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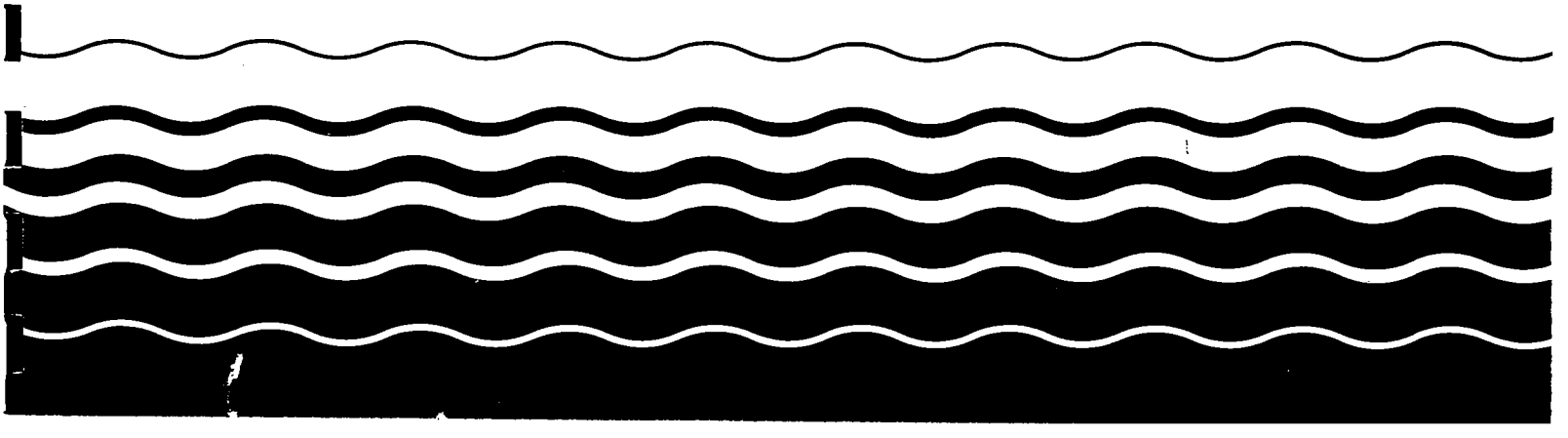
Method 1618: Organo-halide Pesticides, Organo-phosphorus Pesticides, and Phenoxy-acid Herbicides by Wide Bore Capillary Column Gas Chromatography with Selective Detectors



Method 1618 Revision A July 1989

Organo-halide Pesticides, Organo-phosphorus Pesticides, and Phenoxy-acid Herbicides by Wide Bore Capillary Column Gas Chromatography with Selective Detectors

1 SCOPE AND APPLICATION

1.1 This method is designed to meet the survey requirements of the USEPA ITD. The method is used to determine the organo-halide pesticides and polychlorinated biphenyls (PCB's), the organo-phosphorus pesticides, and the phenoxy-acid herbicides and herbicide esters, associated with the Clean Water Act (as amended 1987); the Resource Conservation and Recovery Act (as amended 1986); the Comprehensive Environmental Response, Compensation and Liability Act (as amended 1986); and other compounds amenable to extraction and analysis by automated, wide bore capillary column gas chromatography (GC) with halogen specific and organo-phosphorus detectors.

1.2 The chemical compounds listed in Tables 1 - 3 may be determined in waters, soils, sediments, and sludges by this method. The method is a consolidation of EPA Methods 608, 608.1, 614, 615, 617, 622, and 701. 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 should be applicable to other pesticides and herbicides. The quality assurance/quality control requirements in Section 8.6 of this method give the steps necessary to determine its applicability.

1.3 When this method is applied to analysis of unfamiliar samples, compound identity shall 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 (GCMS) can be used to confirm compounds in extracts produced by this method when analyte levels are sufficient.

1.4 The detection limits of this method are usually dependent on the level of interferences rather than instrumental limitations. The limits in Tables 4 - 6 typify the minimum quantities that can be detected with no interferences present.

1.5 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 Aqueous samples containing 1 - 30 percent solids -- The sample is diluted to one percent solids, if necessary. The pesticides and PCB's are extracted from a one liter sample with methylene chloride using continuous extraction techniques. For the herbicides, the pH of the sample is raised to 12 - 13 to hydrolyze esters, the sample is back-extracted to remove basic and neutral species, the pH is then reduced to less than 2, and the sample is extracted with diethyl ether using separatory funnel techniques.

2.1.3 Samples containing greater than 30 percent solids -- The sample is extracted with acetonitrile and then methylene chloride using ultrasonic techniques. The extract is back extracted with two percent (w/v) sodium sulfate in reagent water to remove water soluble interferences and residual acetonitrile. Samples in which phenoxy-acid herbicides are to be determined are acidified prior to extraction.

2.2 Concentration and cleanup -- For samples in which pesticides are to be determined, each extract is dried over sodium sulfate, concentrated using a Kuderna-Danish evaporator, cleaned up (if necessary) using gel permeation chromatography (GPC),

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 1 - 3.

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 Diazomethane is a toxic carcinogen which can decompose or explode under certain conditions. Solutions decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips. The following operations may cause explosion: heating above 90 °C; use of grinding surfaces such as ground glass joints, sleeve bearings, and glass stirrers; and storage near alkali metals. Diazomethane shall be used only behind a safety screen in a well ventilated hood and should be pipetted with mechanical devices only.

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

4.5 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

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 five percent solids) -- Sample bottle, amber glass, 1 liter or 1 quart, with screw cap.

5.1.1.2 Solid samples (soils, sediments, sludges, filter cake, compost, and similar materials that contain more than five percent 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 Teflon.

5.1.1.5 Cleaning

5.1.1.5.1 Bottles are detergent water washed, then solvent rinsed or baked at 450 °C for one hour minimum before use.

5.1.1.5.2 Liners are detergent water washed, then reagent water and solvent rinsed, and baked at approx 200 °C for one hour minimum 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 - 4 °C during sampling. Glass or Teflon 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 being temperature controlled at 110 ±5 °C.

5.2.2 Dessicator

5.2.3 Crucibles, porcelain

and/or adsorption chromatography, and/or solid phase extraction, and then re-concentrated to one mL. Sulfur is removed from the extract, if required. For samples in which the herbicides are to be determined, each extract is dried over acidified sodium sulfate and the acids are derivatized to form the methyl esters. The solution containing the methyl esters is cleaned up (if necessary) using adsorption chromatography and concentrated to one mL.

2.3 Gas chromatography -- A one uL aliquot of the extract is injected into the gas chromatograph (GC). The compounds are separated on a wide bore, fused silica capillary column. The organo-halide compounds, including the derivatized phenoxy-acid herbicides, are detected by an electron capture, microcoulometric, or electrolytic conductivity detector. The phosphorus containing compounds are detected using a flame photometric detector.

2.4 Identification of a pollutant (qualitative analysis) is performed by (1) comparing the GC retention times of the compound on two dissimilar columns with the respective retention times of an authentic standard, and (2) comparing the concentrations of the compound determined on the primary and confirmatory GC systems. Compound identity is confirmed when the retention times and amounts agree within their respective windows.

2.5 Quantitative analysis is performed by 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 The quality of the analysis 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 analysis 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 one hour minimum 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 clean-up 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 The acid forms of the herbicides are strong acids that react readily with alkaline substances and can be lost during analysis. Glassware and glass wool must be acid rinsed with dilute hydrochloric acid and the sodium sulfate must be acidified with sulfuric acid prior to use.

3.6 Organic acids and phenols cause the most direct interference with the herbicides. Alkaline hydrolysis and subsequent extraction of the basic solution can remove many hydrocarbons and esters that may interfere with the herbicide analysis.

3.7 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 Tables 4 - 6.

5.6.1.3 Syringe filter holder, stainless steel, and glass fiber or Teflon filters (Gelman Acrodisc-CR, 1 - 5 micron, or equivalent).

5.6.1.4 UV detectors -- 254-mu, preparative or semi-prep flow cell: (Isco, Inc., Type 6; Schmadzu, 5 mm path length; Beckman-Altex 152W, 8 uL micro-prep 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 x 22 mm i.d., with Teflon stopcock and coarse frit (Kontes K-42054, or equivalent).

5.6.4 Sulfur removal tubes -- 40 - 50 mL bottle or test tube with Teflon 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 -- 12-15 mL, with screw caps, to fit centrifuge

5.7.4 Funnel, Buchner, 15 cm.

5.7.4.1 Flask, filter, for use with Buchner funnel

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

5.8 Derivatization apparatus -- Diazald kit with clear seal joints for generation of diazomethane (Aldrich Chemical Co. Z10,025-0, or equivalent).

5.9 Miscellaneous glassware

5.9.1 Pipettes, glass, volumetric, 1.00, 5.00, and 10.0 mL

5.9.2 Syringes, glass, with Luerlok tip, 0.1, 1.0 and 5.0 mL. Needles for syringes, two inch, 22 gauge.

5.9.3 Volumetric flasks, 10.0, 25.0, and 50.0 mL

5.9.4 Scintillation vials, glass, 20 - 50 mL, with Teflon-lined screw caps.

5.10 Gas chromatographs -- Two GC's shall be employed. Both shall have splitless or on-column simultaneous automated injection into separate capillary columns with a halide specific detector or flame photometric 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.

5.10.1 GC columns -- Bonded phase fused silica capillary

5.10.1.1 Primary for organo-halide compounds -- 30 ±3 m x 0.5 ±0.05 mm i.d. DB-608, or equivalent).

5.10.1.2 Primary for organo-phosphate compounds -- DB-1 (or equivalent) with same dimensions as column for organo-halide compounds.

5.10.1.3 Confirmatory -- DB-1701, or equivalent, with same dimensions as primary column.

5.10.2 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.

5.10.2.1 Data acquisition -- GC data shall be collected continuously throughout the analysis and stored on a mass storage device.

5.10.2.2 Calibration factors and calibration curves -- The data system shall be used to record and maintain lists of calibration factors, and multi-point calibration curves

5.2.4 Weighing pans, aluminum

5.3 Extraction equipment

5.3.1 Equipment for ultrasonic extraction

5.3.1.1 Sonic disruptor -- 375 watt with pulsing capability and 1/2 or 3/4 in. disruptor horn (Ultrasonics, Inc, Model 375C, or equivalent).

5.3.1.2 Sonabox (or equivalent), for use with disruptor.

5.3.2 Equipment for liquid-liquid extraction

5.3.2.1 Continuous liquid-liquid extractor -- Teflon or glass connecting joints and stopcocks without lubrication, 1.5 - 2 liter 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).

5.3.3 Separatory funnels -- 250, 500, 1000, and 2000 mL, with Teflon stopcocks.

5.3.4 Filtration apparatus

5.3.4.1 Glass powder funnels -- 125 - 250 mL

5.3.4.2 Filter paper for above (Whatman 41, or equivalent)

5.3.5 Beakers

5.3.5.1 1.5 - 2 liter, calibrated to one liter

5.3.5.2 400 - 500 mL

5.3.6 Spatulas -- Stainless steel or Teflon

5.3.7 Drying column -- 400 mm x 15 to 20 mm i.d. Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

5.3.7.1 Pyrex glass wool -- Solvent extracted or baked at 450 °C for one hour minimum.

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 -- Approx 10/40 mesh, extracted with methylene chloride and baked at 450 °C for one hr minimum.

5.4.1.5.2 Teflon (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 - 40 °C (N-Evap, Organomation Associates, Inc., or equivalent).

5.4.4 Sample vials -- Amber glass, 1 - 5 mL with Teflon-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 - 700 mm x 25 mm i.d., 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.

6.6 Sample cleanup

6.6.1 Florisil -- PR grade, 60/100 mesh, activated at 650 - 700 °C, stored in the dark in glass container with Teflon-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 - 200 mesh (Fisher Scientific Certified, or equivalent). Heat for 16 hours at 400 - 450 °C. Seal and cool to room temperature. Add 7 percent w/w reagent water and mix for 10 - 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 Derivatization -- Diazald reagent [N-methyl-(N-nitroso-p-toluene sulfanamide)], fresh and high purity (Aldrich Chemical Co.)

6.8 Reference matrices

6.8.1 Reagent water -- Water in which the compounds of interest and interfering compounds are not detected by this method.

6.8.2 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 percent 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 Teflon-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 Teflon-lined cap.

6.10.2 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Quality control check samples that can be used to determine the accuracy of calibration standards are available from the USEPA, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.10.3 Stock standard solutions shall be replaced after six 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 required 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 solutions

6.12.1 Chlorinated pesticides -- Prepare dibutyl chlorendate at a concentration of 2 ug/mL in acetone.

6.12.2 Phosphorus containing pesticides -- Prepare tributyl phosphate and triphenyl phosphate each at a concentration of 2 ug/mL in acetone.

(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.

5.10.2.3 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.

5.10.3 Detectors

5.10.3.1 Halide specific -- 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 4.

5.10.3.2 Flame photometric -- Capable of detecting 11 pg of malathion under the analysis conditions given in Table 5.

5.10.4 Chromatographs may be configured in one of two ways: (1) Two halide specific detectors (HSD's) in one GC; two flame photometric detectors (FPD's) in the other. With this configuration, the primary and confirmatory columns and detectors are in the same GC. (2) One HSD and one FPD in each GC. With this configuration, the primary columns and detectors are in one GC, the confirmatory columns and detectors are in the other.

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 liter 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 percent. 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 one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw cap which prevents moisture from entering.

6.3.2 Acidified sodium sulfate -- Add 0.5 mL H_2SO_4 and 30 mL ethyl ether to 100 g sodium sulfate. Mix thoroughly. Allow the ether to evaporate completely. Transfer the mixture to a clean container and store at 110 ±5 °C.

6.3.3 Sodium sulfate solution -- Two percent (w/v) in reagent water, pH adjusted to 8.5 - 9.0 with KOH or H_2SO_4.

6.3.4 Sodium sulfate, reagent grade, powdered anhydrous (Baker 73898, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 450 °C for one hour minimum, cooled in a dessicator, and stored in a pre-cleaned glass bottle with screw cap which prevents moisture from entering. NOTE: The powdered sodium sulfate is used only in ultrasonic extraction of samples containing 30 percent solids or greater, and not for drying of sample extracts. Use of granular sodium sulfate during ultrasonic extraction may lead to poor recovery of analytes.

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

7.4 Combined QC standards -- To preclude periodic analysis of all of the individual calibration groups of compounds (Section 7.3.1), 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. These combined QC standards are prepared at the level of the mid-range calibration standard (7.3.1).

7.4.1 Analyze the combined QC standards on their respective column/detector pairs.

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 (Section 7.3.1), and the calibration factor using the primary column shall be within ±20 percent of the calibration factor in the medium level standard (Section 7.3.4).

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 14.2 and 14.5) and for precision and recovery studies (Section 14.6).

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 4) is suggested. The referenced procedure determines the adsorption of lauric acid (in mg/g 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 ASSURANCE/QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 5). 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 matrix spike and matrix spike duplicate (MS/MSD) samples to assess accuracy and precision. 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 6.8.2) is substituted for the reagent water (Section 6.8.1) 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.

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 17).

8.1.4 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the combined QC standard (Section 7.4) that the analysis system is in control. These procedures are described in Sections 14.1, 14.5, and 14.6.

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.

6.12.3 Phenoxyacid herbicides -- Prepare 2,4-dichlorophenylacetic acid at a concentration of 2 ug/mL in acetone.

6.13 DDT and endrin decomposition solution -- Prepare a solution containing endrin at a concentration of 1 ug/mL and DDT at a concentration of 2 ug/mL.

6.14 Stability of solutions -- All standard solutions (Sections 6.9 - 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 percent of the area obtained in the initial analysis of the standard.

7 SETUP AND CALIBRATION

7.1 Configure the GC systems in one of the two ways given in Section 5.10.4 and establish the operating conditions in Tables 4 - 5.

7.2 Attainment of Method Detection Limit (MDL) and DDT/Endrin decomposition requirements -- Determine that each column/detector system meets the MDL's (Tables 4 - 6) and that the organohalide systems meet the DDT and Endrin decomposition test (Section 14.4).

7.3 Calibration

7.3.1 Calibration solutions -- Prepare calibration standards at a minimum of three concentration levels for each compound of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane or isooctane. The lowest concentration solution should be at a concentration near, but above, the MDL's (Tables 4 - 6). The highest concentration solution should be near, but below, the maximum linear range of the analytical system. The other concentration(s) should be ideally equally spaced on a logarithmic scale between the lowest and highest concentration solutions. The ratio between the highest and lowest concentration should be 100 or greater. Note: the GC retention time overlap between analytes requires that the compounds separated and analyzed as groups. Divide the single component analytes into three or four calibration groups each for the organo-halide and organo-phosphorus compounds with an approximately equal number of analytes per group. The compound pairs specified for GC resolution (Section 14.3) shall be in the same group. PCB 1254 or 1260 and Toxaphene are calibrated separately.

7.3.2 Inject the calibration solutions into the GC column/detector pairs appropriate for the mixture, 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 multicomponent analytes (PCB's, toxaphene), store the retention time and peak area for the five largest peaks.

7.3.3 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.

7.3.3.1 If the difference between the maximum and minimum retention times for any compound is less than five 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.

7.3.3.2 Retention time calibration curve (retention time vs amount) -- If the retention time for a compound in the lowest level standard is more than five 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.

7.3.4 Calibration factor (ratio of area to amount injected)

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

7.3.4.2 Linearity -- If the calibration factor for any compound is constant (Cv < 20 percent) 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.

standard solution and analyze them to determine the concentrations after spiking (A) of each analyte. Calculate the percent recovery (P) of each analyte in each aliquot:

$$P = 100 (A - B) / T$$

where T is the true value of the spike.

8.4.3 Compare the percent recovery for each analyte with the corresponding QC acceptance criteria in Tables 7 - 9. If any analyte fails the acceptance criteria for recovery, the sample is complex and must be diluted and reanalyzed per Section 17.

8.4.4 Determine the precision of the MS/MSD analyses by comparing the recoveries calculated in 8.4.2 of each spiked analyte in both aliquots. Calculate the relative percent difference (RPD) of the recoveries (not the concentrations) of each analyte with MS/MSD aliquots as:

$$RPD = \frac{P_{MS} - P_{MSD}}{(P_{MS} - P_{MSD})/2} \times 100$$

8.4.5 As part of the QA 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, compute the average percent recovery (P) and the standard deviation of the percent recovery (sp) for each compound (or co-eluting compound group). Express the accuracy assessment as a percent recovery interval from P - 2sp to P + 2sp for each matrix. For example, if P = 90% and sp = 10% for five analyses of compost, the accuracy interval is expressed as 70 - 110%. Update the accuracy assessment for each compound in each matrix on a regular basis (e.g., after each 5 - 10 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 one liter reagent water blank or a high solids reference matrix blank with each sample lot (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 14.6) to demonstrate freedom from contamination.

8.5.2 If any of the compounds of interest (Tables 1 - 3) or any potentially interfering compound is found in an aqueous blank at greater than 0.05 ug/L, or in a high solids reference matrix blank at greater than 1 ug/kg (assuming the same calibration factor as aldrin and diazinon for compounds not listed in Tables 1 - 3), 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 (sn) for the 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 ±2sn for the new analyte and add the limit to Table 7, 8, or 9.

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 14.5), and for initial (Section 8.2) and ongoing (Section 14.6) 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

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 accuracy -- 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 one-liter aliquots of reagent water spiked with the combined QC standard (Section 7.4) according to the procedure in Section 10. Alternatively, sets of four replicates of the individual calibration groups (Section 7.3) may be used. For samples containing high solids, sets of four 30 gram 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 (Cv) 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 Tables 7 - 9. For coeluting compounds, use the coeluted compound with the least restrictive specification (largest Cv 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 limit 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 surrogate compound(s).

8.3.3 The recovery of the surrogate compound shall be within the limits of 40 to 120 percent. If the recovery of any 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 17.

8.4 Method accuracy and precision -- The laboratory shall spike (matrix spike) at least ten percent of the samples from a given site type (e.g., influent to treatment, treated effluent, produced water, river sediment) in duplicate (MS/MSD). If only one sample from a given site type is analyzed, two aliquots of that sample shall be spiked.

8.4.1 The concentration of the analytes spiked into the MS/MSD 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 spiking level shall be at that limit or at one to five 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 (Section 7.4) or at one to five 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 five times the expected background concentration or at the concentration of the combined QC standard (Section 7.4).

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 one to five times the background concentration. Spike two additional sample aliquots with the

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

10.2.2.5 Spike 0.5 mL of the appropriate 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 3/4 in. horn on the ultrasonic probe approx 1/2 in. below the surface of each sample aliquot and pulse at 50 percent for three 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 ±0.1 liter with reagent water.

10.2.3 Preparation of QC aliquots for samples containing <30 percent solids.

10.2.3.1 For each sample or sample lot (to a maximum of 20) to be extracted at the same time, place two 1.0 ±0.01 liter aliquots of reagent water in clean 1.5 - 2.0 liter beakers. For the phenoxy-acid herbicides, place two additional one liter aliquots in clean beakers.

10.2.3.2 To serve as a blank, spike 0.5 mL of the pesticide surrogate spiking solution (Section 6.12.1 and 6.12.2) into one reagent water aliquot, and 0.5 mL of the herbicide surrogate spiking solution (Section 6.12.3) into a second reagent water aliquot.

10.2.3.3 Spike the combined QC standard (Section 7.4) into a reagent water aliquot. For the herbicides, spike the herbicide standard 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 - 2 hours. Extract the samples and QC aliquots per Section 10.3.

10.2.5 Samples containing 30 percent solids or greater

10.2.5.1 Mix the sample thoroughly

10.2.5.2 Weigh 30 ±0.3 grams into a clean 400 - 500 mL beaker. For the herbicides, weigh an additional two 30 gram aliquots into clean beakers. Discard all sticks, rocks, leaves and other foreign material prior to weighing.

10.2.5.3 Herbicide acidification -- Add 50 mL of reagent water to one of the herbicide sample aliquots and stir on a stirring plate for one hour minimum. Using a pH meter, determine and record the sample pH while stirring. Slowly add H_2SO_4 while stirring and determine and record the amount of acid required to acidify the sample to pH <2. Discard this aliquot. The volume of H_2SO_4 will be used during the extraction of the samples in Section 10.4.6.

10.2.5.4 Spike 0.5 mL of the appropriate surrogate spiking solution (Section 6.12) into the pesticide and herbicide aliquots.

10.2.5.5 QC aliquots -- For each sample or sample lot (to a maximum of 20) to be extracted at the same time, place two 30 ±0.3 gram aliquots of the high solids reference matrix in clean 400 - 500 mL beakers. For the herbicides, place three additional aliquots in clean beakers and use one of these to determine the amount of acid required for acidification per step 10.2.5.3. Discard this aliquot.

10.2.5.6 To serve as a blank, spike 0.5 mL of the pesticide surrogate spiking solution (Section 6.12.1 and 6.12.2) into one aliquot of the high solids reference matrix, and 0.5 mL of the herbicide surrogate spiking solution (Section 6.12.3) into a second aliquot of the high solids reference matrix.

10.2.5.7 Spike the combined QC standard (Section 7.4) into a high solids reference matrix aliquot. For the herbicides, spike the herbicide standard into the remaining high solids reference matrix aliquot. Extract the high solids samples per Section 10.4.

10.3 Extraction of low solids (aqueous) samples

10.3.1 Continuous extraction of pesticides/PCB's -- Place 100 - 150 mL methylene chloride in each continuous extractor and 200 - 300 mL in each distilling flask.

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 6), 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 - 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 7).

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

10 SAMPLE EXTRACTION AND CONCENTRATION

Figure 1 outlines the extraction and concentration steps. Samples containing one percent solids or less are extracted directly using continuous liquid/liquid extraction techniques (Section 10.2.1). Samples containing one through 30 percent solids are diluted to the one percent level with reagent water (Section 10.2.2) and extracted using continuous liquid/liquid extraction techniques. Samples containing greater than 30 percent solids are extracted using ultrasonic techniques (Section 10.2.5). For determination of the phenoxy-acid herbicides, a separate sample aliquot is extracted, derivatized, and cleaned up. The derivatized extract may be combined with the organo-chlorine extract for gas chromatography.

10.1 Determination of percent solids

10.1.1 Weigh 5 - 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 ±5 °C, and cool in a dessicator.

10.1.3 Determine percent solids as follows:

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

10.2 Preparation of samples for extraction

10.2.1 Samples containing one percent solids or less -- Pesticides and PCB samples are extracted directly using continuous liquid/liquid extraction techniques; herbicides are extracted using separatory funnel techniques.

10.2.1.1 Shake the samples to ensure thorough mixing and measure 1.00 ±0.01 liter of each sample into a separate clean 1.5 - 2.0 liter beaker. Measure a separate one liter aliquot for each sample to be tested for the phenoxy-acid herbicides.

10.2.1.2 Spike 0.5 mL of the surrogate spiking solution (Section 6.12) into the sample aliquot. For the phenoxy-acid herbicides, spike 0.5 mL of the herbicide surrogate spiking solution into the herbicide aliquot. Proceed to preparation of the QC aliquots for low solids samples (Section 10.2.3).

10.2.2 Samples containing one to 30 percent solids -- Samples are diluted to one percent solids and then extracted.

10.2.2.1 Mix sample thoroughly.

10.2.2.2 Using the percent solids found in 10.1.3, determine the weight of sample required to produce one liter of solution containing one percent solids as follows:

$$\text{sample weight} = \frac{1000 \text{ grams}}{\% \text{ solids}}$$

10.2.2.3 Place the weight of sample as determined in 10.2.2.2 in a clean 1.5 - 2.0 liter beaker. For the phenoxy-acid herbicides, place a separate aliquot in a clean beaker. Discard all sticks, rocks, leaves and other foreign material prior to weighing.

drying agent. Concentrate the extract to 5 mL per Sections 10.5 through 10.7.

10.4 Ultrasonic extraction of high solids aliquots

10.4.1 Add 60 g powdered (not granular) anhydrous sodium sulfate to the sample and the QC aliquots. Add 100 ±10 mL acetonitrile to each of the aliquots (Section 10.2.5) and mix thoroughly, to produce a free-flowing mixture.

10.4.2 Place the 3/4 in. horn on the ultrasonic probe approx 1/2 in. below the surface of the solvent but above the solids layer and pulse at 50 percent for three 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. Clean the horn with five percent aqueous sodium bicarbonate immediately after sonicating any of the herbicide aliquots to prevent acid damage to the horn.

10.4.3 Decant the pesticide and herbicide extracts through filter paper into 1000 - 2000 mL separatory funnels.

10.4.4 Repeat the extraction and filtration steps (Sections 10.4.2 - 10.4.3) using a second 100 ±10 mL of acetonitrile.

10.4.5 Repeat the extraction step (Section 10.4.2) using 100 ±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.

10.4.6 For each extract, prepare 1.5 - 2 liters of reagent water containing two percent sodium sulfate. For the pesticide extracts, adjust the pH of the water to 6.0 - 9.0 with NaOH or H_2SO_4. For the herbicide extracts, adjust the pH of the water to <2.

10.4.7 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 - 1000 mL graduated cylinder. Filter the herbicide extracts similarly using acidified sodium sulfate. Record the final extract volume.

10.4.8 Filter the extracts through Whatman #41 paper into 500 mL K-D evaporator flasks equipped with 10 mL concentrator tubes. Rinse the graduated cylinder or centrifuge tube with 30 - 50 mL of methylene chloride and pour through the filter to complete the transfer. Concentrate the extracts per Sections 10.5 through 10.7.

10.5 Concentration

10.5.1 Concentrate the extracts in separate 500 mL K-D flasks equipped with 10 mL concentrator tubes. Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the column by adding approx one 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 one 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 - 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 - 10 minutes.

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

10.3.1.2 Extraction -- Adjust the pH of the waters in the extractors to 5 - 9 with NaOH or H_2SO_4 while monitoring with a pH meter.

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

10.3.1.4 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 (acidified sodium sulfate for the herbicides). Rinse the distilling flask with 30 - 50 mL of methylene chloride and pour through the drying column. For pesticide extracts and for herbicide 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, and concentrate per Sections 10.5 through 10.7.

10.3.2 Hydrolysis and back-extraction of herbicides

10.3.2.1 Pour the sample and QC aliquots into separate 1.5 - 2 L separatory funnels. Add 250 g NaCl and shake to dissolve.

10.3.2.2 Add 17 mL of 6 N NaOH to each separatory funnel and shake to mix thoroughly. Check the pH of the sample and QC aliquots and adjust to >12 if required. Periodically shake the aliquots during a 1 - 2 hour hydrolysis period.

10.3.2.3 Rinse each beaker used for measurement of the sample and QC aliquots with 60 mL of methylene chloride, add to its respective separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase. If the emulsion cannot be broken, continuous liquid/liquid extraction techniques may be used. Check and adjust the pH of the sample to >12 with NaOH if required.

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

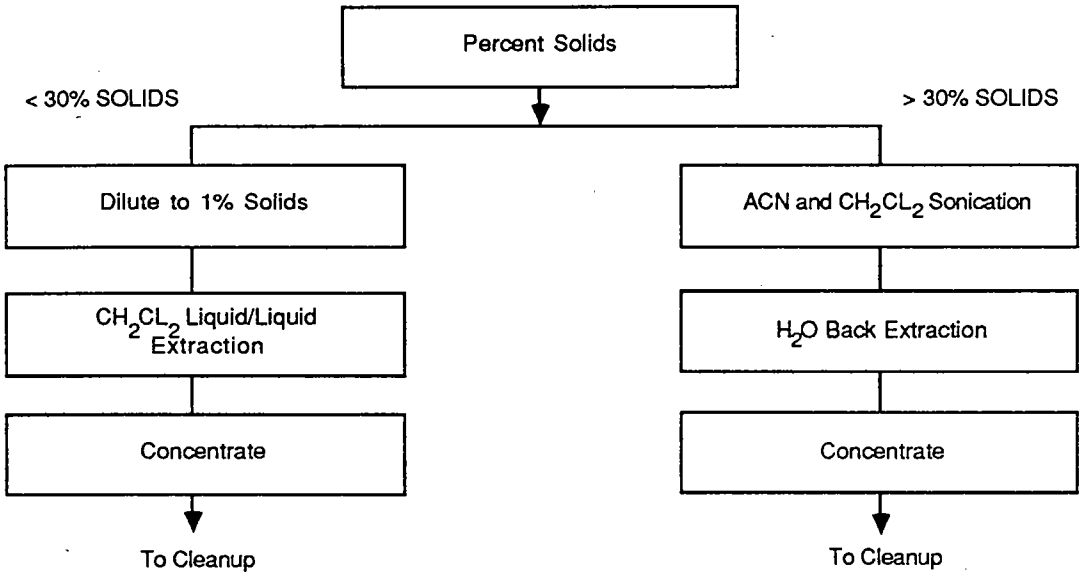
10.3.3 Extraction of the herbicides

10.3.3.1 Add 17 mL of 12 N H_2SO_4 to the sample and QC aliquots. Seal and shake to mix. Caution: some samples require acidification in a hood because of the potential for generating hydrogen sulfide. Check and adjust the pH of the sample to <2 if required.

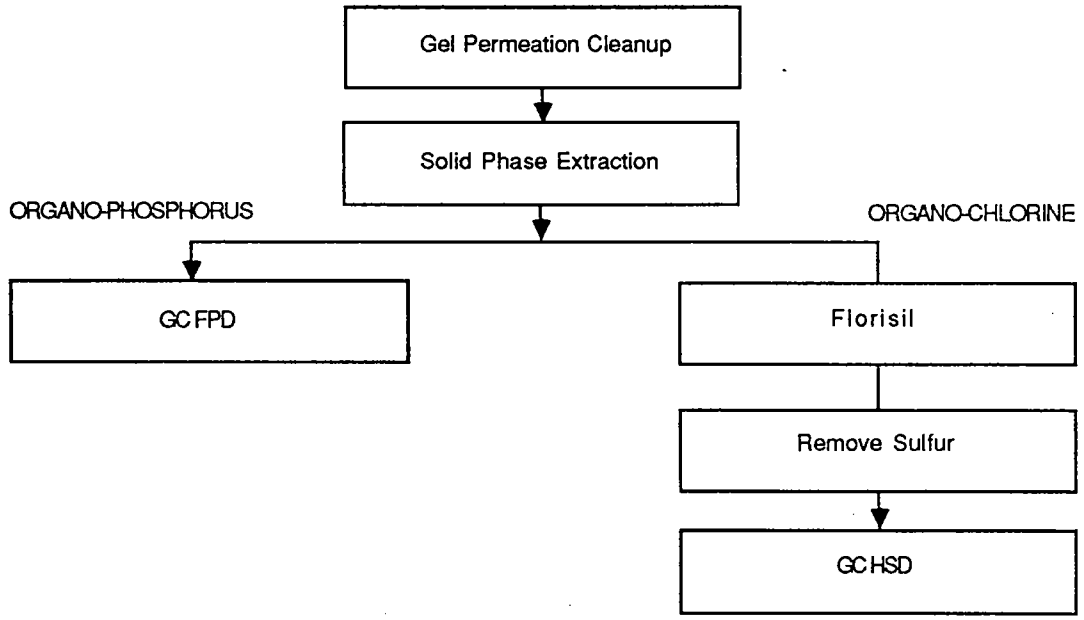
10.3.3.2 Add 120 mL ethyl ether to the sample and QC aliquots. Seal and extract per Section 10.3.2. Drain the aqueous phase completely into the respective beaker used for measurement of aliquot volume. Drain the ether phase into 500 mL round-bottom flask containing approx 10 g of acidified sodium sulfate making certain that the amount of water drained into the flask is minimized. Periodically, shake the round-bottom flask to mix the ether solution and the drying agent.

10.3.3.3 Return the aqueous phase to the separatory funnel, add a 60 mL volume of ether, and repeat the extraction a second time. Drain the aqueous phase completely into the beaker used for measurement of aliquot volume and the ether phase into the round-bottom flask.

10.3.3.4 Repeat the extraction a third time, combining the ether with the other extracts in the round-bottom flask. Allow the sodium sulfate to remain in contact with the ether solution for a minimum of two hours, periodically shaking the round-bottom flask to mix the ether and the



Method 1618 - Extraction and Concentration Steps



Method 1618 - Cleanup and Analysis Steps

FIGURE 1 Method 1618 - Extraction, Cleanup, and Analysis

10.6.2 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 - 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 percent loss in the GPC cleanup). Clean up the extracts using the Florisil, silica gel, and/or sulfur removal procedures in Section 11.

10.7 Herbicide extracts -- These extracts are concentrated to 5 - 10 mL and the herbicides are derivatized per Section 12.

11 CLEANUP AND SEPARATION

11.1 Cleanup procedures may not be necessary for relatively clean samples (treated effluents, groundwater, 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. It is used for cleanup of organo-chlorine and organo-phosphate extracts.

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

11.1.4 Alumina column cleanup (Section 11.5) may also be used for cleanup of the organo-chlorine compounds.

11.1.5 Elemental sulfur, which interferes with the electron capture gas chromatography of some of the pesticides and herbicides, is removed using GPC, mercury, or activated copper. Sulfur removal (Section 11.6) from extracts containing organo-chlorine is required when sulfur is known or suspected to be present. Mercury and copper should not be used for sulfur removal from extracts expected to contain the organo-phosphorus pesticides because some of these analytes are also removed (Reference 8).

11.2 Gel permeation chromatography (GPC)

11.2.1 Column packing

11.2.1.1 Place 70 - 75 g of SX-3 Bio-beads in a 400 - 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 - 5.5 mL/min prior to connecting the column to the detector.

11.2.1.4 After purging the column with solvent for 1 - 2 hours, adjust the column head pressure to 7 - 10 psig, and purge for 4 - 5 hours to remove air. Maintain a head pressure of 7 - 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-ethyl hexyl) phthalate, pentachlorophenol, perylene, and sulfur.

11.2.2.3 Set the "dump time" to allow >85 percent removal of the corn oil and >85 percent 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 percent. If calibration is not verified, the system shall be recalibrated using the calibration

the extract was subjected to GPC cleanup, and proceed to Section 13 for GC analysis.

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 - 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 six percent ethyl ether in hexane (v/v) at a rate of approx 5 mL/min. Remove the K-D flask. Elute fraction 2 with 200 mL of 15 percent ethyl ether in hexane (v/v) into a second K-D flask. Elute fraction 3 with 200 mL of 50 percent ethyl ether in hexane (v/v).

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 13.

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 - 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 Teflon-sealed vial. Add 1 - 2 drops of mercury or 100 mg of activated copper powder and seal (Reference 9). 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 - 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.

11.6.3 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.

11.6.4 If TBA sulfite is used, add 5 mL of reagent water and shake for 1 - 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 13.

12 ESTERIFICATION OF PHENOXY-ACID HERBICIDES

12.1 Concentrate the extract to approximately 5 mL per Section 10.5 and further concentrate the extract to near dryness using the nitrogen blowdown apparatus. Bring the volume to 5 mL with isooctane. If desired, the extract may be transferred to a 10 mL sample vial and stored at -20 to -10 °C.

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 over loaded. The column specified in this method is designed to handle a maximum of 0.5 gram of high molecular weight material in a 5 mL extract. If the extract is known or expected to contain more than 0.5 gram, 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 gravimetricly by evaporating the solvent from a 50 uL 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 - 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 extracts per Sections 10.5 - 10.7.

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 - 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 (6.6.2.2) using vacuum for five 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 7.4). Elute the mixture using the procedure in 11.3.4.

11.3.3.2 Concentrate the eluant to 1.0 mL and inject 1.0 uL of the concentrated eluant into the GC using the procedure in Section 13. The recovery of all organo-chlorine or organo-phosphorus analytes (including the unresolved GC peaks) shall be within the ranges for recovery specified in Tables 7 - 8, 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. Reestablish the vacuum at 5 - 10 psia.

11.3.4.2 Using a pipet or a one 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 elutions solvent (6.6.2.2), using vacuum for five 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. Adjust the final volume to 5 or 10 mL (per Section 10.6), depending on whether or not

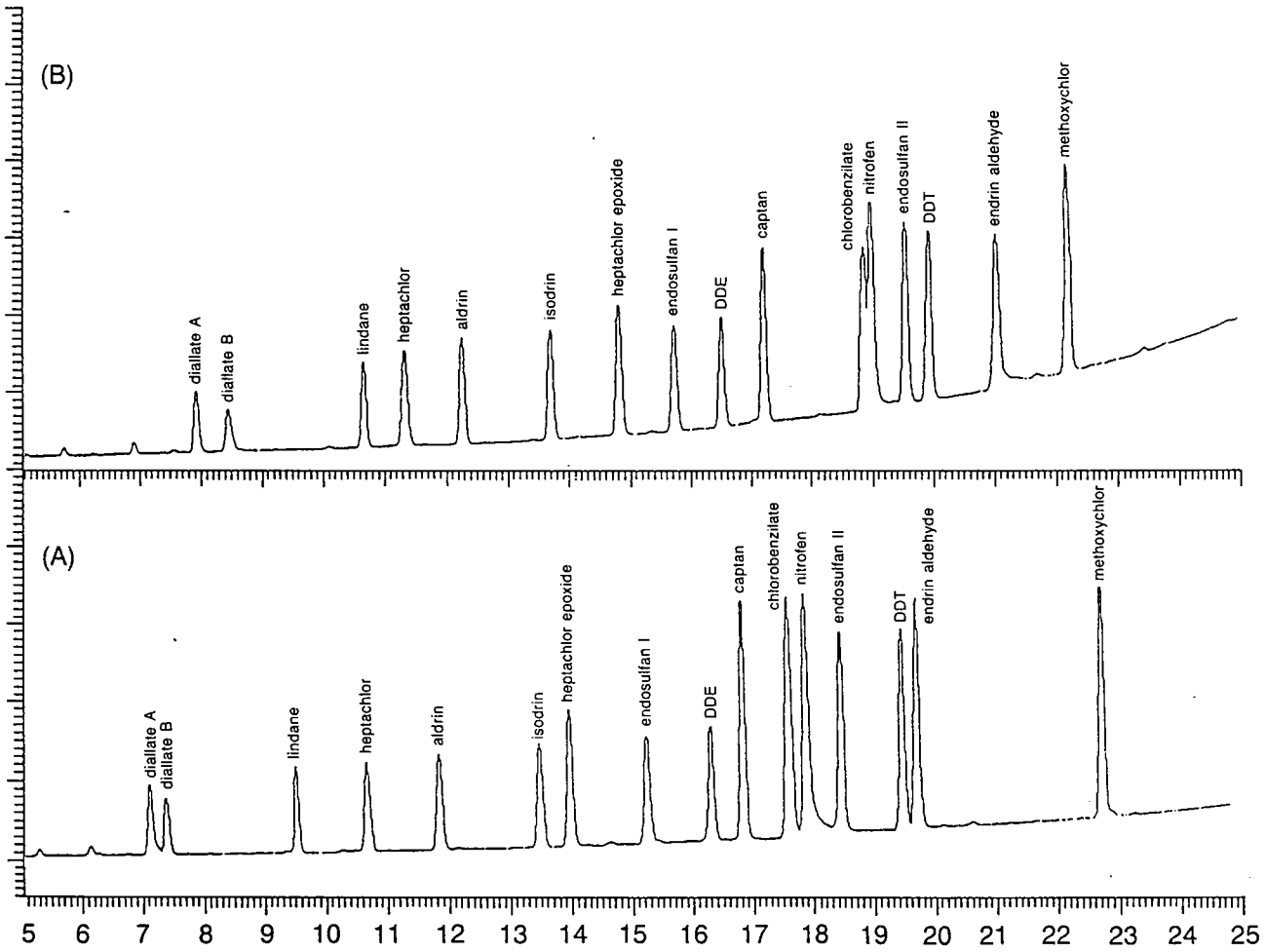


FIGURE 2 Organochlorine Mix A [(A) DDB-608 and (B) DB-1701].

12.2 Esterification -- Observe the safety precautions regarding diazomethane in Section 4.

12.2.1 Set up the diazomethane generation apparatus as given in the instructions in the Diazald kit.

12.2.2 Transfer one mL of the isooctane solution (Section 12.1) to a clean vial and add 0.5 mL of methanol and 3 mL of ether. For extracts that have been cleaned up by GPC, use 2 mL to account for the loss.

12.2.3 Add two mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of diazomethane should persist throughout this period. If the yellow color disappears, add two mL of diazomethane solution and allow to stand, with occasional swirling, for another 10 minutes. Colored or complex samples will require at least 4 mL of diazomethane to ensure complete reaction of the herbicides. Continue adding diazomethane in 2 mL increments until the yellow color persists for the entire 10 minute period or until 10 mL of diazomethane solution has been added.

12.2.4 Rinse the inside wall of the container with 0.2 - 0.5 mL of diethyl ether and add 10 - 20 mg of silicic acid to react excess diazomethane. Filter through Whatman #41 paper into a clean sample vial. If the solution is colored or cloudy, evaporate to near dryness using the nitrogen blowdown apparatus, bring to 10 mL with hexane, and proceed to Section 11.3 for SPE cleanup. If the solution is clear and colorless, evaporate to near dryness, bring to 1.0 mL with hexane and proceed to Section 13 for GC analysis.

13 GAS CHROMATOGRAPHY

Tables 4 through 6 summarize the recommended operating conditions for the gas chromatographs. Included in these tables are the retention times and estimated detection limits that can be achieved under these conditions. Examples of the separations achieved by the primary and confirmatory columns are shown in Figures 2 through 6.

13.1 Calibrate the system as described in Section 7.

13.2 Combining pesticide and herbicide extracts

13.2.1 Pesticide extracts cleaned up by solid phase extraction -- Combine the 1.0 mL final organo-chlorine pesticide extract (Section 11.3.4.5 or 11.5.4) with the 1.0 mL final herbicide extract (Section 11.3.4.5 or 11.5.4 if the herbicide extract required cleanup; Section 12.2.4 if it did not).

13.2.2 Pesticide extracts cleaned up by Florisil -- Combine 1.0 mL of the 5.0 mL or 10.0 mL pesticide extract (Section 11.4.5) with the 1.0 mL final herbicide extract (Section 11.3.4.5 or 11.5.4 if the herbicide extract required cleanup; Section 12.2.4 if it did not).

13.3 Set the injection volume on the autosampler to inject 1.0 uL of all standards and extracts of blanks and samples.

13.4 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.

14 SYSTEM AND LABORATORY PERFORMANCE

14.1 At the beginning of each eight hour shift during which analyses are performed, GC system performance and calibration are verified for all pollutants and surrogates on all column/detector systems. For these tests, analysis of the combined QC standard (Section 7.4) 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.

14.2 Retention times -- The absolute retention times of the peak maxima shall be within ±10 seconds of the retention times in the initial calibration (Section 7.4.1).

14.3 GC resolution -- Resolution is acceptable if the valley height between two peaks (as measured from the baseline) is less than 10 percent of the taller of the two peaks.

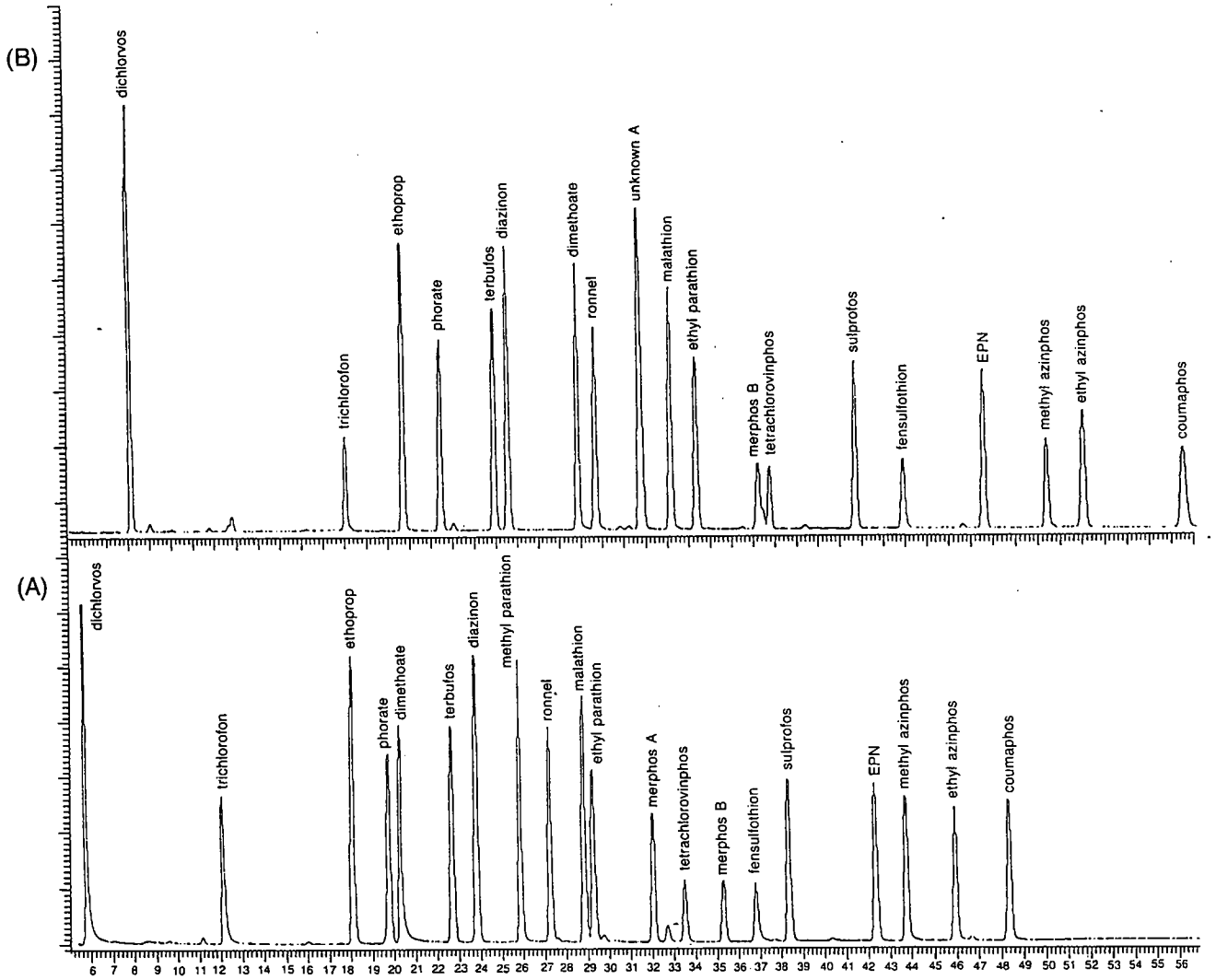


FIGURE 4 Organophosphate Mix A [(A) DB-1 and (B) DB-1701].

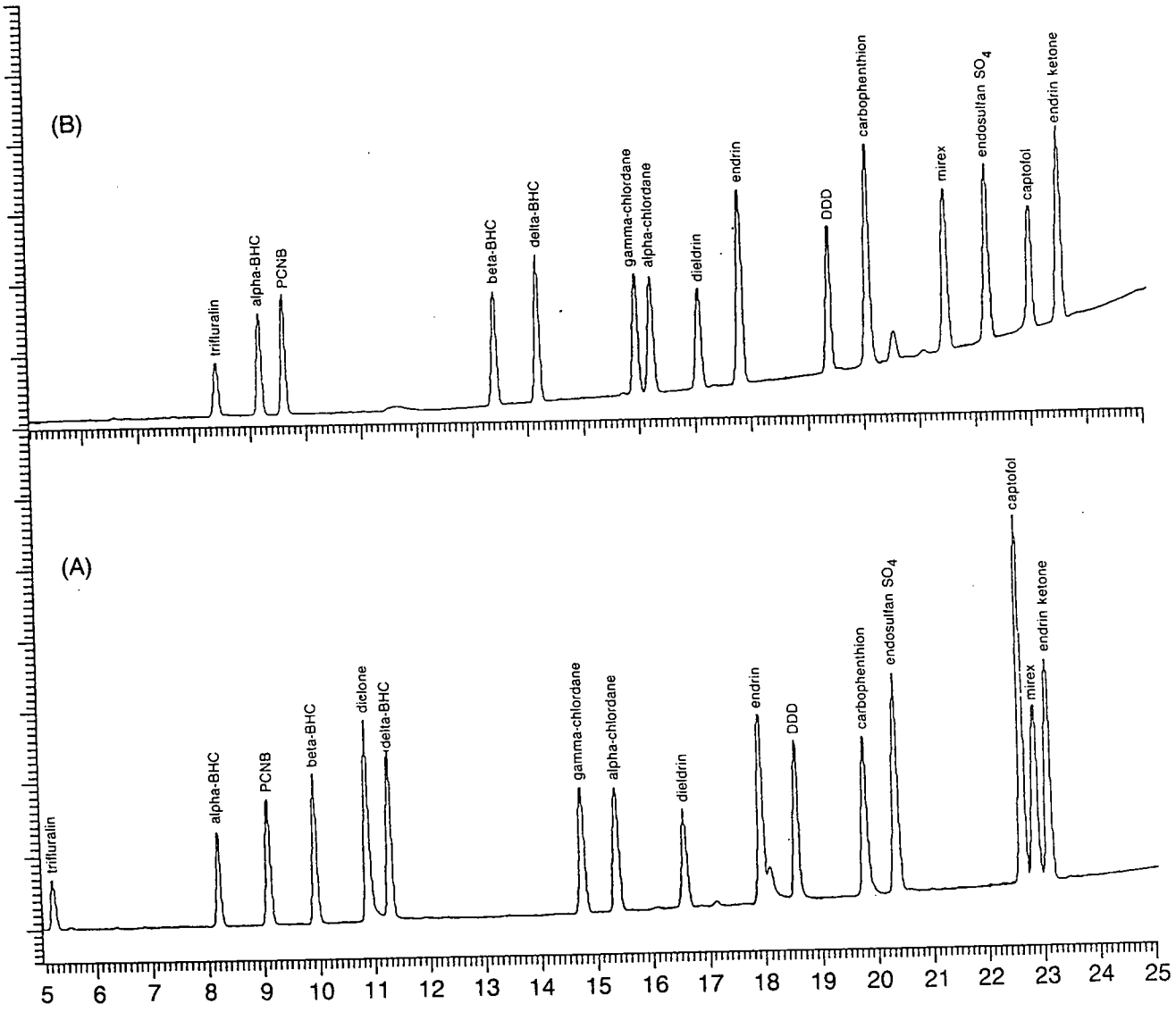


FIGURE 3 Organochlorine Mix B [(A) DB-608 and (B) DB-1701].

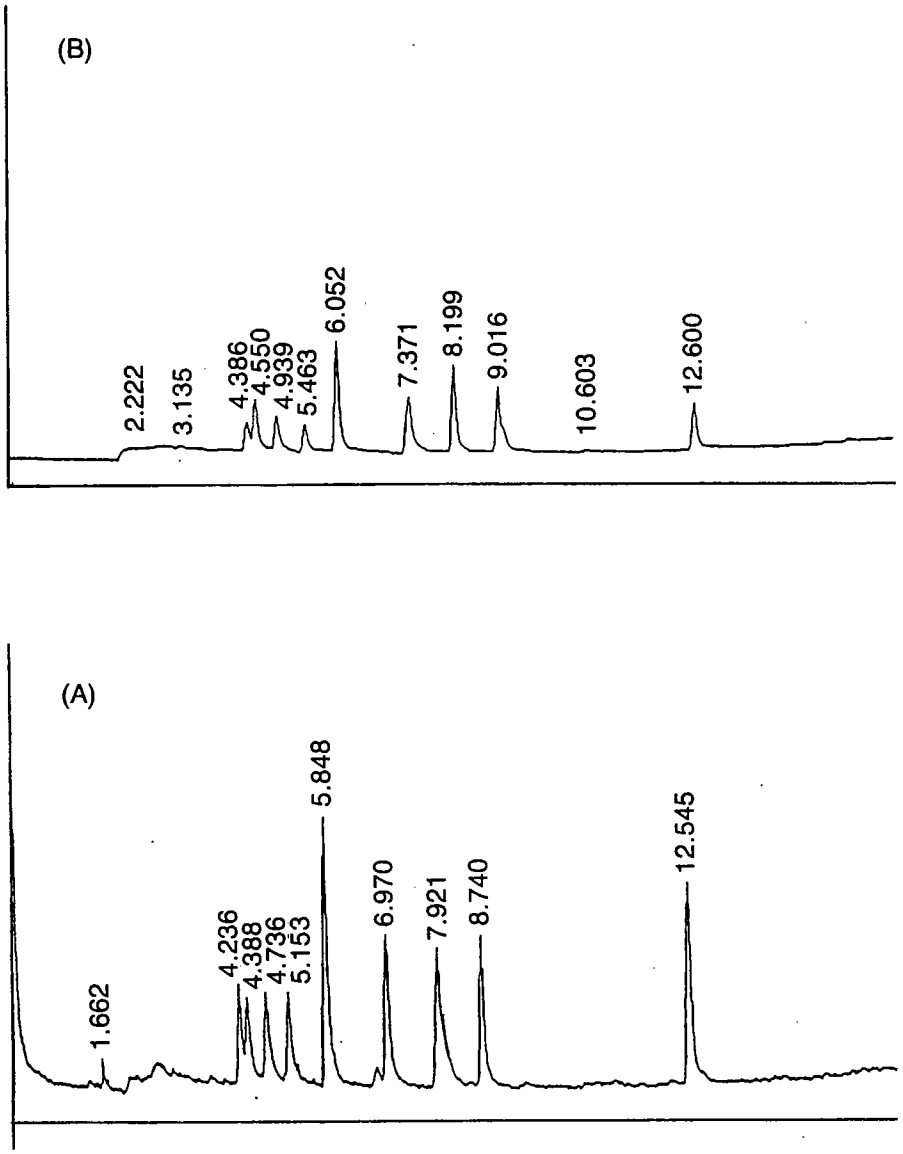


FIGURE 6 Phenoxy-acid Herbicides [(A) DB-608 and (B) DB-1701]

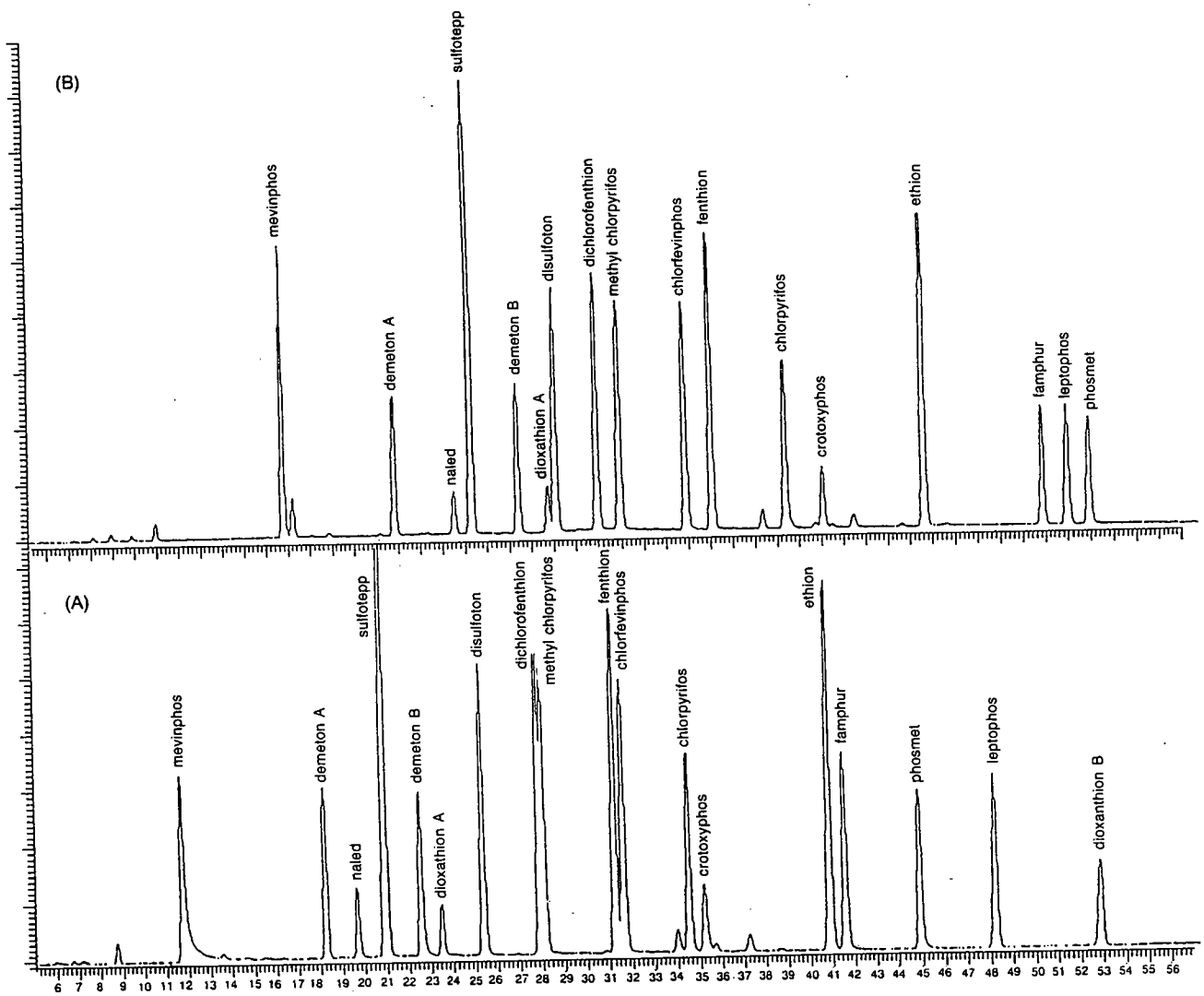


FIGURE 5 Organophosphate Mix B [(A) DB-1 and (B) DB-1701].

15 QUALITATIVE DETERMINATION

15.1 Qualitative determination is accomplished by comparison of data from analysis of a sample or blank with data from analysis of the shift standard (Section 14.2), and with data stored in the retention time and calibration libraries (Section 7.3.3 and 7.3.4.1). Identification is confirmed when retention time and amounts agree per the criteria below.

15.2 For each compound on each column/detector system, establish a retention time window ±20 seconds on either side of the retention time in the calibration data (Section 7.3.3). For compounds that have a retention time curve (Section 7.3.3.2), establish this window as the minimum -20 seconds and maximum +20 seconds. For the multi-component analytes, use the retention times of the five largest peaks in the chromatogram from the calibration data (Section 7.3.3).

15.2.1 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 15.2) 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 16) on each system (primary and confirmatory) agree within a factor of three.

15.2.2 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 15.2) 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 ±30 seconds of the retention times for the computed amounts (Section 16), as determined by the retention time calibration curve (Section 7.3.3.2), and (2) the computed amounts (Section 16) on each system (primary and confirmatory) agree within a factor of three.

16 QUANTITATIVE DETERMINATION

16.1 Using the GC data system, compute the concentration of the analyte detected in the extract (in ug/mL) using the calibration factor or calibration curve (Section 7.3.3.2).

16.2 Liquid samples -- Compute the concentration in the sample using the following equation:

$$Cs = \frac{10\ (Cex)}{(Vs)}$$

where,

Cs = the concentration in the sample in ug/L.
10 = extract total volume in mL.
Cex = concentration in the extract in ug/mL.
Vs = volume of sample extracted in liters.

16.3 Solid samples -- Compute the concentration in the solid phase of the sample using the following equation:

$$Cs = \frac{10\ (Cex)}{1000\ (Ws)\ (\%\ solids)}$$

where,

Cs = concentration in the sample in ug/kg.
10 = extract total volume in mL.
Cex = concentration in the extract in ug/mL.
1000 = used to convert grams to kilograms.
Ws = sample weight in grams.
% solids = percent solids as determined in Section 10.1.3.

16.4 If the concentration of any analyte exceeds the calibration range of the system, the extract is diluted by a factor of 10, and a one uL aliquot of the diluted extract is analyzed.

16.5 Two or more PCB's in a given sample are quantitated and reported as total PCB.

16.6 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.

14.3.1 Organo-halide compounds

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

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

14.3.2 Organo-phosphorus compounds

14.3.2.1 Primary column (DB-1) -- Malathion and ethyl parathion.

14.3.2.2 Confirmatory column (DB-1701) -- Terbufos and diazinon.

14.4 Decomposition of DDT and endrin

14.4.1 Analyze a total of 2 ng DDT and 1 ng endrin on each organo-chlorine column using the analytical conditions specified in Table 4.

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

14.4.3 The area of peaks other than the sum of the areas of the DDT and endrin peaks shall be less than 20 percent 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 14.1 - 14.4) shall be repeated 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.

14.5 Calibration verification -- Calibration is verified for the combined QC standard only.

14.5.1 Inject the combined QC standard (Section 7.4)

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

14.5.3 For each compound or coeluted compounds, compare this calibration verification recovery with the corresponding limits for ongoing accuracy in Tables 7 - 9. 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 (PCB's and toxaphene).

14.6 Ongoing precision and recovery

14.6.1 Analyze the extract of the precision and recovery standard extracted with each sample lot (Sections 10.2.3.3 and 10.2.5.7).

14.6.2 Compute the percent recovery of each analyte and coeluting compounds.

14.6.3 For each compound or coeluted compounds, compare the percent recovery with the limits for ongoing recovery in Tables 7 - 9. 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 lot, and repeat the ongoing precision and recovery test.

14.6.4 Add results which pass the specifications in Section 14.6.3 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 calculating the average percent recovery (R) and the standard deviation of percent recovery sr. Express the accuracy as a recovery interval from R - 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85 - 105%.

Table 1
ORGANO-HALIDE PESTICIDES DETERMINED BY WIDE BORE, FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH HALIDE SPECIFIC DETECTOR

EGD No.	Compound	CAS Registry
089	Aldrin	309-00-2
102	alpha-BHC	319-84-6
103	beta-BHC	319-85-7
105	delta-BHC	319-86-8
104	gamma-BHC (Lindane)	58-89-9
434	Captafol	2425-06-1
433	Captan	133-06-2
441	Carbophenothion	786-19-6
091	Chlordane	57-74-9
431	Chlorobenzilate	510-15-6
094	4,4'-DDD	72-54-8
093	4,4'-DDE	72-55-9
092	4,4'-DDT	50-29-3
432	Diallate	2303-16-4
478	Dichlone	117-80-6
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
100	Heptachlor	76-44-8
101	Heptachlor epoxide	1024-57-3
437	Isodrin	465-73-6
439	Kepone	143-50-0
430	Methoxychlor	72-43-5
438	Mirex	2385-85-5
436	Nitrofen (TOK)	1836-75-5
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
113	Toxaphene	8001-35-2
442	Trifluralin	1582-09-8

NON-ITD ORGANO-HALIDE COMPOUNDS THAT CAN BE ANALYZED BY THIS METHOD

Compound	CAS Registry
Chloroneb	2675-77-6
Chloropropylate	5836-10-2
DBCP	96-12-8
Dicofol	115-32-2
Etridiazole	2593-15-9
Perthane (Ethylan)	72-56-0
Propachlor	1918-16-7
Strobane	8001-50-1

Table 2
ORGANO-PHOSPHORUS PESTICIDES DETERMINED BY WIDE BORE, FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH FLAME PHOTOMETRIC DETECTOR

EGD No.	Compound	CAS Registry
468	Azinphos ethyl	2642-71-9
453	Azinphos methyl	86-50-0
461	Chlorfevinphos	470-90-6
469	Chlorpyrifos	2921-88-2
443	Coumaphos	56-72-4
479	Crotoxyphos	7700-17-6
471	Demeton	8065-48-3
460	Diazinon	333-41-5
450	Dichlorvos	62-73-7
455	Dicrotophos	141-66-2
449	Dimethoate	60-51-5
452	Dioxathion	78-34-2
458	Disulfoton	298-04-4
467	EPN	2104-64-5
463	Ethion	563-12-2
446	Famphur	52-85-7
454	Fensulfothion	115-90-2
447	Fenthion	55-38-9
464	Hexamethylphosphoramide	680-31-9
474	Leptophos	21609-90-5
475	Malathion	121-75-5
456	Methyl parathion	298-00-0
444	Mevinphos	7786-34-7
470	Monocrotophos	6923-22-4
459	Naled	300-76-5
448	Parathion	56-38-2
457	Phorate	298-02-2
465	Phosmet	732-11-6
473	Phosphamidon	13171-21-6
477	Sulfotepp	3689-24-5
476	TEPP	107-40-3
472	Terbufos	13071-79-9
466	Tetrachlorvinphos	961-11-5
445	Trichlorofon	42-68-6
451	Tricresylphosphate	78-30-8
462	Trimethylphosphate	512-56-1

NON-ITD ORGANO-PHOSPHATE COMPOUNDS THAT CAN BE ANALYZED BY THIS METHOD

Compound	CAS Registry
Bolstar	35400-43-2
Dichlorofenthion	97-17-6
Ethoprop	13194-48-4
Merphos	150-50-5
Methyl chlorpyrifos	5598-13-0
Methyl trithion	953-17-3
Ronnel	299-84-3
Sulprofos	35400-43-2
Tokuthion	34643-46-4
Trichloronate	327-98-0

17 ANALYSIS OF COMPLEX SAMPLES

17.1 Some samples may contain high levels (>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.

17.2 The analyst shall attempt to clean up all samples using GPC (Section 11.2), and the SPE cartridge (Section 11.3), and samples for the organo-halide compounds by florisil (Section 11.4) or alumina (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 16.4).

17.3 Recovery of surrogates -- 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, the sample shall be reextracted and reanalyzed. If the surrogate recovery is still outside this range, the sample is diluted by a factor of 10 and reanalyzed (Section 16.4).

17.4 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 Tables 7 - 9, 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 does not apply to the sample being analyzed and the result may not be reported for regulatory compliance purposes.

18 METHOD PERFORMANCE

18.1 Development of this method is detailed in Reference 10.

REFERENCES

1 "Working with Carcinogens," DHEW, PHS, CDC, NIOSH, Publication 77-206, (August 1977).

2 "OSHA Safety and Health Standards, General Industry" OSHA 2206, 29 CFR 1910 (January 1976).

3 "Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety (1979).

4 Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Adsorbent Capacity and Its Use in Standardizing Florisil Columns," J. Assoc. Off. Analytical Chemists, 51, 29 (1968).

5 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL, Cincinnati, OH 45268, EPA-600/4-79-019 (March 1979).

6 "Standard Practice for Sampling Water," ASTM Annual Book of Standards, ASTM, Philadelphia, PA, 76 (1980).

7 "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL, Cincinnati, OH 45268, EPA 600/4-70-020 (March 1979).

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

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

10 "Consolidated GC Method for the Determination of ITD/RCRA Pesticides using Selective GC Detectors," Report Reference 32145-01, Document R70, S-CUBED, A Division of Maxwell Laboratories, Inc, PO Box 1620, La Jolla, CA, 92038-1620 (September 1986).

Table 4
GAS CHROMATOGRAPHY OF ORGANO-HALIDE PESTICIDES

EGD No.	Compound	Retention Time (1) DB-608	Retention Time (1) DB-1701	MDL (2) (ng/L)
442	Trifluralin	5.16	8.58	50 est
432	Diallate-A	7.15	8.05	45
	Diallate-B	7.42	8.58	32
102	alpha-BHC	8.14	9.45	6
440	PCNB	9.03	9.91	6
104	gamma-BHC (Lindane)	9.52	10.84	11
103	beta-BHC	9.86	13.58	7
100	Heptachlor	10.66	11.56	5
478	Dichlone	10.80	(3)	(4)
105	delta-BHC	11.20	14.39	5
089	Aldrin	11.84	12.50	8
437	Isodrin	13.47	13.93	13
101	Heptachlor epoxide	13.97	15.03	12
	gamma-Chlordane	14.63	16.20	9
091	alpha-Chlordane	15.24	16.48	8
095	Endosulfan I	15.25	15.96	11
093	4,4'-DDE	16.34	16.76	10
090	Dieldrin	16.41	17.32	6
433	Captan	16.83	17.32	(4)
431	Chlorobenzilate	17.58	18.97	25
098	Endrin	17.80	18.06	4
436	Nitrofen (TOK)	17.86	19.14	13
439	Kepone	17.92	25.03	(4)
094	4,4'-DDD	18.43	19.56	5
096	Endosulfan II	18.45	19.72	8
092	4,4'-DDT	19.48	20.10	12
441	Carbophenothion	19.65	20.21	50
099	Endrin aldehyde	19.72	21.18	11
097	Endosulfan sulfate	20.21	22.36	7
434	Captafol	22.51	23.11	(4)
438	Mirex	22.75	21.82	4
430	Methoxychlor	22.80	22.34	30
435	Endrin ketone	23.00	23.71	8
106	PCB-1242			
109	PCB-1232			
112	PCB-1016			
108	PCB-1221			
110	PCB-1248			
107	PCB-1254			
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	

(1) Columns: 30 m x 0.53 mm i.d.; DB-608: 0.83 micron; DB-1701: 1.0 micron.
Conditions: 150 °C for 0.5 min, 150 - 270 @ 5 °C per minute, 270 °C until endrin ketone elutes.
Carrier gas flow rate: approximately 7 mL/min.

(2) 40 CFR Part 136, Appendix B (49 FR 43234). Detection limits for soils (in ng/kg) are estimated to be 30 - 100 times this level.

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

(4) Not recovered from water at levels tested.

Table 3
PHENOXYACID HERBICIDES DETERMINED BY WIDE BORE, FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH HALIDE SPECIFIC DETECTOR

EGD No.	Compound	CAS Registry
481	2,4-D	94-75-7
480	Dinoseb	88-85-7
482	2,4,5-T	93-76-5
483	2,4,5-TP	93-72-1

NON-ITD PHENOXYACID HERBICIDES THAT CAN BE ANALYZED BY THIS METHOD

Compound	CAS Registry
Dalapon	75-99-0
2,4-DB (Butoxon)	94-82-6
Dicamba	1918-00-9
Dichlorprop	120-36-5
MCPA	94-74-6
MCPP	93-65-2

Table 6
GAS CHROMATOGRAPHY OF PHENOXY-ACID HERBICIDES

EGD No.	Compound	Retention Time (1) DB-608	DB-1701	MDL (2) (ng/L)
481	2,4-D	5.85	6.05	100
480	Dinoseb			100 est
482	2,4,5-T	7.92	8.20	50
483	2,4,5-TP (Silvex)	6.97	7.37	40
	Dalapon			1000 est
	2,4-DB (Butoxon)	8.74	9.02	50
	Dicamba	4.39	4.39	110
	Dichlorprop	5.15	5.46	40
	MCPA	4.74	4.94	90
	MCPP	4.24	4.55	56

(1) Columns: Same as for the organo-chlorine pesticides. See Table 4.
Conditions: 175 °C for 0.5 min, 175 - 270 @ 5 °C per minute.
Carrier gas flow rate: approximately 7 mL/min.

(2) 40 CFR Part 136, Appendix B (49 FR 43234). Detection limits for soils (in ng/kg) are estimated to be 30 - 100 times this level.

Table 5
GAS CHROMATOGRAPHY OF ORGANO-PHOSPHORUS PESTICIDES

EGD No.	Compound	Retention Time (1) DB-608	Retention Time (1) DB-1701	MDL (2) (ng/L)
450	Dichlorvos	6.56	9.22	4
444	Mevinphos	11.85	16.20	74
445	Trichlorofon	12.69	18.85	150 (3)
471	Demeton-A	17.70	20.57	19
	Ethoprop	18.49	21.43	7
459	Naled	18.92	23.00	18
455	Dicrotophos	19.33	26.30	81
470	Monocrotophos	19.62	29.24	85
477	Sulfotepp	20.04	23.68	6
457	Phorate	20.12	23.08	10
449	Dimethoate	20.59	29.29	27
	Demeton-B	21.40	25.52	21
452	Dioxathion	22.24	26.70	121
472	Terbufos	22.97	24.55	26
473	Phosphamidon-E	23.70	29.89	28
458	Disulfoton	23.89	27.01	32
460	Diazinon	24.03	26.10	38
	Tributyl phosphate (surr)	24.50	17.20	-
	Phosphamidon-Z	25.88	32.62	116
456	Methyl parathion	25.98	32.12	18
	Dichlorofenthion	26.11	28.66	6
	Methyl chlorpyrifos	26.29	29.53	13
	Ronnel	27.33	30.09	11
475	Malathion	28.87	33.49	11
447	Fenthion	29.14	32.16	22
448	Parathion (ethyl)	29.29	34.61	10
469	Chlorpyrifos	29.48	32.15	4
	Trichloronate	30.44	32.12	14
461	Chlorfevinphos	32.05	36.08	2
479	Crotoxyphos	32.65	37.58	81
	Tokuthion	33.30	37.17	2
466	Tetrachlorvinphos	33.40	37.85	12
	Merphos-B	35.16	37.37	18
454	Fensulfothion	36.58	43.86	104
	Methyl trithion	36.62	40.52	10
463	Ethion	37.61	41.67	13
	Sulprofos (Bolstar)	38.10	41.74	6
446	Famphur	38.24	46.37	27
465	Phosmet	41.24	48.22	14
467	EPN	41.94	47.52	9
453	Azinphos methyl	43.33	50.26	9
474	Leptophos	44.32	47.36	14
468	Azinphos ethyl	45.55	51.88	22
	Triphenyl phosphate (surr)	47.68	40.43	-
443	Coumaphos	48.02	56.44	24

(1) Columns: 30 m x 0.53 mm i.d.; DB-1: 1.5 micron; DB-1701: 1.0 micron.
Conditions: 110 °C for 0.5 min, 110 - 250 @ 3 °C per minute, 250 °C until coumaphos elutes.
Carrier gas flow rate: approximately 7 mL/min.

(2) 40 CFR Part 136, Appendix B (49 FR 43234).

(3) Estimated: Detection limits for soils (in ng/kg) are estimated to be 30 - 100 times this level.

Table 8
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS FOR ORGANO-PHOSPHORUS COMPOUNDS

EGD No.	Compound	Spike level (ng/L)	Acceptance Criteria: Initial precision and accuracy Sec 8.2 (%) s	X	Calibration verification Sec 14.5 (ug/mL)	Recovery Sec 8.4 Ongoing accuracy Sec 14.6 R (%)
468	Azinphos ethyl	100	10	71 - 117	77 - 127	59 - 129
453	Azinphos methyl	100	10	52 - 112	83 - 119	37 - 127
461	Chlorfevinphos	50	11	56 - 132	83 - 114	37 - 151
469	Chlorpyrifos	50	10	61 - 112	80 - 119	48 - 125
443	Coumaphos	50	10	78 - 104	82 - 120	72 - 110
479	Crotoxyphos	200	46	28 - 116	68 - 136	6 - 138
471	Demeton-S	200	23	33 - 101	64 - 123	16 - 118
460	Diazinon	100	10	70 - 110	86 - 114	60 - 120
450	Dichlorvos	50	18	52 - 106	77 - 103	39 - 119
455	Dicrotophos (1)					78 - 122
449	Dimethoate	100	89	27 - 100	73 - 127	22 - 100
452	Dioxathion	600	22	59 - 101	79 - 121	49 - 111
458	Disulfoton	100	30	46 - 98	70 - 118	33 - 111
467	EPN	100	13	74 - 124	81 - 108	62 - 136
463	Ethion	100	11	72 - 134	70 - 118	47 - 149
446	Famphur	200	12	81 - 101	81 - 113	76 - 106
454	Fensulfothion	200	65	13 - 115	42 - 139	0 - 141
447	Fenthion	100	13	69 - 101	73 - 137	61 - 109
464	Hexamethylphosphoramide (1)					70 - 130
474	Leptophos	100	10	85 - 105	85 - 112	80 - 110
475	Malathion	100	10	75 - 109	82 - 108	66 - 118
456	Methyl parathion	100	15	72 - 112	89 - 114	61 - 123
444	Mevinphos	100	23	24 - 100	73 - 135	7 - 107
470	Monocrotophos (1)					19 - 206
459	Naled	100	10	0 - 148	77 - 114	0 - 176
448	Parathion	100	10	71 - 111	79 - 110	61 - 121
457	Phorate	100	19	54 - 100	70 - 118	43 - 109
465	Phosmet	200	39	44 - 119	61 - 159	25 - 138
473	Phosphamidon-Z	330	45	0 - 100	81 - 102	0 - 100
477	Sulfotepp	50	10	70 - 120	75 - 115	58 - 132
476	TEPP (1)					70 - 130
472	Terbufos	100	23	60 - 110	82 - 111	47 - 123
466	Tetrachlorvinphos	100	11	48 - 110	73 - 119	32 - 126
445	Trichlorofon (1)					70 - 130
451	Tricresylphosphate	300	10	81 - 101	70 - 130	74 - 114
462	Trimethylphosphate (1)					70 - 130
	Dichlorofenthion	100	10	75 - 115	80 - 110	65 - 125
	Ethoprop	100	14	79 - 103	84 - 108	73 - 109
	Merphos-B	200	10	68 - 102	72 - 118	59 - 111
	Methyl chlorpyrifos	100	10	88 - 108	81 - 114	83 - 113
	Methyl trithion	100	20	21 - 137	78 - 122	0 - 166
	Ronnel	100	10	79 - 111	78 - 113	71 - 119
	Sulprofos (Bolstar)	50	10	75 - 100	81 - 118	70 - 100
	Tokuthion	100	17	73 - 105	70 - 130	65 - 113
	Trichloronate	100	10	82 - 102	80 - 113	77 - 107

(1) Not recovered.

Table 7
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS FOR ORGANO-HALIDE COMPOUNDS

EGD No.(1)	Compound	Spike level (ng/L)	Acceptance Criteria: Initial precision and accuracy Sec 8.2 (%) s	X	Calibration verification Sec 14.5 (ug/mL)	Recovery Sec 8.4 Ongoing accuracy Sec 14.6 R (%)
089	Aldrin	100	12	82 - 108	79 - 113	76 - 114
102	alpha-BHC	100	10	57 - 135	69 - 108	38 - 154
103	beta-BHC	100	10	66 - 130	85 - 102	50 - 146
105	delta-BHC	100	24	60 - 122	79 - 103	45 - 136
104	gamma-BHC (Lindane)	100	10	66 - 112	75 - 119	55 - 123
434	Captafol (2)				70 - 107	
433	Captan (2)				49 - 114	
441	Carbophenothion	1000	10	63 - 141	79 - 102	43 - 161
091	Chlordane-alpha	100	10	79 - 122	73 - 102	69 - 133
	Chlordane-gamma	100	13	32 - 140	79 - 113	4 - 169
431	Chlorobenzilate	500	19	58 - 118	54 - 129	43 - 133
094	4,4'-DDD	100	12	69 - 117	77 - 109	57 - 129
093	4,4'-DDE	200	13	66 - 114	81 - 121	54 - 126
092	4,4'-DDT	200	19	86 - 112	77 - 118	79 - 119
432	Diallate	250	16	44 - 120	70 - 124	24 - 139
478	Dichlone (2)			79 - 110		
090	Dieldrin	100	11	66 - 140	48 - 115	48 - 158
095	Endosulfan I	200	14	41 - 133	78 - 119	18 - 156
096	Endosulfan II	200	19	78 - 142	76 - 119	62 - 158
097	Endosulfan sulfate	100	17	50 - 130	70 - 109	31 - 149
098	Endrin	100	13	17 - 149	5 - 117	0 - 182
099	Endrin aldehyde	200	13	0 - 149	86 - 117	0 - 190
435	Endrin ketone	100	25	36 - 126	68 - 135	14 - 148
100	Heptachlor	100	12	78 - 104	80 - 114	71 - 111
101	Heptachlor epoxide	100	13	63 - 117	79 - 117	49 - 131
437	Isodrin	100	15	69 - 113	71 - 126	45 - 127
439	Kepone (2)				47 - 134	
430	Methoxychlor	200	19	50 - 136	47 - 128	28 - 158
438	Mirex	100	23	25 - 155	78 - 114	0 - 188
436	Nitrofen (TOK)	200	22	15 - 139	59 - 142	0 - 170
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	100	11	49 - 129	78 - 101	29 - 149
113	Toxaphene	5000	20	82 - 112	68 - 134	76 - 122
442	Trifluralin	200	12	32 - 148	47 - 134	3 - 177

(1) Reference numbers beginning with 0 or 1 indicate a pollutant quantified by the internal standard method.

(2) Not recovered.

Table 9
ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS FOR PHENOXY-ACID COMPOUNDS

EGD No.	Compound	Spike level (ng/L)	Acceptance Criteria: Initial precision and accuracy Sec 8.2 (%) s	X	Calibration verification Sec 14.5 (ug/mL)	Recovery Sec 8.4 Ongoing accuracy Sec 14.6 R (%)
481	2,4-D	200	16	41 - 107	70 - 130	23 - 131
480	Dinoseb	100	17	30 - 132	70 - 130	5 - 158
482	2,4,5-T	100	14	36 - 120	70 - 130	15 - 141
483	2,4,5-TP (Silvex)					
	Dalapon	100	16	22 - 118	70 - 130	0 - 142
	2,4-DB (Butoxon)	200	18	37 - 145	70 - 130	10 - 172
	Dicamba	100	14	49 - 133	70 - 130	28 - 154
	Dichlorprop	200	14	46 - 130	70 - 130	25 - 151
	MCPA	400	14	65 - 149	70 - 130	42 - 170
	MCPP					