



Research Article

Determination of polybrominated diphenyl ethers and metabolites by single-drop microextraction and GC–MS/MS



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Abstract

A simple, fast and virtually solvent-free method for the simultaneous determination of 13 polybrominated diphenyl ethers (PBDEs) congeners and their metabolites in aqueous samples was developed using single-drop microextraction (SDME) coupled with gas chromatography-tandem mass spectrometry (GC–MS/MS). Optimization over GC–MS/MS parameters of both electron ionization (EI) and negative chemical ionization (NCI) sources were studied and compared with a result that EI is more sensitive and selective, especially for lower brominated congeners. Optimization of SDME was subsequently conducted. Under optimum conditions (1 μL drop of chlorobenzene in 2 mL sample solution, pH 5.0, 30 min extraction time, stirring rate of 400 rpm), the assay linearity of target PBDEs was confirmed over 2–3 orders of magnitudes, with a coefficient of determination (r^2) ranged from 0.9929 to 0.9998. The limit of detection (LODs) and limit of quantification (LOQs) for lower brominated congeners were found to be better than $6 \text{ ng}\cdot\text{L}^{-1}$ and $20 \text{ ng}\cdot\text{L}^{-1}$, respectively. Real sample analysis with an isotopic internal standard was carried out. The recoveries, relative standard deviation (RSD) and enrichment factors obtained ranged from 73.4 to 128.0%, 7.52 to 25.0% and 8 to 60, respectively, indicating the developed method is suitable for the determination of PBDE congeners in aqueous samples.

Keywords GC–MS/MS · Single-drop microextraction (SDME) · Metabolites · Polybrominated diphenyl ethers (PBDEs)

1 Introduction

Polybrominated diphenyl ethers (PBDEs) constitutes 209 possible congeners which are widely used as brominated fire retardants in a variety of commercial or household products, such as textiles, plastic, furniture, and electronic components [1]. However, PBDEs may enter the environment through emission from the manufacturing, recycling and disposal processes of these products [2–4]. As lipophilic and persistent chemicals, PBDEs bind strongly to soil, sediments and airborne particulate matter, and tend to accumulate in the environment for years without

significant degradation [5]. Also, PBDEs are bio-accumulative and biomagnified in adipose tissues of animals and human, which leads to growing concerns. Toxicology studies have speculated the hazards of PBDEs toward human health in terms of neurotoxicity [6–8], thyrotoxicity [9–11], estrogenicity [12–14], carcinogenicity, [15–17] cellular toxicity [18, 19], and cognitive disorder [20, 21]. In view of the risk of human exposure to PBDEs in the environment, the U.S. EPA have assigned an oral slope factor of $7 \times 10^{-4} \text{ mg/kg/day}$ for carcinogenic risk. Thus, PBDEs have emerged as one of the major environmental pollutants.

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The congeners of PBDEs show different properties. For instance, lower brominated congeners are more persistent and bioaccumulated in the environment, while higher brominated congeners tend to bind to sediment or soil particles [2]. Therefore, congener-specific analysis is of researchers' interest. To achieve this, the identification and quantification of PBDEs in various kinds of environmental samples are required with specific analytical techniques with high selectivity, sensitivity and precision. Current analytical determination methods are mostly based on gas chromatography for separation of target compounds, coupling with mass spectrometry (GC-MS) for targets detection. More recently, to achieve better selectivity, isotope dilution and internal standard with gas chromatography/high resolution mass spectrometry (GC/HRMS) for samples of water, soil, sediment and tissues were employed in the U.S. EPA Method 1614 [22] to detect PBDEs. Electron ionization (EI) was used as the ionization source in this method, as well as in some other studies [23, 24] due to the abundant generation of highly specific molecular ions ($[M]^{+}$) or high-mass fragment ions (i.e. $[M-Br]^{+}$). However, the use of strong electron energy may lead to a loss of unstable molecular ions. Negative chemical ionization (NCI) as a popular alternate, has been proven to be highly sensitive and selective for the determination of electrophilic molecules such as PBDEs [25, 26]. Concerns do exist over its specificity because quantification is dominated by non-specific bromide ions ($[Br]^{-}$, m/z 79 and 81). Moreover, only ^{13}C isotope labeled PBDEs are commercially available for GC-EI-MS, which makes it difficult to find suitable internal standard for GC-NCI-MS if bromide ions are the only quantification ions. Past studies have compared the use of GC-EI-MS and GC-NCI-MS for PBDEs determination [26–28], but few have investigated the use of a gas chromatography tandem mass spectrometry (GC-MS/MS) which is believed to surpass GC-MS over analytical selectivity and specificity. GC-MS/MS provides adequate precursor and product ion selection that allows identification at trace levels in complicated matrixes. The product ion spectra could eliminate inferences and reduce chemical background noises, which may decrease the detection limit. Thus, the present study utilizes GC coupled with triple quadrupole mass spectrometry and compares the performances of EI and NCI as ionization sources for congener-specific PBDEs analysis after the optimization of instrumental parameters.

Due to the complicated matrices and the relatively low concentrations of PBDEs in the environment, different sample treatment procedures such as extraction, concentration, cleanup and fractionation may be required accordingly before the final instrumental analysis. For liquid samples, conventional sample treatment employs liquid-liquid extraction [29–31], and solid-phase extraction

[32–35]. Although these extraction techniques were capable for the extraction of PBDEs with a decent recovery, the main drawbacks such as time consuming and highly manipulated procedures, limited their applications. In the present work, the single drop microextraction (SDME) was employed as sample treatment method to be coupled with GC-MS/MS so as to achieve a simple, fast and virtually solvent-free method for PBDEs determination in aqueous samples. SDME is an analytical technique which uses only a small amount of water-immiscible solvent for concentrating analytes from aqueous samples [36]. Because of its advantages over simplicity, low cost and the potential for automation or high-throughput designs, it has been a rapidly developing technique for various applications such as the extraction of volatile organic compounds [37], chlorobenzenes [38], phenols [39, 40] and bisphenol A [41] in aqueous media. Herein, SDME was performed by suspending a drop of organic solvent directly from the tip of a micro-syringe needle, which was immersed in a stirred aqueous solution. The extraction drop was retracted back into the syringe after a prescribed period of time, then it was transferred to GC-MS/MS for further analysis without other apparatuses [42]. Since most PBDEs have high log-Kow value, SDME would be a suitable extraction method for PBDEs detection in water samples.

This study optimized GC-MS/MS conditions in order to characterize their relative effects on sensitivity and specification. The performances of EI and NCI ionization sources for congener-specific analysis were compared. Direct immersion SDME was performed to extract PBDEs from aqueous samples. The operation parameters were optimized to achieve higher enrichment factors that consequently allowed better sensitivity. Analysis of real samples were conducted based on the optimized conditions and satisfied results were obtained for 8 PBDEs, 3 methylated PBDEs and 2 hydroxylated PBDEs.

2 Materials and methods

2.1 Reagents and apparatus

Standards of PBDEs and metabolites (details in Table 1) were purchased from AccuStandard (New Haven, CT, USA, 99.9% for BDE209 and the rest of PBDEs with concentration of $50 \text{ mg}\cdot\text{L}^{-1}$ in hexane). The internal standard, ^{13}C labeled 2,2',3,4,4',5-Hexabromodiphenylether ($(^{13}C_{12})$ BDE138), was purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA). Chromatographic grade n-hexane, methanol and acetone, were from Burdick & Jackson (Muskegon, MI, USA), CNW Technologies (Düsseldorf, Germany) and Merck (Darmstadt, Germany), respectively. Analytical grade chlorobenzene, toluene,

Table 1 GC retention time, ion pairs and optimum EI parameters of target PBDE congeners

PBDE congeners	Retention time (min)	Pair I				Pair II			
		Precursor ions (m/z)	Product ions (m/z)	Electron energy (eV)	Collision energy (V)	Precursor ions (m/z)	Product ions (m/z)	Electron energy (eV)	Collision energy (V)
2,4,4'-Tribromodiphenyl ether (BDE28)	5.57	406	246	65	17	406	299	65	19
2'-hydroxy-2,4,4'-Tribromodiphenyl ether (2'-OH-BDE28)	6.62	424	264	65	17	424	236	65	21
2'-methoxy-2,4,4'-Tribromodiphenyl ether (2'-MeO-BDE28)	6.67	436	342	65	19	436	276	65	13
2,2',4,4'-Tetrabromodiphenyl ether (BDE47)	7.21	486	326	65	18	486	245	65	37
3-hydroxy-2,2',4,4'-Tetrabromodiphenyl ether (3-MeO-BDE47)	8.99	516	356	65	19	516	341	65	31
2,2',4,4',6-Pentabromodiphenyl ether (BDE100)	9.09	566	406	65	17	566	484	65	13
3-hydroxy-2,2',4,4'-Tetrabromodiphenyl ether (3-OH-BDE47)	9.33	502	342	65	18	342	262	65	21
2,2',4,4',5-Pentabromodiphenyl ether (BDE99)	9.76	566	406	65	21	566	486	65	13
6'-methoxy-2,2',4,4',5-Pentabromodiphenyl ether (6'-MeO-BDE99)	11.35	596	436	65	23	596	502	65	21
2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE154)	11.92	644	484	65	18	484	404	65	25
2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE153)	13.15	644	484	65	20	484	406	65	25
2,2',3,3',4,4',6,6'-octabromodiphenyl ether (BDE197)	16.86	642	533	65	40	802	642	65	33
2,2',3,3',4,4',5,5',6,6'-deca-bromodiphenyl ether (BDE209)	20.76	800	642	65	46	958	800	65	17
(¹³ C ₁₂)BDE138	14.78	656	496	65	20	496	416	65	25

xylylene, cyclohexane, sodium chloride, sulfuric acid and sodium hydroxide were supplied by the Guangzhou Chemical Reagent Factory (Guangzhou, China).

Except for BDE154, BDE153, BDE197 and BDE209, individual stock standard solutions (1 mg·L⁻¹) of each target compound were prepared in hexane. The 100 mg·L⁻¹ stock solution of BDE209 was prepared by dissolving 1 mg of the standard with hexane in a 10 mL volumetric flask. A mixed-standard solution of all target compounds with different concentrations were prepared by diluting the above stock solution in acetone (BDE28, BDE47, 2'-OH-BDE28, 2'-MeO-BDE28 and 3-MeO-BDE47: 10 µg·L⁻¹; 3-OH-BDE47, 6'-MeO-BDE99, BDE100 and BDE99: 100 µg·L⁻¹; BDE154, BDE 153 and BDE197: 1 mg·L⁻¹; BDE209: 10 mg·L⁻¹). The working standard solutions were freshly prepared by diluting the mixed-standard solution in ultra-pure water, spiked with the internal standard at a concentration of 100 µg·L⁻¹.

Ultra-pure water was supplied by Milli-Q apparatus from Merck Millipore (Darmstadt, Germany).

2.2 GC-EI-MS/MS and GC-NCI-MS conditions

A Thermo Fischer Trace 1310-TSQ Quantum XLS Gas Chromatography-Triple Quadrupole Mass Spectrometer (GC-MS/MS), with a TG-5HT GC column (15 m × 0.25 mm I.D. × 0.1 µm) was employed. The GC injection port was set as the splitless mode for 0.8 min, holding isothermally at 280 °C. The injection volume was 1 µL. High purity helium (99.99%) was used as the carrier gas at a flow rate of 1.5 mL·min⁻¹ under the constant flow rate mode. The temperature program was set as follows: 120 °C isothermal for 2 min, 30 °C·min⁻¹ to 200 °C, 3 °C·min⁻¹ to 230 °C, 40 °C·min⁻¹ to 300 °C, and 300 °C isothermal for 6 min. When GC-MS/MS was operated with EI source, the selected reaction monitoring (SRM) mode was used,

with a source temperature of 300 °C, electron energy of 65 eV, collision energy of 13–46 V. When operated with NCI source, selected ion monitoring (SIM) mode was conducted, with a source temperature at 200 °C, electron energy of 70 eV, methane as the reaction gas at a constant flow rate of 2.7 mL/min. Masses of the characteristic ions and the brominated ions for each congener were monitored according to the ionization sources. Identification of each congener was based on the selected m/z values determined and characterized experimentally, at the corresponding retention time (details in Table 1). Internal standard calibration was used for quantification of target compounds.

2.3 Procedure of single-drop microextraction

The SDME procedure followed the proposed method by Jeannot and Cantwell [42]. The optimized SDME procedure was as follows: in a 2 mL GC vial, a 1 μ L drop of chlorobenzene suspended from the tip of a GC micro-syringe needle was immersed in a 2 mL sample solution which was previously adjusted to pH 5.0, at a constant stirring rate of 400 rpm. After 30 min, the extraction solvent was withdrawn back into the micro-syringe, and then be directly injected to GC-MS/MS for further analysis.

3 Results and discussion

3.1 Optimization of GC-EI-MS/MS and GC-NCI-MS conditions

Due to the fact that the sensitivities of different compounds differ, 'normalized response' was calculated and used to interpolate the optimization procedure so that the responses for all the compounds can be brought into the same scale. For the same target compound, normalized response was calculated by dividing peak area of selected ion pair in an individual condition by the maximum peak area within the same optimization procedure. It was used for the SDME optimization as well.

3.1.1 Selection of ion pairs

Both EI and NCI sources are capable for the determination of PBDEs. Nevertheless, NCI could not deliver product ion spectra for PBDEs detection since only fragment ions $[\text{Br}]^-$ (m/z 79 and 81) and $[\text{HBr}_2]^-$ (m/z 159, 161 and 163) meet the criteria peak intensity (Supplementary Fig. S1 b)), but bromine ions could not deliver further fragmentation, thus the product ion spectra was not feasible for NCI. When operated with EI, precursor ions are either molecular ions $[\text{M}]^+$ or fragment ions with the loss of two

bromine atoms $[\text{M}-\text{Br}_2]^+$ (Fig. S1 a)). Two ion-pairs were selected for each target congener, according to their relative abundances (Table 1).

3.1.2 Optimization of EI conditions

Since the ionization potential of most organic compounds is about 7–15 eV, the EI electron energy of 70 eV is sufficient to generate plenty of fragments, but risking a loss of molecular ions or high-mass fragments which are often selected as precursor ions. Tuning down the electron energy could increase the abundance of these precursor ions and consequently enhance the intensity of product ions. Therefore, the electron energy was optimized between 35 and 70 eV (Fig. 1a and b). Results show that responses of lower brominated congeners fluctuate mildly between 35 and 65 eV due to the stabilities of their molecular ions within this range. The electron energy over 65 eV leads to a loss of response for most target congeners. Best ionization efficiency for most target congeners was achieved at 65 eV. An improvement of ionization efficiency for higher brominated congeners was observed when operated at 70 eV, indicating the increasing stability with more bromine substituents. Hence, for compromise, the electron energy was set to 65 eV for further study.

Due to the high boiling point of PBDEs (310–425 °C), the ionization efficiency could be affected by the source temperature of EI. Thus, the influence of source temperature from 200 to 300 °C on ionization intensity was investigated. Seeing from Fig. 1c, significant improvement of intensity was observed with the increasing source temperature. Due to the limitation of the instrument itself, 300 °C was selected as source temperature.

To generate product ions from the precursor ions in the collision cell, helium was introduced with a certain pressure. The optimization of collision energy for each precursor was carried out to improve the sensitivity (details in Table 1).

3.1.3 Optimization of reaction gas flow rate for NCI

Methane was used as the reaction gas. In order not to interfere the high vacuum, the flow rate of methane was optimized within the range of 1.5–2.7 mL/min to improve ionization. Results demonstrate enhancing responses for most congeners with increasing flow rate (Fig. 2). Nevertheless, a slight decrease on the ionization intensity for higher brominated congeners was observed. For further NCI analysis, optimum flow rate was fixed at 2.7 mL/min.

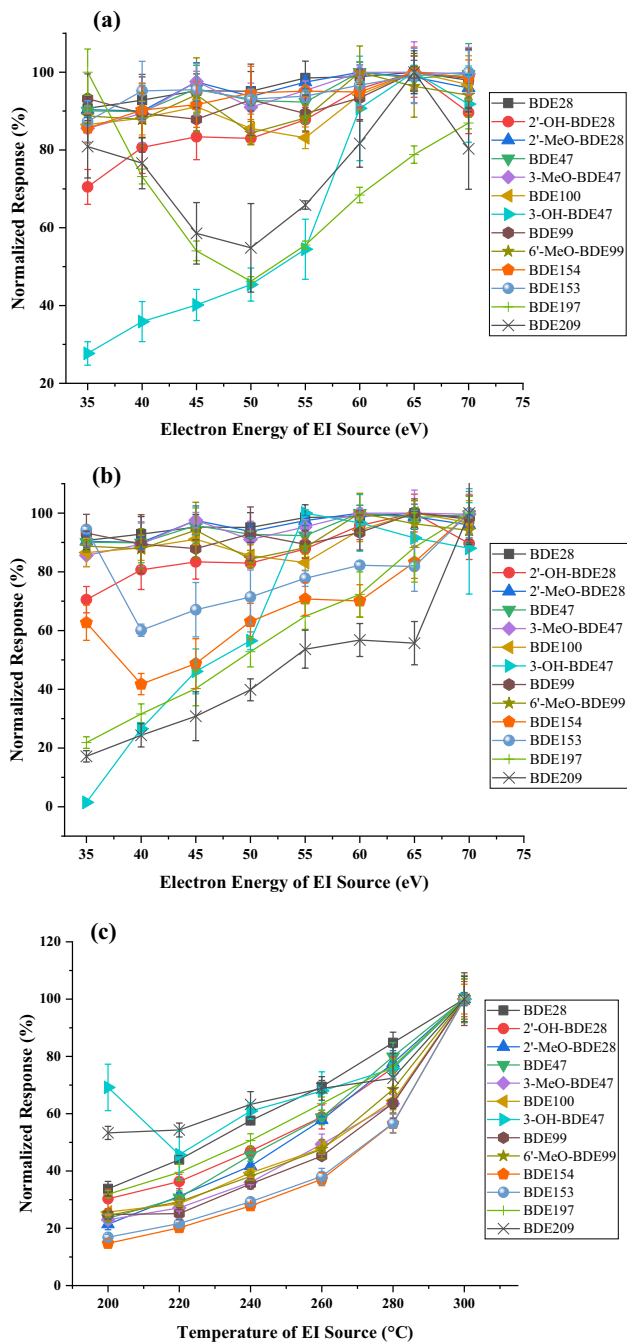


Fig. 1 Effects of EI conditions on ion intensity, **a** electron energy (the first pair of ions); **b** electron energy (the second pair of ions); **c** source temperature (using mix-standard solution)

3.2 Comparison of EI with NCI

The comparison of GC-EI-MS/MS and GC-NCI-MS was conducted under the above optimum conditions (Fig. 3). It can be seen that for GC-EI-MS/MS, better performances in terms of peak area and S/N ratios are found for penta- or lower brominated congeners while GC-NCI-MS, gaining

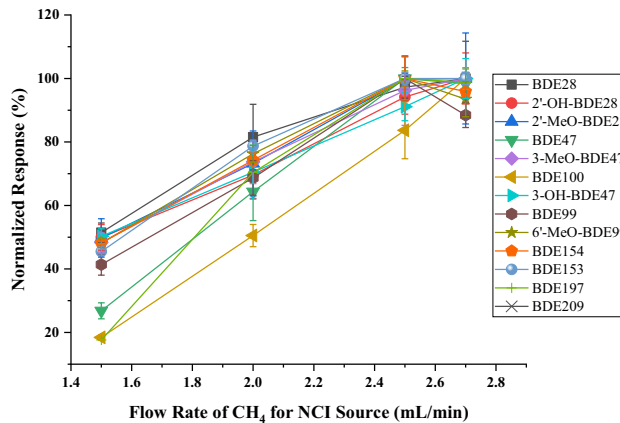


Fig. 2 Effects of methane flow rate on ionization intensity

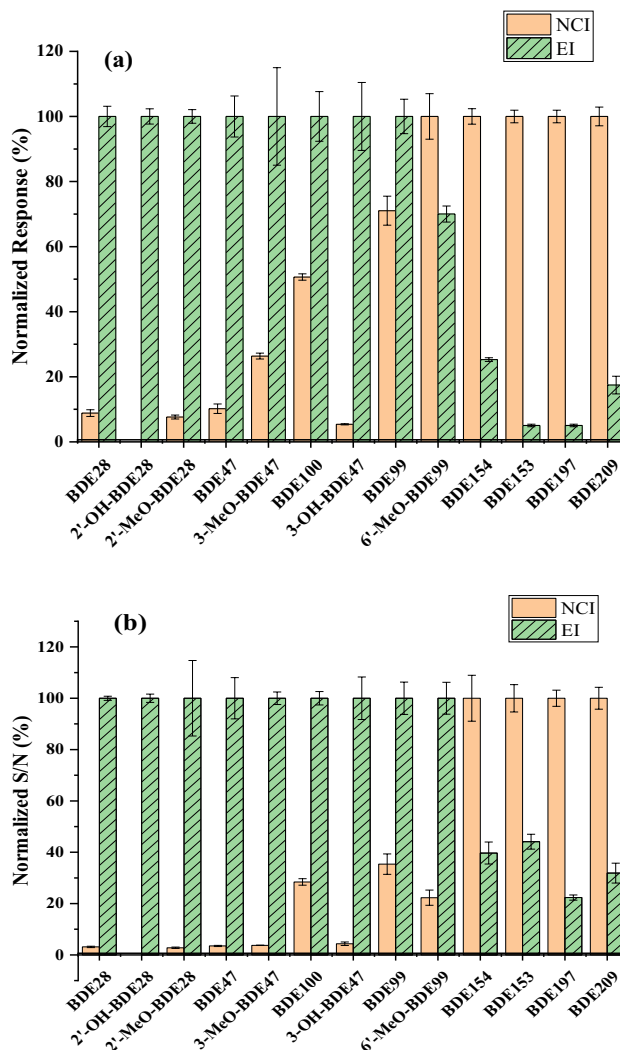


Fig. 3 Comparison of EI and NCI for **a** normalized peak area and **b** normalized S/N ratio for target PBDE congeners and metabolites

from its specificity for brominated species, delivers significant increase in sensitivity for higher brominated congeners. This opposite pattern is a consequence of the different fragmentation schemes. EI provides certain ionization energy that does not distinct between congeners. Hence, to compromise the major congeners, the sensitivity of higher brominated congeners would be sacrificed. NCI, on the other hand, focuses on the bromine ions. With more bromine ions, better specificity and sensitivity are gained, so it would be preferable for the determination PBDEs with 6 or more bromine atoms. It should be pointed out that even without the help of tandem mass, the performance of GC-NCI-MS surpass GC-EI-MS/MS for highly brominated congeners. Nevertheless, in the case of 6'-MeO-BDE99, NCI provides evidently higher intensity while EI presented much better S/N ratio. This indicates that tandem mass spectra do avoid interferences and reduce background noise remarkably, benefiting the selectivity when analyzing samples with complicated matrixes. Furthermore, 2'-OH-BDE28 and 2'-MeO-BDE28 have very close retention time, making it impossible to detect 2'-OH-BDE28 by NCI. In contrast, EI could separate these two congeners with different selected ion pairs. This reveals another advantage of GC-EI-MS/MS, that is, tandem mass could achieve separation for chemically or structurally similar compounds which could not be separated completely. Last but not least, with the sufficient ionization and fragmentation, EI Provides detailed structural information such as the molecular weights and the sequential loss of bromine atoms.

To summarize, the choice of ionization source depends on the target PBDE congeners. If highly

brominated congeners are the only targets in a simple matrix, GC-NCI-MS would be the best approach as a more commonly accessible instrument. For metabolism, distribution or other studies that require a comprehensive understanding of all PBDE congeners, especially for samples with complicated matrixes, GC-EI-MS/MS would be a better choice.

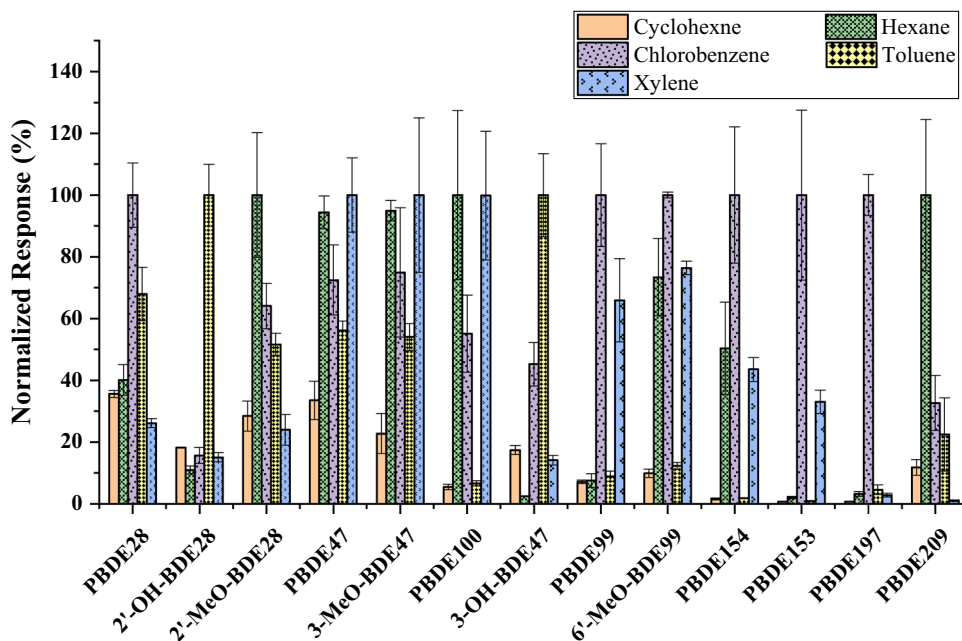
3.3 Optimization of SDME

Based on the above study, GC-EI-MS/MS was selected for the further study on the determination of target PBDE congeners in aqueous samples.

3.3.1 Optimization of extraction solvents

The choice of the extraction solvent is crucial for SDME as it greatly affects the enrichment efficiency. It would follow the basis: (a) good solubility for target compounds and water-immiscible; (b) with strong surface tension to maintain a stable extraction drop; (c) without interferences during the instrumental analysis. Therefore, n-hexane, cyclohexane, toluene, xylene and chlorobenzene were selected for the optimization. As shown in Fig. 4, toluene delivers good extraction results for hydroxylated PBDEs while n-hexane would be the first choice for methylated PBDEs. Benefiting from the halogen group and the structural similarity with target PBDE congeners, chlorobenzene demonstrates better extraction results in general. Thus, it was selected for SDME procedure.

Fig. 4 Comparison of different extraction solvents for SDME



3.3.2 Optimization of stirring rate

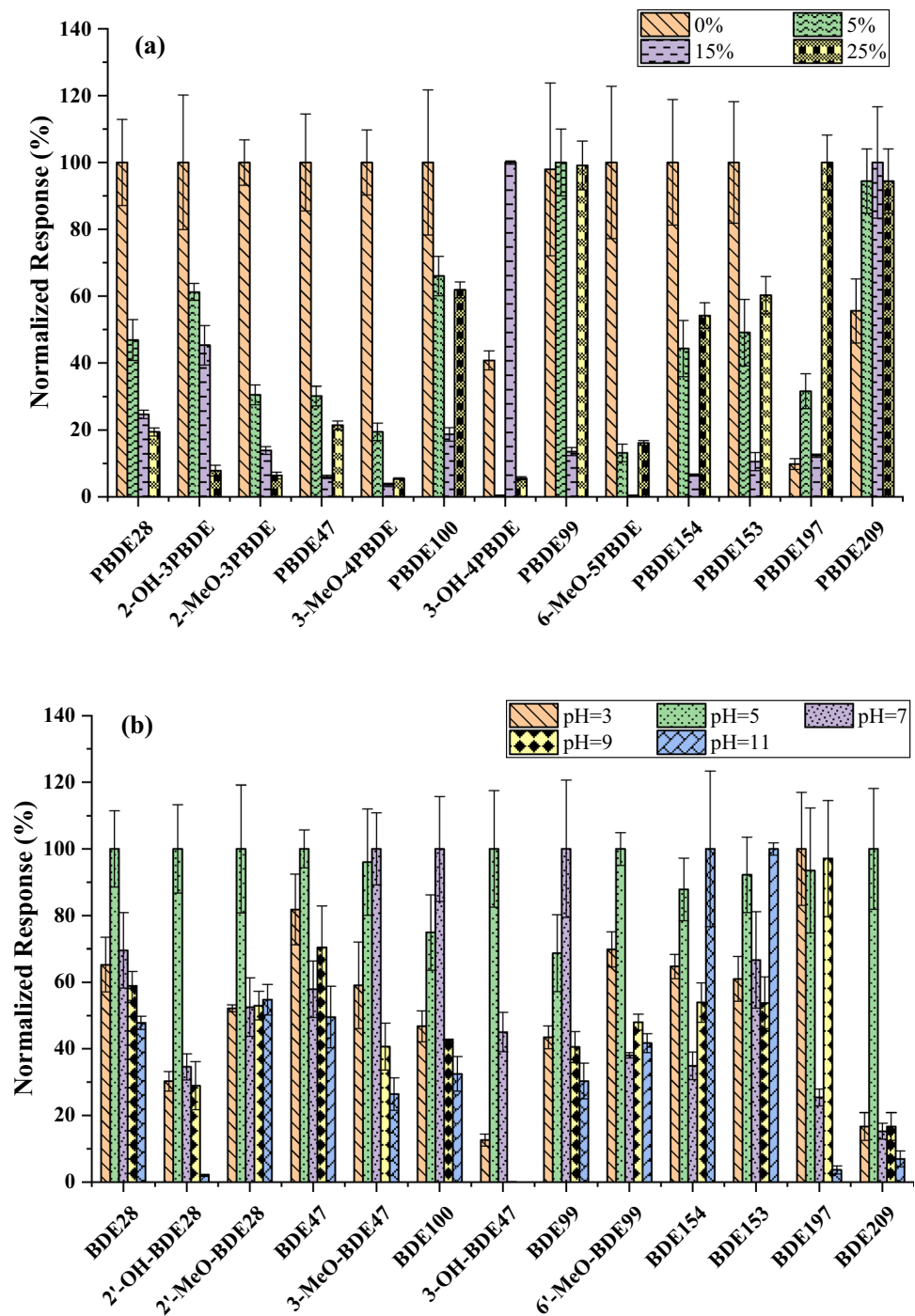
During the SDME procedure, a suitable stirring rate is important to maximize the mass transfer efficiency. By testing stirring rates from 60 to 600 rpm, results demonstrate the optimized stirring rate was 400 rpm (Supplementary Fig. S3). Decrease occurred with a stirring rate of 60 or 200 rpm due to the inefficient mass transfer. Increasing the stirring to 600 rpm might enhance dissolution of

the extraction solvents in the aqueous media, which leads to a loss of extractants. The extraction drop became unstable when operated at 800 rpm.

3.3.3 Effects of salinity and pH

A certain amount of NaCl was added to adjust the salinity from 0 to 25% to investigate the effect of ionic strength on the extraction efficiency (Fig. 5a). For highly

Fig. 5 Effect of **a** salinity and **b** pH on normalized peak area for PBDE congeners and metabolites



brominated congeners, slight enhancement on extraction was found with 25% NaCl because of their decreased solubility in matrixes with strong ionic strength. The extraction of methoxylated or hydroxylated PBDEs on the other hand, was not benefited from the addition of NaCl. The interaction of NaCl with methoxy group and hydroxy group possibly kept the targets stay in the sample solutions rather than be extracted. In general, the addition of inorganic salts is not necessary for an efficient SDME procedure.

The pH value of sample was also optimized. From Fig. 5b), the optimum pH is 5 for most of the target congeners, changing the pH value draws only slight differences on the extraction of PBDEs.

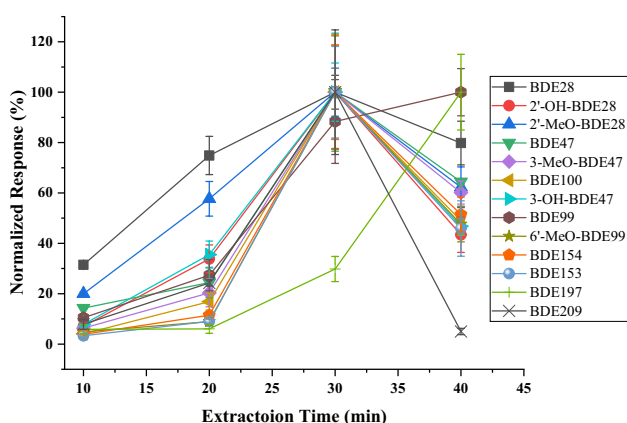


Fig. 6 Effect of SDME extraction time on normalized peak area for PBDE congeners and metabolites

3.3.4 Effect of extraction time

The duration of suspending a micro-drop was optimized to achieve sufficient extraction as well as to obtain reasonable sample throughput. Extraction time in the range of 10–40 min was tested. According to the results shown in Fig. 6, the response of most congeners peaked with an extraction time of 30 min, indicating the equilibrium of extraction has achieved. Extending the extraction time may cause a loss of the extraction solvent. Thirty minutes was chosen as optimum extraction time.

3.4 Determination of PBDEs congeners in lake water and method validation

Under the optimized SDME and GC-EI-MS/MS conditions, the linearity of calibration curve, relative standard deviation (RSD, n = 6), limit of detection (LOD, S/N = 3) and limit of quantification (LOQ, S/N = 10) were investigated. As shown in Table 2, the linear ranges of all target congeners spanned over 3 orders of magnitudes, and for some lower brominated congeners, achieved 4 orders of magnitudes. The determination coefficients (r^2) ranged from 0.9929 to 0.9998. In comparison with the limits of detection reported by Akerman et al. [25], the resulted sensitivity by SDME-GC-EI-MS/MS is much improved.

Real water sample was collected in Southern campus of Sun Yat-sen University. Except for simple filtration, no other pretreatment was required before SDME procedure. Under the optimized conditions, analysis of target PBDE congeners as well as recoveries investigation was carried out. None of target compounds was found in the collected

Table 2 Linear range, LOD, LOQ, RSD and r^2 , recovery and enrichment factor under optimized conditions

PBDE congeners	Linear range ($\mu\text{g L}^{-1}$)	Determination coefficient (r^2)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Lake water Spiked concentration ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%)	Enrichment factor
2'-OH-BDE28	0.001–1	0.9986	0.40×10^{-4}	0.13×10^{-3}	0.02	119	10.9	52
2'-MeO-BDE28	0.001–0.1	0.9929	0.20×10^{-4}	0.63×10^{-4}	0.02	128	8.06	60
BDE47	0.001–0.5	0.9970	0.30×10^{-4}	0.11×10^{-3}	0.02	107	7.52	12
3-MeO-BDE47	0.001–1	0.9995	0.43×10^{-3}	1.4×10^{-3}	0.02	74.7	20.4	24
BDE100	0.01–10	0.9933	3.3×10^{-3}	11×10^{-3}	8.00	90.0	14.2	32
3-OH-BDE47	0.01–10	0.9998	0.27×10^{-3}	0.88×10^{-3}	8.00	130	21.2	41
BDE99	0.01–5	0.9997	5.7×10^{-3}	19×10^{-3}	0.20	70.7	21.4	24
6'-MeO-BDE99	0.01–5	0.9997	6.0×10^{-3}	20×10^{-3}	0.20	101	25.0	25
BDE154	0.1–50	0.9996	25×10^{-3}	83×10^{-3}	2.00	73.4	4.17	15
BDE153	0.1–50	0.9988	14×10^{-3}	45×10^{-3}	2.00	71.8	15.9	13
BDE197	1–100	0.9983	0.30	1.1	2.00	98.7	13.3	12
BDE209	20–1000	0.9991	6.0	20	20.00	100	17.3	8

lake water. For recoveries experiment, the lake water was spiked with target compounds with different concentration. As the presented in Table 2, the recoveries ranged from 74.7 to 130%, and the enrichment factors (calculated as the ratio of calibration slope with and without SDME) ranged from 8 to 60, indicating the SDME treatment is relatively stable and sufficient for PBDEs detection. The RSD ($n=6$) varies upon congeners, ranging from 4.17% to 25.00%, which reveals the decent precision and reproducibility of GC-EI-MS/MS.

4 Conclusions

The present study developed the single-drop microextraction, coupling with gas chromatography-tandem mass spectrometry for the determination of PBDE congeners and their metabolites in water samples. By optimizing high mass fragment ion abundance over a range of EI parameters, GC-EI-MS/MS provides better identification between congeners. In addition, the use of tandem mass delivers better S/N ratio, which enables the congener-specific analysis in complicated matrixes. In comparison, GC-NCI-MS is more suitable for the analysis of highly brominated PBDEs. The single-drop microextraction has been proved to be a simple, fast and one-step extraction technique, coupling with GC, for PBDEs determination in aqueous samples. With the optimization over the extraction conditions, reliable quantification of 13 PBDE congeners in real water samples has been achieved with satisfied precision and sensitivity.

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Data availability We declared that materials described in the manuscript, including all relevant raw data, will be freely available to any scientist wishing to use them for non-commercial purposes, without breaching participant confidentiality.

Compliance with ethical standards

Conflicts of interest We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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