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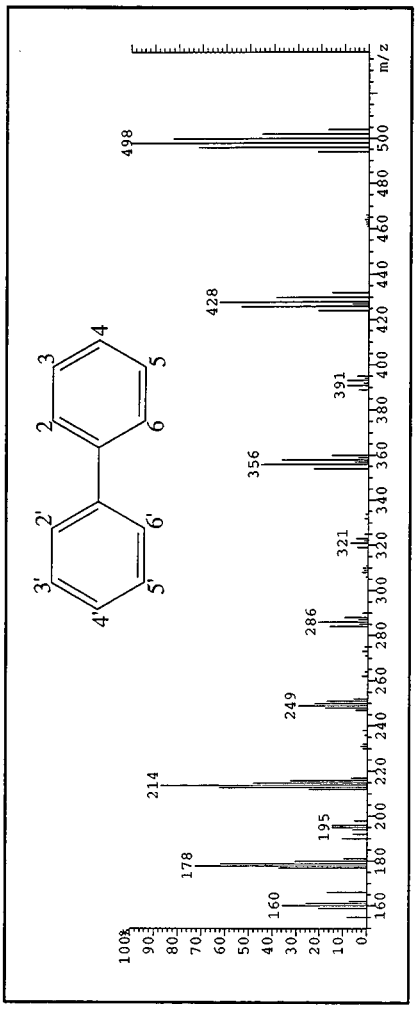

Reference Method for the Analysis of Polychlorinated Biphenyls (PCBs)

Report EPS 1/RM/31
March, 1997

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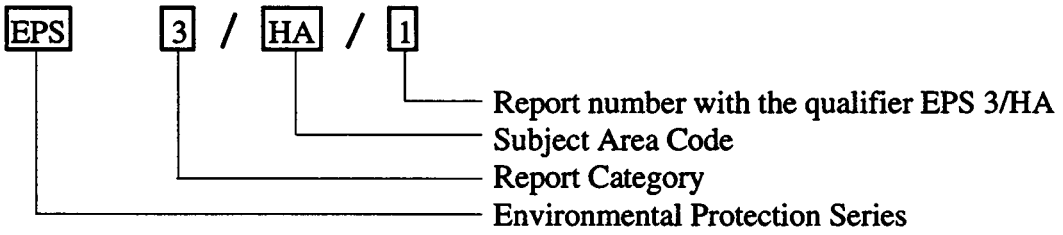

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Reference Method for the Analysis of Polychlorinated Biphenyls (PCBs)

Analysis and Methods Division
Environmental Technology Advancement Directorate
Environment Canada

Report EPS 1/RM/31
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Preamble

A comprehensive analytical procedure has been developed for analyzing polychlorinated biphenyls (PCBs). It is intended for use in support of the various regulations that govern the use and disposal of PCB-containing materials. A screening method that uses gas chromatography - electron capture detection (GC-ECD) with simple cleanup to determine the level of PCBs is described (Section 1) as well as a confirmative method that uses gas chromatography - mass spectrometry analysis (GC-MS), carbon-13 labelled surrogates (isotope dilution), and thorough cleanup to unambiguously identify and quantify total PCBs (Section 2).

Methods are written in a performance-based format. ***Mandatory procedures written in bold type and underlined must be followed.*** *Depending on the experience and equipment available to the user, procedures that are not written in bold type may be modified. There is a prerequisite to validate analytical performance of the method to be used before the samples are processed.*

Polychlorinated biphenyl (PCB) regulations under the Canadian Environmental Protection Act *(CEPA) define PCBs as chlorobiphenyls that have the molecular formula* $C_{12}H_{10-n}Cl_n$ *in which "n" is greater than 2 (i.e., tri- to deca-chlorobiphenyls)*. Standards with respect to various PCB regulations are summarized in Table A6 (Appendix A). The reporting of dioxin-like PCB congeners is not currently required for CEPA regulations. Determination of these individual congeners is therefore not in the scope of this protocol.*

Application of this reference method for compliance testing requires strict adherence to all mandatory procedures in this method. Throughout this report, such mandatory procedures are identified by bold type and underline . Deviation from the mandatory procedures of this method may invalidate the test results and therefore, any deviation must be approved in writing by Environment Canada before testing. If deviations are made without prior approval, the validity of the test results shall be determined by Environment Canada on a case-by-case basis.

* Re: The List of Toxic Substances, Schedule 1 to the *Canadian Environmental Protection Act*, June 1988.

Avant Propos

Pour l'analyse des biphényles polychlorés (BPC), on a mis au point une méthode analytique complète. Cette méthode est destinéé à appuyer les divers réglements régissant l'emploi et l'élimination des matières renfermant des BPC. Dans la Première partie, *nous dérivons une méthode de dépistage fondée sur la chromatographie en phase gazeuse à détecteur à capture électronique (CPG-DCE), avec une étape simple de purification en vue du dosage des BPC. Dans la* Partie 2, *on trouvera une méthode de confirmation fondée sur la chromatographie en phase gazeuse accouplée à la spectrométrie de masse (CPG-SM), l'emploi de substituts marqués au carbone 13 (dilution isotopique) et la purification poussée, afin d'indentifier et de doser avec certitude tous les BPC.*

La rédaction des méthodes obéit à un souci de performance. ***Les modes opératoires en lettres grasses soulignées sont obligatoires.*** *Selon l'expérience et les matériels dont il dipose, l'utilisateur pourra modifier les marches à suivre en maigre. Il faudra au préalable valider les performances analytiques de la méthode à utiliser avant de passer aux échantillons.*

Le Règlement sur les biphényles polychlorés *(BPC), promulgué sous le régime de la* Loi canadienne sur la protecion de l'environnement *(LCPE), définit les BPC comme des chlorobiphényles possédant la formule brute* $C_{12}H_{10-n}Cl_n$ *où* n *est supérieur à 2 (c'est-à-dire la série des trichlorobiphenyls au décachlorobiphényle)*. Le tableau A6 (annexe A) résume les normes découlant des divers réglements sur les BPC. Les réglements sous le régime de la LCPE n'exigent pas, actuellement, que l'on signale les divers BPC dont la molécule ressemble à celle de la dioxine. Leur détermination n'entre donc pas dans le cadre du présent protocole.*

L'application de la présente méthode de référence aux épreuves de conformité exige que l'on adhère scrupuleusement à toutes les marches à suivre obligatoires de cette méthode. Tout au long du rapport, les passages en gras identifient cas marches à suivres obligatoires. Le fait de s'en écarter par écrit, par Environnement Canada, avant d'entreprendre les épreuves, fauts de quoi Environnement Canada devra déterminer cas par cas la validité des résultats.

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*Cf: La liste des substances toxiques, annexe I de la *Loi canadienne sur la protection de l'environnement*, juin, 1988.

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Acknowledgements

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This method was prepared by C. Chiu, G. Poole, and M. Tardif of the Analysis and Methods Division, Environmental Technology Advancement Directorate.

Section 1

Screening Analysis of Polychlorinated Biphenyls

1.1 Summary

This screening method is designed to be a fast, economical way of determining if polychlorinated biphenyls (PCBs) are present in a sample, and their approximate concentration. The measurement technique is based on high resolution gas chromatography - electron capture detection (HRGC-ECD). However, **confirmative analysis of a second subsample using gas chromatography - mass spectrometry (GC-MS) is required if the PCB concentration determined by GC-ECD is greater than 60% of the regulatory limits (> limit × 0.6).** Standards with respect to various federal PCB regulations are summarized in Appendix A (Table A6).

For oil samples, 1.0 g of the oil is diluted with iso-octane at a minimum dilution ratio of 1:25. An aliquot of the diluted oil sample is subjected to one or more cleanup procedures to minimize matrix interferences. Solid samples are extracted with toluene using a Soxhlet extractor or extracted with hexane/acetone under microwave energy. An aqueous sample is extracted with dichloromethane in a separatory funnel. Following cleanup, the extract is injected into a gas chromatograph equipped with a capillary column, an electron capture detector, and a computerized data station.

Identification of PCBs in a sample is achieved, whenever possible, by matching the profile of the sample GC-ECD chromatogram to profiles of one or more of the commercial PCB mixtures (typically Aroclors 1242, 1254, 1260). If the PCB chromatogram does not match any of the Aroclor patterns, a trichlorobiphenyl standard is used for quantification. Concentrations of PCBs in samples are measured as μg/g for solids and oils, and ng/L for aqueous samples. **This screening method may not be applicable to oil samples containing Aroclor PCBs in concentrations less than 3 μg/g.**

1.2 Contamination and Interferences

Contamination from solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines that could lead to elevated detection limits and/or inability to detect PCBs that may be present. Reagents should be of high purity, and in some cases, may require further purification before use.

Proper cleaning of the glassware is essential to minimize contamination. Glassware should be washed with a detergent solution soon after use followed by solvent rinsing to remove most of the contaminants. Sonication of glassware filled with a detergent solution can also be performed as an aid to cleaning.

Matrix interferences may be present if a chromatographic profile of a PCB sample does not closely match any of the commercial Aroclor mixture standards. Certain interferences may be minimized or eliminated by subjecting the sample to one or more cleanup methods (see Section 1.5) before analysis.

Oil samples analyzed using an ECD without the addition of an appropriate internal standard could yield PCB concentrations significantly lower than the true values. This error is due to the quenching of the detector response by the high-boiling hydrocarbons in oil. The magnitude of this error, typically 20 to 30%, is matrix and detector dependent.

1.3 Safety

Polychlorinated biphenyls are bioaccumulative and persistent in the environment. Some of the PCB congeners appear to elicit the same toxicity and effects on biological activities as 2,3,7,8-

substituted polychlorinated dibenzo-*para*-dioxins and dibenzofurans (PCDDs/PCDFs) (Safe *et al.*, 1990). Some of these toxic chlorobiphenyls are present in commercial products containing PCBs (Voogt *et al.*, 1990). Oils containing PCBs may contain trace amounts of PCDFs (Mitchell *et al.*, 1984). Each sample, therefore, should be treated as a potential health hazard and personal exposure should be minimized.

All work pertaining to the analysis of PCBs, including preparation, handling, and storage of all samples must be carried out in an adequately ventilated laboratory.

Personnel in the laboratory must wear protective clothing at all times consisting of safety glasses, lab coat, and disposable, powder-free gloves as a minimum. Common laboratory safety equipment and facilities, such as sinks, first aid kits, eye wash stations and fire extinguishers must be easily accessible. In addition, all safety equipment and materials required to contain and clean up a spill must be on hand.

Only experienced and well-trained personnel, who are fully aware of the hazards associated with all the chemicals pertaining to sample processing as well as any safety regulations within the jurisdiction, should be involved with these analyses.

Laboratory safety protocols, covering such topics as safe and secure handling and storage of PCBs, housekeeping, spill containment and cleanup, and disposal of solid and liquid wastes, must be provided to laboratory personnel. These protocols must be strictly adhered to.

1.4 Apparatus and Reagents

1.4.1 Apparatus

The following lists the apparatus to be used for the screening analysis of PCBs.

- **Evaporative Concentrator**... rotary evaporator and/or nitrogen blow down device
- **Balance**... top-loading macro balance, readability to 0.01 g
- **Pipets**... electronic or mechanical pipets with capacities from 10 to 1000 μL
- **Oven**... range to 225°C for conditioning sodium sulphate
- **Tube Furnace**... for activating alumina at 350°C
- **Beakers**... assorted volumes
- **Volumetric Flasks**... 25 mL and up
- **Buchner Funnels**... 12-cm diameter
- **Erlenmeyer Flask**... 25 mL
- **Filtration Flasks**... 500 and 1000 mL
- **Separatory Funnels**... 125 mL and up
- **Calibrated Centrifuge Tubes**... 5 and 15 mL
- **Pasteur Pipets**... 22 cm, disposable
- **Teflon® Squeeze Bottles**
- **Glass Wool**
- **Vials**... assorted capacities from 1.5 to 40 mL, amber glass, screw cap with Teflon®-faced septum
- **Soxhlet Extractors**... 200 mL Soxhlet body (Dean Stark moisture trap optional), condensers, 45 x 125 mm glass or cellulose thimble, and heating mantles
- **Microwave Oven**... see Subsection 1.5.4 (Solids)
- **Gas Chromatograph**... see Section 1.6

1.4.2 Reagents

The following reagents are used for the screening analysis of PCBs.

- **Solvents**... all solvents are distilled-in-glass quality; those required include toluene, hexane, iso-octane, dichloromethane, and acetone
- **Gases**... high purity grade nitrogen and helium
- **Water**... high purity distilled or deionized water
- **Copper**... powder, chips, or turnings pretreated with 6 N HCl and rinsed with acetone
- **Standards**... the complete line of commercial PCB Aroclor mixtures available in Canada and the United States; consists of Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, and

1268; reference standard inventories must include, at minimum, Aroclors 1242, 1254 and 1260 and 2,4',5-trichlorobiphenyl (PCB-31)

- **Chemicals Required for Cleanup**... basic alumina, silica, sodium sulphate, sodium hydroxide, silver nitrate and sulphuric acid [all are American Chemical Society (ACS) reagent grade or better].

1.5 Sample Collection, Handling, and Workup Procedures

Through the advancement of technology, new analytical techniques using supercritical fluid extraction/chromatography, solid phase extraction, and accelerated solvent extraction, as well as others, exist. The use of alternative methods is acceptable if it has been demonstrated that their application will produce equivalent or better precision and accuracy than the method presented herein. The application of cleanup methods depends on the concentration of PCBs and the level of interferences present in the sample extract. A sample containing little or no interferences may require little or no cleanup, whereas a sample containing a high level of background interferences may require adherence to most of the following cleanup procedures.

1.5.1 Sample Collection, Preservation, and Storage

The integrity of measurement depends on how the sample was collected. It is important, therefore, that the sample collected is representative and free from any outside contamination. Consideration must be given to all facets of sample collection, preservation, shipment, and handling to maintain the integrity of the sample.

In general, representative samples should be collected in pre-proofed amber jars having Teflon®-lined lids. Samples should be kept in the dark at a temperature less than 10°C from the time of collection until receipt in the laboratory. Upon arrival at the laboratory, samples should be stored in the dark below 10°C until extraction.

1.5.2 Sample Handling and Custody

Upon arrival at the laboratory, samples must be inspected immediately for their physical condition and to ensure proper labelling. Inform the client of any potential problem concerning the integrity of samples. After logging and labelling with laboratory code numbers, samples should be processed as soon as possible. The sample-tracking report sheet submitted with samples is completed and signed by authorized laboratory personnel. Samples must be maintained below 10°C from the time of receipt until extraction. A subsample is taken for analysis only when the sample appears to be homogeneous.

1.5.3 Performance Validation

Before sample analysis, the laboratory must demonstrate the ability to achieve acceptable precision and accuracy of the method used by validating the analytical performance as follows:

Conduct analyses of three subsamples of a certified reference material containing Aroclors or three matrix blanks (e.g., oil, soil water, solvent, XAD) spiked with an Aroclor 1254/1260 (1:1) mixture at a concentration near the regulatory limit. The sample matrix chosen should be similar to the type of sample to be analyzed. For each of the three analyses, PCB recovery must be within 75 to 125% of the actual value. No sample should be processed until the performance validation test yields acceptable results. The test must be repeated within a 6-month period before sample processing begins.

1.5.4 Sample Preparation

The minimum sample size used for compliance testing must be able to achieve a detection limit that is not greater than 30% of the regulatory limits. Suggested sample size and achievable detection limits for individual Aroclors are given in Table 1.

Each batch of up to 15 test samples must contain at least one method blank sample and one control sample. The acceptance limit for

Table 1 Suggested Sample Size and Achievable Detection Limits

Matrix	Suggested Sample Size	Achievable Detection Limit for Aroclor 1242, 1254, and 1260
Solid	2 g (or more)*	20 ng/g (or less)
Aqueous	1 L (or more)	40 ng/L (or less)
Oil	0.5 g	1000 to 2000 ng/g

* A subsample less than 2 g can be used if the particle size of the sample is less than 250μm.

PCB presence in the method blank sample is 25 ng per congener and up to 100 ng in total PCB. As a control sample, a certified reference material or fortified sample with a PCB concentration near the regulated limit, is processed with each batch of samples. The recovery of total PCBs in the control sample must be within 75 to 125% of the actual value.

Particular attention should be given to ensure that the sample is homogeneous before a subsample is taken. Grinding and blending a solid sample may be necessary to improve homogeneity. Splitting an aqueous sample containing particulate is not recommended. If a subsample must be taken, one must ensure that a representative sample is obtained.

Sample Extraction. The following extraction techniques have undergone rigorous testing and will produce data meeting the performance criteria set out in Subsection 1.5.3. Other validated extraction techniques may be used providing the aforementioned performance criteria are met.

Solids. Solid samples may include filtered solids, sludges, soils, sediments, ashes, and feed (solid waste). They may contain various amounts of moisture; therefore, results should be reported on a dry weight basis.

Dry weight determination - Determine the dry weight of the sample as follows:

A representative amount of sample (typically 5 g) is weighed in a preweighed weighing boat and placed in an oven at 100°C overnight. The sample is weighed until a constant weight is achieved.

The dry weight of the sample used for PCB analysis is determined by :

$$M_{sd} = M_{sw} \cdot M_d / M_s$$

where:

M_{sd} = the dry weight of the sample used for analysis

M_{sw} = the wet weight of the sample used for analysis

M_d = the dry weight of the sample aliquot used in the determination (not to be used for analysis)

M_s = the wet weight of the sample aliquot used in the determination

For sample analysis, accurately weigh an appropriate amount of the finely-divided sample (use a mortar and pestle when necessary). Polychlorinated biphenyls in solid samples are extracted with solvent using the Soxhlet Extractors or the Microwave Assisted Process (MAP™) for soil and sediment samples.

Soxhlet extraction - Insert a cellulose or glass fibre thimble into the Soxhlet body and blank the Soxhlet apparatus overnight with toluene.

Discard the toluene along with three toluene rinses of the entire apparatus. Remove the pre-extracted thimble from the Soxhlet body and allow it to air dry in a beaker. Quantitatively transfer the air dried sample into the thimble and cover the sample with a layer of glass wool. Place the thimble into the Soxhlet apparatus. Fill the bottom flask with 350 mL (or an appropriate amount) of toluene. The addition of 10% (v/v) polar solvent such as acetone is recommended for samples which have not been thoroughly dried. A Dean-Stark apparatus may be used as an alternative to remove moisture from a moist solid sample. Connect the apparatus to the water-cooled condenser and wrap the Soxhlet apparatus with aluminum foil as a heat insulator. Reflux the sample for 20 hours at a rate of three to four cycles each hour. When the extraction is complete, rinse the inner surface of the condenser with toluene and allow the apparatus to cool. Siphon the solvent from the Soxhlet body into the extraction flask. Rinse the Soxhlet apparatus three times with toluene, siphoning each rinse into the flask. Concentrate the toluene extract to a few millilitres by rotary evaporation. Change the solvent to cyclohexane by adding 100 mL of cyclohexane to the flask and concentrating to a few millilitres (this will remove toluene before column cleanup).

Dry the sample by passing it through cyclohexane-rinsed sodium sulphate and glass wool held in a powder funnel positioned over a 250 mL boiling flask. Complete the transfer by rinsing first the extraction flask, then the sodium sulphate, with three, 5-mL portions of cyclohexane. Concentrate the sample to a few millilitres. The sample is now ready for cleanup.

Microwave extraction - This technique has been tested satisfactorily for soil and sediment samples. Studies are needed for the extraction of PCBs in other matrices. **Do not use this method for solids other than soil and sediment samples unless a proof of compatible extraction efficiency to the Soxhlet method has been established and documented.** Using microwave energy for sample extraction has the advantage of being faster and consuming less energy and solvents than the conventional Soxhlet method.

A laboratory microwave apparatus (MSE-1000, of CEM Corporation) equipped with a temperature control device and safety features such as solvent vapour alarm, pressure-relief device, and protective shield is used. Because of the potential hazards with use at elevated temperature and pressure, safety precautions, especially solvent leakage and vessel pressure, should be observed at all times. Extraction should be stopped immediately if a spark inside a vessel is observed.

The model MSE-1000 is equipped with only one fiberoptic temperature probe that is inserted into one of the sample vessels. The temperature in this vessel is used as a reference for the control of microwave energy. Since the heating rate, the time required to reach 100°C, at a set microwave power depends on the matrix, the size, and moisture content of the sample, **samples with different matrices, size, or moisture content must not be extracted simultaneously.** A sample containing metals should not be extracted under microwave because it may cause a spark.

Quantitatively transfer the sample material into the Teflon® extraction vessel (120 mL). Add 20 or 30 mL of hexane/acetone mixture (1:1 ratio) and ensure all solid material is covered with solvent. Connect vessels with the control and monitoring device on the vessel carousel following the manufacturer's instructions. If more than one vessel is extracted simultaneously, these vessels are placed evenly in the carousel to ensure uniformity during extraction. Extract for 10 to 20 minutes at 100°C using 500 watts or higher microwave energy. After extraction, remove the sample vessels from the microwave oven and cool to room temperature in a running water bath.

Construct a filtration apparatus by adding a few grams of the precleaned and oven-dried anhydrous sodium sulphate (Na_2SO_4) on a medium porosity filter paper inside a glass funnel. Wash the apparatus with 5 mL of hexane/acetone. Transfer the sample extract through the filtration apparatus into a round bottom flask. Wash the solid sample three times each with several millilitres of hexane/acetone and transfer these rinses into the apparatus. Add 1 mL of iso-octane to the sample

Aqueous. Aqueous samples could consist of industrial effluents or runoffs, the condensate of a stack sampling train, and waters from rivers, lakes, or marine environments. **Any particulate in the aqueous sample is filtered out of the sample and extracted as a solid sample before being combined with the extract of the aqueous phase before cleanup.** Extraction procedures are shown schematically in Figure 1.

Visually inspect each sample for the presence of organic phases. Any organic phase should be separated from the aqueous phase before extraction and recombined with the sample extract before cleanup.

Weigh the liquid sample to the nearest gram on a top-loading balance. Weight is converted to volume by assuming a sample density of 1.0 g/mL. Alternatively, the aqueous sample volume is measured using a graduated cylinder.

Extraction of suspended particulate - Suction filter the sample, if suspended particulate is present, through a pre-wet, glass fibre filter into an appropriately sized filtration flask. Complete the transfer with several portions of deionized water to remove any remaining particulate. Retain the sample container for later use. Continue suction until the flow of filtrate stops completely. Transfer the filter and any particulate still adhering to the walls of the Buchner funnel to a Petri dish and allow the solids to dry in a clean environment. This solid fraction is extracted using the Soxhlet apparatus or MAP™.

Extraction of filtrate - Quantitatively transfer the filtrate from the flask to a clean separatory funnel using three rinses of deionized water. Add three, 50-mL rinses of dichloromethane (CH_2Cl_2) to the retained empty sample container, shaking or swirling each rinse in the container before transferring to the separatory funnel. Extract the filtrate with these rinses by shaking the separatory funnel vigorously for two minutes, releasing pressure buildup as required. Allow the sample to stand for at least ten minutes to ensure separation of the aqueous and organic layers. Drain the organic layer through a powder funnel containing pre-rinsed sodium sulphate and glass wool, into a 500-mL round bottom flask. Persistent emulsions may be drained off into a clean, large beaker and broken using mechanical means, such as passage through loosely packed glass wool. Emulsions may also be broken under microwave energy.

Repeat these extraction procedures twice using 50 mL of dichloromethane each time. Rinse the separatory funnel with an additional 30 mL of dichloromethane. Complete the transfer by rinsing the sodium sulphate three times with several millilitres of dichloromethane. Concentrate the combined extracts and rinses to a few millilitres before combining with the extract from the particulate fraction of the sample. Change the solvent to cyclohexane by adding 100 mL of cyclohexane to the flask and concentrate to a few millilitres. The sample is now ready for cleanup.

Sample Cleanup.

Sulphuric acid cleanup for oil sample. A dilution of the oil is required to reduce the quenching effect on the ECD. This method may not be applicable to determine Aroclor PCBs in oil samples at a concentration less than 3 μg/g.

Tare a 25- or 50-mL volumetric flask on the balance. Weigh 1.00 g of the oil into the bottom of the volumetric flask and top up to the calibration mark with iso-octane using a pipet. Mix well to ensure the sample is homogeneous.

Pipet 10 mL of concentrated sulphuric acid into a pre-cleaned, 25-mL amber vial with a Teflon®-lined cap. Carefully transfer 10 mL of the diluted sample to the vial containing the acid. **CAUTION: THERE COULD BE AN EXOTHERMIC REACTION.** Shake the vial vigorously for two minutes. Allow the sample to settle out for at least 10 minutes. When the sample is partitioned into two discrete layers, remove 1.00 mL of the top layer (sample) and transfer to a 1.5-mL amber vial with a Teflon®-lined cap. For a dirty oil sample, apply the sample to one or more of the cleanup columns described

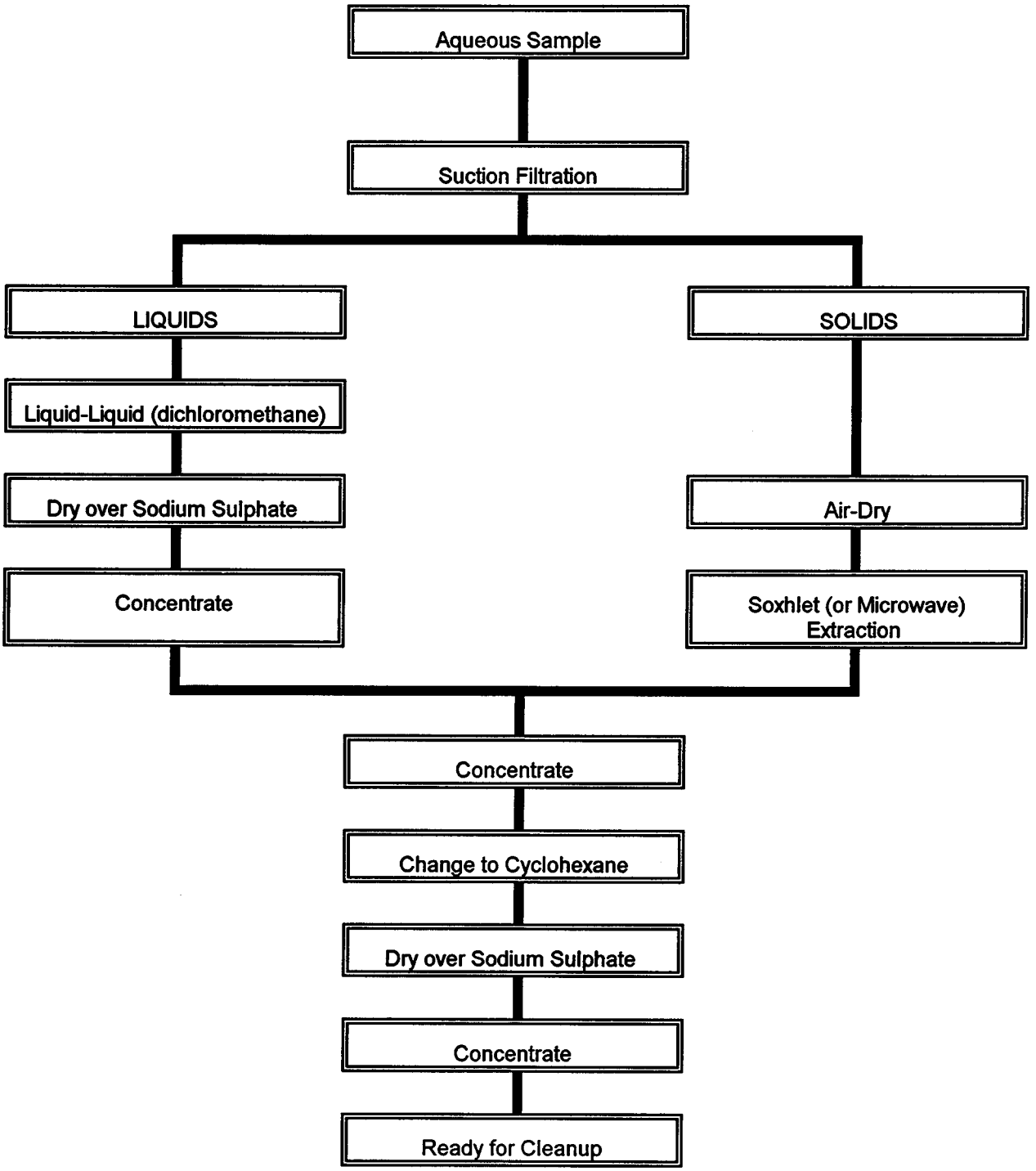


Figure 1 **Extraction Schematic for Polychlorinated Biphenyl in Aqueous Samples - Screening Analysis**

in the next subsection, then concentrate the cleaned extract to 1.00 mL. Add a known amount of the internal standard solution (see Subsection 1.6.1) to the sample and mix well. Store the sample vial below 10°C until GC-ECD analysis.

Cleanup for solid and aqueous samples. It is recommended that all sample extracts be subjected to some form of cleanup before the GC-ECD analysis. Depending on the complexity of the sample matrix, one or two of the following techniques can be applied:

- Sulphuric Acid
- Modified Silica Column
- Copper
- Alumina Column
- Florisil Column
- Disposable Sep-Pak Column

Since no surrogate is added to correct for the possible loss of PCBs during sample workup, cleanup steps should be minimized.

Sulphuric acid cleanup - Transfer the concentrated extract with three, 5 mL hexane rinses of the flask into a 60- or 125-mL separatory funnel. Add 20 mL of concentrated sulphuric acid to the funnel and shake vigorously for two minutes carefully discharging any gas buildup. Allow the two phases to separate for at least ten minutes.

When the sample has partitioned into two discrete layers drain off and discard the acid layer. Rinse the solvent layer with approximately 5 mL of deionized water which is drained out and discarded. Dry the sample extract by passage through pre-rinsed sodium sulphate and rinsing the funnel and sodium sulphate three times with hexane.

Modified silica column- Preparation of the reagents can be found in Subsection 2.4.4. Plug the tip of the column with glass wool and add the following in the order specified:

1.5 g of 10% silver nitrate/silica (bottom layer);
1 g of silica ;
2 g of the 33% 1 *M* sodium hydroxide/silica;
1 g of silica;
4 g of 44% sulphuric acid/silica;
2 g of silica; and
approximately 1 g of sodium sulphate to top off the column.

After each reagent has been added, gently tap the column to ensure even layering. Pre-wash the prepared column with 30 mL of 3% dichloromethane in hexane (v/v). Just as the solvent reaches the top of the sodium sulphate layer, place a 250-mL boiling flask under the column. Using a Pasteur pipet, transfer the concentrated raw extract onto the column, followed by three, 5-mL rinsings of the sample flask, using the same pipet each time.

When the third rinse has drained to the top of the sodium sulphate layer, pour an additional 50 mL of 3% dichloromethane in hexane (v/v) into the column. When the solvent has drained, assess the column for saturation of the acid/silica layer and the silver nitrate/silica layer. This is indicated by the appearance of colour throughout the reagent layer.

Saturation of the acid/silica layer suggests that the sample extract (in hexane) should be washed with concentrated sulphuric acid in a separatory funnel, repeating the washes (maximum of four washings) with fresh acid until no colour is observed in the acid layer. Wash the extract sequentially with deionized water, 1 *M* sodium hydroxide, and a final wash with deionized water. Dry the extract by passing it through sodium sulphate, as previously described.

Saturation of the silver nitrate/silica layer requires passage of the concentrated sample extract through an additional column containing 2.5 g of 10% silver nitrate/silica to remove sulphur-containing compounds which may interfere in the analysis. Elute the sample extract through the pre-washed column with 30 mL of 3% dichloromethane in hexane.

Copper cleanup - Some oils and sediment extracts may contain high levels of elemental sulphur which will cause significant interference

on the ECD. Add approximately 0.5 g of freshly treated copper to a 5-mL aliquot of the sample extract in a small Erlenmeyer flask. Swirl the flask and allow the extract to stand for approximately 10 minutes. Add another 0.5 g of copper and repeat until no further reactions (copper turns black) are observed. Quantitatively transfer the sample extract through a filter paper or glass wool to remove the copper.

Alumina column cleanup - Prepare the basic alumina and the alumina column using the procedures described in Subsections 2.4.4 and 2.5.6. Add 15 mL of hexane to wash the column. When the hexane has drained just to the top of the sodium sulphate layer, place a 250-mL boiling flask under the column for sample collection. Using a Pasteur pipet, transfer the sample extract onto the alumina column following with 30 mL of hexane. When this solvent has drained to the top of sodium sulphate layer, add 30 mL of freshly prepared 5% dichloromethane in hexane to the column.

After final cleanup, add 1 mL of iso-octane, concentrate the sample to a known small volume, and then add a known amount of the internal standard solution to the sample. Transfer the sample to a precleaned amber vial and store below 10°C until GC-ECD analysis.

1.6 Gas Chromatography - Electron Capture Detection Analysis

1.6.1 Gas Chromatograph and Calibration

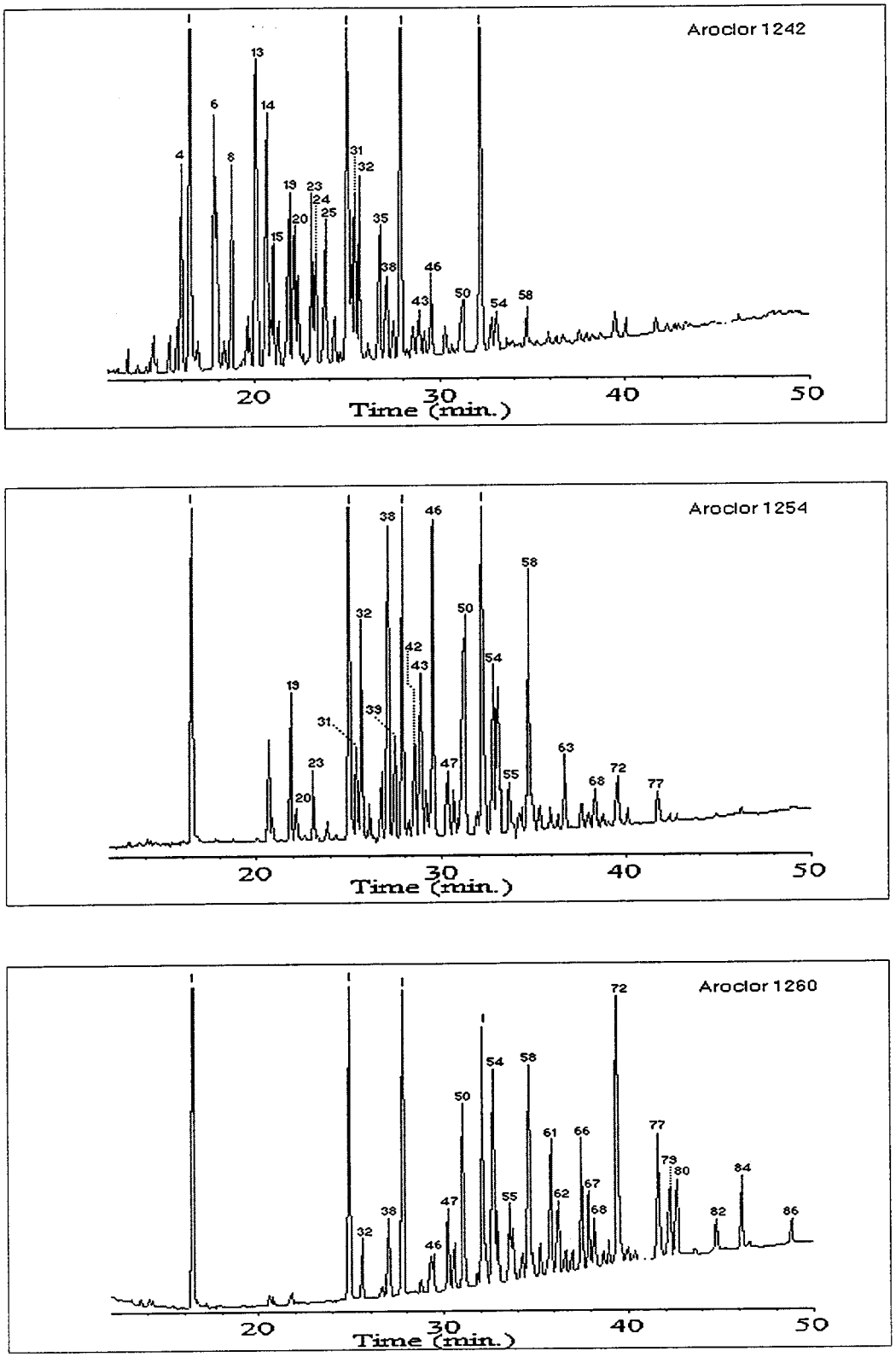
The gas chromatograph should be equipped with a temperature-programmable oven, a temperature-controlled split/splitless or on-column injector, a ^{63}Ni electron capture detector, and a computerized data station. A 30-m, DB-5 (5% phenyl substituted methyl polysiloxane), or equivalent capillary column, is required to achieve adequate gas chromatographic separation of Aroclor PCBs.

The analysis of PCBs in samples is based on fingerprint pattern recognition of each particular Aroclor or Aroclor mixture. Many types of Aroclor standards (see Subsection 1.4.2) are commercially available. **As a minimum, calibration solutions of Aroclors 1242, 1254, and 1260 and Aroclor mixtures 1242/1254, 1254/1260 and 1242/1260 at 1:1 ratio should be prepared. For non-Aroclor PCBs, the 2,4', 5-trichlorobiphenyl (PCB-31) is used as a calibration standard for total PCBs.** (This standard is present in the certified reference material CLB-1 solution A at 6.6 μg/mL; NRCC). Prepare PCB standards in iso-octane.

The presence of oil in a sample will result in a quenching of the detector response, loss of resolution for some closely eluting congeners, and a shift in retention time. Therefore, to facilitate accurate analysis, oil samples should be quantitated against a standard containing the same approximate concentration of oil as the sample.

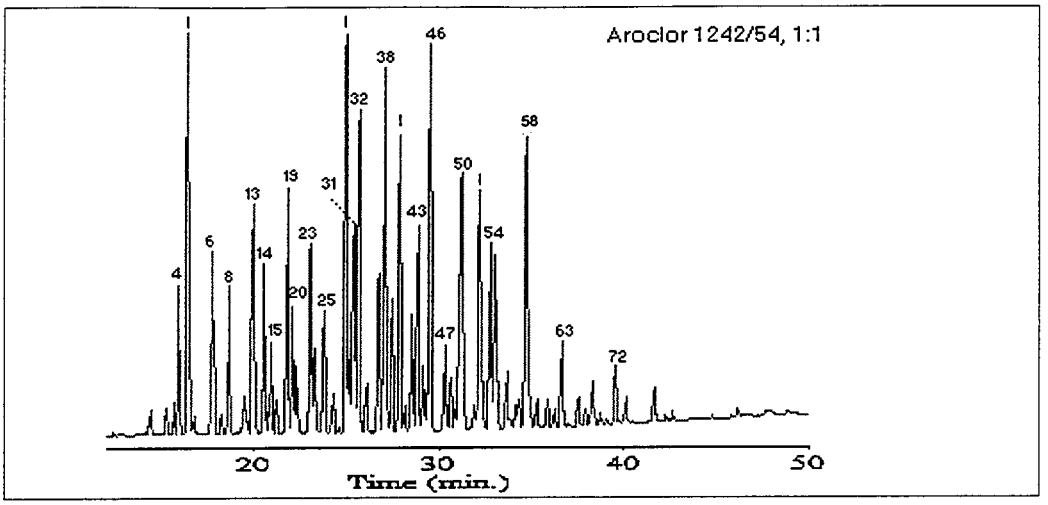
Internal standard(s) must be added to the calibration solution and sample extracts before analysis to correct for possible variations in injection volume, sensitivity, quenching effect, and evaporation loss during GC analysis. Internal standards must have a response to the ECD and GC column similar to PCBs and must not co-elute with target PCBs.
Compounds such as:
PCB-29 (2,4,5-trichlorobiphenyl),
PCB-34 (2',3,5-trichlorobiphenyl),
PCB-35 (3,3',4-trichlorobiphenyl),
PCB-83(2,2',3,3',5-pentachlorobiphenyl),
PCB-103(2,2',4,5',6-pentachlorobiphenyl),
PCB-119 (2,3',4,4',6-pentachlorobiphenyl),
PCB-122 (2',3,3',4,5-pentachlorobiphenyl),
PCB-169 (3,3',4,4',5,5'-hexachlorobiphenyl),
PCB-189 (2,3,3',4,4',5,5'-heptachlorobiphenyl),
PCB-198 (2,2',3,3',4,5,5',6-octachlorobiphenyl),
can be considered as internal standards. It is wise to add more than one internal standard to a sample so that the most appropriate one can be used. Congeners with higher chlorine substitution such as octa-, nona-, and deca-chlorobiphenyls are expected to yield relatively lower (poor) precision than other PCBs.

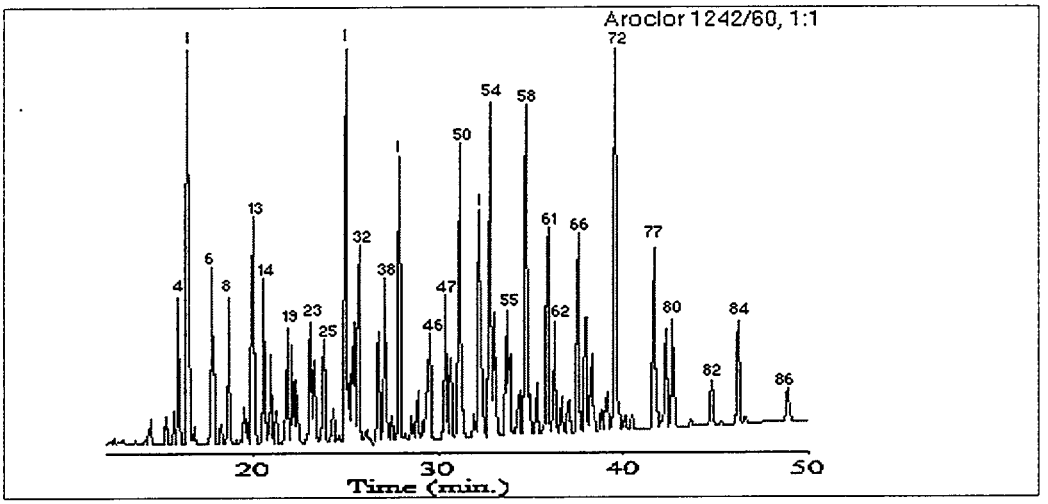
Figures 2 and 3 are typical GC-ECD profiles for various Aroclors and Aroclor mixtures. To help peak identification, each characteristic peak is identified with a domain number (Schulz *et al.*,

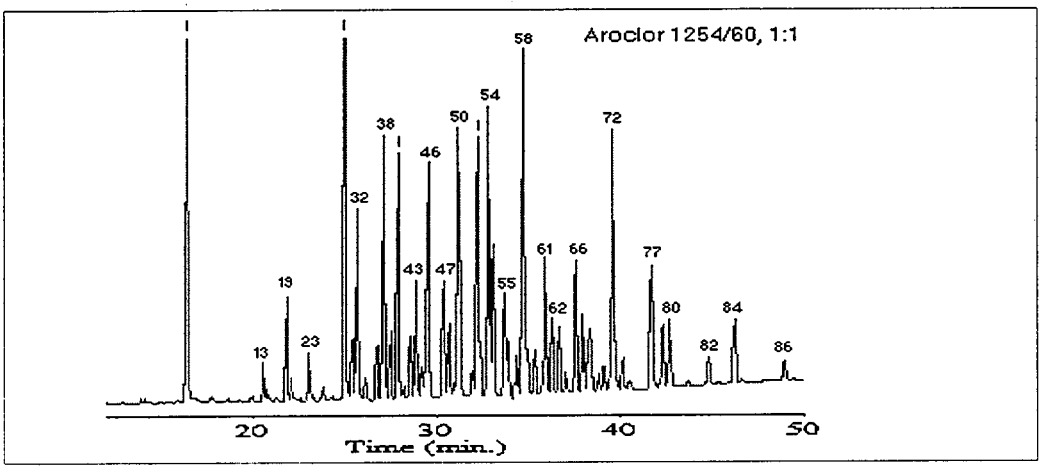


Note: 'I' represents internal recovery standard hexachlorobenzene, octachlorostyrene, PCB-83 and PCB-122 in order of elution.

Figure 2 **Gas Chromatography - Electron Capture Detection Profiles of Aroclor 1242, 1254, and 1260 on a DB-5 Column**







Note: 'I' represents internal recovery standard hexachlorobenzene, octachlorostyrene, PCB-83 and PCB-122 in order of elution.

Figure 3 **Gas Chromatography - Electron Capture Detection Profiles of Aroclor 1242/1254, 1242/1260, and 1254/1260 Mixtures on a DB-5 Column**

1989), each of which contains either one well-resolved peak or a cluster of unresolved peaks. Each domain should be separated from neighbouring domains. Typical GC parameters used for obtaining these chromatograms are:

- injector: 2 μL injection at splitless mode, 290°C
- detector temperature: 320°C
- oven temperature program: 90°C for 0.5 min, 15°C/min to 200°C and hold for 5 min
- 2.5°C/min to 285°C and hold for 5 min
- GC Column: DB-5, 30 m, 0.25-mm ID, 0.25 μm film

Aroclor profiles could vary slightly among suppliers and also from batch to batch; however, characteristic peaks should remain the same. The typical Aroclor 1242 should have major domain peaks # 4, 6, 8, 13, and 14 at the early elution times and the minor peaks of # 46, 50, 54, and 58 at the later elution times. The presence of domain peaks # 79, 80, 82, 84, and 86 at later elution times, and the absence of peaks before # 32 are unique for Aroclor 1260. In addition to possessing the dominant peaks #38, #43, and #46, Aroclor 1254 shares the major peaks with Aroclor 1242 on domain #19, #31, and #32, and with Aroclor 1260 on domain #50, #54, and #58. Aroclor mixtures (e.g., 1242/1260) should have the characteristic peaks of the combined Aroclors. Domain numbers and percent contributions of individual PCB congeners in Aroclors are tabulated in Table A7 (Appendix A).

When analysis yields measurable peaks, determine the type of PCBs by comparing the sample chromatogram to reference chromatograms of the various Aroclors. The best way for matching Aroclor patterns is to set the highest (largest) PCB peak at full (100%) scale for every chromatogram. **The GC parameters used to obtain reference chromatograms must match those used for sample analysis.**

The linear calibration range bracketing the relevant regulation limit must be established by using a minimum four levels of calibration standard (e.g., Aroclor1242/1260 mixture). Linearity of the calibration curve is verified when the correlation coefficient is not less than 0.995. Linearity must be re-established when the column or any GC parameter has been changed. Once the Aroclor pattern of the sample is identified, a calibration solution with a similar Aroclor pattern and a concentration close to the regulated limit should be used for PCB quantitation. This calibration solution is analyzed at least twice with each batch of samples.

1.6.2 Quantification

Sample Containing a Single Aroclor or a Mixture of Aroclors.

For samples containing a single or a mixture of identified Aroclors, PCB concentration is calculated by comparing the summed response (area) of all identified PCB peaks, or at least eight major peaks, in the sample chromatogram to the summed response (area) for the corresponding peaks in the calibration standard chromatogram. Due to Aroclor pattern variations and possible interferences, serious errors may result if calculation is based upon only a few PCB peaks.

Assuming equal injection volume for both sample and standard, the PCB concentration of a sample is calculated as:

$$PCB\ concentration = \frac{(\sum_{k=1}^{n} A_k) \cdot C \cdot F \cdot A_c}{(\sum_{ck=1}^{n} A_{ck}) \cdot W \cdot A_s}$$

where:

$\sum_{k=1}^{n} A_k$ = sum of the peak area for "n" identified PCB peaks in the sample chromatogram

$\sum_{ck=1}^{n} A_{ck}$ = sum of the peak area for the corresponding "n" PCB peaks in the calibration standard

C = PCB concentration of the calibration standard

W = size of sample used, in grams for solid and oil samples , in litres for aqueous samples

F = dilution factor or volume of sample extract

A_c = peak area of the internal standard in the calibration standard

A_s = peak area of the internal standard in the sample

Sample Containing Non-patterned Polychlorinated Biphenyls (PCBs).

Sample GC profiles which do not closely match any single Aroclor or mixture of Aroclors should be treated as non-patterned PCBs. In these cases, areas of all possible PCB peaks of the sample chromatogram, within the retention time window between the first eluting PCB congener peak (domain-5 containing PCB-19, PCB-30, and PCB-18 on a DB-5 column), **and the last eluting PCB congener** (decachlorobiphenyl, PCB-209, or domain-87 on a DB-5 column), **should be summed and quantified against the 2,4',5 trichlorobiphenyl (PCB-31).**

PCB-31 has an ECD response close to the mean response of trichlorobiphenyl isomers (see Table A1, Appendix A). The mean response of each isomer group, in general, increases with the degree of chlorination; however, the coefficient of variation of relative response factors (RRF) within each homologue is as high as 42%. A total of 36 PCB congeners within the tri- to octa-homologues may have RRF values (relative to octachloronaphthalene) lower than the PCB-31 (Mullin *et al.*, 1984).

Assuming equal injection volume for both sample and standard, the PCB concentration of a sample is calculated as:

$$PCB\ concentration = \frac{(\sum_{k=1}^{n} A_k) \cdot C \cdot F \cdot A_c}{A \cdot W \cdot A_s}$$

where:

$\sum_{k=1}^{n} A_k$ = sum of the peak area for "n" possible PCB peaks in the sample chromatogram excluding the internal standard

A = peak area of PCB-31 standard

C = concentration of PCB-31 calibration standard

W = size of sample used, in grams for solid and oil samples or litres for liquids

F = dilution factor or volume of sample extract

A_c = peak area of the internal standard in the calibration standard

A_s = peak area of the internal standard in the sample

An alternative approach is to identify and quantify each PCB peak by using as many of the available PCB congeners of tri- to deca-homologues as possible and a good separation technique such as multidimensional gas chromatography or dual column gas chromatography. **Documentation must be made to demonstrate that under no circumstances would this alternate procedure underestimate PCB concentrations.**

1.6.3 Detection Limits and Precision

The detection limit of a sample is affected by sample size, dilution, and concentration factor, injection volume, and instrumental sensitivity. The GC-ECD sensitivity is generally determined on the basis of the signal-to-noise ratio for a single compound. A GC chromatogram of an Aroclor may contain 20 or more eluting peaks. It

is appropriate to use at least eight major peaks for pattern recognition and quantification. The detection limit for Aroclors is therefore determined by the minimum abundance of those selected major peaks. It is estimated that under ideal operating conditions, the detection limit of Aroclor 1242 in iso-octane is 0.04 to 0.1 μg/mL (ppm). The detection limit of Aroclor 1242 in oil, however, is estimated to be 1 to 2 μg/g because of the dilution required to reduce the quenching effect of the oil on the EC detector. For oils containing non-Aroclor PCBs, the detection limit is approximately 0.2 μg/g per congener peak using the PCB-31 for calibration.

Intralaboratory precisions for the analysis of various Aroclors and Aroclor mixtures in solvent and in a diluted transformer oil are found in Tables A2, A3, and A4 (Appendix A). An HP 5890 series II GC equipped with a 7673A autosampler was used with the operational conditions specified in Subsection 1.6.1. The concentration of PCBs used in this study were slightly higher than the detection limits. The analytical precision (% RSD) would be moderately improved if the level of Aroclor in the sample is significantly above the detection limit. Variations are expected to be greater if sample cleanup steps are required.

Interlaboratory variations in PCB analysis for the Canadian Association for Environmental Analytical Laboratories' (CAEAL) studies undertaken in 1993, 1994, and 1995 are presented in Table A5, Appendix A. For these studies, participating labs used their own GC-ECD method, with the exception of a few labs using a GC-MS method. Study results suggested that the deviation from the reference value at 95% confidence is between 25 and 46% for oil with single Aroclor pattern and between 33 and 50% for oil containing Aroclor mixtures.

1.7 Data Reporting

Reporting of GC-ECD screening results and relevant QA/QC data is necessary only if GC-MS analysis has not been carried out.

Submission of sample results must be accompanied by a good photocopy of the corresponding sample submission/custody sheet (Figure 4).

A PCB screening report (Figure 5) must include information on sample identity, matrix, dilution factor, PCB concentration, type of Aroclor(s), GC column, and date of analysis.

Quality Assurance/Quality Control (QA/QC) data including calibrations, control samples, method blanks, detection limits and results of the most recent performance validation test must be made available to Environment Canada upon request. An example is shown in Figures 6 and 7.

Laboratories must maintain all original sample and supporting QA/QC data on file for a minimum of three years for auditing purposes.

1.8 Quality Assurance

The following quality assurance procedures must be followed and performance criteria must be met to minimize potential bias and errors.

(a) Performance Validation (Subsection 1.5.3):
Before sample analysis, the laboratory must demonstrate the ability to achieve acceptable recoveries of PCBs by conducting analyses of three subsamples of a certified reference material containing Aroclors or the matrix blanks spiked with an Aroclor 1254/1260 mixture at a concentration near the regulatory limit. The sample matrix chosen should be similar to the type of sample to be analyzed. For each of the three analyses, PCB recovery must be within 75 to 125% of the actual value. No sample should be processed until the performance validation test yields acceptable results. The test must be repeated within a 6-month period before sample processing begins.

(b) Control Sample (Subsection 1.5.4):
A certified reference material with a matrix

similar to test samples is analyzed with each batch of up to 15 samples. This could be replaced with a blank matrix similar to the test samples and fortified as in Subsection 1.5.3 when reference material is not available. The recovery of PCBs in the control sample must be within 75 to 125% of the actual value.

(c) Method Blank (Subsection 1.5.4):
A blank matrix sample (free of PCBs) is analyzed with each batch of up to 15 test samples to assess any cross-contamination that would interfere with PCB analysis.

(d) Internal Standard (Subsection 1.6.1):
Compounds that respond to the GC-ECD in a similar manner to PCBs and do not co-elute with target PCBs can be used as internal standards. Internal standard(s) must be added to the final sample extract before analysis to correct for analytical variations from run to run.

(e) Calibration Standard (Subsection 1.6):
The accuracy of working calibration standards must be verified against reference standards at least once every 12 months.

(f) Detection Limit (Subsection 1.5.4):
The detection limit of a PCB sample must not exceed 30% of the regulatory limit.

(g) GC-MS Confirmation (Section 2):
Confirmative analysis using gas chromatography-mass spectrometry is required if the screening result is greater than 60% of the regulatory limit (> limit × 0.6).

Sample Submission/Custody Sheet

Date: _____ Submitted by: _____

Project: _____ Phone No: _____

Submitted to: _____ Fax No: _____

Storage Conditions during shipment: _____

Sample ID	Date and Time Collected	Sampling Location	Matrix and Size	Container Type and Size	Analysis Requested and Expected Concentration

Remarks:

CHAIN OF CUSTODY RECORD

Relinquished by:	Date: / Time:	Received by:	Date: / Time:	Remarks:
Relinquished by:	Date: / Time:	Received by:	Date: / Time:	Remarks:
Relinquished by:	Date: / Time:	Received by:	Date: / Time:	Remarks:
Relinquished by:	Date: / Time:	Received by:	Date: / Time:	Remarks:

Figure 4 Example of a Sample Submission/Custody Sheet

PCB Screening Report

Lab:_____ GC Column: _____
Project/Client: _____ Approved By: _____
Analysis Date: _____ Date: _____
Batch No.: _____

1. Sample ID: _____ Matrix: _____ Size and Dilution Factor: _____
   PCB Concentration:_____Aroclor Type: _____

2. Sample ID: _____ Matrix: _____ Size and Dilution Factor: _____
   PCB Concentration: _____Aroclor Type: _____

3. Sample ID: _____ Matrix: _____ Size and Dilution Factor: _____
   PCB Concentration: _____Aroclor Type: _____

4. Sample ID: _____ Matrix: _____ Size and Dilution Factor: _____
   PCB Concentration: _____Aroclor Type: _____

5. Sample ID: _____ Matrix: _____ Size and Dilution Factor: _____
   PCB Concentration: _____Aroclor Type: _____

6. Sample ID: _____ Matrix: _____ Size and Dilution Factor: _____
   PCB Concentration: _____Aroclor Type: _____

7. Sample ID: _____ Matrix: _____ Size and Dilution Factor: _____
   PCB Concentration: _____Aroclor Type: _____

Figure 5 Example of a Polychlorinated Biphenyl Screening Report

Quality Assurance/Quality Control Data Report A

Lab: _____ GC Column: _____
Project/Client: _____ Approved By: _____
Analysis Date: _____ Date: _____
Batch No.: _____

Performance Validation Test

Expected PCB Concentration: _____ Aroclor Type: _____ Matrix:_____

Recovery: Analysis 1_____ %
Analysis 2 _____ %
Analysis 3 _____ %

Figure 6 **Example of Quality Assurance/Quality Control Data Report for Performance Validation Test**

Quality Assurance/Quality Control Data Report B

Lab: _____ GC Column: _____
Project/Client: _____ Approved By: _____
Analysis Date: _____ Date: _____
Batch No.: _____

A. Control Sample(s)

Expected PCB Concentration: _____ Aroclor Type: _____ Matrix:_____
% Recovery: _____

B. Method Blank(s)

PCB Concentration: _____ Aroclor Type: _____ Matrix:_____

C. Detection Limit(s)

Estimated Detection Limit for Aroclor _____ in ____ (Matrix) was _____ μg/g (ng/L)

Figure 7 **Example of a Quality Assurance/Quality Control Data Report for Control Sample, Method Blank, and Detection Limit**

Section 2

Confirmative Analysis of Polychlorinated Biphenyls

2.1 Summary

The confirmative analysis of PCBs comprises the application of isotopically-labelled PCB surrogates (isotope dilution), thorough cleanup to remove oil and/or other interfering organics, and mass spectroscopy for analysis. This analysis provides the unambiguous identification and quantification of PCBs in samples. **Confirmative analysis of a second subsample is required when the PCB concentration, determined by the screening method (Section 1), is greater than 60% of the regulatory limits (> limit × 0.6).** This method can also be applied directly without screening analysis. Standards with respect to various federal PCB regulations are summarized in Appendix A (Table A6).

Before sample processing, each sample is spiked with a surrogate mixture of isotopically-labelled PCBs. The accurately weighed solid sample is Soxhlet extracted with toluene for 16 to 20 hours. Alternatively, the solid sample is extracted with hexane/acetone under microwave energy for 10 minutes.

An aqueous sample is extracted with dichloromethane in a separatory funnel. Particulate, if present in the aqueous sample, are filtered and extracted using a Soxhlet or microwave apparatus. Raw extracts of the particulate phase and the aqueous phase are combined before cleanup.

Each oil sample is washed with concentrated sulphuric acid followed by liquid-liquid extraction with dimethyl sulphoxide/water mixture (97.5/2.5%) using separatory funnels. The latter step separates PCB from the oil matrix to facilitate gas chromatography - mass spectrometry (GC-MS) analysis.

The concentrated raw extract is passed through one or two columns which remove, by reaction and/or selective adsorption, the bulk of the organic matrix co-extracted with PCBs. Further cleanup using gel permeation chromatography (GPC) or high performance liquid chromatography (HPLC) may be required. The resulting PCB fraction is concentrated to a known volume (typically 0.5 mL) for analysis.

The qualitative and quantitative analysis for PCBs is performed with a GC-MS system. Polychlorinated biphenyls are quantified on a total homologue basis as opposed to individual congeners or Aroclors. Three characteristic ions are selectively monitored for each PCB homologue. Analyte identification is confirmed when target ions detected in the established retention time windows have correct abundance ratios. Quantification is based on the use of relative response factors of the ratio of PCBs to surrogates. The PCB concentration is, therefore, automatically corrected for the recovery of surrogates. An isotopically-labelled standard added to sample extracts immediately before analysis, serves as a recovery standard for the quantification of surrogate recovery.

2.2 Contamination and Interferences

Contamination from solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines that could lead to elevated detection limits and/or inability to detect PCBs that may be present. Reagents should be of high purity, and in some cases, may require further purification before use.

Proper cleaning of the glassware is essential to minimize contamination. Glassware should be rinsed with solvents soon after use, then washed with a detergent solution followed by solvent rinsing to remove most of the contaminants. Sonication of glassware filled with a detergent solution can also be performed as an aid to cleaning.

It must be demonstrated that all materials used in the analysis are free from interferences by conducting proofing analysis initially and method blanks with each sample set of up to 15 samples.

Interferences co-extracted from samples will vary considerably from source to source depending on the nature of the sample matrix. Interfering compounds may be present at concentrations several orders of magnitude higher than any PCBs that may be present. Interfering co-extractants must therefore be eliminated or reduced to the maximum extent practicable to ensure reliable quantification of trace amounts of PCBs. The cleanup procedures described herein can effectively remove many potential interferents.

Despite rigorous cleanup procedures, matrix interference may still be a possibility. If detection limits are seriously affected by excessive background (non-discrete interference), the sample extract will have to be re-processed using alternative cleanup techniques.

2.3 Safety

It is suspected that most PCB congeners do not have any acute toxic effects other than their persistence in the environment. There are some congeners, however, that appear to elicit the same toxicity and effects on biological activities as polychlorinated dibenzo-*para*-dioxins and dibenzofurans (PCDDs/PCDFs) (Safe *et al.*, 1990). Some of these toxic chlorobiphenyls are present in commercial products containing PCBs (Voogt *et al.*, 1990). Oils containing PCBs may contain trace amounts of PCDFs (Mitchell *et al.*, 1984). Each sample, therefore, should be treated as a potential health hazard and personal exposure should be minimized.

All work pertaining to the analysis of PCBs, including preparation, handling, and storage of all samples must be carried out in an adequately ventilated laboratory.

Personnel in the laboratory must wear protective clothing at all times consisting of safety glasses, lab coat, and disposable powder-free gloves as a minimum. Common laboratory safety equipment and facilities, such as sinks/safety showers, first aid kits, eye wash stations, and fire extinguishers must be easily accessible. In addition, all safety equipment and materials required to contain and clean up a spill must be on hand.

Only experienced and well-trained personnel, who are fully aware of the hazards associated with all the chemicals pertaining to sample processing as well as any safety regulations within the jurisdiction, should be involved with these analyses.

Laboratory safety protocols, covering such topics as safe and secure handling and storage of PCBs, housekeeping, spill containment and cleanup, and disposal of solid and liquid wastes, must be provided to laboratory personnel. These protocols must be strictly adhered to.

2.4 Apparatus and Reagents

2.4.1 Equipment and Supplies

The following equipment and supplies are used for the confirmative analysis of PCBs.

- **Extraction Apparatus...** 200-mL Soxhlet body (Dean Stark moisture trap optional), condenser, 45 × 125-mm glass or cellulose thimble, and a temperature controlled heating mantle
- **Evaporative Concentrator...** Buchi R-110 rotary evaporator or equivalent or Zymark Turbo-Vap
- **Balance...** top-loading macro balance, capacity to 1600 g, readability to 0.01 g, for weighing samples and reagents
- **Pipets...** electronic or mechanical pipets with capacities from 10 to 1000 μL
- **Oven...** range to 225°C, for conditioning silica, reagent-coated silica, sodium sulphate, and glass wool
- **Tube Furnace...** Lindberg, Model 59344 or equivalent, for activating alumina at 350°C
- **Ultrasonic Bath...** 1-litre capacity
- **Pumps...** pressure/vacuum with vacuum to 85 kPa (25 in. Hg) for rotary evaporation and suction filtration
- **Filters...** various diameters, glass fibre filter with 1.2 μm pore size
- **Teflon® Squeeze Bottles**
- **Weighing Paper**
- **Forceps, Spatulas, Scoops**
- **Desiccators**
- **Glassware Washing Equipment**

- **GC-MS...** see Section 2.6
- **HPLC...** see Subsection 2.5.6
- **GPC...** see Subsection 2.5.6

2.4.2 Glassware

The following glassware is used in the confirmative analysis of PCBs.

- **Beakers...** assorted volumes from 150 to 1000 mL
- **Buchner Funnels...** 12 cm diameter
- **Filtration Flasks...** 500 and 1000 mL
- **Separatory Funnels...** 125, 250, 1000, 2000 mL
- **Boiling Flasks...** 250 and 500 mL
- **Erlenmeyer Flasks...** 500 mL with glass stopper
- **Powder Funnels...** 7 cm diameter
- **Graduated cylinders...** 10, 50, 100, and 250 mL
- **Volumetric Flasks...** 10 and 50 mL
- **Calibrated Centrifuge Tubes...** 5 and 15 mL
- **Calibrated Chromatography Sample Tubes...** 2 mL
- **Pasteur Pipets...** 22 cm, disposable
- **Petri Dishes...** 14 cm diameter
- **Glass Column...** minimum 1L capacity, Teflon® stopcock, for solvent washing of silica, sodium sulphate, and glass wool
- **Cleanup Columns...** acid/base, alumina (see Figure 12)
- **Alumina Conditioning Column...** (see Figure 8)
- **Calibrated Pipets...** 5 and 10 mL, graduated at 0.1 mL intervals
- **Vials...** assorted capacities from 1.5 to 40 mL, amber glass, screw cap with Teflon®-faced septum

2.4.3 Reagents

The following reagents are used for the confirmative analysis of PCBs.

- **PCB Standards...** PCB standards, carbon-13-labelled standards, window-defining mixtures and column performance mixtures are commercially available. Reference standard solutions are available from the National Research Council (NRC) in Canada and the National Institute of Standards and Technology (NIST) in the United States.

- **Solvents...** all solvents are distilled-in-glass quality or better; those required include toluene, hexane, iso-octane, cyclohexane, dichloromethane, dimethyl sulphoxide (DMSO), and acetone.

- **Gases...** high purity grade nitrogen and helium

- **Others...** silica (100 to 200 mesh, 50 Å pore diameter), S-X3 beads, and basic alumina (AG 10, 100 to 200 mesh) are commercially available; all other reagents, including sulphuric acid, sodium hydroxide, silver nitrate, and sodium sulphate are American Chemical Society (ACS) reagent grade or better.

2.4.4 Glassware and Material Preparation

Glassware: All reusable glassware must be scrupulously cleaned as soon as possible after use. Glassware is sequentially rinsed with the last solvent contained in that piece of glassware, followed by rinses of hexane and acetone. This is followed by washing with hot detergent solution and sequential rinsing with hot water, deionized water, and three portions each of acetone, hexane, and dichloromethane. For severely contaminated glassware, treatment in an ultrasonic bath filled with detergent solution is often beneficial. If a brush is used to scrub glassware, great care must be taken to ensure that glass surfaces are not scratched. Glassware is either air-dried or dried in an oven, and then stored in a contaminant-free area.

A glassware-proofing sample must be analyzed before actual test samples are processed. Each piece of glassware to be used with test samples, must be rinsed with hexane and dichloromethane. The rinses are combined into one sample, which is spiked with surrogates, cleaned up (if required) and analyzed by GC-MS. Test sample analysis may proceed only if any PCB present in the proofing sample is below 25 ng per congener and less than 100 ng in total PCB.

DMSO/water 97.5/2.5 (v/v): Add 40 mL of deionized water that has been saturated with sodium sulphate to 1560 mL of DMSO and extract three times in a 2000 mL separatory funnel with 100 mL of hexane for two minutes each time. Store the precleaned solvent in a glass bottle with a Teflon®-lined lid.

Glass Wool: Compress a quantity of glass wool into a large glass column (1 L capacity or larger) and wash sequentially with hexane and dichloromethane. The volume of solvent used for each wash should be twice the estimated volume of glass wool in the column. Transfer the washed glass wool into a large beaker. Loosely cover the mouth of the beaker with aluminium foil previously rinsed with hexane and dichloromethane, allow the glass wool to air dry in a fume hood, and then condition overnight at 225°C in a vented oven. Store in a clean, wide-mouth, glass-stoppered bottle.

Sodium Sulphate: Wash the granular, anhydrous sodium sulphate in the same column used for preparing glass wool. Sequentially wash the sodium sulphate twice with hexane and twice with dichloromethane. The volume of solvent used for each washing should be twice the estimated volume of sodium sulphate in the column. Transfer to a large beaker, cover the mouth loosely with solvent-rinsed aluminum foil, and oven dry at 50°C for several hours before conditioning overnight at 225°C. Store in a desiccator in a clean, screw-capped bottle fitted with a Teflon®-lined cap.

Silica: Transfer approximately 350 g of silica to the large glass column used for preparing glass wool and sodium sulphate. Sequentially wash with hexane and dichloromethane as previously described. Oven dry the silica at 50°C for several hours in a beaker loosely covered with solvent-rinsed aluminum foil, then condition at 180°C overnight. Store in a desiccator in an amber jar with a Teflon®-lined lid.

44% (w/w) Sulphuric Acid on Silica: Add 78.6 g of concentrated sulphuric acid in a stepwise manner (5 mL at a time), to 100 g of freshly-conditioned silica in a 500-mL glass-stoppered Erlenmeyer flask. After each addition, shake the flask vigorously to remove all clumps. Store this material in the stoppered flask. Preparation of larger batches is not recommended. (**Caution**: This material has all the properties of concentrated sulphuric acid. Handle with care!)

33% (w/w) of 1 *M* Sodium Hydroxide on Silica: Add 24.6 g of a 1 *M* sodium hydroxide solution, stepwise, to 50 g of freshly-conditioned silica in a glass-stoppered Erlenmeyer flask. After each addition, shake the flask to remove all clumps. Store this material in a screw-capped bottle fitted with a Teflon®-lined cap.

10% (w/w) Silver Nitrate on Silica: Dissolve 5.6 g of silver nitrate in 21.5 mL of deionized water. Add this solution, in a stepwise manner, to 50 g of freshly-conditioned silica in a glass-stoppered Erlenmeyer flask. Between additions, shake the flask until a uniformly-coated, free-flowing powder is produced. When all silver nitrate has been added, allow the material to stand for approximately 30 minutes, cover the mouth of the flask with solvent-rinsed aluminum foil, and place in an oven at 30°C. Over a five-hour period, gradually raise the oven temperature to 180°C, and continue to condition overnight at this temperature. Cool to room temperature and immediately transfer to an amber glass, screw-capped bottle fitted with a Teflon®-lined cap. Minimize exposure of this material to light. Store this material in a desiccator until use.

Basic Alumina (optional): Weigh out 2 to 3 g more alumina than is required (2.5 g/sample) for the number of samples to be batch-processed at one time. Add the alumina to the conditioning column (Figure 8), and wash with dichloromethane, then hexane (two portions each). The volume of solvent used for each wash should be two to three times the estimated volume of alumina in the conditioning column. After draining, insert a pre-cleaned glass wool plug into the column to immobilize the alumina. Drain as much solvent as possible from the wet alumina by applying suction at the end of the column, then place the column in the tube furnace. Connect the glass-jointed end of the column to a cylinder of nitrogen. With the furnace off, purge the alumina with nitrogen at 200 to 400 mL/min for approximately 30 minutes. While maintaining the nitrogen purge, condition the alumina at 350°C for a minimum of two hours. Conditioned

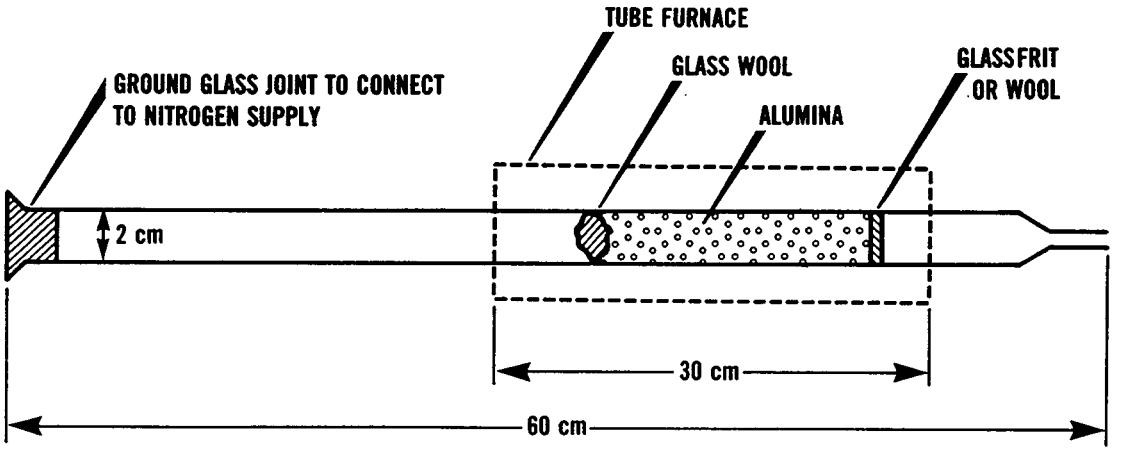


Figure 8 **Alumina Conditioning Column**

alumina should be used immediately after removal from the tube furnace. Do not store this material for later use. **(Caution: Hot glass.)**

It is highly recommended that reagent blank samples are prepared and assessed for contamination and recovery whenever a new lot of reagents are used (Subsection 2.5.3)

2.5 Sample Collection, Handling, and Workup Procedures

2.5.1 Sample Collection and Storage

The integrity of measurement depends on how the sample was collected. It is important, therefore, that the sample collected is representative and free from any outside contamination. Consideration must be given to all facets of sample collection, preservation, shipment, and handling to maintain the integrity of the sample.

In general, samples should be collected in pre-proofed amber jars having Teflon®-lined lids. Samples should be kept at a temperature less than 10°C from the time of collection until receipt at the laboratory. Upon arrival at the laboratory, samples should be stored in the dark below 10°C until extraction (do not the allow the aqueous sample in a glass jar to freeze).

2.5.2 Sample Handling and Custody

Upon arrival at the laboratory, samples must be inspected immediately for their physical condition and to ensure proper labelling. Inform the client of any potential problem concerning the integrity of samples. After logging and labelling with laboratory code numbers, samples should be processed as soon as possible. The sample-tracking report sheet submitted with samples is completed and signed by authorized laboratory personnel.

2.5.3 Performance Validation

Before sample analysis, the laboratory must demonstrate the ability to achieve acceptable precision and accuracy by validating the analytical performance as follows.

Three spiked matrix samples similar to the samples being analyzed must be prepared, processed and analyzed according to the procedures used for actual samples. Each of these validation samples must be fortified with the following:

a) Aroclor 1254/1260 mixture (1:1) close to the regulated limit, or an amount not more than 125 ng each of the 20 native PCB congeners specified in Table 5; and

b) $^{13}C_{12}$-labelled surrogates - a minimum of one surrogate for each PCB homologue containing more than two chlorines. Spiking each sample with 200 ng of each of the surrogates listed in Table 2 is recommended. These surrogates can be substituted with different $^{13}C_{12}$-labelled PCB isomers.

Standard reference materials, of the matrix being analyzed may substitute for fortified samples when available.

The average labelled surrogate recovery for each sample must be within the 50 to 120% range with no individual surrogate recovery less than 30% or greater than 130%. The recovery of deca- and nona-PCB surrogates are exempted from this criteria for an oil sample that contains mainly Aroclors. The total PCB recovery for each of the three samples must be within the range of 75 to 120% of the actual value.

No field sample shall be processed until the performance validation test yields acceptable results. This test should be repeated whenever extraction or cleanup procedures are modified, whenever the analyst has been changed, or if the performance validation test has not been conducted in the preceding six-month period.

The values obtained from control samples may be used instead of repeating the performance validation tests every six months if the following conditions are met:

i) Control samples consist of a certified reference material or a matrix blank fortified with Aroclor 1254/1260 (1:1) at a concentration close to the regulated limit, or a mixture containing no more than 125 ng each of the 20 native PCB congeners specified in Table 5. A control sample should possess matrices similar to the test sample.

ii) No less than three control samples have been processed in the last 6 months.

iii) The mean PCB value of all control samples within the last 6 months is within ± 25% of the actual value with no more than 20% of individual values over the ± 25% limit.

2.5.4 Sample Preparation

The minimum sample size used for compliance testing must be able to achieve a detection limit that is not greater than 30% of the regulatory limits. Recommended sample sizes are provided in Table 3.

Before a sample is spiked with the surrogates, the anticipated PCB concentration should be assessed. For samples containing a high concentration of PCB, it may be practical to clean up and analyze only a portion of the sample extract. **Particular attention must be paid to ensure that the sample is homogeneous before a subsample is taken.** This can be achieved by vigorously grinding and mixing the sample to be analyzed. An aqueous sample, if possible, should not be divided into subsamples.

Sample Extraction. Through advancement of technology, new techniques using supercritical fluid extraction, microwave assisted processing, solid phase extraction, and accelerated solvent extraction, as well as others, exist. The use of alternative extraction methods is acceptable if it has been demonstrated their application will produce equivalent or better extraction efficiency and precision than the method presented herein.

The following extraction techniques have undergone rigorous testing and will produce data meeting the performance criteria set out in Subsection 2.5.3.

Each batch of up to 15 test samples must contain at least one method blank sample and one control sample. A method blank consisting of a clean matrix spiked with surrogates is processed with each batch of samples. The acceptance limit for PCB presence in the method blank sample is 25 ng per congener and up to 100 ng in total PCB. As a control sample, a certified reference material or fortified sample with a PCB concentration near the regulated limit, is processed with each batch of samples. The recovery of total PCBs in the control sample should be within 75 to 125% of the actual value.

Table 2 Recommended Constituents of Polychlorinated Biphenyl Surrogate Solution

Surrogate (in iso-octane)*	Congener No. (IUPAC)	Concentration (µg/mL)
$^{13}C_{12}$-Trichlorobiphenyl (2,4,4')	28	2.0
$^{13}C_{12}$-Tetrachlorobiphenyl (2,2'5,5')	52	2.0
$^{13}C_{12}$-Pentachlorobiphenyl (2,3',4,4',5)	118	2.0
$^{13}C_{12}$-Hexachlorobiphenyl (2,2',4,4',5,5')	153	2.0
$^{13}C_{12}$-Heptachlorobiphenyl (2,2',3,4,4',5,5')	180	2.0
$^{13}C_{12}$-Octachlorobiphenyl (2,2',3,3',4,4',5,5')	194	2.0
$^{13}C_{12}$-Nonachlorobiphenyl (2,2',3,3',4,5,5',6,6') or (2,2',3,3',4,4',5,5',6)	208 (or 206)	2.0
$^{13}C_{12}$-Decachlorobiphenyl (2,2',3,3',4,4',5,5',6,6')	209	2.0

*surrogates can be substituted with different isomers

Table 3 Suggested Sample Size and Achievable Sample Detection Limits (SDL)

Matrix	Suggested Sample Size	Achievable SDL*	
		per Congener Peak**	per Aroclor
Solid	2 g (or more)***	2.5 ng/g (or less)	50 ng/g (or less)
Aqueous	1 L	5 ng/L	100 ng/L
Oil	0.5 g	20 ng/g	400 ng/g
Ambient Air	500 m^3	0.01 ng/m^3	0.2 ng/m^3
Sampling Train	entire sample	5 ng/sample	100 ng/sample

* SDL values are based on assumption of low processing losses and final extracts (0.5 mL) that are free from interference

** congener of tri- through hepta-homologue; double the value for octa-, nona-, and deca-homologue

*** a subsample less than 2 g can be used if the size of particles in the sample is less than 250 μm

Solids. Solid samples may include filtered solids, sludges, soils, sediments, ashes, feed (solid waste), particulate on a filter and the Amberlite XAD of a sampling train. Various amounts of moisture may be contained in solid samples. Sample concentrations are normally reported on a dry weight basis.

Refer to Subsection 2.5.5 for samples containing a high level of PCBs.

Dry weight determination - A representative amount of sample (typically 5 g) is weighed in a tared weighing boat and placed in an oven at 100°C overnight. The sample is weighed until a constant weight is achieved.

The dry weight of the sample used is determined by:

$$M_{sd} = M_{sw} \cdot M_d / M_s$$

where:

M_{sd} = the dry weight of the sample used for analysis
M_{sw} = the wet weight of the sample used for analysis
M_d = the dry weight of the sample aliquot used in the determination (not to be used for analysis)
M_s = the wet weight of the sample aliquot used in the determination

Accurately weigh an appropriate amount of the finely-divided sample (use a mortar and pestle when necessary) into a beaker. **Spike the sample with a known amount of the PCB surrogate solution** (or 0.1 mL of the solution suggested in Table 2) **and allow to age for thirty minutes (minimum).** Polychlorinated biphenyls in solid samples are extracted with solvent using the Soxhlet extractors or the MAP™ for soil and sediment samples.

Soxhlet extraction - Insert a cellulose or glass fibre thimble into the Soxhlet body and blank the Soxhlet apparatus overnight with toluene. Discard the toluene along with three toluene rinses of the entire apparatus. Remove the pre-extracted thimble from the Soxhlet body and allow it to air dry in a beaker. Quantitatively transfer the sample into the thimble and cover the sample with a layer of glass wool. Place the thimble into the Soxhlet apparatus. Fill the bottom flask with 350 mL (or an appropriate amount) of toluene. The addition of 10% (v/v) polar solvent such as acetone is recommended for samples which have not been thoroughly dried. A Dean-Stark apparatus may be used as an alternative to a Soxhlet apparatus to remove moisture from a moist solid sample. Connect the apparatus to the water-cooled condenser and wrap the Soxhlet apparatus with aluminum foil as a heat insulator. Reflux the sample for 20 hours at a rate of three to four cycles each hour.

When the extraction is complete, rinse the inner surface of the condenser with toluene and allow the apparatus to cool. Siphon the solvent from the Soxhlet body into the extract flask. Rinse the Soxhlet apparatus three times with toluene, siphoning each rinse into the flask. Concentrate the toluene extract to a few millilitres by rotary evaporation. Change the solvent to cyclohexane by adding 100 mL of cyclohexane to the flask and concentrate to a few millilitres. This step will remove toluene before column cleanup.

Dry the sample by passing it through cyclohexane rinsed sodium sulphate and glass wool held in a powder funnel positioned over a 250 mL boiling flask. Complete the transfer by rinsing first the extraction flask, then the sodium sulphate, with three, 5-mL portions of cyclohexane. Concentrate the sample to a few millilitres. The sample is now ready for cleanup (Subsection 2.5.6).

Microwave extraction -This technique has been tested satisfactorily for soil and sediment samples. Studies are needed for the extraction of PCBs in other matrices. **Do not use this method for solids other than soil and sediment samples unless a proof of compatible extraction efficiency to the Soxhlet method has been established and documented.** Using microwave energy for sample extraction has the advantage of being faster and consuming less energy and solvents than the conventional Soxhlet method.

A laboratory microwave apparatus (MSE-1000, CEM Corporation) equipped with a temperature control device and safety features such as solvent vapour alarm, pressure-relief device, and protective shield is used. Because of the potential hazards using the elevated temperature and

Extraction of filtrate - Quantitatively transfer the filtrate from the flask to a clean separatory funnel using three rinses of deionized water. Add three, 50-mL rinses of dichloromethane to the retained empty sample container, shaking or swirling each rinse in the container before transferring to the separatory funnel. Extract the filtrate with these rinses by shaking the separatory funnel vigorously for two minutes, releasing pressure buildup as required. Allow the sample to stand for at least ten minutes to ensure separation of the aqueous and organic layers. Drain the organic layer through a powder funnel containing pre-rinsed sodium sulphate and glass wool, into a 500-mL round bottom flask. Persistent emulsions may be drained off into a clean, large beaker and broken using mechanical means, such as passage through loosely packed glass wool. Emulsions may also be broken under microwave energy for 20 seconds.

Repeat these extraction procedures two more times using 50 mL of dichloromethane each time. Rinse the separatory funnel with an additional 30 mL of dichloromethane. Complete the transfer by rinsing the sodium sulphate three times with several millilitres of dichloromethane. Concentrate the combined extracts and rinses to a few millilitres before combining with the extract from the particulate fraction of the sample. Change the solvent to cyclohexane by adding 100 mL of cyclohexane to the flask and concentrate to a few millilitres. The sample is now ready for cleanup.

Oils. An oil sample may consist of the oil from a transformer, capacitor, hydraulic device, or motor. The following extraction procedure should be used on any oil or sample extract containing more than 0.2% oil (2 mg/g) to facilitate analysis and quantification. A schematic summary of the extraction procedures is found in Figure 10. Following these procedures, adequate recovery of PCBs except for nona- and deca-homologues is anticipated. Since the total weight of nona- and deca chlorobiphenyls in Aroclors is less than 0.8%, the weak recovery of these congeners would not have a significant effect on the quantification of Aroclor in oil.

Weigh out exactly 0.50 g of oil into a 15-mL centrifuge tube using a disposable glass pipet. Add a known amount of surrogate solution to the sample then dilute with 5 mL of hexane. Using another clean pipet, quantitatively transfer the oil with several rinses of hexane into a 125-mL separatory funnel so that the final volume is approximately 20 mL.

If the sample has been diluted following the procedure for high level samples (Subsection 2.5.5), transfer exactly 0.5 mL of the diluted oil sample directly into a 125-mL separatory funnel, spike with the surrogate solution, and add hexane to a final volume of 20 mL.

Add 20 mL of concentrated sulphuric acid and shake vigorously for 2 minutes allowing any pressure buildup to be released. **Caution: An exothermic reaction may occur.**

Allow the mixture to settle for at least 15 minutes or until the two phases have completely separated before draining the acid layer into a waste container. Add 5 mL of deionized water and drain off the excess acid.

Add 75 mL of pre-extracted DMSO/water (Subsection 2.4.4) to the separatory funnel and vigorously shake for two minutes. Allow the phases to separate completely (for at least 10 minutes) before draining the DMSO/water into a 250 mL separatory funnel. Repeat this procedure twice with 50 mL of the DMSO/water solution each time. Care should be taken to ensure none of the hexane/oil fraction is transferred with the DMSO. Discard or archive the hexane/oil fraction.

Add 20 mL of hexane to the combined DMSO solution and vigorously shake for 1 minute to remove oil which may have been carried over. Allow the solution to stand for 10 minutes. Transfer the DMSO layer into a 1- or 2-L separatory funnel.

Extract the hexane twice with 30 mL of DMSO/water and then combine the DMSO extracts with the original extracts. Discard or archive the hexane layer.

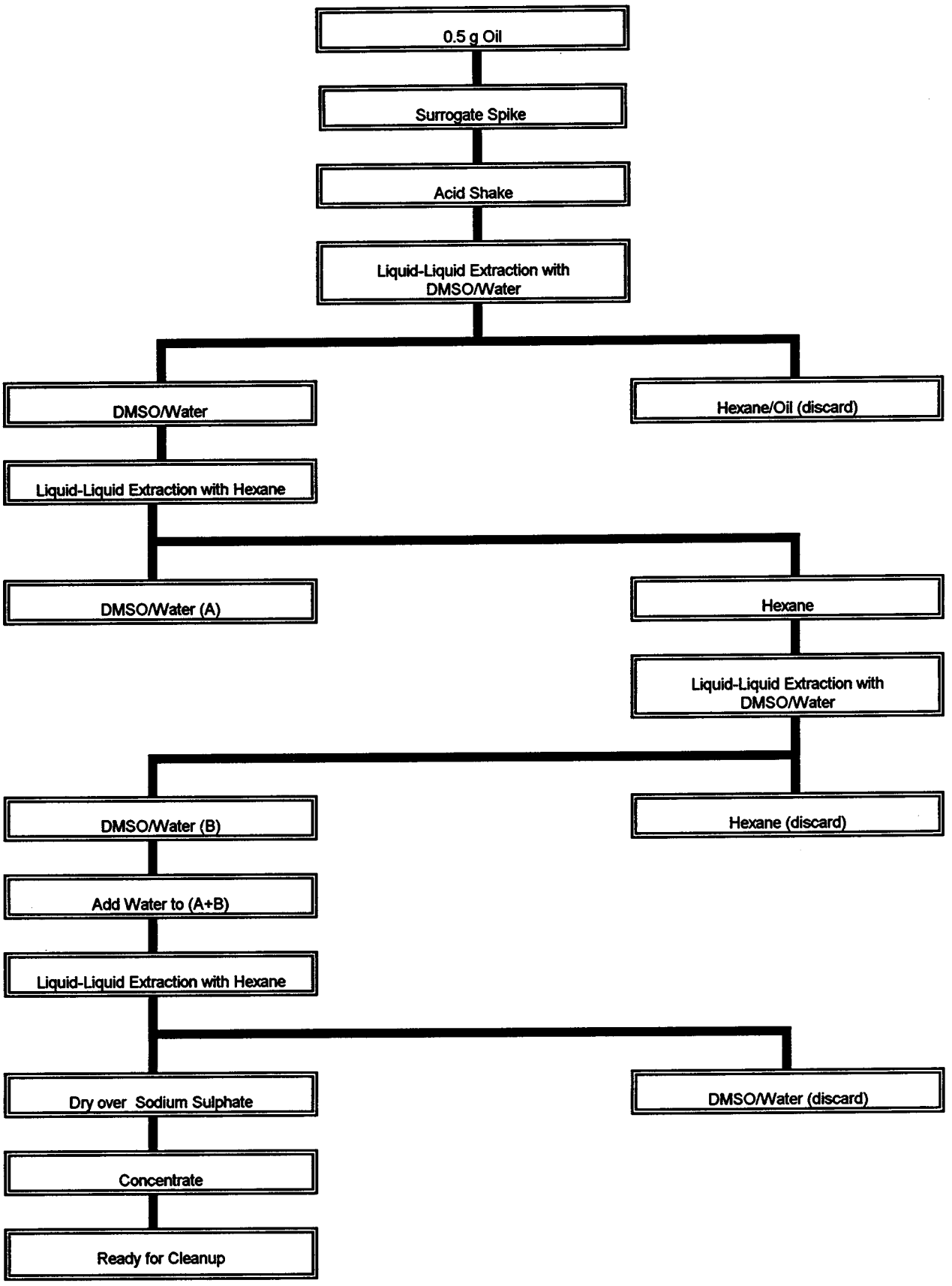


Figure 10 Extraction Schematic for Polychlorinated Biphenyl in Oil Matrices

pressure process, all safety precautions, especially solvent leakage and vessel pressure, should be observed at all times. Extraction should be stopped immediately if a spark inside a vessel is observed.

The model MSE-1000 is equipped with only one fibre-optic temperature probe that is inserted into one of the sample vessels. The temperature in this vessel is used as a reference for the control of microwave energy. Since the heating rate, the time required to reach 100°C, at a set microwave power depends on the matrix, size, and moisture content of the sample, **samples with different matrices, sizes, or moisture contents must not be extracted simultaneously.** A sample containing metals should not be extracted under microwave because it may cause a spark.

Quantitatively transfer the preweighed sample material into the Teflon® extraction vessel (120 mL). Add 20 mL or more of hexane/acetone mixture (1:1 ratio) to ensure all solid material is covered with solvent. Connect vessels with the control and monitoring device on the vessel carousel following the manufacturer's instructions. If more than one vessel is extracted simultaneously, these vessels are placed evenly in the carousel to ensure uniformity during extraction. Extract for 10 to 20 minutes at 100 °C using 500 watts or higher microwave energy. After extraction, remove the sample vessels from the microwave oven and cool to room temperature in a running water bath.

Construct a filtration apparatus by adding a few grams of the precleaned and oven-dried anhydrous sodium sulphate on a medium porosity filter paper inside a glass funnel. Wash the apparatus with 5 mL of hexane/acetone. Transfer the sample extract through the filtration apparatus into a round bottom flask. Wash the solid sample three times each with several millilitres of hexane/acetone and transfer these rinses into the apparatus. Add 1 mL of iso-octane to the sample extract as a keeper and concentrate the extract to a few millilitres. This sample extract is ready for cleanup.

Aqueous. Aqueous samples could consist of industrial effluents or runoffs, the condensate of a stack sampling train, and waters from rivers, lakes, or marine environments. **Any particulate in the aqueous sample is filtered out of the sample and extracted as a solid sample before being combined with the extract of the aqueous phase before cleanup**. Extraction procedures are shown in Figure 9.

Visually inspect each sample for the presence of organic phases. Any organic phase should be separated from the aqueous phase before extraction and recombined with the sample extract before cleanup.

For each batch of samples processed, prepare a fresh dilution of the PCB surrogate solution (Table 2) by adding 0.1 mL of the stock solution to 1.9 mL (1 × 20 dilution) of a polar solvent such as propanol for each sample being prepared.

Weigh out an appropriate size of sample to the nearest gram in a suitably sized beaker or bottle on a top-loading balance. **Taking a subsample from an aqueous sample containing particulate is not recommended. If a subsample must be taken, one must ensure that a representative sample is obtained.** Weight is converted to volume by assuming a sample density of 1.0 g/mL. Alternatively, the aqueous sample volume is measured by using a 1-L graduated cyclinder.

Spike the sample with 2.0 mL of the freshly diluted surrogate solution. Carefully shake the sample container several times or mix the solution with a magnetic stirrer to allow the surrogates to equilibrate within the raw sample matrix.

Extraction of suspended particulate - Suction filter the sample, if suspended particulate is present, through a pre-wet, glass fibre filter into an appropriately sized filtration flask. Complete the transfer with several portions of deionized water to remove any remaining particulate. Retain the sample container for later use. Continue suction until the flow of filtrate stops completely. Transfer the filter and any particulate still adhering to the walls of the Buchner funnel to a Petri dish and allow the solids to dry in a desiccator or air dry in a clean environment. This solid fraction is extracted using the Soxhlet apparatus or MAP™.

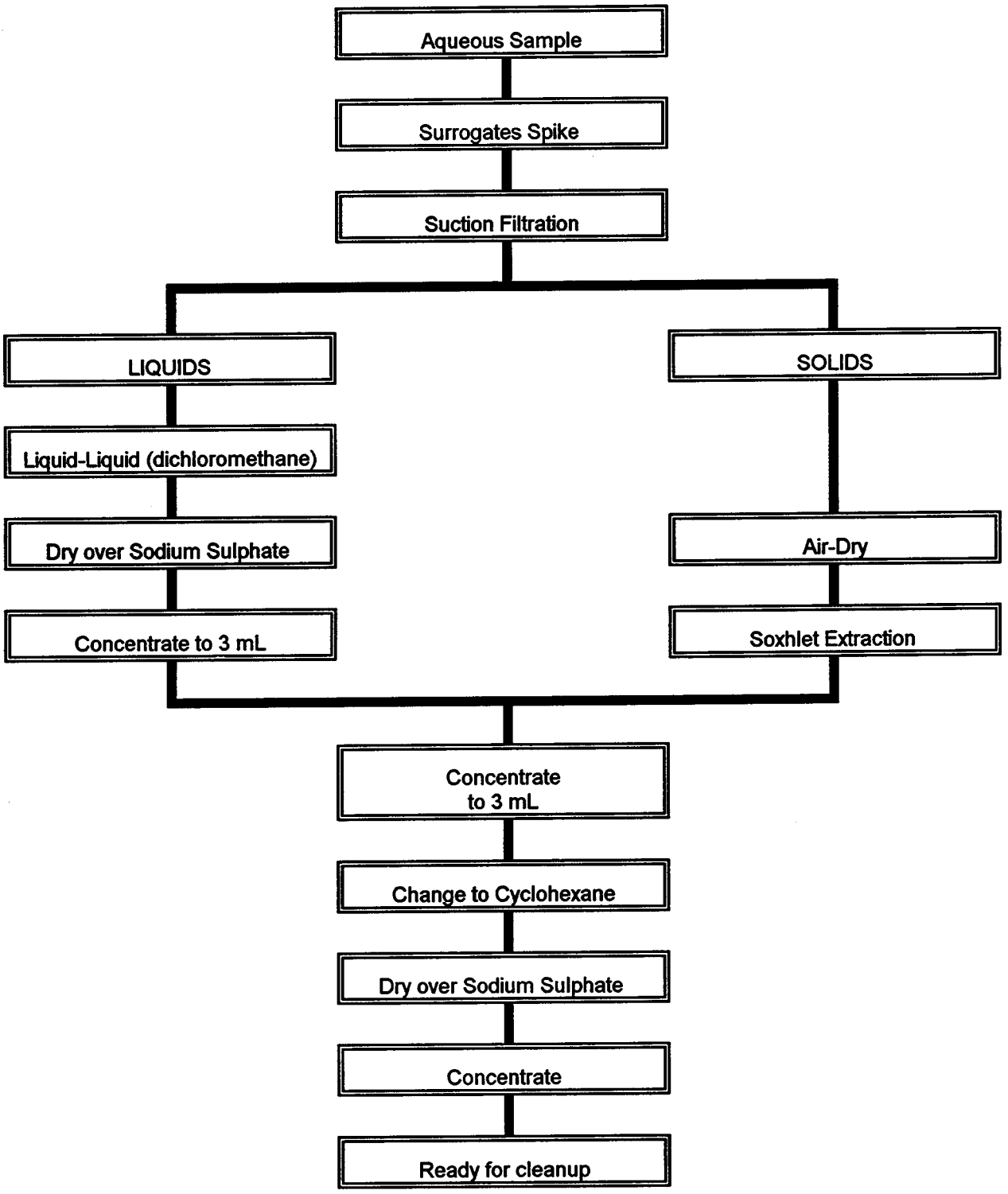


Figure 9 **Extraction Schematic for Polychlorinated Biphenyl in Aqueous Samples - Confirmative Analysis**

Add 750 mL of deionized water to the DMSO and extract three times with 100, 50, 50 mL of hexane as previously described. Dry the hexane fraction by passing through a powder funnel containing pre- rinsed sodium sulphate. Collect the sample in a 500 mL flask. Complete the transfer by rinsing first the extraction funnel, then the sodium sulphate, with three 5-mL portions of hexane. Concentrate the sample to several millilitres. The sample is now ready for cleanup (Subsection 2.5.6)

2.5.5 High-level Samples

Solids. High concentrations of PCBs (greater than 500 ppm) can be found in solid samples such as contaminated soils and waste feed from a PCB-treatment or destruction systems. It may not be practical to spike such high PCB samples with the PCB surrogates since a large ratio of dilution is required to bring the PCB concentration into the linear calibration range for GC-MS quantification. Instead the following procedures should be used for these types of samples.

Weigh out an appropriate amount of the sample and perform extraction for solids as previously described. Concentrate or dilute the sample extract to a known volume before determining the approximate concentration using GC-ECD.

Serially dilute the sample extract to bring the concentration of PCBs into the linear range of the GC-MS and pipette out the diluted extract. Add an appropriate amount of the surrogate solution containing 200 ng of each surrogate to the diluted extract. The sample is now ready for further cleanup [include the procedures in Subsection 2.5.6 (Acid/Base/Silver Nitrate/Silica Column) as a minimum].

Oil. Waste oils from electrical capacitors and transformers may contain high concentrations of PCBs which require dilution to bring the concentration into the linear calibration range. The following procedure is recommended for the analysis of these samples.

Determine the approximate concentration of PCB in the oil by analyzing a diluted oil sample using GC-ECD.

Weigh 0.50 g of the oil into an appropriately sized volumetric flask and perform an accurate serial dilution with hexane to bring the concentration of PCBs into the linear range of the GC-MS.

Pipette out 0.5 mL of the diluted oil and spike this aliquot with a solution containing 200 ng of each of the surrogates. Samples which have been diluted by less than a factor of 500 will require an extraction to remove the oil matrix which will interfere with the GC-MS analysis (Subsection 2.5.4; Oils). As a minimum, the sample cleanup should include passage through a multi-layered silica column (Subsection 2.5.6).

2.5.6 Sample Cleanup

The application of cleanup methods depends on the concentration of PCBs and the level of interferences present in the sample extract. A sample containing little or no interferences, therefore, may require little or no cleanup, whereas a sample containing a high level of background interferences may require adherence to most of the following cleanup procedures. Just before GC/MS analysis each sample is made up to the final volume after the addition of a known concentration of the recovery standard(s). This serves as a retention time reference for labelled surrogates and as the basis for the calculation of surrogate recoveries.

The basic cleanup procedures recommended for sample extracts are shown in Figure 11. Cleanup columns required in this method are shown in Figure 12.

Acid/Base/Silver Nitrate /Silica Column

Plug the tip of the column with glass wool and add the following in the order specified:

1.5 g of 10% silver nitrate/silica (bottom layer);
1 g of silica ;
2 g of the 33% 1 *M* sodium hydroxide/silica;
1 g of silica;
4 g of 44% sulphuric acid/silica;
2 g of silica; and
approximately 1 g of sodium sulphate to top off the column.

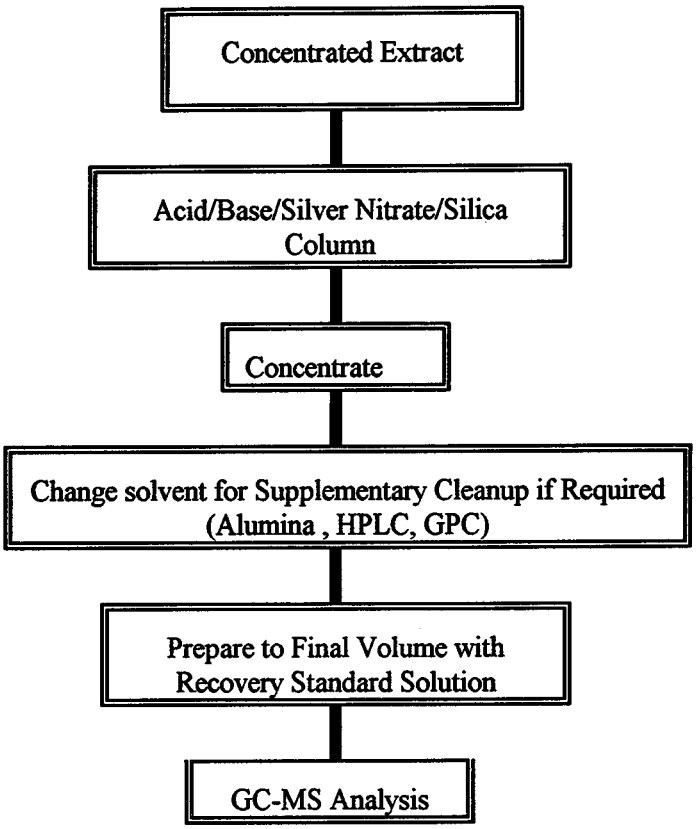


Figure 11 Cleanup and Analysis Schematic for Polychlorinated Biphenyls

After each reagent has been added, gently tap the column to ensure even layering.

Pre-wash the prepared column with 30 mL of 3% dichloromethane in hexane (v/v). Just as the solvent reaches the top of the sodium sulphate layer, place a 250-mL boiling flask under the column. Using a Pasteur pipet, transfer the concentrated raw extract onto the column, followed by three 5-mL rinsings of the sample flask, using the same pipet each time.

When the third rinse has drained to the top of the sodium sulphate layer, pour an additional 50 mL of 3% dichloromethane in hexane (v/v) into the column. When the solvent has drained, assess the column for saturation of the acid/silica layer and the silver nitrate/silica layer. This is indicated by an appearance of colour throughout the reagent layer.

Saturation of the acid/silica layer suggests that the sample extract (in hexane) should be washed with concentrated sulphuric acid in a separatory funnel, repeating the washes (maximum of four washings) with fresh acid until no colour is observed in the acid layer. Wash the extract sequentially with deionized water, 1 *M* sodium hydroxide and a final wash with deionized water. Dry the extract by passing it through sodium sulphate, as previously described.

Saturation of the silver nitrate/silica layer requires passage of the concentrated sample extract through an additional column containing 2.5 g of 10% silver nitrate/silica to remove sulphur-containing compounds which may interfere in the analysis. Elute the sample extract through the pre-washed column with 30 mL of 3% dichloromethane in hexane. Pretreated copper may be used to remove sulphur as an alternative.

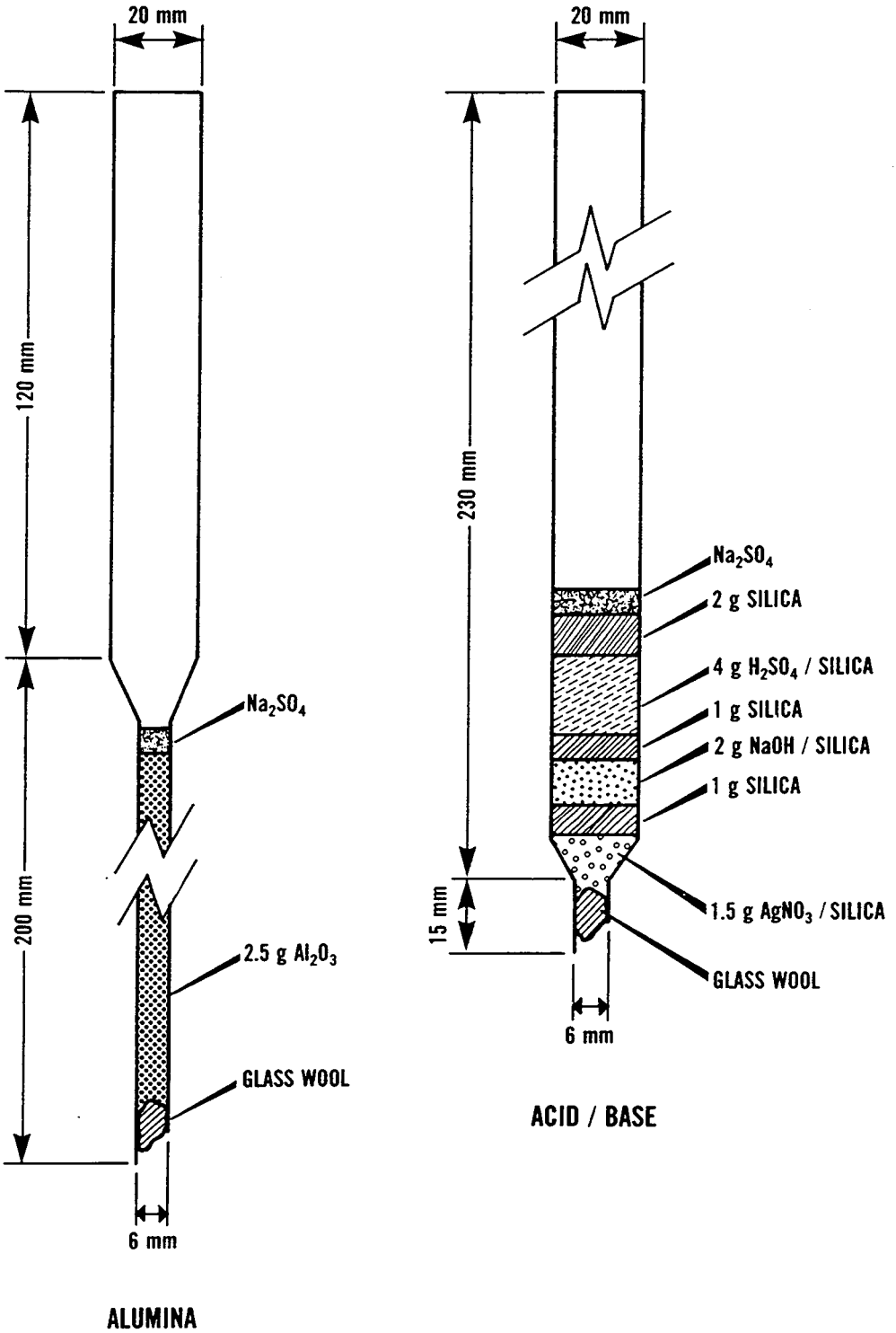


Figure 12 Cleanup Columns

It is recommended that the extract from an oil-containing sample be screened using GC/FID before the addition of the recovery standards to determine if further cleanup is necessary.

Concentrate the final column extract to a few millilitres. Change the solvent to hexane for samples which require an alumina column cleanup . Samples for HPLC and GPC cleanup are changed to dichloromethane.

Samples which are ready for analysis are transferred to a pre-calibrated centrifuge tube containing 0.5 mL of iso-octane and concentrated to approximately 0.4 mL before the addition of a known amount (200 ng) of the recovery standard. The sample is then made up to 0.5 mL and transferred to a 1.5 mL amber vial with a Teflon®-lined lid and stored refrigerated until analysis.

Copper Cleanup

Some oils and sediment extracts may contain high levels of elemental sulphur which will cause significant interference on the electron capture detection. Add approximately 0.5 g of freshly treated copper to a 5-mL aliquot of the sample extract in a small Erlenmeyer flask. Swirl the flask and allow the extract to stand for approximately 10 minutes. Add another 0.5 g of copper and repeat until no further reactions (copper turns black) are observed. Quantitatively transfer the extract through a filter paper or glass wool to remove the copper then concentrate to a small volume before the addition of the internal standard. Make the extract to a known volume and store below 10°C until analysis.

Alumina Column Chromatography

Plug the tip of the alumina column with glass wool and add 2.5 g of freshly prepared basic alumina (Subsection 2.4.4). Top off the column with 0.5 cm of sodium sulphate. Add 15 mL of hexane to pre-wash the column. When the hexane has drained just to the top of the sodium sulphate layer, immediately place a 250-mL boiling flask under the column tip.

Using a Pasteur pipet, transfer the concentrated extract from the acid/base/silver nitrate/silica column onto the alumina column, followed, just as the sample extract reaches the sodium sulphate layer, by three, 5-mL hexane rinsings of the sample flask. Add an additional 30 mL of hexane (2 × 15 mL) to the column just as the flask rinsings reach the top of the sodium sulphate layer. When this solvent has drained to the top of the sodium sulphate layer, add 20 mL of freshly prepared 5% dichloromethane in hexane to the column. This combined fraction contains the PCB.

Concentrate the eluent to a few millilitres. Transfer the extract to a pre-calibrated centrifuge tube containing 0.5 mL of iso-octane with three, 0.5-mL hexane rinses and concentrate to 0.5 mL under a gentle stream of nitrogen for further cleanup or with the recovery standard added for analysis as previously described.

Cleanup Using High Performance Liquid Chromatography (HPLC)

When the sample extract contains excessive amounts of oil (> 0.2%), determined by GC/FID, the following procedures may be used after the Acid/Base column cleanup to further reduce the oil residue. This procedure could also be used on an oil sample containing a high concentration of PCB. The oil sample should be diluted by a factor of 100 or more. An aliquot of the diluted sample is spiked with surrogates and subjected to a silica column cleanup as previously described.

The equipment and parameters which are suitable for the HPLC cleanup of PCB samples are:

- **HPLC...** Hewlett Packard Model 1090 or equivalent
- **Injector...** Rheodyne Model 7125 with 100 μL sample loop and 6 port valve or equivalent
- **Detector...** UV detector monitoring at 254 nm
- **Syringe...** 100 μL gas tight with a 5-cm, square end, 22 gauge needle
- **Column...** Waters, Energy Analysis - NH_2 Preparative Column (7.8 mm ID, 30 cm long) with in-line precolumn filter (APS-Hypersil-NH_2 , 5 μm, 20 × 21mm)
- **Flow rate...** 1.0 mL/minute
- **Solvent...** hexane/dichloromethane 9:1 (v/v)
- **Pressure...** 3500 kPa
- **Injection Volume...** 100 μL
- **Collection Window...** 12.75 to 18.00 minutes

Sparge the solvent with helium at a rate of 10 mL/min for 15 minutes before commencing flow to the column. Allow the column to equilibriate at a flow rate of 1 mL/min for 30 minutes before introduction of the sample.

The retention time window of PCBs, adequate separation of PCBs from oil, and acceptable recovery of PCBs using this cleanup technique should be confirmed before any sample is processed.

A control sample containing a known amount of PCB spiked with the surrogates, should be run daily to confirm the collection window and to assess recovery.

Inject 0.1 mL of the sample containing not more than 1 mg of oil into the sample loop and collect three fractions as follows:

Fraction 1: 0 to 12.75 min (archive)
Fraction 2: 12.75 to 18.00 min (for analysis)
Fraction 3: 18.00 to 25 min. (archive)

Fraction 2 is collected in a 2.0 mL chromatography sample tube precalibrated to 0.2 mL with iso-octane.

Concentrate the sample extract to just under 0.2 mL with a gentle stream of nitrogen, periodically rotating the sample to rinse the walls of the tube.

Add the recovery standard and make the sample up to exactly 0.2 mL with iso-octane.

Transfer the extract to a 1.5 mL amber vial or an autosampler vial with a Teflon®-lined cap for GC-MS analysis.

Cleanup Using Gel Permeation Chromatography (GPC)

Gel permeation chromatography may be used as an alternative technique to HPLC to separate the PCBs from an excess of oil (> 0.2%) remaining in the sample extract. As in the case of the HPLC cleanup, this technique could also be used to prepare an oil sample for analysis. The oil sample should be diluted by at least a factor of 100, spiked with surrogates and subjected to the silica column cleanup before injection.

The method allows for many different types of GPC including standard S-X3 chromatography, automated S-X3 chromatography and HPLC/GPC chromatography providing that the performance criteria set out in Subsection 2.5.3 (Performance Validation) are met.

The following equipment is used for this cleanup procedure:

- **Pump...** capable of constant flow from 0.1 to 7.0 mL/min at no more than 689 kPa (100 psi)
- **Injector...** 5.0 mL sample loop
- **Syringe...** 10 mL with luerlok fitting
- **Chromatographic Column...** 600 to 700 mm × 25 mm ID glass column with associated endcaps and fittings for upward flow

GPC Column Preparation: Prepare the column by swelling approximately 70 g of the resin overnight in dichloromethane. Build the column by gently pouring small amounts of the slurry into the column. To ensure a uniform packing, vibrate the column using a small handheld vibrator as the slurry is settling.

The solvent (dichloromethane) is purged with UHP Helium for at least 15 min at 100 mL/min before eluting the column. Sparge rate is then reduced to 30 mL/min.

Once the column is built, elute the solvent through at a flow rate of 1 to 2 mL/min for several hours to eliminate any air. Periodically tighten the column to eliminate solvent pockets.

Increase the flow to 7 mL/min and adjust the pressure of the column to 3 kg/cm^2 (300 kPa).

The column must be calibrated to determine adequate separation of the oil from the PCB, the retention time of the analyte, and the anticipated recovery of the PCB before any samples are applied.

GPC Column Calibration: Calibration of the column is facilitated with the use of a UV detector monitoring the column eluent at a wavelength of 254 nm. To do this, prepare a standard containing 20 μg of Aroclor 1242/1254/1260 at a 1:1:1 ratio in dichloromethane. Transfer 0.5 mL into a 1.5 mL vial. Draw the standard and four, 1-mL dichloromethane rinses of the vial, into the 5 mL sample loop and inject onto the column. Monitoring the eluent at 254 nm will define the PCB elution window. Collect the PCB fraction and concentrate to a final volume of 0.5 mL after adding the internal standards. Quantify the recovery of PCBs using GC-ECD. A calibration standard containing the internal standards, and 20 ppm of the Aroclor mixture should be used to quantify the results.

Calibration is also possible using gravimetric means coupled with GC-ECD/FID analysis of the eluent. To do this, prepare a standard containing 0.25 g of blank matrix oil [available from the National Institute of Standards and Technology (NIST)] spiked with 20 μg of Aroclor 1242/1254/1260 at a 1:1:1 ratio in dichloromethane. Make up to 0.5 mL with dichloromethane in a 1.5 mL vial. Draw the sample and four, 1- mL dichloromethane rinses of the vial, into the 5 mL sample loop and inject onto the column.

The eluent is collected from 10 to 30 minutes at 2 minute intervals and each fraction is evaporated to dryness. The elution profile of the oil is determined gravimetrically. An oil of similiar matrix as the sample should be used, if possible, as different oils will elute during different time intervals.

The PCB elution profile is determined by collecting the eluent from 20 to 35 minutes at one minute intervals. Each fraction is concentrated to 0.5 mL and analyzed using GC-ECD to determine the elution profile and GC/FID to determine the amount of oil in each fraction. The optimum PCB collection window should have the highest recovery of PCBs with the least amount of oil.

GPC Column Cleanup: Void the sample loop of all solvent. Draw the sample containing not more than 5 mg of oil in 0.5 mL of dichloromethane into the sample loop with four, 1-mL dichloromethane rinses of the vial to complete the transfer via a gastight syringe. A prefilter in the sample loading line will eliminate particulate in the sample from damaging the valves or the column.

Ensure that the sample is drawn through the loop by monitoring a small air pocket. Minimize the amount of air entering the loop to maintain the integrity of the column.

Inject the sample onto the column and collect the predetermined PCB fraction into a 125-mL flask. The fractions collected before and after the PCB fraction could be archived until analysis is complete.

Concentrate the sample extract to a few millilitres by rotary evaporation at 30°C before transferring to a centrifuge tube precalibrated to 500 μL. Complete the transfer, concentrate the sample to 0.5 mL containing the recovery standard, and store in a 1.5 mL vial until analysis, as previously described.

Flush the sample loading line and the sample loop several times with fresh solvent before loading another sample to eliminate any carry over.

A control sample consisting of a known concentration of analyte(s) and surrogates should be injected into the system each day of sample processing to monitor the recovery and the retention time window.

2.6 Gas Chromatography - Mass Spectrometry Analysis

2.6.1 Instrumentation

Requirements for the gas chromatograph (GC) are: it exhibits isothermal temperature stability of ± 0.2°C or better over its specified range of operation; it has the ability to accommodate a minimum of three temperature ramps; and it is configured for use with a capillary column. The capillary column is directly coupled to a low-resolution mass spectrometer (MS). The MS is operator-programmed for time-sequenced acquisition of selected MS data for PCB homologues. The MS is operated in the electron impact (EI) and selected ion monitoring (SIM) modes.

2.6.2 *Gas Chromatograph (GC) Parameters*

To achieve acceptable gas chromatographic separation on a 30-m, DB-5 (5% phenylsubstituted methyl polysiloxane) or equivalent column, the following set of parameters may be used as a starting point.

Injector temperature: 300°C for split-splitless or ambient temperature for on-column injection; Interface temperature: 290°C; Temperature program:

1) initial temperature of 100°C for split-splitless or 90°C for on-column and hold for 2 minutes;

2) 15°C/min to 180°C;

3) 3°C/min to 240°C;

4) 10°C/min to 285°C; and

5) hold at 285°C for 10 minutes.

Optimum settings for GC parameters and appropriate retention time windows for time-sequenced SIM mode analysis on a capillary column are established from the analysis of the Window Defining Mixture containing the first and the last eluting congeners within each homologue of analytes. Polychlorinated biphenyl congeners can overlap up to three levels of chlorine substitution (e.g., 3Cl/4Cl/5Cl, 4Cl/5Cl/6Cl... etc.) within a homologue window on a DB-5 column. The overlapped retention time windows for PCB congener groups are illustrated in Table 4.

Other well-documented and commercially available GC columns (not described in this method), may also be used if the user can demonstrate that adequate retention time windows for PCBs are established.

2.6.3 *Mass Spectrometer (MS) Parameters*

The mass spectrometer is operated under electron impact (EI) and selected ion monitoring (SIM) modes with a dwell time of 50 to 100 ms/ion. Perfluorotributylamine (PFTBA), introduced into the MS ion source, is used to calibrate the mass scale of the MS system. Periodically, following major upsets such as power failures or ion source servicing, ion source parameters should be tuned to achieve a PFTBA spectrum consistent with optimal sensitivity, peak shape, and mass resolution requirements throughout the mass range of interest.

A known volume (typically 1 to 2 μL) of PCB calibration standard PCS-3 (Table 5) is injected into the GC-MS system. **The isotope abundance ratio for every native analyte must agree with the corresponding theoretical ratio within the control limits given in Table 6. If any ratio is outside its control limits, a problem clearly exists which must be identified and corrected before proceeding further. Calibration standard PCS-1 is used to assess instrumental detection limits. Injection of 20 pg of any individual congener of tri through hepta-chlorobiphenyls must result in a peak response which is at least three times the background noise level (i.e., S/N ≥ 3) for each of the two monitored quantification ions. If these levels cannot be detected, then instrument parameters are to be adjusted accordingly.**

Because of the overlapping elution of homologues, total PCBs can be monitored with four acquisition windows as defined in Table 7. With this setting, the number of characteristic ions required for each acquisition window varies from 8 to 14 depending on the number of overlapping homologues.

Under the electron impact ionization mode, the loss of the two chlorine (M-70) cluster is normally in the range of 50 to 100% of the parent ion cluster. Some congeners may have cluster ions of one chlorine loss (M-35) at low intensity. These daughter ions (M +1-35)may cause interferences when homologues overlap. Thus, the presence or absence of the confirmation ions specified in Table 6 should always be verified as part of the quantification process. Relative intensities of molecular and fragmentation ions are shown in Table B1 (Appendix B).

Table 4 Elution Order of Polychlorinated Biphenyl Window-defining Mixture on a 30-m, DB-5 Column

PCB Homologue	First Eluting Isomer (IUPAC No.)	Last Eluting Isomer (IUPAC No.)	Retention Time Window[a] (min)
Trichloro	19/30 [b]	37	11.0 to 15.5
Tetrachloro	54	77	13.0 to 20.0
Pentachloro	104	126	15.0 to 24.0
Hexachloro	155	169	17.5 to 29.0
Heptachloro	188	189	22.0 to 30.0
Octachloro	202	194/205 [c]	26.0 to 32.0
Nonachloro	208	206	30.0 to 33.0
Decachloro	209	209	35.0

[a]Based on the temperature program given in Subsection 2.6.2 and the GC column with 0.25 mm ID and 0.25 μm film; [b] first and second closely eluted isomers; [c] second to last and the last closely eluted isomers

2.6.4 Criteria for Analyte Identification

Sample components are identified as PCBs if their GC-MS data satisfy the following criteria:

- **peak response for each of the two selected molecular cluster ions must be at least three times the background noise level (i.e., S/N ≥ 3);**
- **the abundance ratio of the two major characteristic ions must be within ± 20% of the theoretical value or the value established using calibration standards;**
- **ion of 2 Cl loss (M-2Cl) must be confirmed when concentration is sufficient for detection;**
- **the absence of responses for M+2Cl (molecular plus two chlorine) ions must be confirmed for tri- through hepta-chlorobiphenyl;**
- **the peak maxima for the specified characteristic ions must be coincident within 2 scan units (3 seconds maximum); and**
- **identified compounds within each homologous group must fall within their pre-defined retention time windows as established by the analysis of the Window-defining Standard.**

2.6.5 Quantification

Quantification is based on the use of Relative Response Factors (RRFs) established from calibration runs. For native standards, the RRF is the ratio of analyte response factor to the response factor of the corresponding labelled surrogate. These RRFs remain unchanged over the range of concentration for which MS response is linear.

Using these RRFs, along with native and surrogate responses from the sample run, recovery-corrected concentrations of PCBs are calculated directly. Surrogate recoveries are calculated using the recovery standards that are added to the sample extract before GC-MS analysis. These surrogate recoveries reflect the overall quality of the data being reported.

A total of 20 PCB congeners (three congeners for each of the tri- through octa-homologues and one for nona- and deca-chlorobiphenyl) representing some of the major compounds in Aroclors, are selected as calibration standards. Since isomer-specific analysis is not required, the average response of the three congeners

Table 5 Constituents of Polychlorinated Biphenyl Calibration Standards

PCB Congener (IUPAC No.)	Homologue	ng/mL (in iso-octane)				
		PCS-1[a]	PCS-2	PCS-3[b]	PCS-4	PCS-5
PCB-18	Tri	20	50	200	800	2000
PCB-28	Tri	20	50	200	800	2000
PCB-33	Tri	20	50	200	800	2000
PCB-52	Tetra	20	50	200	800	2000
PCB-44	Tetra	20	50	200	800	2000
PCB-70	Tetra	20	50	200	800	2000
PCB-101	Penta	20	50	200	800	2000
PCB-118	Penta	20	50	200	800	2000
PCB-105	Penta	20	50	200	800	2000
PCB-153	Hexa	20	50	200	800	2000
PCB-138	Hexa	20	50	200	800	2000
PCB-128	Hexa	20	50	200	800	2000
PCB-187	Hepta	20	50	200	800	2000
PCB-180	Hepta	20	50	200	800	2000
PCB-170	Hepta	20	50	200	800	2000
PCB-199	Octa	20	50	200	800	2000
PCB-195	Octa	20	50	200	800	2000
PCB-194	Octa	20	50	200	800	2000
PCB-206	Nona	20	50	200	800	2000
PCB-209	Deca	20	50	200	800	2000
$^{13}C_{12}$-Surrogate (IUPAC No.)						
PCB-28	Tri	400	400	400	400	400
PCB-52	Tetra	400	400	400	400	400
PCB-118	Penta	400	400	400	400	400
PCB-153	Hexa	400	400	400	400	400
PCB-180	Hepta	400	400	400	400	400
PCB-194	Octa	400	400	400	400	400
PCB-208 (or 206)	Nona	400	400	400	400	400
PCB-209	Deca	400	400	400	400	400
$^{13}C_{12}$-Recovery Standard						
PCB-101[c]	Penta	400	400	400	400	400
PCB-202[d]	Octa	400	400	400	400	400

[a] used to assess detection limits; [b] used to verify calibration and abundance ratios; [c] retention time marker and recovery standard for tri- to hexa-homologue; [d] retention time marker and recovery standard for hepta- to deca-homologue

Table 6 Selected Ion Masses for Polychlorinated Biphenyl Analysis

Homologue	No. of Isomers	Quantification Ions		Control Limits for Isotope Ratio[a]	Confirmation Ions
		Mass (m/z)	Ion Type		Mass (m/z)
T_3CB	24	256/258	M/M+2	1.03 ± 20%	188(186) 326[b]
T_4CB	42	290/292	M/M+2	0.78 ± 20%	222(220) 360[b], 326[c]
P_5CB	46	324/326 (326/328)	M/M+2 (M+2/M+4)	0.62 ± 20% (1.55 ± 20%)	256 396[b], 360[c]
H_6CB	42	358/360 (360/362)	M/M+2 (M+2/M+4)	0.52 ± 20% (1.24 ± 20%)	290 430[b], 394[c]
H_7CB	24	394/396	M+2/M+4	1.04 ± 20%	324 464[b], 430[c]
O_8CB	12	428/430	M+2/M+4	0.89 ± 20%	358, 464[c]
N_9CB	3	462/464	M+2/M+4	0.78 ± 20%	394
$D_{10}CB$	1	498/500	M+4/M+6	1.17 ± 20%	428
$^{13}C_{12}$-T_3CB		270(268)	M+2 (M)		
$^{13}C_{12}$-T_4CB		304(302)	M+2 (M)		
$^{13}C_{12}$-P_5CB		338(336)	M+2 (M)		
$^{13}C_{12}$-H_6CB		372(374)	M+2 (M+4)		
$^{13}C_{12}$-H_7CB		406(408)	M+2 (M+4)		
$^{13}C_{12}$-O_8CB		442(440)	M+4 (M+2)		
$^{13}C_{12}$-N_9CB		476(474)	M+4 (M+2)		
$^{13}C_{12}$-$D_{10}CB$		510(512)	M+4 (M+6)		

ion mass in bracket is optional; [a] based on theoretical values; [b] response of this ion (M+2CL) must be absent; [c] response of this ion (M+CL) signifies a possibility of coelution of congeners from two neighbouring homologues (M and M+CL)

Table 7 Acquisition Windows for Polychlorinated Biphenyl Analysis

Homologue	Minimum Number of Ions Monitored	Retention Time Windows (min)*	Homologue Absent
tri, tetra	8	10 to 14	penta to deca
tri, tetra, penta, and hexa	13	14 to 21	hepta to deca
penta, hexa, hepta, and octa	14	21 to 30	tri, tetra, nona, and deca
octa, nona, and deca	10	30 to 37	tri to hepta

* based on the temperature program given in Subsection 2.6.2

within a homologue is used to quantify all congeners within that homologue. Calibration standards must consist of the 20 PCB congeners specified in Table 5. $^{13}C_{12}$-labelled surrogates and recovery standards, however, can be substituted with different isomers.

Relative response factors for the native standard (RRF_n) and for the surrogate standard (RRF_r) are calculated using the following equations.

$$RRF_n = \frac{A_n \cdot C_s}{A_s \cdot C_n}$$

and

$$RRF_r = \frac{A_s \cdot C_r}{A_r \cdot C_s}$$

where:

RRF_n = relative response factor, native standard to surrogate standard

RRF_r = relative response factor, surrogate standard to recovery standard

A_n = quantification ion (single or both ions) peak area for native standard

A_s = quantification ion peak area for the appropriate surrogate standard

A_r = quantification ion peak area for the recovery standard ($^{13}C_{12}$-PCB-101 or $^{13}C_{12}$-PCB-202)

C_n = concentration of the native standard (pg/μL)

C_s = concentration of the appropriate surrogate standard (pg/μL)

C_r = concentration of the recovery standard ($^{13}C_{12}$-PCB-101 or $^{13}C_{12}$-PCB-202)

Using the RRFs, PCB concentrations (C) and surrogate standard recoveries (%R) can be calculated as:

$$C(X) = \frac{(\sum_{k=1}^{m} A_k) \cdot Q_s}{A_s' \cdot RRF_n \cdot S}$$

and

$$\%R(X) = \frac{A_s' \cdot Q_r \cdot 100}{A_r' \cdot Q_s \cdot RRF}$$

where:

$C(X)$ = recovery-corrected concentration of homologue X

A_k = quantification ion (single or both ions) peak area for the "k"th homologous isomer ("m" is the number of isomer peaks detected)

Q_s = amount of surrogate standard for homologue X added to the sample

A_s' = quantification ion peak area of surrogate standard for homologue X in sample extract

S = sample size (i.e., g or L, dependent on sample type)

$\%R(X)$ = percent recovery of surrogate standard for homologue X

Q_r = amount of the recovery standard in sample extract

A_r' = quantification ion peak area for the recovery standard in sample extract.

For homologues represented by more than one isomer in the calibration standard solution, the "homologue-average" RRF is used to quantify all isomers in the same homologue.

The calibration data from which RRFs are calculated must be of good and definable quality. For initial calibration, RRFs are calculated by analyzing at least four levels of calibration standard solutions bracketing the regulatory limit (the suggested concentrations are given in Table 5). **The Relative Standard Deviation (RSD) of the four to five RRFs must be less than 20% for all native analytes. This value effectively corresponds to the response linearity criterion. If this criterion is met, then the calibration is successful, and the mean RRF values are used for quantification of subsequent target analyte data. The established calibration curve must be verified by analyzing the calibration verification standard, with a midpoint concentration such as PCS-3, at least once during every 12-hour period in which sample analysis occurs. The calculated PCB concentrations of the verification run must be within 20% of their design values. The surrogate recovery must be within the range of 75 to 125%.**

Although the 20 PCB congeners specified in Table 5 must be used as calibration standards, the calibration range and concentrations can be altered as needed. The calibration range, however, must bracket the regulated limit. Surrogates and recovery standards specified in Table 5 can be replaced with other $^{13}C_{12}$-labelled PCB isomers. A minimum of one surrogate for each PCB homologue is required. The concentration of surrogates and recovery standards in the calibration solutions should not be less than 200 ng/mL.

Although a minimum of one recovery standard is required, the use of two recovery standards, one for tri- through hepta-homologue and one for octa- through deca-homologue is recommended.

The ion abundance could vary significantly among isomers within a homologue. To illustrate the degree of variation in response, RRFs of 53 congeners to the $^{13}C_{12}$-PCB-101 are tabulated in Table B2 (Appendix B). Although some of the isomers' RRFs are significantly different from the mean, the homologue average RRFs for PCS-3 agree very well with the average value for the reference material CLB-1. Aroclor standards have been quantified using procedures described herein. Calculated concentrations and their weight

distribution among homologues for Aroclor 1242, 1254, 1260 and mixture 1254/1260 are presented in Table B3. Results show that the quantified values are approximately 66, 84, 87, and 89% of the design values for Aroclor 1242, 1254, 1260, and mixture 1254/1260 respectively. This discrepancy is partly a result of many minor PCB congeners of an Aroclor being too small to be quantified. For Aroclor 1242, mono- and di-chlorobiphenyls accounting for 15% of total PCBs are excluded from quantification resulting in a greater difference in concentration.

2.6.6 Detection Limit

The sample detection limit (SDL) is defined as the minimum concentration of analyte in the sample that will produce clearly defined peaks with an acceptable chlorine isotope ratio, and with a signal-to-noise ratio equal to three. Variables, such as sample matrix, sample size, final extract volume, injection volume used in analysis, surrogate recovery, GC column performance, chromatographic parameters, electronic noise, and instrument sensitivity may directly influence the SDL. **Reported SDL must be corrected for surrogate recovery and is calculated as:**

$$SDL = \frac{3 \cdot N \cdot Q_s}{H \cdot RRF_n \cdot S}$$

where:

N = estimated sum of electronic and chemical (matrix) noise expressed as peak height (single or both ions)

H = peak height of the surrogate standard peak

Q_s = amount of surrogate standard added

RRF_n = relative response factor, as defined in the preceding subsection

S = sample size

The noise for each homologue group must be determined electronically or manually from the actual sample chromatograms. If a quantification ion channel contains one or more large peaks that prevent observation of the noise, a portion of the chromatogram should be re-scaled so that the noise level can be assessed. The requirement of instrumental detection limit is given in Subsection 2.6.3.

Based on these procedures, assuming adequate surrogate recoveries, achievable SDL for various matrices are listed in Table 3. **The SDL calculated using the previous equation must be reported when a target analyte (PCB homologue) is nondetectable.**

Method detection limits (MDLs) for PCB congeners in clean oil were statistically determined as:

$$MDL = t_{n-1} \cdot s$$

where:

t_{n-1} = the student's value (one-side test) at a specific confidence level

s = the standard deviation of n replicate analyses

Method detection limits for PCB in clean oil as presented in Table B5 (Appendix B) are in the range of 4 to 27 ng/g and 6 to 42 ng/g per congener at 95% and 99% confidence level, respectively.

2.7 Data Reporting

Submission of sample results must be accompanied by a clear photocopy of the corresponding sample submission/custody form. An example of the sample submission/custody sheet is given in Figure 4.

For every sample analyzed, information on sample identity, sample size, GC column, concentration of target analytes, detection limits, number of isomer peaks identified for each homologue, amounts of surrogates added, and surrogate recoveries must be reported (Figure 13).

Quality Assurance/Quality Control data that must be archived and submitted to Environment Canada upon request include:

results of the validation of performance (Figure 14), multipoint calibration (Figure 15), calibration verification (Figure 16), control samples (Figure 17), method blank, glassware proof rinse, and GC-MS chromatograms of samples, blanks, standards, detection limit verification, and window-defining mixture runs.

All original sample data and supporting QA/QC data must be archived for a minimum of three years for possible audit.

2.8 *Quality Assurance Summary*

Required quality assurance elements are:

(a) Glassware proof (Subsection 2.4.4):
Before any sample is processed, all pre-cleaned glassware, including Soxhlet Apparatus, concentrators, columns, flasks, and vials, are rinsed with dichloromethane (or hexane). Rinses of glassware required for one sample or a set of samples are combined and processed in the same manner as test samples. Contamination levels of individual congeners in the combined glassware-proof rinse must not exceed 25 ng per congener and total PCB contamination levels must not exceed 100 ng per sample.

(b) Performance Validation (Subsection 2.5.3):
Before any sample is processed, the laboratory must demonstrate the ability to achieve acceptable recovery of PCBs by conducting analyses of three matrix blanks spiked with native and labelled PCB standards. Criteria for accuracy and surrogate recoveries described in Subsection 2.5.3 must be met. This matrix blank analysis can be substituted with the analysis of standard reference materials or recent (within 6 months) control samples, providing the acceptance criteria are met.

(c) Surrogate Spike (Subsection 2.5.4):
Before extraction, each sample is spiked with a mixture of isotopically-labelled surrogates to assess and correct any analyte loss during sample workup. The surrogate mixture must contain, at minimum, one isotopically-labelled congener per homologue of tri- through octa-chlorobiphenyls. If the recovery of any surrogate (except for nona and deca in oil matrix) is outside the range of 30 to 130% , the sample must be re-processed and re-analyzed.

(d) Recovery Standard (Subsections 2.5.5 and 2. 6.5):
A known concentration of the recovery standards are added to each sample extract immediately before GC-MS analysis. These compounds serve as retention time references for labelled surrogates and as the basis for calculating surrogate recoveries.

(e) Method Blank (Subsection 2.5.4):
In addition to field blank samples, a method blank, consisting of clean matrix spiked with surrogates, is processed with each batch of up to 15 test samples. The acceptance limit for PCB presence in method blank samples is 25 ng per congener and up to 100 ng in total PCB.

(f) Control Sample (Subsection 2.5.4):
As a control sample, a certified reference material or fortified sample with known PCB concentration is processed with each batch of up to 15 test samples. The recovery of total PCBs in the control sample should be within the range of 75 to 125% of the actual value.

(g) Retention Time Window (Subsection 2.6.2):
A Window Defining Mixture containing the first and last eluting isomer within each homologous group of PCB must be used to correctly define retention time windows for selected ion monitoring of individual homologues. This analysis must be repeated weekly or whenever the column is cut, changed, or when any GC parameter has been modified.

(h) Calibration (Subsection 2.6.5):
Before sample analysis, calibration curves are constructed by analyzing at least four levels of calibration solutions to verify linearity of MS response and establish RRFs for all homologues. The calibration range must bracket the target regulatory level. Subsequent calibrations are performed as required. Native PCB congeners listed in Table 5 must be used as calibration standards.

Sample Data Sheet

Laboratory: _____ GC Column and MS: _____
Project: _____ Calibration Date: _____
Sample ID: _____ Analysis Date: _____
Sample Size: _____ File: _____
Approved by: _____

PCB Homologue	Concentration (Units)	SDL	NP
Trichlorobiphenyl			
Tetrachlorobiphenyl			
Pentachlorobiphenyl			
Hexachlorobiphenyl			
Heptachlorobiphenyl			
Octachlorobiphenyl			
Nonachlorobiphenyl			
Decachlorobiphenyl			
Total			

$^{13}C_{12}$-Surrogate (IUPAC No.)	Amount Added (pg)	% Recovery
PCB-28		
PCB-52		
PCB-118		
PCB-153		
PCB-180		
PCB-202		
PCB-208		
PCB-209		

Note: 1. Results are corrected for surrogate recoveries
2. SDL = sample detection limit (per analyte peak)
3. ND = not detected
4. NP = number of peaks detected

Figure 13 Example of a Sample Data Sheet

Performance Validation Data Sheet

Lab: _____ GC Column and MS: _____

Project: _____ Calibration Date: _____

Sample Matrix and Size: _____ Analysis Date: _____

Sample ID: _____ File: _____

Standard(s): _____ Approved by: _____

PCB Homologue	Calculated Value					
	#1		#2		#3	
	Amount	NP	Amount	NP	Amount	NP
Tri						
Tetra						
Penta						
Hexa						
Hepta						
Octa						
Nona						
Deca						
Total						

Total PCB (Tri-Deca) Amount Added (pg)	% Recovery		
	#1	#2	#3

$^{13}C_{12}$-Surrogate (IUPAC No.)	Amount Added (pg)	% Recovery		
		#1	#2	#3
PCB-28				
PCB-52				
PCB-118				
PCB-153				
PCB-180				
PCB-202				
PCB-208				
PCB-209				
	Average:			

NP = number of peaks detected

Figure 14 Example of a Performance Validation Data Sheet

Multipoint Calibration Data Sheet

Lab: _____ GC Column and MS: _____

Project: _____ File: _____

Calibration Date: _____ Approved by: _____

PCB Homologue (IUPAC No.)	Relative Response Factor (RRF)*				Mean RRF	%RSD
	PCS-#	PCS-#	PCS-#	PCS-#		
Tri (PCB-18, 28, 33)						
Tetra (PCB-44, 52, 70)						
Penta (PCB-101, 105, 118)						
Hexa (PCB-128, 138, 153)						
Hepta (PCB-170, 180, 187)						
Octa (PCB-194, 195, 199)						
Nona (PCB-206)						
Deca (PCB-209)						

* the average response of the specified congeners within each homologue is used

Figure 15 Example of a Multipoint Calibration Data Sheet

Calibration Verification Data Sheet

Lab: _____ GC Column and MS: _____

Project: _____ Verification Date and Time: _____

Calibration Date: _____ File: _____

Standards: _____ Approved by: _____

PCB Homologue	Concentration		Ratio of: Calculated Value / Actual Value
	Calculated Value	Actual Value	
Tri			
Tetra			
Penta			
Hexa			
Hepta			
Octa			
Nona			
Deca			

$^{13}C_{12}$- Surrogate (IUPAC#)	Calculated % Recovery
PCB-28	
PCB-52	
PCB-118	
PCB-153	
PCB-180	
PCB-202	
PCB-208	
PCB-209	

Figure 16 Example of a Calibration Verification Data Sheet

Control Sample Data Sheet

Lab: _____ GC Column and MS: _____

Project: _____ Analysis Date: _____

Sample ID: _____ File: _____

Sample Matrix and Size: _____ Approved by: _____

PCB Homologue	Calculated Value	Actual Value	Ratio of: Calculated Value / Actual Value
Tri			
Tetra			
Penta			
Hexa			
Hepta			
Octa			
Nona			
Deca			

$^{13}C_{12}$-Surrogate (IUPAC#)	Amount Added	% Recovery
PCB-28		
PCB-52		
PCB-118		
PCB-153		
PCB-180		
PCB-202		
PCB-208		
PCB-209		

Figure 17 Example of a Control Sample Data Sheet

(i) Calibration Verification (Subsection 2.6.5):
The established calibration must be verified by analyzing a mid-level calibration verification standard (e.g., PCS-3) at least once during every 12-hour period in which sample analysis occurs. Using average RRFs obtained from initial calibration runs, the calculated concentrations of all native analytes must be within 20% of their respective true concentrations. The recovery of each surrogate must be within the range of 75 to 125%. Remedial action is required whenever any native analyte or surrogate fails this verification test.

(j) Detection Limit (Subsections 2.6.3 and 2.6.6):
Gas chromatograph-mass spectrometer (GC-MS) detection limits must be confirmed by analyzing the lowest concentration (PCS-1) standard solution. This analysis must be repeated daily.

(k) Accuracy of Standards:
The accuracy of the calibration standards must be verified periodically (no longer than 12 months) against freshly unsealed certified reference standards (e.g., CLB-1 solution from the National Research Council of Canada).

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Appendix A

Data for Gas Chromatography - Electron Capture Detection Analysis

Table A1 **Relative Response Factors of Polychlorinated Biphenyls for Electron Capture Detection** (Mullin *et al.*, 1984)

	Octachloro-naphthalene	PCB-31	tri	tetra	penta	hexa	hepta	octa	nona	deca
No. of Isomers Used	1	1	24	42	46	42	24	12	3	1
Average RRF	1	0.562	0.563	0.675	0.716	0.877	1.153	1.072	1.391	1.05
Standard Deviation	-	-	0.229	0.199	0.212	0.242	0.371	0.445	0.255	-
% Relative SD	-	-	40.7	29.5	29.6	27.7	32.2	41.5	18.3	-

Table A2 **Precision on Peak Ratios for Aroclor in Iso-octane**

			Percent Relative Standard Deviation (RSD), n=10			
	µg/mL	Replicates	HCB/PCB*	OCS/PCB*	#83/PCB*	#122/PCB*
Aroclor 1242	0.2	10	2.3	3.4	3.0	6.7
Aroclor 1254	0.2	10	2.7	6.6	1.3	2.2
Aroclor 1260	0.2	10	2.8	2.1	0.7	4.4
Aroclor 1242/1254	0.4	10	2.5	1.9	1.9	3.9
Aroclor 1242/1260	0.4	10	4.7	5.2	3.2	3.6
Aroclor 1254/1260	0.4	10	3.1	2.5	2.4	0.6

* ratio of internal standard to the sum of 10 major Aroclor peaks

Table A3 Precision on Peak Ratios for Aroclor in Clean Oil

			Percent Relative Standard Deviation, n=10			
	μg/mL**	Replicates	HCB/PCB*	OCS/PCB*	#83/PCB*	#122/PCB*
Aroclor 1242	5	10	3.6	3.2	6.7	6.8
Aroclor 1254	5	10	4.8	5.3	1.9	3.6
Aroclor 1260	5	10	9.0	1.7	1.9	9.4
Aroclor 1242/1254	10	10	6.2	5.7	6.3	6.1
Aroclor 1242/1260	10	10	5.3	2.7	2.0	2.8
Aroclor 1254/1260	10	10	5.1	4.6	0.7	1.1

* ratio of internal standard to the sum of 10 major Aroclor peaks
** concentration in oil before the 25 times dilution with iso-octane

Table A4 Analytical Precision for Aroclors in Iso-octane (iso) and Oil

	Design Value	Analytical Value		Percent Relative Standard Deviation, n=10									
	(μg/mL)	(μg/mL)**		uncorrected		HCB*		OCS*		#83*		#122*	
Aroclor		iso	oil	iso	oil	iso	oil	iso	oil	iso	oil	iso	oil
1242	5	5.9	5.3	24.4	22.1	5.2	3.6	4.5	2.4	4.4	3.8	5.7	4.0
1254	5	5.2	4.9	33.1	32.3	4.5	4.7	6.3	5.5	1.8	1.9	3.4	3.5
1260	5	4.9	5.2	6.5	28.5	13	11	2.5	1.7	1.8	1.9	10	10
1242/1254	10	10	9.3	19.6	25.1	6.1	5.7	5.5	5.3	4.9	5.9	5.8	5.8
1242/1260	10	11.3	9.9	17.4	19.3	7.3	5.9	5.6	2.7	3.5	2.0	4.5	2.9
1254/1260	10	9.9	9.9	8.0	14.3	6.5	5.7	5.5	4.9	2.9	0.7	0.7	1.1

* value corrected for the internal standard response for 10 replicate analyses
**mean of the mean values corrected for the responses of individual internal standards

Table A5 Variations in PCB Analysis - CAEAL's Interlab Studies

Date of Study	No. of Labs	Sample ID	Aroclor in Oil	Reference Value (μg/g)	AD Value* (95% Confidence) (μg/g)	AD Value x 100 / Ref. Value (%)
October 1995	55	C8-1	1254/1260	19.1	7.7	40.3
		C8-2	1254/1260	19.1	7.7	40.3
		C8-3	1254/1260	59.5	21.8	36.8
		C8-4	1254/1260	97.2	37.0	38.1
March 1995	55	C8-1	1254/1260	20.5	9.2	44.9
		C8-2	1254/1260	50.7	18.2	35.9
		C8-3	1254/1260	71.9	24.6	34.2
		C8-4	1254/1260	103.0	34.0	33
October 1994	49	C8-1	1254/1260	20.2	10.1	50.0
		C8-2	1254/1260	20.2	10.1	50.0
		C8-3	1254/1260	62.1	24.7	39.8
		C8-4	1254/1260	103.0	38.9	37.8
March 1994	51	C8-1	1254/1260	19.8	8.3	41.9
		C8-2	1254/1260	49.9	21.0	42.1
		C8-3	1254/1260	49.9	21.0	42.1
		C8-4	1254/1260	105.0	44.0	41.9
October 1993	45	C8-1	1254	18.5	8.6	46.5
		C8-2	1254	45.4	16.6	36.6
		C8-3	1254	87.5	29.2	33.4
		C8-4	1254	107.0	35.1	32.8
March 1993	48	C8-1	1260	24.6	6.2	25.2
		C8-2	1260	44.2	11.0	24.9
		C8-3	1260	86.5	21.6	25.0
		C8-4	1260	120.4	30.1	25.0

*CAEAL's Accepted Deviation Value based on 95% confidence level

Table A6 **Summary of Polychlorinated Biphenyl Limits under *Canadian Environmental Protection Act* (CEPA) Regulations**

Regulations	Enforcement	PCB Limits
Federal Mobile PCB Treatment and Destruction Regulations	Emission and discharge	2 mg/kg for oil; 1 mg/kg feed for gases (efficiency of 99.9999%) 5 μg/L for liquid 0.5 mg/kg for solid
Storage of PCB Materials Regulations	Storage	50 mg/kg for all materials
PCB Waste Export Regulations	Export	50 mg/kg for PCB waste (liquid, solid, and equipment)
Ocean Dumping Regulations	Dredged sediment disposal	0.1 mg/kg for sediment
Chlorobiphenyl Regulations (under review)	Products	50 mg/kg
	Release	50 mg/kg for liquids 5 mg/kg for road oiling 1 g/day for equipment in operation, maintenance, decommissioning, transportation, and storage

Table A7 **Domain Numbers and Percent Contribution of Polychlorinated Biphenyl Congeners in Aroclors** (Schulz *et al.*, 1989)

Domain No.	IUPAC No.	Chlorine Position	Aroclor Weight Percent Contribution % 1016	1242	1254	1260	PCB< 0.05%
1	10	26	0.37	0.20			
	4	22'	3.89	3.89			
2	7	24	0.60	0.60			
	9	25	0.95	0.54			
3	6	23'	1.83	1.38			
4	8	24'	10.8	7.65			
	5	23	0.13	0.06			
							14
5	19	22'6	0.96	0.53			
							30,11,12,13
6	18	22'5	9.03	6.28	0.41		
	17	22,4	3.84	2.88	0.19		
	15	44'	2.90	1.51			
7	24	236	0.30	0.22			
	27	23'6	0.47	0.28			
8	16	22'3	2.86	2.01			
	32	24'6	1.34	0.88			
							23
9	34	2'35	0.12	0.05			54
10	29	245	0.19	0.10			
11	26	23'5	1.92	1.33			
12	25	23'4	1.19	0.79			
13	31	24'5	6.40	4.59	0.22	0.05	50
	28	244'	8.71	6.52	0.25	0.05	
14	20	233'	1.00	0.29			21
	33	2'34	6.25	4.79	0.14		
	53	22'56'	0.55	0.64	0.09		
15	51	22'46'	0.36	0.23			
	22	234'	4.80	3.41			
							36
16	45	22'36	1.66	1.16			
17	46	22'36'	0.70	0.49			
							39
18	69	23'46		0.11			
19	52	22'55'	4.46	4.04	5.18	0.56	73
20	49	22'45'	4.31	3.60	1.64		43,38
21	47	22'44'	1.11	0.94	0.17	0.11	
	48	22'45	0.98	0.82	0.14	0.09	
	75	244'6	0.08	0.11			
							65,62
22	35	33'4	0.08	0.11			
23	44	22'35'	3.50	3.20	2.03	104	
24	37	344'	0.30	0.27			
	59	233'6	0.29	0.34			72,71
	42	22'34'	0.55	0.83	0.23		
25	41	22'34	2.24	1.86	0.64	0.14	
	64	234'6	1.80	1.64	0.45		
							68
26	96	22'366'			0.08		

			1016	1242	1254	1260	PCB< 0.05%
27	40	22'33'	0.96	0.89	0.20		
							103,57
28	100	22'44'6			0.10		
	67	23'45	0.27	0.41	0.09		
							58
29	63	234'5	0.15	0.23	0.05		
30	74	244'5	0.89	2.17	0.78		94,61
31	70	23'4'5	1.20	3.89	3.21	0.09	76
							98,102
32	66	23'44'	1.60	1.66	0.59		93,80
	95	22'35'6	0.55	2.87	6.02	3.04	
33	88	22'346					
							121
34	91	22'34'6	0.15	0.17	0.83		55
35	60	2344'	0.07	1.33	0.54		155
	56	233'4'	0.10	1.60	0.58		
36	92	22'355'		0.25	1.58	0.59	
37	84	22'33'6	0.14	0.72	1.95	0.25	
							89
38	90	22'34'5		0.32	0.93	0.56	
	101	22'455'	0.15	1.33	7.94	5.02	
							113
39	99	22'44'5		0.86	3.60	0.11	
						79	
40	119	23'44'6		0.05	0.14		150
							112
41	83	22'33'5		0.12	0.45		78,109
							152
42	97	22'3'45		0.65	2.55	0.23	86
							125,145,81,117,116
43	87	22'345'		0.77	3.78	0.77	
	115	2344'6			0.30	0.05	
							111
44	85	22'344'		0.53	1.66	0.05	
							148
45	136	22'33'66'		0.07	1.12	2.23	120
46	77	33'44'		0.45			
	110	233'4'6		1.53	5.85	1.90	
47	82	22'33'4		0.44	0.95		154
	151	22'355'6			1.17	3.67	
48	135	22'33'56'		0.08	1.62	2.56	144
							124,147
49	107	233'4'5		0.07	0.72		108
50	123	2'344'5			0.81		106
	149	22'34'5'6		0.63	2.21	7.83	
	118	23'44'5		1.62	6.39	0.57	
							140,139
51	134	22'33'56			0.49	0.62	143
52	114	2344'5					142,133
	131	22'33'46			0.16	0.16	
	122	2'33'45			0.50	0.30	
							188,165
53	146	22'34'55'			0.83	1.49	
							161,184
54	132	22'33'46'		0.3	1.98	3.69	
	153	22'44'55'		0.68	4.26	10.80	
	105	233'44'		0.86	3.83	0.07	
							168,127
55	141	22'3455'			1.04	2.56	
	179	22'33'566'			0.21	1.79	
56	130	22'33'45'			0.63	0.08	

			1016	1242	1254	1260	PCB< 0.05%
57	176	22'33'466'			0.32	0.95	
	137	22'344'5			0.25	0.06	
58	160	233'456				0.05	163,164,186
	138	22'344'5'	0.19	0.54	3.20	6.13	
	158	233'44'6			0.77	1.55	
59	129	22'33'45			0.23	1.11	
	126	33'44'5					
	178	22'33'55'6			1.35	1.62	
							166
60	175	22'33'45'6			0.05	0.23	
61	187	22'34'55'6			0.32	3.97	182,159
62	183	22'344'5'6			0.17	1.76	
							162
63	128	22'33'44'			2.07	1.06	
64	167	23'44'55'			0.21	0.26	
65	185	22'3455'6				1.34	
66	174	22'33'456'			0.34	3.85	181
67	177	22'33'4'56			0.21	2.21	
68	202	22'33'55'66'				0.50	
	171	22'33'44'6		0.05	0.50	2.16	
	156	233'44'5		0.09	1.62	0.88	
69	173	22'33'456			0.09	0.36	
	157	233'44'5'				0.14	
	201	22'33'45'66'			0.68	0.99	
							204
70	172	22'33'455'			0.050	0.75	192
71	197	22'33'44'66'				0.12	
72	180	22'344'55'		0.06	0.38	7.12	
73	193	233'4'55'6				0.66	
74	191	233'44'5'6				0.25	
75	200	22'33'4566'				0.45	
76	169	33'44'55'				0.05	
77	170	22'33'44'5		0.11	0.31	3.91	
	190	233'44'56			0.08.	0.79	
78	198	22'33'455'6				0.09	
79	199	22'33'455'6'				1.31	
80	203	22'344'55'6				0.99	
	196	22'33'44'5'6				0.69	
81	189	233'44'55'				0.11	
82	208	22'33'455'66'				0.17	
	195	22'33'44'56				0.68	
83	207	22'33'44'566'				0.05	
84	194	22'33'44'55'				1.30	
85	205	233'44'55'6				0.15	
86	206	22'33'44'55'6				0.45	
87	209	22'33'44'55'66'				0.05	

Appendix B

Data for Gas Chromatography - Mass Spectrometry Analysis

Table B1 Relative Intensities of Molecular and Fragmentation Ions

Congener	Chlorine Positions	Ions	Relative Intensities	
			NIST Library	Lab Data
PCB-18	2,2',5	258/256/222/186/188	48/50/8/100/39	93/100/8/96/31
PCB-28	2,4,4'		74/83/1/100/31	95/100/2/51/16
PCB-33	2',3,4		96/100/0/94/32	98/100/3/57/18
PCB-44	2,2',3,5'	292/258/256/220/222	77/6/7/100/68	100/6/8/86/58
PCB-52	2,2',5,5'		100/5/6/95/59	100/5/6/72/49
PCB-70	2,3',4',5		100/0/0/93/48	100/2/3/45/31
PCB-101	2,2',4,5,5'	326/292/290/256/258	100/2/3/60/20	100/5/3/58/17
PCB-105	2,3,3',4,4'		100/0/0/56/17	100/3/6/38/13
PCB-118	2,3',4,4',5		100/0/0/53/15	100/3/2/35/11
PCB-128	2,2',3,3',4,4'	360/326/324/290/292	100/5/4/78/37	100/8/6/72/37
PCB-138	2,2',3,4,4',5		94/6/0/100/40	100/6/4/64/32
PCB-153	2,2',4,4',5,5'		100/0/0/76/37	100/0/0/56/27
PCB-170	2,2',3,3',4,4',5	394/360/358/324/326	100/0/0/82/48	100/9/6/79/53
PCB-180	2,2',3,4,4',5,5'		100/0/0/84/53	100/6/4/70/48
PCB-187	2,2',3,4',5,5',6		100/0/0/73/45	100/7/4/69/46
PCB-194	2,2',3,3',4,4',5,5'	430/396/394/358/360	100/4/3/77/61	100/7/8/70/51
PCB-195	2,2',3,3',4,4',5,6		100/10/3/78/56	100/8/9/73/57
PCB-199	2,2',3,3',4,5,6,6'		100/0/0/45/39	100/7/8/64/50
PCB-206	2,2',3,3',4,4',5,5',6	464/430/428/394/396	100/21/20/79/40	100/11/9/60/33
PCB-209	2,2',3,3',4,4',5,5',6,6'	498/464/462/428/430	100/1/1/64/39	100/8/5/50/37

Note: Lab data was obtained using SIM mode. Relative intensities may vary depending upon MS acquisition parameters used.

Table B2 Comparison of RRFs for Calibration Standard and Standard Reference Materials

Congener and Homologue	CLB-1A RRF	CLB-1B RRF	CLB-1C RRF	CLB-1D RRF	PCS-3 RRF	PCS-3 Homologue Average	CLB-1 Homologue Average
13C12-PCB-101	1.00	1.00	1.00	1.00	1.00		
18	1.17 (3.6)				1.04 (8.8)		
28					1.54 (7.8)		
31	1.85 (3.1)						
33					1.52 (7.7)		
T3CB						**1.37 ± 0.28**	**1.51**
40	0.84 (3.4)						
44	1.04 (3.4)				0.96 (3.6)		
49	1.09 (2.8)						
52		1.41 (6.6)			1.24 (10.8)		
54	1.27 (2.7)						
60		1.71 (4.0)					
70					1.52 (5.6)		
77	1.45 (4.3)						
T4CB						**1.24 ± 0.28**	**1.26 ± 0.29**
86	0.72 (0.78)						
87	0.86 (6.2)						
101				0.98 (1.8)	0.87 (1.2)		
103		0.97 (4.2)					
105		1.43 (2.7)			1.16 (4.1)		
114			1.37 (6.5)				
118				1.22 (7.6)	1.31 (3.8)		
121	1.24 (3.2)						
P5CB						**1.12 ± 0.22**	**1.10 ± 0.23**
128		0.74 (7.8)			0.73 (6.5)		
129			0.74 (5.1)				
137			0.84 (6.9)				
138				0.82 (8.1)	0.80 (7.1)		
141				0.79 (7.2)			
143		0.74 (4.5)					
151				0.69 (6.2)			
153	0.85 (3.7)			0.91 (9.8)	0.93 (4.8)		
154		0.85 (4.3)					
156	1.00 (4.9)						
159	0.90 (6.4)						
H6CB						**0.82 ± 0.10**	**0.84 ± 0.10**
170				0.6 (6.3)	0.69 (8.0)		
171			0.62 (8.1)				
173		0.55 (5.1)					
180				0.62 (5.8)	0.62 (5.1)		
182		0.64 (5.3)					
183			0.61 (6.8)				
185			0.64 (5.3)				
187				0.63 (6.3)	0.59 (3.4)		
189		0.90 (5.3)					
191		0.77 (7.4)					
H7CB						**0.63 ± 0.05**	**0.66 ± 0.10**
194				0.51 (5.1)	0.42 (6.9)		
195				0.42 (8.2)	0.41 (7.6)		
196				0.38 (5.7)			
199			0.37 (5.8)	0.36 (8.7)	0.45 (9.3)		
201			0.50 (6.9)				
202		0.55 (6.0)					
203			0.52 (4.7)				
205		0.53 (11.1)					
O8CB						**0.43 ± 0.02**	**0.46 ± 0.08**
206			0.27 (7.2)		0.25 (12.8)		
207		0.28 (10.0)					
208		0.36 (9.5)					
N9CB						**0.25**	**0.30 ± 0.05**
209	0.23 (11.7)	0.24 (8.8)	0.24 (6.1)	0.24 (10.3)	0.21 (9.2)		
D10CB						**0.21**	**0.24**

note: values in brackets represent %RSD of six analyses. CLB-1 is a set of reference standards from NRCC.

Table B3 GC/MS Results of Aroclor 1242, 1254, 1260, and 1254/1260 in Iso-octane

Aroclor 1242 at 5μg/mL

PCB	GC/MS Value			Reference Value**	
Homologue	Mean (n=5)	RSD	Weight*	Weight*	No. of Domain Peaks
	μg/mL	%	%	%	
Tri	1.99 (8 to 9)	2.1	52.0	42.2	13
Tetra	1.55 (14 to 16)	5.8	40.5	38.9	18
Penta	0.28 (12 to 14)	4.8	7.31	15.8	16
Hexa	0.009(1 to 3)	4.5	0.24	2.86	6
Hepta	ND		0	0.26	3
Octa	ND		0	0	0
Nona	ND		0	0	0
Deca	ND		0	0	0
Total PCBs	**3.829**	**2.2**	**100**	**100**	

Aroclor 1254 at 5 μg/mL

PCB	GC/MS Value			Reference Value**	
Homologue	Mean (n=5)	RSD	Weight	Weight	No. of Domain Peaks
	μg/mL	%	%	%	
Tri	0.028 (2 to 4)	15	0.67	1.21	3
Tetra	0.623 (7 to 10)	6.3	14.8	13.4	14
Penta	2.190 (13 to 16)	6.0	52.1	54.17	18
Hexa	1.185 (14 to 15)	3.8	28.2	23.86	16
Hepta	0.166 (8 to 9)	3.7	3.95	4.38	14
Octa	0.011(1 to 3)	37	0.26	0.68	1
Nona	ND		0	0	0
Deca	ND		0	0	0
Total PCBs	**4.203**	**4.4**	**100**	**100**	

Aroclor 1260 at 5 μg/mL

PCB Homologue	GC/MS Value Mean (n=5) μg/mL	RSD %	Weight %	Reference Value** Weight %	No. of Domain Peaks
Tri	0.012(2)	15	0.28	0.1	1
Tetra	0.012(1)	3.0	0.28	0.99	4
Penta	0.409(6 to 10)	8.2	9.45	13.51	12
Hexa	1.910(9 to 11)	4.4	44.12	46.84	18
Hepta	1.638(12 to 14)	2.1	37.84	33.84	17
Octa	0.336(7 to 8)	7.1	7.76	7.27	10
Nona	0.027(1 to 2)	22	0.62	0.67	3
Deca	ND		0	0.05	1
Total PCBs	**4.329**	**1.2**	**100**	**100**	

Aroclor 1254/1260 at 6.67 μg/mL

PCB Homologue	GC/MS Value Mean (n=5) μg/mL	RSD %	Weight %	Reference Value** Weight %	No. of Domain Peaks
Tri	0.034(4)	2.4	0.57	0.66	3
Tetra	0.423(6 to 8)	4.0	7.13	7.19	14
Penta	1.944(12 to 15)	4.9	30.64	33.84	18
Hexa	2.090(13 to 15)	2.5	38.04	35.35	18
Hepta	1.248(12 to 13)	0.9	21.04	19.11	17
Octa	0.155(4 to 6)	32	2.61	3.98	10
Nona	0.020(1 to 2)	26	0.34	0.34	3
Deca	0.003(1)	16	0.05	0.03	1
Total PCBs	**5.931**	**2.3**	**100**	**100**	

Note: numbers in bracket represent number of analyte peaks detected
'ND'- denotes values below the detection limit of 0.005 to 0.02 μg/mL
* weight % excludes the mono and dichlorobiphenyls
** (Schulz *et al.*, 1989)

Table B4 Method Detection Limits for Polychlorinated Biphenyls in Clean Oil

Congener (IUPAC No.)	Homologue	Mean (n=10) (ng/g)	Standard Deviation (ng/g)	MDL* 95% Confidence (ng/g)	MDL* 99% Confidence (ng/g)
18	Tri	87.6	5.0	9.2	14.1
28	Tri	130.5	14.7	26.9	41.5
33	Tri	103.9	12.6	23.1	35.6
52	Tetra	92.4	6.0	11.0	16.9
44	Tetra	79.9	6.9	12.6	19.6
70	Tetra	118.3	11.9	21.8	33.7
101	Penta	72.6	3.0	5.5	8.4
118	Penta	107.5	4.3	7.9	12.2
105	Penta	94.3	5.4	9.9	15.2
153	Hexa	111.0	3.1	5.7	8.8
138	Hexa	98.1	5.0	9.2	14.1
128	Hexa	92.1	6.4	11.7	17.9
187	Hepta	82.4	2.9	5.3	8.3
180	Hepta	84.9	2.6	13.5	7.4
170	Hepta	88.3	4.8	8.8	13.5
195	Octa	79.6	4.0	7.3	11.2
194	Octa	81.0	5.9	10.8	16.7
206	Nona	36.3	2.2	4.0	6.3
209	Deca	193.5	11.4	20.9	32.2
			Average	**11.8**	**17.6**

* $MDL = t_{n-1} \cdot s$

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