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# MULTI-CLASS METHOD FOR THE ANALYSIS OF ORGANOCHLORINATED PESTICIDES POLYCHLORINATED BIPHENYLS, CHLOROBENZENES AND NEUTRAL HERBICIDES IN SEDIMENTS

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## 1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the qualitative and quantitative gas chromatographic determination of 18 organochlorinated pesticides (OCs), polychlorinated biphenyls (PCBs), hexachlorobutadiene (HCBD), 10 chlorobenzenes (CBs) and seven neutral herbicides (NHs) in sediments.

1.2 The practical limits of measurement based on a 50 g sediment sample with a 30% moisture content and using a Nitrogen-Phosphorus detector for Atrazine and electron capture detection for the remaining compounds are as follows:

| Compound | Method Detection Limits* (µg/kg) | NAQUADAT No. |
|---|---|---|
| **Chlorobenzenes:** | | |
| 1,3-dichlorobenzene (1,3-DCB) | 5.0 | |
| 1,4-dichlorobenzene (1,4-DCB) | 5.0 | |
| 1,2-dichlorobenzene (1,2-DCB) | 5.0 | |
| Hexachlorobutadiene (HCBD) | 0.25 | |
| 1,3,5-trichlorobenzene (1,3,5-TCB) | 1.0 | |
| 1,2,4-trichlorobenzene (1,2,4-TCB) | 1.0 | |
| 1,2,3-trichlorobenzene (1,2,3-TCB) | 1.0 | |
| 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB) | 1.0 | |
| 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB) | 1.0 | |
| Pentachlorobenzene PeCB) | 1.0 | |
| Hexachlorobenzene (HCB) | 0.4 | |
| **Organochlorinated Pesticides:** | | |
| α-BHC | 1.0 | |
| β-BHC | 1.0 | |
| γ-BHC (lindane) | 1.0 | |
| Aldrin | 1.0 | |
| Heptachlor | 1.0 | |
| Heptachlor Epoxide | 1.0 | |
| α-Chlordane (cis-) | 5.0 | |
| γ-Chlordane (trans-) | 5.0 | |
| α-Endosulfan | 10.0 | |
| β-Endosulfan | 10.0 | |
| Dieldrin | 1.0 | |
| Endrin | 10.0 | |
| p,p'-DDE | 1.0 | |
| p,p'-DDD (p,p'-TDE) | 1.0 | |
| o,p'-DDT | 1.0 | |
| p,p'-DDT | 1.0 | |
| p,p'-methoxychlor | 10.0 | |
| Mirex | 1.0 | |
| **PCBs:** | | |
| AROCLOR 1242 | 3 | |
| AROCLOR 1254 | 3 | |
| AROCLOR 1260 | 3 | |
| Total PCBs | 9 | |
| **Neutral Herbicides:** | | |
| Trifluralin (Treflan) | 0.1 | |
| Diallate | 2.0 | |
| Triallate | 0.2 | |
| Atrazine | 2.0 | |
| Barban | 2.0 | |
| Diclofop-Methyl (Hoegrass) | 1.0 | |
| Benzoylprop-Ethyl (Endaven) | 0.5 | |

* Note: These concentration levels have been validated for each class of compounds individually.

## 2.0 PRINCIPLE AND THEORY

2.1 The sediment sample at neutral pH is extracted in a Soxhlet apparatus with an acetone-hexane solvent mixture.

2.2 The organic extract is base partitioned with a 2% potassium bicarbonate solution to remove any acidic co-extractives. Dichloromethane rinsings of this aqueous solution are then added to the original organic extract.

2.3 The combined organic extract is dried through anhydrous sodium sulphate and concentrated to approximately 3 mL.

2.4 Cleanup and fractionation on a 10% deactivated Florisil column provides two fractions which are then concentrated to approximately 3 mL.

2.5 The concentrated extract of the first fraction is applied to an activated Florisil column for further fractionation of the organic compounds of interest.

2.6 The three final fractions are made up to 10.0 mL and analyzed by GLC using electron capture and nitrogen-phosphorus detection.

2.7 The method presented here can readily be modified for the analysis of any one of, or combination of the four classes of compounds, if required.

## 3.0 INTERFERENCES

3.1 Organic compounds co-extracted from the sediment are potential interferences. 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.

3.3 Other pesticide residues, metabolites or degradation products may interfere in the GLC analysis. As many of these organic compounds have properties similar to those of the compounds of interest, confirmation of the identity of the latter is important.

3.4 Elemental sulphur or reactive sulphur-containing compounds may interfere with the analysis of Fraction C containing PCBs. These must be removed prior to GLC analysis by shaking the extract with clean mercury until HgS no longer precipitates as a black solid.

## 4.0 SAMPLING PROCEDURE AND STORAGE

4.1 Sediment samples should be collected and frozen immediately in an all-glass system or metal container.

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

4.3 Samples should be kept frozen in the dark, and extracted as soon as possible.

## 5.0 SAMPLE PREPARATION

5.1 No special preparation is required.

## 6.0 APPARATUS

6.1 Capillary GLC analyses.

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): 12 m x 0.2 mm i.d. column, coated with cross-linked dimethyl silicone gum (0.33 µm thickness) and surface deactivated by siloxane, such as Hewlett-Packard OV-1 (Part No. 19091-60312) or equivalent.

6.1.4 Chromatographic conditions for analysis of OCs in Fractions B and D:

Injection Port: spitless mode, splitless valve on for 30s
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: 12.5 psi
Column Temperature Initial: 70°C, hold for 0.5 min
Programming Rate 1: 30°C/min (70° to 160°C),
Programming Rate 2: 2°/min (160° to 220°C), hold at 220°C for 5.0 min
Column Post-Run Final Temperature: 220°C for 15 min

6.1.5 Chromatographic conditions for analysis of (OCs + PCBs + CBs) in Fraction C:

Injection Port: spitless mode, splitless valve on for 30s
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: 12.5 psi
Column Temperature Initial: 40°C, hold for 0.5 min
Programming Rate 1: 30°C/min (40° to 80°C), hold at 80°C for 5.0 min
Programming Rate 2: 8°/min (80° to 140°C)
Programming Rate 3: 4°C/min (140° to 220°C), hold for 15.0 min
Column Post-Run Final Temperature: 220°C for 15 min
Chart Speed: 0.75 cm/min

6.2 Packed Column GLC Analysis.

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 Hewlet-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 of neutral herbicides in Fractions B and D:

Injection Port Temperature: 200°C
Detector: Ni-63 ECD
Detector Temperature: 300°C
Oven Temperature: isothermal at 185°C
Carrier Gas: Argo/Methane (95+5) at 24 mL/min

NOTE: Preliminary priming of the column with a 10 ng/µL concentrated Barban solution is recommended to improve the sensitivity to this herbicide.

6.2.5 Chromatographic conditions for GC-NPD of Atrazine in Fraction B:

Injection Port Temperature: 200°C
Detector: Nitrogen-specific, NPD collector voltage at 14.5 V
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

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 1x32 or similar is obtained.

6.3 Soxhlet Apparatus.

6.3.1 Electrothermal extraction apparatus with thermostatted heating mantles to accommodate 500 mL round-bottom flasks.

6.3.2 Allihn condensers (250 mm x 50 mm i.d.)

6.3.3 Soxhlet extraction tubes (200 mL capacity).

6.3.4 Glass extraction thimbles (130 mm x 45 mm i.d.) with coarse (40-60 µm) porosity fritted disc.

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

6.5 Heating Mantles with power regulators, to accommodate 500-mL round-bottom flasks.

6.6 Three-stage Snyder columns with a tapered ground-glass joint to fit the neck of the 500 mL round-bottom flasks.

6.7 Boiling chips, Soxhlet-cleaned for 24 hours with Acetone/Hexane (59+41).

6.8 Oven, capable of maintaining 200°C.

6.9 Hamilton micro-syringes (500 µL, 100 µL, 10 µL).

6.10 Disposable Pasteur Pipettes.

6.11 Silanized glass wool.

6.12 Volumetric flasks, "low-actinic" (100 mL).

6.13 Separatory funnels with Teflon stop-cocks (1000 mL).

6.14 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.

6.15 Round-bottom flasks (500 mL).

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

6.17 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 should be dried at 130°C for at least two hours. Thorough rinsing with organic solvent immediately prior to using the glassware is recommended.

## 7.0 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 Acetone.
7.1.2 Hexane.
7.1.3 Dichloromethane (methylene chloride).
7.1.4 Benzene.
7.1.5 Methanol.
7.1.6 Iso-octane.
7.1.7 Pentane.
7.1.8 Acetonitrile.
7.1.9 Toluene.

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

7.2.1 Celite 545 (not Acid-washed), available from Fisher Scientific Company.
7.2.2 Purified (organic-free) water. Pass distilled water through Millipore Super-Q unit (Millipore Corp.). Alternatively, extract 1 L distilled water three times by stirring with 50 mL dichloromethane for 30 minutes. Discard organic layers.
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 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.
7.2.5 Activated 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.

7.2.6 10% Deactivated Florisil. Add 10 g purified (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. All herbicides and pesticides 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 compound of interest by dissolving 100 mg of pure analytical standard in the appropriate solvent and diluting to 100.0 mL in "low-actinic" volumetric flasks. The stock solution for each Aroclor, chlorobenzene and most OCs is prepared in iso-octane. The solvent for β-BHC is toluene/iso-octane (1+1), for α-Endosulfan is toluene/iso-octane (10+90), and for Endrin is toluene/iso-octane (20+80). The neutral herbicide stock solutions are prepared in toluene with the exception of that for atrazine, which is prepared in methanol. Store all stock solutions at 4°C in the dark.

7.3.2 Prepare mixed stock solutions for each class of compounds by combining appropriate aliquots of each individual stock solution and diluting to 100.0 mL with either iso-octane (OCs, NHs) or toluene (PCBs, CBs).

7.3.3 Prepare an OC Standard Solution in iso-octane for calibration of Fractions B and D by capillary GLC.

7.3.4 Prepare a mixed Standard Solution of OCs, PCBs and CBs in iso-octane for calibration of Fraction C by capillary GLC.

7.3.5 Prepare a Neutral Herbicide Standard Solution in iso-octane/methanol (99+1) and store at 4°C in the dark. This standard may be used to calibrate the packed-column GLC-ECD analyses of Fractions B and D, as well as the GLC-NPD analysis of Atrazine in Fraction B.

## 8.0 PROCEDURE

### 8.1 Sediment Extraction

8.1.1 Weigh a 50.0 g sample of homogeneous sediment into an extraction thimble containing 50 mm Celite 545.

8.1.2 At the same time,weigh representative sample aliquots of the sediment into tared containers and heat at 105°C to constant weight for moisture content determination.

8.1.3 Place the glass thimble containing the Celite and sediment into a Soxhlet extraction tube fitted with a 500 mL round-bottom flask containing 350 mL acetone/hexane (59+41) and a few boiling chips.

8.1.4 Adjust the temperature of the Soxhlet heating mantles to obtain a reflux rate of 6-8 cycles/hour.

8.1.5 After extracting for 20 hours, dismantle the Soxhlet apparatus and discard the sediment. When the solvent in the 500 mL round-bottom flask has cooled, transfer quantitatively to a 1000 mL separatory funnel.

8.1.6 Add 200 mL of potassium bicarbonate solution (2%) to the 1000 mL separatory funnel containing the acetone/hexane 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).

8.1.7 Allow the layers to separate and drain the aqueous (lower) layer into the 500 mL round-bottom flask used for the Soxhlet extraction.

8.1.8 Drain the organic layer through a (vacuum) sintered glass filter funnel containing 50 mm of anhydrous sodium sulphate. Collect the dried extract in a clean 500 mL round-bottom flask.

8.1.9 Return the aqueous layer to the 1000 mL separatory funnel and add 500 mL of potassium bicarbonate solution (2%). Rinse the 500 mL round-bottom flask with (30+20) mL of dichloromethane and add to the aqueous solution in the 1000 mL separatory funnel. Shake vigorously for 2 min and allow the layers to separate. Drain the organic layer through the sodium sulphate-filled filter funnel. Discard the aqueous layer.

8.1.10 Rinse the 1000-mL separatory funnel twice with 25 mL dichloromethane and pass the rinsings through the sodium sulphate column.

8.1.11 Wash the sodium sulphate column with 50 mL dichloromethane and apply a vacuum until the sodium sulphate is dry. Remove the column and add 3 mL iso-octane to the 500 mL round-bottom flask as a keeper.

8.1.12 Add several boiling chips to the dichloromethane extract and add a three-stage Snyder column to the 500 mL round-bottom flask. Wet the Snyder column with 5 mL hexane and clamp securely in a heating mantle.

8.1.13 Gently evaporate the methylene chloride to about 10 mL. Slowly add 50 mL hexane through the Snyder column to the 500 mL round-bottom flask and repeat evaporation to 3 mL. Do not let the extract go dry!

**CAUTION: All Snyder column evaporation steps must be performed in a Fume Hood.**

8.2 Column Cleanup with 10% Deactivated Florisil

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

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

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

8.2.4 When the extract just enters the sodium sulphate layer, elute the column with 200 mL of a benzene/hexane (25+75) solution into a clean 500 mL round-bottom flask. This is Fraction A.

8.2.5 Elute the column with 250 mL of a benzene/methanol (98+2) solution into another clean 500 mL round-bottom flask. This is Fraction B.

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

8.2.7 Quantitatively transfer the concentrated Fraction B extract to a 15 mL graduated centrifuge tube and make up to 10.00 mL with iso-octane/methanol (99+1).

8.2.8 Add 3 mL iso-octane and several boiling chips to the 500 mL round-bottom flask containing Fraction A. Clamp securely in a heating mantle and add a three-stage Snyder column. Wet the column with 5 mL hexane.

8.2.9 Gently evaporate the solvent to about 10 mL. Slowly add 50 mL hexane through the Snyder column to the 500 mL round-bottom flask and repeat evaporation to 3 mL. Do not let the extract go dry!

8.3 Column Cleanup with Activated Florisil

8.3.1 Prepare macro-columns by filling chromatographic columns (500 x 20 mm i.d.) with 20 g of fully activated Florisil. Tap columns gently to uniformly settle the solid. Add 1 cm anhydrous sodium sulphate on top of the Florisil layer.

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

8.3.3 Quantitatively transfer the concentrated Fraction A extract (from step 8.2.9) plus rinsings onto the column with a disposable Pasteur pipette.

8.3.4 When the extract just enters the sodium sulphate layer, elute the column with 200 mL of a dichloromethane/pentane (20+80) solution into a clean 500 mL round-bottom flask. This is Fraction C.

8.3.5 Elute the column with 250 mL of a dichloromethane/acetonitrile (99.5 + 0.5) solution into another clean 500 mL round-bottom flask. This is Fraction D.

8.3.6 Add 3 mL iso-octane and several boiling chips to the 500 mL round-bottom flask containing Fraction C. Clamp securely in a heating mantle. Add a three-stage Snyder column and wet with 5 mL hexane.

8.3.7 Gently evaporate the solvent to about 10 mL. Slowly add 50 mL hexane through the Snyder column to the 500-mL round-bottom flask. Repeat evaporation to 3 mL, taking care not to let the extract go dry.

8.3.8 Quantitatively transfer the concentrated Fraction C extract to a 15-mL graduated centrifuge tube and make up to 10.00 mL with iso-octane.

8.3.9 Remove any sulphur-containing compounds in Fraction C by shaking the concentrated extract with successive drops of clean, triple-distilled mercury until HgS no longer precipitates as a black solid and the mercury drop remains shiny.

8.3.10 Add 3 mL iso-octane to Fraction D and evaporate the solvent to about 10 mL on a rotary evaporator (water bath temperature at 35°C). Add 50 mL hexane and repeat evaporation to 3 mL.

8.3.11 Quantitatively transfer the concentrated Fraction D extract to a 15-mL graduated centrifuge tube and make up to 10.00 mL with iso-octane/methanol (99+1).

8.4 GLC Analysis

8.4.1 Fraction B is divided into three portions and analyzed as follows:

(i) for β-Endosulfan and Endrin by capillary GLC as per conditions in section 6.1.4,

(ii) for Barban, Hoegrass and Endaven by packed column GLC-ECD as per section 6.2.4, and

(iii) for Atrazine by GLC-NPD as described in section 6.2.5.

8.4.2 Fraction C is analyzed by capillary GLC as outlined in section 6.1.5. This fraction contains the PCBs, chlorobenzenes and some OCs.

8.4.3 Fraction D is divided into two portions and analyzed as follows:

(i) for the remaining OCs by capillary GLC as per the conditions outlined in section 6.1.4, and

(ii) for Treflan, Diallate and Triallate by packed column GLC-ECD as per section 6.2.4.

## 9. CALCULATIONS

9.1 The concentration of each compound of interest 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:

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

where $X_{sam}$ = concentration of organic compound in original sediment sample (µg/kg);

$H_{sam}$ = 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);

$X_{std}$ = concentration of organic compound in standard solution (pg/µL);

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

$W_{sam}$ = weight of original sediment sample extracted (g).

9.2 For recovery studies, PCB quantitation was performed by a modified Webb and McCall method, whereby the areas of three PCB peaks in the capillary gas chromatogram of Fraction C were used to represent total PCBs.

9.3 For real samples, packed column quantitation by the method of Webb and McCall is recommended (Ref. 13.4).

9.4 The determination of moisture content in the sediment samples is as follows:

$$\% \text{ moisture} = \left( \frac{A-B}{A} \right) \times 100$$

where A = weight in grams of a homogeneous sediment subsample before drying, and

B = weight in grams of the same sample after being dried to constant weight at 105°C.

## 10. PRECISION AND ACCURACY

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

| Compound | Fortification Level in 50 g Sediment (µg/kg) | Mean Recovery (%) | Relative Standard Deviation (%) |
|---|---|---|---|
| Neutral Herbicides: | | | |
| Trifluralin | 2.0 | 102 | 3.3 |
| Diallate | 40.0 | 88 | 7.4 |
| Triallate | 4.0 | 90 | 3.4 |
| Atrazine | 80.0 | 95 | 2.7 |
| Diclofop-methyl | 20.0 | 93 | 1.7 |
| Benzoylprop-ethyl | 10.0 | 99 | 3.0 |
| Chlorobenzenes: | | | |
| 1,3-DCB | 200.0 | 87 | 2.6 |
| 1,4-DCB | 200.0 | 86 | 2.2 |
| 1,2-DCB | 200.0 | 85 | 1.5 |
| HCBD | 10.0 | 85 | 1.9 |
| 1,3,5-TCB | 20.0 | 89 | 1.5 |
| 1,2,4-TCB | 20.0 | 90 | 2.7 |
| 1,2,3-TCB | 20.0 | 86 | 2.8 |
| 1,2,4,5-TeCB | 20.0 | 87 | 2.2 |
| 1,2,3,4-TeCB | 20.0 | 87 | 1.5 |
| PeCB | 20.0 | 87 | 1.0 |
| HCB | 20.0 | 89 | 0.9 |
| Organochlorinated Pesticides: | | | |
| α-BHC | 5.0 | 87 | 5.0 |
| β-BHC | 5.0 | 88 | 2.4 |
| γ-BHC | 5.0 | 84 | 6.3 |
| Aldrin | 5.0 | 86 | 1.5 |
| Heptachlor | 5.0 | 86 | 2.3 |
| Heptachlor Epoxide | 5.0 | 86 | 1.5 |
| α-Chlordane | 10.0 | 86 | 2.4 |
| γ-Chlordane | 10.0 | 88 | 1.4 |
| α-Endosulfan | 20.0 | 88 | 1.4 |
| β-Endosulfan | 20.0 | 80 | 2.9 |
| Dieldrin | 10.0 | 84 | 2.5 |
| Endrin | 20.0 | 90 | 4.2 |
| p,p'-DDE | 10.0 | 90 | 2.6 |
| p,p'-DDD | 10.0 | 86 | 4.0 |
| o,p'-DDT | 20.0 | 85 | 3.1 |
| p,p'-DDT | 20.0 | 81 | 3.0 |
| Methoxychlor | 100.0 | 95 | 4.6 |
| Mirex | 10.0 | 88 | 1.8 |
| Total PCBs | 120.0 | 90 | 2.2 |

Note: (a) Validation data were obtained from fortified 50 g subsamples of a Lake Superior/Battle River blended sediment having approximately 30% moisture content.
(b) Fortification levels were calculated on a "wet-sediment" basis.
(c) No. of replicates = 5.

## 11. REMARKS

11.1 In natural sediment samples with high humic content, emulsions can form at the solvent/water interface during extraction with dichloromethane. If this happens, the emulsion should remain with the aqueous layer until the final organic extraction, at which point it is included in the organic phase. For severe cases, extra washes of the potassium bicarbonate layer with 50 mL dichloromethane may be required. This permits the emulsion to be extracted further and prevents the sodium sulphate in the filter funnel from becoming saturated.

11.2 Extreme care must be exercised by the analyst in the steps in which extracts are concentrated. Samples must never be allowed to go dry, as all chlorobenzenes and some chlorinated insecticides and neutral herbicides are quite volatile.

11.3 All concentration steps using a Snyder column for evaporation of the solvent must be carried out in a Fume Hood.

11.4 It is strongly recommended that the use and handling of benzene be restricted to a Fume Hood.

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

11.6 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. 13.2).

11.7 Addition of 1% methanol (or acetone) to neutral herbicide solutions containing Benzoylprop-Ethyl is recommended to increase and stabilize the GLC response to this herbicide. (Ref. 13.2).

11.8 Electron capture detection 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.

11.9 The analysis of 1,2,3,5-tetrachlorobenzene was omitted because it could not be resolved from 1,2,4,5-tetrachlorobenzene on the 12 m OV-1 FSCC. They may be resolved, however, on a Carbowax-20M or DX-4 FSCC, if required.

11.10 It has been demonstrated elsewhere that the basic analytical scheme is also effective in the determination of other classes of compounds such as phthalate esters and polynuclear aromatic hydrocarbons (PAHs).

## 12. CONFIRMATION OF IDENTITY

12.1 The identity of each peak in the sample extracts may be assigned by comparison with the retention time of each compound analyzed individually under identical chromatographic conditions.

12.2 Additional confirmation of identity may also be obtained by combined GC-MS, chemical derivatization or some other suitable technique.

## 13. REFERENCES

13.1 Stokker, Yvonne D. 1986. Multi-Class Method for the Analysis of Organochlorinated Pesticides, Polychlorinated Biphenyls, Chlorobenzenes and Neutral Herbicides in Natural Waters. (NWRI Contribution No. 86- ).

13.2 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. 66[3]: 651-658.

13.3 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. 66[6]:1332-1326.

13.4 Webb, Ronald G. and Ann C. McCall. 1973. Quantitative PCB Standards for Electron Capture Gas Chromatography. J. Chromatogr. Sci. 11: 366-373.

13.5 Chau, A.S.Y. and R.C.J. Sampson. 1975. Electron Capture Gas Chromatographic Methodology for the Quantitation of Polychlorinated Biphenyls: Survey and Compromise. Environ. Lett. 8(2): 89-101.

13.6 Oliver, Barry G. and Karen D. Bothen. 1980. Determination of Chlorobenzenes in Water by Capillary Gas Chromatography. Anal. Chem. 52: 2066-2069.

## APPENDIX

1. Figure A-1. Gas chromatogram of a standard mixture of 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.

| | Neutral 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 |

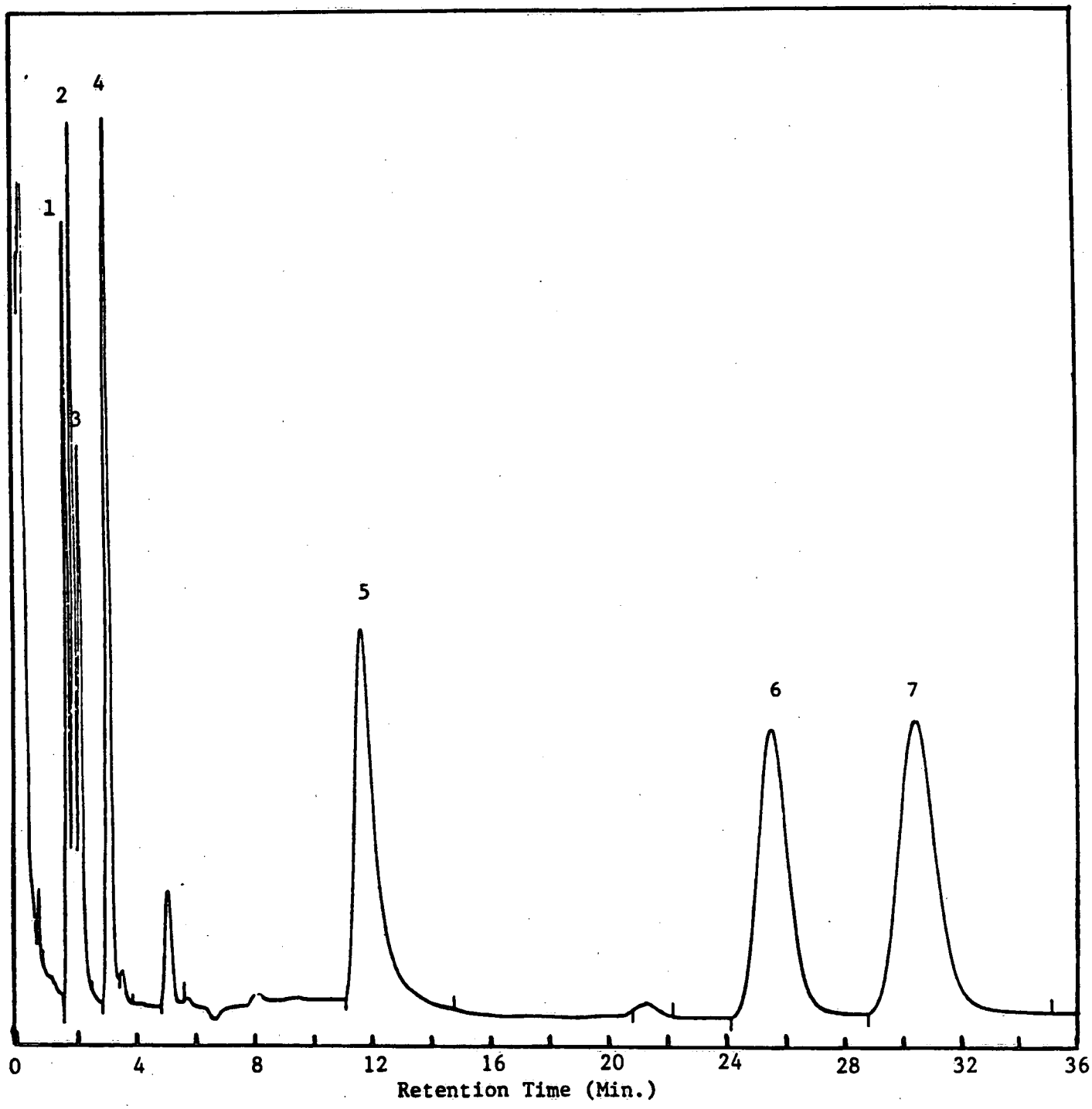


Figure A-1. 7 Neutral Herbicides

2. Figure A-2. Gas chromatogram of a standard mixture of 18 organochlorinated pesticides as resolved on a 12 m x 0.2 mm i.d. OV-1 fused silica capillary column. GLC conditions are outlined in section 6.1.

| OC | Amount Injected (pg) | Retention Time (min) |
|---|---|---|
| 1. α-BHC | 50 | 7.87 |
| 2. β-BHC | 50 | 8.27 |
| 3. γ-BHC | 50 | 8.87 |
| 4. Heptachlor | 50 | 12.46 |
| 5. Aldrin | 50 | 14.31 |
| 6. Heptachlor Epoxide | 50 | 16.31 |
| 7. γ-Chlordane | 100 | 17.67 |
| 8. α-Endosulfan | 200 | 18.52 |
| 9. α-Chlordane | 100 | 18.80 |
| 10. Dieldrin | 100 | 20.22 |
| 11. p,p'-DDE | 100 | 20.50 |
| 12. β-Endosulfan | 200 | 21.60 |
| 13. p,p'-DDD | 100 | 23.01 |
| 14. o,p'-DDT | 200 | 23.62 |
| 15. p,p'-DDT | 200 | 26.10 |
| 16. Endrin | 200 | 27.50 |
| 17. p,p'-Methoxychlor | 1000 | 30.67 |
| 18. Mirex | 100 | 33.47 |

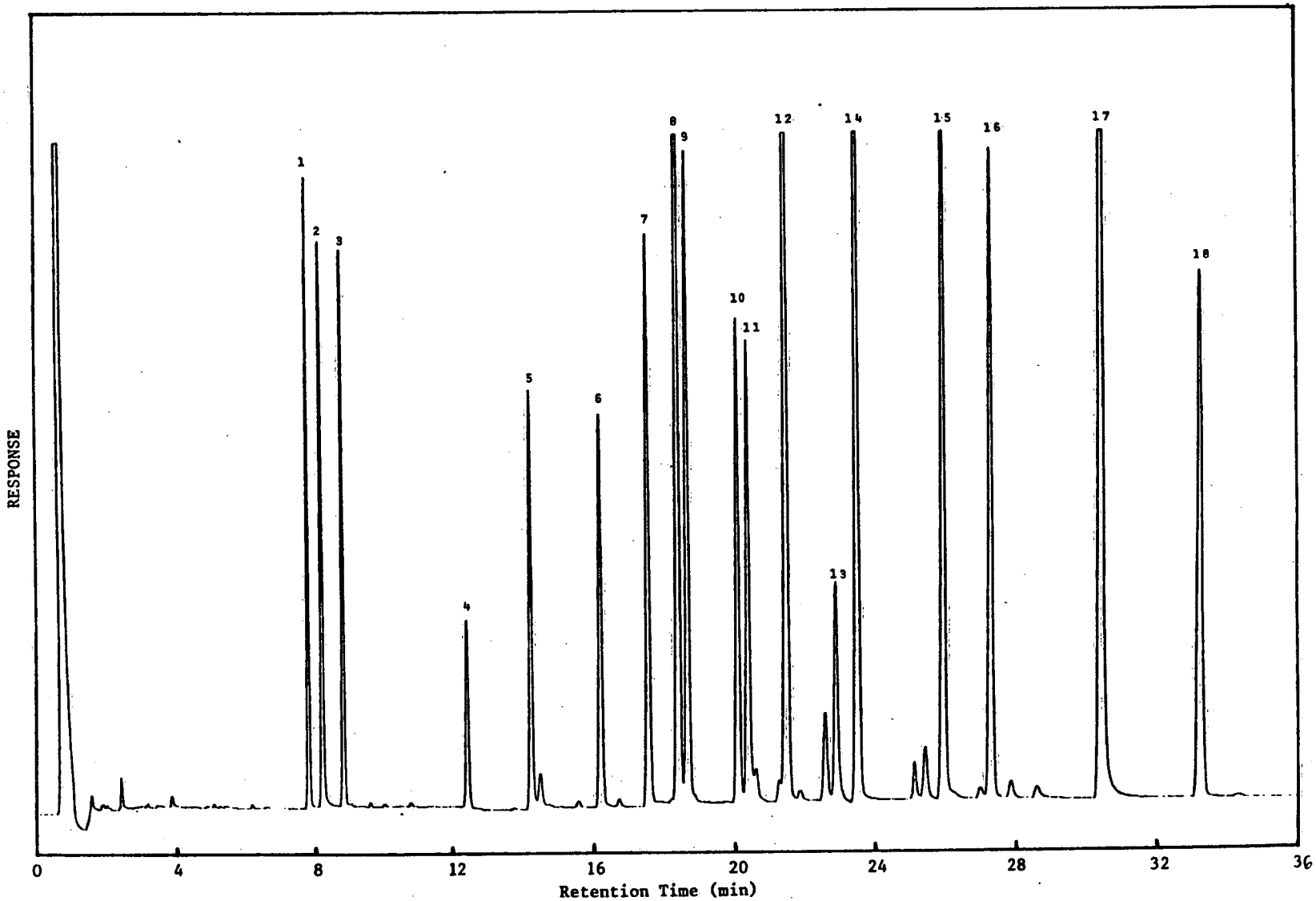


Figure A-2. 18 Organochlorinated Pesticides

3. Figure A-3. Gas chromatogram of a standard mixture of 18 organochlorinated pesticides, 11 chlorobenzenes and Aroclors 1242, 1254 and 1260, as resolved on a 12 m x 0.2 mm i.d. OV-1 fused silica capillary column. GLC conditions are outlined in section 6.1.

| | Peak Identification | Amount Injected (pg) | Retention Time (min) |
|---|---|---|---|
| 1. | 1,3-DCB | 2000 | 4.28 |
| 2. | 1,4-DCB | 2000 | 4.38 |
| 3. | 1,2-DCB | 2000 | 4.80 |
| 4. | 1,3,5-TCB | 200 | 7.67 |
| 5. | 1,2,4-TCB | 200 | 8.88 |
| 6. | 1,2,3-TCB | 200 | 9.78 |
| 7. | HCBD | 100 | 10.35 |
| 8. | 1,2,4,5-TeCB | 200 | 12.63 |
| 9. | 1,2,3,4-TeCB | 200 | 13.52 |
| 10. | PeCB | 200 | 16.38 |
| 11. | α-BHC | 50 | 19.75 |
| 12. | β-BHC | 50 | 20.29 |
| 13. | HCB | 200 | 20.50 |
| 14. | γ-BHC | 50 | 21.09 |
| 15. | PCB-1* | - | 24.09 |
| 16. | Heptachlor | 50 | 24.92 |
| 17. | Aldrin | 50 | 26.54 |
| 18. | Heptachlor Epoxide | 50 | 28.14 |
| 19. | γ-Chlordane | 100 | 29.15 |
| 20. | α-Endosulfan | 200 | 29.77 |
| 21. | α-Chlordane | 100 | 29.95 |
| 22. | Dieldrin | 100 | 30.92 |
| 23. | p,p'-DDE | 100 | 31.08 |
| 24. | PCB-2* | - | 31.28 |
| 25. | β-Endosulfan | 200 | 31.84 |
| 26. | PCB-3* | - | 32.52 |
| 27. | p,p'-DDD | 100 | 32.69 |
| 28. | o,p'-DDT | 200 | 33.07 |
| 29. | PCB-4* | - | 33.71 |
| 30. | p,p'-DDT | 200 | 34.56 |
| 31. | PCB-5* | - | 34.78 |
| 32 | Endrin | 200 | 35.57 |
| 33. | p,p'-methoxychlor | 1000 | 37.60 |
| 34. | PCB-6* | - | 38.79 |
| 35. | Mirex | 100 | 40.34 |

* Aroclor 1242, Aroclor 1254 and Aroclor 1260 were each present in the standard mixture at a level of 200 pg/μL. Therefore, total PCBs injected are 1200 pg.

NOTE: While six "PCB peaks" are identified in the chromatogram, only Peaks 15, 29 and 34 were used to quantitate Total PCBs in the recovery studies.

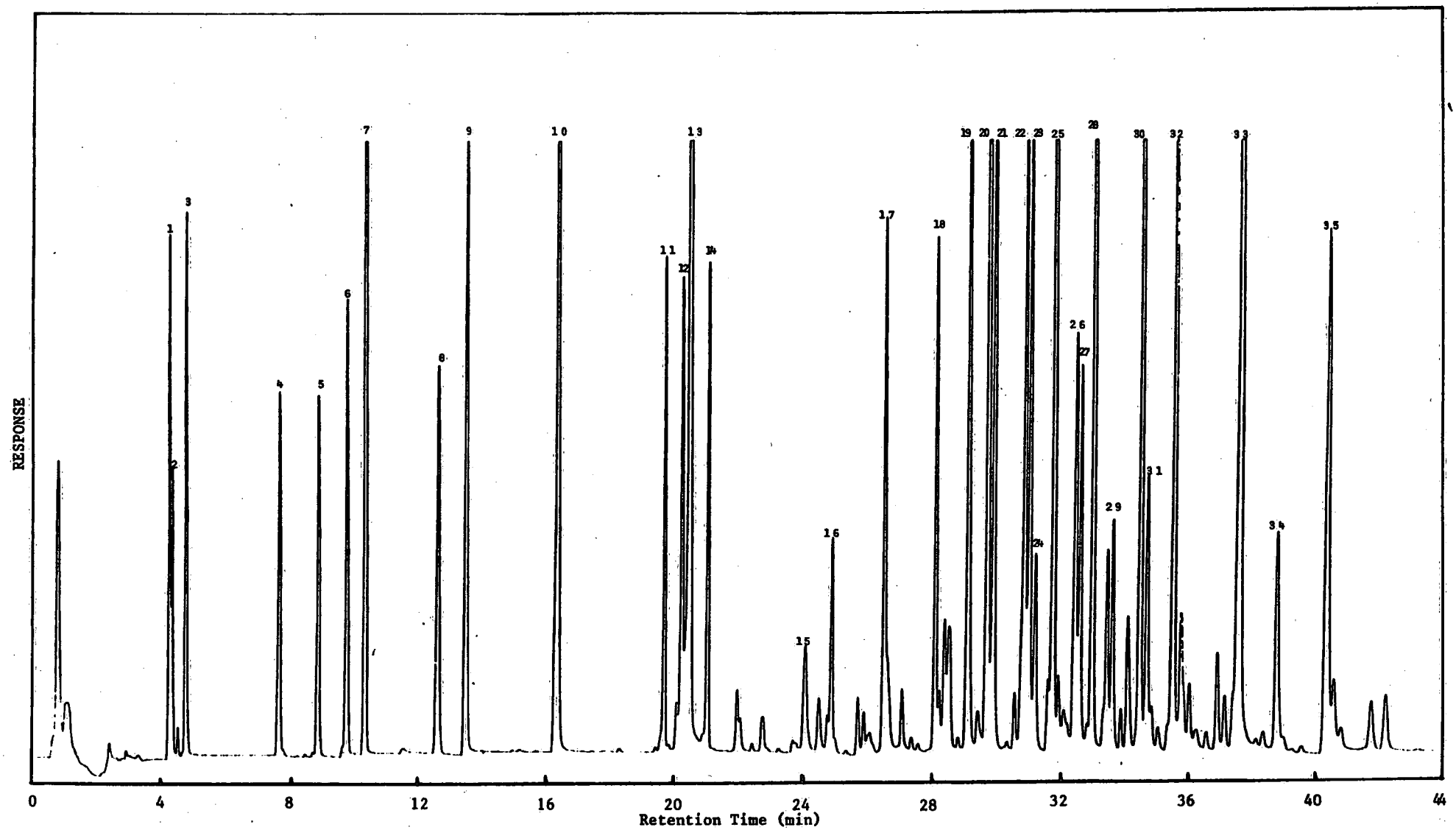


Figure A-3. Organochlorinated Pesticides, PCB's and Chlorobenzenes