Use of fluorinated polybrominated diphenyl ethers and simplified cleanup for the analysis of polybrominated diphenyl ethers in house dust

Walter Weathers[1], Maribel Colón, Avis Hines[1], Elin M. Ulrich*

U.S. Environmental Protection Agency, 109 T W Alexander Dr., Maildrop D205-05, Research Triangle Park, NC USA 27711

[1] Retired

Email addresses: colon.maribel@epa.gov; ulrich.elin@epa.gov

*Corresponding author Phone: 1+ (919) 541-3717, Fax: 1+ (919) 541-3527

Abstract

A simple, cost-effective method is described for the analysis of polybrominated diphenyl ethers (PBDEs) in house dust using pressurized fluid extraction, cleanup with modified silica solid phase extraction tubes, and fluorinated internal standards. There are 14 PBDE congeners included in the method, some typically contained in the commercial mixtures used as flame retardants, and some which are not routinely reported in the peer-reviewed literature. A gas chromatographic-mass spectrometry instrumental method provides baseline separation in < 20 minutes, detection limits <20 ng/g, and quantitation limits <60 ng/g for most congeners. Method blanks contained an average concentration < 9 ng/g for all congeners except BDE209 which had an average around 40 ng/g. Spiked samples showed good accuracy with relative percent difference (RPD) <7%, and good precision with relative standard deviation <22% for all congeners except BDE209. The method was applied to the analysis of a standard dust (NIST Standard Reference Material 2585) and showed good accuracy with RPD <25% except for BDE154. Overall, this method exhibited good performance characteristics in all categories including simplicity, cost, sensitivity, selectivity, accuracy, and precision.

Highlights

- Using F-PBDEs saves over $400 per standard compared to ^{13}C-labeled.
- Surrogate recovery was over 80% in performance standards.
- Relative percent difference (RPD) was generally <7% in spiked samples.
- Concentrations found in SRM were generally within 20% of reported value.

Keywords: Flame retardants; polybrominated diphenyl ethers; house dust; fluorinated PBDEs; solid phase extraction

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are among a class of brominated flame retardants (BFRs) that have widely been used in consumer products. In a typical home, PBDEs can be found in electronic products, textiles such as mattresses and carpets, and furniture. PBDEs are typically additive flame retardants, meaning that they are physically bound to the substrate. Since

they are not chemically bound, PBDEs tend to migrate from the product into the indoor environment [1], particularly to dust which is a substantial source of exposure [2-5]. PBDEs are of concern because of potential health impacts including disruption of thyroid hormones [6], neurodevelopmental consequences [7-9] and endocrine disruption [10,11]. While the PBDEs have been or will be removed from U.S. products due to growing concerns about potential health risks[12,13], products containing these chemicals will remain in household use for the foreseeable future. Thus it is important to continue adding and improving the methods for assessing the presence of these chemicals.

There are several important issues that complicate the study of PBDEs in house dust (e.g., matrix complexity, range of physical chemical properties). To facilitate the analysis of PBDEs, sample extracts are cleaned up to isolate analytes from the other components of the dust. These procedures tend to be time consuming and use complex cleanup columns. Therefore, this work developed simple yet effective methods for the cleanup using commercial SPE tubes modified to improve their performance.

Alternatives to the ^{13}C-labeled PBDE internal standards are needed because the labeled PBDEs are relatively expensive and have analytical challenges, particularly ion selection issues and breakdown during analysis [14]. Gas chromatographic mass spectrometry (GC/MS) with negative chemical ionization (NCI) is the method of choice for the analysis of PBDEs in environmental samples. However, labeled PBDEs cannot be used in the NCI analysis because for most congeners, the 79/81 bromide ions are used for quantitation for sensitivity reasons and no differentiation can be made between the labeled and unlabeled congeners. If different analytical instrumentation, ionization modes, or NCI ion selections were made to allow the use of isotopically labeled standards, it is very likely the sensitivity would be diminished and/or the cost of analysis would increase. In the case of higher brominated congeners where alternate ion selection can differentiate between labeled and unlabeled molecules, we have found that there is not a significant methodological advantage over less expensive alternative internal standards. The use of fluorinated PBDEs reduces or eliminates degradation of highly brominated internal standards to lower brominated BDEs generated during analysis. In this work we demonstrate the analysis of 14 PBDEs using three fluorinated PBDEs (F-PBDEs) as internal standards. Fluorinated PBDEs have different retention time than the parent PBDE from which it was derived, and are less costly than labeled PBDEs.

2. Materials and methods

A variety of methods have been recently published for the extraction (Soxhlet [15], PFE [16], sonication [17]), cleanup (manually packed columns [18], SPE [19], on-line [20], in-cell [21]), and surrogate/internal standards (^{13}C-BDE(s) [22], native BDEs [23], F-BDEs [24], non-BFR compounds [25]), and instrumental analysis (GC-EI [18], GC-ECNI [26], GC-ECD [27], GC-MS/MS [28], LC-MS/MS[29]) for different combinations of PBDE congeners in dust. The method presented here is similar to that described by Stapleton, et al. [30] in that both use pressurized fluid extraction (PFE; ASE 200; Dionex Corp., Sunnyvale, CA), commercially available solid phase extraction (SPE) cartridges, analysis by GC/MS with NCI, and MCDE 86L as a surrogate (recovery) standard. In contrast, this method decreases the volume of dichloromethane, pressure and temperature used for extraction; uses modified SPE cleanup cartridges, a thinner film in the GC column with Guard column and heated injection; adds both

surrogate recovery and internal standards; and quantitates different congeners and monitors different ions in the mass spectrometer. The exact conditions for this method are described below and are displayed in Figure 1A-C.

2.1 Extraction

Figure 1B shows the assembly of the PFE cells to extract house dust mixed with Ottawa sand (Fisher Scientific, Fair Lawn, NJ). 200 ng of MCDE 86L (Wellington Laboratories, Ontario, Canada) and PBDE 181 (Cambridge Isotope Laboratories, Andover, MA) surrogate recovery standards (SRS) were added to the dust prior to extraction. Table 1 details which SRS was used for each measured congener. Each sample was extracted twice and collected in separate 60 mL vials that were later combined. Additional extraction details are included in Figure 1A.

2.2 Cleanup

Sample cleanup was accomplished using two modified 3-mL, SPE cartridges (Sigma-Aldrich, St. Louis, MO) in tandem. The bottom SPE cartridge was modified by adding 500 µL 95-98% sulfuric acid:water (1:1) and was used without drying. The top SPE cartridge was modified as shown in Figure 1C. The SPE cartridges were flushed three times with 2 mL of hexane:dichloromethane (4:1). The concentrated sample extract was loaded onto the top cartridge, and eluted as shown in Figure 1A. After concentration to 1 mL, 500 ng of F-BDEs 69 and 160 and 1000 ng of F-BDE 208 internal standards (Cambridge Isotope Laboratories or Chiron AS, Trondheim, Norway) were added to the extract. Table 1 details which internal standard was used for each measured congener.

2.3 GC/MS analysis

GC/MS analyses were performed on an Agilent Technologies (Santa Clara, CA) 6890N GC equipped with a model 5973 inert MS. The GC column specifications (Agilent Technologies and Restek, Bellefonte, PA), GC temperature program and select MS conditions are shown in Figure 1A. Helium carrier gas was used at a constant flow rate of 3.2 mL/minute. Injections were made in the splitless mode with the inlet temperature set at 260 °C. The ion source and quadrupole temperatures were 150 °C and methane reagent gas was used. Table 1 shows the retention time and ions monitored for each congener.

2.4 Detection/Quantitation limit determination and calibration

To determine the detection and quantitation limits for the target congeners, eight PFE cells containing 0.5g each of diatomaceous earth were spiked with 0 (blank), 1, 5, 10, 25, 50, 250, and 500 ng of each PBDE, respectively. These were prepared in triplicate and taken through the complete analytical procedure.

The procedure recommended by The International Conference on Harmonization of Technical Requirements for Registration of Pharmaceuticals for Human Use [31] was followed to determine the detection limit (DL) and quantitation limit (QL) for the method. Using this procedure, $DL = 3.3*\sigma/S$, where σ is the standard deviation of the y-intercept and S is slope of

the calibration curve. The QL = 10* σ /S or 3*DL. A plot was prepared of the spiked amount versus the average concentration determined for each congener. The four lowest spiked amounts that produced a response (above the blank) were used to determine S and σ were determined. The DL and QL found for each congener is shown in Table 1.

Calibration of the mass spectrometer was conducted at least weekly using the instrument's autotune functionality. The instrument response was calibrated for a low (25-500 ng/mL in hexane) and high (50-1000 ng/mL in hexane) range for 13 PBDEs, and at double the concentration for BDE209. Linear regression, with inverse concentration weighting and without origin forcing, was performed for both the low and high ranges for each sample set. Samples above the high calibration range were diluted and reanalyzed. Concentrations were converted to a mass/mass basis using the quantity of dust extracted.

2.5 Quality assurance

A sample run using this method consisted of field collected samples, a method blank, method spike, and 100% recovery spike. For the method spike, a specific concentration of the SRS and PBDE solution are added to 0.5 g diatomaceous earth (DE; used as blank matrix; Sigma Aldrich) prior to the extraction and cleanup process. For the 100% recovery spike, the SRS and the PBDE solution are added to the extract resulting from the extraction and cleanup of the blank DE immediately prior to GC/MS analysis. Standard Reference Material (SRM) 2585 (NIST, Gaithersburg, MD) was also analyzed with the run.

Regression lines were considered acceptable with $R^2 \geq 0.98$. Calibration check standards were run at least once per sample set, inserted every 5-6 samples. If check standards were outside the ±25% nominal concentration criteria, the instrument was retuned and recalibrated. For quantification, an experienced analyst considered the retention time, ion presence, and ion ratios to confirm the identity of PBDE analytes of interest; strict performance criteria for these values were not used due to the complexity of the dust sample matrix and chromatograms.

3. Results and discussion

This exact combination of cleanup conditions had not previously been reported, and produced good recovery of target analytes and produced purified extracts. Because PBDEs are stable under acidic conditions, acidified silica is used to remove hydrophobic interferences from samples [32]. Alumina further eliminates polar interferences, and has the added benefit of separating PBDEs from newer brominated flame retardants such as TBB which can coelute with BDE99 [33].

Diatomaceous earth proved to be a good dust surrogate since it is difficult or impossible to find house dust that does not contain PBDEs [25]. A 0.5 g sample of DE is used rather than the 1g of dust because it has a lower density and therefore fills a larger volume. This mass of DE also proved to be sufficient to absorb spikes.

Good baseline separation was achieved for all congeners using the guard and 15 meter DB-5MS columns (Figure 2A), and showed minimal interferences for a SRM 2585 housedust sample (Figure 2B). As previously reported, the instrument responses decreased with the increasing PBDE masses, in part due to thermal breakdown in the injector and column [14]. It is likely that the response of the higher PBDEs could be improved with the use of a programmable

temperature vaporization inlet, on column injection, and shorter or narrow bore columns [14].

Table 2 shows method performance data for method blanks (N = 32), spikes (N = 17) and 100% recovery (N = 17) samples. All concentrations were adjusted based on the recoveries of the two surrogate recovery standards. MCDE 86L was used for the correction of BDEs 47 through 183 while BDE181 was used for the correction of BDEs 190 through 209. Percent recovery of SRS in these 83 quality control samples (including 17 SRMs in Table 3) was 87.8 ± 23.4% for MCDE-86L (mean ± standard deviation) and 81.9 ± 21.8% for BDE181.

The blank samples contained a maximum of 28.4 ng/g for individual PBDE congeners, excepting BDE 209 (Table 2). For BDE209, the concentration in blanks averaged 39.2 ± 35.6 ng/g and was found in all but four samples, which may reflect the ubiquitous nature of this compound. For BDEs 190 and 206, no detectable concentrations were found in any blank sample. The 100% recovery and method spikes were amended with 300 ng/g of each congener except BDE209 for which the concentration was doubled. The 100% recovery spikes had mean concentrations within 10% of the actual concentrations as shown by the relative percent difference (RPD) in Table 2, absolute standard deviation (SD) less than 65 ng/g for most congeners and relative standard deviations (RSD) < 34%. The method spikes had mean concentrations within 13% of the actual concentrations, absolute SD less than 55 ng/g for most congeners and RSD < 20% for most congeners. In all cases, the RPD and SD were largest for BDE209. The decreased accuracy and precision for BDE209 are likely due to previously mentioned analytical difficulties with this compound, including the likelihood of inadvertent contamination, photo and thermal degradation [14]. The performance of this method was considered very good for all aspects of laboratory created samples.

Table 3 shows the concentrations measured from the analysis of SRM 2585 (House Dust) used to evaluate this method. The seventeen SRM samples were analyzed over a year period during the analysis of environmental dust samples (to be reported separately). The precision of the method can be assessed by the RSD of the repeat measurements. The RSD ranges from 16 to 43% which is reasonable for an environmentally derived sample. The results were in close agreement with the SRM certified values [34] with the relative percent difference (RPD) for individual congeners ranging from 2.5 to 35%, with six of the nine congeners below 15%, showing good accuracy of the method.

Table 3 also shows SRM 2585 results using other methods reported in the literature, grouped by instrumental method. The RSD for this method was usually higher than other methods reported by a few percent (0-15%), however, for this study N = 17 over a year period, while in others N = 3-6. Using this method, the RPD for all congeners except BDE154 is in the same range as other methods. Two congeners do not have a NIST reported reference value (BDEs 197 and 207). For BDE 197 our mean concentration (28.5 ng/g) was within the range of other reported concentrations (10-33 ng/g) and for BDE 207 our mean concentration was quite similar to the one other reported value (124 vs 120 ng/g).

4. Conclusion

A simple and cost effective method is presented for the analysis of PBDEs in house dust samples. This method makes use of F-PBDEs as internal standards, which we have demonstrated

to be just as effective as isotopically labeled standards. For 1 mL of a 50 μg/mL solution of $^{13}C_{12}$ BDE209, the cost is $725; fluorinated BDE standards in the same volume and concentration cost $295, a savings of over $400 per standard. Also, the method uses a dust cleanup procedure using modified commercial SPE cartridges that is simpler, more consistent, and requires less time than hand-packed, and/or multiple column procedures. Only BDEs 99, 118 and 209 had average blank concentrations above the detection limit (none were above the quantitation limit). Spiked laboratory samples had good accuracy and precision. The method was also used to measure the PBDE concentration of a dust standard reference material. The results show the method produced results in the expected range of values for SRM and compared well with other reported values. Results from the full study of house dust present in Southern California homes will be presented in future papers.

Disclaimer

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Figure Captions:

Figure 1. Analytical procedure flow diagram (A) and drawings of extraction (B) and cleanup (C) steps.

Figure 2. Total ion chromatogram (using SIM conditions noted in Table 1) of a 500 ng/mL standard (A) and SRM 2585 House Dust extract (B) with internal and surrogate standards.

Compound identification: (1) MCDE 86L,(2) F-BDE69, (3) BDE47, (4) BDE100, (5) BDE99, (6) BDE118, (7) BDE154, (8) BDE153, (9) F-BDE160, (10) BDE183, (11) BDE181, (12) BDE190, (13) BDE197, (14) BDE203, (15) BDE205, (16) F-BDE208, (17) BDE207, (18) BDE206, (19) BDE209

A

Sieve 1 g dust to <150 µm

Pressurized Fluid Extraction

- Hexane: DCM 4:1
- Two static cycles: Heat and Static times 5 min
- 1500 psi, 75 °C, 50% flush, 60 sec purge

Cleanup

- 2 stacked SupelClean™ LC-Si SPE cartridges
- Bottom cart. acidified 500 µL sulfuric acid:water 1:1

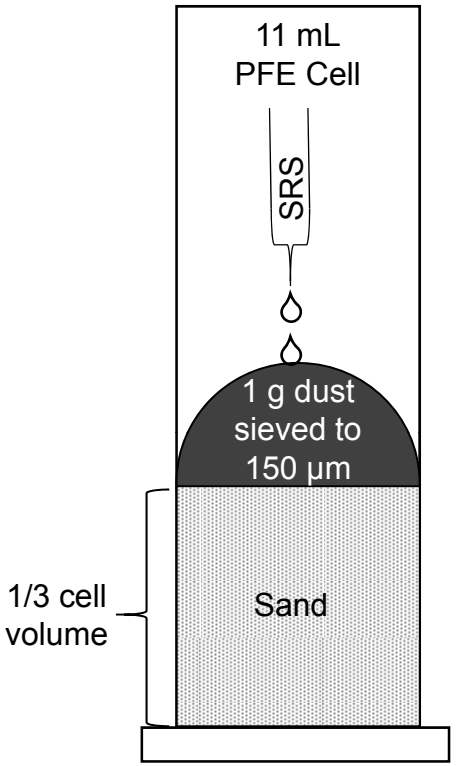
Solvent concentration

- Internal Standards added

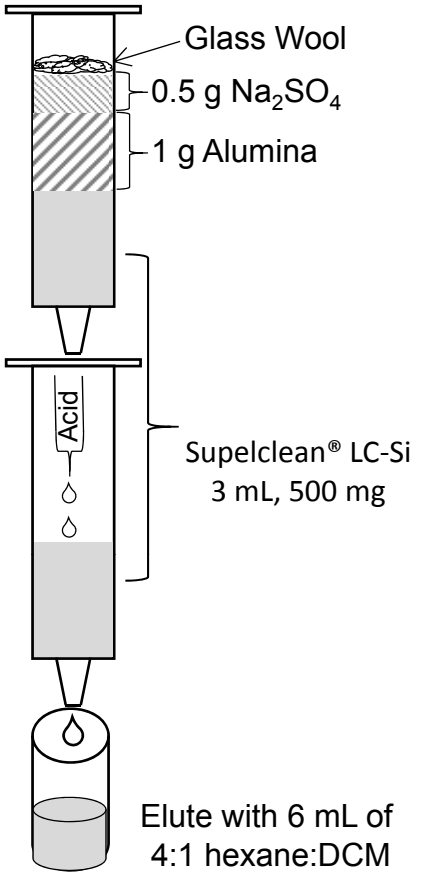
GC/MS Analysis

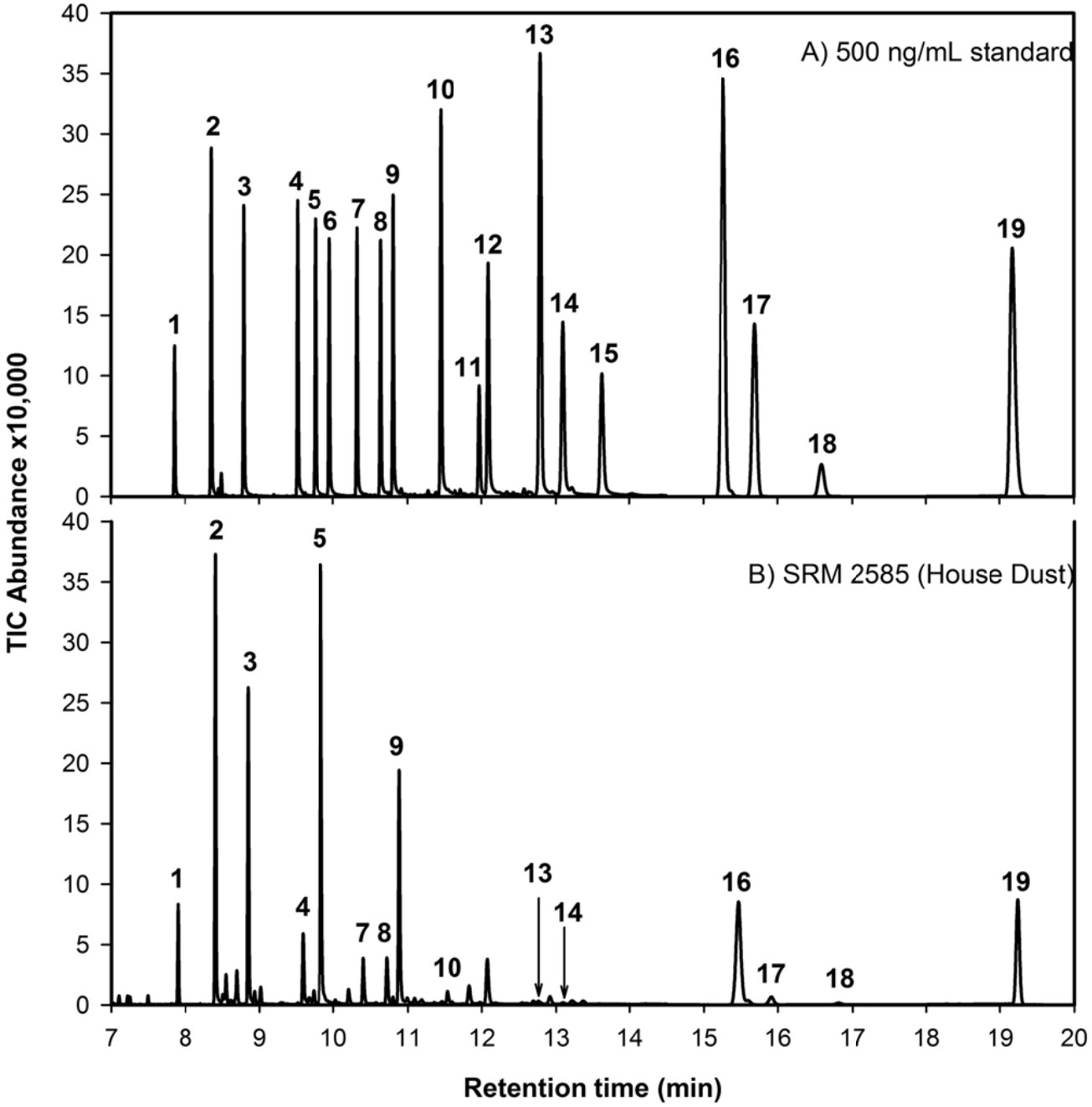
- DB-5MS 15m × 0.25 mm ID × 0.1 µm film with Siltek® deactivated guard column (5 m × 0.25 mm I.D)
- GC conditions: initial 95 °C hold 2 min; 20 °C/min to 280 °C hold 6 min; 35 °C/min to 310 °C hold 5 min
- Negative Chemical Ionization, Selected Ion Monitoring

B



C




A) 500 ng/mL standard
B) SRM 2585 (House Dust)
TIC Abundance x10,000
Retention time (min)
1
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Use of fluorinated polybrominated diphenyl ethers and simplified cleanup for the analysis of polybrominated diphenyl ethers in house dust

Walter Weathers[1], Maribel Colón, Avis Hines[1], Elin M. Ulrich*

U.S. Environmental Protection Agency, 109 T W Alexander Dr., Maildrop D205-05, Research Triangle Park, NC USA 27711

[1] Retired

Email addresses: colon.maribel@epa.gov; ulrich.elin@epa.gov

*Corresponding author Phone: 1+ (919) 541-3717, Fax: 1+ (919) 541-3527

Table 1. Retention times, ions monitored, detection (DL) and Quantitation Limits (QL) for PBDE analysis.

Congener	Ret. time (min)	Target ion *(m/z)*	Qualifier ion #1 *(m/z)*	Qualifier Ion #2 *(m/z)*	DL ng/g	QL ng/g
			Target analytes			
BDE47[b, d]	8.8	81.0	79.0	161.0	20	59
BDE100[b, d]	9.6	81.0	79.0	161.0	7	20
BDE99[b, d]	9.8	81.0	79.0	161.0	32	96
BDE118[b, d]	10.0	81.0	79.0	161.0	2	6
BDE154[b, d]	10.4	81.0	79.0	562.0	6	17
BDE153[b, d]	10.7	81.0	79.0	562.0	6	19
BDE183[b, e]	11.5	81.0	79.0	562.0	3	9
BDE190[c, e]	12.1	81.0	79.0	562.0	10	31
BDE197[c, e]	12.9	409.7	79.0	81.0	7	21
BDE203[c, e]	13.2	81.0	79.0	561.7	6	18
BDE205[c, e]	13.8	81.0	79.0	561.7	7	20
BDE207[c, f]	15.9	486.6	488.6	—[a]	8	24
BDE206[c, f]	16.8	486.6	488.6	641.6	125	378
BDE209[c, f]	19.3	488.6	486.6	—	26	78
			Internal standards and surrogates			
F-BDE69	8.4	81.0	79.0	161.0		
F-BDE160	10.9	81.0	79.0	502.0		
F-BDE208	15.4	486.6	488.6	—		
MCDE 86L	7.9	318.0	354.0	—		
BDE181	12.0	81.0	79.0	562.0		

[a] No additional qualifier ion used

[b] Compounds corrected by MCDE 86L surrogate standard

[c] Compounds corrected by BDE181 surrogate standard

[d] Compounds quantitated by F-BDE69 internal standard

[e] Compounds quantitated by F-BDE160 internal standard

[f] Compounds quantitated by F-BDE208 internal standard

Table 2. Method performance for blank (N = 32), 100% recovery (N = 17), and spiked (N = 17) samples (300 ng/g except BDE209 at 600 ng/g) including mean ±standard deviation (SD; ng/g), range (ng/g), relative standard deviation (RSD) and percent difference (RPD) from the nominal spike concentration.

Congener	Method Blank	100% Recovery Spike		Method Spike	
	Mean±SD (min-max) ng/g	Mean ± SD (min-max) ng/g	RPD RSD %	Mean±SD (min-max) ng/g	RPD RSD %
BDE47	5.45±4.16 0.52-16.6	287±48.3 153-392	4.26 16.8	286±37.7 205-383	4.69 13.2
BDE99	7.80±7.06 0-28.2	284±51.5 157-382	5.31 18.1	293±39.2 211-376	2.44 13.4
BDE100	3.44±4.28 0-19.6	281±56.3 157-389	6.48 20.1	280±53.9 170-393	6.80 19.3
BDE118	5.28±5.28 0-24.6	290±48.2 155-382	3.18 16.6	296±39.4 207-374	1.47 13.3
BDE154	2.07±3.70 0-19.5	292±47.7 161-386	2.73 16.3	292±41.5 217-391	2.82 14.2
BDE153	2.96±4.79 0-21.2	290±48.4 158-378	3.48 16.7	286±40.5 211-380	4.83 14.2
BDE183	1.76±2.67 0-13.6	298±55.0 144-402	0.78 18.5	286±39.5 192-360	4.79 13.8
BDE190	0±0 0	291±46.0 140-349	2.90 15.8	288±35.7 187-329	3.88 12.4
BDE197	1.89±5.77 0-28.4	283±52.2 132-392	5.60 18.4	284±44.4 179-376	5.22 15.6
BDE203	0.79±2.20 0-9.05	287±54.4 121-378	4.47 19.0	282±44.9 160-350	6.02 15.9
BDE205	0.31±1.73 0-9.79	284±59.4 111-365	5.46 20.9	275±49.5 146-329	8.34 18.0
BDE206	0±0 0	295±65.3 136-418	1.52 22.1	289±53.8 201-424	3.60 18.6
BDE207	1.47±4.51 0-23.4	298±56.6 143-378	0.63 19.0	292±49.2 193-392	2.60 16.8
BDE209	39.2±35.6 0-172	538±181 151-917	10.3 33.6	524±202 200-969	12.7 38.5

Table 3. BDE congener mean ±standard deviation or range of means (ng/g; first line) with Relative Standard Deviation (second line) and Relative Percent Difference (third line) for various methods vs. NIST certified value for SRM 2585.

BDE	This method[a]	GC-ECNI-MS [1-5]	GC-EI-MS [6,7]	GC-MS/MS [8-10]	GC-ECD [11,12]	LC-NI-APPI-MS/MS [13]	NIST [14]
47	484±77.9	390-520	445±29	486-526	537±26	561±36	497±46[d]
RSD[b]	16.1	3.2-12	6.5	2.1-9.5	4.8	6.4	
RPD[c]	2.55	0.20-22	10	0.60-5.8	8.0	13	
99	858±133	680-1110	838±67	803-952	890±36	883±26	892±53[d]
	15.5	5.6-13	8.0	5.6-6.8	4.0	2.9	
	3.85	2.1-24	6.1	1.9-10	0.22	1.0	
100	149±34.0	110-158	140±13	135-147	160.7±5.6	143±5	145±11[d]
	22.8	3.3-13	9.3	3.4-8.9	3.5	3	
	2.72	3.7-24	3.4	0.69-6.9	11	1.4	
154	113±22.1	70-95	87.8	77-81	96±12	77.4±4.2	83.5±2.0[e]
	19.5	7.9-12	8.9	6.2-13	13	5.4	
	35.3	5.6-16	5.1	3.0-7.8	15	7.3	
153	131±24.6	90-124	118	118-133	127.1±8.8	132±6	119±1[d]
	18.7	1.6-13	8.5	5.7-14	6.9	5	
	10.3	0-24	0.84	0.84-12	6.8	11	
183	40.0±11.4	25-62	NR[f]	44±4	42.5±5.2	43.3±4.7	43±3.5[d]
	28.6	3.2-17		9.1	12	11	
	6.83	1.6-44		2.3	1.2	0.70	
197	28.5±9.22	10-33	NR	NR	NR	NR	NR[f]
	32.3	20-61					
	NA[g]	NA					
203	29.2±8.01	10-20.6	NR	NR	41.3±4.8	NR	36±6.4[e]
	27.4	0-12			12		
	19.0	43-72			15		
206	204±59.0	157-159	188	NR	NR	NR	271±42[e]
	28.9	19-21	7.4				
	24.6	41-42	31				
207	124±23.4	120±40	NR	NR	NR	NR	NR
	18.9	33.3					
	NA	NA					
209	2670±1140	2050-2800	2703	2971±333	2091-2706	2580±140	2510±190[e]
	42.8	8.5-25	5.2	11	2.8-7.2	5.4	
	6.34	1.2-18	7.7	18	7.8-17	2.8	

[a] N = 17

[b] Relative standard deviation

[c] Relative percent difference from the NIST reported value.

[d] Certified values are weighted means of the results from four analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2 (approximately 95% confidence) except for PBDE 153 with a coverage factor of 10, calculated by combining a between-source variance incorporating inter-method bias with a pooled within-source variance.

[e] Certified values are unweighted means of the results from two or three analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance with a pooled, within-method variance.

[f] Not reported

g Not applicable- RPD cannot be calculated when a reference value is not reported.

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