

## CONCENTRATIONS OF DIOXIN-LIKE PCB CONGENERS IN UNWEATHERED AROCLORS BY HRGC/HRMS USING EPA METHOD 1668A

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### **Introduction**

Polychlorinated biphenyls (PCBs) were once commercially produced in the U.S. under the brand name "Aroclor" and used in industry as heat transfer fluids, hydraulic lubricants, flame retardants, plasticizers, and as dielectric fluids in electronic components such as capacitors and transformers. The reaction conditions for production of each Aroclor favor the synthesis of certain of the 209 PCB congeners, giving each Aroclor a unique signature or pattern based on its congener composition.

Determination of PCBs in the environment has traditionally focused on identifying and quantifying the Aroclor(s) by gas chromatography with an electron capture detector (GC/ECD)<sub>1</sub>. An alternative to GC/ECD Aroclor analysis involves quantifying the concentrations of individual congeners in using GC/ECD, GC/LRMS, or GC/HRMS. Such techniques provide a more accurate estimate of the total PCB concentration in an environmental sample.

Congener composition of the Aroclors has been studied extensively by Frame et. al.<sub>2-6</sub>. These and other studies established Aroclor composition to approximately the 0.01 percent (100 parts per million; ppm) level<sub>7-8</sub>. Several groups have reported results to approximately the 5 ppm level<sub>9-11</sub>. None of the above researchers quantitated all the dioxin-like congeners in all Aroclors.

In this study, the concentration of individual congeners in each of nine different Aroclors was determined to the sub-ppm level using HRGC/HRMS. The analysis used silica and carbon cleanup columns and multiple GC columns to separate co-eluting congeners, and the most modern HRMS to achieve low detection levels. This analytical system facilitates the isolation and quantification of all of the dioxin-like congeners.

### **Methods and Materials**

*EPA Method 1668A* - The U.S. Environmental Protection Agency has developed Method 1668A for determination of the concentrations of individual PCB congeners, especially the dioxin-like

congeners<sup>12</sup>. Method 1668A uses <sup>13</sup>C<sub>12</sub>-labeled PCB congeners for isotope dilution quantification of the dioxin-like PCB congeners and of congeners with the earliest and latest retention time at each level of chlorination (LOC). Other congeners are quantified against the mean response of the labeled compounds at each LOC using the internal standard quantification technique.

*Selection of Aroclors as analytical standards* - Different batches and lots of Aroclor have been produced, both for distribution in commerce and for analytical chemical standards. The Aroclor standards used in this study were supplied by AccuStandard, Inc.

*Congener analyses* - HRGC/HRMS analyses using EPA Method 1668A were performed by Axys Analytical Laboratories in Sidney, British Columbia, Canada. Aroclor standards were prepared by dilution to 7.5-15 ppm in isooctane and 15  $\Phi$ L aliquots of each were spiked with a suite of <sup>13</sup>C<sub>12</sub>-labeled PCB congener standards to give a 5 to 10 ppm Aroclor working concentration in the 20  $\Phi$ L final volume. These solutions were subsequently analyzed on 30-m SPB-Octyl and DB-1 columns coupled to Micromass Ultima HRMS instruments. Further details of the analysis are given in EPA Method 1668A.

### Results and Discussion

Results of determination of each of the 12 dioxin-like congeners for Aroclors 1248, 1254, and 1250 by HRGC/HRMS, in ug/g (ppm), are presented in Table 1. Data for the other Aroclors has been presented elsewhere<sup>13</sup>. Each congener is identified by its IUPAC number, as listed in EPA Method 1668A<sup>14</sup>. The bottom (bolded) row in Table 1 shows the TEQ for each Aroclor and can be used to estimate dioxin-like risk from historical Aroclor data.. The TEQs were calculated by multiplying the concentration of each dioxin-like congener by its respective TEF<sup>15</sup>. The TEFs for mammals (including humans) are also shown in Table 1. Complete concentration data for all 209 PCB congeners in all 9 Aroclors are available electronically as Supporting Information<sup>16</sup>.

Table 1 also identifies which GC column was used for quantification and whether carbon column fractionation was applied to obtain each result. For the purpose of this study, the carbon column fractionation procedure in EPA Method 1668A was adjusted to collect both the co-planar (non-*ortho*-substituted) congeners and the dioxin-like mono-*ortho*-substituted congeners while excluding as many other congeners as possible.

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### References

1. Erickson, M.D. (1997) Analytical Chemistry of PCBs, CRC Press, New York City, Chapter 2, pp.17-96.
2. Frame, G.M.; Cochran, J.W.; Bowadt S.S. (1996) *J. High Resol. Chromatogr.* 19, 657-668.
3. Frame, George M. (1997) *Fresenius J. Anal. Chem.* 357, 701-713.
4. Frame, George M. (1997) *Fresenius J. Anal. Chem.* 357, 714-722.
5. Frame, George M. (1999) *Anal. Chem.* 69, 468A-475A
6. Frame, George M. (1999) *J. High Resol. Chromatogr.* 22, 533-540.
7. Schulz, D.E.; Petrick, G.; Duinker, J.C. (1989) *Environ. Sci. Tech.* 23, 852.
8. Duinker, Jan C.; Schulz, Detlef E.; Petrick, Gert (1988) *Anal. Chem.* 60, 478-482.
9. Hong, Chia-Swee; Bush, Brian; Xiao, Ju; Qiao, Huancheng (1993) *Arch. Environ. Contam. Toxicol.* 25, 118-123.
10. Schwartz, Ted R., Tillitt, Donald E. (1993) *Chemosphere* 26, 1443-1460.
11. Kannan, Narayanan; Tanabe, Shinsuke; Wakimoto, Tadaaki; Tatsukawa, Ryo (1987) *J. Assoc. Off. Anal. Chem.* 70, 451-454.
12. EPA (1999) Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS (EPA-821-R-00-002), available from the EPA Sample Control Center operated by DynCorp I&ET, 6101 Stevenson Av, Alexandria, VA 22304, [scc@dyncorp.com](mailto:scc@dyncorp.com); also as: <http://www.epa.gov/region08/water/wastewater/biohome/biosolidsdown/methods/1668a5.pdf> (accessed August 2002).
13. Rushneck, D. R., Andy Beliveau, Brian Fowler, Coreen Hamilton, Dale Hoover, Katharine Kaye, Marlene Berg, Terry Smith, William A. Telliard, Henry Roman, Eric Ruder, and Liza Ryan (2003) Submitted to *Chemosphere*.
14. Guitart R.; Puig P.; Gomez-Catalan, J. (1993) *Chemosphere* 27, 1451-1459.
15. Van den Berg, M.; Birnbaum, L.; Bosveld A.T.C.; Brunstrom B.; Cook P.; Feeley M.; Giesy J.P.; Hanberg A.; Hasegawa R.; Kennedy S.W.; Kubiak, Timothy; Larsen, John Christian; van Leeuwen, F.X. Rolaf; Djien Liem, A.K.; Nolt, Cynthia; Peterson, Richard E.; Poellinger, Lorenz; Safe, Stephen; Schrenk, Dieter; Tillit, Donald; Tysklind, Mats; Younes, Maged; Waern, Fredrik; Zacharewski, Tim (1998). *Environ. Health Perspect.* 106, 75-792.
16. EPA (2002) Concentrations for all 209 congeners in all Aroclors are available at: <http://www.epa.gov/superfund/resources/pcb/index.htm> (accessed August 2002).

**Table 1: Dioxin-Like PCB Congener Concentrations and Aroclor TEQ ( $\Phi$ g/g; ppm)**

Congener	IUPAC Number	WHO TEF	Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268
<b>3,3',4,4'-TeCB</b>	77	0.0001	12.6	2150	40.9	2590	4440	174	33.8	84.6	36.1
<b>3,4,4',5-TeCB</b>	81	0.0001	0.51	111	1.96	156	221	16.4	3.33	4.63	1.35
<b>2,3,3',4,4'-PeCB</b>	105	0.0001	55.9	3030	69.5	4840	17300	33800	434	764	107
<b>2,3,4,4',5-PeCB</b>	114	0.0005	4.04	248	6.03	443	1320	1930	17.0	46.0	5.86
<b>2,3',4,4',5-PeCB</b>	118	0.0001	88.1	4460	110	6980	24200	78900	5610	1980	101
<b>2',3,4,4',5-PeCB</b>	123	0.0001	3.33	164	4.72	277	806	1150	5.02	27.8	3.24
<b>3,3',4,4',5-PeCB</b>	126	0.1	0.28	21.0	0.56	33.6	98.0	37.3	2.13	2.28	1.76
<b>2,3,3',4,4',5-HxCB</b>	156	0.0005	7.49	90.7	3.72	255	654	8440	4860	946	17.6
<b>2,3,3',4,4',5'-HxCB</b>	157	0.0005	1.46	22.0	1.03	70.9	171	1870	252	63.8	R 7.92
<b>2,3',4,4',5,5'- HxCB</b>	167	0.00001	2.52	32.4	1.10	80.7	207	3100	1990	278	4.96
<b>3,3',4,4',5,5'-HxCB</b>	169	0.01	U 0.08	U 0.17	0.13	R 0.11	0.21	0.81	U 0.82	0.40	U 0.32
<b>2,3,3',4,4',5,5'- HpCB</b>	189	0.0001	1.17	4.36	0.12	4.53	11.0	246	1290	451	4.40
<b>Aroclor total TEQ</b>			<b>0.05</b>	<b>3.3</b>	<b>0.09</b>	<b>5.2</b>	<b>15</b>	<b>21</b>	<b>3.5</b>	<b>1.1</b>	<b>0.21</b>

U= not detected at given detection limit

R = peak detected, but did not meet identification criteria

If congener qualified with "U" or "R", concentration is estimated maximum, but Aroclor TEQs are minimum values (i.e., "U" and "R" values were not included in TEQ calculations).