

METHOD 8150B

CHLORINATED HERBICIDES BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides. The following compounds can be determined by this method:

Compound Name	CAS No. ^a
2,4-D	94-75-7
2,4-DB	94-82-6
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5
Dalapon	75-99-0
Dicamba	1918-00-9
Dichloroprop	120-36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2

^a Chemical Abstract Services Registry Number.

1.2 Table 1 lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

1.3 When Method 8150 is used to analyze unfamiliar samples, compound identifications should 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. Sec. 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.4 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (the compound is explosive and carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium

hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (Goerlitz and Lamar, 1967). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

3.2.1 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.5 Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and

glass wool must be acid rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

3.7 Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1a and 1b - 1.8 m x 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.1.2.2 Column 2 - 1.8 m x 4 mm ID glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.1.2.3 Column 3 - 1.98 m x 2 mm ID glass, packed with 0.1% SP-1000 on 80/100 mesh Carbowax C or equivalent.

4.1.3 Detector - Electron capture (ECD).

4.2 Erlenmeyer flasks - 250 and 500 mL Pyrex, with 24/40 ground glass joint.

4.3 Beaker - 500 mL.

4.4 Diazomethane generator - Refer to Sec. 7.4 to determine which method of diazomethane generation should be used for a particular application.

4.4.1 Diazald kit - recommended for the generation of diazomethane using the procedure given in Sec. 7.4.2 (Aldrich Chemical Co., Cat. No. 210,025-2 or equivalent).

4.4.2 Assemble from two 20 x 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Sec. 7.4.3.

4.5 Vials - 10 to 15 mL, amber glass, with Teflon lined screw cap or crimp top.

4.6 Separatory funnel - 2000 mL, 125 mL, and 60 mL.

4.7 Drying column - 400 mm x 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.8 Kuderna-Danish (K-D) apparatus

4.8.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts

4.8.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps or equivalent.

4.8.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.9 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.11 Microsyringe - 10 μL .

4.12 Wrist shaker - Burrell Model 75 or equivalent.

4.13 Glass wool - Pyrex, acid washed.

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

4.15 Syringe - 5 mL.

4.16 Glass rod.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the

specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid solution

5.3.1 ((1:1) (v/v)) - Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.3.2 ((1:3) (v/v)) - Slowly add 25 mL H_2SO_4 (sp. gr. 1.84) to 75 mL of organic-free reagent water.

5.4 Hydrochloric acid ((1:9) (v/v)), HCl . Add one volume of concentrated HCl to 9 volumes of organic-free reagent water.

5.5 Potassium hydroxide solution (KOH) - 37% aqueous solution (w/v). Dissolve 37 g potassium hydroxide pellets in organic-free reagent water, and dilute to 100 mL.

5.6 Carbitol (Diethylene glycol monoethyl ether), $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$. Available from Aldrich Chemical Co.

5.7 Solvents

5.7.1 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.7.2 Methanol, CH_3OH - Pesticide quality or equivalent.

5.7.3 Isooctane, $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)_2$ - Pesticide quality or equivalent.

5.7.4 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.7.5 Diethyl Ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$. Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.8 Sodium sulfate (granular, acidified, anhydrous), Na_2SO_4 . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Acidify by slurring 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 mL of organic-free reagent water and measure the pH of the mixture. It must be below a pH of 4. Store at 130°C .

5.9 N-Methyl-N-nitroso-p-toluenesulfonamide (Diazald), $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}(\text{CH}_3)\text{NO}$. Available from Aldrich Chemical Co.

5.10 Silicic acid. Chromatographic grade, nominal 100 mesh. Store at 130°C.

5.11 Stock standard solutions - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the acids in pesticide quality acetone and dissolve the esters in 10% acetone/isooctane (v/v) and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.11.2 Transfer the stock standard solutions into vials with Teflon lined screw caps or crimp tops. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.11.3 Stock standard solutions of the derivatized acids must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem. Stock standard solutions of the free acids degrade more quickly and should be replaced after two months, or sooner if comparison with check standards indicates a problem.

5.12 Calibration standards - A minimum of five calibration standards for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.13 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.13.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Sec. 5.12.

5.13.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane.

5.13.3 Analyze each calibration standard per Sec. 7.0.

5.14 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with one or two herbicide surrogates (e.g. herbicides that are not expected to be present in the sample). The surrogates selected should elute over the range of the temperature program used in this method. 2,4-Dichlorophenylacetic acid (DCAA) is recommended as a surrogate compound. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Preparation of waste samples

7.1.1 Extraction

7.1.1.1 Follow Method 3580 except use diethyl ether as the dilution solvent, acidified anhydrous sodium sulfate, and acidified glass wool.

7.1.1.2 Transfer 1.0 mL (a lesser volume or a dilution may be required if herbicide concentrations are high) to a 250 mL ground glass-stoppered Erlenmeyer flask. Proceed to Sec. 7.2.2 hydrolysis.

7.2 Preparation of soil, sediment, and other solid samples

7.2.1 Extraction

7.2.1.1 To a 500 mL, wide mouth Erlenmeyer flask add 50 g (dry weight as determined in Method 3540, Sec. 7.2.1) of the well mixed, moist solid sample. Adjust the pH to 2 (See Method 9045) with concentrated HCl and monitor the pH for 15 minutes with occasional stirring. If necessary, add additional HCl until the pH remains at 2.

7.2.1.2 Add 20 mL acetone to the flask and mix the contents with the wrist shaker for 20 minutes. Add 80 mL diethyl ether to the same flask and shake again for 20 minutes. Decant the extract and measure the volume of solvent recovered.

7.2.1.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 minutes and the acetone-ether extract decanted.

7.2.1.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2 liter separatory funnel containing 250 mL of reagent water. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.2.1.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 minute and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract phase (top layer) in a 500 mL ground glass-stoppered Erlenmeyer flask. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500 mL Erlenmeyer flask.

7.2.1.6 An alternative extraction procedure using ultrasonic extraction can be found in Sec. 7.2 of Method 8151.

7.2.2 Hydrolysis

7.2.2.1 Add 30 mL of organic-free reagent water, 5 mL of 37% KOH, and one or two clean boiling chips to the flask. Place a three ball Snyder column on the flask, evaporate the diethyl ether on a water bath, and continue to heat until the hydrolysis step is completed (usually 1 to 2 hours).

7.2.2.2 Remove the flask from the water bath and allow to cool. Transfer the water solution to a 125 mL separatory funnel and extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for the layers to separate and discard the ether layer each time. The phenoxy-acid herbicides remain soluble in the aqueous phase as potassium salts.

7.2.3 Solvent cleanup

7.2.3.1 Adjust the pH to 2 by adding 5 mL cold (4°C) sulfuric acid (1:3) to the separatory funnel. Be sure to check the pH at this point. Extract the herbicides once with 40 mL and twice with 20 mL of diethyl ether. Discard the aqueous phase.

7.2.3.2 Combine ether extracts in a 125 mL Erlenmeyer flask containing 5-7 g of acidified anhydrous sodium sulfate. Stopper and allow the extract to remain in contact with the

acidified sodium sulfate. If concentration and esterification are not to be performed immediately, store the sample overnight in the refrigerator.

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free-flowing crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held overnight in contact with the sodium sulfate.

7.2.3.3 Transfer the ether extract, through a funnel plugged with acid washed glass wool, into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.2.3.4 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.2.3.5 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5 mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 minutes. When the apparent volume of the liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether. Proceed to Sec. 7.4 for esterification.

7.3 Preparation of aqueous samples

7.3.1 Extraction

7.3.1.1 Using a 1 liter graduated cylinder, measure 1 liter (nominal) of sample, record the sample volume to the nearest 5 mL, and quantitatively transfer it to the separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Adjust the pH to less than 2 with sulfuric acid (1:1).

7.3.1.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 seconds to rinse the walls. Transfer the solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer for a minimum of 10 minutes. If the emulsion interface between layers is more than one third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Drain the aqueous phase into a 1 liter Erlenmeyer flask. Collect the solvent extract in a 250 mL ground glass Erlenmeyer flask containing 2 mL of 37% KOH. Approximately 80 mL of the diethyl ether will remain dissolved in the aqueous phase.

7.3.1.3 Repeat the extraction two more times using 50 mL of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1 liter flask with each additional aliquot of extracting solvent.)

7.3.2 Hydrolysis

7.3.2.1 Add one or two clean boiling chips and 15 mL of organic-free reagent water to the 250 mL flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Place the apparatus on a hot water bath (60°-65°C) so that the bottom of the flask is bathed with hot water vapor. Although the diethyl ether will evaporate in about 15 minutes, continue heating until the hydrolysis step is completed (usually 1 to 2 hours). Remove the apparatus and let stand at room temperature for at least 10 minutes.

7.3.2.2 Transfer the solution to a 60 mL separatory funnel using 5-10 mL of organic-free reagent water. Wash the basic solution twice by shaking for 1 minute with 20 mL portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

7.3.3 Solvent cleanup

7.3.3.1 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for

2 minutes. Drain the aqueous layer into a 250 mL Erlenmeyer flask, and pour the organic layer into a 125 mL Erlenmeyer flask containing about 5-7 g of acidified sodium sulfate. Repeat the extraction twice more with 10 mL aliquots of diethyl ether, combining all solvent in the 125 mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hours.

NOTE: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held overnight in contact with the sodium sulfate.

7.3.3.2 Transfer the ether extract, through a funnel plugged with acid washed glass wool, into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.3.3.3 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.3.3.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5 mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 minutes. When the apparent volume of the liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

7.4 Esterification

7.4.1 Two methods may be used for the generation of diazomethane: the bubbler method (set up shown in Figure 1) and the Diazald kit method. The bubbler method is suggested when small batches (10-15) of samples require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g. aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g., samples such as soils that result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method). The diazomethane derivatization (U.S. EPA, 1971) procedures, described below, will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. The following precautions should be taken:

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90°C -- EXPLOSION may result.
- Avoid grinding surfaces, ground glass joints, sleeve bearings, 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 powder, calcium chloride, and boiling chips.

7.4.2 Diazald kit method - Instructions for preparing diazomethane are provided with the generator kit.

7.4.2.1 Add 2 mL of diazomethane solution and let sample stand for 10 minutes with occasional swirling.

7.4.2.2 Rinse inside wall of the ampule with several hundred μ L of diethyl ether. Allow solvent to evaporate spontaneously at room temperature to about 2 mL.

7.4.2.3 Dissolve the residue in 5 mL of hexane. Analyze by gas chromatography.

7.4.3 Bubbler method - Assemble the diazomethane bubbler (see Figure 1).

7.4.3.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1-0.2 g Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract.

Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1-0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

7.4.3.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 minutes.

7.4.3.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.5 Gas chromatographic conditions (Recommended)

7.5.1 Column 1a

Carrier gas (5% methane/95% argon) flow rate: 70 mL/min
Temperature program: 185°C, isothermal.

7.5.2 Column 1b

Carrier gas (5% methane/95% argon) flow rate: 70 mL/min
Initial temperature: 140°C, hold for 6 minutes
Temperature program: 140°C to 200°C at 10°C/min, hold until last compound has eluted.

7.5.3 Column 2

Carrier gas (5% methane/95% argon) flow rate: 70 mL/min
Temperature program: 185°C, isothermal.

7.5.4 Column 3

Carrier gas (ultra-high purity N₂) flow rate: 25 mL/min
Initial temperature: 100°C, no hold
Temperature program: 100°C to 150°C at 10°C/min, hold until last compound has eluted.

7.6 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.6.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.6.2 The following gas chromatographic columns are recommended for the compounds indicated:

<u>Analyte</u>	<u>Column</u>	<u>Analyte</u>	<u>Column</u>
Dicamba	1a,2	Dalapon	3
2,4-D	1a,2	MCPD	1b
2,4,5-TP	1a,2	MCPA	1b
2,4,5-T	1a,2	Dichloroprop	1b
2,4-DB	1a	Dinoseb	1b

7.7 Gas chromatographic analysis

7.7.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 μ L of internal standard to the sample prior to injection.

7.7.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration check standard after each group of 10 samples in the analysis sequence.

7.7.3 Examples of chromatograms for various chlorophenoxy acid herbicides are shown in Figures 2 through 4.

7.7.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.7.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.7.6 If calibration standards have been analyzed in the same manner as the samples (e.g. have undergone hydrolysis and esterification), then the calculation of concentration given in Method 8000 should be used. However, if calibration is done using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.7.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000.

8.2.1 Select a representative spike concentration for each compound (acid or ester) to be measured. Using stock standards, prepare a quality control check sample concentrate in acetone 1,000 times more concentrated than the selected concentrations.

8.2.2 Table 3 indicates single operator accuracy and precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if none of the above checks reveal a problem.
- Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.4 GC/MS confirmation

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

8.4.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, using organic-free reagent water and effluents from publicly owned treatment works (POTW), the average recoveries presented in Table 3 were obtained. The standard deviations of the percent recoveries of these measurements are also included in Table 3.

10.0 REFERENCES

1. U.S. EPA, National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II, Method for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents, Cincinnati, Ohio, 1971.
2. Goerlitz, D.G., and W.L. Lamar, "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography," U.S. Geol. Survey Water Supply Paper, 1817-C, 1967.
3. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.
4. U.S. EPA, "Extraction and Cleanup Procedure for the Determination of Phenoxy Acid Herbicides in Sediment," EPA Toxicant and Analysis Center, Bay St. Louis, Mississippi, 1972.
5. "Pesticide Methods Evaluation," Letter Report #33 for EPA Contract No. 68-03-2697. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
6. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Analytical Chemistry, 47, 995, 1975.
7. Glaser, J.A. et.al., "Trace Analysis for Wastewaters," Environmental Science & Technology, 15, 1426, 1981.
8. Gurka, D.F., Shore, F.L., Pan, S-T, "Single Laboratory Validation of EPA Method 8150 for Determination of Chlorinated Herbicides in Hazardous Waste", JAOAC, 69, 970, 1986.
9. U.S. EPA, "Method 615. The Determination of Chlorinated Herbicides in Industrial and Municipal Wastewater," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, June 1982.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS
FOR CHLORINATED HERBICIDES

Compound	Retention time (min) ^a				Method detection limit (µg/L)
	Col.1a	Col.1b	Col.2	Col.3	
2,4-D	2.0	-	1.6	-	1.2
2,4-DB	4.1	-	-	-	0.91
2,4,5-T	3.4	-	2.4	-	0.20
2,4,5-TP (Silvex)	2.7	-	2.0	-	0.17
Dalapon	-	-	-	5.0	5.8
Dicamba	1.2	-	1.0	-	0.27
Dichloroprop	-	4.8	-	-	0.65
Dinoseb	-	11.2	-	-	0.07
MCPA	-	4.1	-	-	249
MCPP	-	3.4	-	-	192

^aColumn conditions are given in Secs. 4.1 and 7.5.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION
LIMITS (EQL) FOR VARIOUS MATRICES^a

Matrix	Factor
Ground water (based on one liter sample size)	10
Soil/sediment and other solids	200
Waste samples	100,000

^aEQL = [Method detection limit (see Table 1)] X [Factor found in this table]. For non-aqueous samples, the factor is on a wet weight basis. Sample EQLs are highly matrix dependent. The EQLs to be determined herein are provided for guidance and may not always be achievable.

TABLE 3.
SINGLE OPERATOR ACCURACY AND PRECISION^a

Compound	Sample Type	Spike (µg/L)	Mean Recovery (%)	Standard deviation (%)
2,4-D	DW	10.9	75	4
	MW	10.1	77	4
	MW	200	65	5
Dalapon	DW	23.4	66	8
	MW	23.4	96	13
	MW	468	81	9
2,4-DB	DW	10.3	93	3
	MW	10.4	93	3
	MW	208	77	6
Dicamba	DW	1.2	79	7
	MW	1.1	86	9
	MW	22.2	82	6
Dichlorprop	DW	10.7	97	2
	MW	10.7	72	3
	MW	213	100	2
Dinoseb	MW	0.5	86	4
	MW	102	81	3
	MW	102	81	3
MCPA	DW	2020	98	4
	MW	2020	73	3
	MW	21400	97	2
MCPP	DW	2080	94	4
	MW	2100	97	3
	MW	20440	95	2
2,4,5-T	DW	1.1	85	6
	MW	1.3	83	4
	MW	25.5	78	5
2,4,5-TP	DW	1.0	88	5
	MW	1.3	88	4
	MW	25.0	72	5

^aAll results based upon seven replicate analyses. Esterification performed using the bubbler method. Data obtained from reference 8.

DW = ASTM Type II

MW = Municipal water

FIGURE 1.
DIAZOMETHANE GENERATOR

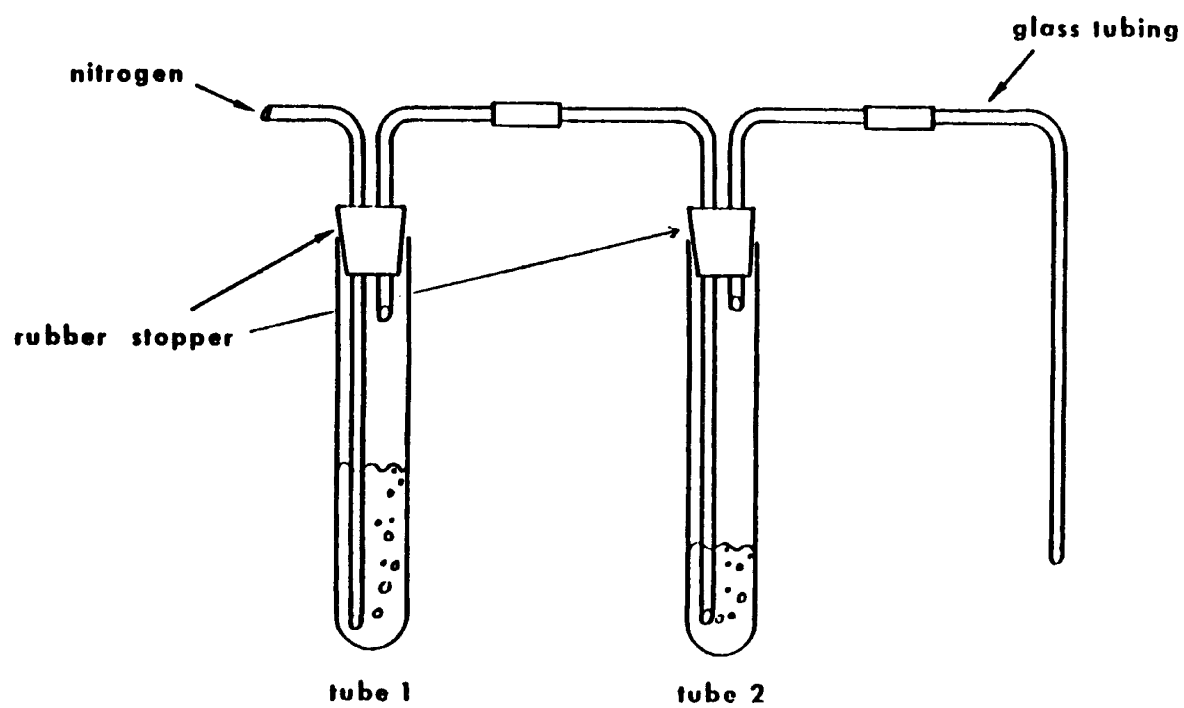


FIGURE 2.
GAS CHROMATOGRAM OF CHLORINATED HERBICIDES

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

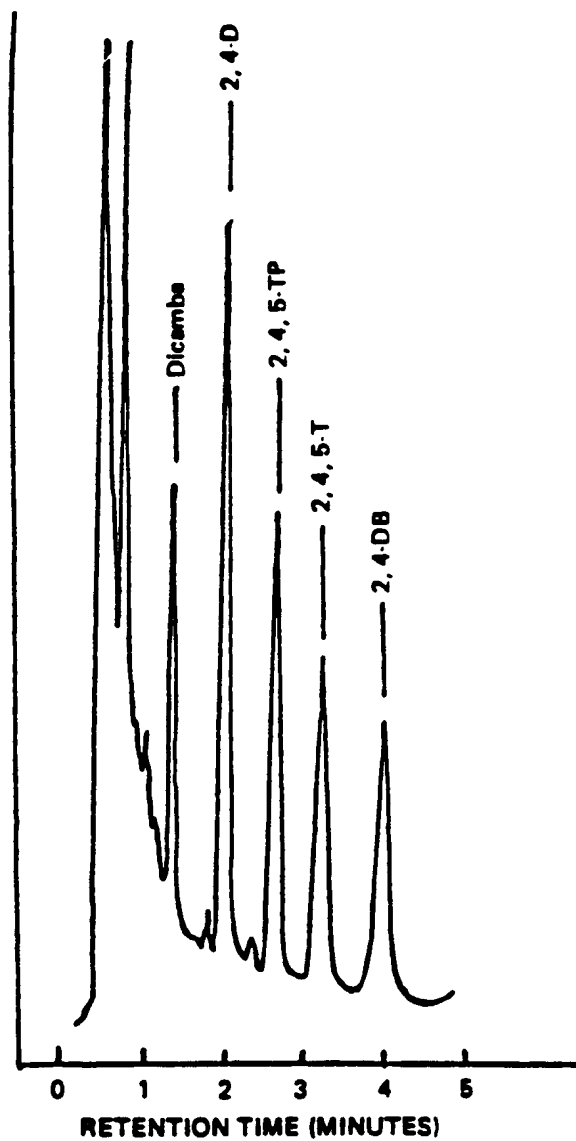


FIGURE 3.
GAS CHROMATOGRAM OF CHLORINATED HERBICIDES

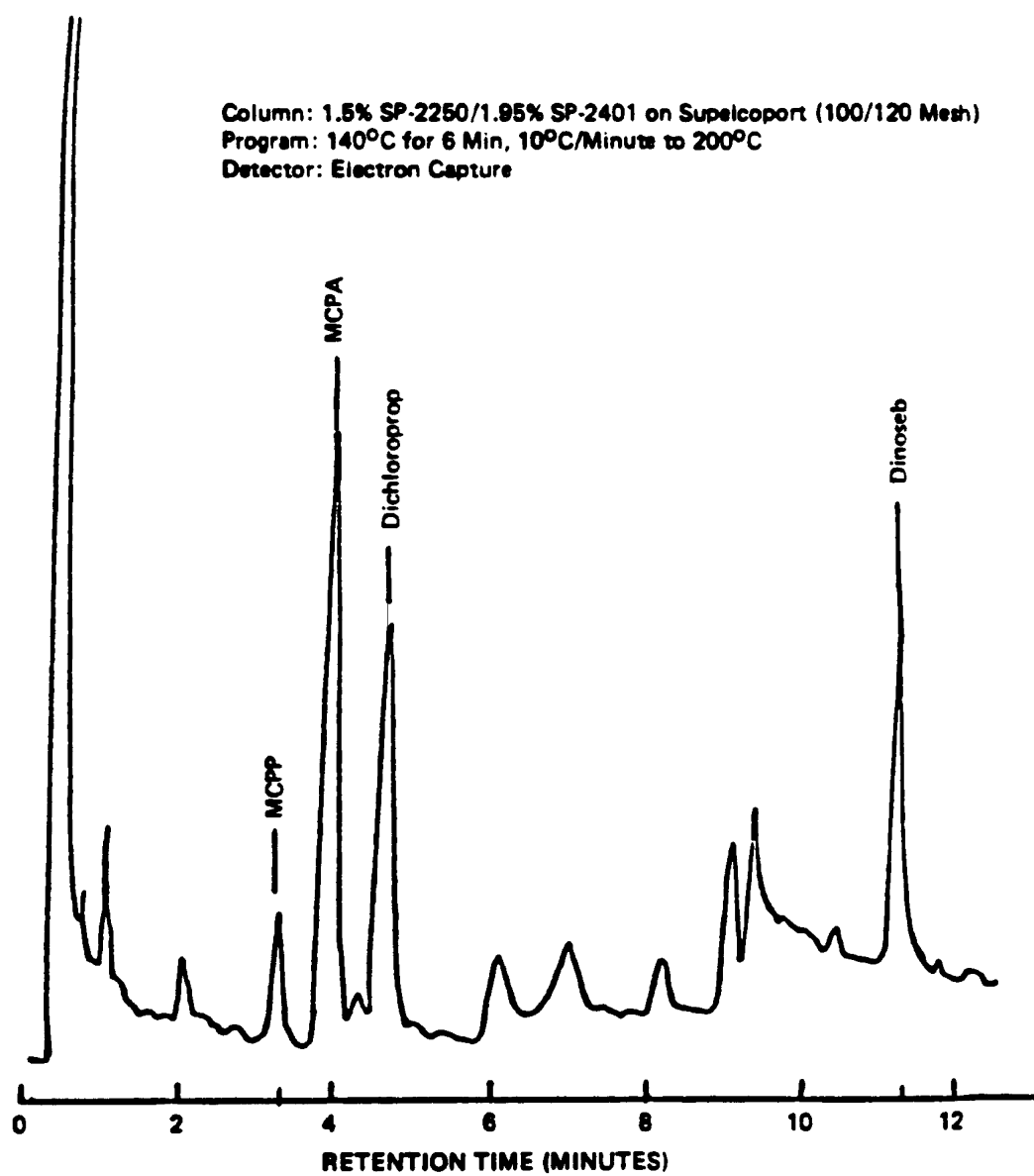
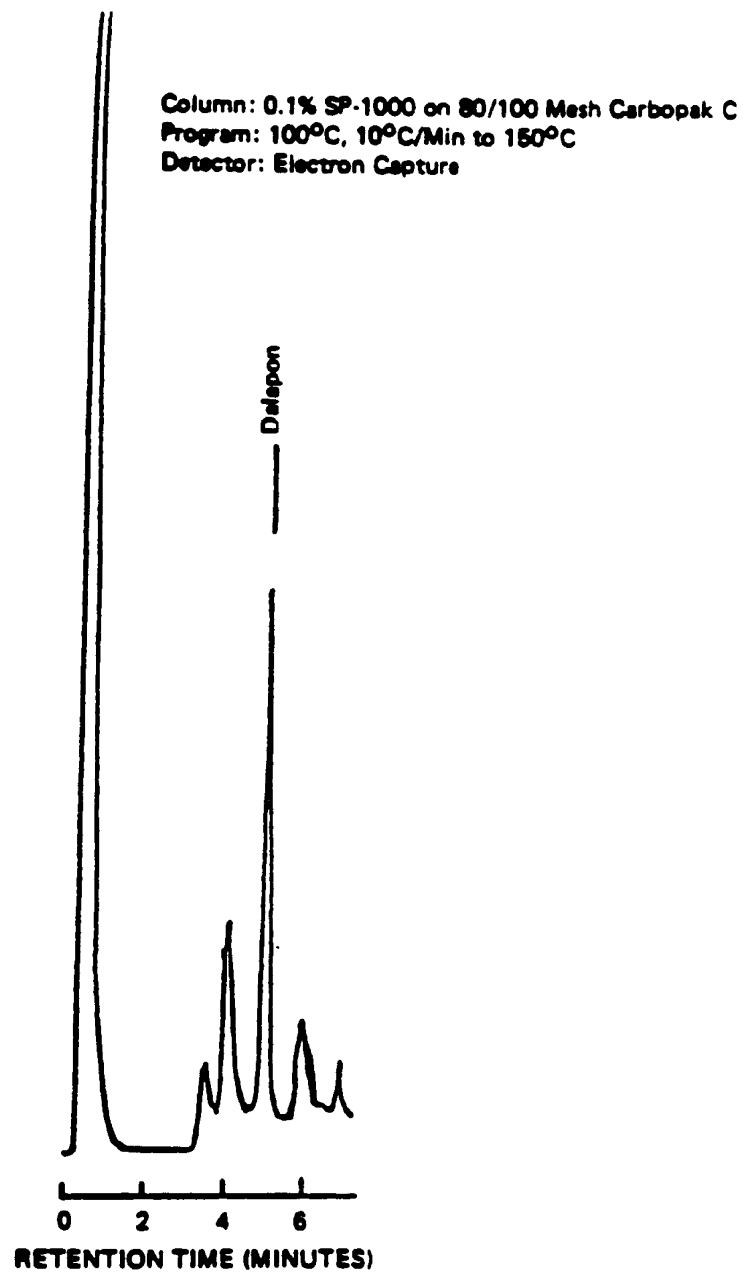
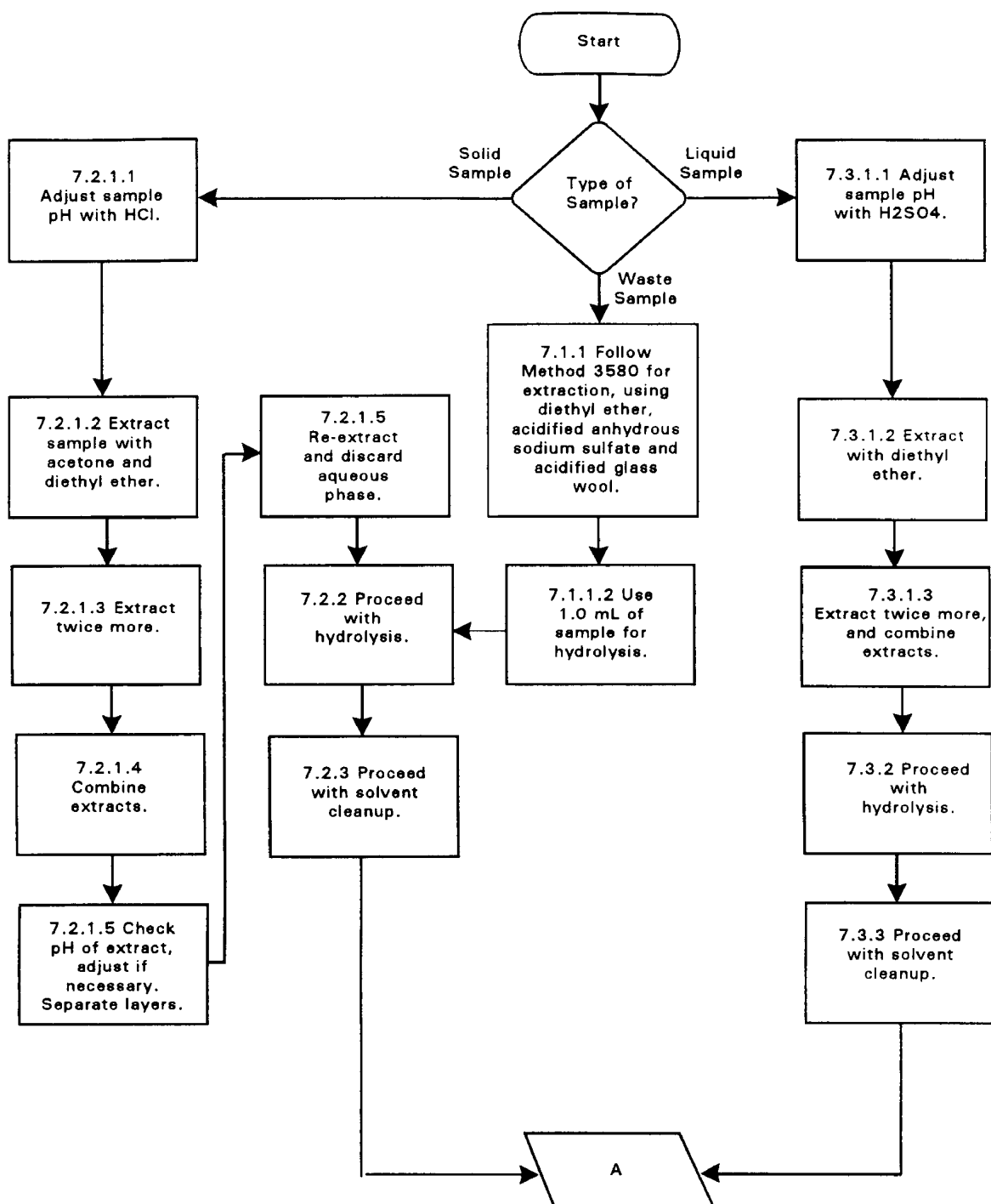


FIGURE 4.
GAS CHROMATOGRAM OF DALAPON, COLUMN 3



METHOD 8150B
CHLORINATED HERBICIDES BY GAS CHROMATOGRAPHY



METHOD 8150B
(Continued)

