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Determination of Nine Hydroxylated Polybrominated Diphenyl Ethers and Forty Polybrominated Diphenyl Ethers in Atmospheric Fine Particles by Precolumn Derivatization-GC-MS/GC

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Abstract

Environmental context: Hydroxylated polybrominated diphenyl ethers (OH-PBDEs) and polybrominated diphenyl ethers (PBDEs) in $PM_{2.5}$ can be toxic to humans and ecosystems, because they will show endocrine disrupting activity. It is thus important to understand the contamination level of PBDEs and OH-PBDEs in $PM_{2.5}$. In this paper, a method has been applied to the analysis and separation of trace PBDEs and OH-PBDEs in $PM_{2.5}$, in order to understand the pollution levels, migration and transformation of PBDEs/OH-PBDEs in $PM_{2.5}$.

In this study, we demonstrate a method for simultaneously analyzing 9 OH-PBDEs and 40 PBDEs existed in $PM_{2.5}$. Quantitative analysis was conducted by using gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) combined with a precolumn derivatization. To achieve accurate detection, the extraction solvents and clean-up condition were optimized. The working curves were obtained via dissolving standards in blank matrix extracts. The linear range of 9 OH-PBDEs was from 15 pg m^{-3} to 3875 pg m^{-3}, and limits of detection and quantification ranged from 4.95 pg m^{-3} to 24.33 pg m^{-3} and 16.48 pg m^{-3} to 81.09 pg m^{-3}, respectively. The linear range of 40 PBDEs was from 1.25 pg m^{-3} to 5000 pg m^{-3}, and limits of detection and quantification ranged from 0.37 pg m^{-3} to 38.19 pg m^{-3} and 1.25 pg m^{-3} to 127.29 pg m^{-3}, respectively. The results showed that the recoveries were in the range of 72.1%-104.7% and the relative standard deviations were less than 13.6%. This method was suitable for simultaneous analysis of PBDEs and OH-PBDEs in $PM_{2.5}$ with the advantages of high sensitivity, time saving and easy operation. The applicability of the method has been successfully validated on atmospheric samples collected in Baoding, China. Six PBDEs and five OH-PBDEs were detected in all the samples. Among the detected PBDEs and OH-PBDEs, detection rate of BDE-47, BDE-99, BDE-100 and BDE-209 were relatively higher than that of others. The results indicated that the concentration of BDE-209 might be affected by the concentration of $PM_{2.5}$.

Keywords: Gas chromatography; Mass spectrometry; Gas chromatography; Hydroxylated polybrominated diphenyl ethers; Polybrominated diphenyl ethers; Deteminaion; $PM_{2.5}$

Introduction

Polybrominated diphenyl ethers (PBDEs) are one class of brominated flame retardants (BFRs). Hydroxy polybrominated diphenyl ethers (OH-PBDEs) as metabolites of PBDEs in the environment, are potentially more toxic than their parent PBDEs [1]. At present, PBDEs and OH-PBDEs are ubiquitous in all environmental media (air, soil, sediment, indoor air), organisms (fish, birds, mammals) and in human body (breast milk, blood, tissue and bile) [2,3], etc. The PBDEs in the environment can be transported and transformed over long distances through the atmosphere, causing harm to the ecological environment and human health [4]. Thus the analysis of these organic pollutants in the atmosphere has major significance for studying $PM_{2.5}$ source apportionment and transformation of organic pollutants.

The issue of air pollution has raised public concern in China. $PM_{2.5}$ is one of the prime pollutant parameters that affect urban air quality. $PM_{2.5}$ are harmful to human health not only because they can enrich most organic pollutants [5] and heavy metal elements, but also because they are small enough to penetrate deeply into the lungs. The chemical composition of $PM_{2.5}$ in the atmosphere is very complex. Besides heavy metals, alkanes, polycyclic aromatic hydrocarbons (PAHs), esters, heterocyclic compounds [6-8], and persistent organic pollutants such as PBDEs and OH-PBDEs are all present in $PM_{2.5}$. Current research about the noxious pollutants in $PM_{2.5}$ are extensively focused on heavy metals, PAHs and on phthalic acid ester [REF]. However, the studies about pollution level and source of PBDEs in $PM_{2.5}$ are rather limited.

Furthermore, there is little information available in literature about the pollution of OH-PBDEs in $PM_{2.5}$. The ecotoxicological studies found that OH-PBDEs are stronger endocrine disruptors than their precursor PBDEs. For example, OH-PBDEs will disrupt thyroid hormone action and possess pseudo/anti estrogenic activities even in a low concentration range of micromolar per liter [9-11]. Therefore, it is considerably important to understand the contamination level of PBDEs and OH-PBDEs in $PM_{2.5}$. However, determination of PBDEs and OH-PBDEs in $PM_{2.5}$ is difficult due to the following reasons: 1) the concentration of PBDEs and OH-PBDEs in $PM_{2.5}$ is very low; 2) the complex composition of $PM_{2.5}$ induces matrix interference; 3) Considering the weak polarity of the phenol hydroxyl group in OH-PBDEs, simultaneously extracting and separating PBDEs and OH-PBDEs from $PM_{2.5}$ are not trivial. Currently the main pretreatment methods for analyzing different polarity fractions require several steps, including extraction, separation and clean-up. Numerous techniques have been developed for extracting analytes, such as accelerated solvent extraction (ASE) [12], Soxhlet

extraction (SE) [13], and ultrasound assisted extraction (UAE) [14]. Among them, SE was widely used in the extraction of air filters. The methods for separation of the neutral (PBDEs) and phenol (OH-PBDEs) analytes involves partitioning with potassium hydroxide were widely used [15-21]. Another common technique to separate different polarity components is gel-permeation chromatography. However, this method is laborious, sophisticated and consumes a large amount of organic solvent [22,23]. Regardless of separation technique, analyzing PM$_{2.5}$ samples requires complicated clean-up procedure to reduce matrix interference. Florisil [24] silicon gel [25] and alumina [26] are often used in clean-up procedure. Among them, silicon gel can be used in clean-up procedure for the separation of analytes from interfering compounds of a different chemical polarity.

This paper presents an approach for simultaneous analyzing PBDEs and OH-PBDEs with an improved sample pretreatment. Different polar fractions were separated via controlling pH of liquid-liquid extraction and then purified by acidic silica columns. PBDEs were analyzed by GC-ECD. OH-PBDEs were analyzed by GC-MS after derivatization with N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) [27]. BSTFA was used as derivatization reagent in OH-PBDEs determination. Compared with diazomethane and dimethyl sulfate, it has the advantages of low toxicity, minimal interference, and easy operation [16,28]. This method for determining 9 OH-PBDEs and 40 PBDEs in atmospheric fine particles was highly efficient and sensitive, requiring small amount of samples and reagents. Meanwhile, it can eliminate the interference induced by impurities in the atmosphere. This method will provide a practical reference to understand the pollution levels, migration and transformation of PBDEs/OH-PBDEs in atmospheric fine particles.

Experimental

Chemicals and reagents

Standard solutions, 2'-hydroxy-4-monobromodiphenyl ether (2'-OH-BDE-3), 3'-hydroxy-2,4-dibromodiphenyl ether (3'-OH-BDE-7), 2'-hydroxy-2,4,4'-tribromodiphenyl ether (2'-OH-BDE-28), 3'-hydroxy-2,4,4'-tribromodiphenyl ether (3'-OH-BDE-28), 4'-hydroxy-2,2',4-tribromodiphenyl ether (4'-OH-BDE-17), 2'-hydroxy-2,3',4,5'-tetrabromodiphenyl ether (2'-OH-BDE-68), 5-hydroxy-2,2',4,4'-tetrabromodiphenyl ether (5-OH-BDE-47), 6-hydroxy-2,2',4,4'-tetrabromodiphenyl ether (6-OH-BDE-47), 5'-hydroxy-2,2',4,4',5-pentabromodiphenyl ether (5'-OH-BDE-99), BDE-209 and the standard solution of 39 PBDE congeners (BDE-1, 2, 3, 7, 8, 10, 11, 12, 13, 15, 17, 25, 28, 30, 32, 33, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 116, 118, 119, 126, 138, 153, 154, 155, 166, 181, 183, 190) were purchased from Accustandard (New Haven, CT, USA). Acetonitrile, isooctane, dichloromethane, hexane, methyl tert-butyl ether and N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) (98%) were obtained from J&K Scientific Ltd (Beijing). Isopropyl alcohol was purchased from Tedia (USA). Acetone and toluene were obtained from JT Baker (Phillipsburg, NJ, USA). Alcohol was purchased from Fisher Scientific. All of the above solvents were HPLC grade. Hydrochloric acid (HCl), concentrated sulfuric acid (H$_2$SO$_4$), sodium hydroxide (NaOH), sodium chloride (NaCl), anhydrous sodium sulfate (Na$_2$SO$_4$) and silica (100-200 mesh) were analytical grade. Glass fiber filters [effective diameter (90 ±1) mm] applied to collect PM$_{2.5}$ were obtained from Whatman (Loughborough, UK). Glass chromatography columns (30 cm × 1.0 cm i.d) applied to clean up were purchased from Beijing Xingyun Kenuo trading company (Beijing, China).

Equipment

7890A Gas chromatography with 5975C mass spectrometry, 7890B Gas chromatography (Agilent Technologies, Ltd.), Termovap sample concentrator BF-2000M (Beijing eight Century Technology Co. Ltd.), Rotary evaporator RV 10 control (IKA Works Guangzhou), Vortex shaker WH-861 (Taicang Hualida laboratory equipment company), Electric thermostatic drying oven DHG-9053A (Shanghai Feiyue Experimental Instrument Co. Ltd.), P8846X high volume mass flow controlled system for PM$_{10}$/PM$_{2.5}$ sampler with the flow rate of 1 m^3 min^{-1} (Tisch Environmental Inc, OH, USA). Analytical balance AB 135-S (METTLER TOLEDO Co. Ltd.).

Sampling

PM$_{2.5}$ samples were collected on the top of a university building at a height of approximately 10 m (38°52′17.99″N, 115°30′35.06″E) from September 2016 to January 2017. Active sampling using glass fiber filters is routinely employed for sampling PM$_{2.5}$. The sampling duration was 8 h either during daytime from 10:00 to 18:00 or at night from 22:00 to 06:00 using a P8846X high volume mass flow controlled system for PM$_{10}$/PM$_{2.5}$ sampler with the flow rate of 1 m^3 min^{-1}. Before collecting PM$_{2.5}$, the glass fiber filters were pre-baked at 500°C for 4 h and stored in the dryer at room temperature and relative humidity (40%-60%) for at least 24 h. The filters were weighed in the electronic balance (0.01 mg precision) with gravimetric methods before and after sampling, respectively. All collected samples were wrapped by aluminum foil and stored at ≤ -18°C in the freezer prior to analysis.

Sample preparation

Standard mixture solutions and spiking solutions series preparation: According to the response value, the standard solutions of nine OH-PBDEs were diluted with acetonitrile to the following concentrations: 12 µg mL^{-1} 2'-OH-BDE-3, 12 µg mL^{-1} 3'-OH-BDE-7, 10 µg mL^{-1} 2'-OH-BDE-28, 8 µg mL^{-1} 3'-OH-BDE-28, 12.5 µg mL^{-1} 4'-OH-BDE-17, 11 µg mL^{-1} 5-OH-BDE-47, 10 µg mL^{-1} 6-OH-BDE-47, 10 µg mL^{-1} 2'-OH-BDE-68, and 10 µg mL^{-1} 5'-OH-BDE-99. Then they are mixed together in a ratio of 2:5:10:12:10:10:10:10:31 (v/v). The final concentration was 0.24, 0.6, 1.0, 0.96, 1.25, 1.1, 1.0, 1.0, 3.1 µg mL^{-1}, respectively. 2 mg of decabromodiphenyl ether (BDE-209) was put into 50 mL hexane. Then the solution is placed in an ultrasonic chamber for 20 mins for complete dissolution. 1 mL 40 µg mL^{-1} BDE-209 solution was diluted 20 times with hexane to obtain the standard solution of 2 µg mL^{-1} BDE-209. Similarly, we obtained the standard solution of BDE-47, BDE-99, BDE-100 with the same procedure. Then all standard solutions were stored at ≤ -18°C.

Silica gel preparation: Activated silica gel: 20 g of silica gel (100-200 mesh) was pre-washed with 50 mL methanol to remove high polar impurities, and then with 50 ml hexane/dichloromethane (DCM) (1:1, v/v, the following was the same) to get rid of weak polar and nonpolar impurities. Cleaned silica gel was dried and activated at 135°C for 4 h. Acid silica gel (H$_2$SO$_4$, 30%) was prepared by adding 8.6 g of sulfuric acid into 20 g of activated silica. Anhydrous sodium sulfate was baked at 660°C for 6 h and cooled to 150°C. All of them were reserved in the dryer before use.

Extraction procedures: Air filter was extracted by Soxhlet extractor for 12 h with 200 mL of hexane/DCM. The extract was concentrated by rotary evaporation to 5 mL, and then adjusted to acidity with 1 mL of 6mol L^{-1} HCl. After that, 5 mL of isopropyl alcohol and 10 mL of methyl tert-butyl ether (MTBE)/hexane mixture (1:1, v/v) were added into the extracted sample. The extract was washed three times with a total of 30 mL (10+10+10 mL) of 3% NaCl solution and the organic

layer was transferred to a separatory funnel. Then, 15 mL of 1mol L^{-1} NaOH/alcohol (1:1, v/v) was added into the separatory funnel to separate the neutral fractions and the weak acid fractions with hydroxyl component. PBDEs was contained in organic phase (I) and OH-PBDEs was contained in water phase. The pH of water layers containing OH-PBDEs was adjusted to acidity with 0.1 mL of H_2SO_4 (50%). Then the water phase were extracted three times with a total of 20 mL of methyl tert-butyl ether (MTBE)/hexane mixture (1:1, v/v, 10+5+5 mL) and then organic fractions (II) containing OH-PBDEs were collected.

Clean up and derivation: The volumes of two organic fractions ((I), (II)) were both concentrated to 1 mL before being subjected to silica gel column. The concentrated solutions were cleaned-up using two acid-base silica gel columns (30 cm i.d) Both of the acid-base silica gel columns were packed from the bottom to the top with absorbent cotton, 0.5 g of activated silica gel, 2 g of acid silica geland 3 cm of anhydrous sodium sulfate. The two columns were pre-washed with 45 mL of hexane/DCM. Then organic phase (I) containing PBDEs was added into a column and eluted with 40 mL of hexane/DCM. Organic phase (II) containing OH-PBDEs was added into the other column and eluted with 35 mL of hexane/DCM. Both of eluates were collected and evaporated to almost dryness under a stream of nitrogen. Then 100 μL of BSTFA was added to elution fraction (II) containing OH-PBDEs and vortex mixed for 1 min. Elution fraction (II) was incubated at 90°C for 30 min, then cooled at room temperature. Ultimately, fraction (I) containing PBDEs and fraction (II) containing OH-PBDEs were nitrogen evaporated to almost dryness and reconstituted in 100 μL of hexane prior to instrumentally analyzed by GC-ECD and GC-MS, respectively (Figure 1).

Instrumental analysis

GC conditions: The quantification of PBDEs was performed with GC with DB-5HT column (15 m × 0.25 mm i.d. × 0.10 μm). High purity nitrogen (purity ≥ 99.999%) was used as carrier gas at a constant flow rate of 1.0 mL min^{-1}. Sample injection was set at 1 μL in chromatographic method. The injection temperature and detector temperature were set at 300°C and 340°C, respectively. The programmed GC oven temperature was initiated at 45°C, held 1.0 min, ramp 25°C min^{-1} to 150°C, held 1.0 min, ramp 4°C min^{-1} to 320°C and held 3.0 mins. Chromatogram of the forty PBDEs were shown in Figure 2.

GC-MS conditions

Chromatographic separation: The quantification of OH-PBDEs was performed with a GC-MS. Compounds separation was achieved using a DB-35MS column (30 m × 0.32 mm i.d. × 0.25 μm) with high purity helium (purity ≥ 99.999%) as the carrier gas at a constant flow of 1.0 mL min^{-1}. Sample injection was set at 1 μL and the injection temperature was set at 250°C. The programmed GC oven temperature was initially 45°C, held for 1 min, increased to 200°C at 15°C min^{-1}, then to 300°C at 8°C min^{-1}, and held for 10 mins.

Mass parameters: Electron ionization (EI) was used in mass spectrometer with an electron energy of 70 eV. The temperatures of ion source and the transfer line were set at 230°C and 280°C, respectively. The mass spectrometer was operated in SIM mode and SCAN mode, respectively. Selected ion chromatogram of the nine OH-PBDEs was shown in Figure 1. Retention times of 9 OH-PBDEs and 40 PBDEs were listed in Tables 1 and 2.

Results and Discussion

Conditions optimization

Optimization of cleanup conditions: Two acid-base silica gel columns were rinsed with 45 mL of hexane/DCM. After that 1 mL of 9 OH-PBDEs mixture and 1 mL of 4 PBDEs mixture were poured over the columns, respectively. Hexane, dichloromethane and hexane/ DCM were used as elution solvents. The eluent was collected every 5 mL and was determined to investigate three solvents' elution.

Optimization of elution solvent: If hexane was used as the elution solvent, only BDE-209 could be eluted completely. If dichloromethane was used as the elution solvent, the low-BDEs could be eluted completely. While hexane/DCM as eluent solvent, low-BDEs, high-BDEs and hydroxylated polybrominated diphenyl ethers could be all flown out. Therefore, the mixed hexane/DCM was considered to be the most suitable elution solvent.

Optimization of elution volume: When hexane/DCM was used as the elution solvent, BDE-47/99/100 began to flow out at 0-5 mL and reached the maximum value at 5-10 mL. 35 mL of solvent can elute BDE-47/99/100 entirely. BDE-209 reached the maximum value at 5-10 mL and it was eluted entirely at an elution volume of 40 mL; Therefore, 40 mL of hexane/DCM was the optimum elution volume to elute polybrominated diphenyl ethers.
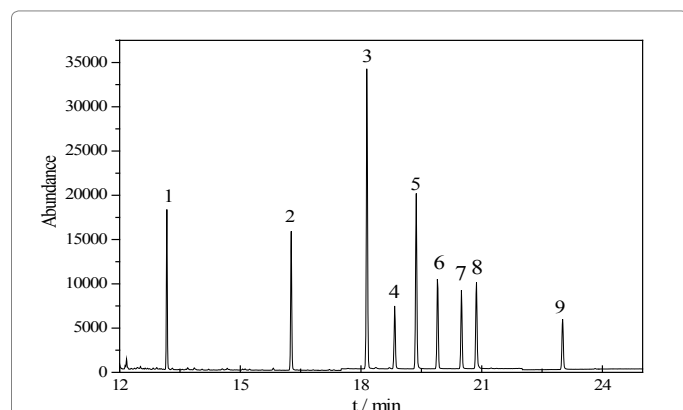

Figure 1: Selected ion chromatogram of the nine OH-PBDEs. 1. 2'-OH-BDE-3; 2. 3'-OH-BDE-7; 3. 2'-OH-BDE-28; 4. 3'-OH-BDE-28; 5. 4'-OH-BDE-17; 6. 6-OH-BDE-47; 7. 2'-OH-BDE-68; 8. 5-OH-BDE-47; 9. 5'-OH-BDE-99.

Figure 2: Chromatogram of the forty PBDEs. 1. BDE-1; 2. BDE-2; 3. BDE-3; 4. BDE-10; 5. BDE-7; 6. BDE-11/8; 7. BDE-12/13; 8. BDE-15; 9. BDE-30; 10. BDE-32; 11. BDE-17; 12. BDE-25; 13. BDE-33/28; 14.BDE-35; 15.BDE-37; 16. BDE-75; 17. BDE-49; 18. BDE-71.19. BDE-47; 20. BDE-66; 21. BDE-77; 22. BDE-100; 23. BDE-119; 24. BDE-99; 25. BDE-116; 26. BDE-118; 27. BDE-85; 28. BDE-126/155; 29. BDE-154; 30. BDE-153; 31. BDE-138/166; 32. BDE-183; 33. BDE-181; 34. BDE-190; 35. BDE-209.

No.	Date	Pollution degree	Weather condition	Before sampling (g)	After sampling (g)	PM$_{2.5}$ concentration (µg m^{-3})
1	2016.09.23	Unhealthy	17-27°C Sunny-Cloudy Winds S at 1-2 grade	2.84985	2.92226	150.85
2	2016.09.23-24	Very Unhealthy	17-27°C Sunny-Cloudy Winds S at 1-2 grade	2.85687	2.95291	200.08
3	2016.10.09	Moderate	7-19°C Sunny-Cloudy Winds S at 1-2 grade	2.84197	2.88048	80.23
4	2016.10.11-12	Unhealthy for Sensitive Groups	9-22°C Sunny Winds N at 1-2grade	2.85953	2.90739	99.71
5	2016.10.13	Very Unhealthy	11-23°C Sunny Winds S at 1-2 grade	2.8539	2.99769	299.56
6	2016.11.03	Hazardous	4-17°C Sunny Winds S at 1-2 grade	2.84406	2.88739	90.27
7	2016.12.05	Good	-7-8°C Sunny Winds WN 3-4 grade	2.81252	2.82936	35.08
8	2016.12.19	Hazardous	-5-5°C Hazy Winds S at1-2grade	2.83884	3.08326	509.21
9	2016.12.23	Moderate	-6-4°C Sunny Winds N at 1-2 grade	2.85998	2.89188	66.46
10	2016.12.28	Unhealthy	-10-3°C Cloudy-Sunny Winds WN 1-2 grade	2.83508	2.84318	16.875
11	2017.01.03	Hazardous	-4-5°C Hazy Winds S at 1-2 grade	2.86693	3.13337	555.08
12	2017.01.03-04	Very Unhealthy	-4-5°C Hazy Winds S at 1-2 grade	2.8583	2.9897	273.75
13	3017.01.04	Hazardous	-3-2°C Hazy-Foggy Winds EN 1-2 grade	2.84725	2.99875	315.63
14	2017.01.04-05	Hazardous	-3-2°C Hazy-Foggy Winds EN 1-2 grade	2.86268	3.05032	807.58
15	2017.01.05	Very Unhealthy	-3-2°C Hazy Winds EN 1-2 grade	2.85528	2.96285	224.10
16	2017.01.05 -06	Very Unhealthy	-3-2°C Hazy Winds EN 1-2 grade	2.86845	2.99295	259.38

Table 1: Records of weather conditions and mass concentration of PM$_{2.5}$ during sampling

Name	Retention time (min)	Name	Retention time (min)	Name	Retention time (min)
2'-OH-BDE-3	13.602	BDE12/13	11.436	BDE-100	24.143
3'-OH-BDE-7	16.779	BDE-15	11.842	BDE-119	24.486
2'-OH-BDE-28	18.7	BDE-30	13.746	BDE-99	25.167
3'-OH-BDE-28	19.404	BDE-32	15.028	BDE-116	25.409
4'-OH-BDE-17	19.929	BDE-17	15.488	BDE-118	25.971
6-OH-BDE-47	20.473	BDE-25	15.576	BDE-85	26.875
2'-OH-BDE-68	21.068	BDE-28/33	16.117	BDE-126/155	27.168
5-OH-BDE-47	21.445	BDE-35	16.55	BDE-154	27.908
5'-OH-BDE-99	23.604	BDE-37	17.04	BDE-153	29.273
BDE-1	7.254	BDE-75	19.559	BDE-138/166	31.016
BDE-2	7.404	BDE-49	19.975	BDE-183	33.096
BDE-3	7.571	BDE-71	20.097	BDE-181	35.024
BDE-10	9.858	BDE-47	20.715	BDE-190	35.304
BDE-7	10.74	BDE-66	21.362	BDE-209	46.632
BDE-11/8	11.164	BDE-77	22.386		

Table 2: Retention times of the nine OH-PBDEs and the forty PBDEs.

Among of 9 OH-PBDEs, 4'-OH-BDE-17 began to flow out at 0-5 mL. while other OH-PBDEs were not detected at 0-5 mL. Except for 2'-OH-BDE-3 and 2'-OH-BDE-28, the others were eluted entirely at an elution volume of 30 mL. 2'-OH-BDE-3 and 2'-OH-BDE-28 were eluted entirely at an elution volume of 35 mL. The elution amount of 9 OH-PBDEs reached the maximum value at 5-10 mL and eluted entirely at an elution volume of 35 mL. Therefore, 35 mL of hexane/DCM was used to elute hydroxylated polybrominated diphenyl ethers. This results were shown in Figure 3.
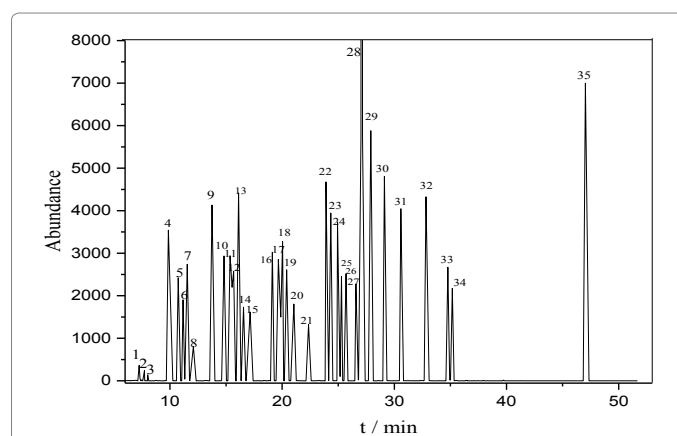
Selection of extraction solvent

A certain amount of standard mixture was added to glass fiber membrane, then 200 mL of different solvents (toluene, acetone, hexane, dichloromethane and hexane/DCM) were tested for extraction
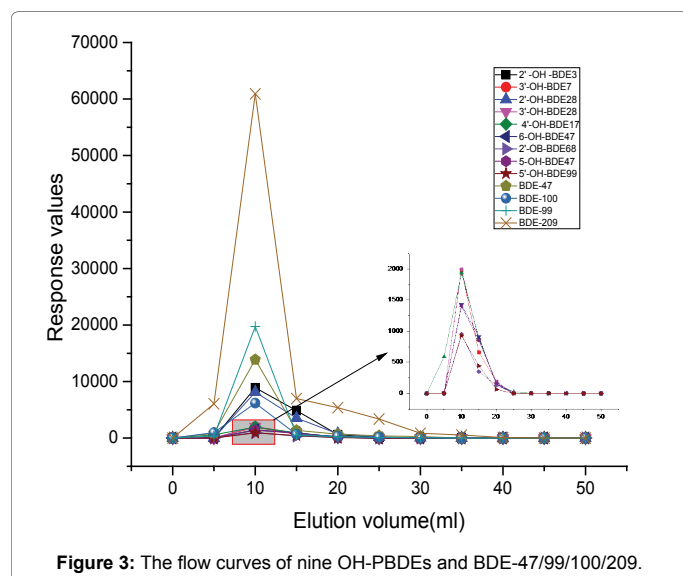
Figure 3: The flow curves of nine OH-PBDEs and BDE-47/99/100/209.

efficiency of the targets, respectively. The comparison of extraction efficiency was in the following sequence: toluene≈hexane/DCM>acetone>hexane>dichloromethane. The experimental results were shown in Figure 4. It could be seen from Figure 4, both of toluene and hexane/DCM could achieved satisfactory extraction effects. Extraction efficiency of toluene was slightly higher than hexane/DCM, whereas the blank value of solution extracted by toluene was higher than by hexane/DCM. The nitrogen blowing of toluene solution spent longer time than that of hexane/DCM. Therefore, hexane/DCM was the optimum extraction solvent.

Performance of the method

Linear equations, correlation coefficients (r^2), limits of detection (LOD) and limits of quantification (LOQ): 5, 10, 20, 50 and 100 μL of 9 OH-PBDEs standard mixture were added to blank membrane, then we could obtain OH-PBDEs series concentration of 62.5, 125, 250, 625, 1250 pg m^{-3}, respectively. Similarly, 5, 20, 50, 100 and 200 μL of 39 PBDEs standard mixture were added to blank membrane, and obtained the concentration of 1.25, 5, 12.5, 25 and 50 pg m^{-3} PBDEs, respectively. We could obtain BDE-209 series concentration of 125, 500, 1250, 2500 and 5000 pg m^{-3} by adding 5, 20, 50, 100 and 200 μL of BDE-209 standard solution to blank membrane, respectively. The quality assurance and quality control procedures included procedural blank and parallel duplicate samples. The measurement values were the average value of three parallel determinations. Based on measurement values of peak area and concentration, linear equations were generated. The linear range of 9 OH-PBDEs was from 15 pg m^{-3} to 3875 pg m^{-3}. The linear range of PBDEs was from 1.25 pg m^{-3} to 5000 pg m^{-3}. Limits of detection (LODs) were calculated as the minimum amount of analyte that produces a peak with a signal-to-noise ratio of 3. The limits of quantification (LOQs) were calculated as the minimum amount of analyte that produces a peak with a signal-to-noise ratio of 10. The results were shown in Table 3.

Recoveries and precision: Recoveries were performed at two different spiked levels with three parallel experiments for each level. 10 μL and 50 μL of 9 OH-PBDEs standard mixture were spiked to two extracts of winter atmospheric PM$_{2.5}$, respectively. Recoveries of OH-PBDEs were 72.1%-104.7% and relative standard deviations were lower than 13.6%. Similarly, 20 μL and 100 μL of 39 PBDEs standard mixture

were spiked to two extracts of winter atmospheric PM$_{2.5}$, respectively. We obtained the recoveries of PBDEs were between 74.6% and 104.5%. Relative standard deviations were lower than 13.5%. Two extracts of winter atmospheric PM$_{2.5}$ were spiked with 20 μL and 100 μL of BDE-209 standard solution, respectively. The recoveries and relative standard deviations for BDE-209 were 76.1%-83.0% and lower than 5.9% (Table 4).

OH - PBDEs qualitative analysis: The mass spectra of nine OH-PBDEs and BSTFA derivatives were shown in Figure 5.

Application to atmospheric samples study

We used established method to determine trace amounts of PBDEs and OH-PBDEs in PM$_{2.5}$, which were collected from Baoding, China. The information of samples collection was shown in Table 1. The test results of real atmospheric samples were shown in Table 5. Considering the range of PM$_{2.5}$, the concentration of winter is obviously higher than that of autumn, which suggests winter heating contribute significantly to PM$_{2.5}$ concentration. Six PBDEs and five OH-PBDEs were detected in all the samples. The total concentrations of 40 PBDEs in atmospheric samples ranged from 147.1 to 8663.4 pg m^{-3}, while BDE-209 was the largest contributor to PBDEs, ranged from 137 to 5248 pg m^{-3}.

The results indicated that the concentration level and distribution of PBDEs in the atmosphere were influenced by weather conditions. Meanwhile, it was found that the concentration of BDE-209 in the atmosphere was mainly affected by PM$_{2.5}$ concentration. The higher the pollution degree was, the higher the PM$_{2.5}$ concentration was and the greater the BDE-209 concentration was. The detection rates of BDE-47, BDE-99, BDE-100 and BDE-209 were relatively higher, while the detection rate of BDE-100 was 100%. It is probably because the penta-BDE commercial mixtures were widely used in China. The detectable amount of BDE-66, BDE-153 and 5 OH-PBDEs was relatively lower. It was found that the total detectable amount of low-brominated OH-PBDEs was higher than high-brominated OH-PBDEs, and it is possiblely related to the content of bromine atoms of PBDEs. The less bromine atoms content of PBDEs' are, the faster their oxidation rates are. There is a certain relationship between the content of OH-PBDEs and weather conditions. The total detectable amount of OH-PBDEs was relatively lower in clean and sunny weather, while the total detectable amount of OH-PBDEs was relatively higher in heavy haze.
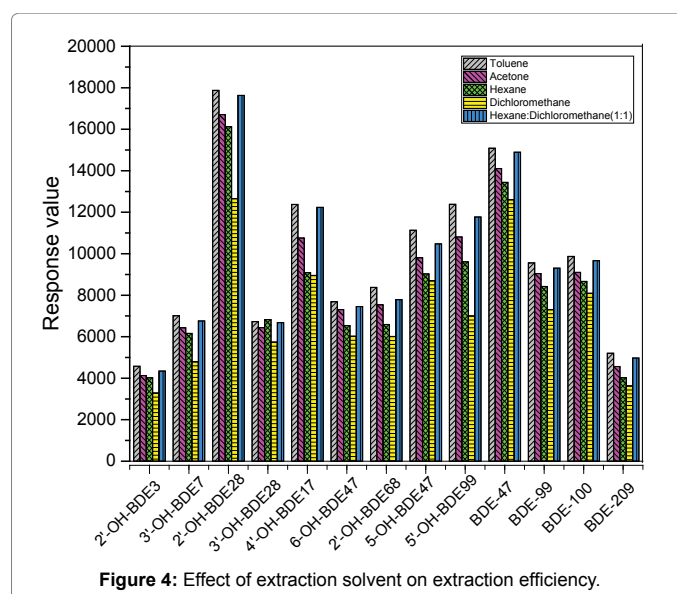

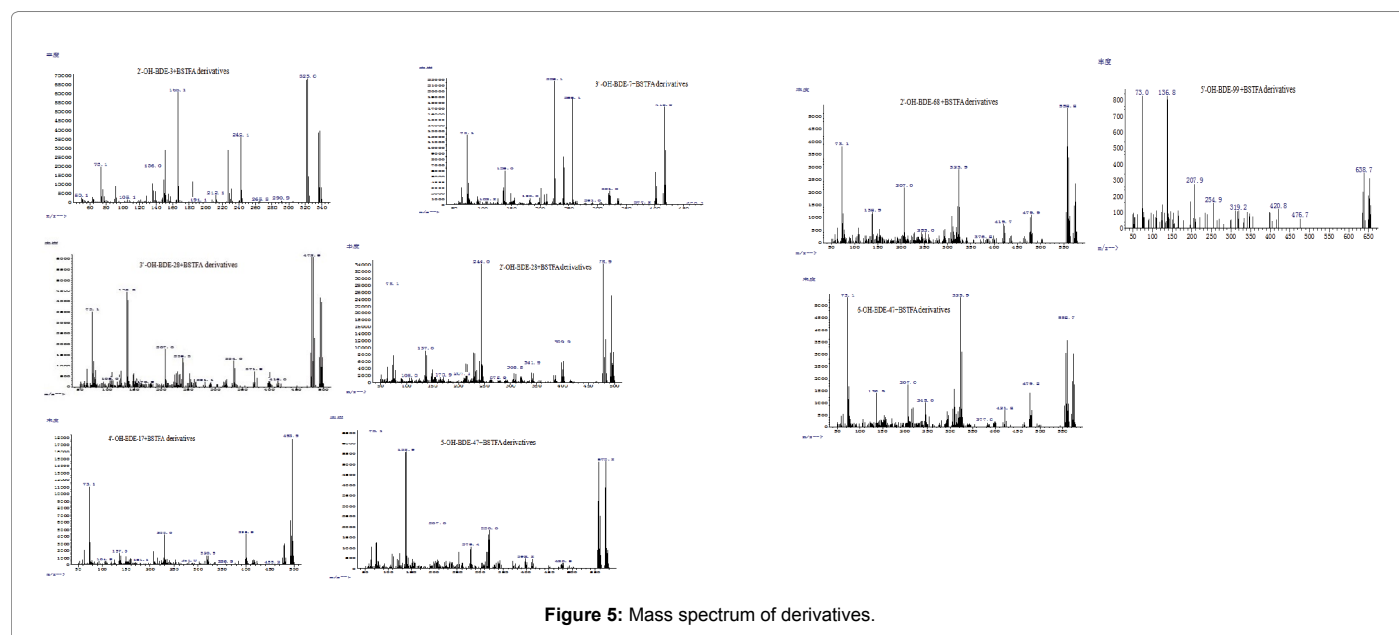**Figure 4:** Effect of extraction solvent on extraction efficiency.

Figure 5: Mass spectrum of derivatives.

OH-PBDEs/PBDEs	Linear equation	r^2	LOD (ng m^{-3} × 10^{-3})	LOQ (ng m^{-3} × 10^{-3})
2'-OH-BDE-3	$y^1=629177x^2+5704.3$	0.9942	4.95	16.48
3'-OH-BDE-7	$y=382634x+10117$	0.9994	6.06	20.19
2'-OH-BDE-28	$y=484845x+21149$	0.9955	6.25	20.82
3'-OH-BDE-28	$y=208191x+2762.8$	0.9994	13.31	44.38
4'-OH-BDE-17	$y=370617x+688.63$	0.9979	15.20	50.68
5-OH-BDE-47	$y=340213x+16888$	0.9955	8.05	26.85
6-OH-BDE-47	$y=238751x+4113.3$	0.9959	12.08	40.27
2'-OH-BDE-68	$y=195558x+6964.9$	0.9972	6.22	20.72
5'-OH-BDE-99	$y=103934x+2267.5$	0.9946	24.33	81.09
BDE-1	$y=49372x+39.943$	0.9991	4.93	16.45
BDE-2	$y=37219x+31.632$	0.9990	6.94	23.15
BDE-3	$y=25864x+17.083$	0.9987	7.98	26.59
BDE-10	$y=691123x+46.784$	0.9997	1.28	4.28
BDE-7	$y=526756x+34.181$	0.9989	1.83	6.09
BDE-11/8	$y=597150x+62.428$	0.9994	2.02	6.72
BDE-12/13	$y=977883x+92.783$	0.9997	1.21	4.02
BDE-15	$y=332913x+48.892$	0.9992	2.05	6.83
BDE-30	$y=801171x+92.29$	0.9989	1.62	5.39
BDE-32	$y=613788x+61.055$	0.9985	2.10	7.02
BDE-17	$y=560725x+64.222$	0.9987	2.30	7.67
BDE-25	$y=635891x+70.115$	0.9984	2.14	7.14
BDE-33/28	$y=1E+06x+122.31$	0.9990	0.75	2.51
BDE-35	$y=661255x+52.25$	0.9985	1.97	6.58
BDE-37	$y=734232x+77.468$	0.9987	1.86	6.22
BDE-75	$y=757348x+76.051$	0.9986	0.50	1.67
BDE-49	$y=640812x+35.11$	0.9986	2.00	6.68
BDE-71	$y=660109x+50.656$	0.999	2.12	7.06
BDE-47	$y=804617x+75.571$	0.9992	0.38	1.27
BDE-66	$y=714850x+99.093$	0.9986	1.76	5.86
BDE-77	$y=780365x+90.701$	0.9991	1.41	4.71
BDE-100	$y=2E+06x+52.542$	0.9990	0.37	1.25
BDE-119	$y=666848x+63.729$	0.9999	0.69	2.33
BDE-99	$y=1E+06x+63.563$	0.9991	0.41	1.38
BDE-116	$y=385855x+62.261$	0.9992	2.48	8.29
BDE-118	$y=677724x+81.653$	0.9988	1.97	6.58

BDE-85	y=562398x+95.43	0.9988	2.85	9.51
BDE-126/155	y=1E+06x+131.59	0.9990	1.15	3.85
BDE-154	y=646329x+68.595	0.9993	1.54	5.13
BDE-153	y=693962x+95.181	0.9989	2.21	7.37
BDE-138/166	y=822492x+134.26	0.9991	2.53	8.44
BDE-183	y=501972x+67.883	0.9990	2.92	9.74
BDE-181	y=349427x+62.037	0.9998	3.81	12.70
BDE-190	y=373594x+83.883	0.9999	4.22	14.08
BDE-209	y=175426x+20.48	0.9992	38.19	127.29

[1]y represents peak area; [2]x reperesents mass concentration, ng m^{-3} × 10^{-3}

Table 3: Linear equations, r^2, LOD and LOQ of OH-PBDEs and PBDEs (n=3).

OH-PBDEs/PBDEs	Level 1		Level 2	
	Recovery/%	RSD/%	Recovery/%	RSD/%
2'-OH-BDE-3	89.4	8.4	85.5	1.9
3'-OH-BDE-7	84.0	7.0	94.0	1.6
2'-OH-BDE-28	92.3	13.6	99.5	8.5
3'-OH-BDE-28	86.6	10	104.7	3.3
4'-OH-BDE-17	72.7	10.5	76.9	6.9
5-OH-BDE-47	85.0	13.1	74.5	5.2
6-OH-BDE-47	89.7	2.3	98.8	3.4
2'-OH-BDE-68	72.1	7.4	97.6	6.6
5'-OH-BDE-99	96.9	6.8	91.8	9.7
BDE-10	93.2	4.8	88.1	14.0
BDE-7	95.2	1.5	95.2	12.8
BDE-11/8	103.3	8.2	97.0	10.7
BDE-12/13	84.4	7.4	86.2	13.0
BDE-15	75.9	4.1	93.1	8.3
BDE-30	90.1	3.0	86.1	12.6
BDE-32	84.5	6.8	90.6	9.8
BDE-17	75.7	2.4	90.8	13.1
BDE-25	75.7	3.6	90.7	13.2
BDE-33/28	76.5	5.3	92.3	13.2
BDE-35	74.6	1.9	94.9	13.5
BDE-37	75.5	3.6	94.9	11.2
BDE-75	75.1	5.1	84.2	10.6
BDE-49	86.1	4.9	91.0	13.4
BDE-71	76.9	2.6	91.2	12.9
BDE-47	75.2	5.2	98.2	12.1
BDE-66	76.1	2.2	88.5	12.0
BDE-77	75.3	2.2	96.5	12.8
BDE-100	75.9	10.3	82.8	2.0
BDE-119	77.3	2.9	84.9	13.2
BDE-99	76.5	13.5	104.5	10.7
BDE-116	74.6	5.4	90.5	13.0
BDE-118	83.3	2.6	92.1	13.5
BDE-85	89.1	2.3	99.8	13.0
BDE-126/155	79.8	0.9	100.2	10.4
BDE-154	89.2	5.2	95.6	10.4
BDE-153	74.5	3.2	94.9	13.5
BDE-138/166	76.3	5.5	94.2	8.1
BDE-183	74.6	4.5	85.0	12.2
BDE-181	74.9	12.6	84.5	12.1
BDE-190	76.6	4.6	79.2	11.9
BDE-209	76.1	5.6	83	5.9

[1]y represents peak area; [2]x reperesents mass concentration, ng m^{-3} × 10^{-3}

Table 4: Recoveries and relative standard deviations (RSDs) of OH-PBDEs and PBDEs spiked at two levels (n=3).

No.	BDE-47 (pg m⁻³)	BDE-66 (pg m⁻³)	BDE-99 (pg m⁻³)	BDE-100 (pg m⁻³)	BDE-53 (pg m⁻³)	BDE-209 (pg m⁻³)	3'-OH-BDE-7 (pg m⁻³)	2'-OH-BDE-28 (pg m⁻³)	4'-OH-BDE-17 (pg-m⁻³)	5-OH-BDE-47 (pg-m⁻³)	5'-OH-BDE-99 (pg m⁻³)
1	79.36	NDᶜ	678.73	122.39	ND	606	ND	ND	ND	ND	87
2	94.55	ND	941.07	301.75	302.05	2812	27	ND	67	ND	ND
3	ND	14.01	16.21	24.22	ND	229	ND	ND	ND	ND	ND
4	9.32	ND	ND	141.32	ND	ND	ND	ND	ND	34	ND
5	ND	ND	49.11	70.07	ND	815	82	ND	ND	29	ND
6	64.10	ND	72.26	681.21	ND	223	175	ND	ND	ND	ND
7	10.45	ND	36.18	43.47	ND	346	ND	ND	ND	ND	ND
8	50.03	62.21	ND	779.30	ND	1319	ND	ND	ND	30.10	ND
9	19.34	ND	ND	227.84	ND	ND	ND	ND	ND	ND	ND
10	ND	ND	7.26	2.82	ND	137	ND	ND	ND	ND	ND
11	669.23	ND	ND	1408.60	ND	828	ND	182	997	ND	ND
12	32.69	ND	13.53	342.73	ND	519	ND	125	ND	ND	ND
13	62.24	118.15	326.76	248.96	ND	3182	ND	426	ND	ND	ND
14	ND	ND	17.68	275.66	ND	5248	ND	648	ND	ND	ND
15	82.93	ND	46.58	1576.80	ND	3069	ND	499	ND	ND	ND
16	193.66	ND	103.96	4352.77	ND	4013	ND	584	ND	ND	ND
Total	1367.9	194.37	2309.33	10599.9	302.05	23346	284	2464	1064	93.10	87

Table 5: Detectable amount of PBDEs/OH-PBDEs in16 real samples (n=3).

Conclusions

The method has been applied to the analysis and separation of trace PBDEs and OH-PBDEs in $PM_{2.5}$, which were collected from Baoding, China. Under the optimum experimental conditions, six PBDEs and five OH-PBDEs were detected in all the samples collected in Baoding, China, and the detection rate of BDE-47, BDE-99, BDE-100 and BDE-209 were relatively higher. The results confirmed that the method is simple, convenient, highly sensitive, easy to operate and suitable for the analysis of PBDEs and trace OH-PBDEs in $PM_{2.5}$.

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