Organohalogen Compounds, Volume 60, Pages 190-194 (2003)

Estimating Detection Limits for PCB Congeners Using EPA Method 1668A

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Introduction

Method 1668 Revision A**,** published in 1999 by the US EPA Office of Science and Technology, applies high resolution gas chromatography, high resolution mass spectrometry (HRGC/HRMS) and isotope dilution techniques to analyze polychlorinated biphenyl (PCB) congeners at parts per trillion levels in solid samples and parts per quadrillion levels in aqueous samples[1].

The reporting limit defined in this method is the minimum level (ML) of reliable quantitation. The method's application of the laboratory-specific ML approach using historical blank data (Ferrario, et al) sets the ML at the mean blank concentration plus 2 standard deviations[2]. However, laboratories are frequently requested to report results below the ML[3,4]. In these cases, some estimate of the detection limit (DL) must be made. Two approaches are available for estimating the DL for an individual sample. One is to perform a laboratory-specific method detection limit (MDL) study [5,6,7,8]. After making adjustments for sample size and dilutions, the MDL value is used as a sample-specific censoring level. Another approach is to calculate the sample-specific estimated detection limit (EDL), based on the signal-to-noise ratio achieved for the congener during sample data acquisition.[9,10,11]. Since the DL for an individual sample depends on the extent of chemical interferences present, as well as the momentary performance of the analytical system, the DLs for an individual sample may diverge significantly from the MDL. The direction and magnitude of divergence between the two estimates can be used to help minimize the probability of false positives and false negatives.

The purpose of this paper is to report on a study examining EDLs obtained on field samples received from contaminated sites and watersheds over a 14 month period. EDL summary data is presented for contaminated fish, contaminated sediments and aqueous samples. Comparisons of the average EDL to the laboratory-specific MDL are made for aqueous and solid samples.

Methods and Materials

The method-specified performance assessment was completed prior to the study period. MDL studies were conducted on solid and aqueous matrices for the 29 congeners for which QC acceptance criteria are listed in the method. The MDLs were calculated to be less than 0.333 times the method estimated method detection limits (EMDLs) for all congeners, except for the aqueous MDL for PCB 19 (0.753 times the method EMDL). An examination of all method blanks for a 1 year period for all congeners was conducted. Using Ferrario's method[2], the blank studies supported an estimated minimum level (EML) averaging one half the average EMLs. It should be noted that one method blank was excluded from the study, on the basis of a Grubbs test failure. This outlier was due to a contaminated sample, which affected all extracts in the batch. EDL data for all aqueous, sediment/soil and fish samples analyzed during the next 14 months by the

laboratory using method 1668A were then examined. This included 112 samples of sediment and soil, 68 samples of water and 44 samples of fish tissue. The sediment and soil samples represented 3 watershed studies from the Eastern coastal USA, and five contaminated sites in the Eastern USA. The water samples were from 10 sites in the coastal and interior Eastern USA. The fish samples were from various contaminated rivers and streams in Ohio and Virginia.

A large range of PCB concentrations was found in the solid sample data. Only 5 of the 112 sediment/soil samples and none of the fish samples had all congeners within the method calibration range. To bring the highest level samples into the method calibration range, samples were further prepared by 3 additional protocols, designated High, Medium, and Low. Table 1 summarizes the differences among the protocols. The upper screening limit in the table refers to the highest concentration of any congener in the sample.

Table 1. Summary of Protocols

Matrix (Protocol)	Upper Screening Limit (ppb)	Sample Amount Extracted	Percent of Extract Used	MDL final Volume	Bench Dilution	Effective Final Volume
Aqueous	0.2	1 L	100	0.1 mL	1	0.1
Sed/Soil (Clean)	20	10g	100	0.1 mL	1	0.1
Sed/Soil (Low)	100	10 g	100	0.1 mL	5	0.5
Sed/Soil (Med)	800	10 g	25	0.1 mL	10	4
Sed/Soil (High)	4000	2 g	25	0.1 mL	10	20
Fish (Clean)	20	10 g	100	0.1 mL	1	0.1
Fish (Low)	100	10 g	100	0.1 mL	5	0.5
Fish (Med)	200	10 g	100	0.1 mL	10	1
Fish (High)	2000	0.1 g	100	0.1 mL	1	0.1

Samples were excluded from the data set for one or more of the following reasons:

A. The sample required greater than a 10-fold dilution, thereby requiring post-extraction addition of internal standards.
B. The sample was run under conditions for which there were less than 10 data points.
C. The sample had 1 or more EDLs failing a Grubbs test for outliers.

A total of 187 of the original 226 samples remained in the data set after all of the exclusions were made. Table 2 summarizes the exclusions and the resulting number of samples (n) used for each matrix.

Table 2. Summary of Sample Exclusions

Matrix (Protocol)	Beginning Pool (n)	Reason for Exclusion A (n)	Reason for Exclusion B (n)	Reason for Exclusion C (n)	Included Samples (n)
Aqueous	69	0	0	4	65
Sed/Soil (Low)	46	0	5	2	39
Sed/Soil (Medium)	19	0	0	0	19

Sed/Soil (High)	48	8	13	0	27
Fish (Low)	18	7	0	0	11
Fish (Medium)	12	0	0	0	12
Fish (High)	14	0	0	0	14

The EDL results were grouped by matrix and protocol. They were checked using the Grubbs test for outliers (Table 2) and the results for each congener were averaged. An adjusted MDL value (AMDL) was calculated by multiplying the MDL value by an adjustment factor (effective final volume/MDL final volume). The ratio of the average EDL to the AMDL was calculated for each congener for each matrix/protocol. Because an insufficient number of data points were collected, four of the initial twenty-nine congeners (BZ 104, 105, 170, 180) were excluded from the study. Those remaining include the WHO dioxin-like congeners and representatives within each chlorination level.

Results and Discussion

The MDL and mean EDL results are shown in Table 3. The MDLs and EDLs are both significantly below the method EMDLs, as would be expected since these terms do not account for variance in method blank contamination. The values are useful for predicting the lower limit to which congeners can be detected using these protocols. It is important to note that detections at these levels disregard the source (sample vs. laboratory). The EDL/AMDL ratios show steady increases across the following matrices/protocols: aqueous < solid/low < solid/medium < solid/high. As it is derived from the signal-to-noise ratio, the EDL is a more specific measure than the AMDL for any given sample, and by extension, for any group of samples. Thus, EDL/AMDL ratios less than 1, as observed in the aqueous group, indicate that the AMDL is biased high for that group. EDL/AMDL ratios greater than 1, as observed in the contaminated solids, indicate that the AMDL is biased low for that group. It is noteworthy that the range of EDL/AMDL ratios (0.63 to 2.02) closely resembles the 95% confidence interval for the MDL (0.64 to 2.20)[8]. Programs and researchers relying on the MDL as an estimate of the detection limit need to evaluate the impact of these biases on their studies. In studies of contaminated samples, the MDL may underestimate the DL. In studies of relatively clean matrices, the MDL may overestimate the DL. Further study, which includes evaluating the statistical significance of the differences between the groups, is planned.

Table 1

Summary of MDLs, Mean EDLs and EDL/AMDL Ratios

Matrix >>	Aqueous		Sediment and Soil				Fish Tissue		
Protocol >>				Low	Med.	High	Low	Med.	High
		Mean		Mean	Mean	Mean	Mean	Mean	Mean
Type DL >>	MDL	EDL	MDL	EDL	EDL	EDL	EDL	EDL	EDL
Analyte	pg/L	pg/L	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g	pg/g
Mo CB 1	10.2		2.38						
Di CB 3	7.87	4.01	1.22	2.59	26.0	120		15.8	34.8
Di CB 4	27.4		3.02						
Tri CB15	20.1	25.5	1.03	9.96	120	689		23.4	200
Tri CB19	31.6	6.44	2.97						
Tri CB 28				3.46	63.8	339			

Tri CB 31				3.69	65.0	345	6.9	12.7	111
Tri CB 37	16.1	6.60	0.65						
Tetra CB 77	11.3	6.68	0.93	5.50	68.6	438	13.1	19.2	192
Tetra CB 81	4.00	6.57	0.65	5.28	67.6	435	12.5	19.0	184
Penta CB 105	14.0	5.87	0.53	5.23	65.1	361	12.7	15.0	135
Penta CB 114	10.2	5.82	1.58	5.17	66.0	360	12.5	14.8	135
Penta CB 118	18.0	6.21	1.76	5.61	70.3	382	13.3	15.9	144
Penta CB 123	9.44	6.29	0.91	5.43	69.4	372	13.3	15.5	142
Penta CB 126	7.95	6.40	1.44	5.47	71.5	401.6	14.0	16.5	133.9
Hexa CB 156	16.8	7.28	0.66	8.15	104.0	575.0	23.5	19.0	170.8
Hexa CB 157	12.7	7.29	0.96	8.14	107.6	575.0	23.5	19.0	170.8
Hexa CB 167	10.1	6.07	1.09	6.53	82.4	437.1	18.0	14.4	133.9
Hexa CB 169	10.1	6.39	1.53	6.73	90.6	498.0	22.4	17.8	122.7
Hepta CB 189	11.5	5.58	0.50	5.25	78.4	374.5	13.7	11.6	83.5
Octa CB 194				6.35	76.1	391.0	18.0	14.2	107.7
Octa CB 202	22.7	7.52	2.32						
Octa CB 205	10.4		0.86						
Nona CB 206	13.7	11.7	1.68	8.15	67.8	353.2	15.5	16.1	128.0
Deca CB 209	14.4	7.68	1.89	6.54	37.7	235.9	15.7	11.3	104.6
EDL/AMDL Ratio		**0.63**		**1.17**	**1.84**	**2.02**			

Acknowledgements

The author wishes to thank Jennifer Bonin and Tim Wilson of USGS-New Jersey, Dan Gobich, Melissa Davidson, David McNeil, Snell Mills, Susan Oxendine, Trish Parsly, Vahnsengh Khounlavong, Syed Ahmed, Nena Meehan, Allan Sudderth, Jon Nordquist, Bruce Wagner, Cornelia Apahidean, Chase Adams, Carole Jackson, Chris Rigell, Scot Goss, and Michael Tiller for their contributions. The author thanks Tom Yoder and STL management for their support.

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