TITLE: STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF TOTAL POLY-CHLORINATED BIPHENYLS (PCBs)

(KEY WORDS: PCBs, CONGENER, GC/ECD, CAPILLARY)
(BASED ON: EPA SW-846 8082 and EPA Report 600/4-81-045, 1982)

1. SCOPE AND APPLICATION

1.1 This document describes Safety-Kleen's Standard Operating Procedure (SOP) for the analysis of Total Polychlorinated Biphenyls (PCBs) in hydrotreated base stocks.

1.2 Having the ability to quantify Total PCBs rather than Aroclors as is done in SK9202 allows for any PCB, that may remain after the hydrotreating process, to be quantified even if it does not produce a familiar Aroclor pattern.

1.3 PCBs were prepared industrially in the United States and Great Britain by the *Monsanto Chemical Corp*. under the trade name of *Aroclor*.® Although, strictly speaking, PCBs exist as a family of 209 *congeners*. Because it is not possible to get the necessary separation of all 209 congeners on a GC ECD, this method uses a standard made up of the 19 most prevalent congeners found in Aroclors and quantifies all PCBs based on how their retention times relate to the retention times of the standard peaks. It is assumed here that congeners with similar retention times will share similar calibration factors for the purposes of quantification in this method.

2. SAFETY AND WASTE HANDLING

NOTE: Please refer to the latest version of Safety-Kleen's Chemical Hygiene Plan (CHP) for more comprehensive and authoritative safety information. The information provided in this section is to be used as guidance. The information given in the CHP supercedes the information provided here.

2.1 **Fire** – Some of the materials are highly flammable. Be sure that there are no open flames nearby while testing or cleaning. The fumes released may be flammable and migrate to open flames. Also the carrier gas, hydrogen, is an immediate fire and explosion hazard.

Fire – If any spill occurs, wipe up with an absorbent wipe. Used wipes and plastic pipettes must be placed in a metal container lined with a plastic trash bag. The metal top must be kept on the container at all times except to add or to remove the contents. In the event of a fire, the top should quickly smother it. Any fires involving these materials must be treated as Class A fires. The contents must be disposed of according to facility policy and local regulators.

2.2 **Eye Contact** – Special eye protection procedures are required when using concentrated acids and bases. When using concentrated sulfuric acid, the use of a face shield and safety glasses or goggles is required.

Eye Contact – Regular safety glasses with side shields provide adequate protection from an accidental sample splash.

2.3 **Hand Contact** – Use of disposable nitrile gloves provide adequate protection from contact with the samples and minor exposure to sulfuric acid; however, anytime that the gloves come into contact with the sulfuric acid, they should be changed within a reasonable amount of time. All skin contact must be washed off immediately, especially any acid contact.

2.4 **Respiratory** – Exposure to the vapors from the sample should be kept to a minimum by working in a well-ventilated area. The sample container must be opened in a hood and only long enough to obtain a sample. A fitted respirator must be available for use in case of sample spills.

2.5 **Waste Disposal** – The remainder of the sample in the original container must be returned to sample storage for future testing or later disposal.

Waste Disposal – The hexane extracts containing greater than 50 mL volume must be retained until it is determined whether or not they contain PCBs. If the extract does not contain concentrations of PCBs above 2.0 µg/mL, it may be disposed of in the regular solvent waste. If the extract is determined to contain PCBs above 2.0 µg/mL, then the extract must be segregated and held for special disposal. PCB warning labels must be attached to containers derived from waste known to contain PCB at or above 2.0 µg/g.

Waste Disposal – If a waste sample is determined to contain PCBs, the sample container must be properly labeled with PCB warning stickers. Waste samples containing PCBs at or above the concentration of 2.0 mg/kg must be segregated for special disposal.

Waste Disposal, Acid Hazard – Sulfuric acid must either be neutralized to a pH between 5 and 9 by careful drop-wise addition of the acid to 20% sodium carbonate (w/v), or segregated for proper disposal.

2.6 **Toxics** – PCBs have been found to be potentially carcinogenic. The standards of these compounds must be handled with proper safety and hygiene precautions. Work areas handling PCB sample preparation and analyses must be monitored semiannually (or more frequently, if contamination is suspected), using wipe tests, to determine if PCB contamination is present.

3. SUMMARY OF METHOD

3.1 Hydrotreated base stocks are analyzed by Capillary Gas Chromatography using Electron Capture Detection (GC/ECD). Samples are prepared for chromatographic analysis by dilution and/or extraction with hexane and cleaned-up (as appropriate) with sulfuric acid and adsorbent materials such as Florisil and/or Silica Gel. Any peak present on the chromatogram will be considered to be one of the 209 congeners and will be quantified in accordance with its proximity to one of the 19 standard congeners.

3.2 Quantitation is performed using an External Standards Method (ESTD). The technique involves determining retention time windows for each of the 19 standard peaks, finding into which window the unknown peak falls and quantifying that peak with the five point calibration curve of the standard from which that window was derived. Calibration is verified by evaluation of the results obtained from the analysis of a midpoint Calibration Check Standard (CCS) against the initial calibration.

3.3 The MDL and LLOQ for this method are listed in Table 1 in Appendix A.

3.4 Analytical results are reported as either "Regulatory limit of <2.0 ug/g" or the calculated value is given in units of ug/g to three significant figures.

4. SAMPLE HANDLING AND PRESERVATION

NOTE: Sample storage, preservation, and holding times are detailed in the Safety-Kleen Quality Assurance Manual.

4.1 No sample preservation is required, however, samples should be stored at a temperature between 40°F and 90°F to prevent physical damage to the container due to freezing or pressure build up. Short term elevated/reduced temperatures experienced during sample shipment will not significantly affect sample integrity.

4.2 Erroneous results may be obtained if precautions are not taken to avoid the loss of volatile material. Do not open containers unnecessarily. Results for samples from leaky containers must be marked to indicate that the sample integrity was not maintained during shipping/storage.

4.3 Plastic containers or lids must not be used for the storage of samples due to the possibility of contamination from the phthalate esters and other hydrocarbons within the plastic. For shipment of samples, use a plastic-coated wide mouth glass bottle with a polytetrafluoroethylene (PTFE) lined cap. For samples to be used on location, any clean glass bottle is satisfactory, but some secondary containment must be provided when transporting the sample. The bottle should be filled at least 75% full but should not be more than 90% full.

5. INTERFERENCES

5.1 The Electron Capture Detector (ECD) has selective sensitivity to alkyl halides, conjugated carbonyls, nitrates, organometallics, and sulfur.

5.2 Care must be given to assure purity of the carrier gas. For example, in-line scrubbers may be required.

5.3 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to the analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by the analysis of Method Blanks.

5.4 Interferences by phthalate esters can pose a major problem when using ECD. Phthalates generally appear in the chromatogram as broad late eluting peaks. Since phthalates are commonly used as plasticizers and are easily extracted from plastic, all contact of samples and extracts with plastic should be avoided unless the materials are demonstrated to be free of interferences by the analysis of Method Blanks.

6. APPARATUS

NOTE: Unless indicated as mandatory, all references to manufacturer and catalog numbers are provided as examples of acceptable items.

6.1 **Gas Chromatograph** – A temperature programmable gas chromatograph suitable for splitless injections; equipped with an Electron Capture Detector (ECD). (Hewlett-Packard 5890 Series II, or, HP 6890 Gas Chromatographs.)

6.2 **Data System** – A computer and data system capable of GC control and data acquisition and processing; able to provide qualitative and quantitative results. (HP ChemStation).

6.3 **Analytical GC Column (Mandatory)** – Cross-bonded 5% Diphenyl – 95% Dimethyl Poly-Siloxane; 0.32 mm ID ×30 m × 0.25 µm film thickness (stable to 340°C). (Restek Rtx-5, Cat. # 10224; J&W, DB-5, Cat. # 9381).

6.4 **Autosampler** – HP Autosampler tower designed for the specific GC to be used (HP 7673).

6.5 **Autosampler Vials** – For GC autosampler, 11 mm with 1.8 mL capacity. (Fisher Cat. # 03-340-50A for standard opening; # 03-340-5K for larger opening to accept inserts).

6.6 **Autosampler Vial Crimp Caps** – 11 mm crimp caps for crimp top vials. (Fisher Cat. # 06-406-19B).

6.7 **Nitrogen Regulator** – 3000 psi service, 380 CGA fittings. (Restek Cat. # 20606).

6.8 **Hydrogen Regulator** – 3000 psi service, 350 CGA fittings. (Restek Cat. # 20607).

6.9 **Gas Traps/Scrubbers**

6.9.1 **Oxygen** – Restek Cat. # 20601.

6.9.2 **Moisture** – Restek Cat. # 20601.

6.9.3 **Hydrocarbon** – Alltech Cat. # 8131.

6.10 **Vortex Mixer** – Fisher Scientific (Cat. # 12-814-54).

6.11 **Preparation Vials** (Available from Scientific Specialties, 1-800-648-7800)

6.11.1 **20 mL Vials** – Vial and PTFE lined cap (Cat. # B-75520-SK).

6.11.2 **40 mL Vials** – Vial and PTFE lined cap (Cat. # B-75540-SK).

6.12 **Disposable 3 mL Polyethylene Pasteur Pipets** – For non-quantitative transfers and making cleanup columns. (Baxter Cat. # P5214-19, standard size bulb; P5214-21, larger bulb).

6.13 **Graduated Disposable 3 mL Polyethylene Pasteur Pipets** – For taking 3 mL sample sizes of pipettable samples. (Baxter Cat. # P5214-33).

6.14 **Disposable Borosilicate Glass Transfer Pipets**

6.14.1 1.0 mL in 0.01 mL gradations (Baxter Cat. # P4650-11X).

6.14.2 5.0 mL in 0.1 mL gradations (Baxter Cat. # P4650-15).

6.14.3 10.0 mL in 0.1 mL gradations (Baxter Cat. # P4650-110).

6.15 **Centrifuge** – Capable of accommodating 20 mL prep vials (Fisher Cat. # 05-100-25). Four-place rotor (Fisher Cat. # 05-100-28), Shield (Fisher Cat. # 05-100-36).

6.16 **Volumetric Automatic Dispensers**

6.16.1 **Hexane/Acetone**: 10 – 50 mL (Fisher Cat. # 13-688-85).

6.16.2 **Hexane**: 2 – 10 mL (Fisher Cat. # 13-688-83).

6.16.3 **Sulfuric Acid**: 1 – 10 mL, with bottle (Fisher Cat. # 13-687-55).

6.17 **Glass Wool** – Silanized, for packing cleanup columns (Supelco Cat. #. 2-0411).

6.18 **Disposable Gloves** – N-Dex® 4 mil Nitrile Gloves (Fisher Cat. # 11-388-32).

6.19 **GC Injection Port Septa** – Low bleed/high temperature (HP No. 5080-8896). Optional: Merlin Microseal mechanical septa (HP No. 5181-8816).

6.20 **GC Injection Port Liners** – Split/Splitless, 4 mm ID, glass wool packed. (Supelco Cat. # 2-0486,05). (Many other acceptable styles).

6.21 **Compressed Gases** – (Available from Air Products: 1-800-224-2724).

6.21.1 Hydrogen – UHP (Zero grade).

6.21.2 Nitrogen – UHP (Zero grade).

6.22 **100 µL Fixed Volume Disposable Tip Pipette** – For adding the surrogate standard, DCB, to sample preparations. Fisher/Wheaton Micropipetter (Fisher Car. # 13-707-11). Yellow Disposable Pipette Tips – (Fisher Cat. # 13-707-69).

6.23 **Microsyringes** – 10 µL, 25 µL, 50µL, 100 µL, 250 µL, and 500 µL. (Fisher Cat. #s 14-824,14-824-7, 14-824-5, 14-824-6, 14-824-2, 14-824-9).

6.24 **Class A Volumetric Flasks** – 5 mL, 10 mL, 25 mL, 50 mL, 100 mL, 200 mL, 250 mL. For making standard dilutions. (Fisher Cat. #s 10-209M, 10-209A, 10-209B, 10-209C, 10-209D, 10-209E, 10-209F).

6.25 **Class A Volumetric Pipets** – 1 mL, 2 mL, 5 mL, 10 mL, 20 mL, 25 mL. (Fisher Cat. #s 13-650- 2B, 13-650- 2C, 13-650- 2F, 13-650- 2L, 13-650- 2N, 13-650- 2P).

7. REAGENTS AND STANDARDS

NOTE: The use of method specific standards provided/subcontracted by the Safety-Keen Technical Center is mandatory.

NOTE: Reagents and Standards Labeling Requirements.

Reagents must have the following clearly identified:

Container: Description, Source, Lot #, Purity (or grade), Date of Receipt.

Logbook: Description, Source, Lot #, Purity (or grade), Date of Receipt.

Standards and all solutions must have the following clearly identified:

Container: Description, Nominal Conc., Date Prepared, Expiration Date.

Logbook: Standard/solution Name, Sources, Lot #s, Purities (or grades), Concentrations, Preparer's Name, Date Prepared, Expiration Date.

7.1 **Hexane** – Pesticide Grade (Fisher Cat. # H300-4).

7.2 **Acetone** – Pesticide Grade (Fisher Cat. # A40-4).

7.3 **Hexane/Acetone** – 90% Hexane/10% Acetone (V/V).

7.4 **Methanol** – Pesticide Grade (Fisher Cat. # A450-4).

7.5 **Isooctane** – Pesticide Grade (Fisher Cat. # 0297-4).

7.6 **Sulfuric Acid** – ACS Grade (Fisher Cat. # A300S-212).

7.7 **Silylation Reagent** – For silanizing injection port liners if they are not obtained pre-silanized. Supelco Sylon-CT (Supelco Cat. # 3-3065).

7.8 **Sodium Sulfate Anhydrous** – ACS Grade, Granular (Fisher Cat. # S415-1). Dry at 130°C and cool in a desiccator for at least 30 minutes before use.

7.9 **Florisil® Adsorbent** – Pesticide Residue Grade (60/100 mesh); purchase-activated at 677°C (1250°F), stored in glass containers with ground glass stoppers or foil lined screw caps. (Supelco Cat. # 2-0280).

> **NOTE: Just before use, activate each batch at least 4 hours at 130°C in a glass container loosely covered with aluminum foil, alternatively, store the Florisil in an oven at 130°C. Cool the Florisil in a desiccator for 30 minutes before use.**

7.10 **Florisil Cartridge** – 1000 mg, 6 mL Tubes. (Supelco Cat. # 5-7057 or Altech Cat. # 207930).

7.11 **Silica Gel Adsorbent** – Chromatographic Silica Gel, 100-200 mesh, Grade 634 Type 60A (Fisher Cat. # S734-1).

7.12 Strata® FL-PR Florisil, 1 g / 6 ml or 2g / 12 ml. (Phenomenex Cat# 8B-S013-JCH, 8B-S013-KDG)

7.13 **Surrogate Spiking Standard, Decachlorobiphenyl (DCB)** – The Stock Surrogate Spiking Standard is an iso-Octane solution of decachlorobiphenyl at a concentration of 1500 µg/mL, which is to be diluted 1:100 with iso-Octane to give a 15 ug/mL working spiking solution. This surrogate spiking solution is appropriate for spiking sample preparations diluted by a factor of 10-fold and results in an instrument concentration of 0.05 ug/mL. The Surrogate Spiking Standard must be stored in tightly sealed vials with

PTFE-lined caps at a temperature of 4°C with minimal headspace. Shelf life is six months.

7.14 **Calibration Standards** – The calibrations standards contain the 19 congeners plus DCB at the concentrations listed in TABLE 2 in a solution of iso-Octane and 10% 120HT. Calibration Standards must be stored in tightly sealed vials with PTFE-lined caps at a temperature of 4°C with minimal headspace. Shelf life is six months.

7.15 **Calibration Check Standard (CCS)** – The Calibration Check Standard is an iso-Octane and 10% 120HT solution of the 19 congeners plus DCB listed in TABLE 1at the midpoint concentration . The CCS must be stored in a tightly sealed vial with PTFE-lined caps at a temperature of 4°C with minimal headspace. Shelf life is six months.

7.17 **Matrix Spiking Standard** – The Matrix Spiking Standard is an isooctane solution of Aroclor 1254 or an alternative aroclor at a concentration of 250 µg/mL. Spiking 3 mL of sample with 100 µL (0.100 mL) of this solution gives a 0.831 µg/mL Total PCB instrument concentration:

$$\frac{(250\mu g/mL)(0.100mL)}{(30.1mL)} = 0.831\mu g/mL$$

The Matrix Spiking Standard must be stored in tightly sealed vials with PTFE-lined caps at a temperature of 4°C with minimal headspace. Shelf life is six months.

8. PREVENTIVE MAINTENANCE

8.1 Clean all contamination, both spillage and routine handling, from the hood and instrument surfaces. Check for proper autosampler syringe operation (plunger is not sticky and syringe is correctly aligned with injection port). Fill the syringe wash solvent vials in the autosampler.

8.2 Change the septum and injection port liners as needed. Low recoveries of surrogate in the analysis of the CCS may indicate a dirty injection port liner.

8.3 New columns may need to be conditioned at the recommended temperature and flow. When using hydrogen, the column flow should be vented outside the oven during column conditioning and the ECD cell capped off with make-up gas flowing.

8.4 All maintenance must be documented in the instrument maintenance log book or alternative.

8.5 Injection of methanol after injection port liner replacement is sometimes effective in cleaning a GC channel.

9. TROUBLESHOOTING AND CORRECTIVE ACTION

NOTE: Guidance concerning the corrective action which is required when method QC is out of control, is given in the Safety-Kleen Laboratory Quality Assurance Manual.

9.1 If results obtained for the method quality control (i.e., CCS, MB, surrogate, MS/MSD/LCS), are not within the control limits, corrective action must be taken and documented.

9.2 If the DCB surrogate peak is not present, the following may be useful in identifying the source of the problem:

- Check for proper addition and surrogate.
- Check for leaking septum, dirty injection port liner and drifting baseline.
- Look for major interfering peaks.
- Look for sample preparation problems, including overly aggressive clean-up.
- Reanalyze sample, on different channel, if possible.
- Re-evaluate surrogate standard solution.

9.3 Effective troubleshooting of GC/ECD instrumentation begins by isolation of the problem to either the supply gasses, inlet manifold, column, or the ECD. Check for septum leakage and syringe operation first. If these appear to be acceptable, replace the injection port liner and septum. Low surrogate recoveries usually indicate that the injection port liner needs replacement. Build up of residue on the injection port liner may lead to loss of recovered Congener due to adsorption on the residue. If the problem is still not corrected, cut off the first few inches, up to one foot, of the injection port side of the column and reconnect. If the problem is still not resolved, it may be necessary to rebuild the chromatographic system. An elevated background signal produced by the ECD indicates contamination of the detector, requiring bake-out of the detector at 390°C for periods of 4 hrs. (Make sure the hydrogen valve is shut off and column is disconnected from the detector and inlet capped and oven is cooled off).

10. QUALITY CONTROL

NOTE: Calculation of the common quality control parameters (e.g., percent recovery, percent difference, relative percent difference (RPD), and relative standard

deviation (RSD)), are given the Safety-Kleen Laboratory Quality Assurance Manual.

NOTE: Corrective action to be taken when the following quality control parameters are out-of-control is given in the Safety-Kleen Quality Assurance Manual.

10.1 Initial Calibration – A complete instrument calibration consists of the following:

1. A five-point calibration the 19 Congeners, with DCB.
2. CCS to independently verify the initial calibration.

10.2 Calibration of 19 Congeners and DCB – The instrument calibration consists of at least five (5) concentrations for each congener, typically at the concentrations given in section 7.14. Alternate calibration ranges can be used to meet other concentration ranges of interest; however, the laboratory's justification for this change must be documented.

Data systems typically use a statistical *least squares regression analysis* of the calibration data to determine a calibration curve (e.g., HP ChemStation and Multichrom). The regression analysis must be *linear*, *unweighted* and the origin must be *ignored* (not *included* or *forced*). The average correlation coefficient (of all 19 Congeners and DCB) must be ≥ 0.99 to demonstrate linearity. Recalibration is required only when the calibration verification criteria cannot be met.

10.3 Calibration Verification – Every analytical batch of no more than twenty (20) samples, the instrument calibration must be verified by the analysis of a calibration check standard (CCS). The CCS contains the same 19 congeners plus DCB and must be from a different source or Lot number than the initial calibration solutions. The QC acceptance criterion for the CCS is less than or equal to ± 20% difference from the initial calibration for each Congener. If the CCS results indicate that the calibration is outside control limits, and corrective actions do not correct the problem, the GC/ECD *must* be recalibrated.

10.4 Surrogate Standard – The surrogate standard, Decachlorobiphenyl (DCB), must be added to all samples and method blank preparations. The accuracy requirement for the surrogate standard is 40% – 150% recovery. Sample dilution beyond the standard 10-fold dilution may result in an undetectable surrogate standard which is an acceptable situation. In this case document the Surrogate as "diluted out" and indicate the total sample dilution factor.

10.5 Method Blanks – Every preparation batch of no more than twenty (20) samples, a Method Blank must be prepared and analyzed by processing the dilution/extraction solvents, *with surrogate,* through the identical preparation and cleanup procedure as used for the samples. No interferences prohibiting the identification or quantitation

of any congener may be present, nor can any congener be present at or above the MDL.

10.6 Matrix Spike/Matrix Spike Duplicates (MS/MSD) – Every preparation batch (EPB) of no more than twenty (20) samples, a sample must be Matrix Spiked in duplicate. Matrix Spike and Matrix Spike Duplicate sample recovery limits are 70% – 130%, of the spiked Aroclor concentration. These recovery limits will be updated when at least 20 batches have been analyzed. QC acceptance criteria for the precision between MS and MSD is 20% RPD.

10.7 Laboratory Control Samples (LCS) – Every preparation batch of no more than twenty (20) samples, a Laboratory Control Sample must be prepared and analyzed. A laboratory Control sample is a "spiked blank" using the same spiking solution as is used to spike the MS/MSD samples. These control samples are used to demonstrate the performance of the entire method (preparation and instrumental analysis) without the influence of the sample matrix. The control limits for the LCS are 70 – 130 % Recovery of Aroclor 1254 or alternative Aroclor. These recovery limits will be updated when at least 20 batches have been analyzed.

11. PROCEDURE

11.1.1 Sample Preparation– Transfer the weight of sample equivalent to a volume of 3 mL (e.g., 2.4 grams for a material with a density of 0.8 g/mL) to a 40 mL vial and record the weight to the nearest 0.01 gram. Spike the sample with 100 µL of Decachlorobiphenyl Surrogate Spiking Solution (15 µg/mL for 10-fold dilutions). Dispense 27 mL of hexane into the vial. Cap the vial and vortex vigorously for *at least* 30 seconds. This yields a 1:10 sample dilution. Transfer 10 mL of the 1:10 sample dilution into a 40 mL vial.

11.2.1 Method Blanks – Pipet or transfer 3 mL of the hexane diluent used to prepare samples, to a 40 mL vial and spike with 100 µL of the Surrogate Spiking Solution (12 µg/mL for 10-fold dilutions). Proceed with its preparation in identical manner to sample preparations.

11.2.2 Matrix Spikes – Pipet or transfer 3 mL of sample to a 40 mL vial and spike with 100 µL of the Matrix Spiking Solution (250 µg/mL for 10-fold dilutions). This concentration gives and Aroclor 1254 instrument concentration of 0.831 µg/mL Total PCB. Proceed with its preparation in identical manner to sample preparations.

11.2.3 Laboratory Control Samples – Pipet or transfer 3 mL of hexane to a 40 mL vial and spike with 100 µL of the Matrix Spiking Solution (250 µg/mL for 10-fold dilutions). This concentration gives an Aroclor 1254 instrument concentrations of 0.831 µg/mL. Total PCB. Proceed with its preparation in identical manner to sample preparations.

11.3 Sample Cleanup Procedures – Samples analyzed with this method including quality control samples will be processed through the clean-up procedure described below.

11.3.1 Sulfuric Acid Treatment – Concentrated Sulfuric Acid may be used to cleanup the sample dilutions prepared above. This is a "brute force" chemical treatment as this strong mineral acid decomposes many potentially interfering compounds. The PCBs however, by virtue of their chemical inertness, are not labile to the action of this acid and are not destroyed (within limits).

To the sample dilution prepared above, add 3 mL of Sulfuric Acid, cap tightly, and vortex well. Allow the phases to separate (the acid will settle to the bottom of the vial). If an emulsion has formed, centrifugation is very effective in separating these two phases which have widely differing densities (H_2SO_4 ~1.84 g/mL, hexane ~0.67 g/mL). This treatment may be repeated up to *six times,* after which, PCB degradation may occur. Record the number of acid treatments used.

11.3.2 Florisil and Silica Gel Slurries – Adsorbent slurries are able to remove some of the interfering materials which are not decomposed by the Sulfuric Acid. To treat, transfer 4 – 8 mL of the acid treated extract*, free of any acid,* into another 20 mL vial, containing approximately 0.25 gram of anhydrous Sodium Sulfate and 0.5 gram activated Florisil. Alternatively, use 0.25 gram anhydrous Sodium Sulfate and 0.5 gram activated Silica Gel. Cap, vortex well, and allow the adsorbent Florisil or Silica Gel to settle by gently tapping the vial or by centrifugation. These two adsorbents may be used together in a mixed slurry, or, in succession if required by a particularly persistent interference. When used in succession, the Florisil treatment is typically followed by a Silica Gel treatment.

11.3.3 Adsorbent Column Cleanup – Florisil and Silica Gel adsorbents are able to remove certain interfering materials by selectively retaining more polar interferents in a gravity-flow chromatographic column, while allowing the less polar PCB congeners to elute through the column. While any small bore pipet may be used to prepare these cleanup columns, the disposable plastic 3 mL polyethylene Pasteur pipets (Section 6.12) have been found to be quite convenient and are indicated in the suggested procedure given below (pre-made columns may be purchased (Section 7.12) for the clean-up process).

To prepare, cut the top "dome" portion off the bulb of a pipet leaving the opened "bulb" to serve as a reservoir for the sample extract at the top the column. Using a 1 mL disposable transfer pipet, push a small wad of glass wool down the newly opened end and pack it into the taper at the other end of the column. Packing should be just tight enough to prevent the adsorbent from passing through the column but not so tight as to slow the eluent flow. Add the equivalent depth of 0.25 mL of anhydrous Sodium Sulfate, 1 to 2 mL of activated Florisil or activated Silica Gel (or ~ 1 mL each), and top it off with another 0.25 mL of anhydrous Sodium Sulfate. These columns may be prepared in advance and, because of their small size, stored in a standard size desiccator until needed.

Transfer approximately 8 mL of acid treated sample dilution, *free of any acid,* to the reservoir of an adsorbent cleanup column. Allow as much of the sample to pass through the column as possible before collecting any eluent for chromatographic analysis. (The absolute minimum eluent volume is 3 mL, however, due to the possibility of PCB material being retained on the column, 5 mL is preferable.) These first few milliliters of eluent are diminished in PCB concentration (assuming PCBs are present) and should be discarded. Continue to add sample extract to the reservoir to maintain proper column flow. Once at least 3 mL have passed through the column, place a GC autosampler vial under the column (the column tip should just fit inside the vial mouth), collect about 1.5 mL of eluent, and crimp cap the vial. Alternatively, collect the entire eluent in an appropriate vial (e.g., a 20 mL prep vial) and transfer 2 mL of the collected eluent to a GC autosampler vial. Discard any further column eluent and the column itself. The sample is now ready for gas chromatographic analysis.

11.4 Instrument Conditions – The temperature programs for Congeners is a 12 minute program and is allowed for analyses *on instruments equipped with Electronic Pressure Control* (EPC).

The column flow rate (column head pressure) must be adjusted so that DCB elutes between 9.5 – 10.1 minutes using the 12 minute temperature program.

Injection Port Temperature:	280°C
Detector Temperature:	325°C (350°C for μ-ECD)
Carrier Gas:	Hydrogen
Column Head Pressure:	Dependent on DCB RT (approx. 15 psi.)
Column Flow Rate:	~ 3 mL/min (EPC in Constant Flow mode.)
Purge Off Time:	Initially (Time = 0 min.)
Purge On Time:	1.0 min.
Gas Saver Mode:	20 mL/min at 2 min (EPC only)
Purge Vent (Septum Purge):	~ 2.5 mL/min.
Split Vent (Inlet Purge):	~ 50 mL/min.
Injection Volume:	1.0 μL for 12 min (5 or 10 μL syringe)
ECD make-up gas & rate:	Nitrogen @ ~65 mL/min.

11.4.1 Twelve (12) Minute Temperature Program

Initial Oven Temperature:	130°C
Initial Time:	2 minutes
Ramp Rate:	20 C°/min.
Final Oven Temperature:	270°C
Final Time:	3 minutes

Total Run time: 12 min.

11.5 Instrument Calibration – Because the level of interest is typically 2 mg/kg (ppm) Total PCBs, and a 1:10 sample preparation dilution is typically employed, the GC is calibrated at the concentrations listed in Table 1 in Appendix A. and verified with a CCS at the midpoint. In order to accommodate the need for other levels of interest, alternative calibration ranges are allowed, provided that screening is performed at the actual level of interest and all of the relevant quality control criteria are met. The laboratory must document its justification for the use of alternate calibration ranges.

11.6. Quantitative – The instrument calibration consists of a five-concentration multipoint calibration for all 19 Congeners and DCB.

11.6.1. Calibration of 19 Congeners and DCB – Analyze the 19 Congener/ DCB mixture (Section 7.14) at the five (5) concentrations bracketing the concentration range of interest . Alternate calibration ranges can be used to meet other concentration ranges of interest, however, the laboratory's justification for this change must be documented.

Establish a first-order, linear, calibration model from the calibration data using an unweighted least squares regression analysis, ignoring the origin. The average correlation coefficient must be ≥ 0.99 for each congener and DCB to demonstrate linearity.

11.6.2. Calibration Sequence

1. Reagent Blank(s) (as necessary).
2. 19 Congener standard with DCB (5-point multilevel calibration).
3. CCS to independently verify the initial calibration.

11.7 Instrumental Analysis

11.7.1 Quantitative Instrumental Analysis – The 12 minute temperature program is required. The sample injection volume, as well as all other instrumental conditions, must be the same for the samples as those used for the calibration standards.

11.7.2 Typical Analytical Sequence

1. CCS
2. Method Blank
3. LCS
4. Unspiked Sample

5. MS/MSD
6. Samples 1-20

Continue as long as the system remains stable and in-control as verified by the method quality control.

11.7.3 Congener Identification – Because this method will only be used to analyze hydrotreated base stocks, it will be assumed that any peak present on the chromatogram after the appropriate clean-up measures given in section 11.3 have been performed will be a congener. The peak will be calculated by applying to it the calibration factor of the standard peak nearest in retention time. These results will be in the same units as those used for the calibration standards, µg/mL, and are called *Instrument Concentrations*.

12. CALCULATIONS

12.1 Data System Quantitation – The data system which has been calibrated for the individual Congeners will give the congener concentration of the sample extract analyzed on the instrument, the *Instrument Concentration,* in µg/mL. This concentration must be multiplied by factors representing the sample preparation procedure to arrive at the original *Sample Concentration*. Sample results are reported in units of ug/g to three significant figures.

12.2 Manual Quantitation – Quantitate congener samples by totaling the peak areas in each of the 19 retention time windows which are determined by taking the retention time of each standard peak and subtracting half of the time between it and the preceding peak to get the lower end of the retention time window and adding half of the time between the standard peak and the next peak to get the upper end of the retention time window (except in the case of the first and last standard peaks where the actual peak retention time will represent the lower and upper end of the retention times for those peaks respectively). Once the areas for all peaks in a given retention time window have been totaled, plug that total into the line equation for the standard peak representing the window. This will give the instrument concentration for congeners that window. Once this has been done for all retention time windows containing peaks, total all window concentrations to obtain the total PCB instrument concentration. An example of this calculation is shown in Appendix B

12.3 Typical 1:10 Dilution

$$Total\ Sample\ PCB\ \left(\frac{\mu g}{g}\right) = \frac{(Istrument\ Conc.\left(\frac{\mu g}{mL}\right))(30mL)}{(Sample\ Mass\ (g))}$$

Where:

Sample Aroclor Conc. = *Aroclor concentration in the original sample in µg/g (equivalent to mg/kg) on a wet weight basis.*

Instrument Conc. = *Concentration of PCB in the sample extract/dilution in µg/mL obtained by interpolation from the calibration curve.*

Sample Mass = *Mass of the sample in grams.*

12.2 Additional Dilutions – If further dilutions were used to bring the instrument concentration within the calibration range, multiply the Congener concentration determined above by the additional dilution factor (*DF*):

$$Total\ Sample\ PCB\ \left(\frac{\mu g}{g}\right) = \frac{(Istrument\ Conc.\left(\frac{\mu g}{mL}\right))(30mL)DF}{(Sample\ Mass\ (g))}$$

13 REFERENCES

NOTE: All EPA OSWER SW-846 Methods are available on the world wide web at http://www.epa.gov/epaoswer/hazwaste/test/main.htm, and all ASTM methods are available at http://www.astm.org (The EPA methods are free while ASTM charges a fee).

13.1 See SK9202

List of Appendices

Appendix A 19 Congeners

Appendix B Sample Calculations

Appendix A

Table 1: List of all congeners used in this method and their corresponding standard concentrations, MDL, and LLOQ (LLOQ as the level 1 standard has the units of ug/mL).

Congener	MDL (µg/g)	LLOQ (µg/g)	Level 2 (ug/mL)	Level 3 (ug/mL)	Level 4 (ug/mL)	Level 5 (ug/mL)
2-Clorobiphenyl	0.010	0.005	0.01	0.02	0.04	0.08
2,3-Dichlorobiphenyl	0.011	0.005	0.01	0.02	0.04	0.08
2,2,5-Trichlorobiphenyl	0.003	0.005	0.01	0.02	0.04	0.08
2,4,5-Trichlorobiphenyl	0.005	0.0025	0.005	0.01	0.02	0.04
2,2,5,5-Tetrachlorobiphenyl	0.007	0.004	0.008	0.016	0.032	0.064
2,2,3,5-Tetrachlorobiphenyl	0.006	0.004	0.008	0.016	0.032	0.064
2,3,4,4-Tetrachlorobiphenyl	0.003	0.0025	0.005	0.01	0.02	0.04
2,2,4,5,5-Pentachlorobiphenyl	0.005	0.0025	0.005	0.01	0.02	0.04
2,2,3,4,5-Pentachlorobiphenyl	0.002	0.001	0.002	0.004	0.008	0.016
2,3,3,4,6-Pentachlorobiphenyl	0.008	0.0025	0.005	0.01	0.02	0.04
2,2,3,5,5,6-Hexachlorobiphenyl	0.003	0.0025	0.005	0.01	0.02	0.04
2,2,4,4,5,5-Hexachlorobiphenyl	0.002	0.0025	0.005	0.01	0.02	0.04
2,2,3,4,5,5-Hexachlorobiphenyl	0.004	0.0025	0.005	0.01	0.02	0.04
2,2,3,4,4,5-Hexachlorobiphenyl	0.006	0.0025	0.005	0.01	0.02	0.04
2,2,3,4,5,5,6-Heptachlorobiphenyl	0.005	0.0025	0.005	0.01	0.02	0.04
2,2,3,4,4,5,6-Heptachlorobiphenyl	0.002	0.0025	0.005	0.01	0.02	0.04
2,2,3,4,4,5,5-Heptachlorobiphenyl	0.002	0.004	0.008	0.016	0.032	0.064
2,2,3,3,4,4,5-Heptachlorobiphenyl	0.002	0.0025	0.005	0.01	0.02	0.04
2,2,3,3,4,4,5,5,6-Nonachlorobiphenyl	0.002	0.0025	0.005	0.01	0.02	0.04
Decachlorobiphenyl		0.006	0.012	0.024	0.048	0.096
Total instrument PCB	0.0088	0.0580	0.116	0.232	0.464	0.928
Total Sample PCB	0.088	0.580	1.16	2.32	4.64	9.28

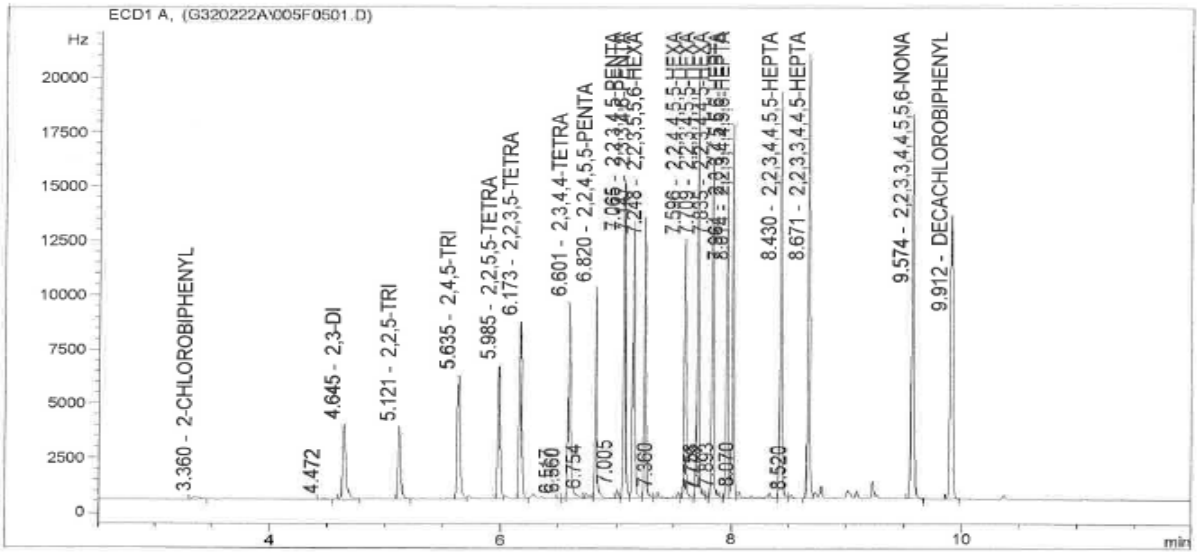

Figure 1: Chromatogram of a 12 minute run using 19 congeners plus DCB.

Appendix B

Calculating the total PCB concentration of a sample.

1. Determining the retention time windows from the standard

   Example: Find the retention time window for peak 2, when there are three peaks with the following retention times: Peak A at 2 minutes, Peak B at 5 minutes and Peak C at 6 minutes is calculated in the following manner:

   Low end of the retention time window = $Peak\ B - \frac{|Peak\ B\ R.T - Peak\ A\ R.T|}{2}$

   = 5min-$\frac{|5min-2min|}{2} = 5min - 1.5min = 3.5min$

   High end of the retention time window = Peak B + $\frac{|Peak\ B\ R.T - Peak\ C\ R.T|}{2}$

   =5min+$\frac{|5min-6min|}{2} = 5min + 0.5min = 5.5min$

   Therefore the retention time window for Peak B is from 3.5min-5.5min

2. Using the total area of the peaks in a retention time window to calculate the instrument concentration of total

   Example: The peak area in the retention time window 3.5-5.5 minutes is 10000.

   $$y = mx + b$$

   Where: y= window area
   x=Instrument amount in ug/mL
   m=slope of the line=1,000,000
   b=y-intercept=-163

   $$x = \frac{y-b}{m} = \frac{10{,}000-(-163)}{1{,}000{,}000} = 0.010ug/mL$$

3. Determining the sample concentration assuming only one R.T window contained any peaks (If there were others, they would be calculated as above and summed. That sum would be used in the following calculation to determine the total PCB for the sample).

   Example: Instrument concentration for total PCB is 0.010ug/mL

   $$Total\ PCB\ in\ Sample = \frac{(instrument\ amount\ \frac{ug}{mL})(30mL)}{(Sample\ amount\ g)}$$

   $$Total\ PCB\ in\ Sample = \frac{(0.010ug/mL)(30mL)}{3.00g} = 0.1ug/g$$