

**EPA Contract No. 68-W6-0042  
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**FINAL  
SAMPLING AND ANALYSIS PLAN  
FOR  
TECHNICAL ASSISTANCE**

**APPENDIX B: DAS SPECIFICATIONS**

**Ottati and Goss/Kingston Steel Drum Superfund Site  
Kingston, New Hampshire**

**May 1999**



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**FINAL SAMPLING AND ANALYSIS PLAN  
TECHNICAL ASSISTANCE  
OTTATI AND GOSS SUPERFUND SITE  
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## **B-1. DAS ANALYTICAL SERVICES SPECIFICATIONS**

**FINAL SAMPLING AND ANALYSIS PLAN  
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**ANALYTICAL SPECIFICATION  
FOR THE ANALYSIS OF  
VOLATILE ORGANIC COMPOUNDS  
IN SOIL SAMPLES**

***Prepared by:***

**Metcalf & Eddy Inc.  
Wakefield, Massachusetts  
Revision 1  
July 1998**

## **1. SCOPE**

This specification is for the analysis of volatile organic compounds (VOCs) in soil samples using a modified version of the EPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Organics Analysis, OLM03.2. This specification includes procedures described in Method 5035 from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition including updates, for the collection and analysis of soil samples for VOC analysis. Quality assurance/quality control (QA/QC) requirements are adapted from SW-846 as well as the EPA SOW OLM03.2. The target compounds and the required reporting limits are presented in Attachment A. Performance evaluation (PE) samples may be submitted for analysis. If PE samples are submitted, instructions for preparation and analysis will be provided in the sample shipping container.

## **2. PURPOSE**

The data derived using this specification will be used to: determine if ecological and human health risk criteria have been exceeded, provide input to risk assessments, define the nature and extent of volatile organic contamination in soil samples, establish excavation limits, determine the efficacy of remedial activities, provide a measure of the quality of data generated by another consultant, and/or for other purposes.

## **3. DEFINITION OF WORK**

Soil samples will be analyzed in accordance with this specification for volatile organic compounds. Field samples plus the associated QC samples will be submitted for analysis. Soil samples for VOC analysis will be collected into five gram Encore™ soil samplers in accordance with the procedures presented in EPA Method 5035. Soil samples will be shipped in the Encore samplers to the laboratory daily by an overnight courier.

Soil matrix samples are to be analyzed by EPA SOW OLM03.2 with the modifications presented within. These modifications are described in Section 7, Analytical Procedures. Samples will be submitted in sample delivery groups (SDGs). An SDG is as defined in EPA SOW OLM03.2 Exhibit A, Section 4.2.2.1.1. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that the last sample in the SDG is received.

### **Laboratory Soil Sampler Requirements**

The laboratory will provide a total of three Encore, 5 gram capacity, soil samplers for each sampling location. Two of these samplers will be submitted for low concentration VOC analysis. The third sampler will provide soil for high concentration (VOCS > 200 µg/Kg) analysis if this is necessary. M&E will provide an additional sample jar to allow a percent solids determination for each sample and possibly for sample screening.

#### **4. SCHEDULE**

Target sampling dates will be provided in each work order. Samples will be shipped daily. Saturday delivery may be required. An overnight delivery service will be used. Contacts for shipping will be provided in each work order. Data delivery inquiries may be made to Bruce Livingston, Metcalf & Eddy Inc. at (781) 224-6437 or the person specified in the work order.

##### Holding Times

The samples must be analyzed within 48 hours of sample collection. If analysis is not possible within 48 hours of sample collection, the soil must be transferred to soil sample vials containing organic-free water and sodium bisulfate for the low concentration analysis and methanol for the high concentration analysis in accordance with Method 5035. Transferred soil samples must be analyzed within 14 days of sample collection.

##### Delivery of Data

All sample data must be delivered under chain of custody. Data delivered to M&E will be sent to the following:

Mr. Bruce Livingston  
Metcalf & Eddy, Inc.  
30 Harvard Mill Square  
Wakefield, MA 01880-5371  
Phone (781) 224-6437  
Fax (781) 245-6293

#### **5. ANALYTICAL REFERENCES**

The analytical method reference is the EPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM03.2. Reference is also made to Method 5035, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition with updates. Quality assurance/quality control (QA/QC) requirements are adapted from OLM03.2. The target compounds and the required reporting limits are presented in Attachment A.

#### **6. SAMPLE PRESERVATION**

##### Sample Collection and Preservation

All soil samples not intended for percent solids determination will be collected using five gram Encore soil samplers. A four ounce wide mouth jar will be filled to capacity and

provided to the laboratory for percent solids determination and possibly for sample screening. All samples will be iced or refrigerated to 4° C ( $\pm$  2° C) from the time of collection and the samples will also be protected from light by the Encore samplers. Cooler temperature indicators will be placed in the sample shipping containers. If the cooler temperature exceeds 6° C upon sample receipt, the laboratory will contact M&E immediately regarding the temperature deviation to obtain direction on whether or not to prepare and analyze the affected samples. The temperature of the cooler is the only physical requirement the laboratory needs to record upon sample log-in. A sample pH check is not required at log-in.

#### Procedure for Sample Storage

The samples must be refrigerated from the time of receipt until 60 days after delivery of a complete, reconciled, sample-data package. After 60 days, disposal of the samples may be performed in accordance with all applicable regulations.

The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants. If analysis for VOCs is not conducted within 48 hours, the soil samples must be transferred to soil sample vials containing organic-free water and sodium bisulfate for the low concentration analysis and methanol for the high concentration analysis in accordance with Method 5035.

### **7. ANALYTICAL PROCEDURES**

#### Percent Solids Determination

A percent solids determination will be conducted on all soil samples using the sample bottle submitted expressly for this purpose. The laboratory must use the percent moisture determination provided in OLM03.2 Exhibit D Volatiles, Section 10.3.

#### Sample Preparation

Prior to sample analysis, all soil samples will be transferred to sample analysis vials. The laboratory must determine the mass of the vials, organic-free water and sodium bisulfate before sample addition and after the samples are extruded from the Encore samplers to determine the mass used for analysis. In accordance with OLM03.2, results must be recorded to the nearest 0.1 grams. The results must be recorded in a laboratory notebook and submitted with the data package.

#### Laboratory Fortified Blank

One LFB meeting the criteria presented in Section 8 will be analyzed daily prior to sample analysis on each instrument used for sample analysis according to this specification. The LFB will consist of 5 grams of VOC-free soil matrix placed into a VOC analysis vial spiked with all of the target compounds specified in Attachment A, such that LFB concentrations are at the specified reporting limits. The parent LFB spiking solution must be from a source other

than the initial and continuing calibration standards.

The LFB target compounds must meet the percent recovery criteria provided in Section 8, Quality Control Requirements, prior to sample analysis. The LFB surrogates and internal standards must also meet the recovery criteria presented in Section 8.

#### Matrix Spike/Matrix Spike Duplicate

Selection and analysis of MS/MSDs will be performed according to OLM03.2, Exhibit D, Volatiles, Section 12.2. If the sampling chain of custody forms do not identify the samples to be used for the MS/MSD, the laboratory will contact M&E to obtain additional instructions.

Matrix spike recovery and relative percent difference will be calculated according to the equations presented in OLM03.2, Exhibit D, Volatiles Sections 12.2.4.1 and 12.2.4.2. Technical acceptance criteria will be as specified in Section 12.2.5 of the same exhibit. All MS/MSDs must be analyzed on a GC/MS system meeting the BFB tuning criteria, the initial calibration and continuing calibration technical acceptance criteria, the blank technical acceptance criteria, and the frequency described in Section 12.2.2 of the same exhibit. The percent recovery and RPD criteria for each spiking compound are presented in Section 8, Quality Control Requirements, and corrective actions are as per OLM03.2, Exhibit D, Volatiles, Section 12.2.6.

#### Instrument Tuning

The GC/MS system must be tuned using bromofluorobenzene to meet the ion abundance criteria presented in Table 1 of Exhibit D VOA of OLM03.2. The tuning must be performed prior to initial and continuing calibration and before samples are analyzed.

#### Initial and Continuing Calibration

Initial and continuing calibration of the GC/MS system must be performed in accordance with OLM03.2. The acceptance criteria for the initial and continuing calibration are the same as OLM03.2 and these are presented in Section 8 of this specification.

#### Internal Standards

The internal standards must be the same compounds specified as in OLM03.2 and they must be spiked at the concentrations presented in Exhibit D VOA Section 7.2.4.3. Internal standard responses for all samples and calibration checks must not differ by more than a factor of two (- 50% to + 100%) when compared to the appropriate calibration standard specified by OLM03.2. As with all target compounds, internal standards must be within  $\pm$  0.5 minutes between any sample and the most recent continuing calibration standard analysis.

### Surrogate Compounds

All field samples and QA/QC samples including standards and method blanks will be monitored with the use of the surrogate compounds or system monitoring compounds specified in OLM03.2. Recovery of all surrogates must be as per Table 7 of Exhibit D Volatiles of OLM03.2 for all samples and QC samples. If these criteria are not met, the sample or QC sample must be reanalyzed. If in the second analysis, the surrogate recoveries again fall outside of criteria, report both analyses, note the problem in the case narrative, and flag the data with an asterisk. Surrogate standards must fall within  $\pm 0.06$  RRT units of its relative retention time in the continuing calibration standard.

### Method Blanks

Method blanks must be analyzed at the frequency specified in OLM03.2. The frequency, procedure, technical acceptance criteria, and corrective actions are specified in Exhibit D VOA Section 12.1.

## 8. QUALITY CONTROL REQUIREMENTS

The following QC checks must achieve the limits provided and be analyzed at the designated frequencies.

| QC Check                | Frequency                                                                                                               | Acceptance Limits                                                                                                             | Corrective Action                                                                           |
|-------------------------|-------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|
| Sample Preservation     | Every field sample and field QC sample                                                                                  | Analyze within 48 hours of sample collection or transfer to analysis vial                                                     | Notify M&E immediately if analysis is beyond 48 hours and the samples were not transferred. |
| GC/MS Instrument Tuning | Every 12 hours                                                                                                          | As per Table 1 of Exhibit D VOA of OLM03.2                                                                                    | As per Section 9.2.5 of Exhibit D VOA in OLM03.2                                            |
| Initial Calibration     | When a corrective action may change the initial calibration or if the continuing calibration criteria have not been met | RSD $\leq$ 20.5%, and RRF must meet minimum for all target compounds and surrogates as designated in Table 5 of Exhibit D VOA | Reanalyze ICAL. Perform system maintenance to remedy cause of problem                       |
| Continuing Calibration  | Every 12 hours                                                                                                          | %D $\leq$ 25%, and RRF must meet minimum for all target compounds and surrogates as designated in Table 5 of Exhibit D VOA    | Reanalyze CCAL, reanalyze ICAL if necessary                                                 |

| QC Check                                                                            | Frequency                                                                                      | Acceptance Limits                                                                                 | Corrective Action                                                                                                                                 |
|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| Surrogate (System Monitoring Compound) Recoveries                                   | All samples, QC samples and standards                                                          | As per Table 7 of Exhibit D Volatiles of OLM03.2                                                  | As per Section 11.4.3.1 of Exhibit D Volatiles of OLM03.2                                                                                         |
| Internal Standard Areas                                                             | All samples, QC samples and standards                                                          | -50% to +100% of the area of the corresponding IS in the most recent cont. calibration standard   | As per Section 11.4.3.1 of Exhibit D Volatiles of OLM03.2                                                                                         |
| Method Blank                                                                        | After initial calibration sequence, after each continuing standard, before sample analysis.    | Target analytes < ½ of the quantitation limits presented in Attachment A.                         | Must be met prior to sample analysis. Find the source of problem and reanalyze. Blank must be compliant before analysis of samples.               |
| Solid Matrix Lab Fortified Blank form a source other than the calibration standards | At the beginning of each 24 hour period during which samples are run, prior to sample analysis | Percent recovery must be 60-140% for all target compounds.                                        | Reanalyze CCAL and LFB until met; If necessary, perform ICAL, CCAL, and LFB until met. LFB must be compliant before analysis of samples.          |
| Matrix Spike/Matrix Spike Duplicate                                                 | 1 per SDG                                                                                      | Recoveries and Precision must be as in Table 8 Exhibit D Volatiles of OLM03.2, and Section 12.2.6 | Because the values in Table 8 are advisory no corrective action for recoveries is required. Flag the QC noncompliance on Form 3B as per OLM03.2 . |
| Performance Evaluation Sample                                                       | 1 per SDG                                                                                      | Not Relinquished                                                                                  | Will be conducted on a case by case basis.                                                                                                        |

## 9. ANALYTICAL DELIVERABLES

- A. Whenever possible, the forms provided in OLM03.2 must be used, and instructions presented in Exhibit B, Section 3, Forms Instructions, OLM03.2, must be followed. All information for which QC criteria are presented in this specification must be clearly presented on such forms. Additional instructions follow.

- A case narrative must be provided that contains a detailed description of the sample preparation and analysis methodology employed, any deviations from the requirements of this analytical specification, problems encountered and their resolution, and any anomalies in the reported data. The laboratory sample identification numbers and the M&E-assigned sample numbers must be cross-referenced in the Case Narrative. An example calculation must be provided for positive results and quantitation limits reported. If there are no detected compounds in the field samples, then the laboratory must use the matrix spike results for the example calculations.
- A copy of this analytical specification must be provided.
- Results for all samples, blanks, LFBs, MS/MSDs, and PE samples must be reported on Form Is that include all target compounds. All sample results must be reported on a dry-weight basis in  $\mu\text{g/kg}$ . The data qualifiers provided in OLM03.2 must be applied to the data generated. Laboratory qualifiers may be used by the laboratory, however they must be completely defined in the Case Narrative.
- The data package must be paginated and good copy quality is required.
- The CLP SOW-required header information must be supplied on all Forms whenever applicable. The volume of methanol from any high concentration samples which is injected into 5 ml purge volume and analyzed must be recorded on the Form I. On Form IA, this information will be placed in the "Soil Aliquot Volume" field.
- Surrogate recoveries will be presented on Form IIF. All standards, blanks, samples, and QC samples that were analyzed must be reported on the form. The results must be flagged according to OLM03.2 procedures.
- The matrix spike and matrix spike duplicate sample results must be reported on a form similar to OLM03.2 Form IIIB for the spiked compounds. The results must be flagged according to the procedures presented in Section 8 of this specification. Raw data must be included. Unspiked or "native" volatile organic compounds must be reported in the MS/MSD as per OLM03.2.
- The method blanks and associated samples must be summarized on OLM03.2 Form IVA.
- Continuing calibration checks will be presented on Form VIIA. The concentration and source of the standards analyzed must be provided. Raw data must be included for all standards analyzed.



- Results for the internal standards used must be provided on Form VIIIA. The retention time and area or height of the peak for the internal standards in all blanks, samples and QC samples must be reported on this form.
- The analytical sequences will be presented on Form VIID.
- All raw data must be provided for all blanks, spikes, standards, PE samples and field samples as per OLM03.2. All chromatograms must indicate the peaks used for quantitation, chromatographic conditions, instrument identification number, and injection volume. Quantitation reports must provide area counts (or peak heights) for all peaks present in the chromatograms.
- The Laboratory Fortified Blank (LFB) must be reported in tabular format on Form I. Raw data must be included. The source of the spike and the QC acceptance limits must also be reported. The percent recoveries for all compounds in the LFB will be calculated and presented on forms similar to Form III.
- All sample tracking reports (shipper information), sampling chain-of-custody forms, and custody seals must be provided in the data package.
- Copies of sample log-in/tracking sheets indicating the cooler temperature and the sample arrival time and date, the M&E chain of custody, and any telephone logs referring to the samples, must be provided in the data package.
- The laboratory must provide photocopies of any logbook or notebook pages that the laboratory generated in processing the samples including, but not limited to, the following: pages indicating all weights recorded for each sample and internal standard concentrations and volumes added.
- The laboratory must include the concentration of the surrogates, calibration standards, LFB, and matrix spike components on all relevant reporting Forms and raw data.
- The source, including the manufacturer, lot number, and concentration, of all reference materials must be provided in the data package.

**B. Complete Sample Delivery Group File (CSF) Audit**

All analytical data and all tabulated raw or supporting data must be delivered under custody seal for each SDG. The CSF Completeness Evidence Audit Forms, which are included in Attachment B, must be completed by the laboratory for the data package deliverables submitted for each SDG. Using those audit forms, the

laboratory must demonstrate that all tabulated and raw data for all field samples, standards, blanks, and QC samples, as well as any other documents required by OLM03.2 and this analytical specification are contained in the data package deliverable for each SDG.

Resubmittals for missing, inaccurate, and/or questionable data will be requested by facsimile followed by a telephone call. The resubmittals must be accompanied by additional completed CSF Completeness Evidence Audit Forms.

## **10. EXCEPTIONS**

If the laboratory has any questions, or if the laboratory experiences problems during any time from the sample scheduling/receipt through analysis, immediately contact:

Mr. Bruce Livingston  
Metcalf & Eddy, Inc.  
30 Harvard Mill Square  
Wakefield, MA 01880-5371  
Phone (781) 224-6437  
Fax (781) 245-6293

**ATTACHMENT A**  
**TARGET COMPOUND LIST**

| <u>Target Compound</u>   | <u>Required Quantitation<br/>Limit (µg/Kg)</u> |
|--------------------------|------------------------------------------------|
| Chloromethane            | 5.0                                            |
| Bromomethane             | 5.0                                            |
| Vinyl Chloride           | 5.0                                            |
| Chloroethane             | 5.0                                            |
| Methylene Chloride       | 5.0                                            |
| Acetone                  | 25                                             |
| Carbon Disulfide         | 5.0                                            |
| 1,1-Dichloroethene       | 5.0                                            |
| 1,1-Dichloroethane       | 5.0                                            |
| cis-1,2-Dichloroethene   | 5.0                                            |
| trans-1,2-Dichloroethene | 5.0                                            |
| Chloroform               | 5.0                                            |
| 1,2-Dichloroethane       | 5.0                                            |
| 2-Butanone               | 25                                             |
| 1,1,1-Trichloroethane    | 5.0                                            |
| Carbon Tetrachloride     | 5.0                                            |
| Bromodichloromethane     | 5.0                                            |
| 1,2-Dichloropropane      | 5.0                                            |
| cis-1,3-Dichloropropene  | 5.0                                            |
| Trichloroethene          | 5.0                                            |
| Dibromochloromethane     | 5.0                                            |
| 1,1, 2-Trichloroethane   | 5.0                                            |
| Benzene                  | 5.0                                            |

| <u>Target Compound</u>    | <u>Required Quantitation<br/>Limit (µg/Kg)</u> |
|---------------------------|------------------------------------------------|
| trans-1,3-Dichloropropene | 5.0                                            |
| Bromoform                 | 5.0                                            |
| 4-Methyl-2-Pentanone      | 25                                             |
| 2-Hexanone                | 25                                             |
| Tetrachloroethene         | 5.0                                            |
| 1,1,2,2-Tetrachloroethane | 5.0                                            |
| Toluene                   | 5.0                                            |
| Chlorobenzene             | 5.0                                            |
| Ethylbenzene              | 5.0                                            |
| Styrene                   | 5.0                                            |
| Total Xylenes             | 5.0                                            |

# DRAFT

## TECHNICAL SPECIFICATION

TOXIC POLYCHLORINATED BIPHENYLS AND TOTAL HOMOLOGUES ANALYSIS IN  
MULTI-MEDIA, MULTI CONCENTRATION SAMPLES BY ISOTOPE DILUTION HIGH  
RESOLUTION GAS CHROMATOGRAPHY/HIGH RESOLUTION MASS SPECTROMETRY  
(HRGC/HRMS) U.S.EPA METHOD 1668, MARCH 1997 AND U.S EPA METHOD  
680, NOVEMBER 1985

FOR  
U.S. ENVIRONMENTAL PROTECTION AGENCY

JUNE 1998

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(HRGC/HRMS) U.S.EPA METHOD 1668, MARCH 1997 AND U.S EPA METHOD  
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## 1.0 INTRODUCTION

Superfund site activities involve analyzing sediment, soil, sludge, ash, aqueous, tissue and other sample matrices for the Toxic PCB congeners and PCB homologues. The following specifications are for laboratory services to provide analysis of multi-media, multi-concentration samples via modified HRGC/HRMS USEPA Method 1668, March 1997 and USEPA Method 680, November 1985, for the Toxic Polychlorinated Biphenyls and Total Homologues.

## 2.0 SCOPE

Analytical services require the analysis of sediment, soil, sludge, ash, aqueous, tissue, and other sample matrices by isotope dilution techniques High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) for selected toxic PCB congeners and PCB homologues listed in Table 1. This technical specification is based on the combination of EPA Method 680 to measure PCB homologues, and EPA Method 1668 to extract, clean-up sample extracts, and measure toxic PCB congener target compounds.

The minimum required quantitation limits are presented in Table 1. In order for the laboratory to demonstrate their qualifications for this analysis an acceptable Initial Precision and Recovery (IPR) study must be submitted upon request, for each matrix being analyzed, as described in Section 9.2 of Method 1668, that was prepared within one year. The recovery of the compounds must meet the acceptance criteria presented in Table 4.

The results will be reported as a complete data package, data will be summarized on forms with the raw data which support the results. The summary forms are provided in Attachment A. The complete data package must be delivered within 35 days of last sample receipt in each sample delivery group (SDG = 20 or fewer field samples received over a period not exceeding 14 calendar days). Data package deliverables are described in Section 8.

The contractor is responsible for returning the empty coolers to the provider using the carrier account provided. The contractor is responsible for disposal of the unused samples one year after delivery of the complete data package.

## 3.0 SCHEDULE

Sample analysis will be scheduled by groups of samples. Each defined as a Case and identified by a unique EPA Case number. A Case signifies a group of samples collected at one site or geographical area over a finite time period and includes one or more field samples with associated blanks. Samples may be shipped to the contractor in a single shipment or multiple shipments over a period of time, depending on the size of the Case.

A case consists of one or more Sample Delivery Group(s). A Sample Delivery Group (SDG) is defined by the following, whichever is the most frequent:

- Each Case of field samples received, OR

- Each 20 field samples or less within a Case, OR
- Each 14 calendar day period during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG).

Samples may be assigned to SDGs by matrix (e.g., all soil samples in one SDG, all water samples a second SDG, and all fly ash in a third SDG), at the discretion of the laboratory. Such assignments must be made at the time the samples are received and may not be made retroactively.

Data for all samples in a SDG must be submitted together. The SDG number is the EPA sample number of the first sample received in the SDG. When several samples are received in the first SDG shipment, the SDG number will be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. The SDG number is reported on all data reporting forms.

### 3.1 Sample Collection

The sampling contractor will provide the laboratory with the airbill number and number of samples shipped prior to the arrival of each shipment to the laboratory. If the shipment does not arrive as scheduled, the laboratory will use the airbill number to track the shipment and notify the contractor. Within two days of sample receipt, the laboratory will fax a signed copy of the sample chain-of-custody or other form identifying the number and condition of samples received to the contractor.

### 3.2 Holding Times

All sediment, soil, sludge, ash, aqueous, tissue, and other sample matrices must be refrigerated at 0-4°C in the dark at the time of collection. At the time of sample receipt aqueous samples must be stored in the dark at 0-4°C. Sediment, soil, sludge, ash, tissue, and other solid matrices will be stored in the dark at < -10°C.

The PCB sample extraction must start within 7 days (aqueous) and 14 days (sediment, soil, sludge, ash, aqueous, tissue, and other sample matrices) from sample collection and the PCB analysis must be performed within 40 days from sample collection. Sample extraction and analysis of frozen tissue must be completed within 60 days of sample collection. Once frozen tissue samples are thawed, tissue samples must be extracted within 24 hours.

The laboratory is responsible for disposal of the unused samples one year after delivery of the data results, unless other provisions are established.

These turnaround times are recommended. The site data quality objective can augment this recommendation.



#### 4.0 ANALYTICAL REFERENCES

The toxic congeners and PCB homologues will be analyzed according to the following methods: Draft EPA Method 680, November 1985 and by EPA Method 1668, March 1997.

#### 5.0 SAMPLE PRESERVATION AND DETECTION LIMITS

Maintain samples per section 3.2 of this technical specification.

Minimum quantitation limits for aqueous, solid, and tissue samples are detailed in Table 1.

#### 6.0 SPECIAL TECHNICAL INSTRUCTIONS

All toxic PCB congeners must be individually separated. All analytical, sample preparation, and extraction instructions in EPA Method 1668 (Attachment B) must be adhered to by the laboratory.

- 6.1 The laboratory must submit an Initial Precision and Recovery (IPR) study upon request, conducted within one year, for each matrix being analyzed, as described in Section 9.2 of Method 1668. The recovery of the compounds must meet the acceptance criteria presented in Table 4. OPR data are acceptable instead of IPR. The IPR results must be submitted with the first data package.
- 6.2 Sample preparation and extraction are performed as specified in EPA Method 1668, Sections 11 and 12.
- 6.3 Aqueous samples (samples containing less than one percent solids) - The stable isotopically labeled analogs listed above are spiked into a one liter sample, and the sample is vacuum filtered through a glass-fiber filter on top of a solid phase extraction (SPE) disk. Sample components on the filter and disk are eluted with methylene chloride and the eluant is concentrated for clean up.
- 6.4 For solid samples, percent solids must be determined prior to sample allocation. If the percent solids are below 30%, then the analyst must take more sample to bring the solid content to 20g. Samples containing multiple phases are pressure filtered and any aqueous liquid is discarded or may require analysis depending on project request. Course solids are ground or homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted in an SDS extractor. The extract is concentrated for clean-up.
- 6.5 Solid, semi-solid, and multi-phase samples (but not tissue) - The labeled compounds are spiked into a sample containing 20g (dry weight) of solids.
- 6.6 Large rocks or extraneous materials must be removed, coarse soils must be ground, per Method 1668, Section 11.7, and the sample homogenized

prior to performing percent moisture determination and sample extraction. Two sample aliquots are taken, one for extraction and one for percent moisture determination. The sediment and soil samples must be dried overnight at 60 degrees centigrade for moisture determination.

6.7 Fish and other tissue - A 30g aliquot of sample is homogenized, and a 20g aliquot is spiked with the labeled isotope compounds. The sample is mixed with sodium sulfate, allowed to dry for 12-24 hours and extracted for 18-24 hours using methylene chloride:hexane (1:1) in a soxhlet extractor. The extract is evaporated to dryness, and the lipid content is determined per Method 1668, Section 12.4.9.

6.8 A solution containing the following labeled congeners will be spiked into all samples, blanks and standards as internal standards used for quantitation via isotope dilution techniques.

<sup>13</sup>C<sub>12</sub>-4-Monochlorobiphenyl (#3)  
<sup>13</sup>C<sub>12</sub>-4,4'-Dichlorobiphenyl (#15)  
<sup>13</sup>C<sub>12</sub>-2,4,4'-Trichlorobiphenyl (#28)  
<sup>13</sup>C<sub>12</sub>-3,3',4,4'-Tetrachlorobiphenyl (#77)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4'-Pentachlorobiphenyl (#105)  
<sup>13</sup>C<sub>12</sub>-2,3,4,4',5-Pentachlorobiphenyl (#114)  
<sup>13</sup>C<sub>12</sub>-2,3',4,4',5-Pentachlorobiphenyl (#118)  
<sup>13</sup>C<sub>12</sub>-2',3,4,4',5-Pentachlorobiphenyl (#123)  
<sup>13</sup>C<sub>12</sub>-3,3',4,4',5-Pentachlorobiphenyl (#126)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4',5-Hexachlorobiphenyl (#156)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4',5'-Hexachlorobiphenyl (#157)  
<sup>13</sup>C<sub>12</sub>-2,3',4,4',5,5'-Hexachlorobiphenyl (#167)  
<sup>13</sup>C<sub>12</sub>-3,3',4,4',5,5'-Hexachlorobiphenyl (#169)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3',4,4',5'-Heptachlorobiphenyl (#170)  
<sup>13</sup>C<sub>12</sub>-2,2',3,4,4',5,5'-Heptachlorobiphenyl (#180)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4',5,5'-Heptachlorobiphenyl (#189)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3',5,5',6,6'-Octachlorobiphenyl (#202)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl (#208)  
<sup>13</sup>C<sub>12</sub>-Decachlorobiphenyl (#209)

a. The recoveries will be reported in a tabular format for each sample. The recoveries must meet the criteria specified Table 4.

6.9 After extraction, samples are cleaned up using back-extraction with sulfuric acid and/or base, and gel permeation, silica gel, florisil, and activated carbon chromatography per EPA Method 1668, Section 13.

a. Prior to the clean-up procedures cited above, add the clean-up standards <sup>13</sup>C<sub>12</sub>-3,4,4',5-Tetrachlorobiphenyl (#81) and <sup>13</sup>C<sub>12</sub>-2,3,3',5,5'-Pentachlorobiphenyl (#111) per Method 1668, Section 7.11.

b. Additionally, tissue extracts are cleaned up using an anthropogenic isolation column according to Method 1668, Section 13.6.

- 6.10 After clean-up extracts are concentrated to near dryness. Recovery standards [ $^{13}\text{C}_{12}$ -2,2',5,5'-Tetrachlorobiphenyl (#52),  $^{13}\text{C}_{12}$ -2,2',4,5,5'-Pentachlorobiphenyl (#101),  $^{13}\text{C}_{12}$ -2,2',3,4,4',5'-Hexachlorobiphenyl (#138), and  $^{13}\text{C}_{12}$ -2,2',3,3',5,5',6-Heptachlorobiphenyl (#178)] are added to each extract per Method 1668, Section 7.12 and an aliquot of the extract is injected per EPA Method 1668, Section 14.
- 6.11 For the measurement of PCB congeners and PCB homologues, the GC/MS system must be calibrated using concentrations listed in Table 3.
- 6.12 An individual PCB congener is identified by comparing the GC retention time and ion abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion abundance ratio of the two exact m/z's per Method 1668, Section 16.0. Isomer specificity for toxic PCBs may require several GC columns to achieve resolution of the individual congeners from the other PCBs.
- 6.13 The Total homologues are determined by summing the areas for all isomers identified at each level of chlorination in a retention time window established per Method 680, Section 11.4.4 using the calibration standards listed in Table 3.
- 6.14 Quantitative analysis is performed using Selected Ion Current Profile (SICP) areas, in one of two ways per Method 1668, Section 17.0:
- a. For PCB congeners, the GC/MS system is calibrated, and the concentration of each compound is determined using internal standard technique per Method 1668, Section 17.1. For PCB congener measurements which exceed the 5-point calibration curve dilution of sample extracts is required.
  - b. For PCB homologues, the GC/MS system will be calibrated and the concentration of each compound determined using the associated internal standard as listed in Table 2 of this technical specification. For PCB congeners measurements which exceed the 5-point calibration curve dilution of sample extracts is required.
  - c. PCB homologues will be calibrated and the concentrations determined using the congeners listed in Table 3.
- 6.15 A method blank must be prepared and analyzed with each group of field samples of the same matrix extracted at the same time, as described in EPA method 1668, Sections 9.5 and 15.6. The method blank must not have any target PCBs at concentrations above one tenth the QL (Table 1) found in any method blank. If limits are exceeded, corrective actions must be performed and the associated samples must be re-analyzed. Where sample weight and volumes are adjusted to keep contaminated samples within the calibration range of the instrument, the adjusted quantitation limits should be used for judging method blank contaminants.
- 6.16 A five-point initial calibration for all target congeners, homologues

and the labeled analogs listed in Table 3 of this technical specification must be analyzed at the frequency specified in EPA Method 1668, Sections 10.5 and 10.6.

- a. The unlabeled PCB congeners should be quantitated against the response for the corresponding isotopically-labeled PCB congeners. The mean relative response of all the labeled congeners should be used if more than one labeled congener in a homologue group was used.
  - b. The linearity of the unlabeled congeners calculated by isotope dilution method must meet a relative standard deviation (RSD) limit below or equal to 20 percent.
  - c. The same analytical conditions must be used for the initial calibration and for analysis of all the quality control and field samples.
  - d. The initial calibration curve will be determined at a maximum less than one year from the time the first samples of an SDG are measured by the laboratory.
  - e. The window defining mix must be analyzed before every initial and continuing calibration and after instrument maintenance.
- 6.17 Native and labeled congeners in the calibration verification standard (CS3) and in the Ongoing Precision and Recovery (OPR) will meet the acceptance criteria specified in Table 4. If the VER and/or OPR does not meet recovery criteria, a new initial calibration must be analyzed.
- 6.18 Results are reported in ng/L for aqueous sample and in ug/Kg for solid and tissue samples. The solid sample results must be reported on a dry weight basis. Tissue samples are reported on a wet weight basis.
- 6.19 The calculation of the total PCB for each homologue group, e.g., total monochlorobiphenyls, is performed by calculating the concentration of each congener that occurs in the homologue and adding the concentrations of all congeners for that particular homologue group. For the measurement of PCB homologues, scan the masses listed in Tables 8a thru 8c. Include the [M-70]<sup>+</sup> ion for homologue confirmation, and the [M-35]<sup>+</sup> and [M-70]<sup>+</sup> ions to check for interferences from higher molecular weight PCB homologues which may elute at the same time as the target compounds homologues. The case narrative will specify if the concentrations were corrected for fragmentation. The concentration of each congener is calculated using the isotopically-labeled internal standard in the respective homologue. The estimated maximum possible concentration (EMPC) values will be calculated and reported in a separate EMPC/EDL column. EMPC values and/or non-detected congeners results must not be included in the total homologue calculation, e.g. do not add the "detection limit" for congeners that are not present. EMPC concentrations are reported in the EMPC/EDL column. Also, report the

number of PCB congeners (or peaks) used in calculating the total homologue concentrations.

#### 6.20 Identification criteria

- a. The signals for the two extract m/z's must be present, and must maximize within plus or minus 2 seconds of one another as per EPA Method 1668, Section 16.1.
- b. The signal-to-noise ratio (S/N) of each of the two exact m/z's must be greater than or equal to 2.5 for a sample extract, and greater than or equal to 10 for a calibration standard per EPA Method 1668, Section 16.2.
- c. The ratio of the integrated ion currents (SICPs) of both the exact possible m/z's monitored must be within the limits specified in Table 6 of this specification. Sample results which do not meet ion ratio criteria will be reported as EMPC.
- d. The relative retention times (RRT) of the peaks representing an unlabeled PCB congener must be within 5% of the labeled analogue.
- e. The measurement of PCBs 156 and 157 on the primary SPB-Octyl GC column must be confirmed by a confirmatory column such as DB-1. All QC requirements of EPA Method 1668 must be met on both the primary and secondary GC columns per EPA Method 1668, Section 16.5.
- f. The laboratory will flag data "I" when the ion ratios do not meet criteria and "S" when the S/N criteria are out. The concentration will be reported as EMPC values when the ion ratios do not meet criteria. Concentrations will be reported as EDLs when the S/N criteria are not met.

6.21 The operation conditions of the HRGC/HRMS described in EPA Method 1668, Section 10.1 must be obtained. A MS static resolution power of at least 10,000 at the appropriate m/z must be demonstrated according to EPA Method 1668, Section 15.2 before analysis is started.

6.22 The detection limits will be reported as Estimated Detection limits (EDLs) for each PCB congener and total homologue. The estimated detection limits are calculated using the following formula:

$$EDL = \frac{2.5 \times H_n \times Q_{is}}{H_{is} \times W \times RRF}$$

Where:

EDL = sample specific, Estimated Detection Limit,  
 $H_n$  = noise height (peak to Peak),  
 $H_{is}$  = peak height of the internal standard,  
 $Q_{is}$  = quantity, in pg, of the internal standard added to the sample  
 Before extraction,  
 $W$  = weight of the sample (solid dry weight or liquid), and  
 RRF = calculated relative response factor for the analyte.

6.23 The laboratory will follow the analytical sequence listed in Table 5 of this specification.

#### 7.0 QUALITY CONTROL REQUIREMENTS

All quality control criteria specified in section 7.0 of this technical specification must be followed.

| AUDITS REQUIRED                                                      | FREQUENCY OF AUDITS                                                                                                                                 | CRITERIA                                                                                                                                       | CORRECTIVE ACTIONS                                                                                                                                                       |
|----------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| IPR<br>Method 1668, Section 9.2                                      | Prepared within one year for each sample matrix.                                                                                                    | Per Section 6.1 and Table 4                                                                                                                    | Criteria must be met prior to sample analysis.                                                                                                                           |
| MS Resolution Determination<br>Method 1668, Sections 10.1.2 and 15.2 | At the beginning and end of each 12 hour period.                                                                                                    | Per Method 1668, Sections 10.1.2 and 15.2                                                                                                      | Initial criteria must be met prior to sample analysis. If the MS resolution fails criteria at the end of the 12 hour period, the entire sample batch must be reanalyzed. |
| Window Defining Mix<br>Section 6.16e                                 | Before every initial and continuing calibration and after instrument maintenance.                                                                   | According to Table 7.                                                                                                                          | If criteria are not met adjust the instrument conditions and re-analyze the window defining mix or re-calibrate.                                                         |
| Initial Calibration<br>Method 1668, Section 10.6                     | Five point initial calibration, according to Table 3. Within one year of sample analysis.                                                           | Congeners calculated using isotope dilution technique<br>RSD $\leq$ 20%.                                                                       | Criteria must be met prior to sample analysis.                                                                                                                           |
| Method Blank<br>Method 1668, Sections 9.5 and 15.6                   | Once each sample SDG (20 samples or less) per matrix prepared at one time. Method Blank will be analyzed immediately following OPR or VER analysis. | No target compounds from Table 1 at levels equal to or greater than one tenth the QL. All internal and recovery standard criteria must be met. | If criteria are not met, the entire batch must be re-prepared and re-analyzed, according to EPA Method 1668, Section 9.5.2.                                              |

| AUDITS REQUIRED                                                                 | FREQUENCY OF AUDITS                        | CRITERIA                                                                     | CORRECTIVE ACTIONS                                                                                                  |
|---------------------------------------------------------------------------------|--------------------------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|
| Continuing Calibration and VER Method 1668, Section 15                          | At the beginning of each 12 hour period.   | %D < 30% for CS3. VER criteria per Table 3.                                  | Criteria must be met prior to sample analysis. If criteria are not met, a new initial calibration must be analyzed. |
| Quality Control Check Sample Method 1668, Section 7.16                          | Quarterly, report the most recent analysis | Results must be within the acceptance windows specified by the manufacturer. | If criteria are not met, recalibrate the instrument. Criteria must be met prior to sample analysis.                 |
| CS1 as defined in Table 3                                                       | At the end of each 12 period.              | The CS1 must meet all calibration criteria. Per Method 1668, Section 10.6.   | If the CS1 fails criteria, the entire sample batch must be reanalyzed.                                              |
| Internal Standards, Recovery Standards, and Clean-up Standards per Section 6.3. | Add to all samples spikes, and blanks      | Per Form 1PCB.                                                               | If criteria are not met, re-analyze once. If the reanalysis do not meet criteria report both results.               |

Additional QC may be requested:

| AUDITS REQUIRED       | FREQUENCY OF AUDITS      | CRITERIA              | CORRECTIVE ACTIONS                                 |
|-----------------------|--------------------------|-----------------------|----------------------------------------------------|
| Laboratory Duplicates | As specified on the COC. | RPD < 50%             | Report results from sample and duplicate analysis. |
| Matrix Spike          | As specified on the COC. | As specified per DQOs | As specified per DQOs                              |

## 8.0 ANALYTICAL DELIVERABLES

The following items are required as deliverables for each data package: (See attachment A).

1. The data package will be prepared to resemble as close as possible, a CLP deliverable package. The required information will be reported on Forms I through X. The laboratory may use their own forms modified to include all the required information on Forms I through X. The laboratory will submit a signed PCB DC-2 form.
2. The laboratory will use the EPA identification numbering system when reporting sample results. In addition, the EPA identification number must be included in the header of the raw data for each sample; it may be hand written, if necessary.
3. A case narrative which summarizes the method used, clean-up procedures,

type of mass spectrometer used, problems encountered, and problem resolutions must be provided. The narrative must include a table showing the laboratory sample numbers and their corresponding EPA sample numbers. The case narrative will specify if the sample results were corrected for fragmentation.

4. The internal, recovery, and clean-up standard recoveries must be reported in tabular format. Non-spiked PCB congeners detected must be quantitated and reported (Form 1PCB-2 and Form 1PCB-4).
5. Positive results and non-detected PCB congeners and total homologue concentrations must be reported in tabular form for each sample analyzed (Form 1PCB and Form 1PCB-2). Laboratory duplicate sample results must be reported (Form 9PCB), as well as the method and instrument blanks (Form 1PCB and Form 1PCB-2). Concentrations, EDL and EMPC values will be reported on these forms.
6. PCB window defining mix results must be summarized, indicating the first and last eluting PCB congeners (Form 6PCB-1).
7. PCB chromatographic resolution must be summarized (Form 6PCB-2).
8. The PCB analytical sequence must be reported in a tabular form. The Analytical Sequence Summary will include all standards, window defining mix, sample QC (if required), and field samples (Form 4PCB).
9. The PCB method blank summary must be reported in a tabular form. The method blank summary will include all standards, window defining mix, sample QC, and field samples (Form 2PCB).
10. PCB initial calibration response factors must be tabulated, including the mean RRF and the percent RSD for all labeled and unlabeled compounds (Form 3PCB-1 and Form 3PCB-2).
11. The laboratory must submit an Initial Precision and Recovery (IPR) study with the first data package, which has been conducted within one year, for each matrix being analyzed (Form 7PCB-1 and Form 7PCB-2).
12. The PCB calibration verification results must also be tabulated and reported, including the RRF, the mean RRF from the initial calibration, and the percent difference (Form 5PCB-1). The calibration verification retention time must be reported in a tabular form (Form 5PCB-2). The calibration verification percent recoveries and ion ratio must be reported in a tabular form (Form 8PCB).
13. The solid samples must be reported in ug/Kg (dry basis), tissue samples must be reported in ug/Kg (wet weight), and aqueous samples must be reported in ng/L.
14. All sample tracking reports, original signed chain-of-custody forms, sample tags, custody seals, airbill, and any telephone logs referring to



TABLE 1  
PCB TARGET COMPOUNDS AND QUANTITATION LIMITS

| Target Compound <sup>1</sup>        | IUPAC Number | CAS Number | Quantitation Limits <sup>2</sup> |             |              |
|-------------------------------------|--------------|------------|----------------------------------|-------------|--------------|
|                                     |              |            | Aqueous ng/L                     | Solid ug/Kg | Tissue ug/Kg |
| 3,3',4,4'-TetCB                     | 77           | 32598-13-3 | 0.020                            | 0.002       | 0.002        |
| 2,3,3',4,4'-PeCB                    | 105          | 32598-14-4 | 1                                | 0.1         | 0.1          |
| 2,3,4,4',5-PeCB                     | 114          | 74472-37-0 | 2                                | 0.2         | 0.2          |
| 2,3'4,4',5-PeCB                     | 118          | 31508-00-6 | 0.2                              | 0.02        | 0.02         |
| 2',3,4,4',5-PeCB                    | 123          | 65510-44-3 | 0.1                              | 0.01        | 0.01         |
| 3,3'4,4',5-PeCB                     | 126          | 57465-28-8 | 0.1                              | 0.01        | 0.01         |
| 2,3,3'4,4',5-HxCB                   | 156          | 38380-08-4 | 0.2                              | 0.02        | 0.02         |
| 2,3,3',4,4',5'-HxCB                 | 157          | 69782-90-7 | 0.2                              | 0.02        | 0.02         |
| 2,3',4,4',5,5'-HxCB                 | 167          | 52663-72-6 | 0.2                              | 0.02        | 0.02         |
| 3,3',4,4',5,5'-HxCB                 | 169          | 32774-16-6 | 0.2                              | 0.02        | 0.02         |
| 2,2',3,3',4,4',5'-HpCB              | 170          | 35065-30-6 | 0.2                              | 0.02        | 0.02         |
| 2,2',3,4,4',5,5'-HpCB               | 180          | 35065-29-3 | 0.2                              | 0.02        | 0.02         |
| 2,3,3',4,4',5,5'-HpCB               | 189          | 39635-31-9 | 0.2                              | 0.02        | 0.02         |
| Total MCB Homologues <sup>3</sup>   |              | 27323-18-8 | 0.1                              | 0.01        | 0.01         |
| Total DiCB Homologues <sup>3</sup>  |              | 25512-42-9 | 0.1                              | 0.01        | 0.01         |
| Total TriCB Homologues <sup>3</sup> |              | 25323-68-6 | 0.1                              | 0.01        | 0.01         |
| Total TetCB Homologues <sup>3</sup> |              | 26914-33-0 | 0.1                              | 0.01        | 0.01         |
| Total PeCB Homologues <sup>3</sup>  |              | 25429-29-2 | 0.2                              | 0.02        | 0.02         |
| Total HxCB Homologues <sup>3</sup>  |              | 26601-64-9 | 0.2                              | 0.02        | 0.02         |
| Total HpCB Homologues <sup>3</sup>  |              | 28655-71-2 | 0.2                              | 0.02        | 0.02         |
| Total OCB Homologues <sup>3</sup>   |              | 31472-83-0 | 0.3                              | 0.03        | 0.03         |
| Total NCB Homologues <sup>3</sup>   |              | 53742-07-7 | 0.3                              | 0.03        | 0.03         |
| Total DeCB Homologues <sup>3</sup>  |              | 2051-24-3  | 0.5                              | 0.05        | 0.05         |
| Total PCB Homologues <sup>4</sup>   |              |            | 0.2                              | 0.02        | 0.02         |

<sup>1</sup> - Nomenclature for Polychlorinated Biphenyls:

|       |   |                     |       |   |                     |
|-------|---|---------------------|-------|---|---------------------|
| MCB   | = | Monochlorobiphenyl  | DiCB  | = | Dichlorobiphenyl    |
| TriCB | = | Trichlorobiphenyl   | TetCB | = | Tetrachlorobiphenyl |
| PeCB  | = | Pentachlorobiphenyl | HxCB  | = | Hexachlorobiphenyl  |
| HpCB  | = | Heptachlorobiphenyl | OCB   | = | Octachlorobiphenyl  |
| NCB   | = | Nonachlorobiphenyl  | DeCB  | = | Decachlorobiphenyl  |

<sup>2</sup> - Quantitation limits listed are for soil and fish tissue samples on wet weight basis.

<sup>3</sup> - Quantitation limits listed are based upon the single PCB congener which is used to calibrate for the homologue series.

<sup>4</sup> - Quantitation limits listed for total PCB homologues are based upon the average of the 10 PCB congeners which are used to calibrate for each of the homologue series.

TABLE 2  
PCB TARGET COMPOUNDS, INTERNAL STANDARDS, RECOVERY STANDARDS, CLEAN-UP  
STANDARDS, TOTAL HOMOLOGUE AND CALIBRATION CONGENERS

Target Compound

3,3',4,4'-Tetrachlorobiphenyl (#77)  
2,3,3',4,4'-Pentachlorobiphenyl (#105)  
2,3,4,4',5-Pentachlorobiphenyl (#114)  
2,3'4,4',5-Pentachlorobiphenyl (#118)  
2',3,4,4',5-Pentachlorobiphenyl (#123)  
3,3'4,4',5-Pentachlorobiphenyl (#126)  
2,3,3'4,4',5-Hexachlorobiphenyl (#156)  
2,3,3',4,4',5'-Hexachlorobiphenyl (#157)  
2,3',4,4',5,5'-Hexachlorobiphenyl (#167)  
3,3',4,4',5,5'-Hexachlorobiphenyl (#169)  
2,2',3,3',4,4',5'--Heptachlorobiphenyl (#170)  
2,2',3,4,4',5,5'-Heptachlorobiphenyl (#180)  
2,3,3',4,4',5,5'-Heptachlorobiphenyl (#189)

Monochlorobiphenyl Homologues

Dichlorobiphenyl Homologues

Trichlorobiphenyl Homologues

Tetrachlorobiphenyl Homologues

Pentachlorobiphenyl Homologues

Hexachlorobiphenyl Homologues

Heptachlorobiphenyl Homologues

Octachlorobiphenyl Homologues

Nonachlorobiphenyl Homologues

Decachlorobiphenyl Homologues

Total PCB Homologues

Internal Standards

<sup>13</sup>C<sub>12</sub>-4-Monochlorobiphenyl (#3)  
<sup>13</sup>C<sub>12</sub>-4,4'-Dichlorobiphenyl (#15)  
<sup>13</sup>C<sub>12</sub>-2,4,4'-Trichlorobiphenyl (#28)  
<sup>13</sup>C<sub>12</sub>-3,3',4,4'-Tetrachlorobiphenyl (#77)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4'-Pentachlorobiphenyl (#105)  
<sup>13</sup>C<sub>12</sub>-2,3,4,4'5-Pentachlorobiphenyl (#114)  
<sup>13</sup>C<sub>12</sub>-2,3',4,4',5-Pentachlorobiphenyl (#118)  
<sup>13</sup>C<sub>12</sub>-2',3,4,4'5-Pentachlorobiphenyl (#123)  
<sup>13</sup>C<sub>12</sub>-3,3',4,4',5-Pentachlorobiphenyl (#126)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4',5-Hexachlorobiphenyl (#156)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4',5'-Hexachlorobiphenyl (#157)  
<sup>13</sup>C<sub>12</sub>-2,3',4,4',5,5'-Hexachlorobiphenyl (#167)  
<sup>13</sup>C<sub>12</sub>-3,3',4,4',5,5'-Hexachlorobiphenyl (#169)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3'4,4',5'-Heptachlorobiphenyl (#170)  
<sup>13</sup>C<sub>12</sub>-2,2',3,4,4',5,5'-Heptachlorobiphenyl (#180)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4',5,5'-Heptachlorobiphenyl (#189)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3',5,5',6,6'-Octachlorobiphenyl (#202)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl (#208)  
<sup>13</sup>C<sub>12</sub>-Decachlorobiphenyl (#209)

TABLE 1  
PCB TARGET COMPOUNDS AND QUANTITATION LIMITS

| Target Compound <sup>1</sup>        | IUPAC Number | CAS Number | Quantitation Limits <sup>2</sup> |                |                 |
|-------------------------------------|--------------|------------|----------------------------------|----------------|-----------------|
|                                     |              |            | Aqueous<br>ng/L                  | Solid<br>ug/Kg | Tissue<br>ug/Kg |
| 3,3',4,4'-TetCB                     | 77           | 32598-13-3 | 0.020                            | 0.002          | 0.002           |
| 2,3,3',4,4'-PeCB                    | 105          | 32598-14-4 | 1                                | 0.1            | 0.1             |
| 2,3,4,4',5-PeCB                     | 114          | 74472-37-0 | 2                                | 0.2            | 0.2             |
| 2,3'4,4',5-PeCB                     | 118          | 31508-00-6 | 0.2                              | 0.02           | 0.02            |
| 2',3,4,4',5-PeCB                    | 123          | 65510-44-3 | 0.1                              | 0.01           | 0.01            |
| 3,3'4,4',5-PeCB                     | 126          | 57465-28-8 | 0.1                              | 0.01           | 0.01            |
| 2,3,3'4,4',5-HxCB                   | 156          | 38380-08-4 | 0.2                              | 0.02           | 0.02            |
| 2,3,3',4,4',5'-HxCB                 | 157          | 69782-90-7 | 0.2                              | 0.02           | 0.02            |
| 2,3',4,4',5,5'-HxCB                 | 167          | 52663-72-6 | 0.2                              | 0.02           | 0.02            |
| 3,3',4,4',5,5'-HxCB                 | 169          | 32774-16-6 | 0.2                              | 0.02           | 0.02            |
| 2,2',3,3',4,4',5'-HpCB              | 170          | 35065-30-6 | 0.2                              | 0.02           | 0.02            |
| 2,2',3,4,4',5,5'-HpCB               | 180          | 35065-29-3 | 0.2                              | 0.02           | 0.02            |
| 2,3,3',4,4',5,5'-HpCB               | 189          | 39635-31-9 | 0.2                              | 0.02           | 0.02            |
| Total MCB Homologues <sup>3</sup>   |              | 27323-18-8 | 0.1                              | 0.01           | 0.01            |
| Total DiCB Homologues <sup>3</sup>  |              | 25512-42-9 | 0.1                              | 0.01           | 0.01            |
| Total TriCB Homologues <sup>3</sup> |              | 25323-68-6 | 0.1                              | 0.01           | 0.01            |
| Total TetCB Homologues <sup>3</sup> |              | 26914-33-0 | 0.1                              | 0.01           | 0.01            |
| Total PeCB Homologues <sup>3</sup>  |              | 25429-29-2 | 0.2                              | 0.02           | 0.02            |
| Total HxCB Homologues <sup>3</sup>  |              | 26601-64-9 | 0.2                              | 0.02           | 0.02            |
| Total HpCB Homologues <sup>3</sup>  |              | 28655-71-2 | 0.2                              | 0.02           | 0.02            |
| Total OCB Homologues <sup>3</sup>   |              | 31472-83-0 | 0.3                              | 0.03           | 0.03            |
| Total NCB Homologues <sup>3</sup>   |              | 53742-07-7 | 0.3                              | 0.03           | 0.03            |
| Total DeCB Homologues <sup>3</sup>  |              | 2051-24-3  | 0.5                              | 0.05           | 0.05            |
| Total PCB Homologues <sup>4</sup>   |              |            | 0.2                              | 0.02           | 0.02            |

<sup>1</sup> - Nomenclature for Polychlorinated Biphenyls:

|       |   |                     |       |   |                     |
|-------|---|---------------------|-------|---|---------------------|
| MCB   | = | Monochlorobiphenyl  | DiCB  | = | Dichlorobiphenyl    |
| TriCB | = | Trichlorobiphenyl   | TetCB | = | Tetrachlorobiphenyl |
| PeCB  | = | Pentachlorobiphenyl | HxCB  | = | Hexachlorobiphenyl  |
| HpCB  | = | Heptachlorobiphenyl | OCB   | = | Octachlorobiphenyl  |
| NCB   | = | Nonachlorobiphenyl  | DeCB  | = | Decachlorobiphenyl  |

<sup>2</sup> - Quantitation limits listed are for soil and fish tissue samples on wet weight basis.

<sup>3</sup> - Quantitation limits listed are based upon the single PCB congener which is used to calibrate for the homologue series.

<sup>4</sup> - Quantitation limits listed for total PCB homologues are based upon the average of the 10 PCB congeners which are used to calibrate for each of the homologue series.

TABLE 2  
PCB TARGET COMPOUNDS, INTERNAL STANDARDS, RECOVERY STANDARDS, CLEAN-UP  
STANDARDS, TOTAL HOMOLOGUE AND CALIBRATION CONGENERS

Target Compound

3,3',4,4'-Tetrachlorobiphenyl (#77)  
2,3,3',4,4'-Pentachlorobiphenyl (#105)  
2,3,4,4',5-Pentachlorobiphenyl (#114)  
2,3'4,4',5-Pentachlorobiphenyl (#118)  
2',3,4,4',5-Pentachlorobiphenyl (#123)  
3,3'4,4',5-Pentachlorobiphenyl (#126)  
2,3,3'4,4',5-Hexachlorobiphenyl (#156)  
2,3,3',4,4',5'-Hexachlorobiphenyl (#157)  
2,3',4,4',5,5'-Hexachlorobiphenyl (#167)  
3,3',4,4',5,5'-Hexachlorobiphenyl (#169)  
2,2',3,3',4,4',5'--Heptachlorobiphenyl (#170)  
2,2',3,4,4',5,5'-Heptachlorobiphenyl (#180)  
2,3,3',4,4',5,5'-Heptachlorobiphenyl (#189)  
Monochlorobiphenyl Homologues  
Dichlorobiphenyl Homologues  
Trichlorobiphenyl Homologues  
Tetrachlorobiphenyl Homologues  
Pentachlorobiphenyl Homologues  
Hexachlorobiphenyl Homologues  
Heptachlorobiphenyl Homologues  
Octachlorobiphenyl Homologues  
Nonachlorobiphenyl Homologues  
Decachlorobiphenyl Homologues  
Total PCB Homologues

Internal Standards

<sup>13</sup>C<sub>12</sub>-4-Monochlorobiphenyl (#3)  
<sup>13</sup>C<sub>12</sub>-4,4'-Dichlorobiphenyl (#15)  
<sup>13</sup>C<sub>12</sub>-2,4,4'-Trichlorobiphenyl (#28)  
<sup>13</sup>C<sub>12</sub>-3,3',4,4'-Tetrachlorobiphenyl (#77)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4'-Pentachlorobiphenyl (#105)  
<sup>13</sup>C<sub>12</sub>-2,3,4,4',5-Pentachlorobiphenyl (#114)  
<sup>13</sup>C<sub>12</sub>-2,3',4,4',5-Pentachlorobiphenyl (#118)  
<sup>13</sup>C<sub>12</sub>-2',3,4,4',5-Pentachlorobiphenyl (#123)  
<sup>13</sup>C<sub>12</sub>-3,3',4,4',5-Pentachlorobiphenyl (#126)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4',5-Hexachlorobiphenyl (#156)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4',5'-Hexachlorobiphenyl (#157)  
<sup>13</sup>C<sub>12</sub>-2,3',4,4',5,5'-Hexachlorobiphenyl (#167)  
<sup>13</sup>C<sub>12</sub>-3,3',4,4',5,5'-Hexachlorobiphenyl (#169)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3',4,4',5'-Heptachlorobiphenyl (#170)  
<sup>13</sup>C<sub>12</sub>-2,2',3,4,4',5,5'-Heptachlorobiphenyl (#180)  
<sup>13</sup>C<sub>12</sub>-2,3,3',4,4',5,5'-Heptachlorobiphenyl (#189)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3',5,5',6,6'-Octachlorobiphenyl (#202)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl (#208)  
<sup>13</sup>C<sub>12</sub>-Decachlorobiphenyl (#209)

TABLE 2 (CONTINUED)  
PCB TARGET COMPOUNDS, INTERNAL STANDARDS, RECOVERY STANDARDS, CLEAN-UP  
STANDARDS, TOTAL HOMOLOGUE AND CALIBRATION CONGENERS

Recovery Standards

<sup>13</sup>C<sub>12</sub>-2,2',5,5'-Tetrachlorobiphenyl (#52)  
<sup>13</sup>C<sub>12</sub>-2,2',4,5,5'-Pentachlorobiphenyl (#101)  
<sup>13</sup>C<sub>12</sub>-2,2',3,4,4',5'-Hexachlorobiphenyl (#138)  
<sup>13</sup>C<sub>12</sub>-2,2',3,3',5,5',6-Heptachlorobiphenyl (#178)

Clean-up Standards

<sup>13</sup>C<sub>12</sub>-3,4,4',5-Tetrachlorobiphenyl (#81)  
<sup>13</sup>C<sub>12</sub>-2,3,3',5,5'-Pentachlorobiphenyl (#111)

Total Homologue Calibration Congeners

2-Monochlorobiphenyl (#1)  
2,3-Dichlorobiphenyl (#5)  
2,4,5-Trichlorobiphenyl (#29)  
2,2',4,6-Tetrachlorobiphenyl (#50)  
2,2',3,4,5'-Pentachlorobiphenyl (#87)  
2,2',4,4',5,6'-Hexachlorobiphenyl (#154)  
2,2',3,4',5,6,6'-Heptachlorobiphenyl (#188)  
2,2',3,3',4,5,6,6'-Octachlorobiphenyl (#200)  
2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl (#207)  
Decachlorobiphenyl (#209)

TABLE 3  
CONCENTRATIONS OF PCBs IN CALIBRATION AND CALIBRATION VERIFICATION SOLUTIONS

| Toxic PCB Congener                                       | IUPAC <sup>1</sup> | CS1 | CS2 | CS3 <sup>2</sup> | CS4 | CS5  |
|----------------------------------------------------------|--------------------|-----|-----|------------------|-----|------|
| 3,3',4,4'-TetCB                                          | 77                 | 0.5 | 2   | 10               | 40  | 200  |
| 2,3,3',4,4'-PeCB                                         | 105                | 2.5 | 10  | 50               | 200 | 1000 |
| 2,3,4,4',5-PeCB                                          | 114                | 2.5 | 10  | 50               | 200 | 1000 |
| 2,3'4,4',5-PeCB                                          | 118                | 2.5 | 10  | 50               | 200 | 1000 |
| 2',3,4,4',5-PeCB                                         | 123                | 2.5 | 10  | 50               | 200 | 1000 |
| 3,3'4,4',5-PeCB                                          | 126                | 2.5 | 10  | 50               | 200 | 1000 |
| 2,3,3'4,4',5-HxCB                                        | 156                | 5   | 20  | 100              | 400 | 2000 |
| 2,3,3',4,4',5'-HxCB                                      | 157                | 5   | 20  | 100              | 400 | 2000 |
| 2,3',4,4',5,5'-HxCB                                      | 167                | 5   | 20  | 100              | 400 | 2000 |
| 3,3',4,4',5,5'-HxCB                                      | 169                | 5   | 20  | 100              | 400 | 2000 |
| 2,2',3,3',4,4',5'-HpCB                                   | 170                | 5   | 20  | 100              | 400 | 2000 |
| 2,2',3,4,4',5,5'-HpCB                                    | 180                | 5   | 20  | 100              | 400 | 2000 |
| 2,3,3',4,4',5,5'-HpCB                                    | 189                | 5   | 20  | 100              | 400 | 2000 |
| Internal Standards                                       |                    |     |     |                  |     |      |
| <sup>13</sup> C <sub>12</sub> -4-MCB                     | 3L                 | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -4,4'-DiCB                 | 15L                | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,4,4'-TriCB              | 28L                | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -3,3',4,4'-TetCB           | 77L                | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,3,3',4,4'-PeCB          | 105L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,3,4,4',5-PeCB           | 114L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,3',4,4',5-PeCB          | 118L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2',3,4,4',5-PeCB          | 123L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -3,3',4,4',5-PeCB          | 126L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5-HxCB        | 156L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5'-HxCB       | 157L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,3',4,4',5,5'-HxCB       | 167L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -3,3',4,4',5,5'-HxCB       | 169L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,2'3,3',4,4',5'-HpCB     | 170L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,2',3,4,4',5,5'-HpCB     | 180L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5,5'-HpCB     | 189L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,2',3,3',5,5',6,6'-OCB   | 202L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -2,2',3,3',4,5,5',6,6'-NCB | 208L               | 100 | 100 | 100              | 100 | 100  |
| <sup>13</sup> C <sub>12</sub> -DeCB                      | 209L               | 200 | 200 | 200              | 200 | 200  |

TABLE 3 (Continued)  
CONCENTRATIONS OF PCBs IN CALIBRATION AND CALIBRATION VERIFICATION SOLUTIONS

| Toxic PCB Congener                                   | IUPAC <sup>1</sup><br>No. | CS1<br>ng/ml | CS2<br>ng/ml | CS3 <sup>2</sup><br>ng/ml | CS4<br>ng/ml | CS5<br>ng/ml |
|------------------------------------------------------|---------------------------|--------------|--------------|---------------------------|--------------|--------------|
| Clean-up Standard                                    |                           |              |              |                           |              |              |
| <sup>13</sup> C <sub>12</sub> -3,4,4',5-TetCB        | 81L                       | 0.5          | 2            | 10                        | 40           | 200          |
| <sup>13</sup> C <sub>12</sub> -2,3,3',5,5'-PeCB      | 111L                      | 2.5          | 10           | 50                        | 200          | 1000         |
| Recovery Standards                                   |                           |              |              |                           |              |              |
| <sup>13</sup> C <sub>12</sub> -2,2',5,5'-TetCB       | 52L                       | 100          | 100          | 100                       | 100          | 100          |
| <sup>13</sup> C <sub>12</sub> -2,2',4,5,5'-PeCB      | 101L                      | 100          | 100          | 100                       | 100          | 100          |
| <sup>13</sup> C <sub>12</sub> -2,2',3,4,4',5'-HxCB   | 138L                      | 100          | 100          | 100                       | 100          | 100          |
| <sup>13</sup> C <sub>12</sub> -2,2',3,3',5,5',6-HpCB | 178L                      | 100          | 100          | 100                       | 100          | 100          |
| Total Homologue Calibration Congeners                |                           |              |              |                           |              |              |
| 2-MCB                                                | 1                         | 0.5          | 2            | 10                        | 40           | 200          |
| 2,3-DiCB                                             | 5                         | 0.5          | 2            | 10                        | 40           | 200          |
| 2,4,5-TriCB                                          | 29                        | 0.5          | 2            | 10                        | 40           | 200          |
| 2,2',4,6-TetCB                                       | 50                        | 0.5          | 2            | 10                        | 40           | 200          |
| 2,2',3,4,5'-PeCB                                     | 87                        | 2.5          | 10           | 50                        | 200          | 1000         |
| 2,2',4,4',5,6'-HxCB                                  | 154                       | 5            | 10           | 50                        | 400          | 2000         |
| 2,2',3,4',5,6,6'-HpCB                                | 188                       | 5            | 10           | 50                        | 400          | 2000         |
| 2,2',3,3',4,5,6,6'-OCB                               | 200                       | 5            | 10           | 50                        | 400          | 2000         |
| 2,2',3,3',4,4',5,6,6'-NCB                            | 207                       | 5            | 10           | 50                        | 400          | 2000         |
| DeCB                                                 | 209                       | 5            | 10           | 50                        | 400          | 2000         |

- 1 Suffix "L" indicates labeled compound  
2 Calibration verification solution

TABLE 4  
PRELIMINARY ACCEPTANCE CRITERIA FOR PERFORMANCE TEST WHEN ALL TOXIC PCBs ARE TESTED<sup>1</sup>

| Toxic PCB Congener                                       | IUPAC No. | IPR           |                         |                         |              |               |
|----------------------------------------------------------|-----------|---------------|-------------------------|-------------------------|--------------|---------------|
|                                                          |           | Test<br>ng/ml | s <sup>2</sup><br>ng/ml | X <sup>3</sup><br>ng/ml | OPR<br>ng/ml | VER*<br>ng/ml |
| 3,3',4,4'-TetCB                                          | 77        | 20            | 5.6                     | 16-26                   | 14-32        | 5-15          |
| 2,3,3',4,4'-PeCB                                         | 105       | 1000          | 172                     | 720-1500                | 680-1600     | 25-75         |
| 2,3,4,4',5-PeCB                                          | 114       | 1000          | 390                     | 160-2800                | 130-3300     | 25-75         |
| 2,3'4,4',5-PeCB                                          | 118       | 1000          | 172                     | 720-1500                | 680-1600     | 25-75         |
| 2',3,4,4',5-PeCB                                         | 123       | 1000          | 390                     | 160-2800                | 130-3300     | 25-75         |
| 3,3'4,4',5-PeCB                                          | 126       | 100           | 17                      | 72-150                  | 68-160       | 25-75         |
| 2,3,3'4,4',5-HxCB                                        | 156       | 1000          | 222                     | 740-1600                | 640-1700     | 50-150        |
| 2,3,3',4,4',5'-HxCB                                      | 157       | 1000          | 222                     | 740-1600                | 640-1700     | 50-150        |
| 2,3',4,4',5,5'-HxCB                                      | 167       | 1000          | 222                     | 740-1600                | 640-1700     | 50-150        |
| 3,3',4,4',5,5'-HxCB                                      | 169       | 200           | 45                      | 148-320                 | 148-340      | 50-150        |
| 2,2',3,3',4,4',5'-HpCB                                   | 170       | 200           | 33                      | 152-260                 | 140-280      | 50-150        |
| 2,2',3,4,4',5,5'-HpCB                                    | 180       | 1000          | 165                     | 760-1300                | 760-1400     | 50-150        |
| 2,3,3',4,4',5,5'-HpCB                                    | 189       | 200           | 33                      | 152-260                 | 140-280      | 50-150        |
| Internal Standards                                       |           |               |                         |                         |              |               |
| <sup>13</sup> C <sub>12</sub> -4-MCB                     | 3L        | 50            | 10                      | 35-65                   | 25-150       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -4,4'-DiCB                 | 15L       | 50            | 10                      | 40-60                   | 70-140       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,4,4'-TriCB              | 28L       | 100           | 30                      | 70-130                  | 25-150       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -3,3',4,4'-TetCB           | 77L       | 100           | 37                      | 28-134                  | 20-175       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,3,3',4,4'-PeCB          | 105L      | 100           | 39                      | 16-279                  | 13-328       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,3,4,4',5-PeCB           | 114L      | 100           | 39                      | 16-279                  | 13-328       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,3',4,4',5-PeCB          | 118L      | 100           | 39                      | 16-279                  | 13-328       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2',3,4,4',5-PeCB          | 123L      | 100           | 39                      | 16-279                  | 13-328       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -3,3',4,4',5-PeCB          | 126L      | 100           | 39                      | 16-279                  | 13-328       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5-HxCB        | 156L      | 100           | 34                      | 24-157                  | 17-205       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5'-HxCB       | 157L      | 100           | 43                      | 24-157                  | 17-205       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,3',4,4',5,5'-HxCB       | 167L      | 100           | 43                      | 24-157                  | 17-205       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -3,3',4,4',5,5'-HxCB       | 169L      | 100           | 43                      | 24-157                  | 17-205       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,2',3,3',4,4',5'-HpCB    | 170L      | 100           | 41                      | 28-141                  | 20-186       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,2',3,4,4',5,5'-HpCB     | 180L      | 100           | 41                      | 28-141                  | 20-186       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,3,3',4,4',5,5'-HpCB     | 189L      | 200           | 82                      | 56-282                  | 40-372       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,2',3,3',5,5',6,6'-OCB   | 202L      | 200           | 100                     | 40-260                  | 25-150       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -2,2',3,3',4,5,5',6,6'-NCB | 208L      | 200           | 100                     | 40-260                  | 25-150       | 50-150        |
| <sup>13</sup> C <sub>12</sub> -DeCB                      | 209L      | 1000          | 500                     | 700-1200                | 25-150       | 100-300       |



TABLE 4 (Continued)  
PRELIMINARY ACCEPTANCE CRITERIA FOR PERFORMANCE TEST WHEN ALL TOXIC PCBs ARE  
TESTED<sup>1</sup>

| Toxic PCB Congener                              | IUPAC <sup>1</sup><br>No. | IPR           |                         |                         |              |              |
|-------------------------------------------------|---------------------------|---------------|-------------------------|-------------------------|--------------|--------------|
|                                                 |                           | Test<br>ng/ml | S <sup>2</sup><br>ng/ml | X <sup>3</sup><br>ng/ml | OPR<br>ng/ml | VER<br>ng/ml |
| Clean-up Standard                               |                           |               |                         |                         |              |              |
| <sup>12</sup> C <sub>12</sub> -3,4,4',5-TetCB   | 81L                       | 20            | 7.2                     | 8-31                    | 6-38         | 100-300      |
| <sup>12</sup> C <sub>12</sub> -2,3,3',5,5'-PeCB | 111L                      | 100           | 36                      | 39-154                  | 31-191       | 500-1500     |
| Total Homologues                                |                           |               |                         |                         |              |              |
| MCB                                             |                           | 50            | 10                      | 40-160                  | 70-140       | 5-15         |
| DiCB                                            |                           | 50            | 10                      | 40-160                  | 70-140       | 5-15         |
| TriCB                                           |                           | 50            | 10                      | 40-160                  | 70-140       | 5-15         |
| TetCB                                           |                           | 50            | 10                      | 40-160                  | 70-140       | 25-75        |
| PeCB                                            |                           | 50            | 10                      | 40-160                  | 70-140       | 25-75        |
| HxCB                                            |                           | 50            | 10                      | 40-160                  | 70-140       | 25-75        |
| HpCB                                            |                           | 50            | 10                      | 40-160                  | 70-140       | 25-75        |
| OCB                                             |                           | 50            | 10                      | 40-160                  | 70-140       | 25-75        |
| NCB                                             |                           | 50            | 10                      | 40-160                  | 70-140       | 25-75        |
| DeCB                                            |                           | 50            | 10                      | 40-160                  | 70-140       | 25-75        |

- 1 Preliminary criteria transferred from Method 1613. All criteria given as concentrations in the final extract, assuming a 20ul volume.  
2 s=standard deviation  
3 X=average concentration  
\* The CS3 concentrations are used for the VER test. The acceptance criteria are based on the preliminary criteria of 50-150% recovery.

Table 5 ANALYTICAL SEQUENCE

| <u>Time</u>     | <u>Analysis</u>             |
|-----------------|-----------------------------|
|                 | MS Resolution Determination |
|                 | Window Defining Mix         |
|                 | Resolution Check            |
| 0:00            | IPR                         |
|                 | CS3 (VER)                   |
|                 | CS1                         |
|                 | CS2                         |
|                 | CS4                         |
|                 | CS5                         |
|                 | OPR or VER                  |
|                 | Method blank                |
|                 | Samples                     |
|                 | ●                           |
|                 | ●                           |
|                 | CS1                         |
| 12:00 or 0:00   | MS Resolution Determination |
| Hours following | Window Defining Mix         |
| IPR injection   | Resolution Check            |
|                 | CS3 (VER)                   |
|                 | Method blank                |
|                 | Samples                     |
|                 | ●                           |
|                 | ●                           |
|                 | CS1                         |
| 12:00           | MS Resolution Determination |

Table 6  
THEORETICAL ION ABUNDANCE RATIOS AND QC LIMITS

| Number of Chlorine Atoms | Mass <sup>2</sup> | Ion Type | Theoretical Ratio | Control Limits <sup>1</sup> |       |
|--------------------------|-------------------|----------|-------------------|-----------------------------|-------|
|                          |                   |          |                   | Lower                       | Upper |
| 1                        | 188/190           | M/M+2    | 3.13              | 2.66                        | 3.60  |
| 1L                       | 194/196           | M/M+2    | 3.13              | 2.66                        | 3.60  |
| 2                        | 222/224           | M/M+2    | 1.57              | 1.33                        | 1.81  |
| 2L                       | 234/236           | M/M+2    | 1.57              | 1.33                        | 1.81  |
| 3                        | 256/258           | M/M+2    | 1.04              | 0.88                        | 1.20  |
| 3L                       | 268/270           | M/M+2    | 1.04              | 0.88                        | 1.20  |
| 4                        | 290/292           | M/M+2    | 0.77              | 0.65                        | 0.89  |
| 4L                       | 302/304           | M/M+2    | 0.77              | 0.65                        | 0.89  |
| 5                        | 326/328           | M+2/M+4  | 1.56              | 1.32                        | 1.78  |
| 5L                       | 338/340           | M+2/M+4  | 1.56              | 1.32                        | 1.78  |
| 6                        | 358/360           | M/M+2    | 0.51              | 0.43                        | 0.59  |
| 6L                       | 370/372           | M/M+2    | 0.51              | 0.43                        | 0.59  |
| 6                        | 360/362           | M+2/M+4  | 1.25              | 1.05                        | 1.43  |
| 6L                       | 372/374           | M+2/M+4  | 1.25              | 1.05                        | 1.43  |
| 7                        | 392/394           | M/M+2    | 0.45              | 0.37                        | 0.51  |
| 7L                       | 406/408           | M/M+2    | 0.45              | 0.37                        | 0.51  |
| 7                        | 394/396           | M+2/M+4  | 1.04              | 0.88                        | 1.20  |
| 7L                       | 408/410           | M+2/M+4  | 1.04              | 0.88                        | 1.20  |
| 8                        | 428/430           | M+2/M+4  | 0.89              | 0.76                        | 1.02  |
| 8L                       | 440/442           | M+2/M+4  | 0.89              | 0.76                        | 1.02  |
| 9                        | 464/466           | M/M+2    | 1.34              | 1.14                        | 1.54  |
| 9L                       | 474/476           | M/M+2    | 1.34              | 1.14                        | 1.54  |
| 10                       | 494/496           | M/M+2    | 1.17              | 0.99                        | 1.35  |
| 10L                      | 506/508           | M/M+2    | 1.17              | 0.99                        | 1.35  |
| 10                       | 498/500           | M+4/M+6  | 1.17              | 0.99                        | 1.35  |
| 10L                      | 510/512           | M+4/M+6  | 1.17              | 0.99                        | 1.35  |

1 QC limits represent +/- 15% windows around the theoretical ion abundance ratio. These limits are preliminary.

L Denotes labeled standard

2 Not exact masses - masses rounded to nearest whole number

41

Table 7  
PCB WINDOW DEFINING MIXTURE

| PCB Isomer                  | Eluting Order <sup>1</sup> | Group number |
|-----------------------------|----------------------------|--------------|
| 2-MCB                       | F                          | 1            |
| 4-MCB                       | L                          | 1            |
| 2,6-DiCB                    | F                          | 2            |
| 4,4'-DiCB                   | L                          | 2            |
| 2,4,6-TriCB                 | F <sup>2</sup>             | 2            |
| 2',3,5-TriCB                |                            | 2            |
| 2,2'6,6'TetCB               | F                          | 3            |
| 3,4,4'-TriCB                | L                          | 3            |
| 2,3,3'4-TetCB               |                            | 3            |
| 3,3',4,4'-TetCB             | L                          | 3            |
| 2,2'4,6,6'-PeCB             | F                          | 3            |
| 2,2'4,4'6,6'-HxCB           | F                          | 3            |
| 3,3'4,4'5-PeCB              | L                          | 4            |
| 2,2'3,4,4',6-HxCB           |                            | 4            |
| 2,2'3,4,5,6'-HxCB           |                            | 4            |
| 3,3'4,4'5,5'-HxCB           | L                          | 4            |
| 2,2'3,4',5,6,6'-HpCB        | F                          | 4            |
| 2,2'3,3',4,4',5-HpCB        |                            | 4            |
| 2,2'3,3'5,5'6,6'-OCB        | F                          | 4            |
| 2,3,3'4,4'5,5'-HpCB         | L                          | 5            |
| 2,2'3,3'4,4'5,5'-OCB        | L <sup>3</sup>             | 5            |
| 2,2'3,3',4,5,5',6,6'-NCB    | F                          | 5            |
| 2,2'3,3'4,4'5,5'6-NCB       | L                          | 5            |
| 2,2'3,3'4,4',5,5',6,6'-DeCB | F,L                        | 5            |

- 1 F = First eluting PCB within the homologue group; L = Last eluting PCB within the homologue group.
- 2 The 2,4,6-DiCB is the second eluting DiCB.
- 3 The 2,2'3,3',4,4',5,5'-OCB is the second to the last eluting isomer.

TABLE 8A  
IONS FOR SELECTED ION MONITORING TO DETERMINE PCBs BY ACQUIRING DATA FOR FOUR  
SETS OF  $\leq 35$  IONS EACH

| PCB Isomer Group | Nominal Mol.<br>Wt. Number | Mass or Range<br>to be<br>Monitored | No.<br>of<br>Ions | Ion Sets |                |                |    |
|------------------|----------------------------|-------------------------------------|-------------------|----------|----------------|----------------|----|
|                  |                            |                                     |                   | #1       | #2             | #3             | #4 |
| MCB              | 188                        | 152,186-190                         | 6                 | 6        |                |                |    |
| DiCB             | 222                        | 220-224                             | 5                 | 5        |                |                |    |
| TriCB            | 256                        | 254-260                             | 7                 | 7        | 7              | 1 <sup>a</sup> |    |
| TetCB            | 290                        | 288-294                             | 7                 | 7        | 7              | 1 <sup>b</sup> |    |
| PeCB             | 324                        | 322-328                             | 7                 |          | 7              | 7              |    |
| HxCB             | 358                        | 356-362                             | 7                 |          | 6 <sup>c</sup> | 7              | 7  |
| HpCB             | 392                        | 390-396                             | 7                 |          |                | 6 <sup>d</sup> | 7  |
| OCB              | 426                        | 424-430                             | 7                 |          |                |                | 7  |
| NCB              | 460                        | 460-466                             | 7                 |          |                |                | 7  |
| DeCB             | 494                        | 496-500                             | 5                 |          |                |                | 5  |

- a Monitor m/z 254 to confirm presence of (M-70)<sup>+</sup> for Cl<sub>1</sub>-PCBs.
- b Monitor m/z 288 to confirm presence of (M-70)<sup>+</sup> for Cl<sub>1</sub>-PCBs.
- c Begin range at m/z 357 in ion set #2.
- d Begin range at m/z 391 in ion set #3.

TABLE 8B  
IONS FOR SELECTED ION MONITORING TO DETERMINE PCBs BY ACQUIRING DATA FOR FIVE  
SETS OF  $\leq 20$  IONS EACH

| Ion Set | Isomer Group     | Quant Ion | Confirm Ions  | M-70               | M+70               | M+35               | Ion Measured for Correction |     |
|---------|------------------|-----------|---------------|--------------------|--------------------|--------------------|-----------------------------|-----|
| 1       | Cl <sub>1</sub>  | 188       | 190           | 152, 153           | 256, 258           | 222, 224           | -                           | -   |
|         | Cl <sub>2</sub>  | 222       | 224           | 152, 153, 186, 188 | 290, 292, 294      | 256, 258           | -                           | 221 |
|         | Cl <sub>3</sub>  | 256       | 258           | 186, 188           | -                  | 290, 292, 294      | -                           | 255 |
|         | Cl <sub>4</sub>  | 292       | 290, 294      | 220, 222           | -                  | -                  | -                           | -   |
| 2       | Cl <sub>1</sub>  | 256       | 258           | 186, 188           | 324, 326, 328      | 290, 292, 294      | 254                         | 255 |
|         | Cl <sub>4</sub>  | 292       | 290, 294      | 220, 222           | 360, 362           | 324, 326, 328      | 288                         | 289 |
|         | Cl <sub>6</sub>  | 326       | 324, 328      | 254, 256, 258      | -                  | 360, 362           | -                           | 323 |
|         | Cl <sub>6</sub>  | 360       | 358, 362      | 288, 290, 292      | -                  | -                  | -                           | -   |
| 3       | Cl <sub>6</sub>  | 326       | 324, 328      | 254, 256           | 392, 394, 396, 398 | 360, 362           | 322                         | 323 |
|         | Cl <sub>6</sub>  | 360       | 358, 362      | 288, 290           | -                  | 392, 394, 396, 398 | -                           | 357 |
|         | Cl <sub>7</sub>  | 394       | 392, 396      | 322, 324, 326      | -                  | -                  | -                           | -   |
| 4       | Cl <sub>6</sub>  | 360       | 358, 362      | 288, 290           | 426, 428, 430, 432 | 392, 394, 396      | 356                         | 357 |
|         | Cl <sub>7</sub>  | 394       | 392, 396, 398 | 322, 324           | -                  | 428, 430, 432      | -                           | 391 |
|         | Cl <sub>8</sub>  | 430       | 428, 432      | 356, 358, 360      | -                  | -                  | -                           | -   |
| 5       | Cl <sub>8</sub>  | 430       | 426, 428, 432 | 356, 358, 360      | 494, 496, 498, 500 | 462, 464, 466      | -                           | 425 |
|         | Cl <sub>9</sub>  | 464       | 460, 462, 466 | 390, 392, 394      | -                  | 496, 498, 500      | -                           | -   |
|         | Cl <sub>10</sub> | 498       | 494, 496, 500 | 424, 426, 428, 430 | -                  | -                  | -                           | -   |

TABLE 8C  
IONS FOR SELECTED ION MONITORING TO DETERMINE PCBs BY ACQUIRING DATA FOR FIVE  
SETS OF  $\leq 20$  IONS

| Ion Set No. 1 <sup>a</sup> | Ion Set No. 2 <sup>b</sup> | Ion Set No. 3 <sup>c</sup> | Ion Set No. 4 <sup>d</sup> | Ion Set No. 5 <sup>e</sup> |
|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| 152                        | 186                        | 247                        | 240                        | 356                        |
| 153                        | 188                        | 249                        | 241                        | 358                        |
| 186                        | 220                        | 254                        | 288                        | 360                        |
| 187                        | 222                        | 256                        | 290                        | 390                        |
| 188                        | 254                        | 288                        | 322                        | 392                        |
| 189                        | 255                        | 290                        | 324                        | 394                        |
| 190                        | 256                        | 322                        | 326                        | 424                        |
| 220                        | 258                        | 323                        | 356                        | 425                        |
| 221                        | 288                        | 324                        | 357                        | 426                        |
| 222                        | 289                        | 326                        | 358                        | 428                        |
| 224                        | 290                        | 328                        | 360                        | 430                        |
| 255                        | 292                        | 357                        | 362                        | 432                        |
| 256                        | 294                        | 358                        | 391                        | 462                        |
| 258                        | 323                        | 360                        | 392                        | 464                        |
| 290                        | 324                        | 362                        | 394                        | 466                        |
| 292                        | 326                        | 392                        | 396                        | 496                        |
| 294                        | 328                        | 394                        | 398                        | 498                        |
|                            | 358                        | 396                        | 428                        | 499                        |
|                            | 360                        | 398                        | 430                        | 500                        |
|                            | 362                        |                            | 432                        | 502                        |
| 17 Ions                    | 20 Ions                    | 19 Ions                    | 20 Ions                    | 20 Ions                    |

- a Ions to identify and measure Cl<sub>1</sub>-Cl<sub>4</sub>-PCBs.
- b Ions to identify and measure Cl<sub>1</sub>-Cl<sub>4</sub>-PCBs.
- c Ions to identify and measure Cl<sub>1</sub>-Cl<sub>4</sub>-PCBs.
- d Ions to identify and measure Cl<sub>4</sub>-Cl<sub>1</sub>-PCBs.
- e Ions to identify and measure Cl<sub>1</sub>-Cl<sub>10</sub>-PCBs.

**ATTACHMENT B**  
**ANALYTICAL METHODS**



**ATTACHMENT A**  
**REPORTING FORMS**

LABORATORY NAME \_\_\_\_\_  
CITY/STATE \_\_\_\_\_

CASE NO. \_\_\_\_\_ SDG NO. \_\_\_\_\_ SDG NOS. TO FOLLOW \_\_\_\_\_

PCB COMPLETE SDG FILE (CSF) INVENTORY SHEET  
HIGH RESOLUTION

CONTRACT NO. \_\_\_\_\_ METHOD NO. \_\_\_\_\_

All documents delivered in the complete SDG file must be original documents where possible.

|     |                                                     | PAGE NOS |       | CHECK |       |
|-----|-----------------------------------------------------|----------|-------|-------|-------|
|     |                                                     | FROM     | TO    | LAB   | EPA   |
| 1.  | <u>Inventory Sheet</u> (Form DC-2) (Do not number)  | _____    | _____ | _____ | _____ |
| 2a. | <u>SDG Cover Page</u>                               | _____    | _____ | _____ | _____ |
| 2b. | <u>SDG Narrative</u>                                | _____    | _____ | _____ | _____ |
| 3.  | <u>Traffic Report</u>                               | _____    | _____ | _____ | _____ |
| 4.  | <u>PCB Data</u>                                     | _____    | _____ | _____ | _____ |
| a.  | Sample Data                                         |          |       |       |       |
|     | Toxic PCB and Total Homologue Data Summary          | _____    | _____ | _____ | _____ |
|     | Results (Form I PCB-1 and Form I PCB-2)             | _____    | _____ | _____ | _____ |
|     | Second Column Confirmation Summary                  | _____    | _____ | _____ | _____ |
|     | (Form I PCB-3 and Form I PCB-4)                     | _____    | _____ | _____ | _____ |
|     | Selected Ion Current Profile (SICP) for each        | _____    | _____ | _____ | _____ |
|     | sample and each analysis of each sample             | _____    | _____ | _____ | _____ |
| b.  | Quality Control Data                                |          |       |       |       |
|     | PCB Spiked Sample Summary (Form X PCB)              | _____    | _____ | _____ | _____ |
|     | PCB Duplicate Sample Summary (Form IX PCB)          | _____    | _____ | _____ | _____ |
|     | PCB Method Blank Summary (Form II PCB)              | _____    | _____ | _____ | _____ |
|     | PCB Window Defining Mix Summary (Form VI PCB-1)     | _____    | _____ | _____ | _____ |
|     | PCB Chromatographic Resolution Summary              | _____    | _____ | _____ | _____ |
|     | (Form VI PCB-2)                                     | _____    | _____ | _____ | _____ |
|     | PCB Analytical Sequence Summary (Form IV PCB)       | _____    | _____ | _____ | _____ |
|     | SICP for each QC analysis                           | _____    | _____ | _____ | _____ |
| c.  | Calibration Data                                    |          |       |       |       |
|     | PCB Initial Calibration Response Factor Summary     | _____    | _____ | _____ | _____ |
|     | (Form III PCB-1)                                    | _____    | _____ | _____ | _____ |
|     | PCB Initial Calibration Ion Abundance Ratio Summary | _____    | _____ | _____ | _____ |
|     | (Form III PCB-1)                                    | _____    | _____ | _____ | _____ |
|     | and PCB standard(s) SICPs for the                   | _____    | _____ | _____ | _____ |
|     | initial (five-point) calibration                    | _____    | _____ | _____ | _____ |
|     | PCB Initial Precision and Recovery (IPR)            | _____    | _____ | _____ | _____ |
|     | (Form VII PCB-1 and Form VII PCB-2)                 | _____    | _____ | _____ | _____ |
|     | PCB Continuing Calibration Summary (Form V PCB-1)   | _____    | _____ | _____ | _____ |
|     | PCB Continuing Calibration Retention Time Summary   | _____    | _____ | _____ | _____ |
|     | (Form V PCB-2)                                      | _____    | _____ | _____ | _____ |
|     | and PCB standard(s) SICPs                           | _____    | _____ | _____ | _____ |
|     | for all continuing calibrations                     | _____    | _____ | _____ | _____ |
|     | PCB Calibration Verification (VER)                  | _____    | _____ | _____ | _____ |
|     | (Form VIII PCB)                                     | _____    | _____ | _____ | _____ |
| d.  | Raw Quality Control Data                            |          |       |       |       |
|     | Blank Data and SICPs for each blank analyzed        | _____    | _____ | _____ | _____ |
|     | Spiked Sample Data and SICPs for each               | _____    | _____ | _____ | _____ |
|     | spiked sample analyzed                              | _____    | _____ | _____ | _____ |

PCB COMPLETE SDG FILE (CSF) INVENTORY SHEET (Cont.)  
MODIFIED HIGH RESOLUTION

CASE NO. \_\_\_\_\_ SDG NO. \_\_\_\_\_ SDG NOS. TO FOLLOW \_\_\_\_\_

9. Comments: \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Completed by: \_\_\_\_\_  
(CLP Lab) (Signature) (Printed Name/Title) (Date)

Audited by: \_\_\_\_\_  
(EPA) (Signature) (Printed Name/Title) (Date)

1PCB-1  
TOXIC PCB AND TOTAL HOMOLOGUE SAMPLE DATA SUMMARY  
HRGC/HRMS

EPA SAMPLE NO.

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_

Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_

Matrix: \_\_\_\_\_ (Soil/Sediment/Aqueous/Tissue) Lab Sample ID: \_\_\_\_\_

Sample wt/vol: \_\_\_\_\_ (g/mL) \_\_\_\_\_ Lab File ID: \_\_\_\_\_

Concentrated Extract Volume: \_\_\_\_\_ (uL) \_\_\_\_\_ Date Received: \_\_\_\_\_

Injection Volume: \_\_\_\_\_ (uL) % Solids: \_\_\_\_\_ Date Analyzed: \_\_\_\_\_

GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) \_\_\_\_\_ Dilution Factor: \_\_\_\_\_

CONCENTRATION UNITS: (ng/L or ug/Kg) \_\_\_\_\_

| ANALYTE          | SELECTED IONS | PEAK RT | ION RATIO # | CONCENTRATION # | EMPC/EDL |
|------------------|---------------|---------|-------------|-----------------|----------|
| 33'44'-TetCB     | 290/292       |         |             |                 |          |
| 233'44'-PeCB     | 326/328       |         |             |                 |          |
| 2344'5'-PeCB     | 326/328       |         |             |                 |          |
| 23'44'5'-PeCB    | 326/328       |         |             |                 |          |
| 2'344'5'-PeCB    | 326/328       |         |             |                 |          |
| 33'44'5'-PeCB    | 326/328       |         |             |                 |          |
| 233'44'5'-HxCB   | 360/362       |         |             |                 |          |
| 233'44'5'-HxCB   | 360/362       |         |             |                 |          |
| 23'44'55'-HxCB   | 360/362       |         |             |                 |          |
| 33'44'55'-HxCB   | 360/362       |         |             |                 |          |
| 22'33'44'5'-HpCB | 394/396       |         |             |                 |          |
| 22'344'55'-HpCB  | 394/396       |         |             |                 |          |
| 233'44'55'-HpCB  | 394/396       |         |             |                 |          |
| Total Homologues |               | Peak#   |             |                 |          |
| Total MCB        |               |         | NA          |                 |          |
| Total DiCB       |               |         | NA          |                 |          |
| Total TriCB      |               |         | NA          |                 |          |
| Total TetCB      |               |         | NA          |                 |          |
| Total PeCB       |               |         | NA          |                 |          |
| Total HxCB       |               |         | NA          |                 |          |
| Total HpCB       |               |         | NA          |                 |          |
| Total OCB        |               |         | NA          |                 |          |
| Total NCB        |               |         | NA          |                 |          |
| Total DeCB       |               |         | NA          |                 |          |
| Total PCB        |               |         | NA          |                 |          |

# - Column to be used to flag values outside QC limits.

NOTE: Concentrations, EMPCs, and EDLs are calculated on a dry weight basis.

1PCB-2  
TOXIC PCB AND TOTAL HOMOLOGUE SAMPLE DATA SUMMARY  
HRGC/HRMS

EPA SAMPLE NO. \_\_\_\_\_

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_  
 Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_  
 Matrix: \_\_\_\_\_ (Soil/Sediment/Aqueous/Tissue) Lab Sample ID: \_\_\_\_\_  
 Sample wt/vol: \_\_\_\_\_ (g/mL) \_\_\_\_\_ Lab File ID: \_\_\_\_\_  
 Date Received: \_\_\_\_\_  
 Concentrated Extract Volume: \_\_\_\_\_ (uL) \_\_\_\_\_ Date Extracted: \_\_\_\_\_  
 Injection Volume: \_\_\_\_\_ (uL) % Solids: \_\_\_\_\_ Date Analyzed: \_\_\_\_\_  
 GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) \_\_\_\_\_ Dilution Factor: \_\_\_\_\_

CONCENTRATION UNITS: (ng/L or ug/Kg) \_\_\_\_\_

| INTERNAL<br>STANDARD  | SELECTED<br>IONS | PEAK<br>RT | ION<br>RATIO # | ION RATIO<br>LIMITS | %<br>REC # | RECOVERY<br>LIMITS |
|-----------------------|------------------|------------|----------------|---------------------|------------|--------------------|
| 13C-4-MCB             | 194/196          |            |                | 2.66-3.60           |            | 25-150             |
| 13C-44'-DiCB          | 234/236          |            |                | 1.33-1.81           |            | 25-150             |
| 13C-244'-TriCB        | 268/270          |            |                | 0.88-1.20           |            | 25-150             |
| 13C-33'44'-TetCB      | 302/304          |            |                | 0.65-0.89           |            | 24-169             |
| 13C-233'44'-PeCB      | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-2344'5-PeCB       | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-23'44'5-PeCB      | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-2'344'5-PeCB      | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-33'44'5-PeCB      | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-233'44'5-HxCB     | 372/374          |            |                | 1.05-1.43           |            | 26-152             |
| 13C-233'44'5'-HxCB    | 372/374          |            |                | 1.05-1.43           |            | 26-152             |
| 13C-23'44'55'-HxCB    | 372/374          |            |                | 1.05-1.43           |            | 26-152             |
| 13C-33'44'55'-HxCB    | 372/374          |            |                | 1.05-1.43           |            | 26-152             |
| 13C-22'33'44'5'-HpCB  | 408/410          |            |                | 0.88-1.20           |            | 23-143             |
| 13C-22'344'55'-HpCB   | 408/410          |            |                | 0.88-1.20           |            | 23-143             |
| 13C-233'44'55'-HpCB   | 408/410          |            |                | 0.88-1.20           |            | 23-143             |
| 13C-22'33'55'66'-OCB  | 440/442          |            |                | 0.76-1.02           |            | 25-150             |
| 13C-22'33'455'66'-NCB | 474/476          |            |                | 1.14-1.54           |            | 25-150             |
| 13C-DeCB              | 510/512          |            |                | 0.99-1.35           |            | 25-150             |

| CLEAN-UP<br>STANDARD | SELECTED<br>IONS | PEAK<br>RT | ION<br>RATIO # | ION RATIO<br>LIMITS | %<br>REC # | RECOVERY<br>LIMITS |
|----------------------|------------------|------------|----------------|---------------------|------------|--------------------|
| 13C-344'5-TetCB      | 302/304          |            |                | 0.65-0.89           |            | 35-197             |
| 13C-233'55'-PeCB     | 338/340          |            |                | 1.32-1.78           |            | 35-197             |

| RECOVERY<br>STANDARD | SELECTED<br>IONS | PEAK<br>RT | ION<br>RATIO # | ION RATIO<br>LIMITS | %<br>REC # | RECOVERY<br>LIMITS |
|----------------------|------------------|------------|----------------|---------------------|------------|--------------------|
| 13C-22'55'-TetCB     | 302/304          |            |                | 0.65-0.89           |            | 50-200             |
| 13C-22'455'-PeCB     | 338/340          |            |                | 1.32-1.78           |            | 50-200             |
| 13C-22'344'5'-HxCB   | 372/374          |            |                | 1.05-1.43           |            | 50-200             |
| 13C-22'33'55'6-HpCB  | 408/410          |            |                | 0.88-1.20           |            | 50-200             |

# - Column to be used to flag values outside QC limits.

1PCB-3  
TOXIC PCB AND TOTAL HOMOLOGUE SAMPLE DATA SUMMARY  
SECOND COLUMN CONFIRMATION HRGC/HRMS

EPA SAMPLE NO.

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_

Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_

Matrix: \_\_\_\_\_ (Soil/Sediment/Aqueous/Tissue) Lab Sample ID: \_\_\_\_\_

Sample wt/vol: \_\_\_\_\_ (g/mL) \_\_\_\_\_ Lab File ID: \_\_\_\_\_

Concentrated Extract Volume: \_\_\_\_\_ (uL) \_\_\_\_\_ Date Received: \_\_\_\_\_

Injection Volume: \_\_\_\_\_ (uL) % Solids: \_\_\_\_\_ Date Analyzed: \_\_\_\_\_

GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) \_\_\_\_\_ Dilution Factor: \_\_\_\_\_

CONCENTRATION UNITS: (ng/L or ug/Kg) \_\_\_\_\_

| ANALYTE          | SELECTED<br>IONS | PEAK<br>RT | ION<br>RATIO # | CONCENTRATION | # | EMPC/EDL |
|------------------|------------------|------------|----------------|---------------|---|----------|
| 33'44'-TetCB     | 290/292          |            |                |               |   |          |
| 233'44'-PeCB     | 326/328          |            |                |               |   |          |
| 2344'5-PeCB      | 326/328          |            |                |               |   |          |
| 23'44'5-PeCB     | 326/328          |            |                |               |   |          |
| 2'344'5-PeCB     | 326/328          |            |                |               |   |          |
| 33'44'5-PeCB     | 326/328          |            |                |               |   |          |
| 233'44'5-HxCB    | 360/362          |            |                |               |   |          |
| 233'44'5'-HxCB   | 360/362          |            |                |               |   |          |
| 23'44'55'-HxCB   | 360/362          |            |                |               |   |          |
| 33'44'55'-HxCB   | 360/362          |            |                |               |   |          |
| 22'33'44'5'-HpCB | 394/396          |            |                |               |   |          |
| 22'344'55'-HpCB  | 394/396          |            |                |               |   |          |
| 233'44'55'-HpCB  | 394/396          |            |                |               |   |          |
| Total Homologues |                  | Peak#      |                |               |   |          |
| Total MCB        |                  |            | NA             |               |   |          |
| Total DiCB       |                  |            | NA             |               |   |          |
| Total TriCB      |                  |            | NA             |               |   |          |
| Total TetCB      |                  |            | NA             |               |   |          |
| Total PeCB       |                  |            | NA             |               |   |          |
| Total HxCB       |                  |            | NA             |               |   |          |
| Total HpCB       |                  |            | NA             |               |   |          |
| Total OCB        |                  |            | NA             |               |   |          |
| Total NCB        |                  |            | NA             |               |   |          |
| Total DeCB       |                  |            | NA             |               |   |          |
| Total PCB        |                  |            | NA             |               |   |          |

# - Column to be used to flag values outside QC limits.

NOTE: Concentrations, EMPCs, and EDLs are calculated on a dry weight basis.

1PCB-4  
TOXIC PCB AND TOTAL HOMOLOGUE SAMPLE DATA SUMMARY  
SECOND COLUMN CONFIRMATION HRGC/HRMS

EPA SAMPLE NO. \_\_\_\_\_

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_  
 Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_  
 Matrix: \_\_\_\_\_ (Soil/Sediment/Aqueous/Tissue) Lab Sample ID: \_\_\_\_\_  
 Sample wt/vol: \_\_\_\_\_ (g/mL) \_\_\_\_\_ Lab File ID: \_\_\_\_\_  
 Date Received: \_\_\_\_\_  
 Concentrated Extract Volume: \_\_\_\_\_ (uL) \_\_\_\_\_ Date Extracted: \_\_\_\_\_  
 Injection Volume: \_\_\_\_\_ (uL) % Solids: \_\_\_\_\_ Date Analyzed: \_\_\_\_\_  
 GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) Dilution Factor: \_\_\_\_\_

CONCENTRATION UNITS: (ng/L or ug/Kg) \_\_\_\_\_

| INTERNAL<br>STANDARD  | SELECTED<br>IONS | PEAK<br>RT | ION<br>RATIO # | ION RATIO<br>LIMITS | %<br>REC # | RECOVERY<br>LIMITS |
|-----------------------|------------------|------------|----------------|---------------------|------------|--------------------|
| 13C-4-MCB             | 194/196          |            |                | 2.66-3.60           |            | 25-150             |
| 13C-44'-DiCB          | 234/236          |            |                | 1.33-1.81           |            | 25-150             |
| 13C-244'-TriCB        | 268/270          |            |                | 0.88-1.20           |            | 25-150             |
| 13C-33'44'-TetCB      | 302/304          |            |                | 0.65-0.89           |            | 24-169             |
| 13C-233'44'-PeCB      | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-2344'5-PeCB       | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-23'44'5-PeCB      | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-2'344'5-PeCB      | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-33'44'5-PeCB      | 338/340          |            |                | 1.32-1.78           |            | 21-178             |
| 13C-233'44'5-HxCB     | 372/374          |            |                | 1.05-1.43           |            | 26-152             |
| 13C-233'44'5'-HxCB    | 372/374          |            |                | 1.05-1.43           |            | 26-152             |
| 13C-23'44'55'-HxCB    | 372/374          |            |                | 1.05-1.43           |            | 26-152             |
| 13C-33'44'55'-HxCB    | 372/374          |            |                | 1.05-1.43           |            | 26-152             |
| 13C-22'33'44'5'-HpCB  | 408/410          |            |                | 0.88-1.20           |            | 23-143             |
| 13C-22'344'55'-HpCB   | 408/410          |            |                | 0.88-1.20           |            | 23-143             |
| 13C-233'44'55'-HpCB   | 408/410          |            |                | 0.88-1.20           |            | 23-143             |
| 13C-22'33'55'66'-OCB  | 440/442          |            |                | 0.76-1.02           |            | 25-150             |
| 13C-22'33'455'66'-NCB | 474/476          |            |                | 1.14-1.54           |            | 25-150             |
| 13C-DeCB              | 510/512          |            |                | 0.99-1.35           |            | 25-150             |

| CLEAN-UP<br>STANDARD | SELECTED<br>IONS | PEAK<br>RT | ION<br>RATIO # | ION RATIO<br>LIMITS | %<br>REC # | RECOVERY<br>LIMITS |
|----------------------|------------------|------------|----------------|---------------------|------------|--------------------|
| 13C-344'5-TetCB      | 302/304          |            |                | 0.65-0.89           |            | 35-197             |
| 13C-233'55'-PeCB     | 338/340          |            |                | 1.32-1.78           |            | 35-197             |

| RECOVERY<br>STANDARD | SELECTED<br>IONS | PEAK<br>RT | ION<br>RATIO # | ION RATIO<br>LIMITS | %<br>REC # | RECOVERY<br>LIMITS |
|----------------------|------------------|------------|----------------|---------------------|------------|--------------------|
| 13C-22'55'-TetCB     | 302/304          |            |                | 0.65-0.89           |            | 50-200             |
| 13C-22'455'-PeCB     | 338/340          |            |                | 1.32-1.78           |            | 50-200             |
| 13C-22'344'5'-HxCB   | 372/374          |            |                | 1.05-1.43           |            | 50-200             |
| 13C-22'33'55'6-HpCB  | 408/410          |            |                | 0.88-1.20           |            | 50-200             |

# - Column to be used to flag values outside QC limits.

## EPA SAMPLE NO. .

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|  |
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Date Analyzed: \_\_\_\_\_

[illegible]



3PCB-1  
PCB INITIAL CALIBRATION RESPONSE FACTOR SUMMARY  
HRGC/HRMS

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_  
 Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_  
 GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) Instrument ID: \_\_\_\_\_  
 Init. Calib. Date(s): \_\_\_\_\_  
 Init. Calib. Times: \_\_\_\_\_

| NATIVE ANALYTES<br>VS. INTERNAL STDS | CC1 | CC2 | RRF (N)<br>CC3 | CC4 | CC5 | RRF | %RSD |
|--------------------------------------|-----|-----|----------------|-----|-----|-----|------|
| 33'44'-TetCB                         |     |     |                |     |     |     |      |
| 233'44'-PeCB                         |     |     |                |     |     |     |      |
| 2344'5-PeCB                          |     |     |                |     |     |     |      |
| 23'44'5-PeCB                         |     |     |                |     |     |     |      |
| 2'344'5-PeCB                         |     |     |                |     |     |     |      |
| 33'44'5-PeCB                         |     |     |                |     |     |     |      |
| 233'44'5-HxCB                        |     |     |                |     |     |     |      |
| 233'44'5'-HxCB                       |     |     |                |     |     |     |      |
| 23'44'55'-HxCB                       |     |     |                |     |     |     |      |
| 33'44'55'-HxCB                       |     |     |                |     |     |     |      |
| 22'33'44'5'-HpCB                     |     |     |                |     |     |     |      |
| 22'344'55'-HpCB                      |     |     |                |     |     |     |      |
| 233'44'55'-HpCB                      |     |     |                |     |     |     |      |
| TOTAL HOMOLOGUE<br>NATIVE ANALYTES   |     |     |                |     |     |     |      |
| 2-MCB                                |     |     |                |     |     |     |      |
| 23-DiCB                              |     |     |                |     |     |     |      |
| 245-TriCB                            |     |     |                |     |     |     |      |
| 22'46-TetCB                          |     |     |                |     |     |     |      |
| 22'345'-PeCB                         |     |     |                |     |     |     |      |
| 22'44'56'-HxCB                       |     |     |                |     |     |     |      |
| 22'34'566'-HpCB                      |     |     |                |     |     |     |      |
| 22'33'4566'-OCB                      |     |     |                |     |     |     |      |
| 22'33'44'566'-NCE                    |     |     |                |     |     |     |      |
| DCB                                  |     |     |                |     |     |     |      |
| INTERNAL STANDARDS                   |     |     |                |     |     |     |      |
| 13C-4-MCB                            |     |     |                |     |     |     |      |
| 13C-44'-DiCB                         |     |     |                |     |     |     |      |
| 13C-244'-TriCB                       |     |     |                |     |     |     |      |
| 13C-33'44'-TetCB                     |     |     |                |     |     |     |      |
| 13C-233'44'-PeCB                     |     |     |                |     |     |     |      |
| 13C-2344'5-PeCB                      |     |     |                |     |     |     |      |
| 13C-23'44'5-PeCB                     |     |     |                |     |     |     |      |
| 13C-2'344'5-PeCB                     |     |     |                |     |     |     |      |
| 13C-33'44'5-PeCB                     |     |     |                |     |     |     |      |
| 13C-233'44'5-HxCB                    |     |     |                |     |     |     |      |
| 13C-233'44'5'-HxCB                   |     |     |                |     |     |     |      |
| 13C-23'44'55'-HxCB                   |     |     |                |     |     |     |      |
| 13C-33'44'55'-HxCB                   |     |     |                |     |     |     |      |
| 13C-22'33'44'5'-HpCB                 |     |     |                |     |     |     |      |
| 13C-22'344'55'-HpCB                  |     |     |                |     |     |     |      |
| 13C-233'44'55'-HpCB                  |     |     |                |     |     |     |      |
| 13C-22'33'55'66'-OCB                 |     |     |                |     |     |     |      |
| 13C-22'33'455'66'-NCE                |     |     |                |     |     |     |      |
| 13C-DeCB                             |     |     |                |     |     |     |      |
| RECOVERY STANDARDS                   |     |     |                |     |     |     |      |
| 13C-22'55'-TetCB                     |     |     |                |     |     |     |      |
| 13C-22'455'-PeCB                     |     |     |                |     |     |     |      |
| 13C-22'344'5'-HxCB                   |     |     |                |     |     |     |      |
| 13C-22'33'55'-HpCB                   |     |     |                |     |     |     |      |
| CLEAN-UP STANDARDS                   |     |     |                |     |     |     |      |
| 13C-344'5-TetCB                      |     |     |                |     |     |     |      |
| 13C-233'55'-PeCB                     |     |     |                |     |     |     |      |

QC Limits: %RSD must be less than or equal to 20.0%.

FORM III PCB-1

6/98

3PCB-2  
PCB INITIAL CALIBRATION ION ABUNDANCE RATIO SUMMARY  
HRCG/HRMS

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_  
Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_  
GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) Instrument ID: \_\_\_\_\_  
Init. Calib. Date(s): \_\_\_\_\_  
Init. Calib. Times: \_\_\_\_\_

| NATIVE ANALYTES<br>VS. INTERNAL STDS | SELECTED<br>IONS | ION ABUNDANCE RATIO |     |     |     |     | FLAG | QC<br>LIMITS |
|--------------------------------------|------------------|---------------------|-----|-----|-----|-----|------|--------------|
|                                      |                  | CC1                 | CC2 | CC3 | CC4 | CC5 |      |              |
| 33'44'-TetCB                         | 290/292          |                     |     |     |     |     |      | 0.65-0.89    |
| 233'44'-PeCB                         | 326/328          |                     |     |     |     |     |      | 1.32-1.78    |
| 2344'5-PeCB                          | 326/328          |                     |     |     |     |     |      | 1.32-1.78    |
| 23'44'5-PeCB                         | 326/328          |                     |     |     |     |     |      | 1.32-1.78    |
| 2'344'5-PeCB                         | 326/328          |                     |     |     |     |     |      | 1.32-1.78    |
| 33'44'5-PeCB                         | 326/328          |                     |     |     |     |     |      | 1.32-1.78    |
| 233'44'5-HxCB                        | 360/362          |                     |     |     |     |     |      | 1.05-1.43    |
| 233'44'5'-HxCB                       | 360/362          |                     |     |     |     |     |      | 1.05-1.43    |
| 23'44'55'-HxCB                       | 360/362          |                     |     |     |     |     |      | 1.05-1.43    |
| 33'44'55'-HxCB                       | 360/362          |                     |     |     |     |     |      | 1.05-1.43    |
| 22'33'44'5'-HpCB                     | 394/396          |                     |     |     |     |     |      | 0.88-1.20    |
| 22'344'55'-HpCB                      | 394/396          |                     |     |     |     |     |      | 0.88-1.20    |
| 233'44'55'-HpCB                      | 394/396          |                     |     |     |     |     |      | 0.88-1.20    |
| TOTAL HOMOLOGUE<br>NATIVE ANALYTES   |                  |                     |     |     |     |     |      |              |
| 2-MCB                                | 188/190          |                     |     |     |     |     |      | 2.66-3.60    |
| 23-DCB                               | 222/224          |                     |     |     |     |     |      | 1.33-1.81    |
| 245-TrICB                            | 256/258          |                     |     |     |     |     |      | 0.87-1.18    |
| 22'46-TetCB                          | 290/292          |                     |     |     |     |     |      | 0.65-0.89    |
| 22'345-PeCB                          | 326/328          |                     |     |     |     |     |      | 1.32-1.78    |
| 22'44'56'-HxCB                       | 360/362          |                     |     |     |     |     |      | 1.05-1.43    |
| 22'34'566'-HpCB                      | 394/396          |                     |     |     |     |     |      | 0.88-1.20    |
| 22'33'4566'-OCB                      | 428/430          |                     |     |     |     |     |      | 0.76-1.02    |
| 22'33'44'566'-NCB                    | 464/466          |                     |     |     |     |     |      | 1.14-1.54    |
| DCB                                  | 498/500          |                     |     |     |     |     |      | 0.99-1.35    |
| INTERNAL STANDARDS                   |                  |                     |     |     |     |     |      |              |
| 13C-4-MCB                            | 194/196          |                     |     |     |     |     |      | 2.66-3.60    |
| 13C-44'-DiCB                         | 234/236          |                     |     |     |     |     |      | 1.33-1.81    |
| 13C-244'-TriCB                       | 268/270          |                     |     |     |     |     |      | 0.88-1.20    |
| 13C-33'44'-TetCB                     | 302/304          |                     |     |     |     |     |      | 0.65-0.89    |
| 13C-233'44'-PeCB                     | 338/340          |                     |     |     |     |     |      | 1.32-1.78    |
| 13C-2344'5-PeCB                      | 338/340          |                     |     |     |     |     |      | 1.32-1.78    |
| 13C-23'44'5-PeCB                     | 338/340          |                     |     |     |     |     |      | 1.32-1.78    |
| 13C-2'344'-PeCB                      | 338/340          |                     |     |     |     |     |      | 1.32-1.78    |
| 13C-33'44'5-PeCB                     | 338/340          |                     |     |     |     |     |      | 1.32-1.20    |
| 13C-233'44'5-HxCB                    | 372/374          |                     |     |     |     |     |      | 1.05-1.43    |
| 13C-233'44'5'-HxCB                   | 372/374          |                     |     |     |     |     |      | 1.05-1.43    |
| 13C-23'44'55'-HxCB                   | 372/374          |                     |     |     |     |     |      | 1.05-1.43    |
| 13C-33'44'55'-HxCB                   | 372/374          |                     |     |     |     |     |      | 1.05-1.43    |
| 13C-22'33'44'5'-HpCB                 | 408/410          |                     |     |     |     |     |      | 0.88-1.20    |
| 13C-22'344'55'-HpCB                  | 408/410          |                     |     |     |     |     |      | 0.88-1.20    |
| 13C-233'44'55'-HpCB                  | 408/410          |                     |     |     |     |     |      | 0.88-1.20    |
| 13C-22'33'55'66'-OCB                 | 440/442          |                     |     |     |     |     |      | 0.76-1.02    |
| 13C-22'33'455'66'-NCB                | 474/476          |                     |     |     |     |     |      | 1.14-1.54    |
| 13C-DeCB                             | 510/512          |                     |     |     |     |     |      | 0.99-1.35    |
| RECOVERY STANDARDS                   |                  |                     |     |     |     |     |      |              |
| 13C-22'55'-TetCC                     | 302/304          |                     |     |     |     |     |      | 0.65-0.89    |
| 13C-22'455'-PeCB                     | 338/340          |                     |     |     |     |     |      | 1.32-1.78    |
| 13C-22'344'5'-HxCB                   | 268/270          |                     |     |     |     |     |      | 1.05-1.43    |
| 13C-22'33'55'6-HpCB                  | 408/410          |                     |     |     |     |     |      | 0.88-1.20    |
| CLEAN-UP STANDARDS                   |                  |                     |     |     |     |     |      |              |
| 13C-344'5-TetCB                      | 302/304          |                     |     |     |     |     |      | 0.65-0.89    |
| 13C-233'55'-PeCB                     | 338/340          |                     |     |     |     |     |      | 1.32-1.78    |

QC Limits: %RSD must be less than or equal to 20.0%  
FORM III PCB-2

4PCB  
PCB ANALYTICAL SEQUENCE SUMMARY  
HRGC/HRMS

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_

Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_

GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) Instrument ID: \_\_\_\_\_

Init. Calib. Date(s): \_\_\_\_\_

Init. Calib. Times: \_\_\_\_\_

THE ANALYTICAL SEQUENCE OF STANDARDS, SAMPLES, BLANKS, SPIKES, AND  
 DUPLICATES IS AS FOLLOWS:

[illegible]

5PCB-1  
PCB CONTINUING CALIBRATION SUMMARY  
HRGC/HRMS

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_  
Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_  
GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) Instrument ID: \_\_\_\_\_  
Date Analyzed: \_\_\_\_\_ Time Analyzed: \_\_\_\_\_ Lab File ID: \_\_\_\_\_  
Init. Calib. Date(s): \_\_\_\_\_

| NATIVE ANALYTES                 | SELECTED IONS | RRF | MEAN RRF | %D | RRF FLAG | ION RATIO | ION FLAG | QC LIMITS |
|---------------------------------|---------------|-----|----------|----|----------|-----------|----------|-----------|
| 33'44'-TetCB                    | 290/292       |     |          |    |          |           |          | 0.65-0.89 |
| 233'44'-PeCB                    | 326/328       |     |          |    |          |           |          | 1.32-1.78 |
| 2344'5'-PeCB                    | 326/328       |     |          |    |          |           |          | 1.32-1.78 |
| 23'44'5'-PeCB                   | 326/328       |     |          |    |          |           |          | 1.32-1.78 |
| 2'344'5'-PeCB                   | 326/328       |     |          |    |          |           |          | 1.32-1.78 |
| 33'44'5'-PeCB                   | 326/328       |     |          |    |          |           |          | 1.32-1.78 |
| 233'44'5'-HxCB                  | 360/362       |     |          |    |          |           |          | 1.05-1.43 |
| 233'44'5'-HxCB                  | 360/362       |     |          |    |          |           |          | 1.05-1.43 |
| 23'44'55'-HxCB                  | 360/362       |     |          |    |          |           |          | 1.05-1.43 |
| 33'44'55'-HxCB                  | 360/362       |     |          |    |          |           |          | 1.05-1.43 |
| 22'33'44'5'-HpCB                | 394/396       |     |          |    |          |           |          | 0.88-1.20 |
| 22'344'55'-HpCB                 | 394/396       |     |          |    |          |           |          | 0.88-1.20 |
| 233'44'55'-HpCB                 | 394/396       |     |          |    |          |           |          | 0.88-1.20 |
| TOTAL HOMOLOGUE NATIVE ANALYTES |               |     |          |    |          |           |          |           |
| 2-MCB                           | 188/190       |     |          |    |          |           |          | 2.66-3.60 |
| 23-DiCB                         | 222/224       |     |          |    |          |           |          | 1.33-1.81 |
| 245-TrCB                        | 256/258       |     |          |    |          |           |          | 0.87-1.18 |
| 22'46'-TetCB                    | 290/292       |     |          |    |          |           |          | 0.65-0.89 |
| 22'345'-PeCB                    | 326/328       |     |          |    |          |           |          | 1.32-1.78 |
| 22'44'56'-HxCB                  | 360/362       |     |          |    |          |           |          | 1.05-1.43 |
| 22'34'566'-HpCB                 | 394/396       |     |          |    |          |           |          | 0.88-1.20 |
| 22'33'4566'-OCB                 | 428/430       |     |          |    |          |           |          | 0.76-1.02 |
| 22'33'455'66'-NCB               | 464/466       |     |          |    |          |           |          | 1.14-1.54 |
| DecB                            | 498/500       |     |          |    |          |           |          | 0.99-1.35 |
| INTERNAL STANDARDS              |               |     |          |    |          |           |          |           |
| 13C-4-MCB                       | 194/196       |     |          |    |          |           |          | 2.66-3.60 |
| 13C-44'-DiCB                    | 234/236       |     |          |    |          |           |          | 1.33-1.81 |
| 13C-244'-TriCB                  | 268/270       |     |          |    |          |           |          | 0.88-1.20 |
| 13C-33'44'-TetCB                | 302/304       |     |          |    |          |           |          | 0.65-0.89 |
| 13C-233'44'-PeCB                | 336/338       |     |          |    |          |           |          | 1.32-1.78 |
| 13C-2344'5'-PeCB                | 336/338       |     |          |    |          |           |          | 1.32-1.78 |
| 13C-23'44'5'-PeCB               | 336/338       |     |          |    |          |           |          | 1.32-1.78 |
| 13C-2'344'5'-PeCB               | 336/338       |     |          |    |          |           |          | 1.32-1.78 |
| 13C-33'44'5'-PeCB               | 336/338       |     |          |    |          |           |          | 1.32-1.78 |
| 13C-233'44'5'-HxCB              | 372/374       |     |          |    |          |           |          | 1.05-1.43 |
| 13C-233'44'5'-HxCB              | 372/374       |     |          |    |          |           |          | 1.05-1.43 |
| 13C-23'44'55'-HxCB              | 372/374       |     |          |    |          |           |          | 1.05-1.43 |
| 13C-33'44'55'-HxCB              | 372/374       |     |          |    |          |           |          | 1.05-1.43 |
| 13C-22'33'44'5'-HpCB            | 408/410       |     |          |    |          |           |          | 0.88-1.02 |
| 13C-22'344'55'-HpCB             | 408/410       |     |          |    |          |           |          | 0.88-1.20 |
| 13C-233'44'55'-HpCB             | 408/410       |     |          |    |          |           |          | 0.88-1.20 |
| 13C-22'33'55'66'-OCB            | 440/442       |     |          |    |          |           |          | 0.76-1.02 |
| 13C-22'33'455'66'-NCB           | 474/476       |     |          |    |          |           |          | 1.14-1.54 |
| 13C-DecB                        | 510/512       |     |          |    |          |           |          | 0.99-1.35 |
| RECOVERY STANDARDS              |               |     |          |    |          |           |          |           |
| 13C-22'55'-TetCB                | 302/304       |     |          |    |          |           |          | 0.65-0.89 |
| 13C-22'455'-PeCB                | 336/338       |     |          |    |          |           |          | 1.32-1.78 |
| 13C-22'344'5'-HxCB              | 372/374       |     |          |    |          |           |          | 1.05-1.43 |
| 13C-22'33'55'6-HpCB             | 408/410       |     |          |    |          |           |          | 0.88-1.20 |
| CLEAN-UP STANDARDS              |               |     |          |    |          |           |          |           |
| 13C-344'5'-TetCB                | 302/304       |     |          |    |          |           |          | 0.65-0.89 |
| 13C-233'55'-PeCB                | 336/338       |     |          |    |          |           |          | 1.32-1.78 |

%D must be less or equal to 30.0% for all analytes.  
FORM V PCB-1

5PCB-2  
PCB CONTINUING CALIBRATION RETENTION TIME SUMMARY  
HRGC/HRMS

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_  
 Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_  
 GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) Instrument ID: \_\_\_\_\_  
 Date Analyzed: \_\_\_\_\_ Time Analyzed: \_\_\_\_\_ Lab File ID: \_\_\_\_\_  
 Init. Calib. Date(s): \_\_\_\_\_

| NATIVE ANALYTES       | RRT | RT |
|-----------------------|-----|----|
| =====                 |     |    |
| 33'44'-TetCB          |     |    |
| 233'44'-PeCB          |     |    |
| 2344'5'-PeCB          |     |    |
| 23'44'5'-PeCB         |     |    |
| 2'344'5'-PeCB         |     |    |
| 33'44'5'-PeCB         |     |    |
| 233'44'5'-HxCB        |     |    |
| 233'44'5'-HxCB        |     |    |
| 23'44'55'-HxCB        |     |    |
| 33'44'55'-HxCB        |     |    |
| 22'33'44'5'-HpCB      |     |    |
| 22'344'55'-HpCB       |     |    |
| 233'44'55'-HpCB       |     |    |
| TOTAL HOMOLOGUE       |     |    |
| NATIVE ANALYTES       |     |    |
| =====                 |     |    |
| 2-MCB                 |     |    |
| 23-DiCB               |     |    |
| 245-TriCB             |     |    |
| 22'46'-TetCB          |     |    |
| 22'345'-PeCB          |     |    |
| 22'44'56'-HxCB        |     |    |
| 22'34'566'-HpCB       |     |    |
| 22'33'4566'-OCB       |     |    |
| 22'33'455'66'-NCE     |     |    |
| DeCB                  |     |    |
| INTERNAL STANDARDS    |     |    |
| =====                 |     |    |
| 13C-4-MCB             |     |    |
| 13C-44'-DiCB          |     |    |
| 13C-244'-TriCB        |     |    |
| 13C-33'44'-TetCB      |     |    |
| 13C-233'44'-PeCB      |     |    |
| 13C-2344'5'-PeCB      |     |    |
| 13C-23'44'5'-PeCB     |     |    |
| 13C-2'344'5'-PeCB     |     |    |
| 13C-33'44'5'-PeCB     |     |    |
| 13C-233'44'5'-HxCB    |     |    |
| 13C-233'44'5'-HxCB    |     |    |
| 13C-23'44'55'-HxCB    |     |    |
| 13C-33'44'55'-HxCB    |     |    |
| 13C-22'33'44'5'-HpCB  |     |    |
| 13C-22'344'55'-HpCB   |     |    |
| 13C-233'44'55'-HpCB   |     |    |
| 13C-22'33'55'66'-OCB  |     |    |
| 13C-22'33'455'66'-NCE |     |    |
| 13C-DeCB              |     |    |
| RECOVERY STANDARDS    |     |    |
| =====                 |     |    |
| 13C-22'55'-TetCB      | NA  |    |
| 13C-22'455'-PeCB      | NA  |    |
| 13C-22'344'5'-HxCB    | NA  |    |
| 13C-22'33'55'6-HpCB   | NA  |    |
| CLEAN-UP STANDARDS    |     |    |
| =====                 |     |    |
| 13C-344'5'-TetCB      |     |    |
| 13C-233'55'-PeCB      |     |    |

RRT = (RT of analyte)/(RT of appropriate internal standard)  
FORM V PCB-2

6PCB-1  
PCB WINDOW DEFINING MIX SUMMARY  
HRGC/HRMS

EPA SAMPLE NO.

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_

Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_

GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ (mm) Lab File ID: \_\_\_\_\_

Instrument ID: \_\_\_\_\_ Date Analyzed: \_\_\_\_\_

Time Analyzed: \_\_\_\_\_

| CONGENER | RT<br>FIRST<br>ELUTING | RT<br>LAST<br>ELUTING |
|----------|------------------------|-----------------------|
| MCB      |                        |                       |
| DiCB     |                        |                       |
| TriCB    |                        |                       |
| TetCB    |                        |                       |
| PeCB     |                        |                       |
| HxCB     |                        |                       |
| HpCB     |                        |                       |
| OCB      |                        |                       |
| NCB      |                        |                       |
| DeCB     |                        |                       |

|       |  |  |
|-------|--|--|
| MCB   |  |  |
| DiCB  |  |  |
| TriCB |  |  |
| TetCB |  |  |
| PeCB  |  |  |
| HxCB  |  |  |
| HpCB  |  |  |
| OCB   |  |  |
| NCB   |  |  |
| DeCB  |  |  |

7PCB-1  
PCB INITIAL PRECISION AND RECOVERY (IPR)  
HRGC/HRMS

Lab Name: \_\_\_\_\_ Contract No.: \_\_\_\_\_  
 Lab Code: \_\_\_\_\_ Case No: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No: \_\_\_\_\_  
 Matrix (soil/sediment/aqueous/tissue): \_\_\_\_\_  
 Extraction Date: \_\_\_\_\_ Shift: \_\_\_\_\_  
 IPR1 Data Filename: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ Time: \_\_\_\_\_  
 IPR2 Data Filename: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ Time: \_\_\_\_\_  
 IPR3 Data Filename: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ Time: \_\_\_\_\_  
 IPR4 Data Filename: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ Time: \_\_\_\_\_

ALL CONCENTRATIONS REPORTED ON THIS FORM ARE CONCENTRATIONS IN EXTRACT.

|                  | SPIKE<br>CONC.<br>(ng/ml) | IPR1<br>CONC.<br>FOUND<br>(ng/ml) | IPR2<br>CONC.<br>FOUND<br>(ng/ml) | IPR3<br>CONC.<br>FOUND<br>(ng/ml) | IPR4<br>CONC.<br>FOUND<br>(ng/ml) | X (1)<br>(ng/ml) | s<br>(ng/ml) |
|------------------|---------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------|--------------|
| NATIVE ANALYTES  |                           |                                   |                                   |                                   |                                   |                  |              |
| 33'44'-TetCB     | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 233'44'-PeCB     | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 2344'5-PeCB      | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 23'44'5-PeCB     | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 2'344'5-PeCB     | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 33'44'5-PeCB     | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 233'44'5-HxCB    | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 233'44'5'-HxCB   | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 23'44'55'-HxCB   | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 33'44'55'-HxCB   | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 22'33'44'5'-HxCB | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 22'344'55'-HxCB  | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 233'44'55'-HxCB  | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| TOTAL HOMOLOGUES |                           |                                   |                                   |                                   |                                   |                  |              |
| MCB              | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| DiCB             | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| TriCB            | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| TetCB            | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| PeCB             | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| HxCB             | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| HpCB             | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| OCB              | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| NCB              | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| DeCB             | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |

(1) X = average concentration; s = standard deviation of the concentration. Contract-required limits for X and s are specified in Table 4, Region I Technical Specification.

7PCB-2  
PCB INITIAL PRECISION AND RECOVERY (IPR)  
HRGC/HRMS

Lab Name: \_\_\_\_\_ Contract No.: \_\_\_\_\_  
 Lab Code: \_\_\_\_\_ Case No: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No: \_\_\_\_\_  
 Matrix (soil/sediment/aqueous/tissue): \_\_\_\_\_  
 Extraction Date: \_\_\_\_\_ Shift: \_\_\_\_\_  
 IPR1 Data Filename: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ Time: \_\_\_\_\_  
 IPR2 Data Filename: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ Time: \_\_\_\_\_  
 IPR3 Data Filename: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ Time: \_\_\_\_\_  
 IPR4 Data Filename: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ Time: \_\_\_\_\_

ALL CONCENTRATIONS REPORTED ON THIS FORM ARE CONCENTRATIONS IN EXTRACT.

| LABELED ANALYTES      | SPIKE<br>CONC.<br>(ng/ml) | IPR1<br>CONC.<br>FOUND<br>(ng/ml) | IPR2<br>CONC.<br>FOUND<br>(ng/ml) | IPR3<br>CONC.<br>FOUND<br>(ng/ml) | IPR4<br>CONC.<br>FOUND<br>(ng/ml) | X (1)<br>(ng/ml) | s<br>(ng/ml) |
|-----------------------|---------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------|--------------|
| 13C-4-MCB             | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-44'-DiCB          | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-244'-TriCB        | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-33'44'-TetCB      | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-233'44'-PeCB      | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-2344'5-PeCB       | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-23'44'5-PeCB      | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-2'344'5-PeCB      | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-33'44'5-PeCB      | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-233'44'5-HxCB     | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-233'44'5'-HxCB    | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-23'44'55'-HxCB    | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-33'44'55'-HxCB    | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-22'33'44'5'-HpCB  | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-22'344'55'-HpCB   | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-233'44'55'-HpCB   | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-22'33'55'66'-OCB  | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-22'33'455'66'-NCB | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-DeCB              | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-344'5-TetCB       | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |
| 13C-233'55'-PeCB      | _____                     | _____                             | _____                             | _____                             | _____                             | _____            | _____        |

(1) X = average concentration; s = standard deviation of the concentration. Contract-required limits for X and s are specified in Table 4, Region I Technical Specification.



## 8PCB

## PCB CALIBRATION VERIFICATION (VER)

## HRGC/HRMS

Lab Name: \_\_\_\_\_ Contract No.: \_\_\_\_\_  
 Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_  
 GC Column: \_\_\_\_\_ ID: \_\_\_\_\_ Instrument ID: \_\_\_\_\_  
 VER Data Filename: \_\_\_\_\_ Analysis Date: \_\_\_\_\_ Time: \_\_\_\_\_  
 Initial Calibration Analysis Date(s): \_\_\_\_\_

|                         | M/Z's<br>FORMING<br>RATIO (1) | ION<br>ABUNDANCE<br>RATIO | QC<br>LIMITS (2) | CONC.<br>FOUND<br>(ng/ml) | CONC.<br>RANGE (3) |
|-------------------------|-------------------------------|---------------------------|------------------|---------------------------|--------------------|
| <b>NATIVE ANALYTES</b>  |                               |                           |                  |                           |                    |
| 33'44'-TetCB            | 290/292                       | _____                     | 0.65-0.89        | _____                     | 5-15               |
| 233'44'-PeCB            | 326/328                       | _____                     | 1.32-1.78        | _____                     | 25-75              |
| 2344'5-PeCB             | 326/328                       | _____                     | 1.32-1.78        | _____                     | 25-75              |
| 23'44'5-PeCB            | 326/328                       | _____                     | 1.32-1.78        | _____                     | 25-75              |
| 2'344'5-PeCB            | 326/328                       | _____                     | 1.32-1.78        | _____                     | 25-75              |
| 33'44'5-PeCB            | 326/328                       | _____                     | 1.32-1.78        | _____                     | 25-75              |
| 233'44'5-HxCB           | 360/362                       | _____                     | 1.05-1.43        | _____                     | 50-150             |
| 233'44'5'-HxCB          | 360/362                       | _____                     | 1.05-1.43        | _____                     | 50-150             |
| 23'44'55'-HxCB          | 360/362                       | _____                     | 1.05-1.43        | _____                     | 50-150             |
| 33'44'55'-HxCB          | 360/362                       | _____                     | 1.05-1.43        | _____                     | 50-150             |
| 22'33'44'5'-HpCB        | 394/396                       | _____                     | 0.88-1.20        | _____                     | 50-150             |
| 22'344'55'-HpCB         | 394/396                       | _____                     | 0.88-1.20        | _____                     | 50-150             |
| 233'44'55'-HpCB         | 394/396                       | _____                     | 0.88-1.20        | _____                     | 50-150             |
| <b>TOTAL HOMOLOGUES</b> |                               |                           |                  |                           |                    |
| MCB                     |                               |                           |                  |                           | 5-15               |
| DiCB                    |                               |                           |                  |                           | 5-15               |
| TriCB                   |                               |                           |                  |                           | 5-15               |
| TetCB                   |                               |                           |                  |                           | 25-75              |
| PeCB                    |                               |                           |                  |                           | 25-75              |
| HxCB                    |                               |                           |                  |                           | 25-75              |
| HpCB                    |                               |                           |                  |                           | 25-75              |
| OCB                     |                               |                           |                  |                           | 25-75              |
| NCB                     |                               |                           |                  |                           | 25-75              |
| DeCB                    |                               |                           |                  |                           | 25-75              |
| <b>LABELED ANALYTES</b> |                               |                           |                  |                           |                    |
| 13C-4-MCB               | 194/196                       | _____                     | 2.66-3.60        | _____                     | 50-150             |
| 13C-44'-DiCB            | 234/236                       | _____                     | 1.33-1.81        | _____                     | 50-150             |
| 13C-244'-TriCB          | 268/270                       | _____                     | 0.88-1.20        | _____                     | 50-150             |
| 13C-33'44'-TetCB        | 302/304                       | _____                     | 0.65-0.89        | _____                     | 50-150             |
| 13C-233'44'-PeCB        | 338/340                       | _____                     | 1.32-1.78        | _____                     | 50-150             |
| 13C-2344'5-PeCB         | 338/340                       | _____                     | 1.32-1.78        | _____                     | 50-150             |
| 13C-23'44'5-PeCB        | 338/340                       | _____                     | 1.32-1.78        | _____                     | 50-150             |
| 13C-2'344'5-PeCB        | 338/340                       | _____                     | 1.32-1.78        | _____                     | 50-150             |
| 13C-33'44'5-PeCB        | 338/340                       | _____                     | 1.32-1.78        | _____                     | 50-150             |
| 13C-233'44'5-HxCB       | 372/374                       | _____                     | 1.05-1.43        | _____                     | 50-150             |
| 13C-233'44'5'-HxCB      | 372/374                       | _____                     | 1.05-1.43        | _____                     | 50-150             |
| 13C-23'44'55'-HxCB      | 372/374                       | _____                     | 1.05-1.43        | _____                     | 50-150             |
| 13C-33'44'55'-HxCB      | 372/374                       | _____                     | 1.05-1.43        | _____                     | 50-150             |
| 13C-22'33'44'5'-HpCB    | 408/410                       | _____                     | 0.88-1.20        | _____                     | 50-150             |
| 13C-22'344'55'-HpCB     | 408/410                       | _____                     | 0.88-1.20        | _____                     | 50-150             |
| 13C-233'44'55'-HpCB     | 408/410                       | _____                     | 0.88-1.20        | _____                     | 50-150             |
| 13C-22'33'55'66'-OCB    | 440/442                       | _____                     | 0.76-1.02        | _____                     | 50-150             |
| 13C-22'33'455'66'-NCB   | 474/476                       | _____                     | 1.14-1.54        | _____                     | 50-150             |
| 13C-DeCB                | 510/512                       | _____                     | 0.99-1.35        | _____                     | 100-300            |
| 13C-344'5-TetCB         | 302/304                       | _____                     | 0.65-0.89        | _____                     | 100-300            |
| 13C-233'55'-PeCB        | 338/340                       | _____                     | 1.32-1.78        | _____                     | 500-1500           |

(1) Table 6, Region I Technical Specification for m/z specifications.

(2) Ion Abundance Ratio Control Limits as specified in Table 6, Region I Technical Specification.

(3) Contract required concentration range as specified in Table 4, Region I Technical Specification.

FORM VIII PCB

9PCB  
PCB DUPLICATE SAMPLE SUMMARY  
HRGC/HRMS

EPA SAMPLE NO. \_\_\_\_\_

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_

Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_

Matrix: \_\_\_\_\_ (Soil/Sediment/Aqueous/Tissue)

CONCENTRATION UNITS: (ng/L or ug/Kg) \_\_\_\_\_

| ANALYTE          | SAMPLE<br>CONCENTRATION | DUPLICATE<br>CONCENTRATION | RPD # | QC<br>LIMITS |
|------------------|-------------------------|----------------------------|-------|--------------|
| 33'44'-TetCB     |                         |                            |       | 50           |
| 233'44'-PeCB     |                         |                            |       | 50           |
| 2344'5-PeCB      |                         |                            |       | 50           |
| 23'44'5-PeCB     |                         |                            |       | 50           |
| 2'344'5-PeCB     |                         |                            |       | 50           |
| 33'44'5-PeCB     |                         |                            |       | 50           |
| 233'44'5-HxCB    |                         |                            |       | 50           |
| 233'44'5'-HxCB   |                         |                            |       | 50           |
| 23'44'55'-HxCB   |                         |                            |       | 50           |
| 33'44'55'-HxCB   |                         |                            |       | 50           |
| 22'33'44'5'-HpCB |                         |                            |       | 50           |
| 22'344'55'-HpCB  |                         |                            |       | 50           |
| 233'44'55'-HpCB  |                         |                            |       | 50           |
| Total MCB        |                         |                            |       | 50           |
| Total DiCB       |                         |                            |       | 50           |
| Total TriCB      |                         |                            |       | 50           |
| Total TetCB      |                         |                            |       | 50           |
| Total PeCB       |                         |                            |       | 50           |
| Total HxCB       |                         |                            |       | 50           |
| Total HpCB       |                         |                            |       | 50           |
| Total OCB        |                         |                            |       | 50           |
| Total NCB        |                         |                            |       | 50           |
| Total DeCB       |                         |                            |       | 50           |
| Total PCB        |                         |                            |       | 50           |

If an analyte is not detected in either analysis, enter 0 (zero) as the concentration.

# Column to be used to flag values outside QC limits.

QC limits are advisory

10PCB  
PCB SPIKED SAMPLE SUMMARY  
HRGC/HRMS

EPA SAMPLE NO.

Lab Name: \_\_\_\_\_ Contract: \_\_\_\_\_

Lab Code: \_\_\_\_\_ Case No.: \_\_\_\_\_ DAS No.: \_\_\_\_\_ SDG No.: \_\_\_\_\_

Matrix: \_\_\_\_\_ (Soil/Sediment/Aqueous/Tissue)

CONCENTRATION UNITS: (ng/L or ug/Kg) \_\_\_\_\_

| ANALYTE          | SPIKE<br>ADDED<br>(ng) | SPIKED -<br>SAMPLE<br>CONCENTRATION | SAMPLE<br>CONCENTRATION | #<br>REC # | QC<br>LIMITS |
|------------------|------------------------|-------------------------------------|-------------------------|------------|--------------|
| 33'44'-TetCB     |                        |                                     |                         |            | 40-160       |
| 233'44'-PeCB     |                        |                                     |                         |            | 40-160       |
| 2344'5-PeCB      |                        |                                     |                         |            | 40-160       |
| 23'44'5-PeCB     |                        |                                     |                         |            | 40-160       |
| 2'344'5-PeCB     |                        |                                     |                         |            | 40-160       |
| 33'44'5-PeCB     |                        |                                     |                         |            | 40-160       |
| 233'44'5-HxCB    |                        |                                     |                         |            | 40-160       |
| 23'44'5'-HxCB    |                        |                                     |                         |            | 40-160       |
| 33'44'55'-HxCB   |                        |                                     |                         |            | 40-160       |
| 22'33'44'5'-HpCB |                        |                                     |                         |            | 40-160       |
| 22'344'55'-HpCB  |                        |                                     |                         |            | 40-160       |
| 233'44'55'-HpCB  |                        |                                     |                         |            | 40-160       |

If an analyte is not detected in the unspiked sample, enter 0 (zero) as the "SAMPLE CONCENTRATION."

# Column to be used to flag values outside QC limits.

QC limits are advisory.

**ANALYTICAL SPECIFICATION  
FOR THE ANALYSIS OF  
ORGANOCHLORINE PESTICIDES  
AND POLYCHLORINATED BIPHENYLS (AROCLORS)  
IN SEDIMENT/PEAT SAMPLES**

***Prepared by:***

**Metcalf & Eddy Inc.  
Wakefield, Massachusetts  
Revision 1  
September 1997**

## **1. SCOPE**

This specification is for the analysis of organochlorine pesticides, and polychlorinated biphenyls (PCBs) in sediment/peat samples using a modified version of the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Organic Analysis, OLM03.1 The target compounds are listed in Exhibit C, Section 3 of the SOW with one additional target compound, o,p'-DDT. The target compounds and the required quantitation limits are presented in Attachment A.

Method modifications include lowered quantitation limits, procedures for handling and preparing samples with low solids content, mandatory GPC and sulfur cleanup for all extracts, and mandatory sulfuric acid cleanup for extracts to be analyzed for Aroclors. Mass spectral confirmation of all pesticide and Aroclor detects is required if concentrations permit. These modifications are briefly described below and are detailed in Section 7, Analytical Procedures.

An initial percent solids determination will be conducted on all samples. All samples will be prepared using freeze drying to increase the percent solids. Once the freeze drying is complete, the samples will be ground to a uniform dry solid and the percent solids on the freeze dried samples will then be determined. Additional freeze dried sample weight will be extracted so that 30 grams of dry weight equivalent is extracted. If a minimum percent solids of greater than 50% is not obtained after freeze drying, then the laboratory must immediately contact M&E to obtain additional instructions.

All samples will then be extracted and subjected to GPC and sulfur cleanup. The extracts will be split: one-half will undergo sulfuric acid cleanup and be analyzed for Aroclors. The other half will be analyzed directly for pesticides.

Performance evaluation (PE) samples will be submitted for analysis. Instructions for preparation and analysis of the PE samples will be provided in the sample shipping container.

## **2. PURPOSE**

Data derived using this specification will be used to: determine if ecological and human health risk criteria have been exceeded, provide input to risk assessments, define the nature and extent of pesticide/PCB contamination in sediment/peat samples, establish excavation limits, determine the efficacy of remedial activities, provide a measure of the quality of data generated by another consultant, and/or for other purposes.

## **3. DEFINITION OF WORK**

Sediment/peat samples will be analyzed for organochlorine pesticides and PCBs. The shipment of samples will be assigned a unique Case Number. A Case consists of one or

more Sample Delivery Groups (SDGs). An SDG is defined by the following, whichever is most frequent: each Case of field samples, or each 20 field samples within a Case, or each 14 calendar day period during which field samples in a Case are received by the laboratory. Samples may be assigned to SDGs by matrix at the discretion of the laboratory. The laboratory must use the matrix assigned on the chain-of-custody records to make this determination. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that the last sample in the SDG is received.

The matrix of the samples will be sediment/peat, therefore, provision must be made in laboratory procedures for sample storage and preparation. Additional laboratory sample storage space may be required. Extra bottles will be submitted to provide the sample weight necessary to meet the project objectives. It is expected that the sediment density will be close to but slightly greater than 1.0 gm/ml and the percent solids will be approximately 10%. Given these assumptions, one 32 fluid ounce sample container will hold approximately 94 grams of dry weight sample. M&E will submit two 32 ounce bottles for each sample with six bottles each for MS/MSD and laboratory fortified sample (LFS) designated samples.

#### **4. SCHEDULE**

##### **Holding Times:**

The sediments must be extracted within ten days of sample collection. Samples must be analyzed within forty days following the start of extraction.

The extraction holding times do not apply for PEs received as standard extracts.

##### **Delivery of Data:**

The sampling event data must be delivered to M&E within 35 days of laboratory receipt of the last sample per SDG. Sample data must be delivered under chain of custody. Data delivered to M&E should be sent to:

Mr. Bruce Livingston  
Metcalf & Eddy Inc.  
30 Harvard Mill Square  
Wakefield, MA 01880-5371  
Phone (781) 224-6437  
Fax (781) 245-6293

## 5. ANALYTICAL REFERENCES

The analytical method reference is the USEPA Contract Laboratory Program Statement of Work for Organic Analysis, OLM03.1, soxhlet extraction by SW-846 Method 3540B, and sulfuric acid cleanup of PCB extracts by SW-846 Method 3665, Sulfuric Acid/Permanganate Cleanup, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition (and updates).

## 6. SAMPLE PRESERVATION

### Sample Collection and Preservation

All samples will be iced or refrigerated at 4°C ( $\pm$  2°C) from the time of collection. Cooler temperature indicators will be placed in the sample shipping containers. If the cooler temperature exceeds 6°C upon sample receipt, contact M&E immediately regarding the temperature deviation and to obtain direction on whether or not to prepare and analyze the affected samples. If the initial sample shipments arrive at a temperature above 6°C, M&E will conduct corrective action to include more ice in subsequent shipments to properly chill the samples. If the initial shipments arrive at a temperature below 2°C, the sample storage prior to shipment will be evaluated. The temperature of the cooler is the only physical requirement the laboratory needs to record upon sample log-in. A sample pH check is not required at log-in.

### Procedure for Sample Storage

The samples must be protected from light and refrigerated at 4°C ( $\pm$  2°C) from the time of receipt until 60 days after delivery of a complete reconciled sample data package. After 60 days, disposal of the samples may be performed in accordance with all applicable regulations.

The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

### Procedure for Sample Extract Storage

Sample extracts must be protected from light and refrigerated at 4°C ( $\pm$  2°C) until 365 days after delivery of a complete reconciled data package.

Sample extracts must be stored in an atmosphere demonstrated to be free of all potential contaminants.

Samples, sample extracts and standards must be stored separately.

## 7. ANALYTICAL PROCEDURES

Sediment/peat samples will be submitted to the laboratory.

### Percent Solids Determinations

The laboratory must decant any free standing water, which may develop following sample collection, immediately prior to performing the initial percent solids determination. An initial percent solids determination must be conducted on all sediment/peat samples prior to sample extraction and analysis. A second percent solids determination must be conducted following freeze drying of each sediment sample. Prior to the second percent solids determination, the laboratory must grind the dried sample to a uniform powder using a clean mortar and pestle. All percent solids determinations must be performed according to the requirements contained in Exhibit D Pesticides/Aroclors Section 10.1.5.2. A balance calibration check must be conducted in accordance with guidance from NIST. The NIST guidance references ASTM E 617 which for this application requires Type II S grade weights that meet Class 2 tolerances. Prior to performing the post-drying weighing of samples for any percent solids determination associated with this analytical specification, all samples must be cooled in a desiccator for the same **exact** length of time (to approach room temperature, minimally 10 minutes) and the post-drying weighing of all samples must be completed within 2 minutes of removing all samples from the desiccator. The desiccator cooling time for each sample as well as the start and stop times for the post-drying weighing session must be documented in the sample preparation logbook.

### Sample Preparation, Extraction and Cleanup

All samples will be freeze dried to increase the percent solids content. The nominal freeze drying conditions will include a unit temperature of  $-50^{\circ}\text{C}$ , a condenser temperature of  $-80^{\circ}\text{C}$ , a vacuum of  $133 \times 10^{-3}$  mBar, and a 10 hour minimum (overnight) freeze drying time. However, the laboratory should consult the freeze dryer manufacturer's instructions for the specific model planned for use with this specification. Changes to these nominal operating conditions should be discussed with M&E prior to the initiation of freeze drying. The sediment samples should be frozen using dry ice prior to placement in the freeze drying apparatus. Care should be taken to freeze the samples to create a uniform, as thin as possible, coating of sediment on the inside surface of the freeze drying vessel to promote complete drying.

Following freeze drying the laboratory must grind the dried sample to a uniform powder using a clean mortar and pestle. Using the percent solids following freeze drying, the laboratory will proportionately increase the sample weight extracted to achieve extraction of 30 grams of dry weight sample. The surrogate solution will be added to the sample just prior to sample extraction. The samples must be extracted using 50:50 acetone/hexane for 18 hours in accordance with SW-846 Method 3540B. The extraction start and stop times must be recorded in a laboratory notebook and provided in the final data package. The extracts



must be concentrated and solvent exchanged into hexane following the procedures presented in Method 3540B.

Prior to performing the post-drying weighing of samples subjected to freeze drying, all samples must be cooled in a desiccator for the same **exact** length of time (to approach room temperature, minimally 10 minutes) and the post-drying weighing of all samples must be completed within 2 minutes of removing all samples from the desiccator. The desiccator cooling time for each sample as well as the start and stop times for the post-drying weighing session must be documented in the sample preparation logbook. The laboratory must document when the last desiccant regeneration was performed or when new desiccant was added to each desiccator.

If a minimum percent solids of greater than 50% is not obtained after freeze drying, then the laboratory must immediately contact M&E to obtain additional instructions. Additionally, if the laboratory has difficulty obtaining sufficient percent solids and/or adequate sample weight for any of the sediment/peat samples, then M&E must be immediately contacted to obtain additional instructions.

The laboratory must add the surrogates Tetrachloro-m-xylene (TCX) and Decachlorobiphenyl (DCB) to all field samples, method blanks, and QC samples at a concentration that results in sample surrogate concentrations at the midpoint of both the pesticide and PCB curves (taking into account the increased sample weight extracted and the required extract volume of 1.0 ml that will be split: one-half for analysis of pesticides and one-half for analysis of PCBs). The concentration and volume of surrogate solution added to each sample must be recorded in the sample preparation logbook and copies of those logbook pages must be provided in the final data package.

All field sample, method blank, and QC sample extracts must be subjected to GPC and sulfur cleanup following the OLM03.1 procedures and requirements contained in this analytical specification. The field sample, method blank and QC sample extracts must be concentrated to a volume of 1.0 ml to achieve the required quantitation limits. If concentration of any sample extract to 1.0 ml is problematic, contact M&E immediately to obtain additional instructions. The final concentrated extract volume for each sample must be recorded in the sample preparation logbook and copies of those logbook pages must be provided in the final data package.

The resulting field sample and method blank extracts will be split: one-half of each extract will undergo sulfuric acid cleanup according to SW-846 Method 3665 and shall be analyzed for PCBs (Aroclors) according to the procedures presented later in this section. Applicable PE, LFS, and MS/MSD QC sample extracts shall also undergo sulfuric acid cleanup and be analyzed for PCBs.

The other half of each field sample and method blank extract, and all applicable PE, LFS,

and MS/MSD QC sample extracts, shall be analyzed directly for pesticides following the OLM03.1 procedures and requirements contained in this analytical specification. The final pesticide extract volume and the final PCB extract volume (after sulfuric acid cleanup) must be recorded in the sample preparation logbook and copies of those logbook pages must be provided in the final data package.

#### *Laboratory Fortified Sample (LFS)*

Three aliquots of one field sample per SDG must be prepared as LFS samples. The sampling chain-of-custody forms shall identify the samples to be used for LFS samples. If the sampling chain-of-custody forms do not identify the samples to be used for LFS samples, then contact M&E to obtain additional instructions.

The purpose of the LFSs is to evaluate loss/degradation of target compounds during freeze drying. The laboratory fortified spike solution shall be added to the sample after the initial percent moisture determination has been performed and **before** the sample undergoes freeze drying. The surrogate spike solution shall be added to the sample after the initial percent moisture determination has been performed and **after** freeze drying has been completed.

One sample aliquot shall be spiked with the target compounds in the Individual A pesticide mixture, one shall be spiked with the target compounds in the Individual B pesticide mixture, and one shall be spiked with Aroclor 1232. All spike concentrations shall result in LFS concentrations at the midpoint of the calibration curves (taking into account the increased sample weight extracted and the required final extract volumes). One of the pesticide LFSs must contain o,p'-DDT (as determined by the pesticide calibration resolution requirements which are provided later in this section).

The LFSs must meet the percent recovery criteria provided in Section 8 of this analytical specification. If these criteria are not achieved, then all Form I sample results for that LFS and field samples that underwent freeze drying with that LFS must be flagged and a discussion of those results must be included in the data package narrative.

#### *Matrix Spike/Matrix Spike Duplicate(MS/MSD)*

Three matrix spike/matrix spike duplicate pairs must be extracted and analyzed per SDG. The matrix spike and surrogate spike solutions shall be added to the sample after the initial percent moisture determination has been performed and after freeze drying. The sampling chain-of-custody forms shall identify the samples to be used for matrix spike/matrix spike duplicates. If the sampling chain-of-custody forms do not identify the samples to be used for matrix spike/matrix spike duplicates, then contact M&E to obtain additional instructions.

One pair will be spiked with the target compounds specified in OLM03.1 at concentrations that result in matrix spike concentrations at the midpoint of the calibration curves (taking into account the increased sample weight extracted and the required final extract volumes).

The second pair must be spiked with o,p'-DDT at a concentration that results in matrix spike concentrations at the midpoint of the calibration curve (taking into account the increased sample weight extracted and the required final extract volumes). The o,p'-DDT MS/MSD shall follow the established 4,4'-DDT OLM03.1 criteria for matrix spike/matrix spike duplicate frequency, acceptance limits (recovery and RPD) and corrective action procedures.

The third matrix spike/matrix spike duplicate pair must be spiked with Aroclor 1232 at a concentration that results in matrix spike concentrations at the midpoint of the calibration curve (taking into account the increased sample weight extracted and the required final extract volumes). The PCB MS/MSD pair must be subjected to the same preparation, extraction and cleanup procedures as the field samples. The PCB MS/MSD must meet the percent recovery and RPD criteria provided in Section 8 of this analytical specification. If these criteria are not achieved, then the Form I sample results for the unspiked sample must be flagged and a discussion of those results must be included in the data package narrative.

### Analysis

The calibration requirements presented below apply to both GC columns used for analysis of pesticide and PCB extracts.

GC/MS confirmation of pesticide and PCB results for field samples is required as per Section 11.1.2 of OLM03.1.

All chromatograms must be properly scaled as described in Sections 9.2.5.10, 9.3.5.8, 10.2.3, & 11.3 of OLM03.1.

All technical acceptance criteria for sample analysis must be met as per Section 11.3 or effective corrective actions must be performed as per Section 11.4 of OLM03.1.

### *Pesticide Calibration*

External standard calibration must be performed following Section 9.2 of OLM03.1. Include the additional compound o,p'-DDT in either the Individual A or B standard mixture, whichever provides greater than or equal to 90% resolution of o,p'-DDT with both adjacent peaks in the initial calibration midpoint concentration Individual A or B standard. The concentration of this compound in the low through high point standards must follow the general instructions provided in OLM03.1 Section 7.2: the low point concentration **must be at the quantitation limits required in this analytical specification**, the midpoint concentration must be at 4 times the low point concentration and the high point must be at least 16 times that of the low point (but a higher concentration for the high point initial calibration standard may be chosen by the laboratory if the instrument linearity requirement in Section 8 of this analytical specification is achieved).

Follow the procedures outlined in OLM03.1 Sections 9.2.4, 9.2.5 and 9.2.6 for the determination, acceptance criteria and corrective actions for: initial calibration, absolute

retention times, retention time windows, instrument linearity, calibration factors, percent breakdown of DDT and endrin, PEM percent differences, and all resolution checks. Eliminate the Aroclor standards from the initial calibration sequence (since a separate PCB-only sequence must be performed as outlined in the section below).

Calibration verification must be performed according to Section 9.3 of OLM03.1. Follow the procedures outlined in OLM03.1 Sections 9.3.2 through 9.3.6 for the instrument blanks, PEMs, and midpoint Individual A and B standards, which comprise the calibration verification. The o,p'-DDT must be included in either the Individual A or B standard, whichever had acceptable resolution as determined during the initial calibration procedure.

#### *PCB-only Calibration*

The PCB analytical sequence should be performed as follows:

|    | <b>Initial Calibration</b>              |
|----|-----------------------------------------|
| 1  | Low Aroclor 1016/1260                   |
| 2  | Low Aroclor 1221                        |
| 3  | Low Aroclor 1232                        |
| 4  | Low Aroclor 1242                        |
| 5  | Low Aroclor 1248                        |
| 6  | Low Aroclor 1254                        |
| 7  | Mid Aroclor 1232                        |
| 8  | High Aroclor 1232                       |
| 9  | Method Blank                            |
| 10 | Laboratory Fortified Sample             |
| 11 | Instrument Blank                        |
|    | <b>Continuing Calibration Group 1</b>   |
| 12 | 10 Field Samples (including MS/MSD)     |
| 13 | Method Blank (if needed)                |
| 14 | Laboratory Fortified Sample (if needed) |

|         |                                                                                                                                                                                                                     |
|---------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 15 plus | Continuing Calibration Standard(s):<br>Mid Aroclor #1 (for detected PCBs)<br>High Aroclor #1<br>Mid Aroclor #2, 3, etc. as required (for detected PCBs)<br>High Aroclor #2, 3, etc. as required (for detected PCBs) |
| 16      | Instrument Blank                                                                                                                                                                                                    |
|         | <b>Continuing Calibration Group 2</b>                                                                                                                                                                               |
| 17      | 10 Field Samples                                                                                                                                                                                                    |
| 18      | Method Blank (if needed)                                                                                                                                                                                            |
| 19      | Laboratory Fortified Sample (if needed)                                                                                                                                                                             |
| 20 plus | Continuing Calibration Standard(s):<br>Low Aroclor 1016/1260<br>Mid Aroclor #1<br>High Aroclor #1<br>Mid Aroclor #2, 3, etc. as required<br>High Aroclor #2, 3, etc. as required                                    |
| 21      | Instrument Blank                                                                                                                                                                                                    |
|         | <b>Continuing Calibration Group 3</b>                                                                                                                                                                               |
| 22      | Etc.                                                                                                                                                                                                                |

#### *PCB Initial Calibration Sequence*

Runs 1-11 constitute the initial calibration portion of the PCB analytical sequence.

The concentration of the low point standard for each Aroclor **must be equal to the quantitation limits required in this analytical specification**. The midpoint concentration for all Aroclors in the analytical sequence shall be at 4 times the low point concentration and the high point concentration shall be at least 16 times the low point concentration (but a higher concentration may be used by the laboratory if the linearity criteria provided in Section 8 of this analytical specification are achieved).

A full curve is required for Aroclor 1232 in the initial calibration, since that Aroclor is spiked in the LFS and MS/MSD. The Aroclor 1232 three point calibration curve must meet the linearity criteria provided in Section 8 of this analytical specification prior to the analysis of

the remaining QC samples (method blank, LFS, and instrument blank) in the initial calibration sequence. If the criteria are not achieved, then the laboratory must determine the source of the problem, institute effective corrective action procedures, and re-analyze the three point calibration curve prior to analyzing the remaining QC samples in the PCB initial calibration sequence.

The method blank must meet the frequency, acceptance limits, and corrective action requirements specified in Section 8 of this analytical specification prior to the analysis of the LFS.

The instrument blank must meet the frequency, acceptance limits, and corrective action requirements specified in Section 8 of this analytical specification prior to the analysis of any field samples contained in Continuing Calibration Group 1.

#### *PCB Continuing Calibration Sequence*

The continuing calibration for every 12 hour time period must begin and end with an instrument blank. Run 11 serves as the beginning instrument blank for Continuing Calibration Group (CCG) 1, and the instrument blank that ends the previous CCG serves as the beginning instrument blank for the next CCG.

Each CCG must include at least one midpoint and high point Aroclor standard, which must be analyzed after the field samples as shown in the table above. The Aroclor used for midpoint and high point Aroclor standards must consist of Aroclors detected in the environmental samples. Multiple sets of midpoint/high point standards may have to be analyzed in a single CCG in order to accurately quantitate Aroclors detected in the field samples for that CCG. If more than one Aroclor is detected in the field samples in a CCG, then a midpoint and high point standard for each of those Aroclors must be analyzed during that CCG's continuing calibration. If no Aroclors are detected in the field samples in a particular CCG, then the laboratory must run a midpoint and high point standard containing an Aroclor for which a curve has yet to be generated. All three point calibration curves (generated using the low point standard from the initial calibration and the midpoint and high point standards from the continuing calibration) must meet the linearity criteria provided in Section 8 of this analytical specification. If the criteria are not achieved, then the laboratory must determine the source of the problem, institute effective corrective action procedures, generate new three point calibration curves for the affected Aroclors, and re-analyze all field and QC samples that were quantitated using those curves.

Once a demonstrated linear three point curve has been generated for all 6 Aroclor standards, then the high point standard can be eliminated from the continuing calibration standards for all remaining CCGs. The continuing calibration for those CCGs shall just contain one (or more) midpoint standards for Aroclors detected in the field samples for that CCG (if no Aroclors are detected in the field samples for that CCG, then run a midpoint Aroclor standard for an Aroclor that was detected in any of the field samples in previous

CCGs or, if no Aroclors have been detected in any field samples, then run one of the 6 midpoint Aroclor standards on a rotational basis). The percent difference criteria in Section 8 of this analytical specification must be achieved for those midpoint continuing calibration standards. If the criteria are not achieved, then the laboratory must determine the source of the problem, institute effective corrective action procedures (including curve re-analysis, if necessary), and re-analyze all field and QC samples that were analyzed since the last acceptable midpoint continuing calibration standard for that Aroclor.

In addition, the low point Aroclor 1016/1260 standard must be analyzed once every 24 hour time period after the start of the initial calibration sequence to demonstrate continued instrument sensitivity. If the criteria are not achieved, then the laboratory must determine the source of the problem, institute effective corrective action procedures (including curve re-analysis, if necessary), and re-analyze all field and QC samples that were analyzed since the last acceptable low point Aroclor 1016/1260 standard.

The continuing calibration standards and an instrument blank must be the last analyses performed within the analytical sequence.

If sample concentrations exceed the calibration range, a dilution must be performed to bring the sample concentrations to the mid to upper end of the calibration range. All original and diluted sample analyses must be reported in the final data package.

If, in the analyst's judgement, higher chlorinated Aroclors such as 1262 and/or 1268 appear to be present in any of the field samples, then M&E must be contacted immediately to obtain additional instructions. M&E may instruct the laboratory to analyze standards for those Aroclors and re-analyze field sample extracts for those Aroclors at no additional cost.

## 8. QUALITY CONTROL REQUIREMENTS

### Pesticide/PCB Cleanup:

| QC Check              | Frequency of QC Check                | Acceptance Limits                    | Corrective Action                    |
|-----------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Calibration of GPC    | As per OLM03.1, Section 10.1.8.1.3.2 | As per OLM03.1, Section 10.1.8.1.3.4 | As per OLM03.1, Section 10.1.8.1.3.5 |
| GPC Calibration Check | As per OLM03.1, Section 10.1.8.1.4.2 | As per OLM03.1, Section 10.1.8.1.4.4 | As per OLM03.1, Section 10.1.8.1.4.5 |
| Sulfur Cleanup Blanks | As per OLM03.1, Section 12.1.3.2     | As per OLM03.1, Section 12.1.3.4     | As per OLM03.1, Section 12.1.3.5     |

Pesticide Analysis:

| <b>QC Check</b>                                                                            | <b>Frequency of QC Check</b>                                                                                                       | <b>Acceptance Limits</b>                                                      | <b>Corrective Action</b>                                                      |
|--------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Instrument Blank                                                                           | As per OLM03.1, Section 12.1.4.2                                                                                                   | As per OLM03.1, Section 12.1.4.4 & 11.3                                       | As per OLM03.1, Section 12.1.4.5 & 11.4                                       |
| Method Blank                                                                               | As per OLM03.1, Section 12.1.2.2                                                                                                   | As per OLM03.1, Section 12.1.2.4 & 11.3                                       | As per OLM03.1, Section 12.1.2.5 & 11.4                                       |
| Initial Calibration including o,p'-DDT                                                     | Upon award of this contract and as per OLM03.1, Section 9.2.2 and as per instructions provided in Section 7, Analytical Procedures | As per OLM03.1, Section 9.2.5 & 11.3 (apply these criteria for o,p'-DDT also) | As per OLM03.1, Section 9.2.6 & 11.4 (apply these criteria for o,p'-DDT also) |
| Calibration Verification including o,p'-DDT                                                | As per OLM03.1, Section 9.3.2 and as per instructions provided in Section 7, Analytical Procedures                                 | As per OLM03.1, Section 9.3.5 & 11.3 (apply these criteria for o,p'-DDT also) | As per OLM03.1, Section 9.3.6 & 11.4 (apply these criteria for o,p'-DDT also) |
| Surrogate %Rec. & RT                                                                       | As per OLM03.1, Section 7.2.4.1                                                                                                    | As per OLM03.1, Section 11.2.3.2 & 11.3                                       | As per OLM03.1, Section 11.2.3.3 & 11.4                                       |
| Laboratory Fortified Sample (one with OLM03.1 target compounds and a second with o,p'-DDT) | As per instructions provided in Section 7, Analytical Procedures                                                                   | Recovery 50-150%                                                              | As per instructions provided in Section 7, Analytical Procedures              |



| QC Check                                                                                                | Frequency of QC Check                                                                      | Acceptance Limits                                                                          | Corrective Action                                                                          |
|---------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| Matrix Spike/Matrix Spike Duplicate (one pair with OLM03.1 target compounds and a second with o,p'-DDT) | As per OLM03.1, Section 12.2.2 & instructions provided in Section 7, Analytical Procedures | As per OLM03.1, Section 12.2.5 & instructions provided in Section 7, Analytical Procedures | As per OLM03.1, Section 12.2.6 & instructions provided in Section 7, Analytical Procedures |
| Performance Evaluation Samples                                                                          | one per SDG                                                                                | USEPA will score the results                                                               | Actions will be applied on a case by case basis                                            |

PCB Analysis:

| QC Check                        | Frequency of QC Check                                            | Acceptance Limits                                                                                    | Corrective Action                                                |
|---------------------------------|------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|
| Instrument Blank                | As per OLM03.1, Section 12.1.4.2                                 | As per OLM03.1, Section 12.1.4.4 & 11.3                                                              | As per OLM03.1, Section 12.1.4.5 & 11.4                          |
| Method Blank                    | As per OLM03.1, Section 12.1.2.2                                 | As per OLM03.1, Section 12.1.2.4 & 11.3                                                              | As per OLM03.1, Section 12.1.2.5 & 11.4                          |
| Initial Calibration             | As per instructions provided in Section 7, Analytical Procedures | RSD <20% for Aroclor 1232                                                                            | As per instructions provided in Section 7, Analytical Procedures |
| Continuing Calibration          | As per instructions provided in Section 7, Analytical Procedures | %D <15% for any midpoint Aroclor and for low Aroclor 1016/1260<br><br>RSD <20% for any Aroclor curve | As per instructions provided in Section 7, Analytical Procedures |
| Surrogate %Rec. & RT (DCB only) | As per OLM03.1, Section 7.2.4.1                                  | As per OLM03.1, Section 11.2.3.2 & 11.3                                                              | As per OLM03.1, Section 11.2.3.3 & 11.4                          |

| QC Check                            | Frequency of QC Check                                                             | Acceptance Limits            | Corrective Action                                                |
|-------------------------------------|-----------------------------------------------------------------------------------|------------------------------|------------------------------------------------------------------|
| Laboratory Fortified Sample         | As per instructions provided in Section 7, Analytical Procedures                  | Recovery 50-150%             | As per instructions provided in Section 7, Analytical Procedures |
| Matrix Spike/Matrix Spike Duplicate | One pair per SDG as per instructions provided in Section 7, Analytical Procedures | Rec. 50-150% & RPD <20.      | As per instructions provided in Section 7, Analytical Procedures |
| Performance Evaluation Samples      | one per SDG                                                                       | USEPA will score the results | Actions will be applied on a case by case basis                  |

## 9. DATA PACKAGE DELIVERABLES

The laboratory data package deliverables must resemble as closely as possible the OLM03.1 format. The general deliverables described in Section B--Exhibit 2 and the specific data described in Exhibit B-- Section 2, part 2.6.5 must be provided. That section describes the chromatograms and data system printouts. Modify the appropriate forms to include the additional compound, o,p'-DDT and the PCB only analysis. The data package must be of good readable copy quality and paginated in ascending order.

All analytical data and all tabulated raw or supporting data must be delivered under custody seal for each SDG. The CSF Completeness Evidence Audit Forms, which are included in Attachment C, must be completed by the laboratory for the data package deliverables submitted for each SDG. Using those audit forms, the laboratory must demonstrate that all tabulated and raw data for all field samples, standards, blanks and QC samples as well as any other documents required by OLM03.1 and this analytical specification are contained in the data package deliverable for each SDG.

Resubmittals for missing, inaccurate, and/or questionable data from the laboratory will be requested by facsimile followed by a telephone call. The resubmittals must be provided under custody seal within 48 hours of the date of facsimile request at no additional cost and the resubmittals must be accompanied by additional completed CSF Completeness Evidence Audit Forms.

Data package deliverables for each SDG must include the following:

- A Case Narrative must be provided that contains a detailed description of the sample preparation and analysis methodology employed, any deviations from the requirements of this analytical specification, problems encountered and their resolution, and any anomalies in the reported data. The laboratory sample identification numbers and the EPA assigned sample numbers must be cross-referenced in the Case Narrative. An example calculation for one pesticide target compound and one Aroclor must also be provided in the Case Narrative to demonstrate the derivation of pesticide and Aroclor target compound results that are reported on Form Is. If there are no detected compounds in the field samples, then the laboratory must utilize matrix spike results for the example calculations.
- A copy of this analytical specification must be provided.
- Results for all samples, blanks, LFSs, MS/MSDs, and PE samples must be reported on Form Is that have been modified to include all target compounds. All sample results must be reported on a dry weight basis in  $\mu\text{g}/\text{kg}$ . OLM03.1 sample result qualifiers must be used on all Form Is. Additional sample result qualifiers may be utilized by the laboratory (to meet the requirements contained in Sections 7 and 9 of this analytical specification), however, they must be completely defined in the Case Narrative.
- The SOW-required header information must be supplied on all Forms.
- The surrogate percent recoveries must be calculated and reported on Form IIs.
- The MS/MSD recoveries and RPD results must be reported on modified Form IIIs. Values that exceed the QC limits must be flagged with a “\*”.
- The LFS recoveries must be reported on a modified Form IIIs. Values that exceed the QC limits must be flagged with a “\*”.
- The Method Blank(s) and corresponding samples must be reported on Form IVS.
- The initial calibration results for both the Pesticide and PCB only analyses must be reported on modified Forms VI-1 through VI-7.
- The percent breakdown of DDT and endrin must be reported on Form VII-1.
- The Pesticide and PCB only Calibration Verification results must be reported on modified Form VII-2s.
- Report the pesticide analytical sequence for all columns and instruments on Form VIIIs.

- Report the PCB analytical sequence for all columns and instruments on a modified Form VIIIs.
- Report the results of all extract cleanups on modified Form IXs. Include all samples, blanks, and QC samples on the forms.
- The retention time, retention time windows, results quantitated from each column and percent difference between quantitated results must be summarized for all detected target compounds for each sample on modified Form Xs.
- All raw data, including chromatograms and quantitation reports for all standards, blanks, field samples and QC samples must be provided. All chromatograms must indicate the peaks used for quantitation, chromatographic conditions, instrument identification number, and injection volume. Quantitation reports must provide area counts for all peaks present on the chromatograms.
- All sample tracking reports (shipper information), sampling chain-of-custody forms, and custody seals must be provided in the data package.
- Copies of sample log-in/tracking sheets indicating the cooler temperature and the sample arrival time and date, and any telephone logs referring to the samples, must be provided in the data package.
- Provide all sample logbook pages, which have recorded the results for all % solids determinations with pre/post sample weights, start/stop times for desiccator cooling and start/stop times for post-drying sample weighing, sample weights extracted, surrogate concentrations and volumes added; reagent weights/volumes for sodium sulfate and all extraction solvents; the start and stop times for the 18 hour soxhlet extractions; all initial, intermediate and final pesticide and PCB extract volumes; and pages from any other logbook that the laboratory generated in the processing of the samples.
- Include the concentration of the surrogates, calibration standards (pesticide and PCB initial and verification), LFS, and matrix spike components on all relevant reporting Forms and raw data.
- The source, including the manufacturer, lot number, and concentration, of all reference materials must be provided in the data package.

## **10. EXCEPTIONS**

If the laboratory has any questions or if the laboratory experiences problems during any time from sample scheduling/receipt through analysis contact M&E immediately.

Bruce Livingston  
Metcalf & Eddy Inc.  
30 Harvard Mill Square  
Wakefield, MA 01880-5371  
Phone (781) 224-6437  
FAX (781) 245-6293

| Attachment A<br>Target Compound and Quantitation Limit Requirements |                             |
|---------------------------------------------------------------------|-----------------------------|
| Target Compound                                                     | Quantitation Limits (μg/kg) |
| Aldrin                                                              | 0.17                        |
| α-BHC                                                               | 0.17                        |
| β-BHC                                                               | 0.17                        |
| δ-BHC                                                               | 0.17                        |
| γ-BHC                                                               | 0.17                        |
| Chlordane(Technical)                                                | 0.33                        |
| p,p'-DDD                                                            | 0.33                        |
| p,p'-DDE                                                            | 0.33                        |
| o,p'-DDT                                                            | 0.33                        |
| p,p'-DDT                                                            | 0.33                        |
| Dieldrin                                                            | 0.33                        |
| Endosulfan I                                                        | 0.17                        |
| Endosulfan II                                                       | 0.33                        |
| Endosulfan Sulfate                                                  | 0.33                        |
| Endrin                                                              | 0.33                        |
| Endrin Aldehyde                                                     | 0.33                        |
| Endrin Ketone                                                       | 0.33                        |
| Heptachlor                                                          | 0.17                        |
| Heptachlor Epoxide                                                  | 0.17                        |
| Methoxychlor                                                        | 1.7                         |
| Toxaphene                                                           | 17.0                        |
| Aroclor 1016                                                        | 3.3                         |
| Aroclor 1221                                                        | 6.7                         |
| Aroclor 1232                                                        | 3.3                         |
| Aroclor 1242                                                        | 3.3                         |

| Attachment A<br>Target Compound and Quantitation Limit Requirements |                                          |
|---------------------------------------------------------------------|------------------------------------------|
| Target Compound                                                     | Quantitation Limits ( $\mu\text{g/kg}$ ) |
| Aroclor 1248                                                        | 3.3                                      |
| Aroclor 1254                                                        | 3.3                                      |
| Aroclor 1260                                                        | 3.3                                      |

\* The quantitation limits listed for a solid matrix are based on 30 grams dry weight.

## **1. SCOPE**

This specification is for the analysis of low concentrations of metals in sediment/peat samples using a modified version of the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Inorganics Analysis, Multi-media Multi-concentration ILM04.0. To meet project objectives, modifications to ILM04.0 will be required to achieve lowered detection limits for antimony, arsenic, beryllium, cadmium, mercury and silver. The target analytes and the required quantitation limits are presented in Attachment A.

Method modifications include lowered quantitation limits, and procedures for handling and preparing samples with low solids content. These procedures are briefly described below and are detailed in Section 7, Analytical Procedures and in Attachment B.

The percent solids of all samples will be determined initially upon sample receipt. Percent solids preparation will include decanting any free standing water, which may develop following sample collection, immediately prior to performing the initial percent solids determination. An initial percent solids determination must be conducted on all sediment/peat samples prior to sample digestion. Specific sample preparation steps will be performed as described in the Sample Preparation portion of Section 7. All samples will undergo a drying step after the initial percent solids determination. If the percent solids of the sample after the first drying step is greater than or equal to 50%, then additional sample weight must be digested so that the equivalent dry weight of sample, as described in this specification, is digested (Attachment B). If the percent solids is less than 50%, additional drying steps, as described in Section 7 of this specification, will be necessary. All percent solids determinations must be performed according to the requirements contained in ILM04.0 Exhibit D Part F and these must be documented in a laboratory notebook.

Performance evaluation (PE) samples will be submitted for analysis during the main sampling event only. Instructions for preparation and analysis of PE samples will be provided in the sample shipping container.

## **2. PURPOSE**

Data derived using this specification will be used to: determine if ecological and human health criteria have been exceeded, provide input to risk assessments, define the nature and extent of metals contamination in sediment/peat samples, establish excavation limits, determine the efficacy of remedial activities, provide a measure of the quality of data generated by another consultant, or for other purposes.

## **3. DEFINITION OF WORK**

Sediment/peat samples are to be analyzed for low concentrations of metals. To meet project objectives, modifications to ILM04.0 will be required to achieve lowered detection limits for



**ANALYTICAL SPECIFICATION  
FOR THE ANALYSIS OF  
LOW CONCENTRATION METALS  
IN SEDIMENT/PEAT SAMPLES**

***Prepared by:***

**Metcalf & Eddy, Inc.  
Wakefield, Massachusetts  
Revision 2  
September 1997**

antimony, arsenic, beryllium, cadmium, mercury and silver as presented in Attachment A. The shipment of samples will be assigned a unique M&E DAS Case Number. A Case consists of one or more Sample Delivery Groups (SDGs). An SDG is defined by the following and whichever is more frequent: each Case of field samples, or each 20 field samples within a Case, or each 14 calendar day period during which field samples in a Case are received by the laboratory. Samples may be assigned to SDGs by matrix at the discretion of the laboratory, however, the laboratory must use the matrix assigned on the chain-of-custody records to make this determination. Data for all samples in the SDG are due concurrently. The date of delivery of the SDG or any samples within the SDG is the date that the last sample in the SDG is received.

The matrix of the samples will be sediment/peat of low percent solids, therefore, provisions must be made in the laboratory procedures for sample storage and preparation. Additional laboratory sample storage space may be required. Extra sample bottles will be submitted to provide adequate sample weight to meet the project objectives. It is anticipated that the sediment/peat density will be close to, but slightly greater than 1.0 gm/ml and that the percent solids will be approximately 10%. Based on these assumptions, one (1) 8-ounce, plastic sample container will hold approximately 24 grams of dry weight sample. M&E will submit one 8-ounce bottle for each sample including those designated for MS or MS/MSD analysis.

#### **4. SCHEDULE**

Specific sampling dates will be provided in each work order. Samples will be shipped no more than one day after collection. Saturday delivery may be required. An overnight delivery service will be used. Contacts for shipping will be provided in each work order. Data delivery inquiries may be made to Mr. Bruce Livingston, Metcalf & Eddy (781) 224-6437.

##### **Holding Times:**

The sediment/peat samples must be analyzed for all metals, except mercury, within 180 days of sample collection. Analysis for mercury must be conducted within 26 days of sample collection. Analysis for silver must be conducted within 24 hours after sample digestion.

##### **Delivery of Data:**

The data must be delivered to M&E, within 35 days of laboratory receipt of the last sample in the SDG. Sample data must be delivered under chain of custody. Results delivered to M&E should be sent to:

Mr. Bruce Livingston  
Metcalf & Eddy  
30 Harvard Mill Square  
Wakefield, MA 01880-5371  
Phone (781) 224-6437  
Fax (781) 245-6293

## **5. ANALYTICAL REFERENCE**

The analytical reference method is the EPA CLP Statement of Work for Inorganics Analysis Multi-Media Multi-Concentration ILM04.0. Modifications to reach lower quantitation limits and for handling low solids content samples are provided in Section 7, Analytical Procedures, of this specification.

## **6. SAMPLE PRESERVATION**

### Sample Collection and Preservation

Samples will be preserved by cooling and maintaining them at 4° C ( $\pm 2^{\circ}$ C). USEPA cooler temperature indicators will be placed in the sample shipping containers. If the temperature of the cooler is greater than 6° C or less than 2° C upon sample receipt, the laboratory must contact M&E immediately for instructions regarding analysis of the samples. If the initial sample shipments arrive at a temperature above 6° C, M&E will conduct corrective action to include more ice in subsequent shipments to properly chill the samples. If the initial shipments arrive at a temperature below 2° C, the sample storage prior to shipment will be evaluated. The temperature of the cooler is the only physical requirement the laboratory needs to record upon sample log-in. A sample pH check is not required at log-in.

### Procedure for Sample Storage

The samples must be refrigerated at 4° C ( $\pm 2^{\circ}$ C) from the time of sample receipt until 60 days after delivery of a complete reconciled sample data package. After 60 days, disposal of the samples may be performed in accordance with all applicable regulations.

In addition, the samples must be stored in an atmosphere demonstrated to be free of all potential contaminants. Samples and standards must be stored separately.

## **7. ANALYTICAL PROCEDURES**

The analysis will be performed following the procedures in Sections 6, 7, and 8, with the required percent recovery of 75-125% and RPD of less than or equal to 20% as specified in ILM04.0, Exhibit E, Section V Parts 6 and 7.

### Percent Solids Determinations

The laboratory must decant any free standing water, which may develop following sample collection, immediately prior to performing the initial percent solids determination. An initial percent solids determination must be conducted on all sediment/peat samples, after decanting, but prior to sample digestion. Specific sample preparation steps will be performed as described in the Sample Preparation section below. Multiple percent solids determinations may need to be performed on sediment/peat samples that contain low percent solids, before and after drying. All percent solids determinations must be performed according to the requirements presented in ILM04.0 Exhibit D Part F. A balance calibration check must also be conducted in accordance with guidance from NIST. The NIST guidance references ASTM E 617, which for this application requires Type II S grade weights that meet Class 2 tolerances. Prior to performing the post-drying weighing of samples for any percent solids determination associated with this analytical specification, all samples must be cooled in a desiccator for the same **exact** length of time (to approach room temperature, minimally 10 minutes) and the post-drying weighing of all samples must be completed within 2 minutes of removing all samples from the desiccator. The desiccator cooling time for each sample, as well as the start and stop times for the post-drying weighing session, must be documented in the sample preparation logbook.

### Sample Preparation

Preparation blanks must be carried through all steps that are conducted on sediment/peat samples at a frequency of one per SDG or per batch of samples prepared whichever is more frequent.

The percent solids of all samples will be determined initially upon sample receipt (Attachment B). Each sample will then be dried at 60°C for four hours. All samples must undergo this initial drying regardless of the initial percent solids. If the percent solids of the sample from the determination after initial drying is greater than or equal to 50%, then additional sample weight will be digested so that the equivalent dry weight of sample as specified in ILM04.0 or this specification is digested. If the percent solids is less than 50% after the four hours of drying, then the laboratory will dry the samples at 60°C for 24 hours to remove additional moisture. After 24 hours of drying, a third percent solids determination will be conducted. If the percent solids is greater than or equal to 50% additional sample weight will be digested so that the equivalent dry weight of sample as specified in ILM04.0 or this specification is digested. If the percent solids is less than 50% a second 24 hour drying at 60°C will be conducted. If the percent solids is greater than or equal to 30% after the second 24 hour drying cycle, additional sample weight will be digested so that the equivalent dry weight of sample required is digested. If the percent solids is less than 30% after this second 24 hour drying cycle, the laboratory must contact Mr. Bruce Livingston at M&E (781) 224-6437, to further discuss sample preparation and additional instructions. Preparation of sediment samples using microwave digestion is not acceptable for this

analytical specification.

In order to achieve the quantitation limits required for antimony, arsenic, beryllium, cadmium, and silver the laboratory must conduct analyses for these metals using graphite furnace atomic absorption (GFAA). The laboratory must follow the procedures provided in Methods 204.2, 206.2, 210.2, 213.2 and 272.2 of ILM04.0 for the GFAA analysis of antimony, arsenic, beryllium, cadmium and silver, respectively. Additionally, a standard equal to 2X the required quantitation limits must be analyzed along with the remaining calibration standards required in ILM04.0 for GFAA analysis. The highest concentration standards must define the upper limit of the linear range of the instrument for each metal. Any sample concentrations above the highest concentration standards must be diluted to fall within the upper half of the calibration range. A dry weight equivalent of 2 grams of sediment in 200 ml final volume must be used to ensure the quantitation limits required are achieved.

In order to achieve the quantitation limit required for mercury the initial sample weight must be increased to a dry weight equivalent of 2 grams of sediment in 100 ml final volume as opposed to the 0.2 grams specified in ILM04.0.

A laboratory fortified blank (LFB), consisting of an analyte free solid matrix such as Ottawa sand, must be analyzed with each SDG at the specification required quantitation limits or lower to demonstrate that the laboratory is able to consistently meet these quantitation limits.

The use of ICP "TRACE" analysis is allowable for all metals, except antimony, arsenic, beryllium, cadmium, silver and mercury, if the quantitation limits can be achieved and as long as interference check sample analysis is performed and documented. All requirements presented in Exhibit E Section V number 5 of ILM04.0 for interference check sample analysis must be met.

The sediment/peat samples must be analyzed unspiked and as a matrix spike/matrix spike duplicate. The spiking solution will be added prior to drying the samples at 60°C. The samples will be spiked so that the final concentration will be nominally 2.0 mg/kg on a dry weight basis depending on the actual dry weight of the spiked samples. From the stock mercury solution presented in ILM04.0 Exhibit D Method 245.5, prepare a spiking solution at a concentration of 2.0 µg/ml. Add 2.0 ml of this spike solution to the wet sediment/peat sample aliquot that is equivalent to 2.0 gms of dry weight sample for each MS and MSD. The sediment/peat samples must be oven dried at 60°C for 24 hours independent of the initial percent solids. The SRM will not be analyzed as an MS/MSD.

Along with the sample analysis requirements, the laboratory must also provide one of the following:

- A method detection limit (MDL) study within the last 6 months

demonstrating a quantitation limit for antimony at 0.30 mg/kg, arsenic at 0.20 mg/kg, beryllium at 0.040 mg/kg, cadmium at 0.01 mg/kg, silver at 0.02 mg/kg and mercury at 0.01 mg/kg. The MDL requirements are specified in section 9b.

- Laboratory fortified blank (LFB) results, consisting of an analyte free solid matrix such as Ottawa sand, spiked with all target analytes at concentrations equivalent to the quantitation limits in Attachment A demonstrating that these limits can be achieved.

## 8. QUALITY CONTROL REQUIREMENTS

All quality control elements of ILM04.0 must be conducted, with provisions made to achieve the detection limits provided in Attachment A. The following tables present the QC checks required, the frequency, acceptance limits, and corrective actions for samples analyzed using GFAA and ICP:

### Graphite Furnace Atomic Absorption (GFAA)/Cold Vapor AA (Hg)

| QC Checks Required                                                                    | Frequency of QC Checks                                   | Acceptance Limits                                                                    | Corrective Action                                                                                                                                                                                                                                                                                                                                                     |
|---------------------------------------------------------------------------------------|----------------------------------------------------------|--------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Initial Calibration (See 2x equivalent low concentration standard and Section 7 text) | As per ILM04.0, Exhibit E, Section V, part 1             | As per ILM04.0, Exhibit E, Section V, part 1                                         | Recalibrate until initial calibration criteria are met. Low standard must equal the required quantitation limits in Attachment A.                                                                                                                                                                                                                                     |
| Initial Calibration Verifications (ICVs)                                              | As per ILM04.0, Exhibit E, Section V, part 2, subpart a) | As per ILM04.0, Exhibit E, Section V, part 2                                         | Initial calibration criteria must be met or the analysis terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.                                                                                                                                                                                                              |
| Continuing Calibrations (CCVs)                                                        | As per ILM04.0, Exhibit E, Section V, part 2, subpart b) | 90 to 110 % of true value for all metals by GFAA and 80 to 120% of true value for Hg | Continuing calibration criteria must be met or stop analysis, determine the source of the problem, perform corrective action, the calibration verified and reanalysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification, and begin again with initial calibration prior to sample analysis. |

| QC Checks Required                                                         | Frequency of QC Checks                                                                                                     | Acceptance Limits                                                                                                                                        | Corrective Action                                                                                                                                                                                                                                                                                                                                                                   |
|----------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 2x equivalent Low Quantitation Limit Standard                              | To be conducted with initial calibration at frequency in ILM04.0 Exhibit E Section V, part 1                               | 75-125% of the true value                                                                                                                                | If criteria are exceeded, the calibration and 2x standards will be reprepared and reanalyzed until the analysis is linear.                                                                                                                                                                                                                                                          |
| CRDL Standards (routine limits)                                            | 1 per 20 samples analyzed, at the beginning and end of each sample analysis run, preceding the ICS but not before the ICV. | As per ILM04.0, Exhibit E, Section V, part 3                                                                                                             | If criteria are exceeded, the AA standards will be reprepared and reanalyzed until the analysis is linear.                                                                                                                                                                                                                                                                          |
| Initial Calibration Blanks (ICBs) and Continuing Calibration Blanks (CCBs) | As per ILM04.0, Exhibit E, Section V, part 4, subpart a)                                                                   | The absolute value of the calibration blank must less than or equal to the CRDL                                                                          | If the absolute value of the blank result exceeds the IDL, the result shall be reported as specified in Exhibit B. If the absolute value of the blank result exceeds the CRDL, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding ten analytical samples or all samples analyzed since the last compliant calibration blank. |
| Preparation Blanks                                                         | At least one preparation blank per SDG                                                                                     | As per ILM04.0, Exhibit E, Section V, part 4, subpart b)                                                                                                 | If the criteria are exceeded, all samples associated with the blank shall be redigested and reanalyzed for that analyte.                                                                                                                                                                                                                                                            |
| Solid Matrix Laboratory Control Sample (LCS)                               | As per ILM04.0, Exhibit E, Section V, part 8                                                                               | The required quantitation limits must be met. Recovery not to exceed 125%.                                                                               | If the criteria are not met, terminate the analysis, correct the problem, and redigest and reanalyze the analytical samples associated with the non-compliant LCS.                                                                                                                                                                                                                  |
| Matrix Spike Sample Analysis                                               | 1 per SDG                                                                                                                  | 75 to 125% recovery, except if the native concentration exceeds the spiked concentration by a factor of 4 or more; ILM04.0, Exhibit E, Section V, part 6 | If limits are not within the accepted criteria, note this in the narrative and all samples associated with that spike sample are flagged with the letter "N" on FORMS I-IN and V-IN.                                                                                                                                                                                                |

| QC Checks Required                                                                 | Frequency of QC Checks                                | Acceptance Limits                                                                                                                   | Corrective Action                                                                                                                                     |
|------------------------------------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|
| Duplicate Sample Analysis                                                          | 1 per SDG                                             | 20% for RPD if duplicates are $\geq 5x$ CRDL; $\pm$ CRDL if duplicates are $<5x$ CRDL; as per ILM04.0, Exhibit E, Section V, part 7 | If results are outside the control limits, flag all the data for samples associated with that duplicate sample with an "***" on FORMS I-IN and VI-IN. |
| Solid Matrix Laboratory Fortified Blank spiked at the quant limits in Attachment A | 1 per SDG                                             | 50 to 150% recovery                                                                                                                 | If the recoveries are outside the acceptance limits, note this in the case narrative and flag the results reported on a FORM V.                       |
| Method of Standard Addition                                                        | As per ILM04.0, Exhibit E, Section V, part 13         | As per ILM04.0, Exhibit E, Section V, part 13                                                                                       | Report the data and flag it with a "S" or "+" depending on the exceedance and report the results on FORM I-IN and FORM VIII-IN.                       |
| Instrument Detection Limit (IDL)                                                   | Prior to field sample analysis and reported quarterly | As specified in ILM04.0 in Exhibit E, Section V, part 10                                                                            | If the instrument is adjusted, the IDL for that instrument will be redetermined and established IDLs submitted.                                       |
| Performance Evaluation Sample                                                      | 1 per SDG                                             | USEPA will score the results                                                                                                        | Actions will be applied on a case by case basis.                                                                                                      |

Antimony, arsenic, beryllium, cadmium, silver and any other elements analyzed using GFAA to meet detection limit requirements, must incorporate all QC elements presented in Exhibit E Section V number 13 of ILM04.0.

### Inductively Coupled Plasma (ICP)

| QC Checks Required  | Frequency of QC Checks                       | Acceptance Limits                            | Corrective Action                                       |
|---------------------|----------------------------------------------|----------------------------------------------|---------------------------------------------------------|
| Initial Calibration | As per ILM04.0, Exhibit E, Section V, part 1 | As per ILM04.0, Exhibit E, section V, part 1 | Recalibrate until initial calibration criteria are met. |



| QC Checks Required                                                         | Frequency of QC Checks                                                                                                     | Acceptance Limits                                                                  | Corrective Action                                                                                                                                                                                                                                                                                                                                                            |
|----------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Initial Calibration Verifications (ICVs)                                   | As per ILM04.0, Exhibit E, Section V, part 2, subpart a)                                                                   | As per ILM04.0, Exhibit E, Section V, part 2                                       | Initial calibration criteria must be met or the analysis terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.                                                                                                                                                                                                                     |
| Continuing Calibrations (CCVs)                                             | As per ILM04.0, Exhibit E, Section V, part 2, subpart b)                                                                   | 90 to 110 % of true value for all metals                                           | Continuing calibration criteria must be met or stop analysis, determine the source of the problem, perform corrective action, the calibration verified and reanalysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification, and begin again with initial calibration prior to sample analysis.        |
| CRDL Standards (routine limits)                                            | 1 per 20 samples analyzed, at the beginning and end of each sample analysis run, preceding the ICS but not before the ICV. | As per ILM04.0, Exhibit E, Section V, part 3                                       | If criteria are exceeded, the ICP standards will be reprepared and reanalyzed until the analysis is linear.                                                                                                                                                                                                                                                                  |
| Initial Calibration Blanks (ICBs) and Continuing Calibration Blanks (CCBs) | As per ILM04.0, Exhibit E, Section V, part 4, subpart a)                                                                   | The absolute value of the calibration blank must be less than or equal to the CRDL | If the absolute value of the blank result exceeds the IDL, the result shall be reported as specified in Exhibit B. If the absolute value blank result exceeds the CRDL, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding ten analytical samples or all samples analyzed since the last compliant calibration blank. |
| Preparation Blanks                                                         | At least one preparation blank per SDG                                                                                     | As per ILM04.0, Exhibit E, Section V, part 4, subpart b)                           | If the criteria are exceeded, all samples associated with the blank shall be redigested and reanalyzed for that analyte.                                                                                                                                                                                                                                                     |
| Interference Check Sample (ICS)                                            | 1 per 20 analytical samples, per analysis run; ILM04.0, Exhibit E, Section V, part 5                                       | ±20% of the established mean value for the analyte                                 | If the criteria are not met, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last acceptable ICS.                                                                                                                                                                                           |

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| QC Checks Required                                                                 | Frequency of QC Checks                               | Acceptance Limits                                                                                                            | Corrective Action                                                                                                                                                                                                                                                                                                                                                      |
|------------------------------------------------------------------------------------|------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Solid Matrix Laboratory Control Sample (LCS)                                       | As per ILM04.0, Exhibit E, Section V, part 8         | The required quantitation limits must be met. Recovery not to exceed 125%.                                                   | If the criteria are not met, terminate the analysis, correct the problem, and redigest and reanalyze the analytical samples associated with the noncompliant LCS.                                                                                                                                                                                                      |
| Spike Sample Analysis                                                              | 1 per SDG                                            | 75 to 125% recovery                                                                                                          | If limits are not within the accepted criteria, note this in the narrative and all samples associated with that spike sample are flagged with the letter "N" on FORMS I-IN and V-IN.<br><br>If the sample concentration exceeds the spike concentration by a factor of four, the data shall be reported unflagged, even if the percent recovery criteria are exceeded. |
| Duplicate Sample Analysis                                                          | 1 per SDG                                            | 20% for RPD if duplicates are $\geq 5x$ CRDL; $\pm$ CRDL if duplicates are $<5x$ CRDL; ILM04.0, Exhibit E, Section V, part 7 | If results are outside the control limits, flag all the data for samples associated with that duplicate sample with an "*" on FORMS I-IN and VI-IN.                                                                                                                                                                                                                    |
| Solid Matrix Laboratory Fortified Blank spiked at the quant limits in Attachment A | 1 per SDG                                            | 50 to 150% recovery                                                                                                          | If the recoveries are outside the acceptance limits, note this in the case narrative and flag the results reported on a FORM V.                                                                                                                                                                                                                                        |
| Serial Dilution                                                                    | 1 per SDG                                            | Within 10% of the original determination                                                                                     | If the limit is exceeded, the data for all affected analytes in the samples associated with that serial dilution shall be flagged with an "E" on FORM IX-IN and FORM I-IN.                                                                                                                                                                                             |
| Interelement Correction Factors                                                    | Prior to field sample analysis and reported annually | As specified in ILM04.0, Exhibit E, Section V, part 11                                                                       | If the instrument is adjusted, the IEC for that instrument will be redetermined and established IDLs submitted. Data will be reported on FORM XI-IN.                                                                                                                                                                                                                   |

| QC Checks Required               | Frequency of QC Checks                                | Acceptance Limits                                        | Corrective Action                                                                                               |
|----------------------------------|-------------------------------------------------------|----------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|
| Instrument Detection Limit (IDL) | Prior to field sample analysis and reported quarterly | As specified in ILM04.0 in Exhibit E, Section V, part 10 | If the instrument is adjusted, the IDL for that instrument will be redetermined and established IDLs submitted. |
| Linear Range Analysis (LRA)      | Analyzed and reported quarterly                       | 5% of the true value                                     | If a sample exceeds the linear range it should be diluted and the results reported from the dilution            |
| Performance Evaluation Sample    | 1 per SDG                                             | USEPA will score the results                             | Actions will be applied on a case by case basis.                                                                |

## 9. ANALYTICAL DELIVERABLES

All deliverables specified in Exhibit B of ILM04.0, including all of the data reporting forms and all of the raw or supporting data must be provided. The laboratory data package deliverables must resemble as closely as possible the ILM04.0 format. The data package must be of good readable copy quality and paginated.

All analytical data and all tabulated raw or supporting data must be delivered under custody seal for each SDG. The CSF Completeness Evidence Audit Forms, which are included in Attachment C, must be completed by the laboratory for the data package deliverables submitted for each SDG. Using these audit forms, the laboratory must demonstrate that all tabulated and raw data for all field samples, standards, blanks and QC samples as well as any other documents required by ILM04.0 and this analytical specification are contained in the data package deliverable for each SDG. In addition, all telephone communication logs (telecons) between the laboratory and project personnel must be provided.

Resubmittals for missing, inaccurate, and/or questionable data from the laboratory will be requested by facsimile followed by a telephone call. The resubmittals must be provided under custody seal within 48 hours of the date of facsimile request at no additional cost and the resubmittals must be accompanied by additional completed CSF Completeness Evidence Audit Forms.

Data package deliverables for each SDG must include the following:

- A Case Narrative must be provided that contains a detailed description of the sample preparation and analysis methodology employed, any deviations from the requirements of this analytical specification, problems encountered and their resolution, and any anomalies in the reported data. The laboratory sample identification numbers and the EPA assigned sample numbers must be cross-

referenced in the Case Narrative.

- A copy of this analytical specification must be provided.
- Results for all samples, QC analyses, Quarterly Verification of Instrument Parameters forms, raw and tabulated data, and copies of the digestion logs must be included with the Inorganic Analysis Data Reporting Forms. The sample results for blanks, MS/MSDs, and PE samples must be reported on Form Is that have been modified to include all target compounds. All sample results must be reported on a dry weight basis in mg/kg. ILM04.0 sample result qualifiers must be used on all Form Is. Additional sample result qualifiers may be utilized by the laboratory (to meet the requirements contained in Sections 7 and 9 of this analytical specification), however, they must be completely defined in the Case Narrative.
- The SOW-required header information must be supplied on all Forms.
- The MS recovery results must be reported on FORM V-IN. Values that exceed the QC limits must be flagged with a "N" on FORM I-IN.
- The LFB recoveries must be reported on a FORM V-IN modified to indicate that the results are LFB recoveries.
- The Method Blank(s) and corresponding samples must be reported on FORM III-IN.
- The initial calibration results for ICP and GFAA analyses must be reported on FORM II-IN.
- All raw data, including reports for all standards, blanks, field samples and QC samples must be provided.
- All sample tracking reports (shipper information), sampling chain-of-custody forms, and custody seals must be provided in the data package.
- Copies of sample log-in/tracking sheets indicating the cooler temperature and the sample arrival time and date, and any telephone logs referring to the samples, must be provided in the data package.
- Provide all sample logbook pages, which have recorded the results for all % solids determinations with pre/post sample weights, start/stop times for desiccator cooling and start/stop times for post-drying sample weighing, spikes concentrations and volumes added, all LCS preparation records, and pages from any other logbook that the laboratory generated in the processing of the samples.

- Include the concentration of the spikes, calibration standards, and matrix spike components on all relevant reporting Forms and raw data.
- The source, including the manufacturer, lot number, and concentration, of all reference materials must be provided in the data package.

In addition, the laboratory must provide with the laboratory's bid or with the final data package:

An MDL study to demonstrate that the element analyzed by ICP, cold vapor AA, GFAA, or ICP TRACE can achieve the required quantitation limits presented in Attachment A prior to sample analysis. The MDL study must follow 40 CFR, Part 136, Appendix B. The MDL study must be supplied in tabular form including the standard deviations and an example calculation. Initial and continuing calibration, method blank, and instrument print out data must be provided along with the MDL study.

or

The results of a laboratory fortified blank analyzed at the required quantitation limits or lower to demonstrate the laboratory is able to detect the analytes at the low limits. Initial and continuing calibration, method blank, and instrument print out data must be provided along with the laboratory fortified blank data.

## **10. EXCEPTIONS**

If the laboratory has any questions or if the laboratory experiences problems during any time from sample scheduling/receipt through analysis contact M&E immediately.

Mr. Bruce Livingston  
Metcalf & Eddy Inc.  
30 Harvard Mill Square  
Wakefield, MA 01880-5371  
Phone (781) 224-6437  
FAX (781) 245-6293

## ATTACHMENT A

### Analytes and Required Quantitation Limits

| Element   | Required Quantitation Limit<br>mg/kg on a dry weight basis |
|-----------|------------------------------------------------------------|
| Aluminum  | 4.0                                                        |
| Antimony  | 0.30                                                       |
| Arsenic   | 0.20                                                       |
| Barium    | 2.0                                                        |
| Beryllium | 0.040                                                      |
| Cadmium   | 0.010                                                      |
| Calcium   | 8.0                                                        |
| Chromium  | 1.0                                                        |
| Cobalt    | 2.0                                                        |
| Copper    | 1.0                                                        |
| Iron      | 4.0                                                        |
| Lead      | 0.40                                                       |
| Magnesium | 10                                                         |
| Manganese | 1.0                                                        |
| Mercury   | 0.010                                                      |
| Nickel    | 2.0                                                        |
| Potassium | 80                                                         |
| Selenium  | 1.0                                                        |
| Silver    | 0.020                                                      |
| Sodium    | 50                                                         |
| Thallium  | 0.40                                                       |
| Vanadium  | 1.0                                                        |
| Zinc      | 2.0                                                        |

**ANALYTICAL SPECIFICATION**  
**FOR THE ANALYSIS OF**  
**INORGANIC ANIONS BY ION CHROMATOGRAPHY IN**  
**AQUEOUS SAMPLES (METHOD 300.0)**

*Prepared by:*

**Metcalf & Eddy**  
**Wakefield, Massachusetts**  
**Revision 1**  
**March 1999**

## **1. SCOPE**

This specification is for the analysis of aqueous matrices for the following inorganic anions using ion chromatography: chloride, nitrate, nitrite, and sulfate. The method is based upon Method 300.0: Determination of Inorganic Anions by Ion Chromatography, from *Methods for the Determination of Inorganic Substances in Environmental Samples* - EPA/600/R-93-100, August 1993. Aqueous samples are injected into a stream of carbonate/bicarbonate eluent, and passed through a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

## **2. PURPOSE**

The data derived from these analyses will be used to determine whether natural attenuation of groundwater contaminants is occurring, and the extent to which it is occurring at different locations in the contaminant plume.

## **3. DEFINITION OF WORK**

Aqueous samples, most of which will be groundwater, will be analyzed for inorganic anions in accordance with Method 300.0 including the modifications presented within this specification. It is anticipated that some samples may require multiple analyses since dilution may be required to put some anions within calibration range. The laboratory is required to report results for all diluted and undiluted analyses performed. Although chloride concentrations may be elevated for samples from some sites, M&E requires that at least one analysis of the sample be undiluted, such that the practical quantitation limits are met for each anion. If elevated concentrations are anticipated, M&E will indicate this on the work order and/or chain-of-custody form.

The laboratory must provide with the bid package one of the following proofs of laboratory capability generated during the past year of operation:

- A Method Detection Limit (MDL) study conducted according to 40 CFR Part 136 Appendix B with practical quantitation limits (PQL) less than or equal to those specified in Attachment A for each of the anions listed.
- A laboratory fortified blank (LFB) analysis containing all anions listed above at a concentration equal to the practical quantitation limit reported with a recovery of 90 to 110 percent of the true value.
- An initial calibration (IC) meeting the criteria presented in Section 7, Item B of this specification.



Should one of these proofs of capability not be available for delivery with the bid, it may be submitted after the bid, but one of these will be required to be submitted and accepted by M&E prior to the analysis of any samples.

Performance evaluation (PE) samples may be provided with up to one in each sample delivery group (SDG) to be analyzed along with the field samples. An SDG is defined in Exhibit A, Section II G of the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Inorganics Analysis, Multi-Media, Multi-Concentration (ILM04.0).

#### **4. SCHEDULE**

Target sampling dates will be specified in each work order. Samples will be shipped at most one day after collection. Samples to be analyzed for nitrate and/or nitrite will be shipped the day of collection. Saturday delivery may be required. An overnight delivery service will be used. Contacts for shipping will be provided in each work order. Data delivery inquiries may be made to Mr. Bruce Livingston, Metcalf & Eddy Inc., (781) 224-6437, or the person identified in the work order.

##### **Holding Time:**

Analysis for nitrate and nitrite are required to be performed within forty-eight (48) hours of sample collection for aqueous samples. Analysis for chloride and sulfate are required to be performed within twenty-eight (28) days of sample collection for aqueous samples. Sample preservation will be noted on the chain of custody.

##### **Delivery of Data:**

Data is required to be delivered to M&E or the person identified in the work order within thirty-five (35) days of laboratory receipt of the last sample of each SDG of twenty (20) samples or less. Data must be delivered under chain of custody. Data delivered to M&E must be sent to Mr. Bruce Livingston, Metcalf & Eddy, Inc., 30 Harvard Mill Square, Wakefield, MA 01880-5371.

#### **5. ANALYTICAL REFERENCES**

The reference method is Method 300.0: Determination of Inorganic Anions by Ion Chromatography, from *Methods for the Determination of Inorganic Substances in Environmental Samples* - EPA/600/R-93-100, August 1993. Reference is also made to the USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Inorganics Analysis, Multi-Media, Multi-Concentration (ILM04.0).

## **6. SAMPLE PRESERVATION**

All samples will be preserved by chilling and maintaining them at  $4\pm 2^{\circ}\text{C}$  and protecting them from light. No additional sample preservation is required. USEPA cooler temperature indicators will be placed in the sample shipping containers. If the temperature of the cooler exceeds  $6^{\circ}\text{C}$  upon sample receipt, the laboratory must contact M&E immediately regarding the temperature deviation.

## **7. ANALYTICAL PROCEDURES**

Method 300.0: Determination of Inorganic Anions by Ion Chromatography will be followed as promulgated and will be modified as instructed in the following items:

- A. One of the following must be supplied with the laboratory's bid or proposal or one of these must be conducted prior to the analysis of any samples using this specification:

An MDL study is required. This study must follow the requirements described in 40 CFR Part 136 Appendix B using at least seven replicate analyses of calibration standard at a concentration within three to five times the determined MDLs. The study must demonstrate MDLs and present reporting limits acceptable to M&E. MDL studies not meeting these requirements will not be considered. The MDL study may be a study performed within the last year.

or:

A Laboratory Fortified Blank (LFB) containing all anions listed above at a concentration equal to the practical quantitation limit reported. The percent recovery for each anion must be within 90 to 110 percent of the true value. The LFB must have been performed in the last six months.

or:

An initial calibration meeting the criteria presented under Item B. The initial calibration must have been performed in the last six months.

and:

In addition to one of the preceding choices, the laboratory must submit a successful analysis of a Quality Control Standard (QCS), a secondary source standard, as described in Section 9.2.3 of Method 300.0. The standard concentrations must be within  $\pm 10\%$  of the actual concentration. Concentration of the standard will be equivalent to the midpoint of the calibration curve.

- B. Initial calibration, as described in Section 9.2.2 of Method 300.0- Linear Calibration Range, must be determined initially, and re-established at a minimum of each working day. Initial calibration must also be performed whenever the anion eluent strength is changed, or whenever a significant change in instrument response is observed or expected. Sufficient number of standards must be used to establish linearity throughout the calibration range. At a minimum, three calibration standards and one blank will be used to determine linearity. At a minimum, the first standard concentration will be equivalent to the practical quantitation limit, the second standard concentration will be equivalent to the upper calibration limit, and the third standard concentration will be equivalent to the midpoint of the calibration range. The correlation coefficient must be  $\geq 0.995$  for each anion. Calibration standards should be prepared the day of analysis for nitrite.
- C. Since initial calibration will be performed daily, as described under Item B, verification of linearity of the calibration range, as described in Section 9.2.2 of Method 300.0, need not be performed.
- D. The Quality Control Sample (QCS), a secondary source standard, as described in Section 9.2.3 of Method 300.0, will be analyzed once when beginning the use of this method, and monthly thereafter. The standard concentrations must be within  $\pm 10\%$  of actual concentration. Concentration of the standard will be equivalent to the midpoint of the calibration curve.
- E. A Laboratory Reagent Blank (LRB), as described in Section 9.3.1 of Method 300.0 must be analyzed at the beginning of each sample batch, prior to sample analysis, and after all calibration standards and QC samples. Concentration of any target anion cannot exceed  $\frac{1}{2}$  of the practical quantitation limit for that anion.
- F. A Laboratory Fortified Blank (LFB), as described in Section 9.3.3 of Method 300.0, must be performed once per analytical batch. Initially, LFB recoveries should be reported relative to the 90-110% recovery criteria. Once a minimum of 20 to 30 analyses have been performed, the laboratory may establish QC criteria based on control charts as defined in Section 9.3.3 of Method 300.0.
- G. Instrument Performance Checks (IPC), Continuing Calibration Blanks (CCB), and samples will be analyzed as described in Section 9.3.4 of Method 300.0. In addition, samples for which the concentrations of a target anion exceeds the calibration range must be diluted and reanalyzed.
- H. A Laboratory Fortified Matrix (LFM), discussed in Section 9.4.1 of Method 300.0, as well as an LFM duplicate (also known as a matrix spike/matrix spike duplicate), will be performed on a minimum of one per SDG. M&E will select the field sample for MS/MSD analysis, and indicate the selection on the chain-of-custody form.

Criteria for the recovery of each anion will be 80-120% of spiked concentrations.  
Criteria for percent difference (%D) is  $\leq 15\%$  for each anion.

## 8. QC REQUIREMENTS

| QC Element Required                                                        | Frequency of Performance                                                   | Acceptance Limits                                                                     | Corrective Action                                                                                                                                                                                                     |
|----------------------------------------------------------------------------|----------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| QCS and an MDL Study, LFB, or Initial Calibration                          | Once, to be delivered with laboratory bid, or prior to analysis of samples | Must meet the requirements in Section 7, Item B                                       | Laboratory not considered without QCS and MDL study, LFB or initial calibration proof of capability                                                                                                                   |
| Initial Calibration                                                        | Once per working day, or more frequently as needed                         | $\geq 0.995$ correlation coefficient for all target anions                            | Rerun until all criteria are met. Must meet criteria prior to analysis of samples                                                                                                                                     |
| Quality Control Sample (Secondary Source)                                  | Once initially, as noted above, and monthly thereafter                     | Percent recovery 90-110% of actual for all target anions                              | Determine source of problem and resolve prior to sample analysis.                                                                                                                                                     |
| Instrument Performance Checks (IPC) and Continuing Calibration Blank (CCB) | Every 10 samples, and once at the end of the batch                         | IPC %D $\leq 10\%$ for all target anions                                              | Reanalyze the IPC; If the second analysis does not meet criteria, sample analysis must be discontinued. All samples analyzed after the last acceptable IPC must be reanalyzed. Initial calibration must be performed. |
| Laboratory Reagent (Method) Blanks                                         | At the beginning of each sample batch                                      | Contamination $< \frac{1}{2}$ the practical quantitation limits for all target anions | Determine the source of contamination and rerun all affected samples                                                                                                                                                  |

| QC Element Required                                                   | Frequency of Performance | Acceptance Limits                                                                          | Corrective Action                                                                                                                            |
|-----------------------------------------------------------------------|--------------------------|--------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| Laboratory Fortified Blank                                            | One per sample batch     | Percent recovery 90-110% for all target anions or within laboratory control chart criteria | Reanalyze LFB. LFB criteria must be met prior to sample analysis on a daily basis                                                            |
| Laboratory Fortified Matrix and Laboratory Fortified Matrix Duplicate | One pair per SDG         | Percent recovery 80-120% of actual;<br>RPD ≤ 15%                                           | The LFM/LFMD recovery criteria are advisory. No corrective action is necessary. Flag recoveries or RPDs outside QC criteria on the Form III. |

## 9. ANALYTICAL DELIVERABLES

- a. The laboratory deliverables must resemble as closely as possible the Contract Laboratory Program (CLP) RAS Inorganic SOW OLM04.0 format. Reference is made to data reporting forms provided in SOW OLM04.0. The data package must be of good readable copy quality and any missing deliverable must be provided within 48 hours from the time requested at no additional charge. The following items are required as documented deliverables as well as meeting the required quantitation limits presented in Attachment A:
  - Results for all samples, MDL Study Analyses, Initial Calibration Standards, Quality Control Samples, Instrument Performance Checks, Laboratory Reagent Blanks, Laboratory Fortified Blanks, Continuing Calibration Blanks, Laboratory Fortified Matrix and Laboratory Fortified Matrix Duplicate Samples, and PE sample, if submitted, must be reported on a Form 1 modified to include all target anions. All applicable header information must be retained and information supplied on the modified Form 1 and all other data reporting forms.
  - MDL study raw data, including all calculations performed to arrive at the MDLs.
  - The Laboratory Fortified Matrix / Laboratory Fortified Matrix Duplicate recoveries and RPD must be reported on a modified Form 5. Values that exceed the QC Limits should be flagged with a "\*\*".
  - The Laboratory Fortified Blank recoveries must be reported on a modified Form 5. Values that exceed the QC Limits should be flagged with a "\*\*".

- The Laboratory Reagent Blank(s) must be reported on a modified Form 3.
- All raw data for the initial calibration standards must be reported. Initial calibration results, including correlation coefficients ( $r^2$ ) for each target anion, must be reported on a modified Form 2.
- The Instrument Performance Check results must be reported on a modified Form 2, and should include the standard concentrations, the instrument quantitated concentration, and the RPD.
- Report the analytical sequence for all instruments on Form 14.
- All sample tracking reports, chain of custody forms, custody seals, and any telephone logs referring to the samples must be delivered under chain of custody with the data package.
- The laboratory must provide a copy of this Analytical Specification.
- Copies of sample log in sheets indicating the cooler temperature and the sample arrival time and date must be provided.
- Bench sheets for all standards preparation, including the volume and concentration of all standards analyzed and spikes performed, any sample dilutions, instrument run logs, quantitation dates and instrument run times, dates, and pH determination bench sheets must be provided.
- The Laboratory ID Numbers and concentrations of the calibration standards used for the initial calibration, instrument performance checks, blanks, samples, QC samples, and PE samples must be clearly defined in the data.
- The source of all standardizing materials must be documented. The concentrations of all standards must be indicated.
- An example of an actual calculation where a positive target compound result was found.
- A case narrative explaining the methodology used, including the following: make and model of the anion guard columns, separator columns, analytical columns, suppressor devices, detectors, eluent and regeneration solutions and strengths, sample loop volume, and nominal sample volume injected. The case narrative will also explain any deviations from the method as presented in this specification, any deviations from laboratory Standard Operating

Procedures for this analysis, any problems encountered, problem resolutions, and any factors affecting the validity of the data. The narrative must also show all laboratory sample ID numbers and their corresponding field sample numbers.

- All chromatograms (with peaks used for quantitation noted, chromatographic conditions, volume injected, and instrument number) for calibration verifications, samples, diluted samples, QC samples, PE samples, and spike recoveries must be provided.

b. Complete Sample Delivery Group File (CSF) Audit

Region I EPA requires that all analytical data and all tabulated raw or supporting data be delivered with each SDG. With each SDG the CSF Completeness Evidence Audit must be carried out. The CSF Completeness Evidence Audit Forms are included in Attachment B and must accompany each data package. The laboratory using these audit forms must show that each piece of sample data, raw data, calibration data, QC data and any other requirement of the statement of work or analytical specifications are included in the data package.

The forms included in Attachment B are for all types of data packages. For this analytical specification the laboratory will use the forms supplied to the best of their ability where deliverable items are applicable.

## 10. EXCEPTIONS

If QC requirements are not met or QC acceptance limits are exceeded; or if analytical samples are compromised, destroyed or lost; or if matrix interference is suspected; or there are any other problems immediately contact:

Bruce Livingston  
Metcalf & Eddy Inc.  
30 Harvard Mill Square  
Wakefield, MA 01880-5371  
Phone (978) 224-6437  
FAX (978) 245-6293

## ATTACHMENT A

| Anion    | Practical Quantitation Limit (mg/L) |
|----------|-------------------------------------|
| Chloride | 0.25                                |
| Nitrate  | 0.10                                |
| Nitrite  | 0.10                                |
| Sulfate  | 0.25                                |



**ANALYTICAL SPECIFICATION  
FOR THE ANALYSIS OF  
WATER QUALITY PARAMETERS**

**(Alkalinity, Ammonia, Chloride, Chemical Oxygen Demand,  
Nitrate/Nitrite-N, Phosphorus, Sulfate, Total Dissolved Solids,  
Total Suspended Solids, and Total Organic Carbon)**

***Prepared by:***

**Metcalf & Eddy, Inc.  
Wakefield, Massachusetts  
Revision 2  
March 1999**

## **1. SCOPE**

This specification is for the analysis of water quality parameters in groundwater, surface water, treatability study influents and effluents, or other aqueous matrices. The water quality parameters include: alkalinity, ammonia, chloride, chemical oxygen demand (COD), nitrate/nitrite-N, phosphorus, sulfate, total dissolved solids (TDS), total suspended solids (TSS), and total organic carbon (TOC). Performance evaluation (PE) samples may be submitted for analysis. If PEs are submitted, instructions for preparation and analysis will be provided in the sample shipping container.

The laboratory must meet the required detection limits as detailed in Section 6 and prove their capabilities by delivering a recent MDL study (not more than threemonths old). The MDL study must be provided with the bid package.

## **2. PURPOSE**

The data obtained using this specification will be used to further delineate contamination, characterize the treatability of contaminated water, determine background water quality parameter concentrations, and for other purposes.

## **3. DEFINITION OF WORK**

Aqueous samples will be analyzed for the above referenced water quality parameters. The number of samples and the matrix will be detailed in each individual work order. Samples will be submitted in sample delivery groups (SDGs). An SDG is as defined in EPA statement of work (SOW) ILM04.0, Exhibit A, Section 2G.

## **4. SCHEDULE**

Target sampling dates will be provided in each work order. Samples will be shipped at most one day after collection. Saturday delivery may be required. An overnight delivery service will be used. Contacts for shipping and data delivery requirements will be provided in each individual work order.

**Holding Time and Preservation:** Sample holding times and sample preservation are detailed in Section 6 of this specification.

**Delivery of Data:** Sample data must be delivered to M&E or the person identified in the work order within thirty-five (35) days of laboratory receipt of the last sample in each SDG. Data must be submitted under chain of custody.

Data delivered to M&E must be sent to the project chemist specified in the work order or:

Bruce Livingston  
Metcalf & Eddy, Inc.  
30 Harvard Mill Square  
Wakefield, MA 01880  
Phone: (781) 224-6437  
Fax: (781) 245-6293

## 5. ANALYTICAL REFERENCES

The analytical methods are drawn from EPA Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, with updates to Rev. 3-83. The individual methods to be followed include:

Alkalinity - Method 310.1  
Ammonia - Method 350.2  
Chloride - Method 325.3  
Chemical Oxygen Demand (COD) - Method 410.1  
Nitrate/Nitrate-N - Method 353.1  
Phosphorus - Method 365.4  
Sulfate - Method 375.4  
Total Dissolved Solids (TDS) - Method 160.1  
Total Suspended Solids (TSS) - Method 160.2  
Total Organic Carbon (TOC) - Method 415.2

The laboratory may choose to perform a different but equivalent analytical procedure. If so, they must detail that procedure with an SOP that meets the requirements of this specification.

## 6. SAMPLE PRESERVATION AND DETECTION LIMITS

| Parameter  | Method                                            | Reporting Limit (mg/l) | Holding Time <sup>1</sup> | Preservation                                       |
|------------|---------------------------------------------------|------------------------|---------------------------|----------------------------------------------------|
| Alkalinity | 310.1 - Titrimetric                               | 2.0                    | 14 days                   | Cool 4°C                                           |
| Ammonia    | 350.2 - Colorimetric, Titrimetric; Potentiometric | 0.05                   | 28 days                   | Cool 4°C, H <sub>2</sub> SO <sub>4</sub> to pH < 2 |
| Chloride   | 325.3 - Titrimetric                               | 2.0                    | 28 days                   | Cool 4°C                                           |

## 6. SAMPLE PRESERVATION AND DETECTION LIMITS (Continued)

| Parameter             | Method                                                     | Reporting Limit (mg/l) | Holding Time <sup>1</sup> | Preservation                                          |
|-----------------------|------------------------------------------------------------|------------------------|---------------------------|-------------------------------------------------------|
| COD                   | 410.1 - Titrimetric                                        | 50                     | 28 days                   | Cool 4°C,<br>H <sub>2</sub> SO <sub>4</sub> to pH < 2 |
| Nitrate/<br>Nitrite-N | 353.1 - Colorimetric,<br>Automated, Hydrazine<br>Reduction | 0.1                    | 28 days                   | Cool 4°C,<br>H <sub>2</sub> SO <sub>4</sub> to pH < 2 |
| Phosphorus            | 365.4 - Colorimetric                                       | 0.1                    | 28 days                   | Cool 4°C,<br>H <sub>2</sub> SO <sub>4</sub> to pH < 2 |
| Sulfate               | 375.4 - Turbidimetric                                      | 2.0                    | 28 days                   | Cool 4°C                                              |
| TDS                   | 160.1 - Gravimetric                                        | 10.0                   | 7 days                    | Cool 4°C                                              |
| TSS                   | 160.2 - Gravimetric                                        | 4.0                    | 7 days                    | Cool 4°C                                              |
| TOC -<br>low level    | 415.2 - UV Promoted,<br>Persulfate Oxidation               | 0.1                    | 28 days                   | Cool 4°C,<br>H <sub>2</sub> SO <sub>4</sub> to pH < 2 |

<sup>(1)</sup> Holding time is defined as the time between sample collection and sample preparation/analysis.

All samples will be preserved by chilling and maintaining them at 4 ± 2°C. USEPA cooler temperature indicators will be placed in the sample shipping containers. If the temperature of the cooler exceeds 6°C upon sample receipt, the laboratory must contact M&E immediately regarding the temperature deviation.

## 7. ANALYTICAL PROCEDURES

### a. Alkalinity - Method 310.1 (Titrimetric)

1. Analysis for alkalinity must begin as soon as possible since atmospheric carbon dioxide can affect the results. If portions from the same sample container are to be analyzed for other parameters, complete alkalinity analysis first.
2. Appropriate aliquots should be used to avoid a titration volume greater than 50 mls.
3. Follow Section 4.1 of the method for pH specifications. At least two different pH solutions must be used during standardization. The solutions must bracket the expected pH of the samples. Repeat adjustments of

successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value. A separate source pH check standard must then be analyzed to verify the calibration. In the event that the pH meter is not equipped with temperature compensation, all calibration solutions and standards must be measured at the same temperature. Calibration must be documented in a laboratory notebook and provided with the final data package.

4. A normality check of the titrant must be performed prior to sample analysis. If the normality is within 10% of that initially determined, the newly determined normality must be used in the calculations. If it is not within 10%, a fresh titrant must be prepared. The normality of the fresh titrant must be within 20% of that specified by the method.
5. Follow Section 6.1 of the method for the preliminary titration of the sample to determine the normality of the titrant to be used. Then, follow Section 6.2 for high alkalinity samples or Section 6.3 for low alkalinity samples. The normality of the titrant used for each sample must be documented in a laboratory notebook and included with the final deliverables.
6. Analysis of a method blank, prepared using laboratory pure water (deionized/distilled) and all reagents used for the associated samples, must be performed. The method blank should be run in conjunction with the calibration and following every twenty (20) analytical samples. The method blank must not have an alkalinity more than half the reporting limit of the method, or the source of water must be changed to a cleaner source and all samples relating to that blank must be reanalyzed.
7. One sample in twenty (20) field samples must be analyzed in duplicate and the percent difference between results must be less than 20%. If the difference is greater than 20%, the analysis of both samples must be repeated. If the difference is still >20%, flag the associated results with "\*\*".
8. Initially, an EPA check standard must be analyzed 3 consecutive times with each analytical batch of twenty (20) samples or less, prior to blank and sample analysis. All three (3) analyses must be reported in the deliverable package. The final or third analysis must meet recovery criteria. The EPA check standard must also be analyzed at a frequency of one (1) per ten (10) field samples and at the end of the analytical sequence. If a check sample is not available, a standard with a total alkalinity of 10 mg/L as CaCO<sub>3</sub>, which is from a source independent of that used to check the normality of

the titrant, may be used. Results must agree within 15% of the true value. If the precision criteria are not met, a normality check must be performed. Then, another EPA check standard, method blank, and all associated field samples analyzed since the last compliant calibration check must be reanalyzed.

**b. Ammonia - Method 350.2 (Colorimetric; Potentiometric)**

1. For sample concentrations between 0.05 mg/L to 1.0 mg/L use colorimetric procedure. For sample concentrations between 0.05 mg/L to 1400 mg/L use potentiometric procedure. For sample concentrations between 1 mg/L to 25 mg/L use titrimetric procedure with additional requirements detailed in item c. of this section.
2. A 5-point calibration curve must be generated daily, prior to sample analysis. The lowest standard must be at the reporting limit and the range of the calibration must bracket the concentration of the samples. The calibration coefficient must be greater than 0.995. If the criteria are not met, fresh standards must be prepared and a new standard curve generated. Samples may not be analyzed until the criteria are met. If a sample result falls outside the calibration range, either dilute the sample or recalibrate using standards to span the desired range.
3. An EPA check standard, which is digested with the samples, must be analyzed prior to the samples, every ten (10) samples and at the end of the analytical sequence. If one is unavailable, a 0.1 mg  $\text{NH}_3\text{-N/L}$  standard, which is from a source independent from that of the calibration standards, may be used. The results must be within 15% of the true value. If the results do not agree, a new standard curve must be generated, and all associated QC samples and field samples must be redigested and reanalyzed. Limits must be met prior to sample analysis. Report the source of the check standard in the final deliverables.
4. An EPA check sample which is not digested must be analyzed three (3) consecutive times prior to sample analysis. All three (3) analyses must be reported in the deliverable package. The final or third analysis must meet recovery criteria. If unavailable, a mid-range standard from an independent source may be used. The EPA check standard or standard must also be analyzed one (1) per ten (10) samples and at the end of the analytical sequence. Results must agree within  $\pm 15\%$  of the true value. If the result do not agree within 15%, a reanalysis of the check standard must be conducted. If the results are still not within 15%, a new calibration curve must be prepared and all samples analyzed following the last compliant

check standard must be reanalyzed. Steps taken to remedy the problem must be reported in a laboratory notebook and included in the data package.

5. For every batch of twenty (20) samples or less, a distilled water method blank must be digested. The method blank must be analyzed at the beginning of the analytical sequence, following the analysis of the calibration curve and the check standard, but prior to the analysis of any samples. If contamination is present at concentrations exceeding  $\frac{1}{2}$  RL, redigest a new blank, EPA check standard, and all associated field samples. Criteria must be met prior to sample analysis.
6. A matrix spike must be performed at a frequency of one (1) per twenty (20) field samples. Spike a sample prior to digestion at a concentration equal to the mid point of the calibration curve. Recovery must be within 80-120%. If limits are not met, redigest and reanalyze the spiked sample. If the results are still out, flag the results with a "#".
7. One (1) sample per twenty (20) field samples must be analyzed in duplicate and the percent difference between results must be less than 20%. If the difference is greater than 20%, the analysis of both samples must be repeated. If the difference is still  $>20\%$ , flag the results with "\*\*".

**c. Ammonia - Method 350.2 (Titrimetric)**

1. For sample concentrations between 1 mg/L to 25 mg/L.
2. Four practice runs must be made before field sample analysis begins. They must be clearly documented in the laboratory notebook and provided with the final deliverables.
3. Initially, an EPA check standard must be analyzed three (3) consecutive times with each analytical batch (twenty (20) samples or less), prior to blank and sample analysis. All three (3) analyses must be reported in the data package. The final or third analysis must meet recovery criteria. The EPA check standard must also be analyzed at a frequency of one (1) per ten (10) field samples and at the end of the analytical sequence. If a check sample is not available, a 20 mg/L standard, which is from a source independent of that used to check the normality of the titrant, may be used. Results must agree within  $\pm 15\%$  of the true value. If this criteria is not met, a normality check must be performed. Then, another EPA check standard, method blank, and all associated field samples analyzed prior to the last compliant calibration check must be reanalyzed.

4. A normality check of the titrant must be performed prior to sample analysis. If the normality is within 10% of that initially determined, the newly determined value must be used in the calculations. If it is not within 10%, a fresh titrant must be prepared. The normality of the fresh titrant must be within 20% of that specified by the method.
5. Analysis of a method blank, prepared using laboratory pure water (deionized/distilled) and all reagents used for the associated samples, must be performed. The method blank should be run in conjunction with the standardization and following every twenty (20) analytical samples. The method blank must not contain a concentration of chloride more than half the reporting limit of the method, or the source of water must be changed to a cleaner source and all samples relating to that blank must be reanalyzed.
6. One (1) sample in twenty (20) field samples must be analyzed in duplicate and the percent difference between results must be less than 20%. If the difference is greater than 20%, the analysis of both samples must be repeated. If the difference is still >20%, flag the results with "\*\*".
7. A matrix spike must be performed at a frequency of one (1) in twenty (20) samples. The sample must be fortified at a concentration of 10 mg/L, and the recovery of the spike must be within 80-120%. If the spike is outside the limits, repeat the analysis. If the results are still outside the limits, flag the results with a "#".

**d. Chloride - Method 325.3 (Titrimetric)**

1. A sample aliquot must not contain more than 20 mg Cl per 50 ml, in order to avoid using a large titration volume.
2. Follow the procedure exactly as described in Section 6 of the method, with the following exceptions:

If the sample contains less than 0.1 mg/l, there is no need to concentrate the sample.

If the sample aliquot contains less than 2.5 mg of chloride, another aliquot must be analyzed using 0.0141N mercuric nitrate titrant (in Section 6.6 of the method). Record the normality of the titrant used in a laboratory notebook and include with the final deliverables.



If the end point of the titration is difficult to detect, complete Section 6.7 of the method and report with the sample results.

3. Four practice runs must be made before field sample analysis begins. They must be clearly documented in the laboratory notebook and provided with the final deliverables.
4. Initially, an EPA check standard must be analyzed three (3) consecutive times with each analytical batch (twenty (20) samples or less), prior to blank and sample analysis. All three (3) analyses must be reported in the data package. The final or third analysis must meet recovery criteria. The EPA check standard must also be analyzed at a frequency of one (1) per ten (10) field samples and at the end of the analytical sequence. If a check sample is not available, a 20 mg/L standard, which is from a source independent of that used to check the normality of the titrant, may be used. Results must agree within 15% of the true value. If this criteria is not met, a normality check must be performed. Then, another EPA check standard, method blank, and all associated field samples analyzed prior to the last compliant calibration check must be reanalyzed.
5. A normality check of the titrant must be performed prior to sample analysis. If the normality is within 10% of that initially determined, the newly determined value must be used in the calculations. If it is not within 10%, a fresh titrant must be prepared. The normality of the fresh titrant must be within 20% of that specified by the method.
6. Analysis of a method blank, prepared using laboratory pure water (deionized/distilled) and all reagents used for the associated samples, must be performed. The method blank should be run in conjunction with the standardization and following every twenty (20) analytical samples. The method blank must not contain a concentration of chloride more than half the reporting limit of the method, or the source of water must be changed to a cleaner source and all samples relating to that blank must be reanalyzed.
7. One (1) sample in twenty (20) field samples must be analyzed in duplicate and the percent difference between results must be less than 20%. If the difference is greater than 20%, the analysis of both samples must be repeated. If the difference is still >20%, flag the results with "\*\*".
8. A matrix spike must be performed at a frequency of one (1) in twenty (20) samples. The sample must be fortified at a concentration of 10 mg/L, and the recovery of the spike must be within 80-120%. If the spike is

outside the limits, repeat the analysis. If the results are still outside the limits, flag the results with a "#".

**e. Chemical Oxygen Demand (COD) - Method 410.1 (Titrimetric)**

1. Follow the procedure for sample analysis outlined in Section 7.0 of the method. Since the samples may contain volatile organic compounds, use an Allihn Condenser and add the sulfuric acid-silver sulfate solution (as described in Section 7.1.1 of the method) to avoid volatilization.
2. A normality check of the titrant must be performed prior to sample analysis. If the normality is within 10% of that initially determined, the newly determined value must be used in the calculations. If it is not within 10%, a fresh titrant must be prepared. The normality of the fresh titrant must be within 20% of that specified by the method.
3. For every batch of twenty (20) samples or less, a distilled water method blank must be refluxed. The method blank must be analyzed at the beginning of the analytical sequence, following the analysis of the calibration curve and the check standard, but prior to the analysis of any samples. If contamination is present at concentrations exceeding  $\frac{1}{2}$  reporting limit (RL), redigest a new blank, EPA check standard and all associated field samples. Criteria must be met prior to sample analysis.
4. An EPA check sample must be analyzed (carried through the entire analytical procedure) with each group of samples refluxed. If unavailable, a mid-range potassium acid phthalate standard may be used. Results must agree  $\pm 15\%$  of the true value. If the results do not agree within 15%, a new normality check must be performed and the source of the problem must be identified and corrected prior to sample analysis. All associated samples must be reanalyzed (including the reflux step), and a new EPA check standard must be analyzed. Steps taken to identify and remedy the problem must be recorded in a laboratory notebook and included in the final data package.
5. An EPA check sample, which is not refluxed, must be analyzed three (3) consecutive times prior to sample analysis. All three analyses must be reported in the data package. The final or third analysis must meet recovery criteria. If unavailable, a mid-range potassium acid phthalate standard may be used. The EPA check standard or standard must also be analyzed at a frequency of one (1) per ten (10) samples and at the end of the analytical sequence. Results must agree within  $\pm 15\%$  of the true value. If the results do not agree within 15%, a new normality check must be

performed and the source of the problem must be identified and corrected prior to sample analysis. Steps taken to identify and remedy the problem must be recorded in a laboratory notebook and included in the final data package.

6. Analysis of a method blank, prepared using laboratory pure water (deionized/distilled) and all reagents used for the associated samples, must be performed. The method blank should be run in conjunction with the standardization and following every twenty (20) analytical samples. The method blank must not contain a concentration of COD more than half the reporting limit of the method, or the source of water must be changed to a cleaner source and all samples relating to that blank must be reanalyzed.
7. One (1) sample in twenty (20) field samples must be analyzed in duplicate and the percent difference between results must be less than 20%. If the difference is greater than 20%, the analysis of both samples must be repeated. If the difference is still > 20%, flag the results with "\*\*".

**f. Nitrate/Nitrite-Nitrogen - Method 353.1 (Colormetric, Automated, Hydrazine Reduction)**

1. Check the pH of the sample upon receipt. If the pH is greater than 1, document the pH in the narrative.
2. During the comparison of  $\text{NO}_3$  vs.  $\text{NO}_2$  standards (see Section 7.3 of the method), if the reduction efficiency is not 100%, adjust the concentration of the hydrazine sulfate solution appropriately and repeat the check for reduction efficiency. Reduction efficiency must be 100% prior to sample analysis. Document the results in a laboratory notebook for inclusion with the final deliverables.
3. An EPA check standard must be analyzed after the calibration standards and blank and before the samples, as well as after every ten (10) samples and at the end of the analytical sequence. If an EPA check standard is not available, a 5 mg/L standard from a source independent of the calibration standards may be used. Results must agree within 15% of the true value. If the criteria are not met, a fresh standard curve must be prepared, and all samples analyzed since the previous acceptable check standard must be reanalyzed.
4. A calibration curve must be generated each day that samples are analyzed. The curve must consist of a blank and five (5) standards. The concentration of the lowest standard must be equal to the reporting limit,

and the range of the standards must bracket the concentration of the samples. The correlation coefficient must be greater than 0.995. Calibration criteria must be met prior to any samples being analyzed.

5. A matrix spike must be performed at a frequency of one (1) per twenty (20) samples. The sample must be fortified at a concentration of 0.5 mg/L, and the recovery of the spike must be within 80-120%. If the spike is outside the limits, repeat the analysis. If the results are still outside the limits, flag the results with a "#".
6. Analysis of a method blank, prepared using laboratory pure water (deionized/distilled) and all reagents used for the associated samples, must be performed. The method blank should be run in conjunction with the standardization and before every twenty (20) analytical samples. The method blank must not contain a concentration of nitrate-nitrite more than half the reporting limit of the method, or the source of water must be changed to a cleaner source and all samples relating to that blank must be reanalyzed.
7. One sample in twenty (20) field samples must be analyzed in duplicate and the percent difference between results must be less than 20%. If the difference is greater than 20%, the analysis of both samples must be repeated. If the difference is still >20%, flag the results with "\*\*".

**g. Phosphorus - Method 365.4 (Colorimetric)**

1. Any glassware used must be acid washed in hot 1:1 HCl and rinsed with distilled water (see Method 365.3, Section 6.2). This includes any glassware used in the analysis, as well as that used for the preparation of associated reagents.
2. A 5-point calibration curve must be generated daily, prior to sample analysis. The lowest standard must be at the reporting limit and the range of the calibration must bracket the concentration of the samples. The calibration coefficient must be greater than 0.995. If the criteria are not met, fresh standards must be prepared and a new standard curve generated. Samples may not be analyzed until the criteria are met. If a sample result falls outside the calibration range, either dilute the sample or recalibrate using standards to span the desired range.
3. An EPA check standard, which is digested with the samples, must be analyzed prior to the samples, every ten (10) samples and at the end of the analytical sequence. If one is unavailable, a 0.1 mg P/L standard, which

is from a source independent from that of the calibration standards, may be used. The results must be within 15% of the true value. If the results do not agree, a new standard curve must be generated, and all associated QC samples and field samples must be redigested and reanalyzed. Limits must be met prior to sample analysis. Report the source of the check standard in the final deliverables.

4. An EPA check sample which is not digested must be analyzed three (3) consecutive times prior to sample analysis. All three (3) analyses must be reported in the deliverable package. The final or third analysis must meet recovery criteria. If unavailable, a mid-range standard from an independent source may be used. The EPA check standard or standard must also be analyzed one (1) per ten (10) samples and at the end of the analytical sequence. Results must agree within  $\pm 15\%$  of the true value. If the result do not agree within 15%, a reanalysis of the check standard must be conducted. If the results are still not within 15%, a new calibration curve must be prepared and all samples analyzed following the last compliant check standard must be reanalyzed. Steps taken to remedy the problem must be reported in a laboratory notebook and included in the data package.
5. For every batch of twenty (20) samples or less, a distilled water method blank must be digested. The method blank must be analyzed at the beginning of the analytical sequence, following the analysis of the calibration curve and the check standard, but prior to the analysis of any samples. If contamination is present at concentrations exceeding  $\frac{1}{2}$  RL, redigest a new blank, EPA check standard, and all associated field samples. Criteria must be met prior to sample analysis.
6. A matrix spike must be performed at a frequency of one (1) per twenty (20) field samples. Spike a sample prior to digestion at a concentration equal to the mid point of the calibration curve. Recovery must be within 80-120%. If limits are not met, redigest and reanalyze the spiked sample. If the results are still out, flag the results with a "#".
7. One (1) sample per twenty (20) field samples must be analyzed in duplicate and the percent difference between results must be less than 20%. If the difference is greater than 20%, the analysis of both samples must be repeated. If the difference is still  $> 20\%$ , flag the results with "\*\*".

**h. Sulfate - Method 375.4 (Turbidimetric)**

1. The sample aliquot must not contain more than 40 mg SO<sub>4</sub>.
2. Suspended matter and color will interfere. Perform blank correction by analyzing blanks from which the barium chloride has been omitted as per Sections 2.2 and 6.4 of the method.
3. Record all readings, at thirty (30) second intervals during the four (4) minute period, in a laboratory notebook and provide with a final deliverables.
4. A five-point calibration curve must be generated on any day during which samples are to be analyzed. The lowest standard must be equal to the reporting limit and the range of the standards must bracket the concentrations of the samples. A blank must also be included in the curve. The correlation coefficient must be >0.995. Calibration criteria must be met prior to sample analysis.
5. Analysis of a method blank, prepared using laboratory pure water (deionized/distilled) and all reagents used for the associated samples, must be performed. The method blank should be run in conjunction with the initial calibration and before every twenty (20) analytical samples. The method blank must not have a sulfate concentration more than the reporting limit of the method, or the source of laboratory pure water must be changed.
6. A mid-range continuing calibration check standard from a different source must be analyzed prior to sample analysis, after every four (4) samples and at the end of the analytical sequence. The results must be  $\pm 10\%$  of the true value. If the limits are not met, reanalyze the calibration curve, the continuing calibration check and any samples analyzed since the last acceptable continuing calibration standard before proceeding.
7. A duplicate sample must be analyzed of one (1) per twenty (20) field samples. The percent difference must be less than 20%. If the difference is greater than 20%, the analysis of both samples must be repeated. If the difference is still greater than 20%, flag the associated sample results with an asterisk "\*".
8. A matrix spike must be performed at a frequency of one (1) per twenty (20) field samples. Spike a sample at a concentration equal to the midpoint of the calibration curve. The recovery of the spike must be within  $\pm 20\%$  of

the true value. If the criteria is not met, repeat the analysis. If the results are still outside the criteria, flag the results with a "#".

**I. Total Dissolved Solids - Methods 160.1 (Gravimetric)**

1. The samples must be analyzed as soon as possible, so that in the event that the calibration check standard is outside acceptable limits and all associated samples require reanalysis, all analyses can be completed within the required, seven (7) day holding time.
2. The analytical balance utilized for measurements must be checked using class "S" weights prior to weighing each batch of twenty (20) samples or less to ensure the accuracy of the weight values obtained. The results must be recorded in a log book and supplied in the final deliverable package. The check weight must be within the manufacturer's tolerance range or the balance must be recalibrated prior to weighing the samples.
3. Glass fiber filters must be prepared according to Section 7.1 of the method. The procedure must be documented in a laboratory notebook and must be provided with the final deliverables. The name of the manufacturer and model number of the filters must also be recorded and supplied with the deliverables.
4. The evaporating dishes must be prepared according to Section 7.2 of the method. The procedure must be documented on a laboratory notebook and provided with the final deliverables.
5. Record the temperature of the drying ovens daily and provide the documentation with the final deliverables.
6. Analysis of a method blank, prepared using deionized water and filtered through the same type of filter as that used for the samples, must be preformed. The method blank should be prepared and analyzed for each group of twenty (20) samples or less prepared at the same time. Any concentrations of interference detected must be less than  $\frac{1}{2}$  the reporting limit of the method. If the criteria are not met, the samples, EPA check standard, and another blank must be prepared and weighed. The results must be documented in the final data package.
7. An EPA check standard at 10 mg/L must be prepared and analyzed with each batch of samples and per filter type. The results of the analysis must be within  $\pm 15\%$  of the true value. If the results are not within the criteria,

another EPA check standard, method blank, and all associated field samples analyzed since the last compliant calibration check must be reanalyzed.

**j. Total Suspended Solids - Method 160.2 (Gravimetric)**

1. The samples must be run as soon as possible, so that in the event that the calibration check standard is outside the acceptable limits and all associated samples require reanalysis, all analyses can be completed with the required, seven (7) day holding time.
2. The analytical balance utilized for measurements must be checked using class "S" weights prior to weighing each batch of twenty (20) samples or less to ensure the accuracy of the weight values obtained. The results must be recorded in a log book and supplied in the final deliverable package. The check weight must be within the manufacturer's tolerance range or the balance must be recalibrated prior to weighing the samples.
3. Glass fiber filters must be prepared according to Section 7.1 of the method. The procedure must be documented in a laboratory notebook and must be provided with the final deliverables. The name of the manufacturer and model number of the filters must also be recorded and supplied with the deliverables.
4. Sample volume determination must adhere to Section 7.2 of the method.
5. Record the temperatures of the drying oven daily and provide the documentation with the final deliverables.
6. Analysis of a method blank, prepared using deionized water and filtered through the same type of filter as that used for the samples, must be performed. The method blank should be prepared and analyzed for each group of twenty (20) samples or less prepared at the same time. Any concentration of interference detected must be less than  $\frac{1}{2}$  the reporting limit of the method. If the criteria are not met, the samples, EPA check standard, and another blank must be prepared and weighed. The results must be documented in the final data package.
7. An EPA check standard at 20 mg/L must be prepared and analyzed with each batch of samples and per filter type. The results of the analysis must be within  $\pm 15\%$  of the true value. If the results are not within the criteria, another EPA check standard, method blank, and all associated field samples analyzed since the last compliant calibration check must be reanalyzed.



**k. Total Organic Carbon - Method 415.2**

1. All samples must be analyzed in duplicate and both analyses must be reported. The percent difference between duplicate results must be less than 20%. If the difference is greater than 20%, then the analysis of both samples must be repeated. If the difference is still greater than 20%, flag the results with “\*”.
2. Follow the manufacturer's instructions to set up the instrument. Perform the system clean-up and calibration procedure each day prior to sample analysis (see Section 8.2 of the method).
3. Follow the analytical procedure provided in Section 8.0 of the method. Check the effectiveness of the CO<sub>2</sub> scrubber as described in Section 8.3. The results must be recorded and provided in the final data package.
4. Perform a system blank measurement (as specified in Section 8.2 and defined in Section 3.4 of the method) as part of the initial instrument set up procedure. Analysis of the system blank must be repeated until two consecutive readings are within 10% of each other. If the limit is exceeded, identify the problem, make appropriate corrections, and reanalyze the system blank. Criteria must be met prior to sample analysis.
5. A method blank must be analyzed after calibration of the instrument and prior to sample analysis. The method blank must not contain concentrations of TOC exceeding ½ the reporting limit of the method. The water used for the method blank must be the same as that used for preparation of the calibration standards. If concentrations of TOC in the method blank are greater than ½ the reporting limit, a new source of water which meets criteria must be used.
6. Calibrate the instrument according to Section 8.5 of the method. Analyze a method blank and five standards (at 0.1, 0.2, 0.5, 1.0 and 2.0 ppm). A correlation coefficient equal to or greater than 0.995 must be obtained prior to sample analysis. All sample results must be within the range of the calibration curve.
7. An EPA check standard, or a 100 µg/l QC check standard from a source independent of the calibration standards, must be analyzed prior to sample analysis, after every 10 analyses, and at the end of the analytical sequence. The recovery must be 85% - 115% of the true value, or else the instrument must be recalibrated and all associated analyses must be reanalyzed.

## 8. QUALITY CONTROL REQUIREMENTS

Alkalinity - Method 310.1;  
Ammonia - Method 350.2;  
Chloride - Method 325.3; and  
COD - Method 410.1 (Titrimetric)

| <u>Audits</u>                                                                                                   | <u>Frequency</u>                                                                                                               | <u>Limits</u>                           | <u>Corrective Action</u>                                                                                                                                                                                                                                                                                                        |
|-----------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Normality Check                                                                                                 | Once per day prior to sample analysis                                                                                          | $\pm 10\%$ of that initially determined | If the normality is within the limits, use the newly determined value in the calculations. If outside the limits, prepare a new titrant solution. The normality of the new solution must be within $\pm 20\%$ of the normality specified in the method.                                                                         |
| Method Blank                                                                                                    | Prior to sample analysis and following analysis of every 20 field samples                                                      | $\leq \frac{1}{2}$ Reporting Limit (RL) | If $> \frac{1}{2}$ RL, the source of the contamination must be determined and the problem corrected before sample analysis may begin.                                                                                                                                                                                           |
| EPA Check Standard<br>(Note: There are two for COD analysis. Corrective Actions vary. See Section 7 of method.) | Three times prior to sample analysis (see Attachment I), once per 10 field samples, and at the end of the analytical sequence. | $\pm 15\%$ True Value (TV)              | If outside limits, recheck titrant normality and reanalyze EPA check standard, method blank, and all associated field samples. Limits must be met prior to sample analysis. For COD analysis, redigest blanks, check standards, EPA check standard, and all associated field samples. Blank must meet limits prior to analysis. |
| Matrix Spike (for Chloride and Ammonia only)                                                                    | 1/20 field samples                                                                                                             | $\pm 20\%$ Rec                          | If outside the limits, repeat the analysis. If still outside limits, flag with results with a #.                                                                                                                                                                                                                                |

| <u>Audits</u> | <u>Frequency</u>   | <u>Limits</u> | <u>Corrective Action</u>                                                                                                                   |
|---------------|--------------------|---------------|--------------------------------------------------------------------------------------------------------------------------------------------|
| Duplicate     | 1/20 field samples | %D < 20%      | If outside the limits, repeat the analysis of both the samples and the duplicate. If still outside the limits, flag the results with an *. |

**Nitrate/Nitrite-Nitrogen - Method 353.1 (Colorimetric, Automated, Hydrazine Reduction)**

|                    |                                                                                                |                                 |                                                                                                                                               |
|--------------------|------------------------------------------------------------------------------------------------|---------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|
| Reduction Check    | Prior to sample analysis                                                                       | 100% Reduction efficiency       | Adjust the concentration of the hydrazine sulfate solution and repeat the reduction check. Criteria must be met prior to sample analysis.     |
| Method Blank       | Prior to sample analysis and after calibration                                                 | $\leq 1/2$ Reporting Limit      | If outside limits, the contamination source must be found. Criteria must be met prior to sample analysis.                                     |
| Calibration        | Daily prior to sample analysis                                                                 | Correlation Coefficient > 0.995 | If criteria are not met, generate a new curve. Criteria must be met prior to sample analysis.                                                 |
| EPA Check Standard | Prior to sample analysis, once per 10 field samples and at the end of the analytical sequence. | $\pm 15\%$ True Value           | If outside limits, generate a new standard curve and reanalyze all field samples and QC samples since the previous acceptable check standard. |
| Matrix Spike       | 1/20 field samples                                                                             | $\pm 20\%$ Rec                  | If outside the limits, repeat the analysis. If still outside the limits, flag the results with a #.                                           |

| <u>Audits</u> | <u>Frequency</u>   | <u>Limits</u> | <u>Corrective Action</u>                                                                                                              |
|---------------|--------------------|---------------|---------------------------------------------------------------------------------------------------------------------------------------|
| Duplicate     | 1/20 field samples | % D < 20%     | If outside limits, repeat the analysis of both the sample and the duplicate. If still outside the limits, flag the results with an *. |

**Ammonia - Method 350.2 (Colorimetric; Potentiometric)**  
**Phosphorus - Method 365.4 (Colorimetric)**

|                                                                                  |                                                                                                      |                                 |                                                                                                                                                                                |
|----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|---------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Method Blank                                                                     | 1/20 samples or less digested at the same time                                                       | $\pm 1/2$ Reporting Limit       | If criteria are not met redigest and reanalyze a new method blank, all associated samples and a new EPA Check Standard. Criteria must be met prior to sample analysis.         |
| Calibration                                                                      | Daily prior to sample analysis                                                                       | Correlation Coefficient > 0.995 | If outside limits, prepare fresh standards and reanalyze. Criteria must be met prior to sample analysis.                                                                       |
| EPA Check Standard Note: There are two and Corrective Actions vary see Section 7 | Prior to sample analysis, once per every 10 field samples and at the end of the analytical sequence. | $\pm 15\%$ True Value           | If the criteria are not met, a new standard curve must be generated, a new check standard must be digested, and all associated samples must be reanalyzed prior to proceeding. |
| Matrix Spike                                                                     | 1/20 field samples.                                                                                  | $\pm 20\%$ Rec                  | If outside limits, reprepare and reanalyze the spiked sample. If still outside limits, flag results with a #.                                                                  |

| <u>Audits</u> | <u>Frequency</u>   | <u>Limits</u> | <u>Corrective Action</u>                                                                                                      |
|---------------|--------------------|---------------|-------------------------------------------------------------------------------------------------------------------------------|
| Duplicate     | 1/20 field samples | %D < 20%      | If outside limits, repeat the analysis of both the sample and the duplicate. If still outside limits, flag results with an *. |

#### **Sulfate - Method 375.4 (Turbidimetric)**

|                          |                                                                                               |                                                  |                                                                                                                                                                                                                                          |
|--------------------------|-----------------------------------------------------------------------------------------------|--------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Normality Check          | Prior to sample analysis                                                                      | $\pm 10\%$ of the initially determined normality | If the normality is within the limits, use the newly determined value in the calculations. If outside the limits, prepare a new titrant solution. The new solution must be within $\pm 20\%$ of the normality specified in the method.   |
| Method Blank             | Prior to sample analysis and after every batch (20 samples or less)                           | $\pm 1/2$ Reporting Limit                        | If outside limit, the contamination source must be found and all associated samples must be reanalyzed. Criteria must be met before sample analysis can begin.                                                                           |
| Calibration              | Daily prior to sample analysis                                                                | Correlation Coefficient > 0.995                  | If criteria are not met, the standard must be reprepared and the curve must be regenerated. Criteria must be met before sample analysis can begin.                                                                                       |
| Calibration Verification | Prior to sample analysis, after every four samples and at the end of the analytical sequence. | $\pm 10\%$ True Value                            | If the criteria are not met, a new calibration curve must be generated, another continuing calibration verification sample must be analyzed, and all samples after the last acceptable continuing calibration sample must be reanalyzed. |
| Matrix Spike             | 1/20 field samples                                                                            | $\pm 20\%$ Rec                                   | If outside limits, repeat analysis. If still outside limits, flag the results with a #.                                                                                                                                                  |

| <u>Audits</u> | <u>Frequency</u>   | <u>Limits</u> | <u>Corrective Action</u>                                                                                                       |
|---------------|--------------------|---------------|--------------------------------------------------------------------------------------------------------------------------------|
| Duplicate     | 1/20 field samples | %D < 20%      | If outside limits, repeat the analysis of both the samples and the duplicate. If still outside limits, flag results with an *. |

### **Total Dissolved Solids (TDS), Method 160.1 and Total Suspended Solids (TSS), Method 160.2.**

|                          |                                                                             |                                           |                                                                                                                                           |
|--------------------------|-----------------------------------------------------------------------------|-------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|
| Analytical Balance Check | Daily prior to sample analysis                                              | Within the manufacturer's tolerance range | The balance must be recalibrated by the manufacturer.                                                                                     |
| Method Blank             | 1/20 samples or less prepared at one time and for each type of filter used. | $\pm$ 1/2 Reporting Limit (RL)            | If > 1/2 RL, the samples, EPA check std and another blank must be reprepared.                                                             |
| EPA Check Standard       | 1/batch prior to sample analysis and per filter type used                   | $\pm$ 15% True Value                      | If outside the limits, re-filter another method blank, EPA check standard and all associated field samples.                               |
| Duplicate                | 1/20 field samples                                                          | %D < 20%                                  | If outside the limits, repeat the analysis of both the sample and the duplicate. If still outside the limits, flag the results with an *. |

### **Total Organic Carbon, (TOC) Method 415.2**

|              |                                                                      |                                                                            |                                                                                                                               |
|--------------|----------------------------------------------------------------------|----------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
| System Blank | Daily prior to sample analysis                                       | Two readings within 10% of each other and the last instrument system blank | If criteria are not met identify the problem and make appropriate corrections. Criteria must be met prior to sample analysis. |
| Method Blank | 1/20 samples or less analyzed at one time. Prior to sample analysis. | $\pm$ 1/2 Reporting Limit (RL)                                             | If > 1/2 RL, the samples, EPA check std and another blank must be reanalyzed. Criteria must be met prior to sample analysis.  |

| <u>Audits</u>      | <u>Frequency</u>                                                                                             | <u>Limits</u>                   | <u>Corrective Action</u>                                                                                                                                                        |
|--------------------|--------------------------------------------------------------------------------------------------------------|---------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Calibration        | Daily prior to sample analysis                                                                               | Correlation Coefficient > 0.995 | Criteria must be met prior to sample analysis                                                                                                                                   |
| EPA Check Standard | 1/batch prior to sample analysis, after every ten samples and as the final analysis per each day of analysis | $\pm 15\%$ True Value           | If outside the limits, recalibrate the instrument and reanalyze a check standard before any field samples are analyzed or reanalyze all associated field samples if applicable. |
| Duplicate          | All samples                                                                                                  | %D < 20%                        | If outside the limits, reanalyze the sample and the duplicate. If still outside the limits, flag the results with an *.                                                         |

## 9. ANALYTICAL DELIVERABLES

- a. The following requirements for all analytes must be delivered with each package of data. Data packages must be delivered to M&E under custody seal.
  - A recent (conducted within three (3) months of the analysis) MDL study must be delivered with the bid package. The results of the MDL study must meet the reporting limits detailed in Section 6. The MDL study must have been run as described in 40 CFR Part 136 App. B, Section 10.3.
  - A narrative which must include an explanation of all anomalies and corrective actions performed, and a tabulation of the field sample numbers with the corresponding laboratory sample numbers.
  - All positive results and the reporting limit for non-detected results must be tabulated. The reporting limits are listed in Section 6.
  - Raw data for all field samples, QC samples, and calibration standards must be provided. The raw data must include all bench sheets, preparation logs, analysis logbooks, and instrument strip charts and printouts.
  - The results of all QC checks must be tabulated. These include: duplicate results, %D; matrix spike analyses, %Rec; QC check standards, %Rec; EPA check sample results, %Rec; calibration verification results; normality check results; nitrate reduction results; and blank results. The true value

and the actual concentration of spikes must be provided with the percent recovery tabulation. Raw data, which is specified above, must be provided.

- The calibration curve raw data with print-outs and concentrations must be provided. Plot the standard curves and include the linear regression equation.
- Example calculations which descriptively define the generation of sample results must be provided for each analysis. All equations, dilution factors, and information required to reproduce the laboratory results must be provided.
- Original signed chain-of-custody forms, and shipping air bills must be provided. Copies of the laboratory's telephone logs from any conversation with samplers or project personnel must be provided. A copy of this analytical specification must be completed.
- All log-in sheets and records of the cooler temperature and sample preservation checks on samples upon arrival at the laboratory must be provided.
- Data package must be paginated and of good copy quality.
- The data package must be as much like an EPA CLP package as possible.

**b. Complete sample delivery group file (CSF)**

EPA Region I requires that all analytical data, quality control data, and tabulated or raw supporting data be delivered with each SDG. With each SDG an EPA Region I Complete SDG File (CSF) Inventory Sheet shall be completed. The CSF Inventory Sheets are included in Attachment A and must accompany each SDG. The laboratory using these audit forms, must demonstrate that all sample data, raw data, calibration data, and any other requirements of the statement of work or analytical specification are included in the data package.

The forms included in Attachment A are for all types of data packages. For this analytical specification, the laboratory shall use the inventory sheets for all applicable deliverable items, adapting the sheets where necessary.



## **10. EXCEPTIONS**

If QC requirements are not met or QC acceptance limits are exceeded; or if field samples are compromised, destroyed or lost; or if matrix interference is suspected; or there are any other technical problems, immediately contact:

Bruce Livingston  
Metcalf & Eddy, Inc.  
30 Harvard Mill Square  
Wakefield, MA 01880  
Phone: (781) 224-6437  
Fax: (781) 245-6293

**ATTACHMENT A**  
**CSF AUDIT FORMS**

## **B-2. REFERENCE DOCUMENTS**

# Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique

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## Abstract

The measurement of dissolved gases such as methane, ethane, and ethylene in ground water is important in determining whether intrinsic bioremediation is occurring in a fuel- or solvent-contaminated aquifer. A simple procedure is described for the collection and subsequent analysis of ground water samples for these analytes. A helium headspace is generated above a water-filled bottle. Gases that are dissolved in the water partition between the gas and liquid phases and equilibrate rapidly. An aliquot of this headspace is analyzed by gas chromatography to determine the gases' concentration in this phase. The concentration of the gas dissolved in the water can then be calculated based on its partitioning properties, as indicated by its Henry's Law constant.

## Introduction

Our involvement in ground water sampling and analyses at fuel and/or chlorinated solvent spill sites has required the determination of dissolved methane, ethane, and ethene. These constituents are frequently used to detect biodegradation processes in contaminated aquifers. Presence of the compounds is used to determine whether natural processes of contaminant attenuation and destruction are occurring at a spill site (1). Under anoxic conditions, the bioremediation processes for fuel hydrocarbons shift toward methanogenesis, which forms methane. Under similar conditions, chlorinated solvents such as trichloroethylene are subjected to reduction dechlorination; the final products are ethene and chloride (2).

Techniques for the analysis of dissolved gases in water have included direct aqueous injection into a GC equipped with a flame-ionization detector (FID) (3), membrane inlet mass spectrometry (4), and near-infrared Raman spectroscopy (5). Our

need was for a simplified, rapid technique using readily available equipment to analyze ground water samples simultaneously for methane, ethane, and ethene. Previously, we reported on a gas chromatography (GC) headspace technique that emphasized dissolved oxygen (6). In recent years, the emphasis has been on methane and ethene analysis in water.

## Experimental

### Materials

Gas standards in helium were obtained from Scott Specialty Gases (Plumsteadville, PA). "Scotty II" cylinders of methane, ethane, and ethene at 10, 100, and 1000 ppm were used in addition to standards of methane at 1, 10, and 20%. High-purity helium was used as the GC carrier and as a source to prepare headspace in the sample bottles.

### Instrumentation

Samples were analyzed using a Hewlett-Packard (Palo Alto, CA) 5890 GC equipped with a packed column (6-ft  $\times$  1/8-in. Porapak Q, 80/100) and an FID. The carrier gas was high-purity helium at 20 mL/min. The oven was programmed with an initial temperature of 55°C for 1 min, increased at 20°C/min to 140°C, then held for 5 min. The injector was set at 200°C, and the FID was set at 250°C. The FID hydrogen was set at 40 mL/min, and the air flow was set at 400 mL/min. The FID range and attenuation were both at 0. An HP 3396 Series II integrator was used for signal acquisition and peak integration.

### Sample collection and preparation

Water samples from field monitoring wells were collected into 60-mL serum bottles (Wheaton, Millville, NJ). Water was gently added down the side of the bottle so as not to agitate or create bubbles, which could strip gases dissolved in the water. The

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bottle was completely filled, and several drops of 1:1 sulfuric acid were then added as a preservative. The bottle was capped and sealed using a 20-mm gray butyl rubber, Teflon-faced septum (Wheaton, Millville, NJ) and 20 mm aluminum crimp seal (Wheaton). The samples were kept cold in an ice chest in transit to the laboratory. Samples were kept at 4°C and analyzed within 14 days of collection.

#### GC analysis

The GC was calibrated by injecting 300  $\mu$ L of each of the gas standards as listed in the *Materials* section. The Scotty II cylinders were sampled at atmospheric pressure. This was accomplished by attaching a short piece of  $\frac{1}{4}$ -in. stainless steel tubing with appropriate fittings to the cylinder outlet. At the cylinder outlet, a  $\frac{1}{4}$ -in. "tee" was fitted with a GC septum allowing for insertion of a gas-tight syringe needle into the gas stream. The exit end of the tubing was inserted into a 500-mL beaker of water. As gas "bubbled" through the water, 300  $\mu$ L of the gas standard was removed and injected into the GC. The retention times for methane, ethene, and ethane were near 0.6, 1.9, and 2.5 min, respectively. Peak area counts generated for each sample were compared with a calibration standard curve.

Samples were allowed to reach room temperature prior to analysis. A headspace was prepared by replacing 10% of the bottled sample (in this case, 6 mL) with helium. To generate headspace in the sample bottle, the bottle was placed upside-down in a three-fingered clamp attached to a ring stand. Next, a 20-gauge needle attached to a 10-mL Luerlok glass syringe set for dead volume was inserted through the septum. Then an 8-cm 20-gauge needle attached to Teflon tubing and a needle valve was inserted through the septum up to the bottom of the bottle. The Teflon tubing was plumbed to a two-stage regulator on a cylinder of high-purity helium, and the helium was passed through the needle at 5 mL/min or less. The helium forced water out of the bottle and into the syringe. When the volume of water in the syringe reached 6 mL, the 8-cm needle was pulled out, followed by the syringe. The sample bottle was shaken on a rotary shaker at 1400 rpm for 5 min to allow the gases to equilibrate between the headspace and liquid phases.

A 500- $\mu$ L gas-tight syringe with a sampling valve (Dynatech Precision Sampling, Baton Rouge, LA) and equipped with a side-port needle was used to withdraw 300  $\mu$ L of headspace, which was subsequently injected into the GC. The temperature of the remaining sample was determined. The volume of the sample bottle was measured by filling the bottle with water and pouring the contents into a graduated cylinder.

For purposes of quality control, field trip blanks were included with samples, and 10% of samples were collected in duplicate and analyzed. Prior to analysis and at the end of the day, calibration of the GC was checked by analyzing at least one of the gas standards for each analyte. The GC was considered to be in calibration if the analyzed value was within 15% of that expected. Calibration standards for at least one of the gases were analysed with a frequency of 10%. Control charts were maintained to monitor variability. In addition, a method blank consisting of a serum bottle of deionized, boiled water was analyzed on a daily basis. This was necessary to correct for background levels of methane. Quantitation limits for methane, ethane, and ethene

were 0.001, 0.002, and 0.003 mg/L, respectively. Normally, two samples could be prepared and analyzed per hour.

#### Calculations

The concentrations of the gases dissolved in the water sample were calculated using the partial pressure of the gas, Henry's Law constant, the temperature of the sample, the volume of the sample bottle, and the molecular weight of the gas. Values for Henry's Law constant were obtained from Perry's *Chemical Engineer's Handbook* (7).

The linear regression equation of the standard curve was used to determine the partial pressure ( $p_g$ ) of the gas. The concentrations of the gas standards should be converted to their decimal equivalent before generating the curve (i.e., 10 ppm is equivalent to 0.00001, as is 1% to .01). The sample's area count obtained from the chromatogram peak for the analyzed gas was "inserted" into the equation to determine its partial pressure. For methane, it was necessary to subtract the area count obtained from the analysis of a method blank. The following sequence of equations were used to determine the concentration of the dissolved gas.

For the equilibrium mole fraction of the dissolved gas:

$$x_g = p_g / H \quad \text{Eq 1}$$

where  $H$  is Henry's Law constant for the gas. Let  $n_g$  represent the moles of gas and  $n_w$  the moles of water. Then:

$$x_g = n_g / (n_g + n_w) \text{ and } n_g = x_g (n_g + n_w) \quad \text{Eq 2}$$

Because 1 L of water equals 55.5 g-moles:

$$n_g = x_g (n_g + 55.5) \quad \text{Eq 3}$$

and because:

$$n_g x_g \ll n_g \quad \text{Eq 4}$$

therefore:

$$n_g = x_g (55.5) \text{ or } n_g = 55.5 (p_g / H) \quad \text{Eq 5}$$

For the saturation concentration of the gas:

$$C = n_g (MW) (1000 \text{ mg/g}) \quad \text{Eq 6}$$

where  $MW$  is the molecular weight of the gas. To correct gas density for temperature:

$$D = MW / (22.4 \text{ L/mole}) (ST^\circ \text{K} / 273^\circ \text{K}) \quad \text{Eq 7}$$

where  $ST$  is the sample temperature. Then:

$$A_h = (\text{mL of headspace}) (p_g) = 6 (p_g) \quad \text{Eq 8}$$

where  $A_h$  is the milliliters of analyte in the headspace. Then:

$$A_l = (A_h / V) (D) (1000 \text{ mg/g}) (1 \text{ L} / 1000 \text{ mL}) \quad \text{Eq 9}$$

where  $A_1$  is the analyte in liquid phase and  $V$  is the volume of water (bottle volume-headspace volume) in L; using a 60-mL serum bottle with 6 mL of headspace,  $V$  equals 0.054 L. Then:

$$TC = A_1 + C \quad \text{Eq 10}$$

where  $TC$  is the total concentration of analyte in the original sample, in milligrams of gas per liter of water.

#### Example calculation for methane

Methane will be used as an example of the calculations used for the analysis of dissolved gases. From the analysis of a sample, an area count was determined. This area count was used in the equation for the linear regression of the calibration curve to give its partial pressure ( $p_g$ ). Parameters used for this example are as follows: the sample area count was 978264, the method blank area count was 2766, Henry's Law constant was  $4.13\text{E}+4$  (at  $25^\circ\text{C}$ ), the sample temperature was  $25^\circ\text{C}$  ( $298^\circ\text{K}$ ), the bottle volume was 60 mL, and the headspace volume was 6 mL.

From the equation of a straight line ( $y = mx + b$ ), the calibration standard responses generated the following curve:

$$p_g = (1.814\text{E}-9)x - 6.716\text{E}-6 \quad \text{Eq 11}$$

Therefore, for this sample:

$$\begin{aligned} p_g &= (1.814\text{E}-9)(978264 - 2766) - 6.716\text{E}-6 \\ &= 0.0018 \end{aligned} \quad \text{Eq 12}$$

Then, using the previous equations:

$$x_g = 0.0018/4.13\text{E}+4 = 4.269\text{E}-8 \quad (\text{from Eq 1})$$

$$n_g = 55.5(4.269\text{E}-8) = 2.37\text{E}-6 \quad (\text{from Eq 5})$$

$$C = (2.37\text{E}-6)(16)(1000) = 0.038 \text{ mg methane/L water} \quad (\text{from Eq 6})$$

$$D = (16\text{g/mole})/([22.4 \text{ L/mole}][298/273]) = 0.654 \text{ g methane/L} \quad (\text{from Eq 7})$$

$$A_h = 6(0.0018) = 0.0108 \text{ mL methane} \quad (\text{from Eq 8})$$

$$A_1 = (0.0108 \text{ mL}/0.054 \text{ L})(0.654 \text{ g/L})(1 \text{ L}/1000 \text{ mL})(1000 \text{ mg/g}) = 0.1308 \text{ mg methane/L} \quad (\text{from Eq 9})$$

$$TC = 0.1308 + 0.038 = 0.169 \text{ mg methane/L water} \quad (\text{from Eq 10})$$

## Results and Discussion

Water samples collected at field sites have been analyzed by the described procedure for over eight years. The method is relatively simple and reliable for the analyses of water samples.

A typical chromatogram of a ground water sample from a contaminated site is shown in Figure 1. Table I lists the analytical data for several water samples. Calibration curves were generated using linear regression on a calculator or computer; area counts of the standards were plotted versus their concentrations.

Saturated solutions of methane and ethene in water were prepared with expected concentrations of 22.7 and 131 mg/L, respectively. They were analyzed to determine precision and accuracy. For methane, an average recovery of 87% was obtained for six replicates, the standard deviation was 0.64 mg/L, and the relative standard deviation (RSD) was 3.25%. For ethene, the

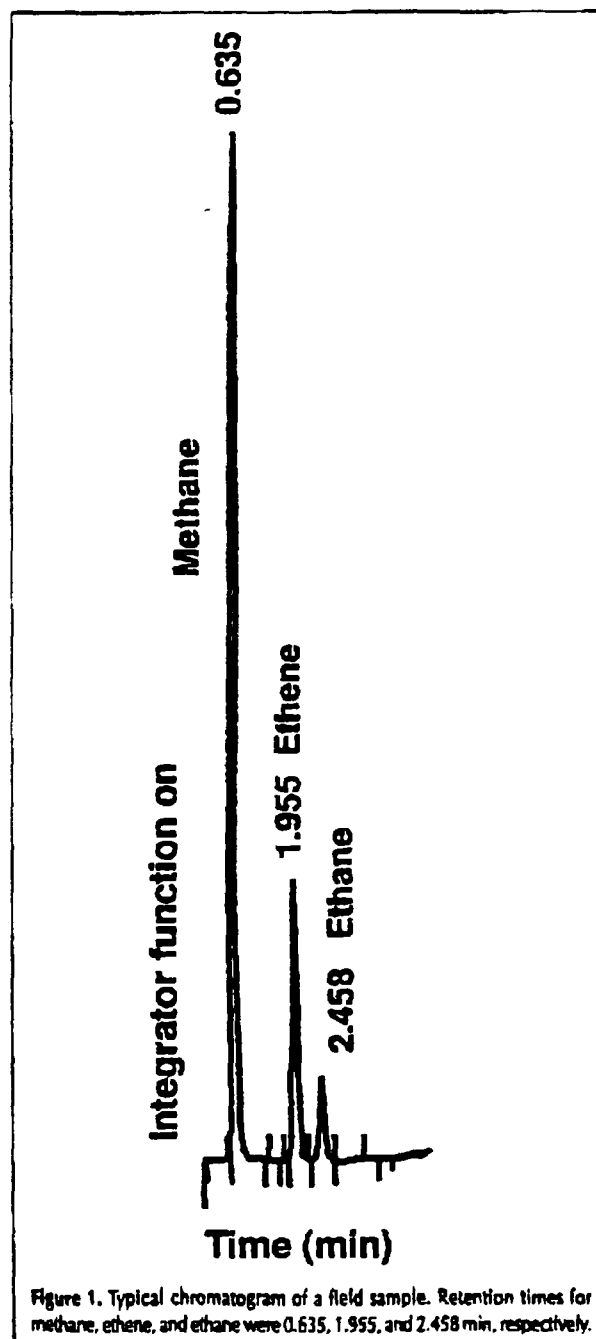


Figure 1. Typical chromatogram of a field sample. Retention times for methane, ethene, and ethane were 0.635, 1.955, and 2.458 min., respectively.

Table 1. Analytical Data of Four Samples from a Field Site

| Sample | Methane<br>(mg/L) | Ethene<br>(mg/L) | Ethane<br>(mg/L) |
|--------|-------------------|------------------|------------------|
| RW-10  | 0.682             | undetected       | 0.027            |
| RW-11  | 4.753             | undetected       | 0.219            |
| RW-12  | 1.268             | undetected       | 0.013            |
| RW-12* | 1.260             | undetected       | 0.013            |
| RW-13  | 3.074             | 0.268            | 0.112            |
| RW-13* | 3.143             | 0.258            | 0.107            |

\* Lab duplicate (i.e., headspace of same sample analyzed twice).  
\* Field duplicate.

average recovery for three replicates was 90%, the standard deviation was 8.8 mg/L, and the RSD was 7.5%. Due to the unavailability of pure ethane in our lab, this exercise was not performed on ethane.

With appropriate GC detectors, this technique should be applicable to other volatile dissolved constituents in water such as carbon dioxide, nitrous oxide, nitrogen, and vinyl chloride. It should be noted that acid preservation should not be used for carbon dioxide analysis because inorganic carbon may be converted to carbon dioxide.

## Conclusion

The sample preparation and analytical technique for dissolved methane, ethane, and ethene in ground water has been used successfully on a routine basis in our lab. We have analyzed thousands of ground water samples from numerous contaminated sites. The data from these analyses have been critical in determining the nature of the degradative processes in contaminated aquifers. This technique will continue to be used for routine analyses on water samples from both lab and field studies.

## Acknowledgments

The authors are grateful to Bryan Newell and Jeff Hickerson of ManTech Environmental Research Services for their support as analysts. Pat Holt of National Risk Management Research Laboratory typed the manuscript. The research described has not been subjected to a review process by the United States Environmental Protection Agency. Therefore, the work does not necessarily reflect the views of the agency, and official endorsement should not be inferred.

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## DISSOLVED OXYGEN AND METHANE IN WATER BY A GC HEADSPACE EQUILIBRATION TECHNIQUE

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*(Received 4 October 1988; in final form 15 March 1989)*

An analytical procedure is described for the determination of dissolved oxygen and methane in groundwater samples. The method consists of generating a helium gas headspace in a water filled bottle, and analysis of the headspace by gas chromatography. Other permanent gases such as nitrogen, and volatile aliphatic hydrocarbons such as ethane, propane, and butane could also be analyzed. BTX analyses could also be done on the sample. Detection limit for oxygen was 0.1 mg/l and 0.002 mg/l for methane. Good agreement was shown between Winkler titration and the GC-Headspace Equilibration Technique for oxygen analyses by a linear regression coefficient,  $R^2=0.998$ . Oxygen was greatly depleted in some field samples when they were stored for 30 days at 4°C without hydrochloric acid preservation.

**KEY WORDS:** Dissolved oxygen, GC, headspace, Henry's law, water, BTX.

### INTRODUCTION

The concentration of dissolved oxygen, methane and aromatic hydrocarbons (BTXs) are important in evaluating biological activity with aquifers contaminated by petroleum fuels. Analytical methods are available for all three parameters, but each requires tedious separate sampling and analysis protocol.

The two methods most widely used for dissolved oxygen determination in water are Winkler titration and direct probe readings.<sup>1</sup> Both are reliable, but they require appreciable volumes of sample. Some gas chromatography methods for determining dissolved gases from solution are by inert gas purging,<sup>2</sup> *in situ* buried diffusion cells or probes,<sup>3</sup> direct injection into a heated column then separation from the vaporized liquid<sup>4,5</sup> or equilibrium of a solution in a closed bottle with an inert gas headspace.<sup>6</sup> The last approach has advantages of simplicity, reliability, and adaptability to routine analyses of samples.



Henry's law states that the equilibrium value of the mole fraction of gas dissolved in a liquid is directly proportional to the partial pressure of the gas above the liquid surface, or  $x_g = p_g/H$ , where  $p_g$  = equilibrium partial pressure of gas,  $x_g$  = mole fraction of dissolved gas,  $H$  = Henry's law constant.<sup>7</sup> Henry's law is applicable at low concentrations and low partial pressures of a gas at or below one atmosphere pressure. Solubility data can be obtained from technical handbooks relating  $H$  values to temperature.<sup>8,9</sup>

Described is a technique for the analysis of dissolved oxygen and methane in water. The method is also applicable to nitrogen and other volatile aliphatic hydrocarbons. The aliquot of water removed during headspace generation can be used for volatile organics analyses by EPA methods 601 or 602.<sup>10</sup>

## EXPERIMENTAL

### *Sample Collection and Preparation*

Water samples collected in the field or prepared in the lab were placed into 50 ml borosilicate glass Hypo-Vials (Pierce, Rockford, IL) and capped with aluminium seals and Teflon faced butyl rubber septa (Wheaton Scientific, Millville, NJ). Actual bottle volume was near 62 ml. Total volume for each bottle was measured by refilling with water and measuring the quantity. Water samples were added to the bottles down the side to prevent agitation and subsequent oxygen contamination. Also, care was taken to make sure that no air bubbles were entrapped in the sample. Initially, field samples were stored at 4°C and analyzed by GC within four to eleven days after collection. In a later sample set, 0.15 ml of 1:1 of water:12 M HCl was added as a preservative. Winkler titrations were fixed and analyzed within 10 minutes of collection to conform to EPA guidelines.<sup>10</sup>

Headspace generation was done by placing the sample bottle upside down in a three finger clamp (Figure 1). A 20 gauge needle on a 10 ml Luerlock glass syringe, set for dead volume, was inserted into the sample by penetrating the septum about one centimeter. An 8 cm 22 gauge needle attached to Teflon tubing via a Mininert syringe valve was then inserted through the septa to the top of the water. A flow of five milliliters per minute of high purity helium was passed through the syringe valve. After six milliliters of water was forced from the bottle into the syringe, both needles were removed. The displaced water could then be used for BTX analysis. The sample bottles, which contained ten percent by volume helium headspace, were shaken five minutes at 1400 rpm on a rotary shaker (Tekmar VRX Vibrax, Thomas Scientific, Swedesboro, NJ) to allow gases to equilibrate between the liquid and gas phases. Samples for headspace analysis of both oxygen and methane were taken immediately after the five minute rotary shaking period.

### *Headspace Analysis*

**Oxygen GC Parameters**—100  $\mu$ l of the headspace was withdrawn with a 500  $\mu$ l

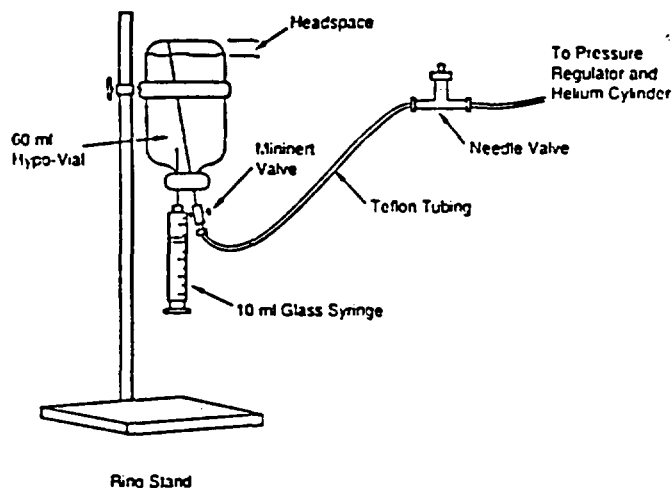


Figure 1 Headspace generation set-up for the headspace equilibration technique.

gas-tight syringe (Precision Scientific, Baton Rouge, LA), and injected into a Varian Vista 6000 GC for oxygen analysis. The column used was  $6' \times 1/8''$  stainless steel, 60/80 molecular sieve 5A (Supelco, Inc., Bellefonte, PA). Two columns were used with one each for the analytical and reference side. Carrier gas was high purity helium at 20 mL/min. The column oven was set at  $50^\circ\text{C}$ , injector at  $120^\circ$ , TCD at  $120^\circ$ , and TCD filament at  $140^\circ$ . The TCD Attenuation = 1, and Range = 0.5 mV. Oxygen and argon chromatogram peaks were not resolved by the molecular sieve column at  $50^\circ\text{C}$  oven temperature. Peak retention times in minutes were 0.98 for oxygen and 2.17 for nitrogen. Ambient air was used for calibration. It was assumed to be 21% oxygen. Detection limit for oxygen was 0.1 mg  $\text{O}_2$ /liter water.

**Background Interference**—Air equivalent to the syringe needle volume was unavoidably introduced into the GC during injection of the  $100\mu\text{l}$  headspace sample. Repeated analyses determined that about  $2\mu\text{l}$  oxygen+argon, which coelute, was introduced with each sample injection. This background may be reduced considerably by pumping the syringe several times into the 6 ml headspace. Confirmation of argon's contribution to the oxygen peak area was done by use of an activated charcoal packed postcolumn. This removed oxygen and left only argon to be measured. During routine analyses, argon was not determined for each sample since reconditioning of the charcoal+molecular sieve columns required a lengthy time period at elevated temperature. The background correction value for argon was determined by analyzing some water samples containing a slight excess of sodium sulfite, which consumed all the dissolved oxygen. Magnitude of the argon peak is shown in the example calculation.

**Calculations**—Pressure was assumed to be one atmosphere. Other variables needed for concentration are temperature and the actual volume of each sample bottle. Water samples were allowed to reach room temperature before generation

of headspace and subsequent analysis. Bottle volumes were determined by emptying refilled bottles into a graduated cylinder and recording the volume.

Example calculation from chromatogram peak areas obtained by analyzing air-saturated water at 20°C.

|                                               | Peak area  |
|-----------------------------------------------|------------|
| 100 $\mu$ l calibration standard, 21 % oxygen | 126450 = A |
| Air-saturated water, oxygen                   | 32759 = B  |
| 2 $\mu$ l syringe needle contribution         | 2360 = C   |
| Background, argon                             | 3649 = D   |

It is assumed that argon partitions the same as oxygen. Then response due to argon in ambient air is 3649/126450 or 2.88%. Then  $E = 1 - 0.0288 = 0.971$ .

$$\text{Partial pressure of oxygen, } P_g = \frac{(B - C) \times E}{A - D} \times 0.21 = 0.050.$$

$$\text{Equilibrium mole fraction of dissolved oxygen, } x_g = \frac{P_g}{H}$$

or

$$\frac{0.050}{4.01 \times 10^4} = 1.247 \times 10^{-6} \text{ moles O}_2.$$

Let

$$n_g = \text{moles gas and } n_w = \text{moles water.}$$

Then

$$x_g = n_g / (n_g + n_w) \text{ and } n_g = x_g (n_g + n_w).$$

Since one liter of water is 55.51 g-moles,

$$n_g = (n_g + 55.5)(1.247 \times 10^{-6}) \text{ and since } n_g (1.247 \times 10^{-6}) \ll n_g,$$

$$n_g \approx 55.5 (1.247 \times 10^{-6}) \text{ or } 6.92 \times 10^{-5} \text{ moles/liter oxygen.}$$

Saturation concentration of oxygen,

$$C = \frac{(n_g)(32 \text{ gm})(100 \text{ mg})}{(\text{mole O}_2)(\text{g})}$$

$$= (6.92 \times 10^{-5})(32)(1000) = 2.21 \text{ mg O}_2/\text{liter headspace oxygen.}$$

$$\text{Density} = 22.4 \text{ liter/mole} \times \frac{293^\circ\text{K}}{273^\circ\text{K}} = 24.04 \text{ liter at } 20^\circ\text{C}$$

or

$$\frac{32 \text{ gm/mole}}{24.04 \text{ liter/mole}} = 1.33 \text{ gm O}_2/\text{liter}.$$

Bottle volume = 62.5 ml and headspace volume = 6 ml.

So,  $6 \times 0.050 = 0.300$  ml oxygen and liquid phase oxygen is

$$\frac{0.300 \text{ ml O}_2}{0.0565 \text{ liter H}_2\text{O}} \times 1.33 = 7.06 \text{ mg O}_2/\text{liter}.$$

Then liquid phase oxygen and headspace oxygen =  $7.06 + 2.21 = 9.27 \text{ mg O}_2/\text{liter}$ . Standard tables list  $20^\circ\text{C}$  air-saturated water to contain  $9.2 \text{ mg O}_2/\text{liter}$ . This is in good agreement with the value of  $9.27 \text{ mg O}_2/\text{liter}$  shown above. Data listed in Table 2 was obtained from four sets of samples. New calibration units  $A$  and  $D$  were determined for each set to obtain a computer entry constant of  $(E)(0.21)/(A-D)$ . Partial pressure of oxygen  $P_g$  for each sample in a set then was determined from  $(B-C) \times$  the constant.

#### *Methane*

GC Parameters—Immediately after oxygen analysis was completed on a sample, analysis for methane was done on the headspace by withdrawing another  $100 \mu\text{l}$  and injecting into a Varian 3300 GC equipped with an FID. Column used was  $5' \times 1/8''$  stainless steel tubing containing Porapak N 80/100. Carrier gas was high purity helium at  $25 \text{ mL/minute}$  flow. Hydrogen and air flow for the detector was 30 and  $300 \text{ mL/minute}$  respectively. The column oven was  $160^\circ\text{C}$ . The injector and detector were both  $190^\circ\text{C}$ . Under these GC conditions, the following retention times in minutes were obtained using a 0.1% "Scotty" hydrocarbon gas standard (Scott Specialty Gases, Plumsteadville, PA): 0.31 for methane, 0.40 for ethane, 0.56 for propane, 0.92 for *n*-butane, 1.64 for pentane, and 3.10 for hexane. Detection limit for methane was  $0.002 \text{ mg CH}_4$  per liter water. Since typical air is essentially methane free and good resolution of GC peaks was obtained, no correction was needed.

## RESULTS AND DISCUSSION

Water samples prepared in the laboratory or collected at a Michigan field site were analyzed by our described procedure with emphasis placed on dissolved oxygen. Table 1 shows analytical data on a water sample that was saturated by purging with air ("oxygen") and natural gas ("methane").

Some chromatograms obtained for the analysis of water samples are shown in Figure 2. Table 2 lists the analytical results obtained from 26 water samples. The

Table 1 Replicate analyses of saturated water

|                                                  | Oxygen | Methane |
|--------------------------------------------------|--------|---------|
| Expected                                         | 9.2    | 23.2    |
| Rep A                                            | 9.17   | 19.2    |
| Rep B                                            | 8.98   | 19.2    |
| Rep C                                            | 9.22   | 19.7    |
| Rep D                                            | 9.62   | 18.5    |
| $\bar{x}$                                        | 9.25   | 19.16   |
| Agreement<br>( $\bar{x}$ /Expected) $\times$ 100 | 100.5% | 83%     |

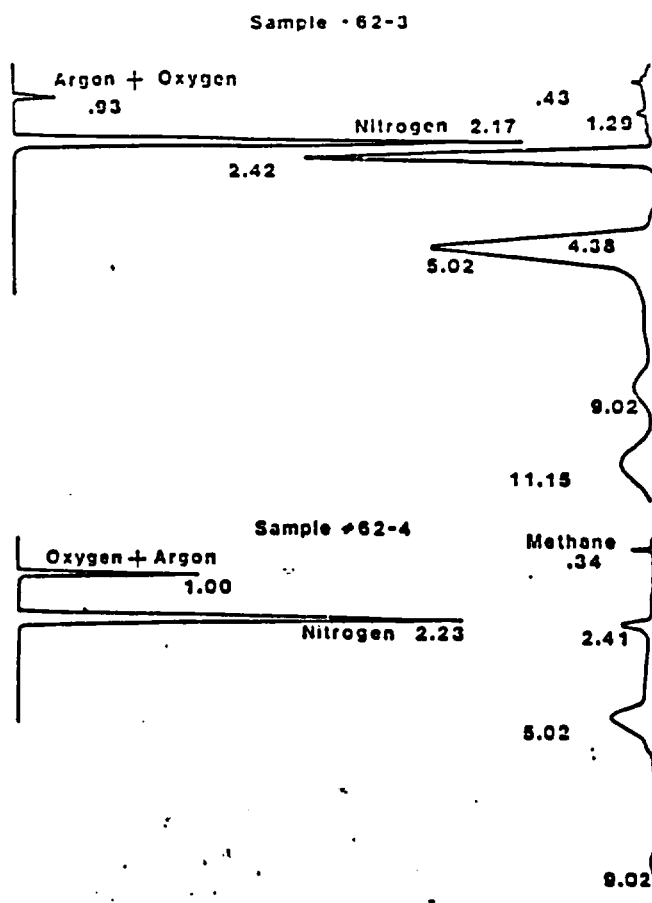


Figure 2 Example chromatograms for two water samples.

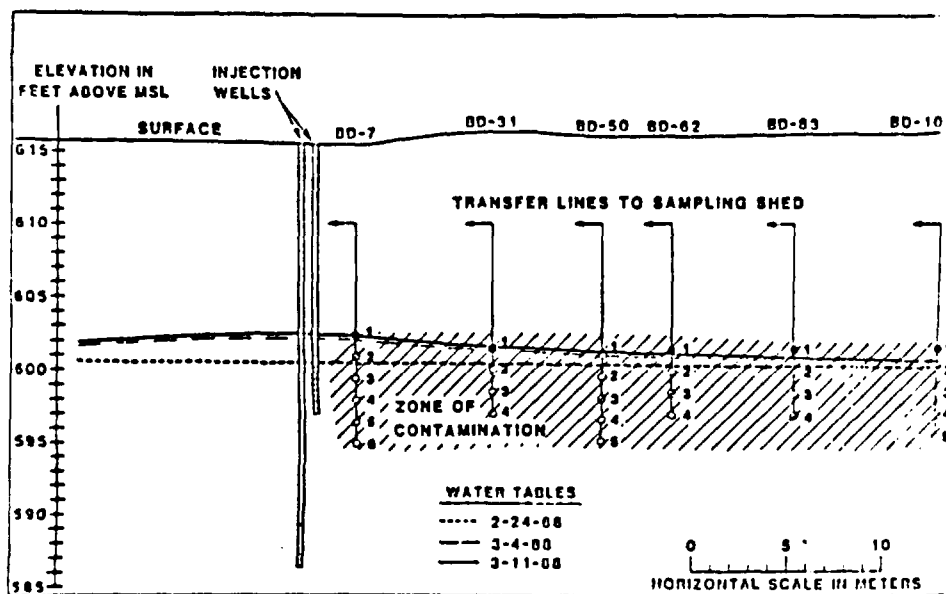


Figure 3 Cross section of pilot scale wells in plume containing gasoline at a remediation site.

first 13 were samples generated in the lab. The rest were collected from an aquifer contaminated with aviation gasoline which was being remediated by injection with water equilibrated with nutrients and pure oxygen. A cross section of the wells are shown in Figure 3. Levels ranged from  $<0.5$  to  $32 \text{ mg O}_2/\text{liter}$ . Methane levels were low where detectable. Aromatic hydrocarbons (BTXs) were determined on the aliquot of headspace-displaced water using a Hewlett-Packard Headspace Sampler and 5890 GC/FID. The Winkler titrations were performed within minutes of collection. The samples labeled "w/HCl" were preserved by adding 0.15 ml of 1:1 water:12 M hydrochloric acid solution. Aquifer samples were taken on 3/11/88 and 5/26/88. Analysis by GC was done on 3/14/88 and 5/31/88.

Acid preservation both extended holding time and maintained integrity of samples. Large oxygen depletions occurred in a 30 day storage test for two of three samples not preserved with HCl (Table 3). A comparison by linear regression through the origin of the two dissolved oxygen methods is shown in Figure 4. A distinct correlation existed between the two methods as indicated by coefficient  $R^2 = 0.998$  for 20 sets of real number data after exclusion of less than values.

## CONCLUSION

The headspace equilibrium technique was successfully used for routine analyses of dissolved oxygen, methane, and indirectly BTXs. Liquid or solid matrix consti-

Table 2 Dissolved oxygen, methane, and aromatic hydrocarbons in water samples

| Sample             | Winkler-O <sub>2</sub><br>mg/l | GC-O <sub>2</sub><br>mg/l | Methane<br>mg/l | Total <sup>a</sup><br>BTXs<br>mg/l |
|--------------------|--------------------------------|---------------------------|-----------------|------------------------------------|
| 1                  | 2.1                            | 2.54, 2.58                | —               | —                                  |
| 2                  | 2.4                            | 3.58                      | —               | —                                  |
| 3                  | 8.8                            | 9.36, 9.32                | —               | —                                  |
| 11                 | <0.5                           | 0.25                      | —               | —                                  |
| 12 replicate of 11 | <0.5                           | 0.42                      | —               | —                                  |
| 21                 | 6.9                            | 7.53                      | —               | —                                  |
| 22 replicate of 21 | 6.9                            | 7.44                      | —               | —                                  |
| 31                 | 7.6                            | 8.00                      | —               | —                                  |
| 32 replicate of 31 | 7.7                            | 8.16                      | —               | —                                  |
| 33 replicate of 31 | 7.7                            | 7.87                      | —               | —                                  |
| 41                 | 8.2                            | 8.52                      | —               | —                                  |
| 42 replicate of 41 | 8.1                            | 8.64                      | —               | —                                  |
| 43 replicate of 41 | 8.0                            | 8.15                      | —               | —                                  |
| 48A-5              | 13.6                           | 15.0                      | 0.005           | <0.006                             |
| 48A-5 replicate    | 14.6                           | 15.1                      | 0.004           | <0.006                             |
| 31-2               | <0.5                           | 0.25                      | 0.002           | 0.073                              |
| 31-3 w/HCl         | <0.5                           | 0.61                      | 0.004           | 0.045                              |
| 31-4 w/HCl         | 31.9                           | 33.1                      | <0.002          | <0.006                             |
| 48A-3              | 1.8                            | 1.94                      | 0.002           | 0.017                              |
| 62-3               | <0.5                           | 0.49                      | <0.002          | 0.072                              |
| 62-4               | 4.2                            | 3.68                      | 0.004           | 0.006                              |
| 50B-2              | <0.5                           | 0.34                      | <0.002          | 0.0031                             |
| 50C-2 w/HCl        | <0.5                           | 0.71                      | <0.002          | 0.038                              |
| 7A-2-1             | 5.9                            | 6.35                      | 0.004           | <0.006                             |
| 7B-4-3             | 2.2                            | 2.64                      | 0.004           | <0.006                             |
| 7A-2-2             | 10.7                           | 11.3                      | 0.005           | <0.006                             |
| 7A-2-3             | 10.8                           | 10.0                      | 0.005           | <0.006                             |

<sup>a</sup>Includes summation of results for benzene, toluene, ethylbenzene, m,p, and o-xylenes, and 1,2,4-trimethylbenzene.

Table 3 Dissolved oxygen change in field samples after 30 days storage at 4 °C by GC-HET

| Initial Winkler<br>mg O <sub>2</sub> /l | No HCl<br>mg O <sub>2</sub> /l | With HCl<br>mg O <sub>2</sub> /l |
|-----------------------------------------|--------------------------------|----------------------------------|
| 3.9                                     | <0.1, 0.48                     | 4.52, 4.50                       |
| 12.2                                    | 0.63                           | 11.6, 11.5                       |
| 5.8                                     | 4.95, 5.15                     | 5.74, 6.07                       |

tients should not interfere with the integrity of the headspace phase. Although the argon chromatogram peak was not separated from the oxygen peak, the additive introduction can be compensated for by reducing D.O. values by a constant. The technique will enable analysis of one bottle of water sample for three chemically different parameters. Because of its convenience and reliability, our headspace equilibrium technique with HCl preservation will be used for routine analysis of dissolved oxygen on samples from both field and lab studies.

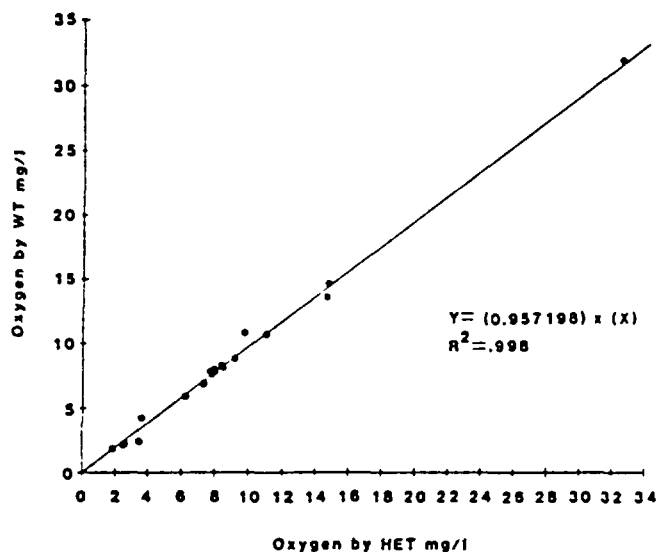


Figure 4 Comparison of dissolved oxygen measurements by Winkler titrations (WT) and headspace equilibrium technique (HET).

#### Acknowledgements

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STANDARD OPERATING PROCEDURE

SAMPLE PREPARATION AND CALCULATIONS FOR DISSOLVED  
GAS ANALYSIS IN WATER SAMPLES USING  
A GC HEADSPACE EQUILIBRATION TECHNIQUE

DISCLAIMER:

This standard operating procedure has been prepared for the use of the R.S. Kerr Environmental Research Laboratory of the United States Environmental Protection Agency and may not be specifically applicable to the activities of other organizations.

1. Purpose: (Scope and Application)

This method is applicable to the preparation of water samples for analysis of the headspace to quantify part-per-million levels of dissolved gases in the water sample. Although this method is specifically for determining methane, ethene, ethane, and nitrous oxide, it has also been used to determine vinyl chloride, nitrogen, oxygen and carbon dioxide in both laboratory and field samples. The number of analyses that can be performed in one eight hour day is approximately 30.

This method is restricted to use by or under the supervision of analysts experienced in sample preparation and in the use of gas chromatography and the interpretation of chromatograms.

2. Summary of Method:

A water sample is collected, in the field or in the laboratory, in a serum bottle and capped using a Teflon faced septum and crimp cap of the appropriate size to fit the bottle. A headspace is prepared using high purity helium. The bottle is shaken for 5 minutes and a sample is taken of the headspace and injected onto a gas chromatographic column where the gaseous components are separated and detected by flame ionization detector or electron capture detector. By using Henry's law, the concentration of the gas in the headspace, the bottle volume, and temperature of the sample, the concentration of dissolved gas in the original water sample can be determined.

3. References:

- 3.1 Kampbell, D. H., J. T. Wilson, S. A. Vandegrift, Dissolved Oxygen and Methane in Water by a GC Headspace Equilibration Technique, International Journal of Environmental Analytical Chemistry, Volume 36, pp. 249-257, 1991.
- 3.2 Vandegrift, S.A., RSKSOP-114, Revision Number 0, January 1991.
- 3.3 Newell, B.S., RSKSOP-147, Revision Number 0, August 1993.
- 3.4 Perry, J.H., *Chemical Engineer's Handbook*, (McGraw-Hill, New York, 1978), 5<sup>th</sup> ed.

4. Procedure:

**Sample Collection and Preparation:**

Water samples should be collected in the field or prepared in the lab by placing the water in a glass bottle. Typically, a 60 milliliter serum bottle is used. Add the water down the side of the bottle so as not to agitate or contaminate the sample. Fill to the top and cap using a butyl rubber Teflon faced septum and the appropriate size aluminum crimp cap. Care should be taken so there are no bubbles in the bottle. Field samples should be fixed with 1:1 hydrochloric acid to a pH less than 2 before they are capped. Do not add acid if carbon dioxide analysis is to be performed since it may convert inorganic carbon to carbon dioxide. Store samples at 4 C and analyze within 14 days of collection.

Remove samples from the refrigerator and allow them to come to room temperature. To generate headspace in the sample bottle, place the bottle upside down in a three finger clamp attached to a ring stand. Next, insert through the septum a 20 gauge needle attached to a 10 ml Luerlock glass syringe set for dead volume. Then insert an 8 cm 20 gauge needle attached to Teflon tubing with needle valve is inserted through the septum to the bottom of the bottle. The Teflon tubing is attached to a two-stage regulator on a cylinder of high purity helium and the helium is passed through the needle at 5 ml per minute or less.

**NOTE:** Helium should be allowed to flow through the Teflon tubing and needle for 30 minutes prior to preparation of the first sample, and flow should continue throughout the day.

The helium forces water out of the bottle and into the glass syringe. The amount of water taken out of the bottle should be 10% of the volume of the sample bottle up to the 100 ml size. If a 160 ml serum bottle is used, remove only 10 ml of the water during sample preparation. After the appropriate amount of water has been removed, pull the 8 cm needle out of the septum. Next, pull the syringe from the septum. The sample bottle is then shaken at 1400 rpm on a rotary shaker for 5 minutes to allow the gases to equilibrate between the headspace and the liquid phase. A portion of the headspace is then taken immediately for analysis on the gas chromatograph. Use a 500 microliter gas tight syringe to take a 300 microliter sample of the headspace. This is done by inserting the syringe needle into the septum so that the side port of the needle is in the headspace. Pull the plunger up to the 300 microliter mark. Close the syringe and withdraw the needle from the septum. Inject the syringe's contents into a gas chromatograph for analysis.

The GC conditions for the analysis of methane, ethane, ethene, and nitrous oxide can be found in RSKSOP-147; for carbon dioxide, oxygen, and nitrogen the conditions for the GC are found in RSKSOP-114. After GC analysis is successfully completed, remove the cap from the bottle.

**CAUTION:** Excessive handling of the sample should be avoided, as this will raise the temperature of the sample.

Record the temperature of the remaining sample using a thermometer, then record the volume of the sample bottle by refilling the bottle and pouring its contents into a Class "A" calibrated to contain (TC) graduated cylinder. Along with the samples a method blank should also be analyzed. The method blank consists of deionized water prepared in the same type of bottle used for the samples. Area count for any detected analyte is subtracted from the area count for each sample. See example calculations.

## 5. Calculations:

### 5a. General Equations:

The calculations for dissolved gas concentration involve several steps. In this section, the general steps and equations will be given; in section 5b a specific example for methane will be shown. Parameters needed are partial pressure of the analyte ( $p_g$ ) (the analyte is the gas in question), Henry's law constant ( $H$ ), temperature of the sample, volume of the sample bottle, and molecular weight of the analyte.

1) From the analysis of the sample, an area count is obtained. Using this area count and the regression equation of the standard curve, the partial pressure is determined.

NOTE: To determine the regression equation, plot area count versus concentration of the standard gas in the decimal fraction i.e. 10 ppm would be 0.00001 on the curve.

NOTE: In these calculations total pressure is assumed to be equal to 1 atmosphere; therefore,  $p_g/p_T = p_g$ .

$$p_g = m(\text{sample area count}) + b \quad \text{Eqn. 1}$$

where  $p_g$  = partial pressure of the gas (decimal fraction)  
 $m$  = slope of the line of the standard curve  
 $b$  = y-intercept of the line.

2) The equilibrium mole fraction of the dissolved gas,  $x_g = p_g/H$  Eqn. 2  
where  $H$  = Henry's law constant for the gas.

3) Let  $n_g$  = moles analyte and  $n_w$  = moles water.  
Then  $x_g = n_g/(n_g + n_w)$  and  $n_g = x_g(n_g + n_w)$ . Eqn. 3

if  $n_g \cdot x_g \ll n_g$ ,  
then  $n_g = x_g \cdot n_w$  or  $n_g = n_w(p_g/H)$   
therefore,  $n_g/V = n_w/V(p_g/H)$  Eqn. 4.

4) One liter of water is 55.5 g-moles,  
 $n_w/V = 55.5 \text{ moles/L}(p_g/H)$

5) Saturation concentration of the gas,  
 $C = (n_g/V)(MW)(1000 \text{ mg/g})$  Eqn. 5  
where  $MW$  = molecular weight of the analyte.

6) Density calculation  
 $p = (\text{molecular weight of the analyte})/(22.4 \text{ l/mole})(ST \text{ in } K/273^\circ K)$   
where  $p$  = density  
 $ST$  = sample temperature

7)  $v = bv_{ml} - hv_{ml}(1L/1000mls)$  Eqn. 7  
where  $bv$  = bottle volume  
 $hv$  = headspace volume

Then,

8)  $A_h = hv_{ml} \cdot p_g$   
where  $A_h$  = ml of analyte in headspace  
then liquid phase analyte ( $A_l$ ) is

$$A_1 = (A_n/(v))(p)(1000\text{mg/g})(11/1000\text{ml}) \quad \text{Eqn. 8.}$$

Then  $TC = A_1 + C$

where  $TC$  = Total Concentration of analyte in the original sample

$A_1$  = liquid phase analyte from Eqn. 8

$C$  = saturation conc. from Eqn. 5.

The result will be in units of milligrams of gas per liter of water.

#### 5b. Example Calculation

Methane will be used as the example of the calculation for dissolved gas concentration in water. From the analysis of the sample, an area count for methane is determined. This area count is used with the equation for the line of the standard curve, which is determined by analyzing a range (10 - 10,000 ppm  $\text{CH}_4$ ) of methane standards, to obtain the partial pressure.

Parameters for this example calculation are as follows:

sample area count = 978264

method blank area count = 2766

Henry's law constant =  $4.13\text{E}+4$  (at 25 C)

sample temperature = 25 C

bottle volume = 60 ml

headspace volume = 6 ml.

1) For this sample the equation for the line of the standard curve is

$$pg = 1.814\text{E}-9x - 6.716\text{E}-6$$

$$\therefore p_g = (1.814\text{E}-9(978264-2766)) - 6.716\text{E}-6 \quad \text{Eqn. 1}$$

$$\text{so, } p_g = 0.0018.$$

2) Using Eqn. 2,  $x_g = 0.0018 / 4.13\text{E}+4$  or  $4.269\text{E}-8$  mole  $\text{CH}_4$ .

3 & 4) Using Eqn. 4 and the value above,  $n_g/V = (55.5)(4.269\text{E}-8)$   
or  $2.37\text{E}-6$  moles  $\text{CH}_4$  / liter  $\text{CH}_4$ .

5) Saturation concentration of  $\text{CH}_4$ , using Eqn. 5 and the value for  $n_g/V$   
 $C = (2.37\text{E}-6)(16)(1000) = 0.038$  mg  $\text{CH}_4$  / liter  $\text{H}_2\text{O}$ .

$$6) p = (16\text{g/mole}) / ((22.4\text{liters/mole})(298/273)) = 0.654 \text{ g } \text{CH}_4 / \text{liter}.$$

$$7) bv = 60 \text{ ml and } hv = 6 \text{ ml,} \\ v = (60 \text{ ml} - 6 \text{ ml})(1\text{L}/1000\text{ml}) = 0.054 \text{ L.}$$

$$8) A_n = 6\text{ml} \cdot 0.0018 = 0.0108 \text{ ml } \text{CH}_4$$

$$A_1 = (0.0108 \text{ ml} / 0.054 \text{ l})(0.654 \text{ g/l})(11/1000\text{ml})(1000\text{mg/g})$$

$$A_1 = 0.1308 \text{ mg } \text{CH}_4 / \text{l } \text{H}_2\text{O}$$

$$9) \text{ then } TC = A_1 + C = 0.038\text{mg/l} + 0.131\text{mg/l} \\ TC = 0.169 \text{ mg } \text{CH}_4/\text{liter } \text{H}_2\text{O}.$$

#### 6. Quality Control:

The use of method blanks, field blanks, field replicates and laboratory duplicates are encouraged. See the SOPs used for the GC analysis for information on analytical quality control.

RSKSOP-175  
Revision No. 0  
Date: 8/11/94  
Page 5 of 5  
Bryan Newell

**PRECAUTIONS:** No special precautions are necessary aside from those used in good laboratory practice.

**NOTE:** See appendix for tables of Henry's law constants.

# Section 14

## Gas Absorption

BY

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Portions of Section 14, "Chemical Engineers' Handbook," 4th ed., are used in this edition without substantial change. Acknowledgment is made of the authorship of that material by R. E. Emmert and R. L. Pigford.

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## GAS ABSORPTION

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### INTRODUCTION

Gas absorption is the unit operation in which one or more soluble components of a gas mixture are dissolved in a liquid. The absorption may be a purely physical phenomenon or may involve solution of the material in the liquid followed by reaction with one or more constituents in the liquid solution. The reverse operation called stripping or desorption is employed to transfer one or more volatile components from a liquid mixture into a gas. The following section is concerned primarily with the calculations and the fundamentals underlying those calculations that are necessary to design commercial equipment for carrying out these operations on a continuous basis.

Many materials are amenable to the gas-absorption process. Table 14-1 lists some absorption systems of commercial importance.

The equipment used for continuous contacting of a vapor and a liquid can be a tower filled with solid packing material, an empty tower into which the liquid is sprayed and through which the gas flows, or a tower that contains a number of bubble-cap, sieve, or valve-type plates. In general, the gas and liquid streams flow countercurrent to each other in order to obtain the greatest concentration driving force and therefore the greatest rate of absorption. Occasionally, absorption operations are carried out in spray columns, wetted-wall columns, stirred vessels, or other types of equipment.

There are three broad steps in the design of an absorption or stripping tower:

1. Data on the vapor-liquid equilibrium relations for the system are needed to determine the quantity of liquid necessary to absorb the required amount of the soluble components from the gas, or the quantity of gas necessary to strip the desired amount of the volatile components from the liquid. (Data of this nature are presented in Sec. 3. Additional sources of data specific to the absorption-stripping process are indicated in the text of this section.)

2. Data on the liquid and vapor capacity of equipment of the type being considered for use are needed to determine the necessary cross-sectional area and size of the equipment. (Data on the design of vapor-liquid equipment are included in Sec. 18. Specific problems peculiar to the absorption-stripping process will be covered in this section.)

3. Equilibrium data and material balances are used in combination with fundamental relations peculiar to the absorption-stripping process to calculate the number of equilibrium stages (theoretical plates or transfer units) required for the separation desired. Difficulty of the separation depends both on the degree of recovery required and the equilibrium for the system being considered.

**Table 14-1. Gas-absorption Systems of Commercial Importance\***

| Solute                             | Solvent                            | Reagent                                                          | Degree of commercial importance |          |     |
|------------------------------------|------------------------------------|------------------------------------------------------------------|---------------------------------|----------|-----|
|                                    |                                    |                                                                  | High                            | Moderate | Low |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | .....                                                            | X                               |          |     |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | Monoethanolamine                                                 | X                               |          |     |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | Diethanolamine                                                   | X                               |          |     |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | Triethanolamine                                                  | ...                             |          | X   |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | Diaminoisopropanol                                               | ...                             |          | X   |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | Methyl diethanolamine                                            | ...                             |          | X   |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | K <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> | X                               |          |     |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | NH <sub>3</sub>                                                  | ...                             | X        |     |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | NaOH, KOH                                                        | ...                             | X        |     |
| CO <sub>2</sub> , H <sub>2</sub> S | Water                              | K <sub>3</sub> PO <sub>4</sub>                                   | ...                             | X        |     |
| CO <sub>2</sub>                    | Propylene carbonate                | .....                                                            | ...                             | X        |     |
| CO <sub>2</sub>                    | Glycerol triacetate                | .....                                                            | ...                             | X        |     |
| CO <sub>2</sub>                    | Butoxy diethylene glycol acetate   | .....                                                            | ...                             | X        |     |
| CO <sub>2</sub>                    | Methoxy triethylene glycol acetate | .....                                                            | ...                             | X        |     |
| HCl, HF                            | Water                              | .....                                                            | X                               |          |     |
| HCl, HF                            | Water                              | NaOH                                                             | X                               |          |     |
| Cl <sub>2</sub>                    | Water                              | .....                                                            | X                               |          |     |
| SO <sub>2</sub>                    | Water                              | .....                                                            | ...                             |          | X   |
| SO <sub>2</sub>                    | Water                              | NH <sub>3</sub>                                                  | ...                             | X        |     |
| SO <sub>2</sub>                    | Water                              | Xylidine                                                         | ...                             | X        |     |
| SO <sub>2</sub>                    | Water                              | Dimethyl aniline                                                 | ...                             | X        |     |
| SO <sub>2</sub>                    | Water                              | Ca(OH) <sub>2</sub> , oxygen                                     | ...                             |          | X   |
| SO <sub>2</sub>                    | Water                              | Aluminum hydroxide-sulfate                                       | ...                             | X        |     |
| NH <sub>3</sub>                    | Water                              | .....                                                            | X                               |          |     |
| NO <sub>2</sub>                    | Water                              | .....                                                            | X                               |          |     |
| HCN                                | Water                              | NaOH                                                             | X                               |          |     |
| CO                                 | Water                              | Copper ammonium salts                                            | X                               |          |     |

\* Kohl and Reisenfeld, *Chem. Eng.*, **66**(12), 127 (1959); Sherwood and Pigford, "Absorption and Extraction," McGraw-Hill, New York, 1952.

Techniques will be presented for determining the necessary time of contact between the flowing streams or the required height of tower.

### EQUILIBRIUM DATA\*

Equilibrium data necessary for absorption calculations include the solubility of the solute gas in the solvent. In order to completely define the solubility, the data must generally state the temperature, the concentration of the solute gas in the liquid phase, the pressure of the solute gas in the gas phase, and the total pressure on the system. At low pressures the total pressure of the system is not so important, but as the total pressure increases, it can have a more significant effect on gas solubility. Equilibrium data will generally be found in one of three forms: solubility data expressed as either solubility in weight or mole per cent or as the Henry's law constant, pure component vapor pressures, or equilibrium distribution coefficients.

**Solubility of Gases in Liquids.** Where Henry's law holds, solubility is defined by giving the Henry's law constant and the temperature  $H = p_a/x_a = \text{atm./mole fraction of solute in solution}$ . For many gases Henry's law holds quite well when the partial pressure of the solute gas is less than 1 atm. For partial pressures of solute gas greater than 1 atm.,  $H$  is seldom independent of the partial pressure of the solute gas. In these instances  $H$  varies with partial pressure, and a given value of  $H$  can be used over only a narrow range of pressures. The use of Henry's law constants in obtaining liquid concentrations from gas solubility data is illustrated in the example below.

**Example 1.** We need to determine how much hydrogen from a gas mixture can be dissolved in 100 lb. of water when the total pressure on the gas is 760 mm. Hg. The partial pressure of hydrogen in the gas mixture is 200 mm. Hg, and the temperature is 20°C.

For partial pressures of hydrogen up to one atmosphere the value of  $H$  is  $6.83 \times 10^4$  at 20°C. ("International Critical Tables," vol. 3, p. 256):

$$x_A = \frac{P_A}{H_A} \quad (14-1)$$

$$P_A = 200 \text{ mm. Hg.} = 0.263 \text{ atm.}$$

$$x_A = \frac{0.263}{6.83 \times 10^4} = 0.385 \times 10^{-5}$$

where  $x_A$  is the mole fraction of hydrogen in the liquid phase. To calculate the pounds of hydrogen per hundred pounds of water we must convert from a molar to a weight basis. In a two-component system, the following formulation may be used:

$$\left(\frac{x_A}{1-x_A}\right)\left(\frac{m_A}{m_B}\right)100 = \left(\frac{0.385 \times 10^{-5}}{1-0.385 \times 10^{-5}}\right)\left(\frac{2.02}{18.02}\right)100$$

$$= 0.431 \times 10^{-4}$$

Thus,  $0.431 \times 10^{-4}$  lb. (g.) of hydrogen is the maximum that can be dissolved in 100 lb. (g.) of water at 20°C. from a gas mixture under a hydrogen partial pressure of 200 mm. Hg.

Obtaining solubility data for the system under consideration can sometimes be a challenging problem. An idea of the range of solutes and solvents that the chemical engineer may encounter in his absorption problems can be gained by studying Table 14-2. The "International Critical Tables" are always an excellent starting point. Markham and Cobey [*Chem. Rev.*, **28**, 519 (1941)] summarized and critically reviewed gas solubility data available before 1941. Battino and Clever [*Chem. Rev.*, **66**, 395-463 (1966)] review more recent data with emphasis on solvents other than water. Osburn and Markovic [*Chem. Eng.*, pp. 105-108, Aug. 25, 1969] present monographs for determining  $H$  at 20°C. when surface tension and molar volume of the solvent are known.

Solubility data for hydrocarbons and oils are usually presented as pure component vapor pressures or as equilibrium constants ( $K = y/x$ , where  $y$  = mole fraction of the solute in the gas phase, and  $x$  = mole fraction of the solute in the liquid phase). Through the use of Raoult's law ( $pp_A = P_A x_A$ , where  $pp_A$  = partial pres-

**Table 14-2. Solutes and Non-aqueous Solvents for Gas Absorption**

| Solutes                                  | Solvents                                                            |
|------------------------------------------|---------------------------------------------------------------------|
| Acetylene, C <sub>2</sub> H <sub>2</sub> | Acetic acid (glacial), C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> |
| Air                                      | Acetic anhydride, C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>      |
| Ammonia, NH <sub>3</sub>                 | Acetone, C <sub>3</sub> H <sub>6</sub> O                            |
| Bromine, Br <sub>2</sub>                 | Amyl alcohol, C <sub>5</sub> H <sub>12</sub> O                      |
| Carbon dioxide, CO <sub>2</sub>          | Aniline, C <sub>6</sub> H <sub>7</sub> N                            |
| Carbon monoxide, CO                      | Benzene, C <sub>6</sub> H <sub>6</sub>                              |
| Chlorine, Cl <sub>2</sub>                | Bromobenzene, C <sub>6</sub> H <sub>5</sub> Br                      |
| Ethane, C <sub>2</sub> H <sub>6</sub>    | Carbon disulfide, CS <sub>2</sub>                                   |
| Ethylene, C <sub>2</sub> H <sub>4</sub>  | Carbon tetrachloride, CCl <sub>4</sub>                              |
| Hydrogen, H <sub>2</sub>                 | Chlorobenzene, C <sub>6</sub> H <sub>5</sub> Cl                     |
| Hydrogen chloride, HCl                   | Chloroform, CHCl <sub>3</sub>                                       |
| Hydrogen sulfide, H <sub>2</sub> S       | Ethyl acetate, C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>         |
| Methane, CH <sub>4</sub>                 | Ethyl alcohol, C <sub>2</sub> H <sub>5</sub> O                      |
| Methyl chloride, CH <sub>3</sub> Cl      | Ethylene chloride, C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>    |
| Nitric oxide, NO                         | Ethyl ether, C <sub>4</sub> H <sub>10</sub> O                       |
| Nitrogen, N <sub>2</sub>                 | Methyl acetate, C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>        |
| Nitrous oxide, N <sub>2</sub> O          | Methyl alcohol, CH <sub>3</sub> O                                   |
| Oxygen, O <sub>2</sub>                   | Nitrobenzene, C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>         |
| Sulfur dioxide, SO <sub>2</sub>          | Propyl alcohol, C <sub>3</sub> H <sub>8</sub> O                     |
| Etc.                                     | Propylene, C <sub>3</sub> H <sub>6</sub>                            |
|                                          | Toluene, C <sub>7</sub> H <sub>8</sub>                              |
|                                          | Etc.                                                                |

sure in gas phase, and  $P_A$  = pure component vapor pressure) vapor pressures can be used to predict solubilities. Extreme care must be taken, however, in attempting to use pure component vapor pressures to predict gas absorption behavior. Both liquid-phase and vapor-phase non-idealities can cause significant deviations from the behavior predicted from pure component vapor pressures combined with Raoult's law. Equilibrium distribution coefficients ( $K$ ) vary with temperature, pressure, and composition, as discussed in Sec. 13. Assuming that data are available for a given system under similar conditions of temperature and pressure, the  $K$  value is a much more reliable tool for predicting vapor-liquid distribution.

Vapor-pressure data are available in Sec. 3 of this handbook for a number of materials. Dreisbach ("Pressure-Volume-Temperature Relationships of Organic Compounds," Handbook Publishers, Sandusky, Ohio, 1952) presents an exhaustive compendium of vapor-pressure data for various families of hydrocarbons.

Values of the equilibrium distribution coefficient  $K$  are given by Katz and Hachmuth [*Ind. Eng. Chem.*, **29**, 1072 (1937)]. See also Sherwood and Pigford ("Absorption and Extraction," McGraw-Hill, New York, 1952) and an extensive series of articles by Sage *et al.* [*Ind. Eng. Chem.*, 1934 to date]. In addition, the "Engineering Data Book" of the Natural Gas Processors Association in both the 1957 and 1966 editions presents significant data, as do Winn [*Petrol. Refiner*, **33**(4), 132 (1954)], Hadden and Grayson [*Hydrocarbon Process. Petrol. Refiner*, **40**(9), 207 (1961)], and Grayson and Streed (6th World Petroleum Congress, 1963). Chao and Seader [*A.I.Ch.E. J.*, **7**, 598-605 (1961)] have presented a wide-ranging correlation which takes into account both the vapor-phase and liquid-phase non-ideality effects up to pressures in the neighborhood of 1500 p.s.i.a.

In the case of absorption combined with chemical reaction, the engineer must be particularly careful that the data he uses include the effect of incomplete stripping on the absorption process. Burns and Maddox [*Oil Gas J.*, **65**, 112 (Sept. 18, 1967)] used data from Kohl and Reisenfeld ("Gas Purification," McGraw-Hill, New York, 1960) to solve in detail a problem illustrating the effect of mutual solubilities and incomplete stripping on absorption of H<sub>2</sub>S and CO<sub>2</sub> in an amine-water solution.

### MASS-TRANSFER FUNDAMENTALS

**Homogeneous Diffusion.** When a homogeneous material—either gas, liquid, or solid—contains two or more components whose concentrations vary from point to point, there is a tendency for

\*Equilibrium solubility data for specific systems are given in Sec. 3.



## 14-4 GAS ABSORPTION

transfer of mass to take place in such a way as to cause the concentrations to become uniform. This phenomenon is associated with the thermal agitation of molecules; in a region where molecules of one kind are concentrated, there is a greater tendency for molecules of this kind to escape than to enter the region. The net rate of diffusion  $N_A$  of material A at a point in a stationary fluid is found from experiment as well as from theory to be proportional to the concentration gradient at the point.

$$N_A = -D_r \frac{\partial c}{\partial s} \quad (14-2)$$

where  $c$  = concentration,  $s$  = distance, and  $D_r$  = diffusivity. If  $c$  is expressed in g.-moles/cu. cm.,  $s$  in cm., and  $D_r$  in sq. cm./sec., then the units of  $N_A$  are g.-moles/(sec.)(sq. cm.). The rate of diffusion is rapid in gases and much slower in liquids.

In the application of the theory of diffusion, it is often desirable to employ integrated forms of the diffusion equation, rather than Eq. (14-2), which is applicable only at a single point. Treatments of the use of Eq. (14-2) for steady-state diffusion are given by Treybal ("Mass-transfer Operations," McGraw-Hill, New York, 1955) and by Sherwood and Pigford ("Absorption and Extraction," McGraw-Hill, New York, 1952).

Several integrated forms of Eq. (14-2) are presented below, along with integrated expressions for the analogous equation for unsteady-state diffusion [Eq. (14-6)]. All these relationships are based on the assumption that diffusivity is not dependent on concentration. This assumption is good for gaseous systems (except at high pressure) and for dilute liquid solutions, but may not be true for concentrated solutions. Dependence on concentration is the result of (1) change of mobility of the solute with concentration because of a change in average molecule size of the medium, and (2) deviations of the mixture from ideal behavior [Wilke, *Chem. Eng. Progr.*, 45, 218 (1949)].

**Steady-state Equimolar Counterdiffusion.** This case is typified by the mixing of two gases in a confined space and by counterdiffusion of two components in distillation. For this case, assuming  $D_r$  constant, Eq. (14-2) integrates to

$$N_A = \frac{D_r}{B_F} (c - c_i) = \frac{D_r P}{RTB_F} (p - p_i) = \frac{D_r P}{RTB_F} (y - y_i) = k_G (y - y_i) \quad (14-3)$$

where concentration  $c$  can be expressed alternatively in terms of partial pressure  $p$  or mole fraction  $y$ . In c.g.s. units,  $N_A$  = g.-moles/(sec.)(sq. cm.);  $D_r$  = sq. cm./sec.;  $c$  = g.-moles/cc.;  $p$  = atm.;  $B_F$  = layer thickness, cm.;  $R$  = universal gas constant, 82.06 (cc.)(atm.)/(g.-mole)(°K.);  $T$  = temperature, °K.;  $P$  = absolute pressure, atm.;  $k_G$  = gas-phase mass-transfer coefficient, g.-moles/(sec.)(sq. cm.)(mole fraction). Subscript  $i$  refers to the interface. Other consistent sets of units may be used with suitable adjustments in the numerical value of  $R$ .

**Steady-state Diffusion of One Component through a Second Stagnant Component.** Examples are absorption of a soluble gas from a second insoluble gas and absorption of a slightly soluble gas into a non-volatile liquid. The integrated equation is

$$N_A = \frac{D_r P}{RTB_F} \frac{y - y_i}{(1 - y)_{lm}} = k_G (y - y_i) \quad (14-4)$$

where  $k_G$  = gas-phase mass-transfer coefficient corrected for inert gas concentration =  $k_G(p_{BM}/P)$ ;  $p_{BM}$  = partial pressure of inert gas;  $lm$  = logarithmic mean; other symbols as defined above.

**Steady-state Diffusion of One Component through a Stagnant Multicomponent Mixture.** According to Wilke [*Chem. Eng. Progr.*, 46, 95 (1950)], Eq. (14-1) may be applied to this case provided an effective diffusivity of the diffusing species A is defined as

$$D_{vA} = \frac{1 - y_A}{(y_B/D_{vAB}) + (y_C/D_{vAC}) + (y_D/D_{vAD}) + \dots} \quad (14-5)$$

**Unsteady-state Diffusion.** Diffusion does not lead to conditions of constant concentration gradient unless a steady state is estab-

lished. It is therefore often necessary to consider the change of concentration  $c$  with time  $t$  caused by diffusion as represented by the differential equation

$$\frac{\partial c}{\partial t} = D_r \frac{\partial^2 c}{\partial s^2} \quad (14-6)$$

where  $s$  = distance and  $D_r$  = diffusivity.

Solutions of this equation for a diversity of physical situations are given by Crank ("Mathematics of Diffusion," Oxford, New York, 1956) and by Jost ("Diffusion," Academic Press, New York, 1952). Figure 14-1 shows the change in average concentration  $\bar{c}$  of a component in a slab, cylinder, or sphere as a function of time  $t$  when a constant surface concentration  $c_i$  is provided to permit that component to diffuse (i.e., where the relative resistance to diffusion in the surrounding medium is negligible). The solution is analogous to that for the conduction of heat under the influence of a temperature gradient. Figure 14-1 is applicable only when the material in which the diffusing component is dispersed is not internally mixed and retains its shape during the period of time involved. This is not the case in packed or plate-column gas absorbers but may be so in some spray, descending-liquid-sheet, or falling-jet devices if the fluid is stagnant or in laminar flow.

**Diffusion with Flow.** If fluid motion is laminar, transfer of mass between adjacent layers of fluid takes place purely by molecular diffusion. If the velocity pattern of the flow is known, it is sometimes possible to calculate the over-all rate of mass transfer into the moving fluid by the use of the basic equations of molecular diffusion. If the flow is turbulent, however, such calculations are generally impossible, since the laws that govern the transport of matter by turbulent mixing of small volumes of fluid are not well enough understood. Prediction of mass-transfer rates under such conditions is based on empirical methods.

**Laminar Flow, Uniform Velocity.** If the velocity of a flowing stream is uniform over a very deep region (thickness  $B_F \gg \sqrt{D_v t}$ ) in which diffusion is taking place, Eq. (14-6) is applicable. It has

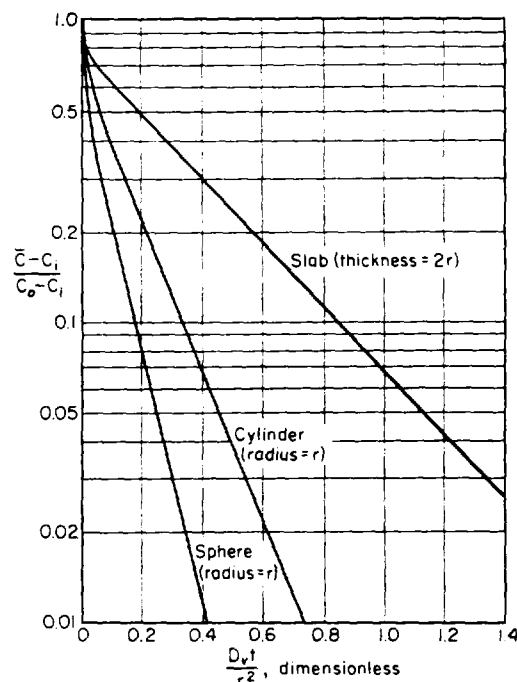


Fig. 14-1. Unsteady-state diffusion:  $c_0$  = uniform initial concentration,  $c_i$  = constant surface concentration,  $\bar{c}$  = average concentration. (Crank, "Mathematics of Diffusion," Oxford, Clarendon, 1956.)

Fig. 14  
t = tin.  
transfer  
(1954).

been integrated by Higbie [*Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935)] to give

$$k_L = \frac{2}{\sqrt{\pi}} \sqrt{\frac{D}{t}} \quad (14-7)$$

where  $k_L$  = liquid-phase mass-transfer coefficient, g.-moles/(sec)(sq. cm.)(g.-moles/cc.);  $D$  = diffusivity, sq. cm./sec.;  $t$  = time, sec.

This equation closely represents gas-absorption data taken with falling laminar jets of liquid [Cullen and Davidson, *Trans. Faraday Soc.*, **53**, 113 (1957); Nijssing and Kramers, *Chem. Eng. Sci.*, **10**, 88 (1959); Scriven and Pigford, *A.I.Ch.E. J.*, **4**, 439 (1958)], and with liquid layers descending in short wetted-wall columns when rippling is absent [Vivian and Peaceman, *A.I.Ch.E. J.*, **2**, 437 (1956)]. In the latter case, Eq. (14-7) predicts rates up to 15 per cent higher than those observed, possibly because of end effects [Lynn, Straatemeier, and Kramers, *Chem. Eng. Sci.*, **4**, 49, 58, 63 (1955)]. Equation (14-7) is applicable only when the diffusing molecules have not completely penetrated the fluid layer in question. It thus must be restricted to short contact times (less than about 1 sec. for freely descending water layers).

**Laminar Flow, Parabolic Velocity Distribution.** Gas absorption or desorption is frequently accomplished into or from liquid layers flowing down a solid surface, as in a wetted-wall column or over packing. The liquid layer in this case moves with maximum velocity at its free surface and zero velocity at the solid surface. The fully established velocity profile appears to be nearly parabolic between these limits as long as ripples are absent, according to the investigation of Grimley [*Trans. Inst. Chem. Engrs. (London)*, **23**, 228 (1945)].

Pigford (Ph.D. Thesis, University of Illinois, 1941) solved the differential equation for this case with the result shown in Fig. 14-2. The dashed line on Fig. 14-2 represents Eq. (14-7) for a uniform velocity profile. Figure 14-2 has been shown to represent wetted-wall column data, as long as rippling is absent, by Emmert and Pigford [*Chem. Eng. Progr.*, **50**, 87 (1954)] and Lynn, Straatemeier, and Kramers (*loc. cit.*). Both investigations avoided rippling by using wetting agents in the liquid or by employing short wetted-wall columns (less than 4 in.).

Ripples are normally present on the surface when the Reynolds number for the liquid exceeds a critical value ( $N_{Re,c}$ ) given by the relation (Grimley, *loc. cit.*)

$$\frac{\gamma^3 \rho}{\mu^4 g} = 0.3(N_{Re,c})^8 \quad (14-8)$$

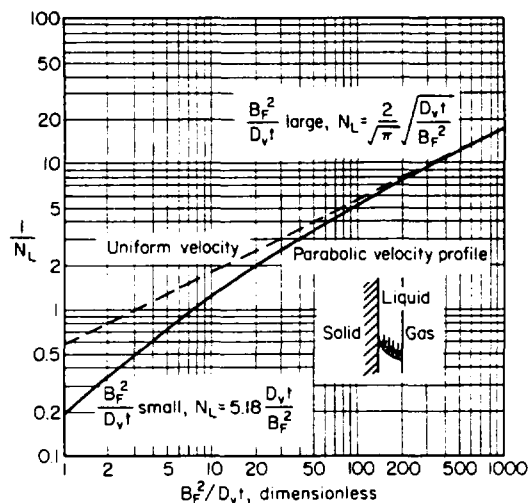


Fig. 14-2. Absorption or desorption to descending liquid:  $t$  = time of surface exposure,  $N_L$  = number of liquid-phase transfer units. [Emmert and Pigford, *Chem. Eng. Progr.*, **50**, 87 (1954).]

where  $\gamma$  = surface tension,  $\rho$  = density,  $\mu$  = viscosity,  $g$  = gravitational constant, all in consistent units. For water, the critical Reynolds number is about 25. Turbulence within the liquid layer begins at a Reynolds number of about 1200 [Thomas and Portalski, *Ind. Eng. Chem.*, **50**, 108 (1958)]. Up to the Reynolds number at which actual turbulence sets in, surface rippling can be avoided by adding certain wetting agents or by employing such a short distance of flow that surface instability does not develop.

Two auxiliary relations are needed for using Fig. 14-2. Film thickness  $B_F$  can be calculated using the Nusselt equation,

$$B_F = \left( \frac{3\mu\Gamma}{g\rho^2} \right)^{1/3} \quad (14-9)$$

which has been confirmed experimentally by Fallah, Hunter, and Nash [*J. Soc. Chem. Ind. London*, **53**, 368 (1934)] and others, even when rippling occurs. In Eq. (14-9),  $\Gamma$  = flow rate per unit of peripheral distance. Contact time  $t$  between gas and liquid is fixed by the velocity  $u$  of the free liquid interface, which is related to the average film velocity by the relation

$$u = \frac{3}{2}u_{avg} \quad (14-10)$$

**Turbulent Flow.** When a fluid phase through which mass transfer is occurring is in turbulent motion, transfer takes place by the relatively fast process of eddy diffusion. Experimental measurements of eddy diffusivities at very high Reynolds numbers in ducts have revealed values in gases as high as 100 times the molecular diffusivities [Sherwood and Woertz, *Trans. Am. Inst. Chem. Engrs.*, **35**, 1034 (1939)], and in liquids as high as 100,000 times the molecular diffusivities [Kalinske and Pien, *Ind. Eng. Chem.*, **36**, 220 (1944)]. The following approximate equation can be fitted to the data of Sherwood and Woertz for gases in turbulent flow through ducts:

$$E_p = 6.6 \times 10^{-5} N_{Re} + 0.2 \quad (14-11)$$

where eddy diffusivity  $E$  is expressed in sq. ft./hr., and density of the medium  $\rho$  is in lb./cu.ft.

When a fluid moves over either a liquid or a solid surface, the eddy motion that causes mass transfer also causes heat transfer and fluid friction because of transfer of heat and momentum, respectively. The close similarity among the transfer of mass, heat, and momentum is brought out by the Reynolds analogy, which states that, when heat, mass, and momentum are supplied to the fluid in corresponding ways, the following ratios are equal:

$$\begin{aligned} & \text{Rate at which mass is transferred from the solid surface} \\ & \text{Total rate at which the component, in excess of the interfacial} \\ & \quad \text{concentration, flows past the surface} \\ & = \frac{\text{rate of heat transfer from the solid surface}}{\text{total rate at which heat, measured above the surface} \\ & \quad \text{temperature, flows past the surface}} \\ & = \frac{\text{rate of momentum loss due to friction}}{\text{total momentum of stream that flows past the surface}} \end{aligned}$$

In terms of mathematical symbols, these statements may be written as

$$\frac{k_G(y - y_i)}{G_M(y - y_i)} = \frac{h(T - T_i)}{c_p G(T - T_i)} = \frac{g_c T_0}{\rho V^2} \quad (14-12)$$

$$\text{or} \quad \frac{k_G}{G_M} = \frac{h}{c_p G} = \frac{f}{2} \quad (14-13)$$

where  $k_G$  = gas-phase mass-transfer coefficient, lb.-moles/(hr.)(sq. ft.)(mole fraction);  $G_M$  = molar mass velocity, lb.-moles/(hr.)(sq. ft.);  $y$  = mole fraction;  $h$  = heat-transfer coefficient, B.t.u./(hr.)(sq. ft.)(°F.);  $c_p$  = specific heat, B.t.u./(lb.)(°F.);  $G$  = mass velocity, lb./(hr.)(sq. ft.);  $T$  = temperature;  $g_c$  = gravitational conversion factor, (lb. mass)(ft.)/(lb. force)(sec.<sup>2</sup>);  $T_0$  = surface frictional stress, lb. force/sq. ft.;  $\rho$  = density, lb./cu. ft.;  $V$  = velocity, ft./sec.;  $f$  = friction factor.

Experimental data for mass transfer into gas streams agree approximately with Eq. (14-12) when the value of the Schmidt number  $\mu/\rho D_v$  is near 1 and when the friction factor is calculated from the

"skin" friction. For flow through a straight tube, or along a flat plate that is parallel to the direction of flow, the pressure drop is due entirely to skin friction against the surface. On the other hand, the frictional force exerted on an immersed body, such as a sphere or a cylinder placed perpendicular to the direction of flow, is due in part to fluid pressure exerted on the front face of the body that is not counterbalanced by equal and opposite pressure on the rear face. Equation (14-11) does not apply in such cases if the friction factor is calculated from the total drag, including the "form" drag.

The limited conditions under which the Reynolds analogy can be expected to hold may be seen from the equations that govern the rate of transfer through a turbulent fluid [von Kármán, *Trans. Am. Soc. Mech. Engrs.*, 61, 705 (1939)]. For mass transfer the assumption is that

$$N_A = N_m + N_t = -(D_v + E) \left( \frac{dc}{ds} \right) \quad (14-14)$$

and for friction

$$\tau = \tau_m + \tau_t = - \left( \frac{\mu + \rho E_v}{g_c} \right) \left( \frac{du}{ds} \right) \quad (14-15)$$

where  $N_m$  = rate of mass transfer due to molecular diffusion, and  $N_t$  = rate of mass transfer due to turbulent mixing, lb.-mole/(hr.)(sq. ft.);  $D_v$  = molecular diffusivity, and  $E$  = eddy diffusivity for mass transfer, sq. ft./hr.;  $c$  = concentration, lb.-moles/cu. ft.;  $s$  = distance, ft.;  $\tau_m$  = shear stress due to molecular motion, and  $\tau_t$  = shear stress due to turbulent mixing, lb. force/sq. ft.;  $\mu$  = viscosity, lb./(ft.)(hr.);  $\rho$  = density, lb./cu. ft.;  $E_v$  = eddy kinematic viscosity, sq. ft./hr.;  $g_c$  = gravitational conversion factor, (lb. mass)/(ft.)(lb. force) (hr.<sup>2</sup>);  $u$  = velocity, ft./hr.

In Eqs. (14-14) and (14-15) the first term in the parentheses gives the rate of transfer of mass or of momentum due to molecular diffusion, and the second term gives the rate due to turbulent mixing. The Reynolds analogy follows from these equations if one assumes that (1) either  $\mu/\rho D_v = 1$  or both  $D_v$  and  $\mu/\rho$  are much smaller than  $E$  and  $E_v$ , (2)  $E = E_v$ , and (3)  $N_A/\tau$  is independent of position  $s$ . Under these conditions the concentration and velocity fields are similar and, just as Reynolds assumed, mass and momentum are transferred in the same way.

The Reynolds analogy thus fails to account for the mass-transfer resistance of the region of fluid near the solid (or liquid) boundary, in which transfer occurs principally by molecular motion. Colburn [*Trans. Am. Inst. Chem. Engrs.*, 29, 174 (1933)] and Chilton and Colburn [*Ind. Eng. Chem.*, 26, 1183 (1934)] showed empirically that the resistance of this laminar sublayer can be expressed by the following modification to the Reynolds analogy:

$$\frac{k_G}{G_M} \left( \frac{\mu}{\rho D_v} \right)^{2/3} = i_M = \frac{h}{c_p G} \left( \frac{c_p \mu}{k} \right)^{2/3} = i_H = \frac{f}{2} \quad (14-16)$$

for turbulent flow through straight tubes and across plane surfaces, and

$$i_M = i_H \leq \frac{f}{2} \quad (14-17)$$

for turbulent flow around cylinders, where  $j_M$  = mass-transfer factor;  $j_H$  = heat-transfer factor;  $k$  = thermal conductivity, B.t.u./ (hr.)(ft.)(°F.); other symbols as defined immediately above. Experimental data show Eqs. (14-16) and (14-17) to be approximately valid for values of  $(\mu/\rho D_v)$  between 0.5 and 2, whereas the Reynolds analogy is substantially in error at these extremes.

**Flow over Packings.** Higbie [*Trans. Am. Inst. Chem. Engrs.*, 31, 365 (1935)] advanced the theory that, in a packed absorption tower, the liquid flows across each packing piece in laminar flow and is mixed with other liquid meeting it at the points of discontinuity between packing elements. Danckwerts [*Ind. Eng. Chem.*, 43, 1460 (1951)] proposed a modification of this theory. It allows for eddy motion in the liquid that continually brings masses of fresh liquid from the interior to the surface, where they are exposed to the gas for a finite length of time before being replaced. Danckwerts assumed that any element has an equal chance of being replaced

regardless of its age. The Higbie model leads to Eq. (14-7), where  $t$  is the time for flow across a single packing piece. The Danckwerts model gives

$$k_L = \sqrt{D s_r} \quad (14-18)$$

where  $s_r$  is the fractional rate of surface renewal.

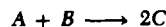
Note that both models predict a dependence on  $\sqrt{D}$ . Few data exist to confirm the validity of this effect of diffusivity. Sherwood and Holloway [*Trans. Am. Inst. Chem. Engrs.*, 36, 39 (1940)] have compared absorption rates in a packed tower for CO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub> and found them to vary nearly as  $\sqrt{D}$ . Danckwerts [*A.I.Ch.E. J.*, 1, 456 (1955)] gives a more thorough treatment of the merits of these models as well as others. No theoretical model has yet proved adequate for predicting absorption rates in packed columns, and empirical correlations (see Sec. 18) are recommended.

**Diffusion with Reaction.** Gas absorptions are often conducted using a solvent which is reactive with the gas or which contains a solute that is reactive. When a chemical reaction takes place in the liquid with the absorbed molecules as they are diffusing, the concentration profiles are altered; hence, the rate of absorption is affected. For a liquid that is stagnant or undergoing rodlike laminar flow, unsteady-state diffusion equations akin to Eq. (14-6) can be written to represent diffusion with reaction of various types. Certain of these differential equations have been solved representing the following cases:

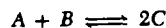
1. Absorption accompanied by first-order reaction [for irreversible reaction, see Danckwerts, *Trans. Faraday Soc.*, 46, 300 (1950); for reversible case, see Sherwood and Pigford, "Absorption and Extraction," McGraw-Hill, New York, 1952]:



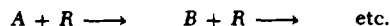
2. Absorption accompanied by very fast second-order reaction (Danckwerts, *loc. cit.*; Sherwood and Pigford, *op. cit.*):



3. Absorption accompanied by finite-rate reversible second-order reaction [Perry and Pigford, *Ind. Eng. Chem.*, 45, 1247 (1953); 49, 1400 (1957)]:



4. Simultaneous absorption of two or more gases which react rapidly with a component in the liquid [Roper, Hatch, and Pigford, *Ind. Eng. Chem., Fund. Quart.*, 1, 144 (1962)]:



5. Two gases that dissolve in an inert medium and then react with each other (Roper, Hatch, and Pigford, *loc. cit.*).

**Absorption with First-order Reaction.** Figure 14-3 shows the relation predicted for first-order reaction. The ordinate  $k_L/k_L^0$  is the ratio of mass-transfer coefficients with and without reaction and thus represents the enhancement due to reaction. Both coefficients are averaged over time period  $t$ . The first-order reaction-rate constant is  $k_1 \text{ sec.}^{-1}$ , and  $K$  is the equilibrium constant. Approximate experimental confirmation of the upper line of Fig. 14-3 has been

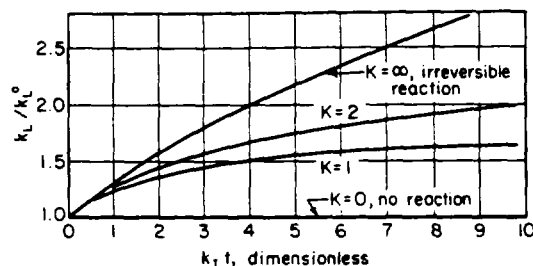


Fig. 14-3. Absorption with first-order reaction. (Sherwood and Pigford, "Absorption and Extraction," McGraw-Hill, New York, 1952.)

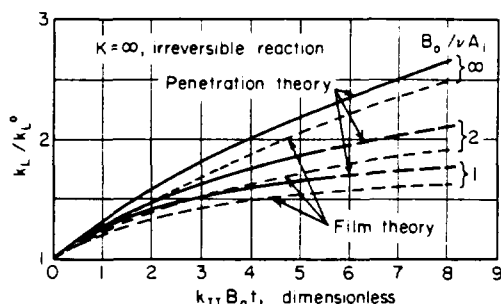


FIG. 14-4. Absorption with second-order irreversible reaction:  $k_{II}$  = second-order reaction-rate constant, liters/(g.)(mole-sec.);  $B_0$  = initial concentration of dissolved reagent, g.-moles/liter;  $t$  = time, sec.;  $\nu$  = stoichiometric coefficient;  $A_i$  = concentration of dissolving gas at liquid interface, g.-moles/liter. [Perry and Pigford, *Ind. Eng. Chem.*, **45**, 1247 (1953); **49**, 1400 (1957).]

obtained for absorption of  $\text{CO}_2$  into alkaline buffer solutions by Danckwerts and Kennedy [*Trans. Inst. Chem. Engrs. (London) Suppl.*, **32**, S49, S53 (1954)], using a rotating-drum apparatus, and by Nijssing and Kramers ("Chemical Reaction Engineering," pp. 81-89, Pergamon Press, London, 1958), using a short wetted-wall column. No adequate data are available to test the allowance the theory makes for effect of the reverse reaction.

**Absorption with Second-order Reaction.** Although the computational methods needed to provide a similar treatment for second-order reaction have been described by Perry and Pigford (*loc. cit.*), solutions have been obtained only for a limited range of the variables of interest. Figure 14-4 shows the results of Perry and Pigford's computations for an irreversible reaction ( $K = \infty$ ) and compares these with the predictions of the film (steady-state) theory of van Krevelen and Hoftijzer [*Rec. Trav. Chim.*, **67**, 563 (1948)]. The film theory, less representative of the actual physical behavior, nevertheless predicts only a slightly lesser degree of enhancement of the absorption coefficient because of reaction for the irreversible case. Until computations for the unsteady-state problem have been extended to cover wider ranges of the parameters, the theory of van Krevelen and Hoftijzer (modified to account for the effect of diffusivity as indicated by the unsteady-state theory) is recommended for use. Figure 14-5 shows the results of this theory so modified.

For very fast reactions, that is, when  $k_{II} B_0 t / (D_B / D_A) (B_0 / \nu A_i) > 10$ , the enhancement of the mass-transfer coefficient can be closely approximated by [Danckwerts, *Trans. Faraday Soc.*, **46**, 300 (1950)]

$$\frac{k_L}{k_L^0} = \frac{1 + (D_B / D_A) (B_0 / \nu A_i)}{(D_B / D_A)^{0.5}} \quad (14-19)$$

where  $k_L / k_L^0$  is the ratio of mass-transfer coefficients with and without reaction;  $k_{II}$  = second-order reaction-rate constant, liters/

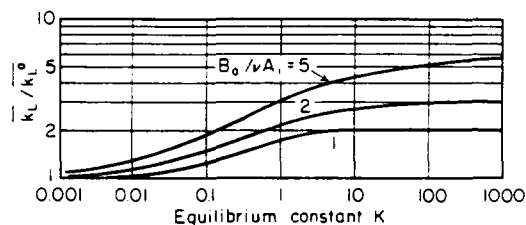
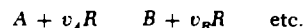


FIG. 14-6. Effect of reversibility on absorption with second-order reaction. (Pigford, *A.I.Ch.E. Meeting, Philadelphia, June 24, 1958*.)

(g.-mole)(sec.);  $B_0$  = initial concentration of dissolved reagent, g.-moles/liter;  $A_i$  = concentration of dissolving gas at liquid interface, g.-moles/liter;  $\nu$  = stoichiometric coefficient relating the number of moles of  $B$  reacting with 1 mole of  $A$ ;  $D_A$  = diffusivity of dissolving gas  $A$ , sq. cm./sec.;  $D_B$  = diffusivity of dissolved reagent, sq. cm./sec.

When several soluble gases ( $A, B, C, \dots$ ) dissolve simultaneously and diffuse to a moving reaction boundary in the liquid, where they all react very quickly with a single reagent  $R$  by the simultaneous reactions,



Eq. (14-19) should be replaced by (Roper, Hatch, and Pigford, *loc. cit.*)

$$\frac{k_L a}{k_L^0 a} = \sqrt{\frac{D_A}{D_R}} \left[ 1 + \frac{1}{(\nu_A A_i / R_0) \left( \frac{D_A}{D_R} \right) + \left( \frac{\nu_B B_i}{R_0} \right) \left( \frac{D_B}{D_R} \right) + \dots} \right] \quad (14-20)$$

Symbols are analogous with those of Eq. (14-19). When  $D_A > 2D_R$ , a more exact solution is to be preferred, and reference to the original paper is recommended.

Both Eq. (14-19) and Fig. 14-5 apply only to irreversible reactions ( $K = \infty$ ). The effect of reversibility can be accounted for by using Fig. 14-6, which, like Eq. (14-19), was derived for very fast reactions but which may also be used as an approximation for slower reactions. Equation (14-19) has been approximately confirmed by Emmert (Ph.D. Thesis, University of Delaware, 1954), who studied absorption of  $\text{CO}_2$  in aqueous monoethanolamine in a short wetted-wall column, and more closely by Nijssing and Kramers (Dissertation, Delft, 1957), who studied the absorption of  $\text{CO}_2$  in  $\text{NaOH}$  and  $\text{KOH}$  solutions in a wetted-wall column.

**Absorption of Two Reacting Gases.** Roper, Hatch, and Pigford (*loc. cit.*) have obtained a theoretical solution for the case where two absorbing gases react with each other. Their results are given in Fig. 14-7A, B, C. Figure 14-7C represents the case of a pseudo-first-order reaction ( $B_0 / \nu A_i = \infty$ ), where the interfacial concen-

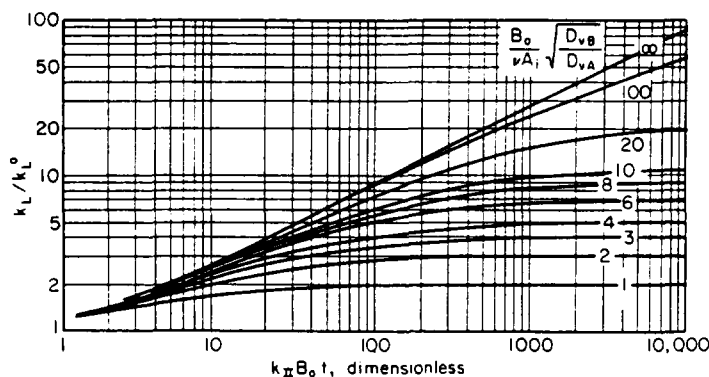


FIG. 14-5. Absorption with very fast second-order reaction.

# 14-8 GAS ABSORPTION

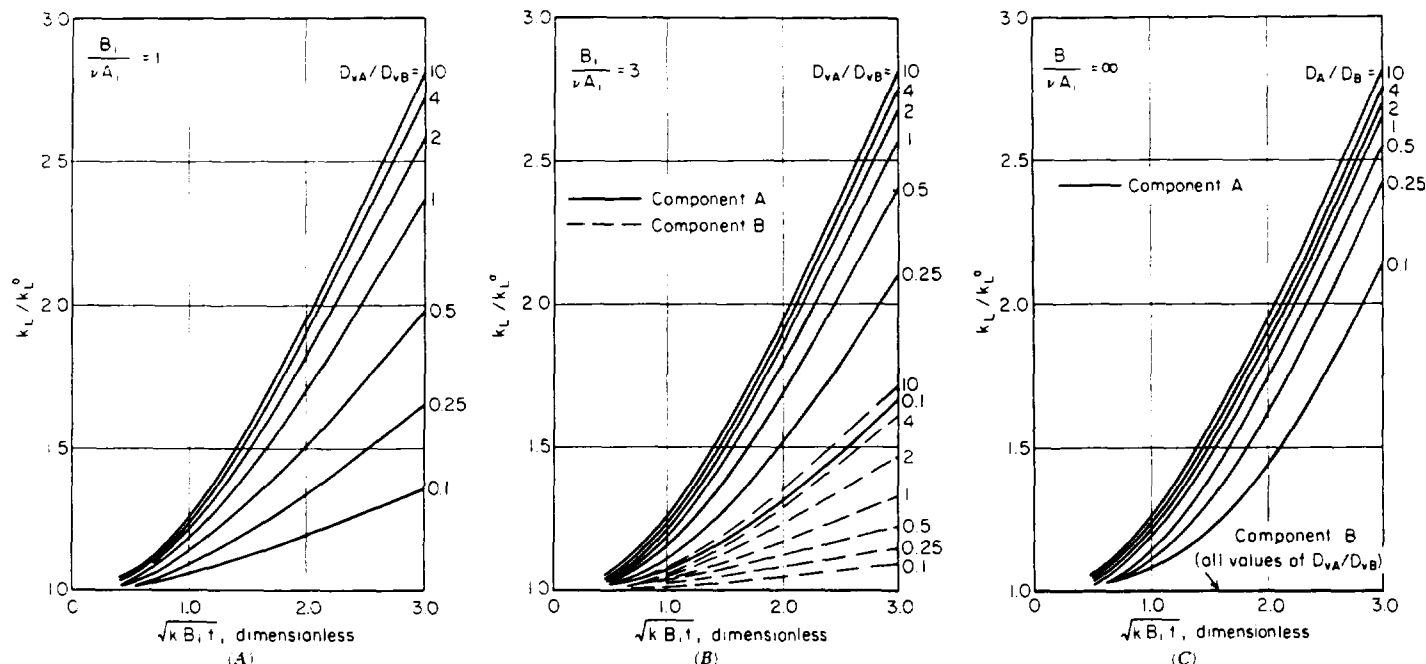


Fig. 14-7. Absorption of two reacting gases:  $k_L/k_G^0$  applies to either A or B. [Roper, Hatch, and Pigford, *Ind. Eng. Chem., Fund. Quart.*, 1, 144 (1962).]

tration of component B far exceeds that of component A. In Fig. 14-7A the value of  $k_L/k_G^0$  applies to both components A and B. In Fig. 14-7B separate curves are given for each component. In Fig. 14-7C,  $k_L/k_G^0$  for component B = 1 for all values of time and diffusivity ratio.

Hatch and Pigford [*Ind. Eng. Chem., Fund. Quart.*, 1, 209 (1962)] describe an experimental study in which  $\text{CO}_2$  and  $\text{NH}_3$  simultaneously dissolve in water and react with each other. Their results confirm the aforementioned theory for the pseudo-first-order case.

**Mass Transfer between Phases.** When material is transferred from one phase to another across an interface that separates the two, the resistance to mass transfer in each phase causes a concentration gradient in each, as shown in Fig. 14-8. The concentrations of the diffusing material in the two phases immediately adjacent to the interface are generally unequal, even if expressed in the same units, but are usually assumed to be related to each other by the laws of thermodynamic equilibrium, as discussed previously.

Rate of transfer varies with time and may be expressed, at least for the laminar sublayer, by the Higbie or Danckwerts equations [Eqs. (14-7) and (14-18)] which predict that the rate of transfer is proportional to the difference between the bulk concentration and the concentration at the interface. Thus

$$N_A = k_L(x - x_i) = k_G(y_i - y) \quad (14-21)$$

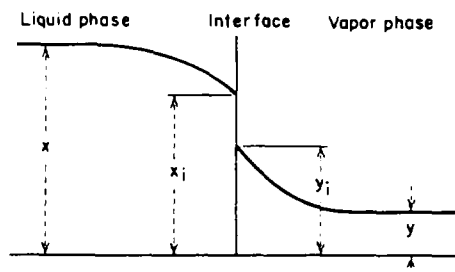


Fig. 14-8. Distribution of concentrations near an interface.

where  $N_A$  = mass-transfer rate, lb.-moles/(hr.)(sq. ft.);  $k_L$  = liquid-phase mass-transfer coefficient, lb.-mole/(hr.)(sq. ft.)(mole fraction);  $x$  = mole fraction in bulk liquid phase;  $x_i$  = mole fraction in liquid at interface;  $y$  = mole fraction in bulk gas phase;  $y_i$  = mole fraction in gas at interface.

This equation may be used to find the interfacial concentrations corresponding to any set of values of  $x$  and  $y$ , provided that the ratio of the individual coefficients is known. Thus

$$\frac{y_i - y}{x - x_i} = \frac{k_L}{k_G} = \frac{L_M H_G}{G_M H_L} \quad (14-22)$$

where  $L_M$  = molar liquid mass velocity, lb.-moles/(hr.)(sq. ft.);  $G_M$  = molar gas mass velocity, lb.-moles/(hr.)(sq. ft.);  $H_L$  = height of a transfer unit based on liquid-phase resistance, ft.;  $H_G$  = height of a transfer unit based on gas-phase resistance, ft.

Equation (14-22) may be solved graphically if a plot is made of the equilibrium vapor and liquid compositions, and a point is located representing the bulk concentrations  $x$  and  $y$  on this same diagram. A construction of this type is shown in Fig. 14-9.

In the design of equipment the rate of mass transfer must be estimated from known or predicted values of the transfer coefficients and the bulk concentrations. This may be done by solving

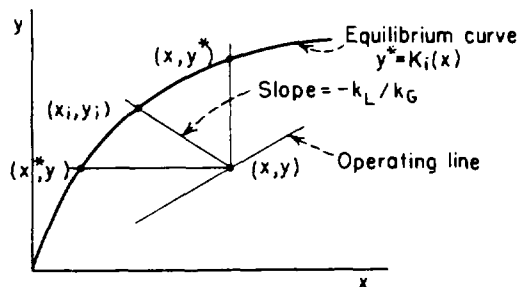


Fig. 14-9. Location of equilibrium concentrations for a point in a countercurrent tower.

Eq. (14-22) simultaneously with the equilibrium relation  $y_i = K_i(x_i)$  to obtain  $y_i$  and  $x_i$ . The rate of transfer may then be calculated from Eq. (14-21).

If the equilibrium relation  $y_i = K_i(x_i)$  is sufficiently simple, i.e., if a plot of  $y_i$  vs.  $x_i$  is a straight line, not necessarily through the origin, the rate of transfer is proportional to the difference in the bulk concentration in one phase and the concentration in that same phase which would be in equilibrium with the bulk concentration in the other phase. One such difference is  $y^* - y$ , and another  $x - x^*$ . In this case there is no need to solve for the interfacial compositions, as may be seen from the following derivation: Since

$$N_A = k_G(y_i - y) = k_L(x - x_i) = K_G(y^* - y) \quad (14-23)$$

where  $K_G$  = over-all gas-phase mass-transfer coefficient and  $y^*$  = vapor composition in equilibrium with  $x$ ,

$$\begin{aligned} \frac{1}{K_G} &= \frac{1}{k_G} \left( \frac{y^* - y}{y_i - y} \right) = \frac{1}{k_G} + \frac{1}{k_G} \left( \frac{y^* - y_i}{y_i - y} \right) \\ &= \frac{1}{k_G} + \frac{1}{k_L} \left( \frac{y^* - y_i}{x - x_i} \right) \end{aligned} \quad (14-24)$$

in view of Eq. (14-22). If the equilibrium curve is a straight line, the term in parentheses is the slope  $m$ . Thus

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L} \quad (14-25)$$

If the units of driving force on which  $k_L$  is based are liquid-phase concentrations expressed in lb.-moles of solute/cu. ft. of liquid, and the units of  $k_G$  are partial pressures in atmospheres, rather than mole fractions, Eq. (14-25) becomes

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{m_c k_L} \quad (14-26)$$

where  $m_c$  is the Henry's law coefficient, lb.-moles/(cu. ft.)(atm.).

When the equilibrium curve is not straight, there is no logical basis for use of an over-all transfer coefficient. Calculation of the rate of transfer in such cases must be made by solving for the interfacial compositions, as described above. A true average value of  $m$  for use in Eq. (14-25) cannot be calculated, since the value used must represent the relation between concentrations in equilibrium at the interface and depends, therefore, on the ratio  $k_L/k_G$ .

If the rate of transfer from the over-all concentration difference based on liquid compositions  $x^* - x$  is to be calculated, the appropriate over-all coefficient  $K_L$  is related to the individual coefficients by the equation

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{m k_G} \quad (14-27)$$

or

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{m}{k_G} \quad (14-28)$$

As in the case of Eq. (14-25), these equations apply only when the equilibrium line is straight.

Experimentally observed rates of mass transfer in diffusional operations equipment are often expressed in terms of over-all transfer coefficients, even when the equilibrium lines are curved. This procedure is purely empirical, since theory indicates that in such cases the rates of transfer may not vary in direct proportion to  $x - x^*$  at all concentration levels, although the rates may be proportional to the concentration difference in each phase taken separately,  $x - x_i$  and  $y_i - y$ .

In most types of diffusional operations equipment, such as packed or spray towers, just what interfacial area is available for mass transfer cannot be determined. For this reason experimentally observed rates of transfer are customarily reported in terms of transfer coefficients based on a unit volume of the apparatus rather than on a unit of interfacial area. Such volumetric coefficients are designated as  $K_G a$ ,  $k_L a$ , etc., where  $a$  represents the interfacial area per unit of volume of the apparatus. Experimentally observed variations in the values of volumetric coefficients due to variations in flow rates, type of packing, etc., may be due as much to changes

in the value of  $a$  as to changes in  $k$ . Calculation of the over-all coefficient from the individual coefficients is made by means of the equations

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{m}{k_L a} \quad (14-29)$$

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{1}{m_c k_L a} \quad (14-30)$$

$$\frac{1}{K_L a} = \frac{1}{k_L a} + \frac{1}{m k_G a} \quad (14-31)$$

$$\frac{1}{K_L a} = \frac{1}{k_L a} + \frac{m}{k_G a} \quad (14-32)$$

Because of the wide variation in the solubilities of gases in liquids, the variation in the value of  $m$  from one system to another sometimes has an important effect on the type of equipment that should be used for contacting. If, for example, an insoluble gas such as oxygen is to be dissolved in water, the large value of  $m$  for this system would cause the liquid-phase part of the over-all resistance to be extremely large in a spray tower, where the poor fluid mixing obtained in the liquid phase might result in a small value of  $k_L$ . On the other hand, this line of reasoning must be applied with caution, since gases with different solubilities are ordinarily absorbed under different conditions of operation; and the effect on the over-all resistance of changes in the solubility is therefore partly counterbalanced by changes in the specific resistance as the flow rates are changed.

**Height Equivalent to a Transfer Unit (H.T.U.).** Frequently the values of individual coefficients of mass transfer vary so rapidly with flow rates that the quantity obtained by dividing each coefficient by the flow rate of the phase to which it applies is more nearly constant than the coefficient itself. The quantity obtained by this division is called [Chilton and Colburn, *Ind. Eng. Chem.*, 27, 255 (1935)] the height of one transfer unit, since it expresses in terms of a single length dimension the height of apparatus required to accomplish a separation of standard difficulty.

The number of over-all gas-phase transfer units  $N_{OG}$  required for changing the composition of the vapor stream from  $y_1$  to  $y_2$  is

$$N_{OG} = \int_{y_2}^{y_1} \frac{dy}{y^* - y} \quad (14-33)$$

for equimolar diffusion, and

$$N_{OG} = \int_{y_2}^{y_1} \frac{(1-y) dy}{(1-y)(y^* - y)} \quad (14-34)$$

for diffusion in one direction only, where  $y$  = mole fraction in gas and  $y^*$  = mole fraction in gas in equilibrium with liquid. Convenient solutions of these equations are given later.

The number of transfer units required for a given separation is closely related to the number of theoretical plates or stages required to carry out the same separation in plate-type or stagewise apparatus. In terms of H.T.U.'s the equations that express the addition of resistances become [Colburn, *Trans. Am. Inst. Chem. Engrs.*, 35, 211 (1939)]

$$H_{OG} = H_G + H_L \left( \frac{m G_M}{L_M} \right) \frac{(1-x)_f}{(1-y)_f} \quad (14-35)$$

$$\text{and} \quad H_{OL} = H_L + H_G \left( \frac{L_M}{m G_M} \right) \frac{(1-y)_f}{(1-x)_f} \quad (14-36)$$

where  $H_{OG}$ ,  $H_{OL}$ ,  $H_G$ , and  $H_L$  = heights of transfer units, ft., based on, respectively, over-all gas-phase resistance, over-all liquid-phase resistance, gas-phase resistance, and liquid-phase resistance;  $(1-y)_f$  = logarithmic mean of  $1-y$  and  $1-y^*$ ;  $(1-x)_f$  = logarithmic mean of  $1-x$  and  $1-x^*$ ;  $x$  = mole fraction in liquid;  $x^*$  = mole fraction in liquid in equilibrium with gas;  $y$ ,  $y^*$ ,  $m$ ,  $G_M$ , and  $L_M$  as defined earlier.

The following relations between the transfer coefficient and the values of H.T.U. apply, where the prime indicates that the coefficient is corrected for inert gas concentration by the factor  $p_{BM}/P$

( $p_{BM}$  = partial pressure of inert gas,  $P$  = total absolute pressure):

$$H_{OG} = \frac{G_M}{K'_G a (1-y)_I} \quad (14-37)$$

$$H_G = \frac{G_M}{k'_G a (1-y)_I} \quad (14-38)$$

$$H_{OL} = \frac{L_M}{K_L a (1-x)_I} \quad (14-39)$$

$$H_L = \frac{L_M}{k_L a (1-x)_I} \quad (14-40)$$

Presence of the factor  $(1-y)_I$  is due to the fact that, in the diffusion of one gas through a second stationary layer of insoluble gas, the resistance to diffusion varies with the concentration of the stationary gas, approaching zero as the concentration of this gas approaches zero. The factor  $(1-x)_I$  cannot be justified on the basis of kinetic theory for the liquid phase but is included in the equations on the assumption that diffusion through liquids is similar to that through gases. (In binary distillation, where both components diffuse simultaneously, both these factors should be omitted.)

H.E.T.P. (height equivalent to one theoretical plate) is another quantity that is used occasionally to express the efficiency of a packing material for carrying out a separation. Experimental data should be reported as H.T.U.'s rather than H.E.T.P.'s, since the former quantity is theoretically correct for equipment, such as packed columns, in which mass is transferred by a differential rather than a stepwise action. If equilibrium and operating lines are parallel, i.e.,  $mG_M/L_M = 1$ , H.E.T.P.'s and H.T.U.'s are equal. If the equilibrium and operating lines are straight, but not parallel,

$$\frac{H_{OG}}{\text{H.E.T.P.}} = \frac{(mG_M/L_M) - 1}{\ln(mG_M/L_M)} \quad (14-41)$$

## DESIGN CALCULATIONS

**Outline of General Design Procedure.** For determination of the number of variables that must be specified in order to fix a unique solution for the design of an absorber, the engineer can use the same phase-rule-type approach discussed in Sec. 13 for distillation. The variables specified will normally include: (1) gas flow rate and composition; (2) operating pressure and pressure drop across the absorber; (3) desired degree of recovery of one or more solutes. In addition, the designer frequently has some degree of freedom concerning the solvent to be employed. Generally, the solvent must be recovered, and the recovery system ordinarily is considered an integral part of the absorption process design.

The designer ordinarily is required to determine (1) the best solvent; (2) the best gas velocity through the absorber (the vessel diameter); (3) the height of the vessel and its internal members, e.g., the depth and type of packing or the number of trays; (4) the optimum rate of solvent circulation through the absorber; (5) temperatures of streams entering and leaving the absorber, and the quantity of heat to be removed to account for heat of solution and other heat effects; (6) the pressures at which the absorber and regenerator will operate; (7) the mechanical design of the absorption and regeneration towers. This section is concerned with all these choices, except the last which is discussed in Sec. 18.

**Selection of Solvent.** The ideal solvent is non-volatile, free, non-corrosive, stable, non-viscous, non-foaming, and non-flammable, and has infinite solubility for the solute. Unfortunately, ideal solvents seldom are found, and so choice is usually based on the most desirable of many alternatives. Where such a choice is possible, preference would be given to a liquid with very high solubility for the solute. The exit gas is usually saturated with solvent, and solvent loss may be costly; so low-cost solvents may be chosen over more expensive ones of higher solubility or lower volatility.

**Selection of Vapor-Liquid Equilibrium or Solubility Data.** Sources of solubility and vapor-liquid equilibrium data have been discussed earlier in this section. Accurate and correct data are very

important because they determine the solvent circulation rate necessary to achieve the specified solute recovery. Experimental data on the particular system of interest are always best. In the absence of specified experimental data, generalized correlations must be referred to.

**Calculation of Liquid-Gas Ratio.** The minimum solvent rate is easily calculated, utilizing the entering-gas composition, and assuming saturation in the solute-rich solvent leaving the absorber. Estimation of the effect of heat of solution of the gas on exit solvent temperature may be necessary. Values of latent and specific heats and heat of solution (at infinite dilution) are given in Sec. 3.

The actual solvent circulation rate will be 25 to 100 per cent greater than the minimum. It will be arrived at on the basis of economic considerations, guided and corrected by judgment and experience.

In some packed-tower applications involving very soluble gases or vacuum operation, the minimum quantity of solvent required for absorption may not be sufficient to keep the packing surface thoroughly wet, leading to poor distribution of the liquid. There is no sharp dividing line of flow rate above which a packing material becomes thoroughly wet and below which flow distribution is poor. However, there is a minimum wetting rate described by Morris and Jackson ("Absorption Towers," Butterworth, London, 1953). The minimum wetting rate (M.W.R.) is computed as  $V_L/a$ , where  $V_L$  = volumetric liquid flow, cu. ft./hr./sq. ft. of tower cross section; and  $a$  = packing surface area, sq. ft./cu. ft. When the net flow of solvent to the packed column is smaller than M.W.R., recirculation of liquid over the packing may be desirable, even at the expense of a reduced mean driving force.

**Selection of Equipment.** Usually packed columns are chosen for corrosive materials, for low pressure drop, for pilot-plant or small-scale operations (say less than 2 ft. in diameter), and for liquids that foam badly. Plate columns are preferred for large-scale operations (they are cheaper), for low liquor rates (where packing would be inadequately wetted), and where internal cooling is desired.

In packed towers the type of packing is chosen for its mechanical strength, resistance to corrosion, cost, capacity, and efficiency. Packings found to be most economical and generally useful are 1- to 2-in. ceramic or carbon rings ( $\frac{1}{2}$ -in. size for columns under 4 in. in diameter), 1-in. saddles, 3-in. spiral or partition rings, drip-point tile, and wood grids.

**Pressure Drop for Both Plate and Pipe Columns.** Methods for estimating pressure drop are given in Sec. 18. Pressure drop at flooding for commonly used packing is around 2 in. of water per foot of packing height. For operation at about 50 per cent of flooding, the pressure drop is roughly  $\frac{1}{2}$  in. water per foot of height. These values are convenient to keep in mind for operating control.

**Height of Column.** Height of the column is primarily dependent on the degree of removal of solute from the gas. To compute the economic recovery, as well as the eventual height, the designer must have values of plate efficiency (plate column) or height of a transfer unit (packed column). Data on plate efficiencies are given in Secs. 13 and 18. For packed columns, over-all values of H.T.U. are used if available for the conditions of the problem; otherwise, separate gas-liquid values of H.T.U. are estimated as shown in Sec. 18 and combined as shown below.

**Computation of Tower Height.** Methods for estimating the height of the active section of an absorber needed to effect a given separation are based on the use of rate expressions for representing mass transfer at a point on the interface, and on material balances to represent the changes in bulk composition in the two phases that flow past each other. Combination of such expressions leads to an integral expression for the number of transfer units, or to very closely related equations for numbers of theoretical plates. The paragraphs immediately below set forth convenient methods for using such equations.

**Rate of Absorption for Packed Columns.** Figure 14-10 shows a section of a packed absorption column, together with the nomenclature that will be used in developing the equations which follow. In the differential section  $dz$  we can equate the rate at which solute is lost from the gas phase to the rate at which it is transferred

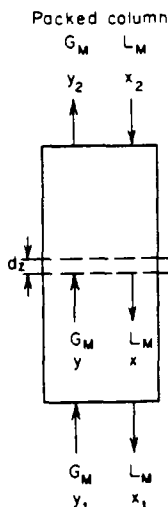


Fig. 14-10. Material balance, operating, and equilibrium lines.

through the gas phase to the interface,

$$-d(G_M y) = -G_M \frac{dy}{(1-y)^2} = k_G a P \frac{y - y_i}{(1-y)_{lm}} dz \quad (14-42)$$

where  $G_M$  = molar mass velocity of the gas stream,  $G_M$  = molar superficial mass velocity of the inert gas,  $k_G$  = gas-phase mass-transfer coefficient,  $a$  = interfacial area per unit of packed volume (smaller than the packing surface  $S$ ),  $P$  = absolute pressure;  $y_i$  = mole fraction solute in the gas at the interface, and  $(1-y)_{lm}$  = logarithmic mean of the mole fraction inert gas in the bulk stream  $(1-y)$  and that at the interface  $(1-y_i)$ . The height of packing  $z$  needed to accomplish a specified change in gas composition is

$$Z = G_M \int_{y_2}^{y_1} \frac{(1-y)_{lm} dy}{k_G a P (1-y)^2 (y - y_i)} \quad (14-43)$$

This expression applies in the most general case and is more complex than normally required. It must be used when the mass-transfer coefficient varies from point to point, as may happen if the gas velocity varies through the absorber, or when the gas is concentrated with solute. Interfacial concentrations ( $y_i$  and  $x_i$ ) are taken to be in equilibrium.

Equation (14-43) can sometimes be simplified by assuming that  $y_i$  equals zero, as would be the case when the solute reacts upon absorption to yield a reactant with negligible solute partial pressure. Frequently, changes in gas flow rate and mole fraction of inert gas are so small that terms such as  $(1-y)$  and  $(1-y)_{lm}$  can be neglected or included in only an approximate way. The following sections illustrate some of these simplified procedures.

**Obtaining Driving Force by Material Balances.** A steady-state material balance around the differential section of the packed column shown in Fig. 14-10 gives

$$d(G_M y) = d(L_M x) \quad (14-44)$$

$$G_M \frac{dy}{(1-y)^2} = L_M \frac{dx}{(1-x)^2} \quad (14-45)$$

where  $L_M$  = molar mass velocity of the liquid stream,  $L_M$  = molar mass velocity of the inert liquid component, and  $x$  = mole fraction in liquid. The reader should realize that  $x$  and  $y$  in Eqs. (14-42) to (14-45) are taken to be the average concentrations of solute in the liquid and vapor, respectively, within the differential packing height  $dz$ .

Integrating Eq. (14-45) around the upper section of packing gives

$$G_M \left( \frac{y}{1-y} - \frac{y_2}{1-y_2} \right) = L_M \left( \frac{x}{1-x} - \frac{x_2}{1-x_2} \right) \quad (14-46)$$

Equation (14-45) is the differential form and Eq. (14-46) is the integral form of the so-called operating line around the upper section of packing. When the mole fractions  $y$  and  $x$  are sufficiently small (dilute solutions), the total molar flows  $G_M$  and  $L_M$  will be very nearly constant. For this case the operating line equation is

$$G_M(y - y_2) = L_M(x - x_2) \quad (14-47)$$

Equation (14-47) is simply a material balance equation giving the relationship between the compositions of the gas and liquid streams at any point in the column. Figure 14-11 shows a plot of the equation in a typical case. Also shown in Fig. 14-11 is the typical equilibrium relationship between interfacial compositions  $y_i$  and  $x_i$ . Once  $y$  is known as a function of  $x$  along the operating line,  $y_i$  can be found at corresponding points from the equilibrium line. The operating line in Fig. 14-11 is straight only under the conditions for which Eq. (14-47) applies, i.e.,  $G_M$  and  $L_M$  constant. The case of curved operating lines has been treated by several authors including Mostafa [Brit. Chem. Eng., 13, 5 (May, 1968)].

**Transfer Units.** The local mass-transfer coefficient  $k_G a P$  in Eq. (14-43) has the units of length. It is called the height of a transfer unit for the gas phase and is symbolized by  $H_G$ . When the local coefficient is proportional to the first power of the point gas velocity  $G_M$ , the term  $G_M/k_G a P(1-y)$  may be taken as a constant. As pointed out in the development of Eq. (14-24), the driving force  $y - y_i$  across the gas phase can be computed from the over-all driving force  $y - y^*$  when the equilibrium line is straight. Since  $(y - y_i)/(y - y^*)$  is equal to  $H_G/H_{OG}$ , the equation for the packed height of the column can be written in two ways:

$$Z = H_G \int_{y_2}^{y_1} \frac{(1-y)_{lm} dy}{(1-y)(y - y_i)} = H_G N_G \quad (14-48a)$$

where  $N_G$  = number of transfer units, based on gas-phase resistance, and

$$Z = H_{OG} \int_{y_2}^{y_1} \frac{(1-y)_{lm} dy}{(1-y)(y - y^*)} = H_{OG} N_{OG} \quad (14-48b)$$

where  $H_{OG}$  = height of a transfer unit, and  $N_{OG}$  = number of transfer units, based on over-all gas-phase resistance. Equation (14-48b) is the more useful equation in a practical sense; it requires either empirical knowledge of or computation of  $H_{OG}$  by adding estimated values of  $H_G$  and  $H_L$ ; it does not, however, require knowledge of or estimation of interfacial compositions as does Eq. (14-48a).

A further convenient simplification of Eqs. (14-48a) and (14-48b) was suggested by Wiegand [Trans. Am. Inst. Chem. Engrs., 35, 679 (1939)], who pointed out that the logarithmic mean mole fraction

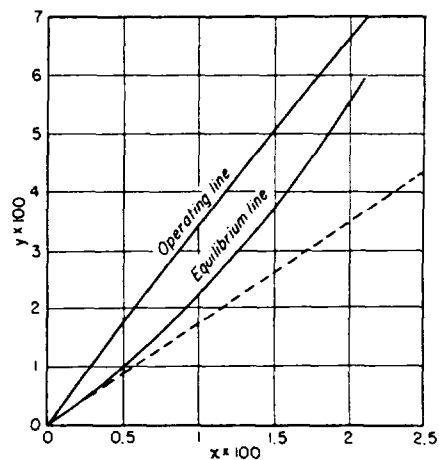


Fig. 14-11. Example of absorption of acetone, with a curved equilibrium line owing to heat of absorption. Dashed line is a tangent to the equilibrium curve at the origin.



## 14-12 GAS ABSORPTION

of inert gas  $(1 - y)_{lm}$  is often very nearly equal to the arithmetic mean. With this substitution the quotient of the first factors in the numerator and denominator of these equations becomes

$$\frac{(1 - y)_{lm}}{1 - y} \approx \frac{(1 - y^*) + (1 - y)}{2(1 - y)} = \frac{y - y^*}{2(1 - y)} + 1 \quad (14-49)$$

and so the equations may be simplified to

$$N_G = \frac{1}{2} \ln \frac{1 - y_2}{1 - y_1} + \int_{y_2}^{y_1} \frac{dy}{y - y_i} \quad (14-50)$$

$$N_{OG} = \frac{1}{2} \ln \frac{1 - y_2}{1 - y_1} + \int_{y_2}^{y_1} \frac{dy}{y - y^*} \quad (14-51)$$

The first terms, frequently amounting to only small corrections, give the effect of the finite level of gas concentration. The second terms give the number of transfer units for infinitely dilute gas. The procedure for applying Eqs. (14-50) and (14-51) involves two steps: evaluation of the integrals, and addition of the corrections corresponding to the first terms in the equations.

The simplest possible case occurs when (1) both the operating and the equilibrium line are straight (dilute solutions), (2) Henry's law is valid ( $y^*/x = y_i/x_i = m$ ), and (3) absorption heat effects are negligible. Under these conditions the integral in Eq. (14-51) may be evaluated explicitly as

$$N_{OG} = \frac{1}{1 - (G_M/L_M)} \ln \left[ \left( 1 - \frac{mG_M}{L_M} \right) \left( \frac{y_1 - mx_2}{y_2 - mx_2} \right) + \frac{mG_M}{L_M} \right] \quad (14-52)$$

Equation (14-52) includes only the evaluation of the second (integral) term of Eq. (14-51) and does not include the correction for the first term on the right side of the equation. It does provide an approximate result even when solutions are concentrated or absorption heat effects are present if, as in many practical examples involving nearly complete cleanup of the gas, the driving forces in the upper part of the tower are much smaller than those at the bottom. In these cases the value of  $mG_M/L_M$  used in the equation should be the ratio of slopes of the equilibrium line  $m$  and the operating line  $G_M/L_M$  in the low-concentration range. Figure 14-12 is a plot of Eq. (14-52) from which the value of  $N_{OG}$  can be read directly as a function of the ratio of the slopes and the ratio of concentrations. This plot and Eq. (14-52) are equivalent to the use of a logarithmic mean of terminal driving forces but are more convenient because they avoid computation of the exit-liquid concentration. For stripping or desorption the change in concentration of the liquid stream is of principal concern. For this case the rate equation is more conveniently formulated in terms of liquid composition  $x$ . This leads to equations defining numbers of transfer units and heights of transfer units based on liquid-phase resistance:

$$Z = H_L \int_{x_2}^{x_1} \frac{(1 - x)_{lm} dx}{(1 - x)(x_i - x)} = H_L N_L \quad (14-53)$$

$$Z = H_{OL} \int_{x_2}^{x_1} \frac{(1 - x)_{lm} dx}{(1 - x)(x^* - x)} = H_{OL} N_{OL} \quad (14-54)$$

When the assumptions applicable are employed, an equation analogous to Eq. (14-52) is obtained.

**Graphical Calculation of Transfer Units.** The number of transfer units required for a given absorption can be obtained graphically. The technique involves the  $x - y$  diagram in a manner similar to that for determination of theoretical stages. Baker [Ind. Eng. Chem., 27, 977 (1935)] presented a technique that involves locating a line vertically halfway between the operating and equilibrium lines, as shown by the dashed line in Fig. 14-13. Starting at point A on the operating line, a line is drawn toward the equilibrium line and extending to a point C such that AB equals BC. Point D on the operating line vertically above C is at a gas composition such that one transfer unit is required to go from A to D. If this procedure is applied successively from exit to inlet gas composition, the number of over-all gas transfer units ( $N_{OG}$ ) results. If  $N_{OL}$  is sought,

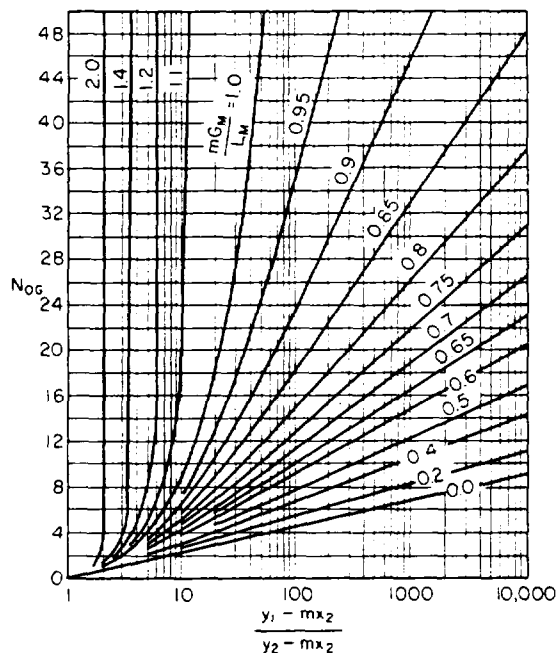


Fig. 14-12. Number of transfer units in an absorption column. Condition of constant  $mG_M/L_M$ , a plot of Eq. (14-52).

the dashed line must be located halfway horizontally between operating and equilibrium lines.

**Multicomponent Systems.** In cases where more than one soluble component is to be absorbed from an insoluble or slightly soluble gas, the method used by the designer will change. In general, a specified percentage of one solute will be recovered. Less volatile components will be recovered almost completely. Absorption of more volatile components will be incomplete, even though the rich solvent leaving the absorber becomes essentially saturated with respect to these components. In these cases calculation procedures derived from consideration of a theoretical plate (see Sec. 13) are generally used. All these procedures utilize, for convenience, an absorption factor  $A = L/KV$ , where  $A$  is the absorption factor for a given component,  $L$  is the total liquid molar flow rate,  $K$  is the equilibrium constant ( $K = y/x$ ), and  $V$  is the total molar gas rate.

The simplest procedure utilizes equations based on analysis of a plate-type absorber by Kremser [Nat. Petrol. News, 22, 48 (May 21, 1930)], as modified by Brown and Souders [Ind. Eng. Chem., 24, 519 (1932)]. Their equations are

$$\frac{Y_{n+1} - Y_1}{Y_{n+1} - Y_0} = \frac{A^{n+1} - A}{A^{n+1} - 1} \quad (14-55)$$

where  $Y$  is the moles of one component in the specified gas stream per mole of entering rich gas.  $A$  is the "average" absorption factor

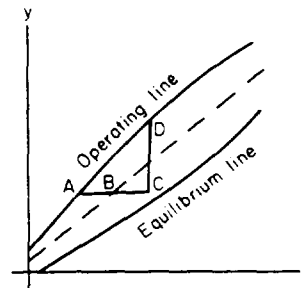


Fig. 14-13. Baker's construction for transfer units.

for that component, and  $n$  is the number of theoretical plates in the absorber.

Use of Eq. (14-55) to yield reliable numbers centers on proper selection of the average absorption factor. Brown and Souders recommend defining the average absorption factor as  $A = L_0/KV_{n+1}$  where  $L_0$  is the rate at which lean solvent flows through the column, and  $V_{n+1}$  is the rate of solute-rich gas flow. If the equilibrium constant is evaluated at a temperature about 15°F. above the average of the lean oil and rich gas temperatures, this will result in estimates of lean oil rates that tend to be slightly higher than those actually required.

In plate-type absorbers utilizing equations similar to (14-55) the number of theoretical plates will generally vary from approximately six to ten. Great caution should be used when estimates result in numbers of theoretical plates greater than ten.

Edmister [Petrol. Eng., 18, 130 (September, 1947)] suggested an "effective" absorption factor which is rigorous for a column with two theoretical plates and is defined as

$$A_e = \sqrt{A_n(A_1 + 1) + 0.25} - 0.5 \quad (14-56)$$

where  $A_n$  and  $A_1$  are the absorption factors on the bottom and top trays, respectively; and  $A_e$  is the effective absorption factor.  $A_e$  from Eq. (14-56) can be used in Eq. (14-55) to estimate the composition of the dry gas leaving the absorber. Estimation of  $A_e$  is more difficult because conditions on both the top and bottom trays of the absorber must be considered. If constant gas shrinkage per tray is assumed, and top and bottom tray temperatures are taken to be 10° to 25°F. higher than entering lean solvent and rich gas temperatures, respectively, estimates of component absorption and other column parameters will usually be reasonably accurate.

For convenience, plots relating the value of the right-hand side of Eq. (14-55) to the value of  $A$  are available (Natural Gas Processors Supplymen's Association, "Engineering Data Book," p. 151, 1966).

The analysis of a plate-type multicomponent absorber can be carried out plate-to-plate. When this is done, an equation similar to (14-57) is developed.

$$\frac{Y_{n+1} - Y_1}{Y_{n+1}} = \left( \frac{A_1 A_2 \cdots A_n + A_2 \cdots A_n + \cdots + A_n}{A_1 A_2 \cdots A_n + A_2 \cdots A_n + \cdots + A_{n+1}} \right) - \frac{L_0 X_0}{V_{n+1} Y_{n+1}} \left( \frac{A_2 A_3 \cdots A_n + A_3 \cdots A_n + \cdots + A_{n+1}}{A_1 A_2 \cdots A_n + A_2 \cdots A_n + \cdots + A_{n+1}} \right) \quad (14-57)$$

where  $X_0$  is the moles of one component in the specified liquid stream per mole of entering lean oil. Analysis of an absorber utilizing Eq. (14-57) is difficult and time consuming. Prediction of the absorption factor on each tray requires knowledge of temperature, vapor-rate, and liquid-rate profiles that are known only after the column has been analyzed. Use of equations similar to (14-57) then are trial and error. One or more profiles for the column must be assumed, with calculations used to check the validity of the assumption. Obviously, procedures such as this are more ideally suited for computer solution. Approaches very similar to those discussed in Sec. 13 on distillation are used, though sometimes special convergence techniques must be employed in order to achieve a closed and unique solution to the absorption calculations.

Edmister [A.I.Ch.E. J., 3, 165 (1957)] presented a variation of the absorption factor analysis. He defined  $\phi_A$  as the fraction of solute not recovered in the absorber,

$$\phi_A = \frac{1}{\Sigma_A + 1}$$

where

$$\Sigma_A = A_1 A_2 \cdots A_n + A_2 \cdots A_n + \cdots + A_n$$

$\psi_A$ , the fraction of a component in the lean solvent that is not lost with the off-gas, was defined as

$$\psi_A = 1 - \frac{\pi_A}{\Sigma_A + 1}$$

where

$$\pi_A = A_1 A_2 \cdots A_n$$

By using these two definitions the material balance equation for a simple absorber can be written as

$$\Sigma v_1 = \Sigma v_{n+1} \phi_A + \Sigma l_0 \psi_A$$

Charts are provided for evaluating  $\psi_A$  and  $\phi_A$  in terms of the average or effective absorption factor and the number of theoretical plates in the column. The real value of this kind of analysis is displayed when more complex towers, such as reboiled absorbers, are considered. Examples of the equations for several more complex column configurations are given in the original article.

All the absorption factor equations can be applied to stripping through use of the stripping factor

$$S = \frac{KV}{L} = \frac{1}{A}$$

The equations that result are:

$$\frac{X_{m+1} - X_1}{X_{m+1} - X_0} = \frac{S_{m+1} - S}{S_{m+1} - 1} \quad (14-58)$$

$$S_e = \sqrt{S_m(S_1 + 1) + 0.25} - 0.5 \quad (14-59)$$

$$\frac{X_{m+1} - X_1}{X_{m+1}} = \left( \frac{S_1 S_2 \cdots S_m + S_2 \cdots S_m + \cdots + S_m}{S_1 S_2 \cdots S_m + S_2 \cdots S_m + \cdots + S_{m+1}} \right) \times \frac{V_0 Y_0}{L_{m+1} X_{m+1}} \left( \frac{S_2 S_3 \cdots S_m + S_3 \cdots S_m + \cdots + S_{m+1}}{S_1 S_2 \cdots S_m + S_2 \cdots S_m + \cdots + S_{m+1}} \right) \quad (14-60)$$

In the case of a stripper, the bottom plate is number 1 and the top plate is  $m$ .

## ECONOMIC DESIGN

Perhaps the most important variables and parameters to be considered in design of the absorption system are those that are most difficult to describe accurately by mathematical expression. Choice of the type of equipment to be used, the internals of that equipment, the liquid-gas ratio, column diameter, and column height are generally chosen on the basis of experience, judgment, and intuition. All these variables can have significant impact on the economics of the absorption-stripping operation and so are worthy of serious considerations and discussion.

**Packed Towers.** There are many instances in which packed towers have significant advantages. These would include:

1. Vacuum operations. The pressure drop through a packed tower can frequently be designed for a lower level than for a plate tower and still obtain adequate vapor-liquid contact.
2. Foaming liquids can frequently be handled more satisfactorily in a packed tower.
3. Liquid holdup is generally less, so that heat-sensitive materials, together with those absorption processes that may have undesirable side reactions may be better handled.
4. Construction is usually simpler and cheaper when the absorption system is corrosive to normal materials of construction.
5. For small columns (less than about 2 ft. in diameter) packed towers will usually be cheaper than plate towers.

**Plate Towers.** Plate-type towers show strong advantages in many areas.

1. Cooling coils are readily installed on plates, making them more desirable when heat of solution requires internal cooling.
2. With proper design for length of liquid cross flow, plate towers can handle higher liquid rates.
3. For extremely low liquid rates (i.e. dehydration of natural gas using a glycol) plate towers have an advantage because they can be designed to hold a given amount of liquid on the tray.
4. Certain types of plate towers may be preferred when there are deposits of solid material that must be periodically removed. Cleaning of plate towers can be accomplished through manholes, whereas packed towers require dumping of the packing to facilitate cleaning.
5. The total weight of a plate tower is usually less than that of a packed tower designed for the same duty. The limited crushing

strength of many packing materials may make use of multiple packing support plates mandatory, to bear the weight of the tall column of packing.

6. Plate columns are generally preferred for operations that require a large number of transfer units or theoretical plates. Packed towers tend to be subject to channeling of vapor and liquid streams, and proper distribution is difficult to maintain without rather elaborate redistribution schemes.

**Liquid-Gas Ratio.**  $mG_M/L_M$  is the design factor of prime importance. It helps to determine the height of a transfer unit, the number of transfer units, and the column diameter. If the solute gas is dilute,  $mG_M/L_M$  is apt to be nearly constant throughout the column. Where the solute gas is not dilute, heat of solution may cause a temperature rise, resulting in a larger value of  $m$  at the bottom of the column than at the top. Where  $mG_M/L_M$  is not constant, choice of the liquid-gas ratio is difficult. Frequently, however, conditions at the dilute end are of most importance. In the case of nearly complete absorption, most of the transfer units will be required in the dilute region.

Choice of the operating magnitude of  $mG_M/L_M$  is based on economic factors. The greater  $mG_M/L_M$ , the closer the solvent circulation is to the minimum value, and the more concentrated the solute-rich solvent leaving the absorber will be. This results in more economical operation because of lessened pumping costs and lowered costs of stripping the solute from the solvent. High values of  $mG_M/L_M$  result in more expensive absorption towers and lessened solute recovery in the absorber. Equation (14-61) represents a balance of the costs of absorption and subsequent stripping to recover the solute. Assumptions in deriving this equation were: the distillation column (stripping of solute from solvent by distillation) produces essentially pure solute overhead; denuded (no solute) solvent is withdrawn from the distillation column for recirculation to the absorber.

$$\left(\frac{L_M}{m_2 G_M} - 1\right)^2 = \frac{BC_3 H_{OG}(K_D - 1)}{C_5 \theta r G_M m_2} \quad (14-61)$$

$$\text{where } B = \left[1 + n \left(\frac{L_M}{m_2 G_M} - 1\right)\right] \times 2.3 \log_{10} \left[ \left(\frac{y_1}{y_2}\right) \frac{(1 - m_2 G_M/L_M)^2}{1 - K_1 G_M/L_M} \right] - \frac{(1 - m_2 G_M/L_M) - 2(K_1/m_2 - 1)}{1 - K_1 G_M/L_M}$$

$K_D = y^*/x$ , of the feed to the stripping column at its boiling point

$m_2$  = slope of equilibrium curve  $y^*/x$  at the temperature of the inlet liquid to the absorption column

$C_3$  = annual cost of apparatus and power for the absorption column, \$/(cu. ft.)(yr.) =  $C_1[(G_{opt}/G) + 0.5(G/G_{opt})^2]$

$C_5$  = total cost of stripping operation, expressed as \$/lb.-mole of vapor supplied to the stripper; includes fixed charges, cost of cooling water, and cost of steam

$y_1/y_2$  = optimum ratio of solute mole fractions in gas stream flowing through absorber

$\theta$  = hr. operation/yr.

$G_M$  = molal gas velocity through absorber, lb.-moles/(hr.)(sq. ft.)

$r$  = (actual reflux ratio in distillation column) + (minimum reflux ratio, defined as ratio of reflux to product)

$n$  = exponent in the relation  $H_{OG} \sim (G/L)^n$

**Column Diameter.** Gas velocity and column diameter are so closely related that they may be thought of interchangeably. The gas velocity for a column is selected by considering first the safe operating velocity with respect to flooding, and then the optimum velocity calculated by an economic balance between column costs and tower cost. Data on flooding velocities for various packings are given in Sec. 18. Design is usually for approximately 60 per cent of flooding to allow for flow fluctuations and a margin of safety to avoid shutdown of the column. An expression for the optimum

gas velocity is

$$G_{opt} = 2680 \phi \frac{4}{3} \left( \frac{C_1}{C_2 \theta b} \right)^{1/3} \quad (14-62)$$

where  $C_1$  = annual cost of packing in the shell, \$/(yr.)(cu. ft.);  $\theta$  = hr./yr. operation;  $\rho$  = gas density;  $\phi = (\rho/0.075)^{1/2}$ ;  $C_2$  = cost of delivered energy, \$/kw.-hr.; and  $b$  = pressure drop, in H<sub>2</sub>O/ft. height at  $G/\phi = 1000$  lb./(hr.)(sq. ft.). Note that  $b$  may be an extrapolated value.

At the economic velocity, according to Eq. (14-62), the annual cost of energy per cubic foot turns out to be approximately one-half the annual cost of the packing and shell ( $C_1$ ), so that the total annual cost of column and energy in dollars per cubic foot becomes approximately equal to  $1.5C_1$ .

**Column Height.** Column height and solute concentration in the exit gas from the absorber are closely related and interdependent. The solute concentration in the exit gas may be determined by an economic balance between the cost of lost solute and the cost of additional column height,

$$(y_2 - mx_2)_{opt} = \frac{C_3 H_{OG}}{C_4 \theta G_M (1 - mG_M/L_M)} \quad (14-63)$$

for packed towers, where  $C_3$  = annual cost of apparatus and energy for pressure drop, \$/(yr.)(cu. ft.);  $C_4$  = value of solute at its concentration in the exit liquor, \$/lb.-mole of solute;  $\theta$  = hr./yr. operation.

A similar result for the plate columns is

$$(y_2 - mx_2)_{opt} = \frac{C_6}{C_4 \theta G_M E (2.3 \log L_M/mG_M)} \quad (14-64)$$

where  $C_6$  = annual cost of column and pressure drop, \$/(yr.)(plate)(sq. ft.); and  $E$  = over-all plate efficiency, fractional. Tiller [Trans. Am. Inst. Chem. Engrs., 40, 331 (1944)] gives an equivalent equation for the optimum number of plates in an absorber.

Optimum exit-liquor strength for a stripping column depends on a balance between the cost of lost solute in the exit liquor and the cost of additional tower height required for more stripping. Equations analogous to those for exit-gas strength in absorption are

$$\left(x_2 - \frac{y_2}{m}\right)_{opt} = \frac{C_3 H_{OL}}{C_4 L_M \theta (1 - L_M/mG_M)} \quad (14-65)$$

for a packed column, and

$$\left(x_2 - \frac{y_2}{m}\right)_{opt} = \frac{C_6}{C_4 L_M \theta E \ln (mG_M/L_M)} \quad (14-66)$$

for a plate column. In these equations,  $C_3$  = annual cost of apparatus (amortization and depreciation of column and packing) and power, \$/(yr.);  $C_6$  = annual cost of apparatus and power, \$/(yr.)(plate)(sq. ft. of cross section);  $C_4$  = value of solute at concentration of exit gas, \$/lb.-mole of pure solute;  $E$  = over-all plate efficiency, fractional;  $H_{OL}$  = over-all H.T.U. based on liquid-phase driving force, ft;  $\theta$  = hr./yr. operation;  $L_M$  and  $G_M$  = molar velocities, lb.-moles/(hr.)(sq. ft.); and  $m$  = slope of equilibrium curve  $y^*/x$  at dilute end of stripper.

**Column Pressure.** The higher the column pressure, the greater the solubility of the solute in the solvent. In cases where gases must be compressed in order to achieve higher pressure, this is seldom economical. Frequently absorption pressure will be set by requirements of other processing steps and thus involve considerable detail in calculations at different absorber pressure levels. As a general rule, the absorber should be operated at the highest possible pressure consistent with other process requirements.

**Lean Solvent Temperature to Absorber.** In continuous operation of an absorber-stripper combination, the lean solvent must be cooled after leaving the bottom of the stripper. Frequently the solvent will be cooled further before entering the absorber or by intercoolers located at intermediate points in the absorber. Cooling the solvent increases the solubility of the solute and decreases the required liquid rate. The economic balance is between savings in stripper costs and lower liquid flows, and cost of additional heat-exchange

equipment and cooling media. Cooling of the solvent substantially below the solute-rich gas temperature is seldom justified.

**Multicomponent Systems.** The simplified equations (14-62) to (14-66) provide only rough guides to optimum design conditions for multicomponent systems. In such cases, detailed computations must be made for alternate designs and alternate operating parameters. Optimum gas velocity will be closely approximated by Eq. (14-62). In general, cooling of solute-rich gas and solvent can be justified to the range of 0°F. or lower for large, high-pressure natural-gas-absorption systems.

**Non-isothermal Absorption.** Computation of tower dimensions and required flows is straightforward when heat effects can be neglected, as indicated above. However, when temperature of the liquid stream varies from point to point in the absorber, owing to heat of solution of the solutes, heat of vaporization of the solvent, or to sensible heat exchange between gas and liquid phases, the problem is more difficult. Computations have to be made differentially from point to point through the absorber if they are to be precise, because solubility of the solute depends on the temperature, and the driving force cannot be found until the temperature profile is known. If the temperature changes are not large, however, approximate procedures may suffice.

**Large Heat Effects.** When the solute has a large heat of solution, or when feed gases containing high percentages of solute are treated, the effects of heat release during absorption may be pronounced. In such cases, heat-transfer surface may be supplied through cooling coils on the plates to remove the heat of absorption. In other cases, the partially saturated solvent will be withdrawn from a point intermediate in the tower and passed through an external heat exchanger for cooling. Provision of adequate heat-removal facilities may be as important in obtaining successful absorber operations as is provision for the absorption process itself.

Absorbers involving large heat effects are frequently operated adiabatically. Treybal [*Ind. Eng. Chem.*, **61**, 36 (1969)] presents a calculational procedure for designing adiabatic packed-tower gas absorbers and strippers. His procedure involves trial-and-error calculation of mass transfer and related heat release across the absorber in stepwise fashion. An example problem is solved in detail.

Mostafa (*op. cit.*) treats the graphical determination of number of transfer units when absorption heat release is considered. His procedure is also trial and error.

**Mild Heat Effects.** The principal object of considering heat effects is to fix the equilibrium line, which depends on liquid temperatures. Mild effects can be allowed for on the basis of estimated liquid temperatures at the top and bottom of the absorber. The former is fixed by external considerations (available cooling capacity applied to the liquid-feed circuit, for example), and the latter can be estimated from an energy balance around the whole absorber. These temperatures fix the gas solubilities at the ends of the absorber. Thus they determine the slope of the equilibrium curve at the inlet-liquid composition and a point on the curve at the proposed exit-liquid composition. If an approximate equilibrium line can be drawn through the end points without very much curvature, it may reasonably be assumed that driving forces are correct.

**Example 2.** Consider the absorption of acetone from air at atmospheric pressure in pure water fed to a packed absorber at 25°C. Inlet gas at 35°C. contains 2 per cent by volume acetone and is 70 per cent saturated with water vapor (4 per cent H<sub>2</sub>O by volume). Mole fraction acetone in the exit gas is to be reduced to  $\frac{1}{400}$  the inlet value. Per 100 lb.-moles of feed-gas mixture, how many pound-moles of fresh water should be fed to provide a positive driving force throughout the packing? How many transfer units will be needed?

Differential heat of solution of acetone vapor in pure water = 2500 p.c.u./lb.-mole acetone, where p.c.u. = pound-Centigrade unit = 1.8 B.t.u. Latent heats at 25°C. are 7220 p.c.u./lb.-mole for acetone and 10,490 for water. Specific heat of air = 7.0 p.c.u./lb.-mole(°C.). Solubilities are given as a function of temperature by the following table:

| $t$ , °C.                                      | 25   | 30   | 35   | 40   |
|------------------------------------------------|------|------|------|------|
| $\gamma_1$ , activity coefficient for acetone  | 6.7  | 7.1  | 7.5  | 7.8  |
| $P_1$ , vapor pressure of pure acetone, mm. Hg | 229  | 283  | 346  | 421  |
| $m = \frac{y^*}{x} = \gamma_1 \frac{P_1}{P}$   | 2.02 | 2.64 | 3.41 | 4.33 |

**Solution.** Relative to dry gas and liquid water at 25°C., the following enthalpies are computed for the inlet- and exit-gas streams (basis = 100 lb.-moles gas entering).

Entering gas:

$$\text{Acetone, } 2(2500 + 7200) = 19,400 \text{ p.c.u.}$$

$$\text{Water vapor, } 4(10,490) = 41,960$$

$$\text{Sensible heat, } (100)(7.0)(35 - 25) = 7,000$$

$$68,360 \text{ p.c.u.}$$

Exit gas (assumed saturated with water at 25°C.):

$$\text{Acetone, } \left(\frac{2}{400}\right)\left(\frac{94}{100}\right)(2500) = 12 \text{ p.c.u.}$$

$$\text{Water vapor, } 94 \left(\frac{23.7}{760 - 23.7}\right)(10,490) = 31,600$$

$$31,612 \text{ p.c.u.}$$

$$\text{Enthalpy change of liquid} = 68,360 - 31,612 = 36,748 \text{ p.c.u.}$$

$$\Delta = \text{temperature rise of liquid} = \frac{36,748}{18L_M}$$

$$L_M = \frac{36,748}{18 \Delta}$$

| $\Delta$ , °C. | $\Delta_1$ , °C. | $L_M$ | $m_1 = y_1^*/x_1$ | $m_1 G_M/L_M$ | $m_2 G_M/L_M$ |
|----------------|------------------|-------|-------------------|---------------|---------------|
| 0              | 25               | ...   | 2.02              | 0             | 0             |
| 2              | 27               | 1022  | 2.26              | 0.221         | 0.198         |
| 3              | 28               | 681   | 2.39              | 0.351         | 0.297         |
| 4              | 29               | 511   | 2.51              | 0.492         | 0.398         |
| 5              | 30               | 409   | 2.64              | 0.645         | 0.494         |
| 6              | 31               | 341   | 2.78              | 0.815         | 0.592         |
| 7              | 32               | 292   | 2.93              | 1.002         | 0.692         |

Evidently,  $\Delta = 6^\circ\text{C.}$  will give an operable absorber, i.e., one having a positive driving force from gas to liquid at all points.  $\Delta = 7^\circ\text{C.}$  is a barely inoperable condition because the equilibrium line touches the operating line. Figure 14-14 shows operating and equilibrium lines for  $L_M = 341$  lb.-mole,

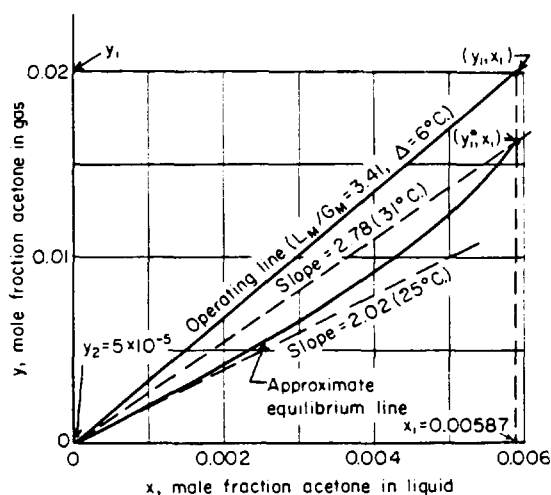


Fig. 14-14. Operating and equilibrium lines in adiabatic acetone absorber, Example 2.

## 14-16 GAS ABSORPTION

the latter being drawn with a French curve so that it has the right slope at the origin and passes through a point corresponding to  $x_1 = 0.02, 100/341 = 0.00587$  mole fraction and  $y_1 = 0.0163$ .

The number of transfer units can be computed from the integral formula, but a quicker method is to use a formula derived by Colburn [*Trans. Am. Inst. Chem. Engrs.*, 35, 211 (1939)] on the assumption that the equilibrium line is a parabolic arc having a slope  $m_2$  at the bottom end and passing through the point  $(x_1, m_1 x_1)$  at the upper end:

$$N_{OG} = \frac{1}{1 - m_2 G_M/L_M} \times \ln \left[ \frac{(1 - m_2 G_M/L_M)^2 y_1 - m_2 x_2}{1 - (m_1 G_M/L_M) y_2 - m_2 x_2} + \frac{m_2 G_M}{L_M} \right] \quad (14.67)$$

In the present instance

$$N_{OG} = \frac{1}{1 - 9.592} \ln \left[ \frac{(1 - 0.592)^2}{1 - 0.815} (400) + 0.592 \right] = 14.4$$

Note that Eq. (14.67) allows for curvature of the equilibrium line in the middle range of  $x$ . Erroneous use of the logarithmic mean of the terminal values of  $y - y^*$ , equal to 0.000543 mole fraction units, gives  $N_{OG} = (y_1 - y_2)/\Delta y_{lm} = 23.8$  and leads to an overestimate of the packed height needed.

**Absorption Accompanied by Chemical Reaction.** There are many systems of industrial importance in which the solute reacts either reversibly or irreversibly with the material used as solvent. Most of these cases involve phenomena that can affect the rate of absorption of solute. Analytical treatment of these cases is not well understood, and for this reason design must be undertaken with particular caution. (See Sec. 18.)

If the reaction occurs in the liquid phase and is rapid and irreversible, the rate of absorption may be controlled primarily by the gas-phase resistance to mass transfer. In these cases the mass-transfer rate may be estimated by the methods outlined above for obtaining  $H_G$ . Absorption of ammonia into acid solution of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  into strong alkali illustrate this situation, so long as there is a stoichiometric excess of the reacting solvent. For the irreversible reaction, calculation of the tower height is also relatively simple because the back pressure of the gas over the solvent is zero. In cases where there is slight reversibility of reaction and therefore a small gas back pressure, the absorption may be gas-phase-controlled. In these cases the  $H_G$  for physical absorption would control the rate of absorption.

Frequently the reaction rate is slow enough that liquid-phase resistance must be considered. Generalized prediction methods for  $H_L$  are unsuitable for application when chemical reaction occurs in the liquid phase. In these cases operating data for the particular system in question must be utilized. Where liquid-phase resistance is important, extreme care must be taken in utilizing experimental data. Extrapolation to different concentration ranges must be made with care and caution. The mass-transfer coefficient may be affected by a reaction which changes concentration gradients near the interface. In many instances there may be competing or parallel reactions of varying rates and equilibrium concentrations. These variables may mask the influences of mass transfer to such an extent that even modest deviations from experimental conditions can lead to serious error.

MANTECH ENVIRONMENTAL RESEARCH SERVICES CORPORATION  
ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY

STANDARD OPERATING PROCEDURE CLEARANCE FORM

Number:

RSKSDP-175

Title:

Sample Preparation and Calculations for Dissolved  
Gas Analysis in Water Samples Using a GC Headspace  
Equilibration Technique

Author(s):

Bryan Newell

<sup>2/15</sup> -  
Kamphill wants us to  
do paper on Cthx in H<sub>2</sub>O

Author's Signature

*B. Newell*

Cthx solubility in water?

20°C.

0.03308 ml/ml water

0.002319 g/100g water

→ 2.32 mg/.1L = 23.2 mg/L

Date 12/31/94

ManTech Analytical  
Section Supervisory

*John*

Date 12/21/94

ManTech QA Coordinator

Powell

*John* <sup>in stock + 500</sup>  
25 → 24.1 mg/L

Date 12/27/94

ManTech Program Manager

Seely

*James Seely*

Date 12/22/94

EPA Technical Monitor

John Wilson

*John Wilson*

Date 1-25-94

EPA Project Officer

Cosby

*Roger L. Cosby*

Date 1-25-95

QA Project Leader

Date

EPA Quality Assurance Officer

D. Bertino

*D. Bertino*

Date 4/4/95

## STANDARD OPERATING PROCEDURE

### GAS CHROMATOGRAPHIC ANALYSIS OF GASEOUS SAMPLES FOR PART-PER-MILLION LEVELS OF NITROUS OXIDE, METHANE, ETHYLENE, AND ETHANE

#### Disclaimer:

This standard operating procedure has been prepared for the use of the Robert S. Kerr Environmental Research Laboratory of the U.S. Environmental Protection Agency and may not be specifically applicable to the activities of other organizations.

#### 1. Purpose: (Scope and Application)

This method is applicable to the analysis of gaseous samples for the quantitation of low part-per-million levels of nitrous oxide (0.3-1000ppm), methane (10ppm-40,000ppm), ethylene (10ppm-10,000ppm), and ethane (10ppm-10,000ppm). The number of analyses that can be performed on one eight hour day is approximately 32.

This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of chromatograms.

#### 2. Summary of Method :

A gas sample is injected onto a gas chromatographic column upon which its hydrocarbon components are separated and detected by a flame ionization detector. One minute after this injection, another sample is taken and injected onto a separate gas chromatographic column where nitrous oxide is separated and detected by an electron capture detector.

3. **References** :

- 3.1 Hewlett Packard 5890 Series II Gas Chromatograph Operator's Manual.
- 3.2 Hewlett Packard 3396 A Integrator Operator's Manual.
- 3.3 Hewlett Packard 3396 Series II Integrator Operator's Manual.
- 3.4 Vandegrift, S., RSKSOP-92, Rev. No. 1, Jan. 1991.
- 3.5 Vandegrift, S., RSKSOP-119, Rev. No. 0, Apr. 1991.

4. **Procedure**:

4.1 **Gas Chromatographic Conditions**

Hewlett Packard 5890 Series II w/ FID and ECD

Oven Temperature Program:

|                      |             |
|----------------------|-------------|
| Initial Temperature: | 55°C        |
| Initial Time:        | 1 minute    |
| Rate:                | 20°C/minute |
| Final Temperature:   | 140°C       |
| Final Time:          | 5 minutes   |

Other Temperatures:

|                  |       |
|------------------|-------|
| Injector (FID):  | 200°C |
| Detector (FID):  | 250°C |
| FID range:       | 0     |
| FID attenuation: | 0     |
| Injector (ECD):  | 120°C |



Detector (ECD): 275°C  
ECD range: 3  
ECD attenuation: 0

Column Type: Both columns are Porapak Q, 80/100,  
6' X 1/8" stainless steel, (Supelco).

Carrier Gas (FID): High Purity Helium at 20 ml/min @ 55°C

Hydrogen: 40 ml/min

Air: 400 ml/min

Column Head Pressure: 14 psi

Carrier Gas (ECD): High Purity 95% Argon, 5% Methane at  
27ml/min @ 40°C

w/ anode purge on: 39 ml/min

Column Head Pressure: 20 psi

Integrator (FID): Hewlett Packard 3396 Series II

Attenuation: 1

Threshold: 1

Chart Speed: 1.0 cm/min

Integrator (ECD): Hewlett Packard 3396A

Attenuation: 4

Threshold: 3

Chart Speed: 0.5 cm/min.

The HP 3396 Series II integrator is on the INET, and the HP 3396A integrator is interfaced to the GC using a signal cable on the SIG 2 output of the GC and a remote cable.

#### 4.2 Gas Chromatograph Preparation

At the beginning of each day, replace the septa in each of the GC injectors.

**-CAUTION: BURN HAZARD!** Be sure to reduce the injector temperatures below 100 degrees C prior to touching the injector nut.

The septum which seems to work best for this application is the Hewlett Packard "red" septum (part no. 5181-1263).

The FID flame is ignited as follows: open the valves on the air and hydrogen cylinders. Open their respective valves for the FID on the GC (labeled detector A). Depress the FID Ignitor button on the GC. There should be a "pop" sound to indicate lighting of the hydrogen flame. Next turn the detector on by depressing the following key sequence: DET A ON. The FID should be ready for analysis in a few minutes.

To prepare the electron capture detector for analysis use the following procedure. Open the ECD Anode Purge valve on detector B. To turn the detector on, use the following key sequence: DET B ON. The ECD should be ready for analysis in a few minutes. The GC oven is kept at 120°C when the instrument is not in use.

#### 4.3 Standards

Scotty standards are available "off the shelf" from Scott Specialty Gases for methane, ethylene, ethane, and nitrous oxide. Their availability is as follows: for methane 10ppm, 100ppm, 1000ppm, 1%, and 4%; for ethylene 10ppm, 100ppm, 1000ppm, and 1%; for ethane 10ppm, 100ppm, 1000ppm, and 1%; and for nitrous oxide 10, 100, and 1000ppm.

A 0.33 ppm nitrous oxide standard can be prepared as follows: immerse a 60 ml serum bottle in a water bath, filling the bottle with water. Displace the water with high purity helium and seal with a gray butyl rubber stopper and aluminum crimp cap. Inject 200ul of the 100 ppm nitrous oxide standard into the bottle. This standard can be used repeatedly, but should be prepared on a daily basis.

#### 4.4 Analysis

A 500 ul gas-tight syringe (Precision Sampling Corporation) is used to withdraw samples and make injections into the GC. Sample volumes of 300 ul are analyzed. Samples are withdrawn without flushing the syringe.

Standards are sampled by "bubbling" the cylinders contents through water via tubing. A septum within a fitting in the tubing can be pierced to retrieve a sample of the standard. A cylinder of high purity helium is available in Lab # 208 to obtain samples for blank runs. The regulator and tubing should be purged for 15 minutes prior to analyzing a sample of the helium. The helium is also sampled by piercing a septa within a fitting in the tubing.

**NOTE:** Methane contamination can be a problem for this analysis; therefore, the syringe should be solvent rinsed after each injection with acetone. Make sure there is no residual solvent left in the syringe.

Retention times for each gas under the conditions listed are as follows: methane 0.6 minutes, ethylene 1.8 minutes, ethane 2.3 minutes, and nitrous oxide 2.2 minutes. (See attached chromatograms.)

#### 4.5 Calibration/Quantitation

For each of the gases a calibration curve is generated on a weekly basis using the standards for each gas. The curve is generated by using linear regression on a calculator or computer. For methane the area count from the blank helium response is entered as the zero concentration. The area counts

for the unknowns can then be used to determine their concentrations. If the unknown's area count is outside of the range of the curve, the accuracy of the calculated concentration is not reliable. If the sample's area count is greater than the highest standard, and more sample is available, another injection using a smaller volume, e.g. 50-100 ul, may be used. The dilution factor, i.e. 300/ ul injected, must be used to correct for the smaller injection.

5. **QUALITY CONTROL:**

Calibration is checked each day prior to analyzing samples, by plotting standard area counts on control charts. For the FID; analyze high purity helium, 100 ppm methane, 100 ppm ethylene, and 100 ppm ethane. For the ECD, analyze high purity helium and 10 ppm nitrous oxide standard prior to analysis of samples. In addition, no fewer than one standard per every tenth sample analyzed should be analyzed.

When reporting results, any extenuating circumstances should be noted.

Control charts of the 100 ppm methane, ethylene, and ethane and of the 10 ppm nitrous oxide standards area counts are kept to monitor variability. If any analysis of these standards falls outside of the control limits, it should be determined why this has occurred, and corrective action should be taken. Some of the things that could be checked are the integrity of the GC septa, plunger "tightness" in the syringe barrel (it should be tight to provide a good seal), column fittings, carrier gas flow rate, air and hydrogen flow rates for the FID, and volume of gas in the standard container (at low pressures the area counts may vary considerably). This is not meant to be a comprehensive list as the analyst or supervisor should have

experience in troubleshooting gas chromatographs, as mentioned under "Purpose." A note should be made on the control chart itself as to the problem and action taken.

The 100 ppm methane standard was analyzed over a four week period on thirteen different occasions (n=13). This resulted in the following statistics:

mean = 60270  
s = 859  
= 1.43 ppm  
CV = 1.43 %

The 100 ppm ethylene standard was analyzed over a four week period on six different occasions (n=6). This resulted in the following statistics:

mean = 106873  
s = 1526  
= 1.43 ppm  
CV = 1.43 %

The 100 ppm ethane standard was analyzed over a four week period on six different occasions (n=6). This resulted in the following statistics:

mean = 108020  
s = 4067  
= 3.77 ppm  
CV = 3.77 %

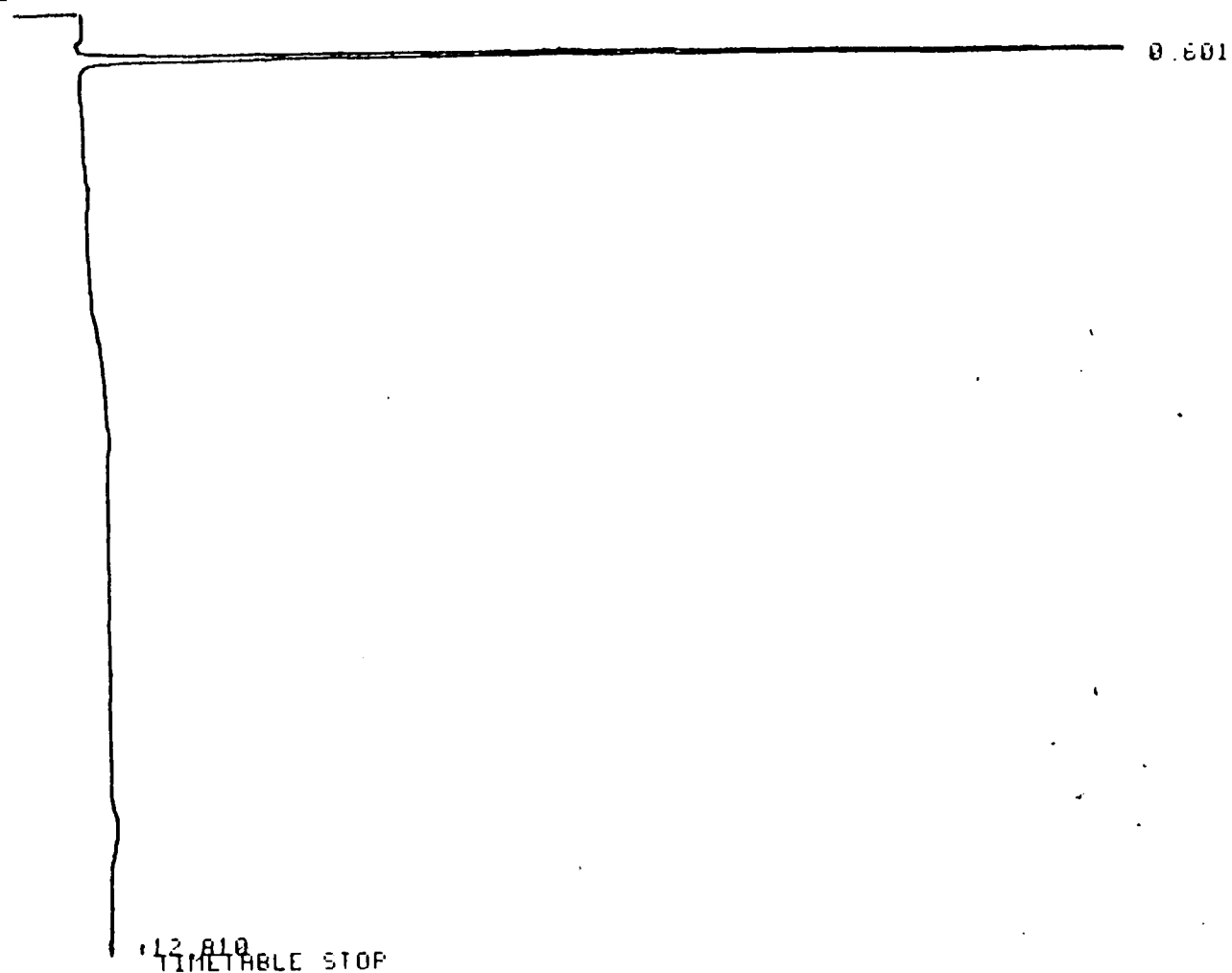
The 10 ppm nitrous oxide standard was analyzed over a four week period on five different occasions (n=5). This resulted in the following statistics:

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mean = 172446  
s = 1568  
= 0.09 ppm  
CV = 0.91 %

**PRECAUTIONS:** Other than as noted, no special precautions are necessary aside from those used in good laboratory practice.

\* RUN # 14 NOV 5, 1992 12:55:03  
START



RUN# 14 NOV 5, 1992 12:55:03

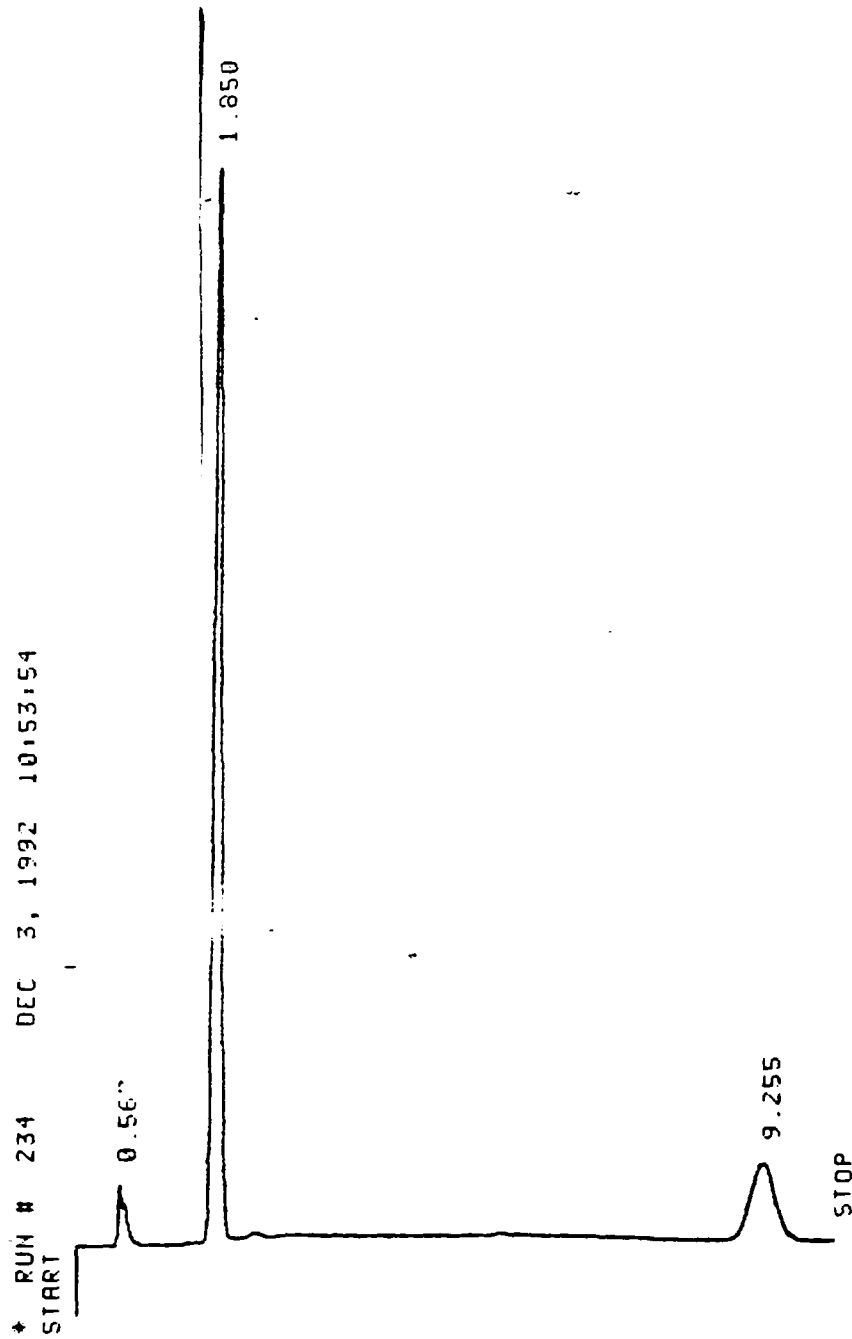
| AREA% | RT   | AREA  | TYPE | WIDTH | AREA%     |
|-------|------|-------|------|-------|-----------|
|       | .601 | 61593 | PB   | .043  | 100.00000 |

TOTAL AREA= 61593  
MUL FACTOR=1.0000E+00

Example Chromatogram of 100 ppm Methane

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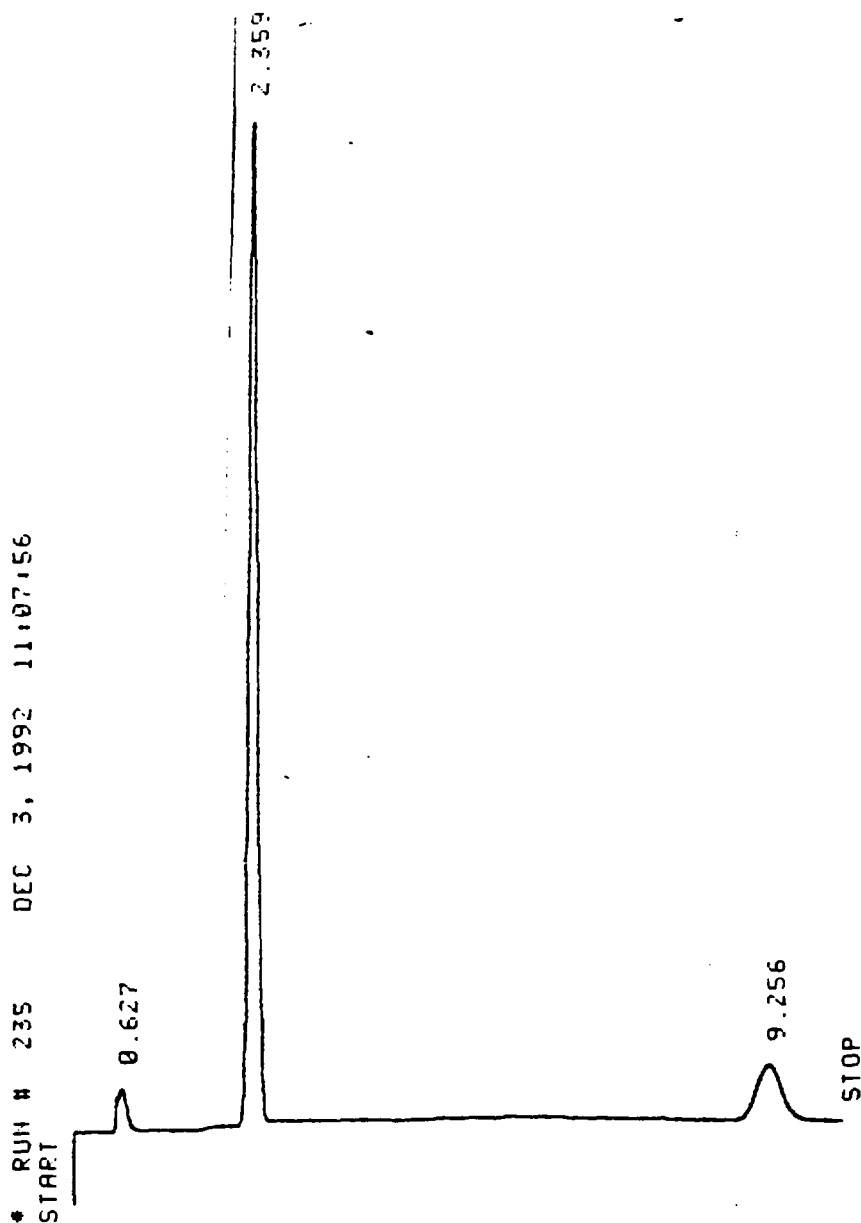
Example Chromatogram of 100 ppm Ethylene



|             |       |             |          |       |          |
|-------------|-------|-------------|----------|-------|----------|
| RUN#        | 234   | DEC 3, 1992 | 10:53:54 |       |          |
| AREA%       | RT    | AREA        | TYPE     | WIDTH | AREA%    |
|             | .567  | 2969        | BU       | .055  | 2.1359   |
|             | 1.850 | 109055      | FB       | .113  | 78.45741 |
|             | 9.255 | 26975       | BP       | .391  | 19.40662 |
| TOTAL AREA= |       |             |          |       | 138999   |



Example Chromatogram of 100 ppm Ethane



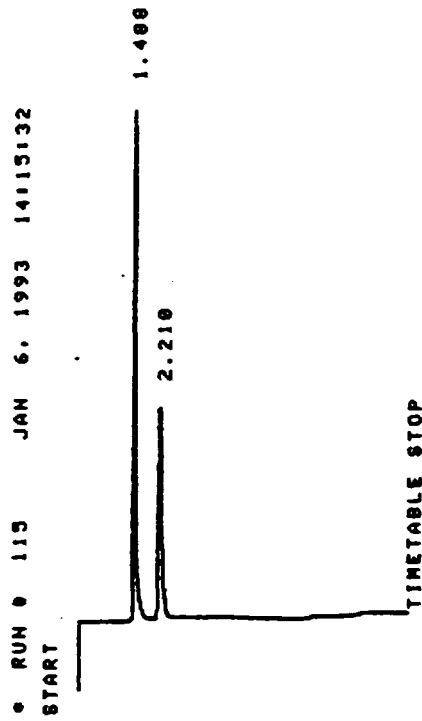
RUN# 235 DEC 3, 1992 11:07:56

| AREA# | RT    | AREA   | TYPE | WIDTH | AREA%    |
|-------|-------|--------|------|-------|----------|
|       | .627  | 5563   | PU   | .144  | 4.10787  |
|       | 2.359 | 110304 | UB   | .125  | 81.45146 |
|       | 9.256 | 19556  | PP   | .393  | 14.44068 |

TOTAL AREA= 135423

NUC FACTOR=1.0000E+00

Example Chromatogram of 10 ppm Nitrous Oxide



RUN 115 JAN 6, 1993 14:15:32

| AREA  | RT     | AREA | TYPE | WIDTH    | AREA |
|-------|--------|------|------|----------|------|
| 1.488 | 229462 | PB   | .063 | 57.38558 |      |
| 2.210 | 170390 | PB   | .112 | 42.61442 |      |

TOTAL AREA= 399860  
 MUL FACTOR=1.0000E+00

**METHOD 300.0**

**DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY**

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## METHOD 300.0

### DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

#### 1.0 SCOPE AND APPLICATION

- 1.1 This method covers the determination of the following inorganic anions:

##### PART A.

|          |                   |
|----------|-------------------|
| Bromide  | Nitrite           |
| Chloride | Ortho-Phosphate-P |
| Fluoride | Sulfate           |
| Nitrate  |                   |

##### PART B.

|          |          |
|----------|----------|
| Bromate  | Chlorite |
| Chlorate |          |

- 1.2 The matrices applicable to each method are shown below:

1.2.1 Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 11.7), leachates (when no acetic acid is used).

1.2.2 Drinking water and reagent waters

- 1.3 The single laboratory Method Detection Limit (MDL defined in Section 3.2) for the above analytes is listed in Tables 1A and 1B. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

- 1.4 Method A is recommended for drinking and wastewaters. The multilaboratory ranges tested for each anion are as follows:

| <u>Analyte</u>    | <u>mg/L</u> |
|-------------------|-------------|
| Bromide           | 0.63 - 21.0 |
| Chloride          | 0.78 - 26.0 |
| Fluoride          | 0.26 - 8.49 |
| Nitrate-N         | 0.42 - 14.0 |
| Nitrite-N         | 0.36 - 12.0 |
| Ortho-Phosphate-P | 0.69 - 23.1 |
| Sulfate           | 2.85 - 95.0 |

- 1.5 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

- 1.6 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest. The fortification procedure is described in Section 11.6.
- 1.7 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedures described in Section 9.0.

## **2.0 SUMMARY OF METHOD**

- 2.1 A small volume of sample, typically 2-3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.
- 2.2 The main differences between Parts A and B are the separator columns and guard columns. Sections 6.0 and 7.0 will elicit the differences.
- 2.3 An extraction procedure must be performed to use this method for solids (See Section 11.7).
- 2.4 Limited performance-based method modifications may be acceptable provided they are fully documented and meet or exceed requirements expressed in Section 9.0, Quality Control.

## **3.0 DEFINITIONS**

- 3.1 **Calibration Blank (CB)** -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.
- 3.2 **Calibration Standard (CAL)** -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.3 **Field Duplicates (FD)** -- Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
- 3.4 **Instrument Performance Check Solution (IPC)** -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

- 3.5 **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.
- 3.6 **Laboratory Fortified Sample Matrix (LFM)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.
- 3.7 **Laboratory Reagent Blank (LRB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 3.8 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.
- 3.9 **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.
- 3.10 **Method Detection Limit (MDL)** -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.
- 3.11 **Performance Evaluation Sample (PE)** -- A solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), U. S. Environmental Protection Agency, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.
- 3.12 **Quality Control Sample (QCS)** -- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

- 3.13 **Stock Standard Solution (SSS)** -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

#### **4.0 INTERFERENCES**

- 4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.
- 4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to 100 mL of each standard and sample.
- 4.3 Method Interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.
- 4.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.
- 4.5 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.
- 4.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.
- 4.7 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.
- 4.8 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample purge the sample with an inert gas (argon or nitrogen) for about five minutes or until no chlorine dioxide remains.

#### **5.0 SAFETY**

- 5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.
- 5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.
- 5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

- 5.3.1 Sulfuric acid (Section 7.4)

## **6.0 EQUIPMENT AND SUPPLIES**

- 6.1 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.
- 6.2 Ion chromatograph -- Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.
  - 6.2.1 Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with a substrate the same as that in the separator column.
  - 6.2.2 Anion separator column: This column produces the separation shown in Figures 1 and 2.
    - 6.2.2.1 Anion analytical column (Method A): The separation shown in Figure 1 was generated using a Dionex AS4A column (P/N 37041). An optional column may be used if comparable resolution of peaks is obtained, and the requirements of Section 9.2 can be met.
    - 6.2.2.2 Anion analytical column (Method B): The separation shown in Figure 2 was generated using a Dionex AS9 column (P/N 42025). An optional column may be used if comparable resolution of peaks is obtained and the requirements of Section 9.2 can be met.
  - 6.2.3 Anion suppressor device: The data presented in this method were generated using a Dionex anion micro membrane suppressor (P/N 37106).
  - 6.2.4 Detector -- Conductivity cell: Approximately 1.25  $\mu$ L internal volume, (Dionex, or equivalent) capable of providing data as required in Section 9.2.



- 6.3 The Dionex AI-450 Data Chromatography Software was used to generate all the data in the attached tables. Systems using a stripchart recorder and integrator or other computer based data system may achieve approximately the same MDL's but the user should demonstrate this by the procedure outlined in Section 9.2.

## 7.0 REAGENTS AND STANDARDS

- 7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.
- 7.2 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.
- 7.3 Eluent solution (Method A and Method B): Sodium bicarbonate (CASRN 144-55-8) 1.7 mM, sodium carbonate (CASRN 497-19-8) 1.8 mM. Dissolve 0.2856 g sodium bicarbonate ( $\text{NaHCO}_3$ ) and 0.3816 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in reagent water (Section 7.2) and dilute to 2 L.
- 7.4 Regeneration solution (micro membrane suppressor): Sulfuric acid (CASRN-7664-93-9) 0.025N. Dilute 2.8 mL conc. sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to 4 L with reagent water.
- 7.5 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 minutes) as listed below.
- 7.5.1 Bromide ( $\text{Br}^-$ ) 1000 mg/L: Dissolve 1.2876 g sodium bromide ( $\text{NaBr}$ , CASRN 7647-15-6) in reagent water and dilute to 1 L.
- 7.5.2 Bromate ( $\text{BrO}_3^-$ ) 1000 mg/L: Dissolve 1.1798g of sodium bromate ( $\text{NaBrO}_3$ , CASRN 7789-38-0) in reagent water and dilute to 1 L.
- 7.5.3 Chlorate ( $\text{ClO}_3^-$ ) 1000 mg/L: Dissolve 1.2753g of sodium chlorate ( $\text{NaClO}_3$ , CASRN 7775-09-9) in reagent water and dilute to 1 L.
- 7.5.4 Chloride ( $\text{Cl}^-$ ) 1000 mg/L: Dissolve 1.6485 g sodium chloride ( $\text{NaCl}$ , CASRN 7647-14-5) in reagent water and dilute to 1 L.
- 7.5.5 Chlorite ( $\text{ClO}_2^-$ ) 1000 mg/L: Dissolve 1.3410g of sodium chlorite ( $\text{NaClO}_2$ , CASRN 7758-19-2) in reagent water and dilute to 1 L.
- 7.5.6 Fluoride ( $\text{F}^-$ ) 1000 mg/L: Dissolve 2.2100g sodium fluoride ( $\text{NaF}$ , CASRN 7681-49-4) in reagent water and dilute to 1 L.
- 7.5.7 Nitrate ( $\text{NO}_3^-$ -N) 1000 mg/L: Dissolve 6.0679 g sodium nitrate ( $\text{NaNO}_3$ , CASRN 7631-99-4) in reagent water and dilute to 1 L.
- 7.5.8 Nitrite ( $\text{NO}_2^-$ -N) 1000 mg/L: Dissolve 4.9257 g sodium nitrite ( $\text{NaNO}_2$ , CASRN 7632-00-0) in reagent water and dilute to 1 L.

7.5.9 Phosphate ( $\text{PO}_4^{3-}\text{-P}$ ) 1000 mg/L: Dissolve 4.3937 g potassium phosphate ( $\text{KH}_2\text{PO}_4$ , CASRN 7778-77-0) in reagent water and dilute to 1 L.

7.5.10 Sulfate ( $\text{SO}_4^{2-}$ ) 1000 mg/L: Dissolve 1.8141 g potassium sulfate ( $\text{K}_2\text{SO}_4$ , CASRN 7778-80-5) in reagent water and dilute to 1 L.

**Note:** Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4°C. Except for the chlorite standard which is only stable for two weeks. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

7.6 Ethylenediamine preservation solution: Dilute 10 mL of ethylenediamine (99%) (CASRN 107-15-3) to 200 mL with reagent water. Use 1 mL of this dilution to each 1 L of sample taken.

## 8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2 Sample preservation and holding times for the anions that can be determined by this method are as follows:

| <u>Analyte</u>                | <u>Preservation</u>                         | <u>Holding Time</u> |
|-------------------------------|---------------------------------------------|---------------------|
| Bromate                       | None required                               | 28 days             |
| Bromide                       | None required                               | 28 days             |
| Chlorate                      | None required                               | 28 days             |
| Chloride                      | None required                               | 28 days             |
| Chlorite                      | Cool to 4°C                                 | immediately         |
| Fluoride                      | None required                               | 28 days             |
| Nitrate-N                     | Cool to 4°C                                 | 48 hours            |
| Combined<br>(Nitrate/Nitrite) | conc. $\text{H}_2\text{SO}_4$<br>to a pH <2 | 28 days             |
| Nitrite-N                     | Cool to 4°C                                 | 48 hours            |
| Orthophosphate-P              | Cool to 4°C                                 | 48 hours            |
| Sulfate                       | Cool to 4°C                                 | 28 days             |

**Note:** If the determined value for the combined nitrate/nitrite exceeds 0.5 mg/L as N, a resample must be analyzed for the individual concentrations of nitrate and nitrite.

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples

be cooled to 4°C and held for no longer than 28 days for Method A and analyzed immediately in Method B.

**Note:** If the sample cannot be analyzed for chlorite within ≤10 minutes, the sample may be preserved by adding 1 mL of the ethylenediamine (EDA) preservation solution (Section 7.6) to 1 L of sample. This will preserve the concentration of the chlorite for up to 14 days. This addition of EDA has no effect on bromate or chlorate, so they can also be determined in a sample preserved with EDA. Residual chlorine dioxide should be removed from the sample (per Section 4.8) prior to the addition of EDA.

## **9.0 QUALITY CONTROL**

**9.1** Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

### **9.2 INITIAL DEMONSTRATION OF PERFORMANCE**

**9.2.1** The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

**9.2.2** Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

**9.2.3** Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

**9.2.4** Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two

to three times the estimated instrument detection limit.<sup>(6)</sup> To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$\text{MDL} = (t) \times (S)$$

where,  $t$  = Student's  $t$  value for a 99% confidence level and a standard deviation estimate with  $n-1$  degrees of freedom [ $t= 3.14$  for seven replicates]

$S$  = standard deviation of the replicate analyses

MDLs should be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response.

### 9.3 ASSESSING LABORATORY PERFORMANCE

- 9.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.
- 9.3.2 Laboratory Fortified Blank (LFB) -- The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery (Section 9.4.2). If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.
- 9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 90-110%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery ( $\bar{x}$ ) and the standard deviation ( $S$ ) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{x} + 3S$$

$$\text{LOWER CONTROL LIMIT} = \bar{x} - 3S$$

The optional control limits must be equal to or better than the required control limits of 90-110%. After each five to 10 new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation ( $S$ ) data should

be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

- 9.3.4 Instrument Performance Check Solution (IPC) -- For all determinations the laboratory must analyze the IPC (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within  $\pm 10\%$  of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within  $\pm 10\%$ . If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

#### 9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

- 9.4.1 Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.1.1 If the concentration of fortification is less than 25% of the background concentration of the matrix the matrix recovery should not be calculated.

- 9.4.2 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%. Percent recovery may be calculated using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where,

R = percent recovery

$C_s$  = fortified sample concentration

C = sample background concentration

s = concentration equivalent of analyte added to sample

- 9.4.3 Until sufficient data becomes available (usually a minimum of 20-30 analysis), assess laboratory performance against recovery limits for Method A of 80-120% and 75-125% for Method B. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery.
- 9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.
- 9.4.5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.
- 9.4.6 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 9.2.
- 9.4.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.
- 9.4.8 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.
- 9.4.9 When using Part B, the analyst should be aware of the purity of the reagents used to prepare standards. Allowances must be made when the solid materials are less than 99% pure.

## **10.0 CALIBRATION AND STANDARDIZATION**

- 10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Tables 1A or 1B.
- 10.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (Section 7.5) to a volumetric flask and diluting

to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

- 10.3 Using injections of 0.1-1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.
- 10.4 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than  $\pm 10\%$ , the test must be repeated, using fresh calibration standards. If the results are still more than  $\pm 10\%$ , a new calibration curve must be prepared for that analyte.
- 10.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). The response of the detector to the sample when diluted 1:1, and when not diluted, should be compared. If the calculated responses are the same, samples of this total anionic concentration need not be diluted.

## **11.0 PROCEDURE**

- 11.1 Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in these tables are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 9.2 are met.
- 11.2 Check system calibration daily and, if required, recalibrate as described in Section 10.0.
- 11.3 Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.
- 11.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.
- 11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

- 11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

**Note:** Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

- 11.7 The following extraction should be used for solid materials. Add an amount of reagent water equal to 10 times the weight of dry solid material taken as a sample. This slurry is mixed for 10 minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45  $\mu$  membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the user's matrix through the use of fortified samples.
- 11.8 It has been reported that lower detection limits for bromate ( $\approx 7 \mu\text{g/L}$ ) can be obtained using a borate based eluent<sup>(7)</sup>. The use of this eluent or other eluents that improve method performance may be considered as a minor modification of the method and as such still are acceptable.
- 11.9 Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

## **12.0 DATA ANALYSIS AND CALCULATIONS**

- 12.1 Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.
- 12.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.
- 12.3 Report results in mg/L.
- 12.4 Report             $\text{NO}_2^-$  as N  
                       $\text{NO}_3^-$  as N  
                       $\text{HPO}_4$  as P

## **13.0 METHODS PERFORMANCE**

- 13.1 Tables 1A and 2A give the single laboratory (EMSL-Cincinnati) MDL for each anion included in the method under the conditions listed.



- 13.2 Tables 2A and 2B give the single laboratory (EMSL-Cincinnati) standard deviation for each anion included in the method in a variety of waters for the listed conditions.
- 13.3 Multiple laboratory accuracy and bias data ( $S_p$ ) and estimated single operator values ( $S_o$ ) for reagent, drinking and waste water using Method A are given for each anion in Tables 3 through 9. Data from 19 laboratories were used for this data.
- 13.4 Some of the bias statements, for example chloride and sulfate, may be misleading due to spiking small increments of the anion into large naturally occurring concentrations of the same anion.

#### **14.0 POLLUTION PREVENTION**

- 14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.
- 14.2 Quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.
- 14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less Is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036, (202) 872-4477.

#### **15.0 WASTE MANAGEMENT**

- 15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

## 16.0 REFERENCES

1. "Determination of Inorganic Disinfection By-Products by Ion Chromatography", J. Pfaff, C. Brockhoff. J. Am. Water Works Assoc., Vol 82, No. 4, pg 192.
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3. Dionex, System 4000 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1988.
4. Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater", J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.
5. American Society for Testing and Materials. Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography D4327-91. Annual Book of Standards, Vol 11.01 (1993).
6. Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.
7. Hautman, D.P. & Bolyard, M. Analysis of Oxyhalide Disinfection By-products and other Anions of Interest in Drinking Water by Ion Chromatography. Jour. of Chromatog., 602, (1992), 65-74.

**17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA**

**TABLE 1A. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS  
IN REAGENT WATER (PART A)**

| Analyte       | Peak # | Retention Time<br>(min) | MDL<br>(mg/L) |
|---------------|--------|-------------------------|---------------|
| Fluoride      | 1      | 1.2                     | 0.01          |
| Chloride      | 2      | 1.7                     | 0.02          |
| Nitrite-N     | 3      | 2.0                     | 0.004         |
| Bromide       | 4      | 2.9                     | 0.01          |
| Nitrate-N     | 5      | 3.2                     | 0.002         |
| o-Phosphate-P | 6      | 5.4                     | 0.003         |
| Sulfate       | 7      | 6.9                     | 0.02          |

Standard Conditions:

Columns: as specified in Section 6.2.2.1

Detector: as specified in Section 6.2.4

Eluent: as specified in Section 7.3

Pump Rate: 2.0 mL/min.

Sample Loop: 50 µL

MDL calculated from data system using a y-axis selection of 1000 ns and with a stripchart recorder with an attenuator setting of 1 uMHO full scale.

\*See Figure 1

**TABLE 1B. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS  
IN REAGENT WATER (PART B)**

| Analyte  | Peak # | Retention Time<br>(min) | MDL<br>(mg/L) |
|----------|--------|-------------------------|---------------|
| Chlorite | 1      | 2.8                     | 0.01          |
| Bromate  | 2      | 3.2                     | 0.02          |
| Chlorate | 4      | 7.1                     | 0.003         |

Standard Conditions:

Column: as specified in Section 6.2.2.2

Detector: as specified in Section 6.2.4

Eluent: as specified in Section 7.3

Pump Rate: 1.0 mL/min.

Sample Loop: 50 µL

Attenuation - 1

y-axis - 500 ns

\*See Figure 2

**TABLE 2A. SINGLE-OPERATOR ACCURACY AND BIAS OF STANDARD ANIONS  
(METHOD A)**

| <b>Analyte</b> | <b>Sample Type</b> | <b>Known Conc.<br/>(mg/L)</b> | <b>Number<br/>of Replicates</b> | <b>Mean<br/>Recovery<br/>%</b> | <b>Standard<br/>Deviation<br/>(mg/L)</b> |
|----------------|--------------------|-------------------------------|---------------------------------|--------------------------------|------------------------------------------|
| Bromide        | RW                 | 5.0                           | 7                               | 99                             | 0.08                                     |
|                | DW                 | 5.0                           | 7                               | 105                            | 0.10                                     |
|                | SW                 | 5.0                           | 7                               | 95                             | 0.13                                     |
|                | WW                 | 5.0                           | 7                               | 105                            | 0.34                                     |
|                | GW                 | 5.0                           | 7                               | 92                             | 0.34                                     |
|                | SD                 | 2.0                           | 7                               | 82                             | 0.06                                     |
| Chloride       | RW                 | 20.0                          | 7                               | 96                             | 0.35                                     |
|                | DW                 | 20.0                          | 7                               | 108                            | 1.19                                     |
|                | SW                 | 10.0                          | 7                               | 86                             | 0.33                                     |
|                | WW                 | 20.0                          | 7                               | 101                            | 5.2                                      |
|                | GW                 | 20.0                          | 7                               | 114                            | 1.3                                      |
|                | SD                 | 20.0                          | 7                               | 90                             | 0.32                                     |
| Fluoride       | RW                 | 2.0                           | 7                               | 91                             | 0.05                                     |
|                | DW                 | 1.0                           | 7                               | 92                             | 0.06                                     |
|                | SW                 | 1.0                           | 7                               | 73                             | 0.05                                     |
|                | WW                 | 1.0                           | 7                               | 87                             | 0.07                                     |
|                | GW                 | 0.4                           | 7                               | 95                             | 0.07                                     |
|                | SD                 | 5.0                           | 7                               | 101                            | 0.35                                     |
| Nitrate-N      | RW                 | 10.0                          | 7                               | 103                            | 0.21                                     |
|                | DW                 | 10.0                          | 7                               | 104                            | 0.27                                     |
|                | SW                 | 10.0                          | 7                               | 93                             | 0.17                                     |
|                | WW                 | 10.0                          | 7                               | 101                            | 0.82                                     |
|                | GW                 | 10.0                          | 7                               | 97                             | 0.47                                     |
|                | SD                 | 10.0                          | 7                               | 82                             | 0.28                                     |
| Nitrite        | RW                 | 10.0                          | 7                               | 97                             | 0.14                                     |
|                | DW                 | 10.0                          | 7                               | 121                            | 0.25                                     |
|                | SW                 | 5.0                           | 7                               | 92                             | 0.14                                     |
|                | WW                 | 5.0                           | 7                               | 91                             | 0.50                                     |
|                | GW                 | 10.0                          | 7                               | 96                             | 0.35                                     |
|                | SD                 | 2.0                           | 7                               | 98                             | 0.08                                     |
| o-Phosphate-P  | RW                 | 10.0                          | 7                               | 99                             | 0.17                                     |
|                | DW                 | 10.0                          | 7                               | 99                             | 0.26                                     |
|                | SW                 | 10.0                          | 7                               | 98                             | 0.22                                     |
|                | WW                 | 10.0                          | 7                               | 106                            | 0.85                                     |
|                | GW                 | 10.0                          | 7                               | 95                             | 0.33                                     |
| Sulfate        | RW                 | 20.0                          | 7                               | 99                             | 0.40                                     |
|                | DW                 | 50.0                          | 7                               | 105                            | 3.35                                     |
|                | SW                 | 40.0                          | 7                               | 95                             | 1.7                                      |
|                | WW                 | 40.0                          | 7                               | 102                            | 6.4                                      |
|                | GW                 | 40.0                          | 7                               | 112                            | 3.2                                      |



**TABLE 2B. SINGLE-OPERATOR ACCURACY AND BIAS OF BY-PRODUCT  
(PART B)**

| <b>Analyte</b> | <b>Sample Type</b> | <b>Spike (mg/L)</b> | <b>Number of Replicates</b> | <b>Mean Recovery %</b> | <b>Standard Deviation (mg/L)</b> |
|----------------|--------------------|---------------------|-----------------------------|------------------------|----------------------------------|
| Bromide        | RW                 | 5.0                 | 7                           | 103                    | 0.07                             |
|                |                    | 1.0                 | 7                           | 98                     | 0.04                             |
|                |                    | 0.1                 | 7                           | 155                    | 0.005                            |
|                |                    | 0.05                | 7                           | 122                    | 0.01                             |
|                | DW                 | 5.0                 | 7                           | 95                     | 0.04                             |
|                |                    | 1.0                 | 7                           | 85                     | 0.02                             |
|                |                    | 0.1                 | 7                           | 98                     | 0.005                            |
|                |                    | 0.05                | 7                           | 98                     | 0.005                            |
| Chlorate       | RW                 | 5.0                 | 7                           | 101                    | 0.06                             |
|                |                    | 1.0                 | 7                           | 97                     | 0.01                             |
|                |                    | 0.1                 | 7                           | 100                    | 0.01                             |
|                |                    | 0.05                | 7                           | 119                    | 0.05                             |
|                | DW                 | 5.0                 | 7                           | 101                    | 0.04                             |
|                |                    | 1.0                 | 7                           | 115                    | 0.01                             |
|                |                    | 0.1                 | 7                           | 121                    | 0.005                            |
|                |                    | 0.05                | 7                           | 110                    | 0.01                             |
| Chlorite       | RW                 | 5.0                 | 7                           | 100                    | 0.04                             |
|                |                    | 1.0                 | 7                           | 98                     | 0.01                             |
|                |                    | 0.1                 | 7                           | 86                     | 0.01                             |
|                |                    | 0.05                | 7                           | 94                     | 0.01                             |
|                | DW                 | 5.0                 | 7                           | 96                     | 0.03                             |
|                |                    | 1.0                 | 7                           | 100                    | 0.02                             |
|                |                    | 0.1                 | 7                           | 76                     | 0.00                             |
|                |                    | 0.05                | 7                           | 96                     | 0.01                             |

RW = Reagent Water  
DW = Drinking Water

**TABLE 3. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR FLUORIDE**

| <b>Water</b>    | <b>Amount<br/>Added<br/>mg/L</b> | <b>Amount Found<br/>mg/L</b> | <b>S<sub>t</sub></b> | <b>S<sub>o</sub></b> | <b>Bias<br/>%</b> |
|-----------------|----------------------------------|------------------------------|----------------------|----------------------|-------------------|
| <b>Reagent</b>  | 0.26                             | 0.25                         | 0.08                 | 0.11                 | -3.8              |
|                 | 0.34                             | 0.29                         | 0.11                 |                      | -14.7             |
|                 | 2.12                             | 2.12                         | 0.07                 | 0.12                 | 0.0               |
|                 | 2.55                             | 2.48                         | 0.14                 |                      | -2.7              |
|                 | 6.79                             | 6.76                         | 0.20                 | 0.19                 | -0.4              |
|                 | 8.49                             | 8.46                         | 0.30                 |                      | -0.4              |
| <b>Drinking</b> | 0.26                             | 0.24                         | 0.08                 | 0.05                 | -7.7              |
|                 | 0.34                             | 0.34                         | 0.11                 |                      | 0.0               |
|                 | 2.12                             | 2.09                         | 0.18                 | 0.06                 | -1.4              |
|                 | 2.55                             | 2.55                         | 0.16                 |                      | 0.0               |
|                 | 6.79                             | 6.84                         | 0.54                 | 0.25                 | +0.7              |
|                 | 8.49                             | 8.37                         | 0.75                 |                      | -1.4              |
| <b>Waste</b>    | 0.26                             | 0.25                         | 0.15                 | 0.06                 | -3.8              |
|                 | 0.34                             | 0.32                         | 0.08                 |                      | -5.9              |
|                 | 2.12                             | 2.13                         | 0.22                 | 0.15                 | +0.5              |
|                 | 2.55                             | 2.48                         | 0.16                 |                      | -2.7              |
|                 | 6.79                             | 6.65                         | 0.41                 | 0.20                 | -2.1              |
|                 | 8.49                             | 8.27                         | 0.36                 |                      | -2.6              |

**TABLE 4. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR  
CHLORIDE**

| <b>Water</b> | <b>Amount<br/>Added<br/>mg/L</b> | <b>Amount Found<br/>mg/L</b> | <b>S<sub>t</sub></b> | <b>S<sub>o</sub></b> | <b>Bias<br/>%</b> |
|--------------|----------------------------------|------------------------------|----------------------|----------------------|-------------------|
| Reagent      | 0.78                             | 0.79                         | 0.17                 | 0.29                 | +1.3              |
|              | 1.04                             | 1.12                         | 0.46                 |                      | +7.7              |
|              | 6.50                             | 6.31                         | 0.27                 | 0.14                 | -2.9              |
|              | 7.80                             | 7.76                         | 0.39                 |                      | -0.5              |
|              | 20.8                             | 20.7                         | 0.54                 | 0.62                 | -0.5              |
|              | 26.0                             | 25.9                         | 0.58                 |                      | -0.4              |
| Drinking     | 0.78                             | 0.54                         | 0.35                 | 0.20                 | -30.8             |
|              | 1.04                             | 0.51                         | 0.38                 |                      | -51.0             |
|              | 6.50                             | 5.24                         | 1.35                 | 1.48                 | -19.4             |
|              | 7.80                             | 6.02                         | 1.90                 |                      | -22.8             |
|              | 20.8                             | 20.0                         | 2.26                 | 1.14                 | -3.8              |
|              | 26.0                             | 24.0                         | 2.65                 |                      | -7.7              |
| Waste        | 0.78                             | 0.43                         | 0.32                 | 0.39                 | -44.9             |
|              | 1.04                             | 0.65                         | 0.48                 |                      | -37.5             |
|              | 6.50                             | 4.59                         | 1.82                 | 0.83                 | -29.4             |
|              | 7.80                             | 5.45                         | 2.02                 |                      | -30.1             |
|              | 20.8                             | 18.3                         | 2.41                 | 1.57                 | -11.8             |
|              | 26.0                             | 23.0                         | 2.50                 |                      | -11.5             |



**TABLE 5. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR  
NITRITE-NITROGEN**

| <b>Water</b>    | <b>Amount<br/>Added<br/>mg/L</b> | <b>Amount<br/>Found<br/>mg/L</b> | <b>S<sub>i</sub></b> | <b>S<sub>o</sub></b> | <b>Bias<br/>%</b> |
|-----------------|----------------------------------|----------------------------------|----------------------|----------------------|-------------------|
| <b>Reagent</b>  | 0.36                             | 0.37                             | 0.04                 | 0.04                 | +2.8              |
|                 | 0.48                             | 0.48                             | 0.06                 |                      | 0.0               |
|                 | 3.00                             | 3.18                             | 0.12                 | 0.06                 | +6.0              |
|                 | 3.60                             | 3.83                             | 0.12                 |                      | +6.4              |
|                 | 9.60                             | 9.84                             | 0.36                 | 0.26                 | +2.5              |
|                 | 12.0                             | 12.1                             | 0.27                 |                      | +0.6              |
| <b>Drinking</b> | 0.36                             | 0.30                             | 0.13                 | 0.03                 | -16.7             |
|                 | 0.48                             | 0.40                             | 0.14                 |                      | -16.7             |
|                 | 3.00                             | 3.02                             | 0.23                 | 0.12                 | +0.7              |
|                 | 3.60                             | 3.62                             | 0.22                 |                      | +0.6              |
|                 | 9.60                             | 9.59                             | 0.44                 | 0.28                 | -0.1              |
|                 | 12.0                             | 11.6                             | 0.59                 |                      | -3.1              |
| <b>Waste</b>    | 0.36                             | 0.34                             | 0.06                 | 0.04                 | -5.6              |
|                 | 0.48                             | 0.46                             | 0.07                 |                      | -4.2              |
|                 | 3.00                             | 3.18                             | 0.13                 | 0.10                 | +6.0              |
|                 | 3.60                             | 3.76                             | 0.18                 |                      | +4.4              |
|                 | 9.60                             | 9.74                             | 0.49                 | 0.26                 | +1.5              |
|                 | 12.0                             | 12.0                             | 0.56                 |                      | +0.3              |

**TABLE 6. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR BROMIDE**

| <b>Water</b>    | <b>Amount<br/>Added<br/>mg/L</b> | <b>Amount<br/>Found<br/>mg/L</b> | <b>S<sub>i</sub></b> | <b>S<sub>o</sub></b> | <b>Bias<br/>%</b> |
|-----------------|----------------------------------|----------------------------------|----------------------|----------------------|-------------------|
| <b>Reagent</b>  | 0.63                             | 0.69                             | 0.11                 | 0.05                 | +9.5              |
|                 | 0.84                             | 0.85                             | 0.12                 |                      | +1.2              |
|                 | 5.24                             | 5.21                             | 0.22                 | 0.21                 | -0.6              |
|                 | 6.29                             | 6.17                             | 0.35                 |                      | -1.9              |
|                 | 16.8                             | 17.1                             | 0.70                 | 0.36                 | +1.6              |
|                 | 21.0                             | 21.3                             | 0.93                 |                      | +1.5              |
| <b>Drinking</b> | 0.63                             | 0.63                             | 0.13                 | 0.04                 | 0.0               |
|                 | 0.84                             | 0.81                             | 0.13                 |                      | -3.6              |
|                 | 5.24                             | 5.11                             | 0.23                 | 0.13                 | -2.5              |
|                 | 6.29                             | 6.18                             | 0.30                 |                      | -1.7              |
|                 | 16.8                             | 17.0                             | 0.55                 | 0.57                 | +0.9              |
|                 | 21.0                             | 20.9                             | 0.65                 |                      | -0.4              |
| <b>Waste</b>    | 0.63                             | 0.63                             | 0.15                 | 0.09                 | 0.0               |
|                 | 0.84                             | 0.85                             | 0.15                 |                      | +1.2              |
|                 | 5.24                             | 5.23                             | 0.36                 | 0.11                 | -0.2              |
|                 | 6.29                             | 6.27                             | 0.46                 |                      | -0.3              |
|                 | 16.8                             | 16.6                             | 0.69                 | 0.43                 | -1.0              |
|                 | 21.0                             | 21.1                             | 0.63                 |                      | +0.3              |

**TABLE 7. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR  
NITRATE-NITROGEN**

| <b>Water</b> | <b>Amount<br/>Added<br/>mg/L</b> | <b>Amount<br/>Found<br/>mg/L</b> | <b>S<sub>t</sub></b> | <b>S<sub>o</sub></b> | <b>Bias<br/>%</b> |
|--------------|----------------------------------|----------------------------------|----------------------|----------------------|-------------------|
| Reagent      | 0.42                             | 0.42                             | 0.04                 | 0.02                 | 0.0               |
|              | 0.56                             | 0.56                             | 0.06                 |                      | 0.0               |
|              | 3.51                             | 3.34                             | 0.15                 | 0.08                 | -4.8              |
|              | 4.21                             | 4.05                             | 0.28                 |                      | -3.8              |
|              | 11.2                             | 11.1                             | 0.47                 | 0.34                 | -1.1              |
|              | 14.0                             | 14.4                             | 0.61                 |                      | +2.6              |
|              |                                  |                                  |                      |                      |                   |
| Drinking     | 0.42                             | 0.46                             | 0.08                 | 0.03                 | +9.5              |
|              | 0.56                             | 0.58                             | 0.09                 |                      | +3.6              |
|              | 3.51                             | 3.45                             | 0.27                 | 0.10                 | -1.7              |
|              | 4.21                             | 4.21                             | 0.38                 |                      | 0.0               |
|              | 11.2                             | 11.5                             | 0.50                 | 0.48                 | +2.3              |
|              | 14.0                             | 14.2                             | 0.70                 |                      | +1.6              |
|              |                                  |                                  |                      |                      |                   |
| Waste        | 0.42                             | 0.36                             | 0.07                 | 0.06                 | -14.6             |
|              | 0.56                             | 0.40                             | 0.16                 |                      | -28.6             |
|              | 3.51                             | 3.19                             | 0.31                 | 0.07                 | -9.1              |
|              | 4.21                             | 3.84                             | 0.28                 |                      | -8.8              |
|              | 11.2                             | 10.9                             | 0.35                 | 0.51                 | -3.0              |
|              | 14.0                             | 14.1                             | 0.74                 |                      | +0.4              |
|              |                                  |                                  |                      |                      |                   |

**TABLE 8. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR  
ORTHO-PHOSPHATE**

| <b>Water</b>    | <b>Amount<br/>Added<br/>mg/L</b> | <b>Amount<br/>Found<br/>mg/L</b> | <b>S<sub>i</sub></b> | <b>S<sub>o</sub></b> | <b>Bias<br/>%</b> |
|-----------------|----------------------------------|----------------------------------|----------------------|----------------------|-------------------|
| <b>Reagent</b>  | 0.69                             | 0.69                             | 0.06                 | 0.06                 | 0.0               |
|                 | 0.92                             | 0.98                             | 0.15                 |                      | +6.5              |
|                 | 5.77                             | 5.72                             | 0.36                 | 0.18                 | -0.9              |
|                 | 6.92                             | 6.78                             | 0.42                 |                      | -2.0              |
|                 | 18.4                             | 18.8                             | 1.04                 | 0.63                 | +2.1              |
|                 | 23.1                             | 23.2                             | 0.35                 |                      | +2.4              |
| <b>Drinking</b> | 0.69                             | 0.70                             | 0.17                 | 0.17                 | +1.4              |
|                 | 0.92                             | 0.96                             | 0.20                 |                      | +4.3              |
|                 | 5.77                             | 5.43                             | 0.52                 | 0.40                 | -5.9              |
|                 | 6.92                             | 6.29                             | 0.72                 |                      | -9.1              |
|                 | 18.4                             | 18.0                             | 0.68                 | 0.59                 | -2.2              |
|                 | 23.1                             | 22.6                             | 1.07                 |                      | -2.0              |
| <b>Waste</b>    | 0.69                             | 0.64                             | 0.26                 | 0.09                 | -7.2              |
|                 | 0.92                             | 0.82                             | 0.28                 |                      | -10.9             |
|                 | 5.77                             | 5.18                             | 0.66                 | 0.34                 | -10.2             |
|                 | 6.92                             | 6.24                             | 0.74                 |                      | -9.8              |
|                 | 18.4                             | 17.6                             | 2.08                 | 1.27                 | -4.1              |
|                 | 23.1                             | 22.4                             | 0.87                 |                      | -3.0              |

**TABLE 9. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR  
SULFATE**

| <b>Water</b>    | <b>Amount<br/>Added<br/>mg/L</b> | <b>Amount<br/>Found<br/>mg/L</b> | <b>S<sub>i</sub></b> | <b>S<sub>o</sub></b> | <b>Bias<br/>%</b> |
|-----------------|----------------------------------|----------------------------------|----------------------|----------------------|-------------------|
| <b>Reagent</b>  | 2.85                             | 2.83                             | 0.32                 | 0.52                 | -0.7              |
|                 | 3.80                             | 3.83                             | 0.92                 |                      | +0.8              |
|                 | 23.8                             | 24.0                             | 1.67                 | 0.68                 | +0.8              |
|                 | 28.5                             | 28.5                             | 1.56                 |                      | -0.1              |
|                 | 76.0                             | 76.8                             | 3.42                 | 2.33                 | +1.1              |
|                 | 95.0                             | 95.7                             | 3.59                 |                      | +0.7              |
| <b>Drinking</b> | 2.85                             | 1.12                             | 0.37                 | 0.41                 | -60.7             |
|                 | 3.80                             | 2.26                             | 0.97                 |                      | -40.3             |
|                 | 23.8                             | 21.8                             | 1.26                 | 0.51                 | -8.4              |
|                 | 28.5                             | 25.9                             | 2.48                 |                      | -9.1              |
|                 | 76.0                             | 74.5                             | 4.63                 | 2.70                 | -2.0              |
|                 | 95.0                             | 92.3                             | 5.19                 |                      | -2.8              |
| <b>Waste</b>    | 2.85                             | 1.89                             | 0.37                 | 0.24                 | -33.7             |
|                 | 3.80                             | 2.10                             | 1.25                 |                      | -44.7             |
|                 | 23.8                             | 20.3                             | 3.19                 | 0.58                 | -14.7             |
|                 | 28.5                             | 24.5                             | 3.24                 |                      | -14.0             |
|                 | 76.0                             | 71.4                             | 5.65                 | 3.39                 | -6.1              |
|                 | 95.0                             | 90.3                             | 6.80                 |                      | -5.0              |

## Method A

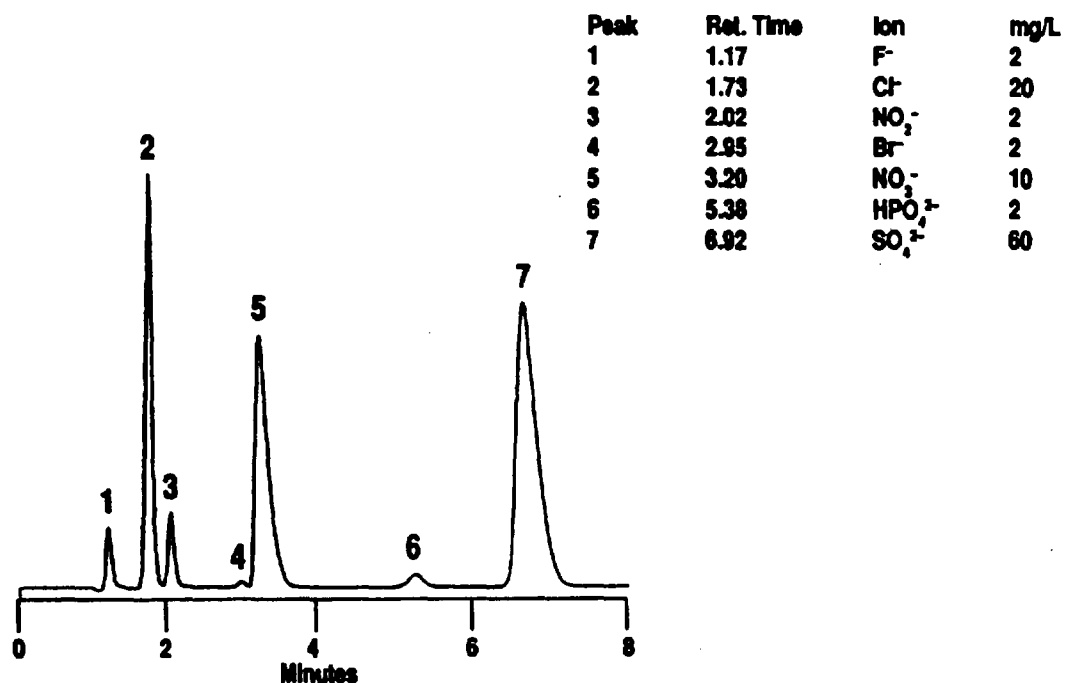


Figure 1. Chromatogram showing separation using the AS4A column

## Method B

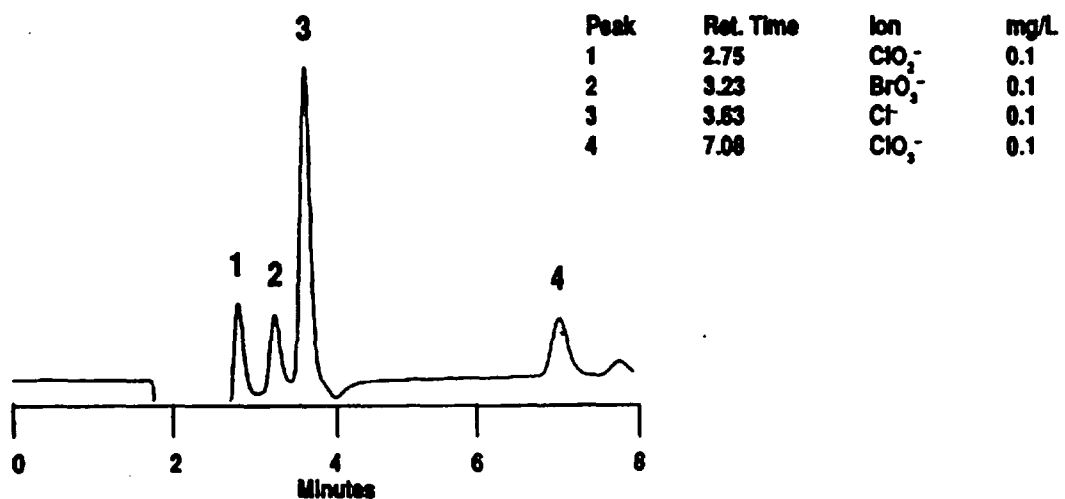


Figure 2. Chromatogram showing separation using the AS9 column

October 4, 1995 Draft

Method 1668 Toxic PCBs by HRGC/HRMS

Questions concerning this draft or its application should be addressed to:

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Toxic PCBs by Isotope Dilution HRGC/HRMS

## 1.0 Scope and Application

- 1.1 This method is for determination of the toxic polychlorinated biphenyls (PCBs) in water, soil, sediment, sludge, tissue, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The method is based on a compilation of methods from the technical literature (References 1-3) and on EPA Method 1613.
- 1.2 The toxic PCBs listed in Table 1 (Reference 4) and other specific congeners may be determined by this method.
- 1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the PCBs can be determined with only common laboratory interferences present. The Method Detection Limit (MDL) for PCB #126 has been determined as 45 pg/L (parts-per-quadrillion) in water using this method.
- 1.4 The GC/MS portions of this method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.
- 1.5 This method is "performance-based". The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met. The requirements for establishing method equivalency are given in Section 9.1.2.
- 1.6 Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

## 2.0 Summary of Method

Flow charts that summarize procedures for sample preparation, extraction, and analysis are given in Figure 1 for aqueous and solid samples, Figure 2 for multi-phase samples, and Figure 3 for tissue samples.

### 2.1 Extraction

- 2.1.1 Aqueous samples (samples containing less than one percent solids)—Stable isotopically labeled analogs of the toxic PCBs are spiked into a one-liter sample, and the sample is vacuum filtered through a glass-fiber filter on top of a solid-phase extraction (SPE) disk. Sample components on the filter and disk are eluted with methylene chloride and the eluant is concentrated for cleanup.
- 2.1.2 Solid, semi-solid, and multi-phase samples (but not tissue)—The labeled compounds are spiked into a sample containing 10 g (dry weight) of solids. Samples containing multiple phases are pressure filtered and any aqueous liquid is discarded. Coarse solids are ground or



homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted in an SDS extractor. The extract is concentrated for cleanup.

- 2.1.3 Fish and other tissue—A 20-g aliquot of sample is homogenized, and a 10-g aliquot is spiked with the labeled compounds. The sample is mixed with sodium sulfate, allowed to dry for 12 - 24 hours, and extracted for 18-24 hours using methylene chloride:hexane (1:1) in a Soxhlet extractor. The extract is evaporated to dryness, and the lipid content is determined.
- 2.2 After extraction, samples are cleaned up using back-extraction with sulfuric acid and/or base, and gel permeation, silica gel, Florisil and activated carbon chromatography. High-performance liquid chromatography (HPLC) can be used for further isolation of specific isomers or congeners. Prior to the cleanup procedures cited above, tissue extracts are cleaned up using an anthropogenic isolation column.
- 2.3 After cleanup, the extract is concentrated to near dryness. Immediately prior to injection, internal standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high-resolution ( $\geq 10,000$ ) mass spectrometer. Two exact  $m/z$ 's are monitored for each analyte.
- 2.4 An individual PCB congener is identified by comparing the GC retention time and ion-abundance ratio of two exact  $m/z$ 's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact  $m/z$ 's. Isomer specificity for the toxic PCBs is achieved using GC columns that resolve these congeners from the other PCBs.
- 2.5 Quantitative analysis is performed using selected ion current profile (SICP) areas, in one of two ways:
  - 2.5.1 For PCBs with labeled analogs (see Table 1), the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique.
  - 2.5.2 For PCBs without labeled compounds, the GC/MS system is calibrated and the concentration of each compound is determined using the internal standard technique.
- 2.6 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

### 3.0 Definitions

Definitions are given in the glossary at the end of this method.

### 4.0 Contamination and Interferences

- 4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse.

The non-coplanar PCB congeners 105, 114, 118, 123, 156, 157, 167, and 180 have been shown to be very difficult to completely eliminate from the laboratory at the MDLs in this method, and baking of glassware in a kiln or furnace at 450 - 500 °C may be necessary to remove these and other contaminants.

- 4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface.
- 4.2.1 Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.
- 4.2.2 After detergent washing, glassware should be rinsed immediately, first with methanol, then with hot tap water. The tap water rinse is followed by another methanol rinse, then acetone, and then methylene chloride.
- 4.2.3 Baking of glassware in kiln or other high temperature furnace (450 - 500 °C) may be warranted after particularly dirty samples are encountered. However, baking should be minimized, as repeated baking of glassware may cause active sites on the glass surface that may irreversibly adsorb PCBs.
- 4.2.4 Immediately prior to use, the Soxhlet apparatus should be pre-extracted with toluene for approximately 3 hours (see Sections 12.3.1-12.3.3). The solid-phase extraction apparatus (Section 6.4.1.5) should be rinsed with methylene chloride/toluene (80/20 mixture).
- 4.3 All materials used in the analysis shall be demonstrated to be free from interferences by running reference matrix method blanks initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).
- 4.3.1 The reference matrix must simulate, as closely as possible, the sample matrix under test. Ideally, the reference matrix should not contain the PCBs in detectable amounts, but should contain potential interferents in the concentrations expected to be found in the samples to be analyzed.
- 4.3.2 When a reference matrix that simulates the sample matrix under test is not available, reagent water (Section 7.6.1) can be used to simulate water samples; playground sand (Section 7.6.2) or white quartz sand (Section 7.3.2) can be used to simulate soils; filter paper (Section 7.6.3) can be used to simulate papers and similar materials; and corn oil (Section 7.6.4) can be used to simulate tissues.
- 4.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCBs. The most frequently encountered interferences are chlorinated dioxins and dibenzofurans, methoxy biphenyls, hydroxy-diphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of PCBs are measured by this method, the elimination of interferences is essential. The cleanup steps given in Section 13 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCBs at the levels shown in Table 2.
- 4.5 Each piece of reusable glassware should be numbered to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

- 4.6 Cleanup of tissue—The natural lipid content of tissue can interfere in the analysis of tissue samples for the PCBs. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for cleanup of sample extracts. Lipids must be removed by the lipid removal procedures in Section 13.6, followed by Florisil (Section 13.7), and carbon (Section 13.4) as minimum additional cleanup steps.

## 5.0 Safety

- 5.1 The toxicity or carcinogenicity of each chemical used in this method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.
- 5.1.1 The PCBs have been tentatively classified as known or suspected human or mammalian carcinogens. On the basis of the available toxicological and physical properties of the PCBs, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.
- 5.1.2 It is recommended that the laboratory purchase dilute standard solutions of the analytes in this method. However, if primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator shall be worn when high concentrations are handled.
- 5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in these analyses. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this method and that the results of this monitoring be made available to the analyst. Additional information on laboratory safety can be found in References 5-8. The references and bibliography at the end of Reference 8 are particularly comprehensive in dealing with the general subject of laboratory safety.
- 5.3 The pure PCBs and samples suspected to contain these compounds are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. Each laboratory must develop a strict safety program for handling these compounds. The practices in Reference 11 for handling chlorinated dibenzo-*p*-dioxins and dibenzofurans (CDDs/CDFs) are also recommended for handling the toxic PCBs.
- 5.3.1 Facility—When finely divided samples (dusts, soils, dry chemicals) are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak tight or in a fume hood demonstrated to have adequate air flow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.

- 5.3.2 **Protective equipment**—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn while working with exposed samples or pure analytical standards. Latex gloves are commonly used to reduce exposure of the hands. When handling samples suspected or known to contain high concentrations of the PCBs, an additional set of gloves can also be worn beneath the latex gloves.
- 5.3.3 **Training**—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.
- 5.3.4 **Personal hygiene**—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).
- 5.3.5 **Confinement**—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.
- 5.3.6 **Effluent vapors**—The effluents of sample splitters from the gas chromatograph (GC) and from roughing pumps on the mass spectrometer (MS) should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols to condense PCB vapors.
- 5.3.7 **Waste Handling**—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.
- 5.3.8 **Decontamination.**
- 5.3.8.1 **Decontamination of personnel**—Use any mild soap with plenty of scrubbing action.
- 5.3.8.2 **Glassware, tools, and surfaces**—Chloroethene NU Solvent is a less toxic solvent that should be effective in removing PCBs. Satisfactory cleaning may be accomplished by rinsing with Chloroethene, then washing with any detergent and water. If glassware is first rinsed with solvent, then the dish water may be disposed of in the sewer. Given the cost of disposal, it is prudent to minimize solvent wastes.
- 5.3.9 **Laundry**—Clothing known to be contaminated should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows of the potential problem. The washer should be run through a cycle before being used again for other clothing.
- 5.3.10 **Wipe tests**—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by GC with an electron capture detector (ECD) can achieve a limit of detection of 0.1 µg per wipe; analysis using this method can achieve an even lower detection limit. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

## 6.0 Apparatus and Materials

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**Note:** *Brand names, suppliers, and part numbers are for illustration purposes only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the laboratory.*

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### 6.1 Sampling equipment for discrete or composite sampling.

#### 6.1.1 Sample bottles and caps.

- 6.1.1.1 Liquid samples (waters, sludges and similar materials containing 5 percent solids or less)—Sample bottle, amber glass, 1.1-L minimum, with screw cap.
- 6.1.1.2 Solid samples (soils, sediments, sludges, paper pulps, filter cake, compost, and similar materials that contain more than 5 percent solids)—Sample bottle, wide mouth, amber glass, 500-mL minimum.
- 6.1.1.3 If amber bottles are not available, samples shall be protected from light.
- 6.1.1.4 Bottle caps—Threaded to fit sample bottles. Caps shall be lined with fluoropolymer.
- 6.1.1.5 Cleaning.
  - 6.1.1.5.1 Bottles are detergent water washed, then solvent rinsed before use.
  - 6.1.1.5.2 Liners are detergent water washed and rinsed with reagent water (Section 7.6.1).

#### 6.1.2 Compositing equipment—Automatic or manual compositing system incorporating glass containers cleaned per bottle cleaning procedure above. Only glass or fluoropolymer tubing shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing shall be thoroughly rinsed with methanol, followed by repeated rinsing with reagent water to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

### 6.2 Equipment for glassware cleaning—Laboratory sink with overhead fume hood.

### 6.3 Equipment for sample preparation.

- 6.3.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.
- 6.3.2 Glove box (optional).
- 6.3.3 Tissue homogenizer—VirTis Model 45 Macro homogenizer (American Scientific Products H-3515, or equivalent) with stainless steel Macro-shaft and Turbo-shear blade.
- 6.3.4 Meat grinder—Hobart, or equivalent, with 3- to 5-mm holes in inner plate.
- 6.3.5 Equipment for determining percent moisture.
  - 6.3.5.1 Oven—Capable of maintaining a temperature of  $110 \pm 5^{\circ}\text{C}$ .
  - 6.3.5.2 Dessicator.

- 6.3.6 Balances.
  - 6.3.6.1 Analytical—Capable of weighing 0.1 mg.
  - 6.3.6.2 Top loading—Capable of weighing 10 mg.
- 6.4 Extraction apparatus.
  - 6.4.1 Water samples.
    - 6.4.1.1 pH meter, with combination glass electrode.
    - 6.4.1.2 pH paper, wide range (Hydron Papers, or equivalent).
    - 6.4.1.3 Graduated cylinder, 1-L capacity.
    - 6.4.1.4 Liquid/liquid extraction—Separatory funnels, 250-, 500-, and 2000-mL, with fluoropolymer stopcocks.
    - 6.4.1.5 Solid-phase extraction.
      - 6.4.1.5.1 1-L filtration apparatus, including glass funnel, frit support, clamp, adapter, stopper, filtration flask, and vacuum tubing (Figure 4). For wastewater samples, the apparatus should accept 90 or 144 mm disks. For drinking water or other samples containing low solids, smaller disks may be used.
      - 6.4.1.5.2 Vacuum source capable of maintaining 25 in. Hg, equipped with shutoff valve and vacuum gauge.
      - 6.4.1.5.3 Glass-fiber filter—Whatman GMF 150 (or equivalent), 1 micron pore size, to fit filtration apparatus in Section 6.4.1.5.1.
      - 6.4.1.5.4 Solid-phase extraction disk containing octadecyl ( $C_{18}$ ) bonded silica uniformly enmeshed in an inert matrix—Fisher Scientific 14-378F (or equivalent), to fit filtration apparatus in Section 6.4.1.5.1.
  - 6.4.2 Soxhlet/Dean-Stark (SDS) extractor (Figure 5 and Reference 12) for filters and solid/sludge samples.
    - 6.4.2.1 Soxhlet—50-mm ID, 200-mL capacity with 500-mL flask (Cal-Glass LG-6900, or equivalent, except substitute 500-mL round-bottom flask for 300-mL flat-bottom flask).
    - 6.4.2.2 Thimble—43 × 123 to fit Soxhlet (Cal-Glass LG-6901-122, or equivalent).
    - 6.4.2.3 Moisture trap—Dean Stark or Barret with fluoropolymer stopcock, to fit Soxhlet.
    - 6.4.2.4 Heating mantle—Hemispherical, to fit 500-mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent).
    - 6.4.2.5 Variable transformer—Powerstat (or equivalent), 110-volt, 10-amp.
  - 6.4.3 Beakers—400- to 500-mL.
  - 6.4.4 Spatulas—Stainless steel.
- 6.5 Filtration apparatus.
  - 6.5.1 Pyrex glass wool—Solvent-extracted by SDS for 3 hours minimum.
  - 6.5.2 Glass funnel—125- to 250-mL.
  - 6.5.3 Glass-fiber filter paper—Whatman GF/D (or equivalent), to fit glass funnel in Section 6.5.2.

- 6.5.4 Drying column—15- to 20-mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug.
- 6.5.5 Buchner funnel—15-cm.
- 6.5.6 Glass-fiber filter paper for Buchner funnel above.
- 6.5.7 Filtration flasks—1.5- to 2.0-L, with side arm.
- 6.5.8 Pressure filtration apparatus—Millipore YT30 142 HW, or equivalent.
- 6.6 Centrifuge apparatus.
  - 6.6.1 Centrifuge—Capable of rotating 500-mL centrifuge bottles or 15-mL centrifuge tubes at 5,000 rpm minimum.
  - 6.6.2 Centrifuge bottles—500-mL, with screw-caps, to fit centrifuge.
  - 6.6.3 Centrifuge tubes—12- to 15-mL, with screw-caps, to fit centrifuge.
- 6.7 Cleanup apparatus.
  - 6.7.1 Automated gel permeation chromatograph (Analytical Biochemical Labs, Inc, Columbia, MO, Model GPC Autoprep 1002, or equivalent).
    - 6.7.1.1 Column—600-700 mm long × 25 mm ID, packed with 70 g of SX-3 Bio-beads (Bio-Rad Laboratories, Richmond, CA, or equivalent).
    - 6.7.1.2 Syringe—10-mL, with Luer fitting.
    - 6.7.1.3 Syringe filter holder—stainless steel, and glass- fiber or fluoropolymer filters (Gelman 4310, or equivalent).
    - 6.7.1.4 UV detectors—254-nm, preparative or semi-preparative flow cell (Isco, Inc., Type 6; Schmadzu, 5-mm path length; Beckman-Altex 152W, 8-μL micro-prep flow cell, 2-mm path; Pharmacia UV-1, 3-mm flow cell; LDC Milton-Roy UV-3, monitor #1203; or equivalent).
  - 6.7.2 Reverse-phase high-performance liquid chromatograph.
    - 6.7.2.1 Column oven and detector—Perkin-Elmer Model LC-65T (or equivalent) operated at 0.02 AUFS at 235 nm.
    - 6.7.2.2 Injector—Rheodyne 7120 (or equivalent) with 50-μL sample loop.
    - 6.7.2.3 Column—Two 6.2 mm × 250 mm Zorbax-ODS columns in series (DuPont Instruments Division, Wilmington, DE, or equivalent), operated at 30°C and 2.0 mL/min with gradient from TBD percent methanol:acetonitrile to 100 percent acetonitrile in TBD minutes.
    - 6.7.2.4 Pump—Altex 110A (or equivalent).
  - 6.7.3 Pipets.
    - 6.7.3.1 Disposable, Pasteur, 150-mm long × 5-mm ID (Fisher Scientific 13-678-6A, or equivalent).
    - 6.7.3.2 Disposable, serological, 50-mL (8- to 10- mm ID).
  - 6.7.4 Glass chromatographic columns.

- 6.7.4.1 150-mm long x 8-mm ID (Kontes K-420155, or equivalent) with coarse-glass frit or glass-wool plug and 250-mL reservoir.
- 6.7.4.2 200-mm long x 15-mm ID, with coarse-glass frit or glass-wool plug and 250-mL reservoir.
- 6.7.4.3 300-mm long x 22-mm ID, with coarse-glass frit, 300-mL reservoir, and glass or fluoropolymer stopcock.
- 6.7.5 Stirring apparatus for batch silica cleanup of tissue extracts.
  - 6.7.5.1 Mechanical stirrer—Corning Model 320, or equivalent.
  - 6.7.5.2 Bottle—500- to 600-mL wide-mouth clear glass.
- 6.7.6 Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature ( $\pm 5^{\circ}\text{C}$ ) in the range of 105-250°C.
- 6.8 Concentration apparatus.
  - 6.8.1 Rotary evaporator—Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath.
    - 6.8.1.1 Vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge.
    - 6.8.1.2 A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.
    - 6.8.1.3 Round-bottom flask—100-mL and 500-mL or larger, with ground-glass fitting compatible with the rotary evaporator.
  - 6.8.2 Kuderna-Danish (K-D) concentrator.
    - 6.8.2.1 Concentrator tube—10-mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.
    - 6.8.2.2 Evaporation flask—500-mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent).
    - 6.8.2.3 Snyder column—Three-ball macro (Kontes K-503000-0232, or equivalent).
    - 6.8.2.4 Boiling chips.
      - 6.8.2.4.1 Glass or silicon carbide—Approximately 10/40 mesh, extracted with methylene chloride and baked at 450°C for one hour minimum.
      - 6.8.2.4.2 Fluoropolymer (optional)—Extracted with methylene chloride.
    - 6.8.2.5 Water bath—Heated, with concentric ring cover, capable of maintaining a temperature within  $\pm 2^{\circ}\text{C}$ , installed in a fume hood.
  - 6.8.3 Nitrogen blowdown apparatus—Equipped with water bath controlled in the range of 30 - 60°C (N-Evap, Organomation Associates, Inc., South Berlin, MA, or equivalent), installed in a fume hood.
  - 6.8.4 Sample vials



- 6.8.4.1 Amber glass, 2- to 5-mL with fluoropolymer-lined screw-cap.
- 6.8.4.2 Glass, 0.3-mL, conical, with fluoropolymer-lined screw or crimp cap.
- 6.9 Gas chromatograph—Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.
  - 6.9.1 GC columns—The pair of GC columns listed below are capable of resolving all 209 PCB congeners. Other GC columns may be used so long as PCBs 126 and 169 are each resolved from their respective most closely eluted leading and trailing congeners. The valley height between PCB 126 or 169 and its respective most closely eluted leading and trailing congeners must be less than 10 percent of the height of the shorter of the pair.
  - 6.9.2 Column #1— $30 \pm 5$ -m long  $\times$   $0.25 \pm 0.02$ -mm ID; 0.25- $\mu$ m film SPB-Octyl (Supelco 2-4218, or equivalent).
  - 6.9.3 Column #2— $30 \pm 5$ -m long  $\times$   $0.25 \pm 0.02$ -mm ID; 0.25- $\mu$ m film DB-1 (J&W, or equivalent).
- 6.10 Mass spectrometer—28- to 40-eV electron impact ionization, shall be capable of repetitively selectively monitoring 12 exact  $m/z$ 's minimum at high resolution ( $\geq 10,000$ ) during a period less than 1.5 seconds, and shall meet all of the performance specifications in Section 10.
- 6.11 GC/MS interface—The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.
- 6.12 Data system—Capable of collecting, recording, and storing MS data.

## 7.0 Reagents and Standards

- 7.1 pH adjustment and back-extraction.
  - 7.1.1 Potassium hydroxide—Dissolve 20 g reagent grade KOH in 100 mL reagent water.
  - 7.1.2 Sulfuric acid—Reagent grade (specific gravity 1.84).
  - 7.1.3 Hydrochloric acid—Reagent grade, 6N.
  - 7.1.4 Sodium chloride—Reagent grade, prepare at 5% (w/v) solution in reagent water.
- 7.2 Solution drying and evaporation.
  - 7.2.1 Solution drying—Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400°C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.
  - 7.2.2 Tissue drying—Sodium sulfate, reagent grade, powdered, treated and stored as above.
  - 7.2.3 Prepurified nitrogen.
- 7.3 Extraction.

- 7.3.1 Solvents—Acetone, toluene, cyclohexane, hexane, methanol, methylene chloride, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences.
- 7.3.2 White quartz sand, 60/70 mesh—For Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9, or equivalent). Bake at 450°C for 4 hour minimum.
- 7.4 GPC calibration solution—Prepare a solution containing 300 mg/mL corn oil, TBD mg/mL PCB 209, 1.4 mg/mL pentachlorophenol, 0.1 mg/mL perylene, and 0.5 mg/mL sulfur. [To be modified if necessary.]
- 7.5 Adsorbents for sample cleanup.
- 7.5.1 Silica gel.
- 7.5.1.1 Activated silica gel—100-200 mesh, Supelco 1-3651 (or equivalent), 100-200 mesh, rinsed with methylene chloride, baked at 180°C for a minimum of 1 hour, cooled in a desiccator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.
- 7.5.1.2 Acid silica gel (30% w/w)—Thoroughly mix 44.0 g of concentrated sulfuric acid with 100.0 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.
- 7.5.1.3 Basic silica gel—Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.
- 7.5.1.4 Potassium silicate.
- 7.5.1.4.1 Dissolve 56 g of high purity potassium hydroxide (Aldrich, or equivalent) in 300 mL of methanol in a 750- to 1000-mL flat-bottom flask.
- 7.5.1.4.2 Add 100 g of activated silica gel (Section 7.4.1.1) and a stirring bar, and stir on a hot plate at 60-70°C for 1-2 hours.
- 7.5.1.4.3 Decant the liquid and rinse the potassium silicate twice with 100-mL portions of methanol, followed by a single rinse with 100 mL of methylene chloride.
- 7.5.1.4.4 Spread the potassium silicate on solvent-rinsed aluminum foil and dry for 2-4 hours in a hood.
- 7.5.1.4.5 Activate overnight at 200-250°C.
- 7.5.2 Carbon.
- 7.5.2.1 Carbopak C—(Supelco 1-0258, or equivalent).
- 7.5.2.2 Celite 545—(Supelco 2-0199, or equivalent).
- 7.5.2.3 Thoroughly mix 18.0 g Carbopak C and 18.0 g Celite 545 to produce a 50% w/w mixture. Activate the mixture at 130°C for a minimum of 6 hours. Store in a desiccator.
- 7.5.3 Anthropogenic isolation column—Pack the column in Section 6.7.4.3 from bottom to top with the following:

- 7.5.3.1 2 g silica gel (Section 7.5.1.1).
- 7.5.3.2 2 g potassium silicate (Section 7.5.1.4).
- 7.5.3.3 2 g granular anhydrous sodium sulfate (Section 7.2.1).
- 7.5.3.4 10 g acid silica gel (Section 7.5.1.2).
- 7.5.3.5 2 g granular anhydrous sodium sulfate.
- 7.5.4 Florisil column
  - 7.5.4.1 Florisil—PR grade, 60-100 mesh (U.S. Silica Corp, Berkeley Springs, WV, or equivalent). Fill a clean 1- to 2-L bottle 1/2 to 2/3 full with Florisil and place in an oven at 130-150 °C for a minimum of three days.
  - 7.5.4.2 Immediately prior to use, dry pack a 300-mm x 22-mm ID glass column (Section 6.7.4.3) bottom to top with 0.5-1.0 cm of anhydrous sodium sulfate (Section 7.2.1), 10-10.5 cm of warm to hot activated Florisil (Section 7.5.4.1), and 1-2 cm of warm to hot anhydrous sodium sulfate. Allow the column to cool and wet immediately with 100 mL of n-hexane to prevent water from entering.
  - 7.5.4.3 Using the procedure in Section 13.7, establish the elution pattern for each carton of Florisil received.
- 7.6 Reference matrices—Matrices in which the PCBs and interfering compounds are not detected by this method.
  - 7.6.1 Reagent water—Bottled water purchased locally, or prepared by passage through activated carbon.
  - 7.6.2 High-solids reference matrix—Playground sand or similar material. Prepared by extraction with methylene chloride and/or baking at 450°C for a minimum of 4 hours.
  - 7.6.3 Paper reference matrix—Glass-fiber filter, Gelman type A, or equivalent. Cut paper to simulate the surface area of the paper sample being tested.
  - 7.6.4 Tissue reference matrix—Corn or other vegetable oil. May be prepared by extraction with methylene chloride.
  - 7.6.5 Other matrices—This method may be verified on any reference matrix by performing the tests given in Section 9.2. Ideally, the matrix should be free of the PCBs, but in no case shall the background level of the PCBs in the reference matrix exceed three times the minimum levels in Table 2. If low background levels of the PCBs are present in the reference matrix, the spike level of the analytes used in Section 9.2 should be increased to provide a spike-to-background ratio in the range of 1:1 to 5:1 (Reference 11).
- 7.7 Standard solutions—Purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with fluoropolymer-lined caps. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, the solution should be replaced.
- 7.8 Stock solutions.

- 7.8.1 Preparation—Prepare in nonane per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories (CIL), Woburn, MA, or equivalent). Observe the safety precautions in Section 5, and the recommendation in Section 5.1.2.
- 7.8.2 Dissolve an appropriate amount of assayed reference material in solvent. For example, weigh 1 to 2 mg of PCB 126 to three significant figures in a 10-mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the PCB is completely dissolved, transfer the solution to a clean 15-mL vial with fluoropolymer-lined cap.
- 7.8.3 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from several vendors.
- 7.9 PAR stock solution.
- 7.9.1 All PCBs—Using the solutions in Section 7.8, prepare the PAR stock solution to contain the PCBs of interest at the concentrations shown in Table 3. When diluted, the solution will become the PAR (Section 7.14).
- 7.9.2 If the toxic, non-ortho, co-planar PCBs (PCBs 77, 126, and 169) only are to be determined, prepare the PAR stock solution to contain these compounds only.
- 7.10 Labeled-compound spiking solution.
- 7.10.1 All toxic PCBs—From stock solutions, or from purchased mixtures, prepare this solution to contain the labeled compounds in nonane at the concentrations shown in Table 3. This solution is diluted with acetone prior to use (Section 7.10.3).
- 7.10.2 If PCBs 77, 126, and 169 only are to be determined, prepare the labeled-compound solution to contain these compounds only. This solution is diluted with acetone prior to use (Section 7.10.3).
- 7.10.3 Dilute a sufficient volume of the labeled compound solution (Section 7.10.1 or 7.10.2) by a factor of 50 with acetone to prepare a diluted spiking solution. Each sample requires 1.0 mL of the diluted solution, but no more solution should be prepared than can be used in one day.
- 7.11 Cleanup standard—Prepare PCBs 81 and 111 in nonane at the concentration shown in Table 3. The cleanup standard is added to all extracts prior to cleanup to measure the efficiency of the cleanup process.
- 7.12 Internal standard(s).
- 7.12.1 All toxic PCBs—Prepare the internal standard solution to contain labeled PCBs 52, 101, 138, 178, and 209 in nonane at the concentration shown in Table 3.
- 7.12.2 If PCBs 77, 126, and 169 only are to be determined, the internal standard solution may be prepared to contain PCBs 52, 101, and 138 only.
- 7.13 Calibration standards (CS1 through CS5)—Combine the solutions in Sections 7.9-7.12 to produce the five calibration solutions shown in Table 4 in nonane. These solutions permit the relative response (labeled to native) and response factor to be measured as a function of concentration. The CS3 standard is used for calibration verification (VER). If the PCBs 77, 126, and 169 only are to be determined, combine the solutions appropriate to these compounds.

- 7.14 Precision and recovery (PAR) standard—Used for determination of initial (Section 9.2) and ongoing (Section 15.5) precision and recovery. Dilute 200 µL of the PAR stock solution (Section 7.9.1 or 7.9.2) to 10 mL with acetone for each sample matrix for each sample batch. One mL of each are required for the blank and OPR with each matrix in each batch.
- 7.15 GC retention time window defining solution and isomer specificity test standard—Used to define the beginning and ending retention times for the PCB congeners and to demonstrate isomer specificity of the GC columns employed for determination of PCB 126. The standard must contain the compounds listed in Table 5 (CIL, or equivalent), at a minimum. It is not necessary to monitor all of the window-defining compounds if PCBs 77, 126, and 169 only are to be determined. In this case, a congener-specificity test standard containing the most closely eluted isomers listed in Table 5 (CIL, or equivalent) may be used.
- 7.16 QC Check Sample—A QC Check Sample should be obtained from a source independent of the calibration standards. Ideally, this check sample would be a certified standard reference material (SRM) containing the PCBs in known concentrations in a sample matrix similar to the matrix under test. The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland has SRMs for several individual PCB congeners, and as Aroclors in transformer and motor oil, in combination with pesticides in cod liver oil, and in combination with 2,3,7,8-TCDD in human serum.
- 7.17 Stability of solutions—Standard solutions used for quantitative purposes (Sections 7.9 through 7.15) should be analyzed periodically, and should be assayed against reference standards before further use.

## 8.0 Sample Collection, Preservation, Storage, and Holding Times.

- 8.1 Collect samples in amber glass containers following conventional sampling practices (Reference 12).
- 8.2 Aqueous samples
- 8.2.1 Samples that flow freely are collected as grab samples or in refrigerated bottles using automatic sampling equipment.
- 8.2.2 If residual chlorine is present, add 80 mg sodium thiosulfate per liter of water. EPA Methods 330.4 and 330.5 may be used to measure residual chlorine (Reference 13).
- 8.2.3 Adjust sample pH 2-3 with sulfuric acid.
- 8.2.4 Maintain aqueous samples in the dark at 0-4°C from the time of collection until receipt at the laboratory. Store in the dark at 0-4°C.
- 8.3 Solid samples
- 8.3.4 Solid samples are collected as grab samples using wide-mouth jars.
- 8.3.4 Maintain solid, semi-solid, oily, and mixed-phase samples in the dark at <4°C from the time of collection until receipt at the laboratory. Store solid, semi-solid, oily, and mixed-phase samples in the dark at <-10°C.
- 8.4 Fish and tissue samples.

- 8.4.1 Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.
- 8.4.2 Fish collected in the field should be wrapped in aluminum foil, and must be maintained at a temperature less than 4°C from the time of collection until receipt at the laboratory.
- 8.4.3 Samples must be frozen upon receipt at the laboratory and maintained in the dark at <-10°C until prepared. Maintain unused sample in the dark at <-10°C.
- 8.5 Holding times.
  - 8.5.1 There are no demonstrated maximum holding times associated with the PCBs in aqueous, solid, semi-solid, tissues, or other sample matrices. If stored in the dark at 0-4°C and preserved as given above (if required), aqueous samples may be stored for up to one year. Similarly, if stored in the dark at <-10°C, solid, semi-solid, multi-phase, and tissue samples may be stored for up to one year.
  - 8.5.2 Store sample extracts in the dark at <-10°C until analyzed. If stored in the dark at <-10°C, sample extracts may be stored for up to one year.

## 9.0 Quality Assurance/Quality Control

- 9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 14). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

If the method is to be applied to sample matrix other than water (e.g., soils, filter cake, compost, tissue) the most appropriate alternate matrix (Sections 7.6.2-7.6.5 and 7.16) is substituted for the reagent water matrix (Section 7.6.1) in all performance tests.
- 9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.
- 9.1.2 In recognition of advances that are occurring in analytical technology, and to allow the analyst to overcome sample matrix interferences, the analyst is permitted certain options to improve separations or lower the costs of measurements. These options include alternate extraction, concentration, cleanup procedures, and changes in columns and detectors. Alternate determinative techniques, such as the substitution of spectroscopic or immunoassay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or better than the specificity of the techniques in this method for the analytes of interest.
  - 9.1.2.1 Each time a modification is made to this method, the analyst is required to repeat the procedure in Section 9.2. If the detection limit of the method will be affected by the change, the laboratory is required to demonstrate that the MDL (40 CFR Part 136, Appendix B) is lower than one-third the regulatory compliance level or one-third the

ML in this method, whichever is higher. If calibration will be affected by the change, the analyst must recalibrate the instrument per Section 10.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modifications.

9.1.2.2.2 A listing of pollutant(s) measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating reason(s) for the modifications.

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

- a) Calibration (Section 10.5-10.7).
- b) Calibration verification (Section 15.3).
- c) Initial precision and recovery (Section 9.2).
- d) Labeled compound recovery (Section 9.3).
- e) Analysis of blanks (Section 9.5).
- f) Accuracy assessment (Section 9.4).

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

- a) Sample numbers and other identifiers.
- b) Extraction dates.
- c) Analysis dates and times.
- d) Analysis sequence/run chronology.
- e) Sample weight or volume (Section 11).
- f) Extract volume prior to each cleanup step (Section 13).
- g) Extract volume after each cleanup step (Section 13).
- h) Final extract volume prior to injection (Section 14).
- i) Injection volume (Section 14.3).
- j) Dilution data, differentiating between dilution of a sample or extract (Section 17.5).
- k) Instrument and operating conditions.
- l) Column (dimensions, liquid phase, solid support, film thickness, etc).
- m) Operating conditions (temperatures, temperature program, flow rates).
- n) Detector (type, operating conditions, etc).
- o) Chromatograms, printer tapes, and other recordings of raw data.
- p) Quantitation reports, data system outputs, and other data to link the raw data to the results reported.

9.1.3 Analyses of method blanks are required to demonstrate freedom from contamination (Section 4.3). The procedures and criteria for analysis of a method blank are described in Sections 9.5 and 15.6.

9.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in Section 9.3. When results of these spikes indicate

- atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits. Procedures for dilution are given in Section 17.5.
- 9.1.5 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the ongoing precision and recovery aliquot that the analytical system is in control. These procedures are described in Sections 15.1 through 15.5.
- 9.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Section 9.4.
- 9.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.
- 9.2.1 For low solids (aqueous) samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with the diluted labeled compound spiking solution (Section 7.10.3) and the precision and recovery standard (Section 7.14) according to the procedures in Sections 11 through 18. For an alternative sample matrix, four aliquots of the alternative reference matrix (Section 7.6) are used. All sample processing steps that are to be used for processing samples, including preparation (Section 11), extraction (Section 12), and cleanup (Section 13), shall be included in this test.
- 9.2.2 Using results of the set of four analyses, compute the average concentration ( $\bar{X}$ ) of the extracts in ng/mL and the standard deviation of the concentration ( $s$ ) in ng/mL for each compound, by isotope dilution for PCBs with a labeled analog, and by internal standard for the PCBs without a labeled analog and the labeled compounds.
- 9.2.3 For each PCB and labeled compound, compare  $s$  and  $\bar{X}$  with the corresponding limits for initial precision and recovery in Table 6. If PCBs 77, 126, and 169 only are to be determined, compare  $s$  and  $\bar{X}$  with the corresponding limits for initial precision and recovery in Table 6a. If  $s$  and  $\bar{X}$  for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual  $s$  exceeds the precision limit or any individual  $\bar{X}$  falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test (Section 9.2).
- 9.3 The laboratory shall spike all samples with the diluted labeled compound spiking solution (Section 7.10.3) to assess method performance on the sample matrix.
- 9.3.1 Analyze each sample according to the procedures in Sections 11 through 18.
- 9.3.2 Compute the percent recovery of the labeled compounds and the cleanup standard using the internal standard method (Section 17.2).
- 9.3.3 The recovery of each labeled compound must be within the limits in Table 7 when all of the toxic PCBs are determined, and within the limits in Table 7a when PCBs 77, 126, and 169 only are determined. If the recovery of any compound falls outside of these limits, method performance is unacceptable for that compound in that sample. Additional cleanup procedures must then be employed to attempt to bring the recovery within the normal range. If the recovery cannot be brought within the normal range after all cleanup procedures have been employed, water samples are diluted and smaller amounts of soils, sludges, sediments, and other matrices are analyzed per Section 18.4.



- 9.4 Recovery of labeled compounds from samples should be assessed and records should be maintained.
  - 9.4.1 After the analysis of five samples of a given matrix type (water, soil, sludge, pulp, etc.) for which the labeled compounds pass the tests in Section 9.3, compute the average percent recovery ( $R$ ) and the standard deviation of the percent recovery ( $S_R$ ) for the labeled compounds only. Express the assessment as a percent recovery interval from  $R - 2S_R$  to  $R + 2S_R$  for each matrix. For example, if  $R = 90\%$  and  $S_R = 10\%$  for five analyses of pulp, the recovery interval is expressed as 70 to 110%.
  - 9.4.2 Update the accuracy assessment for each labeled compound in each matrix on a regular basis (e.g., after each five to ten new measurements).
- 9.5 Method blanks—Reference matrix method blanks are analyzed to demonstrate freedom from contamination (Section 4.3).
  - 9.5.1 Prepare, extract, clean up, and concentrate a method blank with each sample batch (samples of the same matrix started through the extraction process on the same 12-hour shift, to a maximum of 20 samples). The matrix for the method blank shall be similar to sample matrix for the batch, e.g., a 1-L reagent water blank (Section 7.6.1), high-solids reference matrix blank (Section 7.6.2), paper matrix blank (Section 7.6.3); tissue blank (Section 7.6.4) or alternative reference matrix blank (Section 7.6.5). Analyze the blank immediately after analysis of the OPR (Section 15.5) to demonstrate freedom from contamination.
  - 9.5.2 If any PCB (Table 1) is found in the blank at greater than the minimum level (Table 2) or one-third the regulatory compliance level, whichever is greater; or if any potentially interfering compound is found in the blank at the minimum level for each level of chlorination given in Table 2 (assuming a response factor of 1 relative to the internal standard at that level of chlorination for compounds not listed in Table 1), analysis of samples is halted until the blank associated with the sample batch shows no evidence of contamination at this level. All samples must be associated with an uncontaminated method blank before the results for those samples may be reported for regulatory compliance purposes.
- 9.6 QC Check Sample—Analyze the QC Check Sample (Section 7.16) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least quarterly.
- 9.7 The specifications contained in this method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state. The standards used for calibration (Section 10), calibration verification (Section 15.3), and for initial (Section 9.2) and ongoing (Section 15.5) precision and recovery should be identical, so that the most precise results will be obtained. A GC/MS instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of PCBs by this method.
- 9.8 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when the internal standard method is used.

## 10.0 Calibration

10.1 Establish the operating conditions necessary to meet the minimum retention times for the internal standards in Section 10.2.4 and the relative retention times for the PCBs in Table 2.

10.1.1 Suggested GC operating conditions:

Injector temperature: 290°C  
Interface temperature: 290°C  
Initial temperature: 150°C  
Initial time: 2 minutes  
Temperature program: 150 to 200°C at 10°C/minute  
200 to 280°C at 2.0°C/minute

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**Note:** All portions of the column that connect the GC to the ion source shall remain at or above the interface temperature specified above during analysis to preclude condensation of less volatile compounds.

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The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, IPR and OPR aliquots, and samples.

10.1.2 Mass spectrometer (MS) resolution—Obtain a selected ion current profile (SICP) of each analyte in Table 3 at the two exact  $m/z$ 's specified in Table 8 and at  $\geq 10,000$  resolving power by injecting an authentic standard of the PCBs either singly or as part of a mixture in which there is no interference between closely eluted components.

10.1.2.1 The analysis time for PCBs may exceed the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory and a lock-mass  $m/z$  from PFK is used for drift correction. The lock-mass  $m/z$  is dependent on the exact  $m/z$ 's monitored within each descriptor, as shown in Table 8. The level of PFK metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass  $m/z$  signal (regardless of the descriptor number) does not exceed 10% of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

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**Note:** Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source necessitating increased frequency of source cleaning.

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10.1.2.2 If the HRMS has the capability to monitor resolution during the analysis, it is acceptable to terminate the analysis when the resolution falls below 10,000 to save reanalysis time.

- 10.1.2.3 Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley) at  $m/z$  304.9824 or any other reference signal close to  $m/z$  305 (from PeCB). For each descriptor (Table 8), monitor and record the resolution and exact  $m/z$ 's of three to five reference peaks covering the mass range of the descriptor. The resolution must be greater than or equal to 10,000, and the deviation between the exact  $m/z$  and the theoretical  $m/z$  (Table 8) for each exact  $m/z$  monitored must be less than 5 ppm.
- 10.2 Ion abundance ratios, minimum levels, signal-to-noise ratios, and absolute retention times—Choose an injection volume of either 1 or 2  $\mu\text{L}$ , consistent with the capability of the HRGC/HRMS instrument. Inject a 1 or 2  $\mu\text{L}$  aliquot of the CS1 calibration solution (Table 4) using the GC conditions from Section 10.1.1. If PCBs 77, 126, and 169 only are to be determined, the operating conditions and specifications below apply to analysis of those compounds only.
- 10.2.1 Measure the SICP areas for each analyte, and compute the ion abundance ratios at the exact  $m/z$ 's specified in Table 8. Compare the computed ratio to the theoretical ratio given in Table 9.
- 10.2.1.1 The exact  $m/z$ 's to be monitored in each descriptor are shown in Table 8. Each group or descriptor shall be monitored in succession as a function of GC retention time to ensure that all of the toxic PCBs are detected. Additional  $m/z$ 's may be monitored in each descriptor, and the  $m/z$ 's may be divided among more than the descriptors listed in Table 8, provided that the laboratory is able to monitor the  $m/z$ 's of all the PCBs that may elute from the GC in a given retention-time window. If PCBs 77, 126, and 169 only are to be determined, the descriptors may be modified to include only the exact  $m/z$ 's for the tetra-, penta-, and hexa-, congeners, and the lock  $m/z$ 's.
- 10.2.1.2 The mass spectrometer shall be operated in a mass-drift correction mode, using PFK to provide lock  $m/z$ 's. The lock mass for each group of  $m/z$ 's is shown in Table 8. Each lock mass shall be monitored and shall not vary by more than  $\pm 20\%$  throughout its respective retention time window. Variations of the lock mass by more than 20% indicate the presence of coeluting interferences that may significantly reduce the sensitivity of the mass spectrometer. Reinjection of another aliquot of the sample extract will not resolve the problem. Additional cleanup of the extract may be required to remove the interferences.
- 10.2.2 All PCBs and labeled compounds in the CS1 standard shall be within the QC limits in Table 9 for their respective ion abundance ratios; otherwise, the mass spectrometer shall be adjusted and this test repeated until the  $m/z$  ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the test.
- 10.2.3 Verify that the HRGC/HRMS instrument meets the minimum levels in Table 2. The peaks representing the PCBs and labeled compounds in the CS1 calibration standard must have signal-to-noise ratios (S/N) greater than or equal to 10.0. Otherwise, the mass spectrometer shall be adjusted and this test repeated until the minimum levels in Table 2 are met.
- 10.2.4 The absolute retention time of PCB 169 (Section 7.12) shall exceed 20 minutes on the SPB-Octyl column, and the retention time of PCB 157 shall exceed 25 minutes on the DB-

1 column; otherwise, the GC temperature program shall be adjusted and this test repeated until the above-stated minimum retention time criteria are met.

- 10.3 Retention-time windows—Analyze the window defining mixtures (Section 7.15) using the optimized temperature program in Section 10.1. Table 5 gives the elution order (first/last) of the window-defining compounds. If PCBs 77, 126, and 169 only are to be determined, the window-defining tetra-, penta-, and hepta- PCBs are the only compounds that need to be tested.
- 10.4 Isomer specificity
- 10.4.1 Analyze the isomer specificity test standards (Section 7.15) using the procedure in Section 14 and the optimized conditions for sample analysis (Section 10.1.1).
- 10.4.2 Compute the percent valley between the GC peaks that elute most closely to PCB 126 and 169 on the SPB-Octyl column and to PCB 156/157 on the DB-1 column, per Figures 6 and 7.
- 10.4.3 Verify that the height of the valley between the most closely eluted isomers and the PCBs given in Section 10.4.2 is less than 25% (computed as  $100 \times y$  in Figures 6 and 7). If the valley exceeds 25%, adjust the analytical conditions and repeat the test or replace the GC column and recalibrate (Sections 10.1.2 through 10.7).
- 10.5 Calibration by isotope dilution—Isotope dilution calibration is used for the native PCBs for which labeled compounds are added to samples prior to extraction. The reference compound for each native compound is shown in Table 2.
- 10.5.1 A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (RR) (labeled to native) vs. concentration in standard solutions is plotted or computed using a linear regression. Relative response is determined according to the procedures described below. Five calibration points are employed.
- 10.5.2 The response of each native PCB relative to its labeled analog is determined using the area responses of both the primary and secondary exact  $m/z$ 's specified in Table 8, for each calibration standard, as follows:

$$RR = \frac{(A1_n + A2_n) C_l}{(A1_l + A2_l) C_n}$$

Where:

$A1_n$  and  $A2_n$  = The areas of the primary and secondary  $m/z$ 's for the PCB.

$A1_l$  and  $A2_l$  = The areas of the primary and secondary  $m/z$ 's for the labeled compound.

$C_l$  = The concentration of the labeled compound in the calibration standard (Table 4).

$C_n$  = The concentration of the native compound in the calibration standard (Table 4).

- 10.5.3 To calibrate the analytical system by isotope dilution, inject a volume of calibration standards CS1 through CS5 (Section 7.13 and Table 4) identical to the volume chosen in Section 10.2, using the procedure in Section 14 and the conditions in Section 10.1.1 and Table 2. Compute the relative response (RR) at each concentration.

- 10.5.4 **Linearity**—If the relative response for any compound is constant (less than 20% coefficient of variation) over the five-point calibration range, an averaged relative response may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-point calibration range.
- 10.6 **Calibration by internal standard**—The internal standard method is applied to determination of the native PCBs for which a labeled compound is not available, and to the determination of labeled compounds for intralaboratory statistics (Sections 9.4 and 15.5.4).
- 10.6.1 **Response factors**—Calibration requires the determination of response factors (RF) defined by the following equation:

$$RF = \frac{(AI_p + A2_p) C_i}{(AI_i + A2_i) C_p}$$

Where:

- $AI_p$  and  $A2_p$  = The areas of the primary and secondary  $m/z$ s for the PCB.  
 $AI_i$  and  $A2_i$  = The areas of the primary and secondary  $m/z$ s for the internal standard.  
 $C_i$  = The concentration of the internal standard (Table 4).  
 $C_p$  = The concentration of the compound in the calibration standard (Table 4).

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**Note:** There is only one  $m/z$  for PCBs 81 and 111 [This note may not be necessary]. See Table 8.

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- 10.6.2 To calibrate the analytical system by internal standard, inject 1.0 or 2.0  $\mu$ L of calibration standards CS1 through CS5 (Section 7.13 and Table 4) using the procedure in Section 14 and the conditions in Section 10.1.1 and Table 2. Compute the response factor (RF) at each concentration.
- 10.6.3 **Linearity**—If the response factor (RF) for any compound is constant (less than 35% coefficient of variation) over the five-point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the five-point range.
- 10.7 **Combined calibration**—By using calibration solutions (Section 7.13 and Table 4) containing the native PCBs, labeled compounds, and the internal standards, a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (Section 15.3) by analyzing the calibration verification standard (VER, Table 4). Recalibration is required if any of the calibration verification criteria (Section 15.3) cannot be met.
- 10.8 **Data storage**—MS data shall be collected, recorded, and stored.
- 10.8.1 **Data acquisition**—The signal at each exact  $m/z$  shall be collected repetitively throughout the monitoring period and stored on a mass storage device.

- 10.8.2 Response factors and multipoint calibrations—The data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and multipoint calibration curves. Computations of relative standard deviation (coefficient of variation) shall be used to test calibration linearity. Statistics on initial performance (Section 9.2) and ongoing performance (Section 15.5) should be computed and maintained, either on the instrument data system, or on a separate computer system.

## 11.0 Sample Preparation

- 11.1 Sample preparation involves modifying the physical form of the sample so that the PCBs can be extracted efficiently. In general, the samples must be in a liquid form or in the form of finely divided solids in order for efficient extraction to take place. Table 10 lists the phases and suggested quantities for extraction of various sample matrices.
- For samples known or expected to contain high levels of the PCBs, the smallest sample size representative of the entire sample should be used (see Section 17.5).
- For all samples, the blank and IPR/OPR aliquots must be processed through the same steps as the sample to check for contamination and losses in the preparation processes.
- 11.1.1 For samples that contain particles, percent solids and particle size are determined using the procedures in Sections 11.2 and 11.3, respectively.
- 11.1.2 Aqueous samples—Because PCBs may be bound to suspended particles, the preparation of aqueous samples is dependent on the solids content of the sample.
- 11.1.2.1 Aqueous samples containing one percent solids or less are prepared per Section 11.4 and extracted directly using the SPE technique in 12.2.
- 11.1.2.2 For aqueous samples containing greater than one percent solids, a sample aliquot sufficient to provide 10 g of dry solids is used, as described in Section 11.5.
- 11.1.3 Solid samples are prepared using the procedure described in Section 11.5 followed by extraction via the SDS procedure in Section 12.3.
- 11.1.4 Multiphase samples—The phase(s) containing the PCBs is separated from the non-PCB phase using pressure filtration and centrifugation, as described in Section 11.6. The PCBs will be in the organic phase in a multiphase sample in which an organic phase exists.
- 11.1.5 Procedures for grinding, homogenization, and blending of various sample phases are given in Section 11.7.
- 11.1.6 Tissue samples—Preparation procedures for fish and other tissues are given in Section 11.8.
- 11.2 Determination of percent suspended solids.

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**Note:** *This aliquot is used for determining the solids content of the sample, not for determination of PCBs.*

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- 11.2.1 Aqueous liquids and multi-phase samples consisting of mainly an aqueous phase.
- 11.2.1.1 Desiccate and weigh a GF/D filter (Section 6.5.3) to three significant figures.
- 11.2.1.2 Filter  $10.0 \pm 0.02$  mL of well-mixed sample through the filter.
- 11.2.1.3 Dry the filter a minimum of 12 hours at  $110 \pm 5^\circ\text{C}$  and cool in a desiccator.

11.2.1.4 Calculate percent solids as follows:

$$\% \text{ solids} = \frac{\text{weight of sample aliquot after drying (g)} - \text{weight of filter (g)}}{10 \text{ g}} \times 100$$

11.2.2 Non-aqueous liquids, solids, semi-solid samples, and multi-phase samples in which the main phase is not aqueous; but not tissues.

11.2.2.1 Weigh 5 to 10 g of sample to three significant figures in a tared beaker.

11.2.2.2 Dry a minimum of 12 hours at  $110 \pm 5^\circ\text{C}$ , and cool in a desiccator.

11.2.2.3 Calculate percent solids as follows:

$$\% \text{ solids} = \frac{\text{weight of sample aliquot after drying}}{\text{weight of sample aliquot before drying}} \times 100$$

11.3 Determination of particle size.

11.3.1 Spread the dried sample from Section 11.2.2.2 on a piece of filter paper or aluminum foil in a fume hood or glove box.

11.3.2 Estimate the size of the particles in the sample. If the size of the largest particles is greater than 1 mm, the particle size must be reduced to 1 mm or less prior to extraction using the procedures in Section 11.7.

11.4 Preparation of aqueous samples containing one percent suspended solids or less.

11.4.1 Aqueous samples containing one percent suspended solids or less are prepared using the procedure below and extracted using the SPE technique in Section 12.2.

11.4.2 Preparation of sample and QC aliquots.

11.4.2.1 Mark the original level of the sample on the sample bottle for reference. Weigh the sample plus bottle to  $\pm 1$  g.

11.4.2.2 Spike 1.0 mL of the diluted labeled-compound spiking solution (Section 7.10.3) into the sample bottle. Cap the bottle and mix the sample by careful shaking. Allow the sample to equilibrate for 1 to 2 hours, with occasional shaking.

11.4.2.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, place two 1.0-L aliquots of reagent water in clean sample bottles or flasks.

11.4.2.4 Spike 1.0 mL of the diluted labeled-compound spiking solution (Section 7.10.3) into both reagent water aliquots. One of these aliquots will serve as the method blank.

11.4.2.5 Spike 1.0 mL of the PAR standard (Section 7.14) into the remaining reagent water aliquot. This aliquot will serve as the OPR (Section 15.5).

11.4.2.6 Add 5 mL of methanol to the sample and QC aliquots. Cap and shake the sample and QC aliquots to mix thoroughly, and proceed to Section 12.2 for extraction.

**11.5 Preparation of samples containing ~~greater~~ than one percent solids.**

- 11.5.1 Weigh a well-mixed aliquot of each sample (of the same matrix type) sufficient to provide 10 g of dry solids (based on the solids determination in Section 11.2) into a clean beaker or glass jar.
- 11.5.2 Spike 1.0 mL of the diluted labeled compound spiking solution (Section 7.10.3) into the sample.
- 11.5.3 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12 hour shift, weigh two 10-g aliquots of the appropriate reference matrix (Section 7.6) into clean beakers or glass jars.
- 11.5.4 Spike 1.0 mL of the diluted labeled compound spiking solution (Section 7.10.3) into each reference matrix aliquot. One aliquot will serve as the method blank. Spike 1.0 mL of the PAR standard (Section 7.14) into the other reference matrix aliquot. This aliquot will serve as the OPR (Section 15.5).
- 11.5.5 Stir or tumble and equilibrate the aliquots for 1 to 2 hours.
- 11.5.6 Decant excess water. If necessary to remove water, filter the sample through a glass-fiber filter and discard the aqueous liquid.
- 11.5.7 If particles >1 mm are present in the sample (as determined in Section 11.3.2), spread the sample on clean aluminum foil in a hood. After the sample is dry, grind to reduce the particle size (Section 11.7).
- 11.5.8 Extract the sample and QC aliquots using the SDS procedure in Section 12.3.

**11.6 Multiphase samples.**

- 11.6.1 Using the percent solids determined in Section 11.2.1 or 11.2.2, determine the volume of sample that will provide 10 g of solids, up to 1 L of sample.
- 11.6.2 Pressure filter the amount of sample determined in Section 11.6.1 through Whatman GF/D glass-fiber filter paper (Section 6.5.3). Pressure filter the blank and OPR aliquots through GF/D papers also. If necessary to separate the phases and/or settle the solids, centrifuge these aliquots prior to filtration.
- 11.6.3 Discard any aqueous phase (if present). Remove any non-aqueous liquid present and reserve the maximum amount filtered from the sample (Section 11.6.1) or 10 g, whichever is less, for combination with the solid phase (Section 12.3.5).
- 11.6.4 If particles >1 mm are present in the sample (as determined in Section 11.3.2) and the sample is capable of being dried, spread the sample and QC aliquots on clean aluminum foil in a hood. After the aliquots are dry or if the sample cannot be dried, reduce the particle size using the procedures in Section 11.7 and extract the reduced particles using the SDS procedure in Section 12.3. If particles >1 mm are not present, extract the particles and filter in the sample and QC aliquots directly using the SDS procedure in Section 12.3.

**11.7 Sample grinding, homogenization, or blending—Samples with particle sizes greater than 1 mm (as determined in Section 11.3.2) are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix-dependent. In general, hard particles can be reduced by grinding with a mortar and pestle. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or in a blender.**



- 11.7.1 Each size-reducing preparation procedure on each matrix shall be verified by running the tests in Section 9.2 before the procedure is employed routinely.
- 11.7.2 The grinding, homogenization, or blending procedures shall be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.
- 11.7.3 Grinding—Certain papers and pulps, slurries, and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. Grind the sample aliquots from Sections 11.5.7 or 11.6.4 in a clean grinder. Do not allow the sample temperature to exceed 50°C. Grind the blank and reference matrix aliquots using a clean grinder.
- 11.7.4 Homogenization or blending—Particles that are not ground effectively, or particles greater than 1 mm in size after grinding, can often be reduced in size by high speed homogenization or blending. Homogenize and/or blend the particles or filter from Sections 11.5.7 or 11.6.4 for the sample, blank, and OPR aliquots.
- 11.7.5 Extract the aliquots using the SDS procedure in Section 12.3.
- 11.8 Fish and other tissues—Prior to processing tissue samples, the laboratory must determine the exact tissue to be analyzed. Common requests for analysis of fish tissue include whole fish—skin on, whole fish—skin removed, edible fish fillets (filleted in the field or by the laboratory), specific organs, and other portions. Once the appropriate tissue has been determined, the sample must be homogenized.
  - 11.8.1 Homogenization.
    - 11.8.1.1 Samples are homogenized while still frozen, where practical. If the laboratory must dissect the whole fish to obtain the appropriate tissue for analysis, the unused tissues may be rapidly refrozen and stored in a clean glass jar for subsequent use.
    - 11.8.1.2 Each analysis requires 10 g of tissue (wet weight). Therefore, the laboratory should homogenize at least 20 g of tissue to allow for re-extraction of a second aliquot of the same homogenized sample, if re-analysis is required. When whole fish analysis is necessary, the entire fish is homogenized.
    - 11.8.1.3 Homogenize the sample in a tissue homogenizer (Section 6.3.3) or grind in a meat grinder (Section 6.3.4). Cut tissue too large to feed into the grinder into smaller pieces. To assure homogeneity, grind three times.
    - 11.8.1.4 Transfer approximately 10 g (wet weight) of homogenized tissue to a clean, tared, 400- to 500-mL beaker.
    - 11.8.1.5 Transfer the remaining homogenized tissue to a clean jar with a fluoropolymer-lined lid. Seal the jar and store the tissue at <-10°C. Return any tissue that was not homogenized to its original container and store at <-10°C.
  - 11.8.2 QC aliquots.
    - 11.8.2.1 Prepare a method blank by adding approximately 10 g of the oily liquid reference matrix (Section 7.6.4) to a 400- to 500-mL beaker.
    - 11.8.2.2 Prepare a precision and recovery aliquot by adding approximately 10 g of the oily liquid reference matrix (Section 7.6.4) to a separate 400- to 500-mL beaker. Record

the weight to the nearest 10 mg. If the initial precision and recovery test is to be performed, use four aliquots; if the ongoing precision and recovery test is to be performed, use a single aliquot.

### 11.8.3 Spiking.

11.8.3.1 Spike 1.0 mL of the labeled compound spiking solution (Section 7.10.3) into the sample, blank, and OPR aliquot.

11.8.3.2 Spike 1.0 mL of the PAR standard (Section 7.14) into the OPR aliquot.

11.8.4 Extract the aliquots using the procedures in Section 12.4.

## 12.0 Extraction and Concentration

12.1 Extraction procedures include solid phase (Section 12.2) for aqueous liquids; Soxhlet/Dean-Stark (Section 12.3) for solids and filters; and Soxhlet extraction (Section 12.4) for tissues. Acid/base back-extraction (Section 12.5) is used for initial cleanup of extracts.

Macro-concentration procedures include rotary evaporation (Section 12.6.1), heating mantle (Section 12.6.2), and Kuderna-Danish (K-D) evaporation (Section 12.6.3). Micro-concentration uses nitrogen blowdown (Section 12.7).

12.2 SPE of samples containing less than one percent solids.

### 12.2.1 Disk preparation.

12.2.1.1 Remove the test tube from the suction flask (Figure 4). Place an SPE disk on the base of the filter holder and wet with methylene chloride. While holding a GMF 150 filter above the SPE disk with tweezers, wet the filter with methylene chloride and lay the filter on the SPE disk, making sure that air is not trapped between the filter and disk. Clamp the filter and SPE disk between the 1-L glass reservoir and the vacuum filtration flask.

12.2.1.2 Rinse the sides of the reservoir with approx 15 mL of methylene chloride using a squeeze bottle or pipet. Apply vacuum momentarily until a few drops appear at the drip tip. Release the vacuum and allow the filter/disk to soak for approx one minute. Apply vacuum and draw all of the methylene chloride through the filter/disk. Repeat the wash step with approx 15 mL of acetone and allow the filter/disk to air dry.

### 12.2.2 Sample extraction.

12.2.2.1 Pre-wet the disk by adding approx 20 mL of methanol to the reservoir. Pull most of the methanol through the filter/disk, retaining a layer of methanol approx 2 mm thick on the filter. Do not allow the filter/disk to go dry from this point until the extraction is completed.

12.2.2.2 Add approx 20 mL of reagent water to the reservoir and pull most through, leaving a layer approx 2 mm thick on the filter/disk.

12.2.2.3 Allow the sample (Section 11.4.2.2) to stand for 1-2 hours, if necessary, to settle the suspended particles. Decant the clear layer of the sample, the blank (Section 11.4.2.4), or IPR/OPR aliquot (Section 11.4.2.5) into the reservoir and turn on the vacuum to begin the extraction. Adjust the vacuum to complete the extraction in no less than 10

minutes. For samples containing a high concentration of particles (suspended solids), the extraction time may be an hour or longer.

- 12.2.2.4 Before all of the sample has been pulled through the filter/disk, add approx 50 mL of reagent water to the sample bottle, swirl to suspend the solids (if present), and pour into the reservoir. Pull through the filter/disk. Use additional reagent water rinses until all solids are removed.
- 12.2.2.5 Before all of the sample and rinses have been pulled through the filter/disk, rinse the sides of the reservoir with small portions of reagent water.
- 12.2.2.6 Partially dry the filter/disk under vacuum for approx 3 minutes.
- 12.2.3 Elution of the filter/disk.
  - 12.2.3.1 Release the vacuum, remove the entire filter/disk/reservoir assembly from the vacuum flask, and empty the flask. Insert a test tube for eluant collection into the flask. The test tube should have sufficient capacity to contain the total volume of the elution solvent (approx 50 mL) and should fit around the drip tip. The drip tip should protrude into the test tube to preclude loss of sample from spattering when vacuum is applied. Reassemble the filter/disk/reservoir assembly on the vacuum flask.
  - 12.2.3.2 Wet the filter/disk with 4-5 mL of acetone. Allow the acetone to spread evenly across the disk and soak for 15-20 seconds. Pull the acetone through the disk, releasing the vacuum when approx 1 mm thickness remains on the filter.
  - 12.2.3.3 Rinse the sample bottle with approx 20 mL of methylene chloride and transfer to the reservoir. Pull approx half of the solvent through the filter/disk and release the vacuum. Allow the filter/disk to soak for approx 1 minute. Pull all of the solvent through the disk. Repeat the bottle rinsing and elution step with another 20 mL of methylene chloride. Pull all of the solvent through the disk.
  - 12.2.3.4 Release the vacuum, remove the filter/disk/reservoir assembly, and remove the test tube containing the sample solution. Quantitatively transfer the solution to a 250-mL separatory funnel and proceed to Section 12.5 for back-extraction.

### 12.3 SDS extraction of samples containing particles.

- 12.3.1 Charge a clean extraction thimble (Section 6.4.2.2) with 5.0 g of 100/200 mesh silica (Section 7.5.1.1) topped with 100 g of quartz sand (Section 7.3.2).

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**Note:** *Do not disturb the silica layer throughout the extraction process.*

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- 12.3.2 Place the thimble in a clean extractor. Place 30 to 40 mL of toluene in the receiver and 200 to 250 mL of toluene in the flask.
- 12.3.3 Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1 to 2 drops of toluene will fall per second from the condenser tip into the receiver. Extract the apparatus for a minimum of 3 hours.
- 12.3.4 After pre-extraction, cool and disassemble the apparatus. Rinse the thimble with toluene and allow to air dry.

- 12.3.5 Load the wet sample and/or filter from Sections 11.5.8, 11.6.4, 11.7.3, or 11.7.4 and any nonaqueous liquid from Section 11.6.3 into the thimble and manually mix into the sand layer with a clean metal spatula, carefully breaking up any large lumps of sample.
- 12.3.6 Reassemble the pre-extracted SDS apparatus, and add a fresh charge of toluene to the receiver and reflux flask. Apply power to the heating mantle to begin refluxing. Adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction to toluene flow. Frequently check the apparatus for foaming during the first 2 hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.
- 12.3.7 Drain the water from the receiver at 1 to 2 hours and 8 to 9 hours, or sooner if the receiver fills with water. Reflux the sample for a total of 16 to 24 hours. Cool and disassemble the apparatus. Record the total volume of water collected.
- 12.3.8 Remove the distilling flask. Drain the water from the Dean-Stark receiver and add any toluene in the receiver to the extract in the flask.
- 12.3.9 Concentrate the extracts from particles (Sections 11.5-11.7) to approximately 10 mL using the rotary evaporator or heating mantle (Section 12.6.1 or 12.6.2), transfer to a 250-mL separatory funnel, and proceed with back-extraction (Section 12.5).
- 12.4 Extraction of tissue
- 12.4.1 Add 30 to 40 g of powdered anhydrous sodium sulfate to each of the beakers (Section 11.8.4) and mix thoroughly. Cover the beakers with aluminum foil and allow to equilibrate for 12-24 hours. Remix prior to extraction to prevent clumping.
- 12.4.2 Assemble and pre-extract the Soxhlet apparatus per Sections 12.3.1-12.3.4, except use the methylene chloride:hexane (1:1) mixture for the pre-extraction and rinsing and omit the quartz sand. The Dean-Stark moisture trap may also be omitted, if desired.
- 12.4.3 Reassemble the pre-extracted Soxhlet apparatus and add a fresh charge of methylene chloride:hexane to the reflux flask.
- 12.4.4 Transfer the sample/sodium sulfate mixture (Section 12.4.1) to the Soxhlet thimble, and install the thimble in the Soxhlet apparatus.
- 12.4.5 Rinse the beaker with several portions of solvent mixture and add to the thimble. Fill the thimble/receiver with solvent. Extract for 18 to 24 hours.
- 12.4.6 After extraction, cool and disassemble the apparatus.
- 12.4.7 Quantitatively transfer the extract to a macro-concentration device (Section 12.6), and concentrate to near dryness. Set aside the concentration apparatus for re-use.
- 12.4.8 Complete the removal of the solvent using the nitrogen blowdown procedure (Section 12.7) and a water bath temperature of 60°C. Weigh the receiver, record the weight, and return the receiver to the blowdown apparatus, concentrating the residue until a constant weight is obtained.
- 12.4.9 Percent lipid determination—The lipid content is determined by extraction of tissue with the same solvent system (methylene chloride:hexane) that was used in EPA's National Dioxin Study (Reference 15) so that lipid contents are consistent with that study.

- 12.4.9.1 Redissolve the residue in the receiver in hexane and spike 1.0 mL of the cleanup standard (Section 7.11) into the solution.
- 12.4.9.2 Transfer the residue/hexane to the anthropogenic isolation column (Section 13.6.1), retaining the boiling chips in the concentration apparatus. Use several rinses to assure that all material is transferred. If necessary, sonicate or heat the receiver slightly to assure that all material is re-dissolved. Allow the receiver to dry. Weigh the receiver and boiling chips.
- 12.4.9.3 Calculate the lipid content to the nearest three significant figures as follows:

$$\text{Percent lipid} = \frac{\text{Weight of residue (g)}}{\text{Weight of tissue (g)}} \times 100$$

- 12.4.9.4 It is not necessary to determine the lipid content of the blank, IPR, or OPR aliquots.
- 12.5 Back-extraction with base and acid.
  - 12.5.1 Spike 1.0 mL of the cleanup standard (Section 7.11) into the separatory funnels containing the sample and QC extracts from Section 12.2.3.4 or 12.3.9.
  - 12.5.2 Partition the extract against 50 mL of potassium hydroxide solution (Section 7.1.1). Shake for 2 minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the base washing until no color is visible in the aqueous layer, to a maximum of four washings. Minimize contact time between the extract and the base to prevent degradation of the PCBs. Stronger potassium hydroxide solutions may be employed for back-extraction, provided that the laboratory meets the specifications for labeled compound recovery and demonstrates acceptable performance using the procedure in Section 9.2.
  - 12.5.3 Partition the extract against 50 mL of sodium chloride solution (Section 7.1.4) in the same way as with base. Discard the aqueous layer.
  - 12.5.4 Partition the extract against 50 mL of sulfuric acid (Section 7.1.2) in the same way as with base. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.
  - 12.5.5 Repeat the partitioning against sodium chloride solution and discard the aqueous layer.
  - 12.5.6 Pour each extract through a drying column containing 7 to 10 cm of granular anhydrous sodium sulfate (Section 7.2.1). Rinse the separatory funnel with 30 to 50 mL of solvent, and pour through the drying column. Collect each extract in a round-bottom flask. Re-concentrate the sample and QC aliquots per Sections 12.6-12.7, and clean up the samples and QC aliquots per Section 13.
- 12.6 Macro-concentration—Extracts in toluene are concentrated using a rotary evaporator or a heating mantle; extracts in methylene chloride or hexane are concentrated using a rotary evaporator, heating mantle, or Kuderna-Danish apparatus.
  - 12.6.1 Rotary evaporation—Concentrate the extracts in separate round-bottom flasks.

- 12.6.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45°C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, three 2- to 3-mL aliquots of solvent should be rinsed down the feed tube into a waste beaker.
- 12.6.1.2 Attach the round-bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.
- 12.6.1.3 Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15 to 20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask will be steady, but no bumping or visible boiling of the extract will occur.

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**Note:** *If the rate of concentration is too fast, analyte loss may occur.*

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- 12.6.1.4 When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.
  - 12.6.1.5 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.
- 12.6.2 Heating mantle—Concentrate the extracts in separate round-bottom flasks.
- 12.6.2.1 Add one or two clean boiling chips to the round-bottom flask, and attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the round-bottom flask in a heating mantle, and apply heat as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.
  - 12.6.2.2 When the liquid has reached an apparent volume of approximately 10 mL, remove the round-bottom flask from the heating mantle and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the glass joint into the receiver with small portions of solvent.
  - 12.6.2.3 Proceed to Section 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.
- 12.6.3 Kuderna-Danish (K-D)—Concentrate the extracts in separate 500-mL K-D flasks equipped with 10-mL concentrator tubes. The K-D technique is used for solvents such as methylene chloride and hexane. Toluene is difficult to concentrate using the K-D technique unless a water bath fed by a steam generator is used.
- 12.6.3.1 Add 1 to 2 clean boiling chips to the receiver. Attach a three-ball macro Snyder column. Prewet the column by adding approximately 1 mL of solvent through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam.

- 12.6.3.2 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.
- 12.6.3.3 When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of solvent. A 5-mL syringe is recommended for this operation.
- 12.6.3.4 Remove the three-ball Snyder column, add a fresh boiling chip, and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of solvent through the top. Place the apparatus in the hot water bath.
- 12.6.3.5 Adjust the vertical position and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.
- 12.6.3.6 When the liquid reaches an apparent volume of 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes.
- 12.6.3.7 Proceed to 12.6.4 for preparation for back-extraction or micro-concentration and solvent exchange.
- 12.6.4 Preparation for back-extraction or micro-concentration and solvent exchange.
  - 12.6.4.1 For back-extraction (Section 12.5), transfer the extract to a 250-mL separatory funnel. Rinse the concentration vessel with small portions of hexane, adjust the hexane volume in the separatory funnel to 10 to 20 mL, and proceed to back-extraction (Section 12.5).
  - 12.6.4.2 For determination of the weight of residue in the extract, or for clean-up procedures other than back-extraction, transfer the extract to a blowdown vial using 2-3 rinses of solvent. Proceed with micro-concentration and solvent exchange (Section 12.7).
- 12.7 Micro-concentration and solvent exchange.
  - 12.7.1 Extracts to be subjected to GPC or HPLC cleanup are exchanged into methylene chloride. Extracts to be cleaned up using silica gel, carbon, and/or Florisil are exchanged into hexane.
  - 12.7.2 Transfer the vial containing the sample extract to a nitrogen blowdown device. Adjust the flow of nitrogen so that the surface of the solvent is just visibly disturbed.

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**Note:** *A large vortex in the solvent may cause analyte loss.*

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- 12.7.3 Lower the vial into a 45°C water bath and continue concentrating.
  - 12.7.3.1 If the extract is to be concentrated to dryness for weight determination (Sections 12.4.8 and 13.6.4), blow dry until a constant weight is obtained.
  - 12.7.3.2 If the extract is to be concentrated for injection into the GC/MS or the solvent is to be exchanged for extract cleanup, proceed as follows:

- 12.7.4 When the volume of the liquid is approximately 100  $\mu$ L, add 2 to 3 mL of the desired solvent (methylene chloride for GPC and HPLC, or hexane for the other cleanups) and continue concentration to approximately 100  $\mu$ L. Repeat the addition of solvent and concentrate once more.
- 12.7.5 If the extract is to be cleaned up by GPC, adjust the volume of the extract to 5.0 mL with methylene chloride. If the extract is to be cleaned up by HPLC, further concentrate the extract to 30  $\mu$ L. Proceed with GPC or HPLC cleanup (Section 13.2 or 13.5, respectively).
- 12.7.6 If the extract is to be cleaned up by column chromatography (silica gel, Carbopak/Celite, or Florisil), bring the final volume to 1.0 mL with hexane. Proceed with column cleanups (Sections 13.3 - 13.4 and 13.7).
- 12.7.7 If the extract is to be concentrated for injection into the GC/MS (Section 14), quantitatively transfer the extract to a 0.3-mL conical vial for final concentration, rinsing the larger vial with hexane and adding the rinse to the conical vial. Reduce the volume to approximately 100  $\mu$ L. Add 10  $\mu$ L of nonane to the vial, and evaporate the solvent to the level of the nonane. Seal the vial and label with the sample number. Store in the dark at room temperature until ready for GC/MS analysis. If GC/MS analysis will not be performed on the same day, store the vial at  $<-10^{\circ}\text{C}$ .

### 13.0 Extract Cleanup

- 13.1 Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the analyst may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the analyst must demonstrate that the requirements of Section 9.2 can be met using the cleanup procedure. If PCBs 77, 126, and 169 only are to be determined, the cleanup procedures may be optimized for isolation of these compounds.
  - 13.1.1 Gel permeation chromatography (Section 13.2) removes high molecular weight interferences that cause GC column performance to degrade. It should be used for all soil and sediment extracts. It may be used for water extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids). It may also be used for tissue extracts after initial cleanup on the anthropogenic isolation column (Section 13.6).
  - 13.1.2 Acid, neutral, and basic silica gel (Section 13.3) and Florisil (Section 13.7) are used to remove nonpolar and polar interferences.
  - 13.1.3 Carbopak/Celite (Section 13.4) can be used to separate PCBs 77, 126, and 169 from the mono- and di- ortho-substituted PCBs, if desired.
  - 13.1.4 HPLC (Section 13.5) is used to provide specificity for certain congeners and congener groups.
  - 13.1.5 The anthropogenic isolation column (Section 13.6) is used for removal of lipids from tissue samples.
- 13.2 Gel permeation chromatography (GPC).
  - 13.2.1 Column packing.
    - 13.2.1.1 Place 70 to 75 g of SX-3 Bio-beads (Section 6.7.1.1) in a 400- to 500-mL beaker.



- 13.2.1.2 Cover the beads with methylene chloride and allow to swell overnight (a minimum of 12 hours).
- 13.2.1.3 Transfer the swelled beads to the column (Section 6.7.1.1) and pump solvent through the column, from bottom to top, at 4.5 to 5.5 mL/minute prior to connecting the column to the detector.
- 13.2.1.4 After purging the column with solvent for 1 to 2 hours, adjust the column head pressure to 7 to 10 psig and purge for 4 to 5 hours to remove air. Maintain a head pressure of 7 to 10 psig. Connect the column to the detector (Section 6.7.1.4).

### 13.2.2 Column calibration.

- 13.2.2.1 Load 5 mL of the calibration solution (Section 7.4) into the sample loop.
- 13.2.2.2 Inject the calibration solution and record the signal from the detector. The elution pattern will be corn oil, PCB 209, pentachlorophenol, perylene, and sulfur.
- 13.2.2.3 Set the "dump time" to allow >85% removal of the corn oil and >85% collection of PCB 209.
- 13.2.2.4 Set the "collect time" to the peak minimum between perylene and sulfur.
- 13.2.2.5 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the pentachlorophenol is greater than 85%. If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated GPC system.

### 13.2.3 Extract cleanup—GPC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 0.5 g of high molecular weight material in a 5-mL extract. If the extract is known or expected to contain more than 0.5 g, the extract is split into aliquots for GPC, and the aliquots are combined after elution from the column. The residue content of the extract may be obtained gravimetrically by evaporating the solvent from a 50- $\mu$ L aliquot.

- 13.2.3.1 Filter the extract or load through the filter holder (Section 6.7.1.3) to remove the particles. Load the 5.0-mL extract onto the column.
- 13.2.3.2 Elute the extract using the calibration data determined in Section 13.2.2. Collect the eluate in a clean 400- to 500-mL beaker.
- 13.2.3.3 Rinse the sample loading tube thoroughly with methylene chloride between extracts to prepare for the next sample.
- 13.2.3.4 If a particularly dirty extract is encountered, a 5.0-mL methylene chloride blank shall be run through the system to check for carry-over.
- 13.2.3.5 Concentrate the eluate per Section 12.6 and Section 12.7 for further cleanup or injection into the GC/MS.

### 13.3 Silica gel cleanup.

- 13.3.1 Place a glass-wool plug in a 15-mm ID chromatography column (Section 6.7.4.2). Pack the column bottom to top with: 1 g silica gel (Section 7.5.1.1), 4 g basic silica gel (Section

- 7.5.1.3), 1 g silica gel, 8 g acid silica gel (Section 7.5.1.2), 2 g silica gel, and 4 g granular anhydrous sodium sulfate (Section 7.2.1). Tap the column to settle the adsorbents.
- 13.3.2 Pre-elute the column with 50 to 100 mL of hexane. Close the stopcock when the hexane is within 1 mm of the sodium sulfate. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.
- 13.3.3 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.
- 13.3.4 Rinse the receiver twice with 1-mL portions of hexane, and apply separately to the column. Elute the PCBs with 25 mL of hexane and collect the eluate.
- 13.3.5 Concentrate the eluate per Section 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.
- 13.3.6 For extracts of samples known to contain large quantities of other organic compounds (such as paper mill effluents), it may be advisable to increase the capacity of the silica gel column. This may be accomplished by increasing the strengths of the acid and basic silica gels. The acid silica gel (Section 7.5.1.2) may be increased in strength to as much as 44% w/w (7.9 g sulfuric acid added to 10 g silica gel). The basic silica gel (Section 7.5.1.3) may be increased in strength to as much as 33% w/w (50 mL 1N NaOH added to 100 g silica gel), or the potassium silicate (Section 7.5.1.4) may be used.

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**Note:** *The use of stronger acid silica gel (44% w/w) may lead to charring of organic compounds in some extracts. The charred material may retain some of the analytes and lead to lower recoveries of the PCBs. Increasing the strengths of the acid and basic silica gel may also require different volumes of hexane than those specified above to elute the analytes from the column. Therefore, the performance of the method after such modifications must be verified by the procedure in Section 9.2.*

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#### 13.4 Carbon column (Reference 16)

- 13.4.1 Cut both ends from a 50-mL disposable serological pipet (Section 6.7.3.2) to produce a 20-cm column. Fire-polish both ends and flare both ends if desired. Insert a glass-wool plug at one end, and pack the column with 3.6 g of Carbowax/Celite (Section 7.5.2.3) to form an adsorbent bed 20 cm long. Insert a glass-wool plug on top of the bed to hold the adsorbent in place.
- 13.4.2 Pre-elute the column with 20 mL each in succession of toluene, methylene chloride, and hexane.
- 13.4.3 When the solvent is within 1 mm of the column packing, apply the n-hexane sample extract to the column. Rinse the sample container twice with 1-mL portions of hexane and apply separately to the column. Apply 2 mL of hexane to complete the transfer.
- 13.4.4 Elute the column with 25 mL of n-hexane and collect the eluate. This fraction will contain the mono- and di-ortho PCBs. If carbon particles are present in the eluate, filter through glass-fiber filter paper.
- 13.4.5 Elute the column with 15 mL of methanol and discard the eluate. The fraction discarded will contain residual lipids and other potential interferents, if present.

- 13.4.6 Elute the column with 15 mL of toluene and collect the eluate. This fraction will contain PCBs 77, 126, and 169. If carbon particles are present in the eluate, filter through glass-fiber filter paper.
- 13.4.7 Concentrate the fractions per Section 12.6 and 12.7 for further cleanup or injection into the HPLC or GC/MS.
- 13.5 HPLC (Reference 17).
  - 13.5.1 Column calibration.
    - 13.5.1.1 Prepare a calibration standard containing the toxic congeners and other congeners of interest at a concentration of approximately TBD pg/ $\mu$ L in methylene chloride.
    - 13.5.1.2 Inject 30  $\mu$ L of the calibration solution into the HPLC and record the signal from the detector. Collect the eluant for reuse. The elution order will be the mono- through deca- congeners.
    - 13.5.1.3 Establish the collection time for the congeners of interest. Following calibration, flush the injection system with copious quantities of methylene chloride, including a minimum of five 50- $\mu$ L injections while the detector is monitored, to ensure that residual PCBs are removed from the system.
    - 13.5.1.4 Verify the calibration with the calibration solution after every 20 extracts. Calibration is verified if the recovery of the PCBs from the calibration standard (Section 13.6.1.1) is 75 to 125% compared to the calibration (Section 13.5.1.1). If calibration is not verified, the system shall be recalibrated using the calibration solution, and the previous 20 samples shall be re-extracted and cleaned up using the calibrated system.
  - 13.5.2 Extract cleanup—HPLC requires that the column not be overloaded. The column specified in this method is designed to handle a maximum of 30  $\mu$ L of extract. If the extract cannot be concentrated to less than 30  $\mu$ L, it is split into fractions and the fractions are combined after elution from the column.
    - 13.5.2.1 Rinse the sides of the vial twice with 30  $\mu$ L of methylene chloride and reduce to 30  $\mu$ L with the evaporation apparatus (Section 6.8.3).
    - 13.5.2.2 Inject the 30  $\mu$ L extract into the HPLC.
    - 13.5.2.3 Elute the extract using the calibration data determined in Section 13.5.1. Collect the fraction(s) in a clean 20-mL concentrator tube containing 5 mL of hexane:acetone (1:1 v/v).
    - 13.5.2.4 If an extract containing greater than TBD ng/mL of total PCBs is encountered, a 30- $\mu$ L methylene chloride blank shall be run through the system to check for carry-over.
    - 13.5.2.5 Concentrate the eluate per Section 12.7 for injection into the GC/MS.
- 13.6 Anthropogenic isolation column (References 1-2)—Used for removal of lipids from tissue extracts.
  - 13.6.1 Prepare the column as given in Section 7.5.3.
  - 13.6.2 Pre-elute the column with 100 mL of hexane. Drain the hexane layer to the top of the column, but do not expose the sodium sulfate.

- 13.6.3 Load the sample and rinses (Section 12.4.9.2) onto the column by draining each portion to the top of the bed. Elute the PCBs from the column into the apparatus used for concentration (Section 12.4.7) using 200 mL of hexane.
  - 13.6.4 Concentrate the cleaned up extract (Sections 12.6-12.7) to constant weight per Section 12.7.3.1. If more than 500 mg of material remains, repeat the cleanup using a fresh anthropogenic isolation column.
  - 13.6.5 Redissolve the extract in a solvent suitable for the additional cleanups to be used (Section 13.2-13.5 and 13.7).
  - 13.6.6 Spike 1.0 mL of the cleanup standard (Section 7.11) into the residue/solvent.
  - 13.6.7 Clean up the extract using the procedures in Sections 13.2-13.5 and 13.7. Florisil (Section 13.7) and carbon (Section 13.4) are recommended as minimum additional cleanup steps.
  - 13.6.8 Following cleanup, concentrate the extract to 10  $\mu$ L as described in Section 12.7 and proceed with the analysis in Section 14.
- 13.7 Florisil cleanup (Reference 18).
- 13.7.1 Begin to drain the n-hexane from the column (Section 7.5.4). Adjust the flow rate of eluant to 4.5-5.0 mL/min.
  - 13.7.2 When the n-hexane is within 1 mm of the sodium sulfate, apply the sample extract (in hexane) to the column. Rinse the sample container twice with 1-mL portions of hexane and apply to the column.
  - 13.7.3 Elute the mono-ortho and di-ortho PCBs with approx 165 mL of n-hexane and collect the eluate. Elute the non-ortho co-planar PCBs with approx 100 mL of 6% ether:hexane and collect the eluate. The exact volumes of solvents will need to be determined for each batch of Florisil. If the mono/di-ortho PCBs are not to be separated from the non-ortho co-planar PCBs, elute all PCBs with 6% ether:hexane.
  - 13.7.4 Concentrate the eluate(s) per Sections 12.6-12.7 for further cleanup or for injection into the HPLC or GC/MS.

## 14.0 HRGC/HRMS Analysis

- 14.1 Establish the operating conditions given in Section 10.1.
- 14.2 Add 10  $\mu$ L of the appropriate internal standard solution (Section 7.12) to the sample extract immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. If an extract is to be reanalyzed and evaporation has occurred, do not add more instrument internal standard solution. Rather, bring the extract back to its previous volume (e.g., 19  $\mu$ L) with pure nonane only (18  $\mu$ L if 2  $\mu$ L injections are used).
- 14.3 Inject 1.0 or 2.0  $\mu$ L of the concentrated extract containing the internal standard solution, using on-column or splitless injection. The volume injected must be identical to the volume used for calibration (Section 10). Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the  $^{13}\text{C}_{12}$ -PCB 209 has eluted. If PCBs 77, 126, and 169 only are to be determined, stop data collection after  $^{13}\text{C}_{12}$ -PCB 169 has eluted. Return the column to the initial temperature for analysis of the next extract or standard.

## 15.0 System and Laboratory Performance

- 15.1 At the beginning of each 12-hour shift during which analyses are performed, GC/MS system performance and calibration are verified for all native PCBs and labeled compounds. For these tests, analysis of the CS3 calibration verification (VER) standard (Section 7.13 and Table 4) and the congener specificity test standards (Section 7.15 and Table 5) shall be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, IPRs, and OPRs be analyzed.
- 15.2 MS resolution—A static resolving power of at least 10,000 (10% valley definition) must be demonstrated at the appropriate  $m/z$  before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each 12-hour shift according to procedures in Section 10.1.2. Corrective actions must be implemented whenever the resolving power does not meet the requirement.
- 15.3 Calibration verification.
  - 15.3.1 Inject the VER standard using the procedure in Section 14.
  - 15.3.2 The  $m/z$  abundance ratios for all PCBs shall be within the limits in Table 9; otherwise, the mass spectrometer shall be adjusted until the  $m/z$  abundance ratios fall within the limits specified, and the verification test shall be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the verification test.
  - 15.3.3 The peaks representing each native PCB and labeled compound in the VER standard must be present with a S/N of at least 10; otherwise, the mass spectrometer shall be adjusted and the verification test repeated.
  - 15.3.4 Compute the concentration of each native PCB compound by isotope dilution (Section 17.1) for those compounds that have labeled analogs (Table 1). Compute the concentration of each native compound that does not have a labeled analog and of each labeled compound by the internal standard method (Section 17.3). These concentrations are computed based on the calibration data in Section 10.
  - 15.3.5 For each compound, compare the concentration with the calibration verification limit in Table 6. If PCBs 77, 126, and 169 only are to be determined, compare the concentration to the limit in Table 6a. If all compounds meet the acceptance criteria, calibration has been verified and analysis of standards and sample extracts may proceed. If, however, any compound fails its respective limit, the measurement system is not performing properly for that compound. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the resolution (Section 15.2) and verification (Section 15.3) tests, or recalibrate (Section 10).
- 15.4 Retention times and GC resolution.
  - 15.4.1 Retention times.
    - 15.4.1.1 Absolute—The absolute retention times of the GCMS internal standards in the verification test (Section 15.3) shall be within  $\pm 15$  seconds of the retention times obtained during calibration (Section 10.2.4).

- 15.4.1.2 **Relative**—The relative retention times of native PCBs and labeled compounds in the verification test (Section 15.3) shall be within 5 percent of the relative retention times given in Table 2.
- 15.4.2 **GC resolution.**
- 15.4.2.1 Inject the isomer specificity standards (Section 7.15) on their respective columns.
- 15.4.2.2 The valley height between PCBs 123 and 118 at  $m/z$  325.8804 shall not exceed 10 percent on the SPB-Octyl column, and the valley height between PCBs 156 and 157 shall not exceed 10 percent at  $m/z$  359.8415 on the DB-1 column (Figures 6 and 7).
- 15.4.3 If the absolute retention time of any compound is not within the limits specified or if the congeners are not resolved, the GC is not performing properly. In this event, adjust the GC and repeat the verification test (Section 15.3) or recalibrate (Section 10), or replace the GC column and either verify calibration or recalibrate.
- 15.5 **Ongoing precision and recovery.**
- 15.5.1 Analyze the extract of the ongoing precision and recovery (OPR) aliquot (Section 11.4.2.5, 11.5.4, 11.6.2, 11.7.4, or 11.8.3.2) prior to analysis of samples from the same batch.
- 15.5.2 Compute the concentration of each native PCB by isotope dilution for those compounds that have labeled analogs (Section 10.5). Compute the concentration of the native PCBs that have no labeled analog and each labeled compound by the internal standard method (Section 10.6).
- 15.5.3 For each PCB and labeled compound, compare the concentration to the OPR limits given in Table 6. If PCBs 77, 126, and 169 only are to be determined, compare the concentration to the limits in Table 6a. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, the extraction/concentration processes are not being performed properly for that compound. In this event, correct the problem, re-prepare, extract, and clean up the sample batch and repeat the ongoing precision and recovery test (Section 15.5).
- 15.5.4 Add results that pass the specifications in Section 15.5.3 to initial and previous ongoing data for each compound in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each congener in each matrix type by calculating the average percent recovery ( $R$ ) and the standard deviation of percent recovery ( $S_R$ ). Express the accuracy as a recovery interval from  $R - 2S_R$  to  $R + 2S_R$ . For example, if  $R = 95\%$  and  $S_R = 5\%$ , the accuracy is 85 to 105%.
- 15.6 **Blank**—Analyze the method blank extracted with each sample batch immediately following analysis of the OPR aliquot to demonstrate freedom from contamination and freedom from carryover from the OPR analysis. The results of the analysis of the blank must meet the specifications in Section 9.5.2 before sample analyses may proceed.

## 16.0 Qualitative Determination

A PCB or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 16.1 through 16.4 are met.

- 16.1 The signals for the two exact  $m/z$ 's in Table 8 must be present and must maximize within the same two seconds.
- 16.2 The signal-to-noise ratio (S/N) for the GC peak at each exact  $m/z$  must be greater than or equal to 2.5 for each PCB detected in a sample extract, and greater than or equal to 10 for all PCBs in the calibration standard (Sections 10.2.3 and 15.3.3).
- 16.3 The ratio of the integrated areas of the two exact  $m/z$ 's specified in Table 8 must be within the limit in Table 9, or within  $\pm 10$  percent of the ratio in the midpoint (CS3) calibration or calibration verification (VER), whichever is most recent.
- 16.4 The relative retention time of the peak for a toxic PCB must be within 5 percent of the relative retention times listed in Table 2. The retention time of peaks representing PCBs other than the toxic PCBs must be within the retention time windows established in Section 10.3.
- 16.5 Confirmatory analysis—Isomer specificity for PCBs 156 and 157 cannot be achieved on the SPB-Octyl column. Therefore, any sample in which these PCBs are tentatively identified by analysis on the SPB-Octyl column and when rigorous identification is required must have a confirmatory analysis performed on a DB-1 or equivalent GC column. The operating conditions in Section 10.1.1 may be adjusted to optimize the analysis on the second GC column, but the GC/MS must meet the mass resolution and calibration specifications in Section 10.
- 16.6 If the criteria for identification in Sections 16.1-16.5 are not met, the PCB has not been identified and the results may not be reported for regulatory compliance purposes. If interferences preclude identification, a new aliquot of sample must be extracted, further cleaned up, and analyzed.

## 17.0 Quantitative Determination

- 17.1 Isotope dilution quantitation—By adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the PCB can be made because the native compound and its labeled analog exhibit similar effects upon extraction, concentration, and gas chromatography. Relative response (RR) values are used in conjunction with the initial calibration data described in Section 10.5 to determine concentrations directly, so long as labeled compound spiking levels are constant, using the following equation:

$$C_x \text{ (ng/mL)} = \frac{(AI_x + AI_y) C_i}{(AI_i + AI_y) RR}$$

where:

$C_x$  = The concentration of the PCB in the extract, and the other terms are as defined in Section 10.5.2

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

## 17.2 Internal standard quantitation and labeled compound recovery

- 17.2.1 Compute the concentrations of labeled analogs (including the cleanup standard) in the extract using the response factors determined from the initial calibration data (Section 10.6) and the following equation:

$$C_{ex} \text{ (ng/mL)} = \frac{(A1_s + A2_s) C_u}{(A1_{ex} + A2_{ex}) RF}$$

where:

$C_{ex}$  = The concentration of the labeled compound in the extract.

The other terms are defined in Section 10.6.1

- 17.2.2 Using the concentration in the extract determined above, compute the percent recovery of the labeled compounds (including the cleanup standard) using the following equation:

$$\text{Recovery (\%)} = \frac{\text{Concentration found } (\mu\text{g/mL})}{\text{Concentration spiked } (\mu\text{g/mL})} \times 100$$

- 17.3 The concentration of a native PCB in the solid phase of the sample is computed using the concentration of the compound in the extract and the weight of the solids (Section 11.2.2.3), as follows:

$$\text{Concentration in solid (ng/kg)} = \frac{(C_{ex} \times V_{ex})}{W_s}$$

where:

$C_{ex}$  = The concentration of the compound in the extract.

$V_{ex}$  = The extract volume in mL.

$W_s$  = The sample weight (dry weight) in kg.

- 17.4 The concentration of a native PCB in the aqueous phase of the sample is computed using the concentration of the compound in the extract and the volume of water extracted (Section 11.4), as follows:

$$\text{Concentration in aqueous phase (pg/L)} = \frac{(C_{ex} \times V_{ex})}{V_s}$$

where:

$C_{ex}$  = The concentration of the compound in the extract.

$V_{ex}$  = The extract volume in mL.

$V_s$  = The sample volume in liters.



- 17.5 If the SICP area at either quantitation  $m/z$  for any compound exceeds the calibration range of the system, a smaller sample aliquot is extracted.
- 17.5.1 For aqueous samples containing 1% solids or less, dilute 100 mL, 10 mL, etc., of sample to 1 L with reagent water and re-prepare, extract, clean up, and analyze per Sections 11 - 14.
- 17.5.2 For samples containing greater than 1% solids, extract an amount of sample equal to 1/10, 1/100, etc., of the amount used in Section 11.5.1. Re-prepare, extract, clean up, and analyze per Sections 11-14.
- 17.5.3 If a smaller sample size will not be representative of the entire sample, dilute the sample extract by a factor of 10, adjust the concentration of the instrument internal standard to 100 pg/ $\mu$ L in the extract, and analyze an aliquot of this diluted extract by the internal standard method.
- 17.6 Results are reported to three significant figures for the PCBs and labeled compounds found in all standards, blanks, and samples.
- 17.6.1 Reporting units and levels.
- 17.6.1.1 Aqueous samples—Report results in pg/L (parts-per-quadrillion).
- 17.6.1.2 Samples containing greater than 1% solids (soils, sediments, filter cake, compost)—Report results in ng/kg based on the dry weight of the sample. Report the percent solids so that the result may be corrected.
- 17.6.1.3 Tissues—Report results in ng/kg of wet tissue, not on the basis of the lipid content of the sample. Report the percent lipid content, so that the data user can calculate the concentration on a lipid basis if desired.
- 17.6.1.4 Reporting level.
- 17.6.1.4.1 Standards (VER, IPR, OPR) and samples—Report results at or above the minimum level (Table 2). Report results below the minimum level as not detected or as required by the regulatory authority.
- 17.6.1.4.2 Blanks—Report results above the MDL or as required by the regulatory authority. Do not blank-correct results. If a blank accompanying a sample result shows contamination above the MDL for the congener, flag the sample result and report the results for the sample and the accompanying blank.
- 17.6.2 Results for PCBs in samples that have been diluted are reported at the least dilute level at which the areas at the quantitation  $m/z$ 's are within the calibration range (Section 17.5).
- 17.6.3 For PCBs having a labeled analog, results are reported at the least dilute level at which the area at the quantitation  $m/z$  is within the calibration range (Section 17.5) and the labeled compound recovery is within the normal range for the method (Section 9.3 and Tables 6, 6a, 7, and 7a).
- 17.6.4 Additionally, if requested, the total concentration of all congeners at a given level of chlorination (i.e., total TCB, total PeCB, total HxCB, etc.) may be reported by summing the concentrations of all congeners identified in that level of chlorination, including both the toxic and other congeners.

## 18.0 Analysis of Complex Samples

- 18.1 Some samples may contain high levels ( $>10$  ng/L;  $>1000$  ng/kg) of the compounds of interest, interfering compounds, and/or polymeric materials. Some extracts will not concentrate to  $10\ \mu\text{L}$  (Section 12.7); others may overload the GC column and/or mass spectrometer.
- 18.2 Analyze a smaller aliquot of the sample (Section 17.5) when the extract will not concentrate to  $10\ \mu\text{L}$  after all cleanup procedures have been exhausted.
- 18.3 Several laboratories have reported that elimination of several of the toxic PCBs, particularly non-co-planar congeners 105, 114, 118, 123, 156, 157, and 167 are difficult to eliminate. Backgrounds of these congeners can therefore interfere with the determination of these congeners in environmental samples. Care should therefore be exercised in the determination of these congeners.
- 18.4 Recovery of labeled compounds—In most samples, recoveries of the labeled compounds will be similar to those from reagent water or from the alternate matrix (Section 7.6).
  - 18.4.1 If the recovery of any of the labeled compounds is outside of the normal range (Table 7), a diluted sample shall be analyzed (Section 17.5).
  - 18.4.2 If the recovery of any of the labeled compounds in the diluted sample is outside of normal range, the calibration verification standard (Section 7.13) shall be analyzed and calibration verified (Section 15.3).
  - 18.4.3 If the calibration cannot be verified, a new calibration must be performed and the original sample extract reanalyzed.
  - 18.4.4 If the calibration is verified and the diluted sample does not meet the limits for labeled compound recovery, the method does not apply to the sample being analyzed and the result may not be reported for regulatory compliance purposes. In this case, alternate extraction and cleanup procedures in this method must be employed to resolve the interference. If all cleanup procedures in this method have been employed and labeled compound recovery remains outside of the normal range; extraction and/or cleanup procedures that are beyond this scope of this method will be required to analyze these samples.

## 19.0 Pollution Prevention

- 19.1 The solvents used in this method pose little threat to the environment when managed properly. The solvent evaporation techniques used in this method are amenable to solvent recovery, and it is recommended that the laboratory recover solvents wherever feasible.
- 19.2 Standards should be prepared in volumes consistent with laboratory use to minimize disposal of standards.

## 20.0 Waste Management

- 20.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations.

- 20.2 Samples containing HCl or H<sub>2</sub>SO<sub>4</sub> to pH <2 are hazardous and must be neutralized before being poured down a drain or must be handled as hazardous waste.
- 20.3 The PCBs decompose above 800°C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in an appropriate incinerator. Gross quantities (milligrams) should be packaged securely and disposed of through commercial or governmental channels that are capable of handling extremely toxic wastes.
- 20.4 [This section may need to be modified to accommodate the PCBs: Liquid or soluble waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength shorter than 290 nm for several days. Use F40 BL or equivalent lamps. Analyze liquid wastes, and dispose of the solutions when the PCBs can no longer be detected.]
- 20.5 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel" and "Less is Better—Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

## 21.0 Method Performance

For this draft version of Method 1668, performance was validated and preliminary data were collected in a single laboratory.

## 22.0 References

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- 12 "Standard Practice for Sampling Water," ASTM Annual Book of Standards, ASTM, 1916 Race Street, Philadelphia, PA 19103-1187, 1980.
- 13 "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL, Cincinnati, OH 45268, EPA-600/4-70-020, March 1979.
- 14 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA EMSL, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.
- 15 "Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish", U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth MN 55804, EPA/600/3-90/022, March 1990.
- 16 Storr-Hansen, E. and T. Cederberg, "Determination of Coplanar Polychlorinated Biphenyl (CB) Congeners in Seal Tissues by Chromatography on Active Carbon, Dual-Column High Resolution GC/ECD and High Resolution GC/High Resolution MS" *Chemosphere* 24:9, 1181-1196, 1992.
- 17 Workman, S.M., TBD [or Peterman in Reference 2]
- 18 Tessari, J.D., Personal communication with Dale Rushneck, available from the EPA Sample Control Center, operated by DynCorp EE&NSP, 300 N. Lee St., Alexandria, VA 22314 (703-519-1140).

## 23.0 Tables and Figures

Table 1. Toxic Polychlorinated Biphenyls Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

| PCB <sup>1</sup>                                     | Native compound |              | <sup>13</sup> C <sub>12</sub> analog |
|------------------------------------------------------|-----------------|--------------|--------------------------------------|
|                                                      | CAS Registry    | IUPAC        | CAS Registry                         |
| 3,3',4,4'-TCB                                        | 32598-13-3      | <u>77</u> ✓  | 160901-67-7                          |
| 2,3,3',4,4'-PeCB                                     | 32598-14-4      | <u>105</u>   | 160901-70-2                          |
| 2,3,4,4',5-PeCB                                      | 74472-37-0      | <u>114</u>   | 160901-72-4                          |
| 2,3',4,4',5-PeCB                                     | 31508-00-6      | <u>118</u> ✓ | 160901-73-5                          |
| 2',3,4,4',5-PeCB                                     | 65510-44-3      | <u>123</u>   | 160901-74-6                          |
| 3,3',4,4',5-PeCB                                     | 57465-28-8      | <u>126</u>   | 160901-75-7                          |
| 2,3,3',4,4',5-HxCB                                   | 38380-08-4      | <u>156</u>   | 160901-77-9                          |
| 2,3,3',4,4',5'-HxCB                                  | 69782-90-7      | <u>157</u>   | 160901-78-0                          |
| 2,3',4,4',5,5'-HxCB                                  | 52663-72-6      | <u>167</u>   | 161627-18-5                          |
| 3,3',4,4',5,5'-HxCB                                  | 32774-16-6      | <u>169</u> ✓ | 160901-79-1                          |
| 2,2',3,3',4,4',5-HpCB                                | 35065-30-6      | <u>170</u>   | 160901-80-4                          |
| 2,2',3,4,4',5,5'-HpCB                                | 35065-29-3      | <u>180</u>   | 160901-82-6                          |
| 2,3,3',4,4',5,5'-HpCB                                | 39635-31-9      | <u>189</u>   | 160901-83-7                          |
| Cleanup standards                                    |                 |              |                                      |
| <sup>13</sup> C <sub>12</sub> -3,4,4',5'-TCB         |                 | <u>81</u>    | 160901-68-8                          |
| <sup>13</sup> C <sub>12</sub> -2,3,3',5,5'-PeCB      |                 | <u>111</u>   | 160901-71-3                          |
| Internal standards                                   |                 |              |                                      |
| <sup>13</sup> C <sub>12</sub> -2,2',5,5'-TCB         |                 | <u>52</u>    | 160901-66-6                          |
| <sup>13</sup> C <sub>12</sub> -2,2',4,4',5'-PeCB     |                 | <u>101</u>   | 160901-69-9                          |
| <sup>13</sup> C <sub>12</sub> -2,2',3,4,4',5'-HxCB   |                 | <u>138</u>   | 160901-76-8                          |
| <sup>13</sup> C <sub>12</sub> -2,2',3,3',5,5',6-HpCB |                 | <u>178</u>   | 160901-81-5                          |
| Final eluter standard                                |                 |              |                                      |
| <sup>13</sup> C <sub>12</sub> -DCB                   |                 | <u>209</u>   | 160901-84-8                          |

## 1. Polychlorinated biphenyls

|      |   |                     |
|------|---|---------------------|
| TCB  | = | Tetrachlorobiphenyl |
| PeCB | = | Pentachlorobiphenyl |
| HxCB | = | Hexachlorobiphenyl  |
| HpCB | = | Heptachlorobiphenyl |
| DCB  | = | Decachlorobiphenyl  |

Table 2. Retention Time (RT) References, Quantitation References, Relative Retention Ratios, Detection Limits (EMDLs), and Estimated Minimum Levels (EMLs) for the Toxic PCBs

|                                                                                                       |                             |              |                                                |                    |       | Matrix and concentration (3) |      |                          |     |                            |
|-------------------------------------------------------------------------------------------------------|-----------------------------|--------------|------------------------------------------------|--------------------|-------|------------------------------|------|--------------------------|-----|----------------------------|
| IUPAC<br>(1)                                                                                          | Labeled or native PCB       | IUPAC<br>(1) | Retention time and quan-<br>titation reference | RT<br>(min)<br>(2) | RRT   | Water<br>(pg/L;<br>ppg)      |      | Other<br>(ng/kg;<br>ppt) |     | Extract<br>(pg/uL;<br>ppb) |
|                                                                                                       |                             |              |                                                |                    |       | EMDL                         | EML  | EMDL                     | EML | EML                        |
| Tetra congeners using 13C12-2,2',5,5'-TCB (#52L) as the injection internal standard                   |                             |              |                                                |                    |       |                              |      |                          |     |                            |
| 52L                                                                                                   | 13C12-2,2',5,5'-TCB         | 52L          | 13C12-2,2',5,5'-TCB                            | 12.87              | 1.000 |                              |      |                          |     |                            |
| 81L                                                                                                   | 13C12-3,4,4',5-TCB (4)      | 52L          | 13C12-2,2',5,5'-TCB                            | 19.65              | 1.527 |                              |      |                          |     |                            |
| 77L                                                                                                   | 13C12-3,3',4,4'-TCB         | 52L          | 13C12-2,2',5,5'-TCB                            | 20.15              | 1.567 |                              |      |                          |     |                            |
| 77                                                                                                    | 3,3',4,4'-TCB               | 77L          | 13C12-3,3',4,4'-TCB                            | 20.18              | 1.002 | 5                            | 20   | 0.5                      | 2   | 1                          |
| Penta congeners using 13C12-2,2',4,5,5'-PeCB (#101L) as the injection internal standard               |                             |              |                                                |                    |       |                              |      |                          |     |                            |
| 101L                                                                                                  | 13C12-2,2',4,5,5'-PeCB      | 101L         | 13C12-2,2',4,5,5'-PeCB                         | 17.83              | 1.000 |                              |      |                          |     |                            |
| 111L                                                                                                  | 13C12-2,3,3',5,5'-PeCB (4)  | 101L         | 13C12-2,2',4,5,5'-PeCB                         | 20.12              | 1.128 |                              |      |                          |     |                            |
| 123                                                                                                   | 2',3,4,4',5-PeCB            | 118L         | 13C12-2,3',4,4',5-PeCB                         | 21.98              | 0.987 | 40                           | 100  | 4                        | 10  | 5                          |
| 118L                                                                                                  | 13C12-2,3',4,4',5-PeCB      | 101L         | 13C12-2,2',4,5,5'-PeCB                         | 22.27              | 1.249 |                              |      |                          |     |                            |
| 118                                                                                                   | 2,3',4,4',5-PeCB            | 118L         | 13C12-2,3',4,4',5-PeCB                         | 22.30              | 1.001 | 60                           | 200  | 6                        | 20  | 10                         |
| 114                                                                                                   | 2,3,4,4',5-PeCB             | 105L         | 13C12-2,3,3',4,4'-PeCB                         | 22.82              | 0.974 | 600                          | 2000 | 60                       | 200 | 100                        |
| 105L                                                                                                  | 13C12-2,3,3',4,4'-PeCB      | 101L         | 13C12-2,2',4,5,5'-PeCB                         | 23.42              | 1.313 |                              |      |                          |     |                            |
| 105                                                                                                   | 2,3,3',4,4'-PeCB            | 105L         | 13C12-2,3,3',4,4'-PeCB                         | 23.43              | 1.001 | 400                          | 1000 | 40                       | 100 | 50                         |
| 126L                                                                                                  | 13C12-3,3',4,4',5-PeCB      | 101L         | 13C12-2,2',4,5,5'-PeCB                         | 26.55              | 1.489 |                              |      |                          |     |                            |
| 126                                                                                                   | 3,3',4,4',5-PeCB            | 126L         | 13C12-3,3',4,4',5-PeCB                         | 26.56              | 1.001 | 40                           | 100  | 4                        | 10  | 5                          |
| Hexa congeners using 13C12-2,2',3,4,4',5'-HxCB (#138L) as the injection internal standard             |                             |              |                                                |                    |       |                              |      |                          |     |                            |
| 138L                                                                                                  | 13C12-2,2',3,4,4',5'-HxCB   | 101L         | 13C12-2,2',4,5,5'-PeCB                         | 25.35              | 1.422 |                              |      |                          |     |                            |
| 167L                                                                                                  | 13C12-2,3',4,4',5,5'-HxCB   | 138L         | 13C12-2,2',3,4,4',5'-HxCB                      | 28.50              | 1.124 |                              |      |                          |     |                            |
| 167                                                                                                   | 2,3',4,4',5,5'-HxCB         | 167L         | 13C12-2,3',4,4',5,5'-HxCB                      | 28.52              | 1.001 | 60                           | 200  | 6                        | 20  | 10                         |
| 156L                                                                                                  | 13C12-2,3,3',4,4',5-HxCB    | 138L         | 13C12-2,2',3,4,4',5'-HxCB                      | 29.77              | 1.174 |                              |      |                          |     |                            |
| 157L                                                                                                  | 13C12-2,3,3',4,4',5'-HxCB   | 138L         | 13C12-2,2',3,4,4',5'-HxCB                      | 29.77              | 1.174 |                              |      |                          |     |                            |
| 156                                                                                                   | 2,3,3',4,4',5-HxCB          | 156L         | 13C12-2,3,3',4,4',5-HxCB                       | 29.80              | 1.001 | 60                           | 200  | 6                        | 20  | 10                         |
| 157                                                                                                   | 2,3,3',4,4',5'-HxCB         | 157L         | 13C12-2,3,3',4,4',5'-HxCB                      | 29.80              | 1.001 | 60                           | 200  | 6                        | 20  | 10                         |
| 169L                                                                                                  | 13C12-3,3',4,4',5,5'-HxCB   | 138L         | 13C12-2,2',3,4,4',5'-HxCB                      | 33.38              | 1.317 |                              |      |                          |     |                            |
| 169                                                                                                   | 3,3',4,4',5,5'-HxCB         | 169L         | 13C12-3,3',4,4',5,5'-HxCB                      | 33.42              | 1.001 | 60                           | 200  | 6                        | 20  | 10                         |
| Hepta and deca congeners using 13C12-2,2',3,3',5,5',6-HpCB (#178L) as the injection internal standard |                             |              |                                                |                    |       |                              |      |                          |     |                            |
| 178L                                                                                                  | 13C12-2,2',3,3',5,5',6-HpCB | 101L         | 13C12-2,2',4,5,5'-PeCB                         | 25.78              | 1.446 |                              |      |                          |     |                            |
| 180L                                                                                                  | 13C12-2,2',3,4,4',5,5'-HpCB | 178L         | 13C12-2,2',3,3',5,5',6-HpCB                    | 31.30              | 1.214 |                              |      |                          |     |                            |
| 180                                                                                                   | 2,2',3,4,4',5,5'-HpCB       | 180L         | 13C12-2,2',3,4,4',5,5'-HpCB                    | 31.32              | 1.001 | 60                           | 200  | 6                        | 20  | 10                         |
| 170                                                                                                   | 2,2',3,3',4,4',5-HpCB       | 180L         | 13C12-2,2',3,4,4',5,5'-HpCB                    | 32.75              | 1.046 | 60                           | 200  | 6                        | 20  | 10                         |
| 189L                                                                                                  | 13C12-2,3,3',4,4',5,5'-HpCB | 178L         | 13C12-2,2',3,3',5,5',6-HpCB                    | 36.32              | 1.409 |                              |      |                          |     |                            |
| 189                                                                                                   | 2,3,3',4,4',5,5'-HpCB       | 189L         | 13C12-2,3,3',4,4',5,5'-HpCB                    | 36.35              | 1.001 | 60                           | 200  | 6                        | 20  | 10                         |
| 209L                                                                                                  | 13C12-DCB (5)               | 178L         | 13C12-2,2',3,3',5,5',6-HpCB                    | 43.48              | 1.686 |                              |      |                          |     |                            |

Notes:

- (1) Suffix "L" indicates labeled compound
- (2) Retention time data are for SPB-octyl column sorted in ascending retention time order within each congener group
- (3) Some EMDLs and EMLs have been set above the lowest calibration point (Table 4) because backgrounds of these particular congeners are difficult to eliminate from laboratory analytical systems
- (4) Cleanup standard
- (5) Final eluter

Table 3. Concentration of Stock and Spiking Solutions Containing PCBs and Labeled Compounds

| PCB congener                  | IUPAC | Solution concentration (ng/mL) |             |           |             |
|-------------------------------|-------|--------------------------------|-------------|-----------|-------------|
|                               |       | Labeled compound               |             | PAR       |             |
|                               |       | Stock (1)                      | Spiking (2) | Stock (3) | Spiking (4) |
| 3,3',4,4'-TCB                 | 77    | -                              | -           | 220       | 0.4         |
| 2,3,3',4,4'-PeCB              | 105   | -                              | -           | 1000      | 20.0        |
| 2,3,4,4',5-PeCB               | 114   | -                              | -           | 1000      | 20.0        |
| 2,3,4,4',5-PeCB               | 118   | -                              | -           | 1000      | 20.0        |
| 2,3,4,4',5-PeCB               | 123   | -                              | -           | 1000      | 20.0        |
| 3,3',4,4',5-PeCB              | 126   | -                              | -           | 100       | 2.0         |
| 2,3,3',4,4',5-HxCB            | 156   | -                              | -           | 1000      | 20.0        |
| 2,3,3',4,4',5-HxCB            | 157   | -                              | -           | 1000      | 20.0        |
| 2,3,3',4,4',5-HxCB            | 167   | -                              | -           | 1000      | 20.0        |
| 3,3',4,4',5-HxCB              | 169   | -                              | -           | 200       | 4.0         |
| 2,2',3,3',4,4',5-HpCB         | 170   | -                              | -           | 200       | 4.0         |
| 2,2',3,3',4,4',5-HpCB         | 180   | -                              | -           | 1000      | 20.0        |
| 2,2',3,3',4,4',5-HpCB         | 189   | -                              | -           | 200       | 4.0         |
| 13C12-3,3',4,4',5-TCB         | 77L   | 1000                           | 2.0         | -         | -           |
| 13C12-2,3,3',4,4',5-PeCB      | 105L  | 1000                           | 2.0         | -         | -           |
| 13C12-2,3,3',4,4',5-PeCB      | 118L  | 1000                           | 2.0         | -         | -           |
| 13C12-3,3',4,4',5-PeCB        | 126L  | 1000                           | 2.0         | -         | -           |
| 13C12-2,3,3',4,4',5-HxCB      | 156L  | 1000                           | 2.0         | -         | -           |
| 13C12-2,3,3',4,4',5-HxCB      | 157L  | 1000                           | 2.0         | -         | -           |
| 13C12-2,3,3',4,4',5-HxCB      | 167L  | 1000                           | 2.0         | -         | -           |
| 13C12-3,3',4,4',5-HxCB        | 169L  | 1000                           | 2.0         | -         | -           |
| 13C12-2,2',3,3',4,4',5-HpCB   | 180L  | 1000                           | 2.0         | -         | -           |
| 13C12-2,2',3,3',4,4',5-HpCB   | 189L  | 1000                           | 2.0         | -         | -           |
| 13C12-DCB                     | 209L  | 2000                           | 4.0         | -         | -           |
| Cleanup standards (5)         |       |                                |             |           |             |
| 13C12-3,3',4,4',5-TCB         | 81L   | 200                            | 1.0         | -         | -           |
| 13C12-2,3,3',4,4',5-PeCB      | 111L  | 1000                           | 5.0         | -         | -           |
| Internal standards (6)        |       |                                |             |           |             |
| 13C12-2,2',3,3',4,4',5-TCB    | 52L   | 1000                           | -           | -         | -           |
| 13C12-2,2',3,3',4,4',5-PeCB   | 101L  | 1000                           | -           | -         | -           |
| 13C12-2,2',3,3',4,4',5-HxCB   | 138L  | 1000                           | -           | -         | -           |
| 13C12-2,2',3,3',4,4',5,6-HpCB | 178L  | 1000                           | -           | -         | -           |

## Notes:

1. Section 7.10-prepared in nonane and diluted to prepare spiking solution
2. Section 7.10.3-prepared in acetone from stock solution daily
3. Section 7.9-prepared in nonane and diluted to prepare spiking solution. Concentrations are adjusted for expected background levels.
4. Section 7.14-prepared in acetone from stock solution daily. Concentrations are adjusted for expected background levels.
5. Section 7.11-prepared in nonane and added to extract prior to cleanup
6. Section 7.12-prepared in nonane and added to concentrated extract prior to injection

Table 4. Concentration of PCBs in Calibration and Calibration Verification Solutions

| Toxic PCB congener          | IUPAC<br>(1) | Solution concentration (ng/mL) |     |     |     |      |
|-----------------------------|--------------|--------------------------------|-----|-----|-----|------|
|                             |              | VER (2)                        |     |     |     |      |
|                             |              | CS1                            | CS2 | CS3 | CS4 | CS5  |
| 3,3',4,4'-TCB               | 77           | 0.5                            | 2   | 10  | 40  | 200  |
| 2,3,3',4,4'-PeCB            | 105          | 2.5                            | 10  | 50  | 200 | 1000 |
| 2,3,4,4',5-PeCB             | 114          | 2.5                            | 10  | 50  | 200 | 1000 |
| 2,3',4,4',5-PeCB            | 118          | 2.5                            | 10  | 50  | 200 | 1000 |
| 2',3,4,4',5-PeCB            | 123          | 2.5                            | 10  | 50  | 200 | 1000 |
| 3,3',4,4',5-PeCB            | 126          | 2.5                            | 10  | 50  | 200 | 1000 |
| 2,3,3',4,4',5-HxCB          | 156          | 5                              | 20  | 100 | 400 | 2000 |
| 2,3,3',4,4',5'-HxCB         | 157          | 5                              | 20  | 100 | 400 | 2000 |
| 2,3',4,4',5,5'-HxCB         | 167          | 5                              | 20  | 100 | 400 | 2000 |
| 3,3',4,4',5,5'-HxCB         | 169          | 5                              | 20  | 100 | 400 | 2000 |
| 2,2',3,3',4,4',5-HpCB       | 170          | 5                              | 20  | 100 | 400 | 2000 |
| 2,2',3,4,4',5,5'-HpCB       | 180          | 5                              | 20  | 100 | 400 | 2000 |
| 2,3,3',4,4',5,5'-HpCB       | 189          | 5                              | 20  | 100 | 400 | 2000 |
| Labeled congener            |              |                                |     |     |     |      |
| 13C12-3,3',4,4'-TCB         | 77L          | 100                            | 100 | 100 | 100 | 100  |
| 13C12-2,3,3',4,4'-PeCB      | 105L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-2,3',4,4',5-PeCB      | 118L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-3,3',4,4',5-PeCB      | 126L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-2,3,3',4,4',5-HxCB    | 156L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-2,3,3',4,4',5'-HxCB   | 157L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-3,3',4,4',5,5'-HxCB   | 169L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-2,2',3,4,4',5,5'-HpCB | 180L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-2,3,3',4,4',5,5'-HpCB | 189L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-DCB                   | 209L         | 200                            | 200 | 200 | 200 | 200  |
| Cleanup standards           |              |                                |     |     |     |      |
| 13C12-3,4,4',5'-TCB         | 81L          | 0.5                            | 2   | 10  | 40  | 200  |
| 13C12-2,3,3',5,5'-PeCB      | 111L         | 2.5                            | 10  | 50  | 200 | 1000 |
| Internal standards          |              |                                |     |     |     |      |
| 13C12-2,2',5,5'-TCB         | 52L          | 100                            | 100 | 100 | 100 | 100  |
| 13C12-2,2',4,5,5'-PeCB      | 101L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-2,2',3,4,4',5'-HxCB   | 138L         | 100                            | 100 | 100 | 100 | 100  |
| 13C12-2,2',3,3',5,5',6-HpCB | 178L         | 100                            | 100 | 100 | 100 | 100  |

## Notes:

1. Suffix "L" indicates labeled compound
2. Section 15.3, calibration verification solution



Table 5. GC Retention Time Window Defining Solution and Congener Specificity Test Standard (Section 7.15) (1,2)

| Congener group | First eluted (3) |                  | Last eluted |                  |
|----------------|------------------|------------------|-------------|------------------|
| CB             | 54               | 2,2',6,6'        | 77          | 3,3',4,4'        |
| PeCB           | 104              | 2,2',4,6,6'      | 126         | 3,3',4,4',5      |
| HxCB           | 155              | 2,2',4,4',6,6'   | 169         | 3,3',4,4',5,5'   |
| PCB            | 188              | 2,2',3,4',5,6,6' | 189         | 2,3,3',4,4',5,5' |

## PB-Octyl resolution test compounds

|    |                  |
|----|------------------|
| 23 | 2',3,4,4',5-PeCB |
| 18 | 2,3',4,4',5-PeCB |
| 14 | 2,3,4,4',5-PeCB  |

## B-1 column resolution test compounds

|    |                     |
|----|---------------------|
| 56 | 2,3,3',4,4',5-HxCB  |
| 57 | 2,3,3',4,4',5'-HxCB |

## Notes:

- All compounds are at a concentration of 100 ng/mL in nonane.
- It is not necessary to monitor for the earliest eluted compounds if the toxic PCBs only are to be determined. If the co-planar PCBs (77, 126, 169) only are to be determined, it is necessary to resolve these co-planar PCBs and potentially interfering compounds only; i.e., use of the compounds listed in this Table is not required.
- The earliest eluted compound in each congener group is provided for those instances in which all PCBs in that congener group are to be determined. If the toxic PCBs only (Table 1) are to be determined, use of the first eluted compounds is not required.

Table 6. Preliminary Acceptance Criteria for Performance Tests When All Toxic PCBs are Tested<sup>1</sup>

| Congener                   | IUPAC | Test | Concentration (ng/mL) |          |          |          |
|----------------------------|-------|------|-----------------------|----------|----------|----------|
|                            |       |      | IPR (2,3)             |          | OPR      | VER      |
|                            |       |      | s                     | X        |          |          |
| 2,3,3',4,4'-TCB            | 77    | 20   | 5.6                   | 16-26    | 14-32    | 16-26    |
| 2,3,3',4,4'-PeCB           | 105   | 1000 | 172                   | 720-1500 | 680-1600 | 780-1300 |
| 2,3,4,4',5-PeCB            | 114   | 1000 | 390                   | 160-2800 | 130-3300 | 770-1300 |
| 2,3',4,4',5-PeCB           | 118   | 1000 | 172                   | 720-1500 | 680-1600 | 780-1300 |
| 2',3,4,4',5-PeCB           | 123   | 1000 | 390                   | 160-2800 | 130-3300 | 770-1300 |
| 3,3',4,4',5-PeCB           | 126   | 100  | 17                    | 72-150   | 68-160   | 78-130   |
| 2,3,3',4,4',5-HxCB         | 156   | 1000 | 222                   | 740-1600 | 640-1700 | 780-1300 |
| 2,3,3',4,4',5'-HxCB        | 157   | 1000 | 222                   | 740-1600 | 640-1700 | 780-1300 |
| 2,3',4,4',5,5'-HxCB        | 167   | 1000 | 222                   | 740-1600 | 640-1700 | 780-1300 |
| 3,3',4,4',5,5'-HxCB        | 169   | 200  | 45                    | 148-320  | 128-340  | 156-260  |
| 2,2',3,3',4,4',5-HpCB      | 170   | 200  | 33                    | 152-260  | 140-280  | 172-232  |
| 2,2',3,4,4',5,5'-HpCB      | 180   | 1000 | 165                   | 760-1300 | 700-1400 | 860-1160 |
| 2,3,3',4,4',5,5'-HpCB      | 189   | 200  | 33                    | 152-260  | 140-280  | 172-232  |
| 3C12-3,3',4,4'-TCB         | 77L   | 100  | 37                    | 28-134   | 20-175   | 71-140   |
| 3C12-2,3,3',4,4'-PeCB      | 105L  | 100  | 39                    | 16-279   | 13-328   | 77-130   |
| 3C12-2,3',4,4',5-PeCB      | 118L  | 100  | 39                    | 16-279   | 13-328   | 77-130   |
| 3C12-3,3',4,4',5-PeCB      | 126L  | 100  | 39                    | 16-279   | 13-328   | 77-130   |
| 3C12-2,3,3',4,4',5-HxCB    | 156L  | 100  | 43                    | 24-157   | 17-205   | 70-143   |
| 3C12-2,3,3',4,4',5'-HxCB   | 157L  | 100  | 43                    | 24-157   | 17-205   | 70-143   |
| 3C12-3,3',4,4',5,5'-HxCB   | 169L  | 100  | 43                    | 24-157   | 17-205   | 70-143   |
| 3C12-2,2',3,4,4',5,5'-HpCB | 180L  | 100  | 41                    | 28-141   | 20-186   | 72-138   |
| 3C12-2,3,3',4,4',5,5'-HpCB | 189L  | 200  | 82                    | 56-282   | 40-372   | 144-276  |
| Cleanup standards          |       |      |                       |          |          |          |
| 3C12-3,4,4',5'-TCB         | 81L   | 20   | 7.2                   | 8-31     | 6-38     | 15-26    |
| 3C12-2,3,3',5,5'-PeCB      | 111L  | 100  | 36                    | 39-154   | 31-191   | 79-127   |

Table 6a. Preliminary Acceptance Criteria for Performance Tests when PCBs 77, 126, and 169 only are Tested (1)

| Native PCB               | IUPAC | Test | Concentration (ng/mL) |         |         |         |
|--------------------------|-------|------|-----------------------|---------|---------|---------|
|                          |       |      | IPR (2,3)             |         | OPR     | VER     |
|                          |       |      | s                     | X       |         |         |
| 2,3',4,4'-TCB            | 77    | 20   | 5.4                   | 17-25   | 15-30   | 16-25   |
| 3,3',4,4',5-PeCB         | 126   | 100  | 17                    | 72-150  | 68-160  | 78-130  |
| 3,3',4,4',5,5'-HxCB      | 169   | 200  | 45                    | 148-320 | 128-340 | 156-260 |
| 3C12-3,3',4,4'-TCB       | 77L   | 100  | 34                    | 32-115  | 25-141  | 76-131  |
| 3C12-3,3',4,4',5-PeCB    | 126L  | 100  | 17                    | 72-150  | 68-160  | 78-130  |
| 3C12-3,3',4,4',5,5'-HxCB | 169L  | 200  | 45                    | 148-320 | 128-340 | 156-260 |
| Cleanup standards        |       |      |                       |         |         |         |
| 3C12-3,4,4',5'-TCB       | 81L   | 20   | 7.2                   | 8-31    | 6-38    | 15-26   |
| 3C12-2,3,3',5,5'-PeCB    | 111L  | 100  | 36                    | 39-154  | 31-191  | 79-127  |

## Notes:

1. Preliminary criteria transferred from Method 1613. All criteria given as concentration in the final extract, assuming a 20 uL volume.
2. s = standard deviation of the concentration
3. X = average concentration

Table 7. Labeled Compound Recovery in Samples When All PCBs are Tested

| Native PCB                  | IUPAC | Test<br>conc<br>(ng/mL) | Labeled compound<br>recovery |        |
|-----------------------------|-------|-------------------------|------------------------------|--------|
|                             |       |                         | (ng/mL)                      | (%)    |
| 13C12-3,3',4,4'-TCB         | 77    | 100                     | 24-169                       | 24-169 |
| 13C12-2,3,3',4,4'-PeCB      | 105   | 100                     | 21-178                       | 21-178 |
| 13C12-2,3',4,4',5-PeCB      | 118   | 100                     | 21-178                       | 21-178 |
| 13C12-3,3',4,4',5-PeCB      | 126   | 100                     | 21-178                       | 21-178 |
| 13C12-2,3,3',4,4',5-HxCB    | 156   | 100                     | 26-152                       | 26-152 |
| 13C12-2,3,3',4,4',5'-HxCB   | 157   | 100                     | 26-152                       | 26-152 |
| 13C12-2,3',4,4',5,5'-HxCB   | 167   | 100                     | 26-152                       | 26-152 |
| 13C12-3,3',4,4',5,5'-HxCB   | 169   | 100                     | 26-152                       | 26-152 |
| 13C12-2,2',3,4,4',5,5'-HpCB | 180   | 100                     | 23-143                       | 23-143 |
| 13C12-2,3,3',4,4',5,5'-HpCB | 189   | 100                     | 23-143                       | 23-143 |
| Cleanup standards           |       |                         |                              |        |
| 13C12-3,4,4'5-TCB           | 81    | 20                      | 7-40                         | 35-197 |
| 13C12-2,3,3',5,5'-PeCB      | 111   | 100                     | 35-197                       | 35-197 |

Table 7a. Labeled Compound Recovery When PCBs 77, 126, and 169 Only are Tested (1)

| Native PCB                | IUPAC | Test<br>conc<br>(ng/mL) | Labeled compound<br>recovery |        |
|---------------------------|-------|-------------------------|------------------------------|--------|
|                           |       |                         | (ng/mL)                      | (%)    |
| 13C12-3,3',4,4'-TCB       | 77    | 100                     | 29-140                       | 29-140 |
| 13C12-3,3',4,4',5-PeCB    | 126   | 100                     | 21-178                       | 21-178 |
| 13C12-3,3',4,4',5,5'-HxCB | 169   | 100                     | 26-152                       | 26-152 |
| Cleanup standards         |       |                         |                              |        |
| 13C12-3,4,4'5-TCB         | 81    | 20                      | 8-33                         | 42-164 |
| 13C12-2,3,3',5,5'-PeCB    | 111   | 100                     | 35-197                       | 35-197 |

## Note:

1. Preliminary criteria transferred from Method 1613. Criteria are given as concentration in the final extract, assuming a 20 uL volume.

Table 8. Descriptors, Exact  $m/z$ 's,  $m/z$  Types, and Elemental Compositions of the PCBs

| <u>Descriptor</u> | <u>Exact <math>m/z</math> (1)</u> | <u><math>m/z</math> type</u> | <u>Elemental composition</u> | <u>Substance (2)</u> |
|-------------------|-----------------------------------|------------------------------|------------------------------|----------------------|
| 1.                | 289.9224                          | M                            | C12 H6 35Cl4                 | TCB                  |
|                   | 291.9194                          | M+2                          | C12 H6 35Cl3 37Cl4           | TCB                  |
|                   | 292.9825                          | Lock                         | C7 F11                       | PFK                  |
|                   | 301.9626                          | M                            | 13C12 H6 35Cl4               | PeCB (3)             |
|                   | 303.9597                          | M+2                          | 13C12 H6 35Cl3 37Cl          | PeCB (3)             |
|                   | 325.8804                          | M+2                          | C12 H5 35Cl4 37Cl            | PeCB                 |
|                   | 327.8775                          | M+4                          | C12 H5 35Cl3 37Cl2           | PeCB                 |
|                   | 330.9792                          | QC                           | C7 F13                       | PFK                  |
| 2.                | 325.8804                          | M+2                          | C12 H5 35Cl4 37Cl            | PeCB                 |
|                   | 327.8775                          | M+4                          | C12 H5 35Cl3 37Cl2           | PeCB                 |
|                   | 337.9207                          | M+2                          | 13C12 H5 35Cl4 37Cl          | PeCB (3)             |
|                   | 339.9178                          | M+4                          | 13C12 H5 35Cl3 37Cl2         | PeCB (3)             |
|                   | 354.9892                          | Lock                         | C9F13                        | PFK                  |
|                   | 359.8415                          | M+2                          | C12 H4 35Cl5 37Cl            | HxCB                 |
|                   | 361.8385                          | M+4                          | C12 H4 35Cl4 37Cl2           | HxCB                 |
|                   | 371.8817                          | M+2                          | 13C12 H4 35Cl5 37Cl          | HxCB (3)             |
|                   | 373.8788                          | M+4                          | 13C12 H4 35Cl4 37Cl2         | HxCB (3)             |
|                   | 393.8025                          | M+2                          | C12 H3 35Cl6 37Cl            | HpCB                 |
|                   | 395.7996                          | M+4                          | C12 H3 35Cl5 37Cl2           | HpCB                 |
|                   | 405.8428                          | M+2                          | 13C12 H3 35Cl6 37Cl          | HpCB (3)             |
|                   | 407.8398                          | M+4                          | 13C12 H3 35Cl5 37Cl2         | HpCB (3)             |
| 3.                | 442.9728                          | Lock                         | C10 F17                      | PFK                  |
|                   | 509.7229                          | M+4                          | 13C12 35Cl10 37Cl2           | DCB (3)              |
|                   | 511.7199                          | M+6                          | 13C12 35Cl9 37Cl3            | (3)                  |
|                   | 513.7170                          | M+8                          | 13C12 35Cl8 37Cl4            | (3)                  |

## 1. Nuclidic masses used

H = 1.007825      C = 12.00000       $^{13}\text{C}$  = 13.003355  
 $^{35}\text{Cl}$  = 34.968853       $^{37}\text{Cl}$  = 36.965903

2. TCB = Tetrachlorobiphenyl  
 PeCB = Pentachlorobiphenyl  
 HxCB = Hexachlorobiphenyl  
 HpCB = Heptachlorobiphenyl  
 DCB = Decachlorobiphenyl

3.  $^{13}\text{C}$  labeled compound

Table 9. Theoretical Ion Abundance Ratios and QC Limits

| <u>Iodine<br/>forms</u> | <u>m/z's form-<br/>ing ratio</u> | <u>Theoreti-<br/>cal ratio</u> | <u>QC Limit (1)</u> |              |
|-------------------------|----------------------------------|--------------------------------|---------------------|--------------|
|                         |                                  |                                | <u>Lower</u>        | <u>Upper</u> |
| 4                       | M/(M+2)                          | 0.77                           | 0.65                | 0.89         |
| 5                       | (M+2)/(M+4)                      | 1.55                           | 1.32                | 1.78         |
| 6                       | M/(M+2)                          | 0.51                           | 0.43                | 0.59         |
| 6                       | (M+2)/(M+4)                      | 1.24                           | 1.05                | 1.43         |
| 7                       | M/(M+2)                          | 0.44                           | 0.37                | 0.51         |
| 7                       | (M+2)/(M+4)                      | 1.05                           | 0.88                | 1.20         |
| 8                       | (M+2)/(M+4)                      | 0.89                           | 0.76                | 1.02         |

QC limits represent +/- 15 percent windows around the theoretical ion abundance ratio. These limits are preliminary.

Table 10. Suggested Sample Quantities to be Extracted for Various Matrices<sup>1</sup>

| Sample matrix <sup>2</sup> | Example                                                                                  | Percent solids | Phase           | Quantity extracted |
|----------------------------|------------------------------------------------------------------------------------------|----------------|-----------------|--------------------|
| <i>Single-phase</i>        |                                                                                          |                |                 |                    |
| Aqueous                    | Drinking water<br>Groundwater<br>Treated wastewater                                      | <1             | — <sup>3</sup>  | 1000 mL            |
| Solid                      | Dry soil<br>Compost<br>Ash                                                               | >20            | Solid           | 10 g               |
| Organic                    | Waste solvent<br>Waste oil<br>Organic polymer                                            | <1             | Organic         | 10 g               |
| Tissue                     | Fish<br>Human adipose                                                                    | —              | Organic         | 10 g               |
| <i>Multi-phase</i>         |                                                                                          |                |                 |                    |
| <i>Liquid/Solid</i>        |                                                                                          |                |                 |                    |
| Aqueous/Solid              | Wet soil<br>Untreated effluent<br>Digested municipal sludge<br>Filter cake<br>Paper pulp | 1-30           | Solid           | 10 g               |
| Organic/solid              | Industrial sludge<br>Oily waste                                                          | 1-100          | Both            | 10 g               |
| <i>Liquid/Liquid</i>       |                                                                                          |                |                 |                    |
| Aqueous/organic            | In-process effluent<br>Untreated effluent<br>Drum waste                                  | <1             | Organic         | 10 g               |
| Aqueous/organic/solid      | Untreated effluent<br>Drum waste                                                         | >1             | Organic & solid | 10 g               |

1. The quantity of sample to be extracted is adjusted to provide 10 g of solids (dry weight). One liter of aqueous samples containing one percent solids will contain 10 grams of solids. For aqueous samples containing greater than one percent solids, a lesser volume is used so that 10 grams of solids (dry weight) will be extracted.
2. The sample matrix may be amorphous for some samples. In general, when the PCBs are in contact with a multiphase system in which one of the phases is water, they will be preferentially dispersed in or adsorbed on the alternate phase because of their low solubility in water.
3. Aqueous samples are filtered after spiking with the labeled compounds. The filtrate and the materials trapped on the filter are extracted separately, and the extracts are combined for cleanup and analysis.

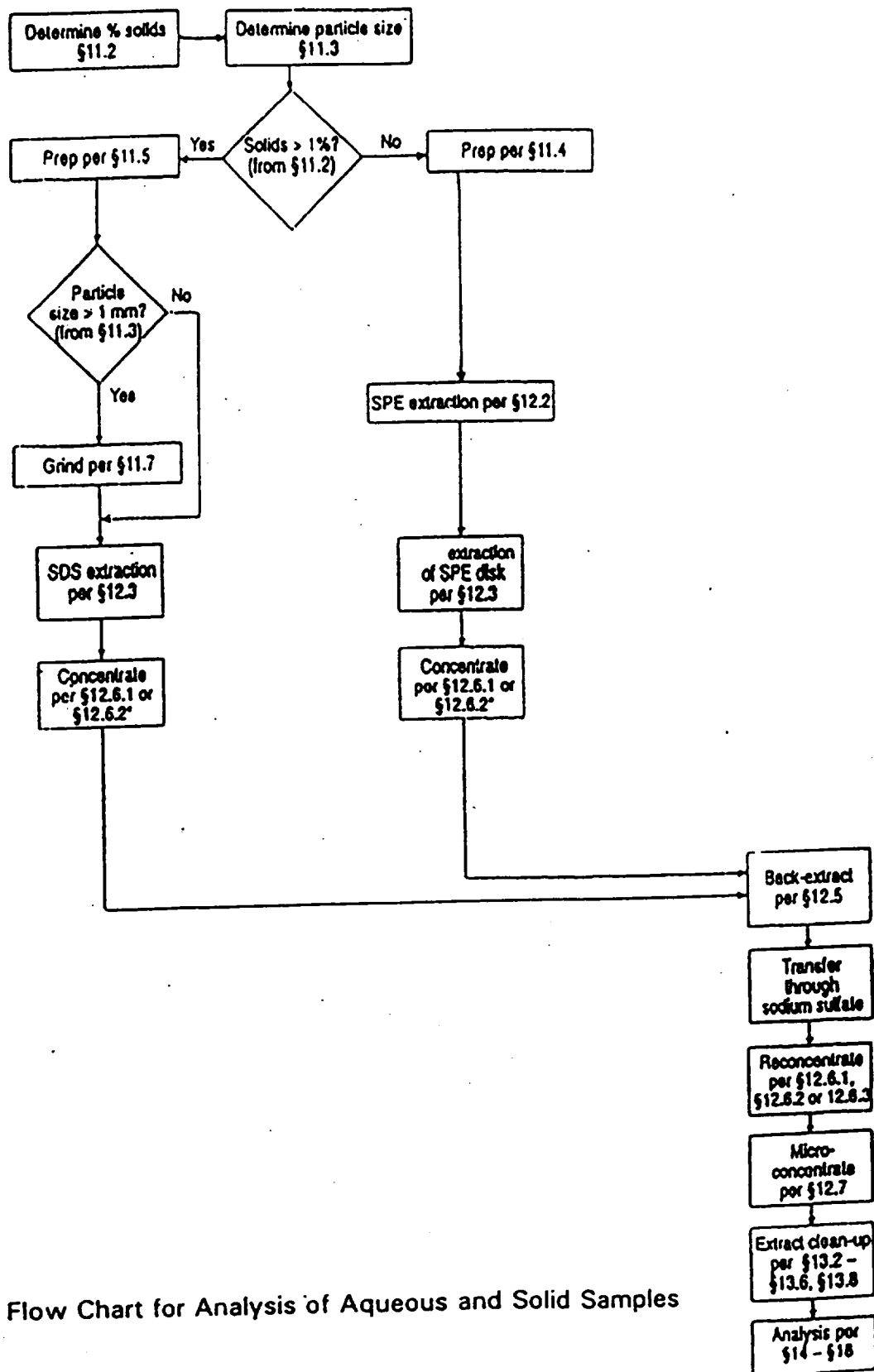


Figure 1 Flow Chart for Analysis of Aqueous and Solid Samples

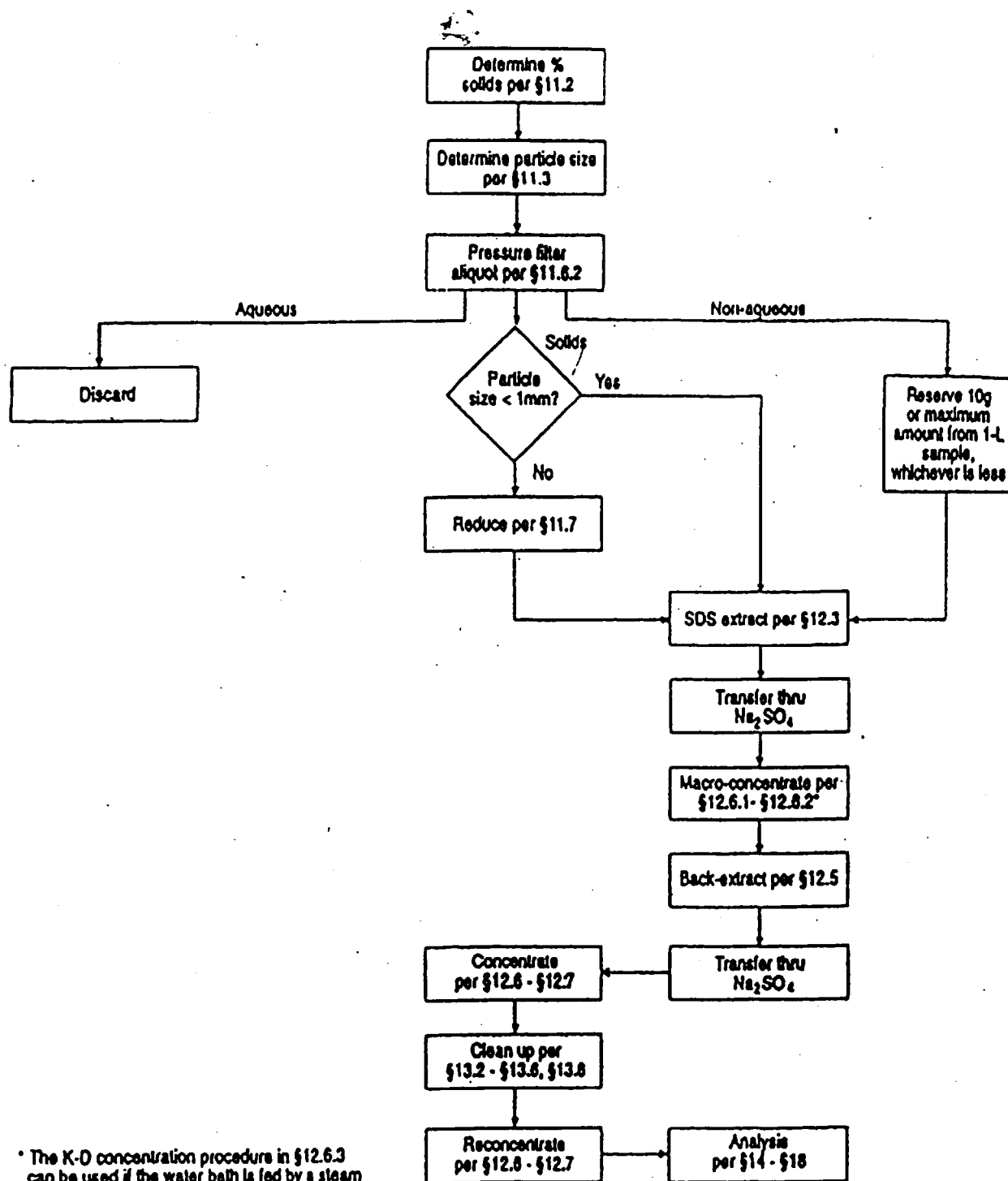


Figure 2 Flow Chart for Analysis of Multi-Phase Samples



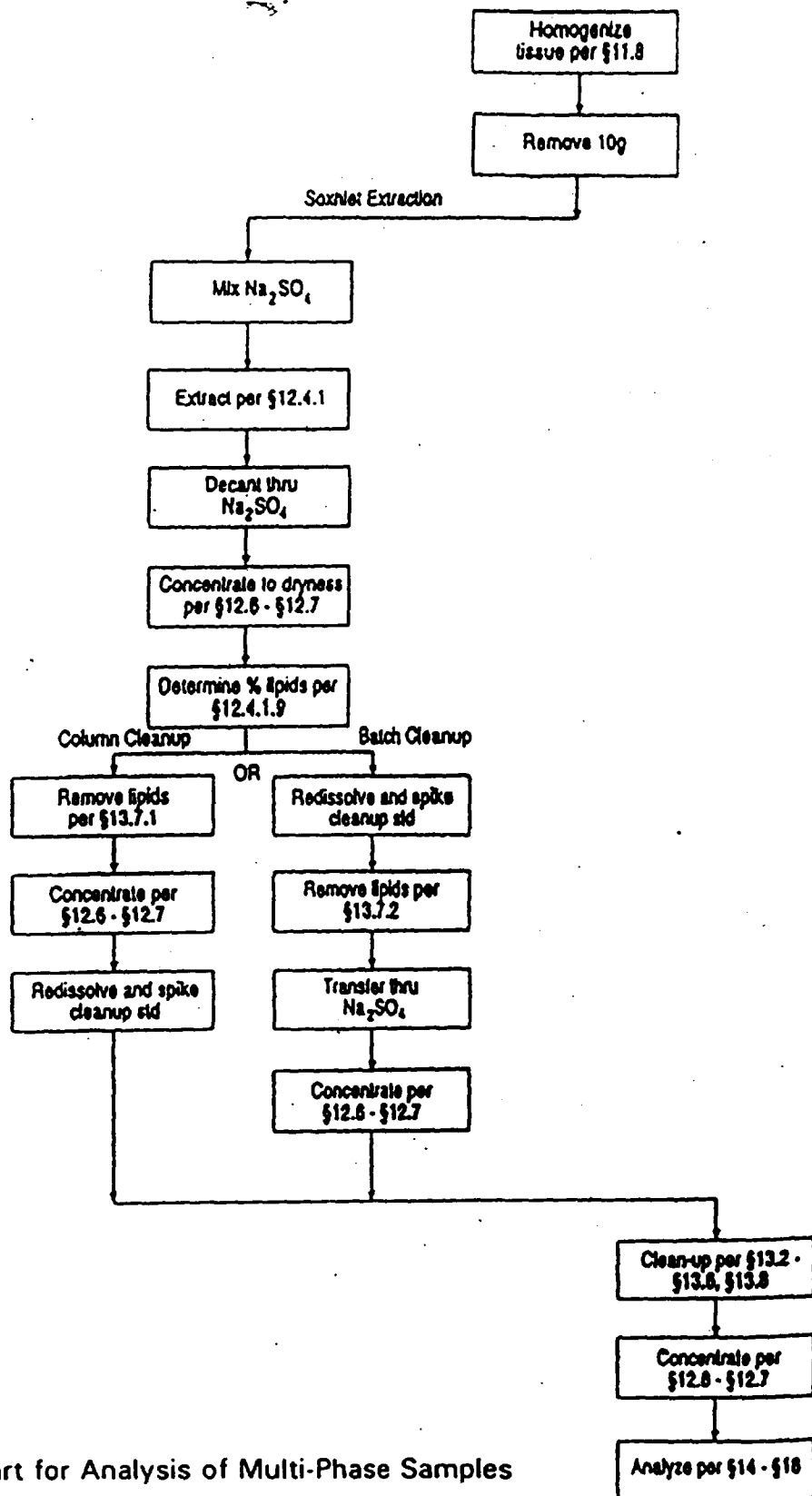


Figure 3 Flow Chart for Analysis of Multi-Phase Samples

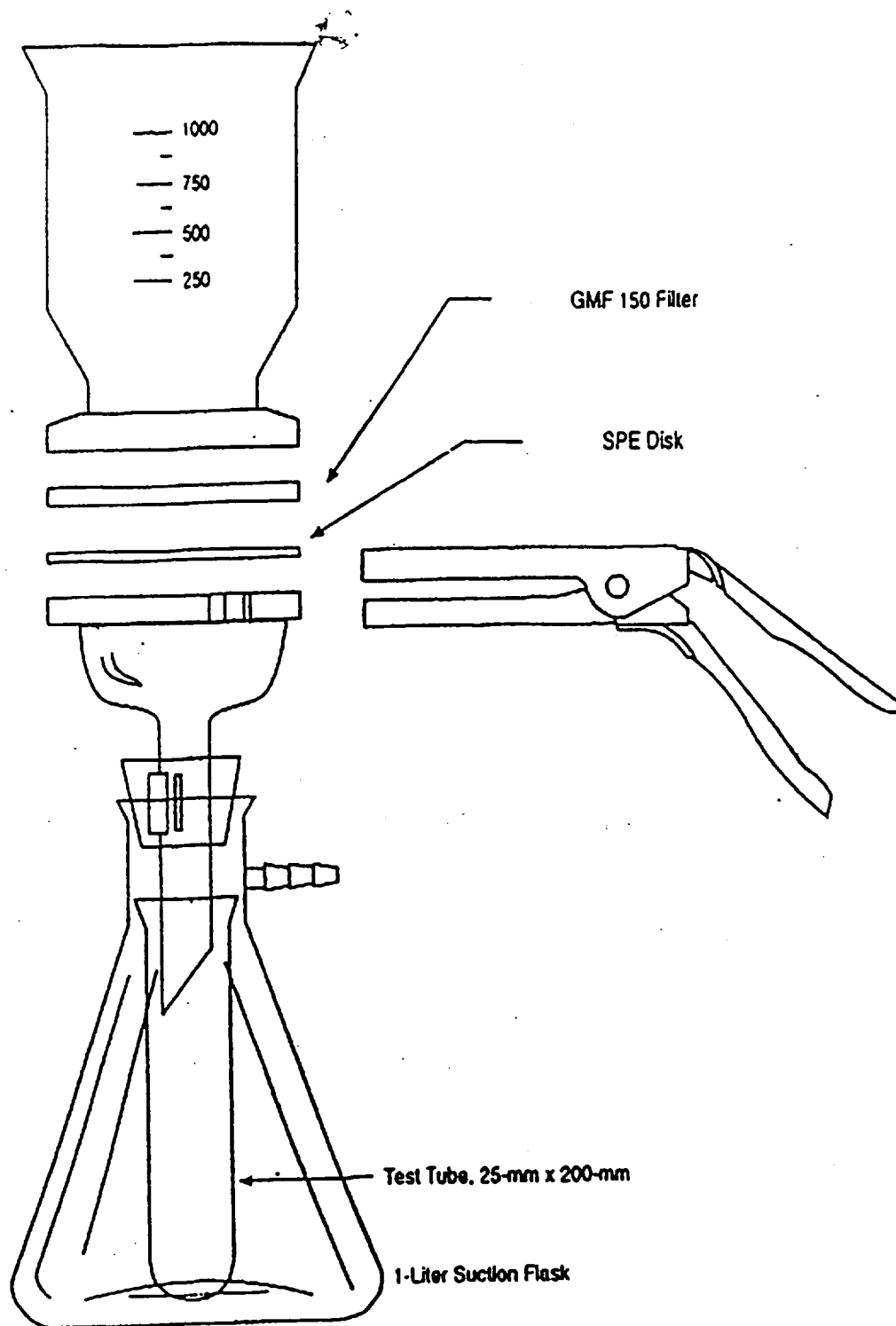
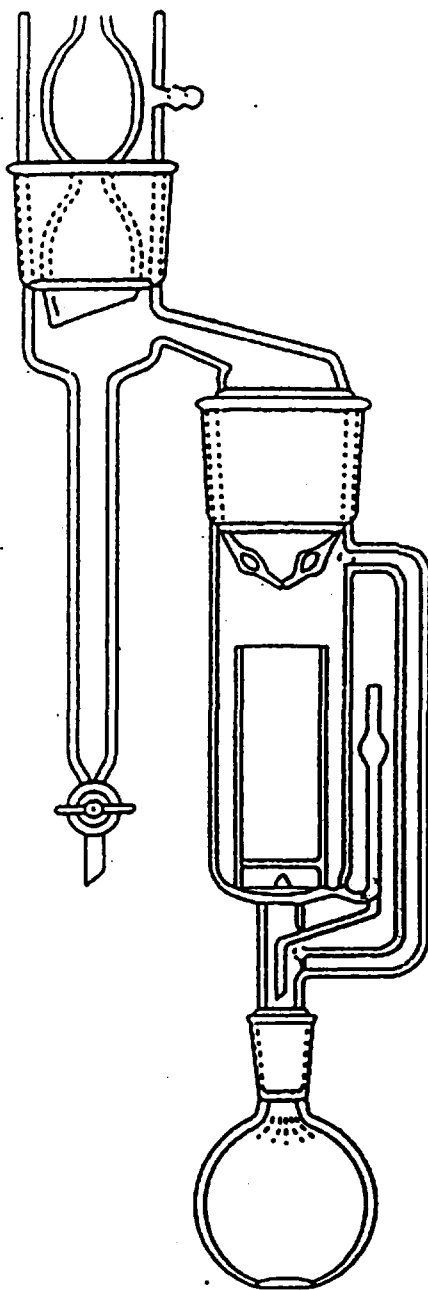


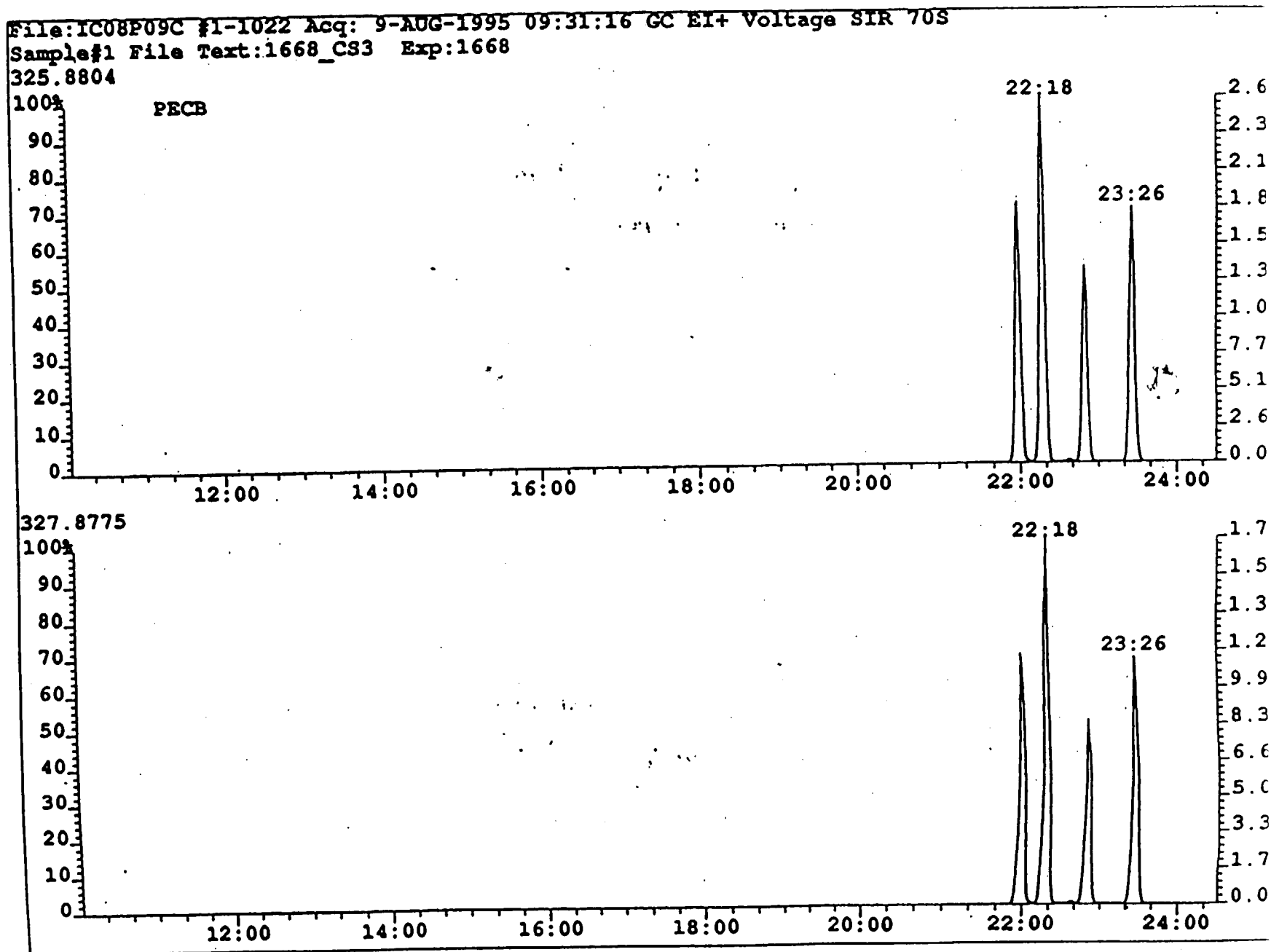
Figure 4 Solid-phase Extraction Apparatus



52-Q27-Q2

Figure 5 Soxhlet/Dean-Stark Extractor

Figure 6 Congener-Specific Separation of Resolution Test Compounds on SPB-Octyl Column



## 24.0 Glossary of Definitions and Purposes

These definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

### 24.1 Units of weight and measure and their abbreviations

#### 24.1.1 Symbols

|    |                 |
|----|-----------------|
| °C | degrees Celsius |
| μL | microliter      |
| μm | micrometer      |
| <  | less than       |
| >  | greater than    |
| %  | percent         |

#### 24.1.2 Alphabetical abbreviations

|      |                                                                                                          |
|------|----------------------------------------------------------------------------------------------------------|
| amp  | ampere                                                                                                   |
| cm   | centimeter                                                                                               |
| g    | gram                                                                                                     |
| h    | hour                                                                                                     |
| ID   | inside diameter                                                                                          |
| in.  | inch                                                                                                     |
| L    | liter                                                                                                    |
| M    | Molecular ion                                                                                            |
| m    | meter                                                                                                    |
| mg   | milligram                                                                                                |
| min  | minute                                                                                                   |
| mL   | milliliter                                                                                               |
| mm   | millimeter                                                                                               |
| m/z  | mass-to-charge ratio                                                                                     |
| N    | normal; gram molecular weight of solute divided by hydrogen equivalent of solute, per. liter of solution |
| OD   | outside diameter                                                                                         |
| pg   | picogram                                                                                                 |
| ppb  | part-per-billion                                                                                         |
| ppm  | part-per-million                                                                                         |
| ppq  | part-per-quadrillion                                                                                     |
| ppt  | part-per-trillion                                                                                        |
| psig | pounds-per-square inch gauge                                                                             |
| v/v  | volume per unit volume                                                                                   |
| w/v  | weight per unit volume                                                                                   |

### 24.2 Definitions and acronyms (in alphabetical order).

**Analyte**—A PCB tested for by this method. The analytes are listed in Table 1.

**Calibration standard (CAL)**—A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

Calibration verification standard (VER)—The mid-point calibration standard (CS3) that is used in to verify calibration. See Table 4.

CS1, CS2, CS3, CS4, CS5—See Calibration standards and Table 4.

DCB—Decachlorobiphenyl (PCB 209)

Field blank—An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

GC—Gas chromatograph or gas chromatography.

GPC—Gel permeation chromatograph or gel permeation chromatography.

HpCB—Heptachlorobiphenyl

HPLC—High performance liquid chromatograph or high performance liquid chromatography.

HRGC—High resolution GC.

HRMS—High resolution MS.

HxCB—Hexachlorobiphenyl

IPR—Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

K-D—Kuderna-Danish concentrator; a device used to concentrate the analytes in a solvent.

Laboratory blank—See Method blank.

Laboratory control sample (LCS)—See Ongoing precision and recovery standard (OPR).

Laboratory reagent blank—See Method blank.

May—This action, activity, or procedural step is neither required nor prohibited.

May not—This action, activity, or procedural step is prohibited.

Method blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if

analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

**Minimum level (ML)**—The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

**MS**—Mass spectrometer or mass spectrometry.

**Must**—This action, activity, or procedural step is required.

**OPR**—Ongoing precision and recovery standard (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

**PAR**—Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

**PFK**—Perfluorokerosene; the mixture of compounds used to calibrate the exact  $m/z$  scale in the HRMS.

**Preparation blank**—See Method blank.

**Primary dilution standard**—A solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

**Quality control check sample (QCS)**—A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

**PeCB**—Pentachlorobiphenyl

**PCB**—Polychlorinated biphenyl

**Reagent water**—water demonstrated to be free from the analytes of interest and potentially interfering substances at the method detection limit for the analyte.

**Relative standard deviation (RSD)**—The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

**RF**—Response factor. See Section 10.6.1.

**RR**—Relative response. See Section 10.5.2.

**RSD**—See Relative standard deviation.

SDS—Soxhlet/Dean-Stark extractor; an extraction device applied to the extraction of solid and semi-solid materials (Reference 12 and Figure 5).

Should—This action, activity, or procedural step is suggested but not required.

SICP—Selected ion current profile; the line described by the signal at an exact  $m/z$ .

SPE—Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

Stock solution—A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

TCB—Tetrachlorobiphenyl

VER—See Calibration verification standard.



Method 680. Determination of Pesticides and PCBs  
in Water and Soil/Sediment  
by Gas Chromatography/Mass Spectrometry

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## 1. SCOPE AND APPLICATION

- 1.1. This method provides procedures for mass spectrometric determination of polychlorinated biphenyls (PCBs) and the listed pesticides in water, soil, or sediment. This method is applicable to samples containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. PCBs are identified and measured as isomer groups (i.e., by level of chlorination). The existence of 209 possible PCB congeners makes impractical the listing of the Chemical Abstracts Service Registry Number (CASRN) for each potential method analyte. Because PCBs are identified and measured as isomer groups, the non-specific CASRN for each level of chlorination is used to describe method analytes.

| <u>Analyte(s)</u>     | <u>Formula</u>        | <u>CASRN</u> |
|-----------------------|-----------------------|--------------|
| Aldrin                | $C_{12}H_8Cl_6$       | 309-00-2     |
| BHCs                  |                       |              |
| alpha isomer          | $C_6H_6Cl_6$          | 319-84-6     |
| beta isomer           | $C_6H_6Cl_6$          | 319-85-7     |
| delta isomer          | $C_6H_6Cl_6$          | 319-86-8     |
| gamma isomer(lindane) | $C_6H_6Cl_6$          | 58-89-9      |
| Chlordane (technical) |                       | 57-74-9      |
| alpha-chlordane       | $C_{10}H_6Cl_8$       | 5103-71-9    |
| gamma-chlordane       | $C_{10}H_6Cl_8$       | 5103-74-2    |
| trans-nonachlor       | $C_{10}H_5Cl_9$       | 39765-80-5   |
| 4,4'-DDD              | $C_{14}H_{10}Cl_4$    | 72-54-8      |
| 4,4'-DDE              | $C_{14}H_8Cl_4$       | 72-55-9      |
| 4,4'-DDT              | $C_{14}H_9Cl_5$       | 50-29-3      |
| Dieldrin              | $C_{12}H_8Cl_6O$      | 60-57-1      |
| Endosulfan I          | $C_9H_6Cl_6O_3S$      | 959-98-8     |
| Endosulfan II         | $C_8H_6Cl_6O_3S$      | 33213-65-9   |
| Endosulfan sulfate    | $C_9H_4Cl_6O_4S$      | 1031-07-8    |
| Endrin                | $C_{12}H_8Cl_6O$      | 72-20-8      |
| Endrin aldehyde       | $C_{12}H_8Cl_6O$      | 7421-93-4    |
| Endrin ketone         | $C_{12}H_8Cl_6O$      | 53494-70-5   |
| Heptachlor            | $C_{10}H_5Cl_7$       | 76-44-8      |
| Heptachlor epoxide    | $C_{10}H_5Cl_7O$      | 1024-57-3    |
| Methoxychlor          | $C_{16}H_{15}Cl_3O_2$ | 72-43-5      |
| PCBs                  |                       |              |
| Monochlorobiphenyls   | $C_{12}H_9Cl$         | 27323-18-8   |
| Dichlorobiphenyls     | $C_{12}H_8Cl_2$       | 25512-42-9   |
| Trichlorobiphenyls    | $C_{12}H_7Cl_3$       | 25323-68-6   |
| Tetrachlorobiphenyls  | $C_{12}H_6Cl_4$       | 26914-33-0   |
| Pentachlorobiphenyls  | $C_{12}H_5Cl_5$       | 25429-29-2   |
| Hexachlorobiphenyls   | $C_{12}H_4Cl_6$       | 26601-64-9   |
| Heptachlorobiphenyls  | $C_{12}H_3Cl_7$       | 28655-71-2   |
| Octachlorobiphenyls   | $C_{12}H_2Cl_8$       | 31472-83-0   |
| Nonachlorobiphenyls   | $C_{12}HCl_9$         | 53742-07-7   |
| Decachlorobiphenyl    | $C_{12}Cl_{10}$       | 2051-24-3    |

1.2 Detection limits vary among method analytes and with sample matrix, sample preparation procedures, condition of the GC/MS system, type of data acquisition, and individual samples. The calculated method detection limit (MDL) for each pesticide in fortified reagent water extracts analyzed with full-range data acquisition is presented in Sect. 14. Analysis of calibration solutions indicated that the calculated MDLs do not accurately reflect instrumental detection limits. The following guidance is based on numerous analyses of calibration solutions with one instrument over a period of approximately six months. Pesticide analytes other than endosulfans I and II can be identified and accurately measured when the injected aliquot contains 2 ng of each analyte; the endosulfans require about 4 ng each. With selected-ion-monitoring (SIM) data acquisition, pesticide analyte detection limits are lowered by at least a factor of five. Detection limits for individual PCB congeners increase with increasing number of chlorine atoms, with the detection limit for decachlorobiphenyl being about 5-10 times higher than that of a monochlorobiphenyl. A monochlorobiphenyl can be identified and accurately measured when the injected extract aliquot contains 1 ng and full-range data are acquired. The detection limit for total PCBs will depend on the number of individual PCB congeners present. SIM data acquisition procedures reduce the detection limit for PCBs by at least a factor of three.

## 2. SUMMARY OF METHOD

A 1-L water sample is placed in a separatory funnel and extracted with methylene chloride. Appropriate extraction procedures for soil/sediment samples will be added when results are obtained from ongoing experiments. The extract is dried and exchanged to hexane during concentration to a final volume of 1 mL or less. Sample extract components are separated with capillary column gas chromatography (GC) and identified and measured with low resolution, electron ionization mass spectrometry (MS). An interfaced data system (DS) to control data acquisition and to store, retrieve, and manipulate mass spectral data is essential. Either full-range or selected-ion-monitoring (SIM) data are acquired, depending on the concentration range of concern. If full-range data are acquired, all method analytes can be identified and measured with one GC/MS analysis. If all pesticides and PCBs must be determined and if SIM data are necessary to meet required detection limits, two GC/MS analyses are necessary, one to detect and measure pesticides and one to detect and measure PCBs.

Two surrogate compounds are added to each sample before sample preparation; these compounds are  $^{13}\text{C}_{12}$ -4,4'-DDT and  $^{13}\text{C}_6$ -gamma-BHC. Two internal standards, chrysene- $\text{d}_{12}$  and phenanthrene- $\text{d}_{10}$ , are added to each sample extract before GC/MS analysis and are used to calibrate MS response. Each concentration measurement is based on an integrated ion abundance of one characteristic ion. All pesticides are identified as individual compounds, and a concentration is calculated by relating the MS response of each compound to the MS response of the internal standard with GC retention time nearer that of the pesticide analyte. The extent of sample contamination with technical chlordane is indicated by identification and measurement of the two most persistent components, gamma-chlordane and nonachlor. (Alpha-chlordane and heptachlor, other major components of technical chlordane, may also be present and will be detected and measured with this method.)

PCBs are identified and measured as isomer groups (i.e., by level of chlorination). A concentration is measured for each PCB isomer group; total PCB concentration in each sample extract is obtained by summing isomer group concentrations.

Nine selected PCB congeners are used as calibration standards, and one internal standard, chrysene-d<sub>12</sub>, is used to calibrate MS response to PCBs, unless sample conditions require the use of the second internal standard, phenanthrene-d<sub>10</sub>.

### 3. DEFINITIONS

- 3.1 CONCENTRATION CALIBRATION SOLUTION (CAL) -- A solution of method analytes used to calibrate the mass spectrometer response.
- 3.2 CONGENER NUMBER -- Throughout this method, individual PCBs are described with the number assigned by Ballschmiter and Zell (2). (This number is also used to describe PCB congeners in catalogs produced by Ultra Scientific, Hope, RI.)
- 3.3 INTERNAL STANDARD -- A pure compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.
- 3.4 LABORATORY DUPLICATES (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory are analyzed with identical procedures. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation or storage procedures.
- 3.5 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the GC/MS/DS with respect to a defined set of method criteria.
- 3.6 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or neutral solid reference material that is treated as a sample. It is exposed to all glassware and apparatus, and all method solvents, reagents, internal standards, and surrogate compounds are used. The extract is concentrated to the final volume used for samples and is analyzed the same as a sample extract.
- 3.7 LABORATORY SPIKE DUPLICATE SAMPLE -- One aliquot (LSD) of a sample is analyzed before fortification with any method analytes. In the laboratory, a known quantity of method analytes (LSA) is added to two independent aliquots of the same sample, and final analyte concentrations (LP1 and LP2) are measured with the same analytical procedures used to measure LSD.
- 3.8 LABORATORY SURROGATE SPIKE
  - 3.8.1 Measured Value (LS1) -- Surrogate compound concentration measured with the same procedures used to measure sample components.
  - 3.8.2 Theoretical Value (LS2) -- The concentration of surrogate compound added to a sample aliquot before extraction. This value is determined from standard gravimetric and volumetric techniques used during sample fortification.
- 3.9 METHOD DETECTION LIMIT (MDL) -- A statistically determined value (1) indicating the minimum concentration of an analyte that can be identified and measured in a sample matrix with 99% confidence that the analyte concentration is greater than zero. This value varies with the precision of the replicate measurements used for the calculation.

- 3.10 PERFORMANCE EVALUATION SAMPLE -- A sample containing known concentrations of method analytes that has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte concentrations are unknown to the analyst.
- 3.11 QUALITY CONTROL (QC) CHECK SAMPLE -- A sample containing known concentrations of analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze environmental samples containing the same or similar analytes. Analyte concentrations are known by the analyst. Preparation of the QC check sample by a laboratory other than the laboratory performing the analysis is highly desirable.
- 3.12 SURROGATE COMPOUND -- A compound not expected to be found in the sample is added to a sample aliquot before extraction and is measured with the same procedures used to measure sample components. Associated with the surrogate compound are two values, laboratory surrogate spike-measured value (LS1) and laboratory surrogate spike - theoretical value (LS2). The purpose of a surrogate compound is to monitor method performance with each sample.

#### 4. INTERFERENCES

- 4.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment. Laboratory reagent blanks (LRBs) are analyzed routinely to demonstrate that these materials are free of interferences under the analytical conditions used for samples.
- 4.2 To minimize interferences, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Then wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry and heat in a muffle furnace at 450°C for a few hours. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent. Volumetric glassware should not be heated in a muffle furnace.
- 4.3 For both pesticides and PCBs, interference can be caused by the presence of much greater quantities of other sample components that overload the capillary column; additional sample extract preparation procedures must then be used to eliminate interferences. Capillary column GC retention times and the compound-specific characteristics of mass spectra eliminate many interferences that formerly were of concern with pesticide/PCB determinations with electron capture detection. The approach and identification criteria used in this method for PCBs eliminate interference by most chlorinated compounds other than other PCBs. With the isomer group approach, coeluting PCBs that contain the same number of chlorines are identified and measured together. Therefore, coeluting PCBs are a problem only if they contain a different number of chlorine atoms. This interference problem is obviated by rigorous application of the identification criteria described in this method.
- 4.4 For SIM identification and measurement of pesticides, other chlorinated sample components that produce the same quantitation and confirmation ions may interfere, but only if retention times are nearly equivalent.

## 5. SAFETY

- 5.1 The toxicity or carcinogenicity of each chemical used in this method has not been precisely defined. Therefore, each should be treated as a potential health hazard, and exposure should be reduced to the lowest feasible level. Each laboratory is responsible for safely disposing materials and for maintaining awareness of OSHA regulations regarding safe handling of the chemicals used in this method. A reference file of material data handling sheets should be made available to all personnel involved in analyses. Additional information on laboratory safety is available (3-5).
- 5.2 The following method analytes have been classified as known or suspected human or mammalian carcinogens: BHCs, 4,4'-DDD, 4,4'-DDT, and PCBs. Primary standards of these compounds should be prepared in a hood. A toxic gas respirator should be worn when the analyst handles solutions containing high concentrations of these compounds.

## 6. APPARATUS AND EQUIPMENT

### 6.1 SAMPLING EQUIPMENT

- 6.1.1 Water Sample Bottles -- Meticulously cleaned (Sect. 4.2) 1-L or 1-qt amber glass fitted with a Teflon-lined screw cap. (Bottles in which high purity solvents were received can be used as sample bottles without additional cleaning if they have been handled carefully to avoid contamination during and after use of original contents.)
- 6.1.2 Soil/Sediment Sample Bottles -- Appropriate containers will be specified when appropriate extraction procedures are determined.

### 6.2 GLASSWARE

- 6.2.1 Separatory Funnel -- 2-L with Teflon stopcock.
- 6.2.2 Drying Column -- glass column approximately 400 mm long X 19 mm ID with coarse frit filter disc.
- 6.2.3 Chromatography Column -- glass column approximately 400 mm long X 19 mm ID with coarse frit filter disc and Teflon stopcock.
- 6.2.4 Concentrator Tube -- 10-mL graduated Kuderna-Danish design with ground-glass stopper.
- 6.2.5 Evaporative Flask -- 500-mL Kuderna-Danish design that is attached to concentrator tube with springs.
- 6.2.6 Snyder Column -- three-ball macro Kuderna-Danish design.
- 6.2.7 Vials -- 10- to 15-mL amber glass with Teflon-lined screw caps.

### 6.3 COMPUTERIZED GC/MS SYSTEM

- 6.3.1 The GC must be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. Manual splitless injections were used to acquire data used as the basis for quality control requirements. An automatic injector, however, is desirable, because it should provide more precise retention times and areas. On-column injection with an uncoated precolumn is encouraged, because high mass discrimination and analyte degradation problems are minimized with this technique. With some GCs, however, the irreproducibility of the low initial column temperature required for on-column injections will cause irreproducible retention times (RTs) and relative retention times (RRTs). That can result in an inability to distinguish between two closely-eluting pesticide isomers and may cause ion sets to be changed at inappropriate times during SIM data acquisition. Splitting injections are not recommended.
- 6.3.2 Either full range or SIM mass spectral data are obtained with electron ionization at a nominal electron energy of 70 eV. To ensure sufficient precision of mass spectral data, the required MS scan rate must allow acquisition of at least five full-range mass spectra or five data points for each monitored ion while a sample component elutes from the GC. The MS must produce a mass spectrum meeting all criteria for <20 ng of decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet.
- 6.3.3 An interfaced data system (DS) is required to acquire, store, reduce, and output mass spectral data. The DS must be capable of searching a data file for specific ions and plotting ion abundances versus time or spectrum number to produce selected ion current profiles (SICPs) and extracted ion current profiles (EICPs). Also required is the capability to obtain chromatographic peak areas between specified times or spectrum numbers in SICPs or EICPs. Total data acquisition time per cycle should be  $\geq 0.5$  s and must not exceed 1.5 s.
- 6.3.4 SIM Option -- For SIM data acquisition, the DS must be equipped with software capable of acquiring data for multiple groups of ions, and the DS must allow automated and rapid changes of the set of ions being monitored. To acquire all PCB data needed for implementation of two currently-available automated interpretation procedures, the SIM program must be capable of acquiring data for four groups (or mass ranges) each consisting of  $\leq 35$  ions or for five groups of  $\leq 20$  ions each. The times spent monitoring ions during sample analyses must be the same as the times used when calibration solutions were analyzed.
- 6.4 GC COLUMN -- A 30 m X 0.32 mm ID fused silica capillary column coated with a 0.25  $\mu$ m or thicker film crosslinked phenyl methyl silicone (such as Durabond-5 (DB-5), J and W Scientific, Rancho Cordova, CA) or polydiphenyl vinyl dimethyl siloxane (such as SE-54, Alltech Associates, Deerfield, IL) is required. Operating conditions known to produce acceptable results with these columns are shown in Table 1; separation of pesticide analytes and PCB calibration congeners with a DB-5 column and those operating conditions is shown in Figure 1. Retention times have been reported (6) for all 209 PCB



congeners with an SE-54 column, which provides the same retention order for PCBs and essentially the same separation capabilities as a DB-5 column.

#### 6.5 MISCELLANEOUS EQUIPMENT

- 6.5.1 Volumetric flasks - 2-mL, 5-mL, 10-mL, 25-mL, and 50-mL with ground glass stoppers.
- 6.5.2 Microsyringes - various standard sizes.
- 6.5.3 Boiling Chips -- approximately 10/40 mesh. Heat at 400°C for 30 min or extract with methylene chloride in a Soxhlet apparatus.
- 6.5.4 Water Bath -- heated, with concentric ring cover, capable of temperature control within  $\pm 2^\circ\text{C}$ .
- 6.5.5 Analytical Balance -- capable of accurately weighing to 0.0001 g.

#### 7. REAGENTS AND CONSUMABLE MATERIALS

- 7.1 SOLVENTS -- High purity, distilled-in-glass hexane and methylene chloride. For precise injections with splitless injectors and capillary columns, all samples and standards should be contained in the same solvent. Effects of minor variations in solvent composition (i.e., small percentage of another solvent remaining in hexane extracts) are minimized with the use of internal standards. (External standard calibration is not acceptable.)
- 7.2 SODIUM SULFATE -- ACS, granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.
- 7.3 SODIUM THIOSULFATE -- ACS, granular.
- 7.4 TETRABUTYLAMMONIUM SULFITE REAGENT -- Dissolve 3.39 g of tetrabutylammonium hydrogen sulfate in 100 mL distilled water. To remove impurities extract solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution in an amber bottle with a Teflon-lined screw cap. The solution can be stored at room temperature for at least one month.
- 7.5. MS PERFORMANCE CHECK SOLUTION -- Prepare a 10 ng/uL solution of decafluoro-triphenylphosphine (DFTPP) in an appropriate solvent.
- 7.6 INTERNAL STANDARDS -- Chrysene- $\text{d}_{12}$  and phenanthrene- $\text{d}_{10}$  are used as internal standards. They are added to each sample extract just before analysis and are contained in all calibration/performance check solutions.
- 7.7 SURROGATE COMPOUNDS --  $^{13}\text{C}_{12}$ -4,4'-DDT and  $^{13}\text{C}_6$ -gamma-BEC are added to every sample before extraction and are included in every calibration/performance check solution.
- 7.8 PCB CONCENTRATION CALIBRATION CONGENERS -- The nine individual PCB congeners listed in Table 2 are used as concentration calibration compounds for PCB determinations. One isomer at each level of chlorination is used as the concentration calibration standard for all other isomers at that level of chlorination, except that decachlorobiphenyl ( $\text{Cl}_{10}$ ) is used for both  $\text{Cl}_9$

and Cl<sub>10</sub> isomer groups. The basis for selection of these calibration congeners has been reported (7).

- 7.9 PCB RETENTION TIME CONGENERS FOR SIM DATA ACQUISITION OPTION -- Knowledge of the retention times of certain congeners is necessary to determine when to acquire data with each ion set. Two concentration calibration congeners also serve as retention time congeners; the first eluting Cl<sub>1</sub>-PCB indicates the time when data acquisition must have been initiated for ion set #1, and the Cl<sub>10</sub>-PCB indicates when all PCBs have eluted. Two or three additional PCB congeners are used to establish times to initiate data acquisition with other ion sets (Sect. 9.4).

#### 7.10 PESTICIDE SOLUTIONS

- 7.10.1 Pesticide Stock Solutions -- Prepare from pure standard materials. Weigh approximately 25.0 mg (with accuracy of 0.1 mg) of each surrogate compound and each pure pesticide analyte, except Endosulfan I and Endosulfan II. For those two pesticides, prepare a stock solution twice as concentrated as that prepared for other pesticide analytes. Dissolve each compound in hexane and dilute to volume in a 10-mL (5-mL for the two Endosulfans) volumetric flask. (Concentration of each component = 2.5 mg/mL, except Endosulfans, which should be 5 mg/mL.) Smaller or larger volumes of stock solution may be used if desired. If compound purity is certified at  $\geq 96\%$ , the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standards in hexane can be used at any concentration if they are traceable to USEPA-supplied standards.
- 7.10.2 Pesticide Primary Dilution Solutions -- A convenient approach to solution preparation is to prepare two pesticide primary dilution solutions that are twice the concentration of the highest concentration calibration solution required. These solutions can then be diluted as necessary to prepare all needed calibration solutions. One solution contains endrin aldehyde and one does not, because the medium level calibration solution does not contain endrin aldehyde. Place 1 mL of each pesticide analyte/surrogate compound stock solution in a 25-mL volumetric flask. (Total volume for all 22 pesticide analytes and 2 surrogate compounds = 24 mL.) Make to volume with hexane and mix well. (Concentration of endosulfan sulfate, endosulfan I and endosulfan II = 200 ng/ $\mu$ L; concentration of each other component = 100 ng/ $\mu$ L.)

#### 7.11 PCB SOLUTIONS

- 7.11.1 Stock Solutions of PCB Calibration Congeners -- Prepare a stock solution of each of the nine PCB concentration calibration congeners at a concentration of 1  $\mu$ g/ $\mu$ L in hexane. (If SIM data are to be acquired, prepare a 1  $\mu$ g/ $\mu$ L stock solution of each of the three retention time congeners also.) Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C if solutions are not to be used right away. Solutions are stable indefinitely if solvent evaporation is prevented.
- CAUTION: Each time a vial containing small volumes of solutions is warmed to room temperature and opened, a small volume of solvent in the vial headspace evaporates, significantly affecting concentration.

Solutions should be stored with the smallest possible volume of headspace, and opening vials should be minimized.

- 7.11.2 PCB Primary Dilution Standard -- Take aliquots of the stock solutions of the nine PCB concentration calibration congeners and mix together in the proportions of one part of each solution of the Cl<sub>1</sub> (#1), Cl<sub>2</sub> (#5), and Cl<sub>3</sub> (#29) congeners, two parts of each solution of the Cl<sub>4</sub> (#50), Cl<sub>5</sub> (#87), and Cl<sub>6</sub> (#154) congeners, three parts of each solution of the Cl<sub>7</sub> (#188) and Cl<sub>8</sub> (#200) congeners, and five parts of the Cl<sub>10</sub> (#209) congener solution. (Note: The retention time congeners described in Sect. 7.9 are not included in the PCB primary dilution standard because they are not needed for full-range data acquisition.) This will provide a primary dilution standard solution of the composition shown in Table 3. Calculate the concentration in ug/uL; use three significant figures. Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C. Mark the meniscus on the vial wall to monitor solution volume during storage; solutions are stable indefinitely if solvent evaporation is prevented.
- 7.12 INTERNAL STANDARD (IS) SOLUTIONS -- Two solutions are needed to prepare concentration calibration solutions (CALs).
- 7.12.1 IS solution #1 (for full-range CALS) -- Weigh 7.5 mg ± 0.1 mg each of phenanthrene-d<sub>10</sub> and chrysene-d<sub>12</sub>; dissolve in hexane and dilute to 10 mL in a volumetric flask. (Concentration of each IS = 750 ng/uL)
- 7.12.2 IS solution #2 (for SIM CALS) -- Take 1 mL of IS solution #1 and dilute to 10 mL in a volumetric flask. (Concentration of each IS = 75 ng/uL)
- 7.13 CALS FOR FULL-RANGE DATA ACQUISITION -- Five hexane solutions are required. The solutions contain constant concentrations of the ISs (chrysene-d<sub>12</sub> and phenanthrene-d<sub>12</sub>) and varying concentrations of individual pesticide analytes, the nine PCB calibration compounds, and the two surrogate compounds (<sup>13</sup>C<sub>12</sub>-4,4'-DDT and <sup>13</sup>C<sub>6</sub>-gamma-BHC). (Composition and approximate concentrations are given in Table 4.) Four solutions (high and low concentrations) contain both ISs, both surrogate compounds, the nine PCB concentration calibration congeners, and each of the single-compound pesticide analytes. The fifth solution, the medium level concentration solution, contains all the above compounds except endrin aldehyde, which is not present for reasons described in Sect. 8. The lowest concentration solution contains each individual pesticide analyte and each PCB calibration congener at a concentration near but greater than its anticipated detection limit. (Because MS response to PCBs decreases with increasing level of chlorination, PCB congener concentrations in CALs increase with level of chlorination.) Components of the highest concentration solution (High CAL) are present at a concentration that allow injections of 2-uL aliquots without MS saturation or GC column overloading.
- 7.13.1 The Full-Range High CAL can be prepared by mixing equal portions of the PCB primary dilution solution and the pesticide primary dilution solution that contains endrin aldehyde and then adding an appropriate volume of IS solution #1. For example, 1 mL of each

primary dilution solution and 20  $\mu$ L of IS solution #1 provide the appropriate concentration for High CAL.

- 7.13.2 Other full-range CALS are prepared by diluting the primary dilution standard solutions and adding the appropriate amount of IS solution #1. CAUTION: The pesticide primary dilution standard that does not contain endrin aldehyde must be used for the medium level full-range CAL.
- 7.14 CALS FOR SIM DATA ACQUISITION OPTION -- Two sets of solutions are needed, one set of five solutions for determinations of pesticide analytes, and one set of five solutions for PCB determinations. Appropriate concentrations of SIM CALs are given in Tables 5a and 5b. Solutions are prepared by diluting appropriate primary dilution standards and adding an appropriate volume of IS solution #2.  
CAUTION: The Pesticide SIM Medium CAL does not contain endrin aldehyde; the PCB SIM CALS must include the three PCB retention time congeners. that are used to establish conditions for SIM data acquisition.
- 7.15 Prepare a solution of surrogate compounds in a water miscible solvent to provide a concentration in the sample/blank extract that is near the concentration anticipated for analytes when an aliquot of  $\geq 20$   $\mu$ L is added to the sample before extraction.
- 7.15 Calculate the concentration (two significant figures if  $< 100$  and three significant figures if  $\geq 100$  ng/ $\mu$ L) of each component in each solution.  
Note: Concentrations presented in tables are only approximate.
- 7.16 LABORATORY PERFORMANCE CHECK SOLUTION - For both full-range data acquisition, and the SIM data acquisition option, the Medium CAL is used as the laboratory performance check solution (LPC) to verify response factors and to demonstrate adequate GC resolution and MS performance.

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

### 8.1 WATER SAMPLES

- 8.1.1 Samples must be collected in clean (Sect. 4.2) glass containers.  
Note: When samples are anticipated to contain low concentrations of method analytes, a sample larger than 1-L may be needed. An effective sample collection procedure to minimize losses of hydrophobic analytes is to add a portion of extracting solvent to each sample container when the sample is collected. When a 1-gal sample is collected, an appropriate solvent volume is approximately 100 mL. (The entire sample must be used as one sample aliquot, and blank sample/solvent volumes must be adjusted also.)
- 8.1.2 Samples must be iced or refrigerated at 4°C from time of collection until extraction. If samples will not be extracted within 72 h after collection, use either sodium hydroxide or sulfuric acid to adjust sample pH to within a range of 5 to 9. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. Field test kits are available for measurement of residual chlorine.

8.1.3 Samples should be extracted within 7 days after collection and analyzed within 40 days after extraction.

8.2 SOIL/SEDIMENT SAMPLES -- Appropriate procedures will be specified when results are obtained from ongoing experiments.

## 9. CALIBRATION

Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of continuing calibration checks. After initial calibration is successfully performed, a continuing calibration check is required at the beginning and end of each 12-h period during which analyses are performed. The Medium CALs for pesticide determinations do not include endrin aldehyde. This allows the Medium CAL to be used for continuing calibration checks, including a check to ensure that endrin decomposition is  $\leq 10\%$ . During initial calibration a separate Medium CAL containing endrin aldehyde and the internal standard is analyzed to determine the response factor for endrin aldehyde. Thereafter, if endrin aldehyde is a component of any sample and endrin decomposition is not a problem, the response factor for endrin aldehyde is verified by analyzing a calibration solution containing it.

9.1 DATA ACQUISITION OPTIONS -- Either full-range or SIM data acquisition may be used.

9.1.1 Full-range data acquisition is recommended if sample extract components are anticipated to be at sufficiently high concentrations.

9.1.2 SIM data acquisition will provide an increase in sensitivity by at least a factor of five for pesticide determinations and by at least a factor of three for PCB determinations.

## 9.2. INITIAL CALIBRATION

9.2.1 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer with any necessary modifications to meet USEPA requirements.

9.2.2 Inject a 1-  $\mu$ L or 2- $\mu$ L aliquot of the 10 ng/ $\mu$ L DFTPP solution and acquire a mass spectrum that includes data for m/z 45-450. If the spectrum does not meet all criteria (Table 6), the MS must be hardware tuned to meet all criteria before proceeding with calibration.

9.2.3 Full-Range Calibration -- Inject a 1- or 2- $\mu$ L aliquot of the Medium CAL and acquire data from m/z 45 to 510. Acquire  $\geq 5$  spectra during elution of each GC peak. Total cycle time should be  $\geq 0.5$  s and  $\leq 1.5$  s. Note: Either a 1- or 2- $\mu$ L aliquot should be used consistently for CALs and sample/blank extracts.

9.2.4 SIM Calibration -- Acquire at least five data points for each ion during elution of each GC peak. Total cycle time should be  $\geq 0.5$  s and  $\leq 1.5$  s.

CAUTION: When acquiring SIM data, GC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times; if not, ions will not be monitored at the appropriate times.

#### 9.2.4.1 SIM Calibration for PCB determinations

- 9.2.4.1.1 Two options for SIM data acquisition are provided. Data can be acquired with four sets of <six mass ranges (<35 ions each as shown in Table 7a) or with the five ion sets (<20 ions each) shown in Tables 7b and 7c.
- 9.2.4.1.2 The time (scan number) for initiation of data acquisition with each ion set must be carefully determined from the retention times (scan numbers) of the retention time congeners. Approximate relative retention times of calibration congeners and approximate relative retention time windows for PCB isomer groups are shown in Table 8. (Also see Figures 1 and 2.)
- 9.2.4.1.3 SIM data acquisition with four ion sets. Begin data acquisition with Ion Set #1 before elution of PCB congener #1, the first eluting Cl<sub>1</sub>-PCB. Stop acquisition with Ion Set #1 and begin acquisition with Ion Set #2 just (approximately 10 s) before elution of PCB congener #104, the first eluting Cl<sub>5</sub>-PCB. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 just (approximately 10 s) after elution of PCB congener #77, the last eluting Cl<sub>4</sub>-PCB. Stop acquisition with Ion Set #3 and begin acquisition with Ion Set #4 just (approximately 10 s) after elution of <sup>13</sup>C<sub>12</sub>-4,4'-DDT.
- 9.2.4.1.4 SIM data acquisition with five ion sets. Acquire data with the four Ion Sets described in Sect. 9.2.4.1.3 and add a fifth Ion Set beginning data acquisition with that set just (approximately 10 s) before elution of PCB congener #208, the first eluting Cl<sub>9</sub>-PCB.

- 9.2.4.2 SIM Calibration for Pesticide Determinations -- Three sets of <15 ions each are used (Tables 9-10). Begin data acquisition with Ion Set #1 before elution of alpha-BHC, the first eluting pesticide analyte. Begin data acquisition with Ion Set #2 after elution of aldrin and before elution of heptachlor epoxide. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 after elution of endosulfan II and before 4,4'-DDD.

#### 9.2.5 Performance Criteria

##### 9.2.5.1 Full-Range Data from Analysis of Medium CAL

- 9.2.5.1.1 GC performance -- baseline separation of beta-BHC and gamma-BHC; baseline separation of endrin ketone and chrysene-d<sub>12</sub>; height of Cl<sub>1</sub>-PCB peak >80% beta-BHC peak height; height of chrysene-d<sub>12</sub> peak >60% of the peak height of methoxychlor, which may partially coelute with the Cl<sub>8</sub>-PCB congener.
- 9.2.5.1.2 MS sensitivity -- Signal/noise ratio of >5 for m/z 499 of PCB congener #209, Cl<sub>10</sub>-PCB.

- 9.2.5.1.3 MS calibration -- Abundance of  $\geq 40\%$  and  $\leq 60\%$  of m/z 502 relative to m/z 498 for PCB congener #209.
- 9.2.5.1.4 Lack of degradation of endrin. Examine an extracted ion current profile (EICP) for m/z 67 in the retention time window between 4,4'-DDE and endosulfan sulfate; confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is  $< 10\%$  of the abundance of m/z 67 produced by endrin.
- 9.2.5.1.5 Lack of degradation of  $^{13}\text{C}_{12}$ -4,4'-DDT. Examine EICPs for m/z 258 and m/z 247 in the retention time window that includes 4,4'-DDD, 4,4'-DDE and 4,4'-DDT; m/z 258 would be produced by  $^{13}\text{C}_{12}$ -4,4'-DDE, and m/z 247 by  $^{13}\text{C}_{12}$ -4,4'-DDD. Confirm that the total abundance of both ions is  $< 5\%$  of m/z 247 produced by  $^{13}\text{C}_{12}$ -4,4'-DDT.
- 9.2.5.2 SIM PCB Data
- 9.2.5.2.1 GC separation -- Baseline separation of PCB congener #87 from congeners #154 and #77, which may coelute.
- 9.2.5.2.2 MS sensitivity -- Signal/noise ratio of  $\geq 5$  for m/z 499 of PCB congener #209,  $\text{Cl}_{10}$ -PCB, and for m/z 241 of chrysene- $\text{d}_{12}$ .
- 9.2.5.2.3 MS calibration -- Abundance of  $\geq 70\%$  and  $\leq 95\%$  of m/z 500 relative to m/z 498 for congener #209,  $\text{Cl}_{10}$ -PCB.
- 9.2.5.3 SIM Pesticide Data
- 9.2.5.3.1 GC separation -- Baseline separation of endrin ketone and chrysene- $\text{d}_{12}$ ; baseline separation of beta-BHC and gamma-BHC; baseline separation of endrin ketone and chrysene- $\text{d}_{12}$ ; height of chrysene- $\text{d}_{12}$  peak  $\geq 60\%$  of methoxychlor peak height.
- 9.2.5.3.2 MS sensitivity -- Signal/noise ratio of  $\geq 5$  for m/z 241 of chrysene- $\text{d}_{12}$ .
- 9.2.5.3.3 MS calibration -- Abundance of m/z 241 relative to that of m/z 240 produced by chrysene- $\text{d}_{12}$  is  $> 15\%$  and  $< 25\%$ .
- 9.2.5.3.4 Lack of degradation of endrin. Examine an SICP for m/z 67 in the retention time window between 4,4'-DDE and endosulfan sulfate; confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is  $< 10\%$  that of m/z 67 produced by endrin.
- 9.2.5.3.5 Lack of degradation of  $^{13}\text{C}_{12}$ -4,4'-DDT. Examine SICPs for m/z 258 and m/z 247 in the retention time window that includes 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT; m/z 258 would be produced by  $^{13}\text{C}_{12}$ -4,4'-DDE, and m/z 247 by  $^{13}\text{C}_{12}$ -4,4'-DDD. Confirm that the total abundance of both ions is  $< 5\%$  of m/z 247 produced by  $^{13}\text{C}_{12}$ -4,4'-DDT.

9.2.6 Replicate Analyses of CALs -- If all performance criteria are met, analyze one 1- or 2-uL aliquot of each of the other four CALs.

9.2.7 Response Factor Calculation

9.2.7.1 Calculate five response factors (RFs) for each pesticide analyte, PCB calibration congener, and surrogate compound relative to both ISs (See Sect. 12.3.2), phenanthrene-d<sub>10</sub> and chrysene-d<sub>12</sub>:

$$RF = A_x Q_{IS} / A_{IS} Q_x$$

where  $A_x$  = integrated ion abundance of quantitation ion for a pesticide, a PCB calibration congener or a surrogate compound,

$A_{IS}$  = integrated ion abundance of m/z 240, the quantitation ion when chrysene-d<sub>12</sub> is used as the internal standard or m/z 188, the quantitation ion when phenanthrene-d<sub>10</sub> is used as the internal standard,

$Q_{IS}$  = injected quantity of chrysene-d<sub>12</sub> or phenanthrene-d<sub>10</sub>,

$Q_x$  = injected quantity of pesticide analyte, PCB calibration congener or surrogate compound.

RF is a unitless number, units used to express quantities must be equivalent. Note: The Cl<sub>2</sub>-PCB calibration congener may not be resolved from alpha-BHC. If not, alpha-BHC will contribute to the ion abundance measured for Cl<sub>2</sub>-PCB. To correct for this contribution, subtract 6.7% of the ion abundance of m/z 219 measured for alpha-BHC from the ion abundance measured for m/z 222 for Cl<sub>2</sub>-PCB.

9.2.8 Response Factor Reproducibility -- For each pesticide analyte, PCB calibration congener and surrogate compound, calculate the mean RF from analyses of each of the five CALs. When the RSD exceeds 20%, analyze additional aliquots of appropriate CALs to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance.

9.2.9 SIM Analyte Retention Time Reproducibility

9.2.9.1 PCB determinations - Absolute retention times of PCB congeners #77 and #104 should not vary by more than  $\pm 10$  s from one analysis to the next. (Retention time reproducibility is not as critical for congeners #1 and #209 as for #77 and #104, which are used to determine when ion sets are changed.)

9.2.9.2 Pesticide determinations -- Absolute retention times of gamma-chlordane, endosulfan I, and endosulfan II should not vary by more than  $\pm 10$  s from one analysis to the next.



9.2.10 Record a spectrum of each CAL component.

### 9.3. CONTINUING CALIBRATION CHECK

- 9.3.1 With the following procedures, verify initial calibration at the beginning and end of each 12-h period during which analyses are to be performed.
- 9.3.2 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer.
- 9.3.3 Analyze a 1-uL or 2-uL aliquot of the DFTPP solution and ensure acceptable MS calibration and performance (Table 6).
- 9.3.4 Inject a 1-uL or 2-uL aliquot of the Medium CAL and analyze with the same conditions used during Initial Calibration.
- 9.3.5 Demonstrate acceptable performance for criteria described in Sect. 9.2.5.
- 9.3.6 Determine that neither the area measured for m/z 240 for chrysene-d<sub>12</sub> nor that for m/z 188 for phenanthrene-d<sub>10</sub> has decreased by more than 30% from the area measured in the most recent previous analysis of a calibration solution or by more than 50% from the mean area measured during initial calibration.
- 9.3.7 Response Factor Reproducibility.-- For an acceptable Continuing Calibration Check, the measured RF for each analyte/surrogate compound must be within +20% of the mean value calculated (Sect. 9.2.7) during Initial Calibration. If not, remedial action must be taken; recalibration may be necessary.
- 9.3.8 SIM Analyte Retention Time Reproducibility -- Demonstrate and document acceptable (Sect. 9.2.9) reproducibility of absolute retention times of appropriate pesticide analytes and PCB retention time congeners.
- 9.3.9 Remedial actions must be taken if criteria are not met; possible remedies are:
  - 9.3.9.1 Check and adjust GC and/or MS operating conditions.
  - 9.3.9.2 Clean or replace injector liner.
  - 9.3.9.3 Flush column with solvent according to manufacturers instructions.
  - 9.3.9.4 Break off a short portion (approximately 0.33 m) of the column; check column performance by analysis of performance check solution.
  - 9.3.9.5 Replace GC column; performance of all initial calibration procedures then required.
  - 9.3.9.6 Adjust MS for greater or lesser resolution.
  - 9.3.9.7 Calibrate MS mass scale.

9.3.9.8 Prepare and analyze new concentration calibration/  
performance check solution.

9.3.9.9 Prepare new concentration calibration curve(s).

## 10. QUALITY CONTROL

10.1 LABORATORY REAGENT BLANK (LRB) -- Perform all steps in the analytical procedure (Section 11) using all reagents, standards, surrogate compounds, equipment, apparatus, glassware, and solvents that would be used for a sample analysis; but omit an aliquot of sample (water or soil/sediment). For water samples, substitute 1 L of reagent water. If available, substitute EPA-provided reagent blank solid material for an aliquot of soil/sediment.

10.1.1 An LRB must contain the same amount of surrogate compounds and internal standards that is added to each sample. This amount will vary with sample type and with the type of data acquisition (full-range or SIM).

10.1.2 Analyze an LRB before any samples are extracted and analyzed.

10.1.3 Before a new batch of solvents or reagents is used for sample extraction or for column chromatographic procedures, analyze an LRB. In addition, analyze a laboratory solvent blank (LSB), which is the same as an LRB except that no surrogate compounds or internal standards are added; this demonstrates that reagents contain no impurities producing an ion current above the level of background noise for quantitation ions for those compounds.

10.1.4 Analyze an LRB along with each batch of  $\leq 20$  samples.

10.1.5 An acceptable LRB contains no method analyte at a concentration greater than one half of its MDL and contains no additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte at its MDL. If the LRB that was extracted along with a batch of samples is contaminated, the entire batch of samples must be reextracted and reanalyzed.

10.1.6 Corrective action for unacceptable LRB -- Check solvents, reagents, apparatus and glassware to locate and eliminate the source of contamination before any samples are extracted and analyzed. Purify or discard contaminated reagents and solvents.

10.2 CALIBRATION -- Included among initial and continuing calibration procedures are numerous quality control checks to ensure that valid data are acquired (See Sect. 9). Continuing calibration checks are accomplished with results from analysis of one solution, the medium level calibration solution for the appropriate type of data acquisition, either full-range or SIM.

10.2.1 If some criteria are not met for a Continuing Calibration Check after a 12-h period during which samples were analyzed, those samples must be reanalyzed. Those criteria are: GC performance (Sect. 9.2.5), MS calibration as indicated by DFTPP spectrum, and MS sensitivity as indicated by area of internal standards.

- 10.2.2 When other criteria in Sect. 9.2 are not met, results for affected analytes must be labeled as suspect to alert the data user of the observed problem. Included among those criteria are: response factor check for each analyte or PCB calibration congener, degradation of DDT and endrin, and retention time reproducibility for SIM data acquisition.
- 10.3 INITIAL DEMONSTRATION OF LABORATORY CAPABILITY FOR WATER ANALYSES  
(Insufficient information is currently available for demonstration for soil/ sediment analyses.)
- 10.3.1 Until appropriate Quality Control Check Samples are available, each laboratory should prepare one or more solutions containing each method analyte at a concentration corresponding to that anticipated in samples. Until accuracy and precision limits have been established for PCB isomer groups in appropriate samples, a solution containing an Aroclor mixture may be used; compare total measured PCB concentration to the total Aroclor concentration. Report Aroclor concentration and measured concentrations of PCB isomer groups and total measured PCB concentration.
- 10.3.2 Add an appropriate volume of a solution of method analytes to each of four 1-L aliquots of reagent water. Extract and analyze according to procedures in Sect. 11.
- 10.3.2 For each analyte, calculate measured concentrations, relative standard deviation of the four measurements, and method bias (Sect. 12.6).
- 10.4 LABORATORY PERFORMANCE CHECK SOLUTION -- In this method, the medium level concentration calibration solution also serves the purpose of a laboratory performance check solution.
- 10.5 LABORATORY SURROGATE SPIKE
- 10.5.1 Measure the concentration of both surrogate compounds in every sample and blank.
- 10.5.2 Until performance based acceptance limits have been established for surrogate compounds, the following guidelines are provided: measured bias with LRB = -30% to +10%; measured bias with water or soil/sediment extract = -50% to +25%.
- 10.6 QUALITY CONTROL CHECK SAMPLE -- Not yet available; anticipate need for analysis of one for each batch of <20 samples. If full-range data are acquired, both pesticide and PCB analytes can be determined with one analysis. If SIM data are acquired, one extraction and two GC/MS analyses will be needed to determine both PCBs and pesticides.
- 10.7 LABORATORY SPIKED DUPLICATE SAMPLE -- Select one sample from each batch of <20 samples of similar type and fortify (spike) two aliquots of that sample with a solution containing appropriate concentrations of pesticide analytes and at least one Aroclor mixture. After addition of surrogate compounds, extract and analyze (Sect. 11) these two fortified aliquots along with an additional unfortified sample aliquot. Relative difference (RD) of duplicate results for surrogate compound concentrations should be <40%.

( $RD = [C_1 - C_2 / 0.5 (C_1 + C_2)] 100$ ) Calculate bias (Sect. 12.6) for each analyte and surrogate compound. Insufficient data are currently available to provide guidance for acceptable bias and RD of measured analyte concentrations.

10.8 PERFORMANCE EVALUATION SAMPLE -- Not yet available; to be analyzed periodically when available.

## 11. PROCEDURES

### 11.1 SAMPLE EXTRACTION

#### 11.1.1 Water Samples

- 11.1.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour entire sample into a 2-L separatory funnel. (If a sample larger than 1-L or 1-qt is extracted, the funnel size and solvent volume for samples and blanks must be adjusted also.)
- 11.1.1.2 Add an appropriate volume of surrogate compound solution.
- 11.1.1.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Wait at least 10 min to allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, use mechanical techniques (such as stirring, filtration of emulsion through glass wool, or centrifugation) to complete phase separation. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.
- 11.1.1.3 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.
- 11.1.1.4 Pour the combined extract into a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Rinse the Erlenmeyer flask with a 20 to 30 mL portion of methylene chloride, and add the rinse to the drying column. Collect the combined extract in the K-D concentrator.
- 11.1.1.5 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus

and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

- 11.1.1.6 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Increase the temperature of the hot water bath to about 80°C. Concentrate the extract to approximately 10 mL as in Sect. 11.1.1.5, except use hexane to prewet the column. Elapsed time of concentration should be 5-10 min.
- 11.1.1.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed within a few hours. If the extract will be stored longer than two days, transfer it to a Teflon-sealed screw-cap vial.
- 11.1.1.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.
- 11.1.2 Soil/Sediment Samples -- Appropriate extraction procedures to be specified when results of ongoing experiments are obtained.
- 11.2 Sulfur Removal -- Elemental sulfur can be removed by the procedure described below. (Sulfur is not expected to be a problem in water sample extracts but sulfur removal is recommended for soil/sediment sample extracts.)
  - 11.2.1 Transfer the extract to a 50-mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the extract container with 1.0 mL of hexane, adding the rinse to the 50-mL bottle.
  - 11.2.2 Add 1 mL of Tetrabutylammonium-sulfite reagent and 1 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.
  - 11.2.3 Add 5 mL of distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min and remove the hexane layer (top) for analysis. Dry the extract by passing it through a 10-cm column containing hexane-washed sodium sulfate. Rinse the sodium sulfate with about 30 mL of hexane and add this hexane to the extract. Concentrate the extract to approximately 10 mL with a K-D apparatus. Store in a refrigerator if GC/MS analysis is not to be performed within a few hours.

### 11.3 GC/MS ANALYSIS

- 11.3.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature if necessary. With a stream of dry, filtered nitrogen, reduce the extract/blank volume to the appropriate volume, depending on anticipated analyte concentrations. Add an appropriate volume of the appropriate internal standard stock solution.
  - 11.3.1.1 Internal standard concentration for full-range data acquisition = 7.5 ng/uL of extract.
  - 11.3.1.2 Internal standard concentration for SIM data acquisition = 0.75 ng/uL of extract.
- 11.3.2 Inject a 1-uL or 2-uL aliquot of the blank/sample extract into the GC operated under conditions used to produce acceptable results during calibration.
- 11.3.3 Acquire mass spectral data with either full-range data acquisition conditions or SIM conditions, as appropriate. Use the same data acquisition time and MS operating conditions previously used to determine response factors.
- 11.3.4 Examine data for saturated ions in mass spectra of target compounds, if saturation occurred, dilute and reanalyze the extract after the quantity of the internal standards is adjusted appropriately.
- 11.3.5 For each internal standard, determine that the area measured in the sample extract has not decreased by >30% from the area measured during the most recent previous analysis of a calibration solution or by >50% from the mean area measured during initial calibration. If either criterion is not met, remedial action must be taken to improve sensitivity, and the sample extract must be reanalyzed.

### 11.4 IDENTIFICATION PROCEDURES

- 11.4.1 Using the ions shown in Tables 7a-7c for PCBs or Table 9 for pesticides, examine ion current profiles (ICPs) to locate internal standards, surrogate compounds, pesticide analytes, and PCBs for each isomer group. Use the RRT data in Table 9 as guidelines for location of pesticide analytes and the RRT window data in Table 8 as guidelines for location of PCB isomers. (A reverse search software routine can be used to locate compounds of concern.)
- 11.4.2 Full-Range Data
  - 11.4.2.1 Examine each pesticide and PCB candidate spectrum after background correction routines have been applied. Compare the candidate spectrum with the appropriate standard spectrum measured during calibration. Verify the absence of any ions with mass greater than the highest mass possible for the compound of concern. (Ions in PCB  $M^+$  ion clusters are shown in Table 12.)

- 11.4.2.2 Obtain integrated abundance areas for quantitation and confirmation ions.
- 11.4.3 SIM Data -- Obtain appropriate selected ion current profiles (SICPs) for IS quantitation and confirmation ions, for each ion monitored to detect pesticides and the surrogate compounds (Table 9), and for the quantitation and confirmation ions for each PCB isomer group.
- 11.4.4 PCB Analytes
- 11.4.4.1 For all PCB candidates, confirm the presence of an  $(M-70)^+$  ion cluster by examining ICPs or spectra for at least one of the most intense ions in the appropriate ion cluster.
- 11.4.4.2 For  $Cl_3$ - $Cl_7$  isomer groups, examine ICPs or spectra for intense  $(M+70)^+$  ions that would indicate a coeluting PCB containing two additional chlorines. (GC retention time data show that this is not a potential problem for other PCB isomer groups; see Figure 2.) If this interference occurs, a correction can be made. Obtain and record the area for the appropriate ion (Table 12) for the candidate PCB isomer group. Use the information in Table 13 to correct the measured abundance of  $M^+$ . For example, if a  $Cl_7$ -PCB and a  $Cl_5$ -PCB candidate coelute, the  $Cl_7$ -PCB will contribute to the ion measured for  $m/z$  326 and  $m/z$  324, the quantitation and confirmation ions, respectively, for a  $Cl_5$ -PCB. Obtain and record the area for  $m/z$  322 (the lowest mass ion in the  $(M+70)^+$  ion cluster of a  $Cl_5$ -PCB fragment produced by a  $Cl_7$ -PCB). To determine the  $m/z$  326 and  $m/z$  324 areas produced by the  $Cl_5$  PCB, calculate the  $Cl_7$ -PCB contribution to each and subtract it from the measured area. In this example, 164% of the area measured for  $m/z$  322 should be subtracted from the area measured for  $m/z$  324, and 108% of the  $m/z$  322 area should be subtracted from the area measured for  $m/z$  326 (Table 13).
- 11.4.4.3 For  $Cl_2$ - $Cl_8$ -PCB candidates, examine ICPs or spectra for intense  $(M+35)^+$  ions that would indicate a coeluting PCB containing one additional chlorine. This coelution causes interferences because of the natural abundance of  $^{13}C$ . (This interference will be small and can be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of another PCB containing one more chlorine.) To correct for this interference, obtain and record the area for the appropriate ion (Table 14) from the  $(M-1)^+$  ion cluster, and subtract 13.5% of the area measured for the  $(M-1)^+$  ion from the measured area of the quantitation ion. For example, for  $Cl_5$ -PCB candidates, obtain and record the area for  $m/z$  325; subtract 13.5% of that area from the measured area of  $m/z$  326.
- 11.4.5 All Analytes -- Use ICP data to calculate the ratio of the measured peak areas of the quantitation ion and confirmation ion(s), and compare to the acceptable ratio (Table 9 for pesticides and Table 12 for PCBs). If acceptable ratios are not obtained, a coeluting or partially coeluting compound may be interfering. Examination of data from several scans may provide information that will allow application of additional background corrections to improve the ion ratio.

## 11.5. IDENTIFICATION CRITERIA

### 11.5.1 Internal Standards

- 11.5.1.1 Chrysene- $d_{12}$  -- the abundance of  $m/z$  241 relative to  $m/z$  240 must be  $\geq 15\%$  and  $\leq 25\%$ , and these ions must maximize simultaneously. The area measured for  $m/z$  240 must be within 30% of the area measured during the most recent calibration.
- 11.5.1.2 Phenanthrene- $d_{10}$  -- the abundance of  $m/z$  189 relative to  $m/z$  188 must be  $\geq 10\%$  and  $\leq 22\%$ , and these ions must maximize simultaneously. The area measured for  $m/z$  188 must be within 30% of the area measured during the most recent acceptable calibration.
- 11.5.1.3 Retention time must be within  $\pm 10$  s of that observed during the most recent acceptable calibration.

### 11.5.2 Full-Range Data for Pesticide Analytes and Surrogate Compounds

- 11.5.2.1 Retention time of the sample component must be within  $\pm$  s of the time observed for that same compound when a calibration solution was analyzed. Calculate the value of  $t$  with the equation,  $t = (RT)^{1/3}$ , where  $RT$  = observed retention time (in seconds) of the compound during the last previous acceptable calibration.
- 11.5.2.2 All ions with relative abundance  $>10\%$  in the mass spectrum must be present in the mass spectrum of the candidate sample component; a molecular ion with relative abundance  $>2\%$  in the standard spectrum must be present in the candidate spectrum.
- 11.5.2.3 The ion that was the most abundant (base peak) in the standard spectrum must also be the base peak in the candidate spectrum.
- 11.5.2.4 For all ions with relative abundance  $>20\%$  in the standard spectrum, the relative abundance in the candidate spectrum must not vary by more than  $\pm 15\%$  in percentage units (i.e., if 50% in standard, must be  $\geq 35\%$  and  $\leq 65\%$ ).
- 11.5.2.5 Ions with relative abundance  $>10\%$  in the candidate spectrum but not present in the standard spectrum must be considered and accounted for by the analyst. When data processing software is used to obtain candidate spectra, both processed and unprocessed spectra must be evaluated.

### 11.5.3 SIM Data for Pesticide Analytes and Surrogate Compounds

- 11.5.3.1 Absolute retention time of each surrogate compound and pesticide candidate must be within 10 s of that measured during the last previous acceptable calibration.
- 11.5.3.2 All ions monitored for each compound (Table 9) must be present and must maximize simultaneously.



11.5.3.3 In a spectrum averaged across a GC peak and with background correction, if necessary, the most abundant ion must correlate with Table 9 data.

11.5.3.4 Observed relative abundances of the monitored ions must meet the following criteria:

Aldrin --  $m/z$  263 = >20% and  $m/z$  265 = >13%  
BHC (each isomer) --  $m/z$  183 = 70-95% of  $m/z$  181  
 $^{13}\text{C}_6$ -gamma-BHC --  $m/z$  189 = 75-90% of  $m/z$  187  
Chlordane (alpha and gamma) --  $m/z$  375 = 75-99%  
4,4'-DDE --  $m/z$  248 = 45-85%  
4,4'-DDD and 4,4'-DDT --  $m/z$  237 = 45-85%  
 $^{13}\text{C}_{12}$ -4,4'-DDT --  $m/z$  249 = 45-85%  
Dieldrin --  $m/z$  263 = >3% and  $m/z$  108 = >8%  
Endosulfan I and II --  $m/z$  339 = >30% and  $m/z$  341 = >20%  
Endosulfan sulfate --  $m/z$  274 = 60-95%  
Endrin --  $m/z$  263 = >50%  
Endrin aldehyde --  $m/z$  345 = >10%  
Endrin ketone --  $m/z$  317 = >30%  
Heptachlor --  $m/z$  272 = >30% and  $m/z$  274 = >20%  
Heptachlor epoxide --  $m/z$  353 = >60%  
Methoxychlor --  $m/z$  228 = 3-30%  
Nonachlor --  $m/z$  407 = 65-95%

#### 11.5.4 Full-Range and SIM Data for PCBs

- 11.5.4.1 Absolute retention times of surrogate compounds must be within  $\pm 10$  s of that measured during the last previous continuing calibration check.
- 11.5.4.2 Quantitation and confirmation ions for each PCB isomer group must maximize within  $\pm 1$  scan of each other.
- 11.5.4.3 The integrated ion current for each quantitation and confirmation ion must be at least three times background noise and must not have saturated the detector.
- 11.5.4.4 For each PCB isomer group candidate, the ratio of the quantitation ion area to the confirmation ion area must be within limits shown in Table 12; at least one ion in the  $(M-70)^+$  ion cluster must be present.

## 12. CALCULATIONS

- 12.1 From appropriate ICPs of quantitation ions, obtain and record the spectrum number of the chromatographic peak apex and the area of the entire chromatographic peak.
- 12.2 For PCBs, sum the areas for all isomers identified at each level of chlorination (e.g., sum all quantitation ion areas for  $\text{Cl}_4$ -PCBs).
- 12.3 Calculate the concentration of each surrogate compound, pesticide candidate, and PCB isomer group using the formula:

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

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

$A_x$  = the area of the quantitation ion for each pesticide analyte/surrogate compound or the sum of quantitation ion areas for all PCB isomers at a particular level of chlorination,

$A_{is}$  = the area of the internal standard quantitation ion, m/z 240 for chrysene-d<sub>12</sub> or m/z 188 for phenanthrene-d<sub>10</sub>,

$Q_{is}$  = quantity (micrograms) of internal standard added to the extract before GC/MS analysis,

RF = calculated response factor for the surrogate compound, the pesticide standard, or the PCB calibration compound for the isomer group (level of chlorination), and

W = weight (kilograms) of sample extracted. If a liquid sample was extracted, W becomes V, the volume (liters) of water extracted, and concentration units become micrograms per liter.

12.3.1 Use the grand mean RF calculated during Initial Calibration.  
CAUTION: For PCB analyses with automated data interpretation a linear fit algorithm will produce erroneous concentration data.

12.3.2 For pesticides eluting before heptachlor epoxide, use the RF relative to phenanthrene-d<sub>10</sub>; for heptachlor epoxide and later eluting pesticides, use the RF relative to chrysene-d<sub>12</sub>. For PCBs, use the RF relative to chrysene-d<sub>12</sub> unless an interference makes the use of the RF relative to phenanthrene-d<sub>10</sub> necessary.

12.4 Estimation of the Concentration of Technical Chlordane. Technical chlordane is a mixture that contains alpha-chlordane (about 13% by weight), gamma-chlordane (about 18% by weight), heptachlor (about 8%), chlordane (three isomers; about 19%) and a variety of side reaction products (including nonachlor isomers) from chlorination of chlordane. Alpha-chlordane is readily converted to gamma-chlordane, which is persistent in environmental samples. Another persistent component is trans-nonachlor. The presence of gamma-chlordane and trans-nonachlor, with or without alpha-chlordane and heptachlor) indicates that technical chlordane was once present in the sample. Therefore the sum of measured concentrations of alpha-chlordane and gamma-chlordane can be used to estimate the original concentration of technical chlordane.

$$C_{tc} = (C_a + C_g) / 0.31$$

where  $C_a$  = measured concentration of alpha-chlordane,  
 $C_g$  = measured concentration of gamma-chlordane, and  
 $C_{tc}$  = estimated concentration of technical chlordane.

12.5 Report calculated values to two significant figures.

12.6 When samples of known composition or fortified samples are analyzed, calculate the percent method bias using the equation:

$$B = 100 (C_s - C_t) / C_t$$

where  $C_s$  = measured concentration (in micrograms per kilogram or micrograms per liter),

$C_t$  = theoretical concentration (i.e., the quantity added to the sample aliquot/weight or volume of sample aliquot).

Note: The bias value retains a positive or negative sign.

### 13. AUTOMATED IDENTIFICATION AND MEASUREMENT

Special software can be used for automated identification and measurement of PCBs (8) and pesticides. Unprocessed GC/MS data are handled without human interaction with the software operating on the dedicated computer. A concentration for each pesticide and each PCB isomer group is calculated automatically. Contact EMSL-Cincinnati for further information.

### 14. METHOD PERFORMANCE

To obtain single laboratory accuracy and precision data for method analytes, replicate 1-L aliquots of reagent water and river water fortified with known amounts of analytes were extracted and analyzed. Automated procedures were used to identify and measure method analytes in 2-uL aliquots of 1-mL extracts. Because a sufficient quantity of individual PCB congeners was not available, Aroclor mixtures were used to fortify water samples. This is not desirable, because individual PCBs in Aroclors vary in concentration. As Aroclor concentrations decrease in a sample extract, an increasing number of components will fall below the detection limit and will not be identified and measured. In addition, insufficient data are available about Aroclor composition to assess accuracy of isomer group measurements or to assess MDLs for PCBs when Aroclors are used to fortify samples.

14.1 Medium Level Reagent Water Extracts -- Five aliquots of reagent water fortified with each individual pesticide at a concentration of 10 ug/L and Aroclors 1221, 1242, 1254, and 1268 at concentrations of 5 ug/L, 50 ug/L, 50 ug/L and 25 ug/L, respectively, were extracted and analyzed. Method bias for individual pesticides ranged from -10% to +18% with a mean method bias of +2% for all 21 pesticides (Table 15). For individual pesticides, RSDs of measured concentration ranged from 0.61% for endrin ketone to 9.8% for endrin aldehyde. No true values are known for concentrations of PCB isomer groups in Aroclors, but the mean measured total PCB concentration was 110 ug/L (RSD 2.9%), which indicated a method bias of -15%. For individual isomer groups, RSDs of mean measured concentrations ranged from 3.9% to 16%.

14.2 Low Level Reagent Water Extract -- Reagent water was fortified with each pesticide at a concentration of 3 ug/L and a total PCB concentration of 27 ug/L (Aroclors 1221, 1 ug/L; 1242, 10 ug/L; 1254, 10 ug/L; and 1268,

6 ug/L). When seven replicate extracts were analyzed, method bias for individual pesticides ranged from -17% to +20% with a mean method bias of -2% (Table 15). An MDL was calculated for each pesticide using the equation relating the standard deviation of the seven replicate measurement and Student's  $t$  value for a one-tailed test at the 99% confidence level with  $n-1$  degrees of freedom (1). With this calculation, MDL is defined as the minimum concentration that can be measured and reported with 99% confidence that the value is above zero. The excellent precision achieved with these measurements resulted in unrealistically low MDLs ranging from 0.2 to 0.8 ug/L for pesticide analytes (Table 15). A PCB MDL is an individual congener characteristic and cannot be determined with samples fortified with Aroclor mixtures. Estimates of MDLs for individual components of PCB isomer groups were obtained by proportioning the total quantity measured for each isomer group among individual measured isomers. The estimated MDL values for individual PCBs also were unrealistically low (0.01-0.1 ug/L) because of the excellent precision of measurements. A more realistic statement of detection limits for pesticides and PCBs can be found in Sect. 1.2.

- 14.3 River Water Extracts -- Five aliquots of river water fortified with each pesticide at a concentration of 5 ug/L and total PCB concentration of 70 ug/L (Aroclors 1221, 2 ug/L; 1242, 30 ug/L; 1254, 30 ug/L; and 1268, 8 ug/L) were extracted and analyzed. Method bias for individual pesticides ranged from -30% to +8% with a mean of -8% (Table 15). The excellent precision of measured pesticide PCB isomer group concentrations was indicated by RSDs ranging from 1.6% to 7.5%. The mean measured total PCB concentration of 51 ug/L (RSD 2.5%) indicated a method bias of -27%.

## 15. REFERENCES

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Table 1. Recommended GC Operating Conditions

|                                                                                           |                                                                                                                                                                                                                             |
|-------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Column Type:                                                                              | SZ-54 or DB-5                                                                                                                                                                                                               |
| Film Thickness:                                                                           | 0.25 um                                                                                                                                                                                                                     |
| Column Dimensions:                                                                        | 30 m X 0.32 mm                                                                                                                                                                                                              |
| Helium Linear Velocity:                                                                   | 28-29 cm/sec<br>at 250°C                                                                                                                                                                                                    |
| Temperature Program for Splitless Injection:                                              |                                                                                                                                                                                                                             |
| o Full-range data acquisition for PCBs and pesticides<br>(Analysis time = approx. 50 min) | Inject at 80°C and hold 1 min; increase at 30°/min to 160°C and hold 1 min; increase at 3°/min to 310°C.<br><br>or<br><br>Inject at 80°C and hold 1 min; heat rapidly to 160°C and hold 1 min; increase at 3°/min to 310°C. |
| o SIM data acquisition for PCBs<br>(Analysis time = approx. 25 min)                       | Inject at 45°C and hold 1 min; increase at 20°/min to 150°C and hold 1 min; increase at 10°/min to 310°C.                                                                                                                   |
| o SIM data acquisition for pesticides<br>(Analysis time = approx. 30 min)                 | Inject at 80°C and hold 1 min; increase at 30°/min to 160°C and hold 1 min; increase at 3°/min to 250°C; hold past elution time of methoxychlor.                                                                            |

Table 2. PCB Congeners Used as Calibration Standards

| PCB Isomer Group                     | Congener Number <sup>a</sup> | Chlorine Substitution    |
|--------------------------------------|------------------------------|--------------------------|
| Concentration Calibration Standard   |                              |                          |
| Monochlorobiphenyl                   | 1                            | 2                        |
| Dichlorobiphenyl                     | 5                            | 2,3                      |
| Trichlorobiphenyl                    | 29                           | 2,4,5                    |
| Tetrachlorobiphenyl                  | 50                           | 2,2',4,6                 |
| Pentachlorobiphenyl                  | 87                           | 2,2',3,4,5'              |
| Hexachlorobiphenyl                   | 154                          | 2,2',4,4',5,6'           |
| Heptachlorobiphenyl                  | 188                          | 2,2',3,4',5,6,6'         |
| Octachlorobiphenyl                   | 200                          | 2,2',3,3',4,5',6,6'      |
| Nonachlorobiphenyl <sup>b</sup>      | -                            | ---                      |
| Decachlorobiphenyl                   | 209                          | 2,2',3,3',4,4',5,5',6,6' |
| Retention Time Calibration Standards |                              |                          |
| Tetrachlorobiphenyl                  | 77                           | 3,3',4,4'                |
| Pentachlorobiphenyl                  | 104                          | 2,2',4,6,6'              |
| Nonachlorobiphenyl                   | 208                          | 2,2',3,3',4,5,5',6,7'    |

<sup>a</sup> Numbered according to the system of Ballschmiter and Zell (2).

<sup>b</sup> Decachlorobiphenyl is used as the calibration congener for both nona- and decachlorobiphenyl isomer groups.

Table 3. Scheme for Preparation of PCB Primary Dilution Standard

| PCB<br>Cong. | Isomer<br>Group  | Stock Sol.<br>Conc.<br>mg/mL | Proportion<br>for Primary<br>Dil. Sol. | Primary Dil.<br>Std. Conc.<br>ng/uL |
|--------------|------------------|------------------------------|----------------------------------------|-------------------------------------|
| #1           | Cl <sub>1</sub>  | 1.0                          | 1 part                                 | 50                                  |
| #5           | Cl <sub>2</sub>  | 1.0                          | 1 part                                 | 50                                  |
| #29          | Cl <sub>3</sub>  | 1.0                          | 1 part                                 | 50                                  |
| #50          | Cl <sub>4</sub>  | 1.0                          | 2 parts                                | 100                                 |
| #87          | Cl <sub>5</sub>  | 1.0                          | 2 parts                                | 100                                 |
| #154         | Cl <sub>6</sub>  | 1.0                          | 2 parts                                | 100                                 |
| #188         | Cl <sub>7</sub>  | 1.0                          | 3 parts                                | 150                                 |
| #200         | Cl <sub>8</sub>  | 1.0                          | 3 parts                                | 150                                 |
| #209         | Cl <sub>10</sub> | 1.0                          | 5 parts                                | 250                                 |

Total 20 parts

Table 4. Composition and Approximate Concentrations of Calibration Solutions for Full-Range Data Acquisition

| Analyte/Int. Std./<br>Surrogate Compound | Concentration (ng/uL) |       |       |       |       |
|------------------------------------------|-----------------------|-------|-------|-------|-------|
|                                          | CAL 1                 | CAL 2 | CAL 3 | CAL 4 | CAL 5 |
| <b>PCB Cal. Congeners</b>                |                       |       |       |       |       |
| Cl <sub>1</sub> (#1)                     | 0.5                   | 2.5   | 5     | 10    | 25    |
| Cl <sub>2</sub> (#5)                     | 0.5                   | 2.5   | 5     | 10    | 25    |
| Cl <sub>3</sub> (#29)                    | 0.5                   | 2.5   | 5     | 10    | 25    |
| Cl <sub>4</sub> (#50)                    | 1                     | 5     | 10    | 20    | 50    |
| Cl <sub>5</sub> (#87)                    | 1                     | 5     | 10    | 20    | 50    |
| Cl <sub>6</sub> (#154)                   | 1                     | 5     | 10    | 20    | 50    |
| Cl <sub>7</sub> (#188)                   | 1.5                   | 7.5   | 15    | 30    | 75    |
| Cl <sub>8</sub> (#200)                   | 1.5                   | 7.5   | 15    | 30    | 75    |
| Cl <sub>10</sub> (#209)                  | 2.5                   | 12.5  | 25    | 50    | 125   |
| <b>Pesticides</b>                        |                       |       |       |       |       |
| Aldrin                                   | 1                     | 5     | 10    | 20    | 50    |
| BHC, each isomer                         | 1                     | 5     | 10    | 20    | 50    |
| Chlordane, each isomer                   | 1                     | 5     | 10    | 20    | 50    |
| 4,4'-DDD                                 | 1                     | 5     | 10    | 20    | 50    |
| 4,4'-DDE                                 | 1                     | 5     | 10    | 20    | 50    |
| 4,4'-DDT                                 | 1                     | 5     | 10    | 20    | 50    |
| Dieldrin                                 | 1                     | 5     | 10    | 20    | 50    |
| Endosulfan I                             | 2                     | 10    | 20    | 40    | 100   |
| Endosulfan II                            | 2                     | 10    | 20    | 40    | 100   |
| Endosulfan sulfate                       | 2                     | 10    | 20    | 40    | 100   |
| Endrin                                   | 1                     | 5     | 10    | 20    | 50    |
| Endrin aldehyde                          | 1                     | 5     | --    | 20    | 50    |
| Endrin ketone                            | 1                     | 5     | 10    | 20    | 50    |
| Heptachlor                               | 1                     | 5     | 10    | 20    | 50    |
| Heptachlor epoxide                       | 1                     | 5     | 10    | 20    | 50    |
| Methoxychlor                             | 1                     | 5     | 10    | 20    | 50    |
| Nonachlor, each isomer                   | 1                     | 5     | 10    | 20    | 50    |
| <b>Internal Standards</b>                |                       |       |       |       |       |
| Chrysene-d <sub>12</sub>                 | 7.5                   | 7.5   | 7.5   | 7.5   | 7.5   |
| Phenanthrene-d <sub>10</sub>             | 7.5                   | 7.5   | 7.5   | 7.5   | 7.5   |
| <b>Surrogate Compounds</b>               |                       |       |       |       |       |
| <sup>13</sup> C <sub>6</sub> -gamma BHC  | 1                     | 5     | 10    | 20    | 50    |
| <sup>13</sup> C <sub>12</sub> -4,4'-DDT  | 1                     | 5     | 10    | 20    | 50    |



Table 5a. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for PCB Determinations

| Compound                                | Concentration (ng/uL) |       |       |       |       |
|-----------------------------------------|-----------------------|-------|-------|-------|-------|
|                                         | CAL 1                 | CAL 2 | CAL 3 | CAL 4 | CAL 5 |
| <b>Cal. Congeners</b>                   |                       |       |       |       |       |
| Cl <sub>1</sub> (#1)                    | 0.1                   | 0.5   | 1     | 2     | 5     |
| Cl <sub>2</sub> (#5)                    | 0.1                   | 0.5   | 1     | 2     | 5     |
| Cl <sub>3</sub> (#29)                   | 0.1                   | 0.5   | 1     | 2     | 5     |
| Cl <sub>4</sub> (#50)                   | 0.2                   | 1.0   | 2     | 4     | 10    |
| Cl <sub>5</sub> (#87)                   | 0.2                   | 1     | 2     | 4     | 10    |
| Cl <sub>6</sub> (#154)                  | 0.2                   | 1     | 2     | 4     | 10    |
| Cl <sub>7</sub> (#188)                  | 0.3                   | 1.5   | 3     | 6     | 15    |
| Cl <sub>8</sub> (#200)                  | 0.3                   | 1.5   | 3     | 6     | 15    |
| Cl <sub>10</sub> (#209)                 | 0.5                   | 2.5   | 5     | 10    | 25    |
| <b>RT Congeners</b>                     |                       |       |       |       |       |
| Cl <sub>4</sub> (#77)                   | 0.2                   | 1     | 2     | 4     | 10    |
| Cl <sub>5</sub> (#104)                  | 0.2                   | 1     | 2     | 4     | 10    |
| Cl <sub>9</sub> (#208)                  | 0.4                   | 2     | 4     | 8     | 20    |
| <b>Internal Standards</b>               |                       |       |       |       |       |
| Chrysene-d <sub>12</sub>                | 0.75                  | 0.75  | 0.75  | 0.75  | 0.75  |
| Phenanthrene-d <sub>10</sub>            | 0.75                  | 0.75  | 0.75  | 0.75  | 0.75  |
| <b>Surrogate Compounds</b>              |                       |       |       |       |       |
| <sup>13</sup> C <sub>6</sub> -gamma-BHC | 0.2                   | 1     | 2     | 4     | 10    |
| <sup>13</sup> C <sub>12</sub> -4,4'-DDT | 0.2                   | 1     | 2     | 4     | 10    |

Table 5b. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for Pesticide Determinations

| Analyte/Internal Std/<br>Surrogate Compound | Concentration (ng/uL) |       |       |       |       |
|---------------------------------------------|-----------------------|-------|-------|-------|-------|
|                                             | CAL 1                 | CAL 2 | CAL 3 | CAL 4 | CAL 5 |
| <b>Pesticide Analytes</b>                   |                       |       |       |       |       |
| Aldrin                                      | 0.2                   | 1     | 2     | 5     | 10    |
| BHC, each isomer                            | 0.2                   | 1     | 2     | 5     | 10    |
| Chlordane, each isomer                      | 0.2                   | 1     | 2     | 5     | 10    |
| 4,4'-DDD                                    | 0.2                   | 1     | 2     | 5     | 10    |
| 4,4'-DDE                                    | 0.2                   | 1     | 2     | 5     | 10    |
| 4,4'-DDT                                    | 0.2                   | 1     | 2     | 5     | 10    |
| Dieldrin                                    | 0.2                   | 1     | 2     | 5     | 10    |
| Endosulfan I                                | 0.4                   | 2     | 4     | 10    | 20    |
| Endosulfan II                               | 0.4                   | 2     | 4     | 10    | 20    |
| Endosulfan sulfate                          | 0.2                   | 1     | 2     | 5     | 10    |
| Endrin                                      | 0.2                   | 1     | 2     | 5     | 10    |
| Endrin aldehyde                             | 0.2                   | 1     | -     | 5     | 10    |
| Endrin ketone                               | 0.2                   | 1     | 2     | 5     | 10    |
| Heptachlor                                  | 0.2                   | 1     | 2     | 5     | 10    |
| Heptachlor epoxide                          | 0.2                   | 1     | 2     | 5     | 10    |
| Methoxychlor                                | 0.2                   | 1     | 2     | 5     | 10    |
| Nonachlor, each isomer                      | 0.2                   | 1     | 2     | 5     | 10    |
| <b>Internal Standards</b>                   |                       |       |       |       |       |
| Chrysene-d <sub>12</sub>                    | 0.75                  | 0.75  | 0.75  | 0.75  | 0.75  |
| Phenanthrene-d <sub>10</sub>                | 0.75                  | 0.75  | 0.75  | 0.75  | 0.75  |
| <b>Surrogate Compounds</b>                  |                       |       |       |       |       |
| <sup>13</sup> C <sub>6</sub> -gamma-BHC     | 0.2                   | 1     | 2     | 5     | 10    |
| <sup>13</sup> C <sub>12</sub> -4,4'-DDT     | 0.2                   | 1     | 2     | 5     | 10    |

Table 6. Criteria for DFTPP Spectrum

| <u>m/z</u> | <u>Relative Abundance</u> |
|------------|---------------------------|
| 127        | 40-60%                    |
| 197        | <1%                       |
| 198        | 100% (Base Peak)          |
| 199        | 5-9%                      |
| 275        | 10-30%                    |
| 365        | >1%                       |
| 441        | Present and <m/z 443      |
| 442        | >40%                      |
| 443        | 17-23% of m/z 442         |

Table 7a. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Four Sets of <35 Ions Each

| PCB Isomer Group/<br>Int.Std./Surr.Cmpd. | Nominal<br>Mol. Wt. | Mass or Range<br>to be Monitored | No. of<br>Ions | Ion Sets       |                |                |    |
|------------------------------------------|---------------------|----------------------------------|----------------|----------------|----------------|----------------|----|
|                                          |                     |                                  |                | #1             | #2             | #3             | #4 |
| Monochlorobiphenyls                      | 188                 | 152; 186-190                     | 6              | 6              |                |                |    |
| Dichlorobiphenyls                        | 222                 | 220-224                          | 5              | 5              |                |                |    |
| Trichlorobiphenyls                       | 256                 | 254-260                          | 7              | 7              | 7              | 1 <sup>a</sup> |    |
| Tetrachlorobiphenyls                     | 290                 | 288-294                          | 7              | 7              | 7              | 1 <sup>b</sup> |    |
| Pentachlorobiphenyls                     | 324                 | 322-328                          | 7              |                | 7              | 7              |    |
| Hexachlorobiphenyls                      | 358                 | 356-362                          | 7              |                | 6 <sup>c</sup> | 7              | 7  |
| Heptachlorobiphenyls                     | 392                 | 390-396                          | 7              |                |                | 6 <sup>d</sup> | 7  |
| Octachlorobiphenyls                      | 426                 | 424-430                          | 7              |                |                |                | 7  |
| Nonachlorobiphenyls                      | 460                 | 460-466                          | 7              |                |                |                | 7  |
| Decachlorobiphenyl                       | 494                 | 496-500                          | 5              |                |                |                | 5  |
| Chrysene-d <sub>12</sub>                 | 240                 | 240-241                          | 2              |                |                |                | 2  |
| Phenanthrene-d <sub>10</sub>             | 188                 | 188-189                          | 2              | 2 <sup>e</sup> |                |                |    |
| <sup>13</sup> C <sub>6</sub> -gamma-BHC  | 294                 | 187, 189                         | 2              | 2 <sup>f</sup> |                |                |    |
| <sup>13</sup> C <sub>12</sub> -4,4'-DDT  | 364                 | 247; 249                         | 2              |                |                | 2              |    |
| Total # ions                             |                     |                                  |                | 25             | 27             | 24             | 35 |

<sup>a</sup>Monitor m/z 254 to confirm presence of (M-70)<sup>+</sup> for Cl<sub>5</sub>-PCBs.

<sup>b</sup>Monitor m/z 288 to confirm presence of (M-70)<sup>+</sup> for Cl<sub>6</sub>-PCBs.

<sup>c</sup>Begin range at m/z 357 in Ion Set #2.

<sup>d</sup>Begin range at m/z 391 in Ion Set #3.

<sup>e</sup>M/z 188 and 189 included among ions used to detect and measure monochlorobiphenyls.

<sup>f</sup>M/z 187 and 189 included among ions used to detect and measure monochlorobiphenyls.

Table 7b. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Sets of <20 Ions Each

| Ion Set | Isomer Group/<br>IS/Surrogate           | Quant.<br>Ion | Confirm.<br>Ions | M-70<br>Ions                    | M+70<br>Ions       | M+35<br>Ions       | Ion Measured <sup>a</sup><br>for Correction |     |
|---------|-----------------------------------------|---------------|------------------|---------------------------------|--------------------|--------------------|---------------------------------------------|-----|
| 1       | Cl <sub>1</sub>                         | 188           | 190              | 152, 153 <sup>b</sup>           | 256, 258           | 222, 224           | -                                           | -   |
|         | Cl <sub>2</sub>                         | 222           | 224              | 152, 153, 186, 188 <sup>c</sup> | 290, 292, 294      | 256, 258           | -                                           | 221 |
|         | Cl <sub>3</sub>                         | 256           | 258              | 186, 188                        | -                  | 290, 292, 294      | -                                           | 255 |
|         | Cl <sub>4</sub>                         | 292           | 290, 294         | 220, 222                        | -                  | -                  | -                                           | -   |
|         | <sup>13</sup> C <sub>6</sub> -gamma-BHC | 187           | 189              | -                               | -                  | -                  | -                                           | -   |
|         | Phenanthrene-d <sub>10</sub>            | 188           | 189              | -                               | -                  | -                  | -                                           | -   |
| 2       | Cl <sub>3</sub>                         | 256           | 258              | 186, 188                        | 324, 326, 328      | 290, 292, 294      | 254                                         | 255 |
|         | Cl <sub>4</sub>                         | 292           | 290, 294         | 220, 222                        | 360, 362           | 324, 326, 328      | 288                                         | 289 |
|         | Cl <sub>5</sub>                         | 326           | 324, 328         | 254, 256, 258                   | -                  | 360, 362           | -                                           | 323 |
|         | Cl <sub>6</sub>                         | 360           | 358, 362         | 288, 290, 292                   | -                  | -                  | -                                           | -   |
| 3       | Cl <sub>5</sub>                         | 326           | 324, 328         | 254, 256                        | 392, 394, 396, 398 | 360, 362           | 322                                         | 323 |
|         | Cl <sub>6</sub>                         | 360           | 358, 362         | 288, 290                        | -                  | 392, 394, 396, 398 | -                                           | 357 |
|         | Cl <sub>7</sub>                         | 394           | 392, 396         | 322, 324, 326                   | -                  | -                  | -                                           | -   |
|         | <sup>13</sup> C <sub>12</sub> -4,4'-DDT | 247           | 249              | -                               | -                  | -                  | -                                           | -   |
| 4       | Cl <sub>6</sub>                         | 360           | 358, 362         | 288, 290                        | 426, 428, 430, 432 | 392, 394, 396      | 356                                         | 357 |
|         | Cl <sub>7</sub>                         | 394           | 392, 396, 398    | 322, 324                        | -                  | 428, 430, 432      | -                                           | 391 |
|         | Cl <sub>8</sub>                         | 430           | 428, 432         | 356, 358, 360                   | -                  | -                  | -                                           | -   |
|         | Chrysene-d <sub>12</sub>                | 240           | 241              | -                               | -                  | -                  | -                                           | -   |
| 5       | Cl <sub>8</sub>                         | 430           | 426, 428, 432    | 356, 358, 360                   | 494, 496, 498, 500 | 462, 464, 466      | -                                           | 425 |
|         | Cl <sub>9</sub>                         | 464           | 460, 462, 466    | 390, 392, 394                   | -                  | 496, 498, 500      | -                                           | -   |
|         | Cl <sub>10</sub>                        | 498           | 494, 496, 500    | 424, 426, 428, 430              | -                  | -                  | -                                           | -   |

<sup>a</sup> See Tables 12-13.

<sup>b</sup> Cl<sub>1</sub>-PCBs lose HCl.

<sup>c</sup> Some Cl<sub>2</sub>-PCBs lose Cl<sub>2</sub> and some lose HCl.

Table 7c. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of <20 Ions

| Ion Set<br>No. 1 <sup>a</sup> | Ion Set<br>No. 2 <sup>b</sup> | Ion Set<br>No. 3 <sup>c</sup> | Ion Set<br>No. 4 <sup>d</sup> | Ion Set<br>No. 5 <sup>e</sup> |
|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 152                           | 186                           | 247                           | 240                           | 356                           |
| 153                           | 188                           | 249                           | 241                           | 358                           |
| 186                           | 220                           | 254                           | 288                           | 360                           |
| 187                           | 222                           | 256                           | 290                           | 390                           |
| 188                           | 254                           | 288                           | 322                           | 392                           |
| 189                           | 255                           | 290                           | 324                           | 394                           |
| 190                           | 256                           | 322                           | 326                           | 424                           |
| 220                           | 258                           | 323                           | 356                           | 425                           |
| 221                           | 288                           | 324                           | 357                           | 426                           |
| 222                           | 289                           | 326                           | 358                           | 428                           |
| 224                           | 290                           | 328                           | 360                           | 430                           |
| 255                           | 292                           | 357                           | 362                           | 432                           |
| 256                           | 294                           | 358                           | 391                           | 462                           |
| 258                           | 323                           | 360                           | 392                           | 464                           |
| 290                           | 324                           | 362                           | 394                           | 466                           |
| 292                           | 326                           | 392                           | 396                           | 496                           |
| 294                           | 328                           | 394                           | 398                           | 498                           |
|                               | 358                           | 396                           | 428                           | 499                           |
|                               | 360                           | 398                           | 430                           | 500                           |
|                               | 362                           |                               | 432                           | 502                           |
| 17 ions                       | 20 ions                       | 19 ions                       | 20 ions                       | 20 ions                       |

<sup>a</sup> Ions to identify and measure Cl<sub>1</sub>-Cl<sub>4</sub>-PCBs, phenanthrene-d<sub>10</sub>, and <sup>13</sup>C<sub>6</sub>-gamma-BHC.

<sup>b</sup> Ions to identify and measure Cl<sub>3</sub>-Cl<sub>6</sub>-PCBs.

<sup>c</sup> Ions to identify and measure Cl<sub>5</sub>-Cl<sub>7</sub>-PCBs and <sup>13</sup>C<sub>12</sub>-4,4'-DDT.

<sup>d</sup> Ions to identify and measure Cl<sub>6</sub>-Cl<sub>8</sub>-PCBs and chrysene-d<sub>12</sub>.

<sup>e</sup> Ions to identify and measure Cl<sub>8</sub>-Cl<sub>10</sub>-PCBs.

Table 8. Retention Time Data for PCB Isomer Groups and Calibration Congeners

| <u>Isomer Group</u>  | <u>Approximate<br/>RRT Range<sup>a</sup></u> | <u>Cal. Cong.<br/>Number</u> | <u>Cal. Cong.<br/>RRT<sup>a</sup></u> |
|----------------------|----------------------------------------------|------------------------------|---------------------------------------|
| Monochlorobiphenyls  | 0.30-0.35                                    | 1                            | 0.30                                  |
| Dichlorobiphenyls    | 0.38-0.50                                    | 5                            | 0.43                                  |
| Trichlorobiphenyls   | 0.46-0.64                                    | 29                           | 0.54                                  |
| Tetrachlorobiphenyls | 0.55-0.82                                    | 50                           | 0.56                                  |
| Pentachlorobiphenyls | 0.64-0.92                                    | 87                           | 0.80                                  |
| Hexachlorobiphenyls  | 0.75-1.1                                     | 154                          | 0.82                                  |
| Heptachlorobiphenyls | 0.88-1.2                                     | 188                          | 0.88                                  |
| Octachlorobiphenyls  | 0.99-1.21                                    | 200                          | 1.03                                  |
| Nonachlorobiphenyls  | 1.16-1.28                                    | -                            | -                                     |
| Decachlorobiphenyl   | 1.3                                          | 209                          | 1.3                                   |

<sup>a</sup> Retention time relative to chrysene-d<sub>12</sub> with a 30 m X 0.31 mm ID SE-54 fused silica capillary column and the following GC conditions: splitless injection at 80°C; hold for 1 min; heat rapidly to 160°C and hold 1 min; increase at 3°C/min to 310°C.

Table 9. Ions for Selected Ion Monitoring Data Acquisition for Pesticide Analytes, Internal Standards and Surrogate Compounds (Ordered by Retention Time)

| <u>Ion Set</u> | <u>Analyte/Internal Std/<br/>Surrogate Compound (MW)</u> | <u>Approx.<br/>RRT</u> | <u>Quant.<br/>Ion</u> | <u>Ions (Approximate<br/>Relative Abundance)</u> |
|----------------|----------------------------------------------------------|------------------------|-----------------------|--------------------------------------------------|
| 1              | Alpha-BHC (288)                                          | 0.43                   | 219                   | 181 (100), 183 (90), 219 (70)                    |
|                | Beta-BHC (288)                                           | 0.47                   | 219                   | 181 (100), 183 (90), 219 (70)                    |
|                | Gamma-BHC (288)                                          | 0.48                   | 219                   | 181 (100), 183 (90), 219 (75)                    |
|                | <sup>13</sup> C <sub>6</sub> -gamma-BHC (294)            | 0.48                   | 225                   | 187 (100), 189 (90), 225 (80), 227 (40)          |
|                | Phenanthrene-d <sub>10</sub> (188)                       | 0.49                   | 188                   | 188 (100), 189 (15)                              |
|                | Delta-BHC (288)                                          | 0.51                   | 219                   | 181 (100), 183 (90), 219 (70)                    |
|                | Heptachlor (370)                                         | 0.58                   | 272                   | 100 (100), 272 (60), 274 (40)                    |
|                | Aldrin (362)                                             | 0.64                   | 263                   | 66 (100), 263 (40), 265 (25)                     |
| 2              | Heptachlor epoxide (386)                                 | 0.70                   | 353                   | 81 (100), 353 (80), 355 (65)                     |
|                | Gamma-chlordane (406)                                    | 0.74                   | 373                   | 373 (100), 375 (95)                              |
|                | Endosulfan I (404)                                       | 0.76                   | 195                   | 195 (100), 339 (50), 341 (35)                    |
|                | Alpha-chlordane (406)                                    | 0.76                   | 373                   | 373 (100), 375 (95)                              |
|                | Trans-nonachlor (440)                                    | 0.77                   | 409                   | 409 (100), 407 (85)                              |
|                | Dieldrin (378)                                           | 0.80                   | 79                    | 79 (100), 263 (10), 108 (15)                     |
|                | 4,4'-DDE (316)                                           | 0.81                   | 246                   | 246 (100), 248 (65)                              |
|                | Endrin (378)                                             | 0.83                   | 81                    | 81 (100), 263 (75)                               |
|                | Endosulfan II (404)                                      | 0.85                   | 195                   | 195 (100), 339 (50), 341 (35)                    |
| 3              | 4,4'-DDD (318)                                           | 0.87                   | 235                   | 235 (100), 237 (65), 165 (65)                    |
|                | Endrin aldehyde (378)                                    | 0.88                   | 67                    | 67 (100), 345 (30)                               |
|                | Endosulfan sulfate (420)                                 | 0.92                   | 272                   | 272 (100), 274 (80), 387 (50)                    |
|                | 4,4'-DDT (352)                                           | 0.93                   | 235                   | 235 (100), 237 (65), 165 (65)                    |
|                | <sup>13</sup> C <sub>12</sub> -4,4'-DDT (364)            | 0.93                   | 247                   | 247 (100), 249 (65)                              |
|                | Endrin ketone (378)                                      | 0.99                   | 67                    | 67 (100), 317 (50)                               |
|                | Chrysene-d <sub>12</sub> (240)                           | 1.00                   | 240                   | 240 (100), 241 (20)                              |
|                | Methoxychlor (344)                                       | 1.03                   | 227                   | 227 (100), 228 (15)                              |



Table 10. Ion Sets for Selected Ion Monitoring of Pesticide Analytes, Internal Standards and Surrogate Compounds (Ordered by Retention Time)

| <u>Ion Set<br/>No. 1</u> | <u>Monitored<br/>Compounds</u>          | <u>Ion Set<br/>No. 2</u> | <u>Monitored<br/>Compounds</u> | <u>Ion Set<br/>No. 3</u> | <u>Monitored<br/>Compounds</u>          |
|--------------------------|-----------------------------------------|--------------------------|--------------------------------|--------------------------|-----------------------------------------|
| 66                       | Alpha-BHC                               | 79                       | Heptachlor                     | 67                       | 4,4'-DDD                                |
| 100                      | Beta-BHC                                | 81                       | epoxide                        | 165                      | Endrin aldehyde                         |
| 181                      | Delta-BHC                               | 108                      | Alpha-chlordane                | 227                      | Endosulfan sulfate                      |
| 183                      | Gamma-BHC                               | 195                      | Gamma-chlordane                | 228                      | 4,4'-DDT                                |
| 187                      | <sup>13</sup> C <sub>6</sub> -gamma-BHC | 246                      | Endosulfan I                   | 235                      | <sup>13</sup> C <sub>12</sub> -4,4'-DDT |
| 188                      | Phenanthrene-d <sub>10</sub>            | 248                      | Trans-nonachlor                | 237                      | Endrin ketone                           |
| 189                      | Heptachlor                              | 263                      | Dieldrin                       | 240                      | Chrysene-d <sub>12</sub>                |
| 219                      | Aldrin                                  | 339                      | 4,4'-DDE                       | 241                      | Methoxychlor                            |
| 225                      |                                         | 341                      | Endrin                         | 247                      |                                         |
| 227                      |                                         | 353                      | Endosulfan II                  | 249                      |                                         |
| 263                      |                                         | 355                      |                                | 272                      |                                         |
| 265                      |                                         | 373                      |                                | 274                      |                                         |
| 272                      |                                         | 375                      |                                | 317                      |                                         |
| 274                      |                                         | 407                      |                                | 345                      |                                         |
|                          |                                         | 409                      |                                | 387                      |                                         |
| 14 ions, 8 compounds     |                                         | 15 ions, 9 compounds     |                                | 15 ions 8 compounds      |                                         |

Table 11. Known Relative Abundances of Ions in PCB Molecular Ion Clusters<sup>a</sup>

| m/z                         | Relative Intensity | m/z                         | Relative Intensity | m/z                        | Relative Intensity |
|-----------------------------|--------------------|-----------------------------|--------------------|----------------------------|--------------------|
| <b>Monochlorobiphenyls</b>  |                    | <b>Hexachlorobiphenyls</b>  |                    | <b>Nonachlorobiphenyls</b> |                    |
| 188                         | 100                | 358                         | 50.9               | 460                        | 26.0               |
| 189                         | 13.5               | 359                         | 6.89               | 461                        | 3.51               |
| 190                         | 33.4               | 360                         | 100                | 462                        | 76.4               |
| 192                         | 4.41               | 361                         | 13.5               | 463                        | 10.3               |
|                             |                    | 362                         | 82.0               | 464                        | 100                |
| <b>Dichlorobiphenyls</b>    |                    | 363                         | 11.0               | 465                        | 13.4               |
| 222                         | 100                | 364                         | 36.0               | 466                        | 76.4               |
| 223                         | 13.5               | 365                         | 4.77               | 467                        | 10.2               |
| 224                         | 66.0               | 366                         | 8.92               | 468                        | 37.6               |
| 225                         | 8.82               | 367                         | 1.17               | 469                        | 5.00               |
| 226                         | 11.2               | 368                         | 1.20               | 470                        | 12.4               |
| 227                         | 1.44               | 369                         | 0.15               | 471                        | 1.63               |
|                             |                    |                             |                    | 472                        | 2.72               |
| <b>Trichlorobiphenyls</b>   |                    | <b>Heptachlorobiphenyls</b> |                    | 473                        | 0.35               |
| 256                         | 100                | 392                         | 43.7               | 474                        | 0.39               |
| 257                         | 13.5               | 393                         | 5.91               |                            |                    |
| 258                         | 98.6               | 394                         | 100                | <b>Decachlorobiphenyl</b>  |                    |
| 259                         | 13.2               | 395                         | 13.5               | 494                        | 20.8               |
| 260                         | 32.7               | 396                         | 98.3               | 495                        | 2.81               |
| 261                         | 4.31               | 397                         | 13.2               | 496                        | 68.0               |
| 262                         | 3.73               | 398                         | 53.8               | 497                        | 9.17               |
| 263                         | 0.47               | 399                         | 7.16               | 498                        | 100                |
|                             |                    | 400                         | 17.7               | 499                        | 13.4               |
| <b>Tetrachlorobiphenyls</b> |                    | 401                         | 2.34               | 500                        | 87.3               |
| 290                         | 76.2               | 402                         | 3.52               | 501                        | 11.7               |
| 291                         | 10.3               | 403                         | 0.46               | 502                        | 50.0               |
| 292                         | 100                | 404                         | 0.40               | 503                        | 6.67               |
| 293                         | 13.4               |                             |                    | 504                        | 19.7               |
| 294                         | 49.4               | <b>Octachlorobiphenyls</b>  |                    | 505                        | 2.61               |
| 295                         | 6.57               | 426                         | 33.4               | 506                        | 5.40               |
| 296                         | 11.0               | 427                         | 4.51               | 507                        | 0.71               |
| 297                         | 1.43               | 428                         | 87.3               | 508                        | 1.02               |
| 298                         | 0.95               | 429                         | 11.8               | 509                        | 0.13               |
|                             |                    | 430                         | 100                |                            |                    |
| <b>Pentachlorobiphenyls</b> |                    | 431                         | 13.4               |                            |                    |
| 324                         | 61.0               | 432                         | 65.6               |                            |                    |
| 325                         | 8.26               | 433                         | 8.76               |                            |                    |
| 326                         | 100                | 434                         | 26.9               |                            |                    |
| 327                         | 13.5               | 435                         | 3.57               |                            |                    |
| 328                         | 65.7               | 436                         | 7.10               |                            |                    |
| 329                         | 8.78               | 437                         | 0.93               |                            |                    |
| 330                         | 21.7               | 438                         | 1.18               |                            |                    |
| 331                         | 2.86               | 439                         | 0.15               |                            |                    |
| 332                         | 3.62               | 440                         | 0.11               |                            |                    |
| 333                         | 0.47               |                             |                    |                            |                    |
| 334                         | 0.25               |                             |                    |                            |                    |

<sup>a</sup>Source: Rote and Morris (9)

Table 12. Quantitation, Confirmation, and Interference Check Ions for PCBs, Internal Standards, and Surrogate Compounds

| Analyte/<br>Internal Std.               | Nom.<br>MW | Quant.<br>Ion | Confirm.<br>Ion | Expected<br>Ratio <sup>a</sup> | Accept.<br>Ratio <sup>a</sup> | M-70             | Interference            |     |
|-----------------------------------------|------------|---------------|-----------------|--------------------------------|-------------------------------|------------------|-------------------------|-----|
|                                         |            |               |                 |                                |                               | Confirm.<br>Ion  | Check Ions<br>M+70 M+35 |     |
| PCB Isomer Group                        |            |               |                 |                                |                               |                  |                         |     |
| Cl <sub>1</sub>                         | 188        | 188           | 190             | 3.0                            | 2.5-3.5                       | 152 <sup>b</sup> | 256                     | 222 |
| Cl <sub>2</sub>                         | 222        | 222           | 224             | 1.5                            | 1.3-1.7                       | 152              | 292                     | 256 |
| Cl <sub>3</sub>                         | 256        | 256           | 258             | 1.0                            | 0.8-1.2                       | 186              | 326                     | 290 |
| Cl <sub>4</sub>                         | 290        | 292           | 290             | 1.3                            | 1.1-1.5                       | 220              | 360                     | 326 |
| Cl <sub>5</sub>                         | 324        | 326           | 324             | 1.6                            | 1.4-1.8                       | 254              | 394                     | 360 |
| Cl <sub>6</sub>                         | 358        | 360           | 362             | 1.2                            | 1.0-1.4                       | 288              | 430                     | 394 |
| Cl <sub>7</sub>                         | 392        | 394           | 396             | 1.0                            | 0.8-1.2                       | 322              | 464                     | 430 |
| Cl <sub>8</sub>                         | 426        | 430           | 428             | 1.1                            | 0.9-1.3                       | 356              | 498                     | 464 |
| Cl <sub>9</sub>                         | 460        | 464           | 466             | 1.3                            | 1.1-1.5                       | 390              | -                       | 498 |
| Cl <sub>10</sub>                        | 494        | 498           | 500             | 1.1                            | 0.9-1.3                       | 424              | -                       | -   |
| Internal standards                      |            |               |                 |                                |                               |                  |                         |     |
| Chrysene-d <sub>12</sub>                | 240        | 240           | 241             | 5.1                            | 4.3-5.9                       | -                | -                       | -   |
| Phenanthrene-d <sub>10</sub>            | 188        | 188           | 189             | 6.6                            | 6.0-7.2                       | -                | -                       | -   |
| Surrogate compounds                     |            |               |                 |                                |                               |                  |                         |     |
| <sup>13</sup> C <sub>6</sub> -gamma-BHC | 294        | 187           | 189             | 1.0                            | 0.8-1.2                       | -                | -                       | -   |
| <sup>13</sup> C <sub>12</sub> -4,4'-DDT | 364        | 247           | 249             | 1.5                            | 1.3-1.7                       | -                | -                       | -   |

<sup>a</sup> Ratio of quantitation ion to confirmation ion

<sup>b</sup> Monodichlorobiphenyls lose HCl to produce an ion at m/z 152.

Table 13. Correction for Interference of PCB Containing Two Additional Chlorines

| Candidate<br>Isomer Group | Quant.<br>Ion | Confirm.<br>Ion | Ion Measured<br>to Determine<br>Interference | % of Meas. Ion Area to<br>be Subtracted from |                      |
|---------------------------|---------------|-----------------|----------------------------------------------|----------------------------------------------|----------------------|
|                           |               |                 |                                              | Quant<br>Ion Area                            | Confirm.<br>Ion Area |
| Trichlorobiphenyls        | 256           | 258             | 254                                          | 99%                                          | 33%                  |
| Tetrachlorobiphenyls      | 292           | 290             | 288                                          | 65%                                          | 131%                 |
| Pentachlorobiphenyls      | 326           | 324             | 322                                          | 108%                                         | 164%                 |
| Hexachlorobiphenyls       | 360           | 362             | 356                                          | 161%                                         | 71%                  |
| Heptachlorobiphenyls      | 394           | 396             | 390                                          | 225%                                         | 123%                 |

Table 14. Correction for Interference of PCB Containing One Additional Chlorine

| Candidate<br>Isomer Group | Quant.<br>Ion | Ion Measured<br>to Determine<br>Interference | % of Meas. Ion Area<br>to be Subtracted<br>from Quant. Ion Area |
|---------------------------|---------------|----------------------------------------------|-----------------------------------------------------------------|
|                           |               |                                              |                                                                 |
| Dichlorobiphenyls         | 222           | 221                                          | 13.5%                                                           |
| Trichlorobiphenyls        | 256           | 255                                          | 13.5%                                                           |
| Tetrachlorobiphenyls      | 292           | 289                                          | 17.4%                                                           |
| Pentachlorobiphenyls      | 326           | 323                                          | 22.0%                                                           |
| Hexachlorobiphenyls       | 360           | 357                                          | 26.5%                                                           |
| Heptachlorobiphenyls      | 394           | 391                                          | 30.9%                                                           |
| Octachlorobiphenyls       | 430           | 425                                          | 40.0%                                                           |

Table 15. Accuracy and Precision of Automated Measurements of PCBs and Pesticides in Fortified Water Extracts

| Analyte<br>(Meas. Ion) | Medium Level Reagent Water <sup>a</sup> |                                       |           |  | Low Level Reagent Water <sup>b</sup> |                                       |           |             | Ohio River Water <sup>a</sup> |                                       |           |  |
|------------------------|-----------------------------------------|---------------------------------------|-----------|--|--------------------------------------|---------------------------------------|-----------|-------------|-------------------------------|---------------------------------------|-----------|--|
|                        | True<br>Conc.<br>ug/L                   | Mean Meas.<br>Conc., ug/L<br>(RSD, %) | Bias<br>% |  | True<br>Conc.<br>ug/L                | Mean Meas.<br>Conc., ug/L<br>(RSD, %) | Bias<br>% | MDL<br>ug/L | True<br>Conc.<br>ug/L         | Mean Meas.<br>Conc., ug/L<br>(RSD, %) | Bias<br>% |  |
| Aldrin (263)           | 10                                      | 9.6 (3.6)                             | -4        |  | 3                                    | 2.5 (7.2)                             | -17       | 0.6         | 5                             | 4.7 (3.0)                             | -6        |  |
| BHC, alpha (219)       | 10                                      | 9.8 (4.3)                             | -2        |  | 3                                    | 2.8 (5.0)                             | -7        | 0.4         | 5                             | 4.7 (1.6)                             | -6        |  |
| BHC, beta (219)        | 10                                      | 10.5 (3.6)                            | +5        |  | 3                                    | 3.0 (2.5)                             | 0         | 0.2         | 5                             | 5.1 (2.5)                             | +2        |  |
| BHC, gamma (219)       | 10                                      | 10.2 (4.7)                            | +2        |  | 3                                    | 2.9 (5.3)                             | -3        | 0.5         | 5                             | 4.8 (3.0)                             | -4        |  |
| BHC, delta (219)       | 10                                      | 9.9 (4.2)                             | -1        |  | 3                                    | 2.9 (4.8)                             | -3        | 0.4         | 5                             | 4.8 (2.4)                             | -4        |  |
| Chlordane, alpha (373) | 10                                      | 9.6 (3.9)                             | -4        |  | 3                                    | 2.9 (4.0)                             | -3        | 0.4         | 5                             | 4.6 (4.2)                             | -8        |  |
| Chlordane, gamma (373) | 10                                      | 9.6 (4.6)                             | -4        |  | 3                                    | 2.7 (4.8)                             | -10       | 0.4         | 5                             | 4.4 (3.5)                             | -12       |  |
| 4,4'-DDD (235)         | 10                                      | 10.4 (3.0)                            | +4        |  | 3                                    | 2.9 (3.8)                             | -3        | 0.4         | 5                             | 4.8 (2.5)                             | -4        |  |
| 4,4'-DDE (246)         | 10                                      | 9.8 (3.2)                             | -2        |  | 3                                    | 2.8 (5.4)                             | -7        | 0.5         | 5                             | 4.5 (4.5)                             | -10       |  |
| 4,4'-DDT (235)         | 10                                      | 10.9 (3.0)                            | +9        |  | 3                                    | 2.9 (4.5)                             | -3        | 0.4         | 5                             | 4.7 (3.9)                             | -6        |  |
| Dieldrin (79)          | 10                                      | 10.6 (3.2)                            | +6        |  | 3                                    | 2.9 (7.6)                             | -3        | 0.7         | 5                             | 4.5 (4.3)                             | -10       |  |
| Endosulfan I (195)     | 10                                      | 9.6 (5.8)                             | -4        |  | 3                                    | 3.1 (4.8)                             | +3        | 0.5         | 5                             | 4.4 (5.0)                             | -12       |  |
| Endosulfan II (195)    | 10                                      | 10.2 (4.5)                            | +2        |  | 3                                    | 3.3 (6.3)                             | +10       | 0.7         | 5                             | 3.5 (4.1)                             | -30       |  |
| Endosulfan sulf. (272) | 10                                      | 10.6 (2.3)                            | +6        |  | 3                                    | 3.2 (4.4)                             | +7        | 0.4         | 5                             | 4.8 (1.7)                             | -4        |  |
| Endrin (81)            | 10                                      | 11.8 (2.8)                            | +18       |  | 3                                    | 3.6 (7.0)                             | +20       | 0.8         | 5                             | 5.4 (7.5)                             | +8        |  |
| Endrin aldehyde (67)   | 10                                      | 9.0 (9.8)                             | -10       |  | 3                                    | 2.8 (8.4)                             | -7        | 0.7         | 5                             | 4.4 (4.8)                             | -12       |  |
| Endrin ketone (67)     | 10                                      | 11.5 (0.61)                           | +15       |  | 3                                    | 3.2 (1.9)                             | +7        | 0.2         | 5                             | 4.7 (3.0)                             | -6        |  |
| Heptachlor (272)       | 10                                      | 10.6 (5.1)                            | +6        |  | 3                                    | 2.6 (5.3)                             | -13       | 0.4         | 5                             | 4.9 (3.5)                             | -2        |  |
| Heptachlor epox. (353) | 10                                      | 10.0 (2.5)                            | 0         |  | 3                                    | 3.0 (5.9)                             | 0         | 0.6         | 5                             | 4.8 (3.9)                             | -4        |  |
| Methoxychlor (227)     | 10                                      | 11.4 (1.6)                            | +14       |  | 3                                    | 3.1 (2.3)                             | +3        | 0.2         | 5                             | 4.8 (3.8)                             | -4        |  |
| Nonachlor, trans (409) | 10                                      | 9.5 (4.6)                             | -5        |  | 3                                    | 2.8 (2.4)                             | -7        | 0.2         | 5                             | 4.4 (4.3)                             | -12       |  |
| All pesticides         | 10                                      | 10.2 (7.1)                            | +2        |  | 3                                    | 2.9 (8.6)                             | -2        |             | 5                             | 4.6 (7.7)                             | -8        |  |

Table 15. (Cont.) Accuracy and Precision of Automated Measurements of PCBs and Pesticides in Fortified Water Extracts

| Analyte<br>(Meas. Ion)                        | Medium Level Reagent Water <sup>a</sup> |                                       |                   |   | Low Level Reagent Water <sup>b</sup> |                                       |                   |                            | Ohio River Water <sup>a</sup> |                                       |                   |  |
|-----------------------------------------------|-----------------------------------------|---------------------------------------|-------------------|---|--------------------------------------|---------------------------------------|-------------------|----------------------------|-------------------------------|---------------------------------------|-------------------|--|
|                                               | True<br>Conc.<br>ug/L                   | Mean Meas.<br>Conc., ug/L<br>(RSD, %) | Mean<br>Bias<br>% |   | True<br>Conc.<br>ug/L                | Mean Meas.<br>Conc., ug/L<br>(RSD, %) | Mean<br>Bias<br>% | Method<br>Detect.<br>Limit | True<br>Conc.<br>ug/L         | Mean Meas.<br>Conc., ug/L<br>(RSD, %) | Mean<br>Bias<br>% |  |
| PCBs                                          | 130                                     | 110 (2.9)                             | -15               |   | 27                                   | 21.2 (2.8)                            | -21               | C                          | 70                            | 51.3 (2.5)                            | -27               |  |
| Cl <sub>1</sub> (188)                         | -                                       | 3.6 (9.9)                             | -                 |   |                                      | 0.7 (15)                              | -                 |                            |                               | 1.83 (4.8)                            |                   |  |
| Cl <sub>2</sub> (222)                         | -                                       | 6.5 (5.7)                             | -                 |   |                                      | 1.2 (10)                              | -                 |                            |                               | 3.42 (3.9)                            |                   |  |
| Cl <sub>3</sub> (256)                         | -                                       | 17.2 (5.3)                            | -                 |   |                                      | 3.1 (10)                              | -                 |                            |                               | 10.1 (3.0)                            |                   |  |
| Cl <sub>4</sub> (292)                         | -                                       | 21.7 (4.1)                            | -                 |   |                                      | 4.1 (3.8)                             | -                 |                            |                               | 11.0 (4.5)                            |                   |  |
| Cl <sub>5</sub> (326)                         | -                                       | 28.8 (3.6)                            | -                 |   |                                      | 5.6 (2.8)                             | -                 |                            |                               | 15.4 (3.6)                            |                   |  |
| Cl <sub>6</sub> (360)                         | -                                       | 9.8 (5.7)                             | -                 |   |                                      | 1.6 (3.1)                             | -                 |                            |                               | 4.86 (6.4)                            |                   |  |
| Cl <sub>7</sub> (394)                         | -                                       | 1.3 (4.3)                             | -                 |   |                                      | -                                     | -                 |                            |                               | 0.335 (4.8)                           |                   |  |
| Cl <sub>8</sub> (428)                         | -                                       | 7.1 (3.5)                             | -                 |   |                                      | 1.6 (2.7)                             | -                 |                            |                               | 1.56 (4.3)                            |                   |  |
| Cl <sub>9</sub> (466)                         | -                                       | 12.6 (5.3)                            | -                 |   |                                      | 2.7 (4.6)                             | -                 |                            |                               | 3.00 (1.8)                            |                   |  |
| Cl <sub>10</sub> (500)                        | -                                       | 2.0 (16.0)                            | -                 |   |                                      | 0.6 (12)                              | -                 |                            |                               | 0.442 (1.8)                           |                   |  |
| Surrogate Compounds                           |                                         |                                       |                   |   |                                      |                                       |                   |                            |                               |                                       |                   |  |
| <sup>13</sup> C <sub>6</sub> -gamma-BHC (187) | -                                       | -                                     | -                 | - | 3                                    | 3.0 (3.4)                             | 0                 | 0.3                        | 5                             | 4.9 (1.4)                             | -2                |  |
| <sup>13</sup> C <sub>12</sub> -4,4'-DDT (247) | -                                       | -                                     | -                 | - | -                                    | -                                     | -                 | -                          | 5                             | 4.4 (7.0)                             | -12               |  |

<sup>a</sup> Results of analysis of five replicate extracts of 1-L aliquots of fortified water.

<sup>b</sup> Results of analysis of seven replicate extracts of 1-L aliquots of fortified water.

<sup>c</sup> PCB method detection limits cannot be determined because Aroclor mixtures were used to fortify samples.

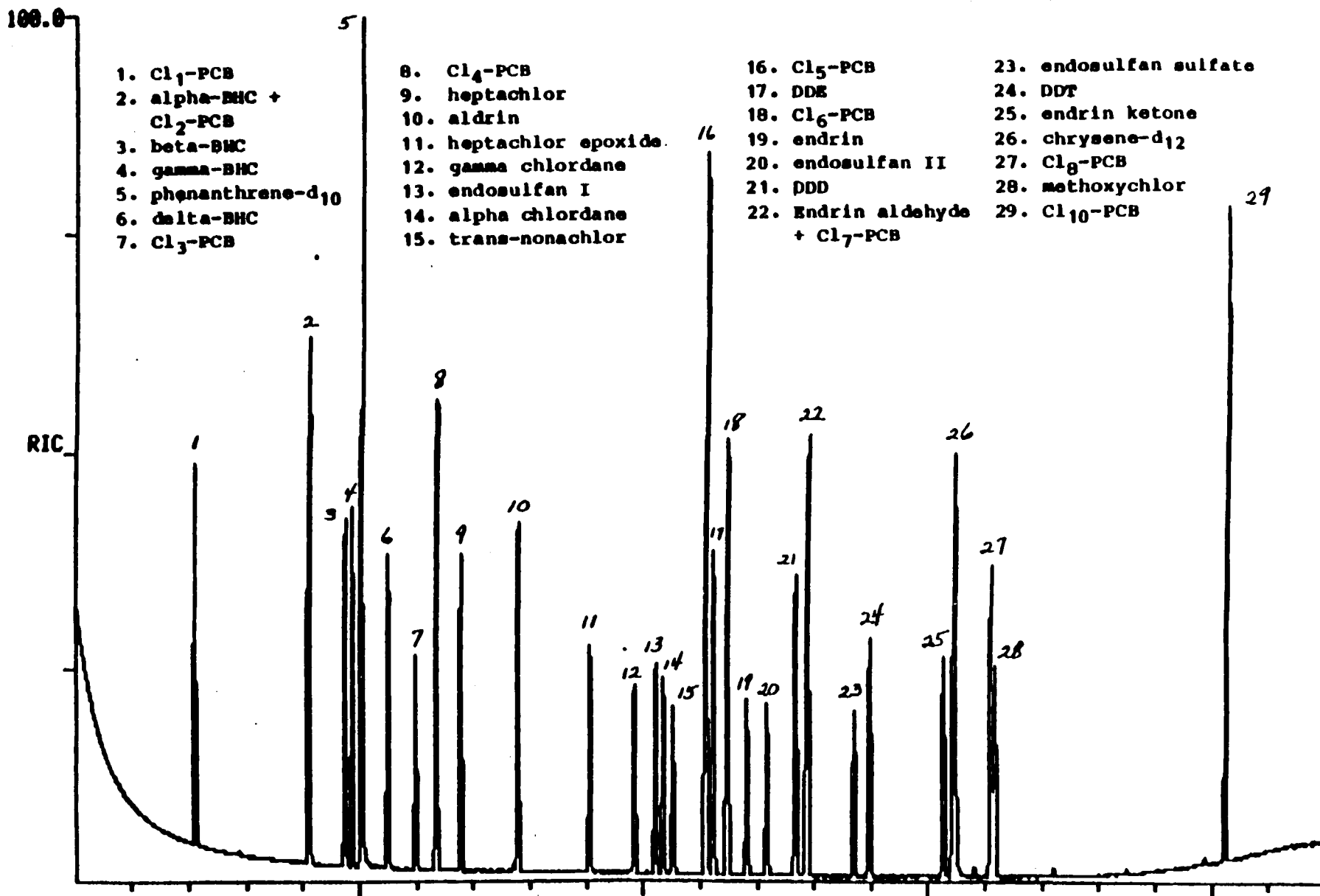


Figure 1. Total Ion Current Profile of PCB Calibration Congeners and Pesticide Analytes.

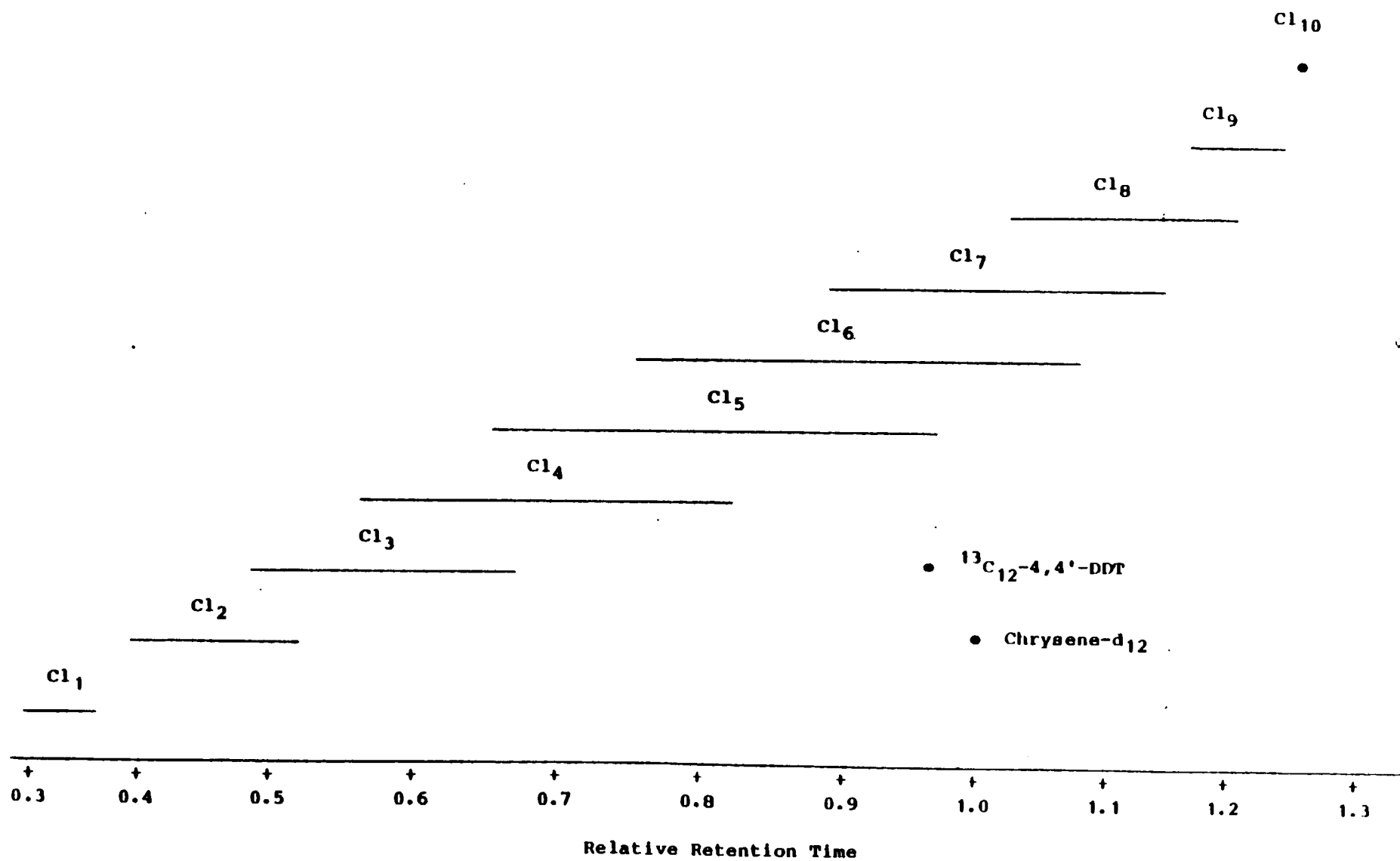


Figure 2. Diagram indicating approximate relative retention times (DB-5 GC column; chrysene-d<sub>12</sub> internal standard) of PCB isomer groups and retention time marker compounds (for PCB SIM data acquisition option).