

# Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## An optimized method based on MAE-SPE-GC-MS for the analysis of thirteen PBDEs in airborne particles

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2014,  
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

[www.rsc.org/](http://www.rsc.org/)

X. Li, X. M. Li, X. X. Yang, Q. Li, B. Huang and X. J. Pan\*

An efficient and reliable analytical method has been developed for determination of polybrominated diphenyl ethers (PBDEs) in atmospheric particulates collected by ultra-fine glass fibre filters. Thirteen PBDEs in atmospheric particulates were extracted through a developed method and determined by Gas Chromatography-Mass Spectrometry (GC-MS). Compared with the classical Soxhlet method and multi-layer silica column purification procedure, the developed method, including microwave assisted extraction (MAE) and solid phase extraction (SPE) procedure, made the pretreatment procedure of atmospheric particulates samples more automatic and faster. Four key conditions of MAE procedure (extraction solvent, solvent volume, extraction temperature and holding time) and three important conditions of SPE procedure (SPE cartridge, elution solvent and pH) were carefully studied and improved. The method achieved good repeatability and reproducibility with RSDs ranged from 2.0% to 11% for all target PBDEs in atmospheric particulate samples. Satisfactory recoveries for spiked particulate samples ranged from 74.0% to 112%. The limits of detection (LOD) and limits of quantification (LOQ) ranged for filter samples were from 0.11 (BDE-17) to 1.23 ng/g dw (BDE-209) and from 0.37 (BDE-17) to 4.10 ng/g dw (BDE-209), respectively. The developed method has been successfully demonstrated to determine the concentrations of the target PBDEs in atmospheric particulates from one of the state air quality controlling sites in Kunming, China. The results showed that the concentration range of target PBDEs was from 4.97 to 376 ng/g dw. BDE-28 (27.9 ng/g dw), BDE-71 (35.4 ng/g dw), BDE-190 (265.4 ng/g dw) and BDE-209 (375.6 ng/g dw) were the four dominant PBDEs in this sampling site.

### Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used in all parts of our lives as flame-retardant, such as electronic appliances (television sets, computers and radios), paints, textiles and furnishings.<sup>1-4</sup> 70000 tons commercial PBDEs products have been consumed around the world in 1999, and the consumption in North America, Asia and Europe were 49%, 37% and 12%, respectively.<sup>5,6</sup> Almost commercial PBDEs products were mixtures, which principally contain Penta-BDE, Octa-BDE and Deca-BDE. In Europe, the consumption of Penta-BDE, Octa-BDE and Deca-BDE in 2001 were 150, 610 and 7600 tons, respectively.<sup>7</sup>

As a consequence of the extensive use of this kind of POPs, PBDEs have been found in the atmosphere,<sup>8-10</sup> soil<sup>11-13</sup> and biota<sup>14,15</sup>. In 2004, Penta-BDE and Octa-BDE mixtures have been banned in Europe, and the flame-retardant production also been ceased voluntarily in North America.<sup>16,17</sup> Unfortunately, China and some other countries are still producing PBDEs.<sup>1</sup> Compared with

polychlorinated biphenyls (PCBs), PBDEs have similar structure. So they have similar behaviors in the environment, such as long distance transportation, persist over long periods of time, bio-accumulating in various biological species and adverse effects on wildlife and human health.<sup>18,19</sup> Nowadays, investigations on the environment concerns of PBDEs have increased rapidly.<sup>1,3,5,12,131</sup>

Since PBDEs were first detected in 1981,<sup>20</sup> PBDEs in matrixes of sediment, atmosphere around the world have been investigated in many literatures.<sup>8-13</sup> For the analysis of PBDEs in different matrixes (sewage sludge, waste electrical and polymers) samples,<sup>21-23</sup> the microwave-assisted extraction (MAE) with low solvent consumption has been widely employed and obtained good results. But, up to now,

Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650500, PR China

\* Corresponding author. Tel./fax: +86 871 65920510.

E-mail address: xjpan@kmust.edu.cn (X.J. Pan).

for atmospheric particulates samples, only classical Soxhlet method was used as the extraction method.<sup>24-32</sup> Using a high volume of organic solvents, a large amount of time and glassware were the disadvantages of Soxhlet method. After Soxhlet procedure, they almost use a multi-layer silica column to purify and concentrate the extracted samples.<sup>24-28</sup> The multi-layer silica column needs to be artificial fill so that waste a lot of the loading time and caused the inevitable artificial error. Therefore, the analysis of PBDEs in atmospheric particulates needs an automated and fast integrated analytical method urgently.

For the instrument analysis process, Gas chromatography-mass spectrometry (GC-MS) has been widely used to determine PBDEs.<sup>33-35</sup> Because of high molecular weight and low volatility of high bromine PBDEs, 10 or 15 m length GC column has a good isolation effect.

The aim of the present work is to develop and validate an efficient and reliable method based on MAE-SPE-GC-MS for the analysis of thirteen PBDEs (BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-138, BDE-153, BDE-154, BDE-183, BDE-190 and BDE-209) in atmospheric particulate samples collected by ultra-fine glass fibre filter. In this paper, four key conditions of MAE procedure (extraction solvent, solvent volume, extraction temperature and holding time) and three important conditions of SPE procedure (SPE cartridge, elution solvent and pH) were carefully studied and developed. Finally, the optimized analytical method was successfully used to analyze the PBDEs in atmospheric particulates collected from one of the state controlling air sampling sites in Kunming, China.

## Experimental

### Reagents and chemicals

The 13 PBDEs standards in this study, 2,2',4-TriBDE (BDE-17, 98%), 2,4,4'-TriBDE (BDE-28, 98%), 2,2',4,4'-TetraBDE (BDE-47, 98%), 2,3',4,4'-TetraBDE (BDE-66, 98%), 2,3',4',6-TetraBDE (BDE-71, 98%), 2,2',3,4,4'-PentaBDE (BDE-85, 98%), 2,2',4,4',5-PentaBDE (BDE-99, 98%), 2,2',3,4,4',5'-HexaBDE (BDE-138, 98%), 2,2',4,4',5,5'-HexaBDE (BDE-153, 98%), 2,2',4,4',5,6'-HexaBDE (BDE-154, 98%), 2,2',3,4,4',5',6-HeptaBDE (BDE-183, 98%), 2,3,3',4,4',5,6-HeptaBDE (BDE-190, 98%), DecaBDE (BDE-209, 98%), and internal standard, 2,2',4,4',6-Penta-<sup>13</sup>C<sub>12</sub>-BDE (BDE-100L, 99%) were supplied by Cambridge Isotope Laboratories, Inc (Andover, MA, USA). HPLC grade acetone, n-hexane, dichloromethane (DCM), ethyl acetate (EA) and methanol (MeOH) were purchased from Merck (Darmstadt, Germany). A Milli-Q ultrapure system (Millipore, Molsheim, France) was used to generate HPLC grade water. Two SPE cartridges, Sep-Pak C-18 (6 mL, 500 mg) and Oasis HLB (6 mL, 500 mg) were obtained from Waters (Milford, MA, USA).

### Sample Collection and Pre-treatment

SC 1160 automatic bottle washer (SalvisLab, Switzerland) was used to clean all glassware. The cleaned glassware was pyrolyzed at 450 °C for 4h before the experiment in order to prevent interference of organic impurities. The ultra-fine glass fibre filter (0.3 μm, 10.2 cm

diameter), aluminum foil, operating scissors, mortar and silica sand were also pyrolyzed at 450 °C for 4 h prior to use.

In order to optimize and verify pretreatment methods, quantitative PBDEs standard was added before the experiment. For the SPE procedure, 100 ng/L of PBDEs standard was spiked in Milli-Q grade water. For the MAE procedure, 100 ng PBDEs standard was spiked in one ultra-fine glass fibre filter. Concentration of injected standard solution was 1 ng/μL.

Atmospheric particulate samples were collected on ultra-fine glass fibre filters from the campus outdoor air using a high-volume glass fibre filter. Preceding sampling, the ultra-fine glass fibre filters were weighed on an electronic balance (± 0.1 mg precision, Denver, USA). After the samples were collected, the filters were covered with aluminum foil and kept cool with ice bags during transport to the laboratory, then stored at about -45 °C until analysis. Before analysis, the filters were freeze-dried for 4 days (Eyela FDU-1200, Japan) into a anhydrous state and then weighed in order to determinate the weight of the total suspended particulate (TSP). Environmental samples were collected from one of the state air quality controlling sites (Yunnan Provincial Hospital of Traditional Chinese Medicine) in Kunming, China to validate the developed method. Throughout the text the concentration of PBDE congeners is reported as ng/g dry weight (dw) basis the TSP in filters.

### Microwave-Assisted Extraction

MAE experiments were performed by ETHOS 1 advanced microwave extraction system (Milestone, Italy). The system was equipped with a 12-sample tray and temperature controlling system. After the weighting of fibre filter, spiked with 100 ng PBDEs standard in a uniform distribution manner, was covered with aluminum foil and left for 48h to allow sorption processes to occur, as in nature. Then the filters was cut into small pieces by operating scissors carefully and put in a mortar. 5 g silica sand and 5 mL extraction solvent were added in the mortar, and then grind them into mud. The mud was transferred into a Teflon lined extraction vessels and washed with the similar solvent for three times. When the temperature program of MAE was finished, the vessels were removed from the instrument and opened after cooled to room temperature. The extracts were carefully filtered through absorbent cotton into the flat-bottomed flasks (250 mL) and washed with 15 mL of the same solvent or solvent mixture for three times. The extracts were concentrated to near dryness leaving a small amount of residue by a rotary evaporator (Buchi Rotavapor RII, Switzerland). In order to purify the residue, a small amount of residue was diluted to a final volume of 250 mL with Milli-Q grade water, and subjected to SPE clean-up procedure.<sup>36</sup>

### Solid Phase Extraction

For Solid Phase Extraction (SPE) process, the pH value of the extracts from the MAE was adjusted by hydrochloric acid or sodium hydroxide. Two different SPE cartridges (Sep-Pak C-18 and Oasis HLB cartridges) were placed into a vacuum manifold (12-port, Supelco, USA), and adjusted vacuum pressure to achieve the required flow rate. All the cartridges were disposed with 5 mL of ethyl acetate to remove residual bonding agents, followed by 5 mL

of methanol soaking for 5 min. Then 3×5 mL Milli-Q grade water was added to the cartridges at a rate of 1–2 mL/min. After that, 250 mL extracts from the MAE process was extracted by SPE cartridges at a flow rate less than 5 mL/min. Then, the cartridges were washed by 2×5 mL Milli-Q grade water:MeOH (9:1, v/v) and then were dried under vacuum for 90 min. The analytes were eluted into 15 mL vials with 15 mL of solvents (e.g. DCM) at a flow rate of 1 mL/min. The eluates were blown down to dryness under a gentle flow of nitrogen and then 100 µL internal standard (1 ng/µL) was added. 1 µL of the mixtures was injected for GC–MS analysis.

### GC–MS Analysis

Gas chromatography-mass spectrometry analysis was performed with a Trace GC (Thermo Fisher Scientific, USA), equipped with a Trace DSQ quadrupole mass spectrometer and an autosampler Triplus AS. A DB-5HT capillary column (15 m length) with a 0.25 mm inner diameter and 0.25 µm film thicknesses (Agilent, USA) were used to separate the compounds. Helium (99.999%) carrier gas was maintained at a constant flow rate of 1 mL/min. At an inlet temperature of 280 °C, a sample volume of 1 µL was injected in splitless mode. The chromatogram information of target compounds were displayed on table 1. The column temperature was maintained at 100°C for 1 min, then programmed at 10 °C/min to 300 °C; held for 1 min, increased to 320 °C at a rate of 8 °C/min, and held for 5 min, the total analysis time was 29.5 min. The MS transfer line temperature was 280 °C, whereas the ion source temperature was 300 °C. Mass spectra were operated in full-scan mode from 50–1000 *m/z* for qualitative analysis and selected ion monitoring (SIM) mode for quantitative analysis. Electron impact ionization energy was 70 eV. Examples of chromatograms for the identification of target compounds in standard solutions were shown in Fig. 1.

Table 1 Chromatogram information of target compounds

PBDEs	Retention time (min)	Quantification ions (m/z)	Confirmation ions (m/z)
BDE-17	10.41	406, 246	408
BDE-28	10.71	406, 246	408
BDE-47	12.51	326, 486	488
BDE-66	12.78	326, 486	488
BDE-71	13.05	326, 486	488
BDE-85	14.27	404, 406	564
BDE-99	14.69	404, 406	564
BDE-138	15.87	482, 484	643
BDE-153	16.44	482, 484	643
BDE-154	17.17	482, 484	643
BDE-183	18.06	456, 562	722
BDE-190	19.00	456, 562	722
BDE-209	24.56	797, 799	959

## Results and Discussion

### Optimization of MAE

In order to effectively extract PBDEs from filter samples by MAE, four key process factors, such as extraction solvent, solvent volume, extraction temperature and holding time, were investigated. For each optimization condition, three parallel ultra-fine glass fibre filters spiked with 100 ng PBDEs standard were analysed. The amounts of the TSP on filter were displayed in the table 2. The air particulate samples collected from the campus were used as model matrix. Three ultra-fine glass fibre filters (TSP: 0.3919, 0.3113 and 0.2813 g) were analyzed to determine possible background concentrations of target compounds in the matrix. The mean concentrations of BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-138, BDE-153, BDE-154, BDE-183, BDE-190 and BDE-209 were 0.66, 0.56, 0.76, 0.97, 1.60, 1.76, 1.40, 1.70, 0.86, 1.24, 1.72, 2.47 and 18.93 ng/g dw, respectively. After deducting the background, the recovery rates were calculated.

Table 2 The information of TSP for optimization of MAE

Optimized conditions of MAE	The amounts of the TSP (g)			
	MeOH	0.3503	0.3891	0.3577
Extraction solvent for MAE	MeOH:DCM (4:1, v/v)	0.2993	0.3203	0.3433
	MeOH:DCM (1:1, v/v)	0.2963	0.3946	0.3794
	Acetone	0.3868	0.3693	0.3655
	Acetone:Hexane (1:1, v/v)	0.3613	0.3279	0.3090
Extraction solvent volume for MAE	15 mL	0.3790	0.3300	0.3266
	20 mL	0.3154	0.3505	0.3023
	25 mL	0.3013	0.3218	0.3197
	30 mL	0.3346	0.3730	0.3813
	90 °C	0.3074	0.3368	0.3730
Extraction temperature for MAE	100 °C	0.3170	0.3246	0.3345
	110 °C	0.3402	0.3852	0.2903
	115 °C	0.3768	0.3398	0.3538
	120 °C	0.3806	0.3313	0.3829
	5 min	0.3907	0.3043	0.3541
Holding time for MAE	10 min	0.3186	0.3768	0.3334
	15 min	0.3397	0.3751	0.2982
	20 min	0.2951	0.4141	0.3105
	30 min	0.4063	0.3377	0.3122

For the effect of extraction solvent, the recoveries of target compounds from spiked filter samples were shown in Fig. 2. The recoveries ranged from 53% to 110% with 30 mL of different solvents at 110 °C for 20 min. According to the MAE operating guide, the extraction energy varies with the extraction temperature, and the limit temperature is two times about boiling point of extraction solvent. So the high boiling point solvent has great extraction energy. However, the methanol has the highest boiling point (64.5 °C), but it is not the best extraction solvent for PBDEs, especially for higher brominated BDEs. The reason mainly was that higher brominated BDEs can be degraded in high temperature.<sup>37</sup> According to Fig. 2, acetone:n-hexane (1:1, v/v) has the highest



recovery effects (63%-102%). Because the n-hexane can't absorb microwave energy so that it can prevent the target compound degraded from the overheated acetone. Thus, in order to obtain higher recovery, acetone:n-hexane (1:1, v/v) was selected as the best solvent for further studies.

According to Fig. 3, the mean recovery of target compounds increased with the volume in the range of 15-30 mL. Solvent volume was chosen as 30 mL, which was the highest solvent volume of extraction vessel (100 mL) for Milestone Ethos 1.

The effects of temperature on the recovery of target compounds were shown in Fig. 4. All the mean recoveries increased with temperature in the range of 90-115 °C. Over the 115 °C, the mean recoveries decreased except for BDE-17, BDE-28 and BDE-47.

The mean recoveries of all the analytes significantly increased with the improvement of holding time from 5 to 20 min, which were shown in Fig. 5. But it has a slight decrease, when holding time increased from 20 to 30 min. Thus, 20 min was chosen as the holding time of extraction. In conclusion, the best operating conditions for the extraction of the target compounds was shown in Table 3. The recoveries of target compounds ranged from 74 to 112%.

**Table 3** The best operating conditions of MAE procedure

Operating conditions			
Solvent	Volume (mL)	Temperature (°C)	holding time (min)
acetone:n-hexane (1:1, v/v)	30	115	20

### Optimization of SPE

For the SPE process, in order to find the optimum conditions, SPE cartridge, elution solvent and pH of samples were investigated. It was important that an appropriate SPE cartridge with different sorbent materials was chosen to achieve a high and reproducible recovery for the target compounds. Spiked water samples were used for recovery experiments, two types of cartridges (Sep-Pak C-18, Oasis HLB) were tested for their extraction efficiencies.

In order to achieve the highest recovery, the SPE cartridge was eluted by the optimal elution solvent. The cartridges were eluted as follows: (1) Sep-Pak C-18 cartridges were eluted with 15 mL of DCM; (2) Oasis HLB cartridges were eluted with 15 mL of ethyl acetate. The pH value of water samples was 7.0. The results were shown in Fig. 6. Sep-Pak C-18 cartridges acquired the better recoveries (47%-105%) compared with Oasis HLB cartridges (33%-104%). Therefore, Sep-Pak C-18 was chosen for further testing.

Sep-Pak C-18 cartridges were eluted with organic solvent to desorb the target compounds. Elution strength for Sep-Pak C-18 cartridge was in the order of: n-hexane > DCM > ethyl acetate, so these solvents and their mixed solution were chosen for preliminary elution solvent. The target compounds displayed different recoveries using different elution solvents (Fig. 7). Hexane showed the worst recoveries (57%-75%) for the target compounds. The effect of elution of DCM was still poor with recoveries ranged from 47% to 104%. For the n-hexane and ethyl acetate mix solution, the recoveries showed increases firstly and then decreases with the ethyl acetate level increased from 0% to 50%. For the DCM and n-hexane

mix solution, the recoveries increased with the increase of n-hexane concentration. The best elution solvent was n-hexane:ethyl acetate (4:1, v/v) with recoveries ranged from 78% to 108% for the target compounds.

The effect of pH on extraction efficiency was studied. The pH value of water sample was adjusted with diluted solutions of sodium hydroxide and hydrochloric acid. As shown in Fig. 8, the extraction recoveries at pH 6.0 and 7.0 were better for all target compounds than other pH values. In consideration of convenience, the best pH value was about 7.0. In conclusion, the best operating conditions of SPE procedure was shown in Table 4.

**Table 4** The best operating conditions of SPE procedure

Choose	Operating conditions		
	SPE cartridge	elution solvent	pH
Sep-Pak C-18	n-hexane:ethyl acetate (4:1, v/v)	7.0	

### Validation of the method

The limit of detection (LOD), the limit of quantification (LOQ), the linear range, mean recovery and precision were used to validate the analytical method. LOD and LOQ were defined as the concentration when signal-to-noise ratios (S/N) were 3:1 and 10:1, respectively, which was used to estimate determination of PBDEs at the levels in particulate samples. A multipoint calibration with thirteen standard solutions at different concentration levels, such as 0.001, 0.005, 0.01, 0.025, 0.05, 0.075, 0.1, 0.25, 0.5, 1, 2.5 and 5 ng/μL were used to determine regression equations of the calibration curve. The internal standard was added to the sample before analyzing and the concentration of internal standard was 1 ng/μL for all points. The calibrations curve correlation coefficient ( $R^2$ ) was higher than 0.995 for the PBDEs analysis. Linear equation, correlation coefficient, linear range, LOD and LOQ of the PBDEs were listed in Table 5. To further validate the precision and accuracy of the method, recovery experiments were carried out by spiking air particulate samples at three levels (10, 100 and 500 ng). The recoveries and relative standard deviations (RSD, n=3) for all the target compounds were 74.0%–112% and 2.0%–11% (Table 6), respectively. The results showed that a high performance could be achieved through optimized method.

**Table 5** Linear equation, correlation coefficient, linear range, LOD and LOQ of the PBDEs

PBDEs	Linear equation	$R^2$	Linear range (ng/g)	LOD in particulates (ng/g)	LOQ in particulates (ng/g)
BDE-17	$y = 2.3762x - 0.0044$	0.999	1.25-1250	0.11	0.37
BDE-28	$y = 2.3058x - 0.0041$	0.999	1.25-1250	0.12	0.40
BDE-47	$y = 1.1586x - 0.0027$	0.999	1.25-1250	0.17	0.57
BDE-66	$y = 1.4392x - 0.0029$	0.999	1.25-1250	0.19	0.63
BDE-71	$y = 1.3441x - 0.0028$	0.999	1.25-1250	0.17	0.57
BDE-85	$y = 0.9075x - 0.002$	0.999	1.25-1250	0.14	0.47
BDE-99	$y = 0.9581x - 0.0026$	0.999	1.25-1250	0.19	0.63
BDE-138	$y = 0.3355x - 0.0019$	0.999	1.875-1875	0.27	0.90
BDE-153	$y = 0.502x - 0.0021$	0.998	1.25-1250	0.20	0.67
BDE-154	$y = 0.6621x - 0.0033$	0.998	1.25-1250	0.21	0.70
BDE-183	$y = 0.1411x + 0.0011$	0.999	1.25-1250	0.18	0.60
BDE-190	$y = 0.1374x + 0.0009$	0.996	1.25-1250	0.31	1.03
BDE-209	$y = 0.0354x - 0.0054$	0.995	5-5000	1.23	4.10

**Table 6** Recoveries and precisions of the PBDEs in spiked air particulate samples

PBDEs	Spiked level 10ng (TSP: 0.3894, 0.3764 and 0.3568 g)		Spiked level 100ng (TSP: 0.4053, 0.3654 and 0.3941 g)		Spiked level 500ng (TSP: 0.3456, 0.3739 and 0.3193 g)	
	Mean Recovery (%)	RSD (%) n=3	Mean Recovery (%)	RSD (%) n=3	Mean Recovery (%)	RSD (%) n=3
BDE-17	90.5	4.2	95.1	2.3	93.0	5.3
BDE-28	95.3	3.2	96.8	2.5	93.8	2.7
BDE-47	100	5.4	110	2.0	106	4.9
BDE-66	109	4.7	112	3.1	110	6.4
BDE-71	108	4.3	104	3.9	94.7	3.7
BDE-85	84.5	4.7	83.3	3.2	89.5	8.9
BDE-99	80.0	5.8	74.0	4.5	83.8	4.6
BDE-138	87.3	8.2	83.1	7.1	88.9	7.8
BDE-153	74.1	3.8	79.5	5.1	80.6	8.7
BDE-154	76.9	9.1	79.2	4.8	74.6	9.1
BDE-183	78.7	8.4	74.1	11	75.4	11
BDE-190	89.1	9.0	97.8	9.6	90.1	5.6
BDE-209	92.4	5.8	89.9	5.1	93.9	4.9

### Analysis of Environmental Samples

The improved method was successfully applied to the analysis of PBDEs in atmospheric particulates, which were collected from one of the state air quality controlling sites in Kunming, China (Yunnan Provincial Hospital of Traditional Chinese Medicine), on April 9, 2012. The amounts of the TSP on filter were 0.4295, 0.4081 and 0.4143g. SIM chromatograms of target compounds in air particulate samples from air sampling site were shown in Fig. 9.

The average concentrations of BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-138, BDE-153, BDE-154, BDE-183, BDE-190 and BDE-209 were 10.7, 27.9, 15.1, 9.6, 35.4, 33.4, 4.97, 9.73, 8.50, 16.2, 19.3, 265 and 376 ng/g dw in air particulates, respectively. To sum up, BDE-28, BDE-71, BDE-190 and BDE-209 were the four dominant PBDEs in this sampling site.

### Conclusions

The integrated method for the analysis of thirteen PBDEs in atmospheric particulates was developed by optimizing the MAE and SPE procedure. For MAE procedure, sufficient extraction was performed with 30 mL of acetone:n-hexane (1:1, v/v) as extraction solvent at 115 °C for 20 min, reducing the time and cost of analysis. For SPE procedure, sufficient isolation of the target compounds was obtained from the matrix by using Sep-PakC-18 cartridges with 15 mL of n-hexane:ethyl acetate (4:1, v/v) as the elution solvent when pH value of water samples was about 7.0. The method can achieve good repeatability and reproducibility with RSDs ranged from 2.0% to 11% for all target PBDEs in atmospheric particulate samples. Satisfactory recoveries of SPE procedure and MAE procedure were 78% to 108% and 74% to 112%, respectively. LOD and LOQ ranged from 0.11 (BDE-17) to 1.23 ng/g dw (BDE-209) and from 0.37 (BDE-17) to 4.10 ng/g dw (BDE-209), respectively.

The developed method has been successfully demonstrated to determine the concentrations of the target PBDEs in atmospheric particulates from one of the state air quality controlling sites in Kunming, China. Thus, the method could be a promising approach for the analysis of thirteen polybrominated diphenyl ethers in

atmospheric particulate samples.

### Acknowledgements

This work was sponsored by the National Natural Science Foundation of China (Grant No. 21267012), the Specialized Research Fund for the Doctoral Program of Higher Education of China (No. 20125314110003), Application Fundamental Key Basic Research Foundation of Yunnan Province, China (Grant No. 2013FA011), China Postdoctoral Science Foundation (Grant No. 2013M531987) and Application Fundamental Research Foundation of Yunnan Province, China (Grant No. 2012FB124).

### References

1. M. Yang, H. Qi, H. L. Jia, N. Q. Ren, Y. S. Ding, W. L. Ma, L. Y. Liu, H. Hung, E. Sverko and Y. F. Li, *Environ. Sci. Technol.*, 2013, **47**, 8978-8984.
2. A. D. St-Amand, P. M. Mayer and J. M. Blais, *Environ. Sci. Technol.*, 2007, **41**, 4234-4239.
3. Z. Y. Xie, A. Möller, L. Ahrens, R. Sturm and R. Ebinghaus, *Environ. Sci. Technol.*, 2011, **45**, 1820-1826.
4. H. B. Moon, K. Kannan, S. J. Lee and M. Choi, *Chemosphere*, 2007, **66**, 585-593.
5. J. Li, Q. L. Li, R. Gioia, Y. L. Zhang, G. Zhang, X. D. Li, B. Spiro, R. S. Bhatia and K. C. Jones, *Atmos. Environ.*, 2011, **45**, 6622-6628.
6. C. A. de Wit, *Chemosphere*, 2002, **46**, 583-6246.
7. R. L. Law, C. R. Allchin., J. De Boer, A. Covaci, D. Herzke, P. Lepom, S. Morris, J. Tronczynski and C. A. de Wit, *Chemosphere*, 2006, **64**, 187-208.
8. F. M. Jaward, G. Zhang, J. J. Nam, A. J. Sweetman, J. P. Obbard, Y. Kobara and K. C. Jones, *Environ. Sci. Technol.*, 2005, **39**, 8638-8645.
9. B. Strandberg, N. G. Dodder, I. Basu and R. A. Hites, *Environ. Sci. Technol.*, 2001, **35**, 1078-1083.
10. E. Hoh and R. A. Hites, *Environ. Sci. Technol.*, 2005, **39**, 7794-7802.
11. A. Hassanin, K. Breivik, S. N. Meijer, E. Steinnes, G. O. Thomas and K. C. Jones, *Environ. Sci. Technol.*, 2004, **38**, 738-745.
12. B. Gevao, A. N. Ghadban, S. Uddin, F. M. Jaward, M. Bahloul and J. Zafar, *Environ. Pollut.*, 2011, **159**, 3666-3672.
13. Y. Wang, C. L. Luo, J. Li, H. Yin, X. D. Li and G. Zhang, *Environ. Pollut.*, 2011, **159**, 2443-2448.
14. S. Hallgren and P. O. Darnerud, *Toxicology*, 2002, **177**, 227-243.
15. P. O. Darnerud, M. Aune, L. Larsson and S. Hallgren, *Chemosphere*, 2007, **67**, 386-392.
16. X. H. Bi, G. O. Thomas, K. C. Jones, W. Y. Qu, G. Y. Sheng, F. L. Martin and J. M. Fu, *Environ. Sci. Technol.*, 2007, **41**, 5647-5653.
17. M. H. Wong, S. C. Wu, W. J. Deng, X. Z. Yu, Q. Luo, A. O. W. Leung, C. S. C. Wong, W. J. Luksemburg and A. S. Wong, *Environ. Pollut.*, 2007, **149**, 131-140.
18. J. P. Boon, W. E. Lewis, M. R. Tjoen-A-Choy, C. R. Allchin, R. J. Law, J. de Boer, C. C. Hallers-Tjabbes and B. N. Zegers, *Environ. Sci. Technol.*, 2002, **36**, 4025-4032.
19. M. Alaei, P. Arias, A. Sjödin and A. Bergman, *Environ. Int.*, 2003, **29**,

- 1 683-689.
- 2 20. Ö. Andersson and G. Blomkvist, *Chemosphere*, 1981, **10**, 1051-1060.
- 3 21. F. Vilaplana, A. Ribes-Greus and S. Karlsson, *Talanta*, 2009, **78**, 33-39.
- 4 22. M. Shin, M. L. Svoboda and P. Falletta, *Anal. Bioanal. Chem.*, 2007, **387**,
- 5 2923-2929.
- 6 23. A. Ranz, E. Maier, C. Trampitsch and E. Lankmayr, *Talanta*, 2008, **76**,
- 7 102-106.
- 8 24. G. Mariani, E. Canuti, J. Castro-Jiménez and E. H. Christoph,
- 9 *Chemosphere*, 2008, **73**, 114-121.
- 10 25. B. Z. Zhang, K. Zhang, S. M. Li, C. S. Wong and E. Y. Zeng, *Environ.*
- 11 *Sci. Technol.*, 2012, **46**, 7207-7214.
- 12 26. K. Tlili, P. Labadie, F. Alliot, C. Bourges, A. Desportes and M.
- 13 Chevreuil, *Water Air Soil Pollut.*, 2012, **223**, 1543-1553.
- 14 27. A. Möller, Z. Xie, R. Sturm and R. Ebinghaus, *Environ. Pollut.*, 2011,
- 15 **159**, 1577-1583.
- 16 28. J. C. Hu, J. Jin, Y. Wang, Z. H. Ma and W. J. Zheng, *Chemosphere*, 2011,
- 17 **84**, 355-360.
- 18 29. A. D. St-Amand, P. M. Mayer and J. M. Blais, *Atmos. Environ.*, 2008, **42**,
- 19 2948-2958.
- 20 30. B. H. Wilford, G. O. Thomas, K. C. Jones, B. Davison and D. K. Hurst,
- 21 *Environ. Int.*, 2008, **34**, 412-419.
- 22 31. Z. F. Ren, X. Xiao, D. Y. Chen, X. H. Bi, B. Huang, M. Liu, J. F. Hu, P.
- 23 A. Peng, G. Y. Sheng and J. M. Fu, *Chemosphere*, 2014, **94**, 143-150.
- 24 32. X. M. Wang, X. Ding, B. X. Mai, Z. Q. Xie, C. H. Xiang, L. G. Sun, G. Y.
- 25 Sheng, J. M. Fu and E. Y. Zeng, *Environ. Sci. Technol.*, 2005, **39**, 7803-7809.
- 26 33. M. Song, S. Chu, R. J. Letcher and R. Seth, *Environ. Sci. Technol.*, 2006,
- 27 **40**, 6241-6246.
- 28 34. U. Sellstrom, C. A. de Wit, N. Lundgren and M. Tysklind, *Environ. Sci.*
- 29 *Technol.*, 2005, **39**, 9064-9070.
- 30 35. A. Binelli, C. Roscioli and L. Guzzella, *J. Chromatogr. A*, 2006, **1136**,
- 31 243-247.
- 32 36. B. Wang, X. Wan and S. M. Zhao, *Chromatographia*, 2011, **74**, 297-306.
- 33 37. H. M. Stapleton. *Anal. Bioanal. Chem.*, 2006, **386**, 807-817.
- 34
- 35
- 36
- 37
- 38
- 39
- 40
- 41
- 42
- 43
- 44
- 45
- 46
- 47
- 48
- 49
- 50
- 51
- 52
- 53
- 54
- 55
- 56
- 57
- 58
- 59
- 60

**Figure captions**

**Fig. 1** SIM chromatogram of target compounds in standard solutions (1ng/μL) (1) BDE-17, (2) BDE-28, (3) BDE-47, (4) BDE-66, (5) BDE-71, (6) BDE-85, (7) BDE-99, (8) I.S. BDE-100L (9) BDE-138, (10) BDE-153, (11) BDE-154, (12) BDE-183, (13) BDE-190 (14) BDE-209

**Fig. 2** The effect of extraction solvent on the mean recovery of target compounds from spiked filter samples (n=3). Note MAE procedure: 30 mL of different solvents as extraction solvent at 110 °C for 20 min in the MAE; SPE procedure: Sep-PakC-18 cartridges with 15 mL of n-hexane:ethyl acetate (4:1, v/v) as the elution solvent; injection solvent: n-hexane; injection volume: 1μL

**Fig. 3** The effect of extraction solvent volume on the mean recovery of target compounds from spiked filter samples (n=3). Note MAE procedure: different solvent volume of acetone:n-hexane (1:1, v/v) as extraction solvent at 110 °C for 20 min in the MAE; SPE procedure: Sep-PakC-18 cartridges with 15 mL of n-hexane:ethyl acetate (4:1, v/v) as the elution solvent; injection solvent: n-hexane; injection volume: 1μL

**Fig. 4** The effect of extraction temperature on the mean recovery of target compounds from spiked filter samples (n=3). Note MAE procedure: 30 mL of acetone:n-hexane (1:1, v/v) as extraction solvent at different temperature for 20 min in the MAE; SPE procedure: Sep-PakC-18 cartridges with 15 mL of n-hexane:ethyl acetate (4:1, v/v) as the elution solvent; injection solvent: n-hexane; injection volume: 1μL

**Fig. 5** The effect of holding time on the mean recovery of target compounds from spiked filter samples (n=3). Note MAE procedure: 30 mL of acetone:n-hexane (1:1, v/v) as extraction solvent at 115 °C for different holding time in the MAE; SPE procedure: Sep-PakC-18 cartridges with 15 mL of n-hexane:ethyl acetate (4:1, v/v) as the elution solvent; injection solvent: n-hexane; injection volume: 1μL

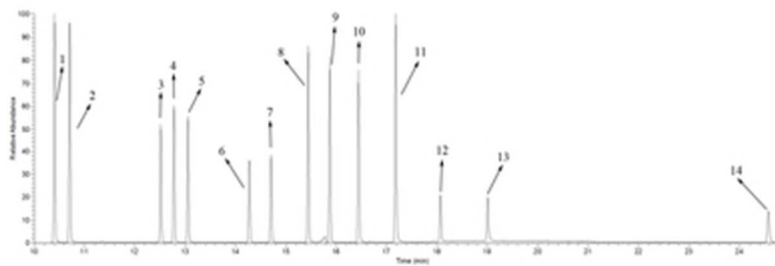
**Fig. 6** The effect of two types of SPE cartridge on the mean recovery of target compounds from spiked water samples (n=3). Note C-18 cartridge with 15 mL of DCM as the elution solvent; HLB cartridge with 15 mL of ethyl acetate as the elution solvent; water sample volume:1000 mL; injection solvent: n-hexane; injection volume: 1μL

**Fig. 7** The effect of different elution solvent on the mean recovery of target compounds from spiked water samples (n=3). Note C-18 cartridge with 15 mL different elution solvent; water sample volume: 1000 mL; injection solvent: n-hexane; injection volume: 1μL

**Fig. 8** The effect of water sample pH on the mean recovery of target compounds from spiked water samples (n=3). Note C-18 cartridge with 15 mL of n-hexane:ethyl acetate (4:1, v/v) as the elution solvent; water sample volume: 1000 mL; injection solvent: n-hexane; injection volume: 1 μL

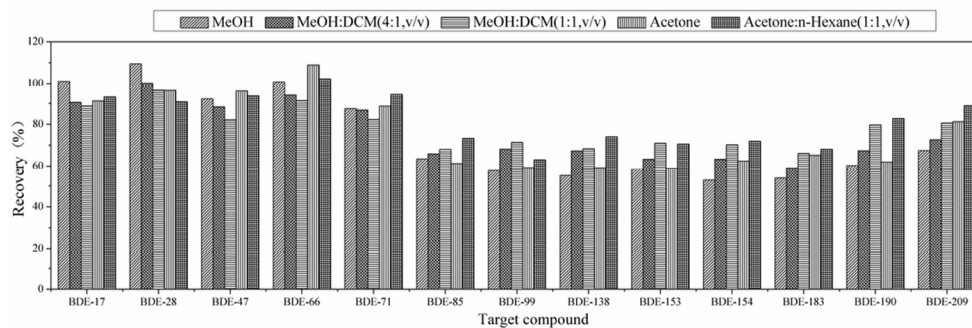
**Fig. 9** SIM chromatogram of target compounds in air particulate samples from air sampling site, and the I.S. concentration was 1 ng/μL (1) BDE-17, (2) BDE-28, (3) BDE-47, (4) BDE-66, (5) BDE-71, (6) BDE-85, (7) BDE-99, (8) I.S. BDE-100L (9) BDE-138, (10) BDE-153, (11) BDE-154, (12) BDE-183, (13) BDE-190 (14) BDE-209



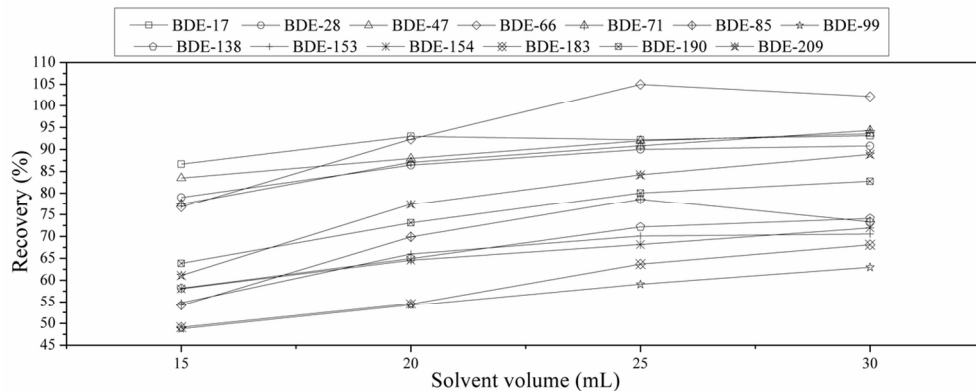


33x11mm (300 x 300 DPI)

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

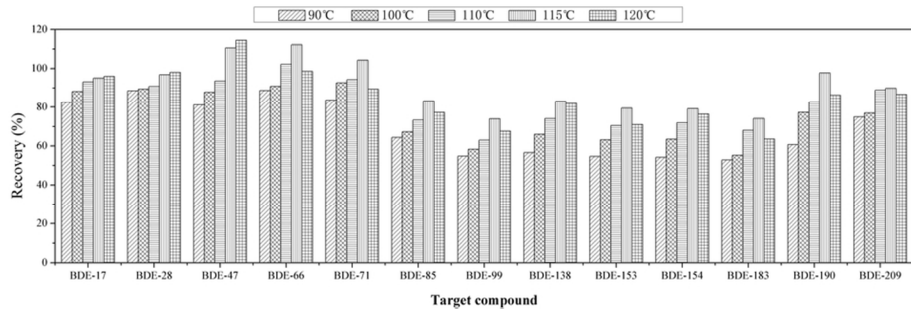


94x31mm (300 x 300 DPI)



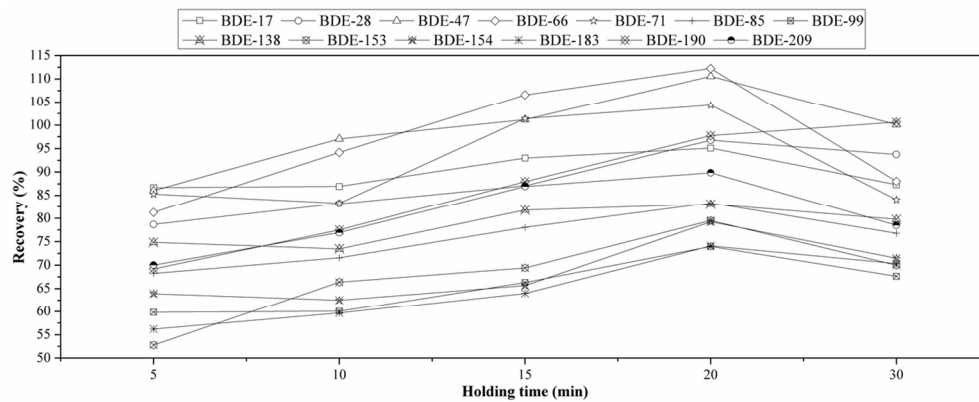
115x46mm (300 x 300 DPI)

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



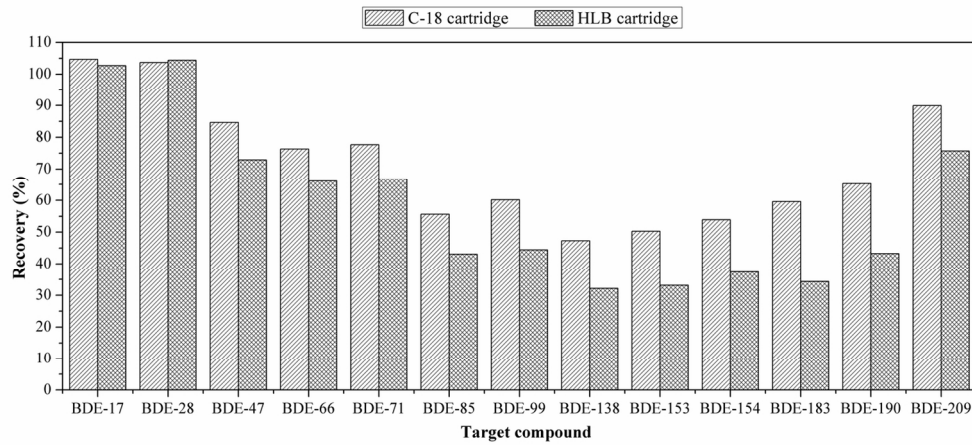
88x27mm (300 x 300 DPI)

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

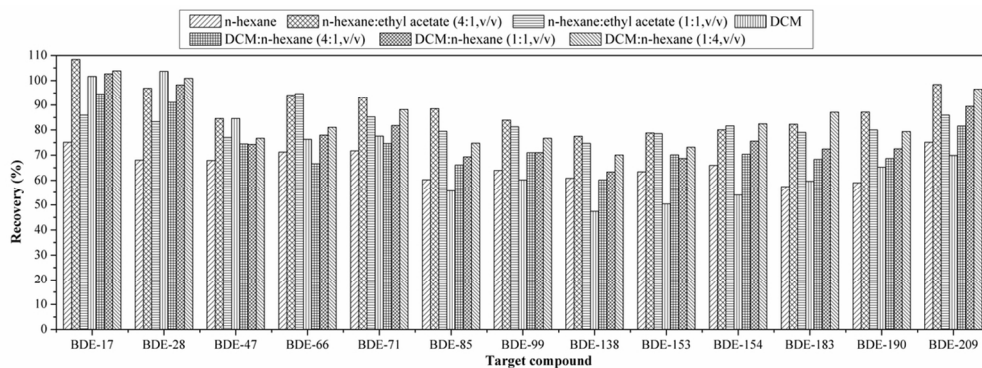


115x46mm (300 x 300 DPI)

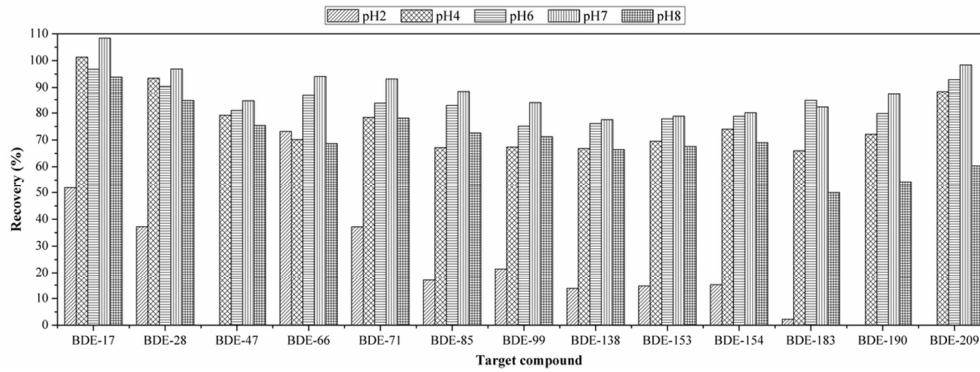




128x57mm (300 x 300 DPI)

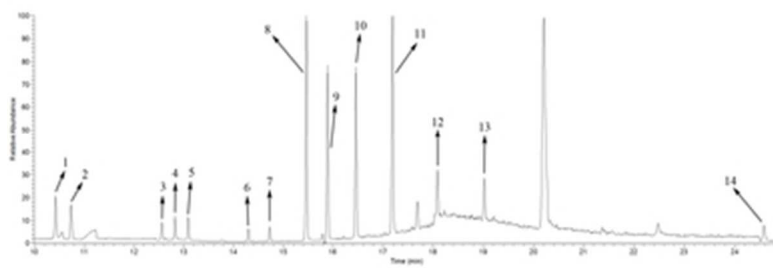


105x38mm (300 x 300 DPI)



105x38mm (300 x 300 DPI)

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



33x11mm (300 x 300 DPI)

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60