METHOD 8082A

POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners in extracts from solid, tissue, and aqueous matrices, using open-tubular, capillary columns with electron capture detectors (ECD) or electrolytic conductivity detectors (ELCD). The target compounds listed below may be determined by either a single- or dual-column analysis system. The Aroclors and PCB congeners listed below have been tested by this method, and the method may be appropriate for additional congeners and Aroclors (see Sec. 1.4). The method also may be applied to other matrices such as oils and wipe samples, if appropriate sample extraction procedures are employed.

Compound	CAS Registry No.	IUPAC #
Aroclor 1016	12674-11-2	-
Aroclor 1221	11104-28-2	-
Aroclor 1232	11141-16-5	-
Aroclor 1242	53469-21-9	-
Aroclor 1248	12672-29-6	-
Aroclor 1254	11097-69-1	-
Aroclor 1260	11096-82-5	-
2-Chlorobiphenyl	2051-60-7	1
2,3-Dichlorobiphenyl	16605-91-7	5
2,2',5-Trichlorobiphenyl	37680-65-2	18
2,4',5-Trichlorobiphenyl	16606-02-3	31
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	44
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	52
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	66
2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	87
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	101
2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	110
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	138
2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	141
2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5	151
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	153
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	180
2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	183
2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	187
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9	206

1.2 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns compared to those of Aroclor standards.

1.3 The seven Aroclors listed in Sec. 1.1 are those that are commonly specified in EPA regulations. The quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment. Therefore, this method provides procedures for the determination of a selected group of the 209 possible PCB congeners, as another means to measure the concentrations of weathered Aroclors. The 19 PCB congeners listed above have been tested by this method and were chosen for testing because many of them represent congeners specific to the common Aroclor formulations (see Table 7). These 19 PCB congeners do not represent the co-planar PCBs or the other PCBs of greatest toxicological significance. The analytical procedures for these 19 congeners may be appropriate for the analysis of other congeners not specifically included in this method and may be used as a template for the development of such a procedure. However, all 209 PCB congeners cannot be separated using the GC columns and procedures described in this method. If this procedure is expanded to encompass other congeners, then the analyst must either document the resolution of the congeners in question, or establish procedures for reporting the results of coeluting congeners that are appropriate for the intended application.

1.4 The PCB congener approach potentially affords greater quantitative accuracy when PCBs are known to be present. As a result, this method may be used to determine Aroclors, some PCB congeners, or "total PCBs," depending on regulatory requirements and project needs. The congener method is of particular value in determining weathered Aroclors. However, analysts should use caution when using the congener method when regulatory requirements are based on Aroclor concentrations. Also, this method is not appropriate as written for the determination of the co-planar PCB congeners at the very low (sub part per trillion) concentrations sometimes needed for risk assessment purposes.

1.5 Compound identification based on single-column analysis should be confirmed on a second column, or should be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS (e.g., Method 8270) is also recommended as a confirmation technique when sensitivity permits (see Sec. 7.10).

1.6 This method includes a dual-column option that describes a hardware configuration in which two GC columns are connected to a single injection port and to two separate detectors. The option allows one injection to be used for dual-column simultaneous analysis.

1.7 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extractions, diluted oil samples, etc.). Example chromatograms and GC conditions are provided as guidance.

1.8 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600,

5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two, Sec. 2.1, for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.9 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.1.1 Aqueous samples may be extracted at neutral pH with methylene chloride using either Method 3510 (separatory funnel), Method 3520 (continuous liquid-liquid extractor), Method 3535 (solid-phase extraction), or other appropriate technique.

2.1.2 Solid samples may be extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540 (Soxhlet), Method 3541 (automated Soxhlet), Method 3545 (pressurized fluid extraction), Method 3546 (microwave extraction), Method 3550 (ultrasonic extraction), Method 3562 (supercritical fluid extraction), or other appropriate technique or solvents.

2.1.3 Tissue samples may be extracted using Method 3562 (supercritical fluid extraction), or other appropriate technique. (The extraction techniques for other solid matrices (see Sec. 2.1.2) may be appropriate for tissue samples).

2.2 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, Method 8082 is not applicable to the analysis of those compounds. Instead, use Method 8081.

2.3 After cleanup, the extract is analyzed by injecting a measured aliquot into a gas chromatograph with either a narrow- or wide-bore fused-silica capillary column and either an electron capture detector (GC/ECD) or an electrolytic conductivity detector (GC/ELCD).

2.4 The chromatographic data may be used to determine the seven Aroclors in Sec. 1.1, selected individual PCB congeners, or total PCBs (see Secs. 7.8 and 7.9).

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Sec. 3.0, in particular), 3600, and 8000 for a discussion of interferences.

3.2 Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into four broad categories:

3.2.1 Contaminated solvents, reagents, or sample processing hardware.

3.2.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.2.3 Compounds extracted from the sample matrix to which the detector responds, such as single-component chlorinated pesticides, including the DDT analogs (DDT, DDE, and DDD).

NOTE: A standard of the DDT analogs should be injected to determine which of the PCB or Aroclor peaks may be subject to interferences on the analytical columns used. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples.

3.2.4 Coelution of related analytes. All 209 PCB congeners cannot be separated using the GC columns and procedures described in this method. If this procedure is expanded to encompass other congeners, then the analyst must either document the resolution of the congeners in question or establish procedures for reporting the results of coeluting congeners that are appropriate for the intended application.

3.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

3.3.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

3.3.2 Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination.

3.3.3 These materials can be removed through the use of Method 3665 (sulfuric acid/permanganate cleanup).

3.4 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned.

3.4.1 Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware, and dry it in an oven at 130EC

for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

NOTE: Oven-drying of glassware used for PCB analysis can increase contamination because PCBs are readily volatilized in the oven and spread to other glassware. Therefore, exercise caution, and do not dry glassware from samples containing high concentrations of PCBs with glassware that may be used for trace analyses.

3.42 Other appropriate glassware cleaning procedures may be employed, such as using a muffle furnace at 430EC for at least 30 minutes. However, analysts are advised not to place volumetric glassware in a muffle furnace, since the heat will burn off the markings on the glassware and may warp the glassware, changing its volume.

3.5 Sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of Method 3660.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - An analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and recorder/integrator or data system. Electrolytic conductivity detectors (ELCDs) may also be employed if appropriate for project needs. If the dual-column option is employed, the gas chromatograph must be equipped with two separate detectors.

4.2 GC columns

This method describes procedures for both single-column and dual-column analyses. The single-column approach involves one analysis to determine that a compound is present, followed by a second analysis to confirm the identity of the compound (Sec. 7.10 describes how GC/MS confirmation techniques may be employed). The single-column approach may employ either narrow-bore (# 0.32-mm ID) columns or wide-bore (0.53-mm ID) columns. The dual-column approach generally employs a single injection that is split between two columns that are mounted in a single gas chromatograph. The dual-column approach generally employs wide-bore (0.53-mm ID) columns, but columns of other diameters may be employed if the analyst can demonstrate and document acceptable performance for the intended application. A third alternative is to employ dual columns mounted in a single GC, but with each column connected to a separate injector and a separate detector.

The columns listed in this section were the columns used to develop the method performance data. Listing these columns in this method is not intended to exclude the use of other columns that may be developed. Laboratories may use other capillary columns or columns of other dimensions, provided that they document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that meet the data quality needs of the intended application.

4.2.1 Narrow-bore columns for single-column analysis (use both columns to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Narrow-bore columns should be installed in split/splitless (Grob-type) injectors.

4.2.1.1 30-m x 0.25-mm or 0.32-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1-µm film thickness.

4.2.1.2 30-m x 0.25-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent), 2.5 µm coating thickness, 1-µm film thickness.

4.2.2 Wide-bore columns for single-column analysis (use two of the three columns listed to confirm compound identifications unless another confirmation technique such as GC/MS is employed). Wide-bore columns should be installed in 1/4-inch injectors, with deactivated liners designed specifically for use with these columns.

4.2.2.1 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5-µm or 0.83-µm film thickness.

4.2.2.2 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

4.2.2.3 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5-µm film thickness.

4.2.3 Wide-bore columns for dual-column analysis (choose one of the three pairs of columns listed below).

4.2.3.1 Column pair 1

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5-µm film thickness.

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

Column pair 1 is mounted in a press-fit Y-shaped glass 3-way union splitter (J&W Scientific, Catalog No. 705-0733) or a Y-shaped fused-silica connector (Restek, Catalog No. 20405), or equivalent.

NOTE: When connecting columns to a press-fit Y-shaped connector, a better seal may be achieved by first soaking the ends of the capillary columns in alcohol for about 10 seconds to soften the polyimide coating.

4.2.3.2 Column pair 2

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 0.83-µm film thickness.

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0-µm film thickness.

Column pair 2 is mounted in an 8-in. deactivated glass injection tee (Supelco, Catalog No. 2-3665M), or equivalent.

4.2.3.3 Column pair 3

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5-µm film thickness.

30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (HP-608, DB-608, SPB-608, RTx-35, or equivalent), 0.5-µm film thickness.

Column pair 3 is mounted in separate injectors and separate detectors.

4.3 Column rinsing kit - Bonded-phase column rinse kit (J&W Scientific, Catalog No. 430-3000), or equivalent.

4.4 Volumetric flasks - 10-mL and 25-mL, for preparation of standards.

5.0 REAGENTS

5.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. 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.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate standards) at 4EC in polytetrafluoroethylene (PTFE)-sealed containers in the dark. When a lot of standards is prepared, it is recommended that aliquots of that lot be stored in individual small vials. All stock standard solutions must be replaced after one year, or sooner if routine QC (Sec. 8.0) indicates a problem. All other standard solutions must be replaced after six months, or sooner if routine QC (Sec. 8.0) indicates a problem.

5.2 Solvents used in the extraction and cleanup procedures (appropriate 3500 and 3600 series methods) include *n*-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane) and they must be exchanged to *n*-hexane or isooctane prior to analysis. Therefore, *n*-hexane and isooctane will be required in this procedure. All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be free of phthalates.

5.3 The following solvents may be necessary for the preparation of standards. All solvent lots must be pesticide quality or equivalent and should be determined to be free of phthalates.

5.3.1 Acetone, $(CH_3)_2CO$

5.3.2 Toluene, $C_6H_5CH_3$

5.4 Organic-free reagent water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.5 Stock standard solutions (1000 mg/L) - May be prepared from pure standard materials or can be purchased as certified solutions.

5.5.1 Prepare stock standard solutions by accurately weighing 0.0100 g of pure compound. Dissolve the compound in isooctane or hexane and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard solution.

5.5.2 Commercially-prepared stock standard solutions may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.6 Calibration standards for Aroclors

5.6.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing multi-point initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample.

Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.6.2 Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards described in Sec. 5.6.1 have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors also may be used to determine the calibration factor for each Aroclor when a linear calibration model through the origin is chosen (see Sec. 7.4). Prepare a standard for each of the other Aroclors. The concentrations should generally correspond to the mid-point of the linear range of the detector, but lower concentrations may be employed at the discretion of the analyst.

5.6.3 Other standards (e.g., other Aroclors) and other calibration approaches (e.g., non-linear calibration for individual Aroclors) may be employed to meet project needs. When the nature of the PCB contamination is already known, use standards of those particular Aroclors. See Method 8000 for information on non-linear calibration approaches.

5.7 Calibration standards for PCB congeners

5.7.1 If results are to be determined for individual PCB congeners, then standards for the pure congeners must be prepared. The table in Sec. 1.1 lists 19 PCB congeners that have been tested by this method along with the IUPAC numbers designating these congeners. This procedure may be appropriate for other congeners as well, but the analyst must either

document the resolution of the congeners in question or establish procedures for reporting the results of coeluting congeners that are appropriate for the intended application.

5.7.2 Stock standards may be prepared in a fashion similar to that described for the Aroclor standards, or may be purchased as commercially-prepared solutions. Stock standards should be used to prepare a minimum of five concentrations by dilution of the stock standard with isooctane or hexane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector.

5.8 Internal standard

5.8.1 When PCB congeners are to be determined, the use of an internal standard is highly recommended. Decachlorobiphenyl may be used as an internal standard, added to each sample extract prior to analysis, and included in each of the initial calibration standards.

5.8.2 When PCBs are to be determined as Aroclors, an internal standard is typically not used, and decachlorobiphenyl is employed as a surrogate (see Sec. 5.9).

5.8.3 When decachlorobiphenyl is an analyte of interest, as in some PCB congener analyses, see Sec. 5.9.3.

5.9 Surrogate standards

The performance of the method should be monitored using surrogate compounds. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards. The choice of surrogate compounds will depend on analysis mode chosen, e.g., Aroclors or congeners. The following compounds are recommended as surrogates. Other surrogates may be used, provided that the analyst can demonstrate and document performance appropriate for the data quality needs of the particular application.

5.9.1 When PCBs are to be determined as Aroclors, decachlorobiphenyl may be used as a surrogate, and is added to each sample prior to extraction. Prepare a solution of decachlorobiphenyl in acetone. The recommended spiking solution concentration is 5 mg/L. Tetrachloro-*m*-xylene also may be used as a surrogate for Aroclor analysis. If used, the recommended spiking solution concentration is 5 mg/L in acetone. (Other surrogate concentrations may be used, as appropriate for the intended application.)

5.9.2 When PCB congeners are to be determined, decachlorobiphenyl is recommended for use as an internal standard, and therefore it cannot also be used as a surrogate. Tetrachloro-*m*-xylene may be used as a surrogate for PCB congener analysis. The recommended spiking solution concentration is 5 mg/L in acetone. (Other surrogate concentrations may be used, as appropriate for the intended application.)

5.9.3 If decachlorobiphenyl is a target congener for the analysis, 2,2',4,4',5,5'-hexabromobiphenyl may be used as an internal standard or a surrogate.

5.10 DDT analog standard - Used to determine if the commonly found DDT analogs (DDT, DDE, and DDD) elute at the same retention times as any of the target analytes (congeners or

Aroclors). A single standard containing all three compounds should be sufficient. The concentration of the standard is left to the judgement of the analyst.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Four, Organic Analytes, Sec. 4.1, for sample collection and preservation instructions.

6.2 Extracts should be stored under refrigeration in the dark and should be analyzed within 40 days of extraction.

NOTE: The holding time above is a recommendation. PCBs are very stable in a variety of matrices, and holding times under the conditions listed above may be as high as a year.

7.0 PROCEDURE

7.1 Sample extraction

7.1.1 Refer to Chapter Two and Method 3500 for guidance in choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510), a continuous liquid-liquid extractor (Method 3520), solid-phase extraction (Method 3535), or other appropriate technique. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using one of the Soxhlet extraction methods (Method 3540 or 3541), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546), ultrasonic extraction (Method 3550), supercritical fluid extraction (Method 3562), or other appropriate technique or solvents. Tissue samples are extracted using supercritical fluid extraction (Method 3562) or other appropriate technique.

NOTE: Use of hexane-acetone generally reduces the amount of interferences that are extracted and improves signal-to-noise.

The choice of extraction solvent will depend on the analytes of interest. No single solvent is universally applicable to all analyte groups. The analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest, for any solvent system employed, *including* those specifically listed in this method. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Sec. 8.2 of Method 3500, using a clean reference matrix. Each new sample type must be spiked with the compounds of interest to determine the percent recovery. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

7.1.2 Reference materials, field-contaminated samples, or spiked samples should be used to verify the applicability of the selected extraction technique to each new sample type. Such samples should contain or be spiked with the compounds of interest in order to determine the percent recovery and the limit of detection for that sample type (see Chapter One). When other materials are not available and spiked samples are used, they should be spiked with the analytes of interest, either specific Aroclors or PCB congeners. When the

presence of specific Aroclors is not anticipated, the Aroclor 1016/1260 mixture may be an appropriate choice for spiking. See Methods 3500 and 8000 for guidance on demonstration of initial method proficiency as well as guidance on matrix spikes for routine sample analysis.

7.1.3 The extraction techniques for solids may be applicable to wipe samples and other sample matrices not addressed in Sec. 7.1.1. The analysis of oil samples may require special sample preparation procedures that are not described here. Analysts should follow the steps described in Sec. 7.1.2 to verify the applicability of the sample preparation and extraction techniques for matrices such as wipes and oils.

7.2 Extract cleanup

Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. Refer to Methods 3660 and 3665 for information on extract cleanup.

7.3 GC conditions

This method allows the analyst to choose between a single-column or a dual-column configuration in the injector port. The columns listed in this section were the columns used to develop the method performance data. Listing these columns in this method is not intended to exclude the use of other columns that may be developed. Wide-bore or narrow-bore columns may be used with either option. Laboratories may use other capillary columns or columns of other dimensions, provided that they document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that meet the data quality needs of the intended application.

7.3.1 Single-column analysis

This capillary GC/ECD method allows the analyst the option of using 0.25-mm or 0.32-mm ID capillary columns (narrow-bore) or 0.53-mm ID capillary columns (wide-bore). Narrow-bore columns generally provided greater chromatographic resolution than wide-bore columns, although narrow-bore columns have a lower sample capacity. As a result, narrow-bore columns may be more suitable for relatively clean samples or for extracts that have been prepared with one or more of the clean-up options referenced in the method. Wide-bore columns (0.53-mm ID) may be more suitable for more complex environmental and waste matrices. However, the choice of the appropriate column diameter is left to the analyst.

7.3.2 Dual-column analysis

The dual-column/dual-detector approach recommends the use of two 30-m x 0.53-mm ID fused-silica open-tubular columns of different polarities, thus, different selectivities towards the target analytes. The columns may be connected to an injection tee and separate electron capture detectors, or to both separate injectors and separate detectors. However, the choice of the appropriate column dimensions is left to the analyst.

7.3.3 GC temperature programs and flow rates

7.3.3.1 Table 2 lists suggested GC operating conditions for the analysis of PCBs as Aroclors for single-column analysis, using either narrow-bore or wide-bore capillary columns. Table 3 lists suggested GC operating conditions for the dual-column analysis. Use the conditions in these tables as guidance and establish the GC temperature program and flow rate necessary to separate the analytes of interest.

7.3.3.2 When determining PCBs as congeners, difficulties may be encountered with coelution of congener 153 and other sample components. When determining PCBs as Aroclors, chromatographic conditions should be adjusted to give adequate separation of the characteristic peaks in each Aroclor (see Sec. 7.4.6).

7.3.3.3 Tables 4 and 5 summarize example retention times of up to 73 Aroclor peaks determined during dual-column analysis using the operating conditions listed in Table 3. These retention times are provided as guidance as to what may be achieved using the GC columns, temperature programs, and flow rates described in this method. Note that the peak numbers used in these tables are *not* the IUPAC congener numbers, but represent the elution order of the peaks on these GC columns.

7.3.3.4 Once established, the same operating conditions must be used for the analysis of samples and standards.

7.4 Calibration

7.4.1 Prepare calibration standards as described in Sec. 5.0. Refer to Method 8000 (Sec. 7.0) for proper calibration techniques for both initial calibration and calibration verification. When PCBs are to be determined as congeners, the use of internal standard calibration is highly recommended. Therefore, the calibration standards must contain the internal standard (see Sec. 5.8) at the same concentration as the sample extracts. When PCBs are to be determined as Aroclors, external standard calibration is generally used.

NOTE: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

7.4.2 When PCBs are to be quantitatively determined as congeners, an initial multi-point calibration must be performed that includes standards for all the target analytes (congeners). See Method 8000 for details on calibration options.

7.4.3 When PCBs are to be quantitatively determined as Aroclors, the initial calibration consists of two parts, described below.

7.4.3.1 As noted in Sec. 5.6.1, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Therefore, an initial multi-point calibration is performed using the mixture of Aroclors 1016 and 1260

described in Sec. 5.6.1. See Sec. 7.0 of Method 8000 for guidance on the use of linear and non-linear calibrations.

7.4.3.2 Standards of the other five Aroclors are necessary for pattern recognition. When employing the traditional model of a linear calibration through the origin, these standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture in Sec. 7.4.3.1 has been used to describe the detector response. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260 standards in Sec. 7.4.3.1. For non-linear calibrations, see Sec. 7.4.3.3.

7.4.3.3 In situations where only a few Aroclors are of interest for a specific project, the analyst may employ a multi-point initial calibration of each of the Aroclors of interest (e.g., five standards of Aroclor 1232 if this Aroclor is of concern and linear calibration is employed) and not use the 1016/1260 mixture described in Sec. 7.4.3.1 or the pattern recognition standards described in 7.4.3.2. When non-linear calibration models are employed, more than five standards of each Aroclor of interest will be needed to adequately describe the detector response (see Method 8000).

7.4.4 Establish the GC operating conditions appropriate for the configuration (single-column or dual column, Sec. 7.3). Optimize the instrumental conditions for resolution of the target compounds and sensitivity. A final temperature of 240-275EC may be required to elute decachlorobiphenyl. The use of injector pressure programming will improve the chromatography of late eluting peaks.

NOTE: Once established, the same operating conditions must be used for both calibrations and sample analyses.

7.4.5 A 2-µL injection of each calibration standard is recommended. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest.

7.4.6 Record the peak area (or height) for each congener or each characteristic Aroclor peak to be used for quantitation.

7.4.6.1 A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.

7.4.6.2 Late-eluting Aroclor peaks are generally the most stable in the environment. Table 6 lists diagnostic peaks in each Aroclor, along with example retention times on two GC columns suitable for single-column analysis. Table 7 lists 13 specific PCB congeners found in Aroclor mixtures. Table 8 lists PCB congeners with example retention times on a DB-5 wide-bore GC column. Use these tables as guidance in choosing the appropriate peaks.

7.4.7 When determining PCB congeners by the internal standard procedure, calculate the response factor (RF) for each congener in the calibration standards relative to the internal standard, decachlorobiphenyl, using the equation that follows.

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

7.4.8 When determining PCBs as Aroclors by the external standard technique, calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards (from either Sec. 7.4.3.1 or 7.4.3.2) using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

Using the equation above, a calibration factor will be determined for each characteristic peak, using the total mass of the Aroclor injected. These individual calibration factors are used to quantitate sample results by applying the factor for each individual peak to the area of that peak, as described in Sec. 7.9.

For a five-point calibration, five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture, e.g., there will be at least 25 separate calibration factors for the mixture. The single standard for each of the other Aroclors (see Sec. 7.4.3.1) will generate at least three calibration factors, one for each selected peak.

If a non-linear calibration model is employed, as described in Method 8000, then additional standards containing each Aroclor of interest will be employed, with a corresponding increase in the total number of calibration factors.

7.4.9 The response factors or calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration, if a linear calibration model is used. This involves the calculation of the mean response or calibration factor, the standard deviation, and the relative standard deviation (RSD) for each congener or Aroclor peak.

When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the linear calibration models must be applied to the other five Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors (see Sec. 7.4.3.3), use the calibration factors from those standards to evaluate linearity.

See Method 8000 for the specifics of the evaluation of the linearity of the calibration and guidance on performing non-linear calibrations. In general, non-linear calibrations also will consider each characteristic Aroclor peak separately.

7.5 Retention time windows

Absolute retention times are generally used for compound identification. When absolute retention times are used, retention time windows are crucial to the identification of target compounds, and should be established by one of the approaches described in Method 8000. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis. Analysts should consult Method 8000 for the details of establishing retention time windows. Other approaches to compound identification may be employed, provided that the analyst can demonstrate and document that they are appropriate for the intended application. When PCBs are determined as congeners by an internal standard technique, absolute retention times may be used in conjunction with relative retention times (relative to the internal standard).

When conducting either Aroclor or congener analysis, it is important to determine that common single-component pesticides such as DDT, DDD, and DDE do not elute at the same retention times as the target congeners. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples. Therefore, in conjunction with determining the retention time windows of the congeners, the analyst should analyze a standard containing the DDT analogs. This standard need only be analyzed when the retention time windows are determined. It is not considered part of the routine initial calibration or calibration verification steps in the method, nor are there any performance criteria associated with the analysis of this standard.

If Aroclor analysis is performed and any of the DDT analogs elute at the same retention time as an Aroclor peak that was chosen for use in quantitation (see Sec. 7.4.6), then the analyst must either adjust the GC conditions to achieve better resolution, or choose another peak that is characteristic of that Aroclor and does not correspond to a peak from a DDT analog. If PCB congener analysis is performed and any of the DDT analogs elute at the same retention time as a PCB congener of interest, then the analyst must adjust the GC conditions to achieve better resolution.

7.6 Gas chromatographic analysis of sample extracts

7.6.1 The same GC operating conditions used for the initial calibration must be employed for the analysis of samples.

7.6.2 Verify calibration at least once each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring reinjection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the

calibration verification standard should be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not *require* analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

7.6.2.1 The calibration factor for each analyte calculated from the calibration verification standard (CF_v) must not exceed a difference of more than ± 15 percent when compared to the mean calibration factor from the initial calibration curve. If a calibration approach other than the RSD method has been employed for the initial calibration (e.g., a linear model not through the origin, a non-linear calibration model, etc.), consult Sec. 7 of Method 8000 for the specifics of calibration verification.

$$\% \text{ Difference } = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

7.6.2.2 When internal standard calibration is used for PCB congeners, the response factor calculated from the calibration verification standard (RF_v) must not exceed a ± 15 percent difference when compared to the mean response factor from the initial calibration. If a calibration approach other than the RSD method has been employed for the initial calibration (e.g., a linear model not through the origin, a non-linear calibration model, etc.), consult Sec. 7 of Method 8000 for the specifics of calibration verification.

$$\% \text{ Difference } = \frac{\overline{RF} - RF_v}{\overline{RF}} \times 100$$

7.6.2.3 If this criterion is exceeded for any calibration factor or response factor, use the approach described in Sec. 7 of Method 8000 to calculate the average percent difference across all analytes. If the average of the responses for all analytes is within ±15%, then the calibration has been verified. However, the conditions in Sec. 7 of Method 8000 also apply, e.g., the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the ±15% limit.

7.6.2.4 If the calibration does not meet the ±15% limit (either on the basis of each compound or the average across all compounds), check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±15%, then a new initial calibration must be prepared. The effects of a failing calibration verification standard on sample results are discussed in Sec. 7.6.6.

7.6.3 Inject a measured aliquot of the concentrated sample extract. A 2-µL aliquot is suggested, however the same injection volume must be used for both the calibration standards and the sample extracts. Record the volume injected and the resulting peak size in area units.

7.6.4 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Sec. 7.7.

7.6.5 Quantitative results are determined for each identified analyte (Aroclors or congeners), using the procedures described in Secs. 7.8 and 7.9 for either the internal or the external calibration procedure (Method 8000). If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area when overlapping peaks cause errors in area integration.

7.6.6 Each sample analysis employing external standard calibration must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour analytical shift), or calibration standards interspersed within the samples. The results from these bracketing standards must meet the calibration verification criteria in Sec. 7.6.2.

Multi-level standards (mixtures or multi-component analytes) are highly recommended to ensure that detector response remains stable for all analytes over the calibration range.

When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that met the QC criteria must be evaluated to prevent misquantitations and possible false negative results, and reinjection of the sample extracts may be required. More frequent analyses of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis.

However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >15%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, since the verification standard has demonstrated that the analyte would have been detected if it were present. In contrast, if an analyte above the QC limits was detected in a sample extract, then reinjection is necessary to ensure accurate quantitation.

If an analyte was not detected in the sample and the standard response is more than 15% below the initial calibration response, then reinjection is necessary. The purpose of this reinjection is to ensure that the analyte could be detected, if present, despite the change in the detector response, e.g., to protect against a false negative result.

7.6.7 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. It is *recommended* that standards be analyzed after every 10 samples (*required* after every 20 samples and at the end of a set) to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative or quantitative QC criteria are exceeded.

7.6.8 The use of internal standard calibration techniques does not require that all sample results be bracketed with calibration verification standards. However, when internal standard calibration is used, the retention times of the internal standards and the area responses of the internal standards should be checked for each analysis. Retention time shifts of more than 30 seconds from the retention time of the most recent calibration standard and/or changes in internal standard areas of more than -50 to +100% are cause for concern and must be investigated.

7.6.9 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample is warranted.

7.6.10 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

7.6.11 If compound identification or quantitation is precluded due to interferences (e.g., broad, rounded peaks or ill-defined baselines are present), corrective action is warranted. Cleanup of the extract or replacement of the capillary column or detector may be necessary. The analyst may begin by rerunning the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to Method 3600 for the procedures to be followed in sample cleanup.

7.7 Qualitative identification

The identification of PCBs as either Aroclors or congeners using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. See Method 8000 for information on the establishment of retention time windows.

Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Confirmation is necessary when the sample composition is not well characterized. See Method 8000 for information on confirmation of tentative identifications. See Sec. 7.10 of this procedure for information on the use of GC/MS as a confirmation technique.

When results are confirmed using a second GC column of dissimilar stationary phase, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. See Sec. 7 of Method 8000 for a discussion of such a comparison and appropriate data reporting approaches.

7.7.1 When simultaneous analyses are performed from a single injection (the dual-column GC configuration described in Sec. 7.3), it is not practical to designate one column as the analytical (primary) column and the other as the confirmation column. Since the calibration standards are analyzed on both columns, both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

7.7.2 The results of a single column/single injection analysis may be confirmed, if necessary, on a second, dissimilar, GC column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition, the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis. That standard may be either the individual congeners, individual Aroclor or the Aroclor 1016/1260 mixture.

7.7.3 When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach should not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document:

- The peaks that were evaluated when comparing the sample chromatogram and the Aroclor standard.
- The absence of major peaks representing any other Aroclor.
- The source-specific information indicating that Aroclors are anticipated in the sample (e.g., historical data, generator knowledge, etc.).

This information should either be provided to the data user or maintained by the laboratory.

7.7.4 See Sec. 7.10 for information on GC/MS confirmation.

7.8 Quantitation of PCBs as congeners

7.8.1 The quantitation of PCB congeners is accomplished by the comparison of the sample chromatogram to those of the PCB congener standards, using the internal standard technique (see Method 8000). Calculate the concentration of each congener.

7.8.2 Depending on project requirements, the PCB congener results may be reported as congeners, or may be summed and reported as total PCBs. The analyst should use caution when using the congener method for quantitation when regulatory requirements are based on Aroclor concentrations. See Sec. 7.9.3.

7.8.3 The analytical procedures for these 19 congeners may be appropriate for the analysis of other congeners not specifically included in this method and may be used as a template for the development of such a procedure. However, all 209 PCB congeners cannot be separated using the GC columns and procedures described in this method. If this procedure is expanded to encompass other congeners, then the analyst must either document the resolution of the congeners in question or establish procedures for reporting the results of coeluting congeners that are appropriate for the intended application.

7.9 Quantitation of PCBs as Aroclors

The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

7.9.1 Use the individual Aroclor standards (not the 1016/1260 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

7.9.2 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the single-point calibration standard for that Aroclor with the peaks observed

in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in Sec. 7.4.6.1. and the calibration model (linear or non-linear) established from the multi-point calibration of the 1016/1260 mixture. Non-linear calibration may result in different models for each selected peak. A concentration is determined using each of the characteristic peaks, using the individual calibration factor calculated for that peak in Sec. 7.4.8, and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

7.9.3 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. If the purpose of the analysis is not regulatory compliance monitoring on the basis of Aroclor concentrations, then it may be more appropriate to perform the analyses using the PCB congener approach described in this method. If results in terms of Aroclors are required, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

7.10 GC/MS confirmation may be used in conjunction with either single-or dual-column analysis if the concentration is sufficient for detection by GC/MS.

7.10.1 Full-scan quadrupole GC/MS will normally require a higher concentration of the analyte of interest than full-scan ion trap or selected ion monitoring techniques. The concentrations will be instrument-dependent, but values for full-scan quadrupole GC/MS may be as high as 10 ng/µL in the final extract, while ion trap or SIM may only require a concentration of 1 ng/µL.

7.10.2 The GC/MS must be calibrated for the target analytes when it is used for quantitative analysis. If GC/MS is used only for confirmation of the identification of the target analytes, then the analyst must demonstrate that those PCBs identified by GC/ECD can be confirmed by GC/MS. This demonstration may be accomplished by analyzing a single-point standard containing the analytes of interest at or below the concentrations reported in the GC/EC analysis. When using SIM techniques, the ions and retention times should be characteristic of the Aroclors to be confirmed.

7.10.3 GC/MS confirmation should be accomplished by analyzing the same extract used for GC/ECD analysis and the extract of the associated blank.

7.11 Chromatographic system maintenance as corrective action

When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

7.11.1 Splitter connections

For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with

a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

7.11.2 Metal injector body

Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.11.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the entire inside of the injector port with acetone and then rinse it with toluene, catching the rinsate in the beaker.

7.11.2.2 Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.

7.11.3 Column rinsing

The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation techniques can be found in Method 3500. If an extract cleanup procedure was performed, refer to Method 3600 for the appropriate quality control procedures. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.2.1 Include a calibration standard after each group of 20 samples (it is *recommended* that a calibration standard be included after every 10 samples to minimize the number of repeat injections) in the analysis sequence as a calibration check. The response factors for the calibration should be within 15 percent of the initial calibration. When this

continuing calibration is out of this acceptance window, the laboratory should stop analyses and take corrective action.

8.2.2 Whenever quantitation is accomplished using an internal standard, internal standard responses must be evaluated for acceptance. The measured area of the internal standard must be no more than 50 percent different from the average area calculated during calibration. When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria must be reanalyzed.

8.3 Initial demonstration of proficiency

8.3.1 Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0, for information on how to accomplish this demonstration.

8.3.2 The QC Reference Sample concentrate (Method 3500) should contain PCBs as Aroclors at 10-50 mg/L in the concentrate for water samples, or PCBs as congeners at the same concentrations. A 1-mL volume of this concentrate spiked into 1 L of reagent water will result in a sample concentration of 10-50 µg/L. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the QC reference sample. See Method 8000, Sec. 8.0, for additional information on how to accomplish this demonstration. Other concentrations may be used, as appropriate for the intended application.

8.3.3 Calculate the average recovery and the standard deviation of the recoveries of the analytes in each of the four QC reference samples. Refer to Sec. 8.0 of Method 8000 for procedures for evaluating method performance.

8.4 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision and accuracy). At a minimum, this includes the analysis of QC samples including a method blank and a laboratory control sample (LCS) in each analytical batch, the addition of surrogates to each field sample and QC sample, and routine analyses of matrix spike and matrix spike duplicate aliquots.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample.

8.4.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0, for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries

The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0, for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined in Chapter One. **MDL data provided in this method are for illustrative purposes only.** Each laboratory should develop its own matrix-specific MDLs, if necessary, using the guidance found in Chapter One. Estimated quantitation limits (EQLs) may be determined using the factors in Table 1.

9.2 The accuracy and precision obtainable with this method depend on the sample matrix, sample preparation technique, optional cleanup techniques, and calibration procedures used. Table 9 provides single laboratory recovery data for Aroclors spiked into clay and soil and extracted with automated Soxhlet. Table 10 provides multiple laboratory data on the precision and accuracy for Aroclors spiked into soil and extracted by automated Soxhlet.

9.3 During method performance studies, the concentrations determined as Aroclors were higher than those obtained using the congener method for the limited set of congeners listed in Sec. 1.1. In certain soils, interference prevented the measurement of congener 66. Recoveries of congeners from environmental reference materials ranged from 51 - 66% of the certified Aroclor values, illustrating the potential difficulties in using congener analysis to demonstrate compliance with Aroclor-based regulatory limits.

9.4 Tables 11 through 13 contain laboratory performance data for several PCB congeners using supercritical fluid extraction (Method 3562) on an HP 7680 to extract solid samples, including soils, sewage sludge, and fish tissue. Seven replicate extractions were performed on each sample. The method was performed using a variable restrictor and solid trapping material (Florisil). Sample analysis was performed by GC/ECD. The following solid samples were used for this study:

9.4.1 Two field-contaminated certified reference materials were extracted by a single laboratory. One of the materials was a lake sediment from Environment Canada (EC-5). The other material was soil from a dump site and was provided by the National Science and Engineering Research Council of Canada (EC-1). The average recoveries for EC-5 are based on the certified value for that sample. The average recoveries for EC-1 are based on the certified value of the samples or a Soxhlet value, if a certified value was unavailable for a specific analyte.

9.4.2 Four certified reference materials were extracted by two independent laboratories. The materials were: a marine sediment from NIST (SRM 1941), a fish tissue from NIST (SRM 2974), a sewage sludge from BCR European Union (CRM 392), and a soil sample from BCR European Union (CRM 481). The average recoveries are based on the certified value of the samples or a Soxhlet value, if a certified value was unavailable for a specific analyte.

9.4.3 A weathered sediment sample from Michigan (Saginaw Bay) was extracted by a single laboratory. Soxhlet extractions were carried out on this sample and the SFE recovery is relative to that for each congener. The average recoveries are based on the certified value of the samples. Additional data are shown in the tables for some congeners for which no certified values were available.

9.5 Tables 14 through 16 contain single laboratory recovery data for Aroclor 1254 using solid-phase extraction (Method 3535). Recovery data at 2, 10, and 100 ug/L are presented. Results represent three replicate solid-phase extractions of spiked wastewaters. Two different wastewaters from each wastewater type were spiked. All of the extractions were performed using 90-mm C_{18} disks.

9.6 Single-laboratory data were developed for PCBs extracted by pressurized fluid extraction (Method 3545) from sewage sludge, a river sediment standard reference material (SRM 1939), and a certified soil reference material (CRM911-050). Certified values were available for five PCB congeners for the sewage sludge and for four congeners in SRM 1939. The soil reference material was certified for Aroclor 1254. All pressurized fluid extractions were conducted using hexane:acetone (1:1), at 100EC, 1300-1500 psi, and a 5-minute static extraction. Extracts were analyzed by GC/ECD. The data are presented in Tables 17 through 19 and are reported in detail in Reference 13.

9.7 Single-laboratory accuracy data were obtained for PCBs extracted by microwave extraction (Method 3546) from three reference materials, EC-1, EC-2, and EC-3, from Environment Canada. Natural soils, glass fiber, and sand samples were also used as matrices that were spiked with PCBs. Concentrations varied between 0.2 and 10 µg/g (total PCBs). All samples were extracted using 1:1 hexane:acetone. Extracts were analyzed by GC/ECD. Method blanks, spikes and spike duplicates were included for the low concentration spikes; matrix spikes were included for all other concentrations. The data are presented in Tables 20 through 22 and are reported in detail in Reference 14.

10.0 REFERENCES

1. Lopez-Avila, V., Baldin, E., Benedicto, J, Milanes, J., Beckert. W.F., Application of Open-Tubular Columns to SW-846 GC Methods", final report to the U.S. Environmental Protection Agency on Contract 68-03-3511, Mid-Pacific Environmental Laboratory, Mountain View, CA, 1990.

2. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 10 - Pesticides and PCB Report for the U.S. Environmental Protection Agency on Contract 68-03-2606.

3. Ahnoff, M., Josefsson, B., "Cleanup Procedures for PCB Analysis on River Water Extracts", Bull. Environ. Contam. Toxicol., 1975, 13, 159.

4. Marsden, P.J., "Performance Data for SW-846 Methods 8270, 8081, and 8141", U.S. Environmental Protection Agency, EMSL-Las Vegas, EPA/600/4-90/015.

5. Marsden, P.J., "Analysis of PCBs", U.S. Environmental Protection Agency, EMSL-Las Vegas, NV, EPA/600/8-90/004.

6. Erickson, M., Analytical Chemistry of PCBs, Butterworth Publishers, Ann Arbor Science Book, (1986).

7. Stewart, J., "EPA Verification Experiment for Validation of the SOXTEC® PCB Extraction Procedure", Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6138, October 1988.

8. Lopez-Avila, V. (Beckert, W., Project Officer), "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments", EPA 600/X-91/140, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV, October 1991.

9. Stewart, J.H., Bayne, C.K., Holmes, R.L., Rogers, W.F., and Maskarinec, M.P., "Evaluation of a Rapid Quantitative Organic Extraction System for Determining the Concentration of PCB in Soils", Proceedings of the U.S. EPA Symposium on Waste Testing and Quality Assurance, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, July 11-15, 1988.

10. Tsang, S.F., Marsden, P.J., and Lesnik, B., "Quantitation of Polychlorinated Biphenyls Using 19 Specific Congeners", Proceedings of the 9th Annual Waste Testing and Quality Assurance Symposium, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC, July 1993.

11. S. Bøwadt, B. Johansson, S. Wunderli, M. Zennegg, L. F. de Alencastro and D. Grandjean, "Independent Comparison of Soxhlet and Supercritical Fluid Extraction for the Determination of PCBs in an Industrial Soil," *Anal. Chem.*, 1995, 67(14) 2424-2430.

12. Markell, C., "3M Data Submission to EPA," letter to B. Lesnik, June 27, 1995.

13. Richter, B, Ezzell, J., and Felix D, "Single Laboratory Method Validation Report - Extraction of Organophosphorus Pesticides, Herbicides and Polychlorinated Biphenyls using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/NPD and GC/ECD," Dionex, Salt Lake City, UT, Document 101124, December 2, 1994.

14. K. Li, J. M. R. Bélanger, M. P. Llompart, R. D. Turpin, R. Singhvi, and J. R. J. Paré. Evaluation of rapid solid sample extraction using the microwave-assisted process (MAP™) under closed-vessel conditions. *Spectros. Int. J.* 13 (1), 1-14 (1997).

TABLE 1

FACTORS FOR DETERMINATION OF ESTIMATED QUANTITATION LIMITS[a] (EQLs)
FOR VARIOUS MATRICES

Matrix	Factor
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]EQL = [MDL for water (see Sec. 1.8)] times [Factor in this table]

For nonaqueous samples, the factor is on a wet-weight basis. Sample EQLs are highly matrix-dependent. EQLs determined using these factors are provided as guidance and may not always be achievable.

TABLE 2

SUGGESTED GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE-COLUMN ANALYSIS

Narrow-bore columns

Narrow-bore Column 1 - 30-m x 0.25 or 0.32-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1 µm film thickness.

Carrier gas (He)	16 psi
Injector temperature	225EC
Detector temperature	300EC
Initial temperature	100EC, hold 2 minutes
Temperature program	100EC to 160EC at 15EC/min, followed by 160EC to 270EC at 5EC/min
Final temperature	270EC

Narrow-bore Column 2 - 30-m x 0.25-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, or equivalent) 25 µm coating thickness, 1 µm film thickness

Carrier gas (N_2)	20 psi
Injector temperature	225EC
Detector temperature	300EC
Initial temperature	160EC, hold 2 minutes
Temperature program	160EC to 290EC at 5EC/min
Final temperature	290EC, hold 1 min

Wide-bore columns

Wide-bore Column 1 - 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, SPB-608, RTx-35, or equivalent), 0.5 µm or 0.83 µm film thickness.

Wide-bore Column 2 - 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with 14% cyanopropylmethylpolysiloxane (DB-1701, or equivalent), 1.0 µm film thickness.

Carrier gas (He)	5-7 mL/minute
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	250EC
Detector temperature	290EC
Initial temperature	150EC, hold 0.5 minute
Temperature program	150EC to 270EC at 5EC/min
Final temperature	270EC, hold 10 min

TABLE 2
(continued)

SUGGESTED GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
SINGLE-COLUMN ANALYSIS

Wide-bore Columns (continued)

Wide-bore Column 3 - 30-m x 0.53-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 1.5 µm film thickness.

Carrier gas (He)	6 mL/minute
Makeup gas (argon/methane [P-5 or P-10] or N_2)	30 mL/min
Injector temperature	205EC
Detector temperature	290EC
Initial temperature	140EC, hold 2 min
Temperature program	140EC to 240EC at 10EC/min, hold 5 minutes at 240EC, 240EC to 265EC at 5EC/min
Final temperature	265EC, hold 18 min

TABLE 3

SUGGESTED GC OPERATING CONDITIONS FOR PCBs AS AROCLORS
FOR THE DUAL-COLUMN METHOD OF ANALYSIS

Column 1 - DB-1701 or equivalent, 30-m x 0.53-mm ID, 1.0 µm film thickness.

Column 2 - DB-5 or equivalent, 30-m x 0.53-mm ID, 1.5 µm film thickness.

Carrier gas (He) flow rate	6 mL/min
Makeup gas (N_2) flow rate	20 mL/min
Temperature program	0.5 min hold 150EC to 190EC, at 12EC/min, 2 min hold 190EC to 275EC, at 4EC/min, 10 min hold
Injector temperature	250EC
Detector temperature	320EC
Injection volume	2 µL
Solvent	Hexane
Type of injector	Flash vaporization
Detector type	Dual ECD
Range	10
Attenuation	64 (DB-1701)/64 (DB-5)
Type of splitter	J&W Scientific press-fit Y-shaped inlet splitter

TABLE 4

EXAMPLE RETENTION TIMES OF AROCLORS
ON THE DB-5 COLUMN[a], DUAL-COLUMN ANALYSIS

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		5.85	5.85				
2		7.63	7.64	7.57			
3	8.41	8.43	8.43	8.37			
4	8.77	8.77	8.78	8.73			
5	8.98	8.99	9.00	8.94	8.95		
6	9.71			9.66			
7	10.49	10.50	10.50	10.44	10.45		
8	10.58	10.59	10.59	10.53			
9	10.90		10.91	10.86	10.85		
10	11.23	11.24	11.24	11.18	11.18		
11	11.88		11.90	11.84	11.85		
12	11.99		12.00	11.95			
13	12.27	12.29	12.29	12.24	12.24		
14	12.66	12.68	12.69	12.64	12.64		
15	12.98	12.99	13.00	12.95	12.95		
16	13.18		13.19	13.14	13.15		
17	13.61		13.63	13.58	13.58	13.59	13.59
18	13.80		13.82	13.77	13.77	13.78	
19	13.96		13.97	13.93	13.93	13.90	
20	14.48		14.50	14.46	14.45	14.46	
21	14.63		14.64	14.60	14.60		
22	14.99		15.02	14.98	14.97	14.98	
23	15.35		15.36	15.32	15.31	15.32	
24	16.01			15.96			
25			16.14	16.08	16.08	16.10	
26	16.27		16.29	16.26	16.24	16.25	16.26
27						16.53	
28			17.04		16.99	16.96	16.97
29			17.22	17.19	17.19	17.19	17.21
30			17.46	17.43	17.43	17.44	
31					17.69	17.69	
32				17.92	17.91	17.91	
33				18.16	18.14	18.14	
34			18.41	18.37	18.36	18.36	18.37
35			18.58	18.56	18.55	18.55	
36							18.68

TABLE 4
(continued)

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
37			18.83	18.80	18.78	18.78	18.79
38			19.33	19.30	19.29	19.29	19.29
39						19.48	19.48
40						19.81	19.80
41			20.03	19.97	19.92	19.92	
42						20.28	20.28
43					20.46	20.45	
44						20.57	20.57
45				20.85	20.83	20.83	20.83
46			21.18	21.14	21.12	20.98	
47					21.36	21.38	21.38
48						21.78	21.78
49				22.08	22.05	22.04	22.03
50						22.38	22.37
51						22.74	22.73
52						22.96	22.95
53						23.23	23.23
54							23.42
55						23.75	23.73
56						23.99	23.97
57							24.16
58						24.27	
59							24.45
60						24.61	24.62
61						24.93	24.91
62							25.44
63						26.22	26.19
64							26.52
65							26.75
66							27.41
67							28.07
68							28.35
69							29.00

[a] GC operating conditions are given in Table 3. All retention times in minutes and are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 5

EXAMPLE RETENTION TIMES OF AROCLORS
ON THE DB-1701 COLUMN[a], DUAL-COLUMN ANALYSIS

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
1		4.45	4.45				
2		5.38					
3		5.78					
4		5.86	5.86				
5	6.33	6.34	6.34	6.28			
6	6.78	6.78	6.79	6.72			
7	6.96	6.96	6.96	6.90	6.91		
8	7.64			7.59			
9	8.23	8.23	8.23	8.15	8.16		
10	8.62	8.63	8.63	8.57			
11	8.88		8.89	8.83	8.83		
12	9.05	9.06	9.06	8.99	8.99		
13	9.46		9.47	9.40	9.41		
14	9.77	9.79	9.78	9.71	9.71		
15	10.27	10.29	10.29	10.21	10.21		
16	10.64	10.65	10.66	10.59	10.59		
17				10.96	10.95	10.95	
18	11.01		11.02	11.02	11.03		
19	11.09		11.10				
20	11.98		11.99	11.94	11.93	11.93	
21	12.39		12.39	12.33	12.33	12.33	
22			12.77	12.71	12.69		
23	12.92			12.94	12.93		
24	12.99		13.00	13.09	13.09	13.10	
25	13.14		13.16				
26						13.24	
27	13.49		13.49	13.44	13.44		
28	13.58		13.61	13.54	13.54	13.51	13.52
29				13.67		13.68	
30			14.08	14.03	14.03	14.03	14.02
31			14.30	14.26	14.24	14.24	14.25
32					14.39	14.36	
33			14.49	14.46	14.46		
34						14.56	14.56
35					15.10	15.10	
36			15.38	15.33	15.32	15.32	
37			15.65	15.62	15.62	15.61	16.61
38			15.78	15.74	15.74	15.74	15.79

TABLE 5
(continued)

Peak No.	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
39			16.13	16.10	16.10	16.08	
40							16.19
41						16.34	16.34
42						16.44	16.45
43						16.55	
44			16.77	16.73	16.74	16.77	16.77
45			17.13	17.09	17.07	17.07	17.08
46						17.29	17.31
47				17.46	17.44	17.43	17.43
48				17.69	17.69	17.68	17.68
49					18.19	18.17	18.18
50				18.48	18.49	18.42	18.40
51						18.59	
52						18.86	18.86
53				19.13	19.13	19.10	19.09
54						19.42	19.43
55						19.55	19.59
56						20.20	20.21
57						20.34	
58							20.43
59					20.57	20.55	
60						20.62	20.66
61						20.88	20.87
62							21.03
63						21.53	21.53
64						21.83	21.81
65						23.31	23.27
66							23.85
67							24.11
68							24.46
69							24.59
70							24.87
71							25.85
72							27.05
73							27.72

[a] GC operating conditions are given in Table 3. All retention times are in minutes and are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

[b] The peaks listed in this table are sequentially numbered in elution order for illustrative purposes only and are not isomer numbers.

TABLE 6

EXAMPLE RETENTION TIMES OF PEAKS DIAGNOSTIC OF PCBs
ON A 0.53-mm ID COLUMNS DURING SINGLE-COLUMN ANALYSIS

Peak No.[a]	RT on DB-608[b]	RT on DB-1701[b]	Aroclor[c]
I	4.90	4.66	1221
II	7.15	6.96	1221, 1232, 1248
III	7.89	7.65	1061, 1221, 1232, 1242
IV	9.38	9.00	1016, 1232, 1242, 1248
V	10.69	10.54	1016, 1232, 1242
VI	14.24	14.12	1248, 1254
VII	14.81	14.77	1254
VIII	16.71	16.38	1254
IX	19.27	18.95	1254, 1260
X	21.22	21.23	1260
XI	22.89	22.46	1260

[a]Peaks are sequentially numbered in elution order and are not isomer numbers

[b]Temperature program: T_i = 150EC, hold 30 seconds; 5EC/minute to 275EC.

[c]Underline indicates the largest peak in the pattern for that Aroclor

All retention times are in minutes and are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 7

SPECIFIC PCB CONGENERS THAT ARE MAJOR COMPONENTS IN COMMON AROCLORS

		Aroclor						
Congener	IUPAC Number	1016	1221	1232	1242	1248	1254	1260
Biphenyl	--		X					
2-CB	1	X	X	X	X			
2,3-DCB	5	X	X	X	X	X		
3,4-DCB	12	X		X	X	X		
2,4,4'-TCB	28*	X		X	X	X	X	
2,2',3,5'-TCB	44			X	X	X	X	X
2,3',4,4'-TCB	66*					X	X	X
2,3,3',4',6-PCB	110						X	
2,3',4,4',5-PCB	118*						X	X
2,2',4,4',5,5'-HCB	153							X
2,2',3,4,4',5'-HCB	138							X
2,2',3,4,4',5,5'-HpCB	180							X
2,2',3,3',4,4',5-HpCB	170							X

*Apparent co-elution of: 28 with 31 (2,4',5-trichlorobiphenyl)
66 with 95 (2,2',3,5',6-pentachlorobiphenyl)
118 with 149 (2,2',3,4',5',6-hexachlorobiphenyl)

This table is not intended to illustrate all of the congeners that may be present in a given Aroclor, but rather to illustrate the major congener components.

TABLE 8
EXAMPLE RETENTION TIMES OF PCB CONGENERS ON THE DB-5 WIDE-BORE COLUMN

IUPAC Number	Retention Time (min)
1	6.52
5	10.07
18	11.62
31	13.43
52	14.75
44	15.51
66	17.20
101	18.08
87	19.11
110	19.45
151	19.87
153	21.30
138	21.79
141	22.34
187	22.89
183	23.09
180	24.87
170	25.93
206	30.70
209 (internal standard)	32.63

All data are provided for illustrative purposes only. Each laboratory must determine retention times and retention time windows for their specific application of the method.

TABLE 9

SINGLE-LABORATORY RECOVERY DATA FOR THE EXTRACTION OF PCBs FROM CLAY AND SOIL BY AUTOMATED SOXHLET (METHOD 3541)[a]

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Clay	1254	5	1	87
			2	93
			3	94
			4	99
			5	79
			6	28
Clay	1254	50	1	65
			2	72
			3	97
			4	80
			5	50
			6	59
Clay	1260	5	1	87
			2	75
			3	61
			4	94
			5	97
			6	113
Clay	1260	50	1	74
			2	70
			3	92
			4	89
			5	90
			6	67

TABLE 9
(continued)

Matrix	Aroclor	Spike Level (ppm)	Trial	Percent Recovery[b]
Soil	1254	5	1	70
			2	89
			3	92
			4	83
			5	63
Soil	1254	50	1	84
			2	78
			3	92
			4	67
			5	82
			6	62
Soil	1260	5	1	84
			2	83
			3	82
			4	96
			5	94
			6	94
			7	98
Soil	1260	50	1	77
			2	69
			3	93
			4	82
			5	83
			6	76

[a]The operating conditions for the automated Soxhlet
Immersion time: 60 min
Reflux time: 60 min

[b]Multiple results from two different extractors

Data from Reference 9

TABLE 10

MULTIPLE-LABORATORY PRECISION AND ACCURACY DATA FOR THE EXTRACTION OF PCBs FROM SPIKED SOIL BY AUTOMATED SOXHLET (METHOD 3541)

		Percent Recovery at Aroclor 1254 Spike Concentration (µg/kg)			Percent Recovery at Aroclor 1260 Spike Concentration (µg/kg)			Mean Recovery
		5	50	500	5	50	500	All Levels
Lab 1	n	3	3		3	3		12
	Mean	101.2	74.0		83.9	78.5		84.4
	S. D.	34.9	41.8		7.4	7.4		26.0
Lab 2	n		6	6		6	6	24
	Mean		56.5	66.9		70.1	74.5	67.0
	S. D.		7.0	15.4		14.5	10.3	13.3
Lab 3	n	3	3		3	3		12
	Mean	72.8	63.3		70.6	57.2		66.0
	S. D.	10.8	8.3		2.5	5.6		9.1
Lab 4	n	6	6		6	6		24
	Mean	112.6	144.3		100.3	84.8		110.5
	S. D.	18.2	30.4		13.3	3.8		28.5
Lab 5	n		3	3		3	3	12
	Mean		97.1	80.1		79.5	77.0	83.5
	S. D.		8.7	5.1		3.1	9.4	10.3
Lab 6	n	2	3		3	4		12
	Mean	140.9	127.7		138.7	105.9		125.4
	S. D.	4.3	15.5		15.5	7.9		18.4
Lab 7	n	3	3		3	3		12
	Mean	100.1	123.4		82.1	94.1		99.9
	S. D.	17.9	14.6		7.9	5.2		19.0
Lab 8	n	3	3		3	3		12
	Mean	65.0	38.3		92.8	51.9		62.0
	S. D.	16.0	21.9		36.5	12.8		29.1
All Labs	n	20	30	9	21	31	9	120
	Mean	98.8	92.5	71.3	95.5	78.6	75.3	87.6
	S. D.	28.7	42.9	14.1	25.3	18.0	9.5	29.7

Data from Reference 7

TABLE 11

PERCENT RECOVERY (BIAS) OF PCBs IN VARIOUS SOILS USING SUPERCRITICAL FLUID EXTRACTION (METHOD 3562)

PCB No.[a]	EC-1 Dump Site Soil Low #1	SRM 1941 Marine Sediment Low #2	EC-5 Lake Sediment Low #3	CRM 481[b] European Soil High #1	Saginaw Bay Sediment High #2	CRM 392 Sewage Sludge High #3	SRM 2974 Fish Tissue Mussel Low #4	Congener Mean
28	148.4	63.3	147.7	67.3	114.7	89.2	101.7	104.6
52	88.5	106.6	115.8	84.5	111.1	96.2	131.4	104.9
101	93.3	91.2	100.2	84.5	111.5	93.9	133.2	101.1
149	92.6	105.1	101.5	73.2	111.2		69.4	92.2
118	89.9	66.1	108.9	82.1	110.8	73.5	82.7	87.7
153	90.8	65.1	95.1	82.8	118.6	97.3	107.5	94.0
105[b]	89.1	72.6	96.6	83.4	111.8		79.4	88.8
138	90.1	57.4	97.9	76.9	126.9		73.1	87.1
128	90.8	69.9	101.2	65.9	87.6		62.5	79.7
156[b]	90.6	88.9	94.3	85.2	101.1		59.3	86.6
180	92.4	142.4	93.3	82.2	109.2	100.5	65.7	98.0
170	91.3	101.1	95.2	80.5			33.0	81.8
Matrix Mean	95.7	85.8	104.0	79.0	108.7	91.8	83.2	92.2

[a] Congeners which are either certified or have had Soxhlet confirmation.

[b] Congener 105 was not resolved from congener 132 and congener 156 was not resolved from congener 171 by the GC method used for samples EC-1 and EC-5.

TABLE 12

PRECISION (AS %RSD) OF PCBs EXTRACTED USING SUPERCRITICAL FLUID EXTRACTION (METHOD 3562)

PCB No.[a]	EC-1 Dump Site Soil Low #1	SRM 1941 Marine Sediment Low #2	EC-5 Lake Sediment Low #3	CRM 481 European Soil High #1	Saginaw Bay Sediment High #2	CRM 392 Sewage Sludge High #3	SRM 2974 Fish Tissue Mussel Low #4	Congener Mean
28	11.5	1.5	3.8	5.6	2.4	1.9	2.7	4.2
52	9.1	3.3	3.9	5.4	2.2	2.9	3.1	4.3
101	9.1	2.9	2.8	4.9	1.4	5.2	2.9	4.2
149	7.1	0.7	3.8	3.9	3.4		2.2	3.0
118	9.8	1.9	4.5	5.4	2.0	3.3	2.4	4.2
153	8.4	1.5	3.0	4.3	4.3	9.5	3.0	4.9
105[b]	6.6	3.7	2.7	4.3	2.7		2.5	3.2
138	9.2	1.8	3.1	4.7	2.3		2.9	3.4
128	6.0	5.3	3.3	4.9	2.8		3.3	3.7
156[b]	8.3	0.0	5.1	4.5	1.9		3.8	3.4
180	8.0	1.3	3.6	4.3	3.1	9.6	2.7	4.7
170	5.7	2.3	3.6	3.9	2.3		4.0	3.1
Matrix Mean	8.2	2.2	3.6	4.7	2.6	2.7	3.0	3.8

[a] Congeners which are either certified or have had Soxhlet confirmation.

[b] Congener 105 was not resolved from congener 132 and congener 156 was not resolved from congener 171 by the GC method used for samples EC-1 and EC-5.

TABLE 13

EXAMPLE METHOD DETECTION LIMITS (MDLs)[a] OF PCBs USING SUPERCRITICAL FLUID EXTRACTION (METHOD 3562)

PCB No.[b]	EC-1 Dump Site Soil Low #1	SRM 1941 Marine Sediment Low #2	EC-5 Lake Sediment Low #3	Saginaw Bay Sediment High #2	CRM 392 Sewage Sludge High #3	SRM 2974 Fish Tissue Mussel Low #4	Congener Mean
28	13.2	0.5	0.6	15.4	5.3	5.0	6.6
52	22.3	0.6	1.9	29.9	6.9	9.1	11.8
101	23.9	0.9	1.9	3.3	20.6	9.7	10.1
149	7.1	0.7	3.8	3.7		4.1	3.2
118	9.8	1.9	4.5	3.3	7.5	6.9	5.7
153	8.4	1.5	3.0	3.5	97.3	9.4	20.5
105[c]	6.6	3.7	2.7	2.6		3.1	3.1
138	9.2	1.8	3.1	1.7		7.2	3.8
128	6.0	5.3	3.3	0.5		0.6	2.6
156[c]	8.3	0.0	5.1	0.2		0.6	2.4
180	8.0	1.3	3.6	1.9	94.5	0.9	18.4
170	5.7	2.3	3.6	0.6		3.1	2.6
Matrix Mean	10.7	1.7	3.1	5.6	19.3	5.0	7.6

[a] MDLs are highly matrix-dependant. MDLs provided in SW-846 are for illustrative purposes only and may not always be achievable. Labs should establish their own in-house MDLs, if necessary, to document method performance.

[b] Congeners which are either certified or have had Soxhlet confirmation.

[c] Congener 105 was not resolved from congener 132 and congener 156 was not resolved from congener 171 by the GC method used for samples EC-1 and EC-5.

TABLE 14

EXAMPLE SINGLE-LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF AROCLOR 1254 FROM WASTEWATER MATRICES SPIKED AT 2 µg/L

Wastewater Type	Mean Conc. (µg/L)	Percent Recovery	Std. Dev. (µg/L)	RSD (%)
Chemical Industry	2.4	120	0.41	17.2
Chemical Industry	0.6	28	0.03	5.4
Paper Industry	3.0	150	0.56	18.5
Paper Industry	2.3	115	0.08	3.7
Pharmaceutical Industry	1.5	76	0.03	1.7
Pharmaceutical Industry	1.0	51	0.03	2.9
Refuse	0.5	27	0.04	6.7
Refuse	0.6	31	0.10	16.0
POTW	1.9	96	0.15	7.8
POTW	2.1	105	0.04	1.8

Results represent three replicate solid-phase extractions of spiked wastewaters. Two different wastewaters from each wastewater type were spiked. All extractions were performed using 90-mm C_{18} extraction disks.

TABLE 15

EXAMPLE SINGLE-LABORATORY RECOVERY DATA FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF AROCLOR 1254 FROM WASTEWATER MATRICES SPIKED AT 10 µg/L

Wastewater Type	Mean Conc. (µg/L)	Percent Recovery	Std. Dev. (µg/L)	RSD (%)
Chemical Industry	8.8	88	1.07	12.2
Chemical Industry	8.1	81	0.06	0.7
Paper Industry	8.9	89	0.71	7.9
Paper Industry	10.1	101	0.15	1.4
Pharmaceutical Industry	9.2	92	0.24	2.6
Pharmaceutical Industry	8.4	84	0.17	2.0
Refuse	8.8	88	0.49	5.6
Refuse	8.0	80	1.44	18.0
POTW	9.5	82	0.17	2.1
POTW	8.2	82	0.17	2.1

Results represent three replicate solid-phase extractions of spiked wastewaters. Two different wastewaters from each wastewater type were spiked. All extractions were performed using 90-mm C_{18} extraction disks.

TABLE 16

EXAMPLE SINGLE-LABORATORY RECOVERY DATA
FOR SOLID-PHASE EXTRACTION (METHOD 3535) OF AROCLOR 1254
FROM WASTEWATER MATRICES SPIKED AT 100 µg/L

Wastewater Type	Mean Conc. (µg/L)	Percent Recovery	Std. Dev. (µg/L)	RSD (%)
Chemical Industry	81.7	82	1.46	1.8
Chemical Industry	89.7	90	0.66	0.7
Paper Industry	73.7	74	3.94	5.3
Paper Industry	95.3	95	1.89	2.0
Pharmaceutical Industry	86.4	86	1.95	2.3
Pharmaceutical Industry	79.2	79	3.92	4.9
Refuse	85.7	86	1.59	1.9
Refuse	71.5	72	1.61	2.2
POTW	87.8	88	1.76	2.0
POTW	80.6	81	0.40	0.5

Results represent three replicate solid-phase extractions of spiked wastewaters. Two different wastewaters from each wastewater type were spiked. All extractions were performed using 90-mm C_{18} extraction disks.

TABLE 17

SINGLE-LABORATORY PCB CONGENER DATA FROM A SEWAGE SLUDGE SAMPLE EXTRACTED BY PRESSURIZED FLUID EXTRACTION (METHOD 3545)

PCB No.	Mean Recovery (%)	%RSD	Certified Value (µg/kg)
52	114	4.7	163
101	143	7.4	161
138	110	3.9	193
153	110	5.8	198
180	160	7.5	207

Percent recoveries are the mean of six replicate extractions.

Data are taken from Reference 13.

TABLE 18

SINGLE-LABORATORY PCB CONGENER DATA FROM A RIVER SEDIMENT REFERENCE MATERIAL EXTRACTED BY PRESSURIZED FLUID EXTRACTION (METHOD 3545)

PCB No.	Mean Recovery (%)	%RSD	Certified Value (µg/kg)
101	89	3.7	780
138	122	2.3	570
153	62	4.1	370
180	112	5.9	180

Percent recoveries are the mean of six replicate extractions.

The river sediment reference material was SRM 1939.

Data are taken from Reference 13.

TABLE 19

SINGLE-LABORATORY AROCLOR 1254 DATA FROM A SOIL REFERENCE MATERIAL EXTRACTED BY PRESSURIZED FLUID EXTRACTION (METHOD 3545)

Replicate Extraction	Aroclor 1254 Concentration (µg/kg)
1	1290
2	1370
3	1280
4	1370
Mean	1330
%RSD	3.5%
Certified value	1340
Mean recovery (%)	99%

Data are taken from Reference 13.

TABLE 20

SINGLE-LABORATORY PCB HOMOLOGUE DATA BY MICROWAVE EXTRACTION (METHOD 3546) FROM A CERTIFIED GREAT LAKE SEDIMENT MATERIAL (EC-2)

	Microwave Extraction			Soxhlet Extraction		
PCB homologue	µg/kg	Peaks[a]	% RSD	µg/kg	Peaks[a]	% RSD
Trichlorobiphenyl	130	4	21.8	100	4	14.6
Tetrachlorobiphenyl	400	10	13.2	390	20	10.2
Pentachlorobiphenyl	310	9	1.9	300	9	8.7
Hexachlorobiphenyl	120	3	0.0	110	3	9.1

[a] Number of PCB peaks detected
Cl_3 to Cl_{10} homologues analyzed
n=3
Data are taken from Reference 14.

TABLE 21

SINGLE-LABORATORY PCB HOMOLOGUE DATA BY MICROWAVE EXTRACTION (METHOD 3546) FROM A CERTIFIED HARBOR SEDIMENT MATERIAL (SRM-1944)

	Microwave Extraction			Soxhlet Extraction		
PCB homologue	µg/kg	Peaks[a]	% RSD	µg/kg	Peaks[a]	% RSD
Trichlorobiphenyl	450	8	10.1	360	6	5.8
Tetrachlorobiphenyl	580	12	3.9	580	11	6.0
Pentachlorobiphenyl	330	9	6.1	330	9	7.9
Hexachlorobiphenyl	260	3	12.4	240	3	5.1
Heptachlorobiphenyl	60	2	43.8	80	2	27.3

[a] Number of PCB peaks detected
Cl_3 to Cl_{10} homologues analyzed
n=3
Data are taken from Reference 14.

TABLE 22

SINGLE-LABORATORY PCB DATA BY MICROWAVE EXTRACTION
(METHOD 3546) FROM CERTIFIED GREAT LAKE SEDIMENT MATERIALS

Sediment	Total Aroclor Concentration (µg/kg)	Standard Deviation (µg/kg)	RSD (%)	n	Certified Value (µg/kg)
EC-1	1850	0.07	3.78	3	2000 ± 54
EC-2	1430	0.09	6.60	4	1160 ± 70
EC-3	670	0.02	3.12	3	660 ± 54

Sample size = 2 g extracted into a final volume of 4 mL

EC-2 and EC-3 certified values were only provisional values at the time the work was conducted. The data presented herein were part of the validation data package used to confirm the certified values.

Data are taken from Reference 14.

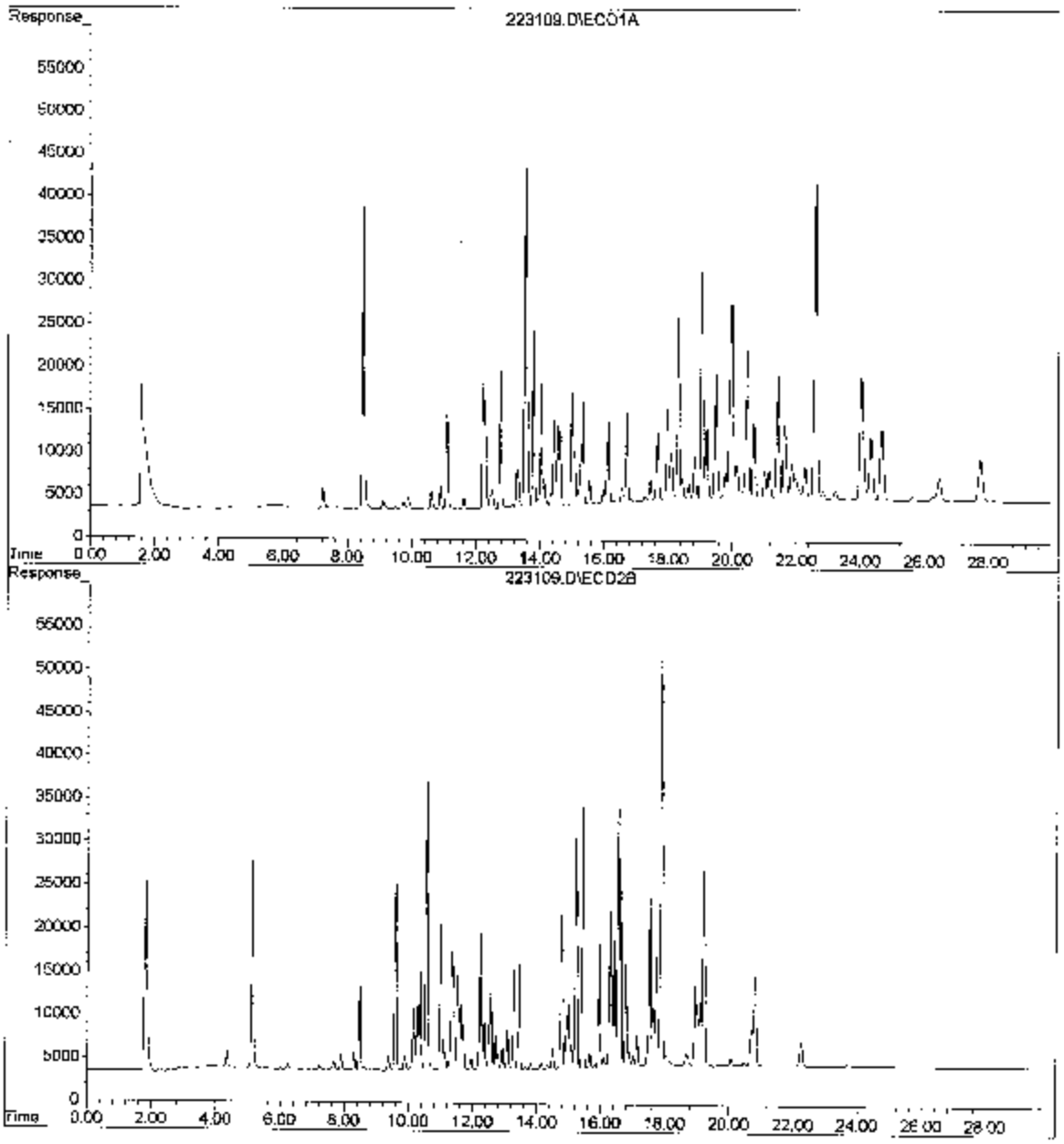

FIGURE 1. Example GC/ECD chromatogram of the Aroclor 1016/1260 mixture analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150EC (1.0 min hold) to 280EC (17 min hold) at 8EC/min.

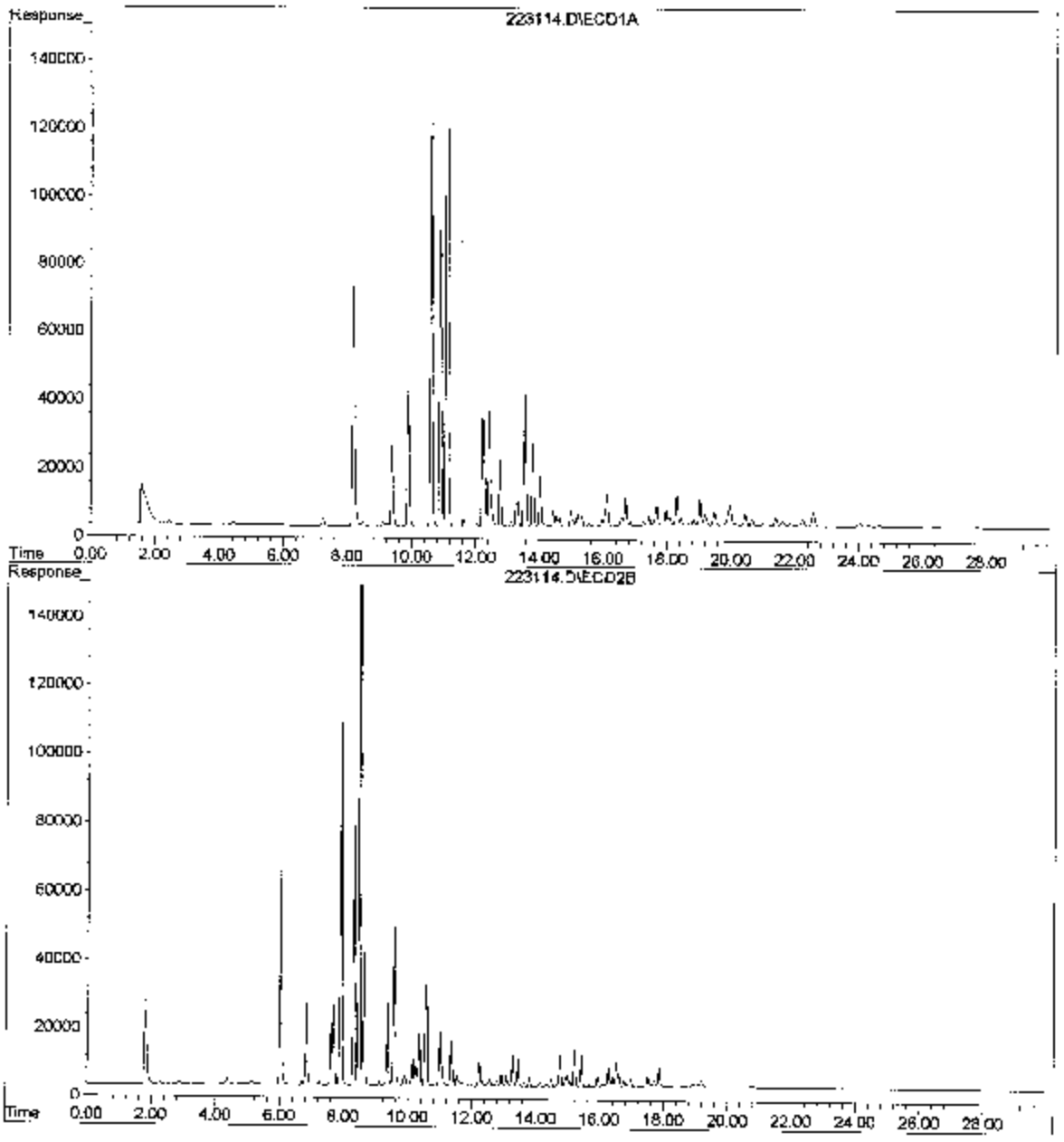

FIGURE 2. Example GC/ECD chromatogram of Aroclor 1221 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150EC (1.0 min hold) to 280EC (17 min hold) at 8EC/min.

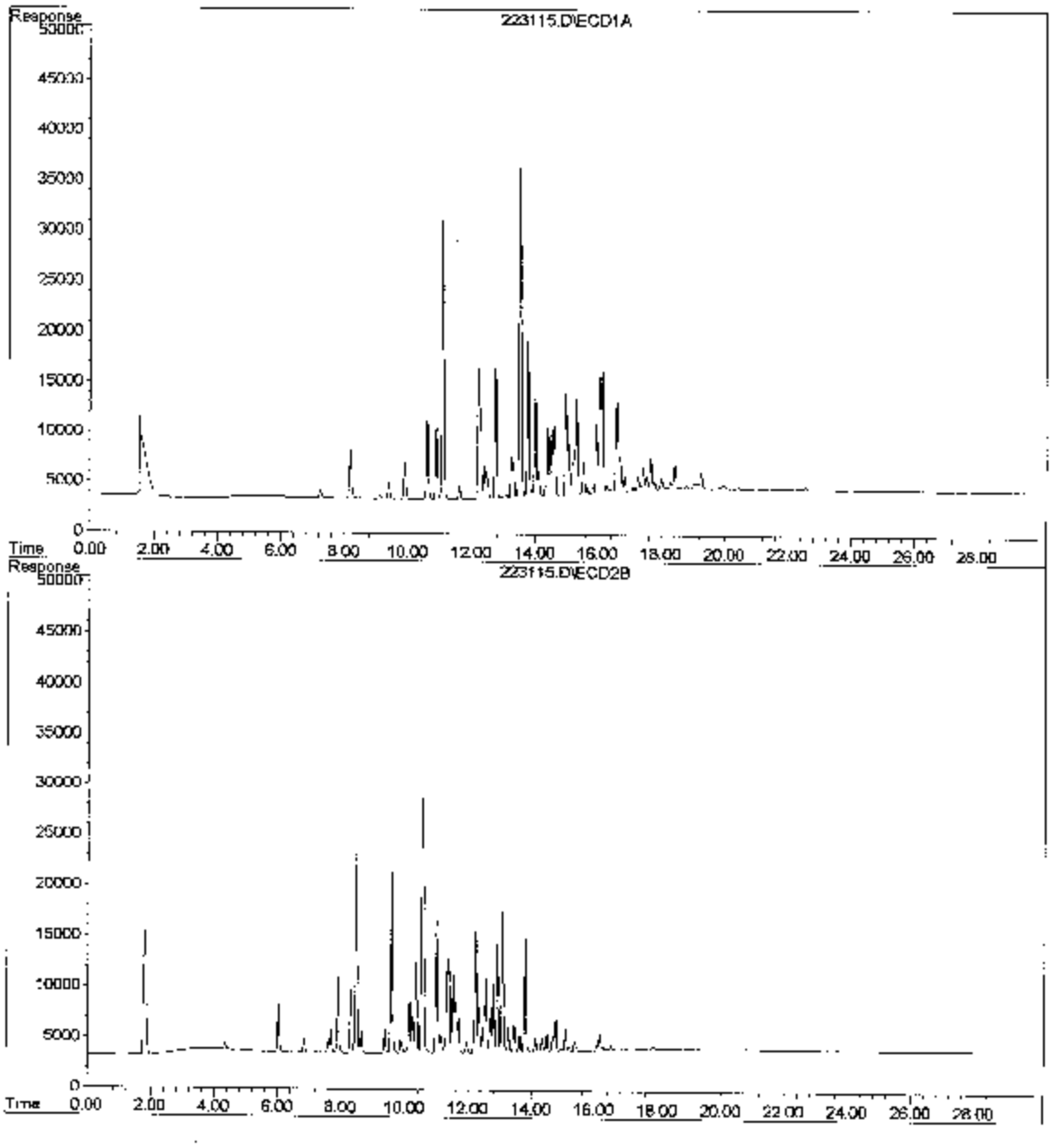

FIGURE 3. Example GC/ECD chromatogram of Aroclor 1232 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150EC (1.0 min hold) to 280EC (17 min hold) at 8EC/min.

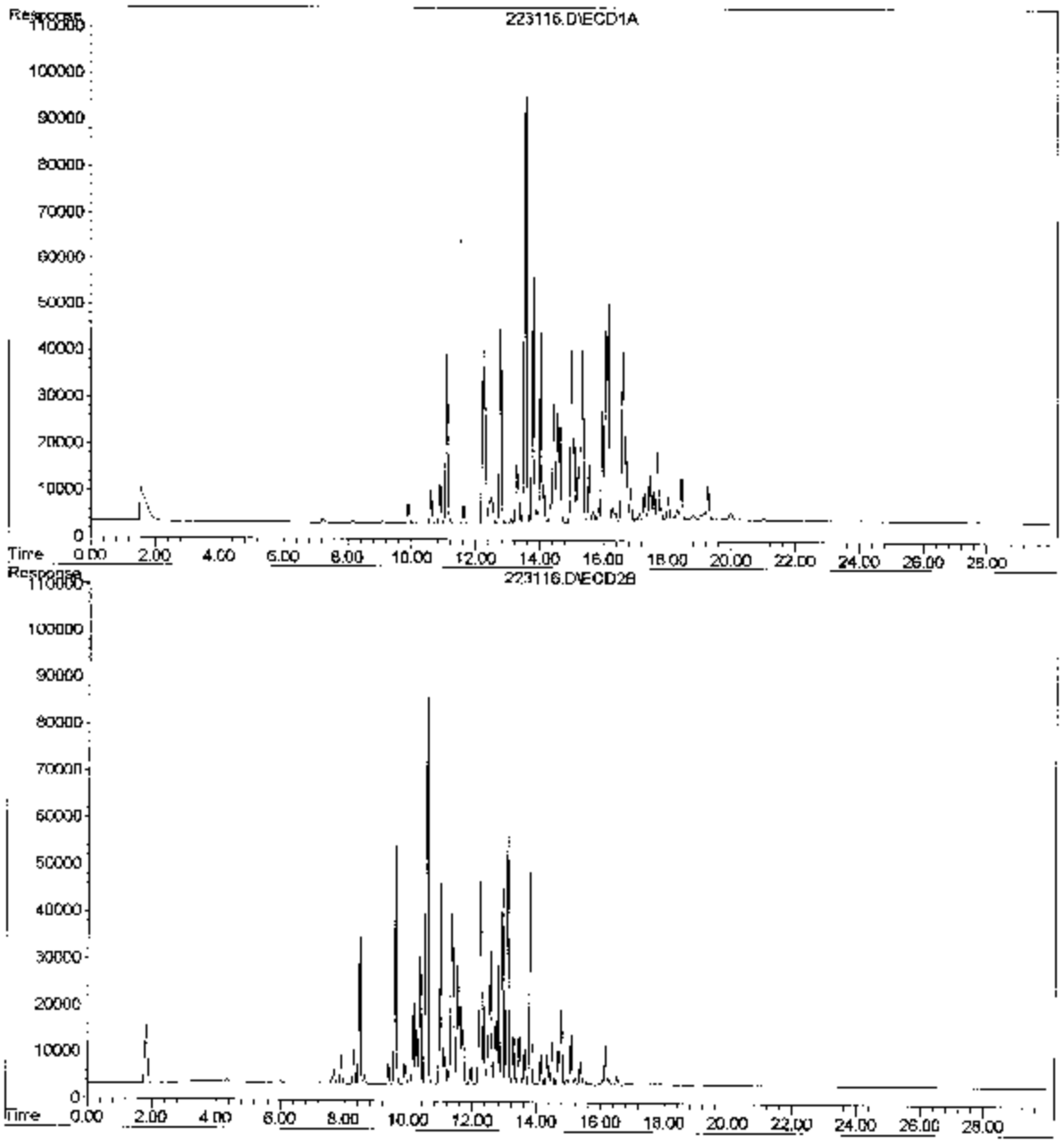

FIGURE 4. Example GC/ECD chromatogram of Aroclor 1242 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150EC (1.0 min hold) to 280EC (17 min hold) at 8EC/min.

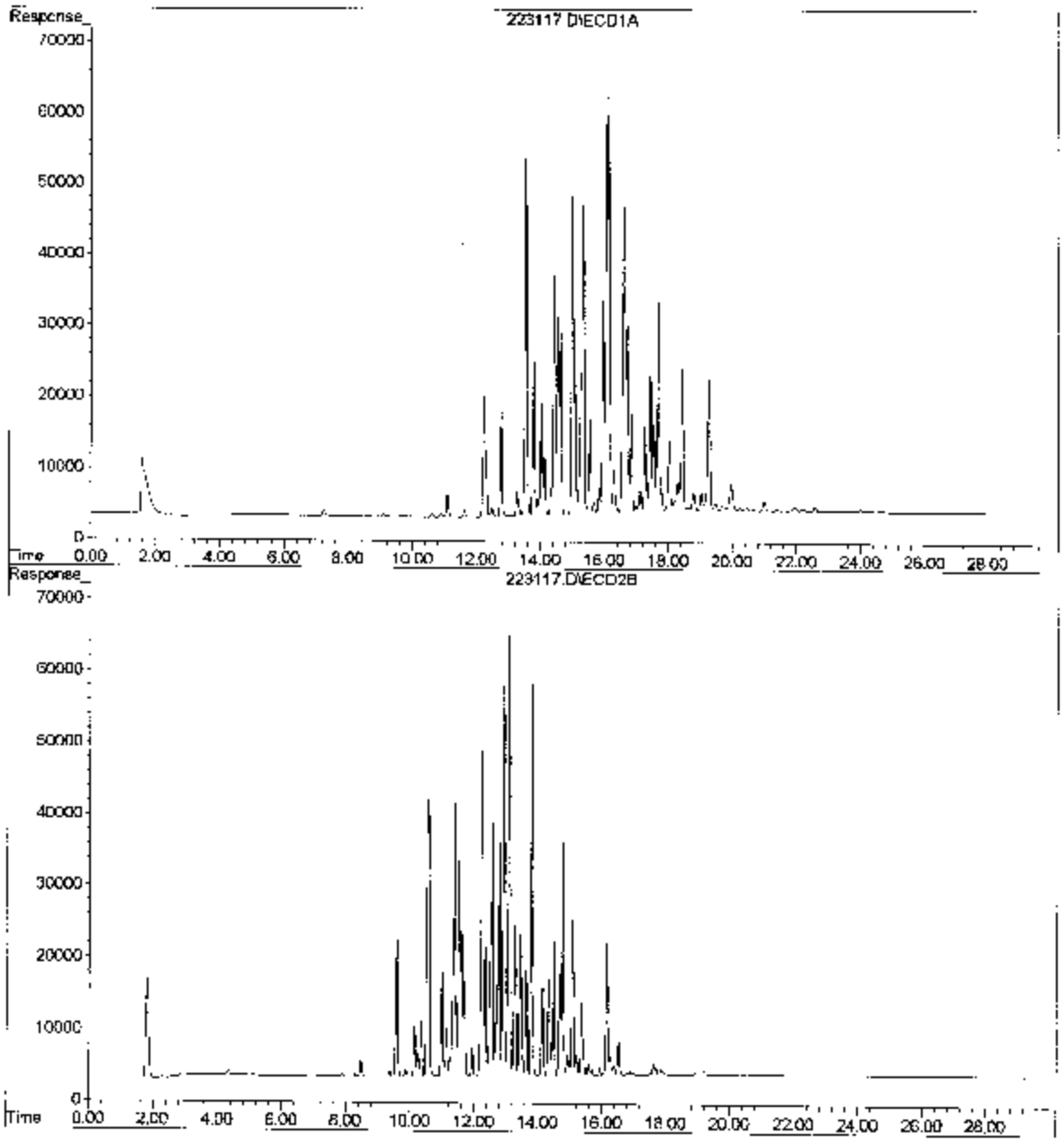

FIGURE 5. Example GC/ECD chromatogram of Aroclor 1248 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150EC (1.0 min hold) to 280EC (17 min hold) at 8EC/min.

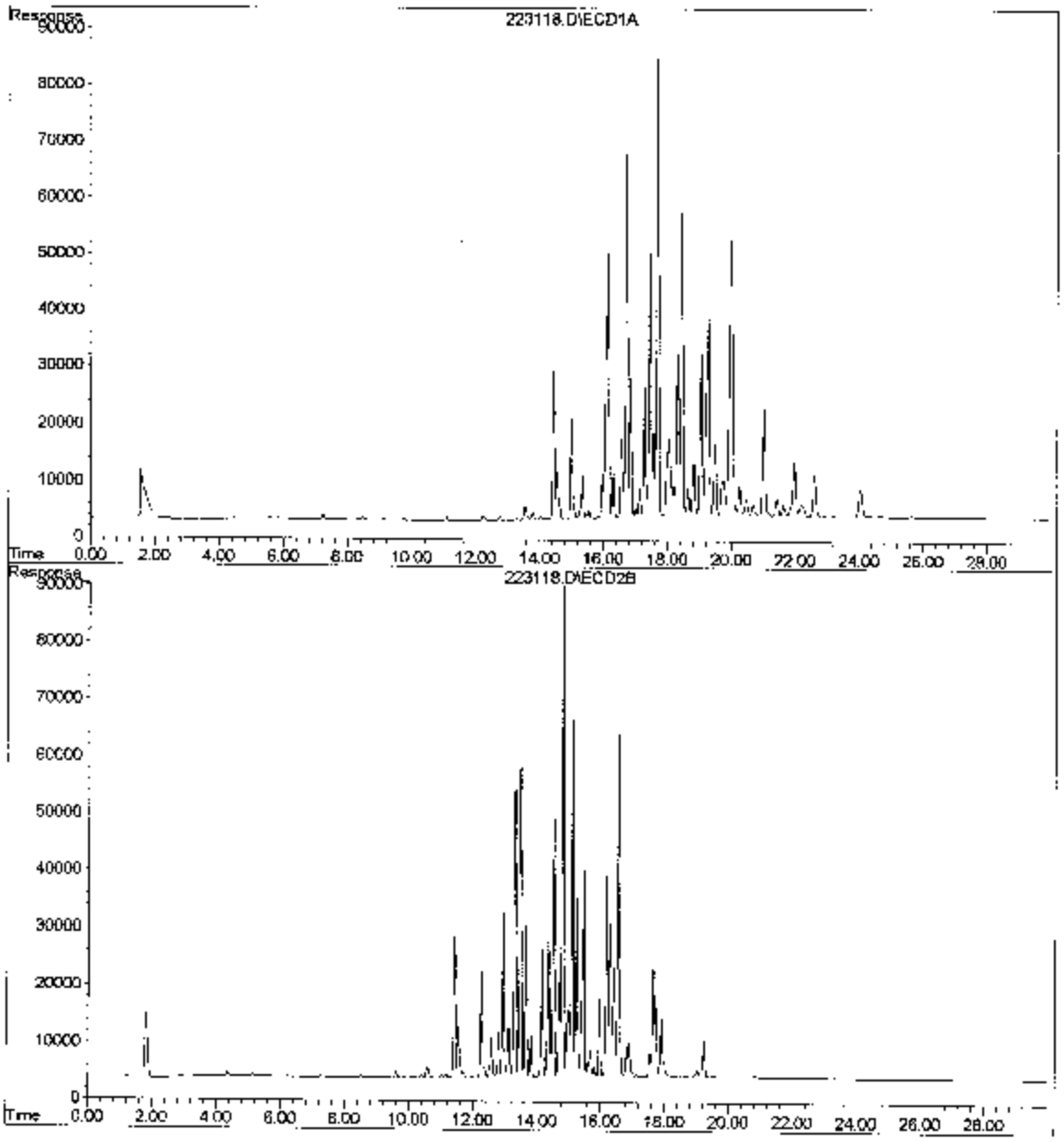

FIGURE 6. Example GC/ECD chromatogram of Aroclor 1254 analyzed on a Rtx-5/HP-608 column pair connected to separate injectors. The top trace is the Rtx-5 column (30-m x 0.53-mm ID, 1.5-µm film thickness) and the bottom trace is the HP-608 column (30-m x 0.53-mm ID, 0.5-µm film thickness). Temperature program: 150EC (1.0 min hold) to 280EC (17 min hold) at 8EC/min.

POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY