EXHIBIT B

Project Specific PCB Homolog

Analytical Method (USEPA Method 680)

Quantitative Environmental Analysis, LLC

STANDARD OPERATING PROCEDURE (SOP) GEHR680

GENERAL ELECTRIC (GE) HUDSON RIVER DESIGN SUPPORT

SEDIMENT SAMPLING AND ANALYSIS PROGRAM

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF PCBs IN SEDIMENT BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY BY EPA METHOD 680

Revision No.: 1

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1. SCOPE AND APPLICATION

1.1. This method provides procedures for mass spectrometric determination of polychlorinated biphenyls (PCBs) in sediment for the GE Hudson River Design Support Sediment Sampling and Analysis Program (SSAP). This method is applicable to samples containing PCBs as single congeners. 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
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
Decachlorobiphenyls	$C_{12}Cl_{10}$	2051-24-3

1.2 A Method Detection Limit (MDL) study will be performed on a representative instrument in accordance with the procedures described in 40 CFR Part 136, Appendix B prior to analysis of sediment samples for the SSAP. A clean sodium sulfate will be used as the matrix for this MDL study. 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. Detection limits for individual PCB congeners increase with increasing number of chlorine atoms, with the detection limit for decachlorobiphenyl being about 2 times higher than that of a monochlorobiphenyl. 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

In general, samples are extracted with a pesticide-grade solvent. The extracts are further processed by concentrating or diluting, depending on the PCB concentration, and carried through a series of cleanup techniques. The sample is then analyzed by injecting the extract onto a gas chromatographic system and the PCBs detected by a mass spectrometer.

This SOP provides detailed instructions for gas chromatographic/mass spectrometer conditions, calibration, and analysis of PCBs by gas chromatography/mass spectrometry (GC/MS). Sediment extraction procedures are covered in separate standard operating procedures. It is expected that the extracts generated for analysis by SOP GEHR8082 will be used for analysis by this method (GEHR680) to provide paired total PCB results by both methods for the same extract.

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. Selected-ion-monitoring (SIM) data are to be acquired.

A Varian Saturn Ion Trap GC/MS will be used by Northeast Analytical, Inc. (NEA) to perform this analysis. Varian uses a proprietary field-modulated Wave-Board technology to selectively trap only those ions of interest. Background ions are not stored. This allows for a much cleaner spectrum and a considerable increase in sensitivity since the trap's capacity is dedicated to these ions of interest. Additionally, the selected storage mass range (Method 680 requires scanning ions across 5 mass ranges) is time programmable so that many different target analytes can be selectively stored relative to the background matrix. Varian refers to this mode of operation as Selected Ion Scanning (SIS) mode. SIS is Varian's term for Selected Ion Monitoring (SIM) common to most other mass spectrometers. SIS allows the Saturn Ion Trap to store many more masses than traditional SIM techniques without a corresponding loss of sensitivity. The more common term SIM (versus SIS) will be used throughout SOP for ease of reference.

Two surrogate compounds are added to each sample before sample preparation; these compounds are tetrachloro-*meta*-xylene (TCMX) and decachlorobiphenyl (DCB). 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.

PCBs are identified and measured as isomer groups or homologs (*i.e.*, by level of chlorination). A concentration is measured for each PCB isomer group total; 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 PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the GC/MS with respect to a defined set of method criteria.

3.5 METHOD BLANK -- 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.

3.6 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. These analyses are more commonly referred to as matrix spike (MS) and matrix spike duplicate (MSD) samples. MS/MSD analyses are not required by US EPA for the GE Hudson River SSAP.

3.7 LABORATORY SURROGATE SPIKE

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

3.7.2 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.

3.8 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.

3.9 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.

3.10 QUALITY CONTROL (QC) CHECK OR LABORATORY CONTROL SAMPLE (LCS) -- 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.

3.11 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. Method blanks 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. Than wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry. Heating in a muffle furnace at 450°C for a few hours may be used as a further cleaning technique, but does not have to be performed provided that method blanks demonstrate glassware cleanliness. 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 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 (refer to the applicable extraction SOPs for extract cleanup procedures). Capillary column GC retention time and the compound-specific characteristics of mass spectra eliminate many interferences that formerly were of concern with 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.

5. SAFETY

5.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

5.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. The analyst should minimize manipulation of sample extracts outside of a fume hood.

5.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions of handling applicable solvents and chemicals used to process samples. The analyst should refer to the project laboratory's internal chemical hygiene plan for further safety information.

5.4 Samples remaining after analysis should be disposed of through the project laboratory's internal disposal plan. Refer to the project laboratory's internal standard operating procedures for disposal of laboratory waste.

6. APPARATUS AND EQUIPMENT

6.1 COMPUTERIZED GC/MS

The specific GC and MS operating parameter to be used are summarized on Table 1.

6.1.1 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. Splitting injections is not recommended.

6.1.2 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.

6.1.3 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.

6.1.4 SIM – 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. The SIM program must be capable of acquiring data for five groups (or mass ranges) each consisting of $\leq$ 27 ions each. The times spent monitoring ions during sample analyses must be the same as the times used when calibration solutions were analyzed.

6.2 GC COLUMN – A 30 m $\times$ 0.25 mm ID fused silica capillary column coated with a 0.25 μm film, Durabond-XLB, Agilent Technologies is required. Operating conditions known to produce acceptable results with this column are shown in Table 1. Separation of PCB calibration congeners with a DB-XLB column and those operating conditions is shown in Figure 1. Figure 2 shows a chromatogram of the PCB Window Defining Mixture used to determine retention time windows for the five ion groups for SIM data acquisitions.

6.3 MISCELLANEOUS EQUIPMENT

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

6.3.2 Microsyringes -- various standard sizes 9.

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

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

7.5 SURROGATE COMPOUNDS – TCMX and DCB are added to every sample before extraction and are included in every calibration/performance check solution and quality control samples.

7.6 PCB CONCENTRATION CALIBRATION CONGENERS - The nine individual PCB congeners listed on 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 (6).

7.7 PCB RETENTION TIME CONGENERS FOR SIM DATA ACQUISITION -- Knowledge of the retention time 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. A PCB Window Defining Mixture Standard (AccuStandard, Inc., catalog item C-WDM or equivalent) is analyzed at a concentration of 2.5ug/mL for each PCB congener. The PCB Window Defining Mixture Standard contains the first and last eluting PCB congener for each Homolog group. The following four congeners are used from this standard to define the five retention time segments for the five Ion Set Groups: BZ#104, BZ#77, BZ#202, and BZ#189. (See Sect. 9.2.3.1.3 for Ion Set Segments).

7.8 PCB SOLUTIONS

7.8.1 Stock Solutions of PCB Calibration Congeners -- Prepare a stock solution of each of the nine PCB concentration calibration congeners at a concentration of 1 μg/μL in hexane. 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.

7.8.2 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. This will provide a primary dilution standard solution of the composition shown on Table 3. Calculate the concentration in μg/μL; 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 in prevented.

7.9 INTERNAL STANDARD (IS) SOLUTION

7.9.1 IS solution (for SIM CALs) – Phenanthrene-d_{10} and chrysene-d_{12} at a concentration of 40 ng/μL (ppm). A stock standard is prepared by transferring 1 mL of 1000 ng/μL phenanthrene-d_{10} and 0.5 mL of 2000 ng/μL chrysene-d_{12} to 25 mL hexane to provide a 40 ng/μL (ppm) solution.

7.10 CAL FOR SIM DATA ACQUISITION -- One set of six solutions is needed for PCB determinations. Appropriate concentrations of SIM CALs are given on Table 4a and 4b. Solutions are prepared by diluting appropriate primary dilution standards and adding an appropriate volume of IS solution #2. Four (4) μL of IS solution (7.9.1) will be added to 200 μL of extract to provide phenanthrene-d_{10} and chrysene-d_{12} at a concentration of 0.80 μg/μL (ppm) in the extract. The CAL6 level is prepared by using 600 μL of primary dilution standard plus 400 μL of Hexane. This gives a concentration for decachlorobiphenyl of 15.0 ug/mL. The GC/MS calibration standard is prepared by taking 200 μL of this standard and spiking with four (4) μL of internal standard. Only decachlorobiphenyl will be calibrated from this sixth standard, leaving all analytes as a five-point calibration.

7.11 Calculate the concentration (two significant figures if <100 and three significant figures if >100 ng/μL) of each component in each solution. Note: Concentrations presented in tables are only approximate.

7.12 LABORATORY PERFORMANCE CHECK SOLUTION - 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.

7.13 PCB Window Defining Mixture Standard – This standard is used as purchased at 2.5ug/mL per congener. It is analyzed by full scan to provide a check on retention time for the four PCB congeners used to established retention time segments for SIM data acquisition.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Sample collection, preservation, and storage of sediment samples is addressed in the Design Support Sediment Sampling Analysis Program Field Sampling Plan (FSP) and Quality Assurance Project Plan (QAPP).

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.

9.1 DATA ACQUISITION -- SIM data acquisition is to be used.

9.1.1 SIM data acquisition will provide an increase in sensitivity from full-range data acquisition 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 requirements defined in this SOP.

9.2.2 Inject a 2-μL aliquot of the 10 ng/μL DFTPP solution and acquire a mass spectrum that includes data for m/z 45-450. If the spectrum does not meet all criteria (Table 5), the MS must be hardware tuned to most all criteria before proceeding with calibration.

9.2.3 SIM Calibration – Inject a 2-μL aliquot of the Medium CAL. Acquire at least five data points for each ion during elution of each GC peak. Total cycle time should be ≥ 0.5 s and <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.

9.2.3.1 SIM Calibration for PCB determinations

9.2.3.1.1 Data will be acquired with the five ion sets (≤ 27 ions each) shown on Tables 6a and 6b.

9.2.3.1.2 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 on Table 7. (Also see Figure 1 and Figure 2.)

9.2.3.1.3 SIM data acquisition with five 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 seconds) 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) before elution of PCB congener #202, the first eluting Cl_8-PCB. Stop acquisition with Ion Set #4 and begin acquisition with Ion Set #5 just (approximately 10 s) after elution of PCB congener #189, the last eluting Cl_7-PCB, stop acquisition of Ion Set #5 after Cl_{10}-PCB elution.

9.2.4 Performance Criteria

9.2.4.1 SIM PCB Data

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

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

9.2.4.1.3 MS calibration -- Abundance of $\geq$ 70% and $\leq$ 95% of m/z 500 relative to m/z 498 for congener #209, Cl_{10}-PCB.

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

9.2.6 Response Factor Calculation

9.2.6.1 Calculate five response factors (RFs) for each PCB calibration congener and surrogate compound relative to both ISs (see Sect. 12.4.2), 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 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 PCB calibration congener or surrogate compound.

RF is a unitless number, units used to express quantities must be equivalent.

9.2.7 Response Factor Reproducibility -- For each 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.

9.2.8 SIM Analyte Retention Time Reproducibility

9.2.8.1 PCB determinations - Absolute retention times of PCB congeners #77, #104, #202, and #189 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 the other four congeners, which are used to determine when ion sets are changed.)

9.2.9 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 2-μL aliquot of the DFTPP solution and ensure acceptable MS calibration and performance (Table 5).

9.3.4 Inject a 2-μL 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. 9.2.4.

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 ±20% of the mean value calculated (Sect. 9.2.6) 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. 9.2.8) reproducibility of absolute retention

times of appropriate PCB retention time congeners by analysis of the PCB Window defining mixture in full scan mode.

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 is 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

The QC sample extracts (method blank and laboratory control sample) associated with the sediment sample extracts will be performed at a frequency of one method blank and one laboratory control sample (LCS) per 20 sample extracts. As many field sediment sample extracts originating from multiple laboratories and analysis extraction batches will be selected for Method 680 analysis, a representative method blank and LCS extract that has passed GEHR8082 acceptance criteria will be selected to be run with up to 20 sediment sample extracts for this analysis. Sediment sample extracts for Method 680 analysis will be selected from SOP GEHR8082 analysis batches where the method blank and LCS passed SOP GEHR8082 criteria. If this is not always possible, then the method and LCS that failed SOP GEHR8082 criteria will also be run by Method 680 (SOP GEHR680).

10.1 Method Blank – The extracts for this analysis will be the same extracts as those generated for the analysis of total PCBs as Aroclors by SOP GEHR8082.

10.1.1 A method blank must contain the same amount of surrogate compounds and internal standards that is added to each sample.

10.1.2 Analyze a method blank before any samples are analyzed.

10.1.3 An acceptable method blank contains no method analyte at a concentration greater than its reporting limit (RL) for the PCB homologue 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 RL. If the method blank that was extracted along with a batch of samples is contaminated, the entire batch of samples must be reanalyzed.

10.1.4 Corrective action for unacceptable method blank -- 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 the medium-level calibration solution and the PCB Window Defining Mixture to monitor criteria times for the five (5) ion sets.

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. 9.2.4), MS calibration as indicated by DFTPP spectrum (Sect. 9.2.2), and MS sensitivity as indicated by area of internal standards (Sect. 9.3.6).

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 PCB calibration congener and retention time reproducibility for SIM data acquisition.

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

10.4 LABORATORY SURROGATE SPIKE

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

10.4.2 Acceptance limits for surrogate compounds will be 60-140% recovery for sediment extracts.

10.5 LABORATORY CONTROL SAMPLE -- A QC reference check standard (LCS) is also prepared and analyzed for Aroclor-1242 at a concentration of 500 ng/mL in the extract. For sediment/solid samples, sodium sulfate is used for the QC reference check standard (LCS). Calculate the percent recovery for the Total PCB Aroclor spike and compare to the project limits of 60-140%. If the percent recovery for the QC reference check standard (LCS) is out of criteria, the analysis is out of the control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be reanalyzed (Exception: If the LCS recovery is high and there were no associated positive results, then address the issue in the Case Narrative and no further action is needed).

10.6 MS/MSD SAMPLES -- At this time, the GE Hudson River Design Support Sediment Sampling and Analysis Program does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, a matrix spike for Aroclor-1242 is to be analyzed at a rate of 1 matrix spike per every 20 samples at a concentration of 20,000 ng/mL in the extract (**Note:** this spike concentration will require a sample dilution to be performed). The result by GEHR680 will be reported as a Total PCB. Also a matrix spike duplicate sample is to be analyzed at a rate of 1 per every 20 samples.

10.6.1 If requested, analyze one unspiked and two spiked samples. Calculate the percent recovery based on Aroclor concentration of both samples as follows:

A = concentration of spiked sample
B = concentration of unspiked sample (background)
T = known true value of the spike

Percent Recovery (p) = 100 (A-B) %/T

Compare the percent recovery calculated with the project limits of 60-140%. If the total PCB concentrations of the matrix spikes are *greater* than four times the calculated sample amount, then the quality control limits should be applied. If the total PCB concentrations of the matrix spikes are *less* than four times the sample, then there are no established limits applicable. If the percent recovery falls outside of the acceptance range for the total PCB used as the spiking analyte, then the matrix spike recovery failed the acceptance criteria. Check for documentable errors (*e.g.,* calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated QC reference check standard

(Laboratory Control Sample [LCS]) is within 60-140%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

A relative percent difference (RPD) must also be calculated on the matrix spike set recoveries. This is calculated as follows:

A = % recovery of matrix spike sample
B = % recovery of matrix spike duplicate sample

RPD = [(A-B)/{(A+B)/2}] x 100
where (A-B) *is taken as an absolute value*

If the total PCB concentrations of the matrix spike set are *greater* than four times the calculated sample amount, then an RPD of 40% or less is acceptable. If the total PCB concentrations of the matrix spike set are *less* than four times the calculated sample amount than there are no established limits applicable to the RPD. If the criterion is not met, check for documentable errors (*e.g.,* calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated LCS is within 60-140%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

11. PROCEDURES

11.1 Sediment Samples – The extracts for this analysis will be the same extracts as those generated for the analysis of total PCBs as Aroclors by SOP GEHR8082.

11.2 GC/MS ANALYSIS

11.2.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature, if necessary. Add an appropriate volume of the appropriate internal standard stock solution.

11.2.1.1 Internal standard concentration for SIM data acquisition = 4 μL of 40 ng/μL solution (of each chrysene-d_{12} and phenenthrene-d_{10}) added to 200 μL of extract for a concentration of 0.80 ng/μL.

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

11.2.3 Acquire mass spectral data with SIM conditions. Use the same data acquisition time and MS operating conditions previously used to determine response factors.

11.2.4 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. In addition, any individual PCB analyte amount that exceeds the high level calibration standard of the calibration curve will require dilution and re-analysis of the extract to place that analyte within the calibration range.

11.2.5 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.

11.3 IDENTIFICATION PROCEDURES

11.3.1 Using the ions shown on Tables 6a-6b for PCBs examine ion current profiles (ICPs) to locate internal standards, surrogate compounds, and PCBs for each isomer group. Use the RRT window data on Table 7 as guidelines for location of PCB isomers. (A reverse search software routine can be used to locate compounds of concern.)

11.3.2 SIM Data -- Obtain appropriate selected ion current profiles (SICPs) for IS quantitation and confirmation ions for the quantitation and confirmation ions for each PCB isomer group.

11.3.3 PCB Analytes

11.3.3.1 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.

11.3.3.2 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.) If this interference occurs, a correction can be made. Obtain and record the area for the appropriate ion (Table 9) for the candidate PCB isomer group. Use the information in Table 10 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 10).

11.3.3.3 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 11) 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.

11.3.4 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). 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.

11.4 IDENTIFICATION CRITERIA

11.4.1 Internal Standards

11.4.1.1 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.

11.4.1.2 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.

11.4.1.3 Retention time must be within ±10 s of that observed during the most recent acceptable calibration.

11.4.2 SIM Data for PCBs

11.4.2.1 Absolute retention times of surrogate compounds must be within ±10 s of that measured during the last previous continuing calibration check.

11.4.2.2 Quantitation and confirmation ions for each PCB isomer group must maximize within ±1 scan of each other.

11.4.2.3 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.

11.4.2.4 For each PCB isomer group candidate, the ratio of the quantitation ion area to the confirmation ion area must be within limits shown on Table 9; at least one ion in the $(M-70)^+$ ion cluster most 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 GC/MS Analytes Detected Above the Initial Low Level Calibration Standard Concentration

Any individual PCB analyte amount in a sample or QC sample above the initial low-level calibration standard concentration will be reported as such with no associated flags. Any individual PCB analyte amount that exceeds the high level calibration standard of the calibration curve will require dilution and re-analysis of the extract to place that analyte within the calibration range.

12.3 GC/MS Analytes Detected Below the Initial Low Level Calibration Standard Concentration

As stated in Section 1.2, a Method Detection Limit (MDL) will be performed in accordance with procedures set forth in 40CFR Part 136, Appendix B. Any individual PCB analyte amount in a sample or QC sample that is above the established MDL but below the initial low level calibration standard concentration will be reported and appropriately flagged with a "J" flag. A "J" flag signifies that the analyte amount was below the initial low level calibration standard concentration but above the determined MDL for the analyte.

12.4 GC/MS Analytes Detected Below the MDL

Any individual PCB analyte amount in a sample or QC sample that is below the established MDL for that analyte or not present will be reported as not detected (ND). The associated MDL concentration value for that analyte will be reported to provide information on the analyte reporting limit.

12.5 PCB Homolog Group Amounts

For each PCB Homolog Group all reportable (both non-flagged and "J" flagged) PCB analytes associated with a given chlorination level (i.e. All dichlorobiphenyls) will be summed and a total provided. No flagging of Homolog Group concentrations will occur. This will provide 10 PCB sub-totals from monochlorobiphenyl to decachlorobiphenyl. If for a given Homolog there are no reportable analytes to report or sum, then a not detected (ND) will be reported. The associated analyte MDL concentration value for that chlorination level will be reported as the Homolog reporting limit.

12.6 Total PCB Amount

The Total PCB amount for a sample or QC sample will be provided by summation of the Homolog Group amounts. No flagging of the Total PCB amount will occur. If all 10 Homolog Groups are reported as not detected (ND), then the Total PCB amount will be reported as not detected (ND). For this reporting condition (i.e. Total PCB amount = ND), the single highest reporting limit from the 10 Homolog groups (highest PCB analyte MDL from MDL study) will be used and will provide the reporting limit for the Total PCB amount.

12.7 All sediment results will be reported on a dry-weight basis using the moisture determined during the GEHR8082 analysis for total PCBs as Aroclors.

12.8 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).

12.9 Calculate the concentration of each surrogate compound and PCB isomer group using the formula:

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

where:

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

A_x = the area of the quantitation ion for each 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 or the PCB calibration compound for the isomer group (level of chlorination), and

W = weight (kilograms) of sample extracted.

D = (100 - % moisture)/100

12.4.1 Use the average RF calculated during Initial Calibration.

12.4.2 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.

12.10 Report calculated values to two significant figures.

12.11 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) and

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

Automated identification and measurement software for PCBs will be used to assist in handling and reducing the data.

14. REFERENCES

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4. “OSHA Safety and Health Standards, General Industry”, 29 CPR 1910, Occupational Safety and Health Administration, OSHA 2206, Revised January 1976.

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Table 1. Recommended GC and MS Operating Parameters

Mass Spectrometer Parameters:

Varian Model Saturn 2000 Ion Trap Mass Spectrometer

Ion Trap Temperature: 200°C
Emission Current: 70 microamps
Scan Time: 0.700 seconds
Ionization Mode: EI AGC
Ion Technique: SIS (Selected Ion scanning, which is Varian's term for SIM)

Gas Chromatograph Parameters:

Varian Model 3800 Gas Chromatograph

Injector Model 1079 (Temperature Programmable):

Coolant: Enabled
Initial Temperature: 50°C
Initial Hold Time: 1.00 minute
Final Temperature: 250°C
Temperature Ramp: 150°C/minute
Final Hold Time: 50 minutes
1079 Valve at 0.0 minutes: split state: on split ratio: 50
1079 valve at 0.50 minutes: split state: off split ratio: off
1079 valve at 3.00 minutes: split state: on split ratio: 50
Constant column flow: 1.0mL/min
Pulsed Pressure: On
Pulse Pressure: 24.0 psi
Pulse Pressure Duration: 0.75 minutes

Oven Temperature Profile:

Initial Temperature: 80°C
Initial Hold Time: 1.00 minute
First Temperature Ramp: 80 °C to 160°C at 30°C/minute, hold 1 minute
Second Temperature Ramp: 160°C to 310°C at 3°C/minute, hold 5.30 minutes

Table 1. Recommended GC and MS Operating Parameters (Cont.)

Sample Injection Parameters:

Syringe Size: 10uL
Solvent Flush: Yes, solvent A then B
Syringe Wash: 20 seconds
Solvent plug size: 0.3uL
Upper Air Gap: Yes
Lower Air Gap: Yes
Injection Rate: 0.5uL/sec
Extract Injection Volume: 2.0uL

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'
Heptachlorobiphenyl	189	2, 3, 3′ 4, 4′, 5, 5′
Octachlorobiphenyl	202	2, 2′, 3, 3′, 5, 5′, 6, 6′

[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 Standards

PCB Cong.	Isomer Group	Stock Sol. Conc. mg/mL	Proportion for Primary Dil. Sol.	Primary Dil. Std. Conc. ng/μL
#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 4a. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for PCB Determinations

Concentration (ng/μL)

Compound	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5	CAL 6
Cal. Congeners						-
Cl_1 (#1)	0.05	0.5	1	2	5	-
Cl_2 (#5)	0.05	0.5	1	2	5	-
Cl_3 (#29)	0.05	0.5	1	2	5	-
Cl_4 (#50)	0.10	1.0	2	4	10	-
Cl_5 (#87)	0.10	1	2	4	10	-
Cl_6 (#154)	0.10	1	2	4	10	-
Cl_7 (#188)	0.15	1.5	3	6	15	-
Cl_8 (#200)	0.15	1.5	3	6	15	-
Cl_{10} (#209)	0.25	2.5	5	10	-	15
Internal Standards						
Chrysene-d_{12}	0.80	0.80	0.80	0.80	0.80	0.80
Phenanthrene-d_{10}	0.80	0.80	0.80	0.80	0.80	0.80
Surrogate Compounds						
TCMX	0.05	0.5	1	2	5	-
DCB	0.05	0.5	1	2	5	-

Table 4b. Retention Time Calibration Standards
Concentration (ng/μL)

Compound	CAL 1
Pentachlorobiphenyl (#014)	2.50
Tetrachlorobiphenyl (#77)	2.50
Octachlorobiphenyl (#202)	2.50
Heptachlorobiphenyl (#189)	2.50

Table 5. 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 6a. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Sets of ≤27 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	-	225
	Cl_4	292	290, 294	220, 222	-	-	-	-
	Phenanthrene-d_{10}	188	189	-	-	-	-	-
2	Cl_3	256	258	188, 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	-	-	-	-
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	-	462, 464, 466	-	425
	Cl_9	464	460, 462, 466	390, 392, 394	-	-	-	-
	Chrysene-d_{12}	240	241	-	-	-	-	-

Table 6a. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Sets of ≤27 Ions Each (Cont.)

Ion Set	Isomer Group/ IS/Surrogate	Quant. Ion	Confirm Ions	M-70 Ions	M+70 Ions	M+35 Ions	Ion Measured[a] for Correction	
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 9-10.
[b]Cl_1-PCBs lose HCl.
[c]Some Cl_2-PCBs lose Cl_2 and some lose HCl.

Table 6b. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤27 Ions

Ion Set #1[a]	Ion Set #2[b]	Ion Set #3[c]	Ion Set #4[d]	Ion Set #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	390	462
258	323	360	391	464
290	324	362	392	466
292	326	392	394	496
294	328	394	396	498
	358	396	398	499
	360	398	425	500
	362		426	502
			428	
			430	
			432	
			460	
			462	
			464	
			466	

Table 6b. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤27 Ions (Cont.)

Scan Range #1	Scan Range #2	Scan Range #3	Scan Range #4	Scan Range #5
145m/z to 330m/z	179m/z to 398m/z	240m/z to 428m/z	233m/z to 520m/z	349m/z to 532m/z
SIS Ion Preparation	**SIS Ion Preparation**	**SIS Ion Preparation**	**SIS Ion Preparation**	**SIS Ion Preparation**
Mass Range 1: 150mz/ to 155m/z	Mass Range 1: 184mz/ to 226m/z	Mass Range 1: 244mz/ to 260m/z	Mass Range 1: 236mz/ to 296m/z	Mass Range 1: 350mz/ to 366m/z
Mass Range 2: 180mz/ to 195m/z	Mass Range 2: 250mz/ to 263m/z	Mass Range 2: 284mz/ to 294m/z	Mass Range 2: 316mz/ to 368m/z	Mass Range 2: 384mz/ to 400m/z
Mass Range 3: 215mz/ to 260m/z	Mass Range 3: 283mz/ to 300m/z	Mass Range 3: 318mz/ to 332m/z	Mass Range 3: 385mz/ to 404m/z	Mass Range 3: 418mz/ to 438m/z
Mass Range 4: 285mz/ to 300m/z	Mass Range 4: 320mz/ to 332m/z	Mass Range 4: 388mz/ to 404m/z	Mass Range 4: 422mz/ to 438m/z	Mass Range 4: 456mz/ to 472m/z
Mass Range 5: not used	Mass Range 5: 355m/z to 368m/z	Mass Range 5: not used	Mass Range 5: 455m/z to 506m/z	Mass Range 5: 490m/z to 508m/z
R.T. Window (minutes)	**R.T. Window (minutes)**	**R.T. Window (minutes)**	**R.T. Window (minutes)**	**R.T. Window (minutes)**
5.00 to 17.21	17.21 to 25.01	25.01 to 30.25	30.25 to 36.35	36.35 to 54.67
Total number of Ions	**Total number of Ions**	**Total number of Ions**	**Total number of Ions**	**Total number of Ions**
17	20	19	27	20

[a] Ions to identify and measure Cl_1 – Cl_4 PCBs and phenanthrene-d_{10}.

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

[c] Ions to identify and measure Cl_5 – Cl_7 PCBs.

[d] Ions to identify and measure Cl_6 – Cl_9 PCBs and chrysene-d_{12}.

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

Table 7. Retention Time Data for PCB Isomer Groups and Calibration Congeners

Isomer Group	Approximate RRT Range[a]	Cal. Cong. Number	Cal. Cong. RRT[a]
Monochlorobiphenyls	0.23-0.28	1	0.23
Dichlorobiphenyls	0.29-0.43	5	0.34
Trichlorobiphenyls	0.36-0.60	29	0.45
Tetrachlorobiphenyls	0.44-0.77	50	0.47
Pentachlorobiphenyls	0.55-0.93	87	0.73
Hexachlorobiphenyls	0.65-1.07	154	0.74
Heptachlorobiphenyls	0.81-1.13	188	0.81
Octachlorobiphenyls	0.95-1.18	200	0.97
Nonachlorobiphenyls	1.11-1.22	-	-
Decachlorobiphenyls	1.26	209	1.26

[a] Retention time relative to chrysene-d_{12} with a 30 m $\times$ 0.25 mm ID DB-XLB fused silica capillary column and the GC conditions set forth in Table 1.

Table 8. Known Relative Abundances of Ions in PCB Molecular Ion Clusters[a]

m/z	Relative Intensity
Monochlorobiphenyls	
188	100.00
189	13.50
190	33.40
192	4.41
Dichlorobiphenyls	
222	100.00
223	13.50
224	66.00
225	8.82
226	11.20
227	1.44
Trichlorobiphenyls	
256	100.00
257	13.50
258	98.60
259	13.20
260	32.70
261	4.31
262	3.73
263	0.47
Tetrachlorobiphenyls	
290	76.20
291	10.30
292	100.00
293	13.40
294	49.40
295	6.57
296	11.00
297	1.43
298	0.95
Pentachlorobiphenyls	
324	61.00
325	8.26
326	100.00
327	13.50
328	65.70
329	8.78
330	21.70
331	2.86
332	3.62
333	0.47
334	0.25
Hexachlorobiphenyls	
358	50.90
359	6.89
360	100.00
361	13.50
362	82.00
363	11.00
364	36.00
365	4.77
366	8.92
367	1.17
368	1.20
369	0.15
Heptachlorobiphenyls	
392	43.70
393	5.91
394	100.00
395	13.50
396	98.30
397	13.20
398	53.80
399	7.16
400	17.70
401	2.34
402	3.52
403	0.46
404	0.40
Octachlorobiphenyl	
426	33.40
427	4.51
428	87.30
429	11.80
430	100.00
431	13.40
432	65.6
433	8.76
434	26.90
435	3.57
436	7.10
437	0.93
438	1.18
439	0.15
440	0.11
Nonachlorobiphenyls	
460	26.00
461	3.51
462	76.40
463	10.30
464	100.00
465	13.40
466	76.40
467	10.20
468	37.60
469	5.00
470	12.40
471	1.63
472	2.72
473	0.35
474	0.39
Decachlorobiphenyl	
494	20.80
495	2.81
496	68.00
497	9.17
498	100.00
499	13.4
500	87.30
501	11.70
502	50.00
503	6.67
504	19.70
505	2.61
506	5.40
507	0.71
508	1.02
509	0.13

[a] Source: Rote and Morris (7)

Table 9. 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	0.9-1.2	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								
TCMX	242	244	242	1.3	1.1-1.5	-	-	-
DCB	494	498	500	1.1	0.9-1.3	424	-	-

[a] Ratio of quantitation ion to confirmation ion.

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

Table 10. 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	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 11. 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%

Figure 1. Merged Ion Current Profile of PCB Calibration Congeners

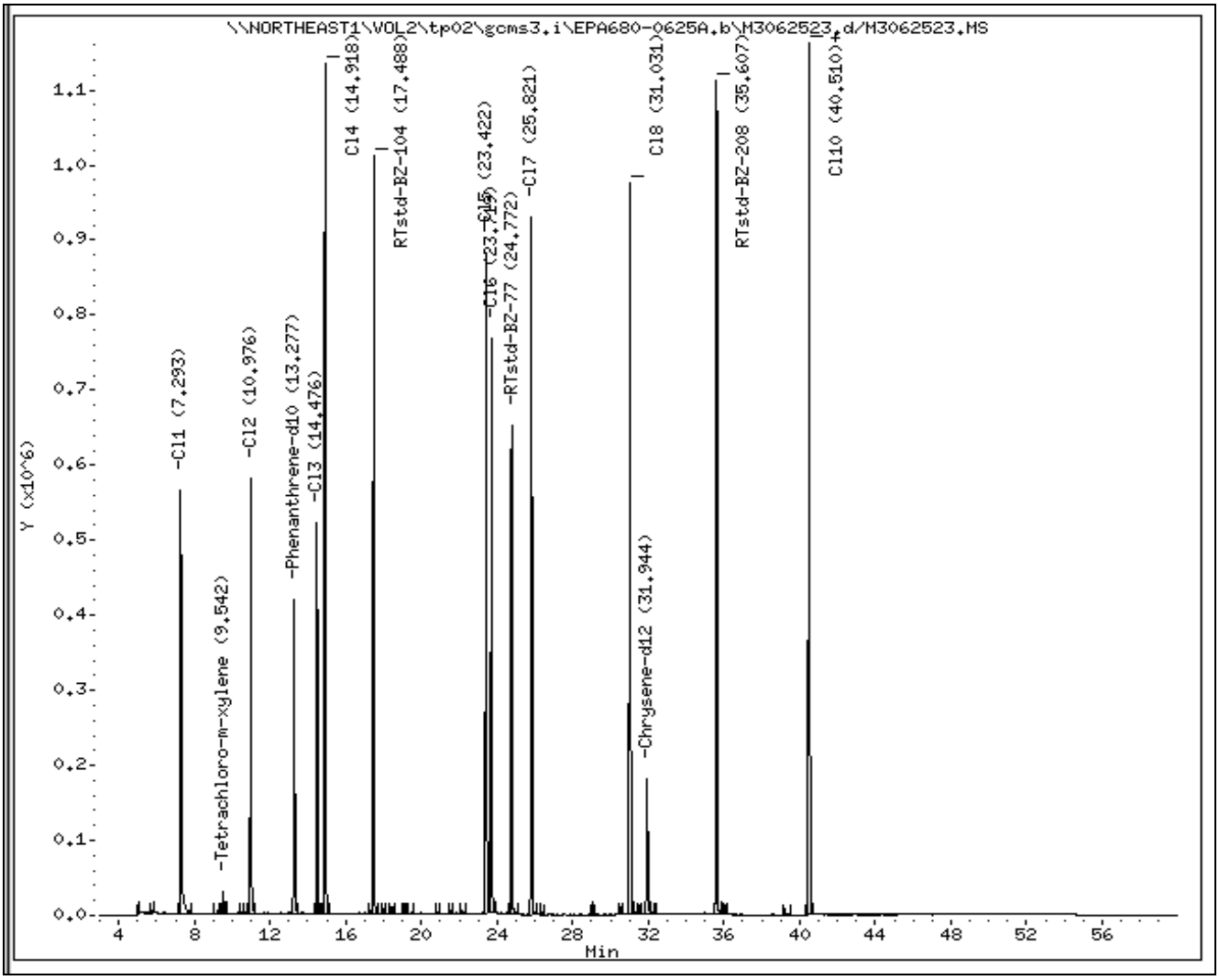

Figure 2: Total Ion Chromatogram of PCB Window Defining Mixture Standard