Method 515: Determination of Chlorinated Herbicides in Drinking Water

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METHOD 515: THE DETERMINATION OF CHLORINATED HERBICIDES IN DRINKING WATER

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of certain chlorinated acid herbicides in drinking water. This method is applicable, but not limited to, the analyses of the following parent acids and salts and esters of these acids. The chemical form of each acid is not distinguished. Results are calculated and reported as total free acid.

Analyte	Chemical Abstract Services Registry Number (CAS)
2,4-D	94-75-7
2,4-DB	94-82-6
Dicamba	1918-00-9
2,4,5-T	93-76-5
2,4,5-TP (Silvex)	93-72-1
Dalapon	75-99-0
Pentachlorophenol (PCP)	87-86-5
Dinoseb	88-85-7
Picloram	1918-02-1

1.2 The estimated detection limit (EDL) for each analyte above is given in Table 1 for capillary column chromatography. The EDLs were determined by the esterification and analyses of replicate 1 mL acid calibration standards as described in Sect. 7.3. Thus the variability represented by the EDL is that of the esterification and analysis portions and not of the total procedure. The method detection limit (MDL) for each analyte is given in Table 2 for packed column chromatography.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of GC and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.3.

1.4 When this method is used to analyze unfamiliar samples for any or all of the analytes above, identifications should be supported by at least one additional qualitative technique.

2. SUMMARY OF METHOD

2.1 A measured volume of sample, ca. 1 liter, is acidified to convert any salts present to the parent acid. The acids and esters are extracted with ethyl ether. The esters are hydrolyzed and

converted to acid salts with potassium hydroxide solution. The aqueous phase containing the acid salts is then solvent washed to remove extraneous organic material. After acidification the acids are extracted into organic phase and the sample volume reduced to 5 mL in methyl-t-butyl ether (MTBE) with a K-D concentrator. The acids are converted to their methyl esters by the use of a micro-diazomethane generator. The samples are then analyzed by either packed or capillary column GC using an electron capture detector (ECD).[1]

2.2 This method is a modified version of EPA Method 615, "The Determination of Chlorinated Herbicides in Industrial and Municipal Wastewater."

3. INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.6.

3.1.1 Glassware must be scrupulously cleaned.[2] Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thoroughly rinsing with dilute acid, tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 15 to 30 min. Do not heat volumetric ware. Thermally stable material, such as PCBs, might not be eliminated by this treatment. Thorough rinsing with acetone and pesticide quality hexane may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 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.

3.2 The acid forms of the herbicides are strong organic acids, which react readily with alkaline substances and can be lost during analysis. Glassware and glass wool must be acid-rinsed with (1+9) hydrochloric acid and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility (See Section 6.5).

3.3 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. 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.

3.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences may vary from source to source, depending upon the municipality sampled. Specific cleanup procedures have not yet been identified for drinking water samples.

4. SAFETY

4.1 The toxicity or carcinogenitity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[3-5] for the information of the analyst.

4.2 Diazomethane is a toxic carcinogen and can explode under certain conditions. The following precautions must be followed:

4.2.1 Use only in a well ventilated hood - do not breath vapors.

4.2.2 Use a safety screen.

4.2.3 Use mechanical pipetting aides.

4.2.4 Do not heat above 90°C - EXPLOSION may result.

4.2.5 Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers - EXPLOSION may result.

4.2.6 Store away from alkali metals - EXPLOSION may result.

4.2.7 Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

5. APPARATUS AND MATERIALS

5.1 Sample bottle - Amber borosilicate or flint glass, 1-liter or 1-quart volume, fitted with screw caps lined with TFE-fluorocarbon or aluminum foil. If amber bottles are not available, protect samples from light. The container and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only).

5.2.1 Separatory funnels - 60-mL and 2000-mL, with TFE-fluorocarbon stopcocks, ground glass or TFE stoppers.

5.2.2 Concentrator tube, Kuderna-Danish - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper is used to prevent evaporation of extracts.

5.2.3 Evaporative flask, Kuderna-Danish - 500-mL (Kontes K-570001-0500 or equivalent). Attached to concentrator tube with springs.

5.2.4 Synder column, or Kuderna-Danish - three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.5 Snyder column, Kuderna-Danish - two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.6 Erlenmeyer flask - Pyrex, 250 mL with 24/40 ground glass joint.

5.2.7 Vials - Amber glass, 10 to 15 mL capacity with TFE-fluorocarbon lined screw cap.

5.3 Boiling chips - approximately 10/40 mesh. Heat at 400°C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath must be located in a hood.

5.5 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

5.6 Diazomethane generator - assemble from two 20 x 150 mm test tubes, two Neoprene rubber stoppers and a source of nitrogen. The generator assembly is shown in Figure 1 along with the diazomethane collection vessel.

5.7 Diazomethane Collector - An approximately 2 liter thermos for ice bath or cryogenically cooled vessel (Thermoelectrics Unlimited Model SK-12 or equivalent).

5.8 Glass wool - Acid washed (Supelco 2-0383 or equivalent).

5.9 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection, split/splitless capillary injection and all required accessories including syringes, analytical columns, gases, detector and strip-chart recorder. A data system is recommended for measuring peak areas.

5.9.1 Column 1 - Capillary, DB-1, 30 m x 0.32 mm ID, 0.25 µm film thickness or equivalent.

5.9.2 Column 2 - Capillary, DB-5, 30m x 0.32 mm ID, 0.25 µm film thickness or equivalent.

5.9.3 Column 3 - 180 cm long x 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

5.9.4 Column 4 - 180 cm long x 4 mm ID glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

5.9.5 Detector - Electron capture. This detector has proven effective in the analysis of drinking water and was used to develop the method performance statements in Section 15. Alternative detectors, including a mass spectrometer, may be used in accordance with the provisions described in Section 12.1.

6. REAGENTS

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

6.2 Methanol - Pesticide quality or equivalent.

6.3 Ethyl ether - (Burdick and Jackson Product No. 107 or equivalent). Nanograde, redistilled in glass if necessary. Ethers must be free of peroxides as indicated by EM Quant test strips · Procedures recommended for removal of peroxides are provided with the test strips. Ethers must be periodically tested (monthly) for peroxide formation during use.

6.4 Methyl-t-butyl ether - (Burdick and Jackson Product No. 242 or equivalent). Nanograde, redistilled in glass if necessary Same peroxide precautions apply as for ethyl ether.

6.5 Sodium sulfate - (ACS) Granular, acidified, anhydrous. Heat treat in a shallow tray at 400°C for a minimum of 4 h to remove phthalates and other interfering organic substances. Alternatively, Soxhlet extract with methylene chloride for 48 h. Acidify by slurrying 100 g sodium sulfate with enough ethyl ether to just cover the solid. Add 0.1 mL concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. It must be below pH 4. Store at 130°C.

6.6 Hydrochloric acid (1+9) - (ACS) Add one volume of conc. HCl to 9 volumes reagent water.

6.8 Potassium hydroxide solution - 37% aqueous solution (W:V). Dissolve 37 g ACS grade KOH pellets in reagent water and dilute to 100 mL.

6.9 Sulfuric acid solution (1+1) - Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

6.10 Sulfuric acid solution (1+3) - Slowly add 25 mL H_2SO_4 (sp. gr. 1.84) to 75 mL of reagent water. Store and maintain at 4°C.

6.11 Carbitol - (Diethylene glycol monoethyl ether), ACS. Available from Aldrich Chemical Co.

6.12 Diazald - (N-methyl-N-nitroso-p-toluenesulfonamide), ACS. Available from Aldrich Chemical Co.

6.13 Diazald Solution - Prepare a solution containing 10 grams Diazald in 100 mL of a 50:50 by volume mixture of ethyl ether and carbitol. This solution is stable for one month or longer when stored at 4°C in an amber colored bottle with a teflon-lined screw cap.

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

6.15 Boiling chips - Approximately 10/40 mesh. Heat at 400°C for 1 h or Soxhlet extract with methylene chloride.

6.16 Stock standard solutions (1.00 µg/µL) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.16.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure acids. Dissolve the material in pesticide quality MTBE 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.

6.16.2 Transfer the stock standard solutions into Telfon-sealed screw-cap vials. 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.

6.16.3 Secondary dilution standard - Use stock standard solutions to prepare secondary dilution standard solutions that contain the analytes in methyl-t-butyl ether. The secondary dilution standard should be prepared at a concentration such that 50 to 200 µL of the solution can be added to 25, 50, or 100 mL of MTBE to prepare calibration solutions that bracket the working concentration range.

7. CALIBRATION

7.1 Establish GC operating parameters equivalent to those indicated in Tables 2 and 3.

7.2 For each analyte of interest, prepare acid calibration standards at a minimum of three concentration levels by adding accurately measured volumes of one or more secondary dilution standards to a volumetric flask and diluting to volume with MTBE. One of the external standards should be representative of a concentration near, but greater than the detection limits. The other concentrations should corres- pond to the range of concentrations expected in the sample concentrates or should define the working range of the detector.

7.3 Prepare methyl ester calibration standards by esterification of 1.00 mL volumes of the working standards as described in Section 11. Inject 1 to 2 µL of each calibration standard and tabulate peak height or area responses against the mass of free acid represented by the injection. The results can be used to prepare 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 concentra- tion. If the relative standard deviation of the calibration factor is less than 10% over the working range, the average calibration factor can be used in place of a calibration curve.

7.4 The working calibration curve or calibration factor must be verified on each working shift by the preparation of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that parameter.

8. QUALITY CONTROL

8.1 Each laboratory using this method is required to operate a formal quality control (QC)program. The minimum requirements of this program consist of an initial demonstration of laboratory capa- bility and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data thus generated. Specific minimum QC requirements consist of:

8.1.1 Demonstration of the ability to generate acceptable accuracy and precision with this method (Section 8.3).

8.1.2 Definition of method performance criteria for each spike concentration and analyte being measured (Section 8.4).

8.1.3 Demonstration of continuing laboratory performance by monitoring analyte recoveries from spiked samples (Section 8.5).

8.1.4 Analysis of reagent blanks to detect introduction of reagent and glassware interferences (Section 8.6).

8.1.5 Confirmation of detected analytes (Section 8.7).

8.1.6 Additional quality assurance (QA) procedures as required (Section 8.7).

8.2 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 8.3.

8.3 Accuracy and Precision - To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.3.1 For each compound to be measured, using stock standards, prepare a QC check sample concentrate in methanol at a concentration of 5 µg/mL.

8.3.2 Using a pipet, add 1.00 mL of the check sample concentrate to each of a minimum of four 1000-mL aliquots of reagent water. Analyze the aliquots according to the method beginning in Section 10.

8.3.3 Calculate the average percent recovery (R), and the standard deviation of the percent recovery (s), for the results.

8.3.4 Using the appropriate data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values calculated in Section 8.3.3. If the data are not comparable, review potential problem areas and repeat the test.

8.4 Method Performance Criteria - The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.4.1 Calculate upper and lower control limits for method performance as follows:

Upper Control Limit (UCL) = R + 2 s
Lower Control Limit (LCL) = R - 2 s

where R and s are calculated as in Section 8.3.3. The UCL and LCL can be used to construct control charts[6] that are useful in observing trends in performance.

8.4.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for drinking water samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of drinking water as described in Section 8.3.2. followed by the calculation of R and s. Alternatively, the analyst may use four drinking water data points gathered through the requirement for continuing quality control in Section 8.5. The accuracy statements should be updated regularly.[6]

8.5 Analyte Recoveries - The laboratory is required to collect in duplicate a portion of their samples to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one spiked sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.3. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 13.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.6 Reagent Blanks - Before processing any samples, the analyst must demonstrate through the analysis of a 1-liter aliquot of reagent water that all glassware and reagents interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

8.7 Additional QC - It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are more productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as GC with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of QC materials and participate in relevant performance evaluation studies.

9. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[7] should be followed; however, the bottle must not be prerinsed with sample before collection.

9.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

9.3 All samples must be extracted within seven days, and completely analyzed within 40 days of extraction.

10. SAMPLE EXTRACTION, HYDROLYSIS AND CONCENTRATION

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-liter separatory funnel. Check the pH with wide-range pH paper and adjust to pH less than 2 with sulfuric acid (1+1). Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Alternatively, the sample volume may be determined by weighing before and after the sample bottle is emptied.

10.2 Add 150 mL ethyl ether to the sample bottle, cap the bottle and shake 30 s to rinse the walls. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation or other physical means. Drain the aqueous phase into a 1000-mL Erlenmeyer flask and collect the extract in a 250-mL ground-glass Erlenmeyer flask containing 2 mL of 37% potassium hydroxide solution. Approximately 80 mL of the ethyl ether will remain dissolved in the aqueous phase.

10.3 Add a 50-mL volume of ethyl ether to a sample bottle and repeat the extraction a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Add 15-mL reagent water and 1 or 2 clean boiling chips to the 250-mL flask and attach a three-ball Snyder column. Prewet the Snyder column by adding 1 mL ethyl ether to the top. Place the apparatus on a hot water bath (60 to 65°C), such that the bottom of the flask is bathed in the water vapor. Although the ethyl ether will evaporate in about 15 min, continue heating for a total of 60 min, beginning from the time the flask is placed on the water bath. Remove the apparatus from the bath and let stand at room temperature for at least 10 min.

10.5 Transfer the solution to a 60-mL separatory funnel using 5 to 10 mL of reagent water. Wash the basic solution twice by shaking for one min with 20-mL portions of ethyl ether. Discard the organic phase. The acid salts remain in the aqueous phase.

10.6 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1+3). Test the pH with indicator paper. Add 20 mL ethyl ether and shake vigorously for 2 min. Drain the aqueous layer into the 250-mL Erlenmeyer, then pour the organic layer into a 125-mL Erlenmeyer flask containing about 5 g of acidified, anhydrous sodium sulfate. Repeat the extraction twice more with 10-mL aliquots of ethyl ether, combining all solvent in the 125-mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 h.

10.7 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

10.8 Pour the combined extract through a funnel plugged with acid washed glass wool, and collect the extract in the K-D concentrator. Use a glass rod to crush any caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20 to 30 mL of ethyl ether to complete the quantitative transfer.

10.9 Add 1 to 2 clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL ethyl ether to the top. Place the K-D apparatus on a hot water bath, 60 to 65°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. 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 and allow it to drain and cool for at least 10 min.

10.10 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of ethyl ether using a disposable pipet or syringe. Add 1 mL MTBE and a fresh boiling chip. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 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 to 10 min. When the apparent volume of liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column and rinse the walls of the concentrator tube while adjusting the volume to 3-4 mL with MTBE.

11. ESTERIFICATION OF ACIDS

11.1 Assemble the diazomethane generator shown in Figure 1 in a hood. The collection vessel is a 10-15 mL vial, equipped with a teflon-lined screw cap and maintained at 0-5°C.

11.2 Add a sufficient amount of ethyl ether to tube 1 to cover the first impinger. Add 5 mL of MBTE to the collection vial. Set the nitrogen flow at 5–10 cm^3/min. Add 2 mL Diazald solution (Sect. 6.13) and 1.5 mL of 37% KOH solution to the second impinger. Connect the tubing as shown and allow the N_2 flow to purge the diazomethane from the reaction vessel into the collection vial for 30 min. Cap the vial when collection is complete and maintain at 0–5°C. When stored at 0–5°C this diazomethane solution may be used over a period of 48 h.

11.3 To each concentrator tube containing sample or standard, add 250 µL methanol and 0.5 mL of diazomethane solution (Sect. 11.2). Dilute to 5.0 mL with MTBE.

11.4 Seal the concentrator tubes with teflon or glass stoppers and store in the hood at room temperature for 5 min.

11.5 Open the concentrator tube and destroy any unreacted diazomethane by adding approximately 0.2 g activated silica to the samples. The samples are now ready for analysis by GC. Analyze as soon as possible. The samples may be stored in the stoppered concentrator tubes at 0–4°C if the analysis cannot be performed immediately. The analysis should be performed within 24 hours.

12. GAS CHROMATOGRAPHY

12.1 Tables 2 and 3 summarize the recommended operating conditions for packed and capillary chromatography. Tables 1 and 2 contain estimated retention times and detection limits that can be achieved by this method. Examples of the separations achieved for the methyl esters are shown in Figures 2 and 3. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.3 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 Inject 1 to 5 µL of the sample extract for packed columns or 1–2 µL for capillary columns. Record the resulting peak size in area or peak height units. An automated system that consistently injects a constant volume of extract may also be used.

12.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

13. CALCULATIONS

13.1 Determine the concentration of individual compounds in the sample. Calculate the amount of the free acid injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated as follows:

$$\text{Concentration, } \mu g/L = \frac{(A)\ (V_t)}{(V_i)\ (V_s)}$$

where:

A = Amount of material injected, in nanograms.

V_i = Volume of extract injected in µL.

V_t = Volume of total extract in µL.

V_s = Volume of water extracted in liters.

13.2 Report results in micrograms per liter as acid equivalent without further correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.3 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.4, data for the affected parameters should be considered unacceptable.

14. METHOD PERFORMANCE

14.1 The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[10] The detection limits listed in Tables 1 and 2 were obtained from reagent water with an electron capture detector.

14.2 In single laboratory evaluations, the average recoveries presented in Tables 4 and 5 were obtained for Column 1 of Table 1 and column 3 of Table 2.[11] The standard deviations of the percent recoveries of these measurements are also included in Tables 4 and 5.

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TABLE 1

CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS
CAPILLARY COLUMNS

Analyte (as methyl ester)	Retention Time, min. Column 1+	Column 2+	Estimated Detection* Limit (EDL) µg/L
Dalapon	3.78	2.99	.001
Dicamba	12.32	10.89	.01
2,4-D	14.63	13.78	.01
PCP	18.65	16.98	.0005
2,4,5-TP	18.98	18.65	.01
2,4,5-T	19.76	20.25	.01
2,4-DB	22.78		.07
Dinoseb	23.47	24.61	.01
Picloram	26.46	32.33	.07

* The EDL is defined here as the student t factor times the standard deviation of at least 7 replicate analyses, of a 1 mL calibration standard at a concentration near but above the EDL. These EDL values were obtained on Column 1.

+ Column 1: DB-1

Column 2: DB-5

TABLE 2

CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS
PACKED COLUMNS

Analyte (as methyl ester)	Retention Time (min.) Column 3	Column 4	Method Detection Limit µg/L
Dicamba	1.2	1.0	0.27
2,4-D	2.0	1.6	1.2
2,4,5-TP	2.7	2.0	0.17
2,4,5-T	3.4	2.4	0.20
2,4-DB	4.1	—	0.91
Dinoseb	11.2	—	0.07

Column 3 conditions: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/ 1.95% SP-2401 packed in a 1.8 m long x 4 mm ID glass column with 95% argon/5% methane carrier gas at a flow rate of 70 mL/min. Column temperature: isothermal at 185°C. An electron capture detector was used to measure MDL.

Column 4 conditions: Gas Chrom Q (100/120 mesh) coated with 5% OV-210 packed in a 1.8 m long x 4 mm ID glass column with 95% argon/5% methane carrier gas at a flow rate of 70 mL/min. Column temperature: isothermal at 185°C.

TABLE 3

Recommended Capillary GC Operating Conditions

Column Type:	DB-1 or DB-5
Film Thickness:	0.25 µm
Column Dimension:	30 m x 0.32 mm
Helium Linear Velocity:	28-29 cm/sec
Injection Port Temp:	200°C
Detector Temp:	Column 3 - 290°C
	Column 4 - 200°C
Temperature Program:	Column 1 - DB-1. Inject at 100°C and program immediately at 12°C/min to 200°C and hold until picloram elutes.
	Column 2 - DB-5. Inject at 80°C and hold 2 min. Program at 16°C/min to 160°C and hold until picloram elutes.

TABLE 4

SINGLE OPERATOR ACCURACY AND PRECISION AS DETERMINED BY CAPILLARY COLUMN GC[a]

Analyte	Spike Level[b] ug/L	AVG[c] Recovery %	% RSD
Dalapon	4.05	91	9
Dicamba	4.13	87	11
2,4-D	4.01	87	11
PCP	1.01	63	11
Silvex	4.05	87	13
2,4,5-T	4.23	85	13
2,4-DB	4.02	63	32
Dinoseb	4.12	56	19
Picloram	4.01	62	14

[a]Data obtained on column 1

[b]The matrix is reagent water

[c]All results based on seven replicate analyses

TABLE 5.

SINGLE OPERATOR ACCURACY AND PRECISION*
FOR PACKED COLUMN GC

Parameter	Sample Type	Spike (µg/L)	Mean Recovery (%)	Standard Deviation(%)
2,4,D	RW	10.9	75	4
	DW	10.1	77	4
	DW	200	65	5
2,4-DB	RW	10.3	93	3
	DW	10.4	93	3
	DW	208	77	6
Dicamba	RW	1.2	79	7
	DW	1.1	86	9
	DW	22.2	82	6
2,4,5-T	RW	1.1	85	6
	DW	1.3	83	4
	DW	25.5	78	5
2,4,5-TP	RW	1.0	88	5
	DW	1.3	88	4
	DW	25.0	72	5
Dalapon	RW	23.4	66	8
	DW	23.4	96	13
Dinoseb	DW	0.5	86	4
	DW	102	81	3

*All results based upon seven replicate analyses.

RW = Reagent water
DW = Drinking water

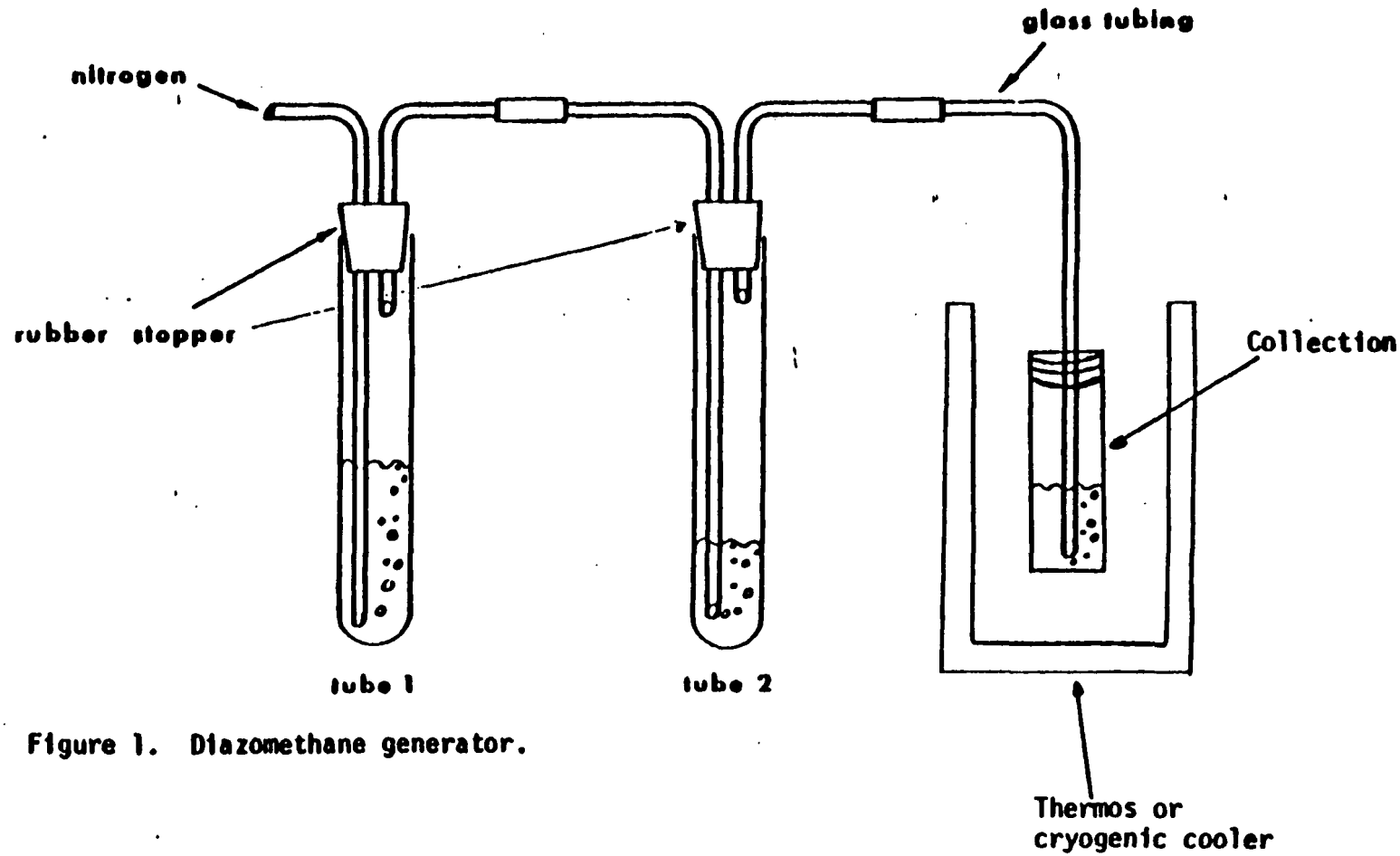

Figure 1. Diazomethane generator.

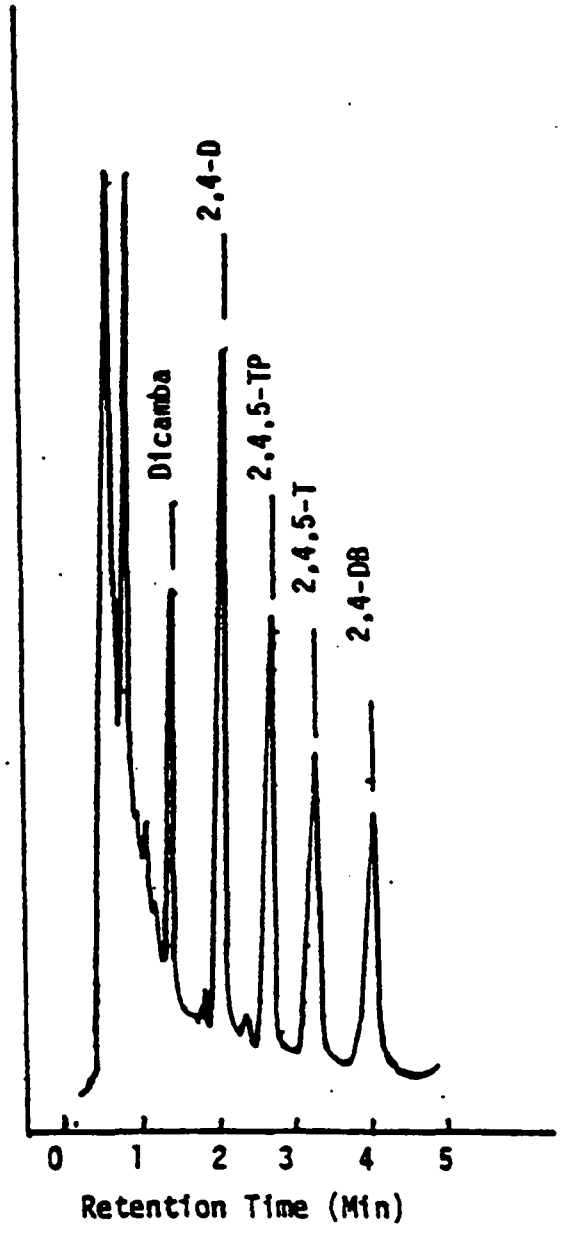

Figure 2. Gas chromatogram of methyl esters of chlorinated herbicides on Column 1. For conditions, see Table 1.

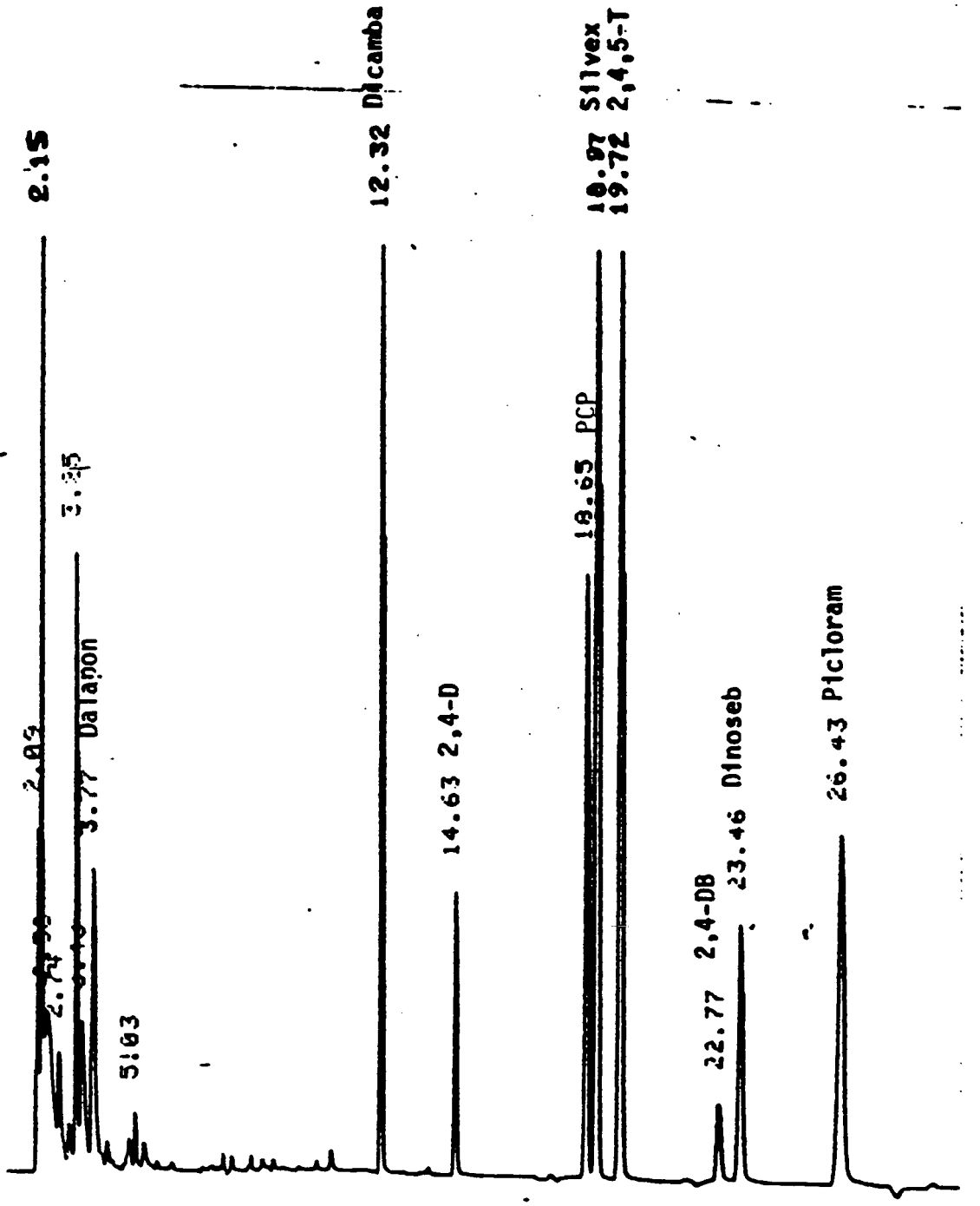

Figure 3. Gas Chromatogram of Methyl Esters of Chlorinated Herbicides on Column 3. For Conditions, See Table 4.