Development of a Low-Resolution GC/MS Method for PCB Congeners in Support of the Clean Water Act

Adrian Hanley, EPA Office of Water, Office of Science and Technology, Engineering and Analysis Division
Harry McCarty and Eric Boring, CSRA

Goal

The goal of this project is to develop a low-resolution GC/MS method for polychlorinated biphenyl (PCB) congeners in wastewater and other matrices that is a significant improvement over Method 608, the only approved PCB method at 40 CFR Part 136 for wastewater. Based on EPA's needs, the PCB congener method must meet the following criteria:

1. Identifies and quantifies PCB contamination using individual congeners, not an estimated quantity based off patterns generated from Aroclor mixtures.
2. Be more sensitive than the currently approved Method 608, but is not so sensitive that it will be compromised by typical laboratory background contamination.
3. Can be implemented at a typical mid-sized full-service environmental laboratory.

Approach

EPA convened a work group of EPA, State, and utility staff, supported by contractors, to identify specific congeners of interest on which to focus, candidate analytical methods, including sample preparation, extraction, cleanup, and instrumental analysis procedures, that were sufficiently well developed to be subjected to single-laboratory testing. The work group prioritized congeners of high priority for this method. There was general consensus that the more important congeners to monitor have the following characteristics:

- Most common in the environment
- Congeners that are known to be most prevalent in human tissue
- Congeners that are present in the largest quantities within the manufactured Aroclor mixtures
- Toxic congeners identified by the World Health Organization (WHO) that are routinely found in environmental matrices

There is significant overlap between the first three of these four categories.

Following the work group deliberations, EPA developed a formal study plan and an associated quality assurance project plan, contracted with a laboratory, selected relevant sources of wastewaters, soils/sediments, biosolids, and fish tissues, and began single-laboratory testing.

Chromatography, Calibration, and Quantification

Analysis is done by GC/MS using a DB-5 chromatography column (60 m, 0.25 mm i.d., 0.10 µm film thickness) operated at a unit mass resolution in the electron ionization (EI) mode using multiple ion detection (MID), acquiring two characteristic ions for each target analyte. The 209 congeners are separated into 167 peaks. Total run time is approximately 48 minutes.

All 209 PCB congeners may be determined by the procedure, but there are 65 congeners of primary interest. The draft method uses a six-point initial calibration and four different quantitation schemes.

- True isotope dilution quantification (ID), whereby the response of the target congener is compared to the response of its $^{13}C_{12}$-labeled analog. **23 target congeners are quantified in this way.**
- Modified isotope dilution (mID), when one or more congeners in the same level of chlorination (LOC) coelute with a congener that has a $^{13}C_{12}$-labeled analog. **14 target congeners are quantified in this way** (6 with $^{13}C_{12}$-labeled analogs and 8 that coelute with one of those 6).
- Extracted internal standard quantification (EIS), whereby the response of the target congener is compared to the response of the $^{13}C_{12}$-labeled analog of another congener in the same level of chlorination (LOC) with which it coelutes. **28 target congeners are quantified in this way.**

The remaining 144 congeners are quantified indirectly using isotope dilution standards of similar congeners with the same level of chlorination. The response factor is assumed to be the same as the reference isotope dilution standard.

Quantitation Scheme	Congeners
Isotope dilution	1, 3, 11, 15, 19, 28, 37, 54, 70, 77, 104, 126, 153, 155, 169, 180, 188, 189, 202, 205, 206, 208, 209
Modified isotope dilution	4 + 10, 52 + 73, 85 + 120, 89 + 90 + 101, 106 + 118, 138 + 163 + 164
Extracted internal standard	5 + 8, 18, 31, 41 + 64, 44, 66 + 80, 61 + 74, 93 + 95, 99, 105 + 127, 110, 132 + 168, 147, 139 + 149, 156, 166, 177, 182 + 187, 199
Indirectly, via another congener	All 144 remaining congeners

Extraction

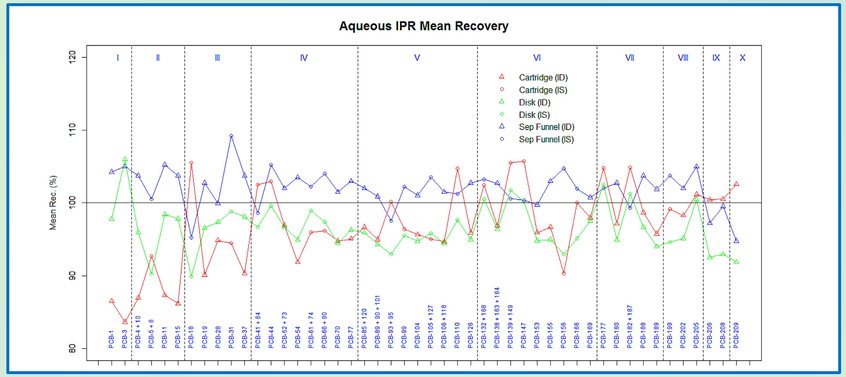
EPA tested three extraction procedures for aqueous samples:

- Separatory funnel extraction
- Disk-based solid-phase extraction (SPE)
- Cartridge-based solid-phase extraction (SPE)

Solid samples were extracted using Soxhlet.

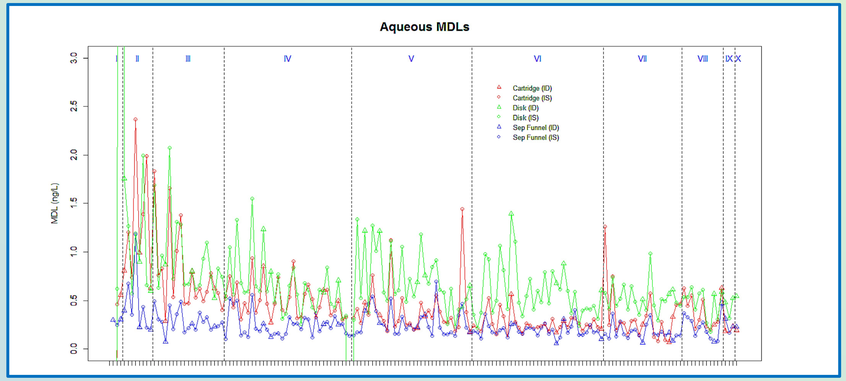
Initial Precision and Recovery

Prior to testing environmental samples, four initial precision and recovery (IPR) samples were analyzed by each extraction technique. The mean IPR recoveries for the congeners of primary interest by the three aqueous extraction techniques are shown below.



Method Detection Limits

Method detection limits (MDLs) were determined using EPA's recently revised MDL procedure. Both the MDL_b and MDL_s were determined. MDL values varied by congener and extraction technique, but generally ranged from approximately 0.06 to 2.37 ng/L. For the separatory funnel procedure, none of the method blank aliquots contained any of the congeners and therefore, MDL_b could not be calculated. For the cartridge-based SPE procedure, only PCB-105+127 was present at a level that allowed the calculation of MDL_b. In contrast, 83 of the 167 congeners or groups of coeluting congeners were present in the blanks from the disk-based SPE procedure at levels that allowed the calculation of MDL_b. However, in all of those instances, the MDL_b value was less than the MDL_s value, and the revised MDL procedure instructs the user to select the greater of the two values as the detection limit to be used. Therefore, none of the calculated MDL_b values affected the final MDL. By and large, the MDL_s values from the separatory funnel extraction are lower than those for either the cartridge-based or disk-based solid-phase extraction. The MDL_s results for all 167 analytes (209 congeners) are presented below, by extraction technique.

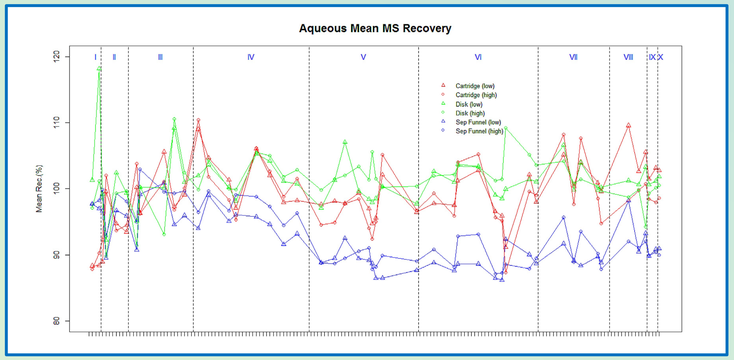


Aqueous Matrix Spike Samples

EPA worked with the laboratory and others to obtain large volumes of wastewater treatment effluents from nine separate sources, including publicly owned treatment works and industrial treatment systems. A 1-liter sample from each source was extracted by the separatory funnel procedure and analyzed to determine background concentrations of the PCB congeners. Three sets of four 1-liter samples of each wastewater were spiked with the 65 congeners of primary interest at two levels determined by the background concentrations.

Matrix Type #	Source	Low Spike (ng/L)	High Spike (ng/L)
1	Pulp and paper effluent	16	160
2	Pulp and paper influent	16	160
3	Municipal primary treatment effluent	16	160
4	Municipal secondary treatment effluent	16	160
5	ASTM synthetic wastewater	16	160
6	Creek water	16	160
7	Unspecific wastewater treatment plan effluent	16	160
8	Recycled paper mill-treatment plant effluent	16	160
9	Aluminum plant final effluent	16	160

One set of four spiked samples was extracted using the three extraction procedures. The mean recoveries of each analyte are shown below, based on the four spiked samples. The recoveries for each technique appear to be independent of the spiking concentration, in that the recoveries for the two levels are consistent within each technique across the long list of analytes. To some extent, the patterns for all three extraction techniques exhibit similarities as well. Regardless of the observed variation across the analytes, all of the mean recoveries are within the range of approximately 85% to 110%, with the exception of PCB-3 in the low-level spiked samples prepared using the disk-based SPE equipment, where the mean recovery is 118%.



Solid Matrix Spike Samples

Matrix spike samples for solid matrices were prepared from four soil/sediments, four biosolids, and four fish tissues from a variety of sources. Based on the observed background concentrations, sets of four aliquots of each sample were spiked with the 65 congeners of primary interest at two or three levels for each matrix type. The range of mean recoveries across all of the congeners in all of the samples in a given spiking level is shown below.

	Low Spike Mean Recovery Range	Medium Spike Mean Recovery Range	High Spike Mean Recovery Range
Soil/Sediment	44 to 128%	53 to 117%	NA
Biosolid	97 to 130%	58 to 216%	52 to 125%
Fish Tissue	89 to 114%	88 to 113%	93 to 116%

Next Steps

EPA plans to proceed with a multi-lab validation study for all three matrices. If your laboratory is interested in participating, please contact:

Adrian Hanley, EPA Office of Water, Engineering and Analysis Division
202-564-1564 · hanley.adrian@epa.gov