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ORIGINAL PAPER

Extraction and determination of polybrominated diphenyl ethers in water and urine samples using solidified floating organic drop microextraction along with high performance liquid chromatography

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Abstract We have developed a method, termed solidification of floating organic drop microextraction (SFOME), for the extraction of polybrominated diphenyl ethers (PBDEs) in water and urine samples, this followed by quantification via HPLC. This method requires very small quantities of organic solvent consumption. It is based on exposing a floating solidified drop of an organic solvent on the surface of aqueous solution in a sealed vial. The organic drop is easily collected with a spatula, molten (at ambient temperature), and then submitted to HPLC. Experimental parameters including extraction solvent and its volume, disperser solvent and its volume, extraction time, ionic strength, stirring speed and extraction temperature were optimized. The enrichment factors of analytes are in the range from 921 to 1,462, and acceptable extraction recoveries (92%–118%) are obtained. The dynamic linear range for five PBDE congeners is in the range of 0.5–75 $\mu g.L^{-1}$ and from 5 to 500 $\mu g.L^{-1}$ for BDE 209. The correlation coefficients range from 0.9960 to 0.9999. The limits of detection (at S/N=3) for PBDE congeners vary between 0.01 and 0.04 $\mu g.L^{-1}$. This method has been successfully applied to detecting PBDEs in two environmental waters and in human urine.

Keywords Solidification of floating organic drop microextraction · Polybrominated diphenyl ethers · Optimization · Urine samples

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Introduction

Polybrominated diphenyl ethers (PBDEs) are man-made chemicals widely used as flame retardants in a wide variety of paints, plastics, textiles, electronic components, etc. [1–3]. They can escape from the surface of manufactured products and release to the environment. Several epidemiological studies have shown PBDEs to pose health risks [4, 5] such as endocrine disruption, adverse neurobehavioral effects to act as reproductive toxicants and probable carcinogens. Furthermore, toxicological test showed that PBDE congeners might be enriched in liver and thyroid [6, 7]. Thus, some commercial mixtures of PBDEs (penta and octa formulations) have been banned in Europe due to their persistence and potential environmental and human health hazard [8]. However, the major PBDE congeners, such as BDE 47, BDE 99, BDE 100, BDE 154, BDE 183 and BDE 209, are ubiquitous in the environment, and rapidly increasing levels have been frequently detected in waters [9–12], sediments [13, 14], marine organism [15, 16] and food [17, 18].

The direct determination of PBDEs is complicated due to their trace level in complex sample matrices, and thus sample cleanup and pretreatment were required. The reported pretreatment methods for PBDEs in different

matrices include stir bar sorption extraction [19, 20], matrix solid-phase dispersion [21], microwave-assisted extraction [22], solid-phase microextraction [23] and dispersive liquid-liquid microextraction [24]. Among them, the dispersive liquid-liquid microextraction is a novel technique, which has been successfully used for extraction and determination of polychlorinated biphenyl [25], polycyclic aromatic hydrocarbons [26], organophosphorus pesticides [27], and some kinds of metal and non-metal in water [28, 29]. The simple and fast microextraction is based on the use of an appropriate extraction and dispersive solvent. The hydrophobic solutes are enriched in the extraction solvent which is dispersed into the bulk aqueous solution. After centrifugation, determination of the analytes in the settled phase can be performed by conventional analytical techniques. However, the extraction solvent in the method is limited. The higher density than water is required for the extraction solvent, the widely used solvents are chlorobenzene, chloroform, tetrachloromethane and carbondisulfide, all of them are toxic and environment-unfriendly [30]. Considering the related problems, another simple, quick and inexpensive microextraction preparation method, i.e., solidification of floating organic drop microextraction (SFOME), has been developed for extraction of analytes from water samples. This technique is based on distribution of analytes between microliter volume of the extraction solvent (floated on the surface of the aqueous sample) and aqueous sample matrix [31].

In SFOME procedures, the suitable organic level at microliter level was floated on the surface of aqueous solution located in a glass vial. The organic solvent must have melting point near room temperature (in the range of 10–30 °C). The aqueous phase was stirred for a selected time [32]. Maximum sensitivity and precision were obtained by stirring the sampling solution until equilibrium was obtained. Then, the sample vial was transferred into a cold water bath for 5 min in order to solidify the organic solvent. The solidified solvent was transferred into a small conical vial by a spatula and melted immediately at ambient temperature. Microliter-level organic solvent was subjected to chromatographic instrument for analysis. This method cannot only avoid using toxic solvent to achieve the idea of green chemistry but also an easy technique compared with other traditional methods. In addition, the experiment time can be shortened from 48 h (Soxhlet extraction) to about 30 min to make the work efficiently [33].

In this study, we used SFOME combined with HPLC to extract six PBDE congeners from water and urine samples, and the main parameters influencing the process were optimized. To the best of authors' knowledge, this study may be the first report describing the application of SFOME as a preconcentration technique for the analysis of PBDEs from human urine samples.

Experimental

Reagent and standards

2,4,4′-tribrominated diphenyl ether (BDE 28), 2,2′,4,4′-tetrabrominated diphenyl ether (BDE 47), 2,2′,4,4′,5-pentabrominated diphenyl ether (BDE 99), 2,2′,4,4′,5,6′-hexabrominated diphenyl ether (BDE 154) and 2,2′,3,4,4′,5′,6-heptabrominated diphenyl ether (BDE 183) were purchased from J&K, Shanghai, China (www.jkchemical.com). 1,1′,2,2′,3,3′,4,4′,5,5′-decabromodi-phenyl ether (BDE 209) was obtained from Sigma–Aldrich, Shanghai, China (www.sigmaaldrich.com). Each PBDE congener was dissolved in acetonitrile to prepare a 50 mg L^{-1} stock solution. All the working standard solutions were prepared by serial dilutions of the stock solution with ultra Milli-Q water (www.millipore.com) prior to analysis. The HPLC-grade acetonitrile and methanol were purchased from Merck Company (www.merck.com.cn). 1-undecanol, 1-dodecanol, 2-dodecanol, bromohexadecane and 1,10-dichlorodecane were obtained from Acros J&K, Shanghai, China (www.jkchemical.com).

Water samples were collected from the region far away from e-waste sites (Taizhou, China) and stored in amber bottles at 4 °C until analysis. Urine samples were collected from healthy individuals and stored in polytetrafluoroethylene flasks at −20 °C until analysis. Prior to the SFOME procedures, water samples were filtered through 0.45 μm membrane to remove particulate matter, while urine samples were removed protein by methanol and then filtered through 0.45 μm membrane.

Instrumentation

PBDEs were analyzed by an Agilent 1200 HPLC equipped with a manual injector and variable wavelength detector (VWD). A Zorbax Eclipse XDB-C18 column (150 mm× 4.6 mm, 5 μm particle size) was used and all injections were performed manually with 20.0-μL sample loop. The operating conditions were as follows: mobile phase, methanol-water, 95:5 (*v*/*v*); flow rate, 1.0 mL min^{-1}; column temperature, 25 ±1 °C and the wavelength of detection, 226 nm.

Stirring of the solution was carried out by a model HJ-6A magnetic heater-stirrer with 8 mm×4 mm string bar, purchased from Jiangsu Jintan Medical Instrument Factory, Jiangsu, China (www.jt-jinyid.com). A 40 mm×60 mm bottle placed on the heater-stirrer was employed to control temperature of the samples.

Extraction procedure

An aqueous or protein-removed urine solution, containing the mixed PBDE congeners at the concentration of 1 μg L^{-1} respect to five congeners and BDE 209 at the concentration of 10 μg L^{-1}, was used in the optimization

studies. Forty milliliters of the standard solution were transferred into 43 mL vial and microliter volume of 2-dodecanol was placed on the surface of the solution by a 25-μL syringe. The vial was sealed and transferred into the water bath and the stirrer was turned on. When the desired extraction time elapsed, the sample vial was transferred into an ice breaker and the organic solvent was solidified after 10 min. Then, the solidified solvent was transferred into the conical vial and melted quickly. Finally, 5.0 μL of the extractant was injected into the HPLC for quantification. Figure 1 shows schematic diagram of the SFOME apparatus.

Results and discussion

Selection of extraction solvent

An appropriate extraction solvent should meet the following requirements: (1) lower density than water, (2) low volatility and low water solubility, (3) good chromatographic behavior, (4) high extraction capability of analytes and (5) melting point near the room temperature (10–30 °C) [31]. According to the previous considerations, 1-undecanol (melting point, 13–15 °C), 1-dodecanol (22–24 °C), 2-dodecanol (17–18 °C), bromohexadecane (17–18 °C) and 1,10-dichlorodecane(14–16 °C) were investigated in this study. For bromohexadecane, its hydrophobicity was so strong that it can't be dissolved in the common organic solvent, so it is not suitable for HPLC analysis. The extraction efficiency and chromatographic performance of 1-undecanol, 1-dodecanol and 1,10-dichlorodecane were very poor . 2-dodecanowas found to give the best extraction efficiency, while its chromatographic peak was easily distinguished from analytes of interest. Also, because of its stability, low vapor pressure and low water solubility at the extraction conditions, 2-dodecanol was thus selected as the extraction solvent in this experiment.

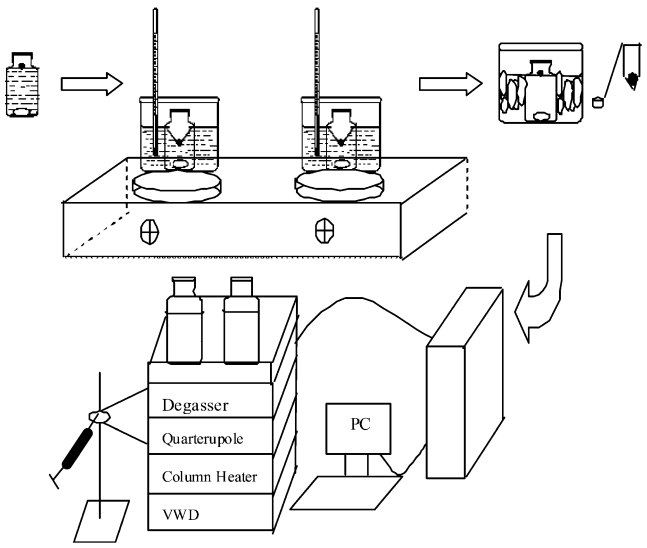

Fig. 1 Schematic diagram of the SFOME apparatus

Effect of extraction solvent volume

The volume of extraction solvent was another important factor in extraction efficiency of analytes. The effect of extraction solvent volume on extraction efficiency was evaluated by using different volumes of 2-dodecanol (15.0, 20.0, 25.0, 30.0 and 35.0 μL) in this experiment. The relationship between volume of extraction solvent and peak areas is shown in Fig. 2. At larger extraction solvent volume, the settled phase volume increased too, which led to the decreasing of peak area. Thus, the volume of extraction solvent was selected to be 25 μL in this study.

Effect of sample volume

The effect of sample volume on analytical performance was studied in the range of 10–43 mL (Fig. 3). The results showed that by increasing of sample volume, the peak areas also increased from 10 to 40 mL. However, with the further increase of volumes (>40 mL), the sample vial became unstable and resulted in decreasing of extraction efficiency. Based on LLE equations, rate of the analytes transported into microdrop is directly related to the interfacial area between two liquid phases and inversely related to the organic-phase volume. Thus, by increasing the drop volume, the effect of the interfacial area predominates and the analytical signals are increased. With further increasing

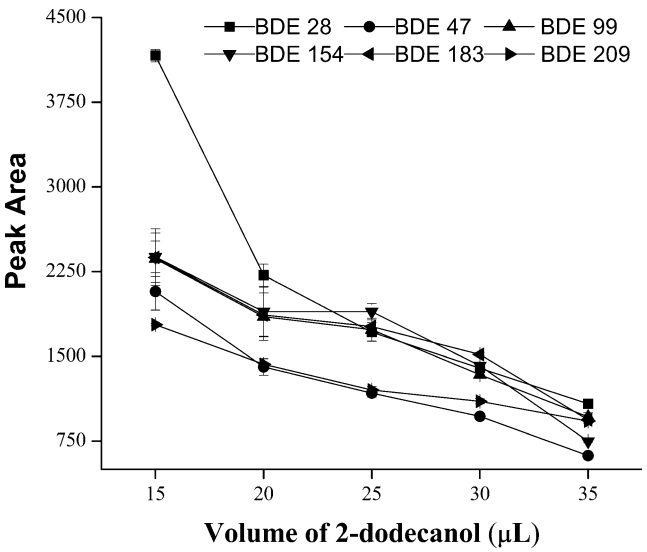

Fig. 2 Effect of volume of extraction solvent. Conditions: stirring rate, 900 rpm; sample solution temperature, 60 °C; sample volume, 40 mL; extraction time, 25 min and without salt addition

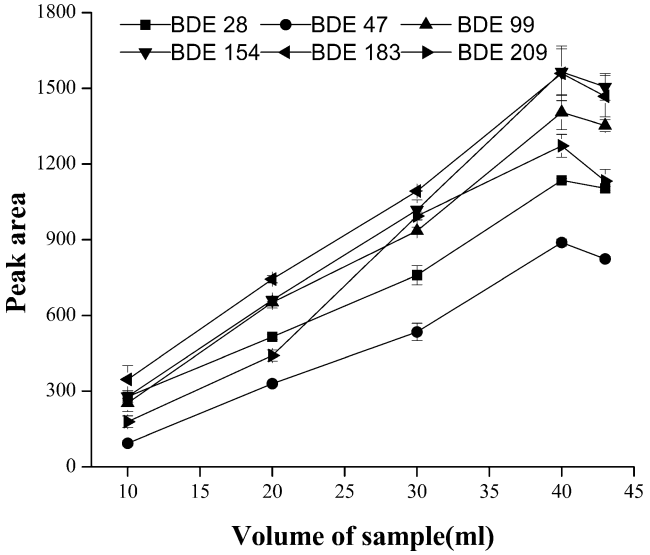

Fig. 3 Effect of sample volume. Conditions: stirring rate, 900 rpm; sample solution temperature, 60 °C; extraction solvent volume, 25 μL; extraction time, 25 min and without salt addition

of the microdrop volume, the effect of the solvent volume was predominated and the analytical signals are decreased [31]. Therefore, the volume of 40 mL was chosen as the optimal sample volume.

Effect of sample solution temperature, stirring rate, extraction time, ionic strength

The effects of sample solution temperature, stirring rate, extraction time, ionic strength on extraction were also studied. After optimization, at 60 °C sample solution temperature, at 900 rpm stirring rate, 25 min of extraction time, and without salt addition were applied in this experiment. More details about the optimization can be found in the supplementary material.

Analytical performance

For the purpose of quantitative analysis, the calibration curve was obtained under the optimized SFOME-HPLC conditions. The precision of the method was evaluated by carrying out five independent measurements of the studied compounds at 5 μg L^{-1}. Several factors, including linearity ranges, correlation coefficients (R^2), and limits of detection were evaluated. As listed in Table 1, the linearity ranges were 0.5–75 μg L^{-1} for BDE 28, and BDE 47, 0.5–50 μg L^{-1} for BDE 99, BDE 154 and BDE 183, and 5–500 μg L^{-1} for BDE 209, respectively. The correlation coefficients (R^2) ranged from 0.9960 to 0.9999. The limits of detection (at S/N=3) were in the range of 0.01–0.04 μg L^{-1}.

As reported by Zanjani et al. (2007), preconcentration factors (PF) were calculated based on the following equation:

$$PF = \frac{C_{o.f}}{C_{aq.ini}}$$

First, an extraction was carried out from a spiked water or urine sample ($C_{aq.ini}$ = 10 μg L^{-1}) by 25 μL 2-dodecanol followed by 5.0 μL injection of the extractant into HPLC. Then a series of standard solutions were prepared in 2-dodecanol as the extraction solution. Finally, by plotting the relative peak area versus concentration for each congener in the standard solutions, the concentrations of PBDE congeners in the organic phase (Co.f) were calculated. From these data, percent extraction (PE) of each PBDE congener extracted into the organic solvent was calculated, using the following equation [31]:

$$PE = \frac{100 \times \left(C_{o.f} V_0\right)}{C_{aq.ini} V_{aq}}$$

The results are summarized in Tables 1 and 2. The PF values ranged from 921 to 1,462, and the PE values varied between 46% and 74%. The previous results demonstrated that SFOME technique had a high preconcentration capacity for PBDE congeners, which increased about 5–20 times compared with those (in the range of 50–200) obtained by technique of dispersive liquid-liquid microextraction [34].

Real sample analysis

The SFOME technique was applied for the determination of PBDEs in two water and urine samples to clarify applicability and reliability of this method. The results showed that the residues of PBDE congeners were all at

Table 1 Analytical performance and preconcentration factors of PBDEs by SFOME technique

LR, R^2, LODs, PF and PE denote abbreviation of linear range, correlation coefficient, limits of detection, preconcentration factor and percent extraction, respectively

Chemical	LR (μg L^{-1})	R^2	LOD (μg L^{-1})	PF	PE (%)
BDE 28	0.5–75	0.9960	0.01	1462	74
BDE 47	0.5–75	0.9969	0.01	1013	50
BDE 99	0.5–50	0.9994	0.04	1210	60
BDE 154	0.5–50	0.9998	0.04	1145	56
BDE 183	0.5–50	0.9999	0.04	1303	66
BDE 209	5–500	0.9980	0.04	921	46

Table 2 Determination of PBDEs in real samples

Congeners	River water 1#			River water 2#			Urine sample		
	Added (μg L^{-1})	Found (μg L^{-1}) ± RSD (%) (n=3)	Relative recovery (%)	Added (μg L^{-1})	Found (μg L^{-1}) ± RSD (%) (n=3)	Relative recovery (%)	Added (μg L^{-1})	Found (μg L^{-1}) ± RSD (%) (n=3)	Relative recovery (%)
BDE 28	5	4.8±1.8	96	5	4.3±3.4	86	5	4.6±2.1	92
	10	8.1±3.9	81	50	43.5±0.9	87	50	48.2±1.3	96
BDE 47	5	5.1±4.6	102	5	5.1±4.6	102	5	5.7±4.2	114
	10	9.1±6.2	91	50	47.2±4.0	94	50	52.9±3.5	106
BDE 99	5	5.2±7.3	104	5	5.7±4.5	114	5	5.4±3.1	108
	10	11.3±4.8	113	50	59.1±1.3	118	50	58.1±2.1	116
BDE 154	5	4.8±4.4	96	5	4.6±1.3	92	5	5.8±5.1	116
	10	11.7±5.5	117	50	58.4±0.7	117	50	53.4±1.8	107
BDE 183	5	4.9±6.3	98	5	4.9±1.6	98	5	5.9±7.8	118
	10	11.7±0.8	117	50	54.3±1.3	109	50	50.3±1.1	101
BDE 209	5	5.1±1.4	102	5	5.4±4.1	108	5	5.1±3.4	102
	10	11.5±0.8	115	50	58.2±5.0	116	50	56.2±4.2	112

below detectable level (<0.01 μg L^{-1}) in water and urine sample with exception that BDE 99 and BDE 183 were detected to be 1.0 and 2.1 μg L^{-1}, respectively, in river water 1#. The previous samples were then spiked with standards of PBDE congeners at different levels to assess the matrix effect. The spiking recoveries of the target PBDEs in the real samples are summarized in Table 3. In the spiked levels of 5, 10 and 50 μg L^{-1}, the relative recoveries ranged from 81% to 118% in water samples. In the spiked level of 5 and 50 μg L^{-1}, the relative recoveries were in the range of 92%–118% in human urine samples. The previous results demonstrated that the SFOME method could be used in trace PBDE analysis for the environmental water and human urine samples. Figure 4 shows the chromatograms attained from blank (a) and spiked urine samples (b) at the concentration level of 50 μg L^{-1} for PBDEs according to SFOME method.

Table 3 Comparison of SFOME with SDME, DLLME and SPME techniques for determination of PBDEs in water samples

Methods	LODs (μg L^{-1})	RSD (%)	PF	References
SDME–HPLC	0.70	4.4	10.6	[34]
SPME–GC–MS	0.03–0.10	8–14	–	[35]
DLLME-HPLC	0.0124–0.0556	3.8–6.3	268–305	[24]
SFOME-HPLC	0.010–0.040	0.8–7.8	921–1462	Represented method

SDME, SPME and DLLME indicate abbreviation of single-drop microextratction, solid-phase microextraction and dispersive liquid-liquid microextraction, respectively

Comparison with other methods

Extraction and determination of PBDEs in water samples by the SFOME-HPLC method was compared with other methods. As summarized in Table 3, lower LODs and RSDs in SFOME-HPLC were obtained. Moreover, the present technique provided higher PF in comparison with SDME-HPLC and DLLME-HPLC. In general, it was a very simple, rapid, inexpensive and environmentally friendly technology.

Conclusions

This study illustrated the successful application of SFOME technique that allows the separation and preconcentration of

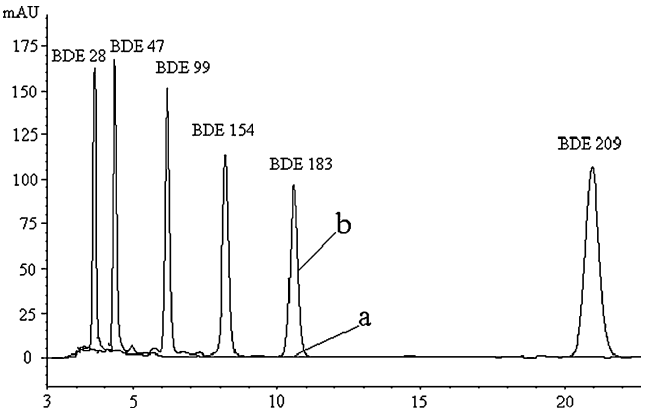

Fig. 4 Chromatograms attained from the blank (**a**) and spiked urine samples (**b**) at the concentration level of 50 μg L^{-1} for PBDEs according to SFOME method

PBDEs present at low concentration levels in environmental water and human urine samples. In comparison with other extraction methods, the present method only requires less-toxic solvent and also has good relative recovery. Additionally, a detection limit at ng.L^{-1} level was achieved due to the higher PF values (921–1,462) compared with dispersive liquid-liquid microextraction (50–500) and single-drop microextraction (20–200) techniques. The main drawback of this pretreatment technique is the limitation on selection of extraction solvent because of overlapping of solvent peak with some analyte peaks. However, many solvents are available that have suitable melting points. Overall, it is an environmentally friendly technique and most importantly, we can shorten the experiment from 48 h (soxhlet extraction) to less than 30 min to make the work efficient. Therefore, this method has a great potential in the routine multi-residual analysis of PBDEs at trace levels in environmental water and human urine samples.

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