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# Method 1656: The Determination of Organo-Halide Pesticides in Municipal and Industrial Wastewater

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## *The Determination of Organo-Halide Pesticides in Municipal and Industrial Wastewater*

### *1. Scope and Application*

**1.1** This method is designed to meet the survey requirements of the Environmental Protection Agency (EPA). It is used to determine (1) the organo-halide pesticides and polychlorinated biphenyls (PCBs) associated with the Clean Water Act, the Resource Conservation and Recovery Act, and the Comprehensive Environmental Response, Compensation and Liability Act; and (2) other compounds amenable to extraction and analysis by wide-bore capillary column gas chromatography (GC) with halogen-specific detectors.

**1.2** The compounds listed in Table 1 may be determined in waters, soils, sediments, and sludges by this method. The method is a consolidation of several EPA wastewater methods. For waters, the sample extraction and concentration steps are essentially the same as in these methods. However, the extraction and concentration steps have been extended to other sample matrices. The method may be applicable to other pesticides as well. The quality control requirements in this method give the steps necessary to determine this applicability. Not all compounds listed in Table 1 have corresponding calibration data in Table 3 and acceptance criteria in Table 4. Calibration data for such analytes may be found in other EPA methods (References 1 and 2).

**1.3** This method is applicable to a large number of compounds. Calibrating the GC systems for all compounds is time-consuming. If only a single compound or small number of compounds is to be tested for, it is necessary to calibrate the GC systems and meet the performance specifications in this method for these compounds only. In addition, the GC conditions can be optimized for these compounds provided that all performance specifications in this method are met.

**1.4** When this method is applied to analysis of unfamiliar samples, compound identity must be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Gas chromatography/mass spectrometry (GC/MS) can be used to confirm compounds in extracts produced by this method when analyte levels are sufficient.

**1.5** The detection limits of this method are usually dependent on the level of interferences rather than instrumental limitations. The limits in Table 2 typify the minimum quantities that can be detected with no interferences present.

**1.6** This method is for use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatographic data. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 8.2.

## 2. SUMMARY OF METHOD

**2.1** Extraction.

**2.1.1** The percent solids content of a sample is determined.

**2.1.2** Samples containing low solids: If the solids content is 1% or less, a 1-L sample is extracted with methylene chloride using continuous extraction techniques.

**2.1.3** Samples containing less than 1% solids.

**2.1.3.1** Non-sludge samples: If the solids content is 1 to 30%, the sample is diluted to 1% solids with reagent water, homogenized ultrasonically, and extracted with methylene chloride using continuous extraction techniques. If the solids content is greater than 30%, the sample is extracted with methylene chloride:acetone using ultrasonic techniques.

**2.1.3.2** Municipal sludge samples and other intractable sample types: If the solids content is less than 30%, the sample is diluted to 1% solids and extracted with methylene chloride using continuous extraction techniques. If the solids content is greater than 30%, the sample is extracted with acetonitrile and then methylene chloride using ultrasonic techniques. The extract is back-extracted with 2% (w/v) sodium sulfate in reagent water to remove water-soluble interferences and residual acetonitrile.

**2.2** Concentration and cleanup: The extract is dried over sodium sulfate, concentrated using a Kuderna-Danish evaporator, cleaned up (if necessary) using gel permeation chromatography (GPC) and/or adsorption chromatography and/or solid-phase extraction, and then concentrated to 1 mL. Sulfur is removed from the extract, if required.

**2.3** Gas chromatography: A 1-$\mu$L aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated on a wide-bore, fused-silica capillary column. The analytes are detected by an electron capture, microcoulometric, or electrolytic conductivity detector.

**2.4** Identification of a pollutant (qualitative analysis) is performed by comparing the GC retention times of the compound on two dissimilar columns with the respective retention times of an authentic standard. Compound identity is confirmed when the retention times agree within their respective windows.

**2.5** Quantitative analysis is performed using an authentic standard to produce a calibration factor or calibration curve, and using the calibration data to determine the concentration of a pollutant in the extract. The concentration in the sample is calculated using the sample weight or volume and the extract volume.

**2.6** Quality is assured through reproducible calibration and testing of the extraction and GC systems.

## 3. CONTAMINATION AND INTERFERENCES

**3.1** Solvents, reagents, glassware, and other sample-processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. All materials used in the anal-

ysis shall be demonstrated to be free from interferences under the conditions of analysis by running method blanks as described in Section 8.5.

**3.2** Glassware and, where possible, reagents are cleaned by solvent rinse and baking at 450°C for a minimum of 1 hour in a muffle furnace or kiln. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment, and thorough rinsing with acetone and pesticide-quality hexane may be required.

**3.3** Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

**3.4** Interference by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. Phthalates usually appear in the chromatogram as large, late-eluting peaks. Phthalates may be leached from common flexible plastic tubing and other plastic materials during the extraction and cleanup processes. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory, or by using a microcoulometric or electrolytic conductivity detector.

**3.5** Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. The cleanup procedures given in this method can be used to overcome many of these interferences, but unique samples may require additional cleanup to achieve the minimum levels given in Table 2.

## 4. SAFETY

**4.1** The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 3 through 5.

**4.2** The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDD, 4,4'-DDT, the BHCs and the PCBs. Primary standards of these compounds shall be prepared in a hood, and a NIOSH/MESA-approved toxic gas respirator should be worn when high concentrations are handled.

**4.3** Mercury vapor is highly toxic. If mercury is used for sulfur removal, all operations involving mercury shall be performed in a hood.

**4.4** Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves that will prevent exposure. The oven used for sample drying to determine percent moisture should be located in a hood so that vapors from samples do not create a health hazard in the laboratory.

## 5. APPARATUS AND MATERIALS

*NOTE: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance meeting requirements of this method is the responsibility of the laboratory.*

**5.1** Sampling equipment for discrete or composite sampling.

**5.1.1** Sample bottles and caps.

**5.1.1.1** Liquid samples (waters, sludges, and similar materials that contain less than 5% solids): Sample bottle, amber glass, 1-L or 1-quart, with screw-cap.

**5.1.1.2** Solid samples (soils, sediments, sludges, filter cake, compost, and similar materials that contain >5% solids): Sample bottle, wide mouth, amber glass, 500-mL minimum.

**5.1.1.3** If amber bottles are not available, samples shall be protected from light.

**5.1.1.4** Bottle caps: Threaded to fit sample bottles. Caps shall be lined with PTFE.

**5.1.1.5** Cleaning.

**5.1.1.5.1** Bottles are detergent-water washed, then rinsed with solvent or baked at 450°C for a minimum of 1 hour before use.

**5.1.1.5.2** Liners are detergent-water washed, then rinsed with reagent water and solvent, and baked at approximately 200°C for a minimum of 1 hour prior to use.

**5.1.2** Compositing equipment: Automatic or manual compositing system incorporating glass containers cleaned per bottle-cleaning procedure above. Sample containers are kept at 0 to 4°C during sampling. Glass or PTFE tubing only shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing shall be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

**5.2** Equipment for determining percent moisture.

**5.2.1** Oven, capable of maintaining a temperature of 110°C (±5°C).

**5.2.2** Desiccator.

**5.2.3** Crucibles, porcelain.

**5.2.4** Weighing pans, aluminum.

**5.3** Extraction equipment.

**5.3.1** Equipment for ultrasonic extraction.

**5.3.1.1** Sonic disrupter: 375 watt with pulsing capability and ½" or ¾" disrupter horn (Ultrasonics, Inc, Model 375C, or equivalent).

**5.3.1.2** Sonabox (or equivalent), for use with disrupter.

**5.3.2** Equipment for liquid-liquid extraction.

**5.3.2.1** Continuous liquid-liquid extractor: PTFE or glass connecting joints and stopcocks without lubrication, 1.5- to 2-L capacity (Hershberg-Wolf Extractor, Cal-Glass, Costa Mesa,California, 1000- or 2000-mL continuous extractor, or equivalent).

**5.3.2.2** Round-bottom flask, 500-mL, with heating mantle.

**5.3.2.3** Condenser, Graham, to fit extractor.

**5.3.2.4** pH meter, with combination glass electrode.

**5.3.2.5** pH paper, wide range (Hydrion Papers, or equivalent).

**5.2.3** Separatory funnels: 250-, 500-, 1000-, and 2000-mL, with PTFE stopcocks.

**5.3.4** Filtration apparatus.

**5.3.4.1** Glass powder funnels: 125- to 250-mL.

**5.3.4.2** Filter paper for above (Whitman 41, or equivalent).

**5.3.5** Beakers.

**5.3.5.1** 1.5- to 2-L, calibrated to 1 L.

**5.3.5.2** 400- to 500-mL.

**5.3.6** Spatulas: Stainless steel or PTFE.

**5.3.7** Drying column: 400 mm long × 15 to 20 mm ID Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

**5.3.7.1** Pyrex glass wool: Extracted with solvent or baked at 450°C for a minimum of 1 hour.

**5.4** Evaporation/concentration apparatus.

**5.4.1** Kuderna-Danish (K-D) apparatus.

**5.4.1.1** Evaporation flask: 500-mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012).

**5.4.1.2** Concentrator tube: 10-mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

**5.4.1.3** Snyder column: Three-ball macro (Kontes K-503000-0232, or equivalent).

**5.4.1.4** Snyder column: Two-ball micro (Kontes K-469002-0219, or equivalent).

**5.4.1.5** Boiling chips.

**5.4.1.5.1** Glass or silicon carbide: Approximately 10/40 mesh, extracted with methylene chloride and baked at 450°C for a minimum of 1 hour.

**5.4.1.5.2** PTFE (optional): Extracted with methylene chloride.

**5.4.2** Water bath: Heated, with concentric ring cover, capable of temperature control (±2°C), installed in a fume hood.

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

**5.4.4** Sample vials: Amber glass, 1- to 5-mL with PTFE-lined screw- or crimp-cap, to fit GC autosampler.

**5.5** Balances.

**5.5.1** Analytical: Capable of weighing 0.1 mg.

**5.5.2** Top loading: Capable of weighing 10 mg.

**5.6** Apparatus for sample cleanup.

**5.6.1** Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc., Columbia, MO, Model GPC Autoprep 1002, or equivalent).

**5.6.1.1** Column: 600 to 700 mm long × 25 mm ID, packed with 70 g of SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA, or equivalent).

**5.6.1.2** Syringe, 10-mL, with Luer fitting.

**5.6.1.3** Syringe-filter holder, stainless steel, and glass fiber or PTFE filters (Gelman Acrodisc-CR, 1 to 5 $\mu$, or equivalent).

**5.6.1.4** UV detector: 254-nm, preparative or semi-prep flow cell: (Isco, Inc., Type 6; Schmadzu, 5 mm path length; Beckman-Altex 152W, 8 $\mu$L microprep flow cell, 2 mm path; Pharmacia UV-1, 3 mm flow cell; LDC Milton-Roy UV-3, monitor #1203; or equivalent).

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

**5.6.2.1** Vacuum system: Capable of achieving 0.1 bar (house vacuum, vacuum pump, or water aspirator), with vacuum gauge.

**5.6.2.2** VacElute Manifold (Analytichem International, or equivalent).

**5.6.2.3** Vacuum trap: Made from 500-mL sidearm flask fitted with single-hole rubber stopper and glass tubing.

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

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

**5.6.3** Chromatographic column: 400 mm long × 22 mm ID, with PTFE stopcock and coarse frit (Kontes K-42054, or equivalent).

**5.6.4** Sulfur removal tubes: 40- to 50-mL bottle or test tube with PTFE-lined screw-cap.

**5.7** Centrifuge apparatus.

**5.7.1** Centrifuge: Capable of rotating 500-mL centrifuge bottles or 15-mL centrifuge tubes at 5,000 rpm minimum.

**5.7.2** Centrifuge bottles: 500-mL, with screw-caps, to fit centrifuge.

**5.7.3** Centrifuge tubes: 12- to 15-mL, with screw-caps, to fit centrifuge.

**5.7.3** Funnel, Buchner, 15 cm.

**5.7.3.1** Flask, filter, for use with Buchner funnel.

**5.7.3.2** Filter paper, 15 cm (Whatman #41, or equivalent).

**5.8** Miscellaneous glassware.

**5.8.1** Pipettes, glass, volumetric, 1.00-, 5.00-, and 10.0-mL.

**5.8.2** Syringes, glass, with Luerlok tip, 0.1-, 1.0- and 5.0-mL. Needles for syringes, 2", 22-gauge.

**5.8.3** Volumetric flasks, 10.0-, 25.0-, and 50.0-mL.

**5.8.4** Scintillation vials, glass, 20- to 50-mL, with PTFE-lined screw-caps.

**5.9** Gas chromatograph: Shall have splitless or on-column simultaneous automated injection into separate capillary columns with a halide-specific detector at the end of each column, temperature program with isothermal holds, data system capable of recording simultaneous signals from the two detectors, and shall meet all of the performance specifications in Section 14.

**5.9.1** GC columns: Bonded-phase, fused-silica capillary.

**5.9.1.1** Primary: 30 m (±3 m) long × 0.5 mm (±0.05 mm) ID DB-608 (or equivalent).

**5.9.1.2** Confirmatory: DB-1701, or equivalent, with same dimensions as primary column.

**5.9.2** Data system: Shall collect and record GC data, store GC runs on magnetic disk or tape, process GC data, compute peak areas, store calibration data including retention times and calibration factors, identify GC peaks through retention times, compute concentrations, and generate reports.

**5.9.2.1** Data acquisition: GC data shall be collected continuously throughout the analysis and stored on a mass storage device.

**5.9.2.2** Calibration factors and calibration curves: The data system shall be used to record and maintain lists of calibration factors, and multi-point calibration curves (Section 7). Computations of relative standard deviation (coefficient of variation) are used for testing calibration linearity. Statistics on initial (Section 8.2) and ongoing (Section 14.6) performance shall be computed and maintained.

**5.9.2.3** Data processing: The data system shall be used to search, locate, identify, and quantify the compounds of interest in each GC analysis. Software routines shall be employed to compute and record retention times and peak areas. Displays of chromatograms and library comparisons are required to verify results.

**5.9.3** Halide-specific detector: Electron capture or electrolytic conductivity (Micoulometric, Hall, O.I., or equivalent), capable of detecting 8 pg of aldrin under the analysis conditions given in Table 2.

## 6. *Reagents and Standards*

**6.1** Sample preservation: Sodium thiosulfate (ACS), granular.

**6.2** pH adjustment.

**6.2.1** Sodium hydroxide: Reagent grade.

**6.2.1.1** Concentrated solution (10N): Dissolve 40 g NaOH in 100 mL reagent water.

**6.2.1.2** Dilute solution (0.1M): Dissolve 4 g NaOH in 1 L of reagent water.

**6.2.2** Sulfuric acid (1 + 1): Reagent grade, 6N in reagent water. Slowly add 50 mL $H_2SO_4$ (specific gravity 1.84) to 50 mL reagent water.

**6.2.3** Potassium hydroxide: 37% (w/v). Dissolve 37 g KOH in 100 mL reagent water.

**6.3** Solution drying and back-extraction.

**6.3.1** Sodium sulfate, reagent grade, granular anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 450°C for a minimum of 1 hour, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw-cap which prevents moisture from entering.

**6.3.2** Sodium sulfate solution: 2% (w/v) in reagent water, pH-adjusted to 8.5 to 9.0 with KOH or $H_2SO_4$.

**6.4** Solvents: Methylene chloride, hexane, ethyl ether, acetone, acetonitrile, isooctane, and methanol; pesticide-quality; lot-certified to be free of interferences.

**6.4.1** Ethyl ether must be shown to be free of peroxides before it is used, as indicated by EM Laboratories Quant Test Strips (Scientific Products P1126-8, or equivalent). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol is added to each liter of ether as a preservative.

**6.5** GPC calibration solution: Solution containing 300 mg/mL corn oil, 15 mg/mL bis (2-ethylhexyl) phthalate, 1.4 mg/mL pentachlorophenol, 0.1 mg/mL perylene, and 0.5 mg/mL sulfur.

**6.6** Sample cleanup.

**6.6.1** Florisil: PR grade, 60/100 mesh, activated at 650 to 700°C, stored in the dark in glass container with PTFE-lined screw-cap. Activate at 130°C for 16 hours minimum immediately prior to use. Alternatively, 500-mg cartridges (J.T. Baker, or equivalent) may be used.

**6.6.2** Solid-phase extraction.

**6.6.2.1** SPE cartridge calibration solution: 2,4,6-trichlorophenol, 0.1 ug/mL in acetone.

**6.6.2.2** SPE elution solvent: Methylene chloride:acetonitrile:hexane (50:3:47).

**6.6.3** Alumina, neutral, Brockman Activity I, 80 to 200 mesh (Fisher Scientific Certified, or equivalent). Heat 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.

**6.6.4** Silicic acid, 100 mesh.

**6.6.5** Sulfur removal: Mercury (triple-distilled), copper powder (bright, non-oxidized), or TBA sodium sulfite. If mercury is used, observe the handling precautions in Section 4.

**6.7** Reagent water: Water in which the compounds of interest and interfering compounds are not detected by this method.

**6.8** High-solids reference matrix: Playground sand or similar material in which the compounds of interest and interfering compounds are not detected by this method. May be prepared by extraction with methylene chloride and/or baking at 450°C for 4 hours minimum.

**6.9** Standard solutions: Purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared 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, standards are stored in the dark at -20 to -10°C in screw-capped vials with PTFE-lined lids. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. The vials are brought to room temperature prior to use. Any precipitate is redissolved and solvent is added if solvent loss has occurred.

**6.10** Preparation of stock solutions: Prepare in isooctane per the steps below. Observe the safety precautions in Section 4.

**6.10.1** Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 10 mg aldrin in a 10-mL ground-glass stoppered volumetric flask and fill to the mark with isooctane. After the aldrin is completely dissolved, transfer the solution to a 15-mL vial with PTFE-lined cap.

**6.10.2** Stock solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards.

**6.10.3** Stock solutions shall be replaced after 6 months, or sooner if comparison with quality control check standards indicates a change in concentration.

**6.11** Secondary mixtures: Using stock solutions (Section 6.10), prepare mixtures at the levels shown in Table 3 for calibration and calibration verification (Sections 7.3 and 14.5), for initial and ongoing precision and recovery (Sections 8.2 and 14.6), and for spiking into the sample matrix (Section 8.4).

**6.12** Surrogate spiking solution: Prepare dibutyl chlorendate (DBC) at a concentration of 2 μg/mL in acetone.

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*NOTE: If DBC is not available, compounds such as tetrachloro-m-xylene or decachlorobiphenyl may be used provided that the laboratory performs the tests described in Section 8.2 using these compounds.*

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**6.13** DDT and endrin decomposition solution: Prepare a solution containing endrin at a concentration of 1 μg/mL and DDT at a concentration of 2 μg/mL.

**6.14** Stability of solutions: All standard solutions (Sections 6.9 through 6.13) shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. Standards will remain acceptable if the peak area remains within ±15% of the area obtained in the initial analysis of the standard.

## 7. SETUP AND CALIBRATION

**7.1** Configure the GC system as given in Section 5.9 and establish the operating conditions in Table 2.

**7.2** Attainment of method detection limit (MDL) and DDT/Endrin decomposition requirements: Determine that each column/detector system meets the MDLs (Table 2), and the DDT and Endrin decomposition test (Section 13.4).

**7.3** Calibration.

**7.3.1** Injection of calibration solutions.

**7.3.1.1** Compounds with calibration data in Table 3: The compounds in each calibration group in Table 3 were chosen so that each compound would be separated from the others by approximately 1 minute on the primary column. The concentrations were chosen to bracket the working range of either the ECD or the ELCD. However, because the response of the ECLD is less for some compounds than that of the ECD, it may be necessary to inject a larger volume of calibration solution when the ELCD is used.

**7.3.1.2** Compounds without calibration data in Table 3: Prepare calibration standards at a minimum of three concentration levels. One of these concentrations should be near, but above, the MDL (Table 2) and the other concentrations should define the working range of the detectors.

**7.3.1.3** Set the automatic injector to inject a constant volume in the range of 0.5 to 5.0 $\mu$L of each calibration solution into the GC column/detector pairs, beginning with the lowest level mixture and proceeding to the highest. For each compound, compute and store, as a function of the concentration injected, the retention time and peak area on each column/detector system (primary and confirmatory). For the multi-componenent analytes (PCBs, toxaphene), store the retention time and peak area for the five largest peaks.

**7.3.2** Retention time: The polar nature of some analytes causes the retention time to decrease as the quantity injected increases. To compensate this effect, the retention time for compound identification is correlated with the analyte level.

**7.3.2.1** If the difference between the maximum and minimum retention times for any compound is less than 5 seconds over the calibration range, the retention time for that compound can be considered constant and an average retention time may be used for compound identification.

**7.3.2.2** Retention time calibration curve (retention time vs. amount): If the retention time for a compound in the lowest level standard is more than 5 seconds greater than the retention time for the compound in the highest level standard, a retention time calibration curve shall be used for identification of that compound.

**7.3.3** Calibration factor (ratio of area to amount injected).

**7.3.3.1** Compute the coefficient of variation (relative standard deviation) of the calibration factor over the calibration range for each compound on each column/detector system.

**7.3.3.2** Linearity: If the calibration factor for any compound is constant ($C_v$ < 20%) over the calibration range, an average calibration factor may be used for that compound; otherwise, the complete calibration curve (area vs. amount) for that compound shall be used.

**7.4** Combined QC standards: To preclude periodic analysis of all of the individual calibration groups of compounds (Table 3), the GC systems are calibrated with combined solutions as a final step. Not all of the compounds in these standards will be separated by the GC columns used in this method. Retention times and calibration factors are verified for the compounds that are resolved, and calibration factors are obtained for the unresolved peaks.

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

**7.4.1.1** For those compounds that exhibit a single, resolved GC peak, the retention time shall be within ±5 seconds of the retention time of the peak in the medium level calibration standard (Table 3), and the calibration factor using the primary column shall be within ±20% of the calibration factor in the medium level standard (Table 3).

**7.4.1.2** For the peaks containing two or more compounds, compute and store the retention times at the peak maxima on both columns (primary and confirmatory), and also compute and store the calibration factors on both columns. These results will be used for calibration verification (Section 13.2 and 13.5) and for precision and recovery studies (Sections 8.2 and 13.6).

**7.5** Florisil calibration: The cleanup procedure in Section 11 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil that is used, the use of the lauric acid value (Reference 6) is suggested. The referenced procedure determines the adsorption of lauric acid (in milligrams per gram of Florisil) from hexane solution. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

## 8. QUALITY CONTROL

**8.1** Each laboratory that uses this method is required to operate a formal quality control program (Reference 7). The minimum requirements of this program consist of an initial demonstration of laboratory capability, an ongoing analysis of standards and blanks as tests of continued performance, and analysis of spiked samples to assess accuracy. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method. If the method is to be applied routinely to samples containing high solids with very little moisture (e.g., soils, compost), the high-solids reference

matrix (Section 6.8) is substituted for reagent water (Section 6.7) in all performance tests, and the high-solids method (Section 10) is used for these tests.

**8.1.1** The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

**8.1.2** The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance requirements are met. Each time a modification is made to the method or a cleanup procedure is added, the analyst is required to repeat the procedure in Section 8.2 to demonstrate method performance. If detection limits will be affected by the modification, the analyst is required to repeat the demonstration of detection limits (Section 7.2).

**8.1.3** The laboratory shall spike all samples with at least one surrogate compound to monitor method performance. This test is described in Section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (Section 16).

**8.1.4** The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the combined QC standard (Section 6.11) that the analysis system is in control. These procedures are described in Sections 13.1, 13.5, and 13.6.

**8.1.5** The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Section 8.4.

**8.1.6** Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in Section 8.5.

**8.1.7** Other analytes may be determined by this method. The procedure for establishing a preliminary quality control limit for a new analyte is given in Section 8.6.

**8.2** Initial precision and recovery: To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations.

**8.2.1** For analysis of samples containing low solids (aqueous samples), extract, concentrate, and analyze one set of four 1-L aliquots of reagent water spiked with the combined QC standard (Section 6.11) according to the procedure in Section 10. Alternatively, sets of four replicates of the individual calibration groups (Table 3) may be used. For samples containing high solids, a set of four 30-g aliquots of the high-solids reference matrix are used.

**8.2.2** Using results of the set of four analyses, compute the average percent recovery (X) and the coefficient of variation ($C_v$) of percent recovery (s) for each compound.

**8.2.3** For each compound, compare s and X with the corresponding limits for initial precision and accuracy in Table 4. For coeluting compounds, use the coeluted compound with the least restrictive specification (largest $C_v$ and widest range). If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limitor or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. In this case, correct the problem and repeat the test.

**8.3** The laboratory shall spike all samples with at least one surrogate compound to assess method performance on the sample matrix.

**8.3.1** Analyze each sample according to the method beginning in Section 10.

**8.3.2** Compute the percent recovery (P) of the DBC or other surrogate.

**8.3.3** The surrogate recovery shall be 40 to 120%. If the recovery of the surrogate falls outside of these limits, method performance is unacceptable for that sample, and the sample is complex. Water samples are diluted, and smaller amounts of soils, sludges, and sediments are reanalyzed per Section 16.

**8.4** Method accuracy: The laboratory shall spike (matrix spike) at least 10% of the samples from a given site type (e.g., influent to treatment, treated effluent, produced water, river sediment). If only one sample from a given site type is analyzed, a separate aliquot of that sample shall be spiked.

**8.4.1** The concentration of the matrix spike shall be determined as follows:

**8.4.1.1** If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the matrix spike shall be at that limit or at 1 to 5 times higher than the background concentration determined in Section 8.4.2, whichever concentration is larger.

**8.4.1.2** If the concentration of an analyte in the sample is not being checked against a limit specific to that analyte, the matrix spike shall be at the concentration of the combined QC standard (Table 3) or at 1 to 5 times higher than the background concentration, whichever concentration is larger.

**8.4.1.3** If it is impractical to determine the background concentration before spiking (e.g., maximum holding times will be exceeded), the matrix spike concentration shall be the regulatory concentration limit, if any; otherwise, the larger of either 5 times the expected background concentration or at the concentration of the combined QC standard (Table 3).

**8.4.2** Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a standard solution appropriate to produce a level in the sample 1 to 5 times the background concentration. Spike a second sample aliquot with the standard solution and analyze it to determine the concentration after spiking (A) of each analyte. Calculate the percent recovery (P) of each analyte:

***Equation 1***

$$P = \frac{100(A-B)}{T}$$

*where*
*T = True value of the spike*

**8.4.3** Compare the percent recovery for each analyte with the corresponding QC acceptance criteria in Table 4. If any analyte fails the acceptance criteria for recovery, the sample is complex and must be diluted and reanalyzed per Section 16.

**8.4.4** As part of the QC program for the laboratory, method accuracy for samples shall be assessed and records shall be maintained. After the analysis of five spiked samples of a given matrix type (water, soil, sludge, sediment) in which the analytes pass the tests in Section 8.4.3, compute the average percent recovery (P) and the standard deviation of the percent recovery ($s_p$) for each compound (or coeluting compound group). Express the accuracy assessment as a percent recovery interval from $P - 2s_p$ to $P + 2s_p$ for each matrix. For example, if $P=90\%$ and $s_p=10\%$ for five analyses of compost, the accuracy interval is expressed as 70 to 110%. Update the accuracy assessment for each compound in each matrix on a regular basis (e.g., after each five to ten new accuracy measurements).

**8.5** Blanks: Reagent water and high-solids reference matrix blanks are analyzed to demonstrate freedom from contamination.

**8.5.1** Extract and concentrate a 1-L reagent water blank or a 30-g high-solids reference matrix blank with each sample batch (samples started through the extraction process on the same 8-hour shift, to a maximum of 20 samples). Analyze the blank immediately after analysis of the combined QC standard (Section 13.6) to demonstrate freedom from contamination.

**8.5.2** If any of the compounds of interest (Table 1) or any potentially interfering compound is found in an aqueous blank at greater than 0.05 μg/L, or in a high-solids reference matrix blank at greater than 1 μg/kg (assuming the same calibration factor as aldrin for compounds not listed in Table 1), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

**8.6** Other analytes may be determined by this method. To establish a quality control limit for an analyte, determine the precision and accuracy by analyzing four replicates of the analyte along with the combined QC standard per the procedure in Section 8.2. If the analyte coelutes with an analyte in the QC standard, prepare a new QC standard without the coeluting component(s). Compute the average percent recovery (A) and the standard deviation of percent recovery ($s_n$) for the new analyte, and measure the recovery and standard deviation of recovery for the other analytes. The data for the new analyte is assumed to be valid if the precision and recovery specifications for the other analytes are met; otherwise, the analytical problem is corrected and the test is repeated. Establish a preliminary quality control limit of $A \pm 2s_n$ for the new analyte and add the limit to Table 4.

**8.7** The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for calibration (Section 7), calibration verification (Section 13.5), and for initial (Section 8.2) and ongoing (Section 13.6) precision and recovery should be identical, so that the most precise results will be obtained. The GC instruments will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of the analytes given in this method.

8.8 Depending on specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

## 9. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

9.1 Collect samples in glass containers following conventional sampling practices (Reference 8), except that the bottle shall not be prerinsed with sample before collection. Aqueous samples which flow freely are collected in refrigerated bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide-mouth jars.

9.2 Maintain samples at 0 to 4°C from the time of collection until extraction. If the samples will not be extracted within 72 hours of collection, adjust the sample to a pH of 5.0 to 9.0 using sodium hydroxide or sulfuric acid solution. Record the volume of acid or base used. If residual chlorine is present in aqueous samples, add 80 mg sodium thiosulfate per liter of water. EPA Methods 330.4 and 330.5 may be used to measure residual chlorine (Reference 9).

9.3 Begin sample extraction within 7 days of collection, and analyze all extracts within 40 days of extraction.

## 10. SAMPLE EXTRACTION AND CONCENTRATION

Samples containing 1% solids or less are extracted directly using continuous liquid-liquid extraction techniques (Section 10.2.1). Samples containing 1 to 30% solids are diluted to the 1% level with reagent water and extracted using continuous liquid-liquid extraction techniques (Section 10.2.2). Samples containing more than 30% solids are extracted using ultrasonic techniques (Section 10.2.5). Figure 1 outlines the extraction and concentration steps.

10.1 Determination of percent solids.

10.1.1 Weigh 5 to 10 g of sample into a tared beaker. Record the weight to three significant figures.

10.1.2 Dry overnight (12 hours minimum) at 110°C (±5°C), and cool in a dessicator.

10.1.3 Determine percent solids as follows:

**Equation 2**

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

10.2 Preparation of samples for extraction

10.2.1 Samples containing 1% solids or less: Extract the sample directly using continuous liquid-liquid extraction techniques.

10.2.1.1 Measure 1.00 L (±0.01 L) of sample into a clean 1.5- to 2.0-L beaker.

10.2.1.2 Spike 0.5 mL of the surrogate spiking solution (Section 6.12) into the sample aliquot. Proceed to preparation of the QC aliquots for low solids samples (Section 10.2.3).

**10.2.2** Samples containing 1 to 30% solids.

**10.2.2.1** Mix sample thoroughly.

**10.2.2.2** Using the percent solids found in Section 10.1.3, determine the weight of sample required to produce 1 L of solution containing 1% solids as follows:

***Equation 3***

$$sample\ weight = \frac{1000\ g}{\%\ solids}$$

**10.2.2.3** Place the weight determined in Section 10.2.2.2 in a clean 1.5- to 2.0-L beaker. Discard all sticks, rocks, leaves, and other foreign material prior to weighing.

**10.2.2.4** Bring the volume of the sample aliquot(s) to 100 to 200 mL with reagent water.

**10.2.2.5** Spike 0.5 mL of the surrogate spiking solution (Section 6.12) into each sample aliquot.

**10.2.2.6** Using a clean metal spatula, break any solid portions of the sample into small pieces.

**10.2.2.7** Place the ¾" horn on the ultrasonic probe approximately ½" below the surface of each sample aliquot and pulse at 50% for 3 minutes at full power. If necessary, remove the probe from the solution and break any large pieces using the metal spatula or a stirring rod and repeat the sonication. Clean the probe with methylene chloride:acetone (1:1) between samples to preclude cross-contamination.

**10.2.2.8** Bring the sample volume to 1.0 L (±0.1 L) with reagent water.

**10.2.3** Preparation of QC aliquots for samples containing low solids (less than 30%).

**10.2.3.1** For each sample or sample batch (to a maximum of 20) to be extracted at the same time, place two 1.0 L (±0.01 L) aliquots of reagent water in clean 1.5- to 2.0-L beakers.

**10.2.3.2** Blank: Spike 0.5 mL of the surrogate spiking solution (Section 6.12) into one reagent water aliquot.

**10.2.3.3** Spike the combined QC standard (Section 7.4) into the remaining reagent water aliquot.

**10.2.3.4** If a matrix spike is required, prepare an aliquot at the concentrations specified in Section 8.4.

**10.2.4** Stir and equilibrate all sample and QC solutions for 1 to 2 hours. Extract the samples and QC aliquots per Section 10.3.

**10.2.5** Samples containing 30% solids or more.

**10.2.5.1** Mix the sample thoroughly.

**10.2.5.2** Weigh 30 g (±0.3 g) into a clean 400- to 500-mL beaker. Discard all sticks, rocks, leaves, and other foreign material prior to weighing.

**10.2.5.3** Spike 0.5 mL of the surrogate spiking solution (Section 6.12) into the aliquot.

**10.2.5.4** QC aliquot: For each sample or sample batch (to a maximum of 20) to be extracted at the same time, place 30 g (±0.3 g) of the high-solids reference matrix in each of two clean 400- to 500-mL beakers.

**10.2.5.5** Blank: Spike 0.5 mL of the surrogate spiking solution (Section 6.12) into one aliquot of the high-solids reference matrix.

**10.2.5.6** Spike the combined QC standard (Section 6.11) into the remaining high-solids reference matrix aliquot. Extract the high-solids samples per Section 10.4.

**10.3** Continuous extraction of low-solids (aqueous) samples: Place 100 to 150 mL methylene chloride in each continuous extractor and 200 to 300 mL in each distilling flask.

**10.3.1** Pour the sample(s), blank, and standard aliquots into the extractors. Rinse the glass containers with 50 to 100 mL methylene chloride and add to the respective extractors. Include all solids in the extraction process.

**10.3.2** Extraction: Adjust the pH of the waters in the extractors to 5 to 9 with NaOH or $H_2SO_4$ while monitoring with a pH meter. Caution: Some samples require acidification in a hood because of the potential for generating hydrogen sulfide.

**10.3.3** Begin the extraction by heating the flask until the methylene chloride is boiling. When properly adjusted, one to two drops of methylene chloride per second will fall from the condenser tip into the water. Test and adjust the pH of the waters during the first 1 to 2 hours of extraction. Extract for 18 to 24 hours.

**10.3.4** Remove the distilling flask, estimate and record the volume of extract (to the nearest 100 mL), and pour the contents through a prerinsed drying column containing 7 to 10 cm of anhydrous sodium sulfate. Rinse the distilling flask with 30 to 50 mL of methylene chloride and pour through the drying column. For extracts to be cleaned up using GPC, collect the solution in a 500-mL K-D evaporator flask equipped with a 10-mL concentrator tube. Seal, label the pesticide and herbicide fractions, and concentrate per Sections 10.5 to 10.6.

**10.4** Ultrasonic extraction of high solids samples: Procedures are provided for extraction of non-municipal sludge (Section 10.4.1) and municipal sludge samples (Section 10.4.2).

**10.4.1** Ultrasonic extraction of non-municipal sludge high-solids aliquots.

**10.4.1.1** Add 60 to 70 g of powdered sodium sulfate to the sample and QC aliquots. Mix each aliquot thoroughly. Some wet sludge samples may require more than 70 g for complete removal of water. All water must be removed prior to addition of organic solvent so that the extraction process is efficient.

**10.4.1.2** Add 100 mL (±10 mL) of acetone:methylene chloride (1:1) to each of the aliquots and mix thoroughly.

**10.4.1.3** Place the ¾" horn on the ultrasonic probe approximately ½" below the surface of the solvent but above the solids layer and pulse at 50% for 3 minutes at full power. If necessary, remove the probe from the solution and break any large pieces using a metal spatula or a stirring rod and repeat the sonication.

**10.4.1.4** Decant the extract through a prerinsed drying column containing 7 to 10 cm anhydrous sodium sulfate into a 500- to 1000-mL graduated cylinders.

**10.4.1.5** Repeat the extraction steps (Sections 10.4.1.3 to 10.4.1.4) twice more for each sample and QC aliquot. On the final extraction, swirl the sample or QC aliquot, pour into its respective drying column, and rinse with acetone: methylene chloride. Record the total extract volume. If necessary, transfer the extract to a centrifuge tube and centrifuge for 10 minutes to settle fine particles.

**10.4.2** Ultrasonic extraction of high-solids municipal sludge aliquots.

**10.4.2.1** Add 100 mL (±10 mL) of acetonitrile to each of the aliquots and mix thoroughly.

**10.4.2.2** Place the ¾" horn on the ultrasonic probe approximately ½" below the surface of the solvent but above the solids layer and pulse at 50% for 3 minutes at full power. If necessary, remove the probe from the solution and break any large pieces using a metal spatula or a stirring rod and repeat the sonication.

**10.4.2.3** Decant the extract through filter paper into a 1000- to 2000-mL separatory funnel.

**10.4.2.4** Repeat the extraction and filtration steps (Sections 10.4.2.2 to 10.4.2.3) using a second 100 mL (±10 mL) of acetonitrile.

**10.4.2.5** Repeat the extraction step (Section 10.4.2.3) using 100 mL (±10 mL) of methylene chloride. On this final extraction, swirl the sample or QC aliquot, pour into its respective filter paper, and rinse with methylene chloride. Record the total extract volume.

**10.4.2.6** For each extract, prepare 1.5 to 2 L of reagent water containing 2% sodium sulfate. Adjust the pH of the water to 6.0 to 9.0 with NaOH or $H_2SO_4$.

**10.4.2.7** Back-extract each extract three times sequentially with 500 mL of the aqueous sodium sulfate solution, returning the bottom (organic) layer to the separatory funnel the first two times while discarding the top (aqueous) layer. On the final back extraction, filter each pesticide extract through a prerinsed drying column containing 7 to 10 cm anhydrous sodium sulfate into a 500- to 1000-mL graduated cylinder. Record the final extract volume.

**10.4.3** For extracts to be cleaned up using GPC, filter these extracts through Whatman #41 paper into a 500-mL K-D evaporator flask equipped with a 10-mL concentrator tube. Rinse the graduated cylinder or centrifuge tube with 30 to 50 mL of methylene chloride and pour through filter to complete the transfer. Seal and label the K-D flasks. Concentrate these fractions per Sections 10.5 through 10.8.

**10.5** Macro concentration.

**10.5.1** Concentrate the extracts in separate 500-mL K-D flasks equipped with 10-mL concentrator tubes. Add one to two clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of methylene chloride through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

**10.5.2** When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes.

**10.5.3** If the extract is to be cleaned up using GPC, 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 in Section 11.

**10.6** Hexane exchange: Extracts to be subjected to Florisil or silica gel cleanup and extracts that have been cleaned up are exchanged into hexane.

**10.6.1** Remove the Snyder column, add approximately 50 mL of hexane and a clean boiling chip, and reattach the Snyder column. Concentrate the extract as in Section 10.5 except use hexane to prewet the column. The elapsed time of the concentration should be 5 to 10 minutes.

**10.6.2** Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. Adjust the final volume of extracts that have not been cleaned up by GPC to 10 mL and those that have been cleaned up by GPC to 5 mL (the difference accounts for the 50% loss in the GPC cleanup). Clean up the extracts using the Florisil, silica gel, and/or sulfur removal procedures in Section 11.

## *11. CLEANUP AND SEPARATION*

**11.1** Cleanup procedures may not be necessary for relatively clean samples (treated effluents, ground water, drinking water). If particular circumstances require the use of a cleanup procedure, the analyst may use any or all of the procedures below or any other appropriate procedure. However, the analyst shall first repeat the tests in Section 8.2 to demonstrate that the requirements of Section 8.2 can be met using the cleanup procedure(s) as an integral part of the method. Figure 1 outlines the cleanup steps.

**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 all soil and

sediment extracts and may be used for water extracts that are expected to contain high molecular weight organic compounds (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 organochlorine compounds and will also eliminate polar interferences.

**11.1.4** Alumina column cleanup (Section 11.5) may also be used for cleanup of the organochlorine compounds.

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

**11.2** Gel permeation chromatography (GPC).

**11.2.1** Column packing.

**11.2.1.1** Place 70 to 75 g of SX-3 Bio-beads 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 1 to 2 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 6.5) 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 the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85%. If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up 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 the 5.0-mL 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 a clean 400- to 500-mL beaker.

**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, a 5.0-mL methylene chloride blank shall be run through the system to check for carry-over.

**11.2.3.5** Concentrate the extract and exchange into hexane per Sections 10.5 and 10.6. Adjust the final volume to 5.0 mL.

**11.3** Solid-phase extraction (SPE).

**11.3.1** Setup.

**11.3.1.1** Attach the Vac-elute manifold 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 psia.

**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 6.6.2.2) 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.

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

**11.3.3.1** To make the test mixture, add the trichlorophenol solution (Section 6.6.2.1) to the combined calibration standard (Section 6.11). Elute the mixture using the procedure in Section 11.3.4.

**11.3.3.2** Concentrate the eluant to 1.0 mL and inject 1.0 μL of the concentrated eluant into the GC using the procedure in Section 13. The recovery of all analytes (including the unresolved GC peaks) shall be within the ranges for recovery specified in Table 4, 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 5.6.2.4) in the vacuum manifold. Re-establish the vacuum at 5 to 10 psia.

**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 5 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 6.6.2.2), using vacuum for 5 minutes after each portion. Collect the eluants in the 50-mL volumetric flasks.

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

**11.3.4.5** Concentrate the eluted extracts to 1.0 mL using the nitrogen blow-down apparatus.

**11.4** Florisil column.

**11.4.1** Place a weight of Florisil (nominally 20 g) predetermined by calibration (Section 7.5) in a chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of 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 10.6.2) onto the column. Complete the transfer with two 1-mL hexane rinses.

**11.4.4** Place a clean 500-mL K-D flask and concentrator tube under the column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. 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. 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.

**11.4.5** Concentrate the fractions as in Section 10.6, except use hexane to prewet the column. Readjust the final volume to 5 or 10 mL as in Section 10.6, depending on whether the extract was subjected to GPC cleanup, and analyze by gas chromatography per the procedure in Section 12.

**11.5** Alumina column.

**11.5.1** Reduce the volume of the extract to 0.5 mL and bring to 1.0 mL with acetone.

**11.5.2** Add 3 g of activity III neutral alumina to a 10-mL chromatographic column. Tap the column to settle the alumina.

**11.5.3** Transfer the extract to the top of the column and collect the eluate in a clean 10-mL concentrator tube. Rinse the extract container with 1 to 2 mL portions of hexane (to a total volume of 9 mL) and add to the alumina column. Do not allow the column to go dry.

**11.5.4** Concentrate the extract to 1.0 mL if sulfur is to be removed, or adjust the final volume to 5 or 10 mL as in Section 10.6, depending on whether the extract was subjected to GPC cleanup, and analyze by gas chromatography per Section 13.

**11.6** Sulfur removal: Elemental sulfur will usually elute entirely in Fraction 1 of the Florisil column cleanup.

**11.6.1** Transfer the concentrated extract into a clean concentrator tube or PTFE-sealed vial. Add 1 to 2 drops of mercury or 100 mg of activated copper powder and seal (Reference 10). If TBA sulfite is used, add 1 mL of the TBA sulfite reagent and 2 mL of isopropanol.

**11.6.2** Agitate the contents of the vial for 1 to 2 hours on a reciprocal shaker. If the mercury or copper appears shiny, or if precipitated sodium sulfite crystals from the TBA sulfite reagent are present, and if the color remains unchanged, all sulfur has been removed; if not, repeat the addition and shaking.

**11.6.2.1** If mercury or copper is used, centrifuge and filter the extract to remove all residual mercury or copper. Dispose of the mercury waste properly. Bring the final volume to 1.0 mL and analyze by gas chromatography per the procedure in Section 13.

**11.6.2.2** If TBA sulfite is used, add 5 mL of reagent water and shake for 1 to 2 minutes. Centrifuge and filter the extract to remove all precipitate. Transfer the hexane (top) layer to a sample vial and adjust the final volume to 5 or 10 mL as in Section 10.6, depending on whether the extract was subjected to GPC cleanup, and analyze by gas chromatography per Section 12.

## *12. GAS CHROMATOGRAPHY*

Table 2 summarizes the recommended operating conditions for the gas chromatograph. Included in these tables are the retention times and minimum levels that can be achieved under these conditions. Examples of the separations achieved by the primary and confirmatory columns are shown in Figure 2.

**12.1** Calibrate the system as described in Section 7.

**12.2** Set the auto-sampler to inject the same volume that was chosen for calibration (Section 7.3.1.3) for all standards and extracts of blanks and samples.

**12.3** 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.

## *13. SYSTEM AND LABORATORY PERFORMANCE*

**13.1** At the beginning of each 8-hour shift during which analyses are performed, GC system performance and calibration are verified for all pollutants and surrogates on both column/detector systems. For these tests, analysis of the combined QC standard (Section 6.11) shall be used to verify all performance criteria. Adjustment and/or recalibration (per Section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, and precision and recovery standards be analyzed.

**13.2** Retention times: The absolute retention times of the peak maxima shall be within $\pm 10$ seconds of the retention times in the initial calibration (Section 7.4.1).

**13.3** GC resolution: Resolution is acceptable if the valley height between two peaks (as measured from the baseline) is less than 10% of the taller of the two peaks.

**13.3.1** Primary column (DB-608): DDT and endrin aldehyde.

**13.3.2** Confirmatory column (DB-1701): Alpha and gamma chlordane.

**13.4** Decomposition of DDT and endrin.

**13.4.1** Analyze a total of 2 ng DDT and 1 ng endrin on each column using the analytical conditions specified in Table 2.

**13.4.2** Measure the total area of all peaks in the chromatogram.

**13.4.3** 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 endrin. In this case, the GC system that failed shall be repaired and the performance tests (Sections 13.1 to 13.4) shall be repeated until the specification is met.

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*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.*

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**13.5** Calibration verification: Calibration is verified for the combined QC standard only.

**13.5.1** Inject the combined QC standard (Section 6.11)

**13.5.2** Compute the percent recovery of each compound or coeluting compounds, based on the calibration data (Section 7.4).

**13.5.3** For each compound or coeluted compounds, compare this calibration verification recovery with the corresponding limits for ongoing accuracy in Table 4. For coeluting compounds, use the coeluted compound with the least restrictive specification (the widest range). If the recoveries for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any recovery falls outside the calibration verification range, system performance is unacceptable for that compound. In this case, correct the problem and repeat the test, or recalibrate (Section 7). If verification requirements are met, the calibration is assumed to be valid for the multicomponent analytes (PCBs and toxaphene).

**13.6** Ongoing precision and recovery.

**13.6.1** Analyze the extract of the precision and recovery standard extracted with each sample batch (Sections 10.2.3.3 and 10.2.5.7).

**13.6.2** Compute the percent recovery of each analyte and for coeluting compounds.

**13.6.3** For each compound or coeluted compound, compare the percent recovery with the limits for ongoing recovery in Table 4. For coeluted compounds, use the coeluted compound 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.

**13.6.4** Add results which pass the specifications in Section 13.6.3 to initial 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 calcualting the average percent recovery (R) and the standard deviation of percent recovery $s_r$. Express the accuracy 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%.

## 14. QUALITATIVE DETERMINATION

**14.1** Qualititative determination is accomplished by comparison of data from analysis of a sample or blank with data from analysis of the shift standard (Section 13.2), and with data stored in the retention-time and calibration libraries (Section 7.3.2 and 7.3.3.2). Identification is confirmed when retention time and amounts agree per the criteria below.

**14.2** For each compound on each column/detector system, establish a retention-time window of 3 RSD on either side of the average retention time in the calibration data (Section 7.3.2). For compounds that have a retention-time curve (Section 7.3.2.2), establish this window as the minimum -10 seconds and maximum +10 seconds. For the multi-component analytes, use the retention times of the five largest peaks in the chromatogram from the calibration data (Section 7.3.2).

**14.2.1** Compounds not requiring a retention-time calibration curve: If a peak from the analysis of a sample or blank is within a window (as defined in Section 14.2) on the primary column/detector system, it is considered tentatively identified. A tentatively identified compound is confirmed when (1) the retention time for the compound on the confirmatory column/detector system is within the retention-time window on that system, and (2) the computed amounts (Section 15) on each system (primary and confirmatory) agree within a factor of three.

**14.2.2** Compounds requiring a retention-time calibration curve: If a peak from the analysis of a sample or blank is within a window (as defined in Section 14.2) on the primary column/detector system, it is considered tentatively identified. A tentatively identified compound is confirmed when (1) the retention times on both systems (primary and confirmatory) are within ±10 seconds of the retention times for the computed amounts (Section 15), as determined by the retention-time calibration curve (Section 7.3.2.2), and (2) the computed amounts (Section 15) on each system (primary and confirmatory) agree within a factor of 3.

## 15. QUANTITATIVE DETERMINATION

**15.1** Using the GC data system, compute the concentration of the analyte detected in the extract (in micrograms per milliliter) using the calibration factor or calibration curve (Section 7.3.3.2).

**15.2** Liquid samples: Compute the concentration in the sample using the following equation:

***Equation 4***

$$C_s = 10\frac{(C_{ex})}{(V_s)}$$

*where*
$C_s$ = *Concentration in the sample, in µg/L*
10 = *Final extract total volume, in mL*
$C_{ex}$ = *Concentration in the extract, in µg/mL*
$V_s$ = *Sample extracted, in L*

**15.3** Solid samples: Compute the concentration in the solid phase of the sample using the following equation:

***Equation 5***

$$C_s = 10\frac{(C_{ex})}{1000(W_s)(solids)}$$

*where*
$C_s$ = *Concentration in the sample, in µg/kg*
10 = *Final extract total volume, in mL*
$C_{ex}$ = *Concentration in the extract, in µg/mL*
1000 = *Conversion factor, g to kg*
$W_s$ = *Sample weight, in g*
*solids* = *Percent solids in Section* 10.1.3 *divided by* 100

**15.4** If the concentration of any analyte exceeds the calibration range of the system, the extract is diluted by a factor of 10, and a 1-µL aliquot of the diluted extract is analyzed.

**15.5** Two or more PCBs in a given sample are quantitated and reported as total PCB.

**15.6** Report results for all pollutants found in all standards, blanks, and samples to three significant figures. Results for samples that have been diluted are reported at the least dilute level at which the concentration is in the calibration range.

## 16. ANALYSIS OF COMPLEX SAMPLES

**16.1** Some samples may contain high levels (greater than 1000 ng/L) of the compounds of interest, interfering compounds, and/or polymeric materials. Some samples may not concentrate to 10 mL (Section 10.6); others may overload the GC column and/or detector.

**16.2** The analyst shall attempt to clean up all samples using GPC (Section 11.2), the SPE cartridge (Section 11.3), by Florisil (Section 11.4) or Alumina (Section 11.5), and sulfur removal (Section 11.6). If these techniques do not remove the interfering compounds, the extract is diluted by a factor of 10 and reanalyzed (Section 15.4).

**16.3** Recovery of surrogate: In most samples, surrogate recoveries will be similar to those from reagent water or from the high solids reference matrix. If the surrogate recovery is outside the range specified in Section 8.3.3, the sample shall be reextracted and reanalyzed. If the surrogate recovery is still outside this range, the extract is diluted by a factor of 10 and reanalyzed (Section 15.4).

**16.4** Recovery of matrix spikes: In most samples, matrix spike recoveries will be similar to those from reagent water or from the high-solids reference matrix. If the matrix spike recovery is outside the range specified in Table 4, the sample shall be diluted by a factor of 10, respiked, and reanalyzed. If the matrix spike recovery is still outside the range, the method may not apply to the sample being analyzed and the result may not be reported for regulatory compliance purposes.

## *17. METHOD PERFORMANCE*

**17.1** Development of this method is detailed in References 11 and 12.

# References


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4. "OSHA Safety and Health Standards, General Industry" (29 *CFR* 1910). Occupational Safety and Health Administration: January 1976.

5. "Safety in Academic Chemistry Laboratories," American Chemical Society Committee on Chemical Safety: 1979.

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7. "Handbook of Quality Control in Wastewater Laboratories," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH: EPA-600/4-79-019, March 1979.

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9. "Methods 330.4 and 330.5 for Total Residual Chlorine," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH: EPA-600/4-70-020, March 1979.

10. Goerlitz, D.F., and Law, L.M., "Bulletin for Environmental Contamination and Toxicology": 6, 9, 1971.

11. "Consolidated GC Method for the Determination of ITD/RCRA Pesticides using Selective GC Detectors," S-CUBED, A Division of Maxwell Laboratories, Inc., La Jolla, CA: Ref. 32145--01, Document R70, September 1986.

12. "Method Development and Validation, EPA Method 1618, Cleanup Procedures," Pesticide Center, Department of Environmental Health, Colorado State University: November 1988 and January 1989.

Table 1. Organo-Halide Pesticides Determined by Large-Bore, Fused-Silica Capillary Column Gas Chromatography with Halide-Specific Detector

| *EPA EGD* | *Compound* | *CAS Registry* |
|---|---|---|
| | Acephate | 30560-19-1 |
| | Alachlor | 15972-60-8 |
| 089 | Aldrin | 309-00-2 |
| | Atrazine | 1912-24-9 |
| | Benfluralin (Benefin) | 1861-40-1 |
| 102 | $\alpha$-BHC | 319-84-6 |
| 103 | $\beta$-BHC | 319-85-7 |
| 104 | $\gamma$-BHC (Lindane) | 58-89-9 |
| 105 | $\delta$-BHC | 319-86-8 |
| | Bromacil | 314-40-9 |
| | Bromoxynil octanoate | 1689-99-2 |
| | Butachlor | 23184-66-9 |
| 434 | Captafol | 2425-06-1 |
| 433 | Captan | 133-06-2 |
| 441 | Carbophenothion (Trithion) | 786-19-6 |
| | $\alpha$-Chlordane (cis-Chlordane) | 5103-71-9 |
| 091 | $\gamma$-Chlordane (trans-Chlordane) | 5103-74-2 |
| 431 | Chlorobenzilate | 510-15-6 |
| | Chloroneb (Terraneb) | 2675-77-6 |
| | Chloropropylate (Acaralate) | 5836-10-2 |
| | Chlorothalonil | 1897-45-6 |
| | DBCP (Dibromochloropropane) | 96-12-8 |
| | DCPA (Dacthal) | 1861-32-1 |
| 094 | 4,4'-DDD (TDE) | 72-54-8 |
| 093 | 4,4'-DDE | 72-55-9 |
| 092 | 4,4'-DDT | 50-29-3 |
| 432 | Diallate (Avadex) | 2303-16-4 |
| 478 | Dichlone | 117-80-6 |
| | Dicofol | 115-32-2 |
| 090 | Dieldrin | 60-57-1 |
| 095 | Endosulfan I | 959-98-8 |
| 096 | Endosulfan II | 33213-65-9 |
| 097 | Endosulfan sulfate | 1031-07-8 |
| 098 | Endrin | 72-20-8 |
| 099 | Endrin aldehyde | 7421-93-4 |
| 435 | Endrin ketone | 53494-70-5 |
| | Ethalfluralin (Sonalan) | 55283-68-6 |
| | Etridiazole | 2593-15-9 |
| | Fenarimol (Rubigan) | 60168-88-9 |
| 100 | Heptachlor | 76-44-8 |
| 101 | Heptachlor epoxide | 1024-57-3 |
| 437 | Isodrin | 465-73-6 |
| | Isopropalin (Paarlan) | 33820-53-0 |
| 439 | Kepone | 143-50-0 |

Table 1. Organo-Halide Pesticides Determined by Large-Bore, Fused-Silica Capillary Column Gas Chromatography with Halide-Specific Detector (cont.)

| *EPA EGD* | *Compound* | *CAS Registry* |
|---|---|---|
| 430 | Methoxychlor | 72-43-5 |
| | Metribuzin | 21087-64-9 |
| 438 | Mirex | 2385-85-5 |
| 436 | Nitrofen (TOK) | 1836-75-5 |
| | Norfluorazon | 27314-13-2 |
| 112 | PCB-1016 | 12674-11-2 |
| 108 | PCB-1221 | 11104-28-2 |
| 109 | PCB-1232 | 11141-16-5 |
| 106 | PCB-1242 | 53469-21-9 |
| 110 | PCB-1248 | 12672-29-6 |
| 107 | PCB-1254 | 11097-69-1 |
| 111 | PCB-1260 | 11096-82-5 |
| 440 | PCNB (pentachloronitrobenzene) | 82-68-8 |
| | Pendamethalin (Prowl) | 40487-42-1 |
| | cis-Permethrin | 61949-76-6 |
| | trans-Permethrin | 61949-77-7 |
| | Perthane (Ethylan) | 72-56-0 |
| | Propachlor | 1918-16-7 |
| | Propanil | 709-98-8 |
| | Propazine | 139-40-2 |
| | Simazine | 122-34-9 |
| | Strobane | 8001-50-1 |
| | Terbacil | 5902-51-2 |
| | Terbuthylazine | 5915-41-3 |
| 113 | Toxaphene | 8001-35-2 |
| | Triadimefon (Bayleton) | 43121-43-3 |
| 442 | Trifluralin | 1582-09-8 |

Table 2. Gas Chromatography of Organo-Halide Pesticides

| EPA EGD | Compound | Retention Time (min)[1] DB-608 | DB-1701 | Method Detection Limit[2] (ng/L) | |
|---|---|---|---|---|---|
| | Acephate | 5.03 | --[3] | 2000 | est (ECD) |
| 442 | Trifluralin | 5.16 | 6.79 | 50 | est |
| | Ethalfluralin | 5.28 | 6.49 | 5 | est (ECD) |
| | Benfluralin | 5.53 | 6.87 | 20 | est (ECD) |
| 432 | Diallate-A | 7.15 | 6.23 | 45 | |
| | Diallate-B | 7.42 | 6.77 | 32 | |
| 102 | α-BHC | 8.14 | 7.44 | 6 | |
| 440 | 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) |
| 104 | γ-BHC (Lindane) | 9.52 | 9.91 | 11 | |
| 103 | β-BHC | 9.86 | 11.90 | 7 | |
| 100 | Heptachlor | 10.66 | 10.55 | 5 | |
| | Chlorothalonil | 10.66 | 10.96 | 15 | est (ECD) |
| 478 | Dichlone | 10.80 | --[3] | --[4] | |
| | Terbacil | 11.11 | 12.63 | 200 | est (ECD) |
| 105 | δ-BHC | 11.20 | 12.98 | 5 | |
| | Alachlor | 11.57 | 11.06 | 20 | est (ECD) |
| | Propanil | 11.60 | 14.10 | | |
| 089 | 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) |
| 437 | Isodrin | 13.47 | 11.12 | 13 | |
| 101 | Heptachlor epoxide | 13.97 | 12.56 | 12 | |
| | Pendamethalin | 14.21 | 13.46 | 30 | |
| | Bromacil | 14.39 | --[3] | 70 | est (ECD) |
| | γ-Chlordane | 14.63 | 14.20 | 9 | |
| | Butachlor | 15.03 | 15.69 | 30 | est (ECD) |
| 091 | α-Chlordane | 15.24 | 14.36 | 8 | |
| 095 | Endosulfan I | 15.25 | 13.87 | 11 | |
| 093 | 4,4'-DDE | 16.34 | 14.84 | 10 | |
| 090 | Dieldrin | 16.41 | 15.25 | 6 | |
| 433 | Captan | 16.83 | 15.43 | 100 | est (ECD) |
| 431 | Chlorobenzilate | 17.58 | 17.28 | 25 | |
| 098 | Endrin | 17.80 | 15.86 | 4 | |
| 436 | Nitrofen (TOK) | 17.86 | 17.47 | 13 | |
| 439 | Kepone | 17.92 | 24.03 | 100 | est (ECD) |
| 094 | 4,4'-DDD | 18.43 | 17.77 | 5 | |
| 096 | Endosulfan II | 18.45 | 18.57 | 8 | |
| | Bromoxynil octanoate | 18.85 | 18.57 | 30 | est (ECD) |
| 092 | 4,4'-DDT | 19.48 | 18.32 | 12 | |
| 441 | Carbophenothion | 19.65 | 18.21 | 50 | |
| 099 | Endrin aldehyde | 19.72 | 19.18 | 11 | |
| 097 | Endosulfan sulfate | 20.21 | 20.37 | 7 | |
| 434 | Captafol | 22.51 | 21.22 | 100 | est (ECD) |

Table 2. Gas Chromatography of Organo-Halide Pesticides (cont.)

| EPA EGD | Compound | Retention Time (min)[1] DB-608 | DB-1701 | Method Detection Limit[2] (ng/L) | |
|---|---|---|---|---|---|
| | Norfluorazon | 20.68 | 22.01 | 50 | est (ECD) |
| 438 | Mirex | 22.75 | 19.79 | 4 | |
| 430 | Methoxychlor | 22.80 | 20.68 | 30 | |
| 435 | 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) |
| 106 | PCB-1242 | | | 150 | est |
| 109 | PCB-1232 | | | 150 | est |
| 112 | PCB-1016 | | | 150 | est |
| 108 | PCB-1221 | | | 150 | est |
| 110 | PCB-1248 | | | 150 | est |
| 107 | PCB-1254 | | | 150 | est |
| 111 | PCB-1260 | 15.44 | 14.64 | 140 | |
| | | 15.73 | 15.36 | | |
| | | 16.94 | 16.53 | | |
| | | 17.28 | 18.70 | | |
| | | 19.17 | 19.92 | | |
| 113 | Toxaphene | 16.60 | 16.60 | 910 | |
| | | 17.37 | 17.52 | | |
| | | 18.11 | 17.92 | | |
| | | 19.46 | 18.73 | | |
| | | 19.69 | 19.00 | | |

Notes:

1. Columns: 30 m long × 0.53 mm ID; DB-608: 0.83 $\mu$; DB-1701: 1.0 $\mu$. Conditions suggested to meet retention times shown: 150°C for 0.5 minutes, 150 to 270° at 5°C/min, 270°C until trans-permethrin elutes. Carrier gas flow rates approximately 7 mL/min.

2. 40 *CFR* Part 136, Appendix B (49 *FR* 43234). MDLs were obtained by a single laboratory with an electrolytic conductivity detector, except as noted. MDL's for soils (in ng/kg) are estimated to be 30 to 100 times this level.

3. Does not elute from DB-1701 column at level tested.

4. Not recovered from water at the levels tested.

Table 3. Concentrations of Calibration Solutions for Electron Capture Detector and Suggested Calibration Groups

| | | Concentration (ng/mL) | | |
|---|---|---|---|---|
| **EPA EGD** | **Compound[1]** | **Low** | **Medium** | **High** |
| *Calibration group 1* | | | | |
| | Acephate | 2000 | 10000 | 40000 |
| | Alachlor | 20 | 100 | 400 |
| | Atrazine | 1000 | 5000 | 20000 |
| 103 | β-BHC | 10 | 50 | 200 |
| | Bromoxynil octanoate | 50 | 250 | 1000 |
| 434 | Captafol | 200 | 1000 | 4000 |
| 432 | Diallate | 200 | 1000 | 4000 |
| 097 | Endosulfan sulfate | 10 | 50 | 200 |
| 098 | Endrin | 20 | 100 | 400 |
| 437 | Isodrin | 10 | 50 | 200 |
| | Pendimethalin (Prowl) | 50 | 250 | 1000 |
| | trans-Permethrin | 200 | 1000 | 4000 |
| *Calibration group 2* | | | | |
| 102 | α-BHC | 5.0 | 25 | 100 |
| | DCPA | 5.0 | 25 | 100 |
| 093 | 4,4'-DDE | 10 | 50 | 200 |
| 092 | 4,4'-DDT | 10 | 50 | 200 |
| 478 | Dichlone | 20 | 100 | 400 |
| | Ethalfluralin | 10 | 50 | 200 |
| | Fenarimol | 20 | 100 | 400 |
| 430 | Methoxychlor | 20 | 100 | 400 |
| | Metribuzin | 10 | 50 | 200 |
| *Calibration group 3* | | | | |
| 105 | γ-BHC (Lindane) | 5 | 25 | 100 |
| 091 | γ-Chlordane | 5 | 25 | 100 |
| 435 | Endrin ketone | 10 | 50 | 200 |
| 101 | Heptachlor epoxide | 5 | 25 | 100 |
| | Isopropalin | 20 | 100 | 400 |
| 436 | Nitrofen (TOK) | 20 | 100 | 400 |
| 440 | PCNB | 5 | 25 | 100 |
| | cis-Permethrin | 200 | 1000 | 4000 |
| 442 | Trifluralin | 10 | 50 | 200 |
| *Calibration group 4* | | | | |
| | Benfluralin | 20 | 100 | 400 |
| 431 | Chlorobenzilate | 50 | 500 | 5000 |
| 090 | Dieldrin | 5 | 20 | 100 |
| 095 | Endosulfan I | 10 | 50 | 200 |
| 438 | Mirex | 20 | 100 | 400 |
| | Terbacil | 200 | 1000 | 4000 |
| | Terbuthylazine | 500 | 2500 | 10000 |
| | Triadimefon | 100 | 500 | 2000 |

Table 3. Concentrations of Calibration Solutions for Electron Capture Detector and Suggested Calibration Groups (cont.)

| | | Concentration (ng/mL) | | |
|---|---|---|---|---|
| EPA EGD | Compound[1] | Low | Medium | High |
| *Calibration group 5* | | | | |
| | α-Chlordane | 10 | 50 | 200 |
| 433 | Captan | 100 | 500 | 2000 |
| | Chlorothalonil | 20 | 100 | 400 |
| 094 | 4,4'-DDD | 20 | 100 | 400 |
| | Norfluorazon | 100 | 500 | 2000 |
| | Simazine | 800 | 4000 | 20000 |
| *Calibration group 6* | | | | |
| 089 | Aldrin | 20 | 100 | 400 |
| 104 | δ-BHC | 5 | 25 | 100 |
| | Bromacil | 100 | 500 | 2000 |
| | Butachlor | 50 | 250 | 1000 |
| 096 | Endosulfan II | 10 | 50 | 200 |
| 100 | Heptachlor | 10 | 50 | 200 |
| 439 | Kepone | 100 | 500 | 2000 |

For compounds listed in Table 2 that are not listed in this table, determine appropriate ranges for calibration standards.

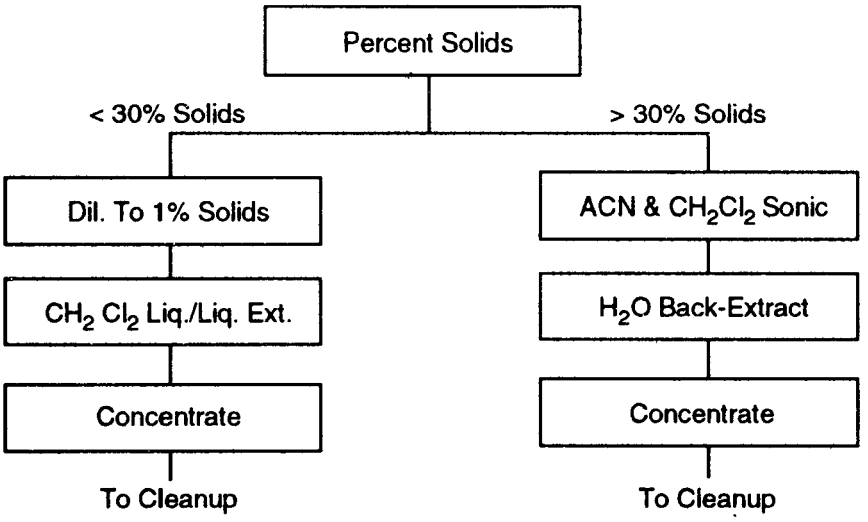
Table 4. Acceptance Criteria for Performance Tests for Organo-Halide Compounds

| EGD No. | Compound | Spike Level (ng/L) | Acceptance Criteria: Initial Precision and Accuracy s | Acceptance Criteria: Initial Precision and Accuracy X | Acceptance Criteria: Calibration Verification* (%) | Acceptance Criteria: Recovery/ Ongoing Accuracy R (%) |
|---|---|---|---|---|---|---|
| | Acephate | 100000 | 94 | 0-195 | 6-194 | 0-209 |
| | Alachlor | 1000 | 20 | 26-100 | 80-120 | 23-101 |
| 089 | Aldrin | 1000 | 12 | 82-108 | 79-113 | 76-114 |
| | Atrazine | 50000 | 26 | 35-129 | 74-126 | 31-132 |
| | Benfluralin | 1000 | 22 | 45-125 | 78-122 | 42-128 |
| 102 | $\alpha$-BHC | 250 | 10 | 57-135 | 69-108 | 38-154 |
| 103 | $\beta$-BHC | 500 | 10 | 66-130 | 85-102 | 50-146 |
| 105 | $\delta$-BHC | 250 | 24 | 60-122 | 79-103 | 45-136 |
| 104 | $\gamma$-BHC (Lindane) | 250 | 10 | 66-112 | 75-119 | 55-123 |
| | Bromacil | 5000 | 84 | 0-263 | 16-184 | 0-275 |
| | Bromoxynil octanoate | 2500 | 28 | 31-131 | 72-128 | 27-135 |
| | Butachlor | 2500 | 32 | 21-137 | 68-132 | 17-141 |
| 434 | Captafol | 10000 | 76 | 0-221 | 24-176 | 0-232 |
| 433 | Captan | 5000 | 32 | 28-144 | 49-114 | 24-148 |
| 441 | Carbophenothion | 1000 | 10 | 63-141 | 79-102 | 43-161 |
| 091 | Chlordane-$\alpha$ | 500 | 10 | 79-122 | 73-102 | 69-133 |
| | Chlordane-$\gamma$ | 250 | 13 | 32-140 | 79-113 | 4-169 |
| 431 | Chlorobenzilate | 5000 | 19 | 58-118 | 54-129 | 43-133 |
| | Chlorothalonil | 1000 | 20 | 37-109 | 80-120 | 34-112 |
| | DCPA | 250 | 20 | 57-129 | 80-120 | 54-132 |
| 094 | 4,4'-DDD | 1000 | 12 | 69-117 | 77-109 | 57-129 |
| 093 | 4,4'-DDE | 500 | 13 | 66-114 | 81-121 | 54-126 |
| 092 | 4,4'-DDT | 500 | 19 | 86-112 | 77-118 | 79-119 |
| 432 | Diallate | 10000 | 16 | 44-120 | 70-124 | 24-139 |
| 478 | Dichlone | 1000 | 20 | 45-117 | 79-110 | 42-120 |
| 090 | Dieldrin | 200 | 11 | 66-140 | 48-115 | 48-158 |
| 095 | Endosulfan I | 500 | 14 | 41-133 | 78-119 | 18-156 |
| 096 | Endosulfan II | 500 | 19 | 78-142 | 76-119 | 62-158 |
| 097 | Endosulfan sulfate | 500 | 17 | 50-130 | 70-109 | 31-149 |
| 098 | Endrin | 1000 | 13 | 17-149 | 5-117 | 0-182 |
| 099 | Endrin aldehyde | 1000 | 13 | 0-149 | 86-117 | 0-190 |
| 435 | Endrin ketone | 500 | 25 | 36-126 | 68-135 | 14-148 |
| | Ethalfluralin | 500 | 24 | 46-132 | 76-124 | 42-136 |
| | Fenarimol | 1000 | 26 | 46-140 | 74-126 | 42-144 |
| 100 | Heptachlor | 500 | 12 | 78-104 | 80-114 | 71-111 |
| 101 | Heptachlor epoxide | 250 | 13 | 63-117 | 79-117 | 49-131 |
| 437 | Isodrin | 500 | 15 | 69-113 | 71-126 | 45-127 |
| | Isopropalin | 1000 | 20 | 47-129 | 80-120 | 54-132 |
| 439 | Kepone | 5000 | 46 | 31-197 | 47-134 | 25-203 |

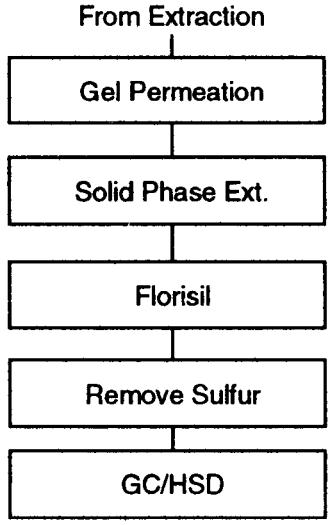
Table 4. Acceptance Criteria for Performance Tests for Organo-Halide Compounds (cont.)

| EGD No. | Compound | Spike Level (ng/L) | Acceptance Criteria: Initial Precision and Accuracy s | Acceptance Criteria: Initial Precision and Accuracy X | Acceptance Criteria: Calibration Verification* (%) | Acceptance Criteria: Recovery/ Ongoing Accuracy R (%) |
|---|---|---|---|---|---|---|
| 430 | Methoxychlor | 1000 | 19 | 50–136 | 47–128 | 28–158 |
| | Metribuzin | 500 | 24 | 54–140 | 76–124 | 50–155 |
| 438 | Mirex | 1000 | 23 | 25–155 | 78–114 | 0–188 |
| 436 | Nitrofen (TOK) | 1000 | 22 | 15–139 | 59–142 | 0–170 |
| | Norfluorazon | 5000 | 20 | 71–143 | 80–120 | 68–146 |
| 112 | PCB-1016 | | | | | |
| 108 | PCB-1221 | | | | | |
| 109 | PCB-1232 | | | | | |
| 106 | PCB-1242 | | | | | |
| 110 | PCB-1248 | | | | | |
| 107 | PCB-1254 | | | | | |
| 111 | PCB-1260 | 1000 | 20 | 82–112 | 79–126 | 75–119 |
| 440 | PCNB | 250 | 11 | 49–129 | 78–101 | 29–149 |
| | Pendimethalin | 2500 | 24 | 32–118 | 76–124 | 28–122 |
| | cis-Permethrin | 10000 | 30 | 45–153 | 70–130 | 41–157 |
| | trans-Permethrin | 10000 | 20 | 59–131 | 80–120 | 56–134 |
| | Simazine | 40000 | 20 | 16–100 | 80–120 | 13–101 |
| | Terbacil | 10000 | 82 | 0–217 | 18–182 | 0–228 |
| | Terbuthylazine | 25000 | 20 | 32–104 | 80–120 | 29–107 |
| 113 | Toxaphene | 5000 | 20 | 82–112 | 68–134 | 76–122 |
| | Triadimefon | 5000 | 54 | 32–104 | 80–120 | 0–107 |
| 442 | Trifluralin | 500 | 12 | 32–148 | 47–134 | 3–177 |

* Verified at the level of the median standard in Table 3.




Extraction and Concentraction Steps




Cleanup and Analysis Steps

A52-002-84

Figure 1. Extraction, Cleanup, Derivatization, and Analysis

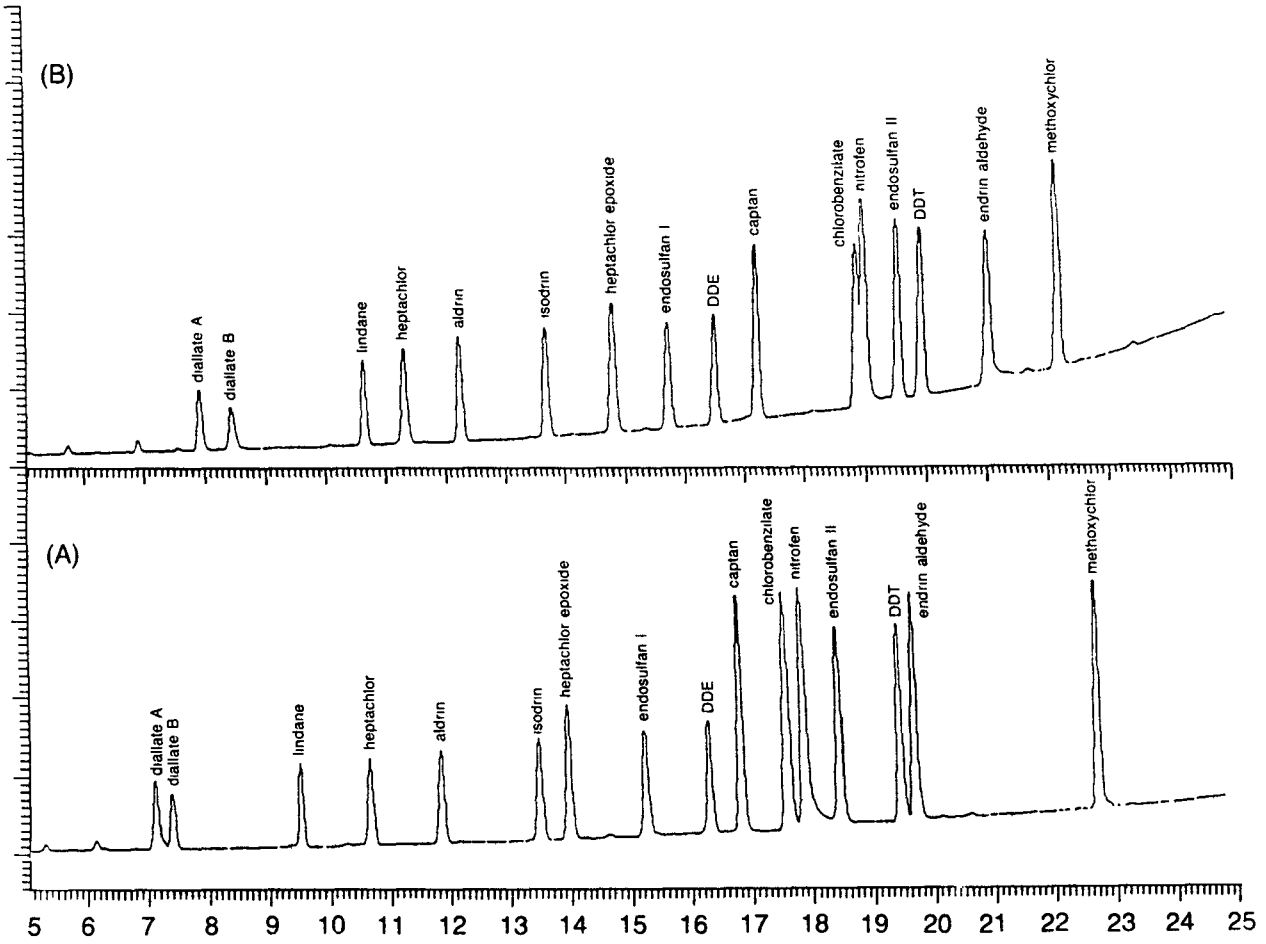



Figure 2. Gas Chromatogram of Selected Organo-Chlorine Compounds