FIELD DETERMINATION OF POLYCHLORINATED BIPHENYL (PCB) CONGENERS IN PRODUCT SAMPLES BY GC/MS AT THE STANDARD CHLORINE-METACHEM SITE

CONTENTS

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1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures to be used for the on-site determination of polychlorinated biphenyl (PCB) congeners by gas chromatography/mass spectrometry (GC/MS) in product and other neat matrices in a field analytical laboratory. On-site field laboratories provide quick turnaround on critical data needed for field decisions concerning site characterization, treatability, separation, and remediation/removal activities. The sample preparation may be modified depending on the type of matrix.

2.0 METHOD SUMMARY

Approximately 0.5 grams (g) of a sample is dissolved in 10 milliliters (mL) of methylene chloride. A one- mL aliquot of the sample solution is spiked with an internal standard and subsequently analyzed by GC/MS. Ten selected PCB compounds from each PCB congener group (i.e., monochloro-, dichloro-, trichloro-, etc.) are used as calibration standards for the calculation of total PCB congener concentrations. PCB congener measurements are based on the peak area integration of each PCB congener group within their respective GC retention time windows.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Samples are typically analyzed immediately upon receipt. In the event samples cannot be diluted and analyzed immediately, samples must be diluted within 14 days and analyzed within 40 days. Sample dilutions should be stored at 4±2 degrees Celsius (^{o}C)when not in use. All unused portions must be maintained in appropriate containers until disposal.

Samples, sample dilutions, and standards must be stored separately in an atmosphere free of all potential contaminants.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

- Peaks having co-eluting retention times can interfere with this method.
- There may be down-time associated with electrical spikes/power outages due to thunderstorms in the site area.
- Improper cleaning or storage of glassware may cause interferences.
- Organic impurities in the carrier gas, the instrument, carryover from a previous sample, or solvents used may contribute to contamination.

5.0 EQUIPMENT/APPARATUS

- GC/MS, capable of temperature programming (Agilent Technologies 6890/5973 GC/MS, equipped with the Chemstation program or equivalent).
- GC column, Rtx-5MS, 30 meter (m) x 0.25 millimeter (mm) inner diameter (ID), 0.50 micron (µm) film thickness, fused silica capillary (Restek Inc., or equivalent).

- Balance, capable of weighing 0.5 g to the nearest 0.001g (Ohaus, Inc., or equivalent).
- Syringes, standard microliter (µL) volume syringes: 25, 100, and 500 µL (Hamilton, Inc., or equivalent).
- Liners, split/splitless low pressure drop liners filled with deactivated glass wool (Restek or equivalent).
- Refrigerators, explosion-proof for sample and standard storage (Lab-Line or equivalent).
- Hot plate, capable of heating up to 120°C (Thermolyne Corp. or equivalent).
- Disposable glass pipets, 10 mL and Pasteur pipettes.
- Glass vials with Teflon-lined crimp caps, 10 mL.
- GC autosampler glass vials with Teflon®-lined crimp caps, 2 mL.

6.0 REAGENTS

- PCB stock calibration standard, commercially available (Accustandard, PCB-SIM or equivalent). Refer to Table 1, Appendix A.
- PCB working calibration standards, prepared from the stock standard mix in methylene chloride at concentrations listed in Table 2, Appendix A.
- Internal Standard (IS), 4,4'-Dibromobiphenyl, 98% (Aldrich or equivalent). Prepare the stock IS solution at 10,000 micrograms per milliliter (µg/mL) in methylene chloride from the neat substance. Prepare the working IS solution at 25 µg/mL in methylene chloride from the stock IS solution. Spike 20 µL of this solution in all calibration standards, blanks, and samples.
- PCB Window Defining Mix, 2.5 µg/mL, commercially available (Accustandard, C-WDM or equivalent)
- Decafluorotriphenylphosphine (DFTPP), 50 µg/mL, commercially available (Supelco or equivalent). The amount of DFTPP injected is 50 nanograms (ng).
- Methylene chloride, capillary GC/GC-MS grade (Burdick & Jackson or equivalent).
- Helium, ultra-high purity, 99.999-99.9999 percent (%), used as GC carrier gas.

7.0 PROCEDURES

7.1 Sample Preparation

Weigh approximately 0.5 g (±0.001 g) of a sample in a 10-mL glass vial. Dissolve the sample in 10 mL of methylene chloride and mix by inverting. One milliliter of the sample solution is transferred to a GC

autosampler vial and spiked with 20 µL of the working IS. A 1-µL aliquot is used for analysis by GC/MS.

7.2 GC/MS Chromatographic Conditions

The typical operating conditions for analysis are as follows:

GC injector temperature:	280°C
Transfer line temperature:	280°C
MS Source temperature:	230°C
GC temperature program	50°C for 1.0 minute (min.) 25°C/min. to 150°C, hold for 0.5 min. 15°C/min. to 300°C, hold for 6.5 min. Total run time of 22 minutes
Column flow:	1.0 mL/min (constant flow)
Injection volume:	1.0 µL
Injection mode:	Splitless (purge time 0.75 minutes)
Scan mode:	Selected Ion Monitoring (SIM) for the following ions:

Mass Ion	Dwell*	Mass Ion	Dwell*	Mass Ion	Dwell*
150.0	10	151.0	10	152.0	10
186.0	10	224.1	10	291.0	10
292.0	10	311.9	10	313.9	10
326.0	10	328.0	10	360.0	10
393.9	10	429.9	10	463.9	10
497.8	10				

* = millisecond (ms)

7.3 DFTPP Tune

Tune the instrument by injecting 50 ng of DFTPP to meet the ion abundance criteria listed in Table 3, Appendix A. Acceptable performance must be achieved every 12 hours prior to sample analysis.

7.4 PCB Congener Retention Time Windows

Inject the PCB Window Defining Mix after tuning criteria have been met to initially establish the retention time window for each congener group (monchloro-, dichloro-, etc.). This mixture need not be run on a routine basis. Inject this mix whenever DFTPP's retention time shifts by 0.05 min. or greater to re-verify the retention window of each PCB congener group. The mix contains two compounds from each congener group (except decachlorobiphenyl, which has one compound) to define their individual retention time windows. A typical chromatogram of the PCB congener window defining mixture is shown in Figure 1, Appendix B. The individual peaks for the various chlorinated congeners are identified by the number of chlorines in the congener. For the monochlorobiphenyls, the retention time window is between 9.9 and 10.55 min., for dichlorobiphenyls between 10.89 and 12.18 min., and so on.

7.5 Initial Calibration

Inject six levels of the working calibration standard mix as described in Sec. 6.0. Figure 2 shows a typical chromatogram of the PCB congener calibration standard. Calculate each PCB congener's relative response factor (RRF), average response factor (RRF_{ave}), standard deviation (SD), and relative standard deviation (%RSD). The equations for RRF, RRF_{ave}, SD, and %RSD are listed in Table 4, Appendix A. The %RSD for the 10 PCB compounds should be ≤30%.

7.6 Continuing Calibration

After a compliant DFTTP tune, inject the continuing calibration standard (Cal4) and calculate percent difference (%D) between RRF_{CC} and RRF_{ave} according to the %D equation in Table 4, Appendix A. The %D should be ≤25% before continuing sample analysis.

Once the continuing calibration passes, update the RRF using the RRF_{CC} for congener concentration calculation. If the continuing calibration fails, re-inject the continuing calibration standard. If the re-injection does not meet the criterion, re-inject the six levels of the working calibration standard mix to generate a new initial calibration before analyzing samples.

7.7 Sample Analysis

Prepare each sample solution as described in Sec. 7.1 for acquisition.

8.0 CALCULATIONS

The concentration of each PCB congener group is calculated based on manual integration of its retention time window. The integration of each PCB congener group is shown in Figures 3A and 3B, Appendix B. Complete instructions for the manual integration of each PCB congener group are provided in Appendix C. Once integration is completed, print out the manual quantitation report. Input the sample information to calculate the total PCB in the sample. Refer to Figure 4, Appendix B.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The following quality assurance/quality control procedures apply:

22. DFTPP Tune - The GC/MS must meet the ion abundance tune criteria specified in Table 3, Appendix A, before initiating acquisition activities involving standards and samples. The tune check ensures correct mass calibration, mass resolution, and mass transmission. It must be performed every 12 hours during analysis.

23. Initial Calibration - An acceptable six-level calibration must be run before sample analysis. The initial calibration is acceptable if the %RSD is ≤30% for each PCB congener.

24. Continuing Calibration - A continuing calibration standard must be run for each 12 hours of sample analysis. The %D must be ≤25%.

25. Internal Standards - The internal standard is added to all standards and samples. The internal standard

area response of the sample must not vary more than 50-200% from the most recent valid calibration check standard. The retention times must not drift more than 0.05 min. from the latest 12-hour calibration check standard.

5. PCB congeners are considered not detected at the detection limits (DL) listed in Table 5, Appendix A.

10.0 DATA VALIDATION

Analytical data will be reviewed by Scientific, Engineering, Response and Analytical Services (SERAS) chemists prior to releasing the data.

1. All samples must be analyzed under an acceptable tune, initial calibration, and continuing calibration check at the required frequency.

2. The QC requirements described in Section 9.0 should be met at all times.

11.0 HEALTH AND SAFETY

Field laboratory instrumentation and analytical methods must meet all relevant United States Environmental Protection Agency/Environmental Response Team (U.S. EPA/ERT), SERAS, and Occupational Safety and Health Administration (OSHA) regulations to ensure the safety of personnel working in the laboratory. All applicable U.S. EPA and U.S. Department of Transportation (DOT) regulations regarding handling, accumulation, storage and removal of hazardous wastes must be met. More specifically, refer to REAC SOP #1501, *Hazardous Waste Management* and SERAS SOP #3013, *REAC Laboratory Safety Program*.

12.0 REFERENCES

U.S. Environmental Protection Agency. 1985. *Analysis of PCBs & Pesticides in Water and Soil/Sediments by GC/MS*, Method 680.

13.0 APPENDICES

A–Tables
B–Figures
C–Manual Integration of PCB Congener Groups

APPENDIX A
Tables
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TABLE 1. PCB Calibration Standard Mix

Analytes	Compound	Formula	Concentration (µg/mL)
Monochlorobiphenyls	2-Chlorobiphenyl	$C_{12}H_9Cl_1$	10
Dichlorobiphenyls	2,3-Dichlorobiphenyl	$C_{12}H_8Cl_2$	10
Trichlorobiphenyls	2,4,5-Trichlorobiphenyl	$C_{12}H_7Cl_3$	10
Tetrachlorobiphenyls	2,2',4,6-Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	20
Pentachlorobiphenyls	2,2',3,4,5'-Pentachlorobiphenyl	$C_{12}H_5Cl_5$	20
Hexachlorobiphenyls	2,2',4,4',5,6'-Hexachlorobiphenyl	$C_{12}H_4Cl_6$	20
Heptachlorobiphenyls	2,2',3,4,5,6,6'-Heptachlorobiphenyl	$C_{12}H_3Cl_7$	30
Octachlorobiphenyls	2,2',3,3',4,5,6,6'-Octachlorobiphenyl	$C_{12}H_2Cl_8$	30
Nonachlorobiphenyls	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl	$C_{12}HCl_9$	50
Decachlorobiphenyl	Decachlorobiphenyl	$C_{12}Cl_{10}$	50

µg/mL = micrograms per milliliter

TABLE 2. PCB Working Calibration Standards (µg/mL)

Standard Identification	Cal 1	Cal 2	Cal 3	Cal4	Cal5	Cal6
	0.02	0.05	0.1	0.5	1	5
2-Chlorobiphenyl	0.02	0.05	0.1	0.5	1	5
2,3-Dichlorobiphenyl	0.02	0.05	0.1	0.5	1	5
2,4,5-Trichlorobiphenyl	0.02	0.05	0.1	0.5	1	5
2,2',4,6-Tetrachlorobiphenyl	0.04	0.1	0.2	1.0	2	10
2,2',3,4,5'-Pentachlorobiphenyl	0.04	0.1	0.2	1.0	2	10
2,2',4,4',5,6'-Hexachlorobiphenyl	0.04	0.1	0.2	1.0	2	10
2,2',3,4,5,6,6'-Heptachlorobiphenyl	0.06	0.15	0.3	1.5	3	15
2,2',3,3',4,5,6,6'-Octachlorobiphenyl	0.06	0.15	0.3	1.5	3	15
2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl	0.08	0.2	0.4	2.0	4	20
Decachlorobiphenyl	0.1	0.25	0.5	2.5	5	25
4,4'-Dibromobiphenyl (IS)	0.5	0.5	0.5	0.5	0.5	0.5

IS = internal standard
µg/mL = micrograms per milliliter

TABLE 3. Ion Abundance Criteria for DFTPP

Mass	Relative Abundance Criteria
51	30-80% of mass 198
68	< 2.0% of mass 69
69	Present
70	< 2.0% of mass 69
127	25-75% of mass 198
197	< 2.0% of mass 198
198	Base peak, 100%
199	5-9% of mass 198
275	10-30% of mass 198
365	>1.0% of mass 198
441	Present but less than mass 443
442	40-110% of mass 198
443	15-24% of mass 442

DFTPP = Decafluorotriphenylphosphine

TABLE 4. Equations for Calculating RRF, %RSD, RFF_{ave},, SD, and %D

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:
Ax = area of analyte X
Ais = area of internal standard
Cis = concentration of internal standard
Cx = concentration of analyte X

$$\%RSD = \frac{SD}{RRF_{avg}} \; x \; 100$$

$$SD = \sqrt{\frac{\sum_{i=} \quad RF_i - \; RF_{ave}}{5}}$$

$$RRF_{ave} = \frac{RF_1 + \; .+ \; RF_6}{6}$$

TABLE 5. Detection Limits (DL) of PCB Congeners

Analytes	DL (µg/kg)
Monochlorobiphenyls	400
Dichlorobiphenyls	400
Trichlorobiphenyls	400
Tetrachlorobiphenyls	800
Pentachlorobiphenyls	800
Hexachlorobiphenyls	800
Heptachlorobiphenyls	1200
Octachlorobiphenyls	1200
Nonachlorobiphenyls	1600
Decachlorobiphenyl	2000

DL = detection limit
µg/kg = micrograms per kilogram

APPENDIX B
Figures
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FIGURE 1. PCB Window Defining Mix

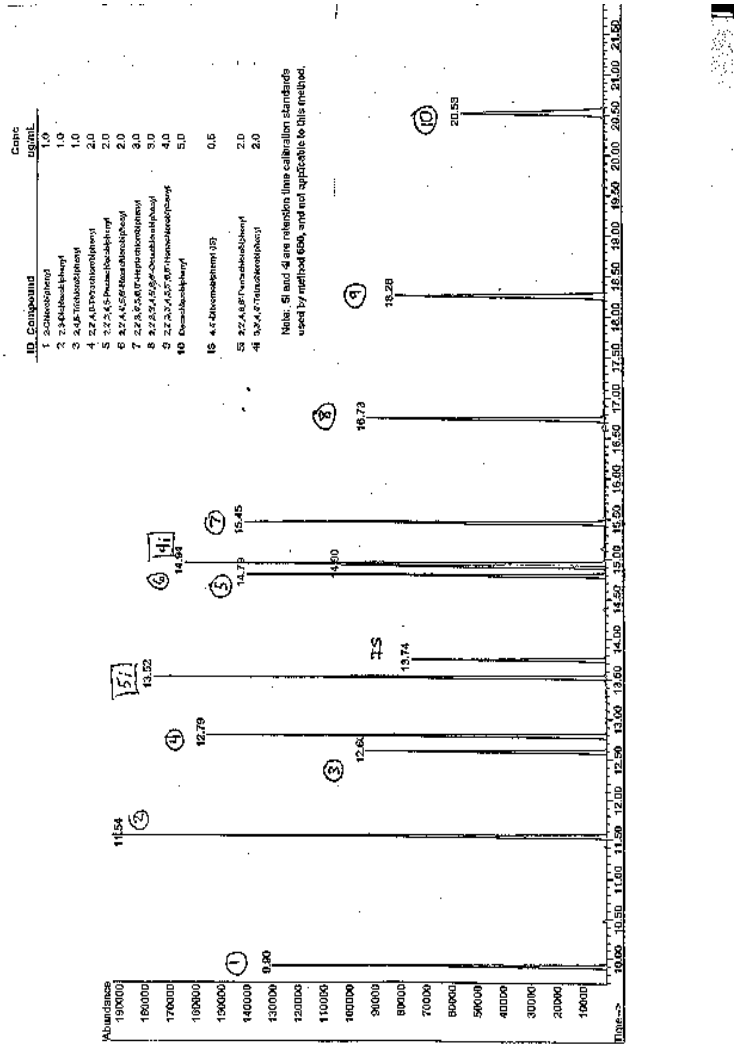

FIGURE 2. PCB Congener Calibration Standard

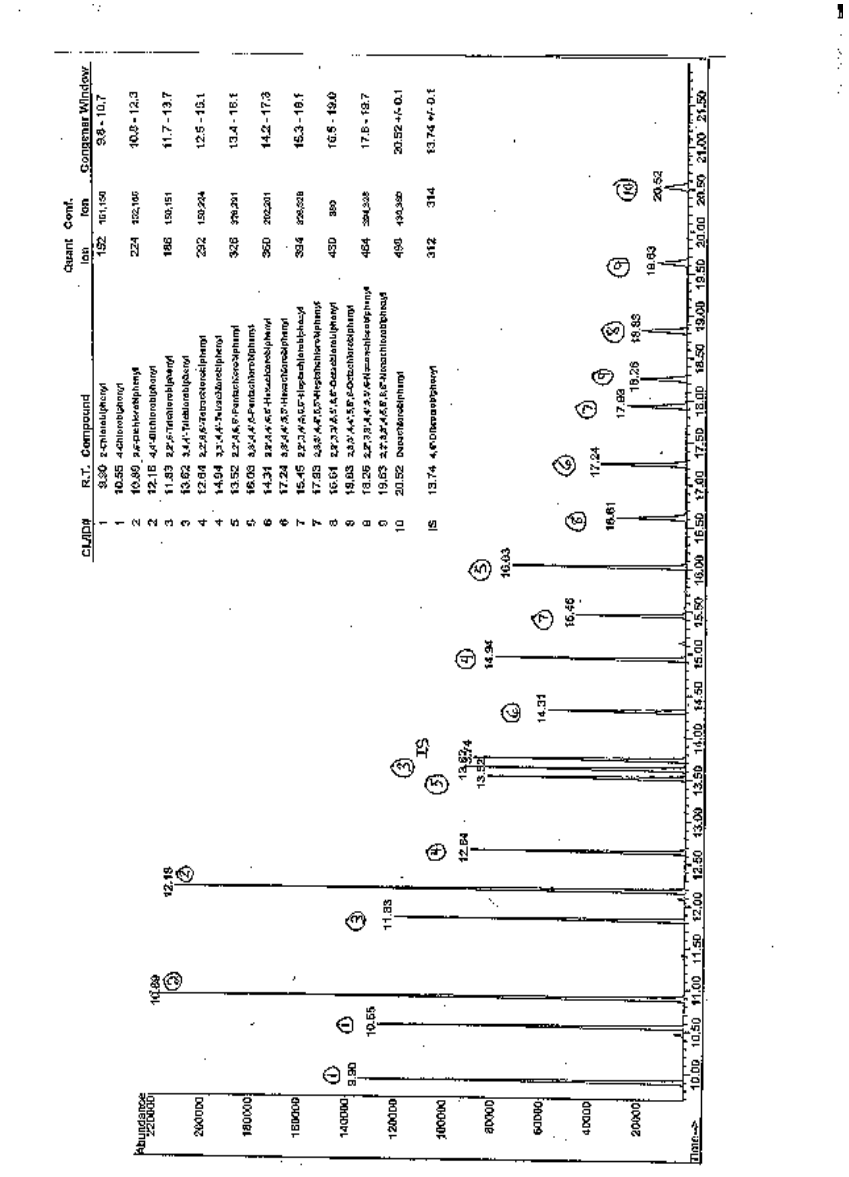

FIGURE 3A. Integration Window of PCB Congener Groups (Cl1-Cl5

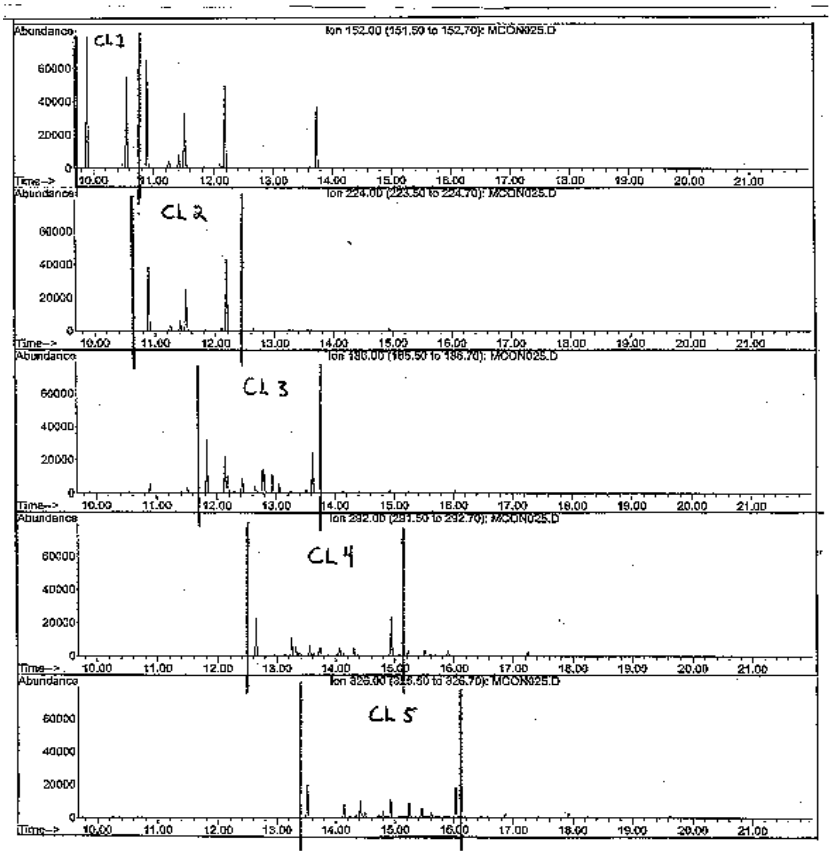

FIGURE 3B. Integration Window of PCB Congener Groups (Cl6-Cl10

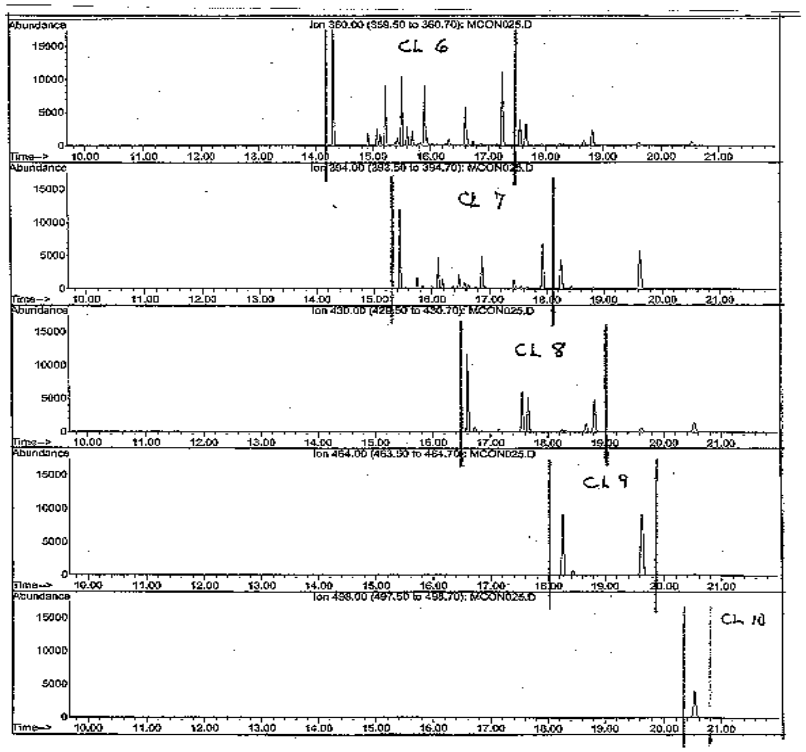

FIGURE 4. PCB Congener Report Sheet

Metachem Sample Data Sheet
PCB Congeners Analysis

Results reported as Total Pcb's

Sample Number:	**Aroclor 1242**		Weight:	1	g
Sample Location:	**10 ppm QC Check**		Final Volume:	1	mL
Date Collected:	05/24/03		Dil. Factor:	1	
Time Collected:	1800	hrs.	Matrix:	Std	

PCB Isomer Group	Conc. µg/g (ppm)		Conc. µg/g (ppm)
Monochlorobiphenyl	0.0557	Mono/50 =	0.0011
Dichlorobiphenyl	1.4143	Di/5=	0.2829
Trichlorobiphenyl	4.8861		
Tetrachlorobiphenyl	3.3362		
Pentachlorobiphenyl	0.8919		
Hexachlorobiphenyl	0.1233		
Heptachlorobiphenyl	U		
Octachlorobiphenyl	U		
Nonachlorobiphenyl	U		
Decachlorobiphenyl	U		

Total PCB's: 10.7075 µg/g

Total PCB's With Mono & Di Correction: 9.5214 µg/g

APPENDIX C
Manual Integration of PCB Congener Groups
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Manual Integration of PCB Congener Groups

1. In the ChemStation program, click [Quant] to open [Qedit Quant Result]
2. In Qedit window, start with monochlorobiphenyl (Cl1) and integrate the retention time window of this group by right-clicking the mouse to draw the baseline along the time axis from left to right.
3. Continue the integration for each PCB congener group following its defined retention time window.
4. Left-click the mouse to zoom in the chromatogram, if necessary, to facilitate the integration.
5. Once the integration is completed, generate the quant report.
6. Open the PCB Congener Report Sheet to enter sample information: sample name, location,sampling time, and weight. Then enter the concentration of each PCB congener group from the quant report.
7. The total PCB congener concentration in the sample is automatically calculated using the template for the sample data sheet shown in Figure 4, Appendix B.
8. Print out the MetaChem Sample Data Sheet.