Analytical Procedures for the Determination of Polybrominated Dibenzo-p-Dioxins and Dibenzofurans in Tetrabromobisphenol A and 2,4,6-Tribromophenol.

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Abstract

Extraction/fractionation and analysis procedures for the determination of ppb and sub-ppb levels of polybrominated dibenzodioxins and dibenzofurans in tetrabromobisphenol A (TBBPA) and 2,4,6-tribromophenol (TBS) are described. Accuracies, as measured from matrix spike studies on TBBPA, averaged 124% (range: 103% to 148%) for TBDD/TBDF, 98% for PeBDD/PeBDF (range: 63% to 174%) and 93% for HxBDD/HxBDF (range: 22% to 138%). Precisions, as determined from the matrix spike studies, ranged from 2% to 43% for tetra- and pentabrominated analytes while they ranged from 8% to 26% for the hexabrominated congeners. Similar results were obtained for TBS.

Introduction

Tetrabromobisphenol A (TBBPA) and 2,4,6-tribromophenol (TBP) are intermediate products used during the preparation of brominated flame retardants. The two chemicals are amongst 32 substances regulated by the Toxic Substances Control Act (TSCA)[1]. The regulation (Test Rule) requires the manufacturers and importers of 12 organic chemicals to test for the presence of chlorinated and brominated dibenzodioxins and dibenzofurans. The testing also applies to 20 additional organic chemicals not currently manufactured or imported in the USA if their manufacture or importation should resume.

At the time the Test Rule was promulgated, no existing analytical methodologies were available in such matrices for the measurement of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/PBDFs) at the targeted limit of quantifications (LOQ) set forth by the Test Rule (Table 1). A draft protocol was developed and evaluated[2] with preliminary results from a single-laboratory evaluation on TBBPA and several polybrominated diphenyloxides presented at the Dioxin'89 conference. Sample size selected at the time and the low recoveries obtained produced data that were outside the Test Rule requirements. Modifications of the methodology were necessary in order to achieve the target LOQs and recoveries above the required 50% mark. The present paper reports on the overall evaluation of the revised analytical methodology for TBBPA and TBS. The results are reported for analyses performed on a 1-g sample. The sample analysis along with a set of matrix spike and matrix spike duplicate analyses are described.

Table 1. Limit of Quantifications for 2,3,7,8-Substituted PBDD/PBDF Congeners

	LOQ in ppb		LOQ in ppb
2,3,7,8-TBDD	0.1	2,3,7,8-TBDF	1
1,2,3,7,8-PeBDD	0.5	1,2,3,7,8-PeBDF	5
1,2,3,4,7,8-HxBDD	2.5	2,3,4,7,8-PeBDF	5
1,2,3,6,7,8-HxBDD	2.5	1,2,3,4,7,8-HxBDF	25
1,2,3,7,8,9-HxBDD	2.5	1,2,3,6,7,8-HxBDF	25
1,2,3,4,6,7,8-HpBDD	100	1,2,3,7,8,9-HxBDF	25
		2,3,4,6,7,8-HxBDF	25
		1,2,3,4,6,7,8-HpBDF	1000
		1,2,3,4,7,8,9-HpBDF	1000

Experimental Section

Sample Fortification and Extraction/Cleanup Procedures

A composite sample for TBBPA was prepared by using an aliquot from the participating manufacturers' supplied samples. All original, individual and composite samples were stored in a refrigerator kept at 4°C. A 1-g portion of the sample was analyzed by dissolving the sample in 20 mL methanol before the addition of an aliquot of the sample fortification mixture to give internal standard concentrations corresponding to the target LOQs.

The methanolic solution was partitioned against 20 mL hexane and 4 mL 5% sodium chloride/water. The methanolic layer was discarded and the partitioning repeated two more times by adding 20 mL methanol and 4 mL 5% sodium chloride/water. The extract was then passed through a funnel containing anhydrous sodium sulfate. After rinsing the sodium sulfate with two 15-mL portions of hexane, the rinsates were combined with the extract and concentrated to near dryness on a rotary evaporator (35° C water bath).

The residue -- dissolved in 2 mL hexane -- was applied to the top of a column prepared by using a disposable pipette (13 mm i.d.) in the following manner: Insert a glass-wool plug into the bottom of the column. Add 4 g of acid-modified silica gel packing material, 1 g of silica gel and 1 g of sodium sulfate. Tap the top of the column gently. The column was eluted with 90 mL hexane which were collected and concentrated to dryness.

GC/MS Analysis

A VG 70S mass spectrometer, operated in the electron ionization mode, was used to perform the analysis by selected ion monitoring. The PBDD/PBDF mass scale was calibrated with perfluorokerosene (PFK). The mass spectrometer resolving power was 5,000 (10% valley definition). A 30-m DB-5 fused-silica capillary column was used.

Table 2. Analytical Results from Matrix Spike (MS) and Matrix Spike Duplicate (MSD). (%Acc. = Percent Accuracy; LOQ in ppb.)

Analyte	TBBPA				TBP			
	MS		MSD		MS		MSD	
	%Acc.	LOQ	%Acc.	LOQ	%Acc.	LOQ	%Acc.	LOQ
2,3,7,8-TBDD	148	0.01	141	0.01	106	0.02	116	0.02
2,3,7,8-TBDF	105	0.10	103	0.09	81	0.22	83	0.19
1,2,3,7,8-PeBDD	174	0.03	112	0.03	65	0.05	118	0.07
1,2,3,7,8-PeBDF	91	0.39	78	0.42	106	0.89	101	0.72
2,3,4,7,8-PeBDF	69	0.39	63	0.42	69	0.89	66	0.72
1,2,3,4,7,8-HxBDD	109	0.16	118	0.16	49	0.27	68	0.37
1,2,3,6,7,8-HxBDD	109	0.16	118	0.16	49	0.27	68	0.37
1,2,3,7,8,9-HxBDD	22	0.03	23	0.03	11	0.05	16	0.07
1,2,3,4,7,8-HxBDF	107	0.31	138	0.34	94	0.72	84	0.58

Results and Discussion

The results show that no 2,3,7,8-substituted PBDD/PBDF congeners are present in TBBPA and TBS with detection limits of less than 0.01 ppb. The procedure is capable of achieving LOQs that are lower than the targeted LOQs with recoveries for the internal standards between 47% and 145%. Matrix spike samples were analyzed to evaluate the analytical method's ability to detect and quantify small quantities of analyte present in the chemicals. A set of matrix spike and matrix spike duplicate samples was prepared. The latter consisted of regular samples to which, in addition to the carbon-labeled internal standards, known quantities of unlabeled PBDD/PBDFs were added. Fortification levels for the unlabeled analytes were at the test rule LOQs. The results, summarized in Table 2, show that the procedure is capable of detecting and quantifying sub-ppb and ppb levels of 2,3,7,8-substituted PBDD/PBDF compounds in TBBPA and TBS with accuracies generally within the 50% to 150% range. This is particularly evident for the compounds for which isotope dilution techniques can be applied (i.e., 2,3,7,8-substituted tetra- and pentabrominated analytes).

Precision data (Table 3; relative percent difference), calculated for the measured analyte quantities in the MS and MSD samples, range for tetra- and pentabrominated compounds from 2% for 2,3,7,8-TBDF, 5% for 2,3,7,8-TBDD to 43% for 1,2,3,7,8-PeBDD when TBBPA is the matrix. Percent recoveries, calculated using $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF as a recovery standard added to the sample extract before GC/MS analysis, range from 78% to 157%. Similar results were obtained for the TBS matrix. No 2,3,7,8-substituted congeners were found in the laboratory method blank with detection limits ranging from 0.01 to 0.03 ppb.

Initial Calibration Relative Response Factors (Table 4)

A set of four calibration solutions (where the 2,3,7,8-TBDD concentration varies from 1 pg/uL to 30 pg/uL) was analyzed and

the unlabeled as well as labeled compounds' relative response factors (RRF) calculated. The variability in the RRFs of the unlabeled analytes range from 6% for the carbon-labeled 2,3,7,8-TBDF to 30% for 1,2,3,4,7,8-HxBDF.

Table 3. Comparison Between Matrix Spike (MS) and Matrix Spike Duplicate (MSD) Analytical Results (%RPD = relative percent difference).

Analyte	TBBPA %RPD	TBP %RPD
2,3,7,8-TBDD	5	9
2,3,7,8-TBDF	2	3
1,2,3,7,8-PeBDD	43	58
1,2,3,7,8-PeBDF	15	6
2,3,4,7,8-PeBDF	8	4
1,2,3,4,7,8-HxBDD	8	33
1,2,3,6,7,8-HxBDD	8	33
1,2,3,7,8,9-HxBDD	4	40
1,2,3,4,7,8-HxBDF	26	11

Table 4. Initial Calibration Relative Response Factors

Analyte	Initial Calibration Sol. Concentration[a]				RRF Mean	RSD %
	1 pg/uL	5 pg/uL	10 pg/uL	30 pg/uL)		
2378-TBDF	1.750	1.890	1.914	1.861	1.854	4
2378-TBDD	0.694	0.653	0.915	1.018	0.820	21
12378-PeBDF	0.926	1.286	1.235	1.258	1.176	14
23478-PeBDF	1.539	2.606	2.245	2.835	2.306	25
12378-PeBDD	0.786	0.733	0.805	0.877	0.800	7
123478-HxBDF	0.276	0.512	0.606	0.531	0.481	30
478/678-HxBDD	1.054	1.314	1.620	1.417	1.351	17
123789-HxBDD	4.644	6.255	7.927	6.779	6.401	21
13C-TBDF	0.795	0.824	0.852	0.905	0.844	6
13C-TBDD	0.579	0.654	0.753	0.541	0.632	15
13C-PeBDF	0.814	0.664	0.927	0.739	0.786	14
13C-PeBDD	0.537	0.576	0.775	0.639	0.632	17

(a) Nominal concentration for 2,3,7,8-TBDD.

References

1. Environmental Protection Agency; Polyhalogenated Dibenzo-p-Dioxins/Dibenzofurans; Testing and Reporting Requirements (Final Rule); Federal Register Vol. 52, No. 108 (1987).

2. Tondeur, Y., Gorsich, R., Mazac, C., Freiberg, M., Hass, J., McAllister, D.; Analytical Protocol for the Analysis of Polybrominated Dibenzodioxins and Dibenzofurans: Data Quality Objectives and Single-Laboratory Evaluation. Chemosphere, in press.