Title: PCB Preparation for Analysis by HRGC/HRMS [Method 1668A]

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1. SCOPE AND APPLICATION

1.1. This SOP is appropriate for the preparation of samples for analysis of mono- through deca-chlorinated biphenyls in a variety of matrices at low part-per-trillion to part-per-billion levels using high resolution gas chromatography and high resolution mass spectrometry, by Method 1668A.

1.2. The calibration range of the procedure for 1 L water is 20 to 20000 ppq, 2 to 2000 ppt for 10.0 g soil, sediment or tissue, and 40-40,000 pg/train (assuming 1/2 sample to 20 uL F.V.) for air train samples for mono-deca PCBs. Analysis of dilutions of aliquots of the sample will permit measurements of concentrations above the upper method calibration limit. The practical limits of detection and quantitation may be different from the lower method calibration limit, depending on the complexity of the matrix and the level of PCB contamination of the reagent and absorbent used in the extraction and cleanup procedure.

1.3. All PCB congener labeling in this document is consistent with IUPAC naming conventions.

1.4. When undertaking projects for the Department of Defense (DOD), the relevant criteria in Policy WS-PQA-021, “DOD QSM and AFCEE QAPP Implementation” must be checked and incorporated.

2. SUMMARY OF METHOD

2.1. This procedure uses matrix specific extraction and analyte specific cleanup techniques.

2.2. An aliquot of a matrix (water, soil, sediment, XAD Resin, filter) is spiked with the solution containing 27 isotopically 13C-labeled PCBs listed in Table I. The sample is then extracted according to matrix specific extraction procedures.

2.3. The extract is then cleaned up.

2.4. The preparation of the final extract for the instrumental analysis is accomplished by adding 5 isotopically (13C12) labeled recovery standards (Table I). Quantitation and analysis is performed as described in the analytical method SOP WS-ID-0013.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Manual (QAM).

3.2. Data qualifiers are defined on each data report. Commonly used data qualifiers are defined in the QAM.

4. INTERFERENCES

4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks. Analysts shall not use PVC gloves.

4.2. The use of high-purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

4.3. Reuse of glassware is to be minimized to avoid the risk of contamination. If samples are known or suspected of containing high analyte levels glassware should be segregated and isolated until analytical results are available. Additional cleaning or disposal of glassware may occur dependent upon analyte levels.

4.4. Interferents co-extracted from the sample will vary considerably from matrix to matrix. PCBs are often associated with other interfering chlorinated substances such as polychlorinated dioxins/furans (PCDD/PCDF), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, methoxy biphenyl hydroxydiphenyl ethers, benzylphenyl ethers, brominated diphenyl ethers, polynuclear aromatics and pesticides that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established. While certain clean-up techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

4.5. A high-resolution capillary column (30 m SPB Octyl) is used to resolve as many PCB isomers as possible; however, no single column is known to resolve all isomers.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Sacramento Addendum to the Corporate EH&S Manual (WS-PEHS-0002), and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. Eye protection that satisfies ANSI Z87.1, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. Nitrile or similar gloves must be used. Latex gloves may be used for methanol.

5.1.2. Exposure to chemicals must be maintained as low as reasonably achievable; therefore all samples must be opened, transferred and prepared in a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.1.3. Laboratory procedures such as repetitive use of pipettes, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.1.4. Hearing protection must be worn when using mechanical systems to grind fish or tissue samples.

5.1.5. When dissecting crawfish abdomens with a scalpel, cut from the hand holding the abdomen toward the tail (away from you).

5.1.6. Finely divided dry soils contaminated with PCBs are particularly hazardous because of the potential for inhalation and ingestion. Such samples are to be processed in a confined environment, such as a hood or a glove box.

5.1.7. Assembly and disassembly of glassware creates a risk of breakage and cuts. All staff members shall wear Kevlar or similar cut-resistant gloves over chemically resistant gloves when assembling and disassembling glassware.

5.1.8. The use of separatory funnels to extract aqueous samples with methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and a face shield must be

worn over safety glasses or goggles when it is performed.

5.1.9. The use of vacuum systems during rotovap concentration presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed or marred in any manner must not be used under vacuum. It must be removed from service and replaced.

5.1.10. Mercury is a highly toxic compound that must be handled with care. The analyst must be aware of the handling and cleanup techniques before handling this material. Spilled mercury requires that special cleanup tools and procedures be used.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table below contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Materials used in this SOP, and their Hazards.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid (1)	Corrosive Oxidizer Dehydradator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Mercury	Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

Materials used in this SOP, and their Hazards.			
Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable Poison Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
Dodecane	Flammable	None listed	May cause respiratory tract, skin or eye irritation.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Cyclohexane	Flammable Irritant	300 ppm TWA	Inhalation of vapors causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. High concentrations have a narcotic effect.
Nonane	Flammable	200 ppm	Primary hazard is flammability. May also cause skin irritation, drowsiness and dizziness if inhaled.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Equipment for sample preparation

6.1.1. Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.1.2. Glove box (optional)

6.1.3. Meat grinder - Hobart, or equivalent, with 3-5 mm holes in inner plate.

6.1.4. Analytical Balance - Capable of weighing 0.1 mg

6.1.5. Top Loading Balance- Capable of weighing 10 mg.

6.2. Extraction Apparatus

6.2.1. Water Samples

6.2.1.1. pH paper, wide range (Hydrion Papers, or equivalent)

6.2.1.2. Graduated cylinder, 1L capacity

6.2.1.3. 1L filtration flasks with side arm, for use in vacuum filtration of water samples

6.2.1.4. Separatory funnels - 250, 500 and 2000 mL, with Teflon stopcocks.

6.2.1.5. Glass fiber filters, Whatman GF-D, GF-F, GMF-150 or equivalent

6.2.2. Soxhlet/Dean-Stark (SDS) extractor

6.2.2.1. Soxhlet – 50 mm i.d., 200 mL capacity with 500 mL flask or 70 mm x 240 mm with 1000 mL round bottom flask.

6.2.2.2. Thimble - 30 x 100 or 43 x 123 mm Glass fiber

6.2.2.3. Moisture trap - Dean-Stark or Barret.

6.2.2.4. Heating mantle - hemispherical, to fit 500 mL or 1000 mL round bottom flask (Cal-Glass LG-8801-112, or equivalent).

6.2.2.5. Variable transformer - Powerstat (or equivalent), 110 volts, 10 amps.

6.2.3. Spatulas - Stainless Steel

6.2.4. Soxtherm extraction apparatus (Gerhardt SE416 or equivalent), including glass thimble holders, glass beakers, and gaskets.

6.3. Filtration Apparatus

6.3.1. Sodium sulfate, granular anhydrous

6.3.2. Pyrex glass wool. (pre-rinsed with methylene chloride)

6.3.3. Glass funnel - 125 - 250 mL.

6.3.4. Glass fiber filter paper (Whatman GF/D, or equivalent).

6.3.5. Drying Column - 15 to 20 mm i.d. Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

6.3.6. Buechner funnel, 15 cm.

6.3.7. Pressure filtration apparatus - Vacuum filtration

6.4. Centrifuge Apparatus

6.4.1. Centrifuge - Capable of rotating 500 mL centrifuge bottles or 15 mL centrifuge tubes at 5000 rpm minimum

6.4.2. Centrifuge tubes - 12-15 mL, with screw caps, to fit centrifuge

6.5. Concentration Apparatus

6.5.1. Rotary evaporator – (Büchi R210 or equivalent) equipped with a variable temperature water bath.

6.5.1.1. A vacuum source is required for use of the rotary evaporator. It must be equipped with a shutoff valve at the evaporator, and preferably, have a vacuum gauge.

6.5.1.2. A recirculation water pump and chiller are recommended, as the use of tap water for cooling the evaporator wastes large volumes of water, and can lead to inconsistent performance because water temperatures and pressures vary.

6.5.1.3. Round bottom flasks - 500 mL and 1000 mL or larger, with ground glass fitting compatible with the rotary evaporator.

6.5.2. Nitrogen blow down apparatus - installed in a fume hood.

6.5.3. Sample vials - 2-5 mL with Teflon-lined screw cap and 200 uL auto-injector insert vials with septum lined screw caps.

7. REAGENTS AND STANDARDS

7.1. pH adjustment and back extraction

7.1.1. Sodium hydroxide - Dilute 50 mL of 20 N NaOH with 50 mL reagent water.

7.1.2. Sulfuric acid - Reagent grade (specific gravity 1.84)

7.2. Solution drying and evaporation

7.2.1. Solution drying - Sodium sulfate, reagent grade, granular anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g) and stored in a pre-cleaned glass bottle with a screw cap that prevents

moisture from entering.

7.2.2. Prepurified nitrogen, reagent grade

7.3. Extraction Solvents: Acetone, toluene, cyclohexane, hexane, dodecane, isooctane, nonane, methanol and methylene chloride (DCM).

7.4. Absorbents for sample cleanup

7.4.1. Silica gel

7.4.1.1. Activated silica gel - Silica Gel 60-Em Science7734-4, 70-230 mesh, rinsed with methylene chloride, baked at 180ºC for one hour minimum, cooled in a desiccator, and stored at 130°C in a covered flask.

7.4.1.2. Acid silica gel (44 percent w/w) - Thoroughly mix 24 mL (44g) of concentrated sulfuric acid with 56.0 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with a Teflon-lined cap.

7.4.2. Alumina—the standard alumina cleanup procedure employs acidic alumina only. Basic alumina may be substituted or added to the cleanup procedure on a project specific basis, provided that the laboratory can meet the QA/QC requirements specified in Section 10. The same type of alumina must be used for all samples, including those used to demonstrate ongoing precision and accuracy (LCS).

7.4.2.1. Acid Alumina - ICN Super A. This alumina is purchased activated and can be used directly from the bottle. A column profile is performed for each new vendor; otherwise a laboratory control sample is used to re-verify new material from an existing vendor.

7.4.3. Mercury: triple distilled. (Mallinckrodt Baker, Inc. or equivalent)

7.5. Reference matrices

7.5.1. Reagent water - Water in which the PCBs and interfering compounds are not detected at above ½ the reporting limit by this method.

7.5.2. High solids reference matrix – sodium sulfate.

7.5.3. Filter paper or extraction thimble - Glass fiber filter papers or extraction thimbles in which the PCBs and interfering compounds are not detected

by this method.

7.5.4. Other matrices - This method may be verified on any matrix if the following criteria are met. Ideally, the matrix should be free of the PCBs, but in no case shall the background level of the PCBs in the reference matrix exceed three times the minimum levels given in Table II (CC1). If low background levels of the PCBs are present in the reference matrix, the spike level of the analytes used in Table III should be increased to provide a spike-to-background ratio in the range of 1:1 to 5:1.

7.5.5. Tissue reference matrix – Canola oil and sodium sulfate.

7.6. Standard solutions - Purchased as solutions or mixtures with certification to their purity, concentration and authenticity, or prepared from materials of known purity and composition. If compound purity is 98 percent or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark in screw-capped vials with Teflon-lined caps in a refrigerator at 4 degrees C. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. If solvent loss has occurred, the solution should be replaced.

7.6.1. Sealed ampoules may be used until the manufacturer's expiration date is exceeded.

7.6.1.1. If no expiration date is provided, then the expiration date will be 10 years from the date the ampoule is opened.

7.6.1.2. The solvent level should be monitored prior to each use to assure there has been no concentration of the standard over time.

7.6.2. All calibration, daily isotope dilution analytes, daily clean up isotope dilution analytes, and daily spiking solutions are stable for one year from preparation.

7.6.2.1. After one year, solutions may be re-verified. The re-verified solution may be used for an additional year, or until there is evidence of compound degradation or concentration.

7.6.2.2. The re-verification must be performed using an unexpired, not previously re-verified solution from a second lot or second vendor.

7.7. Stock solutions

7.7.1. Preparation - Prepare in isooctane or equivalent solvent per the steps

below or purchase as dilute solutions (Cambridge Isotope Laboratories, Cambridge, MA, or equivalent).

7.7.2. Stock standard solutions are prepared from dilutions of neat solutions. Dilutions are performed in volumetric flasks and transferred to a clean vial or amber glass bottle with Teflon-lined cap.

7.8. Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration of performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from Cambridge Isotope Laboratories.

7.9. Secondary standard - Using stock solutions, prepare secondary standard solutions containing the compounds and concentrations shown in Table I in dodecane.

7.10. Labeled compound stock standard - From stock standard solutions prepared as above, or from purchased mixtures, prepare this standard to contain the labeled compounds at the concentrations shown in Table I in isooctane.

7.11. Isotope dilution analytes - Prepare at the concentration shown in Table I in isooctane.

7.12. Clean up Internal standard - Prepare at the concentration shown in Table I in dodecane.

7.13. Calibration standards (CS1 through CS5) - Combine the solutions in Tables I and III to produce the five calibration solutions shown in Table II in dodecane. These solutions permit the relative response (labeled to unlabeled) and response factor to be measured as a function of concentration. The CS3 standard is used for calibration verification (VER).

7.14. Native spike solution - Used for determination of ongoing precision and accuracy, in the form of a laboratory control sample (LCS). This solution contains the analytes and labeled compounds at the concentrations listed in Tables I and III in isooctane.

7.15. GC retention time window defining solutions - Used to define the beginning and ending retention times for mono-deca chlorinated homologue groups.

7.15.1. CS3 is used to define chromatographic windows. (First and last eluters are included with CS3.

7.15.2. The 209 PCB single point calibration solution can also be used to determine the homologue windows.

7.16. Standard solutions will be periodically assayed against reference standards. Continued use of standard solutions past the initially indicated expiration date is

acceptable if concentrations are verified versus the reference standard. Upon acceptable verification, a new expiration/evaluation date will be noted in the standards logbook.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. The sample collection, shipping, handling, and chain-of-custody procedures are not described in the document. The complexity of the method is such that, in order to obtain reliable results, testers should be trained and experienced with sampling and preservation procedures.

8.2. There are no demonstrated maximum holding times associated with the PCBs in aqueous, solid, semi-solid, tissues, or other matrices. If stored in the dark at 0-6°C, and preserved if required, aqueous samples may be stored for up the one year. Similarly, if stored in the dark at <-10 °C, solids, semi-solid, multi-phase, and tissue samples may be stored for up to one year.

8.3. All extracts must be stored capped at room temperature and completely analyzed within 45 days of extraction.

9. QUALITY CONTROL

9.1. One method blank must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The method blank is an aliquot of reference matrix processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when target analytes are detected in the method blank above the acceptance limit or when surrogate recoveries are outside control limits. The associated samples will be evaluated for adverse impact, and flagged or qualified as appropriate. Re-extraction of the blank, other batch QC, and the affected samples are required when the method blank is deemed unacceptable. For any analyte detected in the blank in any of the homologous series of PCBs, the detection limit in the samples analyzed with that blank for the specific isomer or the total for that homologous series is increased to 5 times of the contamination level. Alternatively, both QC and sample results may be reported and qualified as necessary.

9.1.1. Certain programs, such as DOD, may require a more stringent evaluation of the method blank, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit.

9.2. A laboratory control sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. reagent water, Ottawa sand, sodium sulfate, extraction thimble, filter paper, etc.) spiked with 100 uL of Isotope Dilution Analyte

fortification solution (Table 1) and 100 uL of Native Standard fortification solution (Table III). The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside 50-150%, or the control limits provided on the LIMS, or by the client. The associated samples will be evaluated for adverse impact, and flagged or qualified as appropriate. Re-extraction of the blank, other batch QC, and the affected samples are required when the LCS is deemed unacceptable

9.3. A matrix spike/matrix spike duplicate (MS/MSD or MS/SD) pair may be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. MS/MSD are analyzed at the request of the client. An MS/MSD pair is aliquots of a selected field sample spiked with analytes of known identity and concentration. The MS/MSD pair must be processed in the same manner and at the same time as the associated samples. Spiked analytes must be within control limits 50-150%, or the control limits provided on the LIMS, or by the client. The result obtained from MS and MSD samples analysis should agree within 50 percent relative difference. Corrective actions must be documented on a Non-Conformance memo. Outliers with recoveries or precision outside control limits will be flagged and narrated as appropriate.

9.4. The isotope dilution analytes recovery for each sample and method blank should be between 25 and 150 percent. Signal-to-noise of isotope dilution analytes is also evaluated to assess data usability. Signal-to-noise should exceed 10:1 for all isotope dilution analytes.

9.5. Positive results for the 12 coplanar PCBs are reported above the lower calibration limit of 2.0 pg/g for solids assuming a 10.0 g aliquot, 20 pg/L for aqueous assuming a 1.0 liter aliquot, and 40 pg/sample for air train samples assuming a one half split of the sample. For all remaining congeners the reporting limit is ten times the lower calibration limit, unless otherwise specified. Detection limits are reported on a sample specific basis and all results are recovery corrected per the isotope dilution technique. For an analyte reported as ‘Not Detected’ the associated reporting limit represents its maximum possible concentration.

10. CALIBRATION

10.1. On a monthly basis, calibrate any auto-pipettes to be used in accordance with SOP WS-QA-0004.

10.2. On a daily basis, calibrate any balances to be used in accordance with SOP WS-QA-0041.

11. PROCEDURE

One time procedural variations are allowed only if deemed necessary in the professional judgment of a supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Non-Conformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Non-Conformance Memo shall be filed in the project file.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.1. Grinding or Blending of Fish Samples.

If not otherwise specified by the client, the whole fish (frozen) should be blended or ground to provide a homogeneous sample. The use of a stainless steel meat grinder with a 3- to 5-mm hole size inner plate is recommended. In some circumstances, analysis of fillet or specific organs of fish may be requested by the client. If so requested by the client, the above whole fish requirement is superseded.

WARNING: Hearing protection must be worn when grinding samples.

11.2. Phase Separation

Phase separation on very wet (>25 percent water) soil and sediment samples may be accomplished as follows: Place a 50 g portion in a suitable centrifuge bottle and centrifuge for 30 minutes at 2,000 rpm. Remove the bottle from the centrifuge and mark the interface level on the bottle. Estimate the relative volume of each phase. With a disposable pipette, transfer the liquid layer into a clean bottle. Mix the solid with a stainless steel spatula and remove a portion to be weighed and analyzed (percent moisture determination, extraction). Return the remaining solid portion to the original sample bottle (if empty) or to a clean sample bottle that is properly labeled, and store it as appropriate. Analyze the solid phase by using only the soil and sediment method. Take note of the estimated volume of liquid before disposing of the liquid as a liquid waste.

WARNING: Finely divided soils and sediments contaminated with PCBs are hazardous because of the potential for inhalation or ingestion of particles containing PCBs. Such samples should be handled in a confined environment (i.e., a closed hood or a glove box).

11.3. Sample Pre-Treatment

11.3.1. Paper pulp sludges are generally air-dried and ground prior to extraction by either Soxhlet (Section 11.4) or Soxtherm (Section 11.5). Because of the drying procedure, a Dean-Stark water separator may or may not be used for extraction.

11.3.2. Non-Paper pulp sludges are extracted as-is using either Soxhlet (Section

11.4) or Soxtherm (Section 11.5) techniques.

<Soxhlet Extraction see Section 11.4; Soxtherm Extraction see Section 11.5>

11.4. Soxhlet Extraction (Solids, Tissues, Sludges, and Wipes).

11.4.1. Percent moisture is determined in accordance with SOP WS-OP-0013.

11.4.2. If tissues requiring % Lipids are to be extracted, for each sample weigh the concentration vessel with label and boiling chips. Record the mass on the benchsheet.

11.4.3. Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1-2 drops of toluene per second will fall from the condenser tip into the receiver. Extract the apparatus for a minimum of four hours.

WARNING: Open the chiller supply valves about 15 minutes before turning on the heating element and ensure that all of the condensors are cold before you turn the heating element on. Check all of the condensors about 15 minutes after starting the heating process to ensure that they are still cold and functioning properly. If this cleaning cycle is to be left unattended (e.g., overnight) the first chemist to arrive the next morning is to check all condensers to ensure that they are still cold and functioning properly.

11.4.4. After pre-extraction, cool and disassemble the apparatus.

11.4.5. Reassemble the pre-extracted apparatus and add a fresh charge of toluene (250 ml – 350 ml) to the receiver and reflux flask.

NOTE: As an option, sodium sulfate may be mixed with the samples to remove moisture before sample extraction.

11.4.6. Weigh a well-mixed aliquot of each sample (10 g, unless otherwise specified) into a clean Soxhlet thimble. Record the mass to the nearest 0.01g. Use sodium sulfate for the batch QC (MB, LCS) for solids, and a mixture of 9 g sodium sulfate and 1 g canola oil for the batch QC for tissue matrices.

11.4.6.1. In the case of wipes, place the entire wipe sample into the Soxhlet apparatus (no thimble needed), including any liquid present with the sample. Use pre-cleaned wipes for the batch QC samples.

11.4.7. Add 100 µL aliquot of IDA standard in all samples. Add 100 µL of Native Spike to the LCS and matrix spike samples.

11.4.8. Extract the samples in a Soxhlet with a Dean-Stark apparatus with toluene for a minimum of 16 hours. The solvent must cycle completely through the system at least five times per hour.

WARNING: Open the chiller supply valves about 15 minutes before turning on the heating element and ensure that all of the condensers are cold before you turn the heating element on. Check all of the condensers about 15 minutes after starting the heating process to ensure that they are still cold and functioning properly. If this cleaning cycle is to be left unattended (e.g., overnight) the first chemist to arrive the next morning is to check all condensers to ensure that they are still cold and functioning properly.

11.4.9. Drain the water from the receiver if the receiver fills with water. Check and drain when necessary.

Note: If the receiver holds 10 mL of liquid, and 20 g of an approximately 10% solid sample is being extracted, then approximately 9 mL of water will end up in the receiver. In this case, the receiver will not need to be emptied (insufficient liquid to overflow), but it should be checked. If the sample amount is 50, and the percent solids is still 10%, then 45 mL of water will end up in the receiver. In this case, frequent checking is required, and the receiver will need to be emptied at least 5 times.

11.4.10. Cool the sample, then filter the toluene extract, if needed, through a glass-fiber filter or equivalent into a round-bottom flask.

11.4.10.1. If used, rinse the filter with 10 mL toluene, and combine the extract and rinsate.

11.4.11. If samples DO NOT require % lipids, add approximately 100 uL of Dodecane to the round bottom flask to act as a solvent keeper.

11.4.12. Concentrate the combined solutions to near dryness on a rotary evaporator at 70°C using 20-26 psi vacuum. Use of an inert gas to concentrate the extract is also permitted. Proceed with Section 11.12 as necessary.

11.5. Soxtherm Extraction (Solids, Tissues, Sludges, and Wipes)

11.5.1. Prior to loading samples, run the system through two cleaning cycles (approximately 1 hour each).

11.5.2. After pre-extraction, cool and disassemble the apparatus.

11.5.3. Weigh a well-mixed aliquot of each sample (10 g, unless otherwise specified) into a clean Soxhlet thimble. Record the mass to the nearest 0.01g. Use sodium sulfate for the batch QC (MB, LCS) for solids, and a

mixture of 9 g sodium sulfate and 0.250g corn oil for the batch QC for tissue matrices.

11.5.3.1. In the case of wipes, place the entire wipe sample into the Soxhlet apparatus (no thimble needed), including any liquid present with the sample. Use pre-cleaned wipes for the batch QC samples.

11.5.4. Place the thimble into the Soxtherm apparatus.

11.5.5. Spike all samples with 100 uL of isotope dilution analyte solution (2 ng), for a final concentration of 200 pg/g (based on a 10 g sample).

11.5.6. Spike the LCS (and MS/MSD, if present) with 100 uL of native spike.

11.5.7. Reassemble the pre-extracted apparatus and add a fresh charge (150 mL) of toluene to the apparatus.

11.5.8. Program the system to boil for 1 hour, and reduce the toluene volume by 70-90 mL (volume < volume of the thimble).

11.5.9. Continue the extraction for one hour fifteen minutes, reducing the toluene volume by another 15 mL.

11.5.10. After refluxing, allow the apparatus to cool.

11.5.11. Pour the samples into round bottom flasks, and if samples do not require % lipids, add 100 µL of dodecane as a keeper to the round bottom.

11.5.12. Proceed with Section 11.12 as necessary

11.6. Aqueous Samples (no filtration required)

11.6.1. Determine the sample volume by placing the sample bottle on a top-loading balance and taring the balance. Pour the entire sample (approximately 1 L) into a 2 L separatory funnel. Reweigh the empty bottle and record the sample weight. Record the sample weight to the nearest 1 gram.

11.6.2. Add 100 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel.

11.6.3. Add 100 uL of isotope dilution analyte (IDA) solution to the samples and LCSLCSD in the separatory funnel and 100 uL of the native spike to the LCS/LCSD and MS/MSD if applicable.

11.6.4. Extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation.

WARNING: Methylene chloride creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

WARNING: Separatory funnel extraction is a high risk activity. Analyst will wear a face shield over safety glasses/goggles for this extraction. Alternatively, the extraction can take place behind a closed hood sash.

11.6.5. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between the layers is more than one-third the volume of the solvent layer, employ mechanical techniques to complete this operation (e.g., a glass stirring rod or centrifuge). Drain the methylene chloride extract into a solvent rinsed glass funnel approximately one-half full of sodium sulfate. Set up the glass funnel so that it will drain directly into a solvent rinsed 500 mL round bottom.

NOTE: Experience with aqueous samples high in dissolved organic materials (e.g., paper mill effluents) has shown that acidification of the sample prior to extraction may reduce the formation of emulsions. Mechanical techniques may still be necessary to complete the phase separation. Refer to Section 11.11 for techniques to decrease or eliminate emulsions.

11.6.6. Extract the water sample two more times using 100 mL of fresh methylene chloride each time. Drain each extract through the funnel containing the sodium sulfate into the round bottom. After the third extraction, rinse the separatory funnel with at least 20 mL of fresh methylene chloride, and drain this rinse through the sodium sulfate into the round bottom, then add tetradecane.

11.6.7. Dry extract with sodium sulfate: Place glass wool in a precleaned filter funnel. Rinse glass wool with DCM and load funnel with DCM-rinsed Na_2SO_4. Pour extract through Na_2SO_4 to remove water. Rinse Na_2SO_4 with fresh DCM and collect in round bottom flask.

11.6.8. Transfer the extract to a 500-mL round-bottom, add 100 uL of dodecane and concentrate on a rotary evaporator at 60ºC and <10 lbs vacuum at 120-150 RPM. Proceed to Section 11.12 for cleanup options as needed.

NOTE: If no column cleanup is required do not add dodecane as a solvent keeper.

11.7. Aqueous Samples with filtration

Extract the aqueous samples, blanks, and PAR aliquots according to the following procedure.

11.7.1. Determine the sample volume by placing the sample bottle on a top-loading balance and taring the balance.

11.7.2. Spike all samples with 100µL of isotope dilution analyte solution (20 ng) for a final concentration of 20pg/mL (based on a 1 L sample).

11.7.3. Assemble a Buchner funnel on top of a clean 1 L filtration flask. Apply a vacuum to the flask, and pour the entire contents of the sample bottle through a glass fiber filter in the Buchner funnel, swirling the sample remaining in the bottle to suspend any particulates.

***WARNING:* Use of vacuum systems creates a significant risk of implosion. Thoroughly inspect all glassware and do not use any that has been chipped, rubbed, cracked, or marred in any fashion.**

***WARNING:* Ensure that the exhaust line from the vacuum pump is secured well inside of a fume hood so that it cannot fall out of the hood.**

11.7.4. Extract the filter and solid material using either Soxhlet (Section 11.4) or Soxtherm (Section 11.5).

11.7.5. Extract the filtrate using the procedures in Section 11.6, rinsing the filter flask and the sample bottle with DCM.

11.7.6. Perform concentration as detailed in Section 11.10.14.

11.7.7. Combine the concentrated extracts of filtrate and particulate prior to proceeding with cleanup or micro concentration steps.

11.7.8. Proceed to Section 11.12, Extract Cleanup.

11.8. Fish Tissue Lipid Content Determination

11.8.1. The percent lipid of fish samples is determined as follows:

Concentrate the extract from Section 11.4.11 or 11.5.11 on a rotary evaporator until constant weight is attained. An alternative process employing a VOA vial for weighing may be used for samples with expected low lipid amounts. The percent lipid is calculated using the following expression:

Equation 1

$$\text{Percent Lipid} = \frac{\textit{Weight of residue from extraction (g)}}{\textit{Weight of fish tissue portion (g)}} \times 100$$

11.9. Waste Dilution (Still-Bottom/Fuel Oil, and other solvent-miscible materials).

11.9.1. Weigh 1 g of the waste (organic liquids, fuel oils, and solids that will dissolve in a solvent) into a vial.

11.9.2. Add 40 mL of toluene (or other solvent if the material is not miscible/soluble in toluene). Shake gently to dissolve.

11.9.3. Remove a 4.0 mL aliquot (0.1g sample equivalent) and place in a culture tube. Add 1.0 mL of daily internal standard and 1.0 mL of cleanup recovery standard, and proceed to Section 11.12.

11.10. Air train sample – based on Method CARB 428.

11.10.1. There are two options for the preparation of air train sample. The first option is all fractions combined for a single analysis, and the second is to prepare and analyze separate front and back-half extracts.

11.10.2. Preparation of Extraction Thimble

Place a glass extraction thimble into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it. Remove the extraction thimble system and place it in a glass beaker for air drying and for catching rinses. Alternatively, the thimbles may be used directly from the box if the thimbles have been shown to be free of PCBs or interfering compounds at or above the project required reporting limits.

Option 1-Single composite of all air train fractions

11.10.3. Preparation of Container No. 1 (filter)

Place the filter and all particulate matter from Container No. 1 into the cleaned extraction thimble.

11.10.4. Preparation of Adsorbent Cartridge

Suspend the adsorbent module directly over the extraction thimble containing the associated filter. The glass frit of the module should be positioned up. Add a small amount of acetone to the module and discharge the XAD-2 resin into the thimble by using a nitrogen blowing apparatus. Rinse the walls of the module with acetone to remove any excess resin, collect the rinse in the thimble. Rinse the module with toluene and collect the rinses in the thimble containing the XAD-2 resin and filter.

11.10.5. Preparation of Container No. 2 (Front and Back-half Acetone and Methylene Chloride rinses)

Transfer the solvent to a round bottom flask. Rinse the sample container 3 times with methylene chloride and add these to the round bottom flask. Concentrate the solvent to a volume of about 1-5 mL using a rotary evaporator, at a temperature of 60ºC and <10 inches of vacuum at 120-150 RPM.

11.10.6. Preparation of Container No. 3 (Front and Back-half Toluene rinses)

This step can be done one of two ways as dictated by the client:

11.10.6.1. Option 1- Add the toluene rinse to the round bottom flask previously used to concentrate Container No. 2. Rinse the samples container three times with toluene and add the rinses to the round bottom flask. Concentrate the solvent to about 1-5 mL using a rotary evaporator at a temperature of 70ºC and 25 inches of vacuum. Add the rinses to the Soxhlet containing the corresponding filter and XAD resin portions.

11.10.6.2. Option 2- Add the toluene rinse to a pre-cleaned round bottom flask. Rinse the sample container three times with toluene and collect rinses in the round bottom flask. Concentrate the solvent to about 1-5 mL using a rotary evaporator at a temperature of 70°C and 25 inches of vacuum. Do not add the concentrated solvent to the Soxhlet containing the corresponding filter and XAD, instead add 100 uL of isotope dilution analyte (IS) and analyze as a separate sample.

11.10.7. Extraction and Concentration.

11.10.7.1. Surrogate compounds should have been added to the adsorbent cartridge prior to sample collection.

11.10.7.2. Place the extraction thimble containing the filter, XAD resin, and solvent rinses into the Soxhlet extractor. Rinse the beaker three times with toluene and add the rinses to the Soxhlet. Add toluene to the round bottom flask until it is about 2/3 full. Add several Teflon boiling chips to the round bottom flask and assemble the Soxhlet apparatus.

11.10.7.3. Add 100 uL of IDA standard to the thimble, connect the condenser, and adjust the heat source to cause the extractor to cycle approximately three times per hour for a minimum of 16 hours.

11.10.7.3.1. Note: Additional 100 uL volume of IDA standard may be added per split (i.e. ½ arichive = 200 uL total; 1/3 archive, 1/3

Method 0023A, 1/3 1668A = 300 uL; etc.)

11.10.7.4. Allow the Soxhlet to cool and 100 uL of dodecane may be added as a solvent keeper.

11.10.7.5. Concentrate the extract to near dryness using a rotary evaporator at 70ºC and 25 inches of vacuum. Proceed with clean up or splitting of the samples based on client requirements.

***WARNING:* Use of vacuum systems creates a significant risk of implosion. Thoroughly inspect all glassware and do not use any that has been chipped, rubbed, cracked, or marred in any fashion.**

***WARNING:* Ensure that the exhaust line from the vacuum pump is secured well inside of a fume hood so that it cannot fall out of the hood.**

Option 2- Separate Front and Back-half fractions. The Front-half consists of the filter and front-half solvent rinses, the Back-half consists of the XAD resin and Back-half rinses.

11.10.8. Preparation of Container No. 1 (filter)

Place the filter and all particulate matter from Container No. 1 into the cleaned extraction thimble.

11.10.9. Preparation of the Front-half acetone and methylene chloride rinse

Transfer the solvent to a round bottom flask. Rinse the sample container 3 times with methylene chloride and add these to the round bottom flask. Concentrate the solvent to a volume of about 1-5 mL, using a rotary, at a temperature of 60ºC and <10 inches of vacuum at 120-150 RPM. Quantitatively transfer the solvent to the Soxhlet apparatus containing the corresponding filter fraction.

11.10.10. Preparation of the Front-half toluene rinse

Add the toluene rinse to the round bottom flask previously used to concentrate the acetone/methylene chloride rinses. Rinse the samples container three times with toluene and add the rinses to the round bottom flask. Concentrate the solvent to about 1-5 mL using a rotary evaporator at a temperature of 70ºC and 25 inches of vacuum. Add the rinses to the Soxhlet containing the corresponding filter and acetone/methylene chloride fractions.

11.10.11. Preparation of Adsorbent Cartridge

Suspend the adsorbent module directly over a pre-cleaned extraction thimble. The glass frit of the module should be positioned up. Add a small amount of acetone to the module and discharge the XAD-2 resin into the thimble by using a nitrogen blowing apparatus. Rinse the walls of the module with acetone to remove any excess resin, collect the rinse

in the thimble. Rinse the module with toluene and collect the rinses in the thimble containing the XAD-2 resin.

11.10.12. Preparation of the Back-half acetone and methylene chloride rinse

Transfer the solvent to a round bottom flask. Rinse the sample container 3 times with methylene chloride and add these to the round bottom flask. Concentrate the solvent to a volume of about 1-5 mL, using a rotary, at a temperature of 60ºC and <10 inches of vacuum at 120-150 RPM. Quantitatively transfer the solvent to the Soxhlet apparatus containing the corresponding XAD resin fraction.

11.10.13. Preparation of the Back-half toluene rinse

Add the toluene rinse to the round bottom flask previously used to concentrate the acetone/methylene chloride rinses. Rinse the samples container three times with toluene and add the rinses to the round bottom flask. Concentrate the solvent to about 1-5 mL using a rotary evaporator at a temperature of 70ºC and 25 inches of vacuum. Add the rinses to the Soxhlet containing the corresponding XAD resin and acetone/methylene chloride fractions.

11.10.14. Extraction and Concentration.

11.10.14.1. Surrogate compounds should have been added to the adsorbent cartridge prior to sample collection.

11.10.14.2. Place the extraction thimble containing the filter or XAD resin, and its corresponding solvent rinses into the Soxhlet extractor. Rinse the beaker three times with toluene and add the rinses to the Soxhlet. Add toluene to the round bottom flask until it is about 2/3 full. Add several Teflon boiling chips to the round bottom flask and assemble the Soxhlet apparatus.

11.10.14.3. Add 100 uL of IDA standard to the thimble, connect the condenser, and adjust the heat source to cause the extractor to cycle approximately three times per hour for a minimum of 16 hours.

11.10.14.3.1. Note: Additional 100 uL volume of I.S. may be added per split (i.e. ½ arichive = 200 uL total; 1/3 archive, 1/3 Method 0023A, 1/3 1668A = 300 uL; etc.)

11.10.14.4. Allow the Soxhlet to cool and 100 uL of dodecane may be added as a solvent keeper.

11.10.14.5. Concentrate the extract to near dryness using a rotary evaporator at 70ºC and 25 inches of vacuum. Proceed with clean up or splitting of the samples based on client requirements.

WARNING: **Use of vacuum systems creates a significant risk of implosion. Thoroughly inspect all glassware and do not use any that has been chipped, rubbed, cracked, or marred in any fashion.**

WARNING: **Ensure that the exhaust line from the vacuum pump is secured well inside of a fume hood so that it cannot fall out of the hood.**

11.11. There are several useful methods to decrease or eliminate emulsion in aqueous samples when extracting with DCM. These methods may include stirring with a pipette to manually breakup the emulsions or to transfer the sample into centrifuge tubes and centrifuge at approximately 3000 RPM. The most useful method is to use a 1:1 $NaOH/H_2O$ solution to change the pH enough to disrupt the emulsion phase, which works 90% of the time. The following procedure describes how to prepare and use the solution to decrease or eliminate emulsions in aqueous samples during the liquid/liquid extraction step.

11.11.1. Preparing the solution:

Add 1.0 L of reagent grade NaOH solution to an empty 2.0 L NaOH container. Then add 1.0 L of DI H_2O to the container and leave the container in secondary containment with the lid off.

WARNING: The solution will begin to heat so let the solution stand until equilibrium is met and the solution is at room temperature.

When this process is complete, the solution will then be ready for use in the samples.

11.11.2. Using the solution to decrease emulsions:

11.11.2.1. Check the pH of the sample to make sure pH is between 3 and 7, then consult supervisor and client for instructions. Pour approximately 100 mL of 1:1 $NaOH/H_2O$ into a 1.0 L AGB.

11.11.2.2. Pour the solution with DCM back into the same 2.0 L separatory funnel and drain the DCM phase through Na_2SO_4 into a 500mL round bottom. Empty the aqueous waste into the LLE waste drum.

11.12. Cleanup: Depending on the complexity of the matrix, the following clean-up procedures may be employed as necessary or per client requirements.

11.12.1. Add 100 uL of Surrogate Standard to each extract.

11.12.2. Option C (Acid only) **(Required for all solid and tissue matrices)**:

11.12.2.1. Partition the extract in 50-125 mL of hexane against 40 mL concentrated H2SO4 in a separatory funnel. Shake for two minutes. Remove and discard the sulfuric acid layer (bottom). Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

NOTE: Additional rinses may be performed against sodium hydroxide or reagent water if deemed necessary by the laboratory management.

WARNING: Shaking with a concentrated caustic is a high-risk activity. Analyst must wear a face shield over safety glasses/goggles, or the shaking must take behind a closed hood sash.

11.12.3. Silica Gel Column Cleanup. **(Required for all samples)**

11.12.3.1. Add a plug of glass wool to a 20 mm ID disposable column and add 2 grams of activated silica gel, 4 grams of acidic silica gel, 2 grams of activated silica gel, and 1 cm of sodium sulfate.

11.12.3.2. Pre-rinse the column with at least 20 mL of methylene chloride followed by at least 20 mL of hexane.

11.12.3.3. Add the sample extract to the column, and rinse the sample container with 2 x 2 mL hexane rinses. Add the rinses to the column.

11.12.3.4. Elute the column with hexane and collect a total of 90 ml's of hexane.

11.12.3.5. Reduce the volume to about 2 mL under nitrogen and proceed with alumina column cleanup if deemed necessary.

11.12.4. Alumina Column Cleanup. **(Required for all sediment and tissue extracts)**

11.12.4.1. Put a small plug of glass wool in a 16 mm ID column and add 6 grams of acid alumina followed by 1 cm of sodium sulfate.

11.12.4.2. Pre-rinse the column with at least 20 mL of methylene chloride followed by at least 20 mL of hexane.

11.12.4.3. Transfer the sample (in 2 mL hexane) to the acid alumina column. Rinse sample flask with 2 x 2 mL hexane, transfer to acid alumina column.

11.12.4.4. Elute the column with 20 mL of hexane and discard.

11.12.4.5. Elute the column with 30 mL of 65% methylene chloride/hexane and collect.

11.12.5. Sulfur Removal with Elemental Mercury. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

Note: Use mercury sparingly in order to minimize exposure and disposal costs.

11.12.5.1. Transfer 2 mL of sample extract into a clean concentrator tube or Teflon sealed vial.

11.12.5.2. Add one to three drops (about 0.25mL) of mercury to the extract vial and seal.

WARNING: **Only nitrile gloves may be used when working with mercury and organic solvents at the same time.**

11.12.5.3. Shake well for 15-30 seconds.

11.12.5.4. If black precipitate forms, sulfur was present. Centrifuge, then transfer the supernatant to a clean test tube and repeat steps 11.10.5.2 and 11.10.5.3. Do this until relatively little precipitate remains, or a maximum of five sulfur cleanups has been performed.

WARNING: **Do NOT centrifuge glass tubes containing mercury. Due to the density of the mercury, the test tube could break in the centrifuge.**

11.12.5.5. If no precipitate is present, remove the extract from the mercury using a disposable pipette and transfer to a clean vial. Rotate the mercury waste out of the laboratory to the Hazardous Waste storage area for lab pack disposal.

11.12.5.6. Reduce the sample volume under nitrogen and proceed to RS.

11.13. Internal Standard-

11.13.1. Add 20 uL of internal standard in dodecane to a vial.

11.13.2. Transfer the sample contents to the vial containing the internal standard with several rinses of toluene.

11.13.3. Reduce under nitrogen to 20 uL.

11.13.4. Transfer to an injection vial and cap.

11.14. Analysis

11.14.1. The extract is ready for analysis by WS-ID-0013.

12. CALCULATIONS/DATA REDUCTION

Not applicable

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in WS-QA-0006. MDL are available in the Quality Assurance department.

13.2. Initial Demonstration

Each analyst must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration standard.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the historical acceptance criteria.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

14.2. Do not allow waste solvent to evaporate in fume hoods. All solvent waste is stored in capped containers unless transfers are being made.

14.3. The use of rotary evaporator systems to concentrate sample extracts significantly reduces the solvent released into the atmosphere.

15. WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP WS-EHS-0001. The following waste streams are produced when this method is carried out.

15.1. Assorted solvent and methylene chloride from glassware rinsing, glass fiber and sodium sulfate pre-rinsing, and extract rotary evaporator concentration. Collect the waste solvents in tripours during use. Empty the tripours into a 1-liter to 4-liter carboy at the fume hood. When the carboy is full, or at the end of your shift, whichever comes first, empty the carboy into the steel solvent drum in the H3 closet. When the drum is full to between two and six inches of the top, or after no more than 75 days, move the steel drum to the waste collection area for shipment.

15.2. Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous. Place contaminated materials into a yellow contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the dry lab trash into the appropriate steel dry lab trash collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.3. Extracted PUF filters, sodium sulfate, silica gel, alumina, carbon XAD-2 resin, paper funnel filters, glass wool, thimbles, fish/crawfish, ash and soil contaminated with various solvent and eluents. Dump the materials into an orange extracted soil bucket. When the bucket is full or at the end of the day, tie the plastic bag liner shut and put

the lab trash into the incinerate steel extracted solids collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.4. Extracted aqueous samples contaminated with methylene chloride and/or other organic solvents are collected at the fume hood in a 5-gallon or smaller carboy. If the samples are not at a neutral pH, add small quantities of sodium bicarbonate to bring the waste to neutral. Stir well. Once neutralized, immediately pour the carboy contents into a blue plastic LLE drum in the H3 closet. When full to between two and six inches of the top, or after no more than 75 days, move the LLE drum to the waste collection area for shipment.

15.5. Contaminated sulfuric acid used during Option C extract clean-up. Collect the used sulfuric acid in empty, 2.5-liter, plastic coated jars. When full or after no more than one year, whichever comes first, transfer these jars to the waste collection area for shipment.

15.6. Contaminated mercury used during sulfur clean-up. Collect the used mercury in empty 8 ounce plastic jars. When full or after no more than one year, transfer the jar to the waste collection area for shipment.

16. REFERENCES/CROSS REFERENCES

16.1. State of California Air Resources Board Method 428: Determination of Polychlorinated Dibenzo-p-dioxin (PCDD), Polychlorinated Dibenzofuran (PCDF), and Polychlorinated Biphenyl Emissions from Stationary Sources, September 12, 1990.

16.2. EPA Method 1668: Toxic polychlorinated Biphenyls by Isotope Dilution High Resolution Gas Chromatography/High resolution Mass Spectrometry, March 1997.

16.3. Method 1668, Revision A (Method 1668A): Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, August 2003.

17. METHOD MODIFICATIONS

17.1. Deviations from reference Method 1668A

17.1.1. Aqueous samples with < 1% solids are extracted as received, by separatory funnel. Samples with high solids content, > 1% solids, are either shaken well to thoroughly mix the sample followed by extraction by separatory funnel, or separated into two different samples for extraction and analysis, dependent upon client request.

17.1.2. Solid samples are extracted as received, with %-moisture determination

performed simultaneously. Dry weight correction to results is applied at the time of data reporting.

17.1.3. Tissue samples are extracted using toluene.

17.1.4. The sample extract cleanup procedures are all optional, except where noted, and based on analyst judgment. The routine cleanup procedures include acidic silica gel and acidic alumina cleanup columns. The laboratory does not routinely use Florisil, GPC, or anthropogenic column cleanup procedures.

17.1.5. The retention time windows used to identify the chlorination levels is established from the analysis of the native window defining mix included in the calibration curve and native spiking mix.

17.1.6. The laboratory routinely uses a SPB-Octyl column for analysis. Alternate columns such as DB-1 may be used on a project specific basis.

18. ATTACHMENTS

18.1. Table 1 – Composition of the Sample Fortification Solutions

18.2. Table 2 – Instrument Calibration Solution Concentrations

18.3. Table 3 – Composition of the Matrix Spike Fortification Solution

19. REVISION HISTORY

19.1. WS-IDP-0013, Revision 2.2, Effective 04/26/2013

19.1.1. Renamed Internal Standards to Isotope Dilution Analytes.

19.1.2. Renamed Recovery Standards to Internal Standards.

19.1.3. Editorial changes.

19.2. WS-IDP-0013, Revision 2.2, Effective 03/02/2012

19.2.1. Changed Section 11.5.3 from "1.0g canola oil" to "0.250g corn oil"

19.2.2. Editorial revisions.

19.3. WS-IDP-0013, Revision 2.1, Effective 10/14/2011

19.3.1. Inserted Section 11.2 from SOP WS-IDP-0007 as Section 11.7 in this SOP (Aqueous w/filtrate).

19.3.2. Inserted Section 6.2.1.5 – “Glass fiber filters, Whatman GF-D, GF-F, GMF-150 or equivalent.”

19.3.3. Editorial revisions.

19.3.4.

TABLE I
Composition of the Sample Fortification Solutions

	Sample Fortification Solution Concentration (pg/uL in Isooctane)	Recovery Standard Solution (pg/uL in Dodecane)	Clean-up Recovery Standard Solution (pg/uL in Dodecane)
$^{13}C_{12}$-2-MonoPCB (1)	20	--	--
$^{13}C_{12}$-4-MonoPCB (3)	20	--	--
$^{13}C_{12}$-2,2-DiPCB (4)	20	--	--
$^{13}C_{12}$-2,5-DiPCB (9)	--	100	--
$^{13}C_{12}$-4,4'-DiPCB (15)	20	--	--
$^{13}C_{12}$-2,2',6'-TriPCB (19)	20	--	--
$^{13}C_{12}$-2,4,4'-TriPCB (28)	--	--	100
$^{13}C_{12}$-3,4,4'-TriPCB (37)	20	--	--
$^{13}C_{12}$-2,2',5,5'-TetraPCB (52)	--	100	--
$^{13}C_{12}$-2,2',6,6'-TetraPCB (54)	20	--	--
$^{13}C_{12}$-3,3',4,4'-TetraPCB (77)	20	--	--
$^{13}C_{12}$-3,4,4',5-TetraPCB (81)	20	--	--
$^{13}C_{12}$-2,2',4,5,5'-PentaPCB (101)	--	100	--
$^{13}C_{12}$-2,2',4,6,6'-PentaPCB (104)	20	--	--
$^{13}C_{12}$-2,3,3',4,4'-PentaPCB (105)	20	--	--
$^{13}C_{12}$-2,3,3'5,5'-PentaPCB (111)	--	--	100
$^{13}C_{12}$-2,3,4,4',5-PentaPCB (114)	20	--	--
$^{13}C_{12}$-2,3',4,4'5-PentaPCB (118)	20	--	--
$^{13}C_{12}$-2',3,4,4',5-PentaPCB (123)	20	--	--
$^{13}C_{12}$-3,3',4,4',5-PentaPCB (126)	20	--	--
$^{13}C_{12}$-2,2',3',4,4',5'-HexaPCB (138)	--	100	--
$^{13}C_{12}$-2,2',4,4',6,6'-HexaPCB (155)	20	--	--
$^{13}C_{12}$-2,3,3',4,4',5-HexaPCB (156)	20	--	--
$^{13}C_{12}$-2,3,3',4,4',5'-HexaPCB (157)	20	--	--
$^{13}C_{12}$-2,3',4,4',5,5'-HexaPCB (167)	20	--	--
$^{13}C_{12}$-3,3',4,4',5,5'-HexaPCB (169)	20	--	--
$^{13}C_{12}$-2,2',3,3',5,5',6-HeptaPCB (178)	--	--	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HeptaPCB (188)	20	--	--
$^{13}C_{12}$-2,3,3',4,4',5,5'-HeptaPCB (189)	20	--	--
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OctaPCB (194)	--	100	--
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OctaPCB (202)	20	--	--
$^{13}C_{12}$-2,3,3',4,4'5,5',6-OctaPCB (2025	20	--	--
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NonaPCB (206)	20	--	--
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NonaPCB (208)	20	--	--

$^{13}C_{12}$-DecaPCB (209)	20	--	--

TABLE II
Instrument Calibration Solution Concentrations

Compound	IUPAC #(s)	Concentration (pg/uL in Dodecane)				
		CC1	CC2	CC3	CC4	CC5
Unlabelled Analytes						
MonoPCB	1,3	1	5	50	400	2000
DiPCB	4,15	1	5	50	400	2000
TriPCB	19,37	1	5	50	400	2000
TetraPCB	54,77,81	1	5	50	400	2000
PentaPCB	104,105,114,118,123,126	1	5	50	400	2000
HexaPCB	155, 156,157,167,169	1	5	50	400	2000
HeptaPCB	188,189	1	5	50	400	2000
OctaPCB	202,205	1	5	50	400	2000
NonaPCB	206,208	1	5	50	400	2000
DecaPCB	209	1	5	50	400	2000
Internal Standards						
^{13}C-MonoPCB	1,3	100	100	100	100	100
^{13}C-DiPCB	4,15	100	100	100	100	100
^{13}C-TriPCB	19,37	100	100	100	100	100
^{13}C-TetraPCB	54,77, 81	100	100	100	100	100
^{13}C-PentaPCB	104,105,114,118,123,126	100	100	100	100	100
^{13}C-HexaPCB	155,156,157,167,169	100	100	100	100	100
^{13}C-HeptaPCB	188,189	100	100	100	100	100
^{13}C-OctaPCB	202,205	100	100	100	100	100
^{13}C-NonaPCB	206,208	100	100	100	100	100
^{13}C-DecaPCB	209	100	100	100	100	100
Recovery Standards						
^{13}C-DiPCB	9	100	100	100	100	100
^{13}C-TetraPCB	52	100		100	100	100
^{13}C-PentaPCB	101	100	100	100	100	100
^{13}C-HexaPCB	138	100	100	100	100	100
^{13}C-OctaPCB	194	100	100	100	100	100
Cleanup Recovery Standards						
^{13}C-TriPCB	28	100	100	100	100	100
^{13}C-PentaPCB	111	100	100	100	100	100
^{13}C-HeptaPCB	178	100	100	100	100	100

TABLE III
Composition of the Matrix Spike Fortification Solution

Compound (Unlabelled)	IUPAC #(s)	Concentration (pg/uL in isooctane)
MonoPCB	1,3	20
DiPCB	4,15	20
TriPCB	19,37	20
TetraPCB	54,77,81	20
PentaPCB	104,105,114, 118,123,126	20
HexaPCB	155, 156,157,167,169	20
HeptaPCB	188,189	20
OctaPCB	202,205	20
NonaPCB	206,208	20
DecaPCB	209	20