Organohalogen Compounds, Volume 60, Pages 195-198 (2003)

PERFORMANCE OF USEPA METHOD 1668-A IN THE NEW JERSEY TOXIC REDUCTION WORKPLAN FOR THE NEW YORK-NEW JERSEY HARBOR, U.S.A.

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Introduction

As part of ongoing harbor restoration efforts, a study was initiated to determine the sources and concentrations of organic contaminants and sediment in the Newark Bay and Hudson River Estuary system. This project is being conducted by the U.S. Geological Survey in cooperation with the New Jersey Department of Environmental Protection (NJDEP) and the New York State Department of Environmental Conservation (NYSDEC). For this study, concentrations of dissolved and sediment-bound organic contaminants were determined in samples from the major freshwater tributaries, within the saline estuaries, and from major point source discharges to the harbor system. To measure trace level organic concentrations, large volume (>50 liters) sampling methods that use filtration to collect sediment and XAD-2 resin to sequester dissolved compounds were employed. Isotope dilution, high-resolution gas chromatography/high resolution mass spectrometry analyses following U.S. Environmental Protection Agency (USEPA) method 1668-A[1]-modified, were used to measure 98 polychlorinated biphenyl (PCB) congeners.

Many quality-assurance and control checks were instituted to demonstrate the performance of the analytical methods. Accuracy, precision, and efficacy of the analytical methods were estimated by use of the analysis of standard reference material samples (SRMs) of known concentrations and sediments of unknown composition from the National Institute of Science and Technology (NIST) Intercomparsion Exercise for Organic Contaminants in the Marine Environment[2] and the analysis of SRM solutions spiked onto blank XAD sampling columns. Information on the performance of the 1668-A method is provided by the recoveries of labeled internal standards (IS) and the minimum estimated detection limits (EDLs). This paper discusses the performance criteria results for the analysis of PCBs in SRMs, unknown sediments, and samples from freshwater tributaries, as developed in the New Jersey Contaminant Reduction Program.

Methods and Materials

Details of the sampling and analytical methods are presented in previously published papers[3,4]. The SRMs and unknown test sediment used in this work were obtained from NIST and involved replicate analyses of three unknown sediments -- NIST/NOAA QASED99IX, QASED00X, and QASED01XI -- along with NIST SRM 1944 (New York Harbor bottom sediment) or NIST SRM 1941a (Chesapeake Bay sediment) as performance materials. All of these materials contain PCBs. Additional SRM samples were prepared by spiking NIST SRM 2262 into clean XAD resin columns, which were processed along with field samples. The IS used were the labeled compounds injected into each sample before extraction to serve as quantification references for each compound. EDLs were derived for each PCB congener in each sample. In this work, EDLs for a compound not present in a sample were estimated as 2.5 times the area of the chromatographic noise in the corresponding homolog group time window.

Results

The percent recoveries of the SRM solutions that were spiked onto XAD columns are listed in Table 1. Recoveries ranged from 82 to 157 percent, with no systematic variation evident in recovery as a function of homolog group. Overall, the average recoveries of 95 to 106 percent indicate that PCBs can be completely recovered from the XAD resin, at least from resin that has not been exposed to natural waters. As of March 2003, two analyses of SRM 1944 have been completed that provide estimates of the accuracy of the analytical methods and the ability to recover PCBs from dried sediment.

Table 1. Average recoveries of PCBs from SRM solutions spiked onto XAD resin

BZ # and homolog group	1SRM1LPCB percent	2SRM2LPCB percent	3SRM1LPCB percent
8 di	103	100	99
18 Tri	157	90	153
44 to 77 Tetra	91	89	89
87 to 126 Penta	118	93	115
128 to 153 Hexa	92	98	91
170 to 188 Hepta	105	94	104
195 to 201 Octa	117	110	116
206 Nona	83	90	82
209 Deca	91	95	89
Average recovery	**106.3**	**94.8**	**104.2**

The mean of the measured concentrations and the absolute and relative percent differences from the certified values for 25 PCBs are listed in Table 2. With the exception of PCB 44 and 95, the measured concentrations and the certified values agree, with an average difference of 5 nanograms per gram (ng/g). These differences range from –32 to +37 percent, averaging 5.8 percent, and serve as an estimate of the accuracy of the analysis. Only one analysis of SRM 1941a was made; the results were an average absolute difference of 1.6 ng/g and a relative difference of 31 percent

Table 2. Summary of PCBs measured in New York Harbor sediment SRM 1944.

PCB BZ# and homolog group	Mean measured concentration (ng/g)	SRM 1944 certified concentration (ng/g)	Difference (ng/g)	Percent difference
8 Di	21	22.3 ± 2.3	1.3	5.83
18 Tri	59.6	51 ± 2.6	-8.55	-16.76
28	81.6	80.8 + 2.7	-.75	-.93
31	79.8	78.7 +1.6	-1.05	-1.33
44 Tetra	48.2	60.2 ± 2.0	12.05	20.02
49	50.3	53 +1.7	2.75	5.2
52	67.2	79.4 + 2	12.2	15.4
66	64.0	71.9 +4.3	7.95	11.1
95 Penta	50.7	65 ± 8.9	14.35	22.08
99	41.9	37.5 + 2.4	-4.35	-11.6
101/90	70.4	73.4 + 2.5	3.0	4.1
105	21.7	24.5 +1.1	2.85	11.6
118	52.2	58 +4.3	5.85	10.1
128 Hexa	9.84	7.47 ± 0.28	-2.36	-31.66
138/163/164	58.2	62.1 +3	3.95	6.4
149	54.0	49.7 + 1.2	-4.25	-8.55
153	58.9	74 + 2.9	15.1	20.4
156	5.17	6.52 +0.66	1.35	20.7
170/190 Hepta	14.2	22.6 ± 1.4	8.45	37.39
180	37.9	44.3 + 1.2	6.45	14.6
187/159/182	23.5	25.1 + 1.0	1.6	6.37
194 Octa	9.22	11.2 ± 1.4	1.98	17.68
195	3.63	3.75 + 0.39	.12	3.2
206 Nona	6.59	9.21 ± 0.51	2.625	28.50
209 Deca	5.86	6.81 ± 0.33	.95	13.95
		Average for all PCBs in sample	**5.05**	**5.83**

The precision of the method can be estimated from the analysis of unknown sediment measured for the NIST Interlaboratory Comparison Program. Three analyses were made of each of three unknowns. The relative standard deviations are listed in Table 3, along with the average deviation for all PCBs in the sediment. No systematic variation exists as a function of PCB homolog group. Averaged values, which set the precision expected for the sample analyses, ranged from 4.8 to 12.2 percent.

Table 3. Relative standard deviations of three replicate analyses of unknown sediments.

PCB BZ# and homolog group	QA99SED IX percent	QA00SEDX percent	QA01SEDXI percent
8 Di	12.6	20.2	3.53
18 Tri	3.97	14.2	4.68
44 Tetra	6.89	12.4	10.8
95 Penta	3.11	18.9	3.69
128 Hexa	3.48	11.0	7.83
170/190 Hepta	2.02	11.5	5.93
195 Octa	0.00	11.3	7.63
206 Nona	4.98	3.90	3.97
209 Deca	NA	2.10	29.0
Average	**4.77**	**12.2**	**7.49**

A total of 20 analyses of dissolved phase and 21 samples of suspended sediment samples from freshwater tributaries have been made to date, along with 17 XAD blanks and 7 filter blanks. The EDLs produced from these analyses are presented in Table 4. The minimum EDL in each homolog group serves as a reference for the lower limits of detection or sensitivity of the analysis for the respective homolog group. Minimum EDLs for the PCBs measured in the dissolved samples (XAD) ranged from 14 to 21 picograms (pg) and for XAD blanks, 9 to 14 pg. For sediment, the minimum EDLs ranged from 22 to 76 pg for samples and for blanks, 0.1 to 250 pg. It is not clear why some minimum EDLs are higher in the filter blanks than in the samples. Maximum EDLs for the dissolved samples are about 2 ng and as much as 8.5 ng for sediment. Concentration based EDLs were calculated using the volume of water sampled or mass of sediment collected on the filters. The target volumes of 50 liters and 1 to 5 grams of sediment used in this study resulted in minimum concentration-based EDLs for dissolved samples of 0.27 picogram per liter (pg/L) to 0.43 pg/L and for sediment, 7.5 to 25.5 pg/g. Minimum concentration-based EDLs for each homolog group (Table 4), were calculated using a 50-L volume and a 3 gram sediment mass.

Table 4. Estimated detection limits for freshwater samples.

	Dissolved				Sediment			
Homolog Group	Samples n= 20		Blanks n=17		Samples N=21		Blanks n=7	
	Min. EDL (pg)	Equiv. Conc (pg/L)	Min. (pg)	Average (pg)	Min. EDL (pg)	Equiv. conc. (pg/g)	Min. (pg)	Average (pg)
Mono-Di	14.9	0.30	10.6	271	22.4	7.5	0.1	555
Tri	21.4	.43	14.2	206	34.7	11.6	110	369
Tetra	18.8	.37	10.8	110	48.1	16.0	91	278
Penta	17.7	.35	9.6	172	65.1	21.7	100	414
Hexa	16.6	.33	9.6	141	75.0	25.0	110	333
Hepta	15.1	.30	9.1	179	74.2	24.7	120	454
Octa	13.7	.27	8.9	204	76.4	25.5	250	553
Nona-Deca	20.1	.40	12.5	111	47.0	15.7	140	313

The recoveries of the 19 IS show the effects natural water matrixes and laboratory errors have on the analytical procedures (Table 5). Recoveries averaged 59.4 and 75.1 percent for XAD samples and blanks, respectively. Recoveries averaged 44.9 and 69.1 percent for sediment samples and filter blanks, respectively. The lower IS recoveries observed for the samples, as compared with that of their blanks, were likely the result of the complex organic-rich makeup of natural waters that were processed; however, IS recoveries were sufficient to allow accurate quantification of the contaminants in samples containing natural riverine materials.

Table 5. Summary of recoveries of internal standards in samples and blanks

	XAD Samples n=20		Blank XAD n=17		Sediment Samples n=21		Filter blanks n=7	
Internal Standard	**Average percent**	**Percent standard deviation**	**Average percent**	**Percent standard deviation**	**Average percent**	**Percent standard deviation**	**Average percnt**	**Percent standard deviation**
3L	48	35	61	23	49	48	64	13.
15L	54	37	70	19	53	44	67	9.5
28L	50	36	68	19	50	43	66	17
77L	61	39	83	18	54	45	77	11
105L	54	42	66	22	40	47	65	19
114L	54	43	65	23	41	49	65	19
118L	54	42	64	23	39	49	62	19
123L	54	43	65	24	40	49	64	19
126L	52	42	64	23	39	45	66	20
156L	57	37	80	19	48	49	74	13
157L	57	38	79	18	48	48	75	13
167L	57	38	80	18	48	49	74	11
169L	50	38	72	21	43	45	67	15
170L	57	37	78	19	46	49	73	14
180L	56	37	77	19	46	50	71	12
189L	55	42	68	20	40	50	65	18
194L	52	43	66	21	37	49	66	21
206L	56	38	76	19	47	51	77	9.6
209L	56	39	79	24	48	51	74	9.5
Average	**59.4**	**35.4**	**75.1**	**19.7**	**44.**	**48.0**	**69.1**	**14.9**

Conclusions

The results of this study indicate that Method 1668-A provides an accuracy of approximately 6 percent (Table 2) and a precision of 5 to 12 percent (Table 3) when used for analysis of low-level PCB concentrations in SRM materials. Similar values could apply to measurements of suspended sediment and XAD resin. Recoveries of internal standards typically were greater than 40 percent, which allow accurate quantification in samples. Complete recovery of SRMs spiked onto XAD resin indicates that dissolved compounds can be recovered from these sampling media. Minimum EDLs at the target volumes and masses were about 0.5 pg/L and 10 pg/g, respectively, which provides high sensitivity for trace compounds, especially in the dissolved phase.

Acknowledgements

The authors thank Joel Pecchioli, Floyd Genicola, and Gary Buchanan of NJDEP, Scott Douglas of the NJ Department of Transportation, Simon Litten of the NYSDEC, and the analytic group at Severn Trent Laboratories in Knoxville, Tenn. Funding for this study was provided by the Port Authority of New York-New Jersey, and the NJDOT Maritime Resources.

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