EcoNotes

An occasional publication of technical notes from EcoChem, Inc. **Spring 2005**

The Future of Polychlorinated Biphenyls Analysis
No More Aroclors?

A little background

The manufacture and use of polychlorinated biphenyls (PCBs) has been outlawed in the U.S. for almost thirty years, since Congress enacted the Toxic Substances Control Act in 1976. The ban followed several decades of widespread industrial use in the manufacture of lubricants, coolants and insulators for electrical and hydraulic equipment, and plasticizers in paint and plastics.

A high degree of stability was the major reason for such widespread use of PCBs. Now this asset has become a liability, since PCBs are a recognized health risk ubiquitous in our environment today, decades after they were banned.

The EPA has regulated PCB residues in solids, waters and organic liquids (oils and solvents), and PCBs have been the driving force behind several Superfund clean-ups over the years. Therefore, a huge amount of analytical data has been generated. Results have generally been reported as Aroclor concentrations, where Aroclors are trade names for formulations containing certain defined mixtures of PCB compounds. However, it has become apparent that while PCBs remain in the environment for decades, the distribution of PCB compounds in an Aroclor mixture are affected by weathering, metabolism, and the presence of multiple Aroclor mixes. Recent advances in analytical technology have spawned new methods for analysis of individual PCB congeners. The EPA has approved this approach, recognizing that it yields more reliable and accurate results than reporting PCBs as Aroclor mixtures.

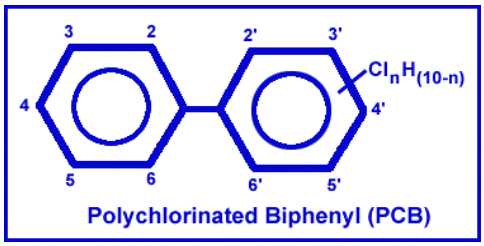

Image source: www.epa.gov/pcb/

PCB Analysis Methods

EPA Method 1668A is the most complete method for analysis of PCB congeners. Issued in 1999, this method employs gas chromatography with high-resolution mass spectrometry (GC/HR-MS) to determine ultra-low (parts per trillion) PCB congener concentrations. HR-MS analytical equipment is highly sophisticated and much more sensitive than the previous generation of MS technology, but remains quite exclusive and expensive. There are an increasing number of laboratories offering this analysis, with a price range of around $600-$900 per sample. The method provides sample preparation and extraction procedures for aqueous and solid samples, multi-phase samples, and tissue samples. Quantitation is performed using the isotope dilution technique, where results are quantitated using the recovery of labeled analogs of the target compounds. HR-MS analysis is typically required for determination of the toxic (coplanar) congeners.

In this issue of EcoNotes:

Analysis using GC with low-resolution mass spectroscopy and selective ion monitoring (GC/LR-MS-SIM) is also feasible for congener determination. A draft procedure, EPA Method 680, was written for this analysis, but was never promulgated. Several laboratories do offer a version of this analysis, which is less expensive – but less sensitive - than the GC/HR-MS option. This technique presents challenges in separating the congeners, often requiring that co-eluting results be reported as a sum of up to five combined congeners. However, some laboratories offer so-called "high-resolution GC/LR-MS", using more selective GC columns with longer run times to optimize congener separations. Sensitivity is in the low parts per billion range – equivalent to GC/ECD (see below) and with better (spectral) identification. However, detection limits are still an order of magnitude higher than for HR-MS analysis. This method of analysis can provide a good way to measure many congeners, but there are limitations in both selectivity and sensitivity, which must be examined carefully before choosing this technique.

EPA Method 8082 is the current method for analysis of PCBs as Aroclor mixtures. This method uses gas chromatography with electron capture detection (GC/ECD). This is a sensitive technique, which has been the most widely used analysis to date. It provides Aroclor detection limits in parts per billion. The main advantage to analyzing PCBs as Aroclors is that the analysis is widely available and relatively inexpensive. As such, it serves as a useful exploratory method for determining the general level of PCB contamination. However, because GC/ECD identifies target compounds solely by retention times, it is not specific enough to identify and quantitate a large number of individual congeners without co-elution problems. Since Method 8082 analysis does not require measurement of individual congeners, variations from a standard Aroclor pattern go undetected. This can lead to significant error in assessing the total concentration of PCBs, since the composition of Aroclor mixtures can become altered by weathering, mixing with other non-target Aroclors, and bioaccumulation. Accurate analysis of PCB concentrations in environmental samples generally requires a congener-specific method.

Whichever analysis method is chosen, a well-designed quality assurance plan can ensure usable data. In addition to the usual quality assurance criteria, consider requesting spikes with specific congeners of interest. Matrix–specific certified reference materials (CRMs) might also be used, particularly for sediments and biological samples such as plant, animal or fish tissues. CRMs provide a measure of the lab's efficiency by providing an independent, real-life sample with a certified concentration of the target compound(s).

Glossary

Aroclor: A range of several established mixtures of PCB congeners, prepared and sold under this trade name from the 1950s until the 1970s for their stability and insulating properties.

Congener: One of 209 individual PCB compounds, each with a unique chlorine substitution pattern (e.g. 2,2',3,4,5'-pentachlorobiphenyl). All congeners can be divided into 10 homologue groups.

Coplanar ("toxic") congeners: Four PCB congeners have a coplanar (dioxin-like) structure, and a further eight have a "near-coplanar" structure. These 12 congeners have been given toxic equivalency factors (TEF) by the World Health Organization, indicating their toxicity relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Extra clean-ups and HR-MS analysis are required to resolve these congeners from others.

Homologue: One of ten classifications (mono- through deca-) for each PCB congener, based on chlorination level (e.g. 2,2', 3,4,5'-pentachlorobiphenyl is one of several congeners from the penta-chlorinated homologue group).

IUPAC Number: A system that identifies each congener by a unique number between 1 and 209 (e.g. 2,2', 3,4,5'-pentachlorobiphenyl may be identified as PCB 87). Also known as the "BZ-number" (from Ballschmitter and Zell). IUPAC and BZ congener numbers were made equivalent in 1993.

PCB: Polychlorinated biphenyl. Strictly refers to any (or all) of the 209 congeners, but is also applied in the context of Aroclors, which are actually *PCB mixtures*.

PCB Web Links

These EPA sites provide general information and specific analytical methods.

EPA PCB Homepage:
www.epa.gov/opptintr/pcb/

EPA Ecological Risk Assessments:
http://cfpub1.epa.gov/ncea/cfm/recordisplay.cfm?deid=52083

EPA Method 1668A (GC/HR-MS analysis method):
www.epa.gov/Region3/1668a.pdf

EPA Method 8082 (GC/ECD analysis method):
www.epa.gov/epaoswer/hazwaste/test/pdfs/8082.pdf

Links to two leading reference material suppliers:

NIST: http:/ts.nist.gov/ts/htdocs/203/232/232.htm

NRC Canada: http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.htm

HOT TOPIC – Polybrominated Flame Retardants

Polybrominated diphenyl ethers (PBDEs) are manufactured chemicals that can be added during the manufacture of plastics and foams as flame retardants (in furnishings, computer monitors, televisions, textiles, etc.). PBDEs are colorless, off-white solids, made up of mixtures of up to 209 congeners (like PCB congeners). They were introduced in the 1970s as a safer alternative to polybrominated biphenyls (PBBs) – a similar class of compounds whose use was discontinued in the U.S. at that time. Production and use of PBDEs has expanded greatly since then, particularly as consumer electronic products flooded the market. Because these brominated compounds are mixed into plastics rather than bound to them, they tend to "migrate" out of the plastic as it degrades, making their way into the environment. Sunlight can degrade some PBDEs in the air, but they are not easily soluble in water, sticking to particles and settling to the bottom of rivers or lakes. From there, the PBDEs are bio-accumulated in marine life, birds and mammals - just like PCBs. Studies have shown their presence in human breast milk, triggering a recent ban on their use in the European Community.

Several agencies list these compounds as suspected human carcinogens, based on laboratory rodent studies, although there are presently no federal guidelines or concentration recommendations for protecting human health from exposure to PBBs or PBDEs. However, following the European lead, the State of California has enacted legislation to ban certain classes of PBDEs (penta-brominated and octa-brominated iphenyl ethers) by 2008. Other states, including Maine and Washington, are considering bans. With this legislation pending, it's inevitable that we're going to start seeing PBDEs as compounds of interest more and more often.

Some laboratories are gearing up for this, while some specialized high-resolution labs have been doing it for years. EcoChem has seen several PBDE data sets recently, and the analyses generally mirror the PCB methods reported elsewhere in this ***EcoNotes*** issue. High-resolution mass spectroscopy (HRMS) provides the best sensitivity and selectivity, providing resolution of dozens of PBDE congeners down to picograms per gram *(parts per trillion)* in solids and picograms per liter *(parts per quadrillion)* in water. A draft EPA Method (1614) for HR-MS analysis of PBDEs is in development, and this is likely to become the method of choice, as Method 1668A has become for PCB congeners.

Example PBDE Detection Limits – HR-MS Analysis

PBDE Homologue (parts per trillion)	Soil/Sediment/Tissue (ng/kg)	Water (pg/L
Tri-, Tetra-, Penta-, Hexa-, Hepta-, Octa-BDEs	5.0	20
Nona-BDEs	10	40
Deca-PBDE	20	100

However, at least one well-known laboratory has developed a PBDE analysis using low resolution MS with selective ion monitoring (LR-MS-SIM). SIM is a proven technique for analysis of several classes of semi-volatile compounds, and has the potential to provide reliable PBDE data, albeit at a higher detection level (parts per billion) and with less ability to identify individual congeners.

As with PCB congener analyses, there is a trade-off between sensitivity and price, which can only be resolved by carefully setting your data quality objectives and selecting the method that will be adequate to meet those objectives. EcoChem has consulted on numerous projects involving PCB and PBDE congener analyses, and can suggest different analytical approaches based on client needs (from screening to health risk). Contact us for more information.

IMPORTANT!

Things to consider when talking with the laboratory about PCB or PBDE analysis methods:

When initiating a new project, it is important that you understand your data quality objectives. Over the course of the project, the proper selection of an analytical procedure will depend on the objectives for data collection (e.g., initial screening, remediation, confirmation sampling, health risk, etc.). Here are a few tips that may be useful:

1. Final EPA policy details are still in flux. We will try to keep you updated. Call us if we can be of assistance.

2. Laboratory performance with the newer PCB congener and PBDE methods is often untested. Quality control review and careful interpretation of your data is essential.

3. Do not make your laboratory selection based solely on price. It is worthwhile in the long run to trust a laboratory with a strong QA program and a proven track record- particularly with complex HRMS congener analyses.

4. Carefully consider your analyte list. Which PCB congeners or PBDEs do you need? Most labs have a standard list, but these can include co-eluting congeners or exclude some of the toxic congeners. How will you determine Total PCBs?

Links to some PBDE information:

US Environmental Protection Agency:
www.epa.gov/Region9/cross_pr/childhealth/pbde.html

Washington State Department of Ecology:
www.ecy.wa.gov/programs/eap/pbt/pbde/index.html

Wisconsin Department. of Natural Resources:
http://dnr.wi.gov/environmentprotect/pbt/chemicals/pbde.htm

EcoChem opens Olympia Office

EcoChem, Inc.
2401 Bristol Court SW
Olympia, WA 98502
Phone: (360)754-2552
Contact: Craig Hutchings
Email: chutchings@ecochem.net

Ann Bailey, President
Linda Bohannon, V.P.

EcoChem, Inc.
405 Westland Building
100 South King Street
Seattle, Washington 98104
Phone (206) 233-9332
Fax (206) 233-0114
www.ecochem.net

This publication is a courtesy of EcoChem, Inc., a leader in providing environmental science, chemistry, and quality assurance support. The content is intended for general purposes only and should not be construed as specific advice or opinion on any specific circumstance.