

# Determination of brominated diphenyl ethers in atmospheric particulate matter using selective pressurized liquid extraction and gas chromatography–mass spectrometry with a negative chemical ionization

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**Abstract** This study describes the development and validation of a sensitive and reliable method for determination of polybrominated diphenyl ethers (PBDEs) in atmospheric particulate matter using selective pressurized liquid extraction (SPLE) and gas chromatography–mass spectrometry with a negative chemical ionization (GC-NCI-MS). Extraction and clean-up were performed using PLE with 2 g florisil and 3 g silica placed in the extraction cells. Under optimal conditions, 14 PBDEs were extracted at 70 °C using hexane/dichloromethane (50:50, v/v) as solvent. Validation of SPLE returned excellent recoveries for most analytes, with relative standard deviations mostly below 20%. Method detection limits ranged from 0.13 to 15.38 ng·mL<sup>-1</sup> for the GC-MS analyses. The method was successfully applied to atmospheric particulate matter of Beijing, where analytes were detected in the range of 182.79 to 468.99 pg·m<sup>-3</sup>.

**Keywords** Brominated diphenyl ethers · Atmospheric particulate matters · Selective pressurised liquid extraction · Gas chromatography-mass spectrometry

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## 1 Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as an additive flame retardant in textiles, electronics, plastics, building materials, and other products (Birgul et al. 2012; Matsukami et al. 2017). However, these chemicals can be easily released to the atmosphere and undergo long-range atmospheric transport. Atmospheric PBDEs can enter the human body through the respiratory system, and have adverse effects on human health (Besis and Samara 2012; Wania and Dugani 2003). Analysis of PBDEs in atmospheric particulate matter (PM) is a key tool in evaluating their characteristics, transport, and transformation through the environment (Arellano et al. 2014; Gouin et al. 2006).

The determination of PBDEs in solid matrices requires efficient extraction and sensitive analytical techniques. Pressurized liquid extraction (PLE) has become an important alternative to traditional extraction techniques, such as classical Soxhlet (Cunha et al. 2010; Moret et al. 2013, 2014), due to its potential for automation and less solvent consumption. A method described as “selective” PLE (SPLE) combines PLE and on-line clean-up procedures. SPLE has been successfully applied to the analysis of persistent and emerging organic pollutants in soil, sediment, and biological samples (Arbelaez et al. 2015; Choi et al. 2016; Pintado-Herrera et al. 2016; Zhang et al. 2012).

The objective of this study was to develop a sensitive, rapid, and reliable SPLE method for the analysis of 14 PBDEs (BDE-17, -28, -47, -66, -71, -85, -99, -100, -138, -153, -154, -183, -190, and -209) in atmospheric PM using gas chromatography–mass spectrometry with a negative chemical ionization (GC-NCI-MS). Advantages of this method were confirmed to include simplicity, automation, less consumption of solvents, and analysis time, and the method was applied to real environmental samples.

## 2 Experiment

Atmospheric PM samples of total suspended particulate were collected on glass fiber filter (GFF, diameter 102 mm, SKC Inc. USA) using high volume air samplers (Echo Tecora Inc., Italy) with a flow rate of 200 L/min for 24 h. After sampling, the GFFs were wrapped in clean aluminum foil, sealed in polyethylene bags, and stored at  $-18^{\circ}\text{C}$  until analysis.

An accelerated solvent extraction system—ASE 350 (Thermo Fisher Scientific)—with 34-mL stainless steel extraction cells was used to perform PLE. Different sorbents were loaded into the PLE cells to achieve purification. Extraction cells were packed, from bottom to top, with two cellulose filters and certain amounts of clean-up sorbents and GFF samples cut into pieces. All sorbents in the different layers in the cell were separated by cellulose filters. The SPLE extracts were evaporated to 1 mL by vacuum rotatory evaporation (Buchi, R-300, Switzerland) and termovap sample concentrator (Organomation, N-EVAP, USA), and then filtered through a 0.22- $\mu\text{m}$  nylon filter for analysis.

PBDE analysis was performed by Agilent 7890A gas chromatograph equipped with a 5975C mass-selective detector operated in NCI mode. The separation of the analytes was carried out using a 15 m Rtx-1614 fused silica column (0.25 mm i.d., film thickness 0.1  $\mu\text{m}$ , Restek Corporation, US). GC-MS was applied in selected ion-monitoring (SIM) mode with NCI to enhance sensitivity.

## 3 Results and discussion

### 3.1 Optimization of selective pressurized liquid extraction

The optimization of SPLE was focused on the extraction solvent, temperature, and clean-up sorbents; other

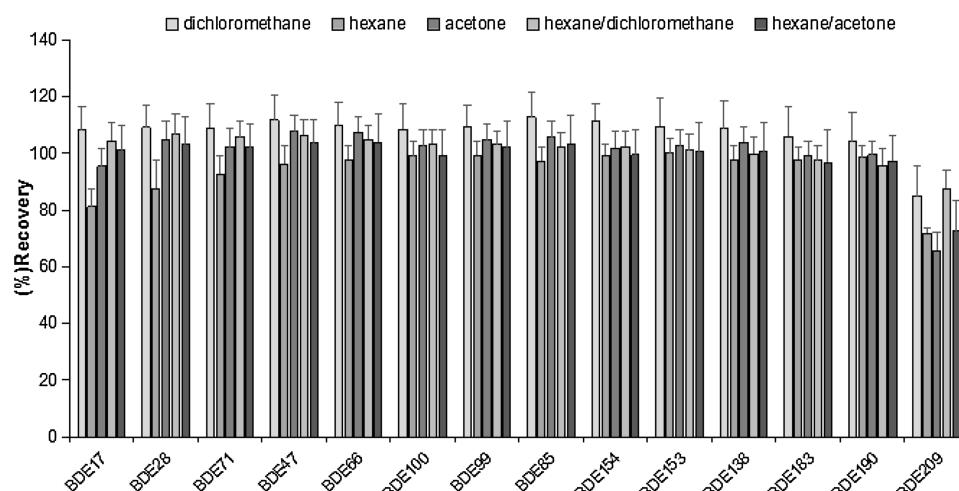
conditions were fixed according to previous studies (Martínez et al. 2010), and all the extractions cycled once for 5 min heated time at 1500 psi with 60% flush volume. Atmospheric PM samples were spiked with PBDE standard of 20 ng BDEs ( $-17$ ,  $-28$ ,  $-47$ ,  $-66$ ,  $-71$ ,  $-85$ ,  $-99$ ,  $-100$ ,  $-138$ ,  $-153$ ,  $-154$ ,  $-183$ , and  $-190$ ) and 100 ng of BDE-209 per film and used in triplicate to perform the following experiments.

Extraction solvent is a crucial parameter in the extraction of selected target compounds. Solvents such as *n*-hexane, dichloromethane, acetone, *n*-hexane/acetone (50:50, v/v), and *n*-hexane/dichloromethane (50:50, v/v) were investigated. Extraction efficiencies are shown in Fig. 1. Good recoveries were detected and there was no significant analytical difference among these solvents except for *n*-hexane, which exhibited lower recoveries because of weak solvent polarity. However, yellow colors were observed in the extracts using acetone as solvent. When *n*-hexane /dichloromethane (50:50, v/v) was used as extraction solvent, cleaner extracts were collected, so it was selected as the optimum extraction solvent.

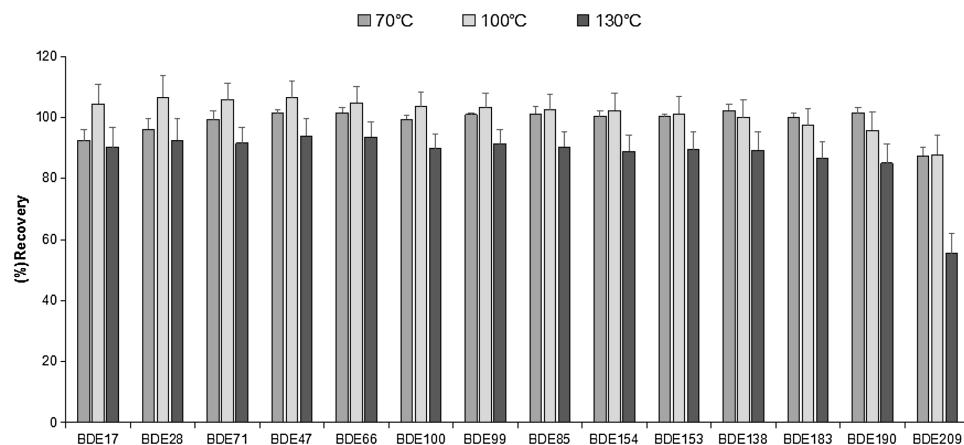
The influence of temperature in the extraction process was studied using a factorial design at three temperatures: 70, 100, and  $130^{\circ}\text{C}$ . Figure 2 shows the effect of temperature in the extraction of 14 PBDEs. Extraction recoveries obtained at 70 and 100  $^{\circ}\text{C}$  were similar to each other and better than those of 130  $^{\circ}\text{C}$ ; the repeatability at 70  $^{\circ}\text{C}$  was the best, with relative standard deviations (RSDs) below 5%. Therefore, SPLE was performed at 70  $^{\circ}\text{C}$  in the subsequent experiments.

The SPLE clean-up process involved placing different types and amounts of sorbents inside the extraction cells. The main objective of this process was to reduce interference and ensure that the extracts were clean enough to inject directly into GC-MS after concentration. Different amounts of alumina, florisil, silica, alumina/silica gel, and florisil/silica gel

**Fig. 1** Extraction recoveries for 14 PBDEs using different solvent from SPLE. Results show mean and RSD ( $n = 3$ )



**Fig. 2** Extraction recoveries for 14 PBDEs at different temperature from SPLE. Results show mean and RSD ( $n = 3$ )



were selected as clean-up sorbents. There were no significant differences of quantitative recoveries with different types and amounts of sorbents, but the cleaner extracts were observed using florisil/silica gel together, and a lower baseline of GC-MS was obtained when increasing the amounts of silica within a certain range. Therefore, 2 g of florisil and 3 g of silica gel were chosen as the most effective options for clean-up.

### 3.2 Method validation

To evaluate the accuracy and precision of the final method, blank GFFs were spiked at three concentrations: 2, 20, and 100 ng of all the target analytes except for BDE-209 (10, 100, and 500 ng). Table 1 shows the recovery data. Good recoveries were obtained for most PBDEs at each of the spiking levels. The best recoveries were observed for all

analytes (from 83.70% to 105.79%) at the medium spiking level, with RSDs below 10%. The recoveries of most analytes at the high spiking level were better than those at the low spiking level. With a RSD of 18.6%, the repeatability of BDE-209 was poor at high-level spikes; BDE-209 was not recovered at the lowest spike level.

Method detection limits (MDLs) of the SPLE method were evaluated from standard deviation(s) of seven replicates by spiking a low concentration (1–5 times the expected MDL) on pre-cleaned filter. The calculated MDL ranged from 0.13 to 15.38 ng·mL<sup>-1</sup> for the 14 PBDEs.

### 3.3 Application to environmental samples

The optimized SPLE method was applied to atmospheric PM samples on different days in Beijing. The results,

**Table 1** Validation data of the optimized SPLE method: recovery percentage, relative standard deviations (RSDs), and method detection limits (MDLs)

Compound	Low spike ( $n = 3$ )		Medium spike ( $n = 3$ )		High spike ( $n = 3$ )		MDLs (ng·mL <sup>-1</sup> )
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
BDE17	74.08	3.3	94.50	3.4	85.63	0.9	0.65
BDE28	76.56	4.2	96.67	4.1	86.26	1.7	0.73
BDE71	74.63	5.8	105.79	5.4	88.03	2.5	0.79
BDE47	85.25	4.1	96.39	3.6	93.23	4.3	0.29
BDE66	88.73	3.2	94.85	5.1	90.63	3.0	0.13
BDE100	71.07	2.9	103.48	2.9	90.32	3.6	0.80
BDE99	81.32	2.2	93.22	4.8	91.23	4.6	0.13
BDE85	73.00	3.5	92.42	3.0	91.58	5.7	0.64
BDE154	81.19	2.2	102.26	5.6	90.46	5.4	0.64
BDE153	79.20	4.2	91.16	5.8	86.15	6.1	0.15
BDE138	83.92	3.0	99.87	4.8	89.96	7.1	0.29
BDE183	80.95	2.4	97.42	5.4	84.42	7.1	0.39
BDE190	86.93	3.9	95.68	6.2	85.69	9.1	0.98
BDE209	N/A	N/A	83.70	6.6	73.90	18.6	15.38

N/A data not available

**Table 2** PBDE concentrations in atmospheric particulate matter on different days in Beijing ( $\text{pg}\cdot\text{m}^{-3}$ )

Compound	S1	S2	S3	S4
BDE17	15.39	5.71	1.15	28.30
BDE28	14.54	8.88	3.94	23.04
BDE71	17.25	41.46	16.70	20.55
BDE47	6.76	16.99	12.94	8.00
BDE66	3.96	9.28	1.54	4.83
BDE100	18.61	24.46	7.68	25.05
BDE99	7.19	20.99	2.15	10.72
BDE85	2.16	2.98	2.01	4.39
BDE154	7.36	15.95	2.06	14.30
BDE153	18.53	13.30	41.93	46.08
BDE138	59.18	8.53	39.48	95.07
BDE183	5.99	18.53	3.48	6.62
BDE190	3.73	5.87	2.93	5.76
BDE209	76.26	276.05	44.80	62.42
$\sum_{14}\text{PBDEs}$	256.90	468.99	182.79	355.13

summarized in Table 2, were similar to a previously reported range (Dong et al. 2015). All 14 PBDEs were detected in real samples, at total concentrations from 182.79 to  $468.99 \text{ pg}\cdot\text{m}^{-3}$ . BDE-209 was measured at the highest concentration, ranging from 44.80 to 276.05  $\text{pg}\cdot\text{m}^{-3}$ .

## 4 Conclusion

A sensitive and reliable method for the simultaneous analysis of 14 PBDEs in atmospheric PM was developed and validated. Advantages of this method were not only the low manipulation of the samples, but also the reduction of extraction solvents and analysis time. Comprehensive extraction of analytes using SPLE was demonstrated by excellent recoveries in spiking experiments, indicating the procedure was highly repeatable and reliable. This method was successfully applied to environmental samples.

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### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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