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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Polychlorinated Biphenyls (PCBs) in Water [1]

This standard is issued under the fixed designation D 3534; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε[1] NOTE—Section 14 was added editorially in June 1995.

1. Scope

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

1.2 The detection limit is in the range from 0.1 to 0.5 µg/L for Aroclor 1254 and 1260 when analyzing 1 L of water using an electron capture detector. The detection limit is compound dependent and is also determined by instrumental sensitivity and interferences present. When using a microcoulometric or conductivity detector, the detection limit is approximately 1.0 µg/L.

1.3 Precision and bias statements reflect recovery of PCB products dosed into water samples. These statements may not apply to environmentally altered PCBs.

1.4 As the precision and bias statements given may apply only to waters used, it is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are provided for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific hazard statement, see Note 2.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 3086 Test Method for Organochlorine Pesticides in Water[4]

D 3304 Method for Analysis of Environmental Materials for Polychlorinated Biphenyls[5]

D 3370 Practices for Sampling Water[3]

D 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents[4]

E 355 Practice for Gas Chromatography Terms and Relationships[6]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129 and Practice E 355.

4. Summary of Test Method

4.1 Polychlorinated biphenyls are extracted by liquid-liquid extraction and are separated from interferences prior to gas chromatographic determination. Sulfuric acid partitioning or a combination of the standard Florisil[7] column cleanup procedure and a silica gel microcolumn separation procedure **(1,2,3)**[8] 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 0.1 µg/L for the PCB mixtures (Aroclors) listed in 1.1 when analyzing 1 L of sample using an electron capture detector. When using a microcoulometric or conductivity detector, the detection limit is approximately 1.0 µg/L. Precision and accuracy statements reflect recovery of PCB products dosed into water samples. These statements do not apply to environmentally altered PCBs.

5. Significance and Use

5.1 The extensive and widespread use of PCBs has resulted in their presence in all parts of the environment. Like the organochlorine pesticides, the PCBs are very persistent. While they are generally less toxic than the organochlorine pesticides, they do have adverse effects on mammals, birds, fish, and other

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[2] Aroclor is a registered trademark of Monsanto Co. All Aroclor production was stopped in 1977. For alternate availability, see paragraph 8.4 of this test method.

[3] *Annual Book of ASTM Standards,* Vol 11.01.

[4] *Annual Book of ASTM Standards,* Vol 11.02.

[5] *Annual Book of ASTM Standards,* Vol 10.03.

[6] *Annual Book of ASTM Standards,* Vol 14.02.

[7] Florisil, a trademark of and available from Floridin Co., Three Penn Center, Pittsburgh, PA 15235, has been found satisfactory for this purpose.

[8] The boldface numbers in parentheses refer to the list of references at the end of this test mthod.

aquatic animals. Thus, we must identify and quantitate the PCBs present in the environment. Because of their cumulative nature and level of occurrence, the method for their determination must be capable of measuring quantities less than 1 µg/L in water.

6. Interferences

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

6.2 Organochlorine pesticides and other halogenated compounds constitute interferences in the determination of PCBs. Most of these are separated by the test method described in this standard. However, certain compounds, if present in the sample, will occur with the PCBs. Included are sulfur, heptachlor, aldrin, DDE, chlordane, mirex, and to some extent *o,p′*-DDT and *p,p′*-DDT. Sulfur may be removed by the addition of elemental mercury **(4)**.

7. Apparatus

7.1 *Glassware*, Kuderna-Danish (K-D).

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[9] (400 mm long by 19-mm inside diameter) with coarse-fritted plate on bottom and TFE-fluorocarbon stopcock; 250-mL reservoir bulb at top of column with flared out funnel shape at top of bulb.

7.3 *Chromatographic Column*, borosilicate glass (approximately 400 mm long by 20-mm inside diameter) with a coarse-fritted plate.

7.4 *Microcolumn*, borosilicate glass, constructed in accordance with Fig. 1.

7.5 *Capillary Pipets*, disposable, 5¾-in. (146 mm), with rubber bulb.

7.6 *Low-Pressure Regulator*, 0 to 5 psig (0 to 34 kPa), 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).

7.11 *Gas Chromatograph* (GC), equipped with an on-column or glass-lined injection port and an electron capture, microcoulometric, or electrolytic conductivity detector. As an option, a capillary column GC with a split, splitless, or on-column injection system (depending on sensitivity required) and one of the above detectors may be used.

7.12 *Sample Container*, 1000-mL glass (amber glass preferred) bottle with TFE-fluorocarbon-lined screw cap. Clean by washing with warm soapy water, remove soap by rinsing with tap water then reagent water, rinse with methylene chloride, final rinse with reagent water followed by heating at 180°C for a minimum of 4 h. Caps and liners should be cleaned similarly without heating. Alternatively, clean bottles following the procedure in Practices D 3694.

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.[10] 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 Specification D 1193, Type II.

8.3 *Antistatic Solution*. [11]

8.4 *PCB Standards* [12]—Aroclors 1221, 1232, 1242, 1248, 1254, 1260, and 1016.

NOTE 1—Polychlorinated biphenyls and their concentrated solutions should be handled so as to avoid contact to the analyst.

8.5 *Diethyl Ether*—Pesticide quality, redistilled in glass, if necessary, and containing 2 % (volume per volume) ethanol.

8.5.1 Ether must be free of peroxides according to the following test: to 10 mL of ether in a glass-stoppered cylinder previously rinsed with ether, add 1 mL of freshly prepared 10 % KI solution. Shake and let stand 1 min. No yellow color should be observed in the ether layer. As an alternative, test strips[13] may be used.

8.5.2 Decompose ether peroxides by adding 40 g of a solution of 30 % (weight per volume) ferrous sulfate solution per litre of solvent.

NOTE 2—**Warning:** Reaction may be vigorous if the solvent contains a high concentration of peroxides.

8.5.3 Distill peroxide-free ether in glass and add 2 % (volume per volume) ethanol.

8.6 *Florisil*, PR grade 60 to 100 mesh; purchase activated at 1250°F (675°C) 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 Annex A1).

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*:

[9] Chromaflex, trademark of Kontes Glass Co., [as a special order (Kontes 42540-9011)], Vineland, NJ 08360, has been found satisfactory for this purpose.

[10] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[11] Stanul, trademark of, and available from Daystrom Inc., Weston Instrument Div., Newark, NJ 07112, has been found satisfactory for this purpose.

[12] The proportions of individual PCB isomers may vary from one lot to another and from one manufacturer to another. Standard solutions are available from US EPA, 26 W. Martin L. King St., Cincinnati, OH 45219.

[13] EM Quant test strips, trademark of, and available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, NY 10523, have been found satisfactory for this purpose. An equivalent may also be used.

8.8.1 Refer to Test Method D 3086.

8.8.2 *Tubing*, borosilicate glass (1800 mm long by 2 to 4-mm inside diameter).

8.8.3 *Glass Wool*, silanized.

8.8.4 *Solid Support, Gas Chrom Q*, [14] 100 to 120-mesh, or equivalent.

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 %.

8.8.6 *Capillary Column*, 20 to 30 m fused silica with bonded methyl silicone or methylphenyl silicone phase or equivalent (needed only for capillary GC option).

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 %)—Mix 0.5 volume of ethyl ether with benzene to make 100 volumes of solvent.

8.11.2 *Ethyl Ether—Petroleum Ether Mixture* (6 %)—Mix 6 volumes of ethyl ether with petroleum ether to make 100 volumes of solvent.

8.11.3 *Ethyl Ether—Petroleum Ether Mixture* (15 %)—Mix 15 volumes of ethyl ether with petroleum ether to make 100 volumes of solvent.

8.11.4 *Ethyl Ether—Petroleum Ether Mixture* (50 %)—Mix 50 volumes of ethyl ether with petroleum ether to make 100 volumes of solvent.

8.11.5 *Methylene Chloride—Hexane Mixture* (15 %)—Mix 15 volumes of methylene chloride with hexane to make 100 volumes of solvent.

8.12 *Petroleum Ether*, pesticide quality, 30 to 60°C boiling range.

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

8.14 *Silica Gel*. [15]

8.15 *Sodium Sulfate*, granular, anhydrous, conditioned for 4 h at 400°C.

8.16 *Methylene Chloride*, pesticide quality.

8.17 *Isooctane*, pesticide quality.

9. Extraction of Sample

9.1 Transfer 1 L of the sample to a 2-L separatory funnel equipped with a TFE-fluorocarbon stopcock. Rinse the 1-L sample bottle and lid with 100 mL of extraction solvent (methylene chloride/hexane mixture) and pour the solvent into the separatory funnel. Extract the water sample by vigorously shaking the separatory funnel for 2 min. Allow the phases to separate and drain the lower phase back into the original sample bottle. Drain the upper phase (solvent) into a clean, unused sample bottle. Extract the water two more times with fresh solvent, compositing the extracts in the second bottle. Discard the aqueous phase after the third extraction.

9.2 Dry the combined extracts by pouring through a 10-cm column of anhydrous sodium sulfate (previously rinsed with hexane). Rinse both bottles with 100 mL of extraction solvent and pour through the sodium sulfate column. Add approximately 5 mL of *iso*octane and concentrate to 3 to 5 mL in a Kuderna-Danish evaporator. Qualitatively analyze the sample by gas chromatography. From the response obtained decide:

9.2.1 If it is obvious that only organochlorine pesticides are present,

9.2.2 If it is obvious that only PCBs are present (negligible amounts or organochlorine pesticides),

9.2.3 If there is a combination of 9.2.1 and 9.2.2, and

9.2.4 If the response is too complex to determine 9.2.1, 9.2.2, or 9.2.3. If no response, concentrate to 1.0 mL or less and repeat the analysis looking for 9.2.1, 9.2.2, 9.2.3, and 9.2.4. Trace quantities of PCBs are often masked by the background which usually occurs in the samples. If detection limits below 100 ng/L are required, proceed as directed in Section 10 even though the presence of PCB peaks is not apparent in the chromatogram.

9.3 If condition 9.2.1 exists, determine the organochlorine pesticides if desired by following the procedure in Test Method D 3086.

9.4 If condition 9.2.2 exists, PCBs only are present and no further separation or clean-up is necessary; then proceed as in 11.2.2 or 11.2.3.

9.5 If condition 9.2.3 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 PCBs present. To separate the PCBs from the organochlorine pesticides, continue as outlined in 9.6.

9.6 If condition 9.2.4 exists, remove interferences by partitioning with sulfuric acid (9.6.1) or Florisil and silica gel column procedure (9.7 and **(5)**).

9.6.1 To remove interferences with sulfuric acid, shake the concentrated extract with 1 to 2 mL of concentrated sulfuric acid for 1 min. Repeat with fresh acid until the acid remains colorless or slightly yellow. Reanalyze the extract and continue to 9.7 if interferences are still present.

9.7 *Florisil Column Procedure*:

9.7.1 Adjust the sample extract volume to 10 mL with petroleum ether.

9.7.2 Place a charge of activated Florisil (weight determined by lauric acid value, see Annex A1) in a Chromaflex column. After settling the Florisil by tapping the column, add about 13-mm layer of anhydrous granular sodium sulfate to the top.

9.7.3 After cooling, preelute the column with 50 to 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/min 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. By using an equivalent quantity of any batch of Florisil as determined by its lauric acid value, the PCBs and pesticides will be separated

[14] Gas Chrom Q is trademark of and is available from Applied Science Laboratories, State College, PA 16801.

[15] Davison code 950-08-226 (60/200 mesh) has been found satisfactory for this purpose.

into the eluates indicated below:

6 % Eluate		
PCBs	DDT	Mirex
Aldrin	Heptachlor	Pentachloronitrobenzene
BHC	Heptachlor Epoxide	
Chlordane	Lindane	Strobane
DDD	Methoxychlor	Toxaphene
DDE		Trifluralin

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 (Vol 1, Section 201) **(6).**

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

9.7.5 To further separate the PCBs from organochlorine pesticides, continue with directions in Section 10 with the 6 % eluate.

10. Silica Gel Microcolumn Separation Procedure

10.1 *Activation of Silica Gel in Microcolumn*—Place about 20 g of silica gel in a 100-mL beaker. Activate at 180°C for approximately 16 h. Transfer the activated silica gel to a 100-mL glass stoppered bottle. When cool, cover with about 35 mL of diethyl ether-benzene, 0.5 % (volume per volume). 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 the bottle (approximately 13 mm above silica gel). Silica gel can be effectively stored in this manner for several days.

10.2 *Preparation of the Chromatographic Column*—Pack the lower 2-mm inside diameter section of the microcolumn with 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 microcolumn. Fill the microcolumn with the ether-benzene solution to the bottom of the 10/30 joint (Fig. 1). Using a disposable capillary pipet, transfer several portions of the silica gel slurry into the microcolumn. After approximately 10 mm of silica gel collects in the bottom of the microcolumn, remove the rubber bulb seal, and tap the column to ensure that the silica gel settles uniformly. Carefully pack the column until the silica gel is within 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 antistatic solution (8.3).

10.2.1 *Deactivation of the Silica Gel*:

10.2.1.1 Fill the microcolumn to the base of the 10/30 joint with the ether-benzene solution, assemble the reservoir (using spring clamps) and fill with approximately 15 mL of 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 the reservoir just as the last of the solvent enters the sodium 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.

10.2.1.2 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) to just elute all of the PCBs 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.

10.2.1.3 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).

10.3 *Determination of Elution Volumes*:

10.3.1 The elution volumes for the PCBs and the pesticides depend upon a number of factors which are difficult to control. These include variations in:

10.3.1.1 Mesh size of the silica gel,

10.3.1.2 Adsorption properties of the silica gel,

10.3.1.3 Polar contaminants present in the eluting solvent,

10.3.1.4 Polar materials present in the sample and sample solvent (found to be a problem in bottom samples which have high levels of polar materials), and

10.3.1.5 Dimensions of the microcolumns. 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.

10.3.1.5.1 Analyze the individual eluates by gas chromatography and determine the cut-off volume for *n*-hexane and for ether-benzene. Refer to Fig. 2 which 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 PCBs, the sample volume (1 mL) and the volume of *n*-hexane (0.5 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 PCBs, the additional volume of hexane to be added should be 8.5 mL.

10.3.3 Fig. 2 shows that as the average chlorine content of a PCB mixture decreases the solvent volume for complete elution increases. Qualitative determination (9.2) indicates which Aroclor standard(s) best represents the PCBs 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 PCBs and ensures the most efficient separation possible for accurate analysis.

10.3.4 For critical analysis where the PCBs and pesticides are not separated completely the column should be accurately calibrated in accordance with 10.3.1, and the percent of material of interest eluting in each fraction must be determined.

10.3.4.1 Flush the column with an additional 15 mL of ether-benzene (0.5 %) solution followed by 5 mL of *n*-hexane, and use the same column for the sample separation. Using this technique one can accurately predict the amount (percent) of materials in each microcolumn fraction.

11. Quantitative Determination

11.1 Measure the volume of solvent containing the PCBs and inject 1 to 5 µL into the gas chromatograph. (Conditions are listed in Figs. 3-9.) If necessary, adjust the injection volume to give linear response to the electron capture detector (detection limit approximately 0.1 ng). A microcoulometric or an electrolytic detector may be employed to improve specificity for samples having higher concentrations of PCBs (detection limit approximately 50 ng).

11.2 *Calculations*:

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

11.2.1.1 As the unchanged commercial product, for example, Aroclor 1242,

11.2.1.2 As a combination of unchanged commercial products, for example, Aroclors 1242 and 1260,

11.2.1.3 As metabolized or biodegraded products of the original commercial product or products, and

11.2.1.4 As a combination of 11.2.1.1, 11.2.1.2, and 11.2.1.3.

11.2.2 For the least complicated situation, 11.2.1.1, compare quantitative Aroclor reference standards (for example 1242, 1260) to the unknown. Measure and sum the areas of the unknown and the reference Aroclor and calculate the result as follows:

$$\text{Concentration, µg/L} = \frac{[A] \times [B] \times [V_t] \times [N]}{[V_i] \times [V_s]} \quad (1)$$

where:

A = ng of standard injected divided by Σ of standard peak areas, mm^2,
B = Σ of sample peak areas, mm^2,
V_i = volume of sample injected, µL,
V_t = volume of extract, µL,
V_s = volume of water sample extracted, mL, and
N = 2 when microcolumn used
N = 1 when microcolumn not used.

11.2.3 For complex situations (11.2.1.2, 11.2.1.3, and 11.2.1.4) the most reproducible calibration and calculation method **(7)** is described in the following sections. This calibration method is applicable only to analyses performed by packed column gas chromatography. The overall accuracy of the test method may decrease as the degree of environmental alteration increases because of changes in the relative concentrations of unresolved components within individual gas chromatographic peaks. Small variations in components between different batches of each Aroclor product may make it necessary to obtain standard samples for which mean weight factors (11.2.3.3) have been determined.

11.2.3.1 Using the OV-1 column referred to in Figs. 3-6, 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 to 2 ng/µL for the Aroclors and 0.02 to 0.2 ng/µL for *p,p′*-DDE.

11.2.3.2 Determine the relative retention time (RRT) of each PCB peak in the resulting chromatograms based on a retention time of 100 for *p,p′*-DDT. See Figs. 3-6.

$$RRT = \frac{RT}{RT_{DDE}} \times 100 \quad (2)$$

where:

RRT = relative retention time of PCB peak,
RT = retention time of peak of interest, and
RT_{DDE} = retention time of *p,p′*-DDE = 100.

Retention time is measured as the distance (millimetres) between the first appearance of the solvent peak and the maximum response for each compound.

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

$$A = H \times P \quad (3)$$

where:

A = area,
H = height, and
P = peak width at ½ height.

$$R = \frac{ng_i \times M/100}{A_m} \quad (4)$$

where:

ng_i = Aroclor standard injected, ng,
mean weight percent = obtained from Tables 1-6,
R = response factor, ng/mm^2,
M = mean weight percent, and
A_m = area of sample peak, mm^2.

11.2.3.4 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 as follows:

$$\text{PCB, ng} = \text{ng/mm}^2 \times A_m \quad (5)$$

where:

A_m = area of sample peak, mm^2, and
ng/mm^2 = response factor for the peak measured.

Then add the nanograms of all PCB peaks present to get the total number of nanograms of PCBs injected. Use the following equation to calculate the concentration of PCBs in the sample:

$$\text{Concentration, µg/L} = \frac{[\Sigma ng] \times [V_t] \times [N]}{[V_s \times [V_i]} \quad (6)$$

where:

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 PCBs for that Aroclor identified, ng, and
N = 2 when microcolumn used, or
= 1 when microcolumn not used.

11.2.3.5 The value can then be reported as micrograms per litre PCBs. For samples containing more than one PCB, use Fig. 10, chromatogram divisional flow chart, to assign a proper response factor to each peak and also identify the "most likely" Aroclors present. Calculate the nanograms of each PCB present (Eq 5); then sum them in accordance with the divisional flow chart using Eq 6 to calculate and report the concentration of the various Aroclors present in the sample.

12. Confirmatory Techniques

12.1 Unequivocal identification of PCBs 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 **(8)**, Eichelberger, et al **(9)**, Goerlitz **(10)**, and Goerlitz and Law **(11)** are useful for this purpose. When GC-MS is not available, separate GC analyses using both nonpolar (Figs. 3-6) and polar columns (Figs. 7-9 and Fig. 11) will give added confidence in the qualitative determination. The use of specific halogen detectors, such as microcoulometric and electrolytic conductivity, eliminates nonhalogen interferences and further supports the identification. The concentration of PCBs required is about 10 ng/µL in the final extract.

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

13. Precision and Bias [16]

13.1 The precision of this test method was tested by 8 laboratories with reagent water, tap water, sea water, well water, and chemical plant effluent.

13.2 Each laboratory received 3 sets of flame sealed ampules containing solutions of PCBs in methyl alcohol. Each set consisted of 4 vials representing 3 concentration levels plus a blank.

13.3 On each analysis day, the laboratories were instructed to prepare one sample of reagent water and one sample of matrix water from each ampule in a set by injecting 100 µL of the methyl alcohol solution into a litre of water.

13.4 The laboratories were then instructed to analyze the water samples following the test method and to identify the unknown PCB formulation, that is, Aroclor 1242, 1248, 1254, etc., and to determine its concentration in the water.

13.5 Precision, single operator (S_o) and overall (S_t), and bias are given in Table 7 for reagent water and Table 8 for matrix water. Precision is plotted as a function of concentration in Fig. 12 for reagent water and in Fig. 13 for matrix water.

13.6 These data may not apply to waters of other matrices, therefore, it is the responsibility of the analyst to assure the validity of this test method in a particular matrix.

14. Keywords

14.1 Arocolor; electron capture detector; gas chromatography; PCBs; polychlorinated biphenyls

[16] Supporting data are available from ASTM Headquarters. Request RR: D19-1113.

ANNEX

(Mandatory Information)

A1. STANDARDIZATION OF FLORISIL COLUMN BY WEIGHT ADJUSTMENT BASED ON ADSORPTION OF LAURIC ACID

A1.1 A rapid method for determining the adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution **(6) (5)**. An excess of lauric acid is used and the amount not adsorbed is measured by alkali titration. The weight of lauric acid adsorbed is used to calculate, by simple proportion, the equivalent quantities of Florisil for batches having different adsorptive capacities.

A1.2 *Apparatus:*

A1.2.1 *Buret*, 25-mL with 1/10-mL graduations.

A1.2.2 *Erlenmeyer Flasks*, 125-mL narrow mouth and 25-mL glass stoppered.

A1.2.3 *Pipet*, 10 and 20-mL transfer.

A1.2.4 *Volumetric Flasks*, 500-mL.

A1.3 *Reagents and Solvents:*

A1.3.1 *Alcohol, Ethyl*, USP or absolute, neutralized to phenolphthalein end point.

A1.3.2 *Hexane*, distilled from all glass apparatus.

A1.3.3 *Lauric Acid*, purified, CP.

A1.3.4 *Lauric Acid Solution*—Transfer 10.000 g of lauric acid to a 500-mL volumetric flask, dissolve in hexane, and dilute to 500 mL (1 mL = 20 mg).

A1.3.5 *Phenolphthalein Indicator*—Dissolve 1 g in alcohol and dilute to 100 mL.

A1.3.6 *Sodium Hydroxide Solution (0.05 N)*—Dissolve 20 g of NaOH (pellets, reagent grade) in water and dilute to 500 mL to prepare a 1 *N* solution. Dilute 25 mL of 1 *N* NaOH solution to 500 mL with water to prepare a (0.05 *N*) solution. Standardize as follows: Weigh 100 to 200 mg of lauric acid into a 125-mL Erlenmeyer flask. Add 50 mL of neutralized

ethyl alcohol and 3 drops of phenolphthalein indicator; titrate to the permanent end point. Calculate the milligrams of lauric acid per millilitre of 0.05 *N* NaOH solution (about 10 mg/mL).

A1.4 *Procedure:*

A1.4.1 Transfer 2.000 g of activated Florisil to a 25-mL glass-stoppered Erlenmeyer flask. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, cool to room temperature, add 20.0 mL of lauric acid solution (400 mg), stopper, and shake occasionally for 15 min. Let adsorbent settle and pipet 10.0 mL of the supernatant into a 125-mL Erlenmeyer flask. Avoid inclusion of any Florisil.

A1.4.2 Add 50 mL of neutral alcohol and 3 drops of indicator solution; titrate with 0.05 *N* NaOH solution to a permanent end point.

A1.5 *Calculation of Lauric Acid Value and Adjustment of Column Weight:*

A1.5.1 Calculate amount of lauric acid adsorbed on Florisil as follows:

$$\text{Lauric acid value, } S_1 = 200 - VS_2$$

where:

S_1 = milligrams of lauric acid per gram of florisil,
S_2 = milligrams of lauric acid per millilitre of 0.05 *N* NaOH solution, and
V = millilitres of 0.05 *N* NaOH solution required for titration.

A1.5.2 To obtain an equivalent quantity of any batch of Florisil, divide 110 by the lauric acid value for that batch and multiply by 20 g. Verify proper elution of pesticides by A1.6.

A1.6 *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 should elute in the 50% eluate and the others in the 6 % eluate.

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(**3**) McClure, V. E., "Precisely Deactivated Adsorbents Applied to the Separation of Chlorinated Hydrocarbons," *Journal of Chromatography*, Vol 70, 1972, p. 168.

(**4**) *Federal Register*, Vol 44, No. 233, Dec. 3, 1979, p. 69503.

(**5**) Mills, P. A.," Variation of Florisil Activity: Simple Method for Measuring Capacity and Its Use in Standardizing Florisil Columns," *Journal of the Association of Official Analytical Chemists*, Vol 51, 1968, p. 29.

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(**7**) Webb, R. G., and McCall, A. C., "Quantitative PCB Standards for Electron Capture Gas Chromatography," *Journal of Chromatographic Science*, Vol 11, 1973, p. 366.

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(**9**) Eichelberger, J. W., et al, "Analysis of the Polychlorinated Biphenyl Problem—Application of Gas Chromatography-Mass Spectrometry with Computer Controlled Repetitive Data Aquisition from Selected Specific Ions," *Analytical Chemistry*, Vol 46, 1974, p. 277.

(**10**) Goerlitz, D. F., private communication, February 1972.

(**11**) Goerlitz, D. F., and Law, L. M., "Chlorinated Naphthalenes in Pesticide Analysis," *Bulletin of Environmental Contamination and Toxicology*, Vol 7, 1972, p. 243.

TABLE 1 Composition of Aroclor 1221 (7)

RRT [A]	Mean Weight Percent	Relative Standard Deviation [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	1.7	48.8	3
40			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 17 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 2 Composition of Aroclor 1232 (7)

RRT [A]	Mean Weight Percent	Relative Standard Deviation [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 (7)

RRT [A]	Mean Weight Percent	Relative Standard Deviation [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.

TABLE 4 Composition of Aroclor 1248 (7)

RRT [A]	Mean Weight Percent	Relative Standard Deviation [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 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.

TABLE 5 Composition of Aroclor 1254 (7)

RRT [A]	Mean Weight Percent	Relative Standard Deviation [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 (7)

RRT [A]	Mean Weight Percent	Relative Standard Deviation [B]	Number of Chlorines [C]
70	2.7	6.3	5
84	4.7	1.6	5
98] 104]	3.8	3.5	5] [D,E] 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] 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	0.6	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.

TABLE 7 Precision and Bias for PCBs in Reagent Water

Aroclor 1254 Amount Added, µg/L	Amount Found, µg/L	Precision, µg/L		Bias	% Bias	Statistically Significant
		S_t	S_o			
1.87	1.89	0.531	0.263	+ 0.02	+ 1.1	No
9.36	8.19	1.45	0.854	−1.17	−12.5	Yes
38.7	33.6	7.43	3.03	−5.10	−13.2	Yes

TABLE 8 Precision and Bias for PCBs in Matrix Water

Aroclor 1254 Amount Added, µg/L	Amount Found, µg/L	Precision, µg/L		Bias	% Bias	Statistically Significant
		S_t	S_o			
1.87	1.71	0.445	0.393	−0.16	−8.6	Yes
9.36	8.12	1.88	1.08	−1.24	−13.2	Yes
38.7	34.8	8.94	5.48	−3.90	−10.1	Yes

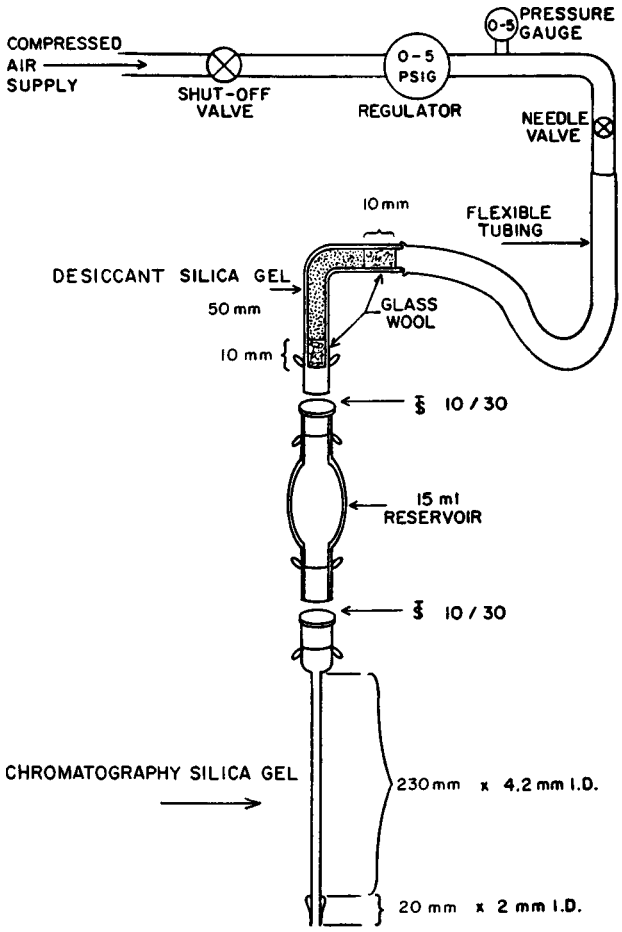

FIG. 1 Microcolumn System

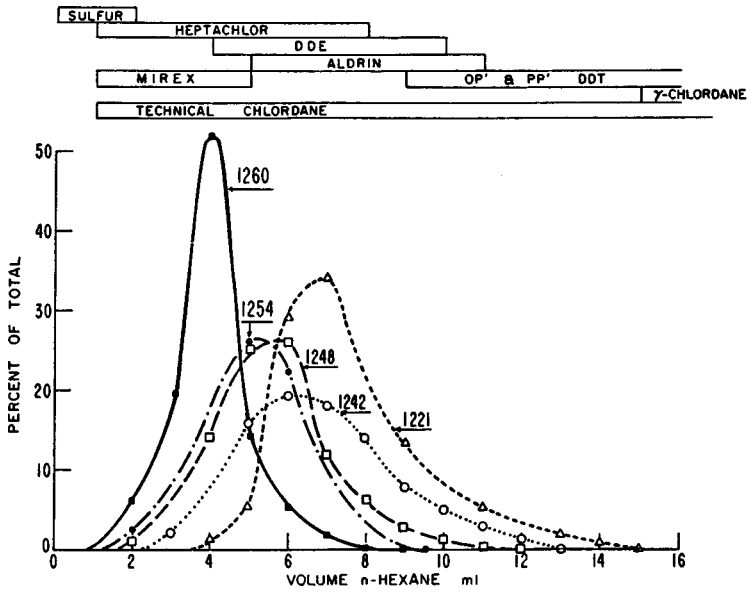

FIG. 2 Aroclor Elution Patterns

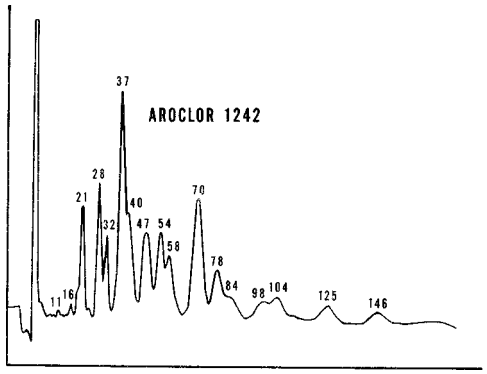

FIG. 3 Column: 3% OV-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 170°C, Detector: Electron Capture

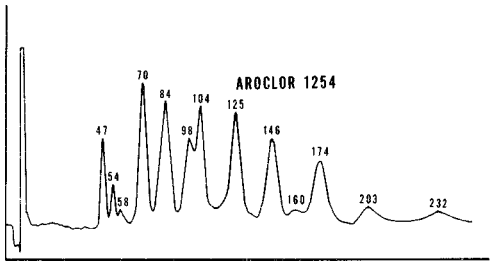

FIG. 4 Column: 3% OV-1, Carrier Gas: Nitrogen at 60 mL/min., Column Temperature: 170°C, Detector: Electron Capture

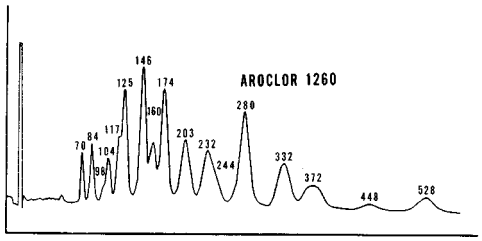

FIG. 5 Column: 3% OV-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 170°C, Detector: Electron Capture

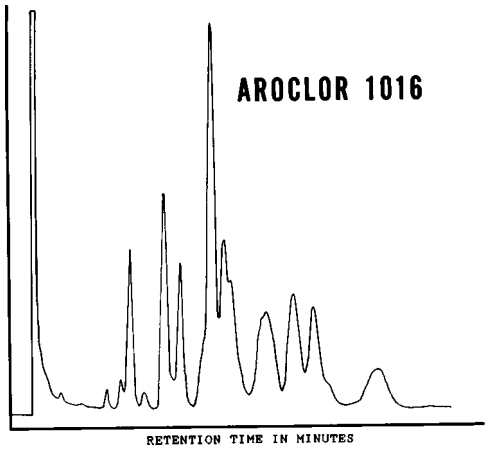

FIG. 6 Column: 3 % OV-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 170°C, Detector: Electron Capture

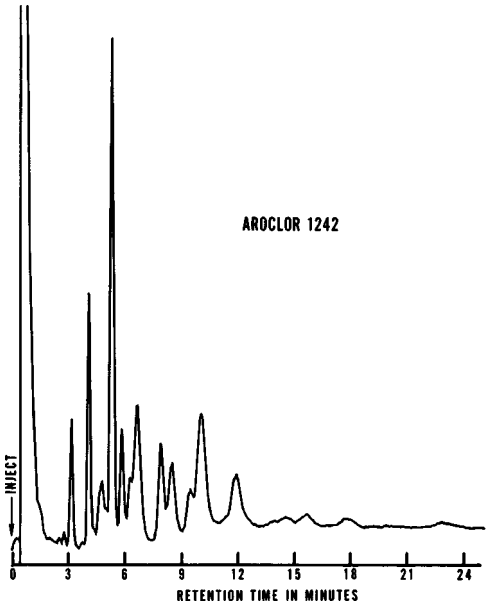

FIG. 7 Column: 1.5 % OV-17 ± 1.95 % QF-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature; 200°C, Detector; Electron Capture

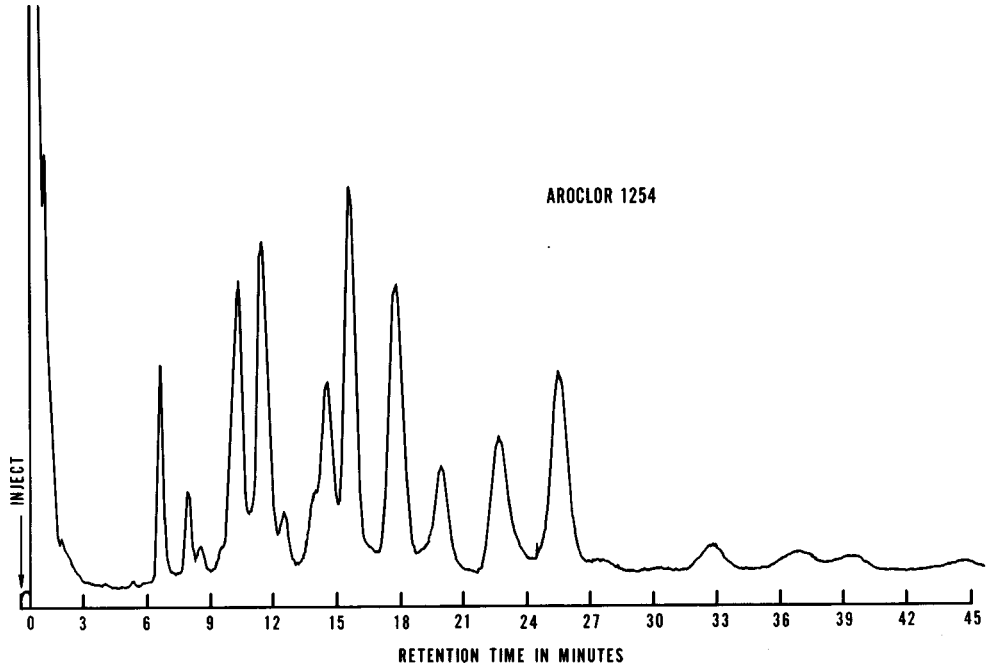

FIG. 8 Column: 1.5 % OV-17 + 1.95 % QF-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 200°C, Detector: Electron Capture

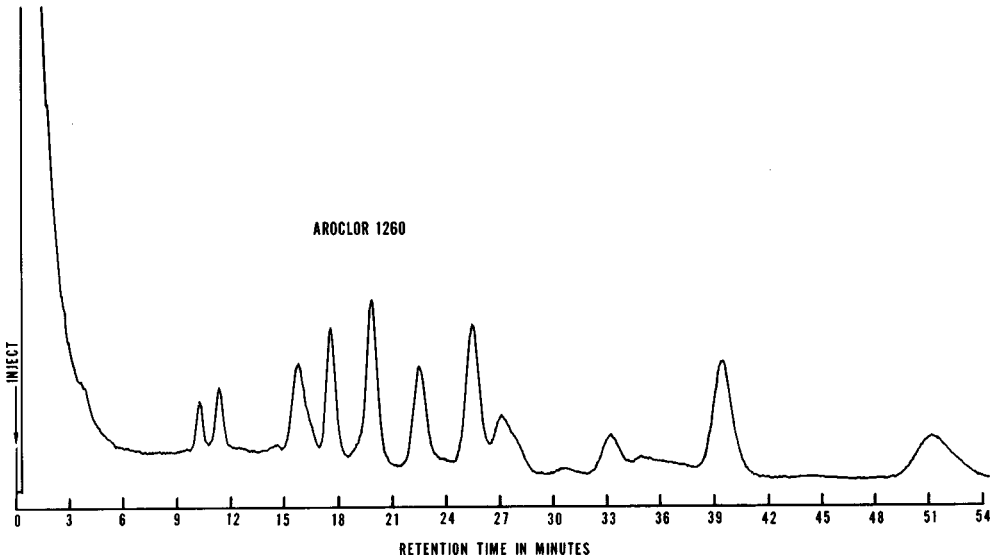

FIG. 9 Column: 1.5 % OV-17 + 1.95 % QF-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 200°C, Detector: Electron Capture

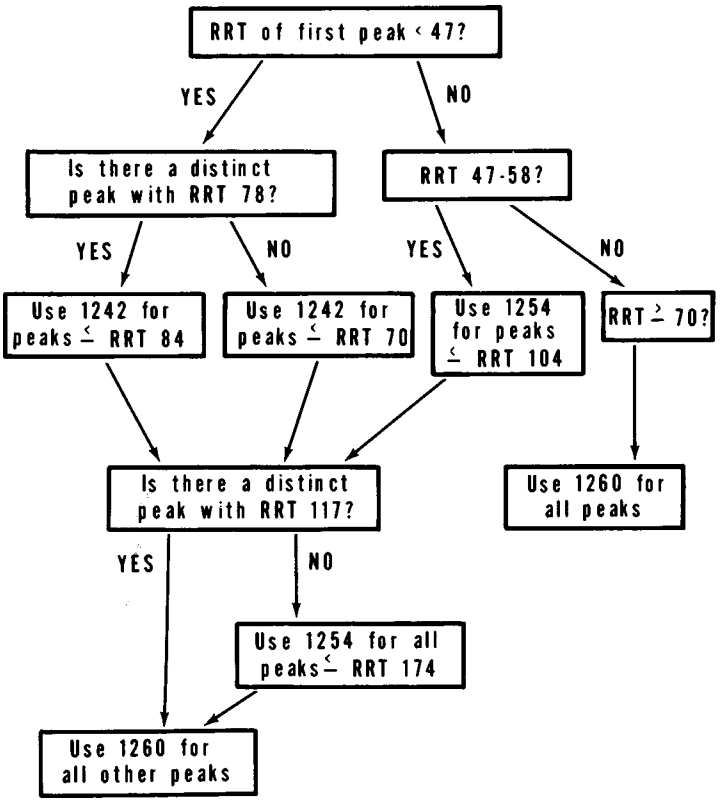

FIG. 10 Chromatogram Division Flowchart (4)

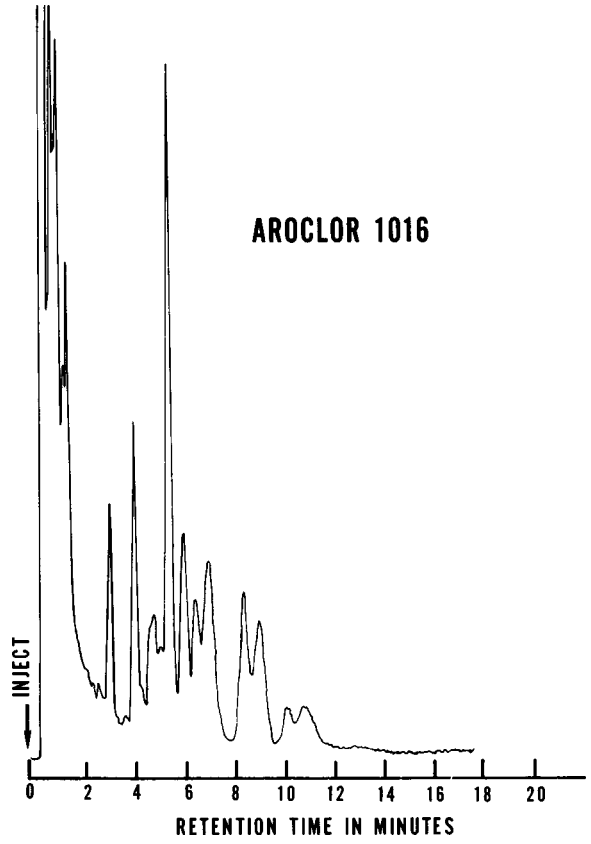

FIG. 11 Column: 1.5 % OV-17 + 1.95 % QF-1, Carrier Gas: Nitrogen at 60 mL/min, Column Temperature: 200°C, Detector: Electron Capture

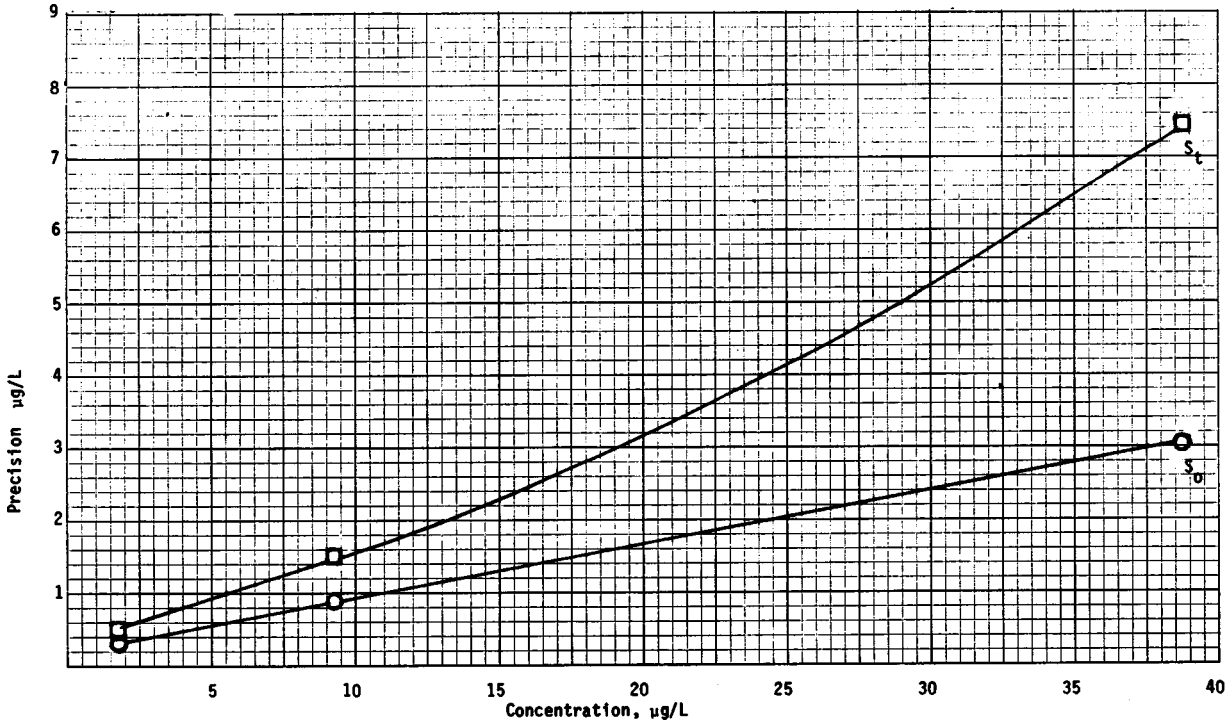

FIG. 12 Precision for the Determination of PCBs in Reagent Water

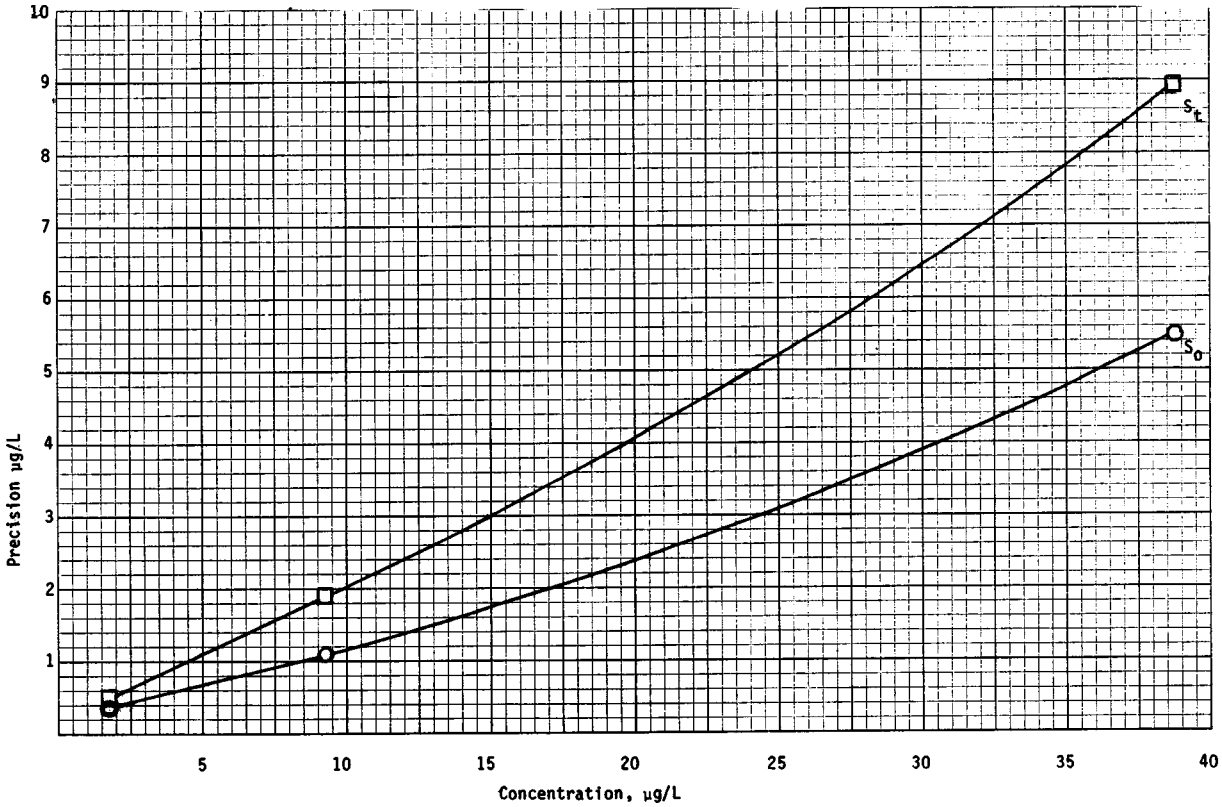

FIG. 13 Precision for the Determination of PCBs in Matrix Water