL portions of the elution solvent (Section 6.7.2.2), using vacuum for five minutes after each portion. Collect the eluants in the 50-mL volumetric flasks.

Comment [BR78]: CLP florisil cleanup is better.

11.3.4.4 Release the vacuum and remove the 50-mL volumetric flasks.

11.3.4.5 Concentrate the eluted extracts per Section 10.3.

11.4 Florisil

Comment [BR79]: Maybe add example florisil cartridge directions here.

11.4.1 Place a weight of Florisil (nominally 20 g) predetermined by calibration (Section 7.9 and Table 7) in a chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of granular anhydrous sodium sulfate to the top.

11.4.2 Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate layer to the air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

11.4.3 Transfer the concentrated extract (Section 10.3.3) onto the column. Complete the transfer with two 1-mL hexane rinses, drawing the extract and rinses down to the level of the sodium sulfate.

11.4.4 Place a clean 500-mL K-D flask and concentrator tube under the column. Elute Fraction 1 with 200 mL of 6% (v/v) ethyl ether in hexane at a rate of

approximately 5 mL/min. Remove the K-D flask and set it aside for later concentration. Elute Fraction 2 with 200 mL of 15% (v/v) ethyl ether in hexane into a second K-D flask. Elute Fraction 3 with 200 mL of 50% (v/v) ethyl ether in hexane into a third K-D flask. The elution patterns for the pesticides and PCBs are shown in Table 7.

11.4.5 Concentrate the fractions as in Section 10.3, except use hexane to prewet the column and set the water bath at about 85 °C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the volume of Fraction 1 to approximately 10 mL for sulfur removal (Section 11.6), if required; otherwise, adjust the volume of the fractions to 10 mL, 1.0 mL, or other volume needed for the sensitivity desired. Analyze the concentrated extract by gas chromatography (Section 12).

11.5 Alumina

11.5.1 Place a small plug of pre-cleaned glass wool in the chromatographic column (Section 5.2.4). Add 10 g of alumina (Section 6.7.3) on top of the plug. Tap the column to settle the alumina. Place 1 - 2 g of anhydrous sodium sulfate on top of the alumina.

11.5.2 Close the stopcock and fill the column to just above the sodium sulfate with hexane. Add 25 mL of hexane. Open the stopcock and adjust the flow rate of hexane to approximately 2 mL/min. Do not allow the column to go dry throughout the elutions.

11.5.3 When the level of the hexane is at the top of the column, quantitatively transfer the extract to the column. When the level of the extract is at the top of the column, slowly add 25 mL of hexane and elute the column to the level of the sodium sulfate. Discard the hexane.

11.5.4 Place a K-D flask (Section 5.2.5.1.2) under the column and elute the pesticides with approximately 150 mL of hexane:ethyl ether (80:20 v/v). It may be necessary to adjust the volume of elution solvent for slightly different alumina activities.

11.5.5 Concentrate the extract per Section 10.3.

11.6 Sulfur removal—Elemental sulfur will usually elute in Fraction 1 of the Florisil column cleanup. If Florisil cleanup is not used, or for removal from any of the Florisil fractions, remove sulfur using one of the procedures below.

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.

11.6.1 Removal with copper (Reference 18)

Note: *If (1) an additional analyte (Table 2) 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 analyte can be successfully extracted and treated with copper in the sulfur matrix. Some of the additional analytes (Table 2) are known not to be amenable to sulfur removal with copper (e.g. Atrazine and Diazinon).*

11.6.1.1 Quantitatively transfer the extract to a 40- to 50-mL flask or bottle. If there is evidence of water in the K-D or round-bottom flask after the transfer, rinse the flask with small portions of hexane:acetone (40:60) and add to the flask or bottle. Mark and set aside the concentration flask for future use.

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

Comment [BR80]: This sounds like a lot.

11.6.1.3 Add activated copper (Section 6.7.4.1.4) 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.

11.6.1.4 After drying and sulfur removal, quantitatively transfer the extract to a nitrogen-evaporation vial or tube and proceed to Section 10.3.3 for nitrogen evaporation and solvent exchange, taking care to leave the sodium sulfate and copper foil in the flask.

11.6.2 Removal with TBA sulfite

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

11.6.2.2 Add 1 - 2 mL of TBA sulfite reagent (Section 6.7.4.2.4), 2 - 3 mL of 2-propanol, and approximately 0.7 g of sodium sulfite (Section 6.7.4.2.2) 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.

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

11.6.2.4 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 10.3.3 for micro-concentration and solvent exchange.

12. Gas Chromatography

12.1 Footnote 2 to Table 3 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDLs that can be achieved under these conditions. Examples of the separations achieved by Column 1 are shown in Figure 1. Other columns, chromatographic conditions, or detectors may be used if QC requirements in this method are met.

12.2 If the internal standard calibration procedure is used, add the internal standard solution (Section 6.9.3) to the extract as close as possible to the time of injection to minimize the possibility of loss by evaporation, adsorption, or reaction. Mix thoroughly.

Comment [BR81]: Delete; the purpose of the internal standard is to correct for those problems.

12.3 Simultaneously inject an appropriate volume of the sample extract or standard solution onto both columns 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 the nearest 0.05 uL.

Comment [BR82]: Allow analysis on one column and then subsequent confirmation of hits.

12.4 Set the data system or GC control to start the temperature program upon sample injection, and begin data collection after the solvent peak elutes. Set the data system to stop data collection after the last analyte is expected to elute and to return the column to the initial temperature.

12.5 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. System and Laboratory Performance

13.1 At the beginning of each 24-hour shift during which standards or extracts are analyzed, GC system performance and calibration are verified for all analytes and surrogates on both column/detector systems. Adjustment and/or recalibration (per Section 7) are performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, and standards be analyzed.

13.2 Inject an aliquot of the ~~combined QC standard~~CCV (Section 6.9.2.1.3) on both columns.

13.3 Retention times—The absolute retention times of the peak maxima shall be within ±10 seconds of the retention times in the first CCV of the day ~~calibration~~ (Section 7.7).

13.4 GC resolution—Resolution is acceptable if the valley height between two peaks (as measured from the baseline) is less than 40% of the shorter of the two peaks.

13.4.1 Primary column (DB-608)—DDT and endrin aldehyde.

13.4.2 Confirmatory column (DB-1701)—Alpha and gamma chlordane.

13.5 Calibration verification

13.5.1 Compute the percent recovery of each analyte and of the coeluting analytes, based on the calibration data (Section 7.7.1.2).

13.5.2 For each analyte or for coeluted analytes, compare the concentration with the limits for calibration verification in Table 5. For coeluting analytes, use the coeluted analyte with the least restrictive specification (the widest range). For analytes in Table 2 not listed in Table 5, QC acceptance criteria must be developed by the laboratory. EPA has provided guidance for development of QC acceptance criteria (References 13 and 14). If the recoveries for all analytes meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue. If, however, any recovery falls outside the calibration verification range, system performance is unacceptable for that analyte. If this occurs, repair the system and repeat the test (Section 13.5), or prepare a fresh calibration standard and repeat the test, or recalibrate (Section 7). See Section 8.1.7 for information on repeated test failures. If verification requirements are met, the calibration is assumed to be valid for the multicomponent analytes (PCBs and toxaphene).

13.6 Decomposition of DDT and endrin—If desired, this test may be performed prior to calibration verification (Section 13.5).

13.6.1 Analyze 1 µL of the DDT and endrin decomposition solution (Section 6.9.5).

13.6.2 Measure the total area of all peaks in the chromatogram.

13.6.3 The area of peaks other than the sum of the areas of the DDT and endrin peaks shall be less than 20% the sum of the areas of these two peaks. If the area is greater than this sum, the system is not performing acceptably for DDT and

Comment [BR83]: First CCV of the day.

Comment [BR84]: ??

Comment [BR85]: Suggest every 20 samples (at a minimum) rather than 24 hours.

Comment [BR86]: Some of these limits need to be changed (e.g., endrin).

Comment [BR87]: Not sure about this; look for better language in CLP or 8081 and use specific degradation products.

endrin. In this case, repair the GC column system that failed and repeat the performance tests (Sections 13.2 to 13.6) until the specification is met.

Note: DDT and endrin decomposition are usually caused by accumulations of particulates in the injector and in the front end of the column. Cleaning and silanizing the injection port liner, and breaking off a short section of the front end of the column will usually eliminate the decomposition problem.

13.7 Laboratory control sample

13.7.1 Analyze the ~~extract of the combined QC standard~~LCS (Section 7.7) extracted with each sample batch (Section 8.4).

13.7.2 Compute the percent recovery of each analyte and of the coeluting analytes.

13.7.3 For each analyte or coeluted analytes, compare the percent recovery with the limits for P in Table 5. For coeluted analytes, use the coeluted analyte with the least restrictive specification (widest range). If all analytes pass, the extraction, concentration, and cleanup processes are in control and analysis of blanks and samples may proceed. If, however, any of the analytes fail, these processes are not in control. In this event, correct the problem, re-extract the sample batch, and repeat the ongoing precision and recovery test.

13.7.4 It is suggested but not required that the laboratory update statements of data quality. Add results that pass the specifications in Section 13.7.3 to initial (Section 8.7) and previous ongoing data. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of percent recovery, s_r. Express the acccuracy as a recovery interval from R - $2s_r$ to R + $2s_r$. For example, if R = 95% and s_r = 5%, the accuracy is 85 to 105%.

Comment [BR88]: Use 3 standard deviations, otherwise average one failure per sample for 20 analytes.

13.8 Internal standard response—If internal standard calibration is used, verify that detector sensitivity has not changed by comparing the response (area or height) of each internal standard in the sample, blank, LCS, MS, and MSD to the response in the ~~combined QC standard~~CCV (Section 7.7.1 or 13.5). The peak area or height of the internal standard should be within 50% to 200% (1/2 to 2x) of its respective peak area or height in the verification standard. If the area or height is not within this range, compute the concentration of the analytes using the external standard method (Section 7.5).

Comment [BR89]: Also CCV should be compared to the initial calibration.

Comment [BR90]: No, reanalyze.

14. Qualitative Identification

Comment [BR91]: Need more guidance on qualitative identification for PCBs and toxaphene.

14.1 Identification is accomplished by comparison of data from analysis of a sample or blank with data from calibration verification (Section 7.7.1 or 13.5), and with data stored in the

retention-time and calibration libraries (Section 7.7). The pesticide window is defined by the CAL data but may be modified by slight changes that will be reflected in calibration verification, blank, LCS, and MS/MSD data. Identification is confirmed when retention time and amounts agree per the criteria below.

14.2 For each analyte on each column/detector system, establish a retention-time window 5 seconds on either side of the retention time in the most recent calibration verification (Section 13.5). For the multi-component analytes, use the retention times of the five largest peaks in the chromatogram. For analytes that have a retention time that varies with concentration (Section 7.4.1.2), establish this window from the calibration data as the minimum -10 seconds and maximum +10 seconds.

14.2.1 Analytes not requiring a retention-time calibration line or curve—If a peak representing an analyte from analysis of a sample or blank is within its ±5 second window on both column/detector systems (as defined in Section 14.2), it is considered identified. Identity is confirmed when the computed amounts (Section 15) on both column/detector systems agree within a factor of 2.

14.2.2 Analytes with a retention-time calibration line or curve—If a peak representing an analyte from the analysis of a sample or blank is within the window established for the retention-time line or curve (Section 14.2), the analyte is considered identified. Identity is confirmed when the computed amounts (Section 15) on both column/detector systems agree within a factor of 2. Because the identification window for an analyte with a retention-time line or curve may be overly broad (Section 14.2), it may be necessary to correlate the retention time to the analyte concentration in the retention time calibration (Section 7.4.1.2) to assure identification.

14.2.3 When the concentration of an analyte is sufficient, ~~or~~ and if the presence or identity is suspect, its presence should be confirmed by GC/MS.

14.2.4 Additional information that may aid the laboratory in the identification of an analyte—The occurrence of peaks eluting near the retention time of an analyte of interest increases the probability of a false positive for the analyte. If the concentration is insufficient for confirmation by GC/MS, the laboratory must use the cleanup procedures in this method (Section 11) to attempt to remove the interferent. After all attempts at cleanup are exhausted, the following steps may be helpful to assure that the substance that appears in the RT windows on both columns is the analyte of interest.

14.2.4.1 Determine the consistency of the RT data for the analyte on each column. For example, if the RT is very stable (i.e., varies by no more than a few seconds) for the calibration, calibration verification, blank, LCS, and MS/MSD, the RT for the analyte of

Comment [BR92]: This is a bit wide; 0.03 minutes is standard.

Comment [BR93]: This is way wide

Comment [BR94]: Delete this RT calibration statement.

Comment [BR95]: This is a bit wide.

Comment [BR96]: What if they do not agree within a factor of 2? Recommend reporting lower number and flag the results. Also suggest 40% rather than a factor of 2 (would be consistent with SW-846).

interest in the sample should be within this variation regardless of the window established in Section 14.2. If the analyte is not within this variation on both columns, it is likely not present.

14.2.4.2 The possibility exists that the RT for the analyte in a sample could shift if extraneous materials are present. This possibility can be confirmed or refuted by the behavior of the surrogates in the sample. If the RTs for the surrogates on both columns are consistent with their RTs in calibration, calibration verification, blank, LCS, and MS/MSD, the RT for the analyte of interest cannot shift.

14.2.4.3 If the RT for the analyte is shifted slightly later on one column and earlier on the other, and the surrogates have not shifted, it is highly unlikely that the analyte is present because shifts nearly always occur in the same direction on both columns.

15.0 Quantitative Determination

Comment [BR97]: Need more detail on quantitative determination of PCBs and toxaphene.

15.1 External standard quantitation—Calculate the concentration of the analyte in the extract using the calibration curve or average calibration factor determined in calibration (Section 7.5.2) and the following equation:

$$C_{ex} = A_s / CF$$

where

C_{ex} = Concentration of the analyte in the extract (ng/mL)
A_s = Peak height or area for the analyte in the standard or sample
CF = Calibration factor, as defined in Section 7.5.1

15.2 Internal standard quantitation—Calculate the concentration of the analyte in the extract using the calibration curve or average response factor determined in calibration (Section 7.6.2) and the following equation:

$$C_{ex} = (A_s \times C_{is}) / (A_{is} \times RF)$$

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where

C_{ex} = Concentration of the analyte in the extract (ng/mL)
A_s = Peak height or area for the analyte in the standard or sample
C_{is} = Concentration of the internal standard (ng/mL)
A_{is} = Area of the internal standard
RF = Response factor, as defined in Section 7.6.1

15.3 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 the following equation:

$$C_s = V_{ex} \times C_{ex} \times DF / V_s$$

where

C_s = Concentration of the analyte in the sample (ng/L)
V_{ex} = Final extract volume (mL)
C_{ex} = Concentration in the extract (ng/mL)
V_s = Volume of sample (L)
DF = Dilution factor

15.4 If the concentration of any target analyte exceeds the calibration range, either extract and analyze a smaller sample volume, or dilute and analyze the diluted extract.

15.5 Reporting of results

15.5.1 Report results in ng/L without correction for recovery. Report all QC data with the sample results.

15.5.2 Reporting level

15.5.2.1 Report the result for each analyte in each sample, blank, or standard (MS/MSD, LCS) at or above the MDL to 3 significant figures. Report a result below the MDL as "<MDL" (where MDL is the concentration at the MDL), or as required by the regulatory authority or permit.

15.5.2.2 ~~Section 15.5.2.1 requires reporting a result for each analyte in each sample, blank, or standard separately (without blank subtraction). In addition to reporting results for samples and blank(s) separately, the concentration of each analyte in a blank or field blank associated with that sample may be subtracted from the result for that sample, or must be subtracted if requested or required by a regulatory authority or in a permit.~~

15.5.2.3 Report the result for a analyte in a sample or extract that has been diluted at the least dilute level at which the peak area is within the calibration range and the MS/MSD recovery and RPD are within their respective QC acceptance criteria (Table 5).

15.5.2.4 Results from tests performed with an analytical system that is not in control must not be reported or otherwise used for permitting or

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Comment [mw98]: RL and flag if between RL and MDL.

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.

15.5.2 Report the lower result from the two columns. Analyze the sample by GC/MS or on a third column when analytes have co-eluted or interfere with determination on both columns.

~~*Note: Dichlone and kepone do not elute from the DB-1701 column and must be confirmed on DB-5 or by GC/MS.*~~

15.6 For multi-component mixtures (chlordane, toxaphene, PCBs) match retention times of peaks in the standard with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add heights or areas of the identified peaks in the chromatogram. Calculate as total response in the sample versus total response in the standard. ~~When two or more Aroclor mixtures are present, the Webb and McCall procedure (Reference 19) may be used to identify and quantify the Aroclors.~~

15.7 Quantitative information that may aid in the confirmation of the presence of an analyte

15.7.1 Sections 14.2.1 and 14.2.2 state that if the amounts on both column/detector systems agree within a factor of 2, the pesticide is present. This factor of 2 is generous and allows for the pesticide that has the largest measurement error. A better indication of the actual measurement error can be gained from IDC and VER data. Using these data, establish a measurement window ±3 standard deviations (or ±3 RSD) around the mean on one column. If the concentration for the pesticide determined on the other column/detector system agrees within this window, and the RT data agree (from Section 14), the pesticide is confirmed.

15.7.2 If the amounts do not agree, and the RT data indicate the presence of the analyte (per Section 14), it is likely that an interference is present on the column that yielded the highest result. Look for a separate peak for this interferent on the other column. It should be near the peak for the analyte of interest, and the area of the peak, when added to the area of the peak for the analyte of interest, should provide an estimate of what the concentration would be if the peaks coincided. This concentration should roughly agree with the concentration determined for the analyte on the column on which the suspected interference occurred. In this event, the pesticide is confirmed and lowest concentration should be reported.

16.0 Analysis of Complex Samples

Comment [BR99]: OK, but consider allowing primary column if results confirm quantitatively.

Comment [BR100]: Normal approach is to select 5 characteristic peaks and use at least 3 for quantitation if there is interference.

Comment [BR101]: And if it is not? Generally there are lots of peaks, and I don't think this paragraph is helpful.

16.1 Some samples may contain high levels (greater than 1000 ng/L) of the analytes of interest, interfering analytes, and/or polymeric materials. Some samples may not concentrate to 1.0 mL (Section 10.3.3.3.2); others may overload the GC column and/or detector.

16.2 When an interference is known or suspected to be present, the laboratory should attempt to clean up the sample using GPC (Section 11.2), the SPE cartridge (Section 11.3), by Florisil (Section 11.4) or alumina (Section 11.5), and/or sulfur removal (Section 11.6). If these techniques do not remove the interference, the extract is diluted by a factor of 10 and reanalyzed (Section 12).

16.3 Recovery of surrogate(s)—In most samples, surrogate recoveries will be similar to those from reagent water. If surrogate recovery is outside the range developed in Section 8.6, the sample is re-extracted and re-analyzed. If the surrogate recovery is still outside this range, 1/10 the amount of sample is analyzed to overcome any matrix interference problems.

16.4 Recovery of the matrix spike and duplicate (MS/MSD)—In most samples, MS/MSD recoveries will be similar to those from reagent water. If either the MS or MSD recovery is outside the range specified in Section 8.3.3, one-tenth the amount of sample is spiked and analyzed. If the matrix spike recovery is still outside the range, the result for the unspiked sample may not be reported or used for permitting or regulatory compliance purposes. Poor matrix spike recovery does not relieve a discharger or permittee of reporting timely results.

Comment [mw102]: Clarify; agree this process is problematic.

Comment [BR103]: This seems problematical

17. Method Performance

17.1 This method was tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4 x MDL to 1000 x MDL with the following exceptions: Chlordane recovery at 4 x MDL was low (60%); Toxaphene recovery was demonstrated linear over the range of 10 x MDL to 1000 x MDL (Reference 3).

17.2 The basic version of this method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations (Reference 2). Concentrations used in the study ranged from 0.5 to 30 µg/L for single-component pesticides and from 8.5 to 400 µg/L for multicomponent analytes. 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 6.

18. Pollution Prevention

18.1 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.

18.2 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.

18.3 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.

19. Waste Management

19.1 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).

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

19.3 Many analytes in this method decompose above 500 ºC. Low-level waste such as absorbent paper, tissues, animal remains, 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 toxic wastes.

19.4 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 N.W., Washington, DC 20036.

20. References

Comment [BR104]: All references need to be checked as some appear to be outdated or no longer relevant.

1. "Determination of Pesticides and PCBs in Industrial and Municipal Wastewaters," EPA 600/4-82-023, National Technical Information Service, PB82-214222, Springfield, Virginia 22161, April 1982.

2. "EPA Method Study 18 Method 608-Organochlorine Pesticides and PCBs," EPA 600/4-84-061, National Technical Information Service, PB84-211358, Springfield, Virginia 22161, June 1984.

3. "Method Detection Limit and Analytical Curve Studies, EPA Methods 606, 607, and 608," Special letter report for EPA Contract 68-03-2606, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, June 1980.

4. ASTM Annual Book of Standards, Part 31, D3694-78. "Standard Practice for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.

5. Giam, C.S., Chan, H.S., and Nef, G.S. "Sensitive Method for Determination of Phthalate Ester Plasticizers in Open-Ocean Biota Samples," *Analytical Chemistry*, *47*, 2225 (1975).

6. Giam, C.S. and Chan, H.S. "Control of Blanks in the Analysis of Phthalates in Air and Ocean Biota Samples," U.S. National Bureau of Standards, Special Publication 442, pp. 701-708, 1976.

7. *Solutions to Analytical Chemistry Problems with Clean Water Act Methods*, EPA 821-R-07-002, March 2007.

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

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

10. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

11. 40 CFR 136.6(b)(5)(*x*)

12. Mills, P.A. "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," *Journal of the Association of Official Analytical Chemists, 51,* 29, (1968).

13. 40 CFR 136.6(b)(2)(*i*)

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

15. 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.)

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

17. Methods 4500 Cl F and 4500 Cl G, *Standard Methods for the Examination of Water and Wastewater*, published jointly by the American Public Health Association, American Water Works Association, and Water Environment Federation, 1015 Fifteenth St., Washington, DC 20005, 20th Edition, 2000.

18. "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.

19. Webb, R.G. and McCall, A.C. "Quantitative PCB Standards for Election Capture Gas Chromatography," *Journal of Chromatographic Science, 11,* 366 (1973).

21. Tables and Figure

Table 1—Pesticides[1]		
Analyte	**STORET number**	**CAS number**
Aldrin	39330	309-00-2
α-BHC	39337	319-84-6
β-BHC	39338	319-85-7
δ-BHC	34259	319-86-8
γ-BHC	39340	58-89-9
α-Chlordane	39350	5103-71-9
γ-Chlordane	39350	5103-74-2
4,4'-DDD	39310	74-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dieldrin	39380	60-57-1
Endosulfan I	34360	959-98-8
Endosulfan II	34356	33212-65-9
Endosulfan sulfate	34351	1031-07-8
Endrin	39390	72-20-8
Endrin aldehyde	34366	7421-93-4
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3

1. All analytes in this table are Priority Pollutants (40 CFR 423, appendix A)

Table 2—Additional analytes		
Analyte	**STORET number**	**CAS number**
Acephate		30560-19-1
Alachlor		15972-60-8
Atrazine		1912-24-9
Benfluralin (Benefin)		1861-40-1
Bromacil		314-40-9
Bromoxynil octanoate		1689-99-2
Butachlor		23184-66-9
Captafol		2425-06-1
Captan		133-06-2
Carbophenothion (Trithion)		786-19-6
Chlorobenzilate		510-15-6
Chloroneb (Terraneb)		2675-77-6
Chloropropylate (Acaralate)		5836-10-2
Chlorothalonil		1897-45-6
Cyanazine		21725-46-2
DCPA (Dacthal)		1861-32-1
2,4'-DDD		53-19-0
2,4'-DDE		3424-82-6
2,4'-DDT		789-02-6
Diallate (Avadex)		2303-16-4
1,2-Dibromo-3-chloropropane (DBCP)		96-12-8
Dichlone		117-80-6
Dichloran		99-30-9
Dicofol		115-32-2
Endrin ketone		53494-70-5
Ethalfluralin (Sonalan)		55283-68-6
Etridiazole		2593-15-9
Fenarimol (Rubigan)		60168-88-9
Hexachlorobenzene [1]		118-74-1
Hexachlorocyclopentadiene [1]		77-47-4
Isodrin		465-73-6
Isopropalin (Paarlan)		33820-53-0
Kepone		143-50-0
Methoxychlor		72-43-5
Metolachlor		51218-45-2
Metribuzin		21087-64-9
Mirex		2385-85-5
Nitrofen (TOK)		1386-75-5
Nonachlor, cis-		5103-73-1
Nonachlor, trans-		39765-80-5
Norfluorazon		27314-13-2

Octachlorostyrene		29082-74-4
Oxychlordane		27304-13-8
PCNB (Pentachloronitrobenzene)		82-68-8
Pendamethalin (Prowl)		40487-42-1
Permethrin, cis-		61949-76-6
Permethrin, trans-		61949-77-7
Perthane (Ethylan)		72-56-0
Propachlor		1918-16-7
Propanil		709-98-8
Propazine		139-40-2
Quintozene		82-68-8
Simazine		122-34-9
Strobane		8001-50-1
Technazene		117-18-0
Terbacil		5902-51-2
Terbuthylazine		5915-41-3
Toxaphene [1]	39400	8001-35-2
Trifluralin		1582-09-8
PCB-1016 [1]	34671	12674-11-2
PCB-1221 [1]	39488	1104-28-2
PCB-1232 [1]	39492	11141-16-5
PCB-1242 [1]	39496	53469-21-9
PCB-1248 [1]	39500	12672-29-6
PCB-1254 [1]	39504	11097-69-1
PCB-1260 [1]	39508	11096-82-5

1. Priority Pollutant (40 CFR 423, appendix A)

Field Code Changed

Comment [mw105]: Revise or eliminate table?

Table 3—Retention times and method detection limits [1]

Analyte	Retention time (min) [2]		Method detection limit (ng/L) [2]	
	DB-608	DB-1701		
Acephate	5.03	– [4]	2000	est (ECD)
Trifluralin	5.16	6.79	50	est (ECD)
Ethalfluralin	5.28	6.49	5	est (ECD)
Benfluralin	5.53	6.87	20	est (ECD)
Diallate-A	7.15	6.23	45	
Diallate-B	7.42	6.77	32	
∀-BHC	8.14	7.44	6	
PCNB	9.03	7.58	6	
Simazine	9.06	9.29	400	est (ECD)
Atrazine	9.12	9.12	500	est (ECD)
Terbuthylazine	9.17	9.46	300	est (ECD)
(-BHC (Lindane)	9.52	9.91	11	
∃-BHC	9.86	11.90	7	
Heptachlor	10.66	10.55	5	
Chlorothalonil	10.66	10.96	15	est (ECD)
Dichlone	10.80	– [5]	– [6]	
Terbacil	11.11	12.63	200	est (ECD)
∗-BHC	11.20	12.98	5	
Alachlor	11.57	11.06	20	est (ECD)
Propanil	11.60	14.10		
Aldrin	11.84	11.46	8	
DCPA	12.18	12.09	3	est (ECD)
Metribuzin	12.80	11.68	5	est (ECD)
Triadimefon	12.99	13.57	50	est (ECD)
Isopropalin	13.06	13.37	20	est (ECD)
Isodrin	13.47	11.12	13	
Heptachlor epoxide	13.97	12.56	12	
Pendamethalin	14.21	13.46	30	
Bromacil	14.39	– [4]	70	est (ECD)
(-Chlordane	14.63	14.20	9	
Butachlor	15.03	15.69	30	est (ECD)
∀-Chlordane	15.24	14.36	8	
Endosulfan I	15.25	13.87	11	
4,4N-DDE	16.34	14.84	10	
Dieldrin	16.41	15.25	6	
Captan	16.83	15.43	100	est (ECD)
Chlorobenzilate	17.58	17.28	25	
Endrin	17.80	15.86	4	
Nitrofen (TOK)	17.86	17.47	13	
Kepone	17.92	– [4]	100	est (ECD)
4,4N-DDD	18.43	17.77	5	
Endosulfan II	18.45	18.57	8	
Bromoxynil octanoate	18.85	18.57	30	est (ECD)

Table 3—Retention times and method detection limits [1]				
	Retention time (min) [2]			
Analyte	**DB-608**	**DB-1701**	**Method detection limit (ng/L) [2]**	
4,4N-DDT	19.48	18.32	12	
Carbophenothion	19.65	18.21	50	
Endrin aldehyde	19.72	19.18	11	
Endosulfan sulfate	20.21	20.37	7	
Captafol	22.51	21.22	100	est (ECD)
Norfluorazon	20.68	22.01	50	est (ECD)
Mirex	22.75	19.79	4	
Methoxychlor	22.80	20.68	30	
Endrin ketone	23.00	21.79	8	
Fenarimol	24.53	23.79	20	est (ECD)
cis-Permethrin	25.00	23.59	200	est (ECD)
trans-Permethrin	25.62	23.92	200	est (ECD)
PCB-1242			150	est (ECD)
PCB-1232			150	est (ECD)
PCB-1016			150	est (ECD)
PCB-1221			150	est (ECD)
PCB-1248			150	est (ECD)
PCB-1254			150	est (ECD)
PCB-1260	15.44	14.64	140	
	15.73	15.36		
	16.94	16.53		
	17.28	18.70		
	19.17	19.92		
Toxaphene	16.60	16.60	910	
	17.37	17.52		
	18.11	17.92		
	19.46	18.73		
	19.69	19.00		

Notes:

1. Data from EPA Method 1656
2. Columns: 30 m long x 0.53 mm ID fused-silica capillary; DB-608, 0.83 µ ; DB-1701, 1.0 µ . Conditions suggested to meet retention times shown: 150 °C ~~F, C~~ for 0.5 minute, 150-270 °C at 5EC/min, 270 °C until trans-Permethrin elutes. Carrier gas flow rates approximately 7 mL/min.
3. 40 *CFR* 136, Appendix B. MDLs were obtained by a single laboratory with an electrolytic conductivity detector, except as noted.
4. Does not elute from DB-1701 column at level tested.
5. Not recovered from water at the levels tested.
6. Dichlone and Kepone do not elute from the DB-1701 column and should be confirmed on DB-5.

Comment [mw105]: Revise or eliminate table?

Comment [mw106]: Eliminate MDLs.

Table 4—Suggested concentrations of calibration solutions and suggested calibration [1]			
	Concentration (ng/mL)		
Analyte	**Low**	**Medium**	**High**
Calibration Group 1			
Acephate	2000	10000	40000
Alachlor	20	100	400
Atrazine	1000	5000	20000
∃-BHC	10	50	200
Bromoxynil octanoate	50	250	1000
Captafol	200	1000	4000
Diallate	200	1000	4000
Endosulfan sulfate	10	50	200
Endrin	20	100	400
Isodrin	10	50	200
Pendimethalin (Prowl)	50	250	1000
trans-Permethrin	200	1000	4000
Calibration Group 2			
∀-BHC	5.0	25	100
DCPA	5.0	25	100
4,4N-DDE	10	50	200
4,4N-DDT	10	50	200
Dichlone	20	100	400
Ethalfluralin	10	50	200
Fenarimol	20	100	400
Methoxychlor	20	100	400
Metribuzin	10	50	200
Calibration Group 3			
(-BHC (Lindane)	5	25	100
(-Chlordane	5	25	100
Endrin ketone	10	50	200
Heptachlor epoxide	5	25	100
Isopropalin	20	100	400
Nitrofen (TOK)	20	100	400
PCNB	5	25	100
cis-Permethrin	200	1000	4000
Trifluralin	10	50	200
Calibration Group 4			
Benfluralin	20	100	400
Chlorobenzilate	50	500	5000
Dieldrin	5	20	100
Endosulfan I	10	50	200
Mirex	20	100	400
Terbacil	200	1000	4000
Terbuthylazine	500	2500	10000
Triadimefon	100	500	2000
Calibration Group 5			
∀-Chlordane	10	50	200
Captan	100	500	2000
Chlorothalonil	20	100	400
4,4N-DDD	20	100	400

Comment [mw107]: Revise or eliminate table

Norfluorazon	100	500	2000
Simazine	800	4000	20000
Calibration Group 6			
Aldrin	20	100	400
∗-BHC	5	25	100
Bromacil	100	500	2000
Butachlor	50	250	1000
Endosulfan II	10	50	200
Heptachlor	10	50	200
Kepone	100	500	2000
Calibration Group 7			
Carbophenothion	80	400	1600
Chloroneb	300	1500	6000
Chloropropylate	200	1000	4000
DBCP	25	125	500
Dicofol	300	1500	6000
Endrin aldehyde	80	400	1600
Etridiazole	80	400	1600
Perthane	1000	5000	20000
Propachlor	500	2500	10000
Propanil	200	1000	4000
Propazine	1000	5000	20000

1. Other calibration solutions and calibration groups may be used provided all QC requirements are met.

Table 5—QC Acceptance Criteria						
Analyte	Calibration verification (%)	Test concen-tration (µg/L)	Limit for s (% SD)	Range for $\bar{X}$ (%)	Range for P (%)	Maximum MS/MSD RPD (%)
Aldrin	75 - 125	2.0	25	54 - 130	42 - 140	35
alpha-BHC	69 - 125	2.0	28	49 - 130	37 - 140	36
beta-BHC	75 - 125	2.0	38	39 - 130	17 - 147	44
delta-BHC	75 - 125	2.0	43	51 - 130	19 - 140	52
gamma-BHC	75 - 125	2.0	29	43 - 130	32 - 140	39
alpha-Chlordane	73 - 125	50.0	24	55 - 130	45 - 140	35
gamma-Chlordane	75 - 125	50.0	24	55 - 130	45 - 140	35
4,4'-DDD	75 - 125	10.0	32	48 - 130	31 - 141	39
4,4'-DDE	75 - 125	2.0	30	54 - 130	30 - 145	35
4,4'-DDT	75 - 125	10.0	39	46 - 137	25 - 160	42
Dieldrin	48 - 125	2.0	42	58 - 130	36 - 146	49
Endosulfan I	75 - 125	2.0	25	57 - 141	45 - 153	28
Endosulfan II	75 - 125	10.0	63	22 - 171	D - 202	53
Endosulfan sulfate	70 - 125	10.0	32	38 - 132	26 - 144	38
Endrin	5 - 125	10.0	42	51 - 130	30 - 147	48
Heptachlor	75 - 125	2.0	28	43 - 130	34 - 140	43
Heptachlor epoxide	75 -125	2.0	22	57 - 132	37 - 142	26
Toxaphene	68 - 134	50.0	30	56 - 130	41 - 140	41
PCB-1016	75 - 125	50.0	24	61 - 103	50 - 140	36
PCB-1221	75 - 125	50.0	50	44 - 150	15 - 178	48
PCB-1232	75 - 125	50.0	32	28 - 197	10 - 215	25
PCB-1242	75 - 125	50.0	26	50 - 139	39 - 150	29
PCB-1248	75 - 125	50.0	32	58 - 140	38 - 158	35
PCB-1254	75 - 125	50.0	34	44 - 130	29 - 140	45
PCB-1260	75 - 125	50.0	28	37 - 130	8 - 140	38

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

Note: These criteria were developed from data in Table 6 (Reference 2). Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those in Table 6.

Table 6—Precision and recovery as functions of concentration			
Analyte	**Recovery, X′ (µg/L)**	**Single analyst precision, s_r′ (µg/L)**	**Overall precision, S′ (µg/L)**
Aldrin	0.81C+0.04	0.16(X-bar) - 0.04	0.20(X-bar) - 0.01
α-BHC	0.84C+0.03	0.13(X-bar)+0.04	0.23(X-bar) - 0.00
β-BHC	0.81C+0.07	0.22(X-bar) - 0.02	0.33(X-bar) - 0.05
δ-BHC	0.81C+0.07	0.18(X-bar)+0.09	0.25(X-bar)+0.03
γ-BHC	0.82C - 0.05	0.12(X-bar)+0.06	0.22(X-bar)+0.04
Chlordane	0.82C - 0.04	0.13(X-bar)+0.13	0.18(X-bar)+0.18
4,4'-DDD	0.84C+0.30	0.20(X-bar) - 0.18	0.27(X-bar) - 0.14
4,4'-DDE	0.85C+0.14	0.13(X-bar)+0.06	0.28(X-bar) - 0.09
4,4'-DDT	0.93C - 0.13	0.17(X-bar)+0.39	0.31(X-bar) - 0.21
Dieldrin	0.90C+0.02	0.12(X-bar)+0.19	0.16(X-bar)+0.16
Endosulfan I	0.97C+0.04	0.10(X-bar)+0.07	0.18(X-bar)+0.08
Endosulfan II	0.93C+0.34	0.41(X-bar) - 0.65	0.47(X-bar) - 0.20
Endosulfan sulfate	0.89C - 0.37	0.13(X-bar)+0.33	0.24(X-bar)+0.35
Endrin	0.89C - 0.04	0.20(X-bar)+0.25	0.24(X-bar)+0.25
Heptachlor	0.69C+0.04	0.06(X-bar)+0.13	0.16(X-bar)+0.08
Heptachlor epoxide	0.89C+0.10	0.18(X-bar) - 0.11	0.25(X-bar) - 0.08
Toxaphene	0.80C+1.74	0.09(X-bar)+3.20	0.20(X-bar)+0.22
PCB-1016	0.81C+0.50	0.13(X-bar)+0.15	0.15(X-bar)+0.45
PCB-1221	0.96C+0.65	0.29(X-bar) - 0.76	0.35(X-bar) - 0.62
PCB-1232	0.91C+10.8	0.21(X-bar) - 1.93	0.31(X-bar)+3.50
PCB-1242	0.93C+0.70	0.11(X-bar)+1.40	0.21(X-bar)+1.52
PCB-1248	0.97C+1.06	0.17(X-bar)+0.41	0.25(X-bar) - 0.37
PCB-1254	0.76C+2.07	0.15(X-bar)+1.66	0.17(X-bar)+3.62
PCB-1260	0.66C+3.76	0.22(X-bar) - 2.37	0.39(X-bar) - 4.86

X′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

Table 7—Distribution of chlorinated pesticides and PCBs into Florisil column fractions			
	Percent recovery by fraction [1]		
Analyte	**1**	**2**	**3**
Aldrin	100	. . . . .	. . . . .
α-BHC	100	. . . . .	. . . . .
β-BHC	97	. . . . .	. . . . .
δ-BHC	98	. . . . .	. . . . .
γ-BHC	100	. . . . .	. . . . .
Chlordane	100	. . . . .	. . . . .
4,4'-DDD	99	. . . . .	. . . . .
4,4'-DDE	98	. . . . .	. . . . .
4,4'-DDT	100	. . . . .	. . . . .
Dieldrin	0	100	. . . . .
Endosulfan I	37	64	. . . . .
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	. . . . .
Endrin aldehyde	0	68	26
Heptachlor	100	. . . . .	. . . . .
Heptachlor epoxide	100	. . . . .	. . . . .
Toxaphene	96	. . . . .	. . . . .
PCB-1016	97	. . . . .	. . . . .
PCB-1221	97	. . . . .	. . . . .
PCB-1232	95	4	. . . . .
PCB-1242	97	. . . . .	. . . . .
PCB-1248	103	. . . . .	. . . . .
PCB-1254	90	. . . . .	. . . . .
PCB-1260	95	. . . . .	. . . . .

[1] Eluant composition:
Fraction 1 - 6% ethyl ether in hexane
Fraction 2 - 15% ethyl ether in hexane
Fraction 3 - 50% ethyl ether in hexane

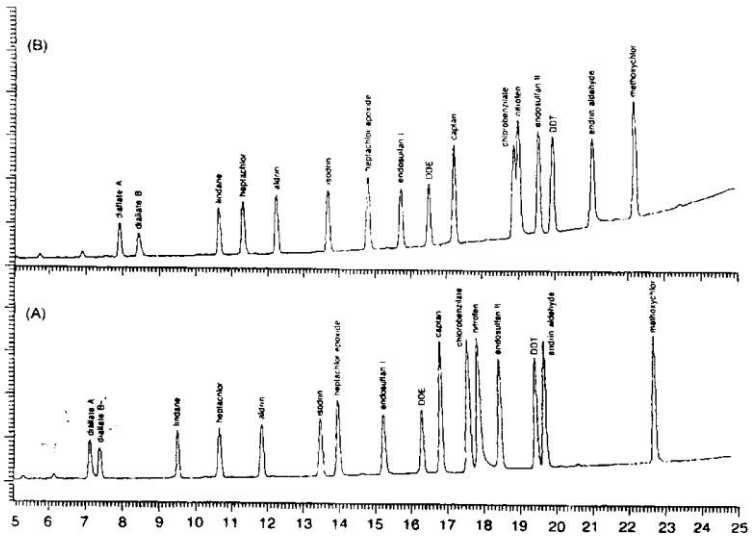

Figure 1 Chromatogram of Selected Organo-chlorine Pesticides

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
µL	microliter
<	less than
>	greater than
%	percent

22.1.2 Abbreviations (in alphabetical order)

cm	centimeter
g	gram
hr	hour
ID	inside diameter
in.	inch
L	liter
M	mole - mass numerically equal to the molecular weight in grams
M	molar solution - one mole or gram molecular weight of solute in one liter of solution
mg	milligram
min	minute
mL	milliliter
mm	millimeter
psig	pounds-per-square inch gauge
v/v	volume per unit volume
w/v	weight per unit volume

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 and 2.

Analytical batch – The set of samples analyzed on a given instrument during a 24-hour period that begins and ends with calibration verification (Sections 7.8 and 13). See also "Extraction batch."

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Blank (method blank; laboratory 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 factor (CF) – See Section 7.5.1.

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

Calibration verification – The process of confirming that the response of the analytical system remains within specified limits of the calibration

Calibration verification standard – The combined QC standard (Section 7.7) used to verify calibration (Section 13.5) and for LCS tests (Section 8.4).

Extraction Batch – A set of up to 20 field samples (not including QC samples) started through the extraction process in a given 24-hour shift. Each extraction batch of 20 or fewer samples must be accompanied by a blank (Section 8.5), a laboratory control sample (LCS, Section 8.4), a matrix spike and duplicate (MS/MSD; Section 8.3), resulting in a minimum of five samples (1 field sample, 1 blank, 1 LCS, 1 MS, and 1 MSD) and a maximum of 24 samples (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 24-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. See also "Blank."

GC – Gas chromatograph or gas chromatography

Gel-permeation chromatography (GPC) – A form of liquid chromatography in which the analytes are separated based on exclusion from the solid phase by size.

GPC – see gel-permeation 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. Also see Internal standard quantitation.

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

IDC – Initial demonstration of capability (Section 8.2); four aliquots of a reference matrix spiked with the analytes of interest and analyzed to establish the ability of the laboratory to generate acceptable precision and recovery. An IDC 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 – See blank

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

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

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

Method detection limit (MDL) – A detection limit determined by the procedure at 40 CFR 136, Appendix B. MDLs are listed in Table 3.

MS – Mass spectrometer or mass spectrometry

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

Preparation blank – See blank

Quality control sample (QCS) – A sample containing analytes of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independent of the normal preparation process.

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

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

RF – Response factor. See Section 7.6.2

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.

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

SPE – Solid-phase extraction; an extraction technique in which an analyte is selectively removed from a sample extract by passage over or through a material capable of reversibly adsorbing the analyte.

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

Surrogate – A compound unlikely to be found in a sample, which is spiked into the sample in a known amount before extraction, and which 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.