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Method for the Analysis of Acid and Neutral Herbicides in Natural Waters (Gas Chromatographic)

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METHOD FOR THE ANALYSIS OF ACID AND NEUTRAL HERBICIDES IN NATURAL WATERS

(Gas Chromatographic)

1. SCOPE AND APPLICATION

1.1 This method is applicable to the qualitative and quantitative gas chromatographic determination of the following ten acid and seven neutral herbicides simultaneously in natural waters:

2-methoxy-3,6-dichlorobenzoic acid	(DICAMBA)
4-chloro-2-methylphenoxyacetic acid	(MCPA)
2-(2,4-dichlorophenoxy)-propionic acid	(2,4-DP)
2,3,6-trichlorobenzoic acid	(2,3,6-TBA)
2,4-dichlorophenoxyacetic acid	(2,4-D)
2-(2,4,5-trichlorophenoxy)-propionic acid	(SILVEX)
2,4,5-trichlorophenoxyacetic acid	(2,4,5-T)
4-(4-chloro-2-methylphenoxy)-butyric acid	(MCPB)
4-(2,4-dichlorophenoxy)-butyric acid	(2,4-DB)
4-amino-3,5,6-trichloropicolinic acid	(PICLORAM)
2,6-dinitro-N,N-dipropyl-4-trifluoromethyl aniline	(TRIFLURALIN)
S-(2,3-dichloroallyl)-N,N-diisopropyl thiocarbamate	(DIALLATE)
S-(2,3,3-trichloroallyl)-N,N-diisopropyl thiocarbamate	(TRIALLATE)
2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine	(ATRAZINE)
4-chloro-2-butynyl-N-(3-chlorophenyl)-carbamate	(BARBAN)
Methyl-2-[4-(2',4'-dichlorophenoxy)-phenoxy]-propionate	(DICLOFOP-METHYL)
Ethyl N-benzoyl-N-(3,4-dichlorophenyl)-2-aminoproprionate	(BENZOYLPROP - ETHYL)

1.2 The practical limits of measurement based on a 1L water sample and utilizing a Nitrogen-Phosphorus Detector for Atrazine and electron capture detection for the remaining herbicides are as follows:

Herbicide	Method Detection Limits* (µg/L)	NAQUADAT No.
Dicamba	.02	
MCPA	.02	
2,4-DP	.02	
2,3,6-TBA	.02	
2,4-D	.02	
Silvex	.02	
2,4,5-T	.04	
MCPB	.04	
2,4-DB	.04	
Picloram	.04	
Trifluralin	.001	
Diallate	.025	
Triallate	.002	
Atrazine	.025	
Barban	.025	
Diclofop-Methyl	.010	
Benzoylprop-Ethyl	.005	

* Based on a 1-L water sample and volume of extract made up to 10 mL for GLC analysis. For definition of Method Detection Limit, see 12.6.

2. PRINCIPLE AND THEORY

2.1 The water sample is acidified to pH 1 or less and extracted with an organic solvent (dichloromethane).

2.2 The acid herbicides are selectively back-extracted into a 2% potassium bicarbonate solution. Dichloromethane rinsings of this solution are then added to the original organic extract. These steps effectively separate the acid and neutral herbicides into aqueous and organic phases, respectively.

2.3 The aqueous phase is acidified to pH 1 or less and extracted with dichloromethane. The solvent is evaporated and the residue is dissolved in acetone in preparation for derivitization.

2.4 The ten acid herbicides are derivitized to their corresponding pentafluorobenzyl esters in order to increase their sensitivity to electron capture. Cleanup and fractionation on a Silica Gel column ready the compounds for determination by EC-GLC analysis.

2.5 The neutral herbicide - containing organic phase (from 2.2) is dried through anhydrous sodium sulphate and concentrated to approximately 3 mL. Cleanup and fractionation on a Florisil column provides two fractions which can then be analyzed by GLC using electron capture and nitrogen-phosphorus detection.

2.6 The method presented here can readily be modified for the analysis of either the acid or neutral herbicides separately, if required.

3. INTERFERENCES

3.1 Extraneous matter, especially in highly coloured water samples, is a potential interference. The cleanup procedures described in this method will usually eliminate this source of interference.

3.2 All reagents must be thoroughly checked and any interferences from this source eliminated.

4. SAMPLING PROCEDURE AND STORAGE

4.1 Water samples should be collected and stored in an all-glass system and acidified immediately to pH 1 or less with dilute sulphuric acid (1+1).

4.2 Teflon-lined bottle caps are recommended to prevent contamination of the water sample from contact with the cap. If Teflon-lined caps are unavailable, the use of solvent-washed aluminum foil beneath the cap is acceptable.

4.3 Samples should be kept in the dark at 4°C and extracted as soon as possible.

5. SAMPLE PREPARATION

5.1 No special preparation.

6. APPARATUS

6.1 Capillary GLC analysis of acid herbicide PFB esters.

6.1.1 A gas chromatograph with good sensitivity equipped with a split/splitless capillary column injection port and an electron capture detector (^{63}Ni) such as Hewlett-Packard Model 5880A or equivalent.

6.1.2 Automatic Liquid Sampler such as Hewlett-Packard Model 7671A or equivalent. If this is not available, use a 10 µL Hamilton micro-syringe and inject 2 µL.

6.1.3 Fused Silica Capillary Column (FSCC): SE-54 or DB-5 FSCC (30 m x .25 mm i.d), .25 µm film thickness, available from J&W Scientific Ltd. or equivalent.

6.1.4 Chromatographic conditions:

Injection Port: splitless mode, splitless valve on for 30 s

Injection Port Temperature: 250°C

Detector: Ni-63 ECD

Detector Temperature: 300°C

Detector Make-Up Gas: Argon/methane (95+5) at 25 mL/min

Carrier Gas: Helium

Column Head Pressure: 20 psi

Column Temperature Initial: 70°C; hold for 0.5 min

Programming Rate 1: 30°C/min (70°-200°C); hold for 10.0 min

Programming Rate 2: 30°C/min (200°-220°C); hold for 10.0 min

Column Post-Run Final Temperature: 250°C for 15-20 min

Chart Speed: 1.0 cm/min.

6.2 Packed Column GLC Analyses

6.2.1 A gas chromatograph with good sensitivity for packed column analyses equipped with an electron capture detector (^{63}Ni) and a nitrogen-phosphorus detector (NPD) such as Hewlett-Packard Model 5710A or equivalent.

6.2.2 Automatic Liquid Sampler such as Hewlett-Packard Model 7671A or 7672A or equivalent. If this is not available, use a 10 µL Hamilton micro-syringe for injections.

6.2.3 GLC glass columns (1.8 m x 2 mm i.d.), packed with 3% OV-1 on Gas Chrom Q, 100/120 mesh, available from Chromatographic Specialties Limited.

6.2.4 Chromatographic conditions for GC-ECD:

Injection Port Temperature:

(a) 250°C for analysis of Picloram-PFB ester;

(b) 200°C for Neutral Herbicide analyses.

Detector: Ni-63 ECD

Detector Temperature: 300°C

Oven Temperature:

(a) 200°C isothermal for Picloram-PFB ester analysis;

(b) 185°C isothermal for Neutral Herbicide analyses.

Carrier Gas: Argon/methane (95+5) at 24 mL/min.

Chart Speed: 0.5 cm/min

Slope Sensitivity: 0.10

Note: Preliminary priming of the column with a high concentration BARBAN solution is recommended to improve the sensitivity to this herbicide.

6.2.5 Chromatographic conditions for GC-NPD (Atrazine analysis):

Injection Port Temperature: 200°C

Detector: Nitrogen-specific; NPD collector voltage at 14.5V

Detector Temperature: 300°C

Detector Gases: Hydrogen at 3 mL/min; Air at 50 mL/min

Oven Temperature: isothermal at 185°C

Carrier Gas: Helium at 20 mL/min

Injection Volume: 3.0 µL

Chart Speed: 15 in/hr.

Note: The voltage of the NPD collector is an arbitrary setting determined by adjustment of the potential until a sensitivity of 50% recorder deflection at attenuation 1 x 32 or similar is obtained.

6.3 Magnetic stirrers with 51 mm x 9.5 mm o.d. Teflon-coated spin-bars.

6.4 Solvent Evaporator with thermostatted bath such as Büchi Rotavapor Model RE-120 or equivalent, available from Brinkman Instruments.

6.5 Oven, capable of maintaining 200°C.

6.6 Centrifuge tube heater such as the Kontes Tube Heater Block or equivalent, set at 60°C, combined with a gentle stream of pure nitrogen gas for controlled evaporation.

6.7 Hamilton micro-syringes (250 µL, 100 µL, 50 µL, 10 µL).

6.8 Disposable Pasteur Pipettes (23 cm x 5 mm i.d.).

6.9 Silanized glass wool.

6.10 Volumetric flasks, "low-actinic" (100 mL, 50 mL, 25 mL).

6.11 Separatory funnels with Teflon stop-cocks (2000 mL, 500 mL, 250 mL).

6.12 Coarse (70-100 µm) sintered-glass filter funnels (100 mm x 40 mm i.d.) with a tapered ground-glass joint and suction side-arm, available from Pegasus Industrial Specialties Ltd.

6.13 Round-bottomed flasks (500 mL).

6.14 Chromatographic columns (20 mm i.d. x 500 mm) with Teflon stop-cocks.

6.15 Graduated centrifuge tubes (15 mL) with ground-glass stoppers.

Note: All glassware must be thoroughly washed with a hot solution of laboratory detergent followed by rinses with hot tap water, 2-3 rinses of distilled water and a final acetone rinse to remove the water. The glassware (except for volumetric pipettes and syringes) should be dried at 130°C for at least two hours. Thorough rinsing with organic solvent immediately prior to using the glassware is recommended.

7. REAGENTS

7.1 All solvents must be Distilled-In-Glass, Pesticide Residue grade and must be checked before use for low blank values.

7.1.1 Dichloromethane (methylene chloride).

7.1.2 Hexane.

7.1.3 Acetone.

7.1.4 Benzene.

7.1.5 Methanol.

7.1.6 Iso-octane.

7.1.7 Toluene.

7.1.8 Ethyl Acetate.

7.2 All chemicals must be of highest purity and should be washed with solvent and preheated where necessary.

7.2.1 Purified (organic-free) water. Pass distilled water through Millipore Super-Q unit (Millipore Corp). Extract 1 L water three times by stirring with 50 mL dichloromethane for 30 minutes. Discard organic layers.

7.2.2 Dilute Sulphuric Acid, ACS grade or better. Prepare a (1+1) v/v solution with purified (organic-free) water.

7.2.3 2% Potassium Bicarbonate Solution. Dissolve 20 g anhydrous $KHCO_3$ in purified (organic-free) water and dilute to 1000 mL.

7.2.4 30% Potassium Carbonate Solution. Dissolve 15 g anhydrous K_2CO_3 in purified (organic-free) water and dilute to 50 mL.

7.2.5 Pentafluorobenzyl Bromide (PFBBr) Reagent. Dissolve 1 g PFBBr (Aldrich Chemical Co.) in 19 mL dry acetone (< .2% water). Keep in the dark at 4°C. Prepare fresh once every two weeks. **CAUTION: Reagent is a strong lachrymator.**

7.2.6 Sodium sulphate (anhydrous, Reagent grade), available from BDH Chemicals. Heat 18 hours at 650°C and store in a clean glass bottle in a dessicator.

7.2.7 5% Deactivated Silica Gel. Activate Silica Gel adsorbent (grade 950 for gas chromatography, 60/200 mesh, Fisher Scientific Co.) by heating for 18 hours at 130°C. Deactivate by adding 5 g purified (organic-free) water to 95 g activated Silica Gel. Mix well by tumbling for 18 hours in a tightly sealed glass container. Prepare fresh weekly.

7.2.8 10% Deactivated Florisil. Florisil PR, 60-100 mesh (Supelco Inc.) should be calcined at 650°C for 24 hours and then stored at 130°C until needed. Deactivate by adding 10 g pure (organic-free) water to 90 g activated Florisil. Mix well by tumbling for 18 hours in a tightly sealed glass container. Prepare fresh weekly.

7.3 Analytical Standards. Herbicidal acids and neutral herbicides should be analytical grade (98+% purity). Obtain from manufacturers or U.S. Environmental Protection Agency and use without further purification.

7.3.1 Prepare 1000 ppm stock solutions of each individual herbicide: (a) dissolve 100 mg of individual acid herbicides in 100 mL ethyl acetate; (b) dissolve 100 mg of individual neutral herbicides in 100 mL toluene. Store at 4°C in the dark.

7.3.2 Prepare a mixed Acid Herbicide Solution by combining appropriate aliquots of the ten individual acid herbicide stock solutions and diluting to 100 mL with acetone. To prepare a GLC standard solution for calibration, derivitize and cleanup 100 µL to 1.0 mL of the mixed solution as per steps 8.2 and 8.3 of the procedure.

7.3.3 Prepare a mixed Neutral Herbicide Standard for GLC calibration by combining appropriate aliquots of the seven individual neutral herbicide stock stolutions and diluting to 100 mL with iso-octane/acetone (99+1). Store at 4°C in the dark.

8. PROCEDURE

8.1 Extraction

8.1.1 Stir a 1-L water sample in a 1.14-L glass bottle on a magnetic stirrer, using a Teflon stirring bar so that the vortex formed at the surface almost reaches the bottom of the bottle. Carefully add dilute sulphuric acid (1+1) in drops until the pH is 1 or less. (Use pH paper).

8.1.2 Add 50 mL of dichloromethane (methylene chloride) and tightly cover the bottle with an aluminum-lined cap. After stirring for 30 min, transfer the contents of the bottle to a 2-L separatory funnel and shake for 1 min.

8.1.3 Transfer the organic layer to a clean 500-mL separatory funnel.

8.1.4 Return the aqueous layer to the original 1.14-L glass bottle. Rinse the 2-L separatory funnel with 50 mL of methylene chloride and transfer to the 1.14-L glass bottle. Tightly cover the bottle with the aluminum-lined cap and stir for 30 min. Transfer the contents of the bottle to the 2-L separatory funnel and shake for 1 min.

8.1.5 Transfer the organic layer to the 500-mL separatory funnel containing the first 50-mL methylene chloride extract.

8.1.6 Repeat steps 8.1.4 and 8.1.5 with another 50 mL methylene chloride. Discard the aqueous layer.

8.1.7 Add 100 mL of potassium bicarbonate solution (2%) to the 500-mL separatory funnel containing the methylene chloride extract and shake vigorously for 2 min. Vent often to release the gas. Ensure the pH of the aqueous layer is 8 or greater (use pH paper). Separate layers and transfer the organic layer to a clean 250-mL separatory funnel.

8.1.8 Add 50-mL of potassium bicarbonate solution (2%) to the methylene chloride in the 250-mL separatory funnel. Shake vigorously for 2 min and allow the layers to separate. Drain the organic layer through a (vacuum) sintered glass funnel containing 75 mm of anhydrous sodium sulphate. Collect the dried extract in a clean 500-mL round-bottomed flask.

8.1.9 Transfer the aqueous layer to the first 500-mL separatory funnel.

8.1.10 Rinse the 250-mL separatory funnel twice with 50 mL methylene chloride and add the rinsings to the aqueous solution in the 500-mL separatory funnel. Shake vigorously 1 min and drain the organic layer through the sodium sulphate column into the 500-mL round-bottomed flask.

8.1.11 Repeat step 8.1.10 with another 50 mL methylene chloride.

8.1.12 Wash the sodium sulphate column with 50 mL methylene chloride and apply a vacuum until the sodium sulphate is dry. Remove the column and add 3 mL iso-octane to the 500-mL round-bottomed flask.

8.1.13 Evaporate the methylene chloride to about 10 mL on a rotary evaporator (water bath temperature at 35°C). Add 50 mL hexane and repeat evaporation to 3 mL. (This extract contains the seven neutral herbicides and is ready for a Florisil Column cleanup).

8.1.14 Acidify the aqueous layer in the 500-mL separatory funnel (from step 8.1.10 and 8.1.11) with dilute sulphuric acid (1+1) until the pH is 1 or less (use pH paper). Agitate the solution to permit CO_2 to escape.

8.1.15 After evolution of the CO_2, extract the aqueous layer with three portions of 50 mL methylene chloride by shaking for 2 min each time. Transfer the organic layers to a clean 500-mL round-bottomed flask. Discard aqueous phase.

8.1.16 Evaporate the methylene chloride to about 20 mL on a rotary evaporator (water bath temperature at 40°C). Add 50 mL benzene and repeat evaporation until just dry.

8.1.17 Dissolve the residue with several 1 to 2 mL portions of acetone, each time transferring the acetone quantitatively into a 15-mL graduated centrifuge tube, the total volume of acetone being about 4 to 5 mL.

8.2 **Esterification by PFBBr**

8.2.1 Add 200 µL of pentafluorobenzyl bromide solution (5%) and 30 µL of potassium carbonate solution (30%) to the 15-mL centrifuge tube.

8.2.2 Stopper the tube and shake it for 1 min. Let the contents react at 60°C for three hours.

8.2.3 After the reaction, evaporate the solution to 1 mL with a gentle stream of nitrogen.

8.2.4 Add 2 mL hexane and repeat evaporation to 0.1 mL.

8.2.5 Add 2 mL of a toluene/hexane (10+90) solution.

8.3 Silica Gel Column Cleanup (of Acid Herbicide-PFB Esters)

8.3.1 Prepare micro-columns by plugging clean disposable pipettes (23 cm x 5 mm i.d.) with a clean piece of silanized glass wool.

8.3.2 Fill the columns with 5 cm of Silica Gel (5% deactivated) and tap them gently with a pencil to uniformly settle the solid. Add 0.5 cm anhydrous sodium sulphate to the top of the column.

8.3.3 Prewet the columns with 5 mL hexane and permit the hexane to drain just to the top of the sodium sulphate layer. Discard hexane eluant.

8.3.4 With a disposable pipette, apply the concentrated sample extract (from step 8.2.5) to the column. Rinse the centrifuge tube 2 mL at a time with toluene/hexane (10+90). Apply the rinses to the column, never permitting the solution to drain below the sodium sulphate layer.

8.3.5 Collect a total of 8.0 mL of the toluene/hexane (10+90) solution in a centrifuge tube. Discard this Fraction A, containing excess reagent and contaminants.

8.3.6 Elute with 8.0 mL of toluene/hexane (75+25) into a clean centrifuge tube. This Fraction B contains the PFB-esters of Dicamba, MCPA, 2,4-DP, 2,3,6-TBA, 2,4-D, Silvex, 2,4,5-T, MCPB and 2,4-DB.

8.3.7 Elute with 8.0 mL of a toluene/methanol (95+5) solution into a clean centrifuge tube. This Fraction C contains the PFB-ester of Picloram.

8.3.8 Analyze for the PFB-esters of the acid herbicides by means of electron capture gas chromatography.

8.4 **Florisil Column Cleanup (of Neutral Herbicides)**

8.4.1 Prepare macro-columns by filling chromatographic columns (500 x 20 mm i.d.) with 20 g of Florisil (10% deactivated). Tap columns gently to uniformly settle the solid. Ad 1 cm anhydrous sodium sulphate on top of the Florisil layer.

8.4.2 Prewet the columns with 100 mL hexane and let the hexane drain just to the top of the sodium sulphate layer. Discard hexane eluant.

8.4.3 Quantitatively transfer the concentrated extract (from step 8.1.13) plus rinsings onto the column with a disposable pipette.

8.4.4 When the extract just enters the sodium sulphate layer, elute the column with 150 mL of a benzene/hexane (25+75) solution into a clean 500-mL round-bottomed flask. This Fraction I contains Trifluralin, Diallate and Triallate.

8.4.5 Elute the column with 200 mL of a benzene/methanol (99+1) solution into a clean 500-mL round-bottomed flask. This Fraction II contains Atrazine, Barban, Diclofop-Methyl and Benzoylprop-Ethyl.

8.4.6 Add 3 mL iso-octane to each fraction and evaporate the solvent to 3 mL on a rotary evaporator (water bath temperature at 35°C).

8.4.7 Quantitatively transfer the concentrated extracts to 15-mL graduated centrifuge tubes and make up to required volume with iso-octane/acetone (99+1).

8.4.8 Analyze the neutral herbicides by means of electron capture gas chromatography. (Use a nitrogen-phosphorus detector for Atrazine quantitation).

9. CALCULATIONS

9.1 The concentration of each herbicide is determined by comparison of peak height or area of the samples with those of the standards. This can be done by using the following equation:

$$X_{sam} = \left(\frac{H_{sam}}{H_{std}}\right) \times \left(\frac{V_{inj\ std}}{V_{inj\ sam}}\right) \times \left(X_{std}\right) \times \left(\frac{V_{ext}}{V_{sam}}\right)$$

where X_{sam} = herbicide concentration in original water sample (µg/L);

H_{sam} = peak height (or area) of sample;

H_{std} = peak height (or area) of standard;

$V_{inj\ std}$ = volume of standard injected (µL);

$V_{inj\ sam}$ = volume of sample injected (µL);

X_{std} = herbicide concentration in standard solution (pg/µL);

V_{ext} = final volume of sample extract (mL); and

V_{sam} = volume of orginal water sample extracted (mL).

10. PRECISION AND ACCURACY

10.1 Data indicating the single-operator precision and accuracy are summarized in the following table:

Herbicide	Fortification Level in 1-L H_2O (µg/L)	No. of Replicates	Mean Recovery (%)	Relative Standard Deviation (%)
Dicamba	0.25	8	85	2.7
MCPA	0.25	8	98	5.2
2,4-DP	0.25	8	101	2.2
2,3,6-TBA	0.25	8	92	3.5
2,4-D	0.25	8	90	4.5
Silvex	0.25	8	92	6.7
2,4,5-T	0.50	8	95	3.4
MCPB	0.50	8	84	2.9
2,4-DB	0.50	8	88	6.8
Picloram	0.50	6	83	5.2
Trifluralin	0.5	8	97	6.5
Diallate	10.0	8	97	4.4
Triallate	1.0	8	94	4.3
Atrazine	20.0	8	98	4.1
Barban	10.0	8	100	3.9
Diclofop-Methyl	5.0	8	90	3.8
Benzoylprop-Ethyl	2.5	8	99	1.8

Note: (a) Samples used for recovery studies were fortified 1-L Lake Ontario water samples.

(b) Recoveries for Picloram, Barban and Atrazine were based on peak height measurements. All other herbicides were measured by peak area.

(c) Atrazine recoveries were measured by GC-NPD.

11. REMARKS

11.1 It is recommended that an acid herbicide standard be prepared alongside each set of water samples to account for any minor variations in the derivitization procedure from one set to another.

11.2 In some natural water samples, emulsions can form during extraction with dichloromethane. If this happens, the emulsion should remain with the aqueous layer until the third extraction at which point it is included in the organic phase for partitioning.

11.3 Organic extracts containing acid herbicides should not be passed through anhydrous sodium sulphate for removal of traces of water. It has been shown that the use of such adsorbents, including acidified ones, can cause irreversible

adsorption and thus low and erratic recoveries of the herbicides. (Ref. 12.2 and 12.4).

11.4 Extreme care must be exercised by the analyst in the steps in which extracts are concentrated.

11.4.1 Neutral herbicide-containing extracts must never become dry, as these herbicides are quite volatile.

11.4.2 In the final extraction step for acid herbicides, the extracts in benzene must be evaporated just to dryness in order to release all of the solvent prior to esterification. When a rotary evaporator at $\leq$40°C was used, no losses of the herbicides were observed. However, prolonged evaporation under reduced pressure after the extract goes dry is not recommended. (Ref. 12.4).

11.4.3 Removal of acetone after esterification by a gentle stream of nitrogen should be done in the presence of hexane. While the PFB esters are relatively non-volatile, evaporation to dryness should be avoided. Care must be taken to ensure that the reaction tubes are tightly sealed after the introduction of the PFBBr reagent. Derivitization of the acid herbicides is a very critical step in their analysis. (Ref. 12.4).

11.5 The presence of too much water in the acid herbicide extract could inhibit esterification and result in low and erratic recoveries. Under these reaction conditions, water is also known to form dipentafluorobenzyl ether and other side products. (Ref. 12.2).

11.6 Since variations in adsorbent activities may be found among different batches of Florisil, it is recommended that the neutral herbicide elution pattern be checked with standard solutions before using the Florisil for sample cleanup.

11.7 The GLC response to Barban may decrease gradually as the column is used for sample analyses. If this occurs, replacement of the silanized glass wool at the column inlet will restore the signal response and reduce tailing. (Ref. 12.1).

11.8 Addition of 1% Acetone to neutral herbicide solutions containing Benzoylprop-ethyl is recommended to increase and stabilize the GLC response to this herbicide. (Ref. 12.1).

11.9 ECD-GLC can be used for the analysis of all seven neutral herbicides. However, for low level samples where greater specificity and sensitivity are needed (as for Atrazine), a

Nitrogen/Phosphorus Detector (NPD) or equivalent is recommended.

11.10 For the determination of just the seven neutral herbicides, acidification of the water sample prior to extraction is not necessary. Also, as the aqueous phase from the potassium bicarbonate partitioning contains acidic co-extractives, it should be discarded and steps 8.1.14 to 8.1.17 may be ignored. Finally, the PFBBr derivitization of acidic compounds (step 8.2) and subsequent Silical Gel cleanup (step 8.3) would, of course, also be omitted.

11.11 To determine just the ten acid herbicides, steps 8.1.7 to 8.1.15, involving the partitioning with potassium bicarbonate followed by the second extraction sequence, may be omitted entirely. Furthermore, the Florisil Column cleanup (step 8.4) may also be eliminated in this simplified procedure.

11.12 It has been demonstrated elsewhere that the basic analytical scheme is also effective in the determination of other classes of compounds such as PCBs, organochlorinated pesticides and chlorobenzenes.

12. REFERENCES

12.1 Lee, Hing-Biu and Alfred S.Y. Chau. 1983. Determination of Trifluralin, Diallate, Triallate, Atrazine, Barban, Diclofop-Methyl and Benzoylprop-Ethyl in Natural Waters at Parts per Trillion Levels. J. Assoc. Off. Anal. Chem. $\underline{66}^3$: 651-658.

12.2 Lee, Hing-Biu and Alfred S.Y. Chau. 1983. Analysis of Pesticide Residues by Chemical Derivitization. VI. Analysis of Ten Acid Herbicides in Sediment. J. Assoc. Off. Anal. Chem. $\underline{66}^4$: 1023-1028.

12.3 Lee, Hing-Biu and Alfred S.Y. Chau. 1983. Gas Chromatographic Determination of Trifluralin, Diallate, Triallate, Atrazine, Barban, Diclofop-Methyl and Benzoylprop-Ethyl in Sediments at Parts per Billion Levels. J. Assoc. Off. Anal. Chem. $\underline{66}^6$; 1322-1326.

12.4 Lee, Hing-Biu, Yvonne D. Stokker and Alfred S.Y. Chau. 1986. Chemical Derivitization Analysis of Pesticide Residues. X. Analysis of Ten Acid Herbicides in Natural Waters. (In press).

12.5 Method for the Analysis of Eight Phenoxy Acid Herbicides in Water by Derivitization with BCl_3/2-Chloroethanol. Water Quality Branch Analytical Methods Manual, Environment Canada.

12.6 Federal Register, US-EPA 40 CFR Part 136. Guidelines Establishing Test Procedures for the Analysis of Pollutants, October 26, 1984, Vol. 29, No. 209, p. 196.

APPENDIX

1. Figure A-1. Gas chromatogram of standard mixture of 9 Acid Herbicide PFB esters on 30 m DB-5 FSCC. 2.0 µL injected. GLC conditions are outlined in section 6.1.

Herbicide (PFB ester)		Amount Injected	Retention Time (min)
1.	Dicamba	20 pg	12.92
2.	MCPA	20 pg	13.23
3.	2,4-DP	20 pg	13.74
4.	2,3,6-TBA	20 pg	13.98
5.	2,4-D	20 pg	15.44
6.	Silvex	20 pg	17.37
7.	2,4,5-T	40 pg	18.91
8.	MCPB	40 pg	19.74
9.	2,4-DB	40 pg	22.02

2. Figure A-2. Gas chromatogram of standard mixture of ~~seven~~ seven Neutral Herbicides on a 3% OV-1 column (1.8 m x 2 mm i.d.) 10.0 µl injected. GLC conditions are outlined in Section 6.2.

	Herbicide	Amount Injected	Retention Time (min)
1.	Trifluralin	50 pg	1.96
2.	Diallate	1 ng	2.18
3.	Atrazine	2 ng	2.38
4.	Triallate	100 pg	3.32
5.	Barban	1 ng	11.68
6.	Diclofop-Methyl	500 pg	25.29
7.	Benzoylprop-Ethyl	250 pg	30.10

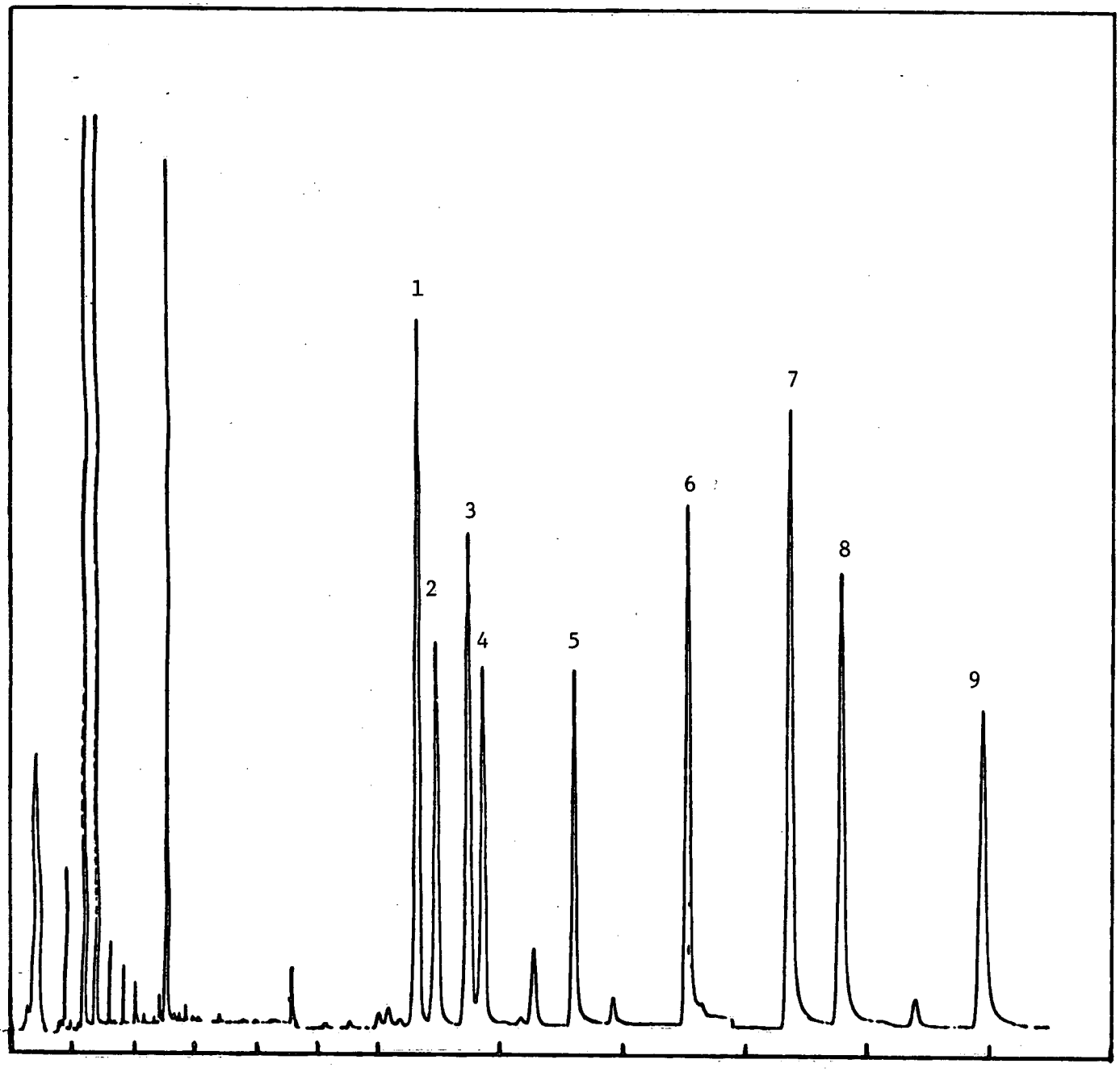

Figure A-1. 9 Acid Herbicide PFB esters

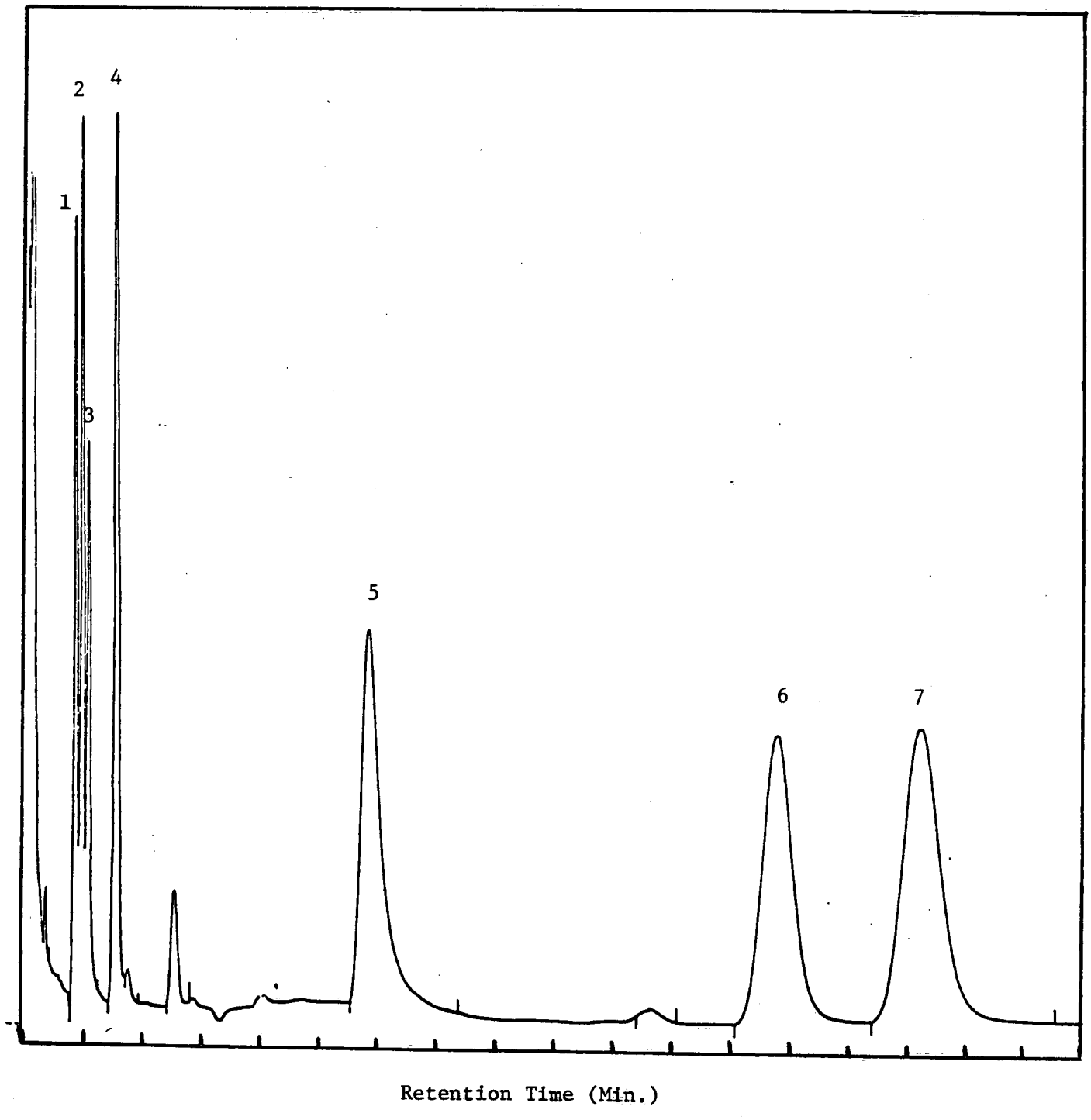

Figure A-2. 7 Neutral Herbicides