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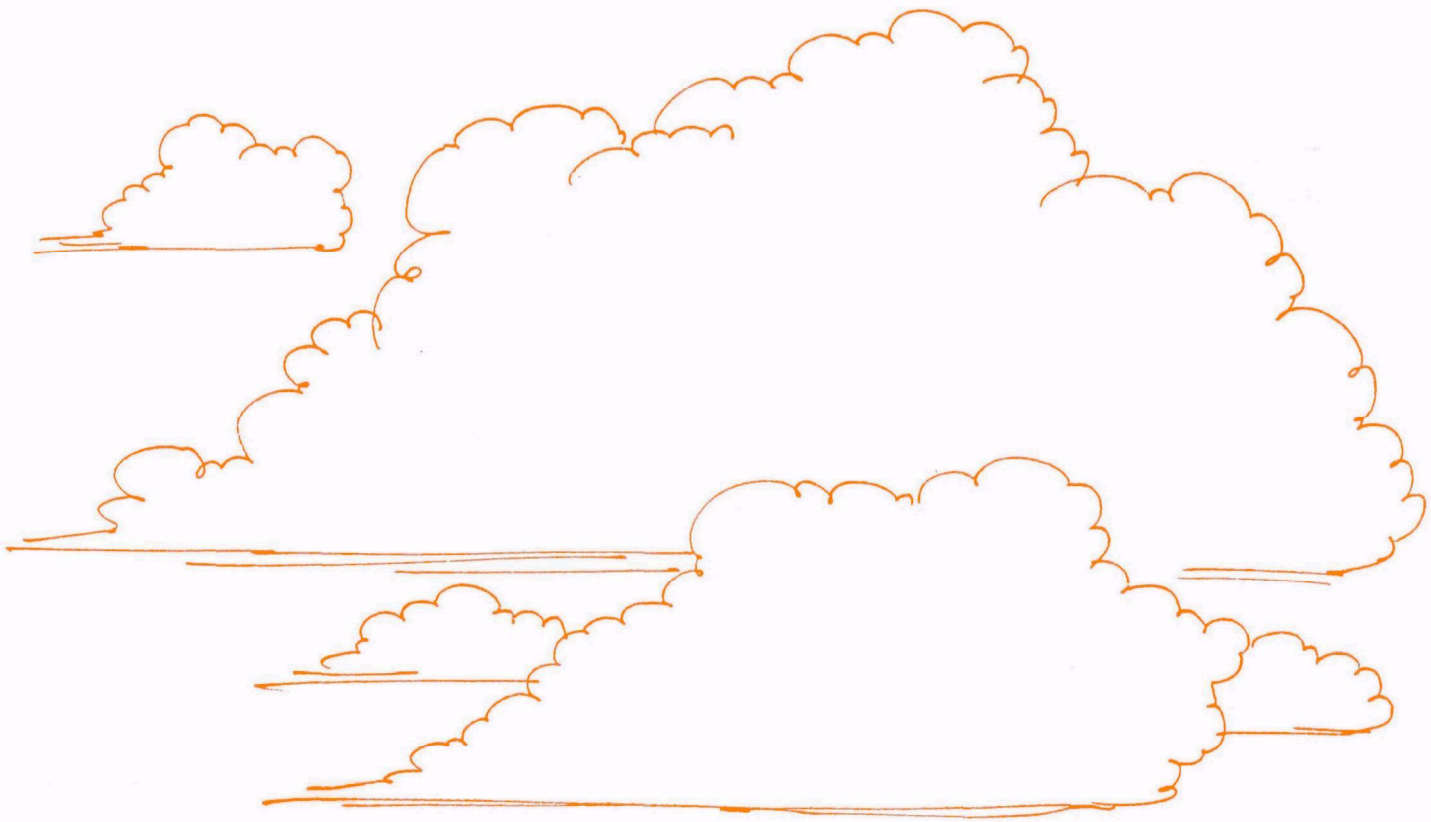
Toxic Substances

EPA

# Analytical Method: The Analysis of By-Product Chlorinated Biphenyls in Air, Revision 2



# ANALYTICAL METHOD: THE ANALYSIS OF BY-PRODUCT CHLORINATED BIPHENYLS IN AIR, REVISION 2

by

Mitchell D. Erickson

WORK ASSIGNMENT NO. 6

SPECIAL REPORT NO. 2

EPA Contract No. 68-02-3938
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For

U.S. Environmental Protection Agency
Office of Toxic Substances
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## DISCLAIMER

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# PREFACE

This report contains an analytical method for the analysis of by-product polychlorinated biphenyls in air. The work was done on Work Assignment No. 6 on US Environmental Protection Agency Contract No. 68-02-3938. This is the second revision of the method. Previous revisions are cited as references 3 and 4 in the method. This report was prepared by Mitchell Erickson. The work on the previous revisions was conducted by Dr. Erickson, John Stanley, Kay Turman, Gil Radolovich, Karin Bauer, Jon Onstot, Donna Rose, Margaret Wickham, and Ruth Blair. The work for the previous revisions was performed on Task 51 of EPA Contract No. 68-01-5915.

Two companion methods have been published which address commercial products and product wastes (Special Report No. 1, EPA Report No. EPA-560/5-85-010) and water (Special Report No. 3, EPA Report No. EPA-560/5-85-012).

The EPA Work Assignment Manager, Daniel T. Heggem, of Field Studies Branch provided helpful guidance.

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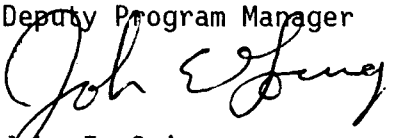

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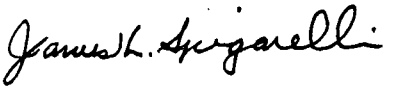

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TABLE OF CONTENTS

## LIST OF TABLES

## LIST OF FIGURES

# THE ANALYSIS OF BY-PRODUCT CHLORINATED BIPHENYLS IN AIR

## 1.0 Scope and Application

1.1 This is a gas chromatographic/electron impact mass spectrometric (GC/EIMS) method applicable to the determination of chlorinated biphenyls (PCBs) in air emitted from commercial production through stacks, as fugitive emissions, or static (room, other containers, or outside) air. The PCBs present may originate either as synthetic by-products or as contaminants derived from commercial PCB products (e.g., Aroclors). The PCBs may be present as single isomers or complex mixtures and may include all 209 congeners from monochlorobiphenyl through decachlorobiphenyl listed in Table 1.

This method was prepared for use in demonstrating compliance with the EPA rules regarding the generation of PCBs as byproducts in commercial chemical production[1,2] and is based on earlier versions.[3,4] This revision includes elimination of a calculation which corrects the native PCB concentration based on the recovery of the $^{13}C$-labeled PCB recovery surrogates. In addition, full scan is now emphasized over the selected ion monitoring and limited mass scan mass spectrometric data collection modes. The latter two techniques provide less qualitative information and should be used only if needed to achieve the required sensitivity. Additional background information on selection of the techniques has also been published.[5]

1.2 The detection and quantitation limits are dependent upon the volume of sample collected, the complexity of the sample matrix and the ability of the analyst to remove interferents and properly maintain the analytical system. The method accuracy and precision will be determined in future studies.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography/mass spectrometry (GC/MS) and in the interpretation of gas chromatograms and mass spectra. Prior to sample analysis, each analyst must demonstrate the ability to generate acceptable results with this method by following the procedures described in Section 15.2.

1.4 During the development and testing of this method, certain analytical parameters and equipment designs were found to affect the validity of the analytical results. Proper use of the method requires that such parameters or designs must be used as specified. These items are identified in the text by the word "must."

TABLE 1. NUMBERING OF PCB CONGENERS[a]

| No. | Structure | No. | Structure | No. | Structure | No. | Structure |
|---|---|---|---|---|---|---|---|
| | **Monochlorobiphenyls** | | **Tetrachlorobiphenyls** | | **Pentachlorobiphenyls** | | **Hexachlorobiphenyls** |
| 1 | 2 | 52 | 2,2',5,5' | 105 | 2,3,3',4,4' | 161 | 2,3,3',4,5',6 |
| 2 | 3 | 53 | 2,2',5,6' | 106 | 2,3,3',4,5 | 162 | 2,3,3',4',5,5' |
| 3 | 4 | 54 | 2,2',6,6' | 107 | 2,3,3',4',5 | 163 | 2,3,3',4',5,6 |
| | | 55 | 2,3,3',4 | 108 | 2,3,3',4,5' | 164 | 2,3,3',4',5',6 |
| | **Dichlorobiphenyls** | 56 | 2,3,3',4' | 109 | 2,3,3',4,6 | 165 | 2,3,3',5,5',6 |
| | | 57 | 2,3,3',5 | 110 | 2,3,3',4',6 | 166 | 2,3,4,4',5,6 |
| 4 | 2,2' | 58 | 2,3,3',5' | 111 | 2,3,3',5,5' | 167 | 2,3',4,4',5,5' |
| 5 | 2,3 | 59 | 2,3,3',6 | 112 | 2,3,3',5,6 | 168 | 2,3',4,4',5',6 |
| 6 | 2,3' | 60 | 2,3,4,4' | 113 | 2,3,3',5',6 | 169 | 3,3',4,4',5,5' |
| 7 | 2,4 | 61 | 2,3,4,5 | 114 | 2,3,4,4',5 | | |
| 8 | 2,4' | 62 | 2,3,4,6 | 115 | 2,3,4,4',6 | | **Heptachlorobiphenyls** |
| 9 | 2,5 | 63 | 2,3,4',5 | 116 | 2,3,4,5,6 | | |
| 10 | 2,6 | 64 | 2,3,4',6 | 117 | 2,3,4',5,6 | 170 | 2,2',3,3',4,4',5 |
| 11 | 3,3' | 65 | 2,3,5,6 | 118 | 2,3',4,4',5 | 171 | 2,2',3,3',4,4',6 |
| 12 | 3,4 | 66 | 2,3',4,4' | 119 | 2,3',4,4',6 | 172 | 2,2',3,3',4,5,5' |
| 13 | 3,4' | 67 | 2,3',4,5 | 120 | 2,3',4,5,5' | 173 | 2,2',3,3',4,5,6 |
| 14 | 3,5 | 68 | 2,3',4,5' | 121 | 2,3',4,5',6 | 174 | 2,2',3,3',4,5,6' |
| 15 | 4,4' | 69 | 2,3',4,6 | 122 | 2',3,3',4,5 | 175 | 2,2',3,3',4,5',6 |
| | | 70 | 2,3',4',5 | 123 | 2',3,4,4',5 | 176 | 2,2',3,3',4,6,6' |
| | **Trichlorobiphenyls** | 71 | 2,3',4',6 | 124 | 2',3,4,5,5' | 177 | 2,2',3,3',4',5,6 |
| | | 72 | 2,3',5,5' | 125 | 2',3,4,5,6' | 178 | 2,2',3,3',5,5',6 |
| 16 | 2,2',3 | 73 | 2,3',5',6 | 126 | 3,3',4,4',5 | 179 | 2,2',3,3',5,6,6' |
| 17 | 2,2',4 | 74 | 2,4,4',5 | 127 | 3,3',4,5,5' | 180 | 2,2',3,4,4',5,5' |
| 18 | 2,2',5 | 75 | 2,4,4',6 | | | 181 | 2,2',3,4,4',5,6 |
| 19 | 2,2',6 | 76 | 2',3,4,5 | | **Hexachlorobiphenyls** | 182 | 2,2',3,4,4',5,6' |
| 20 | 2,3,3' | 77 | 3,3',4,4' | | | 183 | 2,2',3,4,4',5',6 |
| 21 | 2,3,4 | 78 | 3,3',4,5 | 128 | 2,2',3,3',4,4' | 184 | 2,2',3,4,4',6,6' |
| 22 | 2,3,4' | 79 | 3,3',4,5' | 129 | 2,2',3,3',4,5 | 185 | 2,2',3,4,5,5',6 |
| 23 | 2,3,5 | 80 | 3,3',5,5' | 130 | 2,2',3,3',4,5' | 186 | 2,2',3,4,5,6,6' |
| 24 | 2,3,6 | 81 | 3,4,4',5 | 131 | 2,2',3,3',4,6 | 187 | 2,2',3,4',5,5',6 |
| 25 | 2,3',4 | | | 132 | 2,2',3,3',4,6' | 188 | 2,2',3,4',5,6,6' |
| 26 | 2,3',5 | | **Pentachlorobiphenyls** | 133 | 2,2',3,3',5,5' | 189 | 2,3,3',4,4',5,5' |
| 27 | 2,3',6 | | | 134 | 2,2',3,3',5,6 | 190 | 2,3,3',4,4',5,6 |
| 28 | 2,4,4' | 82 | 2,2',3,3',4 | 135 | 2,2',3,3',5,6' | 191 | 2,3,3',4,4',5',6 |
| 29 | 2,4,5 | 83 | 2,2',3,3',5 | 136 | 2,2',3,3',6,6' | 192 | 2,3,3',4,5,5',6 |
| 30 | 2,4,6 | 84 | 2,2',3,3',6 | 137 | 2,2',3,4,4',5 | 193 | 2,3,3',4',5,5',6 |
| 31 | 2,4',5 | 85 | 2,2',3,4,4' | 138 | 2,2',3,4,4',5' | | |
| 32 | 2,4',6 | 86 | 2,2',3,4,5 | 139 | 2,2',3,4,4',6 | | **Octachlorobiphenyls** |
| 33 | 2',3,4 | 87 | 2,2',3,4,5' | 140 | 2,2',3,4,4',6' | | |
| 34 | 2',3,5 | 88 | 2,2',3,4,6 | 141 | 2,2',3,4,5,5' | 194 | 2,2',3,3',4,4',5,5' |
| 35 | 3,3',4 | 89 | 2,2',3,4,6' | 142 | 2,2',3,4,5,6 | 195 | 2,2',3,3',4,4',5,6 |
| 36 | 3,3',5 | 90 | 2,2',3,4',5 | 143 | 2,2',3,4,5,6' | 196 | 2,2',3,3',4,4',5,6' |
| 37 | 3,4,4' | 91 | 2,2',3,4',6 | 144 | 2,2',3,4,5',6 | 197 | 2,2',3,3',4,4',6,6' |
| 38 | 3,4,5 | 92 | 2,2',3,5,5' | 145 | 2,2',3,4,6,6' | 198 | 2,2',3,3',4,5,5',6 |
| 39 | 3,4',5 | 93 | 2,2',3,5,6 | 146 | 2,2',3,4',5,5' | 199 | 2,2',3,3',4,5,6,6' |
| | | 94 | 2,2',3,5,6' | 147 | 2,2',3,4',5,6 | 200 | 2,2',3,3',4,5',6,6' |
| | **Tetrachlorobiphenyls** | 95 | 2,2',3,5',6 | 148 | 2,2',3,4',5,6' | 201 | 2,2',3,3',4,5,5',6' |
| | | 96 | 2,2',3,6,6' | 149 | 2,2',3,4',5',6 | 202 | 2,2',3,3',5,5',6,6' |
| 40 | 2,2',3,3' | 97 | 2,2',3',4,5 | 150 | 2,2',3,4',6,6' | 203 | 2,2',3,4,4',5,5',6 |
| 41 | 2,2',3,4 | 98 | 2,2',3',4,6 | 151 | 2,2',3,5,5',6 | 204 | 2,2',3,4,4',5,6,6' |
| 42 | 2,2',3,4' | 99 | 2,2',4,4',5 | 152 | 2,2',3,5,6,6' | 205 | 2,3,3',4,4',5,5',6 |
| 43 | 2,2',3,5 | 100 | 2,2',4,4',6 | 153 | 2,2',4,4',5,5' | | |
| 44 | 2,2',3,5' | 101 | 2,2',4,5,5' | 154 | 2,2',4,4',5,6' | | **Nonachlorobiphenyls** |
| 45 | 2,2',3,6 | 102 | 2,2',4,5,6' | 155 | 2,2',4,4',6,6' | | |
| 46 | 2,2',3,6' | 103 | 2,2',4,5',6 | 156 | 2,3,3',4,4',5 | 206 | 2,2',3,3',4,4',5,5',6 |
| 47 | 2,2',4,4' | 104 | 2,2',4,6,6' | 157 | 2,3,3',4,4',5' | 207 | 2,2',3,3',4,4',5,6,6' |
| 48 | 2,2',4,5 | | | 158 | 2,3,3',4,4',6 | 208 | 2,2',3,3',4,5,5',6,6' |
| 49 | 2,2',4,5' | | | 159 | 2,3,3',4,5,5' | | |
| 50 | 2,2',4,6 | | | 160 | 2,3,3',4,5,6 | | **Decachlorobiphenyl** |
| 51 | 2,2',4,6' | | | | | | |
| | | | | | | 209 | 2,2',3,3',4,4',5,5',6,6' |

[a]Adopted from Ballschmiter, K. and Zell, M., Fresenius Z. Anal.Chem., 302, 20-31 (1980).

Anyone wishing to deviate from the method in areas so identified must demonstrate that the deviation does not affect the validity of the data. Alternative test procedure approval must be obtained from the Agency. An experienced analyst may make modifications to parameters or equipment identified by the term "recommended." Each time such modifications are made to the method, the analyst must repeat the procedure in Section 15.2. In this case, formal approval is not required, but the documented data from Section 15.2 must be on file as part of the overall quality assurance program.

1.5 This method contains many options because of the diversity of matrices and interferences which may be encountered. Once the appropriate options for each sample type have been selected, each laboratory should prepare a written step-by-step protocol for use by the analysts. The protocol may contain verbatim sections from this method, more detailed steps for certain techniques, or totally different extraction or cleanup techniques.

## 2.0 Summary

2.1 The air must be sampled such that the specimen collected for analysis is representative of the whole. Statistically designed selection of the sampling position (stack, flue, port, etc.) or time should be employed. Gaseous and particulate PCBs should be withdrawn isokinetically from stacks, room air exhausts, process point exhausts, and other flowing gaseous streams using a sampling train. While several sampling methods are available for collection of PCBs, the modified EPA Method 5[6] described herein has been well-validated for PCB collection and recovery. In the modified EPA Method 5, PCBs are collected in a Florisil adsorbent tube and in a series of impingers in front of the adsorbent. Other sample collection systems may be used, provided PCBs are adequately collected by and recovered from the train.

PCBs are sampled from ambient air and other static gaseous sources onto a Florisil adsorbent tube. The sample must be preserved to prevent PCB loss prior to analysis. Storage at 4°C is recommended.

2.2 The Florisil adsorbent is extracted with hexane in a Soxhlet extractor, the aqueous condensate is extracted with hexane and the acetone/hexane impinger rinse is back-extracted with water. All three organic extracts are then combined. Optional cleanup techniques may include sulfuric acid cleanup and Florisil adsorption chromatography. The sample is concentrated to a final known volume for instrumental determination.

2.3 The PCB content of the sample extract must be determined by high resolution (preferred) or packed column gas chromatography/electron impact mass spectrometry (HRGC/EIMS or PGC/EIMS) operated in the full scan, selected ion monitoring (SIM), or limited mass scan (LMS) mode.

2.4 PCBs are identified by comparison of their retention time and mass spectral intensity ratios to those in calibration standards.

2.5 PCBs are quantitated against the response factors for a mixture of 10 PCB congeners using the internal standard technique.

2.6 The PCBs identified by the SIM technique may be confirmed by full scan HRGC/EIMS, retention on alternate GC columns, other mass spectrometric techniques, infrared spectrometry, or other techniques, provided that the sensitivity and selectivity of the technique are demonstrated to be comparable or superior to GC/EIMS.

2.7 The analysis time is dependent on the extent of workup employed. The time required for instrumental analysis of a single sample excluding instrumental calibration, data reduction, and reporting, is typically 30 to 45 min.

2.8 A quality assurance (QA) plan must be developed for each laboratory.

2.9 Quality control (QC) measures include laboratory certification and performance check sample analysis, procedural QC (instrumental performance, calculation checks), and sample QC (blanks, replicates, and standard addition).

2.10 While several options are available throughout this method, the recommended procedure for stack gases to be followed is:

2.10.1 The sample is collected using a modified Method 5 train[6] according to a scheme which permits extrapolation of the sample data to the source being assessed.

2.10.2 The sample is preserved at 4°C to prevent any loss of PCBs or changes in matrix which may adversely affect recovery.

2.10.3 The three sample fractions are extracted and combined.

2.10.4 The extract is cleaned up and concentrated to an appropriate volume. Internal standards are added.

2.10.5 An aliquot of the extract is analyzed by HRGC/EIMS operated in the SIM mode. On-column injections onto a 15-m DB-5 capillary column, programmed (for toluene solutions) from 110° to 325°C at 10°/min after a 2 min hold is used. Helium at 45-cm/sec linear velocity is used as the carrier gas.

2.10.6 PCBs are identified by retention time and mass spectral intensities.

2.10.7 PCBs are quantitated against the response factors for a mixture of 10 PCB congeners.

2.10.8 The total PCBs are obtained by summing the amounts for each homolog found, and the concentration is reported as micrograms per cubic meter.

## 3.0 Interferences

3.1 Method interferences may be caused by contaminants, in sample collection media, solvents, reagents, glassware, and other sample processing hardware, leading to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences by the analysis of laboratory reagent blanks as described in Section 15.

3.1.1 Glassware must be scrupulously cleaned. All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water and rinses with tap water and reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After it is dry and cool, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. It is stored inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required. All solvent lots must be checked for purity prior to use.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sorbent material or impingers. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sources of samples.

## 4.0 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to

the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemical specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 Polychlorinated biphenyls have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood. Personnel must wear protective equipment, including gloves and safety glasses.

Congeners highly substituted at the meta and para positions and unsubstituted at the ortho positions are reported to be the most toxic. Extreme caution should be taken when handling these compounds neat or in concentrated solution. The class includes 3,3',4'4'-tetrachlorobiphenyl (both natural abundance and isotopically labeled).

4.3 Waste disposal must be in accordance with RCRA and applicable state rules.

## 5.0 Apparatus and Materials

All specifications are suggestions only. Catalog numbers and suppliers are included for illustration only.

5.1 Stack sampling train[6] - See Figure 1; a series of four impingers with a solid adsorbent trap between the third and fourth impingers. The train may be constructed by adaptation from a Method 5 train.[3] Descriptions of the train components are contained in the following subsections.

5.1.1 Probe nozzle - Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be $\leq 30^{\circ}$ and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Agency. The wall thickness of the nozzle shall be less than or equal to that of 20 gauge tubing, i.e., 0.165 cm (0.065 in.) and the distance from the tip of the nozzle to the first bend or point of disturbance shall be at least two times the outside nozzle tubing. Other configurations and construction material may be used with approval from the Agency.

5.1.2 Probe liner - Borosilicate or quartz glass equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without sealing greases;

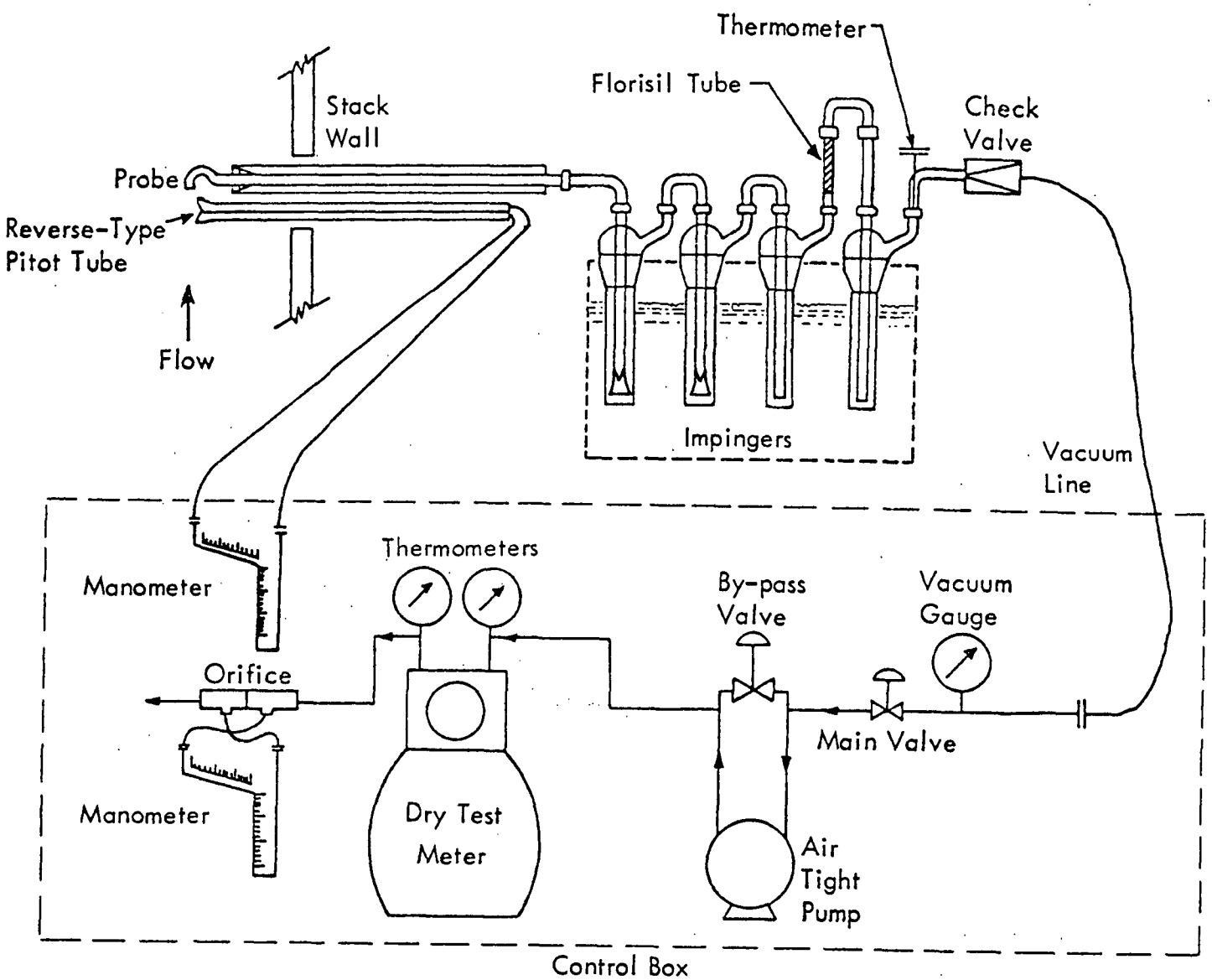


Figure 1. PCB sampling train for stack gases.

such as Kontes Glass Company "O" ring spherical ground ball joints (model K-671300) or University Research Glassware SVL teflon screw fittings.

A stainless steel (316) or water-cooled probe may be used for sampling high temperature gases with approval from the Agency. A probe heating system may be used to prevent moisture condensation in the probe.

5.1.3 Pitot tube - Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other but not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle, which is the largest size nozzle used.

The pitot tube must also meet the criteria specified in Method 2[7] and be calibrated according to the procedure in the calibration section of that method.

5.1.4 Differential pressure gauge - Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, other methods or devices acceptable to the Agency may be used when conditions warrant.

5.1.5 Impingers - Four impingers with connecting fittings able to form leak-free, vacuum tight seals without sealant greases when connected together as shown in Figure 1. The first and second impingers are of the Greenburg-Smith design. The final two impingers are of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

One or two additional modified Greenburg-Smith impingers may be added to the train between the third impinger and the Florisil tube to accommodate additional water collection when sampling high moisture gases. Throughout the preparation, operation, and sample recovery from the train, these additional impingers should be treated exactly like the third impinger.

5.1.6 Solid adsorbent tube - Glass with connecting fittings able to form leak-free, vacuum tight seals without sealant greases (Figure 2). Exclusive of connectors, the tube has a 2.2 cm inner diameter, is at least 10 cm long, and has four deep indentations on the inlet end to aid in retaining the adsorbent. Ground glass caps (or equivalent) must be provided to seal the adsorbent-filled tube both prior to and following sampling.

5.1.7 Metering system - Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within ±3°C (~ 5°F), dry gas meter with 2% accuracy at the required sampling rate, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

5.1.8 Barometer - Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of -2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

5.2 Static air sampling train[6] - The sampling train, see Figure 3, consists of a glass-lined probe, an adsorbent tube containing Florisil, and the appropriate valving and flow meter controls for isokinetic sampling as described in Section 5.1. The sampling apparatus in Figure 3 is the same as that in Figure 1 and Section 5.1, except that the Smith-Greenburg impingers and heated probe are not used. If condensation of significant quantities of moisture prior to the solid adsorbent is expected, Section 5.1 of the method should be used. Since probes and adsorbent tubes are not cleaned up in the field, a sufficient number must be provided for sampling and allowance for breakage.

5.3 Sample recovery

5.3.1 Ground glass caps - To cap off adsorbent tube and the other sample exposed portions of the train.

5.3.2 Teflon FEP® wash bottle - Two, 500 mL, Nalgene No. 0023A59 or equivalent.

5.3.3 Sample storage containers - Glass bottles, 1 liter, with TFE®-lined screw caps.

5.3.4 Balance - Triple beam, Ohaus Model 7505 or equivalent.

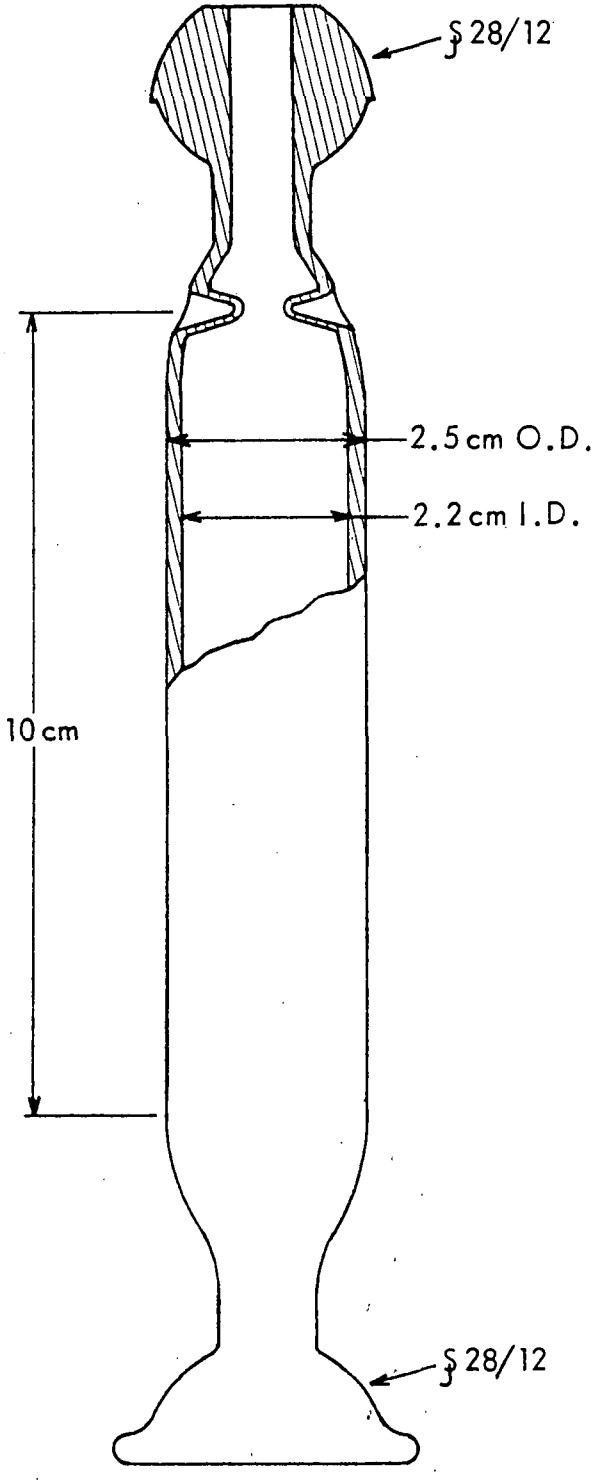


Figure 2. Florisil adsorbent tube.

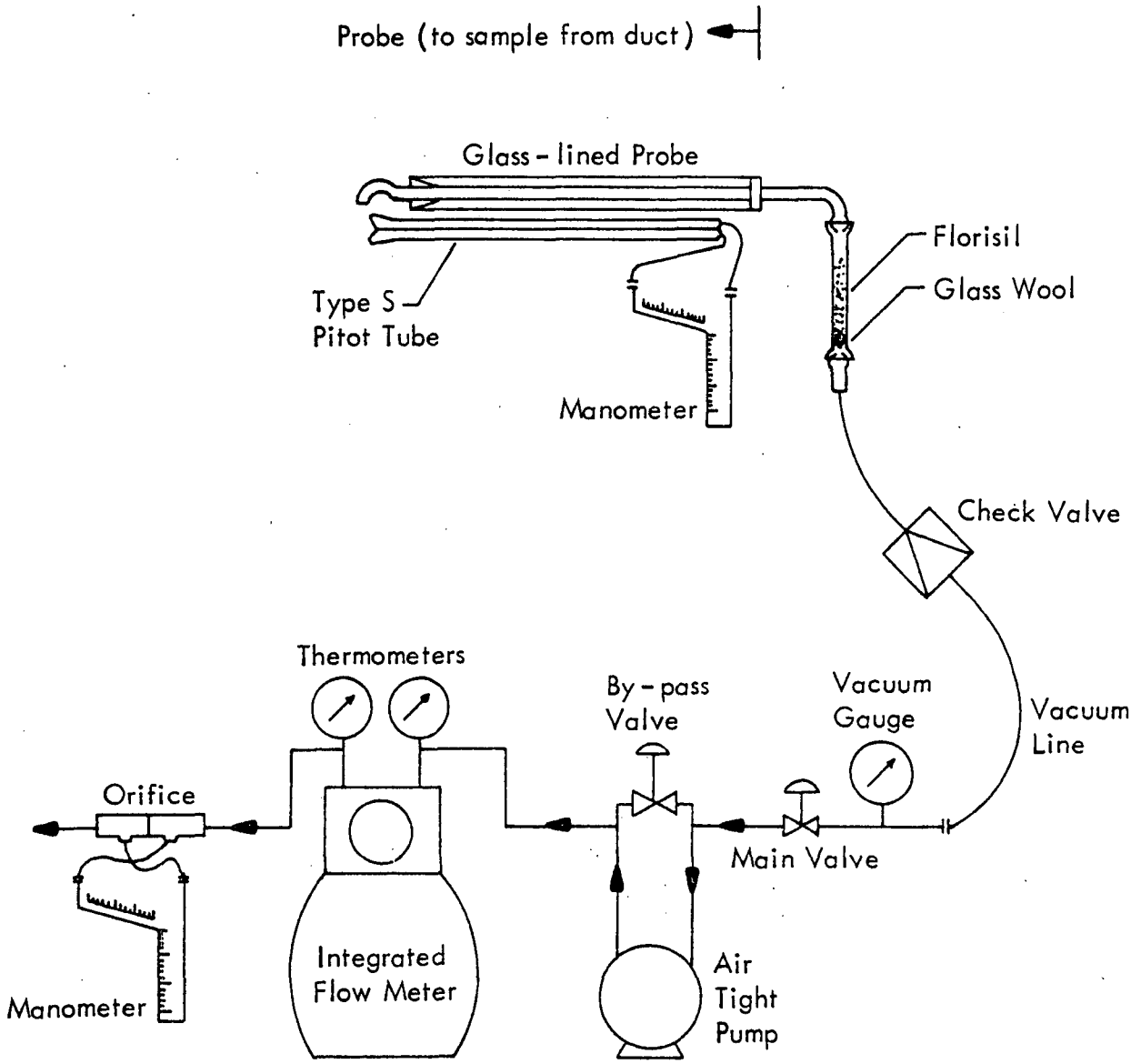


Figure 3. PCB sampling train for static air.

5.3.5 Aluminum foil - Heavy duty.

5.3.6 Metal can - To recover used silica gel.

5.4 Analysis

5.4.1 Glass Soxhlet extractors - 40 mm ID complete with 45/50 S condenser, 24/40 S 250 mL round-bottom flask, heating mantle for 250 mL flask, and power transformer.

5.4.2 Teflon FEP wash bottle - Two, 500 mL, Nalgene No. 0023A59 or equivalent.

5.4.3 Separatory funnel - 1,000 mL with TFE® stopcock.

5.4.4 Kuderna-Danish concentrators - 500 mL.

5.4.5 Steam bath.

5.4.6 Separatory funnel - 50 mL with TFE® stopcock.

5.4.7 Volumetric flask - 25.0 mL, glass.

5.4.8 Volumetric flask - 5.0 mL, glass.

5.4.9 Culture tubes - 13 x 100 mm, glass with TFE®-lined screw caps.

5.4.10 Pipette - 5.0 mL glass.

5.4.11 Teflon®-glass syringe - 1 mL, Hamilton 1001 TLL or equivalent with Teflon® needle.

5.4.12 Syringe - 10 µL, Hamilton 701N or equivalent.

5.4.13 Disposable glass pipettes with bulbs - To aid transfer of the extracts.

5.4.14 Gas chromatography/mass spectrometer system.

5.4.14.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using capillary columns or packed columns. Other capillary injection techniques (split, splitless, "Grob," etc.) may be used provided the performance specifications stated in Section 7.1 are met.

5.4.14.2 Capillary GC column - A 10-30 m long x 0.25 mm ID fused silica column with a 0.25 µm thick DB-5 bonded silicone liquid phase (J&W Scientific) is recommended. Alternate liquid phases may include OV-101, SP-2100, Apiezon L, Dexsil 300, or other liquid phases or columns which meet the performance specifications stated in Section 7.1.

5.4.14.3 Packed GC column - A 180 cm x 0.2 cm ID glass column packed with 3% SP-2250 on 100/120 mesh Supelcoport or equivalent is recommended. Other liquid phases or columns which meet the performance specifications stated in Section 7.1 may be substituted.

5.4.14.4 Mass spectrometer - Must be capable of scanning from m/z 150 to m/z 550 every 1.5 sec or less, collecting at least five spectra per chromatographic peak, utilizing a 70-eV (nominal) electron energy in the electron impact ionizaton mode and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of decafluorotriphenyl phosphine [DFTPP, bis(perfluorophenyl)phenyl phosphine] is injected through the GC inlet. Any GC-to-MS interface that gives acceptable calibration points at 10 ng per injection for each PCB isomer in the calibration standard and achieves all acceptable performance criteria (Section 10) may be used. Direct coupling of the fused silica column to the MS is recommended. Alternatively, GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.4.14.5 A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The data system must have the capability of integrating the abundances of the selected ions between specified limits and relating integrated abundances to concentrations using the calibration procedures described in this method. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number to yield an

Table 2. DFTPP Key Ions and Ion Abundance Criteria

| m/z | Ion abundance criteria |
|---|---|
| 197 | Less than 1% of mass 198 |
| 198 | 100% relative abundance |
| 199 | 5-9% of mass 198 |
| 275 | 10-30% of mass 198 |
| 365 | Greater than 1% of mass 198 |
| 441 | Present, but less than mass 443 |
| 442 | Greater than 40% of mass 198 |
| 443 | 17-23% of mass 442 |

extracted ion current profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.5 Gas chromatograph for GC/FID screening

5.5.1 A temperature-programmable GC equipped with a flame ionization detector Varian 3740 or equivalent.

5.5.2 A 2 m x 2 mm ID glass column packed with 3% SP-2250 on 100/120 mesh Supelcoport or equivalent. A high resolution GC column may also be used.

## 6.0 Reagents

6.1 Sampling

6.1.1 Florisil - Floridin Company, 30/60 mesh, Grade A. The Florisil is cleaned by 8 hr Soxhlet extraction with hexane and then by drying for 8 hr in an oven at 110°C and is activated by heating to 650°C for 2 hr (not to exceed 3 hr) in a muffle furnace. After allowing to cool to near 110°C transfer the clean, active Florisil to a clean, hexane-washed glass jar and seal with a TFE®-lined lid. The Florisil should be stored at 110°C until taken to the field for use. Florisil that has been stored more than 1 month must be reactivated before use.

6.1.2 Glass wool - Cleaned by thorough rinsing with hexane, dried in a 110°C oven, and stored in a hexane-washed glass jar with TFE®-lined screw cap.

6.1.3 Water - Deionized, then glass-distilled, and stored in hexane-rinsed glass containers with TFE®-lined screw caps.

6.1.4 Silica gel - Indicating type, 6-16 mesh. If previously used, dry at 175°C for 2 hr. New silica gel may be used as received.

6.1.5 Crushed ice.

6.2 Solvents - All solvents must be pesticide residue analysis grade. New lots should be checked for purity by concentrating an aliquot by at least as much as is used in the procedure.

6.3 Calibration standard congeners - Standards of the PCB congeners listed in Tables 3 and 4 are available from Ultra Scientific, Hope, Rhode Island; or Analabs, North Haven, Connecticut.

Table 3. Concentrations of Congeners in PCB Calibration Standards for Full Scan Analysis (ng/μL)[a]

| Homolog | Congener no. | FS100 ng PCB | FS050 ng PCB | FS010 ng PCB | FS005 ng PCB | FS001 ng PCB |
|---|---|---|---|---|---|---|
| 1 | 1 | 100 | 50 | 10 | 5 | 1 |
| 2 | 7 | 100 | 50 | 10 | 5 | 1 |
| 3 | 30 | 150 | 75 | 15 | 7.5 | 1.5 |
| 4 | 50 | 200 | 100 | 20 | 10 | 2 |
| 5 | 97 | 200 | 100 | 20 | 10 | 2 |
| 6 | 143 | 200 | 100 | 20 | 10 | 2 |
| 7 | 183 | 300 | 150 | 30 | 15 | 3 |
| 8 | 202 | 300 | 150 | 30 | 15 | 3 |
| 9 | 207 | 450 | 225 | 45 | 22.5 | 4.5 |
| 10 | 209 | 200 | 100 | 20 | 10 | 2 |
| 4 | 210 (IS) | 250 | 250 | 250 | 250 | 250 |
| - | $C_{10}H_7I$ (IS)[b] | 250 | 250 | 250 | 250 | 250 |
| - | $C_{18}D_{12}$ (IS)[c] | 250 | 250 | 250 | 250 | 250 |
| $^{13}C$-$Cl_1$ | 211 (RS) | 100 | 50 | 10 | 5 | 1 |
| $^{13}C$-$Cl_4$ | 212 (RS) | 250 | 125 | 25 | 12.5 | 2.5 |
| $^{13}C$-$Cl_8$ | 213 (RS) | 400 | 200 | 40 | 20 | 4 |
| $^{13}C$-$Cl_{10}$ | 214 (RS) | 500 | 250 | 50 | 25 | 5 |

[a] Concentrations given as examples only.
[b] 1-Iodonaphthalene.
[c] $d_{12}$-Chrysene.

Table 4. Concentrations of Congeners in PCB Calibration Standards for Selected Ion Monitoring and Limited Mass Scan Analysis (pg/μL)[a]

| Homolog | Congener no. | SIM1000 pg PCB | SIM100 pg PCB | SIM050 pg PCB | SIM010 pg PCB |
|---|---|---|---|---|---|
| 1 | 1 | 1,000 | 100 | 50 | 10 |
| 2 | 7 | 1,000 | 100 | 50 | 10 |
| 3 | 30 | 1,500 | 150 | 75 | 15 |
| 4 | 50 | 2,000 | 200 | 100 | 20 |
| 5 | 97 | 2,000 | 200 | 100 | 20 |
| 6 | 143 | 2,000 | 200 | 100 | 20 |
| 7 | 183 | 3,000 | 300 | 150 | 30 |
| 8 | 202 | 3,000 | 300 | 150 | 30 |
| 9 | 207 | 4,500 | 450 | 225 | 45 |
| 10 | 209 | 2,000 | 200 | 100 | 20 |
| 4 | 210 (IS) | 250 | 250 | 250 | 250 |
| - | $C_{10}H_7I$ (IS)[b] | 250 | 250 | 250 | 250 |
| - | $C_{18}D_{12}$ (IS)[c] | 250 | 250 | 250 | 250 |
| $^{13}C$-$Cl_1$ | 211 (RS) | 1,000 | 100 | 50 | 10 |
| $^{13}C$-$Cl_4$ | 212 (RS) | 2,500 | 250 | 125 | 25 |
| $^{13}C$-$Cl_8$ | 213 (RS) | 4,000 | 400 | 200 | 40 |
| $^{13}C$-$Cl_{10}$ | 214 (RS) | 5,000 | 500 | 250 | 50 |

[a] Concentrations given as examples only.
[b] 1-Iodonaphthalene.
[c] $d_{12}$-Chrysene.

6.4 Calibration standard stock solutions - Primary dilutions of each of the individual PCBs listed in Tables 3 and 4 are prepared by weighing approximately 1-10 mg of material within 1% precision. The PCB is then dissolved and diluted to 1.0 mL with hexane. The concentration is calculated in mg/mL. The primary dilutions are stored at 4°C in screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. Primary dilutions are stable indefinitely if the seals are maintained. The stock solutions and dilutions should be clearly labeled with pertinent information such as sample code, solvent, date prepared, initials of person preparing the solution, and notebook reference.

6.5 Working calibration standards - Working calibration standards are prepared that are similar in PCB composition and concentration to the samples by mixing and diluting the individual standard stock solutions. Example calibration solutions are shown in Tables 3 and 4. The mixture is diluted to volume with pesticide residue analysis quality hexane. The concentration is calculated in ng/mL as the individual PCBs. Dilutions are stored at 4°C in narrow-mouth, screw-cap vials with Teflon cap liners. The meniscus is marked on the vial wall to monitor solvent evaporation. These secondary dilutions can be stored indefinitely if the seals are maintained.

These solutions are designated FSxxx ng PCB and SIMxxx pg PCB where the xxx is used to encode the nominal concentration of the lower congeners in ng/μL and pg/μL, respectively. The FS prefix helps aid the analyst in identifying solutions which are appropriate for full scan analysis; the SIM prefix is for solutions to calibrate in the selected ion monitoring and limited mass scan acquisition modes.

6.6 Alternatively, certified stock solutions similar to those listed in Tables 3 and 4 may be available from a supplier, in lieu of the procedures described in Section 6.4.

6.7 DFTPP standard - A 50 ng/μL solution of decafluorotriphenylphosphine (DFTPP), PCR Research Chemicals, Gainesville, Florida, is prepared in acetone or another appropriate solvent.

6.8 Internal standard stock solution - Solutions of $d_6$-3,3',4,4'-tetrachlorobiphenyl (KOR Isotopes, Cambridge, MA) and 1-iodonaphthalene (Aldrich Chemical Company, Milwaukee, WI) or $d_{12}$-chrysene (KOR Isotopes, Cambridge, MA) are prepared at nominal concentrations of 1-10 mg/mL in hexane. The solutions are further diluted to give working standards.

NOTE - Any internal standard may be used, provided it meets the following criteria: (a) it is not already present in the sample, (b) it gives a strong, recognizable mass spectrum, (c) it does not give mass spectral ions which interfere with PCB quantitation, (d) it is chemically stable, and (e) it elutes in the PCB retention window. Ideally, several internal standards are used which

have retention times spanning the PCB retention windows to improve the response factor recision.

Alternatively, the four $^{13}C$-labeled PCBs listed in Table 5 may be used as internal standards. The are available as a certified solution from Toxic and Hazardous Materials Repository, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, 26 West St. Clair Street, Cincinnati, Ohio 45268, (513) 684-7327. This solution may be used as received or diluted further. These solutions are designated "SSxxx," where the xxx is used to encode the nominal concentration in µg/mL.

6.9 Solution stability - The calibration standard, internal standard and DFTPP solutions should be checked frequently for stability. These solutions should be replaced after 6 months, or sooner if comparison with quality control check samples indicates compound degradation or concentration change.

## 7.0 Calibration

Maintain a laboratory log of all calibrations.

### 7.1 Sampling train

7.1.1 Probe nozzle - Using a micrometer, the inside diameter of the nozzle is measured to the nearest 0.025 mm (0.001 in.). Three separate measurements are made using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers must not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they must be reshaped, sharpened, and recalibrated before use.

Each nozzle must be permanently and uniquely identified.

7.1.2 Pitot tube - The pitot tube must be calibrated according to the procedure outlined in Method 2.[7]

7.1.3 Dry gas meter and orifice meter - Both meters must be calibrated according to the procedure outlined in APTD-0581.[8] When diaphragm pumps with bypass valves are used, proper metering system design is checked by calibrating the dry gas meter at an additional flow rate of 0.0057 $m^3$/min (0.2 cfm) with the bypass valve fully opened and then with it fully closed. If there is more than ±2% difference in flow rates when compared to the fully closed position of the bypass valve, the system is not designed properly and must be corrected.

Table 5. Composition of Internal Standard Spiking Solution (SS100) Containing $^{13}C$-Labeled PCBs

| Congener no. | Compound | Abbreviations | Concentration (µg/mL) |
|---|---|---|---|
| 211 | 4-Chloro-(1',2',3',4',5',6'-$^{13}C_6$)-biphenyl | $^{13}C$-$Cl_1$ | 100 |
| 212 | 3,3',4,4'-Tetrachloro-($^{13}C_{12}$)-biphenyl | $^{13}C$-$Cl_4$ | 250 |
| 213 | 2,2',3,3',5,5',6,6'-Octachloro-($^{13}C_{12}$)-biphenyl | $^{13}C$-$Cl_8$ | 400 |
| 214 | Decachloro-($^{13}C_{12}$)-biphenyl | $^{13}C$-$Cl_{10}$ | 500 |

7.1.4 Probe heater calibration - The probe heating system must be calibrated according to the procedure contained in APTD-0581.[8]

7.1.5 Temperature gauges - Dial and liquid filled bulb thermometers are calibrated against mercury-in-glass thermometers. Thermocouples should be calibrated in constant temperature baths.

7.2 The gas chromatograph must meet the minimum operating parameters shown in Tables 6 and 7, daily. If all of the criteria are not met, the analyst must adjust conditions and repeat the test until all criteria are met.

7.3 The mass spectrometer must meet the minimum operating parameters shown in Tables 2, 8, and 9, daily. If all criteria are not met, the analyst must retune the spectrometer and repeat the test until all conditions are met.

7.3.1 Full scan data acquisition - Quadrupole mass spectrometers must meet the tuning criteria in Table 2. The spectrometer must scan between m/z 150-550, although wider scan ranges are permissible.

7.3.2 Limited mass scan data acquisition - Table 10 presents a suggested set of LMS ranges. The mass spectrometer should be set to at least unit resolution. The computer acquisition parameters should utilize the minimum threshold filtering necessary so as not to lose pertinent data. Optimum acquisition parameters will vary depending on the condition of the mass spectrometer and should be checked daily.

The dwell times for the mass ranges given in Table 10 will vary with instrument and should be optimized to allow at least five data points across a chromatographic peak. Maximum sensitivity will be achieved when utilizing maximum dwell time.

Instruments having the capability to switch mass ranges during an analysis required particular attention to the switching points to assure minimal data loss. Switching points can be initially determined by analyzing a highly concentrated Aroclor mixture while in the full scan mode.

7.3.3 Selected ion monitoring data acquisition - Table 11 presents a suggested set of characteristic ions for SIM. The SIM program must include at least two ions for each analyte, generally the primary and secondary ions in Table 11. The spectrometer should be set to at least

Table 6. Operating Parameters for Capillary Column Gas Chromatographic System

| Parameter | Recommended | Tolerance |
|---|---|---|
| Gas chromatograph | Finnigan 9610 | Other[a] |
| Column | 15 -30 m x 0.255 mm ID Fused silica | Other |
| Liquid phase | DB-5 (J&W) | Other nonpolar or semipolar |
| Liquid phase thickness | 0.25 µm | < 1 µm |
| Carrier gas | Helium | Hydrogen |
| Carrier gas velocity | 30-45 cm/s[b] | Optimum performance |
| Injector | "Grob" (split/splitless mode)[c] | Other[c] |
| Injector temperature | 250-270°C | Optimum performance |
| Injection volume | 1.0-2.0 µL | Other |
| Initial column temperature | 60-80°C (2 min)[d] | Other[d] |
| Column temperature program | 70°-300°C at 10°C/min[e] | Other |
| Separator | None[f] | Glass jet or other |
| Transfer line temperature | 280°C | Optimum[g] |
| Tailing factor[h] | 0.7-1.5 | 0.4-3 |
| Peak width[i] | 7-10 s | < 15 s |

[a]Substitutions permitted with any common apparatus or technique provided performance criteria are met.
[b]Measured by injection of air or methane at 270°C oven temperature.
[c]Manufacturer's instructions should be followed regarding injection technique.
[d]With on-column injection, initial temperature equals boiling point of the solvent; in this instance, hexane.
[e]$C_{12}Cl_{10}$ elutes at 270°C. Programming above this temperature ensures a clean column and lower background on subsequent runs.
[f]Fused silica columns may be routed directly into the ion source to prevent separator discrimination and losses.
[g]High enough to elute all PCBs, but not high enough to degrade the column if routed through the transfer line.
[h]Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution FSxxx ng PCB or SIMxxx pg PCB.
[i]Peak width at 10% height for a single PCB congener in FSxxx ng PCB or SIMxxx pg PCB.

Table 7. Operating Parameters for Packed Column Gas Chromatography System

| Parameter | Recommended | Tolerance |
|---|---|---|
| Gas chromatograph | Finnigan 9610 | Other[a] |
| Column | 180 cm x 0.2 cm ID glass | Other |
| Column packing | 3% SP-2250 on 100/120 mesh Supelcoport | Other nonpolar or semipolar |
| Carrier gas | Helium | Hydrogen |
| Carrier gas flow rate | 30 mL/min | Optimum performance |
| Injector | On-column | Other |
| Injector temperature | 250°C | Optimum[b] |
| Injection volume | 1.0 µL | ≦ 5 µL |
| Initial column temperature | 150°C, 4 min | Other |
| Column temperature program | 150°-260°C at 8°/min | Other |
| Separator | Glass jet | Other |
| Transfer line temperature | 280°C | Optimum[b] |
| Tailing factor[c] | 0.7-1.5 | 0.4-3 |
| Peak width[d] | 10-20 sec | < 30 sec |

[a]Substitutions permitted if performance criteria are met.
[b]High enough to elute all PCBs.
[c]Tailing factor is width of front half of peak at 10% height divided by width of back half of peak at 10% height for single PCB congeners in solution FSxxx ng PCB or SIMxxx pg PCB.
[d]Peak width at 10% height for a single PCB congener in FSxxx ng PCB or SIMxxx pg PCB.

Table 8. Operating Parameters for Quadrupole Mass Spectrometer System

| Parameter | Recommended | Tolerance |
|---|---|---|
| Mass spectrometer | Finnigan 4023 | Other[a] |
| Data system | Incos 2400 | Other |
| Scan range | 95-550 | Other |
| Scan time | 1 sec | Other[b] |
| Resolution | Unit | Optimum performance |
| Ion source temperature | 280°C | 200°-300°C |
| Electron energy[c] | 70 eV | 70 eV |

[a]Substitutions permitted if performance criteria are met.
[b]Greater than five data points over a GC peak is a minimum.
[c]Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no solvent venting is used.

Table 9. Operating Parameters for Magnetic Sector Mass Spectrometer System

| Parameter | Recommended | Tolerance |
|---|---|---|
| Mass spectrometer | Finnigan MAT 311A | Other[a] |
| Data system | Incos 2400 | Other |
| Scan range | 98-550 | Other |
| Scan mode | Exponential | Other |
| Cycle time | 1.2 sec | Other[b] |
| Resolution | 1,000 | > 500 |
| Ion source temperature | 280°C | 250-300° |
| Electron energy[c] | 70 eV | 70 eV |

[a]Substitutions permitted if performance criteria are met.
[b]Greater than five data points over a GC peak is a minimum.
[c]Filaments should be shut off during solvent elution to improve instrument stability and prolong filament life, especially if no solvent venting is used.

Table 10. Limited Mass Scanning (LMS) Ranges For PCBs

| Compound | Mass range (m/z) |
|---|---|
| $C_{12}H_9Cl_1$ + $^{13}C_6{}^{12}C_6H_9Cl$ | 186-198 |
| $C_{12}H_8Cl_2$ | 220-226 |
| $C_{12}H_7Cl_3$ | 254-260 |
| $C_{12}H_6Cl_4$ + $C_{12}D_6$ $Cl_4$ + $^{13}C_{12}H_6Cl_4$ | 288-310 |
| $C_{12}H_5Cl_5$ | 322-328 |
| $C_{12}H_4Cl_6$ | 356-362 |
| $C_{12}H_3Cl_7$ | 390-396 |
| $C_{12}H_2Cl_8$ | 426-434 |
| $C_{12}HCl_9$ | 460-468 |
| $C_{12}Cl_{10}$ | 496-502 |
| $C_{10}H_7I$ | 254 |
| $C_{18}D_{12}$ | 240 |
| $^{13}C_{12}H_2Cl_8$ | 440-446 |
| $^{13}C_{12}Cl_{10}$ | 508-514 |

Table 11. Characteristic SIM Ions for PCBs

| Homolog | Ion (relative intensity) | | |
|---|---|---|---|
| | Primary | Secondary | Tertiary |
| $C_{12}H_9Cl$ | 188 (100) | 190 (33) | - |
| $C_{12}H_8Cl_2$ | 222 (100) | 224 (66) | 226 (11) |
| $C_{12}H_7Cl_3$ | 256 (100) | 258 (99) | 260 (33) |
| $C_{12}H_6Cl_4$ | 292 (100) | 290 (76) | 294 (49) |
| $C_{12}H_5Cl_5$ | 326 (100) | 328 (66) | 324 (61) |
| $C_{12}H_4Cl_6$ | 360 (100) | 362 (82) | 364 (36) |
| $C_{12}H_3Cl_7$ | 394 (100) | 396 (98) | 398 (54) |
| $C_{12}H_2Cl_8$ | 430 (100) | 432 (66) | 428 (87) |
| $C_{12}HCl_9$ | 464 (100) | 466 (76) | 462 (76) |
| $C_{12}Cl_{10}$ | 498 (100) | 500 (87) | 496 (68) |
| $C_{10}H_7I$ | 254 (100) | - | - |
| $C_{12}D_6Cl_4$ | 298 (100) | 300 (49) | 296 (76) |
| $C_{18}D_{12}$ | 240 (100) | - | - |
| $^{13}C_6{}^{12}C_6H_9Cl$ | 194 (100) | 196 (33) | - |
| $^{13}C_{12}H_6Cl_4$ | 304 (100) | 306 (49) | 302 (76) |
| $^{13}C_{12}H_2Cl_8$ | 442 (100) | 444 (65) | 440 (87) |
| $^{13}C_{12}Cl_{10}$ | 510 (100) | 512 (87) | 508 (68) |

unit resolution. The computer acquisition parameters should utilize the minimum threshold filtering necessary so as not to lose pertinent data. Optimum acquisition parameters will vary depending on the condition of the mass spectrometer and should be checked daily.

The dwell times for the mass given in Table 11 will vary with instrument and should be optimized to allow at least five data points across a chromatographic peak. Maximum sensitivity will be achieved when utilizing maximum dwell time.

Instruments having the capability to switch mass ranges during an analysis require particular attention to the switching points to assure minimal data loss. Switching points can be initially determined by analyzing a highly concentrated congener or Aroclor mixture while in the full scan mode.

7.4 The PCB response factors ($RF_p$) must be determined in triplicate or other replication, as discussed below, using Equation 7-1 for the analyte homologs.

$$RF_p = \frac{A_p \times M_{is}}{A_{is} \times M_p} \qquad \text{Eq. 7-1}$$

where $RF_p$ = response factor of a given PCB isomer

$A_p$ = area of the characteristic ion for the PCB congener peak

$M_p$ = mass of PCB congener in sample (micrograms)

$A_{is}$ = area of the characteristic ion for the internal standard peak ($d_6$-3,3',4,4'-tetrachlorobiphenyl, iodonaphthalene, $d_{12}$-chrysene or the $^{13}C$-labeled PCBs)

$M_{is}$ = mass of internal standard in sample (micrograms)

If specific congeners are known to be present and if standards are available, selected RF values may be employed. For general samples, solutions in Tables 3 and 4 or a mixture may be used as the response factor solution. The PCB-surrogate pairs to be used in the RF calculation are listed in Table 12.

Generally, only the primary ions of both the analyte and surrogate are used to determine the RF values. If alternate ions are to be used in the quantitation, the RF must be determined using that characteristic ion.

Table 12. Pairings of Analyte and Calibration Compounds

| Analyte | | Calibration standard | |
|---|---|---|---|
| Congener[a] no. | Compound | Congener no. | Compound |
| 1-3 | $C_{12}H_9Cl$ | 1 | 2 |
| 4-15 | $C_{12}H_8Cl_2$ | 7 | 2,4 |
| 16-39 | $C_{12}H_7Cl_3$ | 30 | 2,4,6 |
| 40-81 | $C_{12}H_6Cl_4$ | 50 | 2,2',4,6 |
| 82-127 | $C_{12}H_5Cl_5$ | 97 | 2,2',3',4,5 |
| 128-169 | $C_{12}H_4Cl_6$ | 143 | 2,2',3,4,5,6' |
| 170-193 | $C_{12}H_3Cl_7$ | 183 | 2,2',3',4,4',5',6 |
| 194-205 | $C_{12}H_2Cl_8$ | 202 | 2,2',3,3',5,5',6,6' |
| 206-208 | $C_{12}HCl_9$ | 207 | 2,2',3,3',4,4',5,6,6' |
| 209 | $C_{12}Cl_{10}$ | 209 | $C_{12}Cl_{10}$ |

[a]Ballschmiter numbering system, see Table 1.

The RF value must be determined in a manner to assure ±20% precision. For instruments with good day-to-day precision, a running mean ($\overline{RF}$) based on seven values may be appropriate. A new value is added each day and the oldest dropped from the mean. Other options include, but are not limited to, triplicate determinations of a single concentration spaced throughout a day or determination of the RF at three different levels to establish a working curve.

If replicate RF values differ by greater than ±10% RSD, the system performance should be monitored closely. If the RSD is greater than ±20%, the data set must be considered invalid and the RF redetermined before further analyses are done.

7.5 If the GC/EIMS system has not been demonstrated to yield a linear response or if the analyte concentrations are more than one order of magnitude different from those in the RF solution, a calibration curve must be prepared. If the analyte and RF solution concentrations differ by more than one order of magnitude, a calibration curve should be prepared. A calibration curve should be established with triplicate determinations at three or more concentrations bracketing the analyte levels.

7.6 The relative retention time (RRT) windows for the 10 homologs and surrogates must be determined. If all congeners are not available, a mixture of available congeners or an Aroclor mixture (e.g., 1016/1254/1260) may be used to estimate the windows. The windows must be set wider than observed if all isomers are not determined. Typical RRT windows for one column are listed in Table 13. The windows may differ substantially if other GC parameters are used.

## 8.0 Sample Collection, Handling, and Preservation

The sampling shall be conducted by competent personnel experienced with this test procedure and cognizant of the constraints of the analytical techniques for PCBs, particularly contamination problems.

### 8.1 Stack sampling

While several sampling protocols are available for collection of PCBs, the modified EPA Method 5 described herein has been well validated for PCB collection and recovery.[6] In this protocol, PCBs are collected in a Florisil adsorbent tube and in a series of impingers in front of the adsorbent. Other sample collection protocols may be used, provided that PCBs are quantitatively collected and recovered from the train. A recent protocol for the collection of semivolatile organics using a modified Method 5 train with XAD-2 as the adsorbent represents an attempt to standardize stack gas sampling.[9] This protocol may be considered an alternative to that described herein.

Table 13. Relative Retention Time (RRT) Ranges of PCB Homologs Versus $d_6$-3,3',4,4'-Tetrachlorobiphenyl

| PCB homolog | No. of isomers measured | Observed range of RRTs[a] | Congener no. | Observed RRT[a] | Projected range of RRTs[b] |
|---|---|---|---|---|---|
| Monochloro | 3 | 0.40-0.50 | 1 | 0.43 | 0.35-0.55 |
| Dichloro | 10 | 0.52-0.69 | 7 | 0.58 | 0.45-0.80 |
| Trichloro | 9 | 0.62-0.79 | 30 | 0.65 | 0.55-1.00 |
| Tetrachloro | 16 | 0.72-1.01 | 50 | 0.75 | 0.55-1.05 |
| Pentachloro | 12 | 0.82-1.08 | 97 | 0.98 | 0.80-1.10 |
| Hexachloro | 13 | 0.93-1.20 | 143 | 1.05 | 0.90-1.25 |
| Heptachloro | 4 | 1.09-1.30 | 183 | 1.15 | 1.05-1.35 |
| Octachloro | 6 | 1.19-1.36 | 202 | 1.19 | 1.10-1.50 |
| Nonachloro | 3 | 1.31-1.42 | 207 | 1.33 | 1.25-1.50 |
| Decachloro | 1 | 1.44-1.45 | 209 | 1.44 | 1.35-1.50 |

[a]The RRTs of the 77 congeners and a mixture of Aroclor 1016/1254/1260 were measured versus 3,3',4,4'-tetrachlorobiphenyl-$d_6$ (internal standard) using a 15-m J&W DB-5 fused silica column with a temperature program of 110°C for 2 min, then 10°C/min to 325°C, helium carrier at 45 cm/sec, and an on-column injector. A Finnigan 4023 Incos quadrupole mass spectrometer operating with a scan range of 95-550 daltons was used to detect each PCB congener.

[b]The projected relative retention windows account for overlap of eluting homologs and take into consideration differences in operating systems and lack of all possible 209 PCB congeners.

8.1.1 Pretest preparation - All train components shall be maintained and calibrated according to the procedure described in APTD-0581,[8] unless otherwise specified herein. This should be done in the laboratory prior to sampling.

8.1.1.1 Cleaning glassware - All glass parts of the train upstream of and including the adsorbent tube and impingers, should be cleaned as described in Section 3.1.1. Special care should be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. These grease residues should be removed by soaking several hours in a chromic acid cleaning solution prior to routine cleaning as described above.

8.1.1.2 Solid adsorbent tube - 7.5 g of Florisil activated within the last 30 days and still warm from storage in a 110°C oven, is weighed into the adsorbent tube (prerinsed with hexane) with a glass wool plug in the downstream end. A second glass wool plug is placed in the tube to hold the sorbent in the tube. Both ends of the tube are capped with ground glass caps. These caps should not be removed until the tube is fitted to the train immediately prior to sampling.

8.1.2 Preliminary determinations - The sampling site and the minimum number of sampling points are selected according to Method 1[7] or as specified by the Agency. The stack pressure, temperature, and the range of velocity heads are determined using Method 2[7] and moisture content using Approximation Method 4[7] or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results must be based on actual measurements made during the test.

The molecular weight of the stack gases is determined using Method 3.[7]

A nozzle size is selected based on the maximum velocity head so that isokinetic sampling can be maintained at a rate less than 0.75 cfm. It is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, the nozzle size must not be changed.

A suitable probe length is selected such that all traverse points can be sampled. Sampling from opposite sides for large stacks may be considered to reduce the length of probes.

A sampling time is selected appropriate for total method sensitivity and the PCB concentration anticipated. Sampling times should generally fall within a range of 2 to 4 hr.

A buzzer-timer should be incorporated in the control box (see Figure 1) to alarm the operator to move the probe to the next sampling point.

8.1.3 Preparation of collection train - During preparation and assembly of the sampling train, all train openings must be covered until just prior to assembly or until sampling is about to begin. Immediately prior to assembly, all parts of the train upstream of the adsorbent tube are rinsed with hexane. The probe is marked with heat resistant tape or by some other method at points indicating the proper distance into the stack or duct for each sampling point.

Two hundred milliliters of water is placed in each of the first two impingers, and the third impinger left empty. CAUTION: Sealant greases must not be used in assembling the train. If the preliminary moisture determination shows that the stack gases are saturated or supersaturated, one or two additional empty impingers should be added to the train between the third impinger and the Florisil tube. See Section 5.1.5. Approximately 200 to 300 g or more, if necessary, of silica gel is placed in the last impinger. Each impinger (stem included) is weighed and the weights recorded to the nearest 0.1 g on the impingers and on the data sheet.

Unless otherwise specified by the Agency, a temperature probe is attached to the metal sheath of the sampling probe so that the sensor is at least 2.5 cm behind the nozzle and pitot tube and does not touch any metal.

The train is assembled as shown in Figure 1. Through all parts of this method use of sealant greases such as stopcock grease to seal ground glass joints must be avoided.

Crushed ice is placed around the impingers.

8.1.4 Leak check procedure - After the sampling train has been assembled, the probe heating system(s) is turned on and set (if applicable) to reach a temperature sufficient to avoid condensation in the probe. Time is allowed for the temperature to stabilize. The train is leak checked at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate or 0.0057 $m^3$/min (0.02 cfm) whichever is less, is unacceptable.

The following leak check instruction for the sampling train described in APTD-0581[8] may be helpful. The pump is started with bypass valve fully open and coarse adjust valve completely closed. The coarse adjust valve is partially opened and the bypass valve slowly closed until 380 mm Hg (15 in. Hg) vacuum is reached. The direction of bypass valve must not be reversed. This will cause water to back up into the probe. If 380 mm Hg (15 in. Hg) is exceeded, either the leak check is conducted at this higher vacuum or the leak check is ended as described below and start over.

When the leak check is completed, the plug is first slowly removed from the inlet to the probe and the vacuum pump is immediately turned off. This prevents the water in the impingers from being forced backward into the probe.

Leak checks shall be conducted as described above prior to each test run and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes.

8.1.5 Train operation - During the sampling run, an isokinetic sampling rate within 10%, or as specified by the Agency, of true isokinetic shall be maintained. During the run, the nozzle or any other part of the train in front of and including the Florisil tube must not be changed.

For each run, the data required on the data sheets must be recorded. An example is shown in Figure 4. The dry gas meter readings are recorded at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Other data point readings are taken at least once at each sample point during each time increment and whenever significant changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate.

The portholes are cleaned prior to the test run to minimize change of sampling deposited material. To begin sampling, the nozzle cap is removed, the probe heater operational and temperature up, and the pitot tube and probe positions are verified (if applicable). The nozzle is positioned at the first traverse point with the tip pointing directly into the gas stream. The pump is started and the flow adjusted to isokinetic conditions. Nomographs are available for sampling trains using type S pitot tubes with 0.85 ± 0.02 coefficients ($C_p$), and when sampling in air or a stack gas with equivalent

## FIELD DATA

PLANT _____
DATE _____
SAMPLING LOCATION _____
SAMPLE TYPE _____
RUN NUMBER _____
OPERATOR _____
AMBIENT TEMPERATURE _____
BAROMETRIC PRESSURE _____
STATIC PRESSURE, ($P_s$) _____
FILTER NUMBER (s) _____

PROBE LENGTH AND TYPE _____
NOZZLE I.D. _____
ASSUMED MOISTURE, % _____
SAMPLE BOX NUMBER _____
METER BOX NUMBER _____
METER $\Delta H_@$ _____
C FACTOR _____
PROBE HEATER SETTING _____
HEATER BOX SETTING _____
REFERENCE $\Delta p$ _____

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY _____ MINUTES

| TRAVERSE POINT NUMBER | CLOCK TIME (24-hr CLOCK) / SAMPLING TIME, min | GAS METER READING ($V_m$), $ft^3$ | VELOCITY HEAD ($\Delta p_s$), in. $H_2O$ | ORIFICE PRESSURE DIFFERENTIAL ($\Delta H$), in. $H_2O$ | | STACK TEMPERATURE ($T_s$), °F | DRY GAS METER TEMPERATURE | | PUMP VACUUM, in. Hg | SAMPLE BOX TEMPERATURE, °F | IMPINGER TEMPERATURE, °F |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | DESIRED | ACTUAL | | INLET ($T_{m\ in}$), °F | OUTLET ($T_{m\ out}$), °F | | | |
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COMMENTS:

EPA (Dur) 235
4 72

Figure 4. Field data sheet.

density (molecular weight, $M_d$, equal to 29 ± 4), which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. If $C_p$ and $M_d$ are outside the above stated ranges, the nomograph cannot be used unless appropriate steps are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), the coarse adjust valve must be closed before inserting the probe into the stack to avoid water backing into the probe. If necessary, the pump may be turned on with the coarse valve closed.

When the probe is in position, the openings around the probe and porthole must be blocked off to prevent unrepresentative dilution of the gas stream.

The stack cross section is traversed, as required by Method 1[7] or as specified by the Agency. To minimize chance of extracting deposited material, the probe nozzle should not bump into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes.

During the test run, periodic adjustments are made to keep the probe temperature at the proper value. More ice and, if necessary, salt is added to the ice bath to maintain a temperature of less than 20°C (68°F) at the impinger/silica gel outlet, to avoid excessive moisture losses. Also, the level and zero of the manometer should be periodically checked.

If the pressure drop across the train becomes high enough to make isokinetic sampling difficult to maintain, the test run should be terminated. Under no circumstances should the train be disassembled during the test run to determine and correct causes of excessive pressure drops.

At the end of the sample run, the pump is turned off, the probe and nozzle removed from the stack, and the final dry gas meter reading recorded. A leak check is performed, with acceptability of the test run based on the same criteria as in Section 8.1.4. The percent isokinetic is calculated (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, the Agency should be consulted for possible variance on the isokinetic rates.

8.1.6 Blank train - For each series of test runs, a blank train is set up in a manner identical to that described above, but with the nozzle capped with aluminum foil and the

exit end of the last impinger capped with a ground glass cap. The train is allowed to remain assembled for a period equivalent to one test run. The blank sample is recovered as described in Section 8.3.

8.2 Static air sampling[6] - The sampling procedure for static air is identical to that described in Section 8.1 with the following exceptions: (a) impingers and a heatable probe are not required prior to the adsorbent tube; and (b) the PCB concentrations may dictate a longer or shorter sampling time.

The selection of sampling time and rate should be based on the approximate levels of PCB residues expected in the sample. The sampling rate should not exceed 14 L/min and may typically fall in the range of 5 to 10 L/min. Sampling times should be more than 20 min but should not exceed 4 hr.

8.3 Sample recovery - Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safely handled, all external particulate matter near the tip of the probe nozzle is wiped off. The probe is removed from the train and both ends closed off with aluminum foil. The inlet to the train is capped off with a ground glass cap.

The probe and impinger assembly are transfered to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

The train is inspected prior to and during disassembly and any abnormal conditions noted. The samples are treated as follows:

8.3.1 Adsorbent tube - The Florisil tube is removed from the train and capped with ground glass caps.

8.3.2 Sample Container No. 1 - The first three impingers are removed. The outside of each impinger is wiped off to remove excessive water and other debris. The impingers are weighed (stem included), and the weight recorded on a data sheet. The contents are poured directly into Container No. 1.

8.3.3 Sample Container No. 2 - Each of the first three impingers are rinsed sequentially with 30-mL acetone and then with 30-mL hexane, and the rinses put into Container No. 2. Material deposited in the probe is quantitatively recovered using 100-mL acetone and then 100-mL hexane and these rinses added to Container No. 2.

8.3.4 Silica gel container - The last impinger is removed, and the outside wiped to remove excessive water and other debris. It is weighed (stem included), and the weight recorded on the data sheet. The contents are transferred to the used silica gel can.

8.4 Sample preservation - Samples should be stored in the dark at 4°C. Storage times in excess of 4 weeks are not recommended.

## 9.0 Sample Preparation[6]

### 9.1 Extraction

9.1.1 Adsorbent tube - The entire contents of the adsorbent tube are expelled directly onto a glass wool plug in the sample holder of a Soxhlet extractor. Although no extraction thimble is required, a glass thimble with a coarse-fritted bottom may be used.

The tube is rinsed with 5-mL acetone and then with 15-mL hexane and these rinses put into the extractor. The extraction apparatus is assembled and the adsorbent extracted with 170-mL hexane for at least 4 hr. The extractor should cycle 10 to 14 times per hour. After allowing the extraction apparatus to cool to ambient temperature, the extract is transferred into a Kuderna-Danish evaporator.

The extract is evaporated to about 5 mL on a steam bath and the evaporator allowed to cool to ambient temperature before disassembly. The extract is transferred to a 50-mL separatory funnel and the funnel set aside.

9.1.2 Sample Container No. 1 - The aqueous sample is transferred to a 1,000-mL separatory funnel. The container is rinsed with 20-mL acetone and then with two 20-mL portions of hexane, adding the rinses to the separatory funnel.

The sample is extracted with three 100 mL portions of hexane and the sequential extracts transferred to a Kuderna-Danish evaporator.

The extract is concentrated to about 5 mL and allowed to cool to ambient temperature before disassembly. The extract is filtered through a micro column of anhydrous sodium sulfate into a 50-mL separatory funnel containing the corresponding Florisil extract from Section 9.1.1. The micro column is prepared by placing a small plug of glass wool in the bottom of the large portion of a disposable pipette and then adding anhydrous sodium sulfate until the tube is about half full.

9.1.3 Sample Container No. 2 - The organic solution is transferred into a 1,000-mL separatory funnel. The container is rinsed with two 20-mL portions of hexane and the rinses added to the separatory funnel. The sample is washed with three 100-mL portions of water. The aqueous layer is discarded and the organic layer transferred to a Kuderna-Danish evaporator.

The extract is concentrated to about 5 mL and allowed to cool to ambient temperature before disassembly. The extract is filtered through a micro column of anhydrous sodium sulfate into the 50-mL separatory funnel containing the corresponding Florisil and impinger extracts (Section 9.1.2).

9.2 Cleanup - Two tested cleanup techniques are described below.[10] Depending upon the complexity of the sample, one or both of the techniques may be required to fractionate the PCBs from interferences. If the sample extract is colored, the Florisil column cleanup may be indicated.

9.2.1 Acid cleanup

9.2.1.1 Add 5 mL of concentrated sulfuric acid to the separatory funnel containing the sample extract and shake for 1 min.

9.2.1.2 Allow the phases to separate, transfer the sample (upper phase) with three 1 to 2 mL solvent rinses to a clean continer.

9.2.1.3 Back-extract sample extract with 5-10 drops of distilled water. Pass through a short column of anhydrous sodium sulfate and concentrate to an appropriate volume.

9.2.1.4 Analyze as described in Section 10.0.

9.2.1.5 If the sample is highly contaminated, a second or third acid cleanup may be employed.

9.2.2 Florisil column cleanup

9.2.2.1 Variations among batches of Florisil may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of Florisil can then be adjusted accordingly.

9.2.2.2 Place a 20-g charge of Florisil, activated overnight at 130°C, into a Chromaflex column. Settle the Florisil by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the Florisil. Pre-elute the column with 70-80 mL of hexane. Just before the exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

9.2.2.3 Add the sample extract to the column.

9.2.2.4 Carefully wash down the inner wall of the column with 5 mL of of the hexane.

9.2.2.5 Add 200 mL of 6% ethyl ether/hexane and set the flow to about 5 mL/min.

9.2.2.6 Collect 200 mL of eluate in a Kuderna-Danish flask. All the PCBs should be in this fraction. Concentrate to an appropriate volume.

9.2.2.7 Analyze the sample as described in Section 10.0.

9.3 Optional Screening for Interferences Using GC/FID

Note: Since many sample matrices are one of a kind or infrequently encountered by the analyst, the effectiveness of the extraction and cleanup for a matrix may be unknown. A simple screen to assess whether the interferences have been reduced to a tolerable level can both save GC/MS time and prevent contamination of the GC/MS instrument with very dirty samples. This screen should <u>not</u> be used to determine PCB levels under this analytical method.

9.3.1 Using a GC system as described in Section 5.5.3, analyze for background interferences.

9.3.2 A 2 m x 2 mm glass column packed with 3% SP-2250 on 100/120 Supelcoport or equivalent is suggested. A flow rate of 40 mL/min 95% air/5% methane or nitrogen is recommended. The air and hydrogen flow rates should be sufficient to keep the flame lit and to burn efficiently, e.g., 300 mL/min air and 30 mL/min $H_2$.

9.3.3 The recommended temperature program is from 50 to 250°C at 20°C/min with an initial hold of 3 min and a final hold of 10 min. The injector temperature should be 200°C and the detector 300°C.

9.3.4 Set instrumental sensitivity comparable to the anticipated mass spectral sensitivity. It is advisable to establish criteria for rejection of sample at a given attenuation such as (a) any off-scale peaks in PCB elution window, (b) a baseline rise of 40% full scale, (c) other criteria which are indicative of "problem" samples.

9.3.5 If the FID screen suggests that the sample is not amenable to analysis by GC/EIMS, the analyst may either (a) cycle the sample through the same cleanup again if it appears that the cleanup technique was overloaded by the matrix the first time, (b) submit the extract to another and cleanup techniques which may remove more interferences, or (c) analyze a new aliquot of sample by another extraction or cleanup technique.

## 10.0 Gas Chromatographic/Electron Impact Mass Spectrometric Determination

10.1 Internal standard addition - Pipet an appropriate volume of internal standard solution into the sample. The final concentration of the internal standards must be in the working range of the calibration and well above the matrix background. The internal standards are thoroughly mixed by mechanical agitation.

Note: The volume measurement of the spiking solution is critical to the overall method precision. The analyst must exercise caution that the volume is known ±1% or better. Where necessary, calibration of the pipet is recommended.

Note: If the $^{13}C$-labeled PCB mixture is used for internal standards, this same solution is used as a surrogate standard solution in the method for products/product waste[11] and for water.[12] In this method, the $^{13}C$-labeled PCBs are spiked after extraction, so are used as internal standards.

Alternately, another internal standard solution such as the $d_6$-3,3',4,4'-tetrachlorobiphenyl, 1-iodonaphthalene and $d_{12}$-chrysene used in the product/product waste and water protocols may be used, if acceptable RF precision and accuracy are shown across the homolog range.

10.2 Tables 2, and 6 through 11 summarize the recommended operating conditions for analysis. Figure 5 presents an example of a chromatogram.

The analyst may choose to operate the mass spectrometer at any appropriate sensitivity, using either full scan, limited mass scanning or selected ion monitoring acquisition. The sensitivity selected will depend on anticipated PCB levels and the instrumental

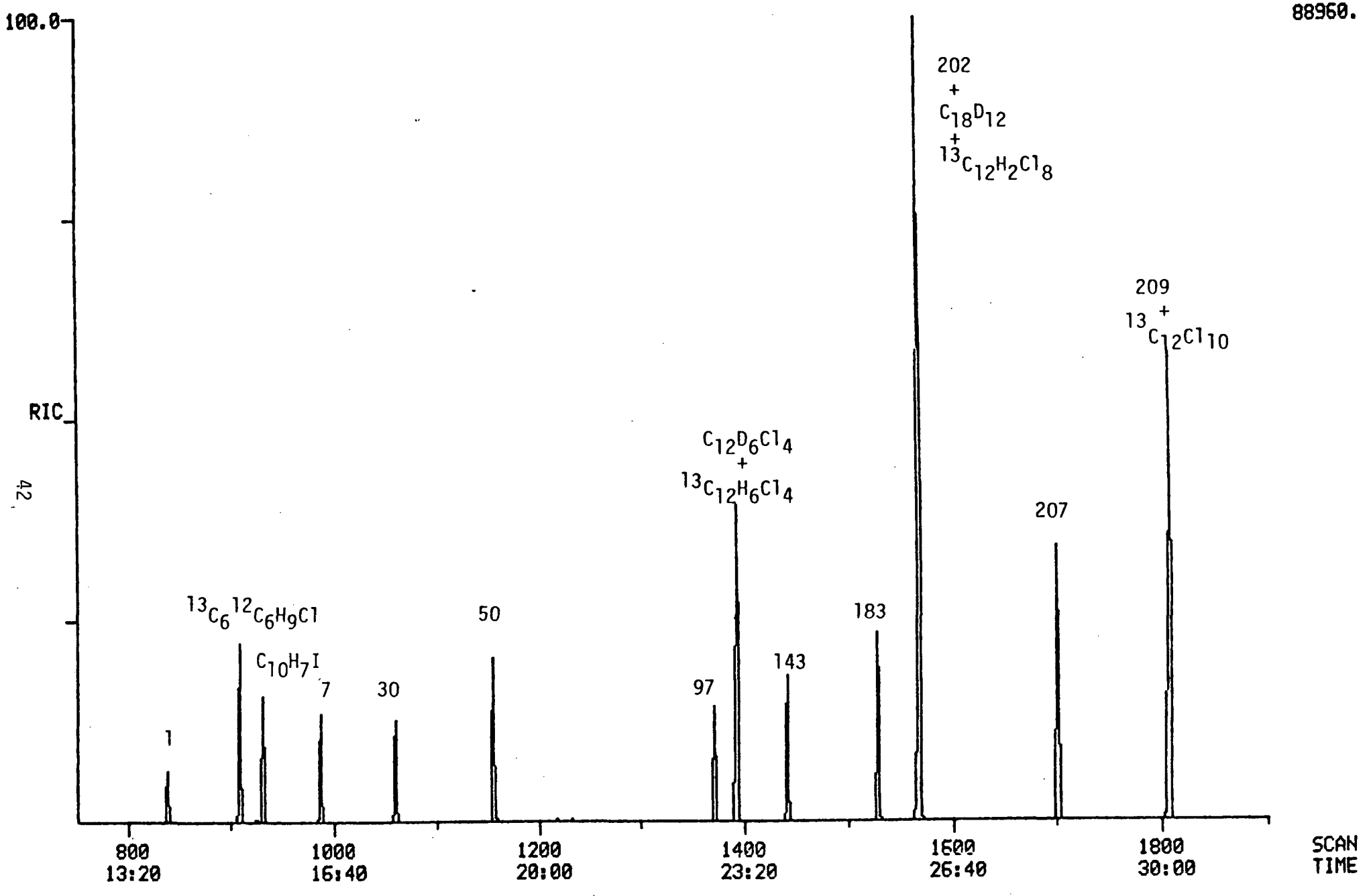


Figure 5. Reconstructed ion chromatogram of calibration solution FS100 ng PCB obtained in the full scan mode. The concentration of the 10 PCB calibration congeners, the four $^{13}C$-labeled PCB recovery surrogates, and the three internal standards are in Table 3. See Table 1 for PCB numbering system, Table 6 for capillary GC parameters, and Table 8 for mass spectrometer operating parameters.

LOQ needed meet the required method LOQ. In general, the more concentrated the PCBs, the greater the precision, accuracy, and qualitative data confidence. Thus, if possible, the amount of sample and concentration factor should be scaled so that full scan acquisition may be utilized.

10.3 While the highest available chromatographic resolution is not a necessary objective of this method, good chromatographic performance is recommended. With the high resolution of HRGC, the probability that the chromatographic peaks consist of single compounds is higher than with PGC. Thus, qualitative and quantitative data reduction should be more reliable.

10.4 After performance of the system has been certified for the day and all instrument conditions set according to Tables 2, and 6 through 11, inject an aliquot of the sample onto the GC column. If the response for any ion, including surrogates and internal standard, exceeds the working range of the system, dilute the sample and reanalyze. If the responses of surrogates, internal standard, or analytes are below the working range, recheck the system performance. If necessary, concentrate the sample and reanalyze.

10.5 Record all data on a digital storage device (magnetic disk, tape, etc.) for qualitative and quantitative data reduction as discussed below.

10.6 The instrumental performance must be monitored from run-to-run. The areas of internal standards must be consistent (e.g., ± 20%). If a low area is encountered, the injection may be suspect.

The resolution and peak shape of the internal standards, surrogates, and other peaks should be monitored during or immediately after data acquisition. Poor chromatography may indicate a bad injection, matrix interferences, or column degradation.

10.7 If a "dirty" sample is encountered, the analyst must employ appropriate measures to demonstrate that there is no memory or carry-over to subsequent samples. To assess the system cleanliness, a standard, blank sample, or solvent blank may be run.

If the system is contaminated, remedial efforts may include (a) changing or cleaning the syringe, (b) cleaning the injector, (c) baking out the column at its maximum temperature, (d) changing to a new column, or (e) cleaning the ion source.

## 11.0 Qualitative Identification

11.1 Full scan data

11.1.1 The peak must elute within the retention time windows set for that homolog (as described in Section 7.5).

11.1.2 The unknown spectrum should be compared to that of an authentic PCB. The intensity of the three largest ions in the molecular cluster (two largest for monochlorobiphenyls) must match the ratio observed for a standard within ± 20%. Fragment clusters with proper intensity ratios should also be present. System noise at low concentration or interferences may skew the ion ratio beyond the ± 20% criteria. If the analyst's best judgement is that a peak, which does not meet the qualitative criteria, is a PCB, the peak may be included in the calculation, with a footnote explaining the data and the reason for relaxing the criteria.

11.1.3 Alternatively, a spectral search may be used to automatically reduce the data. The criteria for acceptable identification include a high index of similarity.

11.2 Selected ion monitoring (SIM) or limited mass scan (LMS) data - The identification of a compound as a given PCB homolog requires that two criteira be met:

11.2.1 (1) The peak must elute within the retention time window set for that homolog (Seciton 7.5); and (2) the ratio of two ions obtained by LMS (Table 10) or by SIM (Table 11) must match the ratio observed for a standard within ± 20%. The analyst must search the higher mass windows, in particular M+70, to prevent misidentification of a PCB fragment ion cluster as the parent. System noise at low concentration or interferences may skew the ion ratio beyond the ± 20% criteria. If the analyst's best judgement is that a peak, which does not meet the qualitative criteria, is a PCB, the peak may be included in the calculation, with a footnote explaining the data and the reason for relaxing the criteria.

11.2.2 If one or the other of these criteria is not met, interferences may have affected the results, and a reanalysis using full scan EIMS conditions is recommended.

11.3 Disputes in interpretation - Where there is reasonable doubt as to the identity of a peak as a PCB, the analyst must either identify the peak as a PCB or proceed to a confirmational analysis (see Section 13.0).

## 12.0 Quantitative Data Reduction

12.1 After a chromatographic peak has been identified as a PCB, the compound is quantitated based either on the integrated abundance of the EICP or the SIM data for the primary characteristic ion in Tables 10 and 11. If interferences are observed for the

primary ion, use the secondary and then tertiary ion for quantitation. If interferences in the parent cluster prevent quantitation, an ion from a fragment cluster (e.g., M-70) may be used. Whichever ion is used, the RF must be determined using that ion. The same criteria should be applied to the internal standard compounds (Table 14).

Note: With the higher homologs, the mass defect from unity is significant. For instance, the mass of the most intense peak for decachlorobiphenyl is 497.6830. Areas, EICPs, etc., must be based on the true mass, not the nominal mass, or erroneous results may be obtained. In addition, the tuning of some quadrupoles may be less stable at high masses. The data quality must be monitored especially carefully for the higher homologs.

12.2 Using the appropriate response factor ($RF_p$) as determined in Section 7.4, calculate the mass of each PCB peak ($M_p$) using Equation 12-1.

$$M_p = \frac{A_p}{A_{is}} \cdot \frac{1}{RF_p} \cdot M_{is} \qquad \text{Eq. 12-1}$$

where $A_p$ = area of the characteristic ion for the analyte PCB peak

$A_{is}$ = area of the characteristic ion for the internal standard peak

$RF_p$ = response factor of a given PCB congener

$M_{is}$ = mass of internal standard added to sample extract (micrograms)

12.3 If a peak appears to contain non-PCB interferences which cannot be circumvented by a secondary or tertiary ion, either:

12.3.1 Reanalyze the sample on a different column which separates the PCB and interferents;

12.3.2 Perform additional chemical cleanup (Section 9) and then reanalyze the sample; or

12.3.3 Quantitate the entire peak as PCB.

12.4 Sum all of the peaks for each homolog and then sum those to yield the total PCB mass, $M_T$, in the sample. If a concentration-per-peak or concentration-per-homolog reporting format is desired, carry each value through the calculations in an appropriate manner. For example, if the analysis is being conducted to satisfy regulatory requirements for by-product PCBs, results may need to be reported on a per resolvable peak basis. One rule[1] states that PCBs in air releases to air must be below the practical limit of

Table 14. Characteristic Ions for Internal Standards and $^{13}C$-Labeled PCB Surrogates

| Compound | Abbreviation | Ion (relative intensity) Primary | Secondary | Tertiary |
|---|---|---|---|---|
| $d_6$-3,4,3',4'-Tetrachlorobiphenyl | $d_6$-$Cl_4$ | 298 (100) | 300 (49) | 296 (78) |
| 1-Iodonaphthalene | INAP | 254 | 127 | - |
| $d_{12}$-Chrysene | DCRY | 240 | - | - |
| $^{13}C_6{}^{12}C_6H_9Cl$ | $^{13}C$-$Cl_1$ | 194 (100) | 196 (33) | - |
| $^{13}C_{12}H_6Cl_4$ | $^{13}C$-$Cl_4$ | 304 (100) | 306 (49) | 302 (78) |
| $^{13}C_{12}H_2Cl_8$ | $^{13}C$-$Cl_8$ | 442 (100) | 444 (65) | 440 (89) |
| $^{13}C_{12}Cl_{10}$ | $^{13}C$-$Cl_{10}$ | 510 (100) | 512 (87) | 514 (50) |

quantitation, defined as "10 micrograms per cubic meter [roughly 0.01 part per million (ppm)] per resolvable chromatographic peak." For regulatory purposes, only peaks greater than the 100 $\mu g/m^3$ cutoff may need to be reported. A second rule[2] requires that inadvertently generated and recycled PCBs "vented to the ambient air are limited to less than 10 ppm" total PCBs.

12.5 Calculation of air sample volume[6]

12.5.1 Nomenclature

$M_p$ = Mass of PCB represented by a chromatographic peak micrograms

$M_T$ = Total mass of PCBs in sample, micrograms

$C_a$ = Concentration of PCBs in air, micrograms per cubic meter, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis

$A_n$ = Cross-sectional area of nozzle, square meter (square feet)

$B_{ws}$ = Water vapor in the gas stream, proportion by volume

I = Percent of isokinetic sampling

$MW_w$ = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)

$P_{bar}$ = Barometric pressure at the sampling site, mm Hg (in. Hg)

$P_s$ = Absolute stack gas pressure, mm Hg (in. Hg)

$P_{std}$ = Standard absolute pressure, 760 mm Hg (29.92 in Hg)

R = Ideal gas constant, 0.06236 mm Hg-$m^3$/K-g-mole (21.83 in. Hg-$ft^3$/°R-lb-mole)

$T_m$ = Absolute average dry gas meter temperature °K (°R)

$T_s$ = Absolute average stack gas temperature °K (°R)

$T_{std}$ = Standard absolute temperature, 293°K (528°R)

$V_{lc}$ = Total volume of liquid collected in impingers and silica gel, milliliters. Volume of water collected equals the weight increase in grams times 1 mL/g

$V_m$ = Volume of gas sample as measured by dry gas meter, dcm (dcf)

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf)

$V_{w(std)}$ = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf)

$V_t$ = Total volume of sample, milliliter

$V_s$ = Stack gas velocity, calculated by EPA Method 2,[7] m/sec (ft/sec)

$\Delta H$ = Average pressure differential across the orifice meter, mm $H_2O$ (in. $H_2O$)

$\rho_w$ = Density of water, 1 g/mL (0.00220 lb/mL)

$\theta$ = Total sampling time, minutes

13.6 = Specific gravity of mercury

60 = Seconds per minute

100 = Conversion to percent

12.5.2 Average dry gas meter temperature and average orifice pressure drop - See data sheet (Figure 4).

12.5.3 Dry gas volume - Correct the sample volume measured by the dry gas meter to standard conditions [20°C, 760 mm Hg (68°F, 29.92 in. Hg)] by using Equation 12-2.

$$V_{m(std)} = V_m \frac{T_{std}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} = K V_m \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m} \qquad \text{Eq. 12-2}$$

where K = 0.3855°K/mm Hg for metric units
= 17.65 °R/in. Hg for English units

12.5.4 Volume of water vapor

$$V_{w(std)} = V_{lc} \frac{\rho_w}{MW_w} \frac{RT_{std}}{P_{std}} = K V_{lc} \qquad \text{Eq. 12-3}$$

where K = 0.00134 $m^3$/mL for metric units
= 0.0472 $ft^3$/mL for English units

12.5.5 Moisture content

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Eq. 12-4}$$

If the liquid droplets are present in the gas stream, assume the stream to be saturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

12.6 Concentration of PCBs in stack gas - Determine the concentration of PCBs in the air according to Equation 12-5 and report in micrograms per cubic meter using Table 15. If an alternate reporting format (e.g., concentration per peak) is desired, a different report form may be used.

$$C_a = K \frac{M_T}{V_{m(std)}} \qquad \text{Eq. 12-5}$$

where $K = 35.31\ ft^3/m^3$

12.7 Isokinetic variation

12.7.1 Calculations from raw data.

$$I = \frac{100\ T_s\ [K\ V_{lc} + (V_m/T_m)\ (P_{bar}) + \Delta H/13.6)]}{60\ \theta\ V_s\ P_s\ A_n} \qquad \text{Eq. 12-6}$$

where K = 0.00346 mm Hg-$m^3$/mL-°K for metric units
= 0.00267 in. Hg-$ft^3$/mL-°R for English units

12.7.2 Calculations from intermediate values

$$I = \frac{T_s\ V_{m(std)}\ P_{std}\ 100}{T_{std}\ V_s\ \Theta\ A_n\ P_s\ 60\ (1-B_{ws})} \qquad \text{Eq. 12-7}$$

$$= K \frac{T_s\ V_{m(std)}}{P_s\ V_s\ A_n\ \Theta\ (1-B_{ws})}$$

where K = 4.323 for metric units
= 0.0944 for English units

12.7.3 Acceptable results - The following range sets the limit on acceptable isokinetic sampling results:

If 90% < I < 110%, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Agency may opt to accept the results.

12.8 Round off all numbers reported to two significant figures.

Table 15. Analysis Report

BY-PRODUCT PCBs IN AIR

Internal Sample No. _____ External Sample No. _____
Notebook No. _____ Sample Source _____
Data File Code _____ Sample Matrix _____
Volume Collected [$V_{m(std)}$] _____ $m^3$

Amount Extracted _____ g Final Volume _____ mL

| Analyte homolog | Mass $M_p$ (µg) | Analyte homolog | Mass $M_p$ (µg) |
|---|---|---|---|
| 1-Cl | | 6-Cl | |
| 2-Cl | | 7-Cl | |
| 3-Cl | | 8-Cl | |
| 4-Cl | | 9-Cl | |
| 5-Cl | | 10-Cl | |
| | | Total ($M_T$) | µg |
| | | Concentration ($C_A$) | µg/$m^3$ |

Estimated Method LOQ _____

Highest concentration per resolvable chromatographic peak _____ µg/µ3

| Reported by: | Internal Audit: | EPA Audit: |
|---|---|---|
| Name | Name | Name |
| Signature/Date | Signature/Date | Signature/Date |
| Organization | Organization | Organization |

## 13.0 Confirmation

If there is significant reason to question the qualitative identification (Section 11), the analyst may choose to confirm that a peak is not a PCB. Any technique may be chosen provided that it is validated as having equivalent or superior selectivity and sensitivity to GC/EIMS. Some candidate techniques include alternate GC columns (with EIMS detection), GC/CIMS, GC/NCIMS, high resolution EIMS, and MS/MS techniques. Each laboratory must validate confirmation techniques to show equivalent or superior selectivity between PCBs and interferences and sensitivity (limit of quantitation, LOQ).

If a peak is confirmed as being a non-PCB, it may be deleted from the calculation (Section 12). If a peak is confirmed as containing both PCB and non-PCB components, it must be quantitated according to Section 12.3.

## 14.0 Quality Assurance

Each participating laboratory must develop a quality assurance plan (QAP) according to EPA guidelines.[13] Additional guidance is also available.[14] The quality assurance plan must be submitted to the Agency (regional QA officer) for approval prior to analysis of samples.

The elements of a QAP include:

- Title Page
- Table of Contents
- Project Description
- Project Organization and Responsibility
- QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability
- Sampling Procedures
- Sample Custody
- Calibration Procedures and Frequency
- Analytical Procedures
- Data Reduction, Validation and Reporting
- Internal Quality Control Checks
- Performance and System Audits

- Preventive Maintenance
- Specific Routine Procedures Used to Assess Data Precision, Accuracy and Completeness
- Corrective Action
- Quality Assurance Reports to Management

## 15.0 Quality Control

15.1 Each laboratory that uses this method must operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial and continuing demonstration of laboratory capability by the analysis of check samples. The laboratory must maintain performance records to define the quality of data that are generated.

15.2 Certification and performance checks - Prior to the analysis of samples, the laboratory must define its routine performance. At a minimum, this must include demonstration of acceptable response factor precision with at least three replicate analyses; and analysis of a blind QC check sample (e.g., the response factor calibration solution at unknown concentration submitted by the QA officer). Acceptable criteria for the response factor precision and the accuracy of the QC check sample analysis must be presented in the QA plan.

Ongoing performance checks should consist of periodic repetition of the initial demonstration or more elaborate measures. More elaborate measures may include control charts and analysis of QC check samples consisting of other congeners or with matrix interferences.

15.3 Procedural QC - The various steps of the analytical procedure should have quality control measures. These include but are not limited to:

15.3.1 GC performance - See Section 7.2 for performance criteria.

15.3.2 MS performance - See Section 7.3 for performance criteria.

15.3.3 Qualitative identification - At least 10% of the PCB identifications, as well as any questionable results, should be confirmed by a second mass spectrometrist.

15.3.4 Quantitation - At least 10% of all manual calculations, including peak area calculations, must be checked. After changes in computer quantitation routines, the results should be manually checked.

15.4 Sample QC - Each sample and each sample set must have QC measures applied to it to establish the data quality for each analysis result. The responses of the internal standards, general spectral data quality, and consistency of the internal standard area are all measures of the data quality on individual samples. Within a sample set, analysis of replicates and standard addition samples are measures of the precision and accuracy, respectively.

15.4.1 The general spectral data quality is indicative of the overall reliability of the data for a sample. The levels of the background, intensity ratios within chlorine clusters, etc., must all be evaluated. If the data quality is marginal, the analyst may footnote results with an explanation regarding any doubts about the data quality. If the data are unacceptable (see Section 11.0), either the GC/MS determination or the entire analysis must be repeated.

15.4.2 An easy and significant assessment of the data quality is the consistency of the internal standard areas. If the internal standard area is consistent, the injection volume was correct and the system is operating within general tolerances (i.e., the chromatography column is transmitting compounds and the spectrometer is detecting them). If the internal standard area does not meet the criteria specified in the QAP, e.g., ± 20% of other injections, the data must be reviewed. If the injection or the GC/MS performance is suspect, the sample must be reanalyzed, or other corrective action taken.

15.4.3 QC for small sample sets - For small sample sets (1-10 samples), the minimum QC requirements can be a heavy burden. Analysts are encouraged to be efficient and bunch similar samples to increase the size of a set. A set is defined as a group of samples analyzed together by the same extraction/cleanup technique and determined on the GC/MS system on the same day or successive days under the same conditions.

At least one method blank must be run. The blank must be exposed to the same sources of contamination--solvent, glassware, etc.--as the samples. If conditions change, additional blanks must be generated. An example would be a new lot of solvent, or a change in dishwashing protocol.

At least one sample must be run in replicate. Triplicates are preferable, but duplicates may be acceptable. The acceptable precision among replicates must be specified in the QAP.

At least one sample must be analyzed by the standard addition technique. The analyst may select the most difficult sample, based on prior knowledge of the sample set, or a random sample. Two aliquots of the sample are analyzed, one "as is" and one spiked (surrogate spiking and equilibration techniques are described in Section 9.2) with Solution FSxxx ng PCB or SIMxxx pg PCB. If the analyst has no prior knowledge of the sample, the spiking level should be in the middle of the calibrated range for the mass spectrometer. If the concentrations of PCBs are known to be high or low, the amount added should be adjusted so that the spiking level is 1.5 to 4 times the measured PCB level in the unspiked sample. The samples should be analyzed together and the quantitative results calculated. The recovery of the spiked compounds (calculated by difference) must be 70-130%. If the sample is known to contain specific PCB isomers, these isomers may be substituted for solution FSxxx ng PCB or SIMxxx pg PCB.

15.4.4 QC for intermediate sample sets - With intermediate (approximately 10-100 samples) sample sets, the number of method blanks, replicates, and standard addition samples must comprise at least 10% each. For example, if 23 samples are to be analyzed as a set, 3 blanks, 3 duplicates, and 3 standard addition samples would be added in to give a total of 32 samples, at a minimum.

15.4.5 QC for large sample sets - When a large sample analysis program is being planned, the QA plan may propose specific QC measures. If none are proposed, the guidelines for intermediate sets may be followed. One QC measure which may increase efficiency is the use of control charts. If, for example, the control charts establish that there is no blank problem over the long term, the percent of blanks may be reduced. Any changes in the procedure (e.g., a new lot of solvent) will still, of course, require a blank.

15.5 It is recommended that the participating laboratory adopt additional QC 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 or triplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

## 16.0 Method Performance

The method performance has not been evaluated. Limits of quantitation; average intralaboratory recoveries, precision, and accuracy; and interlaboratory recoveries, precision, and accuracy will be presented when available.

## 17.0 Documentation and Records

Each laboratory is responsible for maintaining full records of the analysis. Laboratory notebooks should be used for handwritten records. GC/MS data must be archived on magnetic tape, disk, or a similar device. Hard copy printouts may be kept in addition if desired. QC records should be maintained separately from sample analysis records.

The documentation must describe completely how the analysis was performed. Any variances from the protocol must be noted and fully described. Where the protocol lists options (e.g., sample cleanup), the option used and specifies (solvent volumes, digestion times, etc.) must be stated.

The remining samples and extracts should be archived for at least 2 months or until the analysis report is approved, whichever is longer, and then disposed unless other arrangements are made. The magnetic tapes of the analysis and hardcopy spectra, quantitation reports, work sheets, etc., must be archived for at least 3 years.

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15. SUPPLEMENTARY NOTES
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16. ABSTRACT

This is a gas chromatographic/electron impact mass spectrometric (GC/EIMS) method applicable to the determination of chlorinated biphenyls (PCBs) in air emitted from commercial production through stacks, as fugitive emissions, or static (room, other containers, or outside) air. The PCBs present may originate either as synthetic by-products or as contaminants derived from commercial PCB products (e.g., Aroclors). The PCBs may be present as single isomers or complex mixtures and may include all 209 congeners from monochlorobiphenyl through decachlorobiphenyl.

A variety of general and specific sample preparation options are presented in this method. This method takes a different approach from those which rely on Aroclor mixtures for calibration and quantitation. In this method PCBs are detected and quantitated by homolog group. The results can be summed to give a total PCB value comparable to results generated by other methods or they may be presented as 10 individual homolog values. This homolog distribution can provide additional quantitative information on the composition and source of the PCBs.

The method performance is assessed for each sample. A set of four $^{13}C$-labeled PCBs is employed as recovery surrogates. If the surrogates are recovered and other QC parameters are within acceptable limits, then the data may be considered valid.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| PCBs<br>Polychlorinated biphenyls<br>Chlorinated biphenyls<br>Analytical methods<br>Determination<br>By-products Air<br>GC/MS Stack gas | | |

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