

**PERSISTENT, BIOACCUMULATIVE, TOXIC CHEMICALS
Poster Session**

Organized by

R.L. Lipnick

(Pages 167-170 in *Preprints of Extended Abstracts*, Vol. 39 No. 1)

Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
Anaheim, CA March 21-25, 1999

**PROBLEMS WITH CONGENER-SPECIFIC PCB ANALYSIS:
BACKGROUND CONTAMINATION AND CALIBRATION**

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The development of congener-specific techniques and the availability of ^{13}C labelled standards have improved PCB determinations in environmental samples. Congener specific PCB analysis provides critical data on targeted PCBs enabling meaningful measurements and risk assessments. However, congener specific PCB analyses at trace levels still represent a challenge to the analytical and environmental chemist. Background contamination and calibration remain as the two major problems.

Background contamination can be traced to laboratory air, solvents, and adsorbents¹. The air in the laboratory is believed to be the major contamination source, with indoor air concentrations of PCBs higher than those routinely measured outdoors. The air can contaminate samples during their storage and cleanup, as well as calibration standards. Method blanks often show high pg to low ng level of PCBs, particularly PCB 180, 170, 182, 138, and 153. It is interesting to note that many investigators have encountered similar background problems in their laboratories^{2,3}. We concluded that it is impossible to completely eliminate background contamination. Background subtraction is not a practical approach due to large variation in the background level in the method blank. Currently, in our laboratory, we try to enhance the signal by increasing the amount of sample used. This is not always possible, however, particularly with small biological tissues, such as human serum or adipose from biopsies. If a large sample is not available, only the results of "reportable congeners" are reported. To be a "reportable PCB", the congener pattern in the sample should be different from that in the method blank and the level of the individual PCB should be at least 10 times higher than that in the method blank.

The second problem in quantitative trace congener specific analysis of PCB is the selection of a reliable method for calibration. Calibration based on published response factors for ECD have failed because of the poor reproducibility of published data. There is little published information on MS-SIM response factors. Since MS-SIM is the most popular detection method used for congener specific PCB analysis, we have sought to determine if the published response factors can be used for calibration of MS-SIM, and if not, to suggest an alternative method.

A mixture of 41 $^{12}\text{C}_{12}$ -PCB standards (see Table 1) from Cambridge Isotope Laboratory was used to obtain response factors. The 41 $^{12}\text{C}_{12}$ -PCBs were mixed with 10 $^{13}\text{C}_{12}$ labelled PCBs (PCB #s 28, 47, 52, 101, 105, 118, 153, 180, 194 and 209). The concentrations of $^{12}\text{C}_{12}$ PCBs ranged from 25 to 100 pg/uL; $^{13}\text{C}_{12}$ PCBs were 25 pg/uL. Data were acquired on a Varian 3400 GC with a 60 meter DB – 5ms column coupled to a Finnigan MAT 90 high resolution mass spectrometer operated in SIM mode. The two most intense ions in the molecular ion cluster were monitored. Table 1 shows the relative response factors of 41 PCBs vs. PCB 209. It can be seen that the relative response factor (RRF) of the most intense ion in the molecular ion cluster decreases with increase of chlorination. This suggests that there must at least be one standard for each homologue group. It can also be seen that the variation in relative molar response factors of single ion (RmRF) is not significant and the relative molar response factor of molecular ion cluster (RmRfC) increases slightly with increase of chlorination. The CV is less than 20 percent for injections over two days (runs A through E). Within each homologue group, the RRF varied for different isomers. For low chlorinated congeners, the variation can reach a factor of two, which indicates that more than one standard is needed for these homologue groups.

Since only 41 PCBs out of 209 possible congeners were tested in this laboratory, two literature data sets were compiled in Table 2^{4,5}, after recalculating the data relative to the same congener. The PCB numbers in boldface in each homologue group represent its reference congener, with the exception of nonachlorinated congeners (to PCB 209). Table 2 shows that for highly chlorinated PCBs, i.e., hepta- and octachlorinated PCBs (only one set data available for nona- and decachlorinated homologues), the RRFs agreed well among the three studies. For these homologue groups, fewer calibration standards or published RRFs could be used. For low chlorinated homologue series, however, there are greater differences among the three sets. A possible explanation is more coeluting peaks for tetra- and pentachlorinated homologues. In addition, there is more variability in RRFs for the lower chlorinated homologues as shown by the CVs in Table 1.

In summary, it is unnecessary to use 209 PCB congeners to calibrate. Literature data on relative response factors for high chlorinated homologues could be used for quantification. A calibration mixture should always be used to check the response factors. An ideal calibration mixture should not only include PCBs of environmental or toxicological interest, but also PCBs representing different recovery characteristics and

detector response characteristics. We believe that it would be better to have two sets of calibration standards, one for biological samples and one for environmental samples. Since there are generally fewer congeners in biological samples, a mixture of the $^{13}\text{C}_{12}$ standards listed above plus 4 coplanar (77, 126, 169 and 81) with their $^{12}\text{C}_{12}$ -counterparts and a few other $^{12}\text{C}_{12}$ congeners, such as 74, 99, 114, 156, 157, 167, 170, and 189, could be a reasonable calibration standard. For environmental samples, an acceptable calibration mixture should include the $^{13}\text{C}_{12}$ mentioned above and a group of $^{12}\text{C}_{12}$ congeners, representing a group of congeners with similar response factors. Due to the discrepancy shown in Table 2, more work needs to be done to decide which congeners should be included.

Literature:

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Table 2. Comparison of EIMS RRFs

PCBs	Ref ⁴	Ours	Ref ⁵	PCBs	Ref ⁴	Ours	Ref ⁵	PCBs	Ref ⁴	Ours	Ref ⁵
Di- PCB isomers				60	0.55*			158	0.84	0.97*	
4	1.51		0.54	61			1.48	163	0.98*		
	5.00*		0.90	65			1.74	164	0.98*		
6	0.67			66	0.67		1.40	167	0.68		
7	0.83		0.99	70	0.63*	1.70	1.46	169		1.05	
8	0.93		1.10	71	0.69*			Hepta- PCB isomers			
9	0.83		0.97	72	0.69*			170	1.17	1.10	
10			0.81	74		1.70		171	1.02	1.05	
11			1.03	76	0.63*			172	1.14*		
12			0.93	77	0.61		1.13	174	1.15		
14			1.02	Penta- PCB isomers				175	1.26		
15	1.00		1.00	82	0.80	0.73		176	1.18		
Tri- PCB isomers				84	0.61*			177	1.20	1.05	
16	1.24*			87	1.00	1.00	1.00	178	0.98		
17	1.38	0.42*		90	0.75*			179	1.01		
18	1.41	0.42*		92	0.61*			180	1.14	1.30	
19	1.31			95	0.79	1.19		182	1.11*		
21			0.97	97	0.60		0.99	183	1.00	1.00	1.00
22	0.97			99	0.57*	1.11		185	0.97		
24			1.00	101	0.75*	1.23	0.99	187	1.11*	0.94	
25	0.90			105		1.53		190	0.97		
26	0.87		1.03	110	0.58	1.91		191	0.93	1.31	
27	0.87			113	0.57*			192	1.14*		
28	1.08	0.76*	1.03	118	0.88	1.90		193	1.03		
29			1.12	124	0.79			Octa- PCB isomers			
30			0.98	Hexa- PCB isomers				194	1.00	1.00	1.00
31	0.92	0.76*	1.23	128	0.71	0.79	0.83	195	1.00	1.04	
32	1.24*			129	0.99			196	0.97*		
33	1.00	1.00	1.00	130	0.93			198	1.16		
Tetra- PCB isomers				131	0.97			199	0.80	0.73	
40	1.04		0.80	132	0.98	0.69		201	1.04		
41	0.69*			134	1.10			202			1.36
42	0.65			135	1.12			203	0.97*		
44	1.00	1.00	1.00	136			0.90	205	1.36	1.22	
45	0.99			138	0.98*	0.97*	0.84	Nona- PCB isomers			
46	1.07			141	1.07		0.83	206		0.87	
47	0.90		1.05	144	1.03			208		0.98	
48	0.77			146	1.01			Deca- PCB isomers			
49	0.86	0.78	1.18	148	0.77			209		1.00	
51	0.80			149	1.13	0.61		* possible coelution			
52	0.92	0.91	1.23	151	1.03	0.69	0.76				
53	0.81			153	1.00	1.00	1.00				
54			1.41	155			0.96				
56	0.55*			156	0.77	1.05					