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*Quality is  
Always  
our Standard  
Solution*

## Bicoastal Biphenyls: PCB Homologue Group Analysis & Toxicology in Maine and California

Bruce Colby & Therese Anderson

### Homologue Group Analysis of PCBs

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**P**olychlorinated biphenyls (PCBs) have electrical and chemical properties that made their use very attractive for a variety of applications, and by the mid-1970s over one billion pounds of PCBs had been produced and distributed worldwide. PCBs were manufactured by batch chlorination of biphenyl, with longer reaction times producing higher levels of chlorination. Subsequent separation and purification steps generated commercial mixtures containing varying amounts of the 209 possible PCB structures (congeners). These mixtures were most often sold in the US under the trade name "Aroclor" associated with a number indicating the relative level of chlorination. Aroclor 1254, for example, contained 54 weight percent chlorine. Other trade-names such as Chlorestol, Dykanol, Intertween, No-Flamol, Pyanrol, and many more were used in the US and world wide.

As Aroclors became widely distributed, they entered into the environment and subsequently into the food chain, where they exhibited some highly undesirable side effects. Consequently, PCB manufacture was banned and Aroclor mixtures became a major chemical concern in the environment. To this end, the U.S. Environmental Protection Agency (USEPA) developed several methods to characterize and quantitate Aroclors. These include Methods 505, 508, 608 and 8080. All of these methods rely on identifying a characteristic pattern of GC peaks that presumably represent a specific Aroclor mixture.

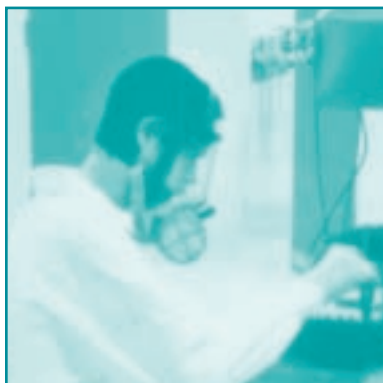
However, there were some problems. First, most environmental assessment work was performed using the Aroclor methods, while research was showing that only a limited number of PCB congeners appeared to have significant health effects. Second, the PCB congener composition of Aroclor mixtures varied from batch to batch due to variations in the manufacturing processes. Third, PCBs found in the environment were frequently present as combinations of Aroclor mixtures. Fourth, different PCB congeners reacted differently to environmental conditions, i.e., they weathered<sup>1</sup> differently. The result was, at best, that an Aroclor determination provided an indirect measure of the health-related congeners, and at worst, PCBs at high levels were not identified because they did not exhibit a characteristic Aroclor peak pattern due to mixing and/or weathering.

*continued on page 2*

The poor relationship between Aroclor measurements and health effects data and the technical problems associated with Aroclor determinations, required the development of new analytical methods. The first attempt was Method 680, a GC/MS method that did not rely on Aroclor mixtures but that failed to provide any congener specific information. The next attempt was Method 8082, a GC-ECD method that provided some congener information but unfortunately not for the congeners that were of most interest from a health effects standpoint (WHO list). Subsequently, Method 1668, an HRGC/HRMS method was drafted in 1995 using Method 1613 (chlorinated dioxins and furans) as a model. It was not Aroclor based, and it addressed the 12 WHO list congeners. While this method did not currently address any of the other 197 congeners, it is being redrafted to correct this situation.

At present there are several organizations in the US performing PCB congener specific analyses using methods of their own design. Although some are performing highly complex, multidimensional GC analyses, most are using GC/MS. With the GC/MS methods, samples are spiked with <sup>13</sup>C labeled PCB analogs, usually one for each homologue group, then solvent extracted. The extracts are cleaned up using some combination of H<sub>2</sub>SO<sub>4</sub> wash, GPC, florisil, silica gel and carbon plus other techniques. The extracts are then concentrated, and just prior to GC/MS analysis, an internal standard is added. The GC/MS is operated in the selected ion mode for increased sensitivity.

Gas chromatography is performed on a variety of columns, but SPB-Octyl is commonly used. Unfortunately, no GC column reliably separates all the PCB congeners from one another, so multiple columns must be used when reporting combined congener concentrations is not acceptable. In addition, the retention time windows for homologue groups overlap one another, so some fairly complex mass descriptor groups are required. Maintaining individual calibration curves for all 209 congeners is also a challenge, so a subset containing the congeners of most interest is frequently used. The non-calibrated congeners can then be reported as summations for homologue groups, with concentrations estimated based on average response factors derived from the calibrated congeners.



## Risk Assessment Methods for Low Resolution PCB Homologue Analysis

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**P**olychlorinated biphenyls (PCBs) are one of several analytes monitored for the State of Maine's Surface Waters Ambient Toxics (SWAT) program. The assessment of risk for PCBs has traditionally been calculated based on the extraction of the compounds from the matrix and the ability of the analyst when comparing and identifying the closest matching Aroclor pattern. Each Aroclor mixture has been assigned a specific risk value. This method works well for fresh spills and for contamination where dechlorination and other forms of metabolism have not taken place. Complex mixtures, and PCBs which have undergone metabolism and bioaccumulated selectively through the food chain, may present a pattern of congeners quite different from the original Aroclor mixtures. Calculating risk based on pattern identification becomes open to personal interpretation and the skill of the analyst.

For the last 4 years, WRI, in conjunction with the Maine Bureau of Health has been working on the development of a method for the identification of risk based on total homologue concentration. The calculation of PCB concentration in a sample is based on the total concentration of each homologue group rather than the summation of the total Aroclor pattern. The ratios of each of the homologue groups (mono-substituted through deca-substituted), calculated for a given sample are compared to standard Aroclor homologue ratios. The risk calculation is then based on the Aroclor standard(s) with the closest ratios, making the calculation of risk less dependent on an individual analyst's skill in interpretation.

The authors can be contacted to discuss their data at [therese@maine.maine.edu](mailto:therese@maine.maine.edu)

<sup>1</sup> "Weathering" is a catchall term used to describe the alteration of chemicals and/or chemical mixtures in the environment. These alterations result from differences in the rates at which individual chemicals are metabolized by living organisms and/or transported to new locations. Transport mechanisms generally involve differences in solubility/volatility in moving media such as water/air.



# CIL Analytical Standards

## for US EPA Method 1668 Revision A:

In 1995 CIL produced the standards used in the first generation of US EPA Method 1668, High Resolution GC/High Resolution MS using Isotope Dilution. Based on the results of the first study, the method and composition of standards was revised and the first draft method 1668 was published in October 1995. CIL produced revised standards that have been used since then for analysis and method validation.

In December 1999, Revision A to Method 1668 was cited in 64 FR 72045 as the "state of the art test method for the measurement of PCB congeners", as part of a proposed rule for 40 CFR part 503. A number of internal standards were added and the novel use of  $^{13}\text{C}$ -PCBs as window definers was also incorporated into the revised method.

The following set of standards is now available for Method 1668A. All standards have been prepared as defined by the method. CIL's highly accurate PCB Certified Standards were used to verify formulation of the  $^{13}\text{C}_{12}$ -PCBs used in the Method 1668A standards, and were also used to formulate the calibration solutions and native stock solution.

CATALOG#	COMPOUND (Isotope, Atom % Enrichment)	PRICE
<b>EC-4976</b>	Calibration Solutions CS1-CS5 (Unlabeled/ $^{13}\text{C}_{12}$ ) (Section 7.10.1, page 21; and Table 5, page 91)	
<b>EC-4976-3</b>	Daily Calibration Solution CS3 (Unlabeled/ $^{13}\text{C}_{12}$ ) (Section 7.10.1, page 21; and Table 5, page 91)	
<b>EC-4976-0.2</b>	High Sensitivity Calibration Solution CS0.2 (Unlabeled/ $^{13}\text{C}_{12}$ ) (Section 7.10.1, page 21; and Table 5, page 91)	
<b>EC-4977</b>	Labeled Toxics/LOC/Window Defining Stock Solution ( $^{13}\text{C}_{12}$ ) (Section 7.9.1, page 21; and Table 3, pages 85 and 86)	
<b>EC-4978</b>	Labeled Clean-up Standard Stock Solution ( $^{13}\text{C}_{12}$ ) (Section 7.9.2, page 21; and table 3, page 86)	
<b>EC-4979</b>	Labeled Injection Internal Standard Stock Solution ( $^{13}\text{C}_{12}$ ) (Section 7.9.3, page 21; and table 3 page 86)	
<b>EC-4989</b>	Native Toxics/LOC Stock Solution - 2 ug/ml in isoctane (Section 7.8.1, page 20; and table 3, page 85)	



# PCB Certified Standards

While CIL's primary environmental contaminants business is isotopically labeled standards, it is important to remember that the accuracy and precision of the native or unlabeled quantitative standards is what determines the accuracy and precision of the quantitative analysis.

When CIL first began to produce <sup>13</sup>C-PCB standards, it was thought that they should be analyzed using native PCBs prepared by external sources. It was discovered, however, that there was quite often substantial variability among native PCB standards. CIL decided to prepare PCB standards of unparalleled accuracy, and the first generation of PCB Certified Standards were prepared.

The overall preparation requires triplicate weighings by three different chemists using NIST-traceable Class S weights on a Sartorius M 3 P microbalance. Three separate solutions are then independently prepared and the relative standard deviations (RSDs) from multiple GC/MS analyses for each individual solution must be less than 5%. The RSD from the combined analyses must also be less than 5%. The solutions are then combined, and the resulting mixture analyzed again.

The US EPA's new draft method 1668A required production of 13 new <sup>13</sup>C<sub>12</sub>-PCBs. Newly acquired GC/MS instrumentation in CIL's QC department gave us the opportunity to reanalyze the entire set of Certified Standards. Certified Standards are used to analyze all individual <sup>13</sup>C<sub>12</sub> PCBs and mixtures, and are used to prepare native solutions and calibration solutions. More than 50 Certified Standards have now been produced, and these products represent exceptional value. The following PCB Certified Standards are now available:

PCB-1-CS	PCB-54-CS	PCB-118-CS	PCB-170-CS
PCB-3-CS	PCB-60-CS	PCB-123-CS	PCB-178-CS
PCB-4-CS	PCB-70-CS	PCB-126-CS	PCB-180-CS
PCB-9-CS	PCB-77-CS	PCB-127-CS	PCB-187-CS
PCB-15-CS	PCB-80-CS	PCB-128-CS	PCB-188-CS
PCB-19-CS	PCB-81-CS	PCB-138-CS	PCB-189-CS
PCB-28-CS	PCB-85-CS	PCB-141-CS	PCB-194-CS
PCB-32-CS	PCB-97-CS	PCB-153-CS	PCB-202-CS
PCB-37-CS	PCB-101-CS	PCB-155-CS	PCB-205-CS
PCB-38-CS	PCB-104-CS	PCB-156-CS	PCB-206-CS
PCB-39-CS	PCB-105-CS	PCB-157-CS	PCB-208-CS
PCB-47-CS	PCB-111-CS	PCB-167-CS	PCB-209-CS
PCB-52-CS	PCB-114-CS	PCB-169-CS	

*All solutions were prepared at 100µg/ml in iso-octane.  
The Certificate of Analysis includes a summary of the data acquired to validate the preparation,  
and a summary of the statistical analysis of the data.*

## JIS PCB Standards

After considerable effort, the Japanese Industrial Standards (JIS) Committee, comprised of leading Japanese analytical chemists from government, industry, and academia, has published guidelines for the measurement of Dioxins and Dioxin-like PCBs in Stationary Source Emissions (JIS K 0311) and in Industrial Water and Waste Water (JIS K 0312).

Calibration solutions have been prepared, as well as an assortment of Sampling, Cleanup and Syringe standards. These are being offered as stock solutions and working solutions for ease of use. Discounts will be applicable to orders for multiple units of the working solutions.

CIL/Radian have also prepared complete sets of Dioxin/Furan standards according to JIS protocol.

Please contact your CIL representative for specific information.



# Brominated Flame Retardant Standards

## From CIL

Generally used as flame-retardants, Brominated Diphenyl Ethers (BDEs) are rapidly emerging as chemicals of environmental concern. While little toxicological information is available, BDEs may be generally considered as persistent and highly lipophilic substances, similar to well known environmental contaminants such as polychlorinated biphenyls (PCBs). However, while production of PCBs has been banned in most countries, brominated flame retardants are still being manufactured, with most reports estimating several thousands of tons being made each year.

In 1996 Cambridge Isotope Laboratories (CIL) first introduced Chlorinated and Brominated Diphenyl Ether analytical standards. Since then, additional studies in Europe, Canada, Japan, and the United States have significantly increased interest in these products, and enabled CIL to extend its Flame Retardant offerings. Since the Brominated Diphenyl Ether product line is constantly growing, please contact your CIL representative for the latest additions.

Solutions of unlabeled  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hexabromocyclododecane (HBCDD) have also been prepared. Solutions are 50 $\mu$ g/ml in toluene

ULM-4834-1.2

$\alpha$ -HBCDD

ULM-4835-1.2

$\beta$ -HBCDD

ULM-4836-1.2

$\gamma$ -HBCDD

$^{13}\text{C}_{12}$  and native tetrabromobisphenol A are available.

CLM-4694-1.2

$^{13}\text{C}_{12}$  Tetrabromobisphenol A

ULM-4694-1.2

Native Tetrabromobisphenol A

## Environmental Products Group Expands

To serve the increasingly complex needs of laboratories performing environmental analysis, the CIL Environmental Products Group now has three chemists dedicated to helping analysts with their environmental standard needs.

Heading the group is Terry Grim, Environmental Sales Manager, who is in his fifth year with the group. Terry manages the group and is directly responsible for sales in California, the Mid-Atlantic, and the Southeast sections of the United States. With over 15 years of experience in analytical instrumentation, Terry contributes to new product development, which includes expansion of existing products, and new areas of analysis.

Last year, Ben Priest, formerly Technical Service Manager with Charm Sciences, joined CIL as Environmental Account Coordinator. As demand for new products grew, he assumed more responsibilities, and is now Environmental Account Manager covering Canada, and the Northeast, Midwest, Southwest, and Northwest sections of the United States.



The newest member of the Environmental Products Group is Jay Grazio, who comes to CIL from A.W. Chesterton, where he was a Product Manager. He is the Environmental Account Coordinator and his duties include addressing customer needs when Terry or Ben are visiting customers or at conferences, and responding to customer inquiries. He will also be working on a number of projects to help the group focus on customer needs, and improve communications between CIL and our environmental customers.

Katherine Belisle, International Account Manager, supports the sales and marketing activities of our overseas representatives and manages the International Sales Department. The department handles all sales inquiries from customers and is the liaison for your technical requirements. International Account Coordinators are Pam Degou, Michael Robey, and Steven Lilly. In addition to the support provided by this group, Terry Grim assists with supporting CIL's environmental representatives in Asia and Southern Europe and Ben Priest assists with Northern Europe and South America.

# WHO PCBs

The World Health Organization (WHO) has made changes to their targeted list of dioxin-like PCBs. The list in 1993 consisted of the coplanar PCBs PCB-77, PCB-126, & PCB-169; mono-ortho PCBs PCB-105, PCB-114, PCB-118, PCB-123, PCB-123, PCB-156, PCB-157, PCB-167, & PCB-189; and di-ortho PCBs PCB-170 & PCB-180. In 1998, the list was modified by adding coplanar PCB-81, and deleting the di-ortho PCBs PCB-170 & PCB-180.

CIL has produced a large number of <sup>13</sup>C-labeled, native, and calibration solution standards for analysis of these dioxin-like PCBs, both with and without PCB-81, PCB-170, & PCB-180. Please contact CIL or one of our International Representatives with specific requests

## Late-Breaking News- Chlorpyrifos Restriction

The US EPA has indicated that they will prohibit use of chlorpyrifos, one of the most commonly available pesticides, as an over-the-counter pesticide. In recent months, the US EPA proposed making the acceptable exposure level of chlorpyrifos one-third of what it is currently, but with the expected recommendation, the level will be one-tenth of what's currently allowed.

The decision is part of a systematic review of the safety of pesticides the US EPA is required to make under the 1996 Food Quality Protection Act, designed to protect children in particular from the toxic effects of pesticides.

Chlorpyrifos is an organophosphorothioate, related to nerve gas compounds used as chemical weapons. The EPA has determined that the compound poses no imminent threat to public health, and hasn't ordered a recall of products containing chlorpyrifos.

CIL has labeled chlorpyrifos, part number DLM-4360-1.2, in stock, for analysts wishing to investigate chlorpyrifos levels.



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An operator will direct your calls from 8:00am-5:30pm eastern US time Monday through Thursday (8:00am-5:00pm Friday).

- Toll-free from the US 800-322-1174
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