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TENTATIVE METHOD OF TEST

FOR POLYCHLORINATED BIPHENYLS (PCB) IN WATER[1]

ASTM DESIGNATION_____-T

1. Scope and Application

1.1 This method covers the determination of certain polychlorinated biphenyls (PCB's) including: Aroclors[2] 1221, 1232, 1242, 1248, 1254, 1260, and 1016.

1.2 The method is an extension of the ASTM Proposed Tentative Method of the Test for Organochlorine Pesticides in Water, D 3086-72[3]T. It is designed so that determination of both the PCB's and the organochlorine pesticides may be made on the same sample.

2. Applicable Documents

2.1 ASTM Standards:

D510 Sampling Water[3]

D1129 Definitions of Terms Relating to Water[3]

D1192 Specifications for Equipment for Sampling Water and Steam[3]

D1193 Specification for Reagent Water[3]

D1496 Sampling Homogenous Waste Water[3]

E260 Recommend Practice for General Gas Chromatography Procedures[4]

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[1] This method is under the jurisdiction of the ASTM Committee D-19 on Water

[2] Trade name of the Monsanto Co., St. Louis, MO

[3] Appears in this publication

[4] 1974 Annual Book of ASTM Standards, Part 42

E355 Recommended Practice for Gas Chromatography Terms and Relationships.[4]

3. Summary

3.1 The PCB's and the organochlorine pesticides are co-extracted by liquid-liquid extraction and, insofar as possible, the two classes of compounds separated from one another prior to gas chromatographic determination. A combination of the standard Florisil[5] column cleanup procedure and a silica gel microcolumn separation procedure (1,2) are employed. Identification is made from gas chromatographic patterns obtained through the use of two or more unlike columns. Detection and measurement is accomplished using an electron capture, microcoulometric, or electrolytic conductivity detector. Techniques for confirming qualitative identification are suggested. The detection limit is approximately 100 ng/l for the PCB mixtures (Aroclors) listed in 1.1 when analyzing 1-liter of sample.

4. Significance

4.1 The extensive and widespread use of PCB's has resulted in their presence in all parts of the environment. Like the organochlorine pesticides, the PCB's are very persistent. While they are generally less toxic than the organochlorine pesticides, they do have lethal effects on mammals, birds, fish, and other aquatic animals. Thus, we must identify and quantitate the PCB's present in the environment. Because of their cumulative nature and level of occurrence, the method must be capable of measuring quantities less than 1 µg/l of the PCB's in water.

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[5] Florisil TM of, and available from Floridin Co., 2 Gateway Center, Pittsburg, PA 15222

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5. Definitions

5.1 For definitions of terms used in these methods refer to ASTM definitions D1129, Terms Relating to Water[3] and ASTM Recommended Practices E-355 for Gas Chromatography Terms and Relationships[4].

6. Interferences

6.1 Certain phthalate esters, organophosphorus pesticides, and elemental sulfur will interfer when using electron capture for detection.

6.2 Organochlorine pesticides and other halogenated compounds constitute interferences in the determination of PCB's. Most of these are separated by the method described below. However, certain compounds, if present in the sample, will occur with the PCB's. Included are sulfur, heptachlor, aldrin, DDE, chlordane, mirex, and to some extent o,p'-DDT and p,p'-DDT.

7. Apparatus

7.1 Kuderna-Danish (K-D) Glassware

7.1.1 Snyder Columns - three ball (macro)

7.1.2 Evaporative flasks - 500 ml

7.1.3 Receiver Ampuls - 10 ml, graduated

7.1.4 Ampul Stoppers

7.2 Chromatographic Column - Chromaflex[6] (400 mm long X 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250 ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes-42540-9011).

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[6] Chromaflex, trademark of Kontes Glass Co., Vineland, NJ 08360

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7.3 Chromatographic Column - borosilicate glass (approximately 400 mm long X 20 mm ID) with a coarse fritted plate.

7.4 Micro Column borosilicate glass - constructed according to Figure 1.

7.5 Capillary pipets disposable (5-3/4 in.) with rubber bulb.

7.6 Low Pressure regulator (0 to 5 PSIG) with low-flow needle valve

7.7 Beaker - 100 ml

7.8 Micro syringe - 10 µl

7.9 Separatory funnel - 2000 ml with TFE-fluorocarbon stopcock

7.10 Centrifuge tubes - Borosilicate glass, calibrated (15 ml)

8. Reagents and Materials

8.1 Purity of Reagents - Reagent grade 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.[7] 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.

8.2 Purity of Water - Unless otherwise indicated, reference to water should be understood to mean reagent water conforming to ASTM Specifications D1193 for Reagent Water, Type II.

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[7] Reagent Chemicals, American Chemical Society Specifications. American Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards", by Joseph Rosin, D. Van Nostrand Co., Inc. New York, N.Y. and the United States Pharmacopeia."

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8.3 Anti-static Solution - STATNUL[8]

8.4 PCB Standards[9]: Aroclors 1221, 1232, 1242, 1248, 1254, 1260 and 1016 from Monsanto Co., St. Louis, MO or commerical sources. Aroclor standard solutions. Environmental Research Laboratory, EPA, GA 30601.

8.5 Diethyl Ether - Pesticide quality, redistilled in glass, if necessary, and contain 2% (v/v) ethanol.

8.5.1 Must be free of peroxides by following test: to 10 ml of ether in glass-stoppered cylinger previously rinsed with ether, add one ml of freshly prepared 10% KI solution. Shake and let stand one minute. No yellow color should be observed in either layer. As alternative, use EM Quant[10] test strips or equivalent.

8.5.2 Decompose either peroxides by adding 40 g of a solution of 30% (w/v) ferrous sulfate solution per liter of solvent. CAUTION! Reaction may be vigorous if the solvent contains a high concentration of peroxides.

8.5.3 Distill deperoxidized ether in glass and add 2% (v/v) ethanol.

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[8] Stanul, TM of and available from Daystrom Inc., Weston Instrument Division, Newark, N.J. 95212

[9] The proportions of individual PCB isomers may vary from one lot to another and from one manufacturer to another.

[10] EM Quant test strips, trade mark of and available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523

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8.6 Florisil - PR grade (60-100 mesh); purchase activated at 1250 F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130 C in foil-covered glass container. Determine lauric-acid value (See Appendix I).

8.7 Ferrous Sulfate Solution (30%). Dissolve 30 g of ferrous sulfate ($FeSO_4$) in water and dilute to 100 ml.

8.8 Gas Chromatographic Materials

8.8.1 Refer to ASTM D3086 Section 7

8.8.2 Tubing - Borosilicate glass (180 cm long X 4 mm ID)

8.8.3 Glass Wool - Silanized

8.8.4 Solid Support - Gas Chrom Q[11] (100-120 mesh)

8.8.5 Liquid Phases - Expressed as weight percent coated on solid support.

8.8.5.1 SE-30 or OV-1, 3%

8.8.5.2 OV-17, 1.5% + QF-1, 1.95%

8.9 Glass Wool - Hexane extracted

8.10 n-Hexane - Pesticide quality (NOT MIXED HEXANES)

8.11 Mixed Solvents - Pesticide quality

8.11.1 Ethyl Ether - Benzene Mixture (0.5%) - Take 1/2 volume of ethyl ether and mix with benzene to 100 volumes.

8.11.2 Ethyl Ether - Petroleum Ether Mixture (6%) - Take 6 volumes of ethyl ether and mix with petroleum ether to 100 volumes.

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[11] Gas Chrom Q, TM of and available from Applied Science Laboratories, State College, PA 16801

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8.11.3 Ethyl Ether - Petroleum Ether Mixture (15%) - Take 15 volumes of ethyl ether and mix with petroleum ether to 100 volumes.

8.11.4 Ethyl Ether - Petroleum Ether Mixture (50%) - Take 50 volumes of ethyl ether and mix with petroleum ether to 100 volumes.

8.11.5 Methylene Chloride - Hexane Mixture (15%) - Take 15 volumes of methylene chloride and mix with n-hexane to 100 volumes.

8.12 Petroleum Ether - Pesticide quality, 30-60 C boil

8.13 Potassium Iodide Solution (10%). Dissolve 10 g of potassium iodide (KI) in water and dilute to 100 ml.

8.14 Silica gel - Davison code 950-08-08-226 (60/200 mesh)[12]

8.15 Sodium Sulfate - Granular, anhydrous, conditioned for 4 hours @ 400 C.

9. Extraction of Sample

9.1 Transfer 1 liter of sample to a 2-liter separatory funnel equipped with a TFE-Fluorocarbon stopcock. Extract the sample three times each with three 60 ml solutions of methylene chloride-hexane 15% (v/v). If a larger volume of sample is to be analyzed, i.e., 3 liters, extract three times with 150 ml the mixed solvent.

9.2 Dry the combined extracts by pouring through a 4-inch column of anhydrous sodium sulfate, (previously rinsed with hexane) contained in a 20 mm ID chromatographic column, and concentrate to 6-10 ml in a Kuderna-Danish evaporator. Qualitatively analyze the sample

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[12] Available from Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219

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by gas chromatography, using the 3% OV-1 column described in Figures 3 to 5, with an electron capture detector. From the response obtained decide:

a. If it is obvious that only organochlorine pesticides are present.

b. If it is obvious that only PCB's are present.

c. If there is a combination of a and b.

d. If the response is too complex to determine a, b, or c.

If no response, concentrate to 1.0 ml or less and repeat the analysis looking for a, b, c, and d. Trace quantities of PCB's are often masked by background which usually occurs in the samples. If detection limits below 100 ng/l are required, continue as in 10. below, even though the presence of PCB peaks is not apparent in the chromatogram.

9.3 If condition a exists, determine the organochlorine pesticides.

9.4 if condition b exists, PCB's only are present, no further separation or clean-up is necessary, proceed to 10.2.2 or 10.2.3 below.

9.5 If condition c exists, compare peaks obtained from sample to those of standard Aroclors and make a judgment as to which Aroclor standard or combination of standards best represents the PCB's present. To separate the PCB's from the organochlorine pesticides, continue as outlined in 9.7.

9.6 If condition d exists, apply standard Florisil column procedure (9.7).

9.7 Florisil Column Procedure

9.7.1 Adust the sample extract volume to 10 ml with petroleum ether.

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9.7.2 Place a charge of activated Florisil (weight determined by lauric-acid value, see Appendix I) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

9.7.3 Pre-elute the column, after cooling, with 50-60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air; quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to three eluates in 500 ml K-D flasks equipped with 10 ml ampuls. (See Eluate Composition below). Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in petroleum ether. Perform the last elution with 200 ml of 50% ethyl ether petroleum ether. Eluate Composition - By using an equivalent quantity of any batch of Florisil as determined by its lauric-acid value, the PCB's and pesticides will be separated into the eluates indicated below:

6% Eluate

PCB's	DDT	Mirex
Aldrin	Heptachlor	Pentachloro-nitrobenzene
BHC	Heptachlor Epoxide	Strobane
Chlordane	Lindane	Toxaphene
DDD	Methoxychlor	Trifluralin
DDE		

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15% Eluate	50% Eluate
Endosulfan I	Endosulfan II
Endrin	Captan
Dieldrin	
Dichloran	

Certain thiophosphate pesticides will occur in each of the above fractions. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (9).

9.7.4 Concentrate the eluates to 6-10 ml in the K-D evaporator in a hot water bath.

9.7.5 To further separate the PCB's from organochlorine pesticides continue on to 10, below with the 6% eluate. Analyze the 15% eluate and the 50% eluate for pesticides.

10. Silica Gel Microcolumn Separation Procedure

10.1 Activation for Silica Gel

10.1.1 Place about 20 gms of silica gel in a 100 ml beaker. Activate at 180 C for approximately 16 hours. Transfer the activated silica gel to a 100 ml glass stoppered bottle. When cool, cover with about 35 cc of diethyl ether-benzene 0.5% (v/v). Keep bottle well sealed. If silica gel collects on the ground glass surfaces, wash off with the above solvent before resealing. Always maintain an excess of the mixed solvent in bottle (approximately 1/2" above silica gel). Silica gel can be effectively stored in this manner for several days.

10.2 Preparation of the Chromatographic Column

10.2.1 Pack the lower 2 mm ID Section of the micro column with

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glass wool. Permanently mark the column 120 mm above the glass wool. Using a clean rubber bulb from a disposable pipet seal the lower end of the micro column. Fill the micro column with the ether-benzene solution to the bottom of the 10/30 joint (Figure 1). Using a disposable capillary pipet, transfer several aliquots of the silica gel-slurry into the micro column. After approximately 1 cm of silica gel collects in the bottom of the micro column, remove the rubber bulb seal, tap the column to insure the silica gel settles uniformly. Carefully pack the column until the silica gel is within $\pm$ 2 mm of the 120 mm mark. Be sure that there are no air bubbles in the column. Add about 10 mm of sodium sulfate to the top of the silica gel. Under low humidity conditions, the silica gel may coat the sides of the column and not settle properly. This can be minimized by wiping the outside of the column with an anti-static solution (8.3).

10.2.2 Deactivation of the Silica Gel

10.2.2.1 Fill the micro column to the base of the 10/30 joint with the ether-benzene solution, assemble reservoir (using spring clamps) and fill with approximately 15 ml ether benzene. Attach the air pressure device (using spring clamps) and adjust the column exit flow to approximately 1 ml/min with the air pressure control. Release the air pressure and detach reservoir just as the last of the solvent enters the sodium

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sulfate. Fill the column with n-hexane to the base of the 10/30 fitting. Evaporate all residual benzene from the reservoir, assemble the column and fill with 5 ml of n-hexane. Apply air pressure and readjust solution flow to 1 ml/min. Release the air pressure and remove the reservoir just as the n-hexane enters the sodium sulfate. The column is now ready for use.

10.2.2.2 Pipet a 1.0 ml aliquot of the concentrated sample extract (previously reduced to a total volume of 2.0 ml) on to the column. As the last of the sample passes into the sodium sulfate layer, rinse down the internal wall of the column twice with 0.25 ml of n-hexane. Then assemble the upper section of the column. As the last of the n-hexane rinse reaches the surface of the sodium sulfate, add enough n-hexane (volume predetermined, see 10.3 below) to just elute all of the PCB's present in the sample. Apply air pressure until the effluent flow is 1 ml/min. Collect the desired volume of eluate in an accurately calibrated ampul. As the last of the n-hexane reaches the surface of the sodium sulfate, release the air pressure and change the collection ampul.

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10.2.2.3 Fill the column with ether-benzene; again apply air pressure and adjust flow to 1 ml/min. Collect the eluate until all of the organochlorine pesticides of interest have been eluted (volume predetermined, see 10.3 below).

10.3 Determination of Elution Volumes

10.3.1 The elution volumes for the PCB's and the pesticides depend upon a number of factors which are difficult to control.

These include variation in:

a. mesh size of the silica gel

b. adsorption properties of the silica gel

c. polar contaminants present in the eluting solvent

d. polar materials present in the sample and sample solvent

e. the dimensions of the micro columns

Therefore, the optimum elution volume must be experimentally determined each time a factor is changed. To determine the elution volumes, add standard mixtures of Aroclors and pesticides to the column and serially collect 1 ml elution volumes. Analyze the individual eluates by gas chromatography and determine the cut-off volume for n-hexane and for ether-benzene. Figure 2 shows the elution patterns of the various PCB components and of the pesticides. Using this information prepare the proper standard mixtures required for analysis of the n-hexane and ether-benzene.

10.3.2 In determining the volume of hexane required to elute the PCB's, the sample volume (1 ml) and the volume of n-hexane (1/2 ml) used to rinse the column wall must be considered. Thus, if it is determined that a 10.0 ml elution volume is required to elute the PCB's, the additional volume of hexane to be added should be 8.5 ml.

10.3.3 Figure 2 shows that as the average chlorine content of a PCB mixture decreases the solvent volume for complete elution increases. Qualitative determination (10.2) indicates which Aroclor standard(s) best represent the PCB's present and provides the basis for selection of the ideal elution volume. This helps to minimize the quantity of organochlorine pesticides which will elute along with the low percent chlorine PCB's and insures the most efficient separation possible for accurate analysis.

10.3.4 For critical analysis where the PCB's and pesticides are not separated completely the column should be accurately calibrated according to 10.3.1 determining the percent of material of interest eluting in each fraction, then flush the column with an additional 15 ml of ether-benzene (0.5%) solution followed by 5 ml of n-hexane, then use the same column for the sample separation. Using this technique one can accurately predict the amount (%) of materials in each micro column fraction.

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11. Quantitative Determination

11.1 Measure the volume of solvent containing the PCB's and inject 1 to 5 µl into the gas chromatograph. (Conditions are listed in Figures 3 to 8). If necessary, adjust the volume of solvent to give linear response to the electron capture detector (detection limit approximately 0.1 ng). The microcoulometric or the electrolytic detector may be employed to improve specificity for samples having higher concentrations of PCB's (detection limit approximately 50 ng).

11.2 Calculations

10.2.1 Since polychlorinated biphenyls occur in the environment in varying degrees of complexity, it is impossible to prescribe a simple method for quantitative determination. They may occur:

a. As the unchanged commercial product, e.g., Aroclor 1242.

b. As a combination of unchanged commercial products, e.g., Aroclors 1242 + 1260.

c. As metabolized or biodegraded products of the original commercial product or products.

d. As a combination of a, b, and c.

11.2.2 For the least complicated situation, a, compare quantitative Aroclor reference standards (e.g., 1242, 1260) to the unknown. Measure and sum the areas of the unknown and the reference Aroclor and calculate the result as follows:

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$$\text{Microgram/liter} = \frac{[A]\,[B]\,[Vt]\,[N]}{[Vi]\quad[Vs]} \qquad \text{(Formula I)}$$

A = $\frac{\text{ng of Standard Injected}}{\text{of Standard Peak Areas}} = \frac{ng}{mm^2}$

B = of Sample Peak Areas $= mm^2$

Vi = Volume of sample injected (μl)

Vt = Volume of extract (μl)

Vs = Volume of water sample extracted (ml)

N = 2 when micro column used
= 1 when micro column not used

11.2.3 For complex situations (b, c, and d) the most practical calibration method is described in (3) below. Small variations in components between different Aroclor batches make it necessary to obtain samples of several specific Aroclors. These reference Aroclors can be obtained from Dr. Ronald Webb, Southeast Environmental Research Laboratory, EPA, Athens, Georgia 30601. The procedure is as follows:

1) Using the OV-1 column described in Figures 3 to 5, chromatograph a known quantity of each Aroclor reference standard. Also chromatograph a sample of p,p'-DDE. Suggested concentration of each standard is 0.1 ng/μl for the Aroclors and 0.02 ng/μl for p,p'-DDE.

2) Determine the relative retention time (RRT) of each PCB peak in the resulting chromatograms using p,p'-DDE as 100. See Figures 3 through 5.

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$$RRT = \frac{RT}{RT_{DDE}} \times 100 \qquad \text{(Formula II)}$$

RRT = Relative retention time

RT = Retention time of peak of interest

RT_{DDE} = Retention time of p,p'-DDE

Retention time is measured as that distance in mm between the first appearance of the solvent peak and the maximum response for each compound.

3) To calibrate the instrument for each PCB, measure the area of each peak. Using Tables 1 through 6 obtain the proper mean weight factor then determine the response factor, ng/mm^2.

Area = height X peak width at 1/2 height (Formula III)

$$ng/mm^2 = \frac{(ng_i)\ (\text{mean weight percent})}{\frac{100}{(\text{Area})}} \qquad \text{(Formula IV)}$$

ng_i = ng of Aroclor Standard Injected

mean weight percent = obtained from Tables 1 through 6.

4) Calculate the RRT value and the area for each PCB peak in the sample chromatogram. Compare the sample chromatogram to those obtained for each reference Aroclor standard. If it is apparent that the PCB peaks present are due to only one Aroclor then calculate the concentration of each PCB using the following formula.

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ng PCB = ng/mm^2 X Area (Formula V)

where Area = (mm^2) of sample peak

ng/mm^2 = Response factor for the peak measured.

Then add all the nanograms of PCB's present in the volume injected to get the total number of nanograms of PCB's present in the sample. Use the following formula to calculate the concentration of PCB's in the sample:

$$\text{Micrograms/liter} = \frac{[\Sigma ng]\ [V_t]\ [N]}{[V_s]\ \ [V_i]} \quad \text{(Formula VI)}$$

V_s = volume of water extracted (ml)

V_t = volume of extract (µl)

V_i = volume of sample injected (µl)

Σng = sum of all the PCB's in nanograms for that Aroclor identified

N = 2 when microcolumn used
= 1 when microcolumn not used

The value can then be reported as:

Micrograms/liter PCB's, and for samples containing more than one PCB use Figure 10 chromatogram divisional flow chart to assign a proper response factor to each peak and also identify the "most likely" Aroclors present. Calculate the ng PCB for each PCB present (Formula V), then sum them up according to the divisional flow chart using Formula VI to calculate and report the concentration of the various Aroclors present in the sample.

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12. Confirmatory Techniques

12.1 Unequivocal identification of PCB's can be made by gas chromatography-mass spectrometry (GC-MS) if present in sufficient concentration (approximately 20 ng/µl in the final extract). The methods described by Bonelli (4), Eichelberger, et al. (5), Goerlitz (6), and Goerlitz and Law (7) are useful for this purpose. When GC-MS is not available, separate GC analysis using both non-polar (Figures 3 to 5) and polar columns (Figures 6 to 9) will give added confidence in the qualitative determination. The use of specific halogen detectors, such as the microcoulometric and electrolytic conductivity, will eliminate non-halogen interferences and further support the identification. The concentration of PCB's required is about 10 ng/µl in the final extract.

12.2 ASTM method D 3304-74 (8) for PCB's which incorporates a two-step chemical treatment - saponification with alcoholic potassium hydroxide followed by sulfuric acid-effectively eliminates many interferences while the PCB's are retained intact. This procedure D 3304-74 may be used for analyses of industrial effluents when the determination of pesticides is not required and when the sensitivity of the method is adequate to meet the need.

13. Precision and Accuracy

13.1 Polychlorinated Biphenyl Recovery and Precision Data

Material	Concentration Range ng/l	Number of Samples	Recovery Average %	Single Operator Precision S_0%
Aroclor 1242	5000	7	104	10.2
Aroclor 1016	1000	27	99	6.9

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14. Standardization of Florisil Column by Weight Adjustment Based on Adsorption of Lauric Acid.

14.1 A rapid method for determining adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution (9) (10). An excess of lauric acid is used and the amount not adsorbed is measured by alkali titration. Weight of lauric acid adsorbed is used to calculate, by simple proportion, equivalent quantities of Florisil for batches having different adsorptive capacities.

14.2 Apparatus

14.2.1 Buret -- 25 ml with 1/10 ml graduations.

14.2.2 Erlenmeyer flasks -- 125 ml narrow mouth and 25 ml, glass stoppered.

14.3.3 Pipet -- 10 and 20 ml transfer

14.3.4 Volumetric flasks -- 500 ml

14.3 Reagents and Solvents

14.3.1 Alcohol, ethyl -- USP or absolute, neutralized to phenolphthalein end point.

14.3.2 Hexane -- Distilled from all glass apparatus.

14.3.3 Lauric acid -- Purified, CP

14.3.4 Lauric acid solution -- Transfer 10.000 g lauric acid to 500 ml volumetric flask, dissolve in hexane, and dilute to 500 ml (1 ml = 20 mg).

14.3.5 Phenolphthalein Indicator -- Dissolve 1 g in alcohol and dilute to 100 ml.

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14.3.6 Sodium hydroxide -- Dissolve 20 g NaOH (pellets, reagent grade) in water and dilute to 500 ml (1N). Dilute 25 ml 1N NaOH to 500 ml with water (0.05N). Standardize as follows: Weigh 100-200 mg lauric acid into 125 ml Erlenmeyer flask. Add 50 ml neutralized ethyl alcohol and 3 drops phenophthalein indicator; titrate to permanent end point. Calculate mg lauric acid/ml 0.05 N NaOH (about 10 mg/ml).

14.4 Procedure

14.4.1 Transfer 2.000 g of activated Florisil to 25 ml glass stoppered Erlenmeyer flasks. Cover loosely with aluminum foil and heat overnight at 130 C. Stopper, cool to room temperature, add 20.0 ml lauric acid solution (400 mg), stopper, and shake occasionally for 15 min. Let adsorbent settle and pipet 10.0 ml of supernantant into 125 ml Erlenmeyer flask. Avoid inclusion of any Florisil.

14.4.2 Add 50 ml neutral alcohol and 3 drops indicator solution; titrate with 0.05 N NaOH to a permanent end point.

14.5 Calculation of Lauric Acid Value and Adjustment of Column Weight

14.5.1 Calculate amount of lauric acid adsorbed on Florisil as follows:

Lauric Acid value = mg lauric acid/g Florisil = 200 - (ml required for titration X mg lauric acid/ml 0.05 N NaOH).

14.5.2 To obtain an equivalent quantity of any batch of Florisil, divide 110 by lauric acid value for that batch and multiply by 20 g. Verify proper elution of pesticides by 13.6

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14.6 Test for Proper Elution Pattern and Recovery of Pesticides:

Prepare a test mixture containing aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, parathion and malathion. Dieldrin and parathion should elute in the 15% eluate; all but a trace of malathion in the 50% eluate and the others in the 6% eluate.

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Table 1

Composition of Aroclor 1221 (3)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
11	31.8	15.8	1
14	19.3	9.1	1
16	10.1	9.7	2
19	2.8	9.7	2
21	20.8	9.3	2
28	5.4	13.9	2 85% 3 15%
32	1.4	30.1	2 10% 3 90%
[37 [40	1.7	48.8	3 3
Total	93.3		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of seventeen results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

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Table 2

Composition of Aroclor 1232 (3)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
11	16.2	3.4	1
14	9.9	2.5	1
16	7.1	6.8	2
[20	17.8	2.4	2
[21			2
28	9.6	3.4	2] 40%
			3] 60%
32	3.9	4.7	3
37	6.8	2.5	3
40	6.4	2.7	3
47	4.2	4.1	4
54	3.4	3.4	3] 33%
			4] 67%
58	2.6	3.7	4
70	4.6	3.1	4] 90%
			5] 10%
78	1.7	7.5	4
Total	94.2		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of four results as a mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 3

Composition of Aroclor 1242 (3)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
11	1.1	35.7	1
16	2.9	4.2	2
21	11.3	3.0	2
28	11.0	5.0	2] 25% 3] 75%
32	6.1	4.7	3
37	11.5	5.7	3
40	11.1	6.2	3
47	8.8	4.3	4
54	6.8	2.9	3] 33% 4] 67%
58	5.6	3.3	4
70	10.3	2.8	4] 90% 5] 10%
78	3.6	4.2	4
84	2.7	9.7	5
98	1.5	9.4	5
104	2.3	16.4	5
125	1.6	20.4	5] 85% 6] 15%
146	1.0	19.9	5] 75% 6] 25%
Total	98.5		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

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Table 4

Composition of Aroclor 1248 (3)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
21	1.2	23.9	2
28	5.2	3.3	3
32	3.2	3.8	3
37	8.3	3.6	3
40	8.3	3.9	3] 85%
			4] 15%
47	15.6	1.1	4
54	9.7	6.0	3] 10%
			4] 90%
58	9.3	5.8	4
70	19.0	1.4	4] 80%
			5] 20%
78	6.6	2.7	4
84	4.9	2.6	5
98	3.2	3.2	5
104	3.3	3.6	4] 10%
			5] 90%
112	1.2	6.6	5
125	2.6	5.9	5] 90%
			6] 10%
146	1.5	10.0	5] 85%
			6] 15%
Total	103.1		

[a]Retention time relative to p,p'-DDE=100. Measured fro first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 5

Composition of Aroclor 1254 (3)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
47	6.2	3.7	4
54	2.9	2.6	4
58	1.4	2.8	4
70	13.2	2.7	4] 25%
			5] 75%
84	17.3	1.9	5
98	7.5	5.3	5
104	13.6	3.8	5
125	15.0	2.4	5] 70%
			6] 30%
146	10.4	2.7	5] 30%
			6] 70%
160	1.3	8.4	6
174	8.4	5.5	6
203	1.8	18.6	6
232	1.0	26.1	7
Total	100.0		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers are bracketed.

Table 6

Composition of Aroclor 1260 (3)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
70	2.7	6.3	5
84	4.7	1.6	5
[98	3.8	3.5	] d
104			5 60%
			6 40%
117	3.3	6.7	6
125	12.3	3.3	5 15%
			6 85%
146	14.1	3.6	6
160	4.9	2.2	6 50%
			7 50%
174	12.4	2.7	6
203	9.3	4.0	6 10%
			7 90%
[232			] e
244	9.8	3.4	6 10%
			7 90%
280	11.0	2.4	7
332	4.2	5.0	7
372	4.0	8.6	8
448	.6	25.3	8
528	1.5	10.2	8
Total	98.6		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of six results as a mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

[d]Composition determined at the center of peak 104.

[e]Composition determined at the center of peak 232.

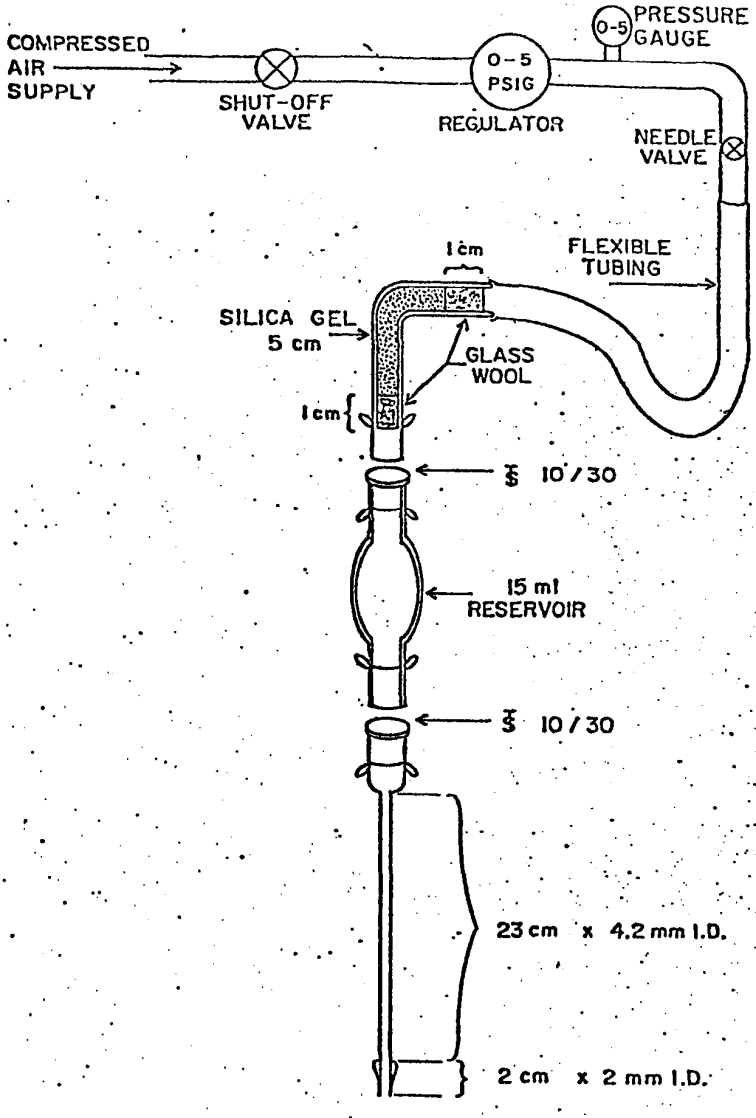
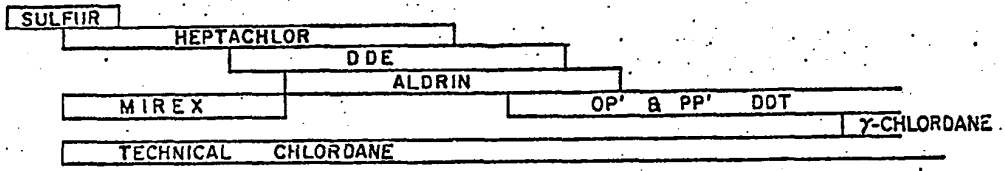
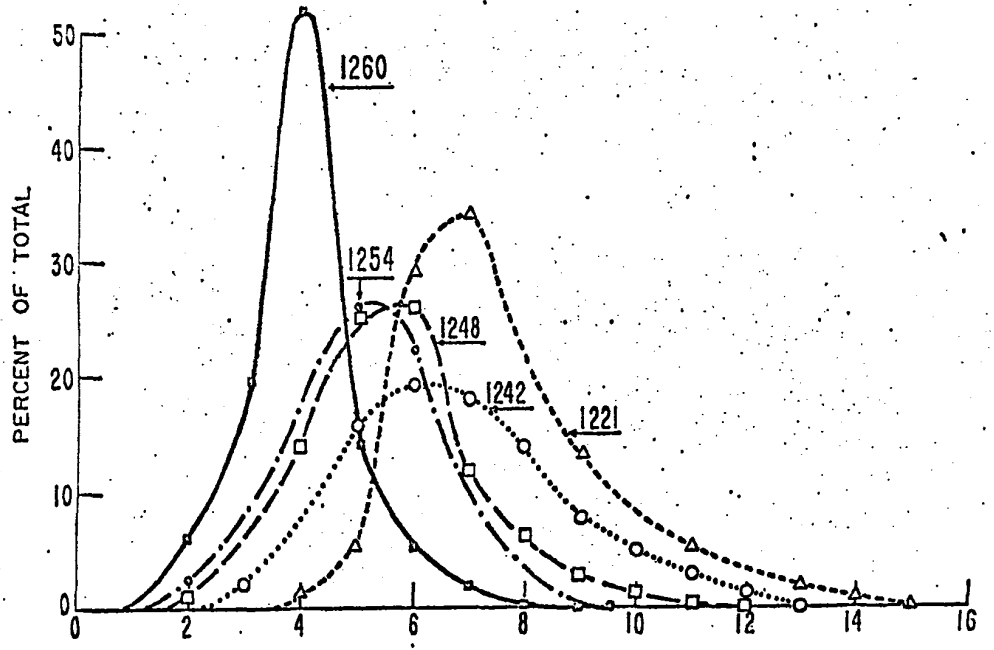


FIGURE 1. MICROCOLUMN SYSTEM

MONS 047486

MONS 047487


SULFUR
HEPTACHLOR
DDE
ALDRIN
MIREX
OP' & PP' DDT
γ-CHLORDANE
TECHNICAL CHLORDANE


PERCENT OF TOTAL
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
1260
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1248
1242
1221

047488
MONS

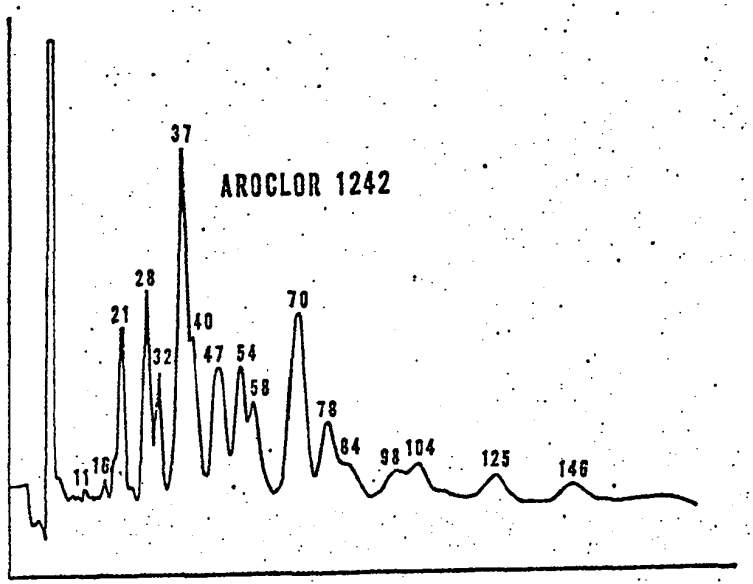


Figure 3. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture

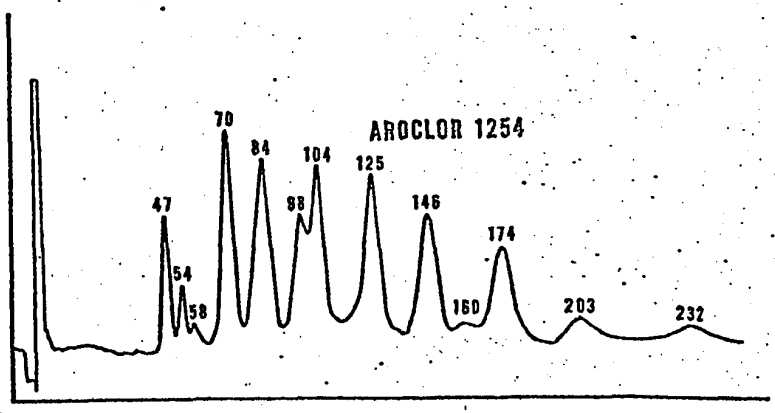


Figure 4. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture.

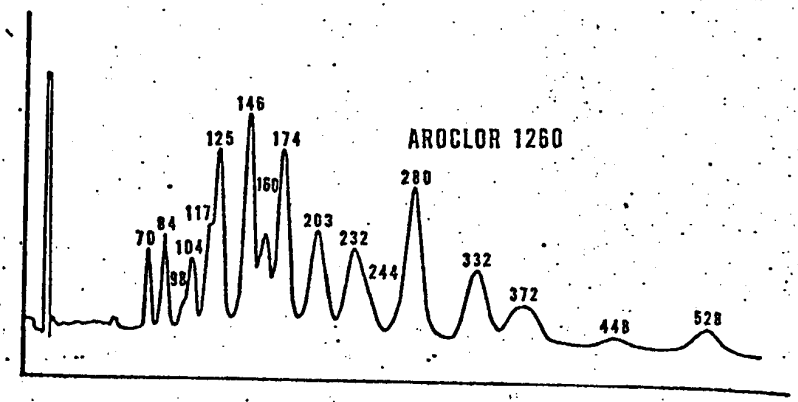


Figure 5. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture.

MONS 047490

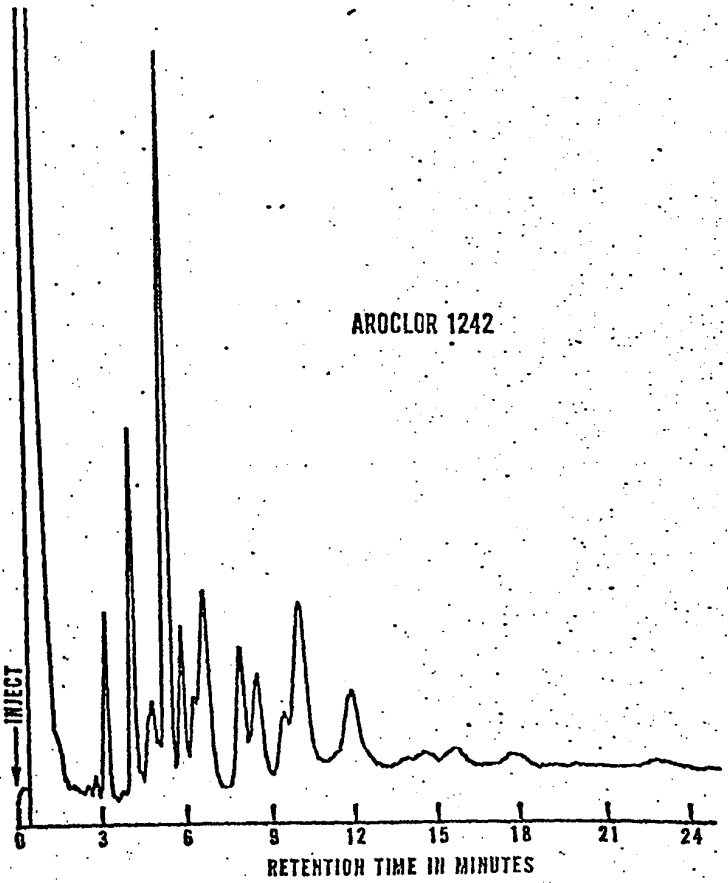


Figure 6. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

MONS 047492

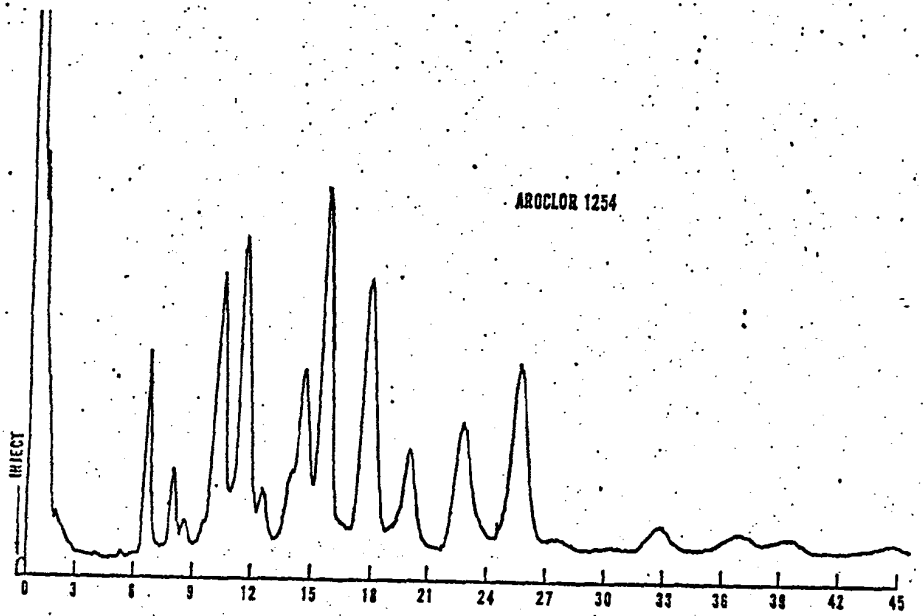
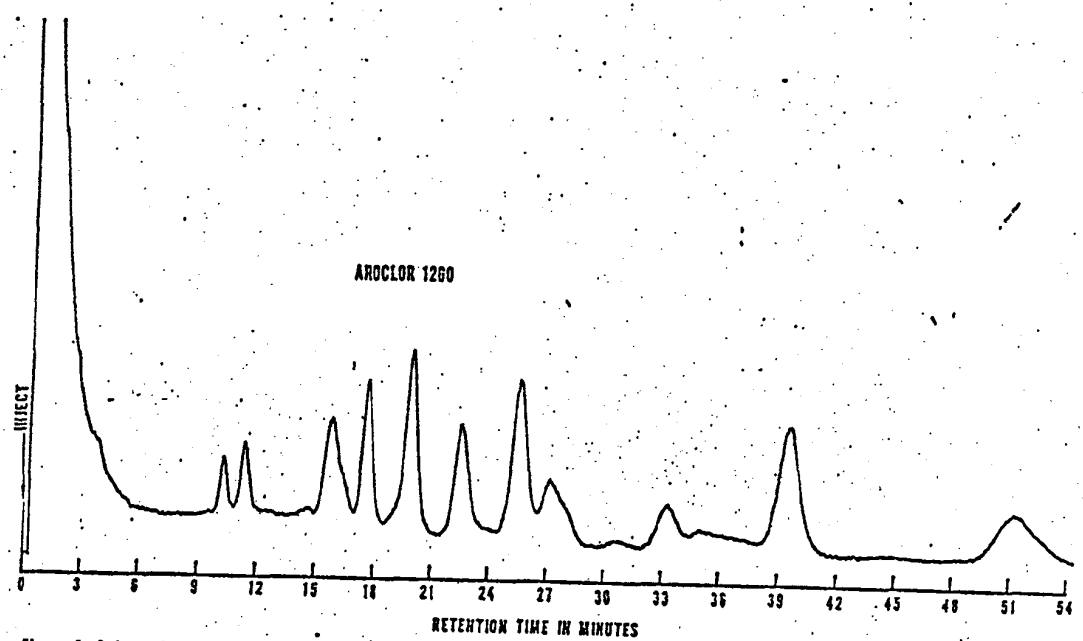


Figure 7. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.



MONS 047493

Figure 8. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200C, Detector: Electron Capture.

Fig 9 Aroclor 1016
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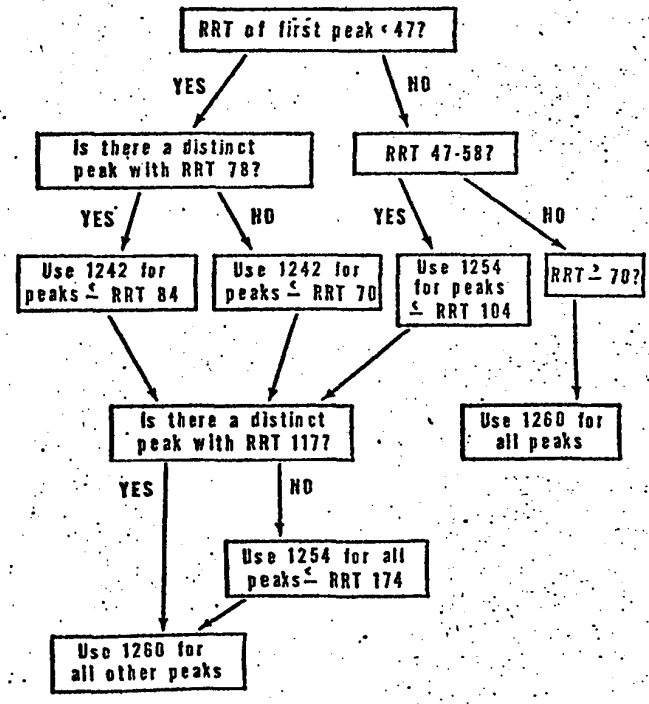

Figure 10. Chromatogram Division Flowchart (3).