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General Electric (GE) Housatonic River Project
Pittsfield, Massachusetts

Contract No. DACW33-94-D-0009

Task Order No. 0032

QUALITY ASSURANCE PROJECT PLAN

Volume II
Appendix A

DCN: GEP2-100598-AADE

October 1998

WESTON SOLUTIONS

FINAL

QUALITY ASSURANCE PROJECT PLAN

GENERAL ELECTRIC (GE) HOUSATONIC RIVER PROJECT PITTSFIELD, MASSACHUSETTS

Volume II—Appendix A

Contract No. DACW33-94-D-0009
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Prepared for

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TABLE OF CONTENTS

APPENDIX A—STANDARD OPERATING PROCEDURES

Appendix A-1—Standard Operating Procedure for Hardness, Total

Appendix A-2—Standard Operating Procedure for Total Dissolved Solids (Residue, Filtered)

Appendix A-3—Standard Operating Procedure for Total Suspended Solids (Residue, Non-Filtered

Appendix A-4—Standard Operating Procedure for Alkalinity as $CaCO_3$ (Titrimetric, pH 4.5)

Appendix A-5—Standard Operating Procedure for Total and Amenable Cyanide

Appendix A-6—Standard Operating Procedure for Ammonia-Nitrogen

Appendix A-7—Standard Operating Procedure for Total Kjeldahl Nitrogen

Appendix A-8—Standard Operating Procedure for Nitrate/Nitrite-N Method

Appendix A-9—Standard Operating Procedure for Nitrite-N

Appendix A-10—Standard Operating Procedure for Phosphate as P

Appendix A-11—Standard Operating Procedure for Orthophosphate as P

Appendix A-12—Standard Operating Procedure for Sulfide (Method 376.2/4500-S^2-D)

Appendix A-13—Standard Operating Procedure for Sulfide in Soil

Appendix A-14—Standard Operating Procedure for Biological Oxygen Demand

Appendix A-15—Standard Operating Procedure for Total Organic Carbon

Appendix A-16—Standard Operating Procedure for Total Organic Carbon in Sediment (Lloyd Kahn Method)

Appendix A-17—Standard Operating Procedure for Percent Solids

Appendix A-18—Standard Operating Procedure for Acid Digestion of Aqueous Samples for Total Metals

Appendix A-19—Standard Operating Procedure for Acid Digestion of Sediments, Sludges, and Soils for Total Metals

Appendix A-20—Standard Operating Procedure for Metals Analysis by ICP

Appendix A-21—Standard Operating Procedure for Mercury Preparation and Cold Vapor Analysis of Aqueous Samples

Appendix A-22—Standard Operating Procedure for Mercury Preparation and Cold Vapor Analysis of Soil Samples

Appendix A-23—Standard Operating Procedure for Organochlorine Pesticides by Gas Chromatography

TABLE OF CONTENTS
(Continued)

Appendix A-24—Standard Operating Procedure for Polychlorinated Biphenyls (PCB) Analysis

Appendix A-25—Standard Operating Procedure for Organophosphorus Pesticides by Capillary GC

Appendix A-26—Standard Operating Procedure for Chlorinated Herbicides by ECD

Appendix A-27—Standard Operating Procedure for Purge and Trap of Aqueous Samples

Appendix A-28—Standard Operating Procedure for Extractable Semivolatile Organic Compounds by GC/MS

Appendix A-29—Standard Operating Procedure for Extractable PAHs by GC/MS Selective Ion Monitoring

Appendix A-30—Standard Operating Procedure for Petroleum Hydrocarbons (by Infrared Spectrophotometry)

Appendix A-31—Standard Operating Procedure for Ignitability

Appendix A-32—Standard Operating Procedure for Reactivity (Cyanide/Sulfide)

Appendix A-33—Standard Operating Procedure for pH

Appendix A-34—Standard Operating Procedure for Volatile Organic Compounds by GC/MS

Appendix A-35—Standard Operating Procedure for Particle Size Analysis

Appendix A-36—Standard Operating Procedure for Polychlorinated Dibenzo Dioxin/Furans

Appendix A-37—Standard Operating Procedure for Polychlorinated Biphenyls and 1,2,4-TCB by GC-ECD (Modified EPA 8082)

Appendix A-38—Standard Operating Procedure for High Resolution Mass Spectrometry Modified Method 1668

Appendix A-39—Standard Operating Procedure for Chlorophyll-A

Appendix A-40—Standard Operating Procedure for Atterberg Limits (Liquid Limit, Plastic Limit, and Plasticity Index in Soil)

Appendix A-41—Standard Operating Procedure for Specific Gravity (for Use in Porosity Calculation)

APPENDIX A

STANDARD OPERATING PROCEDURES

APPENDIX A-35

STANDARD OPERATING PROCEDURE FOR PARTICLE SIZE ANALYSIS

Particle Size Analysis
Method: ASTM D422

Approval and Signatures

QA Officer: Martha E. Roy Date: 6/12/95
Environmental Manager: [signature] Date: 12 June 95

1.0 Scope and Application

1.1 This method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particles sizes larger the 75um (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 um is determined by sedimentation process using a hydrometer.

1.2 The minimum quantity typically ranges from 115 to 230 grams of soil. Larger amounts (from 500 to 5000 grams) are specified for soils with appreciable gravel component.

1.3 There is no holding time requirement.

1.4 This test method is amenable to all soils except possible soils with significant organic content.

2.0 Summary of Method

Soils for particle size analysis are prepared according to ASTM D421 or D2217. The soils are sieved in two steps. The particles greater than 2.00mm (retained on the No. 10 sieve) are sieved after the soil has been prepared. A portion of the soil passing the No. 10 sieve is prepared for hydrometer measurements. Seven hydrometer readings are made over a 24 hour time frame. The soil in the hydrometer is rinsed on a No. 200 (75 um) sieve and dried for sieve analysis of material less than 2.00mm (No. 10 sieve). Calculations are made to determine the percent finer of soil for each sieve and hydrometer reading. These calculations are dependent on percent solid, which is determined during the drying process, and the specific gravity which can be assumed.

3.0 Materials and Reagents

3.1 Balance sensitive to 0.01 grams.

3.2 Mixer and Dispersion cup

3.3 Sodium Hexametaphosphate (dispersion reagent)

3.4 Squirt bottle for De-ionized (DI water).

3.5 1000 ML. sedimentation cylinder for hydrometer test.

3.6 Soil Test Hydrometers meeting specification E 100.

3.7 Sieves of the following size (but not limited to):

3.0 inch (75.00mm)	No. 20 (850.0 um)
2.0 inch (50.00 mm)	No. 40 (425.0 um)
1.5 inch (37.50 mm)	No. 60 (250.0 um)
1.0 inch (25.00 mm)	No. 80 (180.0 um)
3/4 inch (19.00 mm)	No. 100 (150.0 um)
3/8 inch (9.50 mm)	No. 200 (75.0 um)
No. 4 (4.75 mm)	
No. 10 (2.00mm)	

3.8 Oven with temperature range of 60 C to 110 C.

3.9 Thermometer accurate to 0.5 C.

3.10 Timer with second hand and capable of counting up to 25 hours.

3.11 250 ML. and 1000 ML. beakers of glass or plastic.

3.12 Mixing utensils and brushes for homogenization and sample recovery.

3.13 Rototap Machine

4.0 Method Procedures:

4.1 **Large Sieve (dry):** The soil retained on the No. 10 Sieve is used in this step. Rinse the particles on a No. 10 sieve and then place the material in an oven until dry.

Large Sieve (Wet): Take the equivalent of 200 grams of dry soil (use the percent solid table). Place soil on a No. 10 sieve and wash the soil. Take the soil retained on the No. 10 sieve and place in an oven until dry.

4.1.1 Record the weights of the sieves greater than No. 10. Take the dry soil and pour into the sieve stack. Place the sieve stack on the Rototap machine and shake sample for ten minutes.

4.1.2 Weigh and record the contents of each sieve.

4.1.3 Record the maximum particle size. Determine the shape of the particles using the figures in ASTM D422. Determine the hardness of the particles by dropping a hammer on the particle from a height of approximately one foot. Record the hardness as hard, soft or brittle. Save the soil particles.

4.2 **Hydroscopic Moisture (dry prep only):** The soil passing the No 10 sieve is used in this step. Take a small tin, label it and record the weight. Place approximately 10 to 15 grams of soil in the tin. Place the tin in the oven at 110 C for at least 16 hours. Remove the tin and record the weight.

4.3 **Hydrometer Test:** The soil passing the No. 10 sieve is used in this step.

4.3.1 Sample Preparation:

A) Dry Prep: Take a 250ml beaker and tare. Place and record approximately 50 grams for silt or clay particles or 100 grams for sand particles into the beaker. Add 125 ml of a 40 g/L sodium hexametaphosphate solution to sample and allow to soak overnight.

Wet prep: Take a 500ml beaker and tare. Place and record the dry equivalent (use the percent solid table) of approximately 50 grams for silt or clay particles or 100 grams for sand particles into the beaker. Add 125 ml of a 40 g/l sodium hexametaphosphate solution to sample.

B) Dry Prep: Take sample and with DI water rinse the sample into a dispersion cup. Fill the cup to the half way mark with DI water and place cup on a blender. Blenderize sample for approximately one minute. Pour content of cup into a 1000 ml flask. Rinse cup with DI water to wash all the sample into flask. Fill the flask to the 1000 ml line and cover the flask with a sheet of paraffin wax.

Wet Prep: Take sample and with DI water rinse the sample into a dispersion cup. Fill the cup to the half way mark with DI water and place cup on a blender. Blenderize sample for approximately five minute. Pour content of cup through a No. 10 sieve into a 1000 ml flask. Rinse cup with DI water to wash all the sample into flask. Fill the flask to the 1000 ml line and cover the flask with a sheet of paraffin wax. Take the material on the No. 10 sieve, dry it in the oven and record the weight.

4.3.3 After preparing up to 12 flasks, begin setup for hydrometer readings. Paperwork needed is: hydrometer data sheet, hydrometer reading table, and temperature table if conversion from Fahrenheit to Celsius is necessary. Set timer to start counting up from zero. Check readings of hydrometer(s) and temperature probe in a DI water rinse bath. Get the rubber stopper to shack flask and prepare staging and test area.

4.3.4 Initiate timer to indicate the elapsed time. The hydrometer reading table is used to perform activities as indicated (shake, place or read) for each 1000 ml cylinder.

A reading consists of inserting the hydrometer gently into the cylinder about 20 seconds before the actual reading. Read the hydrometer to the nearest 0.0005 at the top of the meniscus. Remove the hydrometer and insert a temperature sensor into the cylinder to the depth where the hydrometer reached. Read the temperature meter to the nearest 0.1 C and remove the temperature sensor. The hydrometer(s) and temperature sensor are rinsed in a DI bath between each reading.

After each cylinder is read, the hydrometer reading, temperature, and time (from table) is entered onto the hydrometer data sheet at the corresponding cylinder (test) number and time portion on the data sheet; deviations from the table schedule are noted on the sheet. The readings are taken at the 2, 5 and 15 minute marks and as close as possible to the 30, 60, 240 and 1440 minute marks.

4.4 **Small Sieve:** Take soils from the hydrometer test and rinse on the No. 200 sieve. Take soil retained on the No. 200 sieve, place in an oven set at 100 C until dry (typically overnight).

4.4.1 Record the weights of the sieves used between No. 10 and No. 200. Take the dry soil and pour into the sieve stack. Place the sieve stack on the Rototap machine and shake sample for ten mimutes.

4.4.2 Weigh and record the contents of each sieve. Save the soil sample.

5.0 Calculations

5.1 Percent Solids (PS) & Hydroscopic Moisture Correction Factor (HMCF)

5.1.1 HMCF is used for air dried samples (dry Prep)

HMCF = (Pan&Bake sample - Pan)/(Pan&Dry sample - Pan) x 100

5.1.2 Wet Method:

PS = (Pan&Dry sample - Pan)/(Pan&Wet Sample - Pan) x 100

Dry Method:

PS = HMCF x (Pan&Dry sample - Pan)/(Pan&Wet Sample - Pan) x 100

5.2 Sample Used (SU):

5.2.1 Wet Method:

SU = (Pan&Wet sample - Pan) x PS

note: for hydrometer SU, subtract the dry weight of any material retained on the No. 10 sieve.

5.2.2 Dry Method:

SU = ((Pan&Dry sample - Pan) - (Pan&Non-soil material - Pan)) x HMCF

5.3 Sieve Analysis (Percent Finer = PF)

5.3.1 Large Sieves:

3 inch: PF = 100 - 100*(Sieve&Sample(3inch) - Sieve(3inch))/SU
2 inch: PF = PF(3 inch) - 100*(Sieve&Sample(2inch) - Sieve(2inch))/SU
and so on through the # 10 sieve.

5.3.2 Small Sieves:

#20: PF=PF(#10)-100*(mass passing #10/sample mass(Hyd))*(sieve&sample(#20)-sieve(#20))/sample used
#40: PF=PF(#20)-100*(mass passing #10/sample mass(Hyd))*(sieve&sample(#40)-sieve(#40))/sample used
and so on through #200 sieve

5.4 Hydrometer Analysis

5.4.1 Particle-Size, Micron

1000*sqrt[930*viscosity/980*(SG-1))*(effective depth/time)]

Viscosity at sample temperature, poises
Effective Depth, cm = 16.29-264.5*(actual Hydrometer reading-1)
above equation for effective depth based on equation found with table 2 in method, in which 16.29 = 0.5*(14.0-67.0/27.8)+10.5
and 264.5 = (10.5-2.3)/0.031
Time, minutes = Time of hydrometer reading from beginning of sedimentation

sqrt - square root
SG - Specific Gravity of soil
Viscosity - is the resistance of a liquid to flow.

4.5.2 Percent Finer (PF):

PF = Constant*(actual hydrometer reading - hydrometer correction factor - 1)
Constant = (100,00/W)*SG/(SG-1)

$$W = \frac{\text{Total sample used} * \text{sample used for hydrometer analysis} * HMCF}{\text{Amount of total sample passing \#10 sieve}}$$

Hydrometer Correction = Slope*sample temperature + Intercept

Slope = ((low temp. reading -1)-(high temp. reading -1)/(low temp. - high temp.))
Intercept = (low temp. reading - 1) - (low temp. *slope)

6.0 Quality Control

6.1 Balance is checked daily with S class weights.

6.2 Sieves are calibrated bi-annually using the National Bureau of Standard Certificate of Calibration, standard reference materials 1017a, 1018a and 1019a calibrated glass beads.

6.3 Hydrometers are calibrated bi-annually, and checked prior to each use.

6.4 Temperature measuring device is checked against similar or more accurate temperature measuring devices.

6.5 Oven temperature is monitored daily in the morning.

6.6 A duplicate analysis is recommended for every set of 20 samples.

APPENDIX A-36

STANDARD OPERATING PROCEDURE FOR POLYCHLORINATED DIBENZO DIOXIN/FURANS

AP No. 2F	Revision: 5	Effective: 4/20/98	Replaces: 2/10/98
POLYCHLORINATED DIBENZO DIOXIN/FURANS **USEPA METHOD 8290**			
Author: Nial M. Maloney			
Management - Date	[signature] 4/20/98		
QA Officer - Date	Shelley A. Weagraff 4/20/98		

1 PURPOSE

1.1 This procedure describes the analytical techniques used for extraction and analysis of aqueous, solid, oil, wipe and waste samples for polychlorinated dibenzo dioxins and furans (PCDD/PCDF) by EPA Method 8290.

2 SCOPE

2.1 All differences between Method 8290 and actual laboratory techniques have been developed to reduce interferences and increase sensitivity.

3 APPARATUS AND MATERIALS

3.1 CTC Autosampler Model A200S.

3.2 DEC Alpha Station 225 with Opus Quan Data System V3.5.

3.3 Neslab HX200 and HX500 Water Cooler.

3.4 VG 70SE & VG Autospec Magnetic Sector High Resolution Mass Spectrometer.

3.5 Micromass Autospec Magnetic Sector High Resolution Mass Spectrometer.

3.6 Pipet, disposable, serological, 10mL.

3.7 Amber glass bottles, 1 liter (teflon-lined screw cap).

3.8 Two liter separatory funnels.

3.9 Teflon boiling chips.

3.10 200mm x 15mm glass chromatographic column used for Silica Filtration.

3.10.1 Place a glass wool plug at the bottom of the column, pack with 12g of silica gel and 5g of Na_2SO_4. Refer to Figure 1.

3.11 200mm x 15mm glass chromatographic column used for Mini-Silica Filtration.

3.11.1 Place a glass wool plug at the bottom of the column, pack with 3g of silica gel, 1cm of 44% H_2SO_4/silica gel, 0.5cm silica gel, 1cm 33% NaOH/silica gel, 0.5cm silica gel, and 1cm Na_2SO_4. Refer to Figure 2.

3.12 Organomation 24-Station N-Evaporator with teflon tubing connection to trap and gas regulator.

3.13 Conical vials, 2mL.

3.14 Glass fiber filters and glass wool plugs.

3.15 Funnels, 100mL (CMS).

3.16 Carbon column preparation: two possible preparations of the packing material are identified below for use in the cleanup procedures outlined in section 8.

3.16.1 Carbon column (gravity flow). Prepare either a carbon/silica gel or carbon/Celite 545 packing material by mixing 5% (by weight) active carbon AX-21, dried at 110°C and 95% (by weight) either silica gel or Celite 545, followed by activation of the mixture at 130°C for 6 hours. Prepare a 10mL disposable serological pipet by cutting off each end to achieve a 9 inch column. Insert a glass wool plug at one end and pack with 1g of the mixture. Cap the packing with a glass wool plug. Refer to Figure 3.

3.16.2 Note: The carbon/Celite 545 packing material has a tendency to "channel and clump" when mixed with AX-21. This packing material will be used only if the carbon/silica gel is not effective.

3.17 Dean-Stark Trap, condenser and flask.

3.18 Buchler Rotary Evaporator.

3.19 Round bottom flasks, 50mL and 500mL.

3.20 Fischer Scientific Top-Loader Balance, Model XL-3000.

3.21 Injection vial inserts, 100µL (Sun International).

3.22 Electrothermal Electromantle six sample and 3000mL capacity.

3.23 VWR Oven.

4 REAGENTS, STANDARDS AND SOLVENTS

4.1 Reagents

4.1.1 Sulfuric acid, concentrated.

4.1.2 Silica gel. Highest purity grade.

4.1.3 Celite 545.

4.1.4 Water, distilled.

4.1.5 Alumina, acid, EMS, 80/100 mesh. Stored in sealed container at 130°C.

4.1.6 Prepurified nitrogen gas.

4.1.7 Anhydrous sodium sulfate. Pour through with several portions of methylene chloride under vacuum.

4.1.8 Sodium Hydroxide. Highest available purity.

4.2 Solvents

4.2.1 Methylene chloride. Highest available purity.

4.2.2 Hexane. Highest available purity.

4.2.3 Benzene. Highest available purity.

4.2.4 Tetradecane. Highest available purity.

4.2.5 Acetone. Highest available purity.

4.2.6 Ethanol. Highest available purity.

4.2.7 Methanol. Highest available purity.

4.3 Standards

4.3.1 Analytical standards (Cambridge Isotope Laboratory, Wooburn, MA).

5 INITIAL CALIBRATION

5.1 An initial calibration curve is created to demonstrate the linearity of the HRMS system over the calibration range. An initial calibration is repeated at least every six months, whenever a new set of spiking calibration standards are created or whenever the continuing calibration falls outside the acceptance criteria.

5.2 Establish the operating conditions necessary to meet the relative retention time specifications established in EPA method 8290. The %RSD for the mean response factors must be within ±20% for the native standards and within ±30% for internal standards.

5.3 Inject the reference compound perfluorokerosene (PFK). PFK provides the required lock masses and is used for tuning the mass spectrometer.

5.3.1 The lock-mass ion from PFK is dependent on the masses of the ions monitored within each descriptor. Each descriptor will be monitored in succession as a function of GC retention time to ensure that all PCDDs and PCDFs are detected.

5.3.2 An appropriate lock mass will be monitored for each descriptor and shall not vary by more than ±20% throughout the respective retention time window.

5.3.3 The instrument is tuned to the minimum required resolving power of 10,000 (10% valley) at a reference signal close to m/z 303.9016.

5.4 Inject 2µL of the Column Performance Check Solution (CPSM). The following criteria must be met:

5.4.1.1 The first and last PCDD/F eluters are verified to be within the eight homologue retention time windows.

5.4.1.2 The chromatographic peak separation between 2,3,7,8-TCDD and the closest eluting isomers must be resolved with a valley of ≤25%.

5.5 Under the same conditions, inject 2µL of each of the six calibration solutions containing all 17 2,3,7,8-substituted isomers. Calibration standard solutions are presented in Table 2.

5.5.1 Fifteen internal standards and three recovery standards are used to improve quantitation.

5.5.2 An initial calibration curve is accepted if the following criteria are met:

5.5.2.1 The signal to noise ratio (s/n) exceeds 10:1 for all ions monitored,

5.5.2.2 The ion abundance ratio measurements are within ± 15% of the theoretical ratio, and

5.5.2.3 An averaged response factor is used for a compound, if the response factor for that compound is less than 20% coefficient of variation. Otherwise, a new initial calibration is reinjected or prepared.

5.5.3 The calibration range for the various types of matrices are as follows:

	Eff/Aqueous (ppq)	Solid (ppt)	Waste (ppt)	Oil (ppt)	Wipes (pg/sample)	Fish/Tissue (ppt)
Cl_4	5.0 - 4000	0.5 - 400	0.5 - 400	0.5 - 400	5.0 - 4000	0.2 - 160
Cl_5-Cl_8	25 - 20,000	2.5 - 2000	2.5 - 2000	2.5 - 2000	25 - 20,000	1.0 - 800
Cl_8	50 - 40,000	5.0 - 4000	5.0 - 4000	5.0 - 4000	50 - 40,000	2.0 - 1600

6 QUALITY CONTROL

6.1 Method Blank (MB): Method blank is a sand or distilled water preparation that is free of native analyte that has been prepared and analyzed using the same procedures followed for the rest of the analytical batch.

6.1.1 A method blank is run with every analytical batch or 20 samples (whichever is less) per matrix type.

6.1.2 For the determination of native 2,3,7,8-substituted isomers the levels measured in the method blank must be less than the method quantitation limit or ten times lower than the concentration found in any sample within the analytical batch.

6.1.3 All samples within an analytical batch are re-extracted and analyzed if the method blank associated with that batch does not meet the criteria described in 6.1.2.

6.2 Laboratory Control Samples (LCS): A laboratory control sample is prepared by adding a known quantity of native standards to an interferant free matrix and used to assess method performance (precision and accuracy).

6.2.1 A 10µL aliquot containing 200pg C_{l4} DD/DF, 1000pg Cl_5-C_{l7} DD/DF & 2000pg Cl_8 DD/DF is used for spiking.

6.2.2 A duplicate pair of LCS samples will be run with each analytical batch.

6.2.3 The LCS of each native isomer should have a relative percent difference of 25% or less.

6.2.4 Internal standard recoveries should range between 40-135%.

6.2.5 If the internal standard recovery of an isomer in the LCS and the associated sample(s) is also out of the range, the sample and the LCS will be re-extracted and analyzed.

6.3 Matrix Spike (MS/MSD): A matrix spike sample is prepared by adding a known quantity of native standards to a sample matrix prior to extraction.

6.3.1 A 10µL aliquot containing 200pg C_{14} DD/DF, 1000pg Cl_5-Cl_7 DD/DF & 2000pg Cl_8 DD/DF is used for spiking.

6.3.2 The relative percent difference between MS/MSD samples should be ≤20%.

6.4 Duplicate Samples: Duplicate samples are two separate aliquots taken from the same source. Duplicate samples are analyzed independently to assess laboratory precision.

6.4.1 If the relative percent difference from duplicate sample analyses is greater than 50%, then both duplicate samples will be reanalyzed.

7 COLLECTION, PRESERVATION, AND HANDLING

7.1 Amber glass bottles and jars must be used for collection.

7.2 Fish tissue is stored at -20°C, all other samples are stored at 4°C, extracted within 30 days and completely analyzed within 45 days of extraction.

8 EXTRACTION AND CLEANUP PROCEDURES

8.1 Extraction

8.1.1 Determine the percent solids on all samples, except oil. Weigh out an appropriate weight or volume, dry overnight in 110°C oven and re-weigh.

8.1.2 All samples are extracted on a wet weight basis. For solid samples, adjust the sample amount for extraction to yield a 10 gram equivalent dry weight based on the percent solids.

8.1.3 In general, if samples are "dirty" or samples contain oil or fuel oil, all cleanup steps may be required.

8.1.4 Add 10µL of internal standard and 10µL of native spike, when appropriate, to 1mL of acetone and use for spiking.

8.1.5 Aqueous or Effluent Samples: If the sample contains >1% solids, the sample must be filtered using a toluene-rinsed glass fiber filter. Spike directly into the separatory funnel containing 1L of sample. Liquid-liquid extract the filtrate by adding 100mL portions of $MeCl_2$ into the sample container, shake and add to a 2L separatory funnel. Extract by shaking the funnel with periodic venting for 2 minutes. Allow the organic layer to separate and collect by passing through a funnel with Na_2SO_4 into a 500mL round bottom. Repeat the process two more times. Add 100-200µL C_{14} to $MeCl_2$ and rotovap to C_{14}. SDS soxhlet extract the filter with toluene for 16 hours. Re-weigh the empty container, cap and record for sample weight calculation. Combine the $MeCl_2$ and toluene extracts and proceed with appropriate cleanup procedures described in section 8.2.

Note: All paper mill effluent samples should be filtered, the isolated solids and filtrate extracted separately, and the extracts recombined.

8.1.6 Solid or Waste Samples: Add 10g of sample directly into a thimble. Spike the sample and Soxhlet/Dean Stark extract for 16 hours with toluene. Proceed with appropriate cleanup procedures described in section 8.2.

8.1.6.1 To separate phases of wet (>25% water) soil, sediment or paper samples, a Soxhlet/Dean Stark extractor system may be used with toluene as the solvent.

8.1.7 Oil Samples: Dilute the sample with 50mL of hexane. Proceed with appropriate cleanup procedures described in section 8.2.

8.2 Cleanups

8.2.1 Add approx. 100µL C_{14} and 10µL of clean-up recovery standard. Rotoevap to C_{14}. Proceed to first cleanup.

8.2.2 ABP-Acid/base partitioning ("dirty" samples only)

8.2.2.1 Add 100mL of hexane to extract in round bottom.

8.2.2.2 Add 50mL of concentrated H_2SO_4 into separatory funnel. Add extract. Shake with periodic venting, allow the layers to separate for a minimum of 5 minutes and discard acid layer. Add 50mL of distilled water into separatory funnel containing sample. Shake and discard. Add 50mL of 10N NaOH into separatory funnel containing sample. Shake and discard. Add 50mL of distilled water into separatory funnel containing sample. Shake and discard.

8.2.2.3 Pass through Na_2SO_4, then roto-evap to C_{14}. Proceed to the next appropriate cleanup procedure.

8.2.3 Silica Filtration (sludge samples only)

8.2.3.1 Roto-evap the extract to C_{14}, then add 10mL $MeCl_2$ and swirl.

8.2.3.2 Add 90mL of hexane, in four portions, while swirling.

8.2.3.3 Pour the solution onto the glass chromatographic column described in section 3.10. Rinse the extract container with a few small portions of hexane and add to the column.

8.2.3.4 When all the solution has passed onto the column, add 90mL of hexane.

8.2.3.5 Collect all eluate in a round bottom flask and roto-evap to the C_{14}. Proceed to cleanup 8.2.5.

8.2.4 Mini-Silica Filtration (soil and water samples)

8.2.4.1 Rinse the glass chromatographic column described in section 3.11 with 20mL of hexane.

8.2.4.2 Roto-evap the extract to C_{14}, quantitatively transfer to column. Collect eluate.

8.2.4.3 Elute and collect 80mL of hexane in a round bottom flask and roto-evap to C_{14}. Proceed to cleanup 8.2.5.

8.2.5 Charcoal/Silica Gel or Charcoal/Celite 545 Column

8.2.5.1 Roto-evap the extract to C_{14}.

8.2.5.2 Pre-rinse the carbon column described in section 3.16 with 5mL of toluene in the forward direction.

8.2.5.3 Invert the column and rinse in the reverse direction with 10mL of 75:20:5 $MeCl_2$:MeOH:Benzene then 5mL of 1:1 $MeCl_2$:Cyclohexane. Discard rinses.

8.2.5.4 Add sample to the column and using a small amount of 1:1 $MeCl_2$:Cyclohexane rinse the flask and transfer to column.

8.2.5.5 Elute the column with 5mL 1:1 $MeCl_2$:Cyclohexane and 5mL of 75:20:5 $MeCl_2$:MeOH:Benzene. Discard rinses.

8.2.5.6 Invert column and elute with 25mL toluene.

8.2.5.7 Roto-evap to approx. 1mL, transfer to a 2mL conical vial containing 10µL of C_{14} and 10µL of recovery standard.

8.2.5.8 N-evap to C_{14}, rinse with hexane and N-evap to C_{14} again (final volume is 20µL).

8.2.5.9 Transfer to autoinjector insert and crimp-top vial.

9 GC/MS ANALYSIS

9.1 Establish the necessary operating conditions. The following GC operating conditions are for guidance and adjustments may be required.

9.1.1

Injector temperature:	270°C
Interface temperature:	290°C
Initial temperature:	200°C
Initial time:	2 minutes
Temperature program:	200 to 220°C, at 5°C/min
	220°C for 16 minutes
	220 to 235°C, at 5°C/min
	235°C for 7 minutes
	235 to 330°C, at 5°C/min

9.2 The reference compound perfluorokerosene (PFK) provides the required lock masses and is used for tuning the mass spectrometer.

9.2.1 The lock-mass ion from PFK is dependent on the masses of the ions monitored within each descriptor. Each descriptor will be monitored in succession as a function of GC retention time to ensure that all PCDDs and PCDFs are detected.

9.2.2 An appropriate lock mass will be monitored for each descriptor and shall not vary by more than ±20% throughout the respective retention time window.

9.2.3 The mass resolution check is achieved before any analysis is performed and at the end of each 12-hour shift.

9.3 Set up the analytical run following this sequential injection pattern: CPSM, CS3, Solvent Blank, Method Blank, Samples, LCS, CS3.

9.4 Continuing Calibration

9.4.1 Inject a column performance standard mix (CPSM) to verify retention time windows. The following criteria must be met:

9.4.1.1 The chromatographic peak resolution between 2,3,7,8-TCDD and the closest eluting isomers must be resolved with a valley of ≤25%.

9.4.1.2 The first and last PCDD/F eluters are verified to be within the eight homologue retention time windows.

9.4.2 Inject a mid-range standard from the initial calibration curve (CS3) at the beginning and end of every 12 hours. The following criteria must be met:

9.4.2.1 The relative response factors for the mid-range standard are within the limits established in method 8290. The %RSD for the mean response factors must be within ±20% for the native standards and within ±30% for internal standards.

9.4.2.2 The ion ratios are within 15% of the theoretical.

9.4.2.3 The signal to noise ratio (s/n) exceeds 10:1 for all ions monitored.

9.4.2.4 The retention times must be within the criteria established in method 8290.

9.5 Qualitative Determination

9.5.1 To identify a chromatographic peak as a PCDD or PCDF(either an unlabeled or a labeled compound). It must meet the following criteria:

9.5.1.1 The signals for the two exact m/z's being monitored must be present and must maximize within ±2 seconds of one another.

9.5.1.2 The signal-to-noise ratio (S/N) of each of the two exact m/z's must be ≥2.5:1 for a sample extract, and ≥10:1 for a calibration standard.

9.5.1.3 The ion abundance ratios must have a ratio within the limits established for the homologous series.

9.5.1.4 The absolute retention times for non-2,3,7,8-substituted congeners must be within the corresponding windows set by the CPSM.

9.5.1.5 The absolute retention times for 2,3,7,8-substituted congeners must be within -1 to +3 seconds of the isotopically labeled standard.

9.6 Quantitative Determination

9.6.1 For peaks which meet the criteria listed above, quantitate the PCDD and PCDF peaks from the mean RRF relative to the appropriate internal standard established in the initial calibration.

9.6.2 Recovery of each internal standard versus the recovery standard should be between 40-135% or have a signal to noise ratio >10:1.

9.6.3 It is recommended that sample recoveries less than 40% or greater than 135% be re-extracted and re-analyzed unless the s/n ratio is >10:1.

9.6.4 Report results in picograms per gram, picograms per liter or picograms per sample.

9.6.5 Any sample in which the 2,3,7,8-TCDF is identified by analysis on a DB-5 GC column must be confirmed on a DB-225 or equivalent GC column.

9.6.6 For 2,3,7,8-substituted congeners that are not identified, calculate a sample specific estimated detection limit.

9.6.7 For a homologous series with no positive identifications, calculate the detection limit.

10 CALCULATIONS

10.1 The concentrations for the PCDD or PCDF compounds are calculated by using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times RRF}$$

Where:

C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g,

A_x = sum of the integrated ion abundances of the quantitation ions (See Table 6 of EPA Method 8290) for unlabeled PCDDs/PCDFs,

A_{is} = sum of the integrated ion abundances of the quantitation ion (See Table 6 of EPA Method 8290) for the labeled internal standards,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight of the sample (solid or liquid), and

RRF = calculated relative response factor for the analyte.

10.2 The detection limits for each absent 2,3,7,8-substituted PCDD/PCDF can be calculated using the following formula:

$$DL = \frac{2.5 \times H_N \times Q_{IS}}{H_{IS} \times W \times RRF}$$

Where:

DL = estimated detection limit for homologous 2,3,7,8-substituted PCDDs/PCDFs,

H_N = Noise height (peak to peak),

H_{IS} = peak height of the internal standard,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight of the sample (solid or liquid), and

RRF = calculated relative response factor for the analyte.

11 REFERENCES

USEPA Method 8290, Revision 0, Dated September 1994.

Figure 1

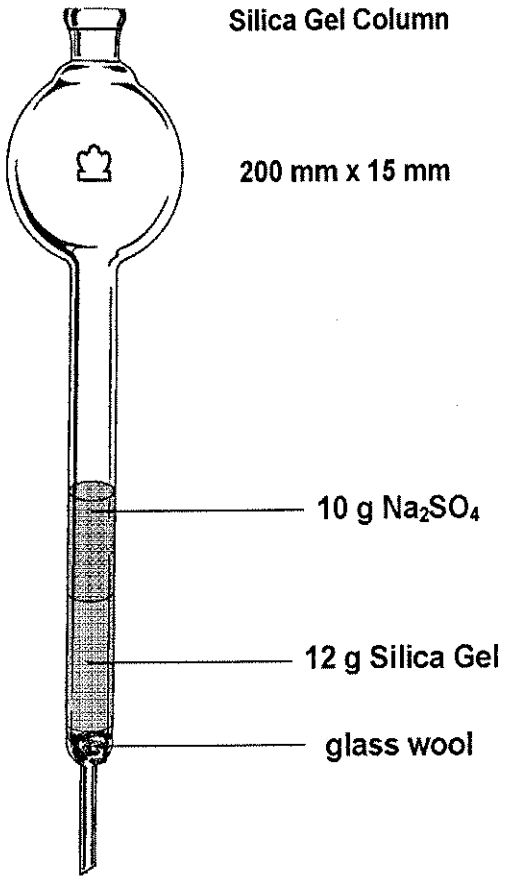
Silica Gel Column
200 mm x 15 mm
10 g Na_2SO_4
12 g Silica Gel
glass wool

Figure 2

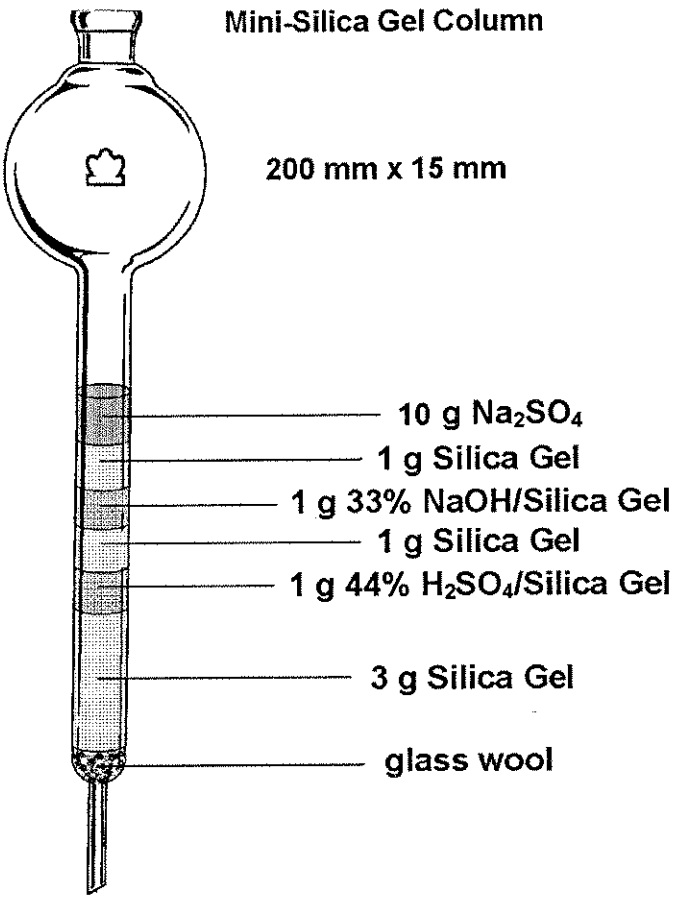
Mini-Silica Gel Column
200 mm x 15 mm
10 g Na_2SO_4
1 g Silica Gel
1 g 33% NaOH/Silica Gel
1 g Silica Gel
1 g 44% H_2SO_4/Silica Gel
3 g Silica Gel
glass wool

Figure 3

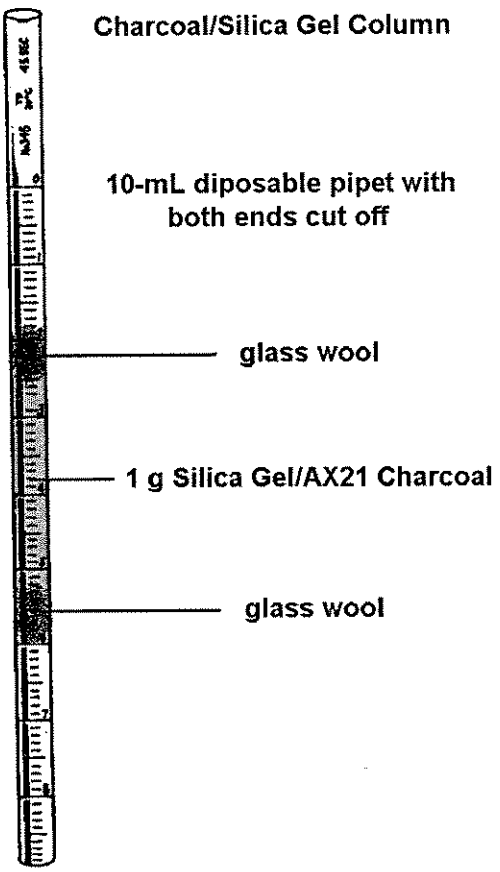
Charcoal/Silica Gel Column
10-mL diposable pipet with both ends cut off
glass wool
1 g Silica Gel/AX21 Charcoal
glass wool

Table 1

Theoretical Ion Abundance Ratios and Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	$\frac{M}{M+2}$	0.77	0.65	0.89
5	$\frac{M+2}{M+4}$	1.55	1.24	1.86
6	$\frac{M+2}{M+4}$	1.24	1.05	1.43
6[a]	$\frac{M}{M+2}$	0.51	0.43	0.59
7[b]	$\frac{M}{M+2}$	0.44	0.37	0.51
7	$\frac{M+2}{M+4}$	1.04	0.88	1.20
8	$\frac{M+2}{M+4}$	0.89	0.76	1.02

(a) Used for ^{13}C-HxCDF (IS) only.

(b) Used for ^{13}C-HpCDF (IS) only

Table 2

Compound	Calibration Solutions (ng/mL)					
Native CDDs and CDFs	CS0	CS1	CS2	CS3*	CS4	CS5
2,3,7,8-TCDD	0.25	0.5	2.0	10	40	200
2,3,7,8-TCDF	0.25	0.5	2.0	10	40	200
1,2,3,7,8-PeCDD	1.25	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	1.25	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	1.25	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	1.25	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	1.25	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	1.25	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	1.25	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	1.25	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	1.25	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	1.25	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	1.25	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	1.25	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	1.25	2.5	10	50	200	1000
OCDD	2.5	5.0	20	100	400	2000
OCDF	2.5	5.0	20	100	400	2000
Labeled Compounds						
13C-2,3,7,8-TCDD	100	100	100	100	100	100
13C-2,3,7,8-TCDF	100	100	100	100	100	100
13C-1,2,3,7,8-PeCDD	100	100	100	100	100	100
13C-1,2,3,7,8-PeCDF	100	100	100	100	100	100
13C-2,3,4,7,8-PeCDF	100	100	100	100	100	100
13C-1,2,3,4,7,8-HxCDD	100	100	100	100	100	100
13C-1,2,3,6,7,8-HxCDD	100	100	100	100	100	100
13C-1,2,3,4,7,8-HxCDF	100	100	100	100	100	100
13C-1,2,3,6,7,8-HxCDF	100	100	100	100	100	100
13C-1,2,3,7,8,9-HxCDF	100	100	100	100	100	100
13C-2,3,4,6,7,8-HxCDF	100	100	100	100	100	100
13C-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	100
13C-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	100
13C-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	100
13C-OCDD	200	200	200	200	200	200
Cleanup Recovery Standard						200
37Cl4-2,3,7,8-TCDD	0.25	0.5	2.0	10	40	200
Recovery Standard						
13C-1,2,3,4-TCDD	100	100	100	100	100	100
13C-1,2,3,4-TCDF	100	100	100	100	100	100
13C-1,2,3,7,8,9-HxCDD	100	100	100	100	100	100

* Calibration Verification Solution

APPENDIX A-37

STANDARD OPERATING PROCEDURE FOR DETERMINATION POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (MODIFIED EPA 8082)

STANDARD OPERATING PROCEDURE FOR DETERMINATION POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY / ELECTRON CAPTURE DETECTOR (MODIFIED EPA 8082)

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Sharon Nordstrom, Project Manager
Roy F. Weston, Inc.

Approved by: Marie Wojtas
Marie Wojtas, Chemist
USACE

1.0 HEALTH AND SAFETY

1.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Treat each chemical as a potential health hazard and minimize potential exposure. Handle stock standard solutions containing these compounds in a fume hood. Wear personal protective equipment such as lab coats, gloves and safety glasses while performing this analysis.

1.2 All reagents and standards used for analysis must be accompanied to the laboratory by manufacturer's Material Data Safety (MSD) Sheets. MSD Sheets are kept on file in the laboratory in binders labeled MSDS on a bookshelf in the data processing area, and are available to all laboratory personnel. As part of the training process, analysts make themselves familiar with the contents of the MSD Sheets.

1.3 Secure all compressed gas cylinders with chains or straps. Train analysts in tank changing procedures.

2.0 SCOPE AND APPLICATION

2.1 The purpose of this SOP is to outline, in detail, the technique of determining polychlorinated biphenyls (PCBs) by GC/ECD. This method is based on Method 8082, SW-846, Rev. 2, Dec 1996. This method is applicable to soil and sediment samples and rinse blank samples collected at the GE Housatonic River Site.

2.2 General method information:

2.2.1 Severe weathering may affect Aroclor patterns. Thus, the experience of the analyst plays a large role in the identification of Aroclors. Samples displaying unusual or significant weathering patterns will be addressed in the report narrative.

2.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method. This includes having the analyst extract four LCS (Laboratory Control Spike) samples. Recoveries of the spiked compounds must be within ±25% of the spiked values, and the Relative Percent Difference (RPD) between the four results must not exceed 20%. Records for each analyst are kept on site for examination.

3.0 SUMMARY OF METHOD

3.1 Thirty (30) g of a soil or sediment sample is dried overnight in an oven at 75 degrees C. A five (5) g aliquot is weighed and dried further using sodium sulfate and methanol, and then extracted using 5 mL of hexane. The sample is vortexed then shaken for an hour on a shaker table and the resulting hexane layer is transferred to a 4.0 mL vial. The extract is then copper cleaned to remove sulfur and then acid cleaned with sulfuric acid.

3.2 For aqueous rinse blank samples, 40 mL of water is extracted with 1 mL of hexane and shaken vigorously for twenty minutes. The hexane layer is drawn off and analyzed. No cleanup procedures are performed on the water samples. If sample shows evidence of Aroclors, it is immediately reported to Weston.

3.3 For hexane rinse blank samples, a 1 mL aliquot is spiked with surrogate and analyzed. No cleanup procedures are performed on the hexane samples. If sample shows evidence of Aroclors, it is immediately reported to Weston.

4.0 INTERFERENCES

4.1 Major contaminant sources are contaminated solvents and glassware used during initial sample extraction and concentration. Ensure that solvents meet ACS certification for pesticide residue and/or HPLC analysis and that glassware is free from contamination. Since new, unused 20mL voa vials are used for every sample, cross contamination from the laboratory is most likely very minimal. Extract a sample blank at the same time and under the same conditions as the samples and analyze before the sample extracts to determine if any contaminants are present. Common contaminants are the phthalate esters, which come from rubber gloves and other rubber materials in the lab in addition to outside sources, and sulfur present in samples.

4.2 Contamination also occurs in the case of carryover, where a low level sample is analyzed immediately following a high concentration sample. Analyze solvent checks following high level samples to determine system carryover. A sample would be considered high concentration if it exceeded 10 times the upper calibration limit. If high level samples are analyzed when an analyst is not present (i.e. overnight using the autosampler), then samples which contain Aroclors analyzed immediately following the high level samples are reanalyzed to confirm the concentration of Aroclor present in the sample.

4.3 Perform adequate maintenance, such as changing septa on GC#1 and changing the injection port liners and clipping columns in order to reduce active sites and improve general chromatography on both GC systems.

5.0 APPARATUS AND MATERIALS

5.1 Hewlett-Packard dual tower 7673 vial autosampler system.

5.2 Gas chromatography/electron capture system (GC/ECD) #1.

5.2.1 Hewlett-Packard 5890A Series II GC.

5.2.2 Hewlett-Packard dual ECD detectors

5.2.3 One Supelco SPB-5 30 m x 0.53 mm ID, 0.5 µm film thickness column
One J&W Scientific DB-5 30 m x 0.53 mm ID, 1.5 µm film thickness column.

5.3 Gas chromatography/electron capture system (GC/ECD) #3:

5.3.1 Hewlett-Packard 6890 Series GC with Electronic Pressure Control (EPC).

5.3.2 Hewlett-Packard dual µECD detectors

5.3.3 Two Supelco SPB-5 30 m x 0.53 mm ID, 0.5 µm film thickness columns.

5.4 Data system

5.4.1 Two computers with enough memory to simultaneously run Excel and Chemstation software.

5.4.2 Hewlett-Packard Chemstation software for integrating and processing signals generated by the GC/ECD system.

5.5 Microsyringes - Hamilton 5-, 10-, 25-, 100-, 250-, 500- and 1000-µL

5.6 AND EK-120, top loading balance, capable of weighing to 0.01 g.

5.7 Disposable Pasteur pipettes, pipette bulbs

5.8 Class A Volumetric glassware - 10 mL and 100 mL

5.9 Stainless steel spatulas

5.10 20mL precleaned VOA vials, with 0.125 inch teflon lined septa

5.11 4 mL vials, with teflon lined caps

5.12 Certified weights, 0.1 g - 100 g.

6.0 REAGENTS AND STANDARDS PREPARATION

6.1 n-Hexane (VWR) - pesticide grade

6.2 Methanol, (VWR) - pesticide grade

6.3 Acetone (VWR) - pesticide grade

6.4 Stock standards

6.4.1 Purchase the following stock standards from ABSOLUTE as certified solutions, and use for PCB/Aroclor calibrations:

- 90127, Aroclor 1248, 1000 µg/mL
- 90128, Aroclor 1254, 1000 µg/mL
- 90129, Aroclor 1260, 1000 µg/mL
- 70103, Decachlorobiphenyl, 1000 µg/mL
- 70273, Tetrachloro-m-Xylene, 1000 µg/mL

6.4.2 Purchase the following stock standards from ACCUSTANDARD as certified solutions, and use for second source verification checks:

- C-248S-H-10X, Aroclor 1248, 1000 µg/mL
- C-254S-H-10X, Aroclor 1254, 1000 µg/mL
- C-260S-H-10X, Aroclor 1260, 1000 µg/mL

6.4.3 Also keep on hand Aroclor 1016, 1221, 1232 and 1242 to analyze in case PCBs other than Aroclor 1248, 1254 or 1260 are detected. PCBs listed above are purchased in 1000 µg/mL solutions, and are prepared as in Sec. 7.1, below. If a sample is suspected of containing one or more of the "non-target" Aroclors, then either a new curve or a midpoint (See Sec 8.1.1. for midpoint definition) is analyzed for each suspected Aroclor and the sample is reanalyzed for the suspected Aroclors.

6.5 Store standards at 4°C.

7.0 CALIBRATION PROCEDURE

7.1 Calibration Curve Preparation for PCBs: Analyze a 6-point initial calibration curve for each Aroclor. Prepare the 6-point curves as below:

Make an initial dilution of each PCB stock standard. All "Standard added" amounts refer to this dilution. Prepare the initial dilution by adding 1 mL of the stock PCB standards to a 10 mL volumetric flask and bring to volume in hexane. The concentration of these standards are 100 µg/mL.

Make an initial dilution of the surrogate standard solution by bringing 1 mL of tetrachloro-m-xylene and 1 mL of decachlorobiphenyl to 10 mL in hexane. The concentration of this standard is 100 µg/mL.

Prepare the working curve standards the following way:

Conc. (PCB/ Surr)	Std added	SS. added	Final volume
10/1µg/mL	1 mL	0.10 mL	10 mL
5/0.5 µg/mL	0.5 mL	0.050 mL	10 mL
3/0.3 µg/mL	0.3 mL	0.030 mL	10 mL
2/0.2 µg/mL	0.2 mL	0.020 mL	10 mL
1/0.1 µg/mL	0.1 mL	0.010 mL	10 mL
0.5/0.05 µg/mL	0.05 mL	0.005 mL	10 mL

This is done for each set of Aroclor standards.

7.1.1 The working range of the method is limited to the upper range of the calibration curve. Samples with analytes that exceed the upper calibration range are reanalyzed at a dilution, with the concentration of the analytes in question ideally falling into the upper half of the calibration range.

7.1.2 "Prime" (deactivate) column before curve is analyzed by injecting the midpoint Aroclor 1260 standard or any midlevel or higher Aroclor standard.

7.2 Curve acceptance criteria for PCBs:

A six-point linear regression calibration curve, which does not pass through the origin, is used to calibrate all three Aroclors (i.e. 1248, 1254, and 1260) and the two surrogates (tetrachloro-m-xylene and decachlorobiphenyl). Seven peaks are chosen for each Aroclor. Peaks for each Aroclor are at least 25% of the height of the largest Aroclor peak. The correlation coefficient generated for each Aroclor peak must be > 0.995 or a new curve must be analyzed. A minimum of five (5) points must be used to generate each calibration curve.

An option for calibration which is not used at the GE Housatonic River Site is an average of Calibration Factors. For the Calibration Factor method seven peaks are chosen for each Aroclor. Peaks for each Aroclor are at least 25% of the height of the largest Aroclor peak.

7.2.1 Calculate the Calibration Factor (CF) for each characteristic Aroclor peak.

$$CF = \frac{\text{Peak Area (or Height) of Compound in Standard}}{\text{Mass of Compound Injected (ng)}}$$

7.2.2 Calculate the mean calibration factor for each characteristic peak using the Chemstation software. The formula is as follows:

$$\text{mean CF} \Rightarrow \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

where n is the number of standards analyzed.

7.2.3 Calculate the standard deviation (SD) and the %RSD of the calibration factors for each Aroclor peak as

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad \%RSD = \frac{SD}{CF} \times 100$$

If the %RSD for each Aroclor Peak is > 25%, a linear regression not forced through the origin (also called a calibration curve) is used to calculate concentrations. The correlation coefficient for each Aroclor Peak must be > 0.995, or a new curve must be analyzed.

In general, the concentration for each individual peak in a given Aroclor is calculated and then they are averaged together. This is done so that if there are interferences, such as other chlorinated analytes (such as pesticides, solvents, chlordane, etc.), the presence of multiple Aroclors, the presence of sulfur, the affect of those interferences can be evaluated on a peak by peak basis to determine if an Aroclor peak should be included in the concentration calculation. Examining each peak is also essential in determining if weathering/degradation has occurred.

7.2.4 Retention time windows: Absolute retention times are essential for compound identification. The retention time for each characteristic Aroclor peak is determined by averaging the retention time over three days and calculating the standard deviation (see formula in Sec. 7.2.3). The width of the of the retention time window is defined as ±3 standard deviations of the average. See Sec. 9.4.2 for further details.

8.0 QUALITY CONTROL

8.1 Before analysis of samples can proceed, calibration verification must occur.

8.1.1 Perform midpoint continuing calibration checks. A 5ppm standard of each Aroclor (i.e. Aroclor 1248, 1254, and 1260) is analyzed as a midpoint continuing calibration check. All Aroclor mixtures must be within ±25% difference of the initial calibration for analysis to continue. The % Difference is calculated as follows:

$$\%\,\mathrm{Diff} = \frac{CF - \overline{CF}_y}{CF} x100$$

This calibration occurs before samples are analyzed. All Aroclors must pass before analysis of samples can occur. After every tenth sample analyze an instrument blank and a midpoint calibration of Aroclor 1260. The instrument blank must be free of extraneous peaks and the recovery of the Aroclor must fall within the ± 25% difference window for analysis to continue. Closing sets of calibration verifications are also analyzed. These consist of an instrument blank, a low level (0.5ppm) and a midpoint (5.0ppm) Aroclor 1260 standard. They must fall within the ± 25% difference window for results to be considered valid. If the 5.0ppm Aroclor 1260 mixture fails to meet criteria then samples must be reanalyzed. If the 0.5ppm Aroclor 1260 mixture fails to meet criteria than all samples that have a concentration of Aroclors below 0.5ppm or have non-detects for the Aroclors are reanalyzed.

Before the opening calibration check, and before each continuing calibration check, an instrument blank is analyzed. The instrument blank must be free of Aroclors or any other potential interfering compounds. Interfering contamination would be Aroclor patterns, or other large peaks that have the potential to bias or interfere with the quantitation of Aroclor concentrations.

9.0 INSTRUMENT CONDITIONS AND SAMPLE ANALYSIS

9.1 Instrument Conditions:

9.1.2 GC #1 conditions (No EPC):

HP 5890 Series II Gas Chromatography/electron capture system

Injection port temperatures:	225 °C
Injection port mode:	Splitless
Carrier Gas Type:	Helium
Makeup Gas Type:	Nitrogen
Detector A temperature:	325 °C
Detector B temperature:	325 °C
Initial temperature:	170 °C
Initial time:	3.0 min
Rate (°C/min):	7.5
Temperature:	200 °C
Hold time:	0.5 min
Rate (°C/min):	12
Final temperature:	260 °C
Final time:	17.0 min

Total time: 29.50 min

9.1.3 GC #3 conditions:

HP 6890 Series Gas Chromatography/electron capture system w/EPC:

Inlets (Front and Back)

Mode:	Splitless
Injection port Temperatures:	250 °C
Pressure:	8.12 psi
Purge Flow:	32.7 mL/min
Gas type:	Nitrogen

Columns (Front and Back)

Supelco 13760-05B
SPB-5 5% Phenyl Methyl Siloxan
30 m x0.53 mm ID, 0.5 µm film thickness

Mode:	constant pressure
Pressure:	8.12 psi
Nominal Initial Flow:	8.9 mL/min
Average Velocity:	72 cm/sec
Outlet Pressure:	ambient

Detectors (Front and Back)

Detector temperature:	300 °C
Constant flow:	60.0 mL/min
Makeup Gas Type:	Nitrogen

Oven

Initial temperature:	140 °C
Initial time:	0.00 min
Rate (°C/min):	10.0
Temperature:	280

Hold time:	6.00 min
Rate (°C/min):	10
Final temperature:	305 °C
Final time:	1.0 min
Total time:	23.50 min

9.1.4 HP 7673 Injectors (Dual Tower, GC #1)

Solvent washes:	5
Sample pumps:	5
Injection volume:	1 µL
Syringe Size:	10 µL
Oncolumn:	No

9.1.5 HP 7683 Injectors (Dual Tower, GC #3)

Solvent washes:	5
Sample pumps:	5
Injection volume:	2 µL
Syringe Size:	10 µL
Plunger Speed:	Fast
Oncolumn:	No

GC #3 is the primary instrument used at the GE Housatonic River Site

9.2 Sample Preparation:

9.2.1 Soil Sample Preparation:

9.2.1.1 Homogenize sample in container by mixing thoroughly with clean stainless steel spatula. Remove any rocks and/or twigs prior to mixing the sample.

9.2.1.2. Weigh out at least 30 g into an aluminum weighing tin. To do this, zero the balance, place the weigh boat on top of the scale and record the weight. Without zeroing, add 30 + g of sample. For the LCS and the blank, use clean, dry sand. Place in an oven at 65-75 °C for 12 hours.

9.2.1.3 At the same time, weigh out at least ten grams of sample into a weigh boat for % solids determination. To do this, zero the balance, place the weigh boat on top of the scale and record the weight. Without zeroing, add 10 + g of sample and record this weight. Place in oven at 105 °C for at least 12 hours and record the final weight. Record date and time into and out of oven. Calculate the %solids (PS1) in the following manner:

$$\%\text{solids (PS1)} = \frac{\text{((dry wt.)-(tin wt.))}}{\text{((wet wt.)-(tin wt.))}} \times 100^{*}$$

* This is the true percent solids of the sample.

9.2.1.4 From the 30 g weighing tin measure a five (5) g (±0.1g) aliquot into a 20 mL pre-cleaned VOA vial. Weigh and record weight of sample remaining in the weighing tin. Place the weighing tin into an oven at 105 °C for approximately 8 hours. After 8 hours remove the tin from the oven and record the weight. Be sure to record date and time placed in and removed from the oven. Calculate percent solids in the following manner:

$$\% \text{ solids (PS2)} = \frac{(\text{dry wt.}) - (\text{tin wt})}{(\text{wet wt.}) - (\text{tin wt.})} \times 100^{**}$$

** This is the percent solids value that will be used in the calculations of the samples.

9.2.1.5 To the 5.0g in the 20 mL voa vial add sodium sulfate that has been solvent rinsed with hexane, muffled overnight at 450 °C, covered with aluminum foil, and stored in a desiccator. The amount of sodium sulfate will vary depending on the amount of moisture left in the sample. Add until completely dry. When sample is completely dry it will have the texture of dry sand.

9.2.1.6 Spike dried samples with 25 µL of surrogate. Add 25 µL of 1,000 µg/mL Aroclor 1260 to the LCS, MS, and MSD. Be sure to clean the syringes by flushing several times with hexane before and after use. Another technician or analyst must witness spiking and initial in the extraction logbook. Add 1.0 mL of methanol and 5.0 mLs of hexane and vortex for thirty (30) seconds. Place samples on shaker table to shake for 60 minutes.

9.2.1.7 After an hour remove the samples from the shaker table. Pipette off the hexane layer and transfer into a 4.0 mL vial. Remove any sulfur from the sample. This is done by first treating approximately 5 g of copper with dilute nitric acid and then rinsing the copper 5 times with distilled water to remove the acid. The copper is then considered "activated", and must either be used immediately, or it can be stored under acetone. If it is stored under acetone, it must be dried for four hours before use. Add approximately 1.0 g of copper to extract and vortex for 15 seconds. Solution will be clear if sulfur is removed. Repeat this step until all sulfur is removed from the sample.

9.2.1.8 When sulfur cleanup is done, pipette extract into another 4.0 mL vial. Approximately a 1: 1 volume of sulfuric acid is added to the extract, and the extract is vortexed for 15 seconds. The acid phase and hexane layer are allowed to separate. Repeat if necessary. Being careful not to transfer any acid, pipette the hexane layer into a clean autosampler vial.

9.2.1.9 Proceed to analysis of samples (Sec. 9.3)

9.2.3 Hexane field blank preparation:

9.2.3.1. Hexane rinse blanks are supplied in 40 mL VOA vials. 1 mL of the hexane is transferred to a 2 mL sample vial, and 5 µL of the 100 µg/mL

Surrogate mixture is added. The sample is then analyzed. No cleanup procedures are performed on the sample.

9.3 Analysis of samples:

9.3.1. Start by analyzing an instrument blank followed by the three Aroclor mixtures. Criteria must meet those outlined in Sec. 8.1.1. Sample analysis follows, generally in the following order: LCS, Blank, samples, MS/MSD. After every ten samples, an instrument blank and midpoint (5 µg/mL) Aroclor 1260 mixture is analyzed, and must meet results listed in Sec. 8.1. A closing check of 0.5 ppm Aroclor is analyzed before the final midpoint Aroclor 1260 check. A sample analytical sequence follows:

Instrument Blank
Opening calibration checks
LCS
Extraction Blank
Samples (up to ten, including LCS & Blank)
Instrument Blank
Continuing 1260 check
Samples (up to ten-- included under the definition of samples are MS/MSD samples)
Instrument blank
0.5 ppm 1260 Check
Closing 1260 Check.

The 0.5 ppm 1260 check must be within ±25% of its true concentration. If it is not within these limits, it could indicate that the instrument is no longer accurately "seeing" and quantitating low level concentrations. Each Aroclor peak in the 0.5 ppm 1260 standard must fall within the windows generated by the low level limit study. See section 10.9.1 for further details. If the 0.5 ppm is out of compliance for Aroclor 1260 all samples which have concentrations of Aroclors below 0.5 ppm or have non-detects for the Aroclors are reanalyzed. This is noted in the case narrative. If the 0.5 ppm standard continues to fail, then a new curve must be analyzed. All non-detected results are "J" qualified as estimates.

9.3.2. Sample results are checked as soon as they come off the instrument as possible. Any sample result that exceeds the upper calibration limit of the instrument is diluted and reanalyzed. This is done by diluting the extract in a known volume of hexane and analyzing. A dilution factor is then incorporated into the final result calculation (Sec. 9.5).

9.4 Qualitative analysis of results

9.4.1 Qualitative results in this analysis are based on retention time of analyte and pattern recognition.

9.4.2 Compounds must also fall within their respective retention time windows. The retention time window is calculated by recording the retention time of an analyte over a 72 hour period, generally using three opening standard data points. The mean retention time and standard deviation is calculated for each analyte. The width of the time window is then defined as ±3 times the standard deviation. Any analyte appearing within this window is considered a positive hit (up to the analyst's discretion).

9.5 Quantitative analysis of results

9.5.1 When linear calibration that does not pass through the origin is employed, the concentration of the analyte is calculated from the area response (y), the slope (a), and the intercept (b). When using this form of linear regression, it is the laboratory's responsibility to ensure that the calculations take into account the volume or weight of the original sample, the dilution factor (if applicable), and the dry weight (as applicable). One approach to this calculation is to perform the original linear regression using the concentration of the analyte in the final extract volume. The concentration of the analyte in the sample may then be calculated as follows:

$$C_s = \frac{(C_{ex})(V_t)}{(W_t)(W_d)}$$

where:

C_s = Concentration in sample
C_{ex} = Concentration in the final extract
V_t = Total volume of the concentrated extract
W_t = Weight of the sample extracted
W_d = Dry weight of the sample extracted

9.5.2 An alternative, which is not used at the GE Housatonic River Site, to calculate quantitative results involves using an external standard response factor from the initial calibration.

9.5.2.1 PCB quantitation. Calculate PCBs using an external calculation. A minimum of three peaks should be used for quantitation. For aqueous samples:

$$\text{Conc. } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(V_s)}$$

where:

A_x = Area of peaks of Aroclor in sample
V_t = Volume of sample extract
D = Dilution factor
CF = Mean calibration factor
V_i = Volume of sample injected (µL)
V_s = Volume of sample extracted, typically 40 mL

For solid samples:

$$\text{Conc. } (\mu g/Kg) = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(W)}$$

All variables are the same except for W, which is the dry weight of the sample.

Dry weight is calculated by multiplying the amount of sample used in the extract by the decimal dry weight value. I.e. if the %solids of sample Y is 86.2%, and 5.02 g was used in the extraction, then the dry weight is calculated in the following manner: 5.02g * 0.862 = 4.33 g.

10.0 ACCEPTANCE OF DATA AND METHOD PERFORMANCE

10.1 All initial calibration data must be within compliances listed in Sec. 7.0.

10.2 All continuing calibration results must be within compliances listed in Sec. 8.1.

10.3 LCS (Laboratory Control Spike) recoveries must be within 50 -130% of the spike value for Aroclor 1260. If these criteria are not met, then the entire batch must be reextracted.

10.4 Extraction blanks must not contain target analytes above ½ the PQL for that specified analyte. If this is not the case, then the entire batch must be reextracted.

10.5 Matrix spikes and LCS recoveries should fall within 50 - 130% of the spiked value. Concentrations that fall outside of this window for MS/MSDs are noted to the client and no corrective action is taken. If concentrations fall outside of the acceptable window for the LCS, then the entire extraction batch is reextracted and reanalyzed. The RPD for MS/MSD should be 40% or less.

10.6 Surrogate recoveries must fall within 30 - 150% of the spiked value. The percent recovery for one of the two surrogates (TCMX and DCBP) must fall within this window. If they do not, then the sample is reextracted. If the surrogate recoveries still fail, then the sample is said to exhibit a matrix effect. Both the original results and the reextracted/reanalyzed results will be reported if the recoveries fail a second time.

10.7 Matrix spike and LCS sample criteria are listed in Sec. 10.5. Outliers are discussed in case narrative, and in the case of failed LCS criteria, the entire extraction batch is reextracted and reanalyzed.

10.8 An independent check standard must be run following each initial calibration. The %DIFF between the original and the independent standards must be < 30%. If the %DIFF exceeds 30% a new standard is prepared and analyzed. If this still fails, a new initial calibration curve will be analyzed and the second source will be reanalyzed upon completion of the new curve. Results of the independent check standard are kept on file at the laboratory.

10.9 MDLs are run once every year, or after major instrumentation changes, such as new columns, new detector, etc. See 40 CFR, Part 136, Appendix B, for details. A minimum of seven samples are analyzed for the MDL.

10.9.1 MDLs are also used to generate low level standard limits for all Aroclors. The acceptance window is determined by averaging the values of each Aroclor peak from the seven MDL samples. The width of this acceptance window is calculated as ±3 standard deviations of the average. Any peak in a 0.5 ppm Aroclor check standard having a value outside this window is not used in the final calculation.

11.0 REFERENCES

1. SW-846, Revision 2, December 1996, Method 8082.

2. Weston SOW for Prime Contract DACW33-94-D-0009

12.0 GLOSSARY

Extraction Blank: A known matrix, usually commercially purchased dried sand, spiked with surrogate solution only. The blank should be free of target analytes and other interfering contaminants. A "clean" extraction blank demonstrates that the extraction process is not introducing target analytes into the samples.

Instrument Blank: Also known as a solvent blank. Hexane is analyzed every ten samples to show that there is no contamination from the instrument being introduced into the samples. Possible sources of instrument contamination are dirty syringes, dirty hexane rinse bottles, dirty injection ports or head of columns, among other sources.

LCS: Laboratory Control Spike. A known matrix, usually commercially purchased dried sand, spiked with a known amount of target analytes in addition to surrogates. The acceptable recovery of these analytes indicates that the extraction process is working correctly.

Matrix Spike: An environmental (i.e. field) sample which is spiked with known amounts of analyte(s). The amount of recovery of these analytes indicates how well the extraction process is working on a particular matrix type. Matrix spike samples are generally analyzed in duplicate and a %RPD is calculated.

STANDARD OPERATING PROCEDURE FOR DETERMINATION POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY / ELECTRON CAPTURE DETECTOR (MODIFIED EPA 8082)

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USACE

1.0 HEALTH AND SAFETY

1.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Treat each chemical as a potential health hazard and minimize potential exposure. Handle stock standard solutions containing these compounds in a fume hood. Wear personal protective equipment such as lab coats, gloves and safety glasses while performing this analysis.

1.2 All reagents and standards used for analysis must be accompanied to the laboratory by manufacturer's Material Data Safety (MSD) Sheets. MSD Sheets are kept on file in the laboratory in binders labeled MSDS on a bookshelf in the data processing area, and are available to all laboratory personnel. As part of the training process, analysts make themselves familiar with the contents of the MSD Sheets.

1.3 Secure all compressed gas cylinders with chains or straps. Train analysts in tank changing procedures.

2.0 SCOPE AND APPLICATION

2.1 The purpose of this SOP is to outline, in detail, the technique of determining polychlorinated biphenyls (PCBs) by GC/ECD. This method is based on Method 8082, SW-846, Rev. 2, Dec 1996. This method is applicable to soil and sediment samples and rinse blank samples collected at the GE Housatonic River Site.

2.2 General method information:

2.2.1 Severe weathering may affect Aroclor patterns. Thus, the experience of the analyst plays a large role in the identification of Aroclors. Samples displaying unusual or significant weathering patterns will be addressed in the report narrative.

2.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method. This includes

having the analyst extract four LCS (Laboratory Control Spike) samples. Recoveries of the spiked compounds must be within ±25% of the spiked values, and the Relative Percent Difference (RPD) between the four results must not exceed 20%. Records for each analyst are kept on site for examination.

3.0 SUMMARY OF METHOD

3.1 Thirty (30) g of a soil or sediment sample is dried overnight in an oven at 75 degrees C. A five (5) g aliquot is weighed and dried further using sodium sulfate and methanol, and then extracted using 5 mL of hexane. The sample is vortexed then shaken for an hour on a shaker table and the resulting hexane layer is transferred to a 4.0 mL vial. The extract is then copper cleaned to remove sulfur and then acid cleaned with sulfuric acid.

3.2 For aqueous rinse blank samples, 40 mL of water is extracted with 1 mL of hexane and shaken vigorously for twenty minutes. The hexane layer is drawn off and analyzed. No cleanup procedures are performed on the water samples. It sample shows evidence of Aroclors, it is immediately reported to Weston.

3.3 For hexane rinse blank samples, a 1 mL aliquot is spiked with surrogate and analyzed. No cleanup procedures are performed on the hexane samples. If sample shows evidence of Aroclors, it is immediately reported to Weston.

4.0 INTERFERENCES

4.1 Major contaminant sources are contaminated solvents and glassware used during initial sample extraction and concentration. Ensure that solvents meet ACS certification for pesticide residue and/or HPLC analysis and that glassware is free from contamination. Since new, unused scintillation vials are used for every sample, cross contamination from the laboratory is most likely very minimal. Extract a sample blank at the same time and under the same conditions as the samples and analyze before the sample extracts to determine if any contaminants are present. Common contaminants are the phthalate esters, which come from rubber gloves and other rubber materials in the lab in addition to outside sources, and sulfur present in samples.

4.2 Contamination also occurs in the case of carryover, where a low level sample is analyzed immediately following a high concentration sample. Analyze solvent checks following high level samples to determine system carryover. A sample would be considered high concentration if it exceeded 10 times the upper calibration limit. If high level samples are analyzed when an analyst is not present (i.e. overnight using the autosampler), then samples which contain Aroclors analyzed immediately following the high level samples are reanalyzed to confirm the concentration of Aroclor present in the sample.

4.3 Perform adequate maintenance, such as changing septa on GC#1 and changing the injection port liners and clipping columns in order to reduce active sites and improve general chromatography on both GC systems.

5.0 APPARATUS AND MATERIALS

5.1 Hewlett-Packard dual tower 7673 vial autosampler system.

5.2 Gas chromatography/electron capture system (GC/ECD) #1.

5.2.1 Hewlett-Packard 5890A Series II GC.

5.2.2 Hewlett-Packard dual ECD detectors

5.2.3 Two Supelco SPB-5 30 m x 0.53 mm ID, 1.0 µm film thickness columns.

5.3 Gas chromatography/electron capture system (GC/ECD) #2:

5.3.1 Hewlett-Packard 5890 Series II GC with Electronic Pressure Control (EPC).

5.3.2 Hewlett-Packard dual ECD detectors

5.3.3 Two Supelco SPB-5 30 m x 0.53 mm ID, 1.0 µm film thickness columns.

5.4 Data system

5.4.1 Two computers with enough memory to simultaneously run Excel and Chemstation software.

5.4.2 Hewlett-Packard Chemstation software for integrating and processing signals generated by the GC/ECD system.

5.5 Microsyringes - Hamilton 5-, 10-, 25-, 100-, 250-, 500- and 1000-µL

5.6 AND EK-120, top loading balance, capable of weighing to 0.01 g.

5.7 Disposable Pasteur pipettes, pipette bulbs

5.8 Class A Volumetric glassware - 10 mL and 100 mL

5.9 Stainless steel spatulas

5.10 20 mL Scintillation Vials, with teflon lined caps

5.11 4 mL vials, with teflon lined caps

5.12 Certified weights, 0.1 g - 100 g.

6.0 REAGENTS AND STANDARDS PREPARATION

6.1 n-Hexane (VWR) - pesticide grade

6.2 Methanol, (VWR) - pesticide grade

6.3 Acetone (VWR) - pesticide grade

6.4 Stock standards

6.4.1 Purchase the following stock standards from ABSOLUTE as certified solutions, and use for PCB/Aroclor calibrations:

- 90127, Aroclor 1248, 1000 µg/mL
- 90128, Aroclor 1254, 1000 µg/mL
- 90129, Aroclor 1260, 1000 µg/mL
- 70103, Decachlorobiphenyl, 1000 µg/mL

- 70273, Tetrachloro-m-Xylene, 1000 µg/mL

6.4.2 Purchase the following stock standards from ACCUSTANDARD as certified solutions, and use for second source verification checks:

- C-248S-H-10X, Aroclor 1248, 1000 µg/mL
- C-254S-H-10X, Aroclor 1254, 1000 µg/mL
- C-260S-H-10X, Aroclor 1260, 1000 µg/mL

6.4.3 Also keep on hand Aroclor 1016, 1221, 1232 and 1242 to analyze in case PCBs other than Aroclor 1248, 1254 or 1260 are detected. PCBs listed above are purchased in 1000 µg/mL solutions, and are prepared as in Sec. 7.1, below. If a sample is suspected of containing one or more of the "non-target" Aroclors, then either a new curve or a midpoint (See Sec 8.1.1. for midpoint definition) is analyzed for each suspected Aroclor and the sample is reanalyzed for the suspected Aroclors.

6.5 Store standards at 4°C.

7.0 CALIBRATION PROCEDURE

7.1 Calibration Curve Preparation for PCBs: Analyze a 5-point initial calibration curve for each Aroclor. Prepare the 5-point curves as below:

Make an initial dilution of each PCB stock standard. All "Standard added" amounts refer to this dilution. Prepare the initial dilution by adding 1 mL of the stock PCB standards to a 10 mL volumetric flask and bring to volume in hexane. The concentration of these standards are 100 µg/mL.

Make an initial dilution of the surrogate standard solution by bringing 2 mL of tetrachloro-m-xylene and 2 mL of decachlorobiphenyl to 10 mL in hexane. The concentration of this standard is 200 µg/mL.

Prepare the working curve standards the following way:

Conc. (PCB/ Surr)	Std added	SS. added	Final volume
20/2 µg/mL	2 mL	0.1 mL	10 mL
10/1µg/mL	1 mL	0.05 mL	10 mL
5//0.5 µg/mL	0.5 mL	0.025 mL	10 mL
1/0.1 µg/mL	0.1 mL	0.005 mL	10 mL
0.5/0.05 µg/mL	0.05 mL	0.0025 mL	10 mL

This is done for each set of Aroclor standards.

7.1.1 The working range of the method is limited to the upper range of the calibration curve. Samples with analytes that exceed the upper calibration range are reanalyzed at a dilution, with the concentration of the analytes in question ideally falling into the upper half of the calibration range.

7.1.2 "Prime" (deactivate) column before curve is analyzed by injecting the midpoint Aroclor 1260 standard or any midlevel or higher Aroclor standard.

7.2 Curve acceptance criteria for PCBs:

There are two methods for calculating the acceptability of the calibration curve. The first is an average of Calibration Factors. The second is a linear regression not forced through the origin. For the Calibration Factor method seven peaks are chosen for each Aroclor. Peaks for each Aroclor are at least 25% of the height of the largest Aroclor peak.

7.2.1 Calculate the Calibration Factor (CF) for each characteristic Aroclor peak.

$$CF = \frac{\text{Peak Area of Compound in Standard}}{\text{Mass of Compound (ng)}}$$

7.2.2 Calculate the mean calibration factor for each characteristic peak using the Chemstation software. The formula is as follows:

$$\text{mean CF} \Rightarrow \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

where n is the number of standards analyzed.

7.2.3 Calculate the standard deviation (SD) and the %RSD of the calibration factors for each Aroclor peak and TCB as

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})2}{n-1}} \qquad \%RSD = \frac{SD}{CF} x100$$

If the %RSD for each Aroclor Peak is < 25%, a linear regression not forced through the origin (also called a calibration curve) is used to calculate concentrations. The correlation coefficient for each Aroclor Peak and TCB must be > 0.995, or a new curve must be analyzed.

In general, the concentration for each individual peak in a given Aroclor is calculated and then they are averaged together. This is done so that if there are interferences, such as other chlorinated analytes (such as pesticides, solvents, chlordane, etc.), the presence of multiple Aroclors, the presence of sulfur, the affect of those interferences can be evaluated on a peak by peak basis to determine if an Aroclor peak should be included in the concentration calculation. Examining each peak is also essential in determining if weathering/degradation has occurred.

7.2.4 Retention time windows: Absolute retention times are essential for compound identification. The retention time for each characteristic Aroclor peak is determined by averaging the retention time over three days and calculating the standard deviation (see formula in Sec. 7.2.3). The width of the of the retention time window is defined as ±3 standard deviations of the average. See Sec. 9.4.2 for further details.

8.0 QUALITY CONTROL

8.1 Before analysis of samples can proceed, calibration verification must occur.

8.1.1 Perform midpoint continuing calibration checks. The midpoint calibration standard in this case is a 5 ppm Aroclor. All Aroclor mixtures (i.e. Aroclor 1248, 1254, etc.) are analyzed and must be within ±25% of the initial calibration for analysis to continue. The % Difference is calculated as follows:

$$\%\,\mathrm{Diff} = \frac{CF - \overline{CF}_y}{CF} x100$$

This calibration occurs before samples are analyzed. All Aroclors must pass before analysis of samples can occur. After every tenth sample analyze an instrument blank and a midpoint calibration of Aroclor 1260. The instrument blank must be free of extraneous peaks and the recovery of the Aroclor must fall within the ± 25% window for analysis to continue. A closing set of an instrument blank/standard analyses must also be analyzed after the last samples, and they must be fall within the ± 25% window for results to be considered valid. If the Aroclor mixture fails to meet criteria then samples must be reanalyzed.

Before the opening calibration check, and before each continuing calibration check, an instrument blank is analyzed. The instrument blank must be free of Aroclors or any other potential interfering compounds. Interfering contamination would be Aroclor patterns, or other large peaks that have the potential to bias or interfere with the calculation of Aroclor concentrations.

9.0 INSTRUMENT CONDITIONS AND SAMPLE ANALYSIS

9.1 Instrument Conditions:

9.1.2 GC #1 conditions (No EPC):

Injection port temperatures:	225 °C
Detector A temperature:	325 °C
Detector A temperature:	325 °C
Initial temperature:	140 °C
Initial time:	1.5 min
Rate (°C/min):	7.5
Temperature:	200 °C
Hold time:	0.5 min
Rate (°C/min):	12
Final temperature:	260 °C
Final time:	5.5 min
Total time:	20.5 min

9.1.3 GC #2 conditions (w/EPC):

Injection port temperatures:	200 °C
Detector A temperature:	300 °C
Detector A temperature:	300 °C
Constant flow:	2.0 mL/min
Initial pressure:	10.0 psi
Initial temperature:	140 °C
Initial time:	1.00 min
Rate (°C/min):	8.0

Temperature:	200
Hold time:	0.00
Rate (°C/min):	12
Final temperature:	265 °C
Final time:	6.5 min
Total time:	20.00 min

9.1.4 HP 7673 Injectors (Dual Tower, both systems)

Solvent washes:	5
Sample pumps:	5
Injection volume:	1 µL
Oncolumn:	No

9.2 Sample Preparation:

9.2.1 Soil Sample Preparation:

9.2.1.1 Homogenize sample in container by mixing thoroughly with clean stainless steel spatula. Remove any rocks and/or twigs prior to mixing the sample.

9.2.1.2. Weigh out at least 30 g into an aluminum weighing tin. To do this, zero the balance, place the weigh boat on top of the scale and record the weight. Without zeroing, add 30 + g of sample. For the LCS and the blank, use clean, qdry sand. Place in an oven at 65-75 °C for 12 hours.

9.2.1.3 At the same time, weigh out at least ten grams of sample into a weigh boat for % solids determination. To do this, zero the balance, place the weigh boat on top of the scale and record the weight. Without zeroing, add 10 + g of sample and record this weight. Place in oven at 105 °C for at least 12 hours and record the final weight. Record date and time into and out of oven. Calculate the %solids (PS1) in the following manner:

$$\%\text{solids (PS1)} = \frac{(\text{(dry wt.)-(tin wt.)})}{(\text{(wet wt.)-(tin wt.)})} \times 100^{*}$$

* This is the true percent solids of the the sample.

9.2.1.4 From the 30 g weighing tin measure a five (5) g (±0.1g) aliquot into a 20 mL pre-cleaned VOA vial. Weigh and record weight of sample remaining in the weighing tin. Place the weighing tin into an oven at 105 °C for approximately 8 hours. after 8 hours remove the tin from the oven and record the weight. Be sure to record date and time placed in and removed from the oven. Calculate percent solids in the following manner:

$$\%\text{ solids (PS2)} = \frac{(\text{(dry wt.) - (tin wt)})}{(\text{(wet wt.) - (tin wt.)})} \times 100^{**}$$

** This is the percent solids value that will be used in the calculations of the samples.

9.2.1.5 To the 5.0g in the 20 mL voa vial add sodium sulfate that has been solvent rinsed with hexane, muffled overnight at 450 °C, and stored in a desiccator. The amount of sodium sulfate will vary depending on the amount of moisture left in the sample. Add completely dry. When sample is completely dry it will have the texture of dry sand.

9.2.1.6 Spike dried samples with 25 µL of surrogate. Add 25 µL of Aroclor 1260 to the LCS, MS, and MSD. Be sure to clean the syringes by flushing several times with hexane before and after use. Another technician or analyst must witness spiking and initial in the extraction logbook. Add 1.0 mL of methanol and 5.0 mLs of hexane and vortex for thirty (30) seconds. Place samples on shaker table to shake for 60 minutes.

9.2.1.7 After an hour remove the samples from the shaker table. Pipette off the hexane layer and transfer into a 4.0 mL vial. Remove any sulfur from the sample. This is done by first treating approximately 5 g of copper with dilute nitric acid and then rinsing the copper 5 times with distilled water to remove the acid. The copper is then considered "activated", and must either be used immediately, or it can be stored under acetone. If it is stored under acetone, it must be dried for four hours before use. Add approximately 1.0 g of copper to extract and vortex for 15 seconds. Solution will be clear if sulfur is removed. Repeat this step until all sulfur is removed from the sample.

9.2.1.8 When sulfur cleanup is done, pipette extract into another 4.0 mL vial. Approximately a 1: 1 volume of sulfuric acid is added to the extract, and the extract is vortexed for 15 seconds. The acid phase and hexane layer are allowed to separate. Repeat if necessary. Being careful not to transfer any acid, pipette the hexane layer into a clean autosampler vial.

9.2.1.9 Proceed to analysis of samples (Sec. 9.3)

9.2.3 Hexane field blank preparation:

9.2.3.1. Hexane rinse blanks are supplied in 40 mL VOA vials. 1 mL of the hexane is transferred to a 2 mL sample vial, and 5 µL of the 200 µg/mL Surrogate mixture is added. The sample is then analyzed. No cleanup procedures are performed on the sample.

9.3 Analysis of samples:

9.3.1. Start by analyzing an instrument blank followed by the three Aroclor mixtures. Criteria must meet those outlined in Sec. 8.1.1. Sample analysis follows, generally in the following order: LCS, Blank, samples, MS/MSD. After every ten samples, an instrument blank and midpoint (5 µg/mL) Aroclor 1260 mixture is analyzed, and must meet results listed in Sec. 8.1. A closing check of 0.5 ppm Aroclor is analyzed before the final midpoint Aroclor 1260 check. A sample analytical sequence follows:

Instrument Blank
Opening calibration checks
LCS
Extraction Blank

Samples (up to ten, including LCS & Blank)
Instrument Blank
Continuing 1260 check
Samples (up to ten-- included under the definition of samples are MS/MSD samples)
0.5 ppm 1260 Check
Instrument blank
Closing 1260 Check.

The 0.5 ppm 1260 check must be within ±25% of its true concentration. If it is not within these limits, it could indicate that the instrument is no longer accurately "seeing" and quantitating low level concentrations. It the 0.5 ppm is out of compliance for Aroclor 1260 all samples which have concentrations of Aroclors below 0.5 ppm or have non-detects for the Aroclors are reanalyzed. This is noted in the case narrative. If the 0.5 ppm standard continues to fail, then a new curve must be analyzed. All non-detected results are "J" qualified as estimates.

9.3.2. Sample results are checked as soon as they come off the instrument as possible. Any sample result that exceeds the upper calibration limit of the instrument is diluted and reanalyzed. This is done by diluting the extract in a known volume of hexane and analyzing. A dilution factor is then incorporated into the final result calculation (Sec. 9.5).

9.4 Qualitative analysis of results

9.4.1 Qualitative results in this analysis are based on retention time of analyte and pattern recognition.

9.4.2 Compounds must also fall within their respective retention time windows. The retention time window is calculated by recording the retention time of an analyte over a 72 hour period, generally using three opening standard data points. The mean retention time and standard deviation is calculated for each analyte. The width of the time window is then defined as ±3 times the standard deviation. Any analyte appearing within this window is considered a positive hit (up to the analyst's discretion).

9.5 Quantitative analysis of results

9.5.1 Quantitative results are calculated using an external standard response factor from the initial calibration.

9.5.1.1 PCB quantitation. Calculate PCBs using an external calculation. A minimum of three peaks should be used for quantitation. For aqueous samples:

$$\text{Conc. } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(V_s)}$$

where:

A_x = Area of peaks of Aroclor in sample
V_t = Volume of sample extract
D = Dilution factor
CF = Mean calibration factor
V_i = Volume of sample injected (µL)
V_s = Volume of sample extracted, typically 40 mL

For solid samples:

$$\text{Conc. } (\mu g/Kg) = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(W)}$$

All variables are the same except for W, which is the dry weight of the sample. Dry weight is calculated by multiplying the amount of sample used in the extract by the decimal dry weight value. I.e. if the %solids of sample Y is 86.2%, and 5.02 g was used in the extraction, then the dry weight is calculated in the following manner: 5.02g * 0.862 = 4.33 g.

Alternately, concentrations are calculated using a linear regression calculation (See Sec.7.2).

10.0 ACCEPTANCE OF DATA AND METHOD PERFORMANCE

10.1 All initial calibration data must be within compliances listed in Sec. 7.0.

10.2 All continuing calibration results must be within compliances listed in Sec. 8.1.

10.3 LCS (Laboratory Control Spike) recoveries must be within 50 -130% of the spike value for Aroclor 1260. If these criteria are not met, then the entire batch must be reextracted.

10.4 Extraction blanks must not contain target analytes above ½ the PQL for that specified analyte. If this is not the case, then the entire batch must be reextracted.

10.5 Matrix spikes and LCS recoveries should fall within 50 - 130% of the spiked value. Concentrations that fall outside of this window for MS/MSDs are noted to the client and no corrective action is taken. If concentrations fall outside of the acceptable window for the LCS, then the entire extraction batch is reextracted and reanalyzed. The RPD for MS/MSD should be 40% or less.

10.6 Surrogate recoveries must fall within 30 - 150% of the spiked value. The percent recovery for one of the two surrogates (TCMX and DCBP) must fall within this window. If they do not, then the sample is reextracted. If the surrogate recoveries still fail, then the sample is said to exhibit a matrix effect. Both the original results and the reextracted/reanalyzed results will be reported if the recoveries fail a second time.

10.7 Matrix spike and LCS sample criteria are listed in Sec. 10.5. Outliers are discussed in case narrative, and in the case of failed LCS criteria, the entire extraction batch is reextracted and reanalyzed.

10.8 An independent check standard must be run following each calibration. The %DIFF between the original and the independent must be < 30%. If of the %DIFF is > 30% then a new standard is prepared. If this still fails, a new initial calibration curve will be analyzed and the second source will be reanalyzed upon completion of the new curve. Results of the independent check standard are kept on file at the laboratory.

10.9 MDLs are run once every year, or after major instrumentation changes, such as new columns, new detector, etc. See 40 CFR, Part 136, Appendix B, for details. A minimum of seven samples are analyzed for the MDL.

11.0 REFERENCES

1. SW-846, Revision 2, December 1996, Method 8082.

2. Weston SOW for Prime Contract DACW33-94-D-0009

12.0 GLOSSARY

Extraction Blank: A known matrix, usually commercially purchased dried sand, spiked with surrogate solution only. The blank should be free of target analytes and other interfering contaminants. A "clean" extraction blank demonstrates that the extraction process is not introducing target analytes into the samples.

Instrument Blank: Also known as a solvent blank. It is hexane spiked with surrogate. It is analyzed every ten samples to show that there is no contamination from the instrument being introduced into the samples. Possible sources of instrument contamination are dirty syringes, dirty hexane rinse bottles, dirty injection ports or head of columns, among other sources.

LCS: Laboratory Control Spike. A known matrix, usually commercially purchased dried sand, spiked with a known amount of target analytes in addition to surrogates. The acceptable recovery of these analytes indicates that the extraction process is working correctly.

Matrix Spike: An environmental (i.e. field) sample which is spiked with known amounts of analyte(s). The amount of recovery of these analytes indicates how well the extraction process is working on a particular matrix type. Matrix spike samples are generally analyzed in duplicate and a %RPD is calculated.

STANDARD OPERATING PROCEDURE FOR DETERMINATION POLYCHLORINATED BIPHENYLS (PCBs) AND 1,2,4-TRICHLOROBENZENE BY GAS CHROMATOGRAPHY / ELECTRON CAPTURE DETECTOR (MODIFIED EPA 8082)

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1.0 HEALTH AND SAFETY

1.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Treat each chemical as a potential health hazard and minimize potential exposure. Handle stock standard solutions containing these compounds in a fume hood. Wear personal protective equipment such as lab coats, gloves and safety glasses while performing this analysis.

1.2 All reagents and standards used for analysis must be accompanied to the laboratory by manufacturer's Material Data Safety (MSD) Sheets. MSD Sheets are kept on file in the laboratory in binders labeled MSDS on a bookshelf in the data processing area, and are available to all laboratory personnel. As part of the training process, analysts make themselves familiar with the contents of the MSD Sheets.

1.3 Secure all compressed gas cylinders with chains or straps. Train analysts in tank changing procedures.

2.0 SCOPE AND APPLICATION

2.1 The purpose of this SOP is to outline, in detail, the technique of determining polychlorinated biphenyls (PCBs) and 1,2,4-trichlorobenzene (TCB) by GC/ECD. This method is based on Method 8082, SW-846, Rev. 2, Dec 1996. This method is applicable to soil and sediment samples and rinse blank samples collected at the GE Housatonic River Site.

2.3 General method information:

2.3.1 Severe weathering may affect Aroclor patterns. Thus, the experience of the analyst plays a large role in the identification of Aroclors. Samples displaying unusual or significant weathering patterns will be addressed in the report narrative.

2.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method. This includes

having the analyst extract four LCS (Laboratory Control Spike) samples. Recoveries of the spiked compounds must be within ±25% of the spiked values, and the Relative Perecent Difference (RPD) between the four results must not exceed 20%. Records for each analyst are kept on site for examination.

3.0 SUMMARY OF METHOD

3.1 Thirty (30) g of a soil or sediment sample is dried overnight in an oven at 75 degrees C. A five (5) g aliquot is weighed and dried further using sodium sulfate and methanol, and then extracted using 5 mL of hexane. The sample is vortexed then shaken for and hour ona shaker table and the resulting hexane layer is transferred to a 4.0 mL vial. The extract is then copper cleaned to remove sulfur and then acid cleaned with sulfuric acid.

3.2 For aqueous rinse blank samples, 40 mL of water is extracted with 1 mL of hexane and shaken vigorously for twenty minutes. The hexane layer is drawn off and analyzed. No cleanup procedures are performed on the water samples. It sample shows evidence of Aroclors, it is immediately reported to Weston.

3.3 For hexane rinse blank samples, a 1 mL aliquot is spiked with surrogate and analyzed. No cleanup procedures are performed on the hexane samples. If sample shows evidence of Aroclors, it is immediately reported to Weston.

4.0 INTERFERENCES

4.1 Major contaminant sources are contaminated solvents and glassware used during initial sample extraction and concentration. Ensure that solvents meet ACS certification for pesticide residue and/or HPLC analysis and that glassware is free from contamination. Since new, unused scintillation vials are used for every sample, cross contamination from the laboratory is most likely very minimal. Extract a sample blank at the same time and under the same conditions as the samples and analyze before the sample extracts to determine if any contaminants are present. Common contaminants are the phthalate esters, which come from rubber gloves and other rubber materials in the lab in addition to outside sources, and sulfur present in samples.

4.2 Contamination also occurs in the case of carryover, where a low level sample is analyzed immediately following a high concentration sample. Analyze solvent checks following high level samples to determine system carryover. A sample would be considered high concentration if it exceeded 10 times the upper calibration limit. If high level samples are analyzed when an analyst is not present (i.e. overnight using the autosampler), then samples which contain Aroclors analyzed immediately following the high level samples are reanalyzed to confirm the concentration of Aroclor present in the sample.

4.3 Perform adequate maintenance, such as changing septa on GC#1 and changing the injection port liners and clipping columns in order to reduce active sites and improve general chromatography on both GC systems.

5.0 APPARATUS AND MATERIALS

5.1 Hewlett-Packard dual tower 7673 vial autosampler system.

5.2 Gas chromatography/electron capture system (GC/ECD) #1.

5.2.1 Hewlett-Packard 5890A Series II GC.

5.2.2 Hewlett-Packard dual ECD detectors

5.2.3 Two Supelco SPB-5 30 m x 0.53 mm ID, 1.0 µm film thickness columns.

5.3 Gas chromatography/electron capture system (GC/ECD) #2:

5.3.1 Hewlett-Packard 5890 Series II GC with Electronic Pressure Control (EPC).

5.3.2 Hewlett-Packard dual ECD detectors

5.3.3 Two Supelco SPB-5 30 m x 0.53 mm ID, 1.0 µm film thickness columns.

5.4 Data system

5.4.1 Two computers with enough memory to simultaneously run Excel and Chemstation software.

5.4.2 Hewlett-Packard Chemstation software for integrating and processing signals generated by the GC/ECD system.

5.5 Microsyringes - Hamilton 5-, 10-, 25-, 100-, 250-, 500- and 1000-µL

5.6 AND EK-120, top loading balance, capable of weighing to 0.01 g.

5.7 Disposable Pasteur pipettes, pipette bulbs

5.8 Class A Volumetric glassware - 10 mL and 100 mL

5.9 Stainless steel spatulas

5.10 20 mL Scintillation Vials, with teflon lined caps

5.11 4 mL vials, with teflon lined caps

5.12 Certified weights, 0.1 g - 100 g.

6.0 REAGENTS AND STANDARDS PREPARATION

6.1 n-Hexane (VWR) - pesticide grade

6.2 Methanol, (VWR) - pesticide grade

6.3 Acetone (VWR) - pesticide grade

6.4 Stock standards

6.4.1 Purchase the following stock standards from ABSOLUTE as certified solutions, and use for PCB/Aroclor calibrations:

- 90127, Aroclor 1248, 1000 µg/mL
- 90128, Aroclor 1254, 1000 µg/mL
- 90129, Aroclor 1260, 1000 µg/mL
- 70103, Decachlorobiphenyl, 1000 µg/mL

- 70273, Tetrachloro-m-Xylene, 1000 µg/mL
- 70289, 1,2,4-Trichlorobenzene, 1000 µg/mL

6.4.2 Purchase the following stock standards from ACCUSTANDARD as certified solutions, and use for second source verification checks:

- C-248S-H-10X, Aroclor 1248, 1000 µg/mL
- C-254S-H-10X, Aroclor 1254, 1000 µg/mL
- C-260S-H-10X, Aroclor 1260, 1000 µg/mL
- CF8S, 1,2,4-Trichlorobenzene, 1000 µg/mL (Purchased from VWR)

6.4.3 Also keep on hand Aroclor 1016, 1221, 1232 and 1242 to analyze in case PCBs other than Aroclor 1248, 1254 or 1260 are detected. PCBs listed above are purchased in 1000 µg/mL solutions, and are prepared as in Sec. 7.1, below. If a sample is suspected of containing one or more of the "non-target" Aroclors, then either a new curve or a midpoint (See Sec 8.1.1. for midpoint definition) is analyzed for each suspected Aroclor and the sample is reanalyed for the suspected Aroclors.

6.5 Store standards at 4°C.

7.0 CALIBRATION PROCEDURE

7.1 Calibration Curve Preparation for PCBs: Analyze a 5-point initial calibration curve for each Aroclor and for TCB. The TCB compound may be included in the Aroclor standard mixture, as it elutes well outside of the expected Aroclor ranges.. Prepare the 5-point curves as below:

Make an initial dilution of each PCB stock standard. All "Standard added" amounts refer to this dilution. Prepare the initial dilution by adding 1 mL of the stock PCB standards to a 10 mL volumetric flask and bring to volume in hexane. The concentration of these standards are 100 µg/mL. In addition, prepare a stock standard of TCB by diluting 100 µL of stock solution into 1 mL of methanol. The concentration of this standard is 100 µg/mL.

Make an initial dilution of the surrogate standard solution by bringing 2 mL of tetrachloro-m-xylene and 2 mL of decachlorobiphenyl to 10 mL in hexane. The concentration of this standard is 200 µg/mL.

Prepare the working curve standards the following way

Conc. (PCB/TCB/Surr)	Std added	TCB added	SS. added	Final volume
20/1/2 µg/mL	2 mL	10 µL*	0.1 mL	10 mL
10/0.5/1 µg/mL	1 mL	0.5 mL	0.05 mL	10 mL
5/0.1/0.5 µg/mL	0.5 mL	0.100 mL	0.025 mL	10 mL
1/0.05/0.1 µg/mL	0.1 mL	50 µL	0.005 mL	10 mL
0.5/0.01/0.05 µg/mL	0.05 mL	10 µL	0.0025 mL	10 mL

* 10 µL of the 1000 µg/mL stock standard is added instead of 1 mL of the 10 µg/mL working standard.
This is done for each set of Aroclor standards.

7.1.1 The working range of the method is limited to the upper range of the calibration curve. Samples with analytes that exceed the upper calibration range are reanalyzed at a dilution, with the concentration of the analytes in question ideally falling into the upper half of the calibration range.

7.1.2 "Prime" (deactivate) column before curve is analyzed by injecting the midpoint Aroclor 1260 standard or any midlevel or higher Aroclor standard.

7.2 Curve acceptance criteria for PCBs and TCB:

There are two methods for calculating the acceptability of the calibration curve. The first is an average of Calibration Factors. The second is a linear regression not forced through the origin. For the Calibration Factor method seven peaks are chosen for each Aroclor, and the TCB is identifed separately. Peaks for each Aroclor are at least 25% of the height of the largest Aroclor peak.

7.2.1 Calculate the Calibration Factor (CF) for each characteristic Aroclor peak.

$$CF = \frac{\text{Peak Area of Compound in Standard}}{\text{Mass of Compound (ng)}}$$

7.2.2 Calculate the mean calibration factor for each characteristic peak using the Chemstation software. The formula is as follows:

$$\text{mean CF} \Rightarrow \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

where n is the number of standards analyzed.

7.2.3 Calculate the standard deviation (SD) and the %RSD of the calibration factors for each Aroclor peak and TCB as

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})2}{n-1}} \qquad \%RSD = \frac{SD}{CF} x100$$

If the %RSD for each Aroclor Peak and TCB is < 25%, a linear regression not forced through the origin (also called a calibration curve) is used to calculate concentrations. The correlation coefficient for each Aroclor Peak and TCB must be > 0.995, or a new curve must be analyzed.

In general, the concentration for each individual peak in a given Aroclor is calculated and then they are averaged together. This is done so that if there are interferences, such as other chlorinated analytes (such as pesticides, solvents, chlordane, etc.), the presence of multiple Aroclors, the presence of sulfur, the affect of those interferences can be evaluated on a peak by peak basis to determine if an Aroclor peak should be included in the concentration calculation. Examining each peak is also essential in determining if weathering/degradation has occured.

7.2.4 Retention time windows: Absolute retention times are essential for compound identification. The retention time for TCB and each characteristic Aroclor peak is

determined by averaging the retention time over three days and calculating the standard deviation (see formula in Sec. 7.2.3). The width of the of the retention time window is defined as ±3 standard deviations of the average. See Sec. 9.4.2 for further details.

8.0 QUALITY CONTROL

8.1 Before analysis of samples can proceed, calibration verification must occur.

8.1.1 Perform midpoint continuing calibration checks. The midpoint calibration standard in this case is a 5 ppm Aroclor/0.1 ppm 1,2,4-TCB standard. All Aroclor mixtures (i.e. Aroclor 1248, 1254, etc.) are analyzed and must be within ±25% of the initial calibration for analysis to continue. This is true for 1,2,4-TCB as well. The % Difference is calculated as follows:

$$\%\,\mathrm{Diff} = \frac{\mathrm{CF} - \overline{\mathrm{CF}}_y}{\mathrm{CF}} x100$$

This calibration occurs before samples are analyzed. All Aroclors must pass before analysis of samples can occur. After every tenth sample analyze an instrument blank and a midpoint calibration of Aroclor 1260/TCB. The instrument blank must be free of extraneous peaks and the recovery of the Aroclor/TCB must fall within the ± 25% window for analysis to continue. A closing set of an instrument blank/standard analyses must also be analyzed after the last samples, and they must be fall within the ± 25% window for results to be considered valid. If the Aroclor/TCB mixture fails to meet criteria then samples must be reanalyzed.

Before the opening calibration check, and before each continuing calibration check, an instrument blank is analzyed. The instrument blank must be free of Aroclors or any other potential interfering compounds. Interfering contamination would be Aroclor patterns, or other large peaks that have the potential to bias or interfere with the calculation of Aroclor concentrations.

9.0 INSTRUMENT CONDITIONS AND SAMPLE ANALYSIS

9.1 Instrument Conditions:

9.1.2 GC #1 conditions (No EPC):

Injection port temperatures:	225 °C
Detector A temperature:	325 °C
Detector A temperature:	325 °C
Initial temperature:	140 °C
Initial time:	1.5 min
Rate (°C/min):	7.5
Temperature:	200 °C
Hold time:	0.5 min
Rate (°C/min):	12
Final temperature:	260 °C
Final time:	5.5 min
Total time:	20.5 min

9.1.3 GC #2 conditions (w/EPC):

Injection port temperatures:	200 °C
Detector A temperature:	300 °C
Detector A temperature:	300 °C
Constant flow:	2.0 mL/min
Initial pressure:	10.0 psi
Initial temperature:	140 °C
Initial time:	1.00 min
Rate (°C/min):	8.0
Temperature:	200
Hold time:	0.00
Rate (°C/min):	12
Final temperature:	265 °C
Final time:	6.5 min
Total time:	20.00 min

9.1.4 HP 7673 Injectors (Dual Tower, both systems)

Solvent washes:	5
Sample pumps:	5
Injection volume:	1 µL
Oncolumn:	No

9.2 Sample Preparation:

9.2.1 Soil Sample Preparation:

9.2.1.1 Homogenize sample in container by mixing thoroughly with clean stainless steel spatula. Remove any rocks and/or twigs prior to mixing the sample.

9.2.1.2. Weigh out at least 30 g into an aluminum weighing tin. To do this, zero the balance, place the weigh boat on top of the scale and record the weight. Without zeroing, add 30 + g of sample and record this weight. For the LCS and the blank, use clean, dry sand. Place in an oven at 65-75 °C for 12 hours. Remove and record final weight. Record date and time into and out of oven. Calculate the % solids (PS2) in the following manner:

$$\%\text{solids (PS2)} = \frac{((\text{wet wt.})-(\text{tin wt.}))}{((\text{dry wt.})-(\text{tin wt.}))} \times 100$$

9.2.1.3 At the same time, weigh out at least ten grams of sample into a weigh boat for % solids determination. To do this, zero the balance, place the weigh boat on top of the scale and record the weight. Without zeroing, add 10 + g of sample and record this weight. Place in oven at 105 °C for at least 12 hours and record the final weight. Record date and time into and out of oven. Calculate the %solids (PS1) in the following manner:

$$\%\text{solids (PS1)} = \frac{((\text{wet wt.})-(\text{tin wt.}))}{((\text{dry wt.})-(\text{tin wt.}))} \times 100$$

9.2.1.4 Final % solids (PS3),which will be used in final calculations, is calculated in the following manner:

Final % solids (PS3) = 100 - | (PS2 - PS1) |

9.2.1.5 From the 30 g weighing tin measure a five (5) g (±0.1g) aliquot into a 20 mL pre-cleaned VOA vial. Add sudium sulfate that has been muffled overnight at 450 °C and stored in a desiccator. The amount of sodium sulfate will vary depending on the amount of moisture left in the sample. Add and stir in sodium sulfate vigorously with a stainless steel spatula until sample is completely dry. When sample is completely dry it will have the texture of dry sand.

9.2.16. Spike dried samples with 25 µL of surrogate. Add 25 µL of 1,2,4-TCB and 50 µL of Aroclor 1260 to the LCS, MS, and MSD. Be sure to clean the syringes by flushing several times with hexane before and after use. Another technician or analyst must witness spiking and initial in the extraction logbook. Add 1.0 mL of methanol and 5.0 mLs of hexane and vortex for thirty (30) seconds. Place samples on shaker table to shake for 60 minutes.

9.2.1.7 After an hour remove the samples from the shaker table. Pipet off the hexane layer and transfer into a 4.0 mL vial. Remove any sulfur from the sample. This is done by first treating approximately 5 g of copper with dilute nitric acid and then rinsing the copper 5 times with distilled water to remove the acid. The copper is then considered "activated", and must either be used immediately, or it can be stored under acetone. If it is stored under acetone, it must be dried for four hours before use. Add approximately 1.0 g of copper to extract and vortex for 15 seconds. Solution will be clear if sulfur is removed. Repeat this step until all sulfur is removed from the sample.

9.2.1.8 When sulfur cleanup is done, pipet extract into another 4.0 mL vial. Approximately a 1: 1 volume of sulfuric acid is added to the extract, and the extract is vortexed for 15 seconds. The acid phase and hexane layer are allowed to separate. Repeat if necessary. Being careful not to transfer any acid, pipet the hexane layer into a clean autosampler vial.

9.2.1.9 Proceed to analysis of samples (Sec. 9.3)

9.2.3 Hexane field blank preparation:

9.2.3.1. Hexane rinse blanks are supplied in 40 mL VOA vials. 1 mL of the hexane is tranferred to a 2 mL sample vial, and 5 µL of the 200 µg/mL Surrogate mixture is added. The sample is then analyzed. No cleanup procedures are performed on the sample.

9.3 Analysis of samples:

9.3.1. Start by analyzing an instrument blank followed by the three Aroclor/TCB mixtures. Criteria must meet those outlined in Sec. 8.1.1. Sample analysis follows, generally in the following order: LCS, Blank, samples, MS/MSD. After every ten samples, an instrument blank and midpoint (5 µg/mL) Aroclor 1260/TCB mixture is analyzed, and must meet results listed in Sec. 8.1. A closing check of 0.5 ppm Aroclor

is analyzed before the final midpoint Aroclor 1260/TCB check. A sample analytical sequence follows:

Instrument Blank
Opening calibration checks
LCS
Extraction Blank
Samples (up to ten, including LCS & Blank)
Instrument Blank
Continuing 1260/TCB check
Samples (up to ten-- included under the definition of samples are MS/MSD samples)
0.5 ppm 1260 Check
Instrument blank
Closing 1260/TCB Check.

The 0.5 ppm/0.010 ppm 1260/TCB check must be within ±25% of its true concentration. If it is not within these limits, it could indicate that the instrument is no longer accurately "seeing" and quantitating low level concentrations. It the 0.5 ppm is out of compliance for Aroclor 1260 all samples which have concentrations of Aroclors below 0.5 ppm or have non-detects for the Aroclors are reanalyzed. This is noted in the case narrative. If the 0.5 ppm standard continues to fail, then a new curve must be analyzed. If the TCB is out of compliance, it is noted in the narrative and all non-detected results are "J" qualified as estimates.

9.3.2. Sample results are checked as soon as they come off the instrument as possible. Any sample result that exceeds the upper calibration limit of the instrument is diluted and reanalyzed. This is done by diluting the extract in a known volume of hexane and analyzing. A dilution factor is then incorporated into the final result calculation (Sec. 9.5).

9.4 Qualitative analysis of results

9.4.1 Qualitative results in this analysis are based on retention time of analyte and pattern recognition.

9.4.2 Compounds must also fall within their respective retention time windows. The retention time window is calculated by recording the retention time of an analyte over a 72 hour period, generally using three opening standard data points. The mean retention time and standard deviation is calculated for each analyte. The width of the time window is then defined as ±3 times the standard deviation. Any analyte appearing within this window is considered a positive hit (up to the analyst's discretion).

9.5 Quantitative analysis of results

9.5.1 Quantitative results are calculated using an external standard response factor from the initial calibration.

9.5.1.1 PCB quantitation. Calculate PCBs using an external calculation. A minimum of three peaks should be used for quantitation. For aqueous samples:

$$\text{Conc. } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(V_s)}$$

where:

A_x = Area of peaks of Aroclor in sample
V_t = Volume of sample extract
D = Dilution factor
CF = Mean calibration factor
V_i = Volume of sample injected (µL)
V_s = Volume of sample extracted, typically 40 mL

For solid samples:

$$\text{Conc. (µg/Kg)} = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(W)}$$

All variables are the same except for W, which is the dry weight of the sample. Dry weight is calculated by multiplying the amount of sample used in the extract by the decimal dry weight value. I.e. if the %solids of sample Y is 86.2%, and 5.02 g was used in the extraction, then the dry weight is calculated in the following manner: 5.02g * 0.862 = 4.33 g.

Alternately, concentrations are calculated using a linear regression calculation (See Sec.7.2).

10.0 ACCEPTANCE OF DATA AND METHOD PERFORMANCE

10.1 All initial calibration data must be within compliances listed in Sec. 7.0.

10.2 All continuing calibration results must be within compliances listed in Sec. 8.1.

10.3 LCS (Laboratory Control Spike) recoveries must be within 50 -130% of the spike value for Aroclor 1260 and TCB. If these criteria are not met, then the entire batch must be reextracted.

10.4 Extraction blanks must not contain target analytes above ½ the PQL for that specified analyte. If this is not the case, then the entire batch must be reextracted.

10.5 Matrix spikes and LCS recoveries should fall within 50 - 130% of the spiked value. Concentrations that fall outside of this window for MS/MSDs are noted to the client and no corrective action is taken. If concentrations fall outside of the acceptable window for the LCS, then the entire extraction batch is reextracted and reanalyzed. The RPD for MS/MSD should be 40% or less.

10.6 Surrogate recoveries must fall within 30 - 150% of the spiked value. The percent recovery for one of the two surrogates (TCMX and TCBP) must fall within this window. If they do not, then the sample is reextracted. If the surrogate recoveries still fail, then the sample is said to exhibit a matrix effect. Both the original results and the reextracted/reanalyzed results will be reported if the recoveries fail a second time.

10.7 Matrix spike and LCS sample criteria are listed in Sec. 10.5. Outliers are discussed in case narrative, and in the case of failed LCS criteria, the entire extraction batch is reextracted and reanalyzed.

10.8 An independent check standard must be run following each calibration. The %DIFF between the original and the independent must be < 30%. If of the %DIFF is > 30% then a new

standard is prepared. If this still fails, a new initial calibration curve will be analyzed and the second source will be reanalyzed upon completion of the new curve. Results of the independant check standard are kept on file at the laboratory.

10.9 MDLs are run once every year, or after major instrumentation changes, such as new columns, new detector, etc. See 40 CFR, Part 136, Appendix B, for details. A minimum of seven samples are analyzed for the MDL.

10.10 Samples found to contain <30% solids will be dried at 65°C for a minimum of 2 hours to reduce the moisture content, and then re-extracted and re-analyzed. A second % solids determination will also be performed on the dried sample.

11.0 REFERENCES

1. SW-846, Revision 2, December 1996, Method 8082.

2. Weston SOW for Prime Contract DACW33-94-D-0009

12.0 GLOSSARY

Extaction Blank: A known matrix, usually commercially purchased dried sand, spiked with surrogate solution only. The blank should be free of target analytes and other interfering contaminants. A "clean" extraction blank demonstrates that the extraction process is not introducing target analytes into the samples.

Instrument Blank: Also known as a solvent blank. It is hexane spiked with surrogate. It is analyzed every ten samples to show that there is no contamination from the instrument being introduced into the samples. Possible sources of instrument contamination are dirty syringes, dirty hexane rinse bottles, dirty injection ports or head of columns, among other sources.

LCS: Laboratory Control Spike. A known matrix, usually commercially purchased dried sand, spiked with a known amount of target analytes in addition to surrogates. The acceptable recovery of these analytes indicates that the extraction process is working correctly.

Matrix Spike: An environmental (i.e. field) sample which is spiked with known amounts of analyte(s). The amount of recovery of these analytes indicates how well the extraction process is working on a particular matrix type. Matrix spike samples are generally analyzed in duplicate and a %RPD is calculated.

TCB: 1,2,4-Trichlorobenzene.

STANDARD OPERATING PROCEDURE FOR DETERMINATION POLYCHLORINATED BIPHENYLS (PCBs) AND 1,2,4-TRICHLOROBENZENE BY GAS CHROMATOGRAPHY / ELECTRON CAPTURE DETECTOR (MODIFIED EPA 8082)

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1.0 HEALTH AND SAFETY

1.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Treat each chemical as a potential health hazard and minimize potential exposure. Handle stock standard solutions containing these compounds in a fume hood. Wear personal protective equipment such as lab coats, gloves and safety glasses while performing this analysis.

1.2 All reagents and standards used for analysis must be accompanied to the laboratory by manufacturer's Material Data Safety (MSD) Sheets. MSD Sheets are kept on file in the laboratory in binders labeled MSDS on a bookshelf in the data processing area, and are available to all laboratory personnel. As part of the training process, analysts make themselves familiar with the contents of the MSD Sheets.

1.3 Secure all compressed gas cylinders with chains or straps. Train analysts in tank changing procedures.

2.0 SCOPE AND APPLICATION

2.1 The purpose of this SOP is to outline, in detail, the technique of determining polychlorinated biphenyls (PCBs) and 1,2,4-trichlorobenzene (TCB) by GC/ECD. This method is based on Method 8082, SW-846, Rev. 2, Dec 1996. This method is applicable to soil and sediment samples and rinse blank samples collected at the GE Housatonic River Site.

2.3 General method information:

2.3.1 Severe weathering may affect Aroclor patterns. Thus, the experience of the analyst plays a large role in the identification of Aroclors. Samples displaying unusual or significant weathering patterns will be addressed in the report narrative.

2.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method. This includes

having the analyst extract four LCS (Laboratory Control Spike) samples. Recoveries of the spiked compounds must be within ±25% of the spiked values, and the Relative Perecent Difference (RPD) between the four results must not exceed 20%. Records for each analyst are kept on site for examination.

3.0 SUMMARY OF METHOD

3.1 Five (5) grams of a soil or sediment sample is placed in a 20 mL scintiallation vial and is dried using sodium sulfate and methanol, and then extracted using 5 mL of hexane. The sample is then mechanically shaken vigorously for twenty minutes and the resulting hexane layer is transferred to a 4 ml glass vial. The extract is then acid cleaned using sulfuric acid, and , depending on sample results, is also copper cleaned to remove sulfur (see Sec. 9.2.1.8).

3.2 For aqueous rinse blank samples, 40 mL of water is extracted with 1 mL of hexane and shaken vigorously for twenty minutes. The hexane layer is drawn off and analyzed. No cleanup procedures are performed on the water samples. It sample shows evidence of Aroclors, it is immediately reported to Weston.

3.3 For hexane rinse blank samples, a 1 mL aliquot is spiked with surrogate and analyzed. No cleanup procedures are performed on the hexane samples. If sample shows evidence of Aroclors, it is immediately reported to Weston.

4.0 INTERFERENCES

4.1 Major contaminant sources are contaminated solvents and glassware used during initial sample extraction and concentration. Ensure that solvents meet ACS certification for pesticide residue and/or HPLC analysis and that glassware is free from contamination. Since new, unused scintillation vials are used for every sample, cross contamination from the laboratory is most likely very minimal. Extract a sample blank at the same time and under the same conditions as the samples and analyze before the sample extracts to determine if any contaminants are present. Common contaminants are the phthalate esters, which come from rubber gloves and other rubber materials in the lab in addition to outside sources, and sulfur present in samples.

4.2 Contamination also occurs in the case of carryover, where a low level sample is analyzed immediately following a high concentration sample. Analyze solvent checks following high level samples to determine system carryover. A sample would be considered high concentration if it exceeded 10 times the upper calibration limit. If high level samples are analyzed when an analyst is not present (i.e. overnight using the autosampler), then samples which contain Aroclors analyzed immediately following the high level samples are reanalyzed to confirm the concentration of Aroclor present in the sample.

4.3 Perform adequate maintenance, such as changing septa on GC#1 and changing the injection port liners and clipping columns in order to reduce active sites and improve general chromatography on both GC systems.

5.0 APPARATUS AND MATERIALS

5.1 Hewlett-Packard dual tower 7673 vial autosampler system.

5.2 Gas chromatography/electron capture system (GC/ECD) #1.

5.2.1 Hewlett-Packard 5890A Series II GC.

5.2.2 Hewlett-Packard dual ECD detectors

5.2.3 Two Supelco SPB-5 30 m x 0.53 mm ID, 1.0 µm film thickness columns.

5.3 Gas chromatography/electron capture system (GC/ECD) #2:

5.3.1 Hewlett-Packard 5890 Series II GC with Electronic Pressure Control (EPC).

5.3.2 Hewlett-Packard dual ECD detectors

5.3.3 Two Supelco SPB-5 30 m x 0.53 mm ID, 1.0 µm film thickness columns.

5.4 Data system

5.4.1 Two computers with enough memory to simultaneously run Excel and Chemstation software.

5.4.2 Hewlett-Packard Chemstation software for integrating and processing signals generated by the GC/ECD system.

5.5 Microsyringes - Hamilton 5-, 10-, 25-, 100-, 250-, 500- and 1000-µL

5.6 AND EK-120, top loading balance, capable of weighing to 0.01 g.

5.7 Disposable Pasteur pipettes, pipette bulbs

5.8 Class A Volumetric glassware - 10 mL and 100 mL

5.9 Stainless steel spatulas

5.10 20 mL Scintillation Vials, with teflon lined caps

5.11 4 mL vials, with teflon lined caps

5.12 Certified weights, 0.1 g - 100 g.

6.0 REAGENTS AND STANDARDS PREPARATION

6.1 n-Hexane (VWR) - pesticide grade

6.2 Methanol, (VWR) - pesticide grade

6.3 Acetone (VWR) - pesticide grade

6.4 Stock standards

6.4.1 Purchase the following stock standards from ABSOLUTE as certified solutions, and use for PCB/Aroclor calibrations:

- 90127, Aroclor 1248, 1000 µg/mL
- 90128, Aroclor 1254, 1000 µg/mL
- 90129, Aroclor 1260, 1000 µg/mL
- 70103, Decachlorobiphenyl, 1000 µg/mL

- 70273, Tetrachloro-m-Xylene, 1000 µg/mL
- 70289, 1,2,4-Trichlorobenzene, 1000 µg/mL

6.4.2 Purchase the following stock standards from ACCUSTANDARD as certified solutions, and use for second source verification checks:

- C-248S-H-10X, Aroclor 1248, 1000 µg/mL
- C-254S-H-10X, Aroclor 1254, 1000 µg/mL
- C-260S-H-10X, Aroclor 1260, 1000 µg/mL
- CF8S, 1,2,4-Trichlorobenzene, 1000 µg/mL (Purchased from VWR)

6.4.3 Also keep on hand Aroclor 1016, 1221, 1232 and 1242 to analyze in case PCBs other than Aroclor 1248, 1254 or 1260 are detected. PCBs listed above are purchased in 1000 µg/mL solutions, and are prepared as in Sec. 7.1, below. If a sample is suspected of containing one or more of the "non-target" Aroclors, then either a new curve or a midpoint (See Sec 8.1.1. for midpoint definition) is analyzed for each suspected Aroclor and the sample is reanalyed for the suspected Aroclors.

6.5 Store standards at 4°C.

7.0 CALIBRATION PROCEDURE

7.1 Calibration Curve Preparation for PCBs: Analyze a 5-point initial calibration curve for each Aroclor and for TCB. The TCB compound may be included in the Aroclor standard mixture, as it elutes well outside of the expected Aroclor ranges.. Prepare the 5-point curves as below:

Make an initial dilution of each PCB stock standard. All "Standard added" amounts refer to this dilution. Prepare the initial dilution by adding 1 mL of the stock PCB standards to a 10 mL volumetric flask and bring to volume in hexane. The concentration of these standards are 100 µg/mL. In addition, prepare a stock standard of TCB by diluting 100 µL of stock solution into 1 mL of methanol. The concentration of this standard is 100 µg/mL.

Make an initial dilution of the surrogate standard solution by bringing 2 mL of tetrachloro-m-xylene and 2 mL of decachlorobiphenyl to 10 mL in hexane. The concentration of this standard is 200 µg/mL.

Prepare the working curve standards the following way

Conc. (PCB/TCB/Surr)	Std added	TCB added	SS. added	Final volume
20/1/2 µg/mL	2 mL	0.100 mL	0.1 mL	10 mL
10/0.5/1 µg/mL	1 mL	0.050 mL	0.05 mL	10 mL
5/0.1/0.5 µg/mL	0.5 mL	0.010 mL	0.025 mL	10 mL
1/0.05/0.1 µg/mL	0.1 mL	0.005 mL	0.005 mL	10 mL
0.5/0.01/0.05 µg/mL	0.05 mL	0.0025 mL	0.0025 mL	10 mL

This is done for each set of Aroclor standards.

7.1.1 The working range of the method is limited to the upper range of the calibration curve. Samples with analytes that exceed the upper calibration range are reanalyzed at a dilution, with the concentration of the analytes in question ideally falling into the upper half of the calibration range.

7.1.2 "Prime" (deactivate) column before curve is analyzed by injecting the midpoint Aroclor 1260 standard or any midlevel or higher Aroclor standard.

7.2 Curve acceptance criteria for PCBs and TCB:

There are two methods for calculating the acceptability of the calibration curve. The first is an average of Calibration Factors. The second is a linear regression not forced through the origin. For the Calibration Factor method seven peaks are chosen for each Aroclor, and the TCB is identifed separately. Peaks for each Aroclor are at least 25% of the height of the largest Aroclor peak.

7.2.1 Calculate the Calibration Factor (CF) for each characteristic Aroclor peak.

$$CF = \frac{\text{Peak Area of Compound in Standard}}{\text{Mass of Compound (ng)}}$$

7.2.2 Calculate the mean calibration factor for each characteristic peak using the Chemstation software. The formula is as follows:

$$\text{mean CF} \Rightarrow \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

where n is the number of standards analyzed.

7.2.3 Calculate the standard deviation (SD) and the %RSD of the calibration factors for each Aroclor peak and TCB as

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad \%RSD = \frac{SD}{CF} x\,100$$

If the %RSD for each Aroclor Peak and TCB is < 25%, a linear regression not forced through the origin (also called a calibration curve) is used to calculate concentrations. The correlation coefficient for each Aroclor Peak and TCB must be > 0.995, or a new curve must be analyzed.

In general, the concentration for each individual peak in a given Aroclor is calculated and then they are averaged together. This is done so that if there are interferences, such as other chlorinated analytes (such as pesticides, solvents, chlordane, etc.), the presence of multiple Aroclors, the presence of sulfur, the affect of those interferences can be evaluated on a peak by peak basis to determine if an Aroclor peak should be included in the concentration calculation. Examining each peak is also essential in determining if weathering/degradation has occured.

7.2.4 Retention time windows: Absolute retention times are essential for compound identification. The retention time for TCB and each characteristic Aroclor peak is determined by averaging the retention time over three days and calculating the standard

deviation (see formula in Sec. 7.2.3). The width of the of the retention time window is defined as ±3 standard deviations of the average. See Sec. 9.4.2 for further details.

8.0 QUALITY CONTROL

8.1 Before analysis of samples can proceed, calibration verification must occur.

8.1.1 Perform midpoint continuing calibration checks. The midpoint calibration standard in this case is a 5 ppm Aroclor/0.1 ppm 1,2,4-TCB standard. All Aroclor mixtures (i.e. Aroclor 1248, 1254, etc.) are analyzed and must be within ±25% of the initial calibration for analysis to continue. This is true for 1,2,4-TCB as well. The % Difference is calculated as follows:

$$\%\,\text{Diff} = \frac{\text{CF} - \overline{\text{CF}}_y}{\text{CF}} x100$$

This calibration occurs before samples are analyzed. All Aroclors must pass before analysis of samples can occur. After every tenth sample analyze an instrument blank and a midpoint calibration of Aroclor 1260/TCB. The instrument blank must be free of extraneous peaks and the recovery of the Aroclor/TCB must fall within the ± 25% window for analysis to continue. A closing set of an instrument blank/standard analyses must also be analyzed after the last samples, and they must be fall within the ± 25% window for results to be considered valid. If the Aroclor/TCB mixture fails to meet criteria then samples must be reanalyzed.

Before the opening calibration check, and before each continuing calibration check, an instrument blank is analzyed. The instrument blank must be free of Aroclors or any other potential interfering compounds. Interfering contamination would be Aroclor patterns, or other large peaks that have the potential to bias or interfere with the calculation of Aroclor concentrations.

9.0 INSTRUMENT CONDITIONS AND SAMPLE ANALYSIS

9.1 Instrument Conditions:

9.1.2 GC #1 conditions (No EPC):

Injection port temperatures:	225 °C
Detector A temperature:	325 °C
Detector A temperature:	325 °C
Initial temperature:	140 °C
Initial time:	1.5 min
Rate (°C/min):	7.5
Temperature:	200 °C
Hold time:	0.5 min
Rate (°C/min):	12
Final temperature:	260 °C
Final time:	5.5 min
Total time:	20.5 min

9.1.3 GC #2 conditions (w/EPC):

Injection port temperatures: 200 °C

Detector A temperature:	300 °C
Detector A temperature:	300 °C
Constant flow:	2.0 mL/min
Initial pressure:	10.0 psi
Initial temperature:	140 °C
Initial time:	1.00 min
Rate (°C/min):	8.0
Temperature:	200
Hold time:	0.00
Rate (°C/min):	12
Final temperature:	265 °C
Final time:	6.5 min
Total time:	20.00 min

9.1.4 HP 7673 Injectors (Dual Tower, both systems)

Solvent washes:	5
Sample pumps:	5
Injection volume:	1 µL
Oncolumn:	No

9.2 Sample Preparation:

9.2.1 Soil Sample Preparation:

9.2.1.1 Homogenize sample in container by mixing thoroughly with clean stainless steel spatula. Remove any rocks and/or twigs prior to mixing the sample. Spatulas are cleaned by first wiping any soil residue with a paper towel. The spatula is then triple rinsed with hexane and dried in the oven for an hour.

9.2.1.2. Weigh out 5 g (±0.1 g) into a 20 mL scintillation vial. For the LCS (Laboratory Control Spike) and the extraction blank, use clean, dry sand. Add enough sodium sulfate to the vial to dry the sample. Also add sodium sulfate to the LCS and extraction blank. Mix well. The sample will have a sandy texture when completely dry.

9.2.1.3 At the same time, weigh out at least ten grams of sample into a weigh boat for % solids determination. To do this, zero the balance, place the weigh boat on top of the scale and record the weight. Without zeroing, add 10 + g of sample and record this weight. Place in oven at 105 °C for at least 12 hours (usually overnight) and record the final weight. Calculate the %solids in the following manner:

$$\%\text{solids} = \frac{((\text{wet wt.})-(\text{tin wt.}))}{((\text{dry wt.})-(\text{tin wt.}))} \times 100$$

9.2.1.4 Spike the sample with 25 µL of Surrogate solution. Also spike LCS, Extraction Blank and MS/MSD samples with surrogate mix. If the sample is an MS/MSD sample, also spike the sample with 25 µL of the 1000 µg/mL Aroclor 1260 standard and 50 µL of the 10 µg/mL TCB standard. Spike the

LCS sample with the Aroclor and TCB standards in addition to the surrogate solution. The concentration of the Aroclor in the LCS and MS/MSD samples is 5 µg/mL; the concentration of the TCB in the LCS and MS/MSD samples is 0.1 µg/mL.

9.2.1.5 Add 1 mL of methanol to the sample and 5 mL of hexane to the sample. Extract the sample on a shaker table for 20 minutes.

9.2.16. After the extract is shaken, the hexane layer is removed from the soil sample and transferred into a clean scintillation vial. A centrifuge can be used to separate layers, if needed.

9.2.1.7 The extract is then acid cleaned using sulfuric acid. Approximately a 1:1 volume of sulfuric is added to the extract, and the extract is vigorously shaken for one to two minutes. The acid phase and the hexane layer are allowed to separate, and the hexane layer is transferred into a clean sample. Care must be taken not to transfer acid to the sample vial.

9.2.1.8 If sulfur is expected to be present in the sample, or if sulfur is found to present in the sample after analysis then in addition to an acid cleanup, a sulfur cleanup must be performed. This is done by first treating approximately 2 g of copper with dilute nitric acid and then rinsing the copper 5 times with distilled water to remove the acid. The copper is then considered "activated", and must either be used immediately, or it can be stored under acetone. If it is stored under acetone, it must be dried for four hours before use. Add approximately 4 mLs of extract to 1 - 2 g of copper turnings and shake for 2 minutes. Solution will be clear if sulfur is removed, and the copper will turn a sooty black in color. This step may be repeated until all the sulfur is removed.

9.2.1.9 Proceed to analysis of samples (Sec. 9.3)

9.2.2 Field blank preparation:

9.2.2.1 Extract the entire 40 mL sample volume provided by the field team with 1 mL of hexane. Add 1 mL of hexane and shake for twenty minutes.

9.2.2.2 Carefully remove the hexane layer, and analyze.

9.2.3 Hexane field blank preparation:

9.2.3.1. Hexane rinse blanks are supplied in 40 mL VOA vials. 1 mL of the hexane is tranferred to a 2 mL sample vial, and 5 µL of the 200 µg/mL Surrogate mixture is added. The sample is then analyzed. No cleanup procedures are performed on the sample.

9.3 Analysis of samples:

9.3.1. Start by analyzing an instrument blank followed by the three Aroclor/TCB mixtures. Criteria must meet those outlined in Sec. 8.1.1. Sample analysis follows, generally in the following order: LCS, Blank, samples, MS/MSD. After every ten samples, an instrument blank and midpoint (5 µg/mL) Aroclor 1260/TCB mixture is

analyzed, and must meet results listed in Sec. 8.1. A closing check of 0.5 ppm Aroclor is analyzed before the final midpoint Aroclor 1260/TCB check. A sample analytical sequence follows:

Instrument Blank
Opening calibration checks
LCS
Extraction Blank
Samples (up to ten, including LCS & Blank)
Instrument Blank
Continuing 1260/TCB check
Samples (up to ten-- included under the definition of samples are MS/MSD samples)
0.5 ppm 1260 Check
Instrument blank
Closing 1260/TCB Check.

The 0.5 ppm/0.010 ppm 1260/TCB check must be within ±25% of its true concentration. If it is not within these limits, it could indicate that the instrument is no longer accurately "seeing" and quantitating low level concentrations. It the 0.5 ppm is out of compliance for Aroclor 1260 all samples which have concentrations of Aroclors below 0.5 ppm or have non-detects for the Aroclors are reanalyzed. This is noted in the case narrative. If the 0.5 ppm standard continues to fail, then a new curve must be analyzed. If the TCB is out of compliance, it is noted in the narrative and all non-detected results are "J" qualified as estimates.

9.3.2. Sample results are checked as soon as they come off the instrument as possible. Any sample result that exceeds the upper calibration limit of the instrument is diluted and reanalyzed. This is done by diluting the extract in a known volume of hexane and analyzing. A dilution factor is then incorporated into the final result calculation (Sec. 9.5).

9.4 Qualitative analysis of results

9.4.1 Qualitative results in this analysis are based on retention time of analyte and pattern recognition.

9.4.2 Compounds must also fall within their respective retention time windows. The retention time window is calculated by recording the retention time of an analyte over a 72 hour period, generally using three opening standard data points. The mean retention time and standard deviation is calculated for each analyte. The width of the time window is then defined as ±3 times the standard deviation. Any analyte appearing within this window is considered a positive hit (up to the analyst's discretion).

9.5 Quantitative analysis of results

9.5.1 Quantitative results are calculated using an external standard response factor from the initial calibration.

9.5.1.1 PCB quantitation. Calculate PCBs using an external calculation. A minimum of three peaks should be used for quantitation. For aqueous samples:

$$\text{Conc. } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(V_s)}$$

where:

A_x = Area of peaks of Aroclor in sample
V_t = Volume of sample extract
D = Dilution factor
CF = Mean calibration factor
V_i = Volume of sample injected (µL)
V_s = Volume of sample extracted, typically 40 mL

For solid samples:

$$\text{Conc. } (\mu g/Kg) = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(W)}$$

All variables are the same except for W, which is the dry weight of the sample. Dry weight is calculated by multiplying the amount of sample used in the extract by the decimal dry weight value. I.e. if the %solids of sample Y is 86.2%, and 5.02 g was used in the extraction, then the dry weight is calculated in the following manner: 5.02g * 0.862 = 4.33 g.

Alternately, concentrations are calculated using a linear regression calculation (See Sec.7.2).

10.0 ACCEPTANCE OF DATA AND METHOD PERFORMANCE

10.1 All initial calibration data must be within compliances listed in Sec. 7.0.

10.2 All continuing calibration results must be within compliances listed in Sec. 8.1.

10.3 LCS (Laboratory Control Spike) recoveries must be within 50 -130% of the spike value for Aroclor 1260 and TCB. If these criteria are not met, then the entire batch must be reextracted.

10.4 Extraction blanks must not contain target analytes above ½ the PQL for that specified analyte. If this is not the case, then the entire batch must be reextracted.

10.5 Matrix spikes and LCS recoveries should fall within 50 - 130% of the spiked value. Concentrations that fall outside of this window for MS/MSDs are noted to the client and no corrective action is taken. If concentrations fall outside of the acceptable window for the LCS, then the entire extraction batch is reextracted and reanalyzed. The RPD for MS/MSD should be 40% or less.

10.6 Surrogate recoveries must fall within 30 - 150% of the spiked value. The percent recovery for one of the two surrogates (TCMX and TCBP) must fall within this window. If they do not, then the sample is reextracted. If the surrogate recoveries still fail, then the sample is said to exhibit a matrix effect. Both the original results and the reextracted/reanalyzed results will be reported if the recoveries fail a second time.

10.7 Matrix spike and LCS sample criteria are listed in Sec. 10.5. Outliers are discussed in case narrative, and in the case of failed LCS criteria, the entire extraction batch is reextracted and reanalyzed.

10.8 An independent check standard must be run following each calibration. The %DIFF between the original and the independent must be < 30%. If of the %DIFF is > 30% then a new standard is prepared. If this still fails, a new initial calibration curve will be analyzed and the second source will be reanalyzed upon completion of the new curve. Results of the independant check standard are kept on file at the laboratory.

10.9 MDLs are run once every year, or after major instrumentation changes, such as new columns, new detector, etc. See 40 CFR, Part 136, Appendix B, for details. A minimum of seven samples are analyzed for the MDL.

10.10 Samples found to contain <30% solids will be dried at 65°C for a minimum of 2 hours to reduce the moisture content, and then re-extracted and re-analyzed. A second % solids determination will also be performed on the dried sample.

11.0 REFERENCES

1. SW-846, Revision 2, December 1996, Method 8082.

2. Weston SOW for Prime Contract DACW33-94-D-0009

12.0 GLOSSARY

Extaction Blank: A known matrix, usually commercially purchased dried sand, spiked with surrogate solution only. The blank should be free of target analytes and other interfering contaminants. A "clean" extraction blank demonstrates that the extraction process is not introducing target analytes into the samples.

Instrument Blank: Also known as a solvent blank. It is hexane spiked with surrogate. It is analyzed every ten samples to show that there is no contamination from the instrument being introduced into the samples. Possible sources of instrument contamination are dirty syringes, dirty hexane rinse bottles, dirty injection ports or head of columns, among other sources.

LCS: Laboratory Control Spike. A known matrix, usually commercially purchased dried sand, spiked with a known amount of target analytes in addition to surrogates. The acceptable recovery of these analytes indicates that the extraction process is working correctly.

Matrix Spike: An environmental (i.e. field) sample which is spiked with known amounts of analyte(s). The amount of recovery of these analytes indicates how well the extraction process is working on a particular matrix type. Matrix spike samples are generally analyzed in duplicate and a %RPD is calculated.

TCB: 1,2,4-Trichlorobenzene.

APPENDIX A-38

STANDARD OPERATING PROCEDURE FOR HIGH RESOLUTION MASS SPECTROMETRY MODIFIED METHOD 1668

AP No. 3D	Revision: 4	Effective: 12/5/97	Replaces: 11/5/97
HIGH RESOLUTION MASS SPECTROMETRY MODIFIED METHOD 1668			
Author: William J. Luksemburg			
Management - Date			12/5/97
QA Officer - Date	Sally A. Weagraff		12/5/97

1 SCOPE AND APPLICATION

1.1 This method is for the determination of coplanar polychlorinated biphenyls (PCBs), mon-ortho substituted PCB congeners, and ten PCB homologues at the quantitation limits listed in Table 1 for water, soil, sediment, sludge, ash, tissue, and other sample matrices by gas chromatography/high resolution mass spectrometry/selective ion monitoring (GC/HRMS/SIM). The method is based upon the combined features of EPA Method 680 to measure PCB homologues, and Method 1668 to extract, cleanup sample extracts, and measure toxic PCB congener target compounds.

1.2 This method may also be used for the determination of coplanar/mono-ortho PCBs only. The quantitation limits for this determination are provided in Table 4.

1.3 Quantitation levels are usually dependent on the level of interferences rather than instrumental limitations. The quantitation limits listed are levels at which the PCBs can be determined with only common laboratory interferences present.

1.4 This method is "performance-based". Modifications to the method to overcome interferences or lower the cost of measurements is permitted, provided that all performance criteria in this method are met.

2 METHOD SUMMARY

2.1 AQUEOUS SAMPLES (<1% solids) - Stable isotopically labeled analogs of PCB target congeners are spiked into a one-liter sample and either vacuum filtered through a glass-fiber filter on top of a solid phase extraction (SPE) disk or liquid-liquid extracted with 3 x 100mL portions of methylene chloride. Sample components on the filter and disk are eluted with methylene chloride and the eluant is concentrated for cleanup or the sample is filtered through a funnel containing cleaned Na_2SO_4 and concentrated for cleanup.

2.2 SOLID, SEMI-SOLID, AND MULTI-PHASE SAMPLES (except tissue) - The labeled compounds are spiked into the sample containing 10-20 g dry weight. If the percent solids is below 30%, then the analyst must take more sample to bring the solid content to 10-20 g. Samples containing multiple phases are pressure filtered and any aqueous liquid is discarded. Coarse solids are ground or homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted in a Soxhlet/Dean Stark (SDS) extractor. The extract is concentrated for cleanup.

2.3 FISH AND TISSUE- A 30 g aliquot of sample is homogenized, and a 25 g aliquot is spiked with the labeled isotope compounds. The sample is mixed with sodium sulfate and extracted for 16 hours using methylene chloride:hexane (1:1) in a Soxhlet extractor. The extract is evaporated to dryness, and the lipid content is determined.

2.3.1 After extraction, samples are cleaned-up using potassium silicate/silica gel chromatography.

2.4 After cleanup, extracts are concentrated to near dryness. Recovery standards are added to each extract and an aliquot of the extract is injected. The analytes are separated by the GC and detected by gas chromatography/high resolution mass spectrometry/selective ion monitoring (GC/HRMS/SIM) to achieve the required quantitation limits of the method. Two exact m/z's are monitored for each homologue.

2.5 For the measurement of PCB congeners and PCB homologues, the GC/MS system should be calibrated using the native and labeled PCB congeners listed in Table 2.

2.5.1 If analyzing coplanar/mono-ortho PCBs only, the GC/MS system should be calibrated using the native and labeled PCB congeners listed in Table 5.

2.6 An individual PCB congener is identified by comparing the GC retention time and ion abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical ion-abundance ratio of the two exact m/z's. Isomer specificity for the toxic PCBs is achieved using GC columns that resolve these congeners from the other PCBs.

2.7 Quantitative analysis is performed using selected ion current profile (SICP) areas, in one of two ways:

2.7.1 For PCB congeners with labeled analogs, the GC/MS system is calibrated, and the concentration of each compound is determined using isotope dilution technique.

2.7.2 For PCB congeners without labeled isotopes, and for PCB homologues, the GC/MS system shall be calibrated and the concentration of each compound determined using internal standard technique.

2.8 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3 CONTAMINATION AND INTERFERENCES

3.1 All materials used in the analysis shall be demonstrated to be free from interferences by running reference matrix method blanks with each sample batch.

3.1.1 The reference matrix should simulate, as closely as possible, the sample matrix under test. Reagent water can be used to simulate water samples; playground sand or white quartz sand can be used to simulate soils; filter paper can be used to simulate papers or similar materials; and corn oil can be used to simulate tissues.

3.2 Interferences coextracted from samples will vary from source to source, depending on the site being sampled. The cleanup steps can be used to reduce or eliminate such interferences.

4 SAFETY

The toxicity or carcinogenicity of each chemical used in this method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in these analyses.

5 APPARATUS AND MATERIALS

5.1 CTC Autosampler Model A200S.

5.2 Alpha Station 255/233.

5.3 Neslab HX200 and HX500 Water Cooler.

5.4 VG 70SE or Micromass (VG) Autospec Magnetic Sector High Resolution Mass Spectrometer.

5.5 Berkel Scharfen Food Slicer.

5.6 Pipets, disposable, serological, 10 mL.

5.7 Pipets, Pasteur.

5.8 Amber glass bottles, 1 liter (teflon-lined screw cap).

5.9 Two liter separatory funnels.

5.10 Teflon boiling chips.

5.11 200mm x 15mm glass chromatographic column used for Mini-Silica Filtration.

5.11.1 Place a glass wool plug at the bottom of the column, pack with 1 g silica gel, 4 g 33% NaOH:silica gel, 1 g silica gel, 8 g 44% H_2SO_4:silica gel, 2 g silica gel and 1 cm Na_2SO_4.

5.12 200mm x 15mm glass chromatographic column used for Silica Filtration.

5.12.1 Place a glass wool plug at the bottom of the column, pack with 12 g of silica gel and 1 g of Na_2SO_4.

5.13 250mm x 30mm glass chromatographic column used for Fish/Tissue sample to remove lipids.

5.13.1 Place a glass wool plug at the bottom of the column, pack with 30 g silica gel, 10 g 44% H_2SO_4:silica gel, 30 g potassium silicate, 2 cm Na_2SO_4.

5.14 Organomation 24-Station N-Evaporator with teflon tubing connection to trap and gas regulator.

5.15 Conical vials, 2 mL.

5.16 Pyrex fiber glass, 8μm sliver (glass wool plug).

5.17 Funnels, 100 mL.

5.18 Carbon column preparation:

5.18.1 Carbon column (gravity flow). Prepare the carbon/silica gel packing material by mixing 5% (by weight) active carbon AX-21, pre-washed with toluene and dried at 110°C and 95% (by weight) silica gel, pre-washed with methylene chloride followed by activation of the mixture at 130°C for 6 hours. Prepare a 10mL disposable glass pipet by cutting off the top end. Insert a glass wool plug at the bottom and pack with 1cm of silica gel followed by 1 g of the mixture. Cap the packing with a glass wool plug.

5.19 Dean-Stark Trap, condenser and flask.

5.20 Buchler Rotary Evaporator.

5.21 Round bottom flasks, 50 mL and 500 mL.

5.22 Top-Loader Balance, Fischer Scientific Model XL-3000.

5.23 Injection vial inserts, 100 uL (Sun International).

5.24 Electrothermal electromantle six sample and 3000 mL capacity.

5.25 Drying oven, VWR Model 1320.

5.26 High Pressure Filtration Apparatus (PFA).

5.27 Whatman glass microfibre filters, 1.2μm.

6 REAGENTS, STANDARDS AND SOLVENTS

6.1.1 ReagentsSulfuric acid, concentrated.

6.1.2 Sodium thiosulfate, 80mg/L.

6.1.3 Silica gel 60 (70-230 mesh).

6.1.4 Water, distilled.

6.1.5 Prepurified nitrogen gas.

6.1.6 Anhydrous sodium sulfate.

6.2 Solvents

6.2.1 Methylene chloride. Highest available purity.

6.2.2 Hexane. Highest available purity.

6.2.3 Tetradecane. Highest available purity.

6.2.4 Methanol. Highest available purity.

6.2.5 Toluene. Highest available purity.

6.3 Standards

6.3.1 PCB Analytical Standards (Cambridge Isotope Labs, Wooburn, MA).

7 SAMPLE COLLECTION, PRESERVATION, STORAGE AND HOLDING TIMES

7.1 Aqueous Samples

7.1.1 At minimum, collect one liter of sample. If residual chlorine is present, add 80mg/L of sodium thiosulfate.

7.1.2 Adjust sample pH 2-3 with sulfuric acid.

7.1.3 Store aqueous samples in the dark at 0-4°C.

7.2 Solid Samples

7.2.1 Solid samples are collected as grab samples using wide-mouth jars.

7.2.2 Store solid, semi-solid, oily, and mixed-phase samples in the dark at <-10°C.

7.3 Fish and Tissue Samples

7.3.1 Fish may be cleaned, filleted, or processed in other ways such that the sample is received as whole fish, fish fillets or other tissues for analysis.

7.3.2 Samples must be frozen and maintained in the dark at <-10°C.

7.4 Holding Times

7.4.1 If stored in the dark at 0-4°C and preserved as described in section 7.3, aqueous samples may be stored for up to one year.

7.4.2 If stored in the dark at <-10°C, solid, semi-solid, oily, multi-phase, fish and tissue samples may be stored for up to one year.

7.4.3 Sample extracts should be stored at <-10°C until analyzed. If stored in the dark at <-10°C, sample extracts may be stored for up to one year.

8 QUALITY CONTROL

Quality control is demonstrated by an initial demonstration of laboratory capability, analysis of spiked samples with labeled compounds to evaluate and document data quality, and the analyses of standards and blanks as a test of continued performance.

8.1 Initial Precision and Recovery (IPR): Four aliquots of the diluted precision and recovery standard are analyzed to establish the ability to generate acceptable precision and accuracy in reference matrix.

8.1.1 An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

8.1.2 Using the results of the set of four analyses, calculate the average concentration (x) and the standard deviation (s) for each compound.

8.1.3 Compare x and s for each native and labeled compound with the limits for IPR in Table 7. If any individual s exceeds the precision limit or any individual x fall outside the range for accuracy, the test must be repeated.

8.2 Method Blank (MB): Method Blank is a sand, distilled water or other appropriate matrix preparation that is free from native analyte that has been prepared and analyzed using the same procedures followed for the rest of the sample batch.

8.2.1 A MB is run with every analytical batch or 20 samples, whichever is less, per matrix type.

8.2.2 Analytical data is accepted (with a data qualifier) if the amount found in the MB is less than one tenth of the level found in any of the associated samples. Otherwise, the samples are re-extracted and analyzed.

8.3 Ongoing Precision and Recovery (OPR): An ongoing precision and recovery sample is prepared by adding a known quantity of native standard to an interferant free matrix and used to assess method performance (precision and recovery).

8.3.1 Spike 50µL (10µL for coplanar/mono-ortho PCBs only) of compound spiking solution into the sample.

8.3.2 An OPR is analyzed with every analytical batch or 20 samples (whichever is less) per matrix type.

8.3.3 For each native and labeled compound, compare the concentration with the limits for ongoing accuracy in Table 7.

8.4 Matrix Spike (MS/MSD): A matrix spike sample is prepared by adding a known quantity of native standard to a sample matrix prior to extraction.

8.4.1 Spike 50µL (10µL for coplanar/mono-ortho PCBs only) of compound spiking solution into the sample.

8.4.2 The relative percent difference between MS/MSD samples should be ≤50%.

9 CALIBRATION

9.1 Inject the reference compound perfluorokerosene (PFK). PFK provides the required lock masses and is used for tuning the mass spectrometer.

9.2 Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 at m/z 304.9824. For each descriptor, monitor and record the resolution and exact m/z of three to five reference peaks covering the range of the descriptor.

9.3 An appropriate lock mass will be monitored for each descriptor and shall not vary by more than ±20% throughout the respective retention time window.

9.4 For the measurement of PCB's, the exact m/z's to be monitored in each descriptor are listed in Table 6.

9.5 Inject 2µL of the Window Defining Mix.

9.5.1 The first and last eluters are verified to be within the appropriate retention time windows for each chlorination level.

9.6 Under the same conditions, inject 2µL of each of the five calibration solutions containing all PCB isomers. Calibration standard solutions are presented in Table 2.

9.6.1 Sixteen internal standards and four recovery standards are used to improve quantitation.

9.6.2 The signal to noise ratio (s/n) must exceed 10:1 for all ions monitored,

9.6.3 The ion abundance ratio measurements must be within ± 15% of the theoretical ratio.

9.7 Calibration by Isotope Dilution: Isotope dilution calibration is used for the native PCBs for which labeled compounds are added to samples prior to extraction.

9.7.1 If the relative response for any compound is less than 20% coefficient of variation over the 5 point calibration range, an averaged relative response is used for that compound; otherwise, the complete calibration curve for that compound is used over the 5 point range.

9.8 Calibration by Internal Standard: Internal standard method is used for the determination of native PCBs for which a labeled compound is not available.

9.8.1 If the response factor for any compound is less than 35% coefficient of variation over the 5 point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point range.

10 SAMPLE EXTRACTION AND CONCENTRATION

10.1 Determine the percent solids on all samples. Weigh 2-10g of sample, dry overnight in 110°C oven and re-weigh.

10.2 AQUEOUS OR SAMPLES WITH <1% SOLIDS: Extract sample using one of the following two extraction procedures:

10.3 Weigh full bottle and cap. Spike 50 µL (10µL for coplanar/mono-ortho PCBs only) internal standard solution into the sample bottle. Into the OPR, spike 50 µL (10µL for coplanar/mono-ortho PCBs only) native spike. Cap and mix. Pre-filter the samples with a 1.2µm glass fiber filter into a 1L bottle. Assemble the Solid-Phase Extraction Apparatus. Condition the disk by soaking it in toluene for one hour. Place the disk onto the apparatus and pre-wash with 20mL of toluene. Apply the vacuum and allow the disk to dry for one minute. Add 20mL of methanol and let the disk soak for three minutes. DO NOT LET THE DISK GO DRY UNTIL ALL OF THE SAMPLE HAS PASSED THROUGH THE DISK. Vacuum most of the methanol through the disk and add approximately 10mL of reagent water and apply the vacuum. Add the sample to the reservoir. Adjust the vacuum to complete the extraction in no less than 10 minutes per 1 liter of sample. Rinse the sample bottle and sides with reagent water and pour into the reservoir. After the sample and rinses have passed through the filter/disk, allow the vacuum to continue for as long as 15 minutes to remove any residual water. Allow the filter/disk to dry. SDS soxhlet extract the filter and disk with toluene for 16 hours. Re-weigh the empty container, cap and record for sample weight calculation. Proceed with cleanup procedures.

10.4 Weigh and record the full sample container and cap. Pour the sample into a 2L separatory funnel. Spike 50µL (10µL for coplanar/mono-ortho PCBs only) internal standard directly into the separatory funnel containing the sample. Into the OPR, spike 50µL (10µL for coplanar/mono-ortho PCBs only) native spike. Liquid-liquid extract the sample by adding 100mL portions of $MeCl_2$ into the sample container, shake and add to a 2L separatory funnel. Extract by shaking the funnel with periodic venting for 2 minutes. Allow the organic layer to separate and collect by passing through a funnel with cleaned Na_2SO_4 into a 500mL round bottom. Repeat the process two more times. Re-weigh the empty container, cap and record for sample weight calculation. Proceed with appropriate cleanup procedures.

10.5 SOIL, SEDIMENT, SLUDGE OR SAMPLES WITH >1% SOLIDS: Spike 50µL (10µL for coplanar/mono-ortho PCBs only) of internal standard solution into the thimble containing 10-20 g equivalent dry weight of sample and 50µL (10µL for coplanar/mono-ortho PCBs only) of native spike into the OPR thimble. SDS soxhlet extract for 16 hours with toluene. Proceed with cleanup procedures.

10.6 MULTI-PHASE SAMPLES: Using the percent solids, determine the volume of sample that will provide 10-20 g of solids, up to 1L of sample. Pressure filter the amount of sample determined through glass-fiber filter paper. If necessary to separate the phases and/or settle the solids, centrifuge the aliquots prior to filtration. Discard any aqueous phase, if present. Remove any non-aqueous liquid present and reserve the maximum amount filtered from the sample or 10 g, whichever is less, for combination with the solid phase.

10.7 ASH SAMPLES: Spike 50µL (10µL for coplanar/mono-ortho PCBs only) of internal standard solution into the thimble containing 5 g of sample and 50µL (10µL for coplanar/mono-ortho PCBs only) of native spike into the OPR thimble. SDS soxhlet extract for 16 hours with toluene. Proceed with cleanup procedures.

10.8 FISH AND TISSUE SAMPLES: Mix 25 g of well ground fish with 60 g of pre-cleaned Na_2SO_4 in a beaker. Stir frequently to remove any lumps. Transfer the mixture to a thimble. Spike 50µL (10µL for coplanar/mono-ortho PCBs only) of internal standard solution into each thimble and 50µL (10µL for coplanar/mono-ortho PCBs only) of native spike into the OPR thimble. Soxhlet extract for 16 hours with 1:1 $MeCl_2$:hexane. Proceed with cleanup procedures. Calculate the % lipids.

10.8.1 % Lipids

10.8.1.1 Roto-evaporate the extract to less than 250mL and transfer to a 250mL mixing cylinder.

10.8.1.2 Adjust the extract to 250mL using 1:1 $MeCl_2$:hexane and mix well.

10.8.1.3 Transfer 25mL of the solution to an aluminum dish that has been pre-weighed on an analytical balance.

10.8.1.4 Allow the extract to air dry completely and then place in a 110°C oven overnight.

10.8.1.5 When the aliquot is dry, re-weigh the dish on an analytical balance and record the weight. Calculate the % lipids using the following equation:

$$\% \text{ lipids} = \frac{\text{lipid residue wt.}}{\text{10\% of sample wt.}} \times 100$$

11 CLEAN-UPS

Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the analyst may use any or all of the procedures below or any other appropriate procedure. Acidic and basic silica gel are used to remove nonpolar and polar interferences.

11.1 If analyzing coplanar/mono-ortho PCBs only, add ~100µL of C_{14} and rotovap to C_{14} prior to cleanup.

11.2 Mini-Silica Filtration (All samples except Fish/Tissue)

11.2.1 Pre-rinse the column described in section 5.11 with 20 mL hexane. Discard rinsate.

11.2.2 Add extract to the top of the column and rinse container with hexane and transfer rinsate.

11.2.3 Elute with 150 mL hexane. Collect entire eluate.

11.2.4 Concentrate the extract to 0.5 mL in hexane. If analyzing for coplanar/mono-ortho PCBs only, proceed to charcoal/silica gel column. Otherwise, transfer to autoinjector insert containing 50µL of recovery standard.

11.3 Silica Filtration (All samples except Fish/Tissue)

11.3.1 Add 10mL $MeCl_2$ and swirl.

11.3.2 Add 90mL of hexane, in four portions, while swirling.

11.3.3 Pour the solution onto the glass chromatographic column described in section 5.12. Rinse the extract container with a few small portions of hexane and add to the column.

11.3.4 When all the solution has passed onto the column, add 90mL of hexane.

11.3.5 Collect all eluate and concentrate to 0.5mL in hexane. If analyzing for coplanar/mono-ortho PCBs only, proceed to charcoal/silica gel column. Otherwise, transfer to autoinjector insert containing 50µL of recovery standard.

11.4 Charcoal/Silica Gel Column (Samples for Coplanar PCBs only)

11.4.1 Roto-evap the extract to C_{14}.

11.4.2 Pre-rinse the column described in section 15.18 with 10 mL hexane. Discard rinsate.

11.4.3 Add sample to the column extract using small hexane rinses.

11.4.4 Elute column with 15 mL hexane. Discard rinsate.

11.4.5 Elute with 30mL 1:1 (v/v) $MeCL_2$:toluene. Collect eluate.

11.4.6 Concentrate to C_{14}. Transfer to autoinjector insert containing 10µL of recovery standard.

If the samples are of a tissue matrix, an anthropogenic isolation column shall be used for removal of lipids from tissue samples (section 5.13).

11.5 Fish/Tissue Glass Chromatographic Column #1 (Potassium silicate/silica gel)

11.5.1 Depending on the lipid content, adjust the remaining extract to 250mL with 1:1 $MeCl_2$:hexane and mix.

11.5.2 Quantitatively transfer the extract to the first column described in Section 5.13 with 1:1 $MeCl_2$:hexane.

11.5.3 As the extract reaches the top of the packing material, add 500mL of 1:1 $MeCl_2$:hexane. Proceed to cleanup column #2 if analyzing for coplanar PCBs only.

11.5.4 Elute, concentrate to ~500µL, transfer to autoinjector insert and crimp-top vial containing 50µL of recovery standard.

11.6 Fish/Tissue Carbon Column #2 (Carbon column: Coplanar PCBs only)

11.6.1 Roto-evap the extract to C_{14}.

11.6.2 Pre-rinse the column described in section 15.18 with 10 mL hexane. Discard rinsate.

11.6.3 Add sample to the column extract using small hexane rinses.

11.6.4 Elute column with 15 mL hexane. Discard rinsate.

11.6.5 Elute with 30mL 1:1 (v/v) $MeCL_2$:toluene. Collect eluate.

11.6.6 Concentrate to C_{14}. Transfer to autoinjector insert containing 10µL of recovery standard.

12 HRMS ANALYSIS

Establish the necessary operating conditions. The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, OPR aliquots and samples. The following GC operating conditions are for guidance and adjustments may be required. These conditions are applicable for analysis using a 60 meter DB-5MS Column.

Injector temperature:	270°C
Interface temperature:	290°C
Initial temperature:	130°C
Initial time:	1.0 minutes
Temperature program:	130 - 200°C at 5°C/min, 200°C for 16 minutes
	200 - 280 at 8°C/min, 280°C for 11 minutes
	280 - 300 at 13°C/min, 300°C for 4.5 minutes

12.1 The reference perfluorokerosene (PFK) provides the required lock masses and is used for tuning the mass spectrometer.

12.1.1 An appropriate lock mass will be monitored for each descriptor and shall not vary by more than ±20% throughout the respective retention time window.

12.1.2 Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 at m/z 304.9824. For each descriptor, monitor and record the resolution and exact m/z of three to five reference peaks covering the range of the descriptor. The mass resolution check is achieved before any analysis is performed and at the end of each 12-hour shift.

12.2 Set up the analytical run following this sequential injection pattern: Window Defining Mix, CS3, Solvent Blank, OPR, Method Blank, Samples.

12.3 Continuing Calibration

12.3.1 Inject 2µL of the Window Defining Mix.

12.3.1.1 The first and last eluters are verified to be within the appropriate retention time windows for each chlorination level.

12.3.2 Inject a mid-range standard from the initial calibration curve (CS3). The following criteria must be met:

12.3.2.1 Calculate the concentration of each native compound either by isotope dilution or internal standard technique. Each compound must be within the verification limits established in Table 6 of Method 1668.

12.3.2.2 The ion ratios must be within 15% of theoretical.

12.3.2.3 The signal to noise ratio (s/n) must exceed 10:1 for all ions monitored.

12.3.2.4 The absolute retention times of the internal standards shall be within ±15 seconds of the retention times obtained during calibration.

13 MONITORING INTERFERING IONS

13.1 For Cl_3-Cl_7 isomer groups, examine SICPs or spectra for intense $(M+70)^+$ ions that would indicate a coeluting PCB containing two additional chlorines. If this interference occurs, obtain and record the area for the appropriate ion (Table 12, Method 680) for the candidate PCB isomer group. Using the information in Table 13 (Method 680), correct the measured abundance of the M^+ ion. For example, if a Cl_7-PCB and a Cl_5-PCB target compound coelute, the Cl_7-PCB interference will contribute to the ion measured at m/z 326 and 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 $(M\pm70)^+$ 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 Cl_5-PCB target compound 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.

13.2 For Cl_2-Cl_8-PCB measurements, examine SICPs 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, Method 680) 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, the computer program shall obtain and record the area for m/z 325; and subtract 13.5% of that area from the measured area of m/z 326.

14 DATA ANALYSIS AND CALCULATIONS

14.1 Qualitative Determination

A chromatographic peak is identified as a PCB or labeled compound when all of the following criteria are met:

14.1.1 The signals for the two exact m/z's being monitored (Table 8 of Method 1668) must be present and must maximize within ±2 seconds of one another.

14.1.2 The signal-to-noise ratio (S/N) of each of the two exact m/z's must be ≥2.5:1 for a sample extract, and ≥10:1 for a calibration standard.

14.1.3 The ratio of the integrated areas of the two exact m/z's must be within the limits established in Table 3.

14.1.4 The relative retention times of the peak for a toxic PCB must be within 5% of the relative retention times listed in Table 2 of Method 1668. The retention times of peaks representing PCBs other than the toxic PCBs must be within the retention time windows established.

14.2 Quantitative Determination

14.2.1 For peaks which meet the criteria listed above (14.3), quantitate the PCB peaks from the response relative to the appropriate internal standard.

14.2.1.1 Any peaks representing the other congeners are quantitated using an average of the response factors from all of the labeled PCBs isomers at the same level of chlorination.

14.2.2 Recovery of each internal standard must be within 25-150%.

14.2.2.1 It is recommended that samples that do not meet the above requirement be re-extracted and re-analyzed.

14.2.3 The OPR results must meet the acceptance criteria reported in Table 7.

14.3 Calculations

14.3.1 The concentrations for PCB compounds are calculated by using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times W \times RRF}$$

Where:

C_x = concentration of unlabeled PCB congeners (or group of coeluting isomers within an homologous series),

A_x = sum of the integrated ion abundances of the quantitation ions for unlabeled PCBs

A_{is} = sum of the integrated ion abundances of the quantitation ion for the labeled internal standards,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight of the sample (solid or liquid), and

RRF = calculated relative response factor for the analyte.

14.3.2 The detection limits can be calculated using the following formula:

$$DL = \frac{2.5 \times H_N \times Q_{IS}}{H_{IS} \times W \times RRF}$$

Where:

DL = sample specific estimated detection limit,

H_N = noise height (peak to peak),

H_{IS} = peak height of the internal standard,

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction,

W = weight of the sample (solid or liquid), and

RRF = calculated relative response factor for the analyte.

15 REFERENCES

15.1 Alford-Stevens, A., Bellar, T. A., Eichelberger, J. W., and W. L. Budde, 1984. Method 680 -- Determination of Pesticides and PCBs in Water and Soil/Sediment by HRGC/LRMS, U. S. EPA. Cincinnati, OH.

15.2 Draft Method 1668. Measurement of Toxic PCB Congeners By Isotope Dilution HRGC/HRMS, Prepared by Analytical Methods Staff, Engineering and Analysis Division (4303), Office of Science and Technology, Office of Water, U. S. Environmental Protection Agency, Washington, DC, March, 1997.

15.3 EPA Region 10 SOP For the Validation of Method 1668 Toxic, Dioxin-Like, PCB Data. Revision 1.0, December 8, 1995.

Table 1. PCB Target Compounds and Quantitation Limits[1]

Coplanar PCB Congeners	IUPAC	Quantitation Limit Water[2] (ng/L)	Quantitation Limit Solid[2] (ng/g)	Quantitation Limit Fish/Tissue[2] (ng/g)
3,3',4,4'-Tetra-CB	77	0.5	0.05	0.02
3,4,4',5-Tetra-CB	81	0.5	0.05	0.02
3,3',4,4',5-Penta-CB	126	0.5	0.05	0.02
3,3',4,4',5,5'-Hexa-CB	169	0.5	0.05	0.02
Toxically Significant Mono-Ortho Substituted PCBs				
2,3,3',4,4'-Penta-CB	105	0.5	0.05	0.02
2,3,4,4',5-Penta-CB	114	0.5	0.05	0.02
2,3',4,4',5-Penta-CB	118	0.5	0.05	0.02
2',3,4,4',5-Penta-CB	123	0.5	0.05	0.02
2,3,3',4,4',5-Hexa-CB	156	0.5	0.05	0.02
2,3,3',4,4',5'-Hexa-CB	157	0.5	0.05	0.02
2,3',4,4',5,5'-Hexa-CB	167	0.5	0.05	0.02
2,3,3',4,4',5,5'-Hepta-CB	189	0.5	0.05	0.02
Other Environmentally Significant PCBs				
2-Mono-CB	1	0.5	0.05	0.02
4-Mono-CB	3	0.5	0.05	0.02
2,4'-DiCB	8	0.5	0.05	0.02
4,4'-DiCB	15	0.5	0.05	0.02
2,2',5-Tri-CB	18	0.5	0.05	0.02
2,4,4'-Tri-CB	28	0.5	0.05	0.02
2,2',3,5'-Tetra-CB	44	0.5	0.05	0.02
2,2',5,5'-Tetra-CB	52	0.5	0.05	0.02
2,3',4,4'-Tetra-CB	66	0.5	0.05	0.02
2,2',3,4,5'-Penta-CB	87	0.5	0.05	0.02
2,2',3,4',5-Penta-CB	90	0.5	0.05	0.02
2,2',4,5,5'-Penta-CB	101	0.5	0.05	0.02
2,2',3,3',4,4'-Hexa-CB	128	0.5	0.05	0.02
2,2',3,4,4',5'-Hexa-CB	138	0.5	0.05	0.02
2,2',4,4',5,5'-Hexa-CB	153	0.5	0.05	0.02
2,2',3,3',4,4',5-Hepta-CB	170	0.5	0.05	0.02
2,2',3,4,4',5,5'-Hepta-CB	180	0.5	0.05	0.02
2,2',3,4,4',5',6-Hepta-CB	183	0.5	0.05	0.02
2,2',3,4,4',6,6'-Hepta-CB	184	0.5	0.05	0.02
2,2',3,4',5,5',6-Hepta-CB	187	0.5	0.05	0.02
2,2',3,3',4,4',5,5'-Octa-CB	194	0.5	0.05	0.02
2,2',3,3',4,4',5,6-Octa-CB	195	0.5	0.05	0.02

2,2',3,3'5,5',6,6'-Octa-CB	202	0.5	0.05	0.02
2,2',3,3',4,4',5,5',6-Nona-CB	206	0.5	0.05	0.02
2,2',3,3',4,4',5,6,6'-Nona-CB	207	0.5	0.05	0.02
Deca-CB	209	0.5	0.05	0.02
Total PCB Homologues				
Monochlorobiphenyl (MCB) Homologues[3]		0.5	0.05	0.02
Dichlorobiphenyl (DiCB) Homologues[3]		0.5	0.05	0.02
Trichlorobiphenyl (TriCB) Homologues[3]		0.5	0.05	0.02
Tetrachlorobiphenyl (TCB) Homologues[3]		0.5	0.05	0.02
Pentachlorobiphenyl (PeCB) Homologues[3]		0.5	0.05	0.02
Hexachlorobiphenyl (HxCB) Homologues[3]		0.5	0.05	0.02
Heptachlorobiphenyl (HpCB) Homologues[3]		0.5	0.05	0.02
Octachlorobiphenyl (OCB) Homologues[3]		0.5	0.05	0.02
Nonachlorobiphenyl (NCB) Homologues[3]		0.5	0.05	0.02
Decachlorobiphenyl (DeCB) Homologues[3]		0.5	0.05	0.02

1 Nomenclature for Polychlorinated Biphenyls

MCB = Monochlorobiphenyl
DiCB = Dichlorobiphenyl
TriCB = Trichlorobiphenyl
TCB = Tetrachlorobiphenyl
PeCB = Pentachlorobiphenyl
HxCB = Hexchlorobiphenyl
HpCB = Heptachlorobiphenyl
OCB = Octachlorbiphenyl
NCB = Nonachlorobiphenyl
DeCB = Decachlorobiphenyl

2 Quantitation limits listed are based upon 1 liter of aqueous sample, 10 grams dry weight solid, and 25 grams fish/tissue sample.

3 Quantitation limits are based upon the single PCB congener which is used to calibrate for the homologue series.

Table 2. Concentration of PCBs in Calibration and Calibration Verification Solutions

		Solution Concentration (pg/µL)				
2a. Coplanar PCB Congeners	IUPAC	CS1	CS2	CS3*	CS4	CS5
3,3',4,4'-Tetra-CB	77	1.0	10	50	100	500
3,4,4',5-Tetra-CB	81	1.0	10	50	100	500
3,3',4,4',5-Penta-CB	126	1.0	10	50	100	500
3,3',4,4',5,5'-Hexa-CB	169	1.0	10	50	100	500

2b. Significant Toxic Mono-Ortho PCBs	IUPAC	CS1	CS2	CS3*	CS4	CS5
2,3,3',4,4'-Penta-CB	105	1.0	10	50	100	500
2,3,4,4',5-Penta-CB	114	1.0	10	50	100	500
2,3',4,4',5-Penta-CB	118	1.0	10	50	100	500
2',3,4,4',5-Penta-CB	123	1.0	10	50	100	500
2,3,3',4,4',5-Hexa-CB	156	1.0	10	50	100	500
2,3,3',4,4',5'-Hexa-CB	157	1.0	10	50	100	500
2,3',4,4',5,5'-Hexa-CB	167	1.0	10	50	100	500
2,3,3',4,4',5,5'-Hepta-CB	189	1.0	10	50	100	500

2c. Environmentally Significant PCBs	IUPAC	CS1	CS2	CS3*	CS4	CS5
2-Mono-CB	1	1.0	10	50	100	500
4-Mono-CB	3	1.0	10	50	100	500
2,4'-DiCB	8	1.0	10	50	100	500
4,4'-DiCB	15	1.0	10	50	100	500
2,2',5-Tri-CB	18	1.0	10	50	100	500
2,4,4'-Tri-CB	28	1.0	10	50	100	500
2,2',3,5'-Tetra-CB	44	1.0	10	50	100	500
2,2',5,5'-Tetra-CB	52	1.0	10	50	100	500
2,3',4,4'-Tetra-CB	66	1.0	10	50	100	500
2,2',3,4,5'-Penta-CB	87	1.0	10	50	100	500
2,2',3,4',5-Penta-CB	90	1.0	10	50	100	500
2,2',4,5,5'-Penta-CB	101	1.0	10	50	100	500
2,2',3,3',4,4'-Hexa-CB	128	1.0	10	50	100	500
2,2',3,4,4',5'-Hexa-CB	138	1.0	10	50	100	500
2,2',4,4',5,5'-Hexa-CB	153	1.0	10	50	100	500
2,2',3,3',4,4',5-Hepta-CB	170	1.0	10	50	100	500
2,2',3,4,4',5,5'-Hepta-CB	180	1.0	10	50	100	500
2,2',3,4,4',5',6-Hepta-CB	183	1.0	10	50	100	500
2,2',3,4,4',6,6'-Hepta-CB	184	1.0	10	50	100	500
2,2',3,4',5,5',6-Hepta-CB	187	1.0	10	50	100	500
2,2',3,3',4,4',5,5'-Octa-CB	194	1.0	10	50	100	500

2c. Environmentally Significant PCBs	IUPAC	CS1	CS2	CS3*	CS4	CS5
2,2',3,3',4,4',5,6-Octa-CB	195	1.0	10	50	100	500
2,2',3,3',5,5',6,6'-Octa-CB	202	1.0	10	50	100	500
2,2',3,3',4,4',5,5',6-Nona-CB	206	1.0	10	50	100	500
2,2',3,3',4,4',5,6,6'-Nona-CB	207	1.0	10	50	100	500
Deca-CB	209	1.0	10	50	100	500

2d. Total PCB Homologues		CS1	CS2	CS3*	CS4	CS5
Monochlorobiphenyl (MCB) Homologues[3]		1.0	10	50	100	500
Dichlorobiphenyl (DiCB) Homologues[3]		1.0	10	50	100	500
Trichlorobiphenyl (TriCB) Homologues[3]		1.0	10	50	100	500
Tetrachlorobiphenyl (TCB) Homologues[3]		1.0	10	50	100	500
Pentachlorobiphenyl (PeCB) Homologues[3]		1.0	10	50	100	500
Hexachlorobiphenyl (HxCB) Homologues[3]		1.0	10	50	100	500
Heptachlorobiphenyl (HpCB) Homologues[3]		1.0	10	50	100	500
Octachlorobiphenyl (OCB) Homologues[3]		1.0	10	50	100	500
Nonachlorobiphenyl (NCB) Homologues[3]		1.0	10	50	100	500
Decachlorobiphenyl (DeCB) Homologues[3]		1.0	10	50	100	500

Internal Standards	IUPAC	CS1	CS2	CS3*	CS4	CS5
^{13}C-4-Mono-CB	3	200	200	200	200	200
^{13}C-2,4,4'-Tri-CB	28	400	400	400	400	400
^{13}C-3,3',4,4'-Tetra-CB	77	400	400	400	400	400
^{13}C-2,2',4,5,5'-Penta-CB	101	400	400	400	400	400
^{13}C-2,3,3',4,4'-Penta-CB	105	400	400	400	400	400
^{13}C-2,3',4,4',5-Penta-CB	118	400	400	400	400	400
^{13}C-3,3',4,4',5-Penta-CB	126	400	400	400	400	400
^{13}C-2,2',3,4,4',5'-Hexa-CB	138	400	400	400	400	400
^{13}C-2,3,3',4,4',5-Hexa-CB	156	400	400	400	400	400
^{13}C-2,3,3',4,4',5'-Hexa-CB	157	400	400	400	400	400
^{13}C-3,3',4,4',5,5'-Hexa-CB	169	400	400	400	400	400
^{13}C-2,2',3,4,4',5,5'-Hepta-CB	180	800	800	800	800	800
^{13}C-2,2',3,3',4,4',5,5'-Octa-CB	194	800	800	800	800	800
^{13}C-2,2',3,3',5,5',6,6'-Octa-CB	202	800	800	800	800	800

Internal Standards	IUPAC	CS1	CS2	CS3*	CS4	CS5
^{13}C-2,2',3,3',4,5,5',6,6'-Nona-CB	208	800	800	800	800	800
^{13}C-Deca-CB	209	2000	2000	2000	2000	2000

Recovery Standards	IUPAC	CS1	CS2	CS3*	CS4	CS5
^{13}C-4,4'-Di-CB	15	200	200	200	200	200
^{13}C-3,4,4',5-Tetra-CB	81	400	400	400	400	400
^{13}C-2,3,3',5,5'-Penta-CB	111	400	400	400	400	400
^{13}C-2,3,3',4,4',5,5'-Hepta-CB	189	400	400	400	400	400

* Calibration Verification Solution

Table 3. Theoretical Ion Abundance Ratios and QC Limits

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits[1]	
			Lower	Upper
1	M/M+2	3.13	2.66	3.60
2	M/M+2	1.57	1.33	1.81
3	M/M+2	1.04	0.88	1.20
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.56	1.32	1.78
6	M/M+2	0.51	0.43	0.59
6	M+2/M+4	1.25	1.05	1.43
7	M/M+2	0.45	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02
9	M/M+2	1.34	1.14	1.54
9	M/M-2	0.78	0.66	0.90
10	M/M+2	1.17	0.99	1.35

(1) Represents ± 15% windows around the theoretical ion abundance ratios.

Table 4. Quantitation Limits for the Determination of Coplanar/Mono-Ortho PCBs Only

Coplanar/Mono-Ortho PCB Target Compounds				
Target Compound	Congener Number	Quantitation Limit[1] Water (pg/L)	Quantitation Limit[1] Solid (pg/g)	Quantitation Limit[1] Fish/Tissue (pg/g)
3,3',4,4'-Tetra-CB	77	50	5.0	2.0
3,4,4',5-Tetra-CB	81	50	5.0	2.0
2,3,3',4,4'-Penta-CB	105	50	5.0	2.0
2,3,4,4',5-Penta-CB	114	50	5.0	2.0
2,3',4,4',5-Penta-CB	118	50	5.0	2.0
2',3,4,4',5-Penta-CB	123	50	5.0	2.0
3,3',4,4',5-Penta-CB	126	50	5.0	2.0
2,3,3',4,4',5-Hexa-CB	156	50	5.0	2.0
2,3,3',4,4',5'-Hexa-CB	157	50	5.0	2.0
2,3',4,4',5,5'-Hexa-CB	167	50	5.0	2.0
3,3',4,4',5,5'-Hexa-CB	169	50	5.0	2.0
2,2',3,3',4,4',5-Hepta-CB	170	50	5.0	2.0
2,2',3,4,4',5,5'-Hepta-CB	180	50	5.0	2.0
2,3,3',4,4',5,5'-Hepta-CB	189	50	5.0	2.0

1 Quantitation limits are based on 1 liter aqueous sample, 10 grams dry weight solid, and 25 grams fish/tissue sample.

Table 5. Concentration of Coplanar/Mono-Ortho PCBs in Calibration Solutions

		Solution Concentration (pg/µL)				
Coplanar/Mono-Ortho PCB Congeners	IUPAC	CS1	CS2	CS3*	CS4	CS5
3,3',4,4'-Tetra-CB	77	1.0	10	50	100	500
3,4,4',5-Tetra-CB	81	1.0	10	50	100	500
2,3,3',4,4'-Penta-CB	105	1.0	10	50	100	500
2,3,4,4',5-Penta-CB	114	1.0	10	50	100	500
2,3',4,4',5-Penta-CB	118	1.0	10	50	100	500
2',3,4,4',5-Penta-CB	123	1.0	10	50	100	500
3,3',4,4',5-Penta-CB	126	1.0	10	50	100	500
2,3,3',4,4',5-Hexa-CB	156	1.0	10	50	100	500
2,3,3',4,4',5'-Hexa-CB	157	1.0	10	50	100	500
2,3',4,4',5,5'-Hexa-CB	167	1.0	10	50	100	500
3,3',4,4',5,5'-Hexa-CB	169	1.0	10	50	100	500
2,2',3,3',4,4',5-Hepta-CB	170	1.0	10	50	100	500
2,2',3,4,4',5,5'-Hepta-CB	180	1.0	10	50	100	500
2,3,3',4,4',5,5'-Hepta-CB	189	1.0	10	50	100	500

Internal Standards	IUPAC	CS1	CS2	CS3*	CS4	CS5
^{13}C-3,3',4,4'-Tetra-CB	77	400	400	400	400	400
^{13}C-2,2',4,5,5'-Penta-CB	101	400	400	400	400	400
^{13}C-2,3',4,4',5-Penta-CB	118	400	400	400	400	400
^{13}C-3,3',4,4',5-Penta-CB	126	400	400	400	400	400
^{13}C-2,2',3,4,4',5'-Hexa-CB	138	400	400	400	400	400
^{13}C-2,3,3',4,4',5-Hexa-CB	156	400	400	400	400	400
^{13}C-2,3,3',4,4',5'-Hexa-CB	157	400	400	400	400	400
^{13}C-3,3',4,4',5,5'-Hexa-CB	169	400	400	400	400	400
^{13}C-2,2',3,4,4',5,5'-Hepta-CB	180	800	800	800	800	800

Recovery Standards	IUPAC	CS1	CS2	CS3*	CS4	CS5
^{13}C-3,4,4',5-Tetra-CB	81	400	400	400	400	400
^{13}C-2,3,3',5,5'-Penta-CB	111	400	400	400	400	400
^{13}C-2,3,3',4,4',5,5'-Hepta-CB	189	400	400	400	400	400

* Calibration Verification Solution

Table 6. Exact Masses Monitored for PCBs

Compound	Native PCBs	Internal Standard PCBs
MonoCB	188.0393, 190.0363	194.0594, 196.0564
DiCB	222.0003, 223.9974	234.0406, 236.0376
TriCB	255.9613, 257.9584	268.0016, 269.9986
TetraCB[1]	289.9224, 291.9194	301.9626, 303.9597
PentaCB[1]	325.8775, 327.8775	337.9207, 339.9177
HexaCB[1]	359.8415, 361.8385	371.8817, 373.8788
HeptaCB[1]	393.8025, 395.7995	403.8457, 405.8428
OctaCB	427.7635, 429.7606	439.8038, 441.8008
NonaCB	463.7216, 465.7186	473.7648, 475.7619
DecaCB	497.6826, 499.6797	509.7229, 511.7199

1 Exact Masses for Coplanar/Mono-Ortho PCB Analysis Only

Table 7. Acceptance Criteria for Concentrations of PCBs in Performance Tests (ng/mL)

Congener	IUPAC	Test	IPR		OPR	Test	VER
			s	x			
3,3',4,4'-Tetra-CB	77	100	14	80-130	70-160	50	40-65
3,4,4',5-Tetra-CB	81	100	10	80-130	70-140	50	35-65
3,3',4,4',5-Penta-CB	126	100	9	72-150	68-160	50	39-65
3,3',4,4',5,5'-Hexa-CB	169	100	11	74-160	64-170	50	39-65
2,3,3',4,4'-Penta-CB	105	100	9	72-150	68-160	50	39-65
2,3,4,4',5-Penta-CB	114	100	20	16-280	14-330	50	39-65
2,3',4,4',5-Penta-CB	118	100	9	72-150	64-160	50	39-65
2',3,4,4',5-Penta-CB	123	100	20	16-280	14-330	50	39-65
2,3,3',4,4',5-Hexa-CB	156	100	11	74-160	64-170	50	39-65
2,3,3',4,4',5'-Hexa-CB	157	100	11	74-160	64-170	50	39-65
2,3',4,4',5,5'-Hexa-CB	167	100	11	74-160	64-170	50	39-65
2,3,3',4,4',5,5'-Hepta-CB	189	100	8	76-130	70-140	50	43-58
2-Mono-CB	1	100	10	70-130	70-140	50	35-65
4-Mono-CB	3	100	10	70-130	70-140	50	35-65
2,4'-DiCB	8	100	10	70-130	70-140	50	35-65
4,4'-DiCB	15	100	10	70-130	70-140	50	35-65
2,2',5-Tri-CB	18	100	10	70-130	70-140	50	35-65
2,4,4'-Tri-CB	28	100	10	70-130	70-140	50	35-65
2,2',3,5'-Tetra-CB	44	100	10	60-130	60-140	50	35-65
2,2',5,5'-Tetra-CB	52	100	10	60-130	60-140	50	35-65
2,3',4,4'-Tetra-CB	66	100	10	70-130	70-140	50	35-65
2,2',3,4,5'-Penta-CB	87	100	10	70-130	70-140	50	35-65
2,2',3,4',5-Penta-CB	90	100	10	70-130	70-140	50	35-65
2,2',4,5,5'-Penta-CB	101	100	10	70-130	70-140	50	35-65
2,2',3,3',4,4'-Hexa-CB	128	100	10	70-130	70-140	50	35-65
2,2',3,4,4',5'-Hexa-CB	138	100	10	70-130	70-140	50	35-65
2,2',4,4',5,5'-Hexa-CB	153	100	10	70-130	70-140	50	35-65
2,2',3,3',4,4',5-Hepta-CB	170	100	8	76-130	70-140	50	43-58
2,2',3,4,4',5,5'-Hepta-CB	180	100	8	76-130	70-140	50	43-58
2,2',3,4,4',5',6-Hepta-CB	183	100	10	70-130	70-140	50	35-65
2,2',3,4,4',6,6'-Hepta-CB	184	100	10	70-130	70-140	50	35-65
2,2',3,4',5,5',6-Hepta-CB	187	100	10	70-130	70-140	50	35-65
2,2',3,3',4,4',5,5'-Octa-CB	194	100	10	70-130	70-140	50	35-65
2,2',3,3',4,4',5,6-Octa-CB	195	100	10	70-130	70-140	50	35-65
2,2',3,3',5,5',6,6'-Octa-CB	202	100	10	70-130	70-140	50	35-65
2,2',3,3',4,4',5,5',6-Nona-CB	206	100	10	70-130	70-140	50	35-65
2,2',3,3',4,4',5,6,6'-Nona-CB	207	100	10	70-130	70-140	50	35-65
Deca-CB	209	100	10	70-130	70-140	50	35-65

Congener	IUPAC	Test	IPR		OPR	Test	VER
			s	x			
Monochlorobiphenyl (MCB) Homologues[3]							
Dichlorobiphenyl (DiCB) Homologues[3]							
Trichlorobiphenyl (TriCB) Homologues[3]							
Tetrachlorobiphenyl (TCB) Homologues[3]							
Pentachlorobiphenyl (PeCB) Homologues[3]							
Hexachlorobiphenyl (HxCB) Homologues[3]							
Heptachlorobiphenyl (HpCB) Homologues[3]							
Octachlorobiphenyl (OCB) Homologues[3]							
Nonachlorobiphenyl (NCB) Homologues[3]							
Decachlorobiphenyl (DeCB) Homologues[3]							
^{13}C-4-Mono-CB	3	100	30	40-160	25-150	100	70-170
^{13}C-2,4,4'-Tri-CB	28	200	30	120-280	50-300	200	140-260
^{13}C-3,3',4,4'-Tetra-CB	77	200	37	56-268	40-350	200	142-280
^{13}C-2,2',4,5,5'-Penta-CB	101	200	40	70-340	50-500	200	154-260
^{13}C-2,3,3',4,4'-Penta-CB	105	200	39	32-558	26-656	200	154-260
^{13}C-2,3',4,4',5-Penta-CB	118	200	39	32-558	26-656	200	154-260
^{13}C-3,3',4,4',5-Penta-CB	126	200	39	32-558	26-656	200	154-260
^{13}C-2,2',3,4,4',5'-Hexa-CB	138	200	40	120-320	50-500	200	140-286
^{13}C-2,3,3',4,4',5-Hexa-CB	156	200	43	48-314	34-410	200	140-286
^{13}C-2,3,3',4,4',5'-Hexa-CB	157	200	43	48-314	34-410	200	140-286
^{13}C-3,3',4,4',5,5'-Hexa-CB	169	200	43	48-314	34-410	200	140-286
^{13}C-2,2',3,4,4',5,5'-Hepta-CB	180	400	41	112-564	80-744	400	288-552
^{13}C-2,2',3,3',4,4',5,5'-Octa-CB	194	400	40	120-680	100-600	400	280-520
^{13}C-2,2',3,3',5,5',6,6'-Octa-CB	202	400	40	120-680	100-600	400	280-520
^{13}C-2,2',3,3',4,5,5',6,6'-Nona-CB	208	400	40	120-680	100-600	400	280-520
^{13}C-Deca-CB	209	1000	50	300-1700	250-1500	1000	700-1300

APPENDIX A-39

STANDARD OPERATING PROCEDURE FOR CHLOROPHYLL-A

8.0 CHLOROPHYLL *a*

8.1 Introduction

The concentration of photosynthetic pigments is used to estimate phytoplankton biomass. All green plants contain chlorophyll *a* and this constitutes 1 to 2% of the dry weight of planktonic algae. Other pigments, such as chlorophyll b and c, as well as chlorophyll degradation products, such as phaeophytins are also found in aquatic environments.

Chlorophyll *a* can be determined by spectrophotometric, fluormetric and high performance liquid chromatographic techniques. The method here employs fluorometry, which is more sensitive than spectrophotometry and utilizes less sample. One drawback, however, is that two common degradation products of chlorophyl *a* and pheophytin *a* can interfere with the chlorophyll *a* determination. These pheopigments can be measured, but are unreliable if chlorophyll *b* is present. Upon acidification of chlorophyll *b*, the resulting fluorescence emission of pheophytion *b* is coincident with that of pheophytin *a*, producing an underestimation of chlorophyll *a* and an overestimation of pheopigments.

In the handling of samples for chlorophyll a samples, the biggest causes of chlorophyll degradation are light, temperature, and acidity.

8.2 Sample Handling

- 100 ml to 200 ml of sample is usually sufficient for chlorophyll *a* analyses.
- Samples should be put in clean glass or plastic containers. If container is not opaque the container should be wrapped in foil.
- Samples should be kept cold (1-4 °C), not frozen, and in the dark from collection time onward.
- If samples are field filtered, following Section 8.3 below, freeze the filters and keep frozen until they have been analyzed.
- Samples should be logged in by sample management in subdued light and transported to microbiology in a cooler as soon as possible after receipt.

8.3 Sample Filtration

8.3.1 Equipment and Reagents

- 100 ml graduated cylinder

- Fiber filters Whatman glass (GF/B) or Gelman (AE)
- Glass filtering apparatus
- Saturated magnesium carbonate solution
- Forceps
- Opaque (black) petri dishes
- Vacuum pump

8.3.2 Laboratory Procedure

- Set up filtering apparatus. Set vacuum on pump to <100 mm Hg.
- Handle filters with designated forceps only, and do not touch the inside of any glassware.
- Carry out the procedure in subdued light.
- Shake sample thoroughly.
- Using the specially prepared graduated cylinder, measure a 100 ml aliquot of sample. Sample volume may vary according to turbidity and algae concentration.
- Record the volume filtered on form.
- After adding the 100 mls of sample into the filtering flask, add 1 ml of saturated magnesium carbonate. Filter sample with 100 mm Hg or less of vacuum. Rinse vessel once with 5 ml deionized water.
- After filtration, remove the filtering funnel and fold the filter in half, using the forceps. Transfer the filter to an opaque (black) petri dish and label each petri dish with sample ID number.
- Rinse the filtering vessel and graduated cylinder twice with deionized water prior to filtering the next sample.
- For each BTR or twenty samples filtered, a reagent blank should be prepared by filtering DI water through a glass fiber filter and processing it as if it were a sample. The volume value for the control is entered as 1.
- When all samples are filtered: 1) rinse all filtering funnel parts and the graduated cylinder with DI water before storing. 2) wrap the perti dishes in batches of eight with aluminum foil. Label with parameter, date, client, and sample numbers. 3) store in freezer in sample management. Filters should be stored in the freezer at least overnight but not more than 21 days. Additional storage time can result in some decrease in chlorphyll a concentration. In addition, if the whole water pH is less

than 5, then the extraction process should be initiated as soon as possible. 4) include date, time, and initials on the chlorophyll *a* analyses worksheet. Fill in the correct information.

8.4 Pigment Extraction

8.4.1 Equipment and Reagents

- Tissue grinder (1/4" drill)
- Glass grinding tube with matching pestle with TFE tip.
- Centrifuge
- 15 ml centrifuge tubes plus caps
- saturated magnesium carbonate
- 90% buffered acetone solution

8.4.2 Laboratory Procedure

- Be sure to turn on the ventilation fan before working with the acetone.
- Allow filters to thaw. Be sure room lighting is subdued before opening.
- Using the designated forceps, insert the filter into the grinding tube. Add 5-10 ml of aqueous acetone.
- With the pestle in the drill bit macerate the filter, at 500 rpm for 1 min. The sample should be well ground.
- Transfer sample to a screw cap centrifuge tube.
- Rinse grinder with 90% aqueous acetone and add to the centrifuge tube. Cap tube.
- Steep sample at least 2 hours, but not more than 24 hours, at 4 °C in the dark.
- Wrap centrifuge tubes in foil during storage.
- Remove the tubes from the refrigerator and allow to warm to room temperature in the dark.
- Mix the tube by inverting and centrifuge at 500 g (2500 rpm) for twenty minutes.
- Decant the clarified extract into a 25 or 50 ml volumetric flask and dilute to volume with 90% aqueous acetone. Stopper the volumetric flask and mix by inversion at least twelve times. This volume is the extract volume and should be entered as such on the chlorophyll *a* worksheet.

8.5 Fluorometric Determination of Chlorophyll *a*

8.5.1 Equipment and Reagents

- Turner design model TD-700 fluorometer equipped with 10-045 Daylight White lamp, photomultiplier tube (red-sensitive), and excitation (10-050R) and emission filters (10-051R) .
- Fluorometer cuvette
- Volumetric flasks
- Glass pipettes
- 1 NHCl
- Aqueous 90% acetone with $MgC0_3$ (for samples)

8.5.2 Laboratory Procedure

8.5.2.1 Fluorometer Calibration

The TD-700 is calibrated and operated in the Multi-Optional Mode - Direct Concentration mode. In this mode the TD-700 will display the actual concentration in the selected units. The calibration procedure for the Multi-Optional Mode is as follows:

- Press <ENT> from the HOME screen, then press <1> for Setup, then <1> again for Mode. Use <↔> to choose the Multi-Optional Mode. Next press <ESC> to return to the previous screen, then press <2> to choose the calibration procedure. Use the <↔> key to choose "Direct Conc" for the Direct Concentration calibration procedure. Next press <ESC> to return to the previous screen, then press <3> to choose the units of measure. Press <ESC> twice to return to the Setup/Cal screen.

- To begin the calibration sequence press <2> from the Cal/Setup screen; the Direct Concentration calibration sequence will appear. When prompted to enter the maximum range (the maximum concentration to be read), press <1> to accept the current value or <9> to enter a new value. The range of acceptable values is 1-1000.

- Next enter the number of standards that will be used to calibrate the TD-700 (1-5 concentrations. It is recommended that a minimum of 3 standards be used.

- When the TD-700 calls for the "HiStd Conc", press <1> to accept the current value and advance to the next screen. Press <9> to change the value. Enter the actual concentration of the highest concentration standard (Hi Std) to be used and press <ENT>. The Hi Std should be about 80% of the Max range previously selected. The acceptable range for all standards is 0.1 to 1000. The concentrations of the

standards selected must be within the max range previously selected and the difference in concentration between any two standards should not be less than 10% of the max range selected. Calibrate using the highest concentration first then use standards 2-5 in any order.

- Fill a clean 13 x 100 mm cuvette with the Hi Std. Wipe the outside of the cuvette dry and insert it into the sample adaptor in the sample chamber and close the lid. Press <*>. The TD-700 will adjust the sensitivity (as shown by the SENS FACTOR) to the level appropriate for that standard then read the standard.

- The TD-700 will prompt you to enter the actual concentration of the second standard (#2 Std) and to insert the second standard, then the third (#3 Std), etc. Use a clean, rinsed cuvette and insert the next standard; press <*>; then <ENT> when finished.

- When all standards have been run, the TD-700 will prompt you to insert the Blank. Fill a clean cuvette with the Blank (90% acetone solution), wipe the outside dry, and insert it into the sample adaptor in the sample chamber. Press <ENT>.

- Wait for the Blank reading to stabilize, the press <0>. The TD-700 will read the Blank, then automatically return to the HOME screen. Calibration data will printout automatically to the laptop computer.

- This calibration procedure must be performed whenever the lamp, or filters are replaced or if the measured concentration of the solid standards differs from the value established during the most recent calibration event by more than 10 percent. The TD-700 must be calibrated at least annually.

- Calculate the "r" factor during calibration by measuring the concentration of a primary standard prior to (R_b) and after (R_a) acidification. Acidify 5 ml of the primary standard by adding 0.15 ml of 0.1 N HCl (3 drops), mix, wait 90 seconds, then record the chlorophyll *a* concentration. Calculate r as follows:

$$r = R_b/R_a$$

8.5.3 Flurometric Standards

- Turner Designs Solid Secondary Chlorophyll *a* standards are calibrated against the liquid primary chlorophyll *a* standards in acetone (the concentration of the primary standards are determined spectrophotometrically by Turner Designs).

- Results should be ± 10% of the calculated value.

- At least one standard is measured per run or with every twenty samples.

8.5.4 Determination of Chlorophyll *a* in Sample

- Insert the appropriate excitation (10-050R) and emission filter (10-051R) as per manufacturer's instructions. Turn on the TD-700 and allow it to warm up for 10 minutes. Make certain the lamp (10-045 Daylight White lamp) is functioning.
-
- From the final extract derived from the extraction procedure in 8.4.2 above the chlorophyll *a* and pheophytin *a* can be determined on a calibrated fluorometer. Add approximately 5 ml of sample to a clean 13 x 100 mm glass cuvette.

- Measure sample fluorescence by placing the cuvette into the sample chamber, close the chamber, then press <*>. The chlorophyll *a* concentration is automatically sent to the computer, however the concentration should also be manually recorded on the chlorophyll *a* analysis benchsheet. This is the R_d value (uncorrected for pheophytin *a* content).

- Remove the cuvette from the fluorometer and acidify the sample by adding 0.15 ml of 0.1 N HCl (3 drops). Shake tube gently to mix the acid and sample.

- Place the cuvette back into the fluorometer, wait 90 seconds, then read and record the chlorophyll *a* concentration. This is the R_c value for the sample.

- Record the R_d and R_c values for each sample. The chlorophyll *a* and pheophytin *a* concentrations are calculated as follows:

$$\text{Chlorophyll } a, \mu g/L = (r/r - 1)(R_d - R_c)$$

$$\text{Pheophytin } a, \mu g/L = (r/r - 1)(rR_c - R_d)$$

where;

r = the before:after ratio of a pure chlorophyll *a* solution
R_d = concentration of a sample extract before acidification
R_c = concentration of a sample extract after acidification

The concentration of chlorophyll *a* and pheophytin *a* in the original sample is calculated by multiplying the results of the above equations by the extraction volume (in milliliters) and dividing by the volume (in milliliters) of sample filtered. Any dilution or concentration factors must also be incorporated accordingly.

- After the sample has been analyzed, pour the acetone extract into a labeled "waste" container to be disposed as "solvent waste" in the Hazardous Waste Room.

- Fill in date, initials, and all other appropriate information on the chlorophyll *a* worksheet.

8.6 Quality Control

A method blank, a blank filter carried through the entire process, is created at the beginning of each run. In addition, a solid secondary chlorophyll *a* standard will be measured at the beginning of each run and after every twenty samples. The measured value should be ± 10% of the standards calculated value. The reporting limit is <0.1 µg/L.

8.7 Cleaning Glassware

It is important that glassware be clean and acid free.

Materials:

Liquinox
$NaHC0_3$
$NaHC0_3$ buffered acetone

8.7.1 Laboratory Procedure

- Wash the glassware in liquinox and water, using the brushes reserved for washing chlorophyll glassware.
- Rinse the glassware thoroughly in tapwater. If the glassware has been in contact with acid, rinse with $NaHC0_3$ solution 2-3 times.
- Rinse again thoroughly with tapwater.
- Rinse once with DI water.
- Triple rinse with 90% $MgC0_3$ buffered acetone.
- Air or oven dry.

8.8 Reagents for Chlorophyll *a* Analysis

8.8.1 Saturated Magnesium Carbonate Solution

Dissolve 1 g $MgC0_3$ in 100 ml DI water or 10 g of $MgC0_3$ in 1 liter of deionized water. Mix thoroughly and allow to settle. Use supernatant to prepare 90% buffered acetone.

8.8.2 Sodium Bicarbonate Solution (1N)

Weigh 8.4g $NaHC0_3$ into a 100 ml flask and dilute to volume with DI water. Mix well before use.

8.8.3 90% Buffered Acetone

For grinding of filters and dilutions of chlorophyll *a* extraction.

Mix 900 parts acetone with 100 parts saturated magnesium carbonate solution. 900 ml acetone plus 100 ml of magnesium carbonate solution will not equal 1L.

8.8.4 1N HCl

Pipette 8.4 ml concentrated HCl into a 100 ml flask. Dilute to volume with DI water an mix well before use.

8.8.5 Sodium Bicarbonate Solution

For rinsing glassware. Dissolve 8.4 g $NaHC0_3$ in 1 L of DI water. Mix well.

8.9 Data Reduction

Using Excel 97, import the TD-700 data text file and calculate the chlorophyll *a* and pheophytin *a* concentrations for each sample. When complete, print the Excel worksheet and attach it to the BTR worksheet.

8.10 Laboratory Transcription

Record corrected, uncorrected and pheophytin *a* values (if requested) on the appropriate BTR worksheets. Be sure to include the units as µg/L. All calculations and transcriptions are QC'd by another laboratory technician, who will sign and date the laboratory analysis worksheet.

8.11 Reporting Results

Enter the concentration data for each sample into the LIMS "Results Entry Form"; when complete, submit all worksheets and reports to the Quality Assurance Officer or other designated person for review. Results will be checked, transcribed and reported according to ABS'S standard operating procedure. BTR's and worksheets will be filed according to ABS'S standard operating procedure.

Reference: Standard Methods for the Examination of Water and Wastewater. 19th ed., 1995. "Instructions for Fluorometric Analyses of Chlorophyll *a*." U.S. EPA, 1992.

APPENDIX A-40

STANDARD OPERATING PROCEDURE FOR ATTERBERG LIMITS (LIQUID LIMIT, PLASTIC LIMIT, AND PLASTICITY INDEX IN SOIL)

(Atterberg Limits)

Liquid Limit, Plastic Limit, and Plasticity Index of Soil
Method: ASTM D4318-93

Approvals and Signatures

QA Officer: Martha Boy Date: 2/21/96

Environmental Manager: Roland Legenby Date: 21 FEB 96

1.0 Scope and Application

1.1 This method covers the determination of liquid limit, plastic limit and plasticity index of soils

1.2 Minimum quantity of sample is 150 grams of soil passing the No. 40 (425 um) sieve.

1.3 There is no holding time requirement. Samples that are being prepared by the wet preparation procedure should be kept in their natural water content and will require refrigeration.

1.4 This analysis is amenable to soils with significant amount of silts and clay particles.

2.0 Summary of Method

2.1 Take a representative portion of the sample, approximately 150 to 200 grams, which has passed through the No. 40 (425 um) sieve. The liquid limit is determined by spreading a portion of the soil in a brass cup and dividing the sample in two parts with a groove tool. The cup is repeatedly dropped with a standard mechanical (liquid limit) device until the sample flows together. This test is repeated several times at the same and/or different water contents. The water content of the soil when it takes 25 drops of the liquid limit device to make the sample flow together is the liquid limit. The plastic limit is determined by repeatedly pressing and rolling the soil into a 3.2 mm (1/8 inch) diameter thread, until the thread

crumbles and can no longer be rolled into a ball or thread. The water content of the soil at this point is the plastic limit. The plasticity index is calculated as the difference between the liquid and plastic limits.

3.0 Material and reagents

3.1 Balance sensitive to 0.01 grams.

3.2 No. 40 (425 um) sieve.

3.3 Liquid limit device which meets the requirements of ASTM D4318

3.4 Flat grooving tool which meets the requirements of ASTM D8314.

3.5 Ground glass plate that is 12 inches square and 3/8 inch thick.

3.6 Spatulas and mixing utensils for mixing and sample recovery.

3.7 Tins for drying samples.

3.8 Storage containers to preserve moisture content.

3.9 Squirt bottles for de-ionized water.

3.10 Oven with temperature control that can maintain a constant temperature of $110 \pm 5°C$.

4.0 Procedures

4.1 Soil Preparation

Wet preparation: This is the preferred method, because the natural water content is maintained. Samples with minimal particles greater than the 425 um should be pressed through the No 40 sieve by hand until 150 to 200 grams of soil has passed through. For samples with significant amount of particles greater than 425 um, the soils should be washed through the No. 40 sieve with de-ionized water. Excess water should be evaporated off by exposing the sample to an air current and/or excess clear water should be decanted from the sample. Avoid over drying the soil by occasionally

mixing the soils. The soils should be brought to a water content by either adding or removing water, so that closure of the soil in the liquid limit device is within 25 to 35 blows based on the analyst judgement. Store the sample in a sealed container for 16 hours.

Dry Preparation: The sample should be allowed to dry at room temperature. Separate the soil particles with a mortar and pestle. Take 150 to 200 grams of soil which has passed through the No. 40 sieve and add de-ionized water. Mix the soil and water until a moisture content is reached that will achieve closure of the soil in the liquid limit device with 25 to 35 blows based on the analyst judgement. Store the sample in a sealed container for 16 hours.

4.2 **Liquid Limit**: Spread the soil to a thickness of 10 mm at its maximum depth in the brass cup of the liquid limit device. Take care to work any air bubbles out of the sample. Divide the sample in two with the groove tool, so that there is no soil in the groove and the sides of the sample are smooth. Turn the crank of the liquid limit device at a rate of two revolutions per second until the soil flows together along a 13 mm (1/2 inch) length. Verify that premature closure has not occurred due to an air bubble. A successful test will achieve closure between 15 to 35 blows depending on the test method below. Take a representative portion of the sample and determine moisture content in accordance to ASTM D2216.

Multipoint Liquid Limit: Repeat the test above at a different water content by adding or evaporating water from the sample. Three test should be completed that have achieved results between 15 to 25 blows, 20 to 30 blows and 25 to 35 blows. If all the tests are below 25 blows, or if the soil keeps crumbling when it is cut, or if the soil keeps sliding in the cup, then the liquid limit cannot be determined; record the soil as non plastic without performing the plastic limit test.

One Point Liquid Limit: This method is successful when closure of the groove is achieved between 20 and 30 blows. Repeated tests are considered successful when closure is achieved with no more than a two drop difference. If all the tests are below 20 or greater than 30 blows, or if the soil keeps crumbling when it is cut, or if the soil keeps sliding in the cup, then the liquid limit cannot be determined; record the soil as non-plastic without performing the plastic limit test.

4.3 **Plastic Limit:** Take approximately 20 grams of soil from the sample prepared for the liquid limit test. Reduce the water content by working the soil on the ground glass plate, exposing it to an air current, and/or blotting it with a paper towel. Adequate moisture content is when the soil can be rolled in ones hand with out sticking to it. Take approximately 1.5 to 2.0 grams of sample for the test. Roll the sample in an ellipsoidal form. Roll the sample between ones fingers and palm and on the glass plate to form a thread with a uniform thickness of 3.2 mm (1/8 inch) thick. The amount of hand and finger pressure will very greatly with different soils. If a thread of uniform thickness is achieved, roll the thread into an ellipsoid again. Repeat this process until the soil cannot be rolled to a 3.2 mm thread or into an ellipsoid. When the soil reaches that state, one trial is completed. Determine the moisture content of the combined soil from three completed trials according to ASTM D2216. Repeat the plastic limit by performing three more trials as described above.

5.0 Calculations

5.1 **Liquid Limit (LL)**

Multipoint Liquid Limit: Plot the relationship between the water content (Wn) and the corresponding number of drops (N) on a semilogarithmic scale. The water content (Wn) is plotted on the X-axis with an arithmetical scale, and the number of blows (N) is plotted on the Y-axis with a logarithmic scale. Draw the best straight line through three or more points. Take the water content that corresponds with 25 drops as the liquid limit.

One-Point Liquid Limit:

$$LL = Wn * (N/25)^{0.121}$$

The liquid limit is the average between two trials. If the difference between the two trials is greater than one percentage point, repeat the test.

5.2 **Plastic Limit (PL):** The plastic limit is the average between the two water contents. The results are considered accurate if the results are within the precision range of Table 2 in ASTM D4318 (typically a difference of 2.6 or less in water content).

5.3 **Plasticity Index (PI):**

$$PI = LL - PL$$

If the liquid limit or plastic limits could not be determined, or the plastic limit is equal to or greater than the liquid limit, report the soil as nonplastic.

6.0 Quality Control Requirements

6.1 Check the balance daily with Class S weights.

6.2 Calibrate the sieves bi-annually or as requested.

6.3 Inspect the Liquid Limit Device prior to each use for wear of the cup, of the cup hanger, of the rubber base and of the cam. Adjust the drop height prior to each use.

6.4 Check the temperature of the 110°C oven daily in the morning.

6.5 A duplicate analysis is recommended for every set of 20 samples.

APPENDIX A-41

STANDARD OPERATING PROCEDURE FOR SPECIFIC GRAVITY (FOR USE IN POROSITY CALCULATION)

Specific Gravity
Method: ASTM D854

Approvals and Signatures

QA Officer: Martha Boy Date: 2/21/96

Environmental Manager: Roland Lupenty Date: 21 FEB 96

1.0 Scope and Application

1.1 This method covers the determination of specific gravity of soil.

1.2 Minimum quantity of sample is 25 grams of dry soil.

1.3 There is no specified holding time.

1.4 This analysis is amenable to sand, silt and clay samples.

2.0 Summary of Method

2.1 Weigh out a representative portion of the sample passing the No. 10 (2.00 mm) sieve (25 to 30 grams) and record this mass. Place the sample in a calibrated volumetric flask, add enough de-ionized (DI) water to cover the sample, and allow the sample to soak overnight. Apply a vacuum to the flask for 30 minutes and periodically tap the flask to dislodge any trapped air. Fill the flask to the referenced volume with DI water. Weigh the flask\sample\water and record the weight and the temperature of the water.

3.0 Materials and Reagents

3.1 Balance sensitive to 0.01 grams

3.2 No. 10 (2.00mm) sieve.

3.3 Volumetric flask, 100 mL or 500 mL.

3.4 Spatulas, brushes and mixing utensils for mixing and sample recovery.

3.5 Squirt bottles for de-ionized water.

3.6 Oven with a temperature control ranging from 60°C to 110°C.

3.7 Mortar and Pestle.

3.8 Blender and dispersion cup as specified in ASTM D422 (wet preparation method only).

3.9 Temperature measuring device accurate to ± 0.5°C.

3.10 1000 mL beaker, plastic or glass.

4.0 Procedures

4.1 **Flask Preparation**

Pycnometer calibration: Weigh the mass of the clean and oven dried volumetric flask. Fill flask with DI water to reference volume line and weigh. Measure temperature of water in degrees Celsius.

Calculations:

Ma at Tx = Mf + (Dw at Tx/(Dw at Ta) * (Ma at Ta - Mf)

Where:
Dw = Density of water
Ma = Mass of pycnometer and water, g
Mf = Mass of pycnometer, g
Ta = Observed temperature of water, °C
Tx = any other desired temperature, °C

Note 1: Density of water is from Table 1 of ASTM D854 or equivalent.

4.2 **Soil Preparation**

Dry : Separate soil particles with mortar and pestle. Remove particles greater than 2.00 mm in size using a No.10 sieve. Tare a calibrated 100 mL volumetric flask. Add 25 grams of a representative soil sample passing the No. 10 sieve, place in the flask and record this mass. Fill flask 3/4 full with DI water and allow to sit overnight.

Wet Prep: Add 25 to 30 grams of the dry soil sample passing the No. 10 sieve into dispersion cup and blenderize for 5 minutes. Pour and wash (using DI water) contents of dispersion cup through No. 10 sieve into a 500 mL volumetric flask. Discard any particles retained on the No. 10 sieve.

4.3 Connect volumetric flask to a vacuum for 30 minutes. Tap flask with a rubber covered pestle to remove air bubbles.

4.4 Fill the volumetric flask to the reference line with DI water, weigh and record mass.

4.5 Measure temperature of water in flask and record.

4.6 If wet preparation was used, weigh and record the mass of 1000 mL beaker. Completely wash contents of volumetric flask into beaker using DI water. Place beaker into 110°C oven until dry. Weigh and record mass of beaker/dry sample.

Calculation:

Mass used in test = Beaker & dry sample - beaker

5.0 Calculation

$$SG \text{ at } Ta = [Mo/(Mo + (Ma - Mb)] \times (Dw \text{ at } Tb/Dw \text{ at } Ta)$$

Where:
SG = Specific Gravity
Mo = Mass of oven dried sample see (note 1)
Ma = Mass of pycnometer filled with DI water at Temp.a (typically 20 C)
Mb = Mass of pycnometer/sample/DI water at Temp.b (observed during step 4.4)
Ta = Temp. of water at desired reference temp. (typically 20 C)

Note 1: If sample was not oven dried, the soil mass is multiplied by the hydroscopic moisture correction factor (see ASTM D422).

6.0 Quality Control Requirements

6.1 Check the balance daily with Class S weight.

6.2 Calibrate the pycnometer bi-annually, as replaced, or as requested.

6.3 Calibrate the sieves bi-annually or as requested.

6.4 Check the temperature of the 110°C oven daily in the morning.

6.5 Temperature measuring device is checked against similar or more accurate temperature measuring device.

6.6 A duplicate analysis is recommended for every set of 20 samples.

NOTE 1—Flask sizes of larger than the specified minimum capacity are recommended. Larger flasks are capable of holding larger specimens and tend to produce better statistical results.

5.2 *Balance*—Meeting the requirements of Specification D 4753 and readable, without estimation, to at least 0.1 % of the specimen mass.

5.3 *Drying Oven*—Thermostatically-controlled oven, capable of maintaining a uniform temperature of 110 ± 5°C (230 ± 9°F) throughout the drying chamber.

5.4 *Thermometer*, capable of measuring the temperature range within which the test is being performed, graduated in a 0.5°C (1.0°F) division scale and meeting the requirements of Specification E 1.

5.5 *Desiccator*—A desiccator cabinet or large desiccator jar of suitable size containing silica gel or anhydrous calcium sulfate.[8]

NOTE 2—It is preferable to use a desiccant that changes color to indicate when it needs reconstitution.

5.6 *Entrapped Air Removal Apparatus*—To remove entrapped air, use one of the following:

5.6.1 *Hot Plate or Bunsen Burner*, capable of maintaining a temperature adequate to boil water.

5.6.2 *Vacuum System*, a vacuum pump or water aspirator, capable of producing a partial vacuum of 100 min or less absolute pressure.

NOTE 3—A partial vacuum of 100 mm Hg absolute pressure is approximately equivalent to a 660 mm (26 in.) Hg reading on vacuum gauge at sea level.

5.7 *Miscellaneous Equipment*, specimen dishes and insulated gloves.

6. Reagents and Materials

6.1 *Purity of Water*—Where distilled water is referred to in this test method, either distilled or demineralized water may be used.

7. Test Specimen

7.1 The test specimen may be oven-dried or moist soil and shall be representative of the total sample. In either case the specimen shall be large enough that its minimum mass in the oven-dried state is in accordance with the following:

Maximum Particle Size (100 % passing)	Standard Sieve Size	Minimum Mass of Test Specimen, g
2 mm	No. 10	20
4.75 mm	No. 4	100

8. Calibration of Pycnometer

8.1 Determine and record the mass of a clean, dry pycnometer, M_f.

8.2 Fill the pycnometer with distilled water to the calibration mark. Visually inspect the pycnometer and its contents to ensure that there are no air bubbles in the distilled water. Determine and record the mass of the pycnometer and water, M_a.

8.3 Insert a thermometer in the water, and determine and record its temperature, T_a, to the nearest 0.5°C (1.0°F).

8.4 From the mass, M_a, determined at the observed temperature, T_a, prepare a table of values of mass, M_a, for a series of temperatures that are likely to prevail when the mass of the pycnometer, soil, and water, M_b, is determined later. These values of M_a can be determined experimentally or may be calculated as follows:

$$M_a \text{ (at } T_x) = [(\text{density of water at } T_x / \text{density of water at } T_a) \times (M_a \text{ (at } T_a) - M_f)] + M_f$$

where:

M_a = mass of pycnometer and water, g,
M_f = mass of pycnometer, g,
T_a = observed temperature of water, °C, and
T_x = any other desired temperature, °C.

NOTE 4—This test method provides a procedure that is more convenient for laboratories making many determinations with the same pycnometer. It is equally applicable to a single determination. Bringing the pycnometer and contents to some designated temperature when masses M_a and M_b are taken, requires considerable time. It is important that masses M_a and M_b be based on water at the same temperature. Values for the density of water at temperatures from 16.0 to 30.0°C are given in Table 1.

9. Procedure

9.1 *Test Method A—Procedure For Oven-Dried Specimens:*

9.1.1 Dry the specimen to a constant mass in an oven maintained at 110 ± 5°C (230 ± 9°F) (See Note 5) and cool it in a desiccator.

NOTE 5—Drying of certain soils at 110°C (230°F) may bring about loss of water of composition or hydration, and in such cases drying may be done in reduced air pressure or at a lower temperature.

9.1.2 Determine and record the mass of a clean, dry, calibrated pycnometer, M_f. Select a pycnometer of sufficient capacity that the volume filled to the mark will be at least 50

TABLE 1 Density of Water and Correction Factor *K* for Various Temperatures

Temperature, °C	Density of Water (g/mL)	Correction Factor *K*
16.0	0.99897	1.0007
16.5	0.99889	1.0007
17.0	0.99880	1.0006
17.5	0.99871	1.0005
18.0	0.99862	1.0004
18.5	0.99853	1.0003
19.0	0.99843	1.0002
19.5	0.99833	1.0001
20.0	0.99823	1.0000
20.5	0.99812	0.9999
21.0	0.99802	0.9998
21.5	0.99791	0.9997
22.0	0.99780	0.9996
22.5	0.99768	0.9995
23.0	0.99757	0.9993
23.5	0.99745	0.9992
24.0	0.99732	0.9991
24.5	0.99720	0.9990
25.0	0.99707	0.9988
25.5	0.99694	0.9987
26.0	0.99681	0.9986
26.5	0.99668	0.9984
27.0	0.99654	0.9983
27.5	0.99640	0.9982
28.0	0.99626	0.9980
28.5	0.99612	0.9979
29.0	0.99597	0.9977
29.5	0.99582	0.9976
30.0	0.99567	0.9974

[8] Anhydrous calcium sulfate is sold under the trade name Drierite.