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CONSOLIDATED GC METHOD FOR THE DETERMINATION OF ITD/RCRA PESTICIDES USING SELECTIVE GC DETECTORS

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1.0 SUMMARY

1.1 This method is a consolidation of methods 608, 614, 615, 617, 622 and 701 that can be used for the analysis of water, solid and multimedia samples. The method has been validated for the analysis of organochlorine and organophosphorous pesticides and industrial chemicals listed as analyzable by "GC/EC" and "GC/NPD" in the ITD/RCRA list of analytes (Appendix I).

1.2 Two separate extraction and sample preparation schemes are required in this method. One for apolar organochlorine (Table 1) and organophosphorous analytes (Table 2). The other for phenoxyacid herbicides and their esters (Table 3). The scheme for the preparation and analyses of all of the method.

1.3 The sample is initially split into separate aliquots for work up by the different procedures. Apolar analytes are extracted from liquid samples with methylene chloride using a continuous liquid extractor or are extracted from solid samples with methylene chloride/acetone using a sonicator. The apolar extracts are cleaned using gel permeation chromatography (GPC) followed by adsorbtion chromatography prior to GC analysis. Phenoxyacid herbicides and their esters are extracted from acidified liquid samples with methylene chloride using a continuous liquid extractor or are extracted from acidified solid samples with methylene chloride/acetone using a sonicator. The extracted phenoxyacids are partitioned into aqueous base and their esters are hydrolyzed to the free acids. The acid fractions are combined and derivatized with diazomethane then cleaned using adsorbtion chromatography prior to GC analysis.

1.4 GC analysis is accomplished on "megabore" capillary columns. Apolar analytes are analyzed using both electron capture detection (ECD) (for organochlorine analytes), and flame photometric detection (FPD) (for organophosphates). Derivatized phenoxyacid herbicides are analyzed by using ECD. The primary column for all analytes is the DB-5 (or equivalent), the confirmation column is the SPB-608.

2.0 REAGENTS AND EQUIPMENT

2.1 REAGENTS

2.1.1 Sodium Sulfate - anhydrous reagent grade, heated at 400°C for four hours, or 120°C for 16 hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous granular, catalog No. 3375 or equivalent.

2.1.2 Methylene chloride, hexane, ethyl ether, acetone, isooctane (optional), and methanol: pesticide quality or equivalent. It is strongly suggested that each lot of solvent used be analyzed to demonstrate that it is free of interferences before use.

2.1.3 Primary pesticide and PCB standards will be obtained from the EPA Quality Assurance Materials Bank, Pesticides and Industrial Chemicals Repository, R.T.P., NC for the purpose of traceability. Commercial standard should be used for working solutions but must be shown to be traceable (quantitatively and qualitatively) to EPA standards.

2.1.4 Mercury (optional)

2.1.5 Copper powder (optional), bright and nonoxidized

2.1.6 Concentrated Sodium hydroxide solution (6 N). Dissolve 24g NaOH in reagent water and dilute to 100 mL.

2.1.7 Sulfuric acid solution (1:1 v/v). Slowly add 50 mL H_2SO_4 (Sp. gr. 1.84) to 50 mL of reagent water.

2.1.8 Potassium hydroxide solution (37% w/v). Dissolve 37g of potassium hydroxide in 100 mL of distilled water.

2.1.9 Diol bonded silica 500-mg or 1-g cartridges with stainless steel frits (Analytichem, Harbor City, CA) or equivalent.

2.1.10 Florisil 500 mg cartridges (J.T. Baker), or equivalent.

2.1.11 2,4,5-trichlorophenol for Diol cartridge performance check, Prepare a 0.1 µg/mL solution in acetone.

2.1.12 Reagent water - Reagent water is defined as a water in which no interferent is observed at the method detection limit of any parameter when 1 liter of the reagent water is extracted and prepared using the sample workup procedures for environmental waters.

2.1.13 N-methyl (N-nitroso-p-toluenesulfanamide) (Diazald) fresh and high purity, Aldrich Chemical Co.

2.1.14 Silicic Acid: 100 mesh powder (optional).

2.1.15 Ten percent acetone in hexane (v/v), prepare by adding 10 mL of acetone to 90 mL of hexane.

2.1.16 GPC calibration solutions:

2.1.16.1 Bis(2-ethylhexyl)phthalate/pentachlorophenol solution 4 mg/mL each in methylene chloride.

2.1.16.2 Corn oil - 200 mg/mL in methylene chloride.

2.1.17 Acidified sodium sulfate. Add 0.5 mL H_2SO_4 to 100 grams of sodium sulfate and 30-mL ethyl ether. Completely evaporate the ether and store at 110°C. (Caution: Transfer the acidified sodium sulfate into a different vessel before placing it in the oven. This is required to ensure no flammable ether residue is placed into a hot oven.)

2.1.18 Dilute sodium hydroxide solution (0.1M). Dissolve 4g NaOH in reagent water and dilute to 1.0L.

2.2 APPARATUS AND MATERIALS

2.2.1 Apparatus for determining percent moisture.

2.2.1.1 Oven, drying.

2.2.1.2 Desiccator.

2.2.1.3 Crucibles, porcelain (optional).

2.2.1.4 Aluminum weighing pans (optional).

2.2.2 Sonic cell disruptor, Heat Systems - Ultrasonics, Inc. Model 375C (or equivalent) (375 watt with pulsing capability 1/2" or 3/4" disruptor horn).

2.2.3 Sonabox (or equivalent) for use with disrupter.

2.2.4 Beakers, 400-mL.

2.2.5 Kuderna-Danish (K-D) apparatus.

2.2.5.1 Concentrator tube - 10-mL, graduated (Kontes K-570040-1029, or equivalent).

2.2.5.2 Evaporative flask - 500-mL (Kontes K-470001-0500, or equivalent).

2.2.5.3 Snyder column - three-ball macro (Kontes K-503000-0121, or equivalent).

2.2.6 Powder funnels, 10-cm diameter, for filtration/drying.

2.2.7 Boiling chips

2.2.7.1 Silicon carbide boiling chips (optional) - approximately 10/40 mesh. Heat to 400°C for 30 minutes or solvent rinse before use.

2.2.7.2 Teflon boiling chips (optional). Solvent rinse before use.

2.2.8 Water bath - heated, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

2.2.9 Top loading balance, capable of accurately weighing to ±0.01 g.

2.2.10 Balance-Analytical, capable of accurately weighing to ±0.0001 g.

2.2.11 Nitrogen evaporation device equipped with a heated bath that can be maintained at 35-40°C, N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent).

2.2.12 Vials and caps, 2-mL for GC auto sampler.

2.2.13 Gel permeation chromatography cleanup device: automated system. Gel permeation chromatograph (GPC) Analytical Biochemical Labs, Inc., GPC Autoprep 1002 (or equivalent) including:

2.2.13.1 25-mm ID x 600 - 700-mm glass column packed with 70 g of Bio-Beads SX-3, Bio-Rad Laboratories (or equivalent).

2.2.13.2 Syringe, 10-mL with luer lock fitting.

2.2.13.3 Syringe filter holder, stainless steel, and filters - TFE (Gelman 4310 or equivalent) or glass fiber.

2.2.13.4 UV detection (optional) Type 6, 254-mμ Isco, Inc., Lincoln, NB (or equivalent).

2.2.14 Vacuum system for eluting multiple cleanup cartridges.

2.2.14.1 Vac Elute Manifold (Analytichem International, Harbor City, CA, J.T. Baker or Supelco) or equivalent.

2.2.14.2 Vacuum trap made from a 500-mL sidearm flask fitted with a 1 hole stopper and glass tubing.

2.2.14.3 Vacuum pressure gauge.

2.2.14.4 Rack for holding 10-mL volumetric flasks in the manifold.

2.2.15 Pyrex glass wool.

2.2.16 Bottle or test tube, 50-mL with Teflon lined screw cap for sulfur removal.

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

2.2.18 Drying column - Chromatographic column approximately 400-mm long x 19-mm ID, with coarse frit. (Substitution of a small pad of disposable Pyrex glass wool for the frit will help prevent cross-contamination of sample extracts.)

2.2.19 Continuous liquid-liquid extractors for use with methylene chloride with Teflon or glass connecting lines. Hershberg-Wolf Extractor, Ace Glass Company, Vineland, NH P/N 6841-10 (or equivalent).

2.2.20 Glass scintillation vials, at least 20-mL, with screw cap and Teflon or aluminum foil liner.

2.2.21 Spatula. Stainless steel or Teflon.

2.2.22 pH Paper. Wide range, Hydrion Papers, Microessential Laboratory, Brooklyn, N.Y. (or equivalent).

2.2.23 Pipet, Volumetric 1.00-mL (optional).

2.2.24 Syringe, 1.00-mL (optional).

2.2.25 Flask, Volumetric 10.00-mL.

2.2.26 Vials, 10-mL, with screw cap and teflon liner (optional).

2.2.27 Tube, centrifuge, 12 to 15-mL with 19-mm ground glass joint, (optional).

2.2.28 Snyder Column, micro with a 19-mm ground glass joint.

2.2.29 Centrifuge, table top (optional).

2.2.30 Centrifuge bottle: 500-mL (Pyrex 1260 or equivalent).

2.2.31 Diazald kit with clear seal joints for generation of diazomethane, Aldrich Chemical Co., catalog No. Z10, 025-0.

2.2.32 Flask, filter, 1-L.

2.2.33 Funnel, Buchner, 15-cm.

2.2.34 Paper, filter (Whatman #1, or equivalent), 15-cm.

2.2.35 Gas chromatographic system including two 0.25-inch injectors, detection makeup gas, an electron capture detector, and a flame photometric detector. It is recommended that the GC be equipped with an integrator or data system rather than a strip chart recorder.

2.3.36 pH Meter with a combination glass electrode.

3.0 EXTRACTIONS-APOLAR

3.1 OVERVIEW

3.1.1 Aqueous samples are extracted using methylene chloride in a continuous liquid-liquid extractor. Extracts are then dried and concentrated by Kuderna-Danish techniques in preparation for cleanup (Section 4) and analysis (Section 5).

3.1.2 Soil or sediment samples are mixed with sodium sulfate and extracted using a 1:1 acetone:methylene chloride solvent by a sonication technique. Extracts are then filtered, dried, concentrated by Kuderna-Danish, and solvent exchanged to methylene chloride in preparation for GPC cleanup (4.2).

3.1.3 Most sludge samples are treated as liquid samples (3.1.1) after 30g of sludge is added to 1-L of reagent water.

3.2 APOLAR PROTOCOL FOR LIQUIDS

3.2.1 Summary of Sample Preparation Method

3.2.1.1 A 1 L volume of a water sample or a mixture of 30 g of sludge and 1 L of reagent water is extracted with methylene chloride using a continuous extractor. The methylene chloride extract is dried, concentrated, exchanged to hexane, and adjusted to a volume of 10.0 mL and a 1.0 mL aliquot is cleaned up on a Diol cartridge prior to GC analysis. Optional GPC (4.2) and sulfur cleanup (4.4) techniques are also allowed.

3.2.2 Liquid Sample Extraction.

3.2.2.1 Liquid samples must be extracted using continuous extraction.

3.2.2.2 It is strongly suggested that 30g of sludge be added to 1 L of reagent water and extracted using the continuous extractor. With some samples, it may be necessary to place a layer of glass wool between the methylene chloride and water layers in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction. Any sample in which solids precipitate through the glass wool must be treated as solids (3.3).

3.2.2.3 The percent weight loss of volatiles from sludge must be determined and reported according to the procedures described in 3.3.1.3.

3.2.2.4 After the sample has been transferred to the extractor, measure and record the pH with wide range pH paper and adjust to between pH 5 and 9 with 6 N sodium hydroxide or 1:1 sulfuric acid solution, if required. Record and report which samples require pH adjustment.

3.2.2.5 Add sufficient methylene chloride to the distilling flask to ensure proper solvent cycling during operation and extract for 18 hours.

3.2.3 Extract Drying and Concentration

3.2.3.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Pour the combined extract through anhydrous sodium sulfate and collect the extract in the K-D concentrator (the sodium sulfate can be held in a drying column filled to a height of about 20-cm or in a powder funnel plugged with glass wool filled to a height of 4-5-cm [3.3.2.5]). Rinse the Erlenmeyer

flask and column with at least one additional 20 to 30 mL portion of methylene chloride to complete the quantitative transfer.

3.2.3.2 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-80°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 3-5 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. Do not allow the evaporator to go dry.

3.2.3.3 If GPC cleanup is to be used, remove the Snyder column, rinse the flask and its lower joint into the concentrator tube, adjust the volume to 10.0 mL with methylene chloride and proceed to Section 4. If no GPC cleanup is required, proceed with the hexane exchange described below.

3.2.4 Exchange into Hexane

3.2.4.1 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. When the apparent volume of liquid reaches 3-5 mL, remove the K-D apparatus and allow

it to drain and cool at least 10 minutes. Do not allow the evaporator to go dry.

3.2.4.2 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane and proceed to Section 4 for Diol cartridge cleanup.

3.3 APOLAR PROTOCOL FOR SOLIDS

3.3.1 Sample Preparation

3.3.1.1 Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Also, decant and discard any standing aqueous phase. The lab must estimate to the nearest 10 percent (by weight) the amount of water decanted (and discarded) from the sample and report that value with the data.

3.3.1.2 Transfer 30 g of sample to 100-mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample using a glass electrode and pH meter while the sample is stirring. Report pH value with the data, but do not attempt to adjust the pH of the sample before extraction. Discard the portion of the sample used for pH determination.

3.3.1.3 Transfer 5 to 10 g of the sediment into a tarred crucible or aluminum weighing pan and weigh to the nearest 0.01 g. Transfer the sediment and weighing pan into an oven monitored at 105°C and dry overnight. Allow the sample and weighing pan to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the nonvolatiles in the sample. (Caution: Gases volatilized from some

soil/sediment samples may require that this drying procedure be carried out in a hood.)

$$\frac{\text{wt of sample - wt of heated sample}}{\text{wt of sample}} \times 100 = \%\ \text{weight loss} \quad (3.1)$$

3.3.2 Extraction with Sonic Agitation

3.3.2.1 Weigh approximately 30 g of sample (to the nearest 0.1 g) into a 400-mL beaker and add 60 g of anhydrous sodium sulfate.

3.3.2.2 Immediately add 80 mL of 1:1 methylene chloride:acetone mixture to the sample.

3.3.2.3 Place the sonicator probe about 1/2 inch below the surface of the solvent but above the sediment layer.

3.3.2.4 Sonicate for 3 min., using the 3/4 inch horn at full power with pulse set at 50 percent. Do not use a microtip.

3.3.2.5 Prepare a filtration/drying bed by placing a plug of glass wool in the neck of a 10-cm powder funnel and filling the funnel to approximately half its depth (4 or 5 cm) with anhydrous sodium sulfate. Decant the extract through the packed funnel and collect it in a 500-mL evaporation (K-D) flask.

3.3.2.6 Repeat the extraction two more times with fresh 80 mL portions of the 1:1 methylene chloride:acetone mixture. Decant the extraction solvent after each sonication. After the final sonication, pour the entire sample into the funnel and rinse with 60-mL portion of 1:1 methylene chloride:acetone mixture.

3.3.2.7 Some samples may require additional clarification before evaporation. These should be vacuum filtered through Whatman #1 paper using a Buchner funnel then transferred to a K-D apparatus.

3.3.2.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 80°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 - 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. In order to remove as much acetone as possible, reduce the apparent volume of liquid to less than 3 mL, but do not take to dryness. Remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Make up a 10 mL final volume with methylene chloride.

Proceed to Part 4.1 for mandatory GPC cleanup.

4.0 EXTRACT CLEANUP-APOLAR

4.1 REQUIREMENTS

4.1.1 GPC cleanup is mandatory for all apolar analyses of soil/sediment and sludge extracts. It can also be used for water samples, if needed. GPC removes many higher molecular weight contaminants which would otherwise accelerate degradation of gas chromatography columns and thus reduce instrument performance. The GPC must meet monthly performance checks.

4.1.2 Diol cartridge cleanup is required for all extracts. It removes polar organic molecules such as phenols. Each lot number of Diol cartridges must pass a cartridge performance check.

4.1.3 Sulfur can be removed by one of two methods, according to laboratory preference. Chromatogram interference due to sulfur is not acceptable.

4.2 EXTRACT CLEANUP BY GEL PERMEATION CHROMATOGRAPHY (GPC)

4.2.1 GPC Setup, Operation and Initial Calibration

4.2.1.1 Packing the column - Place 70 g of Bio Beads SX-3 in a 400-mL beaker. Allow the beads to swell overnight in methylene chloride before packing the column. Transfer the swelled beads to the column and begin pumping solvent through the column, from bottom to top, at a rate of 5.0 mL/min. After approximately 1 hour, adjust the pressure on the column to between 5 and 10 psi and pump an additional 4 hours to remove air from the column. Adjust the column pressure periodically as required to maintain 5 to 10 psi.

4.2.1.2 NOTE: The description of solvent flow rate and column pressure applies only to the ABC GPC apparatus. Laboratories using equivalent equipment must develop the parameters for their apparatus which give acceptable performance (described in Section 4.2.2).

4.2.1.3 The SX-3 Bio Beads column may be used for several months, even if discoloration occurs. System calibration usually remains constant over this period of time if column flow rate remains constant. The calibration must be checked periodically, not less than once every 30 days, using standard pesticide and PCB mixtures.

4.2.1.4 NOTE: Some samples should be centrifuged and/or filtered through an inert filter held in a 25-mm stainless steel holder before loading onto the GPC in order to remove particulate matter.

4.2.1.5 Load the 5.0-mL sample loop using 7.5 mL of the concentrate of the extract of each soil sample (described in 3.3.2.) and of those water samples (described in 3.2.2 or 3.2.3.) to be cleaned up by GPC.

4.2.1.6 NOTE: Some samples may have to be loaded into two or more loops in order to prevent overloading the GPC column. All highly viscous samples or samples known to contain > 1 g of nonvolatile residue should be divided and loaded into two or more loops.

4.2.1.7 Set the instrument terminal for the appropriate number of samples; set the length of the dump, collect and wash cycles for the number of minutes determined by either of the calibra-

tion procedures described below in 4.2.1.9 or 4.2.1.10. Set up and label one collection flask for each loop by placing the appropriate Teflon effluent line into the flask, then covering the flask with aluminum foil. Begin pumping methylene chloride through the column at 5 mL/min. (5 to 10 psi), allow the flow to stabilize for at least 15 minutes, then begin the automatic cleanup sequence by pressing the "auto start" button.

4.2.1.8 After the appropriate GPC fraction has been collected for each sample, evaporate the methylene chloride and exchange to hexane as described in 3.2.5.

4.2.1.9 Two alternate GPC calibration procedures are described below, one of these two must be used. The first is based on a combination of gravimetric and GC analysis of collected GPC fractions, the second is based on monitoring the elution of standards with a UV detector connected to the GPC column. If the UV technique is chosen, care must be taken to account for any difference in volume (elution time) between the GC column and the detector and the GPC column and the collection vial.

4.2.2 Gravimetric GPC Calibration Procedure

4.2.2.1 Set the "dump", "collect" and "wash" times for 00, 02, and 00 minutes, respectively. Set the terminal for 20 samples.

4.2.2.2 Under each of the first twenty receiver lines, place a tared 20-mL scintillation vial.

4.2.2.3 Into Sample No. 1 load 5 mL of 200-mg/mL corn oil solution.

4.2.2.4 Start the auto sequence, collect twenty 10-mL fractions (40 min.).

4.2.2.5 Passively evaporate each fraction to dryness in a fume hood (overnight).

4.2.2.6 Reweigh the vials and record the net weight gain.

4.2.2.7 Plot weight of the elute vs. time to determine the elution profile.

4.2.2.8 Reset the sampling position to 00.

4.2.2.9 Into Sample Loop No. 1, load 5 mL of 0.4-mg/mL PCP/Phthalate Solution.

4.2.2.10 Set the "collect" time to 03 minutes.

4.2.2.11 Under each of the first twenty receiver lines place a clean 20-mL scintillation vial. (NOTE: The vials need not be tared.)

4.2.2.12 Start the auto sequence, collect twenty 15-mL fractions (1 hour).

4.2.2.13 Analyze each fraction by GC to determine the amount of PCP and phthalate.

4.2.2.14 Plot the amounts of PCP and phthalate to determine the elution profiles.

4.2.2.15 Choose the "DUMP" time such that 85+ percent of phthalate is recovered and the corn oil is discarded.

4.2.2.16 Choose the "COLLECT" time to extend 10 minutes after the elution of PCP and set a "WASH" time of 10 minutes.

4.2.3 UV Detector Calibration Procedure

4.2.3.1 Connect the end of the column to a UV detector (254 nm).

4.2.3.2 Zero the detector and start the strip chart recorder.

4.2.3.3 Into Sample Loop No. 1 load 5 mL of 20-mg/mL corn oil solution and into Sample Loop No. 2 load 5 mL of 0.4-mg/mL PCP/phthalate. (NOTE: The corn oil concentration used in this UV procedure is a 10-fold dilution of that used in the gravimetric method.)

4.2.3.4 Inject Sample Loop No. 1, note the injection on the strip chart recorder.

4.2.3.5 After the corn oil elutes, allow the recorder to continue for a few minutes to again establish a baseline.

4.2.3.6 Inject Sample Loop No. 2 and note the injection on the strip chart recorder.

4.2.3.7 Determine the elution times for the corn oil, PCP and phthalate.

4.2.3.8 Choose a "DUMP" time which removes the corn oil yet recovers >85 percent of the phthalate. Choose a "COLLECT" time which continues 10 minutes beyond the elution of pentachlorophenol and a "WASH" time of 10 minutes.

4.2.3.9 NOTE: The DUMP and collect times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask.

4.2.4 Continuing GPC calibration requirement.

4.2.4.1 At least once ever 30 days, the calibration of the GPC must be verified by determining the recovery of 10 method analytes (Tables 1 and 2).

4.2.4.2 The ten analytes used are chosen by each lab. The choice is based on which analytes that were most often detected in their samples during the previous month.

4.2.4.3 The GPC calibration solution is prepared so that the concentration of each analyte is between 0.5 and 5 µg/mL.

4.2.4.4 Using 7.5 mL of the calibration solution loaded into a GPC loop and a fraction using the GPC program established using either of the described procedures (4.2.2 or 4.2.3).

4.2.4.5 The collected GPC calibration fraction is transferred quantitatively to a K-D apparatus and the volume of methylene chloride is reduced (3.2.3). After cooling, the solvent is exchanged to hexane (3.2.4). The final volume is adjusted to 10.0 mL and the sample is analyzed by GC according to the procedures in Section 5.

4.2.4.6 The GPC performance is acceptable if all of the analytes are recovered at 85-110 percent and the column can continue to be used. If the recovery is less than 85 percent, or more than 110 percent, the column must be repacked (4.2.1) and recalibrated before more samples are run.

4.3 DIOL CARTRIDGE CLEANUP

4.3.1 Cartridge Performance Check

Every lot number of Diol cartridges must be tested. A lot of Diol cartridges is demonstrated as acceptable if all apolar analytes are recovered at 80-110 percent and if trichlorophenol is not detected when the compounds are eluted through a cartridge using the method described in 4.3.4.

4.3.2 Nitrogen Blowdown Technique (Taken from ASTM Method D 3086)

4.3.2.1 Place the concentrator tube in a heating bath (35°C) and evaporate the solvent to the final volume using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). The extract must never be allowed to become dry.

4.3.2.2 CAUTION: New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of new tubing must be rinsed several times with hexane then dried prior to use.

4.3.3 Extract Preparation

4.3.3.1 For samples which have been run through the GPC cleanup solvent, exchange to hexane (3.2.4) and adjust the hexane extract volume to 5.0 mL using nitrogen blowdown described in 4.3.2. For those aqueous samples not passed through the GPC step, adjust to 10.0 mL. The different final volumes are required because only half of the methylene chloride concentrates are recovered from the GPC cleanup.

4.3.4 Diol Cartridge Cleanup

4.3.4.1 Attach the Vac-Elute vacuum manifold to a water aspirator or a vacuum pump with a trap installed between the manifold and the vacuum source. Adjust the vacuum pressure in the manifold to between 5 and 10 pounds of vacuum.

4.3.4.2 Most liquid samples can be cleaned using a 500-mg Diol cartridge, the cleanup of soil and sludge extracts must be accomplished using 1 g cartridges.

4.3.4.3 Prior to cleanup of samples, the cartridges must be washed with hexane/acetone (9:1). This is accomplished by placing the cartridge in the vacuum manifold, pulling a vacuum and passing 5 mL of the hexane/acetone solution through the cartridge.

4.3.4.4 After the cartridges in the manifold are washed, the vacuum is released and a rack containing labeled 10-mL volumetric flasks is placed inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is placed inside of the appropriate volumetric flask as the manifold top is replaced.

4.3.4.5 After the volumetric flasks are in place, vacuum to the manifold is restored and a volume of 1.0 mL from each sample, blank or matrix spike extract to be analyzed is transferred to the top frit of the appropriate Diol cartridge.

4.3.4.6 NOTE: Because the volumes marked on concentrator tubes are not necessarily accurate, the use of an 1.00-mL syringe or a volumetric pipet is required.

4.3.4.7 The analytes in the extract concentrates are then eluted through the column with 9 mL of hexane/acetone (9:1) and collected into the 10-mL volumetric flasks held in the rack inside the vacuum manifold.

4.3.4.8 Transfer the eluate in each volumetric flask to a clean centrifuge tube or 10-mL vial. Use two additional 1 mL hexane rinses to ensure quantitative transfer of the cartridge eluate.

4.3.4.9 Concentrate the extract to 1.0 mL using nitrogen blow-down (described in 4.3.2).

4.3.4.10 If crystals of sulfur are evident or sulfur is suspected to be present, proceed to Section 4.4.

4.3.4.11 If the sulfur is not expected to be a problem, transfer the 1.0-mL concentrate to a GC vial and label the vial. The extract is ready for GC analysis, proceed to Section 5. Store the extracts at 4°C in the dark until analyses are performed.

4.4 SULFUR REMOVAL

4.4.1 Two options are available for the removal of sulfur from samples. The mercury technique appears to be the most reliable, but requires the use of small volumes of mercury in the laboratory.

4.4.2 CAUTION: Mercury containing waste should be segregated and disposed of properly.

4.4.3 Mercury Technique

4.4.3.1 Add 1 to 3 drops of mercury for each 1-mL hexane extract in a clean vial. Seal the vial and agitate for 30 seconds. Filter or centrifuge and decant to remove all solid precipitate and liquid mercury. Analyze the extract if the mercury appears shiny. If the mercury turns black, repeat as necessary. Dispose of the mercury waste properly.

4.4.3.2 If only a partial set of samples requires sulfur cleanup, an additional reagent blank is not required.

4.4.4 Copper Technique

4.4.4.1 Bright (non-oxidized) granular copper can be used in place of mercury in the procedure described in Section 4.4.3.1.

5.0 GC ANALYSIS-APOLAR

5.1 SUMMARY

5.1.1 Sample extracts are analyzed by both GC/ECD for organochlorine parameters and by GC/FPD for organophosphorous parameters.

5.1.2 The primary column for both organochlorine and organophosphate analysis is a 15 m x 53 mm id DB-5 megabore capillary column (or equivalent).

5.1.3 The secondary column for both organochlorine and organophosphorous analyses is a 15 m x 0.53 mm id SPB-608 megabore capillary column (or equivalent).

5.2 GC CONDITIONS

5.2.1 Megabore capillary columns can be installed in standard 0.25-inch packed column injector and detector ports using suitable glass adapters and graphite ferrules. Because the column flow used is 5 mL/minute, it is necessary to supply a suitable makeup gas to the detector.

5.2.2 Electron capture detectors should be plumbed with helium or hydrogen carrier and P-10 (Argon/methane) as a detector makeup gas, the detector temperature should be 275°C.

5.2.3 Flame photometric detectors should be plumbed with helium or hydrogen carrier and nitrogen as a detector makeup, the detector temperature should be 250°C.

5.2.4 The temperature program for organochlorine analysis is:

T_i = 50°C
Initial time one minute
Initial temperature ramp 20°/min to 150°C
Second temperature ramp 8°/min to 180°C
Third temperature ramp 3°/min to 250°C
Final hold 15 minutes

Note: It may be necessary to adjust this temperature program for individual gas chromatographs.

5.2.5 The temperature program for organophosphorous analysis is:

T_i = 50°C
Initial time one minute
Initial temperature ramp 5°/min to 140°C, hold 10 minutes
Second temperature ramp 10°/min to 250°C
Five minute final hold.

Note: It may be necessary to adjust this temperature program for individual gas chromatographs.

5.2.6 Injectors should be set at 260°C.

5.3 CALIBRATION

5.3.1 After establishing the appropriate GC operating conditions (5.2) for the method parameters, calibrate the GC system using the external standard technique.

5.3.2 For each parameter of interest, prepare working standards at three concentration levels over a range of a least two orders of magnitude. The low concentration should be near to, but

above, the method detection limit (Section 5.7). The medium concentration must be at least 10 times the low concentration and the high concentration must be at least 10 times the medium concentration (at least 100 times the low concentration). These concentrations define the calibration range in which analytes can be quantitated.

5.3.3 The peak height, or the peak area are plotted against the mass injected and used as a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor for the three concentrations is less than 10% detector linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

5.3.4 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, a new calibration curve or calibration factor must be prepared for that parameter.

5.4 QUANTITATION OF ANALYSES

5.4.1 Analytes can be quantitated using either manual measurement of onscale chromatograms, with a modern electronic integrator, or with a laboratory data system. The analyst can use either peak height or peak area as the basis for quantitation. The use of electronic integration or a laboratory data system is strongly recommended.

5.4.2 If manual quantitation is used, all peaks used for calibration and for sample analysis must be onscale and give at least 20 percent deflection from baseline at maximum height. Guidance in the manual quantitation of peaks is given in the EPA MANUAL OF ANALYTICAL METHODS FOR THE ANALYSIS OF PESTICIDES IN HUMANS AND ENVIRONMENTAL SAMPLES, EPA-600/8-80-038, or in the FDA Pesticide Analytical Manual.

5.4.3 If electronic integration is used, it is the responsibility of the analyst to be sure that the integration parameters are set properly and that off-scale chromatograms are within the dynamic range of the device. The analyst should also check for data flags that indicate improper quantitation of peaks prior to reporting data to the EPA. In addition, the peak width of identified analytes must not be more than 2.0 times the width of the high concentration calibration peak(s) for the same analyte.

5.4.4 The detector response (peak area or peak height) to all of the analytes must lie between the response of the low and high concentrations in the three-point initial calibration in order to be quantitated.

5.4.5 The concentration of the single component analytes are calculated using the following equations:

5.4.5.1 Water

$$\text{concentration} \quad \mu g/L = \frac{(A_x)(V_t)}{(CF)(V_i)(V_x)} \qquad (5.10)$$

Where:

A_x = Response for the parameter to be measured.

CF = Calibration factor for the external standard (5.3.3).

V_t = Volume of total extract (μL) (take into account any dilution).

V_i = Volume of extract injected (μL).

V_x = Volume of water extracted (mL).

5.4.5.2 Sediment/Soil

$$\text{Concentration} \quad \mu g/kg = \frac{(A_x)\ (V_t)}{(CF)\,(V_i)\,(W_s)\,(D)} \qquad (5.10)$$

(Dry weight basis)

Where:

A_x, CF, V_i = same as given above in 5.3.4.1

$D = \frac{100 - \text{percent weight loss}}{100}$ (percent weight loss from Section 3.3)

W_s = Weight of sample extracted (g).

5.4.6 The quantitation of multicomponent pesticide/PCBs must be accomplished by comparing the sum of the heights or the areas of at least three major peaks of the multicomponent analyte in the sample compared with the same peaks in the standard. The concentration of multicomponent analytes are also calculated using equations 5.10 and 5.11 where A_x is the sum of the major peaks of the multicomponent analyte.

5.4.7 The identification and quantitation of multicomponent analytes may be complicated by the environmental alteration of the peak pattern of multicomponent pesticides/PCBs, and by the presence of coeluting analytes and/or matrix interference.

5.4.8 If more than one multicomponent is observed in a sample, the laboratory must chose separate peaks to quantitate the different multicomponent analytes. A peak common to both analytes present in the sample must not be used to quantitate both compounds in the same sample.

5.5 Scheme of Analysis.

5.5.1 A flow scheme for the analysis of samples by this procedure are given in Figure 1.

5.6 Sample chromatograms.

5.6.1 Sample chromatograms of mixtures containing all single component analytes and of all multicomponent analytes for both columns are presented in Figures 2-23.

5.7 Method Detection limits.

5.7.1 Any method is dependent on the complexity of the sample matrix analyzed, but this procedure can be used to determine all of the single component apolar organochlorine analytes (Table 1), except diallate to a detection limit of <50 ppb. If greater sensitivity is required, the 9 mL of extract not subjected to Diol cleanup (4.3) can be blown down to 1 mL and cleaned on a 1 g Diol column. This concentrate can be used to give a method detection limit of <5 ppb.

5.7.2 The procedure can be used to determine all of the single component apolar organophosphate analytes (Table 2) to a detection limit of <500 ppm. If greater sensitivity is required, the 9 mL of extract not subjected to Diol cleanup

(4.3) can be blown down to 1 mL and cleaned on a 1 g Diol column. This concentrate can be used to give a method detection limit of <50 ppb.

6.0 EXTRACTION-PHENOXYACIDS

6.1 OVERVIEW

6.1.1 Phenoxyacids and their esters are extracted from acidified aqueous samples using methylene chloride using a continuous liquid extractor.

6.1.2 Acids and esters are extracted from acidified solid samples using methlene chloride/acetone and a sonicator.

6.1.3 Most sludge samples are treated as liquid samples (6.1.1) after 30g of sludge is added to 1 L of reagent water.

6.1.4 The sample extracts are reduced in volume using a K-D apparatus, the free phenoxyacid herbicides are partitioned into aqueous base and the esters into methylene chloride. The esters are hydrolyzed using aqueous potassium hydroxide and neutral organics are partitioned into methylene chloride and discarded. The two basic aqueous fractions containing phenoxyacids are combined, acidified, and the acids are extracted into methylene chloride. The phenoxyacids are then derivitized with diazomethane, cleaned on adsorption cartridges and analyzed by GC/ECD.

6.2 LIQUID SAMPLE EXTRACTION-PHENOXYACID

6.2.1 Liquid samples must be extracted using continuous extraction. Using a 1 liter graduated cylinder, measure out a 1 liter sample aliquot and place it into the continuous extractor.

6.2.2 It is strongly suggested that 30 g of sludge be added to 1 L of reagent water and extracted using the continuous extrator. With

some samples, it may be necessary to place a layer of glass wool between the methylene chloride and water layers in the extractor to prevent precipitation of suspended solids into the methylene chloride during extraction. Any sample in which solids precipitate through the glass wool must be treated as solids (6.3).

6.2.3 The percent weight loss of volatiles from sludge must be determined and reported according to the procedure described in Section 6.3.1.3.

6.2.4 After the sample has been transferred to the extractor, measure and record the pH of the sample with wide range pH paper and adjust to below 2 with 1:1 sulfuric acid, if required (Caution: some samples should be acidified in the hood because of the potential for generating hydrogen sulfide).

6.2.5 Add sufficient methylene chloride to the distilling flask to ensure proper cycling during operation and extract for 18 hours.

6.2.6 If solids are present in the methylene chloride, after extraction, filter the organic phase through Watman #1 paper.

6.2.7 Transfer the methylene chloride fraction to a 500 mL separatory funnel and proceed to the separation of the phenoxyacids and phenoxyesters (6.4).

6.3 SOLID SAMPLE EXTRACTION-PHENOXYACID

6.3.1 Sample Preparation

6.3.1.1 Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Also,

decant and discard any standing aqueous phase. The lab must estimate to the nearest 10 percent (by weight) the amount of water decanted (and discarded) from the sample and report that value on the data sheet.

6.3.1.2 Transfer 30g of sample to a 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample using a glass electrode and pH meter while the sample is stirring. Report pH value with the data, then determine the amount of 1:1 sulfuric acid/water required to reduce the pH to <2. Discard the portion of the sample used for pH determination.

6.3.1.3 Transfer 5 to 10 g of the sediment into a tarred crucible or aluminum weighing pan and weigh to the nearest 0.01 g. Transfer the sediment and weighing pan into an over monitored at 105°C and dry overnight. Allow the sample and weighing pan to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment. (Caution: Gases volatilized from some soil/sediment samples may require that this drying procedure be carried out in a hood.)

$$\frac{\text{wt of sample} - \text{wt of dry sample}}{\text{wt of sample}} \times 100 = \%\ \text{weight loss} \quad (6.1)$$

6.3.2 Extraction with Sonic Agitation

6.3.2.1 Weigh approximately 30 g of sample (to the nearest 0.1-g) into a 400-mL beaker.

6.3.2.2 Add the amount of 1:1 sulfuric acid/water determined in 6.3.1.2 (Caution: some samples may evolve toxic gases on the addition of acid).

6.3.3.3 Add 60 g of acidified sodium sulfate.

5.3.2.4 Immediately add 80 mL of 1:1 methylene chloride:acetone mixture to the sample.

6.3.2.5 Place the sonicator probe about 1/2 inch below the surface of the solvent but above the sediment layer.

6.3.2.6 Sonicate for 3 min., using the 3/4 inch horn at full power with pulse set at 50 percent. Do not use a microtip.

6.3.2.7 Caution - the sonicator horn must be cleaned in 5% aqueous sodium bicarbonate and methanol between samples. If acid is allowed to remain on the horn, it will be damaged.

6.3.2.8 Prepare a filtration/drying bed by placing a plug of glass wool in the neck of a 10-cm powder funnel and filling the funnel to approximately half its depth (4 or 5 cm) with acidified sodium sulfate. Decant the extract through the packed funnel and collect it in a 500-mL evaporation (K-D) flask, or a 500 mL centrifuge bottle.

6.3.2.9 Repeat the extraction two more times with fresh 80 mL portions of the 1:1 methylene chloride:acetone mixture. Decant the extraction solvent after each sonication. After the final sonication, pour the entire sample into the funnel and rinse with a 60-mL portion of the 1:1 methylene chloride:acetone mixture.

6.3.2.10 If required, centrifuge the combined extract for 10 minutes to settle fine particles then filter the extracts through Whatman #1 filter paper into a 500 mL K-D flask.

6.3.2.11 Transfer the methlene chloride fraction to a 500 mL separatory funnel prior to the separation of the phenoxyacids and phenoxyesters.

6.4 ESTER HYDROLYSIS

6.4.1 Extract the organic phase of the phenoxyacid preparation two times with 100 mL portions of 0.1 N aqueous sodium hydroxide. Combine the aqueous (top) layers containing the free acid herbicides in a beaker and save. The organic (bottom) layer contains the herbicide esters, which must be hydrolyzed.

6.4.2 Transfer the methylene chloride layer into 500-mL Kuderna-Danish flask. Add boiling chips to the K-D and fit it with a three-ball Snyder columns. Wet the Snyder column with 1 mL of methylene chloride and reduce the methylene chloride to a volume of approximately 25 mL on the water bath.

6.4.3 Remove the flask from the water bath and allow it to cool. Then add 5 mL of 37% aqueous potassium hydroxide, 30 mL of distilled water and 40 mL of methanol to the flask.

6.4.4 Add additional boiling chips to the flask. Reflux the mixture in the K-D on the water bath for 2 hours. Remove the flask from the water bath and cool to room temperature.

6.4.5 Transfer hydrolysate from the K-D flask to a 250 mL separatory funnel. Extract the aqueous residue with 50 mL of methylene chloride and discard the methylene chloride (bottom layer) which contains neutral interferents.

6.4.6 At this point the two aqueous solutions containing the free herbicide salts from 6.4.1 and 6.4.5 can be combined (they can be analyzed separately, if required).

6.4.7 Add sulfuric acid to the basic aqueous solutions to adjust the pH to ≤1.

6.4.8 Transfer the acidified aqueous solution into a 500 mL separatory funnel and extract the solution three times with 100 mL portions of methylene chloride.

6.4.9 Combine the organic extracts in 500 mL Kuderna-Danish flasks. Add boiling chips to the extracts in the flasks and fit them with three-ball Snyder columns.

6.4.10 Evaporate the methylene chloride to approximately 5 mL on a hot water bath (the samples may be stored at this stage).

6.4.11 Remove the flasks from water bath. Evaporate the extracts just to dryness under a stream of nitrogen.

6.4.12 Reconstitute with 1 mL of iso-octane and 0.5 mL of methanol. dilute to a volume of 4 mL with ether. The sample is now ready for methylation with diazomethane (the sample should <u>not</u> be stored overnight at this step).

7.0 ESTERIFICATION

7.1 The diazomethane derivatization procedure described below will produce an efficient reaction with all of the chlorinated herbicides described in this method. It should be used only by an experienced analyst, due to the potential hazards associated with its use.

7.2 Diazomethane is a carcinogen and can explode under certain conditions. The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides to reduce potential contact with diazomethane.
- Do not heat above 90°C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers - EXPLOSION may result.
- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper power, calcium chloride, and boiling chips.

7.3 Specific instructions for preparing diazomethane are provided with the generator kit. They must be followed precisely.

7.4 Add 2 mL of diazomethane solution and let the sample stand for 10 minutes with occasional swirling. The yellow color of

diazomethane should be evident and should persist for this period. If the yellow color disappears before 10 minutes has passed, add an additional 2 mL of diazomethane solution. Colored or highly coupler samples will require at least 4 mL of diazomethane to ensure quantitative reaction of all pheoxyacid herbicides.

7.5 After 15 minutes rinse inside wall of ampule with several hundred µL of ethyl ether. Reduce the sample to approximately 1 mL under a stream of nitrogen. Remove any excess diazomethane by reacting it with 10 mg silicic acid.

7.6 Transfer all of the volume of derivatized phenoxyacid to a cleaned Diol cartridge in a vacuum manifold (described in Section 4.3.4) using < 1 mL of additional hexane to complete the transfer.

7.7 Elute the transferred solvent through the cartridge and discard.

7.8 Elute the derivatized analytes through the cartridge with 10 mL of 90:10 hexane/acetone. Collect in a 10 mL volumetric flask.

7.9 Reduce the final sample volume to 1.00 mL under a stream of dry nitrogen (described in 4.3.2) prior to GC analysis.

8.0 GC ANALYSIS-PHENOXYACIDS

8.1 SUMMARY

8.1.1 Extracts are analyzed by GC/ECD for methyl esters of phenoxyacid herbicides.

8.1.2 The primary column for analysis is a 15 m x 0.53 mm ID DB-5 megabore capillary column (or equivalent).

8.1.3 The secondary column for analyses is a 15 m x 0.53 mm ID SPB-608 megabore capillary column (or equivalent).

8.2 GC CONDITIONS

8.2.1 Megabore capillary columns can be installed in 0.25-inch packed column injector and detector ports using suitable glass adapters and graphite ferrules. Because the column flow used will be approximately 5 mL/minute, it is necessary to supply a suitable makeup gas to the detector.

8.2.2 ECD's should be plumbed with helium or hydrogen carrier gas and P-10 as a detector makeup gas.

8.2.3 The initial temperature program to use for phenoxyacid herbicide analysis on both columns is:

T_i = 50°C
Initial time one minute
Initial temperature ramp 20°/min to 150°C
Second temperature ramp 8°/min to 180°C
Third temperature ramp 5°/min to 250°C

it may be necessary to adjust the temperature program for individual gas chromatographs.

8.2.4 GC injectors should be set at 260°C.

8.3 CALIBRATION

8.3.1 After establishing the appropriate GC operating conditions (8.2) for the method parameters, calibrate the GC system using the external standard technique.

8.3.2 For each parameter of interest, prepare working standards at three concentration levels over a range of at least two orders of magnitude by reacting solutions of phenoxyacid standards with diazomethane using the procedure described in Section 7.0 (quantitative yield of methyl esters from standards and samples is assumed). The low concencentration should be near to, but not above, the method detection limit (8.7). The medium concentration must be at least 10 times the low concentration and the high concentration must be at least 10 times the medium concentration (at least 100 times the low concentration). These concentrations define the calibration range in which analytes can be quantitated.

8.3.3 The peak height, or the peak area are plotted against the mass injected and used as a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor for the three concentrations is less than 10%, detector linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

8.3.4 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, a new calibration curve or calibration factor must be prepared for that parameter.

8.4 QUANTITATION OF ANALYSES

8.4.1 Analytes can be quantitated using either manual measurement of onscale chromatograms, with a modern electronic integrator, or with a laboratory data system. The analyst can use either peak height or peak area as the basis for quantitation. The use of manual integration is strongly discouraged.

8.4.2 If manual quantitation is used, all peaks used for calibration and for sample analysis must be onscale and give at least 20 percent deflection from baseline at maximum height. Guidance in the manual quantitation of peaks is given in the EPA MANUAL OF ANALYTICAL METHODS FOR THE ANALYSIS OF PESTICIDES IN HUMANS AND ENVIRONMENTAL SAMPLES, EPA-600/8-80-038, or in the FDA Pesticide Analytical Manual.

8.4.3 If electronic integration is used, it is the responsibility of the analyst to be sure that the integration parameters are set properly and that off-scale chromatograms are within the dynamic range of the device. The analyst should also check for data flags that indicate improper quantitation of peaks prior to reporting data to the EPA. In addition, the peak width of identified analytes must not be more than 2.0 times the width of the high concentration calibration peak(s) for the same analyte.

8.4.4 The detector response (peak area or peak height) to all of the analytes must lie between the response of the low and high concentrations in the three-point initial calibration in order to be quantitated.

8.4.5 The concentration of the surrogate and of the single component analytes are calculated using the following equations:

8.4.5.1 Water

$$\text{concentration} \quad \mu g/L = \frac{(A_x)(V_t)}{(CF)(V_i)(V_x)} \qquad (5.10)$$

Where:

A_x = Response for the parameter to be measured.

CF = Calibration factor for the external standard.

V_t = Volume of total extract (µL) (take into account any dilution).

V_i = Volume of extract injected (µL).

V_x = Volume of water extracted (mL).

8.4.5.2 Sediment/Soil

$$\text{Concentration} \quad \mu g/kg = \frac{(A_x)\ (V_t)}{(CF)(V_i)(W_s)(D)} \qquad (5.10)$$

(Dry weight basis)

Where:

A_x, CF, V_i = same as given above in 5.3.4.1

$$D = \frac{100 - \text{percent weight loss}}{100}$$ (percent weight loss from Section 3.3)

W_s = Weight of sample extracted (g)

8.5 FLOW SCHEME

8.5.1 A flow scheme for the analysis of samples by this procedure are given in Figure 1.

8.6 SAMPLE CHROMATOGRAMS

8.6.1 Sample chromatograms of mixtures containing all single component analytes and of all multi-component analytes are presented in Figures 2-23.

8.7 METHOD DETECTION LIMIT

8.7.1 Any method is dependent on the complexity of the sample matrix analyzed, but this procedure can be used to determine all of the phenoxyacid analytes (Table 3) to a detection limit of <5 ppb.

9.0 QUALITY CONTROL

9.1 Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed to demonstrate that all glassware and reagents are interference-free. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware; these contaminants lead to discrete artifacts, and/or elevated baselines, in gas chromatograms. Interferences by phthalate esters especially can pose a major problem in pesticide analysis when using the electron capture detector. Common flexible plastics contain varying amounts of phthalates which are easily extracted during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

9.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. It is suggested that the response of the external standards be plotted daily as a quality control check. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as GC/MS should be used.

9.3 Waste samples spiked with selected analytes must be analyzed for at least 10% of the samples to validate the accuracy of the analysis. The results of the recovery of spiked analytes must be reported with sample data.

9.4 At the option of the I.T.D., the requirement for spiking at least 10% of the samples with selected herbicides may be replaced with a requirement for analyzing a matrix spike/matrix spike duplicate (MS/MSD) pair for every 20 samples analyzed.

9.5 The MS/MSD pair are prepared by spiking duplicate sample aliquots with the particular matrix spiking solutions described below. The MS/MSD pair as well as the unspiked sample are analyzed by the procedures described in this protocol. The recoveries of the matrix spike compounds are reported with the sample data using the formula below.

$$\text{Matrix spike recovery} = \frac{SSR-SR}{SA} \times 100$$

SSR = Sample spike results
SR = Sample result
SA = Spike added

9.5.1 The apolar MS/MSD samples are each spiked with two solutions. One for organochlorine compounds and the other for organophosphates. The spiking solution for organochlorines is the same one as is used in the CLP analysis of organochlorine pesticides and is listed below.

Pesticide	µg/1.0 mL
gamma-BHC	0.5
Heptachlor	0.5
Aldrin	0.5
Dieldrin	1.0
Endrin	1.0
4,4'-DDT	1.0

The spiking solution for organophosphate pesticides is listed below.

Pesticide	µg/1.0 mL
Chlorpyriophos	100
Fenthion	100
Malathion	100
Parathion, ethyl	100
Carbofenthion	100

The solutions are prepared in acetone and must be allowed to equilibrate at room temperature before they are spiked.

9.5.2 The phenoxyacid MS/MSD samples are spiked with the mixture listed below.

Herbicide	µg/1.0 mL
2,4-D	0.5
2,4,5-T	0.5

The solution is prepared in acetone and must be allowed to equilibrate at room temperature before it is spiked.

9.6 It is critical that analysts become proficient with capillary GC analysis before using this method to generate quantitative results.

9.7 Store stock solutions of standards at 4°C and protect from light. All such solutions must be checked frequently for signs of degradation or evaporation. Organophosphorous standards are particularly prone to hydrolysis during storage.

10.0 REFERENCES

10.1 *Statement of Work - GC Methods for Environment Samples, Pesticides, PCP's (proposed),* Prepared for J. Fisk, Office of Remedial and Emergency Response, USEPA, by P. Marsden and D. Bottrell.

10.2 *Single-Laboratory Validation of EPA Method 8150 for the Analysis of Chlorinated Herbicides in Hazardous Waste,* EPA 600/4-85-060, prepared for D.F. Gurka, QAD, EMSL-LV, by F. Shore, E.N. Amick, and S.T. Pan.

10.3 *Single Laboratory Validation of EPA Method 8140 for the Analysis of Organophosphorous Pesticides in Hazardous Waste (in manuscript),* prepared for D. Betowski, QAD, EMSL-LV, by V. Taylor, D. Hickey, and P. Marsden.

10.4 *Methods for Organic Chemical Analysis of Municipal and Industrial Waste Water,* EPA 600/4-82-057, by J.E. Longbottom and J.J. Lichtenberg.

TABLE 1 AROCLOR ORGANOCHLORINE
PARAMETERS OF THE CONSOLIDATED METHOD

COMPOUND	METHOD	RETENTION TIME DB-5	SPB-608
Aldrin	608,617	17.77	18.3[illegible]
Aroclor 1016	608,617	multiple	multiple
Aroclor 1221	608,617	multiple	multiple
Aroclor 1232	608,617	multiple	multiple
Aroclor 1242	608,617	multiple	multiple
Aroclor 1248	608,617	multiple	multiple
Aroclor 1254	608,617	multiple	multiple
Aroclor 1260	608,617	multiple	multiple
BHC,alpha	608,617	17.77	13.70
BHC,beta	608,617	14.74	15.62
BHC,gamma	608,617	15.01	15.22
BHC,delta	608,617	15.93	17.15
Captan	617	22.07	24.24
Carbophenthion	617,622	28.44	28.69
Chlordane	608,617	multiple	multiple
Chlorobenzylate	608.1	26.49	26.[illegible]
DDD	608,617	26.99	27.10
DDE	608,617	24.70	24.16
DDT	608,617	29.01	28.75
Diallate(cis,trans)	no	13.37,13.91	17.89,1[illegible].20
Dichloran	617	14.31	14.80
Dieldrin	608,617	24.80	24.25
Endosulfan I	608,617	27.54	22.81
Endosulfan II	608.617	26.49	27.15
Endosulfan sulfate	608,617	28.77	29.71
Endrin	608,617	26.0[illegible]	26.11
Endrin Aldehyde	608,617	27.48	28.8[illegible]
Endrin Ketone	no	31.25	31.[illegible]7
Heptachlor	608,617	18.14	16.87
Heptachlor epoxide	608,617	21.69	21.01
Hexachlorobenzene	no	14.24	1[illegible].37
Isodrin	617	21.19	20.[illegible]
Methoxychlor	617	30.17	3[illegible].17
Mirex	no	34.47	32.59
Nitrofen	608.1,617	25.99	2[illegible].[illegible]5
PCNB	617	15.24	14.7[illegible]
Toxaphene		multiple	multiple
Trifluralin		12.95	11.01

COMPOUND	RELATED COMPOUNDS METHOD	DB-5	SPB-608
Captafol	no	31.26	26.83
Chloroneb	608.1	10.46	10.[illegible]7
Chloropropylate	608.1	nd	nd
DBCP	608.1	5.91	5.96
Dicofol	617	32.35	32.76
etridazole	608.1	9.82	9.7[illegible]
Kepone	no	28.04	26.28
Perthane (Ethylan)	no	26.23	26.09
Propachlor	617	nd	nd
Strobane	608,617	multiple	multiple

nd = not determined

TABLE 2 NPOCZR ORGANOPHOSPHORUS
PARAMETERS OF THE CONSOLIDATED METHOD

COMPOUND	METHOD	RETENTION TIME DB-5	SPB-608
Azinphos ethyl	no	39.04	38.49
Azinphos methyl	614,622	38.34	33.04
Carbophenthion	617,622	25.25	35.10
Chlorfenvinphos	no	33.57	31.06
Chlorpyrophos	622	31.17	26.83
Coumophos	622	39.83	38.87
Demeton(mixed)	614,622	18.31,20.96	15.90,18.84
Diazinon	614,622,7	24.27	20.00
Dichlovos	622	9.63	7.91
Dicrotophos		15.27	19.11
Dimethoate		20.64	20.18
Dioxathion		39.97	37.17
Disulfoton	614,622	23.71	19.96
EPN		37.80	36.71
Ethion	614,701	36.17	34.79
Famphur		36.43	35.93
Fensulfothion	627	35.83	35.20
Fenthion	622	31.83	29.45
HMPA		10.69	9.27
Leptophos		38.47	37.25
Malathion	614,701	31.72	28.78
Mevinphos	622	14.18	12.86
Monocrotophos		20.04	20.11
Naled	627	19.01	17.40
Parathion, ethyl	614,701	31.85	27.62
Parathion, methyl	614,622,7	31.83	23.71
Phorate	622	19.94	17.52
Phosmet		37.56	37.20
Phosphamidon		27.05	24.46
Sulfotepp		20.11	18.02
TEPP		6.44	5.12
Terbufos		22.63	18.61
Tetrachlorovinphos		34.65	32.99
TOCP		38.79	37.71
Trichlorofon		11.91	nd
Trimethyl phosphate		2.30	nd

RELATED COMPOUNDS

COMPOUND	METHOD	DB-5	SPB-608
Bolstar	622	36.34	nd
Chlorpyrophos,me	622	nd	nd
Crotoxyphos	no	34.06	33.07
Dichlorfenthion	701	9.63	7.91
Ethoprop	622	18.62	16.48
Merphos	622	nd	36.32
Methyl trithion	701	nd	nd
Ronnel	no	29.27	32.98
Tokuthion	no	34.67	nd
Trichloronate	no	32.19	nd

nd = not determined
Oxydemeton methyl no signal, not a method parameter

TABLE 7 PHENOXYACID
ANALYTES OF CONSOLIDATED METHOD

COMPOUND	METHOD	DB-5	SPB-608
Dinoseb	615		
2,4-D	615		
2,4,5-T	615		
2,4,5-TP	615		
RELATED COMPOUNDS			
Dalapon	615		
2,4-DB	615		
Dicamba	615		
Dichlorprop	615		
MCPA	615		
MCPP	615		

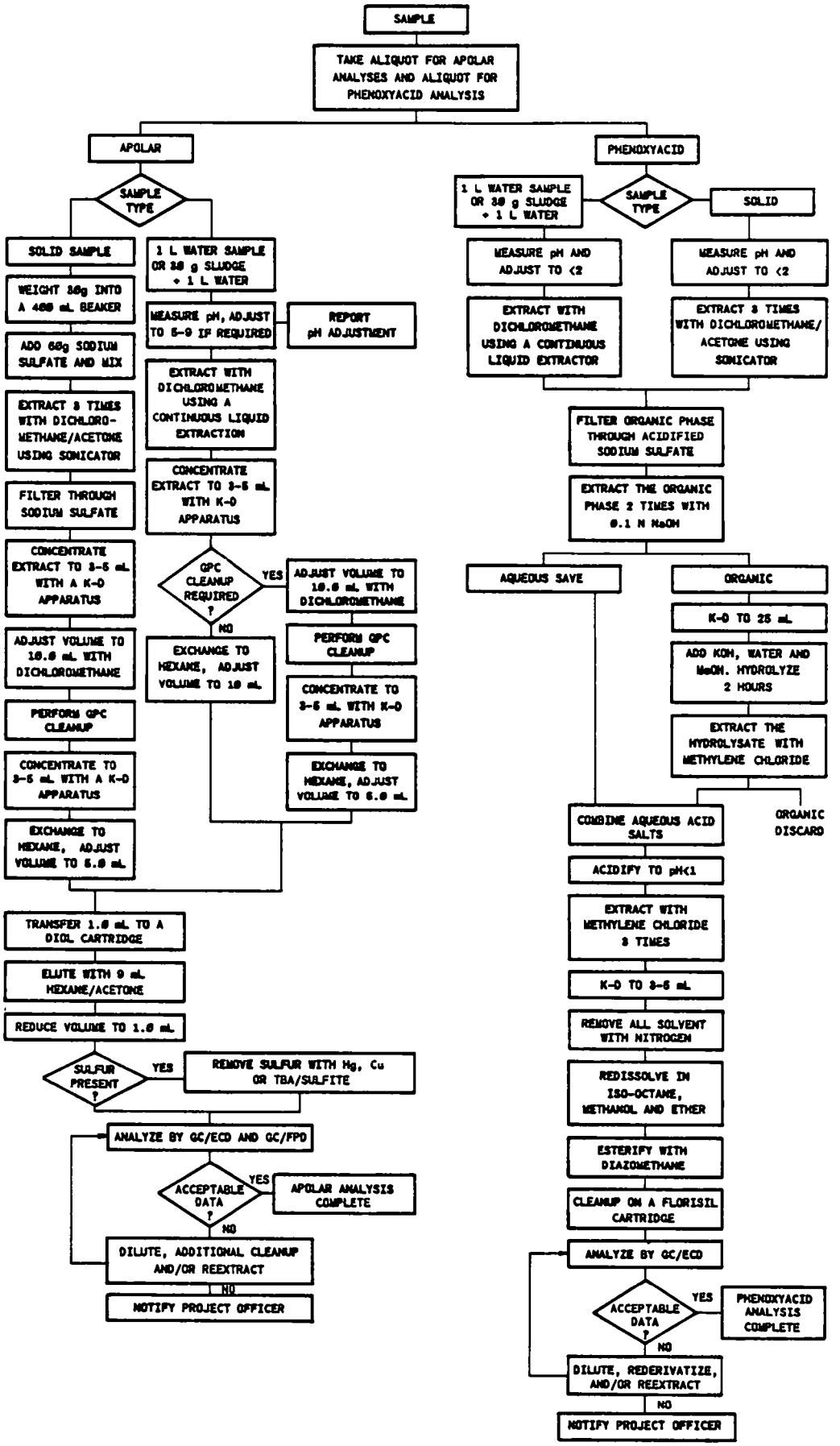

Figure 1. Flow Scheme for the Analysis of Samples.

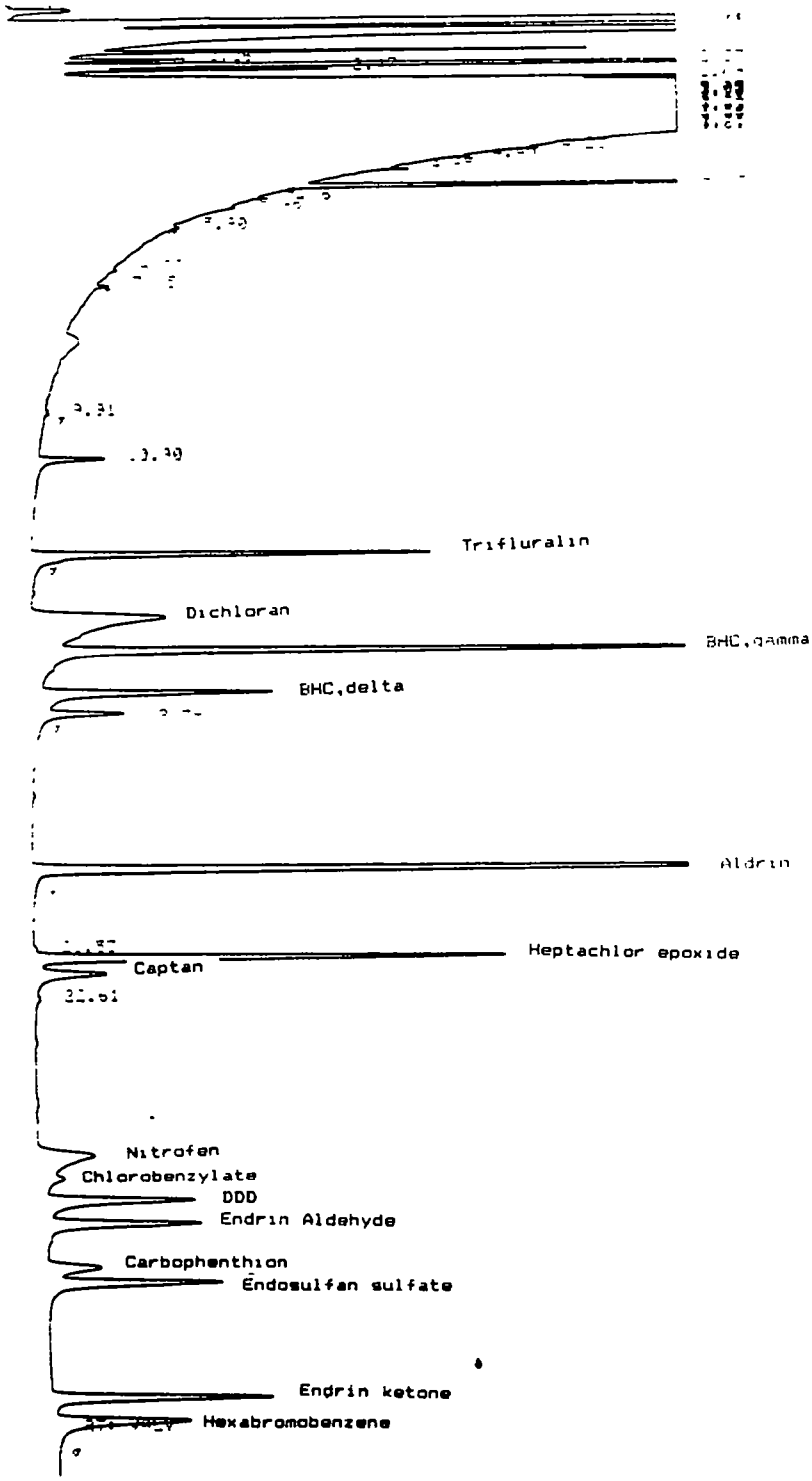

Figure 2A. Sample Chromatogram of Selected Apolar Organochlorine Pesticides on the DB-5.

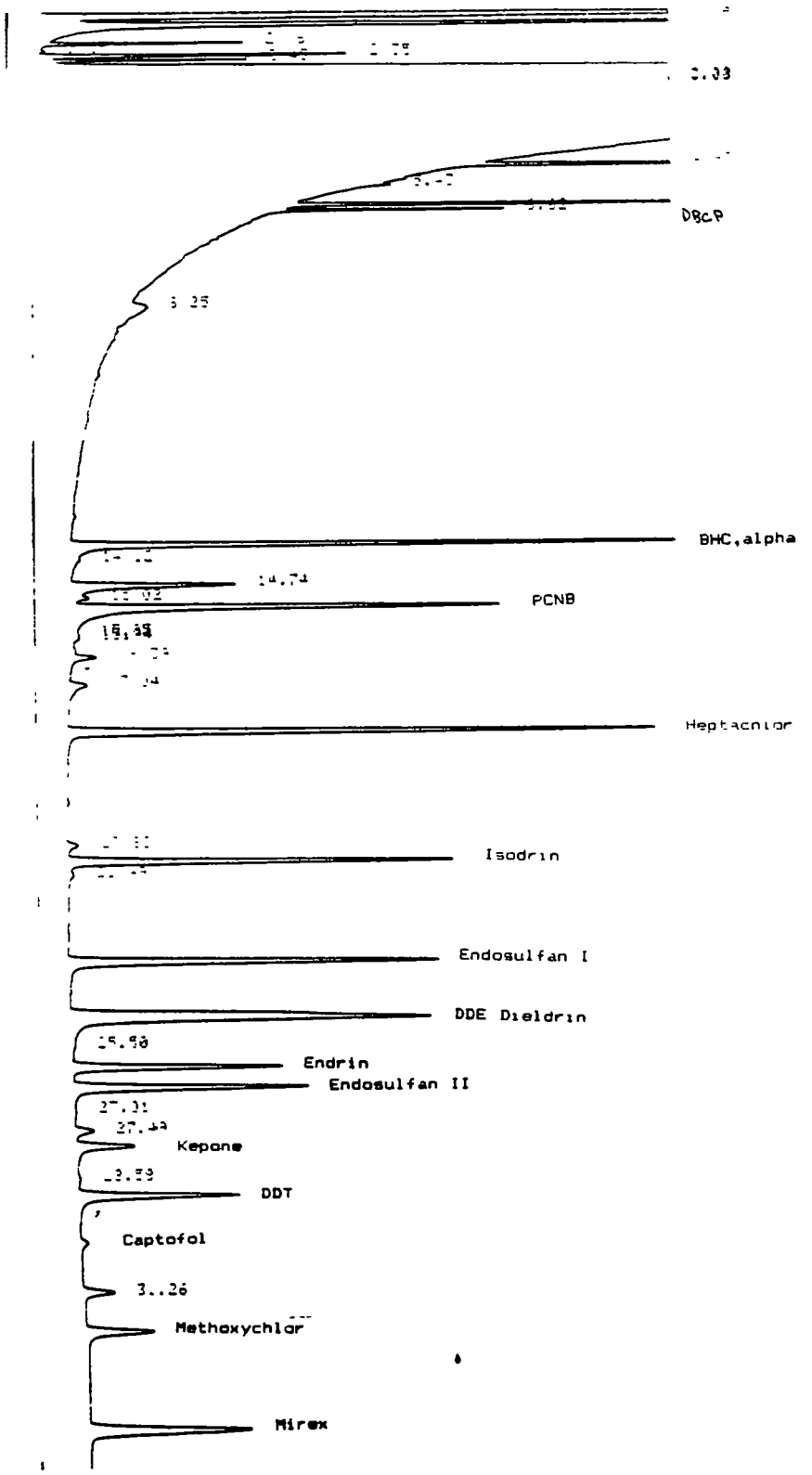

Figure 2B. Sample Chromatogram of Selected Apolar Organochlorine Pesticides on the DB-5.

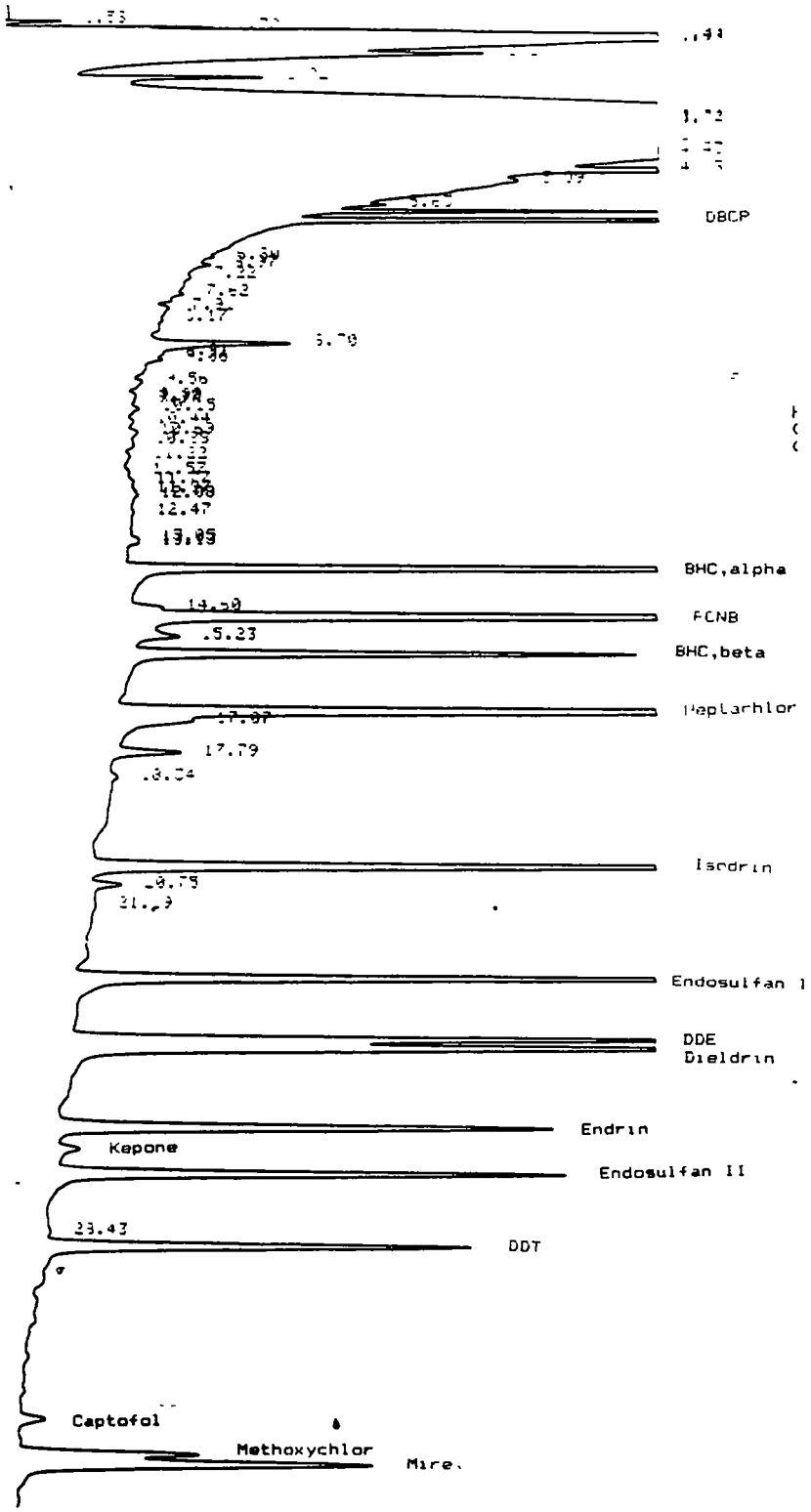

Figure 3A. Sample Chromatogram of Selected Apolar Organochlorine Pesticides on the SPB-608.

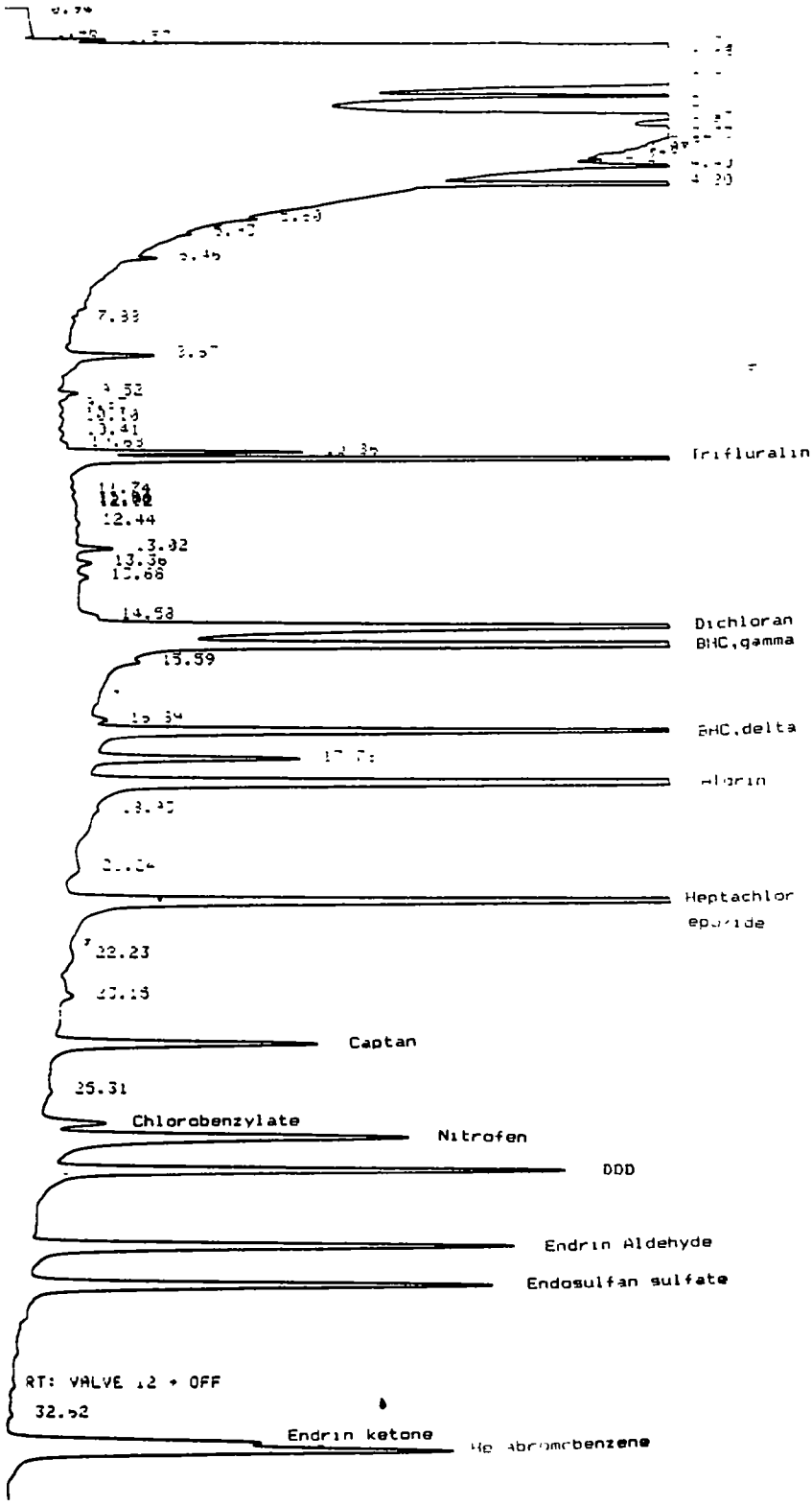

Figure 3B. Sample Chromatogram of Selected Apolar Organochlorine Pesticides on the SPB-608.

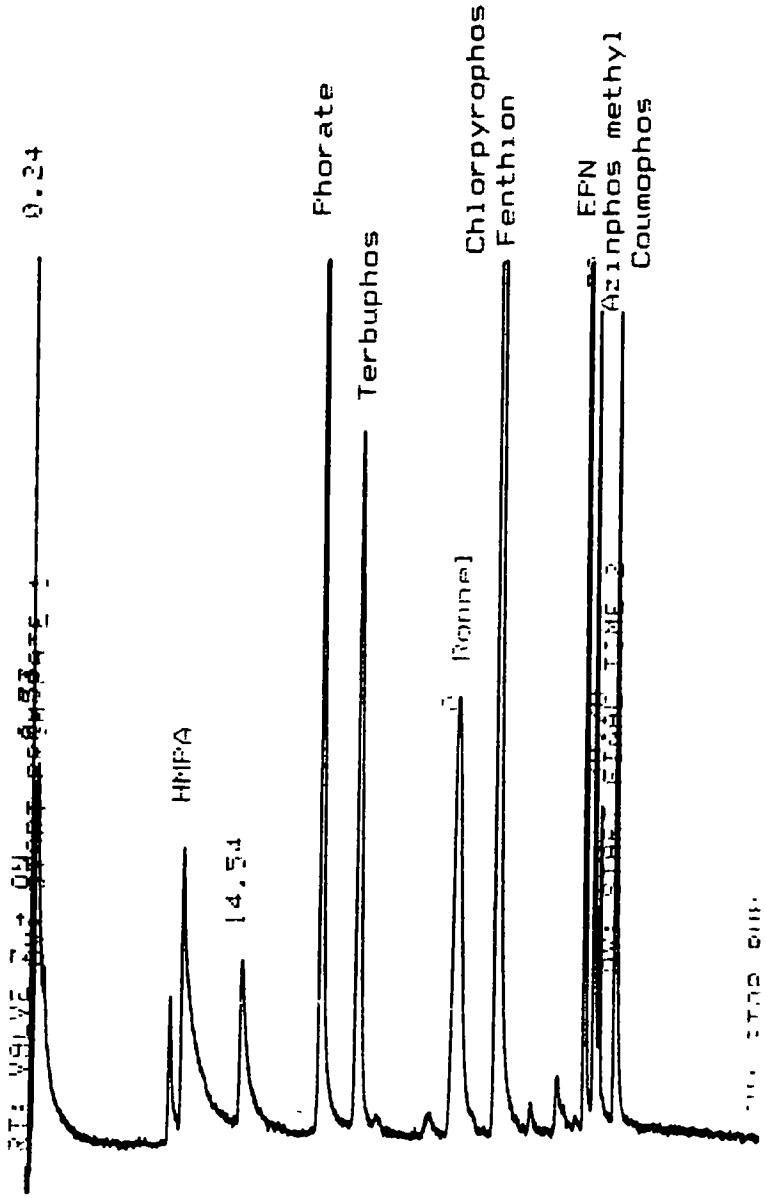

Figure 4A. Sample Chromatogram of Selected Apolar Organophosphorous Pesticides on the DB-5.

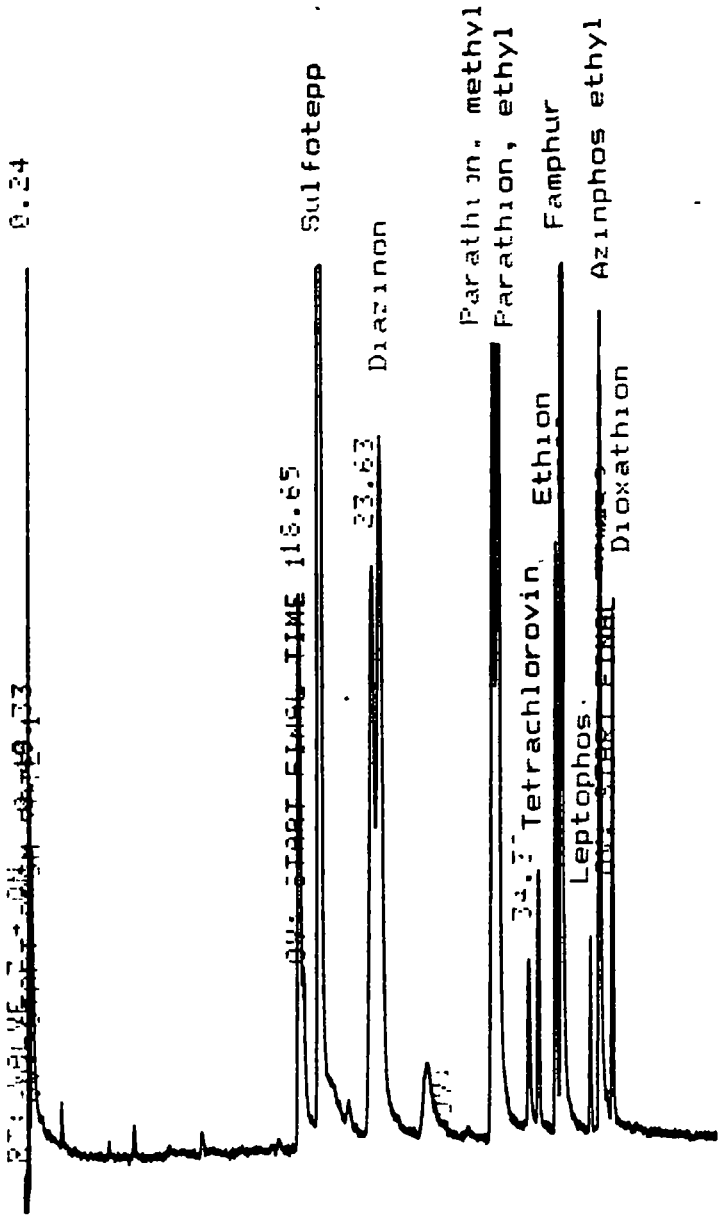

Figure 4B. Sample Chromatogram of Selected Apolar Organophosphorous Pesticides on the DB-5.

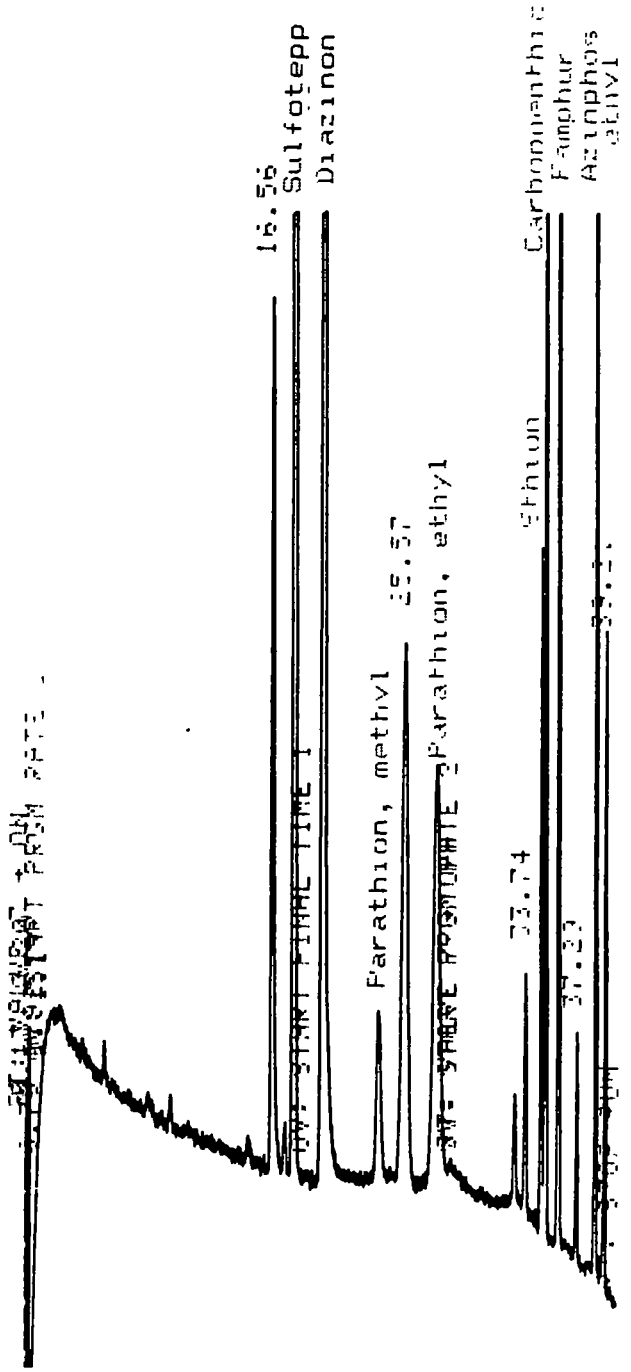

Figure 5A. Sample Chromatogram of Selected Apolar Organophosphorous Pesticides on the SPB-608.

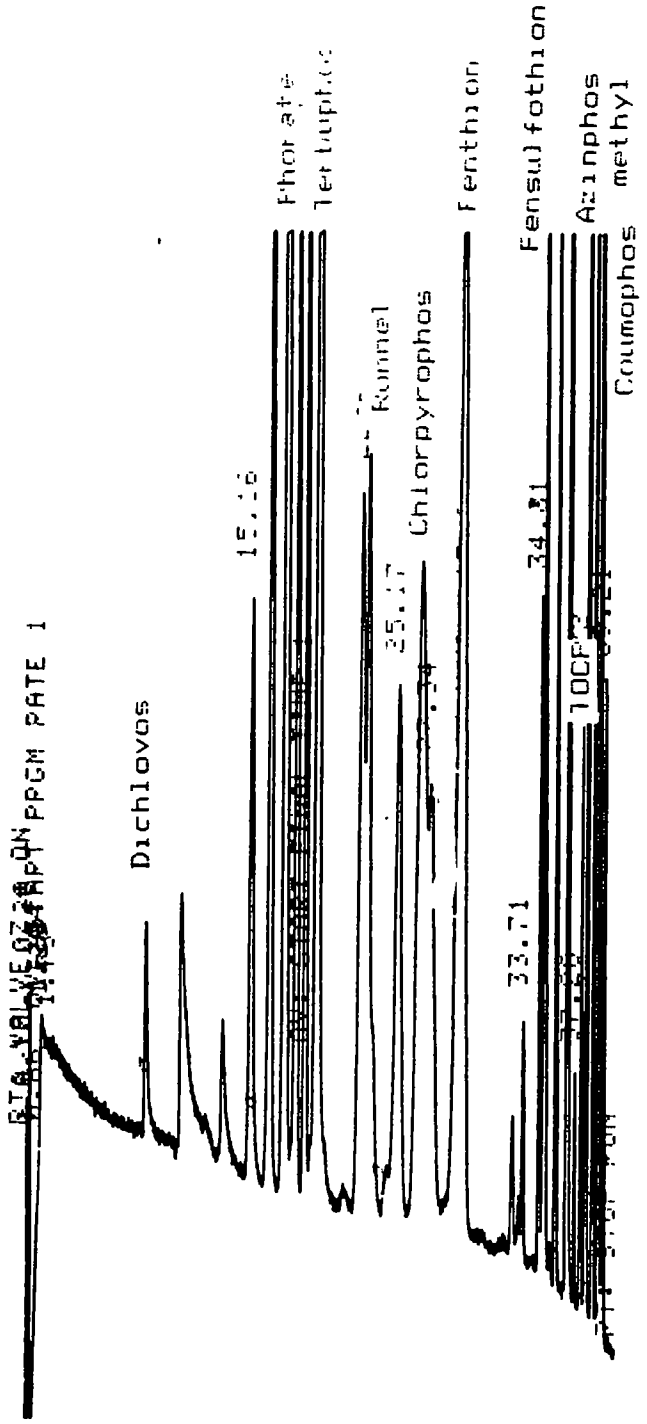

Figure 5B. Sample Chromatogram of Selected Apolar Organophosphorous Pesticides on the SPB-608.

Figure 6. Sample Chromatogram of Phenoxyacids on the DB-5.

Figure 7. Sample Chromatogram of Phenoxyacids on the SPB-608.

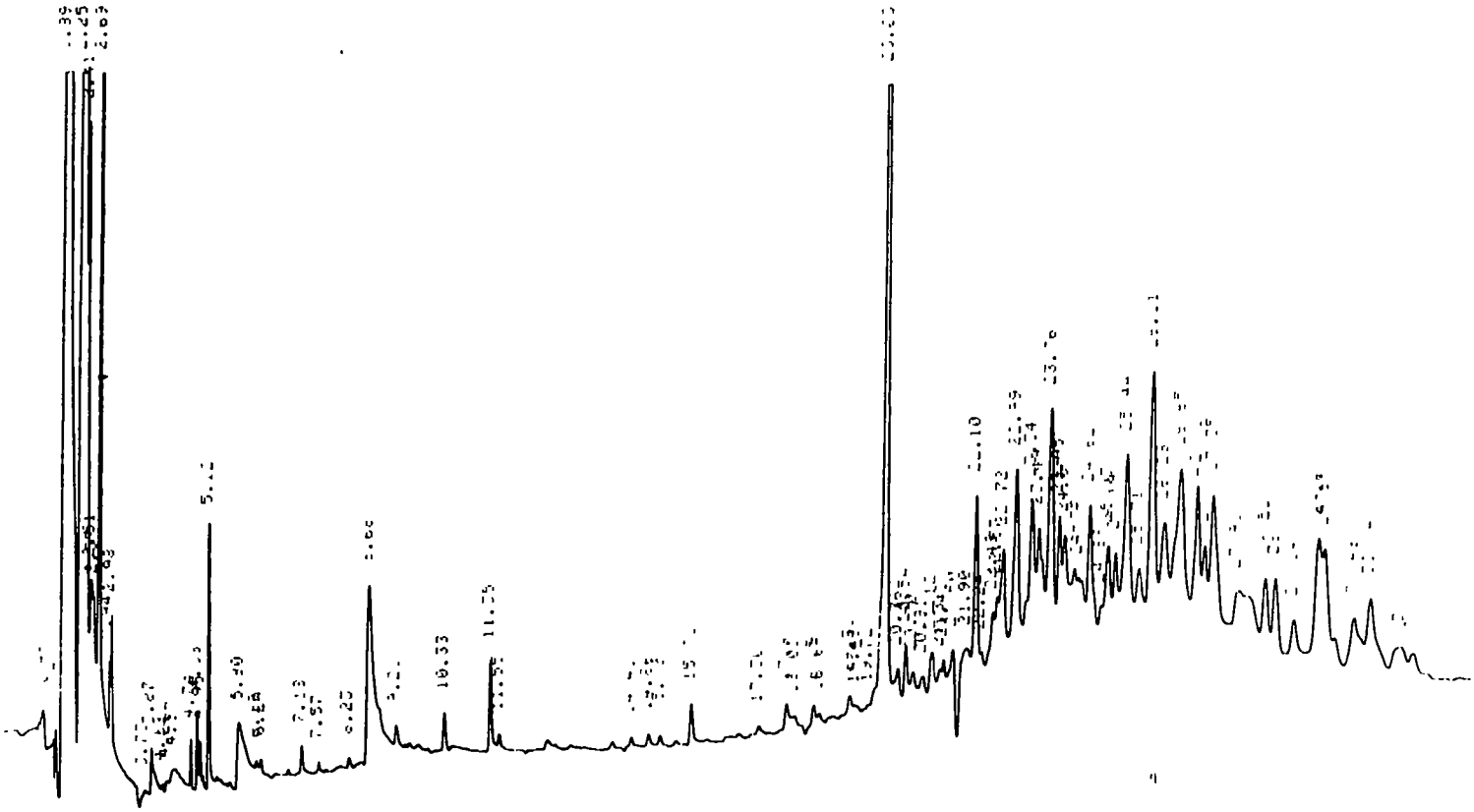

Figure 8. Toxaphene on the DB-5.

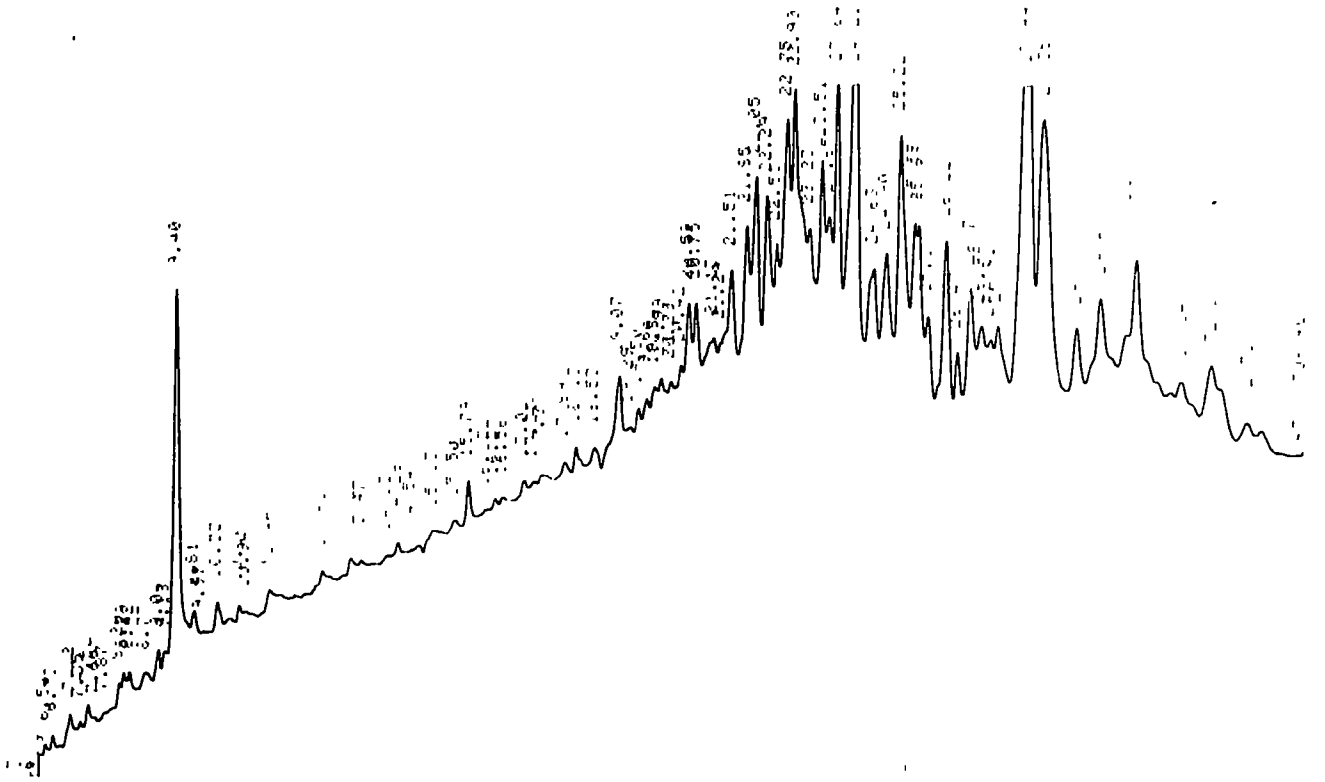

Figure 9. Toxaphene on the SPB-608.

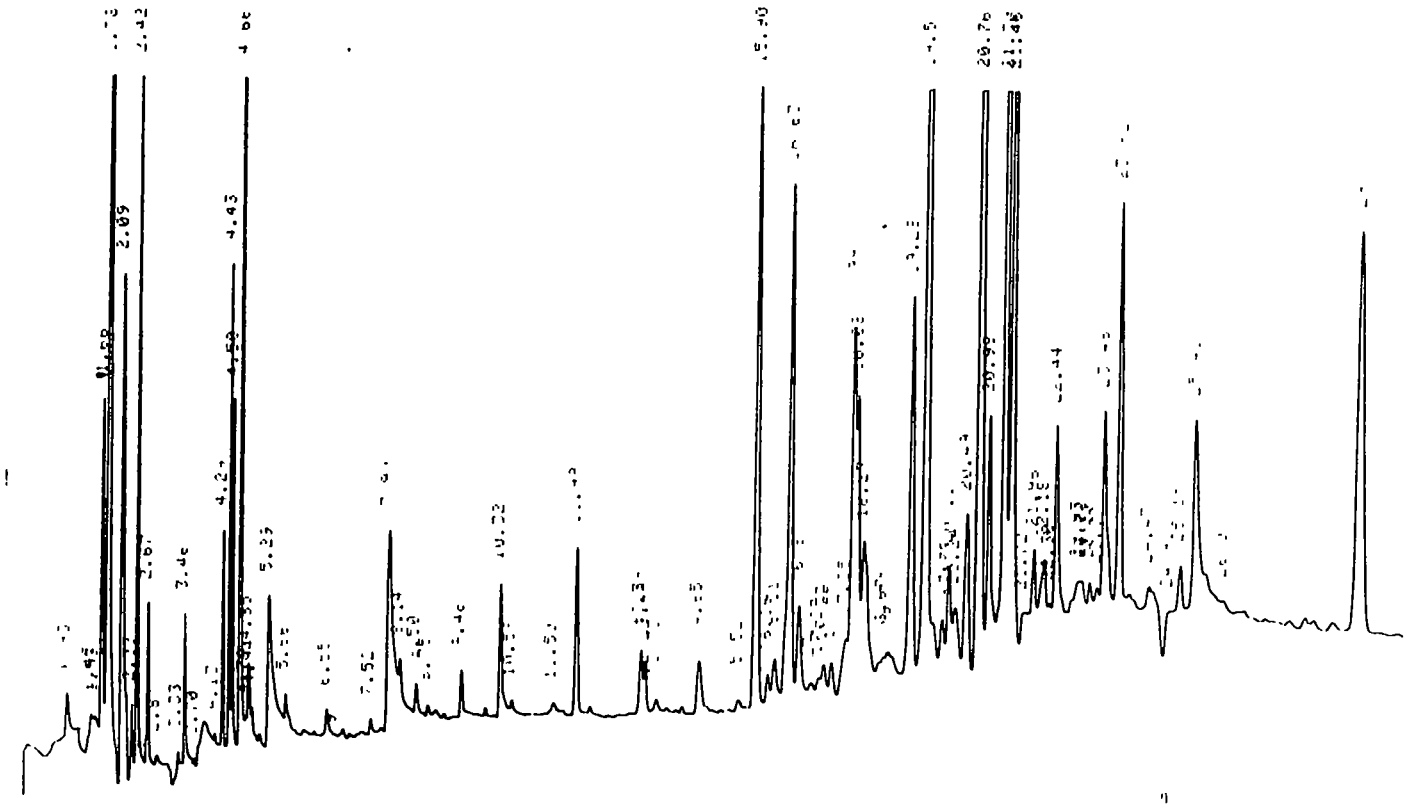

Figure 10. Chlordane on the DB-5.

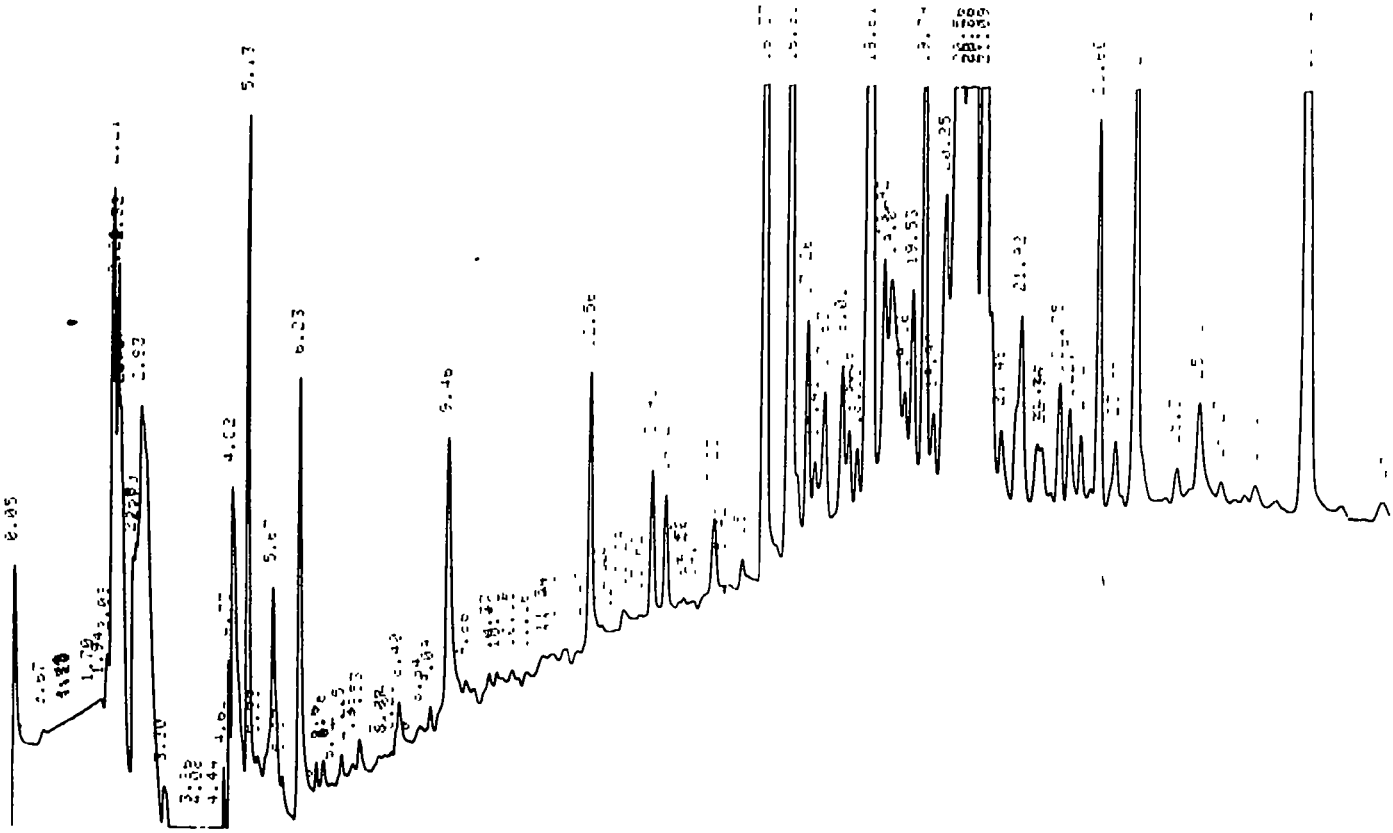

Figure 11. Chlordane on the SPB-608.

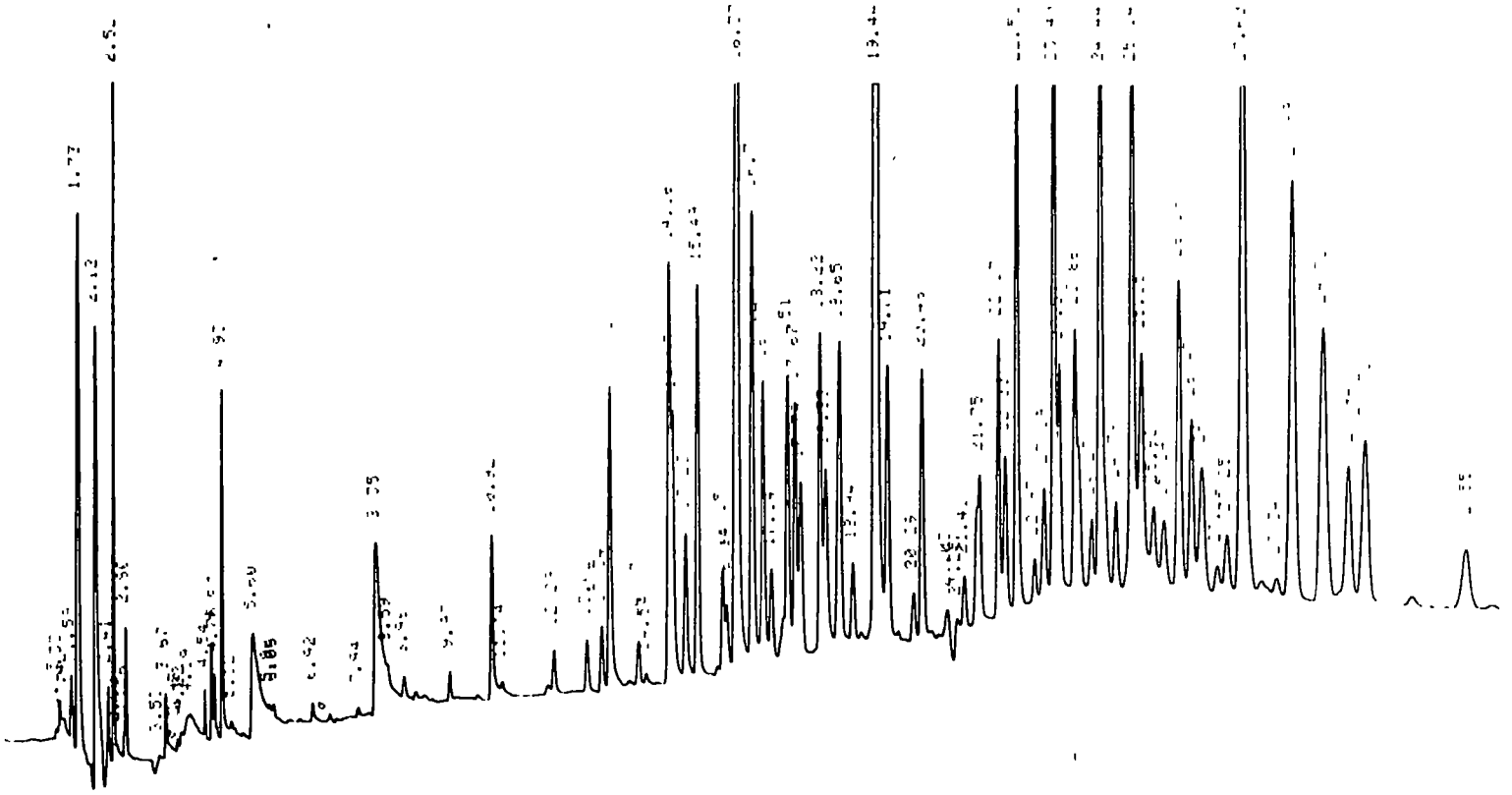

Figure 12. Aroclor 1016/1260 on the DB-5.

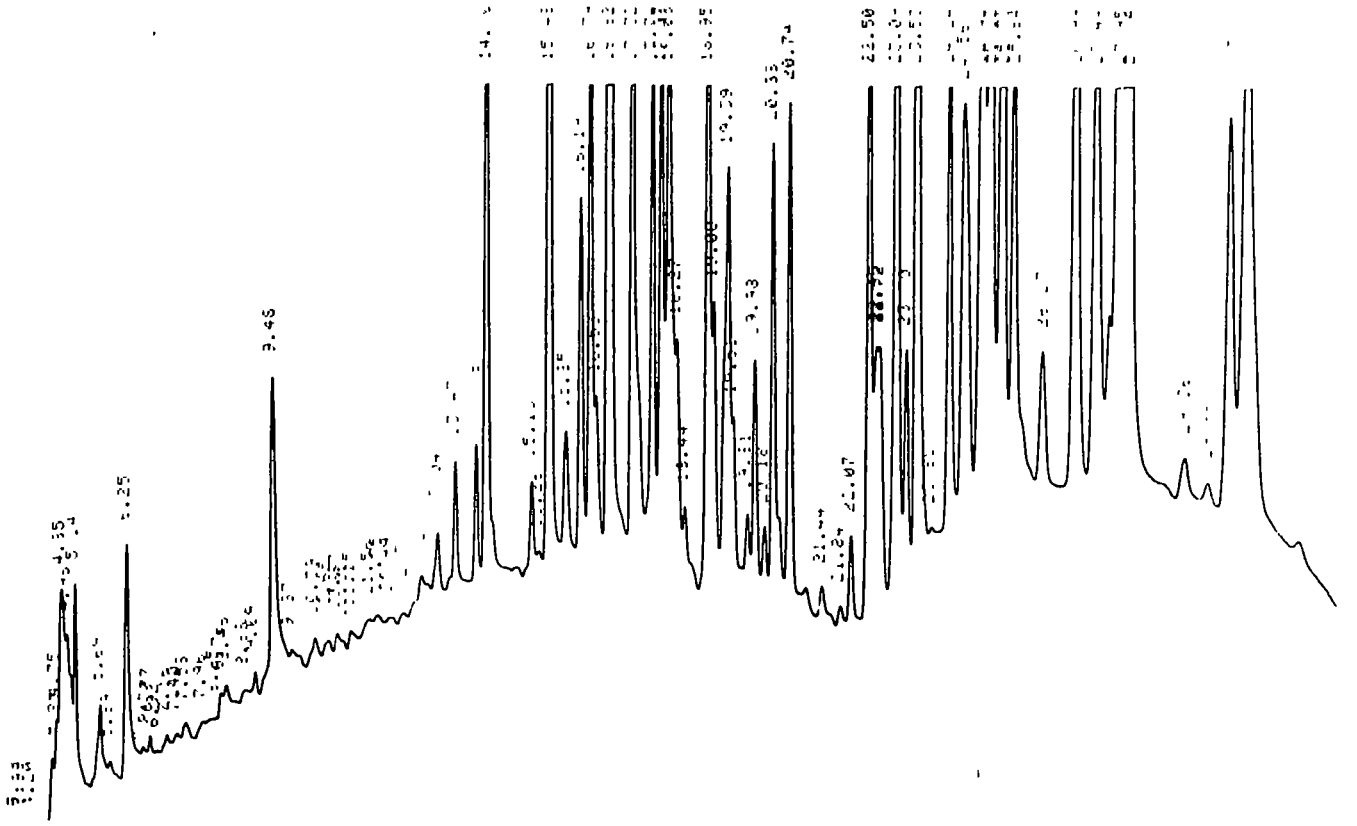

Figure 13. Aroclor 1016/1260 on the SPB-608.

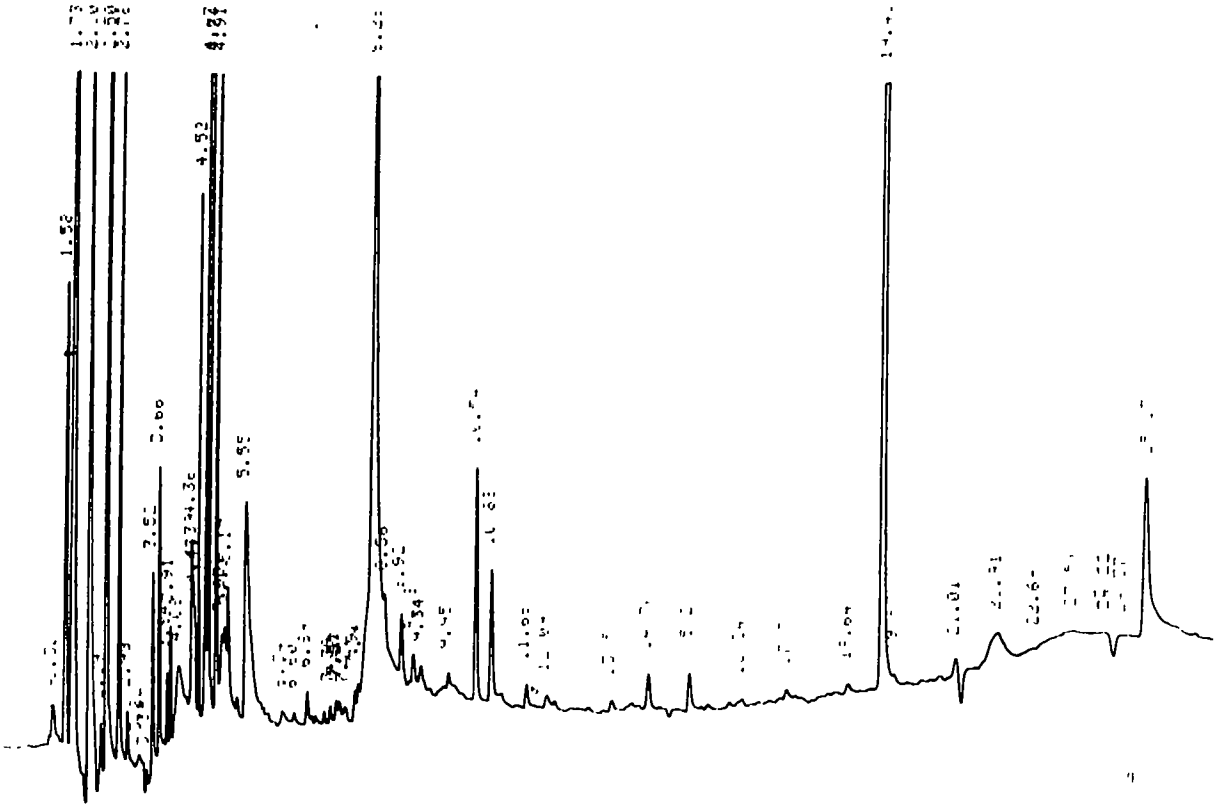

Figure 14. Aroclor 1221 on the DB-5.

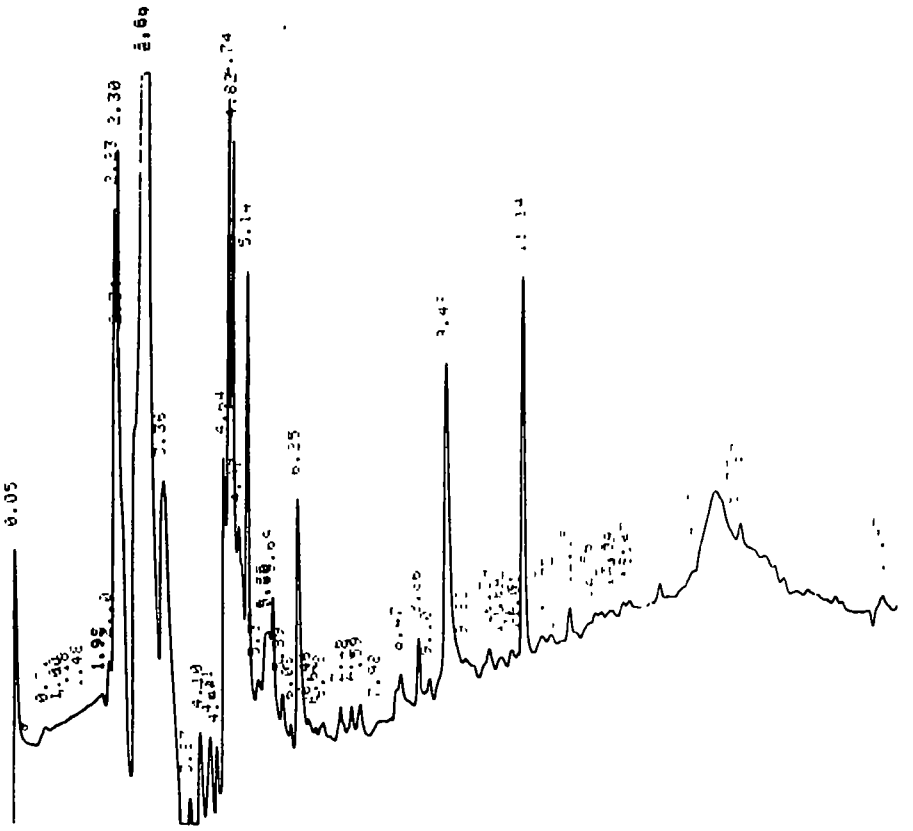

Figure 15. Aroclor 1221 on the SPB-608.

Figure 16. Aroclor 1232 on the DB-5.

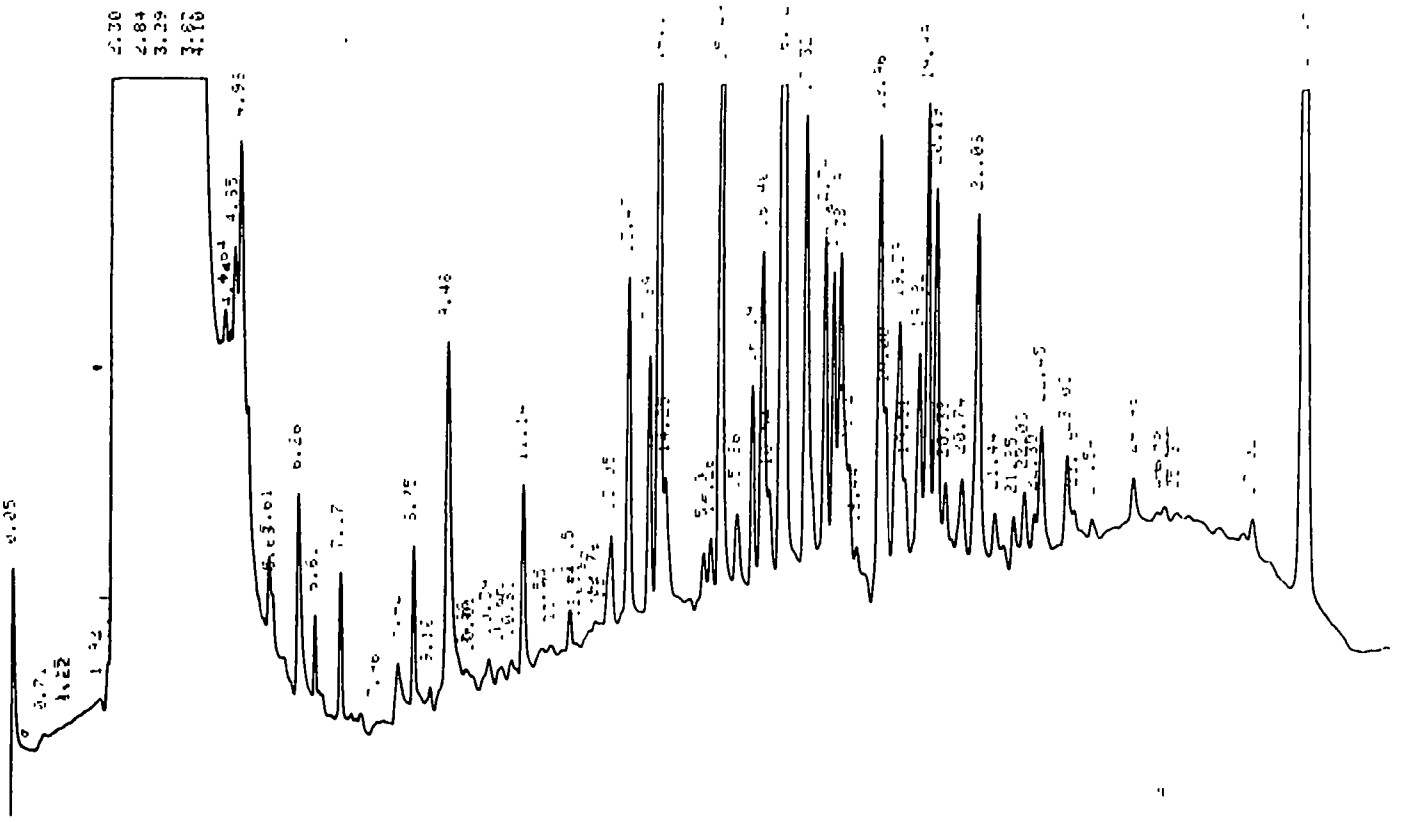

Figure 17. Aroclor 1232 on the SPB-608.

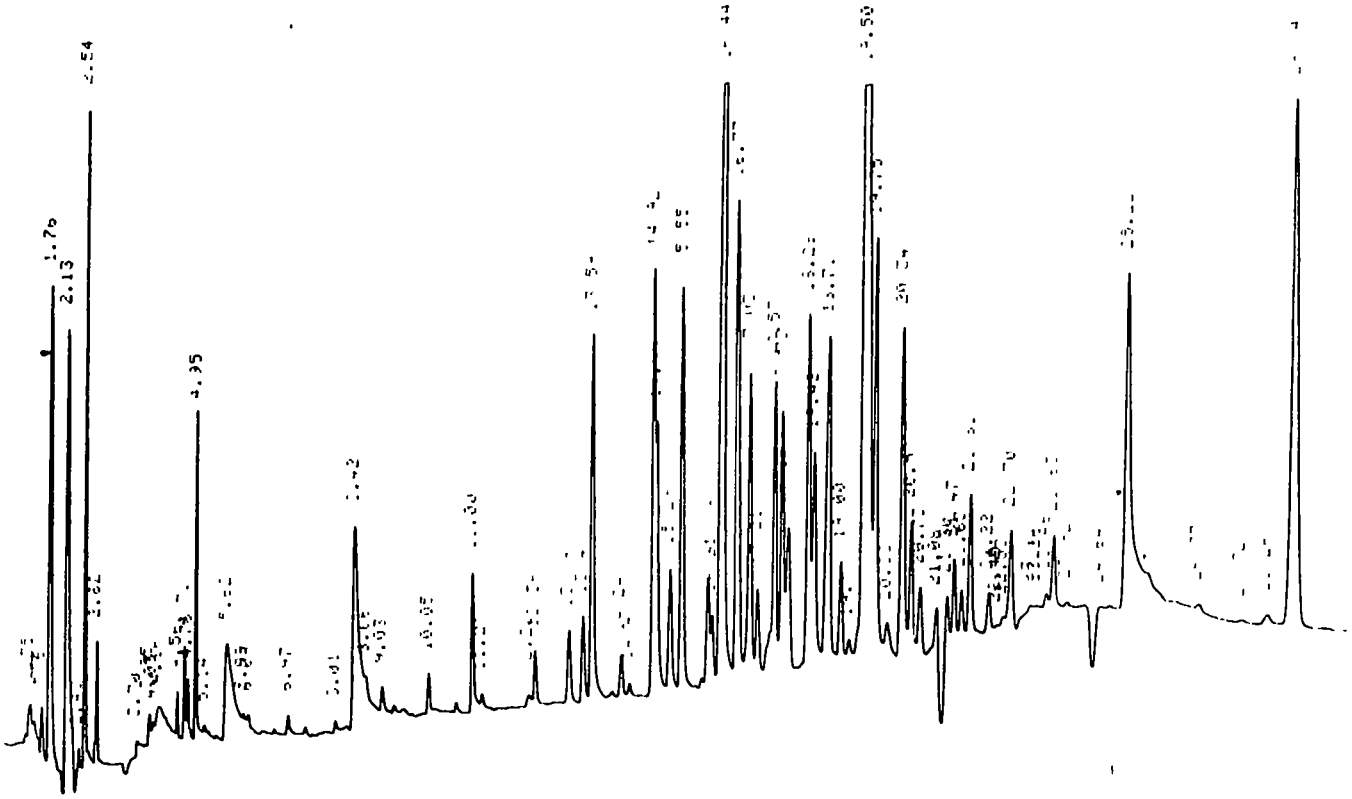

Figure 18. Aroclor 1242 on the DB-5.

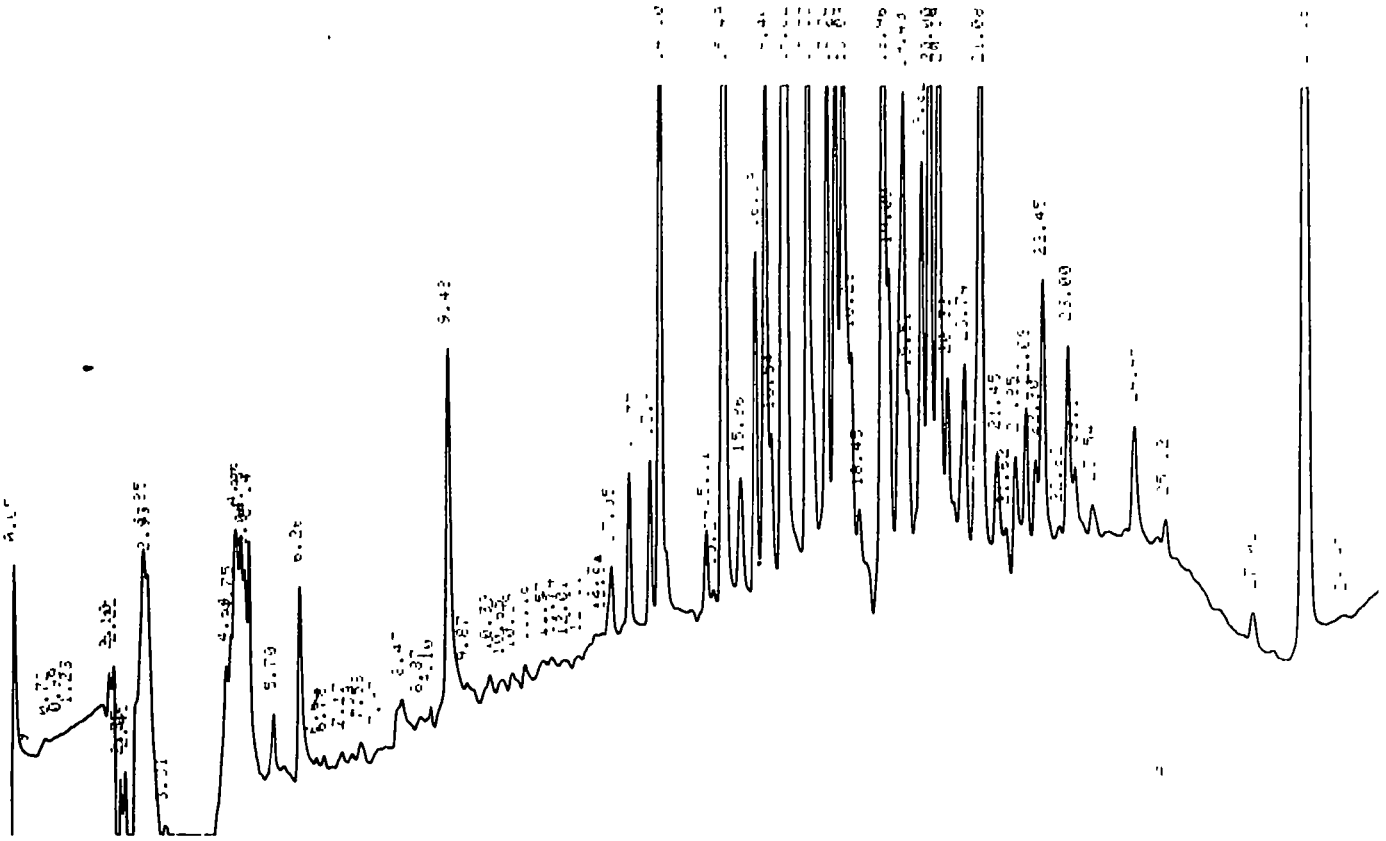

Figure 19. Aroclor 1242 on the SPB-608.

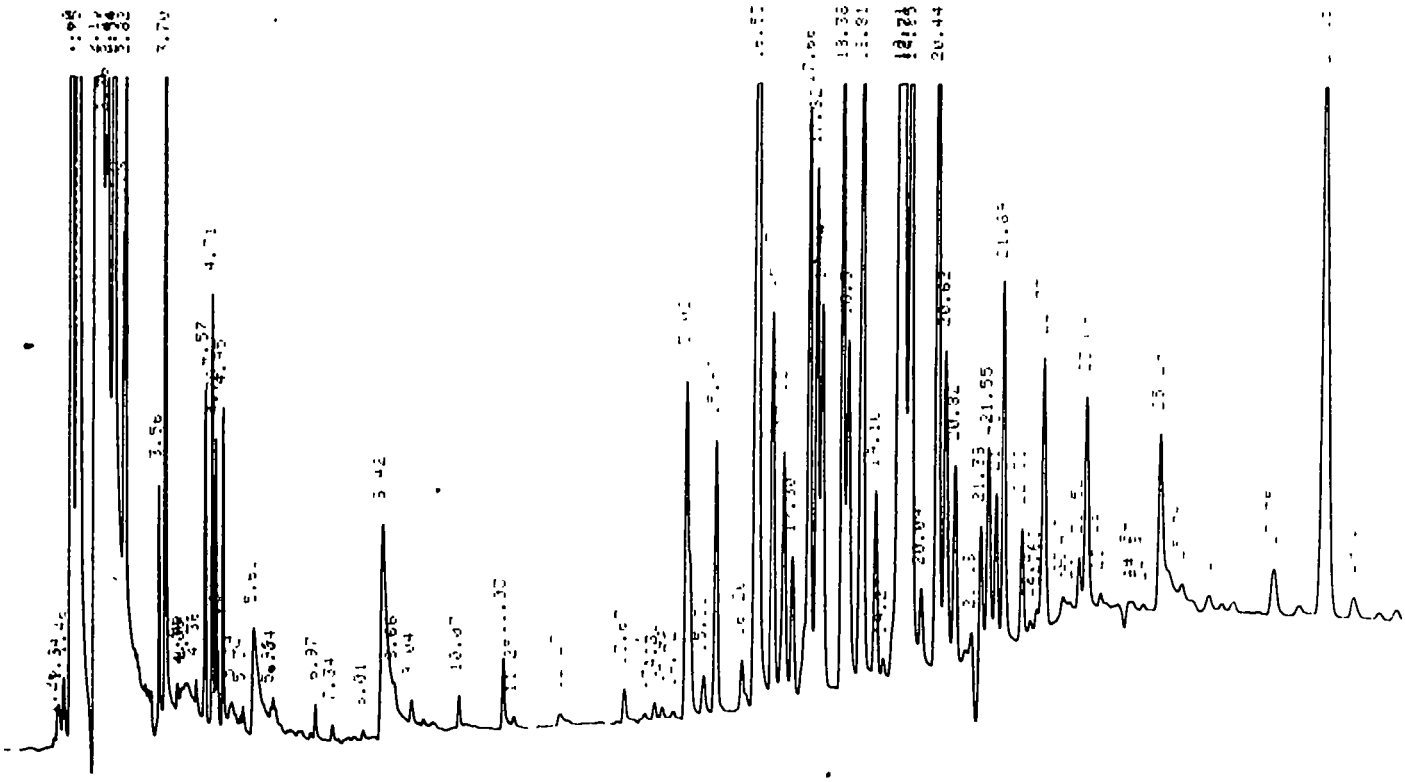

Figure 20. Aroclor 1248 on the DB-5.

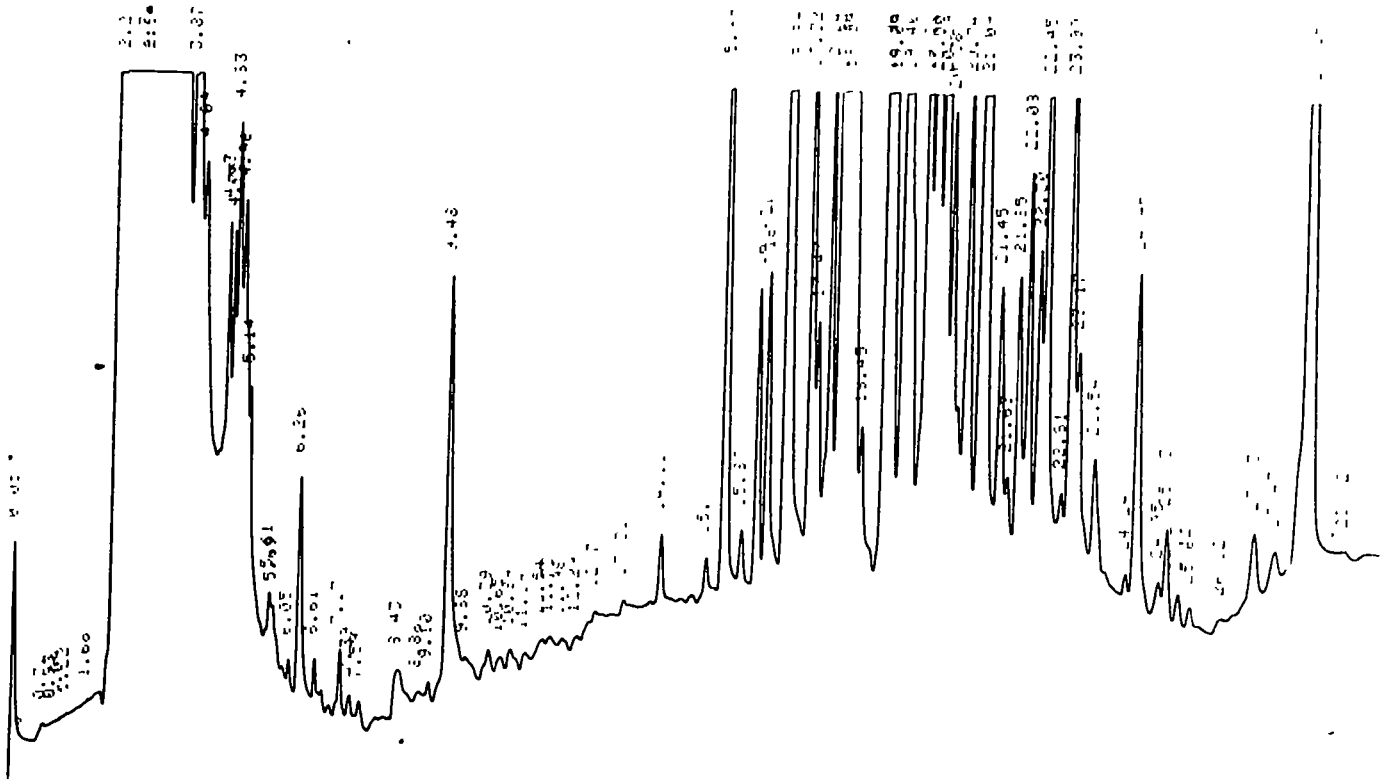

Figure 21. Aroclor 1248 on the SPB-608.

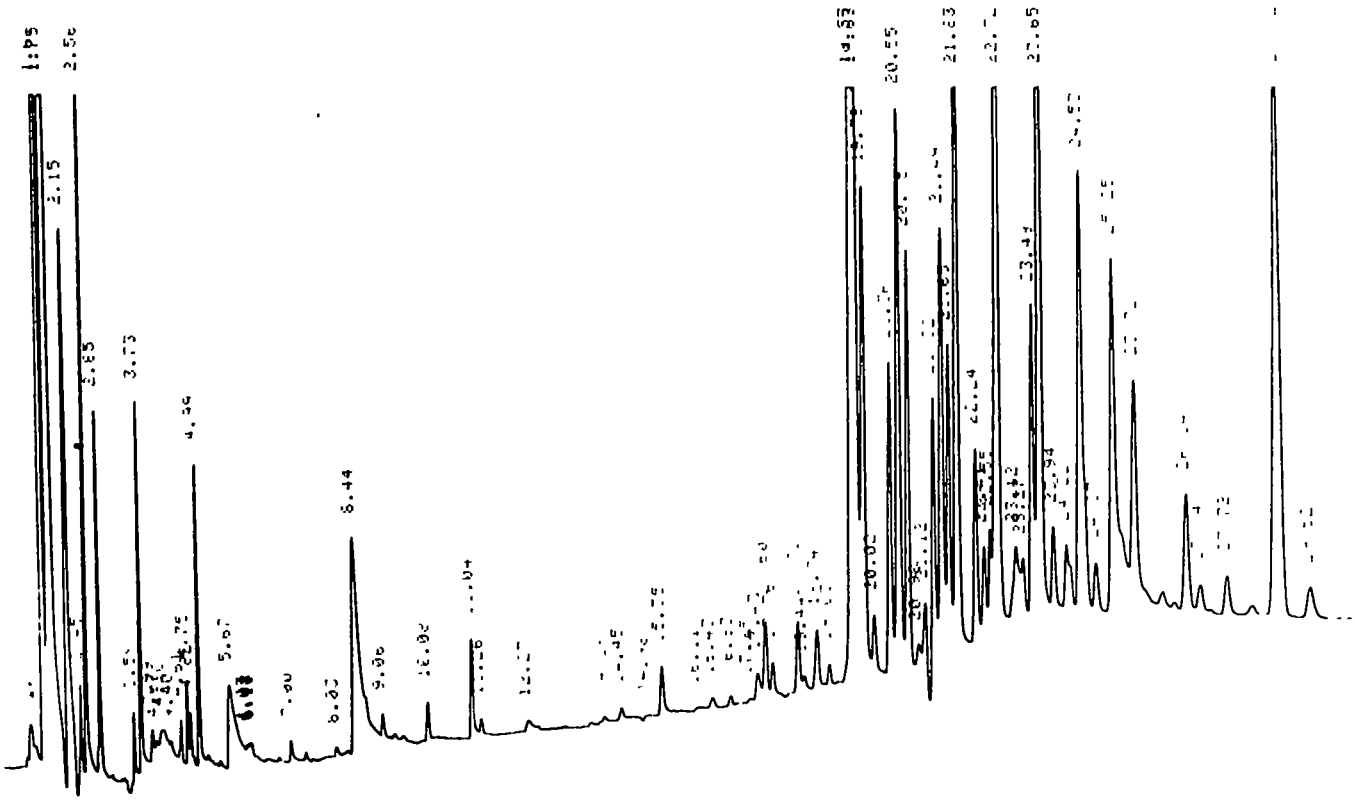

Figure 22. Aroclor 1254 on the DB-5.

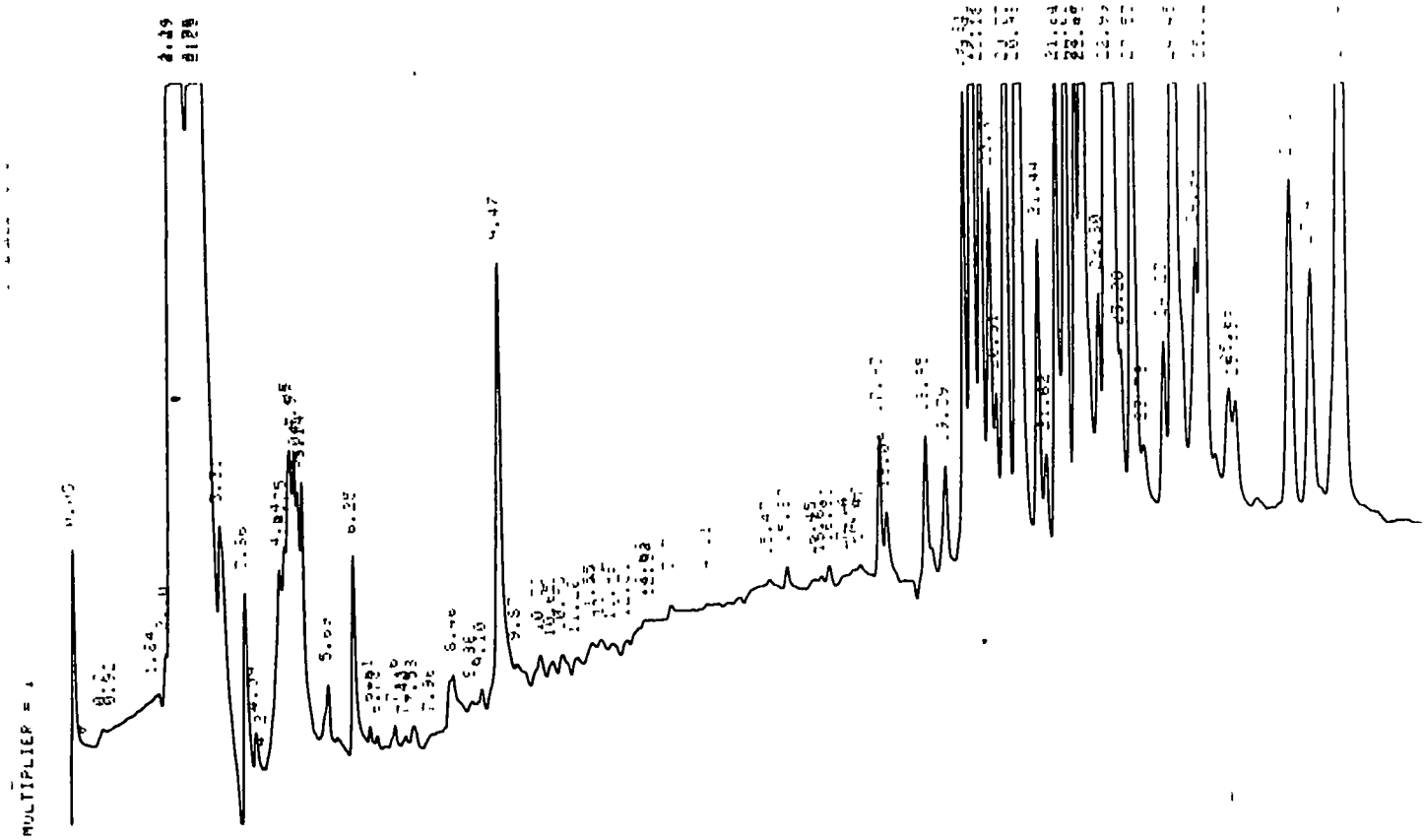

Figure 23. Aroclor 1254 on the SPB-608.