Method 680. Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry

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1. SCOPE AND APPLICATION

1.1. This method provides procedures for mass spectrometric determination of polychlorinated biphenyls (PCBs) and the listed pesticides in water, soil, or sediment. This method is applicable to samples containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. PCBs are identified and measured as isomer groups (i.e., by level of chlorination). The existence of 209 possible PCB congeners makes impractical the listing of the Chemical Abstracts Service Registry Number (CASRN) for each potential method analyte. Because PCBs are identified and measured as isomer groups, the non-specific CASRN for each level of chlorination is used to describe method analytes.

Analyte(s)	Formula	CASRN
Aldrin	$C_{12}H_8Cl_6$	309-00-2
BHCs		
alpha isomer	$C_6H_6Cl_6$	319-84-6
beta isomer	$C_6H_6Cl_6$	319-85-7
delta isomer	$C_6H_6Cl_6$	319-86-8
gamma isomer(lindane)	$C_6H_6Cl_6$	58-89-9
Chlordane (technical)		57-74-9
alpha-chlordane	$C_{10}H_6Cl_8$	5103-71-9
gamma-chlordane	$C_{10}H_6Cl_8$	5103-74-2
trans-nonachlor	$C_{10}H_5Cl_9$	39765-80-5
4,4'-DDD	$C_{14}H_{10}Cl_4$	72-54-8
4,4'-DDE	$C_{14}H_8Cl_4$	72-55-9
4,4'-DDT	$C_{14}H_9Cl_5$	50-29-3
Dieldrin	$C_{12}H_8Cl_6O$	60-57-1
Endosulfan I	$C_9H_6Cl_6O_3S$	959-98-8
Endosulfan II	$C_8H_6Cl_6O_3S$	33213-65-9
Endosulfan sulfate	$C_9H_4Cl_6O_4S$	1031-07-8
Endrin	$C_{12}H_8Cl_6O$	72-20-8
Endrin aldehyde	$C_{12}H_8Cl_6O$	7421-93-4
Endrin ketone	$C_{12}H_8Cl_6O$	53494-70-5
Heptachlor	$C_{10}H_5Cl_7$	76-44-8
Heptachlor epoxide	$C_{10}H_5Cl_7O$	1024-57-3
Methoxychlor	$C_{16}H_{15}Cl_3O_2$	72-43-5
PCBs		
Monochlorobiphenyls	$C_{12}H_9Cl$	27323-18-8
Dichlorobiphenyls	$C_{12}H_8Cl_2$	25512-42-9
Trichlorobiphenyls	$C_{12}H_7Cl_3$	25323-68-6
Tetrachlorobiphenyls	$C_{12}H_6Cl_4$	26914-33-0
Pentachlorobiphenyls	$C_{12}H_5Cl_5$	25429-29-2
Hexachlorobiphenyls	$C_{12}H_4Cl_6$	26601-64-9
Heptachlorobiphenyls	$C_{12}H_3Cl_7$	28655-71-2
Octachlorobiphenyls	$C_{12}H_2Cl_8$	31472-83-0
Nonachlorobiphenyls	$C_{12}HCl_9$	53742-07-7
Decachlorobiphenyl	$C_{12}Cl_{10}$	2051-24-3

1.2 Detection limits vary among method analytes and with sample matrix, sample preparation procedures, condition of the GC/MS system, type of data acquisition, and individual samples. The calculated method detection limit (MDL) for each pesticide in fortified reagent water extracts analyzed with full-range data acquisition is presented in Sect. 14. Analysis of calibration solutions indicated that the calculated MDLs do not accurately reflect instrumental detection limits. The following guidance is based on numerous analyses of calibration solutions with one instrument over a period of approximately six months. Pesticide analytes other than endosulfans I and II can be identified and accurately measured when the injected aliquot contains 2 ng of each analyte; the endosulfans require about 4 ng each. With selected-ion-monitoring (SIM) data acquisition, pesticide analyte detection limits are lowered by at least a factor of five. Detection limits for individual PCB congeners increase with increasing number of chlorine atoms, with the detection limit for decachlorobiphenyl being about 5-10 times higher than that of a monochlorobiphenyl. A monochlorobiphenyl can be identified and accurately measured when the injected extract aliquot contains 1 ng and full-range data are acquired. The detection limit for total PCBs will depend on the number of individual PCB congeners present. SIM data acquisition procedures reduce the detection limit for PCBs by at least a factor of three.

2. SUMMARY OF METHOD

A 1-L water sample is placed in a separatory funnel and extracted with methylene chloride. Appropriate extraction procedures for soil/sediment samples will be added when results are obtained from ongoing experiments. The extract is dried and exchanged to hexane during concentration to a final volume of 1 mL or less. Sample extract components are separated with capillary column gas chromatography (GC) and identified and measured with low resolution, electron ionization mass spectrometry (MS). An interfaced data system (DS) to control data acquisition and to store, retrieve, and manipulate mass spectral data is essential. Either full-range or selected-ion-monitoring (SIM) data are acquired, depending on the concentration range of concern. If full-range data are acquired, all method analytes can be identified and measured with one GC/MS analysis. If all pesticides and PCBs must be determined and if SIM data are necessary to meet required detection limits, two GC/MS analyses are necessary, one to detect and measure pesticides and one to detect and measure PCBs.

Two surrogate compounds are added to each sample before sample preparation; these compounds are $^{13}C_{12}$-4,4'-DDT and $^{13}C_6$-gamma-BHC. Two internal standards, chrysene-d_{12} and phenanthrene-d_{10}, are added to each sample extract before GC/MS analysis and are used to calibrate MS response. Each concentration measurement is based on an integrated ion abundance of one characteristic ion. All pesticides are identified as individual compounds, and a concentration is calculated by relating the MS response of each compound to the MS response of the internal standard with GC retention time nearer that of the pesticide analyte. The extent of sample contamination with technical chlordane is indicated by identification and measurement of the two most persistent components, gamma-chlordane and nonachlor. (Alpha-chlordane and heptachlor, other major components of technical chlordane, may also be present and will be detected and measured with this method.)

PCBs are identified and measured as isomer groups (i.e., by level of chlorination). A concentration is measured for each PCB isomer group; total PCB concentration in each sample extract is obtained by summing isomer group concentrations.

Nine selected PCB congeners are used as calibration standards, and one internal standard, chrysene-d_{12}, is used to calibrate MS response to PCBs, unless sample conditions require the use of the second internal standard, phenanthrene-d_{10}.

3. DEFINITIONS

3.1 CONCENTRATION CALIBRATION SOLUTION (CAL) -- A solution of method analytes used to calibrate the mass spectrometer response.

3.2 CONGENER NUMBER -- Throughout this method, individual PCBs are described with the number assigned by Ballschmiter and Zell (2). (This number is also used to describe PCB congeners in catalogs produced by Ultra Scientific, Hope, RI.)

3.3 INTERNAL STANDARD -- A pure compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

3.4 LABORATORY DUPLICATES (LD1 and LD2) --Two sample aliquots taken in the analytical laboratory are analyzed with identical procedures. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation or storage procedures.

3.5 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the GC/MS/DS with respect to a defined set of method criteria.

3.6 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or neutral solid reference material that is treated as a sample. It is exposed to all glassware and apparatus, and all method solvents, reagents, internal standards, and surrogate compounds are used. The extract is concentrated to the final volume used for samples and is analyzed the same as a sample extract.

3.7 LABORATORY SPIKE DUPLICATE SAMPLE -- One aliquot (LSD) of a sample is analyzed before fortification with any method analytes. In the laboratory, a known quantity of method analytes (LSA) is added to two independent aliquots of the same sample, and final analyte concentrations (LF1 and LF2) are measured with the same analytical procedures used to measure LSD.

3.8 LABORATORY SURROGATE SPIKE

3.8.1 Measured Value (LS1) -- Surrogate compound concentration measured with the same procedures used to measure sample components.

3.8.2 Theoretical Value (LS2) -- The concentration of surrogate compound added to a sample aliquot before extraction. This value is determined from standard gravimetric and volumetric techniques used during sample fortification.

3.9 METHOD DETECTION LIMIT (MDL) -- A statistically determined value (1) indicating the minimum concentration of an analyte that can be identified and measured in a sample matrix with 99% confidence that the analyte concentration is greater than zero. This value varies with the precision of the replicate measurements used for the calculation.

3.10 PERFORMANCE EVALUATION SAMPLE -- A sample containing known concentrations of method analytes that has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte concentrations are unknown to the analyst.

3.11 QUALITY CONTROL (QC) CHECK SAMPLE -- A sample containing known concentrations of analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze environmental samples containing the same or similar analytes. Analyte concentrations are known by the analyst. Preparation of the QC check sample by a laboratory other than the laboratory performing the analysis is highly desirable.

3.12 SURROGATE COMPOUND -- A compound not expected to be found in the sample is added to a sample aliquot before extraction and is measured with the same procedures used to measure sample components. Associated with the surrogate compound are two values, laboratory surrogate spike- measured value (LS1) and laboratory surrogate spike - theoretical value (LS2). The purpose of a surrogate compound is to monitor method performance with each sample.

4. INTERFERENCES

4.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment. Laboratory reagent blanks (LRBs) are analyzed routinely to demonstrate that these materials are free of interferences under the analytical conditions used for samples.

4.2 To minimize interferences, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Then wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry and heat in a muffle furnace at 450°C for a few hours. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent. Volumetric glassware should not be heated in a muffle furnace.

4.3 For both pesticides and PCBs, interference can be caused by the presence of much greater quantities of other sample components that overload the capillary column; additional sample extract preparation procedures must then be used to eliminate interferences. Capillary column GC retention times and the compound-specific characteristics of mass spectra eliminate many interferences that formerly were of concern with pesticide/PCB determinations with electron capture detection. The approach and identification criteria used in this method for PCBs eliminate interference by most chlorinated compounds other than other PCBs. With the isomer group approach, coeluting PCBs that contain the same number of chlorines are identified and measured together. Therefore, coeluting PCBs are a problem only if they contain a different number of chlorine atoms. This interference problem is obviated by rigorous application of the identification criteria described in this method.

4.4 For SIM identification and measurement of pesticides, other chlorinated sample components that produce the same quantitation and confirmation ions may interfere, but only if retention times are nearly equivalent.

5. SAFETY

5.1 The toxicity or carcinogenicity of each chemical used in this method has not been precisely defined. Therefore, each should be treated as a potential health hazard, and exposure should be reduced to the lowest feasible level. Each laboratory is responsible for safely disposing materials and for maintaining awareness of OSHA regulations regarding safe handling of the chemicals used in this method. A reference file of material data handling sheets should be made available to all personnel involved in analyses. Additional information on laboratory safety is available (3-5).

5.2 The following method analytes have been classified as known or suspected human or mammalian carcinogens: BHCs, 4,4'-DDD, 4,4'-DDT, and PCBs. Primary standards of these compounds should be prepared in a hood. A toxic gas respirator should be worn when the analyst handles solutions containing high concentrations of these compounds.

6. APPARATUS AND EQUIPMENT

6.1 SAMPLING EQUIPMENT

6.1.1 Water Sample Bottles -- Meticulously cleaned (Sect. 4.2) 1-L or 1-qt amber glass fitted with a Teflon-lined screw cap. (Bottles in which high purity solvents were received can be used as sample bottles without additional cleaning if they have been handled carefully to avoid contamination during and after use of original contents.)

6.1.2 Soil/Sediment Sample Bottles -- Appropriate containers will be specified when appropriate extraction procedures are determined.

6.2 GLASSWARE

6.2.1 Separatory Funnel -- 2-L with Teflon stopcock.

6.2.2 Drying Column -- glass column approximately 400 mm long X 19 mm ID with coarse frit filter disc.

6.2.3 Chromatography Column -- glass column approximately 400 mm long X 19 mm ID with coarse frit filter disc and Teflon stopcock.

6.2.4 Concentrator Tube -- 10-mL graduated Kuderna-Danish design with ground-glass stopper.

6.2.5 Evaporative Flask -- 500-mL Kuderna-Danish design that is attached to concentrator tube with springs.

6.2.6 Snyder Column -- three-ball macro Kuderna-Danish design.

6.2.7 Vials -- 10- to 15-mL amber glass with Teflon-lined screw caps.

6.3 COMPUTERIZED GC/MS SYSTEM

6.3.1 The GC must be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. Manual splitless injections were used to acquire data used as the basis for quality control requirements. An automatic injector, however, is desirable, because it should provide more precise retention times and areas. On-column injection with an uncoated precolumn is encouraged, because high mass descrimination and analyte degradation problems are minimized with this technique. With some GCs, however, the irreproducibility of the low initial column temperature required for on-column injections will cause irreproducible retention times (RTs) and relative retention times (RRTs). That can result in an inability to distinguish between two closely-eluting pesticide isomers and may cause ion sets to be changed at inappropriate times during SIM data acquistion. Splitting injections are not recommended.

6.3.2 Either full range or SIM mass spectral data are obtained with electron ionization at a nominal electron energy of 70 eV. To ensure sufficient precision of mass spectral data, the required MS scan rate must allow acquisition of at least five full-range mass spectra or five data points for each monitored ion while a sample component elutes from the GC. The MS must produce a mass spectrum meeting all criteria for $\leq$20 ng of decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet.

6.3.3 An interfaced data system (DS) is required to acquire, store, reduce, and output mass spectral data. The DS must be capable of searching a data file for specific ions and plotting ion abundances versus time or spectrum number to produce selected ion current profiles (SICPs) and extracted ion current profiles (EICPs). Also required is the capability to obtain chromatographic peak areas between specified times or spectrum numbers in SICPs or EICPs. Total data acquisition time per cycle should be $\geq$0.5 s and must not exceed 1.5 s.

6.3.4 SIM Option -- For SIM data acquisition, the DS must be equipped with software capable of acquiring data for multiple groups of ions, and the DS must allow automated and rapid changes of the set of ions being monitored. To acquire all PCB data needed for implementation of two currently-available automated interpretation procedures, the SIM program must be capable of acquiring data for four groups (or mass ranges) each consisting of $\leq$35 ions or for five groups of $\leq$20 ions each. The times spent monitoring ions during sample analyses must be the same as the times used when calibration solutions were analyzed.

6.4 GC COLUMN -- A 30 m X 0.32 mm ID fused silica capillary column coated with a 0.25 um or thicker film crosslinked phenyl methyl silicone (such as Durabond-5 (DB-5), J and W Scientific, Rancho Cordova, CA) or polydiphenyl vinyl dimethyl siloxane (such as SE-54, Alltech Associates, Deerfield, IL) is required. Operating conditions known to produce acceptable results with these columns are shown in Table 1; separation of pesticide analytes and PCB calibration congeners with a DB-5 column and those operating conditions is shown in Figure 1. Retention times have been reported (6) for all 209 PCB

congeners with an SE-54 column, which provides the same retention order for PCBs and essentially the same separation capabilities as a DB-5 column.

6.5 MISCELLANEOUS EQUIPMENT

6.5.1 Volumetric flasks - 2-mL, 5-mL, 10-mL, 25-mL, and 50-mL with ground glass stoppers.

6.5.2 Microsyringes - various standard sizes.

6.5.3 Boiling Chips -- approximately 10/40 mesh. Heat at 400°C for 30 min or extract with methylene chloride in a Soxhlet apparatus.

6.5.4 Water Bath -- heated, with concentric ring cover, capable of temperature control within ± 2°C.

6.5.5 Analytical Balance -- capable of accurately weighing to 0.0001 g.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 SOLVENTS -- High purity, distilled-in-glass hexane and methylene chloride. For precise injections with splitless injectors and capillary columns, all samples and standards should be contained in the same solvent. Effects of minor variations in solvent composition (i.e., small percentage of another solvent remaining in hexane extracts) are minimized with the use of internal standards. (External standard calibration is not acceptable.)

7.2 SODIUM SULFATE -- ACS, granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.

7.3 SODIUM THIOSULFATE -- ACS, granular.

7.4 TETRABUTYLAMMONIUM SULFITE REAGENT -- Dissove 3.39 g of tetrabutylammonium hydrogen sulfate in 100 mL distilled water. To remove impurities extract solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution in an amber bottle with a Teflon-lined screw cap. The solution can be stored at room temperature for at least one month.

7.5. MS PERFORMANCE CHECK SOLUTION -- Prepare a 10 ng/uL solution of decafluorotriphenylphosphine (DFTPP) in an appropriate solvent.

7.6 INTERNAL STANDARDS -- Chrysene-d_{12} and phenanthrene-d_{10} are used as internal standards. They are added to each sample extract just before analysis and are contained in all calibration/performance check solutions.

7.7 SURROGATE COMPOUNDS -- $^{13}C_{12}$-4,4'-DDT and $^{13}C_6$-gamma-BHC are added to every sample before extraction and are included in every calibration/performance check solution.

7.8 PCB CONCENTRATION CALIBRATION CONGENERS -- The nine individual PCB congeners listed in Table 2 are used as concentration calibration compounds for PCB determinations. One isomer at each level of chlorination is used as the concentration calibration standard for all other isomers at that level of chlorination, except that decachlorobiphenyl (Cl_{10}) is used for both Cl_9

and Cl_{10} isomer groups. The basis for selection of these calibration congeners has been reported (7).

7.9 PCB RETENTION TIME CONGENERS FOR SIM DATA ACQUISITION OPTION -- Knowledge of the retention times of certain congeners is necessary to determine when to acquire data with each ion set. Two concentration calibration congeners also serve as retention time congeners; the first eluting Cl_1-PCB indicates the time when data acquisition must have been initiated for ion set #1, and the Cl_{10}-PCB indicates when all PCBs have eluted. Two or three additional PCB congeners are used to establish times to initiate data acquisition with other ion sets (Sect. 9.4).

7.10 PESTICIDE SOLUTIONS

7.10.1 Pesticide Stock Solutions -- Prepare from pure standard materials. Weigh approximately 25.0 mg (with accuracy of 0.1 mg) of each surrogate compound and each pure pesticide analyte, except Endosulfan I and Endosulfan II. For those two pesticides, prepare a stock solution twice as concentrated as that prepared for other pesticide analytes. Dissolve each compound in hexane and dilute to volume in a 10-mL (5-mL for the two Endosulfans) volumetric flask. (Concentration of each component = 2.5 mg/mL, except Endosulfans, which should be 5 mg/mL.) Smaller or larger volumes of stock solution may be used if desired. If compound purity is certified at $\geq$96%, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standards in hexane can be used at any concentration if they are traceable to USEPA-supplied standards.

7.10.2 Pesticide Primary Dilution Solutions -- A convenient approach to solution preparation is to prepare two pesticide primary dilution solutions that are twice the concentration of the highest concentration calibration solution required. These solutions can then be diluted as necessary to prepare all needed calibration solutions. One solution contains endrin aldehyde and one does not, because the medium level calibration solution does not contain endrin aldehyde. Place 1 mL of each pesticide analyte/surrogate compound stock solution in a 25-mL volumetric flask. (Total volume for all 22 pesticide analytes and 2 surrogate compounds = 24 mL.) Make to volume with hexane and mix well. (Concentration of endosulfan sufate, endosulfan I and endosulfan II = 200 ng/uL; concentration of each other component = 100 ng/uL.)

7.11 PCB SOLUTIONS

7.11.1 Stock Solutions of PCB Calibration Congeners -- Prepare a stock solution of each of the nine PCB concentration calibration congeners at a concentration of 1 ug/uL in hexane. (If SIM data are to be acquired, prepare a 1 ug/uL stock solution of each of the three retention time congeners also.) Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C if solutions are not to be used right away. Solutions are stable indefinitely if solvent evaporation is prevented.
CAUTION: Each time a vial containing small volumes of solutions is warmed to room temperature and opened, a small volume of solvent in the vial headspace evaporates, significantly affecting concentration.

Solutions should be stored with the smallest possible volume of headspace, and opening vials should be minimized.

7.11.2 PCB Primary Dilution Standard -- Take aliquots of the stock solutions of the nine PCB concentration calibration congeners and mix together in the proportions of one part of each solution of the Cl_1 (#1), Cl_2 (#5), and Cl_3 (#29) congeners, two parts of each solution of the Cl_4 (#50), Cl_5 (#87), and Cl_6 (#154) congeners, three parts of each solution of the Cl_7 (#188) and Cl_8 (#200) congeners, and five parts of the Cl_{10} (#209) congener solution. (Note: The retention time congeners described in Sect. 7.9 are not included in the PCB primary dilution standard because they are not needed for full-range data acquisition.) This will provide a primary dilution standard solution of the composition shown in Table 3. Calculate the concentration in ug/uL; use three significant figures. Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C. Mark the meniscus on the vial wall to monitor solution volume during storage; solutions are stable indefinitely if solvent evaporation is prevented.

7.12 INTERNAL STANDARD (IS) SOLUTIONS -- Two solutions are needed to prepare concentration calibration solutions (CALs).

7.12.1 IS solution #1 (for full-range CALS) -- Weigh 7.5 mg $\pm$ 0.1 mg each of phenanthrene-d_{10} and chrysene-d_{12}; dissolve in hexane and dilute to 10 mL in a volumetric flask. (Concentration of each IS = 750 ng/uL)

7.12.2 IS solution #2 (for SIM CALS) -- Take 1 mL of IS solution #1 and dilute to 10 mL in a volumetric flask. (Concentration of each IS = 75 ng/uL)

7.13 CALS FOR FULL-RANGE DATA ACQUISITION -- Five hexane solutions are required. The solutions contain constant concentrations of the ISs (chrysene-d_{12} and phenanthrene-d_{12}) and varying concentrations of individual pesticide analytes, the nine PCB calibration compounds, and the two surrogate compounds ($^{13}C_{12}$-4,4'-DDT and $^{13}C_6$-gamma-BHC). (Composition and approximate concentrations are given in Table 4.) Four solutions (high and low concentrations) contain both ISs, both surrogate compounds, the nine PCB concentration calibration congeners, and each of the single-compound pesticide analytes. The fifth solution, the medium level concentration solution, contains all the above compounds except endrin aldehyde, which is not present for reasons described in Sect. 8. The lowest concentration solution contains each individual pesticide analyte and each PCB calibration congener at a concentration near but greater than its anticipated detection limit. (Because MS response to PCBs decreases with increasing level of chlorination, PCB congener concentrations in CALs increase with level of chlorination.) Components of the highest concentration solution (High CAL) are present at a concentration that allow injections of 2-uL aliquots without MS saturation or GC column overloading.

7.13.1 The Full-Range High CAL can be prepared by mixing equal portions of the PCB primary dilution solution and the pesticide primary dilution solution that contains endrin aldehyde and then adding an appropriate volume of IS solution #1. For example, 1 mL of each

primary dilution solution and 20 uL of IS solution #1 provide the appropriate concentration for High CAL.

7.13.2 Other full-range CALS are prepared by diluting the primary dilution standard solutions and adding the appropriate amount of IS solution #1. CAUTION: The pesticide primary dilution standard that does not contain endrin aldehyde must be used for the medium level full-range CAL.

7.14 CALS FOR SIM DATA ACQUISITION OPTION -- Two sets of solutions are needed, one set of five solutions for determinations of pesticide analytes, and one set of five solutions for PCB determinations. Appropriate concentrations of SIM CALs are given in Tables 5a and 5b. Solutions are prepared by diluting appropriate primary dilution standards and adding an appropriate volume of IS solution #2.
CAUTION: The Pesticide SIM Medium CAL does not contain endrin aldehyde; the PCB SIM CALS must include the three PCB retention time congeners. that are used to establish conditions for SIM data acquisition.

7.15 Prepare a solution of surrogate compounds in a water miscible solvent to provide a concentration in the sample/blank extract that is near the concentration anticipated for analytes when an aliquot of $\geq$20 uL is added to the sample before extraction.

7.15 Calculate the concentration (two significant figures if <100 and three significant figures if $\geq$100 ng/uL) of each component in each solution. Note: Concentrations presented in tables are only approximate.

7.16 LABORATORY PERFORMANCE CHECK SOLUTION - For both full-range data acquisition, and the SIM data acquisition option, the Medium CAL is used as the laboratory performance check solution (LPC) to verify response factors and to demonstrate adequate GC resolution and MS performance.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 WATER SAMPLES

8.1.1 Samples must be collected in clean (Sect. 4.2) glass containers. Note: When samples are anticipated to contain low concentrations of method analytes, a sample larger than 1-L may be needed. An effective sample collection procedure to minimize losses of hydrophobic analytes is to add a portion of extracting solvent to each sample container when the sample is collected. When a 1-gal sample is collected, an appropriate solvent volume is approximately 100 mL. (The entire sample must be used as one sample aliquot, and blank sample/solvent volumes must be adjusted also.)

8.1.2 Samples must be iced or refrigerated at 4°C from time of collection until extraction. If samples will not be extracted within 72 h after collection, use either sodium hydroxide or sulfuric acid to adjust sample pH to within a range of 5 to 9. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. Field test kits are available for measurement of residual chlorine.

8.1.3 Samples should be extracted within 7 days after collection and analyzed within 40 days after extraction.

8.2 SOIL/SEDIMENT SAMPLES -- Appropriate procedures will be specified when results are obtained from ongoing experiments.

9. CALIBRATION

Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of continuing calibration checks. After initial calibration is successfully performed, a continuing calibration check is required at the beginning and end of each 12-h period during which analyses are performed. The Medium CALs for pesticide determinations do not include endrin aldehyde. This allows the Medium CAL to be used for continuing calibration checks, including a check to ensure that endrin decomposition is $\leq$10%. During initial calibration a separate Medium CAL containing endrin aldehyde and the internal standard is analyzed to determine the response factor for endrin aldehyde. Thereafter, if endrin aldehyde is a component of any sample and endrin decomposition is not a problem, the response factor for endrin aldehyde is verified by analyzing a calibration solution containing it.

9.1 DATA ACQUISITION OPTIONS -- Either full-range or SIM data acquisition may be used.

9.1.1 Full-range data acquisition is recommended if sample extract components are anticipated to be at sufficiently high concentrations.

9.1.2 SIM data acquisition will provide an increase in sensitivity by at least a factor of five for pesticide determinations and by at least a factor of three for PCB determinations.

9.2. INITIAL CALIBRATION

9.2.1 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer with any necessary modifications to meet USEPA requirements.

9.2.2 Inject a 1- uL or 2-uL aliquot of the 10 ng/uL DFTPP solution and acquire a mass spectrum that includes data for m/z 45-450. If the spectrum does not meet all criteria (Table 6), the MS must be hardware tuned to meet all criteria before proceeding with calibration.

9.2.3 Full-Range Calibration -- Inject a 1- or 2-uL aliquot of the Medium CAL and acquire data from m/z 45 to 510. Acquire $\geq$5 spectra during elution of each GC peak. Total cycle time should be $\geq$0.5 s and $\leq$1.5 s. Note: Either a 1- or 2-uL aliquot should be used consistently for CALs and sample/blank extracts.

9.2.4 SIM Calibration -- Acquire at least five data points for each ion during elution of each GC peak. Total cycle time should be $\geq$0.5 s and $\leq$1.5 s.
CAUTION: When acquiring SIM data, GC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times; if not, ions will not be monitored at the appropriate times.

9.2.4.1 SIM Calibration for PCB determinations

9.2.4.1.1 Two options for SIM data acquisition are provided. Data can be acquired with four sets of ≤six mass ranges (≤35 ions each as shown in Table 7a) or with the five ion sets (≤20 ions each) shown in Tables 7b and 7c.

9.2.4.1.2 The time (scan number) for initiation of data acquisition with each ion set must be carefully determined from the retention times (scan numbers) of the retention time congeners. Approximate relative retention times of calibration congeners and approximate relative retention time windows for PCB isomer groups are shown in Table 8. (Also see Figures 1 and 2.)

9.2.4.1.3 SIM data acquisition with four ion sets. Begin data acquisition with Ion Set #1 before elution of PCB congener #1, the first eluting Cl_1-PCB. Stop acquisition with Ion Set #1 and begin acquisition with Ion Set #2 just (approximately 10 s) before elution of PCB congener #104, the first eluting Cl_5-PCB. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 just (approximately 10 s) after elution of PCB congener #77, the last eluting Cl_4-PCB. Stop acquisition with Ion Set #3 and begin acquisition with Ion Set #4 just (approximately 10 s) after elution of $^{13}C_{12}$-4,4'-DDT.

9.2.4.1.4 SIM data acquisition with five ion sets. Acquire data with the four Ion Sets described in Sect. 9.2.4.1.3 and add a fifth Ion Set beginning data acquisition with that set just (approximately 10 s) before elution of PCB congener #208, the first eluting Cl_9-PCB.

9.2.4.2 SIM Calibration for Pesticide Determinations -- Three sets of ≤15 ions each are used (Tables 9-10). Begin data acquisition with Ion Set #1 before elution of alpha-BHC, the first eluting pesticide analyte. Begin data acquisition with Ion Set #2 after elution of aldrin and before elution of heptachlor epoxide. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 after elution of endosulfan II and before 4,4'-DDD.

9.2.5 Performance Criteria

9.2.5.1 Full-Range Data from Analysis of Medium CAL

9.2.5.1.1 GC performance -- baseline separation of beta-BHC and gamma-BHC; baseline separation of endrin ketone and chrysene-d_{12}; height of Cl_1-PCB peak ≥80% beta-BHC peak height; height of chrysene-d_{12} peak ≥60% of the peak height of methoxychlor, which may partially coelute with the Cl_8-PCB congener.

9.2.5.1.2 MS sensitivity -- Signal/noise ratio of ≥5 for m/z 499 of PCB congener #209, Cl_{10}-PCB.

9.2.5.1.3 MS calibration -- Abundance of ≥40% and ≤60% of m/z 502 relative to m/z 498 for PCB congener #209.

9.2.5.1.4 Lack of degradation of endrin. Examine an extracted ion current profile (EICP) for m/z 67 in the retention time window between 4,4'-DDE and endosulfan sulfate; confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is <10% of the abundance of m/z 67 produced by endrin.

9.2.5.1.5 Lack of degradation of $^{13}C_{12}$-4,4'-DDT. Examine EICPs for m/z 258 and m/z 247 in the retention time window that includes 4,4'-DDD, 4,4'-DDE and 4,4'-DDT; m/z 258 would be produced by $^{13}C_{12}$-4,4'DDE, and m/z 247 by $^{13}C_{12}$-4,4'-DDD. Confirm that the total abundance of both ions is <5% of m/z 247 produced by $^{13}C_{12}$-4,4'-DDT.

9.2.5.2 SIM PCB Data

9.2.5.2.1 GC separation -- Baseline separation of PCB congener #87 from congeners #154 and #77, which may coelute.

9.2.5.2.2 MS sensitivity -- Signal/noise ratio of ≥5 for m/z 499 of PCB congener #209, Cl_{10}-PCB, and for m/z 241 of chrysene-d_{12}.

9.2.5.2.3 MS calibration -- Abundance of ≥70% and ≤95% of m/z 500 relative to m/z 498 for congener #209, Cl_{10}-PCB.

9.2.5.3 SIM Pesticide Data

9.2.5.3.1 GC separation -- Baseline separation of endrin ketone and chrysene-d_{12}; baseline separation of beta-BHC and gamma-BHC; baseline separation of endrin ketone and chrysene-d_{12}; height of chrysene-d_{12} peak ≥60% of methoxychlor peak height.

9.2.5.3.2 MS sensitivity -- Signal/noise ratio of >5 for m/z 241 of chrysene-d_{12}.

9.2.5.3.3 MS calibration -- Abundance of m/z 241 relative to that of m/z 240 produced by chrysene-d_{12} is >15% and <25%.

9.2.5.3.4 Lack of degradation of endrin. Examine an SICP for m/z 67 in the retention time window between 4,4'-DDE and endosulfan sulfate; confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is <10% that of m/z 67 produced by endrin.

9.2.5.3.5 Lack of degradation of $^{13}C_{12}$-4,4'-DDT. Examine SICPs for m/z 258 and m/z 247 in the retention time window that includes 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT; m/z 258 would be produced by $^{13}C_{12}$-4,4'-DDE, and m/z 247 by $^{13}C_{12}$-4,4'-DDD. Confirm that the total abundance of both ions is <5% of m/z 247 produced by $^{13}C_{12}$-4,4'-DDT.

9.2.6 Replicate Analyses of CALs -- If all performance criteria are met, analyze one 1- or 2-uL aliquot of each of the other four CALs.

9.2.7 Response Factor Calculation

9.2.7.1 Calculate five response factors (RFs) for each pesticide analyte, PCB calibration congener, and surrogate compound relative to both ISs (See Sect. 12.3.2), phenanthrene-d_{10} and chrysene-d_{12}:

$$RF = A_x Q_{is} / A_{is} Q_x$$

where A_x = integrated ion abundance of quantitation ion for a pesticide, a PCB calibration congener or a surrogate compound,

A_{is} = integrated ion abundance of m/z 240, the quantitation ion when chrysene-d_{12} is used as the internal standard or m/z 188, the quantitation ion when phenanthrene-d_{10} is used as the internal standard,

Q_{is} = injected quantity of chrysene-d_{12} or phenanthrene-d_{10},

Q_x = injected quantity of pesticide analyte, PCB calibration congener or surrogate compound.

RF is a unitless number, units used to express quantities must be equivalent. Note: The Cl_2-PCB calibration congener may not be resolved from alpha-BHC. If not, alpha-BHC will contribute to the ion abundance measured for Cl_2-PCB. To correct for this contribution, subtract 6.7% of the ion abundance of m/z 219 measured for alpha-BHC from the ion abundance measured for m/z 222 for Cl_2-PCB.

9.2.8 Response Factor Reproducibility -- For each pesticide analyte, PCB calibration congener and surrogate compound, calculate the mean RF from analyses of each of the five CALS. When the RSD exceeds 20%, analyze additional aliquots of appropriate CALS to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance.

9.2.9 SIM Analyte Retention Time Reproducibility

9.2.9.1 PCB determinations - Absolute retention times of PCB congeners #77 and #104 should not vary by more than ±10 s from one analysis to the next. (Retention time reproducibility is not as critical for congeners #1 and #209 as for #77 and #104, which are used to determine when ion sets are changed.)

9.2.9.2 Pesticide determinations -- Absolute retention times of gamma-chlordane, endosulfan I, and endosulfan II should not vary by more than ±10 s from one analysis to the next.

9.2.10 Record a spectrum of each CAL component.

9.3. CONTINUING CALIBRATION CHECK

9.3.1 With the following procedures, verify initial calibration at the beginning and end of each 12-h period during which analyses are to be performed.

9.3.2 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer.

9.3.3 Analyze a 1-uL or 2-uL aliquot of the DFTPP solution and ensure acceptable MS calibration and performance (Table 6).

9.3.4 Inject a 1-uL or 2-uL aliquot of the Medium CAL and analyze with the same conditions used during Initial Calibration.

9.3.5 Demonstrate acceptable performance for criteria described in Sect. 9.2.5.

9.3.6 Determine that neither the area measured for m/z 240 for chrysene-d_{12} nor that for m/z 188 for phenanthrene-d_{10} has decreased by more than 30% from the area measured in the most recent previous analysis of a calibration solution or by more than 50% from the mean area measured during initial calibration.

9.3.7 Response Factor Reproducibility -- For an acceptable Continuing Calibration Check, the measured RF for each analyte/surrogate compound must be within $\pm$20% of the mean value calculated (Sect. 9.2.7) during Initial Calibration. If not, remedial action must be taken; recalibration may be necessary.

9.3.8 SIM Analyte Retention Time Reproducibility -- Demonstrate and document acceptable (Sect. 9.2.9) reproducibility of absolute retention times of appropriate pesticide analytes and PCB retention time congeners.

9.3.9 Remedial actions must be taken if criteria are not met; possible remedies are:

9.3.9.1 Check and adjust GC and/or MS operating conditions.

9.3.9.2 Clean or replace injector liner.

9.3.9.3 Flush column with solvent according to manufacturers instructions.

9.3.9.4 Break off a short portion (approximately 0.33 m) of the column; check column performance by analysis of performance check solution.

9.3.9.5 Replace GC column; performance of all initial calibration procedures then required.

9.3.9.6 Adjust MS for greater or lesser resolution.

9.3.9.7 Calibrate MS mass scale.

9.3.9.8 Prepare and analyze new concentration calibration/ performance check solution.

9.3.9.9 Prepare new concentration calibration curve(s).

10. QUALITY CONTROL

10.1 LABORATORY REAGENT BLANK (LRB) -- Perform all steps in the analytical procedure (Section 11) using all reagents, standards, surrogate compounds, equipment, apparatus, glassware, and solvents that would be used for a sample analysis, but omit an aliquot of sample (water or soil/sediment). For water samples, substitute 1 L of reagent water. If available, substitute EPA-provided reagent blank solid material for an aliquot of soil/sediment.

10.1.1 An LRB must contain the same amount of surrogate compounds and internal standards that is added to each sample. This amount will vary with sample type and with the type of data acquisition (full-range or SIM).

10.1.2 Analyze an LRB before any samples are extracted and analyzed.

10.1.3 Before a new batch of solvents or reagents is used for sample extraction or for column chromatographic procedures, analyze an LRB. In addition, analyze a laboratory solvent blank (LSB), which is the same as an LRB except that no surrogate compounds or internal standards are added; this demonstrates that reagents contain no impurities producing an ion current above the level of background noise for quantitation ions for those compounds.

10.1.4 Analyze an LRB along with each batch of $\leq$20 samples.

10.1.5 An acceptable LRB contains no method analyte at a concentration greater than one half of its MDL and contains no additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte at its MDL. If the LRB that was extracted along with a batch of samples is contaminated, the entire batch of samples must be reextracted and reanalyzed.

10.1.6 Corrective action for unacceptable LRB -- Check solvents, reagents, apparatus and glassware to locate and eliminate the source of contamination before any samples are extracted and analyzed. Purify or discard contaminated reagents and solvents.

10.2 CALIBRATION -- Included among initial and continuing calibration procedures are numerous quality control checks to ensure that valid data are acquired (See Sect. 9). Continuing calibration checks are accomplished with results from analysis of one solution, the medium level calibration solution for the appropriate type of data acquisition, either full-range or SIM.

10.2.1 If some criteria are not met for a Continuing Calibration Check after a 12-h period during which samples were analyzed, those samples must be reanalyzed. Those criteria are: GC performance (Sect. 9.2.5), MS calibration as indicated by DFTPP spectrum, and MS sensitivity as indicated by area of internal standards.

10.2.2 When other criteria in Sect. 9.2 are not met, results for affected analytes must be labeled as suspect to alert the data user of the observed problem. Included among those criteria are: response factor check for each analyte or PCB calibration congener, degradation of DDT and endrin, and retention time reproducibility for SIM data acquisition.

10.3 INITIAL DEMONSTRATION OF LABORATORY CAPABILITY FOR WATER ANALYSES (Insufficient information is currently available for demonstration for soil/ sediment analyses.)

10.3.1 Until appropriate Quality Control Check Samples are available, each laboratory should prepare one or more solutions containing each method analyte at a concentration corresponding to that anticipated in samples. Until accuracy and precision limits have been established for PCB isomer groups in appropriate samples, a solution containing an Aroclor mixture may be used; compare total measured PCB concentration to the total Aroclor concentration. Report Aroclor concentration and measured concentrations of PCB isomer groups and total measured PCB concentration.

10.3.2 Add an appropriate volume of a solution of method analytes to each of four 1-L aliquots of reagent water. Extract and analyze according to procedures in Sect. 11.

10.3.2 For each analyte, calculate measured concentrations, relative standard deviation of the four measurements, and method bias (Sect. 12.6).

10.4 LABORATORY PERFORMANCE CHECK SOLUTION -- In this method, the medium level concentration calibration solution also serves the purpose of a laboratory performance check solution.

10.5 LABORATORY SURROGATE SPIKE

10.5.1 Measure the concentration of both surrogate compounds in every sample and blank.

10.5.2 Until performance based acceptance limits have been established for surrogate compounds, the following guidelines are provided: measured bias with LRB = -30% to +10%; measured bias with water or soil/sediment extract = -50% to +25%.

10.6 QUALITY CONTROL CHECK SAMPLE -- Not yet available; anticipate need for analysis of one for each batch of $\leq$20 samples. If full-range data are acquired, both pesticide and PCB analytes can be determined with one analysis. If SIM data are acquired, one extraction and two GC/MS analyses will be needed to determine both PCBs and pesticides.

10.7 LABORATORY SPIKED DUPLICATE SAMPLE -- Select one sample from each batch of $\leq$20 samples of similar type and fortify (spike) two aliquots of that sample with a solution containing appropriate concentrations of pesticide analytes and at least one Aroclor mixture. After addition of surrogate compounds, extract and analyze (Sect. 11) these two fortified aliquots along with an additional unfortified sample aliquot. Relative difference (RD) of duplicate results for surrogate compound concentrations should be $\leq$40%.

(RD = $[C_1 - C_2 / 0.5 (C_1 + C_2)] 100$) Calculate bias (Sect. 12.6) for each analyte and surrogate compound. Insufficient data are currently available to provide guidance for acceptable bias and RD of measured analyte concentrations.

10.8 PERFORMANCE EVALUATION SAMPLE -- Not yet available; to be analyzed periodically when available.

11. PROCEDURES

11.1 SAMPLE EXTRACTION

11.1.1 Water Samples

11.1.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour entire sample into a 2-L separatory funnel. (If a sample larger than 1-L or 1-qt is extracted, the funnel size and solvent volume for samples and blanks must be adjusted also.)

11.1.1.2 Add an appropriate volume of surrogate compound solution.

11.1.1.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Wait at least 10 min to allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, use mechanical techniques (such as stirring, filtration of emulsion through glass wool, or centrifugation) to complete phase separation. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

11.1.1.3 Assemble a Kurderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

11.1.1.4 Pour the combined extract into a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Rinse the Erlenmeyer flask with a 20 to 30 mL portion of methylene chloride, and add the rinse to the drying column. Collect the combined extract in the K-D concentrator.

11.1.1.5 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus

and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

11.1.1.6 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Increase the temperature of the hot water bath to about 80°C. Concentrate the extract to approximately 10 mL as in Sect. 11.1.1.5, except use hexane to prewet the column. Elapsed time of concentration should be 5-10 min.

11.1.1.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed within a few hours. If the extract will be stored longer than two days, transfer it to a Teflon-sealed screw-cap vial.

11.1.1.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.1.2 Soil/Sediment Samples -- Appropriate extraction procedures to be specified when results of ongoing experiments are obtained.

11.2 Sulfur Removal -- Elemental sulfur can be removed by the procedure described below. (Sulfur is not expected to be a problem in water sample extracts but sulfur removal is recommended for soil/sediment sample extracts.)

11.2.1 Transfer the extract to a 50-mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the extract container wtih 1.0 mL of hexane, adding the rinse to the 50-mL bottle.

11.2.2 Add 1 mL of Tetrabutylammonium-sulfite reagent and 1 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

11.2.3 Add 5 mL of distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min and remove the hexane layer (top) for analysis. Dry the extract by passing it through a 10-cm column containing hexane-washed sodium sulfate. Rinse the sodium sulfate with about 30 mL of hexane and add this hexane to the extract. Concentrate the extract to approximately 10 mL with a K-D apparatus. Store in a refrigerator if GC/MS analysis is not to be performed within a few hours.

11.3 GC/MS ANALYSIS

11.3.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature if necessary. With a stream of dry, filtered nitrogen, reduce the extract/blank volume to the appropriate volume, depending on anticipated analyte concentrations. Add an appropriate volume of the appropriate internal standard stock solution.

11.3.1.1 Internal standard concentration for full-range data acquisition = 7.5 ng/uL of extract.

11.3.1.2 Internal standard concentration for SIM data acquisition = 0.75 ng/uL of extract.

11.3.2 Inject a 1-uL or 2-uL aliquot of the blank/sample extract into the GC operated under conditions used to produce acceptable results during calibration.

11.3.3 Acquire mass spectral data with either full-range data acquisition conditions or SIM conditions, as appropriate. Use the same data acquisition time and MS operating conditions previously used to determine response factors.

11.3.4 Examine data for saturated ions in mass spectra of target compounds, if saturation occurred, dilute and reanalyze the extract after the quantity of the internal standards is adjusted appropriately.

11.3.5 For each internal standard, determine that the area measured in the sample extract has not decreased by >30% from the area measured during the most recent previous analysis of a calibration solution or by >50% from the mean area measured during initial calibration. If either criterion is not met, remedial action must be taken to improve sensitivity, and the sample extract must be reanalyzed.

11.4 IDENTIFICATION PROCEDURES

11.4.1 Using the ions shown in Tables 7a-7c for PCBs or Table 9 for pesticides, examine ion current profiles (ICPs) to locate internal standards, surrogate compounds, pesticide analytes, and PCBs for each isomer group. Use the RRT data in Table 9 as guidelines for location of pesticide analytes and the RRT window data in Table 8 as guidelines for location of PCB isomers. (A reverse search software routine can be used to locate compounds of concern.)

11.4.2 Full-Range Data

11.4.2.1 Examine each pesticide and PCB candidate spectrum after background correction routines have been applied. Compare the candidate spectrum with the appropriate standard spectrum measured during calibration. Verify the absence of any ions with mass greater than the highest mass possible for the compound of concern. (Ions in PCB M^+ ion clusters are shown in Table 12.)

11.4.2.2 Obtain integrated abundance areas for quantitation and confirmation ions.

11.4.3 SIM Data -- Obtain appropriate selected ion current profiles (SICPs) for IS quantitation and confirmation ions, for each ion monitored to detect pesticides and the surrogate compounds (Table 9), and for the quantitation and confirmation ions for each PCB isomer group.

11.4.4 PCB Analytes

11.4.4.1 For all PCB candidates, confirm the presence of an $(M-70)^+$ ion cluster by examining ICPs or spectra for at least one of the most intense ions in the appropriate ion cluster.

11.4.4.2 For Cl_3-Cl_7 isomer groups, examine ICPs or spectra for intense $(M+70)^+$ ions that would indicate a coeluting PCB containing two additional chlorines. (GC retention time data show that this is not a potential problem for other PCB isomer groups; see Figure 2.) If this interference occurs, a correction can be made. Obtain and record the area for the appropriate ion (Table 12) for the candidate PCB isomer group. Use the information in Table 13 to correct the measured abundance of M^+. For example, if a Cl_7-PCB and a Cl_5-PCB candidate coelute, the Cl_7-PCB will contribute to the ion measured for m/z 326 and m/z 324, the quantitation and confirmation ions, respectively, for a Cl_5-PCB. Obtain and record the area for m/z 322 (the lowest mass ion in the $(M+-70)^+$ ion cluster of a Cl_5-PCB fragment produced by a Cl_7-PCB). To determine the m/z 326 and m/z 324 areas produced by the Cl_5 PCB, calculate the Cl_7-PCB contribution to each and subtract it from the measured area. In this example, 164% of the area measured for m/z 322 should be subtracted from the area measured for m/z 324, and 108% of the m/z 322 area should be subtracted from the area measured for m/z 326 (Table 13).

11.4.4.3 For Cl_2-Cl_8-PCB candidates, examine ICPs or spectra for intense $(M+35)^+$ ions that would indicate a coeluting PCB containing one additional chlorine. This coelution causes interferences because of the natural abundance of ^{13}C. (This interference will be small and can be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of another PCB containing one more chlorine.) To correct for this interference, obtain and record the area for the appropriate ion (Table 14) from the $(M-1)^+$ ion cluster, and subtract 13.5% of the area measured for the $(M-1)^+$ ion from the measured area of the quantitation ion. For example, for Cl_5-PCB candidates, obtain and record the area for m/z 325; subtract 13.5% of that area from the measured area of m/z 326.

11.4.5 All Analytes -- Use ICP data to calculate the ratio of the measured peak areas of the quantitation ion and confirmation ion(s), and compare to the acceptable ratio (Table 9 for pesticides and Table 12 for PCBs). If acceptable ratios are not obtained, a coeluting or partially coeluting compound may be interfering. Examination of data from several scans may provide information that will allow application of additional background corrections to improve the ion ratio.

11.5. *IDENTIFICATION CRITERIA*

11.5.1 Internal Standards

11.5.1.1 Chrysene-d_{12} -- the abundance of m/z 241 relative to m/z 240 must be $\geq$15% and $\leq$25%, and these ions must maximize simultaneously. The area measured for m/z 240 must be within 30% of the area measured during the most recent calibration.

11.5.1.2 Phenanthrene-d_{10} -- the abundance of m/z 189 relative to m/z 188 must be $\geq$10% and $\leq$22%, and these ions must maximize simultaneously. The area measured for m/z 188 must be within 30% of the area measured during the most recent acceptable calibration.

11.5.1.3 Retention time must be within $\pm$10 s of that observed during the most recent acceptable calibration.

11.5.2 Full-Range Data for Pesticide Analytes and Surrogate Compounds

11.5.2.1 Retention time of the sample component must be within t s of the time observed for that same compound when a calibration solution was analyzed. Calculate the value of t with the equation, $t = (RT)^{1/3}$, where RT = observed retention time (in seconds) of the compound during the last previous acceptable calibration.

11.5.2.2 All ions with relative abundance >10% in the mass spectrum must be present in the mass spectrum of the candidate sample component; a molecular ion with relative abundance >2% in the standard spectrum must be present in the candidate spectrum.

11.5.2.3 The ion that was the most abundant (base peak) in the standard spectrum must also be the base peak in the candidate spectrum.

11.5.2.4 For all ions with relative abundance >20% in the standard spectrum, the relative abundance in the candidate spectrum must not vary by more than $\pm$15% in percentage units (i.e., if 50% in standard, must be $\geq$35% and $\leq$65%).

11.5.2.5 Ions with relative abundance >10% in the candidate spectrum but not present in the standard spectrum must be considered and accounted for by the analyst. When data processing software is used to obtain candidate spectra, both processed and unprocessed spectra must be evaluated.

11.5.3 SIM Data for Pesticide Analytes and Surrogate Compounds

11.5.3.1 Absolute retention time of each surrogate compound and pesticide candidate must be within 10 s of that measured during the last previous acceptable calibration.

11.5.3.2 All ions monitored for each compound (Table 9) must be present and must maximize simultaneously.

11.5.3.3 In a spectrum averaged across a GC peak and with background correction, if necessary, the most abundant ion must correlate with Table 9 data.

11.5.3.4 Observed relative abundances of the monitored ions must meet the following criteria:

Aldrin -- m/z 263 = >20% and m/z 265 = >13%
BHC (each isomer) -- m/z 183 = 70-95% of m/z 181
$^{13}C_6$-gamma-BHC -- m/z 189 = 75-90% of m/z 187
Chlordane (alpha and gamma) -- m/z 375 = 75-99%
4,4'-DDE -- m/z 248 = 45-85%
4,4'-DDD and 4,4'-DDT -- m/z 237 = 45-85%
$^{13}C_{12}$-4,4'-DDT -- m/z 249 = 45-85%
Dieldrin -- m/z 263 = >3% and m/z 108 = >8%
Endosulfan I and II -- m/z 339 = >30% and m/z 341 = >20%
Endosulfan sulfate -- m/z 274 = 60-95%
Endrin -- m/z 263 = $\geq$50%
Endrin aldehyde -- m/z 345 = $\geq$10%
Endrin ketone -- m/z 317 = $\geq$30%
Heptachlor -- m/z 272 = >30% and m/z 274 = >20%
Heptachlor epoxide -- m/z 353 = >60%
Methoxychlor -- m/z 228 = 3-30%
Nonachlor -- m/z 407 = 65-95%

11.5.4 Full-Range and SIM Data for PCBs

11.5.4.1 Absolute retention times of surrogate compounds must be within $\pm$10 s of that measured during the last previous continuing calibration check.

11.5.4.2 Quantitation and confirmation ions for each PCB isomer group must maximize within $\pm$1 scan of each other.

11.5.4.3 The integrated ion current for each quantitation and confirmation ion must be at least three times background noise and must not have saturated the detector.

11.5.4.4 For each PCB isomer group candidate, the ratio of the quantitation ion area to the confirmation ion area must be within limits shown in Table 12; at least one ion in the $(M-70)^+$ ion cluster must be present.

12. CALCULATIONS

12.1 From appropriate ICPs of quantitation ions, obtain and record the spectrum number of the chromatographic peak apex and the area of the entire chromatographic peak.

12.2 For PCBs, sum the areas for all isomers identified at each level of chlorination (e.g., sum all quantitation ion areas for Cl_4-PCBs).

12.3 Calculate the concentration of each surrogate compound, pesticide candidate, and PCB isomer group using the formula:

$$C_x = (A_x \cdot Q_{is})/(A_{is} \cdot RF \cdot W)$$

where C_x = concentration (micrograms per kilogram or micrograms per liter) of surrogate compound, individual pesticide or a PCB isomer group,

A_x = the area of the quantitation ion for each pesticide analyte/surrogate compound or the sum of quantitation ion areas for all PCB isomers at a particular level of chlorination,

A_{is} = the area of the internal standard quantitation ion, m/z 240 for chrysene-d_{12} or m/z 188 for phenanthrene-d_{10},

Q_{is} = quantity (micrograms) of internal standard added to the extract before GC/MS analysis,

RF = calculated response factor for the surrogate compound, the pesticide standard, or the PCB calibration compound for the isomer group (level of chlorination), and

W = weight (kilograms) of sample extracted. If a liquid sample was extracted, W becomes V, the volume (liters) of water extracted, and concentration units become micrograms per liter.

12.3.1 Use the grand mean RF calculated during Initial Calibration. CAUTION: For PCB analyses with automated data interpretation a linear fit algorithm will produce erroneous concentration data.

12.3.2 For pesticides eluting before heptachlor epoxide, use the RF relative to phenanthrene-d_{10}; for heptachlor expoxide and later eluting pesticides, use the RF relative to chrysene-d_{12}. For PCBs, use the RF relative to chrysene-d_{12} unless an interference makes the use of the RF relative to phenanthrene-d_{10} necessary.

12.4 Estimation of the Concentration of Technical Chlordane. Technical chlordane is a mixture that contains alpha-chlordane (about 13% by weight), gamma-chlordane (about 18% by weight), heptachlor (about 8%), chlordene (three isomers; about 19%) and a variety of side reaction products (including *nonachlor isomers*) from chlorination of chlordene. Alpha-chlordane is readily converted to gamma-chlordane, which is persistent in environmental samples. Another persistent component is trans-nonachlor. The presence of gamma-chlordane and trans-nonachlor, with or without alpha-chlordane and heptachlor) indicates that technical chlordane was once present in the sample. Therefore the sum of measured concentrations of alpha-chlordane and gamma-chlordane can be used to estimate the original concentration of technical chlordane.

$$C_{tc} = (C_a + C_g)/0.31$$

where C_a = measured concentration of alpha-chlordane,
C_g = measured concentration of gamma-chlordane, and
C_{tc} = estimated concentration of technical chlordane.

12.5 Report calculated values to two significant figures.

12.6 When samples of known composition or fortified samples are analyzed, calculate the percent method bias using the equation:

$$B = 100\ (C_s - C_t)/\ C_t$$

where C_s = measured concentration (in micrograms per kilogram or micrograms per liter),
C_t = theoretical concentration (i.e., the quantity added to the sample aliquot/weight or volume of sample aliquot).

Note: The bias value retains a positive or negative sign.

13. AUTOMATED IDENTIFICATION AND MEASUREMENT

Special software can be used for automated identification and measurement of PCBs (8) and pesticides. Unprocessed GC/MS data are handled without human interaction with the software operating on the dedicated computer. A concentration for each pesticide and each PCB isomer group is calculated automatically. Contact EMSL-Cincinnati for further information.

14. METHOD PERFORMANCE

To obtain single laboratory accuracy and precision data for method analytes, replicate 1-L aliquots of reagent water and river water fortified with known amounts of analytes were extracted and analyzed. Automated procedures were used to identify and measure method analytes in 2-uL aliquots of 1-mL extracts. Because a sufficient quantity of individual PCB congeners was not available, Aroclor mixtures were used to fortify water samples. This is not desirable, because individual PCBs in Aroclors vary in concentration. As Aroclor concentrations decrease in a sample extract, an increasing number of components will fall below the detection limit and will not be identified and measured. In addition, insufficient data are available about Aroclor composition to assess accuracy of isomer group measurements or to assess MDLs for PCBs when Aroclors are used to fortify samples.

14.1 Medium Level Reagent Water Extracts -- Five aliquots of reagent water fortified with each individual pesticide at a concentration of 10 ug/L and Aroclors 1221, 1242, 1254, and 1268 at concentrations of 5 ug/L, 50 ug/L, 50 ug/L and 25 ug/L, respectively, were extracted and analyzed. Method bias for individual pesticides ranged from -10% to +18% with a mean method bias of +2% for all 21 pesticides (Table 15). For individual pesticides, RSDs of measured concentration ranged from 0.61% for endrin ketone to 9.8% for endrin aldehyde. No true values are known for concentrations of PCB isomer groups in Aroclors, but the mean measured total PCB concentration was 110 ug/L (RSD 2.9%), which indicated a method bias of -15%. For individual isomer groups, RSDs of mean measured concentrations ranged from 3.9% to 16%.

14.2 Low Level Reagent Water Extract -- Reagent water was fortified with each pesticide at a concentration of 3 ug/L and a total PCB concentration of 27 ug/L (Aroclors 1221, 1 ug/L; 1242, 10 ug/L; 1254, 10 ug/L; and 1268,

6 ug/L). When seven replicate extracts were analyzed, method bias for individual pesticides ranged from -17% to +20% with a mean method bias of -2% (Table 15). An MDL was calculated for each pesticide using the equation relating the standard deviation of the seven replicate measurement and Student's t value for a one-tailed test at the 99% confidence level with n-1 degrees of freedom (1). With this calculation, MDL is defined as the minimum concentration that can be measured and reported with 99% confidence that the value is above zero. The excellent precision achieved with these measurements resulted in unrealistically low MDLs ranging from 0.2 to 0.8 ug/L for pesticide analytes (Table 15). A PCB MDL is an individual congener characteristic and cannot be determined with samples fortified with Aroclor mixtures. Estimates of MDLs for individual components of PCB isomer groups were obtained by proportioning the total quantity measured for each isomer group among individual measured isomers. The estimated MDL values for individual PCBs also were unrealistically low (0.01-0.1 ug/L) because of the excellent precision of measurements. A more realistic statement of detection limits for pesticides and PCBs can be found in Sect. 1.2.

14.3 River Water Extracts -- Five aliquots of river water fortified with each pesticide at a concentration of 5 ug/L and total PCB concentration of 70 ug/L (Aroclors 1221, 2 ug/L; 1242, 30 ug/L; 1254, 30 ug/L; and 1268, 8 ug/L) were extracted and analyzed. Method bias for individual pesticides ranged from -30% to +8% with a mean of -8% (Table 15). The excellent precision of measured pesticide PCB isomer group concentrations was indicated by RSDs ranging from 1.6% to 7.5%. The mean measured total PCB concentration of 51 ug/L (RSD 2.5%) indicated a method bias of -27%.

15. REFERENCES

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Table 1. Recommended GC Operating Conditions

Column Type:	SE-54 or DB-5
Film Thickness:	0.25 um
Column Dimensions:	30 m X 0.32 mm
Helium Linear Velocity:	28-29 cm/sec at 250°C
Temperature Program for Splitless Injection:	
o Full-range data acquisition for PCBs and pesticides (Analysis time = approx. 50 min)	Inject at 80°C and hold 1 min; increase at 30°/min to 160°C and hold 1 min; increase at 3°/min to 310°C. or Inject at 80°C and hold 1 min; heat rapidly to 160°C and hold 1 min; increase at 3°/min to 310°C.
o SIM data acquisition for PCBs (Analysis time = approx. 25 min)	Inject at 45°C and hold 1 min; increase at 20°/min to 150°C and hold 1 min; increase at 10°/min to 310°C.
o SIM data acquisition for pesticides (Analysis time = approx. 30 min)	Inject at 80°C and hold 1 min; increase at 30°/min to 160°C and hold 1 min; increase at 3°/min to 250°C; hold past elution time of methoxychlor.

Table 2. PCB Congeners Used as Calibration Standards

PCB Isomer Group	Congener Number[a]	Chlorine Substitution
Concentration Calibration Standard		
Monochlorobiphenyl	1	2
Dichlorobiphenyl	5	2,3
Trichlorobiphenyl	29	2,4,5
Tetrachlorobiphenyl	50	2,2',4,6
Pentachlorobiphenyl	87	2,2',3,4,5'
Hexachlorobiphenyl	154	2,2',4,4',5,6'
Heptachlorobiphenyl	188	2,2',3,4',5,6,6'
Octachlorobiphenyl	200	2,2',3,3',4,5',6,6'
Nonachlorobiphenyl[b]	-	---
Decachlorobiphenyl	209	2,2',3,3',4,4',5,5',6,6'
Retention Time Calibration Standards		
Tetrachlorobiphenyl	77	3,3',4,4'
Pentachlorobiphenyl	104	2,2',4,6,6'
Nonachlorobiphenyl	208	2,2',3,3',4,5,5',6,7'

[a] Numbered according to the system of Ballschmiter and Zell (2).

[b] Decachlorobiphenyl is used as the calibration congener for both nona- and decachlorobiphenyl isomer groups.

Table 3. Scheme for Preparation of PCB Primary Dilution Standard

PCB Cong.	Isomer Group	Stock Sol. Conc. mg/mL	Proportion for Primary Dil. Sol.	Primary Dil. Std. Conc. ng/uL
#1	Cl_1	1.0	1 part	50
#5	Cl_2	1.0	1 part	50
#29	Cl_3	1.0	1 part	50
#50	Cl_4	1.0	2 parts	100
#87	Cl_5	1.0	2 parts	100
#154	Cl_6	1.0	2 parts	100
#188	Cl_7	1.0	3 parts	150
#200	Cl_8	1.0	3 parts	150
#209	Cl_{10}	1.0	5 parts	250
			Total 20 parts	

Table 4. Composition and Approximate Concentrations of Calibration Solutions for Full-Range Data Acquisition

Analyte/Int. Std./ Surrogate Compound	Concentration (ng/uL) CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
PCB Cal. Congeners					
Cl_1 (#1)	0.5	2.5	5	10	25
Cl_2 (#5)	0.5	2.5	5	10	25
Cl_3 (#29)	0.5	2.5	5	10	25
Cl_4 (#50)	1	5	10	20	50
Cl_5 (#87)	1	5	10	20	50
Cl_6 (#154)	1	5	10	20	50
Cl_7 (#188)	1.5	7.5	15	30	75
Cl_8 (#200)	1.5	7.5	15	30	75
Cl_{10} (#209)	2.5	12.5	25	50	125
Pesticides					
Aldrin	1	5	10	20	50
BHC, each isomer	1	5	10	20	50
Chlordane, each isomer	1	5	10	20	50
4,4'-DDD	1	5	10	20	50
4,4'-DDE	1	5	10	20	50
4,4'-DDT	1	5	10	20	50
Dieldrin	1	5	10	20	50
Endosulfan I	2	10	20	40	100
Endosulfan II	2	10	20	40	100
Endosulfan sulfate	2	10	20	40	100
Endrin	1	5	10	20	50
Endrin aldehyde	1	5	--	20	50
Endrin ketone	1	5	10	20	50
Heptachlor	1	5	10	20	50
Heptachlor epoxide	1	5	10	20	50
Methoxychlor	1	5	10	20	50
Nonachlor, each isomer	1	5	10	20	50
Internal Standards					
Chrysene-d_{12}	7.5	7.5	7.5	7.5	7.5
Phenanthrene-d_{10}	7.5	7.5	7.5	7.5	7.5
Surrogate Compounds					
$^{13}C_6$-gamma BHC	1	5	10	20	50
$^{13}C_{12}$-4,4'-DDT	1	5	10	20	50

Table 5a. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for PCB Determinations

	Concentration (ng/uL)				
Compound	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
Cal. Congeners					
Cl_1 (#1)	0.1	0.5	1	2	5
Cl_2 (#5)	0.1	0.5	1	2	5
Cl_3 (#29)	0.1	0.5	1	2	5
Cl_4 (#50)	0.2	1.0	2	4	10
Cl_5 (#87)	0.2	1	2	4	10
Cl_6 (#154)	0.2	1	2	4	10
Cl_7 (#188)	0.3	1.5	3	6	15
Cl_8 (#200)	0.3	1.5	3	6	15
Cl_{10} (#209)	0.5	2.5	5	10	25
RT Congeners					
Cl_4 (#77)	0.2	1	2	4	10
Cl_5 (#104)	0.2	1	2	4	10
Cl_9 (#208)	0.4	2	4	8	20
Internal Standards					
Chrysene-d_{12}	0.75	0.75	0.75	0.75	0.75
Phenanthrene-d_{10}	0.75	0.75	0.75	0.75	0.75
Surrogate Compounds					
$^{13}C_6$-gamma-BHC	0.2	1	2	4	10
$^{13}C_{12}$-4,4'-DDT	0.2	1	2	4	10

Table 5b. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for Pesticide Determinations

Analyte/Internal Std/ Surrogate Compound	Concentration (ng/uL) CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
Pesticide Analytes					
Aldrin	0.2	1	2	5	10
BHC, each isomer	0.2	1	2	5	10
Chlordane, each isomer	0.2	1	2	5	10
4,4'-DDD	0.2	1	2	5	10
4,4'-DDE	0.2	1	2	5	10
4,4'-DDT	0.2	1	2	5	10
Dieldrin	0.2	1	2	5	10
Endosulfan I	0.4	2	4	10	20
Endosulfan II	0.4	2	4	10	20
Endosulfan sulfate	0.2	1	2	5	10
Endrin	0.2	1	2	5	10
Endrin aldehyde	0.2	1	-	5	10
Endrin ketone	0.2	1	2	5	10
Heptachlor	0.2	1	2	5	10
Heptachlor epoxide	0.2	1	2	5	10
Methoxychlor	0.2	1	2	5	10
Nonachlor, each isomer	0.2	1	2	5	10
Internal Standards					
Chrysene-d_{12}	0.75	0.75	0.75	0.75	0.75
Phenanthrene-d_{10}	0.75	0.75	0.75	0.75	0.75
Surrogate Compounds					
$^{13}C_6$-gamma-BHC	0.2	1	2	5	10
$^{13}C_{12}$-4,4'-DDT	0.2	1	2	5	10

Table 6. Criteria for DFTPP Spectrum

m/z	Relative Abundance
127	40-60%
197	<1%
198	100% (Base Peak)
199	5-9%
275	10-30%
365	>1%
441	Present and <m/z 443
442	>40%
443	17-23% of m/z 442

Table 7a. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Four Sets of ≤35 Ions Each

PCB Isomer Group/ Int.Std./Surr.Cmpd.	Nominal Mol. Wt.	Mass or Range to be Monitored	No. of Ions	Ion Sets			
				#1	#2	#3	#4
Monochlorobiphenyls	188	152; 186-190	6	6			
Dichlorobiphenyls	222	220-224	5	5			
Trichlorobiphenyls	256	254-260	7	7	7	1[a]	
Tetrachlorobiphenyls	290	288-294	7	7	7	1[b]	
Pentachlorobiphenyls	324	322-328	7		7	7	
Hexachlorobiphenyls	358	356-362	7		6[c]	7	7
Heptachlorobiphenyls	392	390-396	7			6[d]	7
Octachlorobiphenyls	426	424-430	7				7
Nonachlorobiphenyls	460	460-466	7				7
Decachlorobiphenyl	494	496-500	5				5
Chrysene-d_{12}	240	240-241	2				2
Phenanthrene-d_{10}	188	188-189	2	2[e]			
$^{13}C_6$-gamma-BHC	294	187, 189	2	2[f]			
$^{13}C_{12}$-4,4'-DDT	364	247; 249	2			2	
		Total # ions		25	27	24	35

[a]Monitor m/z 254 to confirm presence of $(M-70)^+$ for Cl_5-PCBs.

[b]Monitor m/z 288 to confirm presence of $(M-70)^+$ for Cl_6-PCBs.

[c]Begin range at m/z 357 in Ion Set #2.

[d]Begin range at m/z 391 in Ion Set #3.

[e]M/z 188 and 189 included among ions used to detect and measure monochlorobiphenyls.

[f]M/z 187 and 189 included among ions used to detect and measure monochlorobiphenyls.

Table 7b. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Sets of ≤20 Ions Each

Ion Set	Isomer Group/ IS/Surrogate	Quant. Ion	Confirm. Ions	M-70 Ions	M+70 Ions	M+35 Ions	Ion Measured[a] for Correction	
1	Cl_1	188	190	152,153[b]	256,258	222,224	-	-
	Cl_2	222	224	152,153,186,188[c]	290,292,294	256,258	-	221
	Cl_3	256	258	186,188	-	290,292,294	-	255
	Cl_4	292	290,294	220,222	-	-	-	-
	$^{13}C_6$-gamma-BHC	187	189	-	-	-	-	-
	Phenanthrene-d_{10}	188	189	-	-	-	-	-
2	Cl_3	256	258	186,188	324,326,328	290,292,294	254	255
	Cl_4	292	290,294	220,222	360,362	324,326,328	288	289
	Cl_5	326	324,328	254,256,258	-	360,362	-	323
	Cl_6	360	358,362	288,290,292	-	-	-	-
3	Cl_5	326	324,328	254,256	392,394,396,398	360,362	322	323
	Cl_6	360	358,362	288,290	-	392,394,396,398	-	357
	Cl_7	394	392,396	322,324,326	-	-	-	-
	$^{13}C_{12}$-4,4'-DDT	247	249	-	-	-	-	-
4	Cl_6	360	358,362	288,290	426,428,430,432	392,394,396	356	357
	Cl_7	394	392,396,398	322,324	-	428,430,432	-	391
	Cl_8	430	428,432	356,358,360	-	-	-	-
	Chrysene-d_{12}	240	241	-	-	-	-	-
5	Cl_8	430	426,428,432	356,358,360	494,496,498,500	462,464,466	-	425
	Cl_9	464	460,462,466	390,392,394	-	496,498,500	-	-
	Cl_{10}	498	494,496,500	424,426,428,430	-	-	-	-

[a] See Tables 12-13.
[b] Cl_1-PCBs lose HCl.
[c] Some Cl_2-PCBs lose Cl_2 and some lose HCl.

Table 7c. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤20 Ions

Ion Set No. 1[a]	Ion Set No. 2[b]	Ion Set No. 3[c]	Ion Set No. 4[d]	Ion Set No. 5[e]
152	186	247	240	356
153	188	249	241	358
186	220	254	288	360
187	222	256	290	390
188	254	288	322	392
189	255	290	324	394
190	256	322	326	424
220	258	323	356	425
221	288	324	357	426
222	289	326	358	428
224	290	328	360	430
255	292	357	362	432
256	294	358	391	462
258	323	360	392	464
290	324	362	394	466
292	326	392	396	496
294	328	394	398	498
	358	396	428	499
	360	398	430	500
	362		432	502
17 ions	20 ions	19 ions	20 ions	20 ions

[a] Ions to identify and measure Cl_1-Cl_4-PCBs, phenanthrene-d_{10}, and $^{13}C_6$-gamma-BHC.

[b] Ions to identify and measure Cl_3-Cl_6-PCBs.

[c] Ions to identify and measure Cl_5-Cl_7-PCBs and $^{13}C_{12}$-4,4'-DDT.

[d] Ions to identify and measure Cl_6-Cl_8-PCBs and chrysene-d_{12}.

[e] Ions to identify and measure Cl_8-Cl_{10}-PCBs.

Table 8. Retention Time Data for PCB Isomer Groups and Calibration Congeners

Isomer Group	Approximate RRT Range[a]	Cal. Cong. Number	Cal. Cong. RRT[a]
Monochlorobiphenyls	0.30-0.35	1	0.30
Dichlorobiphenyls	0.38-0.50	5	0.43
Trichlorobiphenyls	0.46-0.64	29	0.54
Tetrachlorobiphenyls	0.55-0.82	50	0.56
Pentachlorobiphenyls	0.64-0.92	87	0.80
Hexachlorobiphenyls	0.75-1.1	154	0.82
Heptachlorobiphenyls	0.88-1.2	188	0.88
Octachlorobiphenyls	0.99-1.21	200	1.03
Nonachlorobiphenyls	1.16-1.28	-	-
Decachlorobiphenyl	1.3	209	1.3

[a] Retention time relative to chrysene-d_{12} with a 30 m X 0.31 mm ID SE-54 fused silica capillary column and the following GC conditions: splitless injection at 80°C; hold for 1 min; heat rapidly to 160°C and hold 1 min; increase at 3°C/min to 310°C.

Table 9. Ions for Selected Ion Monitoring Data Acquisition for Pesticide Analytes, Internal Standards and Surrogate Compounds (Ordered by Retention Time)

Ion Set	Analyte/Internal Std/ Surrogate Compound (MW)	Approx. RRT	Quant. Ion	Ions (Approximate Relative Abundance)
1	Alpha-BHC (288)	0.43	219	181 (100), 183 (90), 219 (70)
	Beta-BHC (288)	0.47	219	181 (100), 183 (90), 219 (70)
	Gamma-BHC (288)	0.48	219	181 (100), 183 (90), 219 (75)
	$^{13}C_6$-gamma-BHC (294)	0.48	225	187 (100), 189 (90) 225 (80), 227 (40)
	Phenanthrene-d_{10} (188)	0.49	188	188 (100), 189 (15)
	Delta-BHC (288)	0.51	219	181 (100), 183 (90), 219 (70)
	Heptachlor (370)	0.58	272	100 (100), 272 (60), 274 (40)
	Aldrin (362)	0.64	263	66 (100), 263 (40), 265 (25)
2	Heptachlor epoxide (386)	0.70	353	81 (100), 353 (80), 355 (65)
	Gamma-chlordane (406)	0.74	373	373 (100), 375 (95)
	Endosulfan I (404)	0.76	195	195 (100), 339 (50), 341 (35)
	Alpha-chlordane (406)	0.76	373	373 (100), 375 (95)
	Trans-nonachlor (440)	0.77	409	409 (100), 407 (85)
	Dieldrin (378)	0.80	79	79 (100), 263 (10), 108 (15)
	4,4'-DDE (316)	0.81	246	246 (100), 248 (65)
	Endrin (378)	0.83	81	81 (100), 263 (75)
	Endosulfan II (404)	0.85	195	195 (100), 339 (50), 341 (35)
3	4,4'-DDD (318)	0.87	235	235 (100), 237 (65), 165 (65)
	Endrin aldehyde (378)	0.88	67	67 (100), 345 (30)
	Endosulfan sulfate (420)	0.92	272	272 (100), 274 (80), 387 (50)
	4,4'-DDT (352)	0.93	235	235 (100), 237 (65), 165 (65)
	$^{13}C_{12}$-4,4'-DDT (364)	0.93	247	247 (100), 249 (65)
	Endrin ketone (378)	0.99	67	67 (100), 317 (50)
	Chrysene-d_{12} (240)	1.00	240	240 (100), 241 (20)
	Methoxychlor (344)	1.03	227	227 (100), 228 (15)

Table 10. Ion Sets for Selected Ion Monitoring of Pesticide Analytes, Internal Standards and Surrogate Compounds (Ordered by Retention Time)

Ion Set No. 1	Monitored Compounds	Ion Set No. 2	Monitored Compounds	Ion Set No. 3	Monitored Compounds
66	Alpha-BHC	79	Heptachlor	67	4,4'-DDD
100	Beta-BHC	81	epoxide	165	Endrin aldehyde
181	Delta-BHC	108	Alpha-chlordane	227	Endosulfan sulfate
183	Gamma-BHC	195	Gamma-chlordane	228	4,4'-DDT
187	$^{13}C_6$-gamma-BHC	246	Endosulfan I	235	$^{13}C_{12}$-4,4'-DDT
188	Phenanthrene-d_{10}	248	Trans-nonachlor	237	Endrin ketone
189	Heptachlor	263	Dieldrin	240	Chrysene-d_{12}
219	Aldrin	339	4,4'-DDE	241	Methoxychlor
225		341	Endrin	247	
227		353	Endosulfan II	249	
263		355		272	
265		373		274	
272		375		317	
274		407		345	
		409		387	
14 ions, 8 compounds		15 ions, 9 compounds		15 ions	8 compounds

Table 11. Known Relative Abundances of Ions in PCB Molecular Ion Clusters[a]

m/z	Relative Intensity
Monochlorobiphenyls	
188	100
189	13.5
190	33.4
192	4.41
Dichlorobiphenyls	
222	100
223	13.5
224	66.0
225	8.82
226	11.2
227	1.44
Trichlorobiphenyls	
256	100
257	13.5
258	98.6
259	13.2
260	32.7
261	4.31
262	3.73
263	0.47
Tetrachlorobiphenyls	
290	76.2
291	10.3
292	100
293	13.4
294	49.4
295	6.57
296	11.0
297	1.43
298	0.95
Pentachlorobiphenyls	
324	61.0
325	8.26
326	100
327	13.5
328	65.7
329	8.78
330	21.7
331	2.86
332	3.62
333	0.47
334	0.25
Hexachlorobiphenyls	
358	50.9
359	6.89
360	100
361	13.5
362	82.0
363	11.0
364	36.0
365	4.77
366	8.92
367	1.17
368	1.20
369	0.15
Heptachlorobiphenyls	
392	43.7
393	5.91
394	100
395	13.5
396	98.3
397	13.2
398	53.8
399	7.16
400	17.7
401	2.34
402	3.52
403	0.46
404	0.40
Octachlorobiphenyls	
426	33.4
427	4.51
428	87.3
429	11.8
430	100
431	13.4
432	65.6
433	8.76
434	26.9
435	3.57
436	7.10
437	0.93
438	1.18
439	0.15
440	0.11
Nonachlorobiphenyls	
460	26.0
461	3.51
462	76.4
463	10.3
464	100
465	13.4
466	76.4
467	10.2
468	37.6
469	5.00
470	12.4
471	1.63
472	2.72
473	0.35
474	0.39
Decachlorobiphenyl	
494	20.8
495	2.81
496	68.0
497	9.17
498	100
499	13.4
500	87.3
501	11.7
502	50.0
503	6.67
504	19.7
505	2.61
506	5.40
507	0.71
508	1.02
509	0.13

[a]Source: Rote and Morris (9)

Table 12. Quantitation, Confirmation, and Interference Check Ions for PCBs, Internal Standards, and Surrogate Compounds

Analyte/ Internal Std.	Nom. MW	Quant. Ion	Confirm. Ion	Expected Ratio[a]	Accept. Ratio[a]	M-70 Confirm. Ion	Interference Check Ions M+70	Interference Check Ions M+35
PCB Isomer Group								
Cl_1	188	188	190	3.0	2.5-3.5	152[b]	256	222
Cl_2	222	222	224	1.5	1.3-1.7	152	292	256
Cl_3	256	256	258	1.0	0.8-1.2	186	326	290
Cl_4	290	292	290	1.3	1.1-1.5	220	360	326
Cl_5	324	326	324	1.6	1.4-1.8	254	394	360
Cl_6	358	360	362	1.2	1.0-1.4	288	430	394
Cl_7	392	394	396	1.0	0.8-1.2	322	464	430
Cl_8	426	430	428	1.1	0.9-1.3	356	498	464
Cl_9	460	464	466	1.3	1.1-1.5	390	-	498
Cl_{10}	494	498	500	1.1	0.9-1.3	424	-	-
Internal standards								
Chrysene-d_{12}	240	240	241	5.1	4.3-5.9	-	-	-
Phenanthrene-d_{10}	188	188	189	6.6	6.0-7.2	-	-	-
Surrogate compounds								
$^{13}C_6$-gamma-BHC	294	187	189	1.0	0.8-1.2	-	-	-
$^{13}C_{12}$-4,4'-DDT	364	247	249	1.5	1.3-1.7	-	-	-

[a] Ratio of quantitation ion to confirmation ion

[b] Monodichlorobiphenyls lose HCl to produce an ion at m/z 152.

Table 13. Correction for Interference of PCB Containing Two Additional Chlorines

Candidate Isomer Group	Quant. Ion	Confirm. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from Quant Ion Area	% of Meas. Ion Area to be Subtracted from Confirm. Ion Area
Trichlorobiphenyls	256	258	254	99%	33%
Tetrachlorobiphenyls	292	290	288	65%	131%
Pentachlorobiphenyls	326	324	322	108%	164%
Hexachlorobiphenyls	360	362	356	161%	71%
Heptachlorobiphenyls	394	396	390	225%	123%

Table 14. Correction for Interference of PCB Containing One Additional Chlorine

Candidate Isomer Group	Quant. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from Quant. Ion Area
Dichlorobiphenyls	222	221	13.5%
Trichlorobiphenyls	256	255	13.5%
Tetrachlorobiphenyls	292	289	17.4%
Pentachlorobiphenyls	326	323	22.0%
Hexachlorobiphenyls	360	357	26.5%
Heptachlorobiphenyls	394	391	30.9%
Octachlorobiphenyls	430	425	40.0%

Table 15. Accuracy and Precision of Automated Measurements of PCBs and Pesticides in Fortified Water Extracts

Analyte (Meas. Ion)	Medium Level Reagent Water[a]			Low Level Reagent Water[b]				Ohio River Water[a]		
	True Conc. ug/L	Mean Meas. Conc., ug/L (RSD, %)	Bias %	True Conc. ug/L	Mean Meas. Conc., ug/L (RSD, %)	Bias %	MDL ug/L	True Conc. ug/L	Mean Meas. Conc., ug/L (RSD, %)	Bias %
Aldrin (263)	10	9.6 (3.6)	-4	3	2.5 (7.2)	-17	0.6	5	4.7 (3.0)	-6
BHC, alpha (219)	10	9.8 (4.3)	-2	3	2.8 (5.0)	-7	0.4	5	4.7 (1.6)	-6
BHC, beta (219)	10	10.5 (3.6)	+5	3	3.0 (2.5)	0	0.2	5	5.1 (2.5)	+2
BHC, gamma (219)	10	10.2 (4.7)	+2	3	2.9 (5.3)	-3	0.5	5	4.8 (3.0)	-4
BHC, delta (219)	10	9.9 (4.2)	-1	3	2.9 (4.8)	-3	0.4	5	4.8 (2.4)	-4
Chlordane, alpha (373)	10	9.6 (3.9)	-4	3	2.9 (4.0)	-3	0.4	5	4.6 (4.2)	-8
Chlordane, gamma (373)	10	9.6 (4.6)	-4	3	2.7 (4.8)	-10	0.4	5	4.4 (3.5)	-12
4,4'-DDD (235)	10	10.4 (3.0)	+4	3	2.9 (3.8)	-3	0.4	5	4.8 (2.5)	-4
4,4'-DDE (246)	10	9.8 (3.2)	-2	3	2.8 (5.4)	-7	0.5	5	4.5 (4.5)	-10
4,4'-DDT (235)	10	10.9 (3.0)	+9	3	2.9 (4.5)	-3	0.4	5	4.7 (3.9)	-6
Dieldrin (79)	10	10.6 (3.2)	+6	3	2.9 (7.6)	-3	0.7	5	4.5 (4.3)	-10
Endosulfan I (195)	10	9.6 (5.8)	-4	3	3.1 (4.8)	+3	0.5	5	4.4 (5.0)	-12
Endosulfan II (195)	10	10.2 (4.5)	+2	3	3.3 (6.3)	+10	0.7	5	3.5 (4.1)	-30
Endosulfan sulf. (272)	10	10.6 (2.3)	+6	3	3.2 (4.4)	+7	0.4	5	4.8 (1.7)	-4
Endrin (81)	10	11.8 (2.8)	+18	3	3.6 (7.0)	+20	0.8	5	5.4 (7.5)	+8
Endrin aldehyde (67)	10	9.0 (9.8)	-10	3	2.8 (8.4)	-7	0.7	5	4.4 (4.8)	-12
Endrin ketone (67)	10	11.5 (0.61)	+15	3	3.2 (1.9)	+7	0.2	5	4.7 (3.0)	-6
Heptachlor (272)	10	10.6 (5.1)	+6	3	2.6 (5.3)	-13	0.4	5	4.9 (3.5)	-2
Heptachlor epox. (353)	10	10.0 (2.5)	0	3	3.0 (5.9)	0	0.6	5	4.8 (3.9)	-4
Methoxychlor (227)	10	11.4 (1.6)	+14	3	3.1 (2.3)	+3	0.2	5	4.8 (3.8)	-4
Nonachlor, trans (409)	10	9.5 (4.6)	-5	3	2.8 (2.4)	-7	0.2	5	4.4 (4.3)	-12
All pesticides	10	10.2 (7.1)	+2	3	2.9 (8.6)	-2		5	4.6 (7.7)	-8

Table 15. (Cont.) Accuracy and Precision of Automated Measurements of PCBs and Pesticides in Fortified Water Extracts

Analyte (Meas. Ion)	Medium Level Reagent Water[a]			Low Level Reagent Water[b]				Ohio River Water[a]		
	True Conc. ug/L	Mean Meas. Conc., ug/L (RSD, %)	Mean Bias %	True Conc. ug/L	Mean Meas. Conc., ug/L (RSD, %)	Mean Bias %	Method Detect. Limit	True Conc. ug/L	Mean Meas. Conc., ug/L (RSD, %)	Mean Bias %
PCBs	130	110 (2.9)	-15	27	21.2 (2.8)	-21	[c]	70	51.3 (2.5)	-27
Cl_1 (188)	-	3.6 (9.9)	-		0.7 (15)	-			1.83 (4.8)	
Cl_2 (222)	-	6.5 (5.7)	-		1.2 (10)	-			3.42 (3.9)	
Cl_3 (256)	-	17.2 (5.3)	-		3.1 (10)	-			10.1 (3.0)	
Cl_4 (292)	-	21.7 (4.1)	-		4.1 (3.8)	-			11.0 (4.5)	
Cl_5 (326)	-	28.8 (3.6)	-		5.6 (2.8)	-			15.4 (3.6)	
Cl_6 (360)	-	9.8 (5.7)	-		1.6 (3.1)	-			4.86 (6.4)	
Cl_7 (394)	-	1.3 (4.3)	-		- -	-			0.335(4.8)	
Cl_8 (428)	-	7.1 (3.5)	-		1.6 (2.7)	-			1.56 (4.3)	
Cl_9 (466)	-	12.6 (5.3)	-		2.7 (4.6)	-			3.00 (1.8)	
Cl_{10} (500)	-	2.0 (16.0)	-		0.6 (12)	-			0.442 (1.8)	
Surrogate Compounds										
$^{13}C_6$-gamma-BHC (187)	-	- -	-	3	3.0 (3.4)	0	0.3	5	4.9 (1.4)	-2
$^{13}C_{12}$-4,4'-DDT (247)	-	- -	-	-	- -	-	-	5	4.4 (7.0)	-12

[a] Results of analysis of five replicate extracts of 1-L aliquots of fortified water.

[b] Results of analysis of seven replicate extracts of 1-L aliquots of fortified water.

[c] PCB method detection limits cannot be determined because Aroclor mixtures were used to fortify samples.

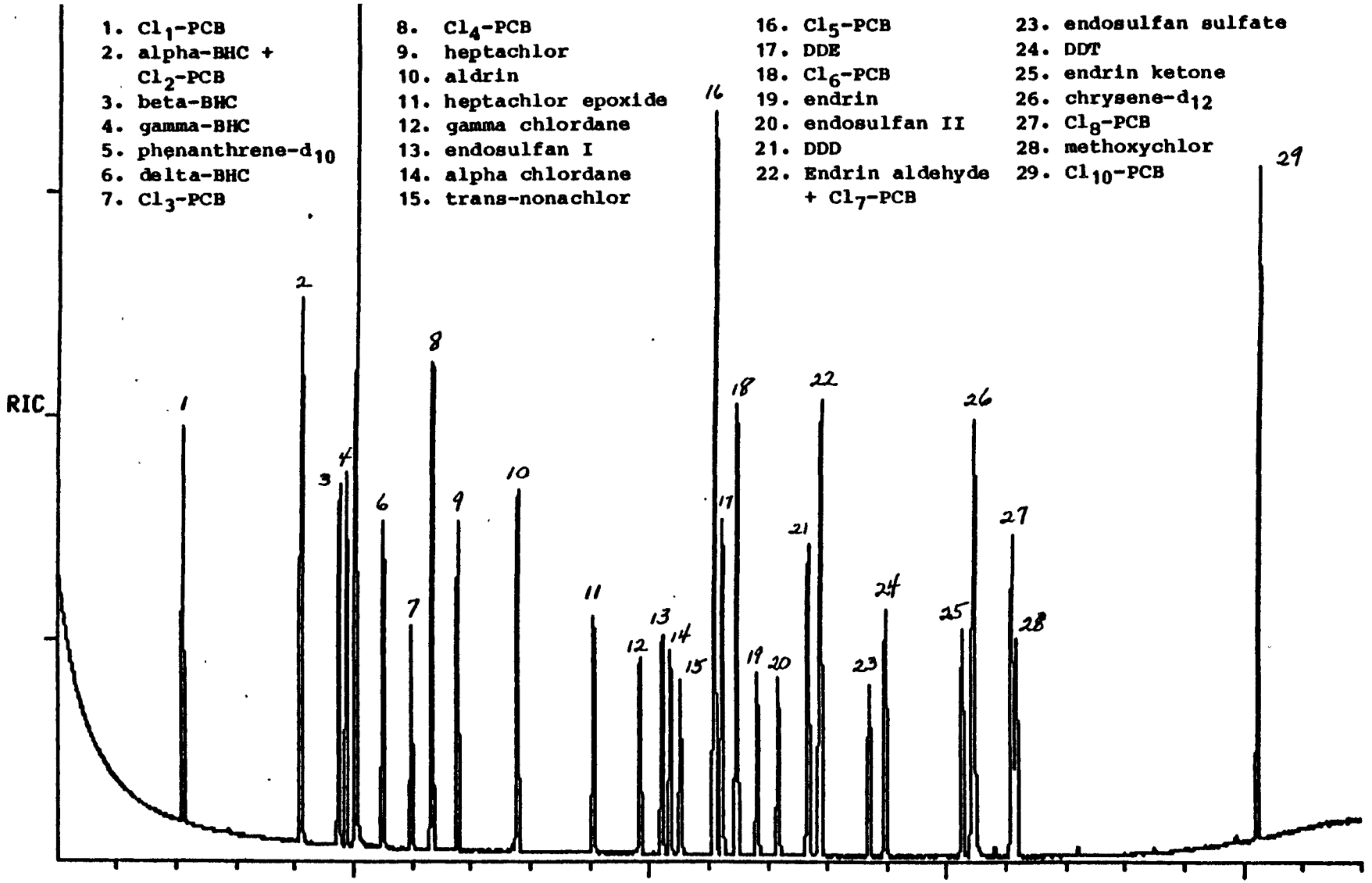

Figure 1. Total Ion Current Profile of PCB Calibration Congeners and Pesticide Analytes.

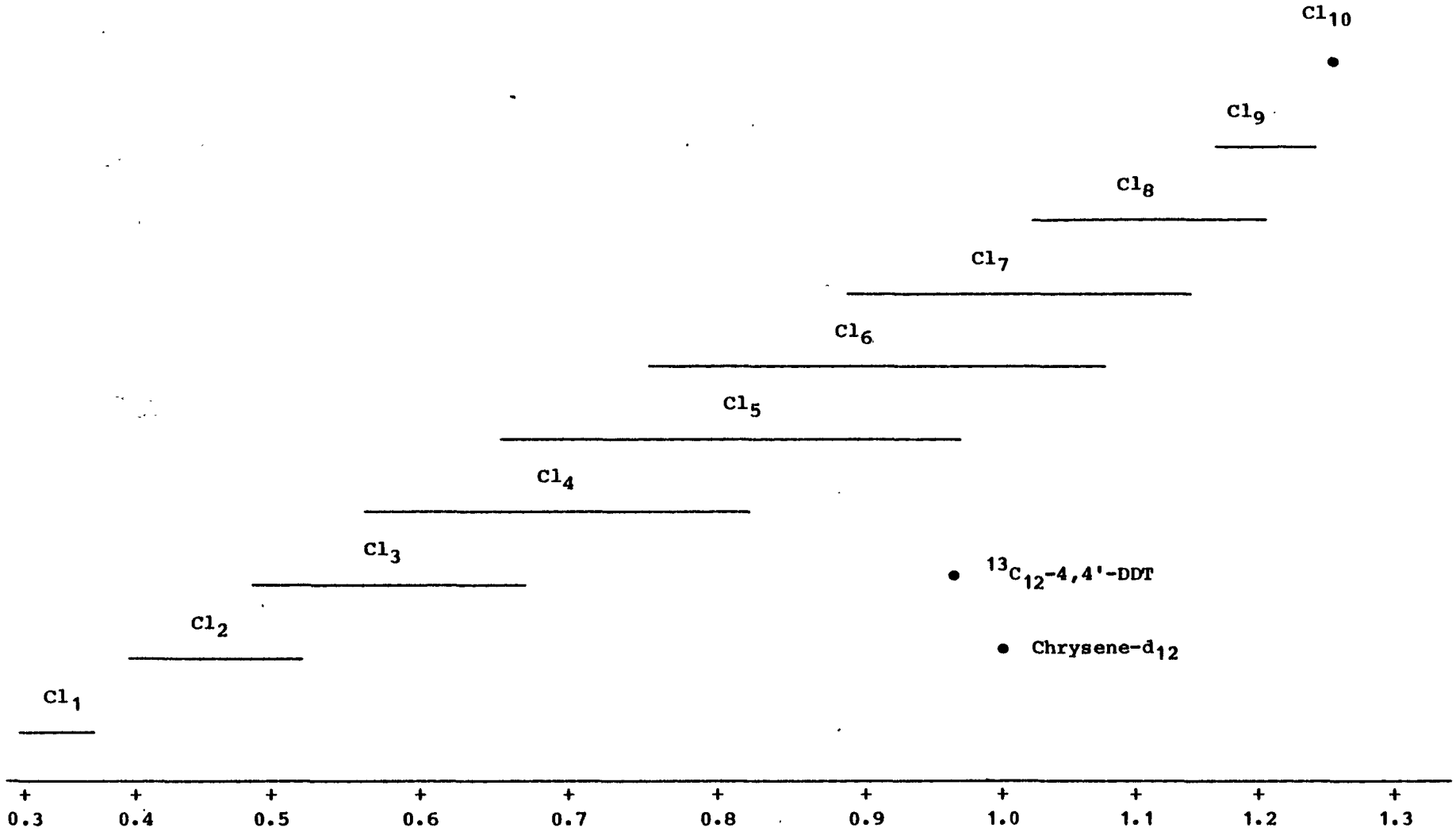

Figure 2. Diagram indicating approximate relative retention times (DB-5 GC column; chrysene-d_{12} internal standard) of PCB isomer groups and retention time marker compounds (for PCB SIM data acquistion option).