

## Combined PBDE/PCB Analysis Using GC/MS With ECNCI Detection

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### Introduction

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are both examples of bioaccumulative compounds that have been found in high concentrations in human populations and in wildlife.<sup>1-3</sup> While PCBs have been banned since the 1970s, they are extremely persistent and are still found throughout the world. Like PCBs, PBDEs are found throughout the world, but their persistence is less well understood. While several PBDE formulations have been banned or are being voluntarily taken off of the market, products containing various PBDE formulations are still in use and will be for years to come. Therefore, the potential for PBDEs to migrate from these products into the environment and then into humans and wildlife will also continue, and so will the need for biomonitoring of PBDEs, as well as of PCBs.

One problem often encountered in the analysis of biological samples is limited sample size, especially samples obtained from human volunteers. To achieve adequate limits of detection when one has only limited amounts of sample, sample extracts are concentrated during preparation to very small sample volumes, typically only a few microliters. Being limited to such small sample sizes becomes problematic when multiple analyses and therefore multiple injections are required for one sample. The ability to analyze more than one class of analyte at one time would reduce the demand on samples with limited volume. In this paper, we describe a combined analysis for PBDEs and select indicator PCBs, and will apply that method to the analysis of breast adipose tissue from Brazilian women.<sup>4</sup>

### Methods and Materials

The samples were analyzed on a Varian (Walnut Creek, CA, USA) 1200L GC/MS system (Varian 3800 GC, Varian 1200L quadrupole mass spectrometer) using a 5% diphenyl/95% dimethylpolysiloxane column (Rtx-5Sil MS, Restek, Bellefonte, PA, USA, 60m x 250 mm i.d. x 0.25 mm film). The mass spectrometer was operated in ECNCI mode using methane as the reagent gas (approximately 6.5 Torr source pressure). The GC was operated in constant flow mode of 1.0 mL/min with helium as the carrier gas. The injector and transfer line temperatures were 280 °C, and the source temperature was 200 °C. The GC temperature program was: 180 °C (2 minute hold time), followed by an increase to 300 °C (10 °/min, 30 minute hold time), with a total run time of 45 minutes. BDEs 17 and 28 (tribromo), 47, 66, and 71 (tetrabromo), 85, 99, and 100 (pentabromo), and 153, 154, 138 (hexabromo) were monitored using masses 79/81. PCBs 118, 138, 153, and 180 were monitored using their molecular masses: 326/338 (PCB-118 / <sup>13</sup>C<sub>12</sub> PCB-118), 360/372 (PCB-138/-153, <sup>13</sup>C<sub>12</sub> PCB-138/-153), and 394/406 (PCB-180 / <sup>13</sup>C<sub>12</sub> PCB-180). PBDE standards and Contaminated Fish Reference Material (EDF-2525) were obtained from Cambridge Isotope Laboratories (CIL, Andover, MA, USA). PCB standards were obtained from CIL and Wellington Laboratories (Guelph, ON, Canada). The whale blubber standard reference material (SRM1945) was obtained from the National Institute of Science and Technology (NIST, Gaithersburg, MD, USA). Sample preparation is described elsewhere.<sup>4</sup>

### Results and Discussion

Figure 1 shows the chromatogram of a standard of mixed PBDEs/PCBs (upper plot) All congeners, with the exception of BDE-71 and the labeled/unlabeled PCB-180 are well resolved. The lower plot is an example of a chromatogram of the NIST Whale Blubber SRM 1945.

Table 1 summarizes the results of a duplicate analysis of the NIST Whale Blubber SRM 1945. Our results also compare favorably with the NIST consensus values for PBDEs.<sup>5</sup> Of the 27 congeners measured by NIST, we

measured 13. Of those 13, NIST measured four as non-detected (17, 71, 85, 138). We measured three of the four as not detected or at very low concentration (17, 71, 85): we measured BDE-138 at a significant concentration, resulting in a very high percent deviation from the NIST value. The percent deviation is below 20% for all other congeners.

Table 2 shows the results of the analysis of the Cambridge Isotope Laboratories' Contaminated Fish Reference Material (EDF-2525).<sup>6</sup>This fish sample was not spiked with PCB internal standards when we prepared the sample, so we can only report PBDE results here. With the exception of BDE-28, our results compare favorably with the CIL values. For five of the seven congeners reported by CIL, our results deviate from the consensus value by 10% or less for five congeners. For BDE-183, we report a non-detect, whereas CIL reports a value of 0.146 ng/g wet weight. Only for BDE-28 did our results differ significantly from the consensus value. As with the analysis of the NIST Whale Blubber SRM, we feel that these results help further define the consensus values for the CIL EDF-2525.

### Acknowledgements and Disclaimer

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### References

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Table 1. Comparison of measured and NIST-preliminary values of PBDEs and certified values of PCBs in Whale Blubber SRM 1945<sup>5</sup>.

Congener	NIST Value ng/g wet	MREF6 ng/g wet	% Deviation	MREF7 ng/g wet	% Deviation	%RPD
BDE 17	< 0.2	0.339	239.00	0.368	268.40	-8.31
28	1.26 ± 0.1	1.44	14.35	1.29	2.45	10.97
66	1.5 ± 0.4	1.35	-10.16	1.38	-7.86	-2.53
47	39.1 ± 2.6	41.3	5.55	41.3	5.69	-0.13
71	< 0.2	0.283	183.40	0.266	166.10	6.30
85	< 0.2	ND	-100.00	ND	-100.00	
99	17.3 ± 1.7	20.3	17.28	20.1	16.40	0.76
100	10.1 ± 0.2	11.5	15.82	11.3	12.00	2.05
153	8.2 ± 0.5	9.50	15.82	9.60	17.03	-1.04
154	15.4 ± 2.6	13.0	-15.34	14.0	-8.71	-7.54
138	< 0.2	8.306	8195.60	9.138	9027.80	-9.55

Table 2. Comparison of measured and reference values of PBDEs and PCBs in CIL's Contaminated Fish Reference Material (EDF-2525).<sup>6</sup>

Congener	CIL Reference Value	Measured Value	% Deviation
BDE	ng/g wet	ng/g wet	
28	1.5± 2.250	0.214	-85.73
47	8.170± 10.4	7.371	-9.77
99	1.910±3.040	1.94	1.68
100	1.360±2.050	1.474	8.38
153	1.980±1.510	1.70	-14.28
154	2.060±2.180	1.84	-10.83
183	0.146	ND	

Figure 1. Chromatograms of mixed PBDE/PCB standard (upper trace) and NIST Whale Blubber SRM 1945 (lower trace).

Chromatogram Plots

Plot 1: c:\anaweb\ed\bb\log\214052005\3x.ms R10 Merged  
 Plot 2: c:\anaweb\ed\bb\log\2140655.ms R10 Merged

