Simultaneous determination of brominated phenols in soils

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Abstract

Brominated phenols (BPs), a widely used group of emerging flame retardants, are important environmental contaminants and exhibit endocrine disrupting potential. Method for simultaneous determination of tetrabromobisphenol A (TBBPA), tribromophenol (TBP), dibromophenols (DBPs) and monobromophenols (MBPs) in soils using gas chromatography-mass spectrometry analysis (GC/MS) was successfully developed. Cleanup methods for soil extracts including several solid-phase extraction cartridges and different elution solvents were compared and optimized. Florisil cartridge with dichloromethane as the elution reagent was selected for sample cleanup owing to its high and reproducible recoveries of the target analytes in soils. Derivatization conditions were tested and the optimal conditions were obtained with 20 μ L silylation reagent at room temperature. The chromatographic separation was optimized with different columns and DB-XLB column was selected for its excellent separation of the analytes. The limits of detection for the target compounds were from 0.04 to 0.19 ng/g. Mean recoveries of the compounds from spiked soils exceeded 84% with a good reproducibility, excepting that the recovery of 2-bromophenol was relatively poor (lower than 55%) due to its instability. The developed method was applied to the determination of the BPs in the soils collected from e-waste sites. The contents of BPs in the soils were at ng/g levels with TBBPA and TBP the most frequently detected. To our knowledge, this is the first report for the simultaneous determination of TBBPA, TBP, DBPs and MBPs in soils.

Key words: brominated phenols; analysis; soil; derivatization; GC/MS

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Introduction

Brominated flame retardants (BFRs), which have been used in a variety of commercial and industrial applications worldwide, cause a great concern as persistent organic contaminants (Covaci et al., 2011; Huang et al., 2010; Guerra et al., 2011; Wang et al., 2011). Among them, brominated phenols (BPs) are a widely used group of BFRs because of their high efficiency and low cost. For example, tetrabromobisphenol A (TBBPA) possesses the largest production volume with the global size of 1.7×10^5 tons in 2004, covering around 60% of the total BFR market (Covaci et al., 2009). Moreover, its use as flame retardants is currently not restricted in many countries such as USA and China (Guerra et al., 2011). Similarly, tribromophenol (TBP) is also used as a reactive flame retardant to a lesser extent than TBBPA and has been recently classified as one of the novel BFRs to replace the banned compounds (Covaci et al., 2011). Due to their wide applications, both TBBPA and TBP have been detected in various environmental media

including water, air, sediment, dust and sewage sludge, together with some biotic samples such as fish, birds and marine and terrestrial mammals (Covaci et al., 2009, 2011; Deng et al., 2010; Haldén et al., 2010). Furthermore, they have also been found to cause adverse health effects such as endocrine disruption, hepatotoxicity and neurotoxicity on humans and other organisms even at environmental levels (Covaci et al., 2009; Deng et al., 2010; Howe et al., 2005; Ezechiáš et al., 2012). Therefore, both TBBPA and TBP are considered as important environmental contaminants with respect to their widely applications and influences on living organisms.

Soil represents a major sink for organic contaminants such as TBBPA and TBP in the terrestrial environment due to their partition ability and low water solubility (Covaci et al., 2009; Hakk and Letcher, 2003). Furthermore, TBBPA and TBP can be partly degraded to lesser brominated analogues in soils mainly due to soil microbe activities and plant-soil interaction (Hakk and Letcher, 2003; Polo et al., 2006; Voordeckers et al., 2002). This not only results in co-contamination of BPs in soils, but also brings additional adverse influences to bear on the environment

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and human health due to their different biological effects compared with their precursor. Therefore, more concern should be given to the environmental presence of TBBPA and TBP together with their possible degradation products of lesser brominated analogues, which firstly necessitates the establishment of analytical methods for simultaneous determination of BPs in soils as well as in other environmental matrices.

Methods for determination of TBBPA and TBP in environmental samples such as water, soil, sediment and air have been established with gas chromatography-mass spectrometry (GC/MS) as the most commonly used analytical tool due to its high selectivity and sensitivity (Covaci et al., 2009; Sánchez-Brunete et al., 2009; López et al., 2009). Simultaneous determination of TBBPA and its degradation products of bisphenol A in sediment and sludge has been established by high performance liquid chromatography-electrospray tandem mass spectrometry (LC-MS/MS) (Chu et al., 2005). However, there are very few validated analytical methods for the determination of simple BPs such as monobromophenols (MBPs) and dibromophenols (DBPs), possible degradation products of TBP in the environment, and no method has been reported for the simultaneous determination of TBBPA, TBP and the lesser BPs in soils. Therefore, the major objective of this study was to develop a fast, selective and sensitive method for the simultaneous determination of BPs including TBBPA, TBP, DBPs and MBPs in soils by GC/MS. In the present work, GC/MS was used due to the reason that in comparison GC/MS is more available although LC-MS/MS method is more robust. Considering the necessity of cleanup and derivatization for sample analysis because of the complex matrices of soils and polarity of the BPs, attentions were mainly paid to optimization of sample cleanup with different solid-phase extraction (SPE) cartridges and derivatization procedure. The established method was verified by analyzing the target compounds in the soils collected from e-waste contaminated sites. To our knowledge, this is the first report for the simultaneous determination of TBBPA, TBP, DBPs and MBPs in soils.

1 Materials and methods

1.1 Chemicals and reagents

The BPs investigated in this study include TBBPA, TBP and MBPs of 2-bromophenol (2-MBP), 3-bromophenol (3-MBP) and 4-bromophenol (4-MBP), and DBPs of 2,4-dibromophenol (2,4-DBP), 2,5-dibromophenol (2,5-DBP), 2,6-dibromophenol (2,6-DBP) and 3,5-dibromophenol (3,5-DBP). Their physicochemical properties are provided in **Table 1**, respectively. TBBPA (> 97%) was obtained from Sigma-Aldrich Chemical Co. (USA). 2,5-DBP was purchased from Accu Standard Co. The other BPs including tetrabromophenol (Tetra-BP) were supplied by Dr. Ehrenstorfer Co. (Germany). However, Tetra-BP was not included in further analysis of the soils due to suitability of the sample pretreatment procedures. ^{13}C -TBBPA and ^{13}C -PCB-208 (> 99%) used as recovery surrogate compound and the internal standard, respectively, were purchased from Cambridge Isotope Laboratories (MA, USA).

Individual standard stock solutions of the BPs were prepared by dissolving each pure compound in ethyl acetate. Working solutions (10 $\mu\text{g/mL}$ for 2,5-dibromophenol and 16 $\mu\text{g/mL}$ for the others) were prepared by mixing individual stock solutions, followed by serial dilution with ethyl acetate. The dosage of 2,5-DBP used in this study was 60% of that of the other eight BPs without special note. ^{13}C -TBBPA and ^{13}C -PCB-208 were used as the recovery surrogate compound and the internal standard at the concentrations of 50 ng/mL and 25 ng/mL, respectively.

All organic solvents used including hexane, dichloromethane, acetone and ethyl acetate were HPLC-grade and purchased from Fisher Scientific (USA). The 12-port Visiprep SPE Vacuum Manifold and the derivatization reagent (BSTFA: TMCS 99:1) were both purchased from Supelco Co. (USA). Anhydrous sodium sulfate was obtained from Beijing Chemical Factory and pretreated by heating in a muffle furnace at 400°C for 4 hr to remove possible organic contaminants. Glassware was washed with detergent solution, rinsed with pure water, air dried and heated at 400°C for 4 hr in sequence prior to use.

Table 1 Physicochemical properties of brominated phenols (BPs) (Kuramochi et al., 2008; Howe et al., 2005)

Compound	Abbreviation	Chemical formula	Molecular mass	Water solubility (mg/L)	K_{ow}	pK_a
2-Monobromophenol	2-MBP	$\text{C}_6\text{H}_5\text{Br}_1\text{O}$	173	–	1.69–2.35	–
3-Monobromophenol	3-MBP	$\text{C}_6\text{H}_5\text{Br}_1\text{O}$	173	–	1.98–2.63	–
4-Monobromophenol	4-MBP	$\text{C}_6\text{H}_5\text{Br}_1\text{O}$	173	17400	1.94–2.63	9.17
2,4-Dibromophenol	2,4-DBP	$\text{C}_6\text{H}_4\text{Br}_2\text{O}$	252	208	2.56–3.48	7.79
2,5-Dibromophenol	2,5-DBP	$\text{C}_6\text{H}_4\text{Br}_2\text{O}$	252	–	2.56	–
2,6-Dibromophenol	2,6-DBP	$\text{C}_6\text{H}_4\text{Br}_2\text{O}$	252	–	2.37	–
3,5-Dibromophenol	3,5-DBP	$\text{C}_6\text{H}_4\text{Br}_2\text{O}$	252	–	–	–
Tribromophenol	TBP	$\text{C}_6\text{H}_3\text{Br}_3\text{O}$	331	59, 61	3.74–4.24	6.08
Tetrabromobisphenol A	TBBPA	$\text{C}_{15}\text{H}_{12}\text{Br}_4\text{O}_2$	544	0.08–4.16	4.50–5.90	7.5, 8.5

“–”: not available.

1.2 Sample preparation

The soil samples (5–25 cm in depth) were collected from the sites contaminated with e-waste dismantling and recycling activities in Guangdong Province of China. After freeze-dried, the soil samples were ground and passed through a 2-mm sieve and then stored at -20°C in sealed plastic bags before use. The mixture of 2 g soils with 2 g anhydrous sodium sulfate was homogenized and transferred to extraction thimble. Then 20 μL of surrogate compound ^{13}C -TBBPA solution (1 $\mu\text{g}/\text{mL}$) was spiked into the soil samples. After the added organic solvent evaporated (about 2 hr), the samples were Soxhlet extracted for 24 hr with 100 mL hexane and acetone mixture (1:1, V/V). The extract was rotary evaporated to 1–2 mL and transferred to 10 mL centrifuge tube with 2 mL hexane and acetone mixture (1:1, V/V) as the rinsing reagent. The extract was then dried with a soft nitrogen flow at room temperature and 1 mL hexane was added to dissolve the residue.

Cartridge purification was performed on SPE Vacuum Manifold. Five kinds of different cartridges were obtained from three manufactures with the detail information as follows: acidic alumina, 2 g/6 mL; florisil, 1 g/6 mL; silica gel-1, 1 g/6 mL; silica gel-2, 500 mg/6 mL; silica gel-3, 500 mg/6 mL. The cartridges were conditioned with 10 mL hexane before use. Then the extract was allowed to pass through the cartridge drop by drop with the gravitational flow rate. The cartridge was washed with 10 mL hexane which was discarded and the analytes were eluted with different solvents (10 mL) for comparison with the flow rate at approximately 1 mL/min.

The collected eluate was concentrated to dryness under a gentle stream of nitrogen and reconstituted in ethyl acetate. The derivative reagent was added and the derivatization conditions (dosage of the derivative reagent and temperature) were optimized. Then the sample with the final volume of 400 μL was filtered through the nylon membrane (0.22 μm) before GC/MS analysis.

1.3 GC/MS analysis

The measurement of the BPs was performed by an Agilent 7890 GC/MS (5975 inert) (USA). Columns of HP-5MS (30 m $\times$ 0.25 mm $\times$ 0.25 μm) and DB-XLB (30 m $\times$ 0.25 mm $\times$ 0.25 μm) were compared for separation efficiency. The gas of helium with high purity (99.99%) was applied with the flow rate of 1 mL/min. The volume of injection was 1 μL with the non-split model. The temperature program was set as follows: oven temperature held at 75°C for 1 min, then increased to 150°C at the rate of $20^{\circ}\text{C}/\text{min}$ and held for 7 min, then increased to 300°C with the rate of $35^{\circ}\text{C}/\text{min}$ and held for 6 min. The total running time was 22 min. The temperatures of oven and injection inlet were set at 300°C and 250°C , respectively. The temperatures of ion source, transfer line and quadrupole were maintained at 230°C , 280°C and

150°C , respectively. For mass spectrometry information, the characteristic ions of the target compounds, surrogate compound and internal compound were determined by full scan model. SIM mode was applied in the further analysis. The quantification ions and the retention time to identify target compounds were also included.

2 Results and discussion

2.1 Optimization of sample pretreatment and analysis

2.1.1 Soil extraction and cleanup

Soxhlet extraction with a mixture of hexane and acetone (volume of 100 mL at 1:1 mixture ratio) has been successfully applied to extract some organic contaminants such as PCBs, PBDEs, TBBPA and HBCD with different polarities in various environmental media such as soils (Huang et al., 2010, 2011; Wang et al., 2011), sediments (Mai et al., 2005), plant (Huang et al., 2010; Wang et al., 2011) and bird tissue samples (He et al., 2010). Therefore it was adopted in the present study. Extract for 24 hr was shown to achieve quantitative recoveries of all the target compounds from soils.

Cleanup step is a key procedure for the determination of target compounds in soils to reduce or eliminate the matrix interferences. Silica, florisil and aluminium oxide are the commonly used adsorbents for the separation of polar phenolic compounds in soils, sediments and other solid matrices (Sánchez-Brunete et al., 2009; López et al., 2009; Chu et al., 2005; Blanco et al., 2006; Liu et al., 2004). Therefore optimization of cartridge with different adsorbent materials is significant in achieving a high and reproducible recovery together with an effective cleanup of sample extract. In this study, five kinds of cartridges with various filling materials provided by different producers were compared for their recoveries. A mixture of the nine BPs (20 ng of each compound) was uploaded onto the cartridges. Different recoveries were obtained after eluting by 10 mL dichloromethane as shown in **Fig. 1**, which was probably attributed to the differences among the cartridges including packing material properties, size and porosity. The poorest recovery was obtained for the acidic alumina oxide cartridge in which the fillings strongly retained the polar compounds with the recovery less than 40% for all the target compounds at the optimized experimental condition. The florisil cartridge showed the best recoveries (73% for 2-MBP and over 82% for the other BPs) and was therefore used for further analysis, whereas the other cartridges were not suitable for simultaneous determination of all the BPs. The recovery obtained by the relatively lower polar solvent (hexane:dichloromethane, 1:1, V/V, 10 mL) as the elution solvent for the selected cartridge was not satisfactory (data not shown) and consequently dichloromethane was chosen as the elution solvent. Moreover, the soil extracts became clear after purification with

Fig. 1 Recoveries of the BPs from cartridge cleanup.

the selected cartridge.

2.1.2 Derivatization

The silylation reagent of BSTFA:TMCS (99:1, V/V) was used to increase the volatility, thermal stability and detector response of the BPs. Heating at 70°C or 60°C has been chosen for derivatization of phenols previously (Liu et al., 2004; Sánchez-Brunete et al., 2009). The impact of heating on derivatization was investigated at the temperature of 26, 40, 60 and 80°C controlled by water bath for 1 hr (256 ng of each compound with enough derivative reagent of 100 µL). The results showed that the increase of temperature did not improve the derivative efficiency. Therefore, heating was unnecessary for the derivatization reaction and room temperature was used in the following experiments with the derivatization time controlled for at least 1 hr.

Different dosages of derivative reagent (10, 20, 40, and 100 µL) were applied to compare the derivatization efficiency. A mixture of nine BPs with each one at the final concentration of 640 ng/mL was used and the derivative time was 1 hr at room temperature. The results showed that the response did not change significantly with the increase of the derivative reagent dosage, and 20 µL was sufficient for complete derivatization and was applied in the following experiments.

2.1.3 Optimization of GC/MS parameters

Considering the polarity differences of the BPs, two different chromatography columns of distinct polarities (non-polarity and weak polarity) were applied to the separation of the nine BPs using the same oven temperature program. HP-5MS capillary column is an excellent non-polarity column coated with (5%-phenyl)-methylpolysiloxane. It has been recommended for the separation of organic contaminants such as PCBs, chlorinated pesticides, phenols and BPDEs (Gu et al., 2011; Huang et al., 2010, 2011; Wang et al., 2011). DB-XLB column has low polarity with unique selectivity and exceptional low bleed. The

chromatograms for the separation of the target compounds on the two columns are shown in Fig. 2. Even though HP-5MS column gave symmetrical chromatographic peaks, peaks for 3,5-DBP and 2,6-DBP overlapped seriously. Whereas DB-XLB column showed high resolution and selectivity for the separation of the nine BPs in both the mixed standard solution and soil extracts (Fig. 3). This demonstrates an obvious advantage of DB-XLB column over HP-5MS column for the separation of the DBP isomers. Therefore, the DB-XLB column was selected for the analysis considering its excellent separation potential. The characteristic ions with their abundance percent and retention time of the analytes are listed in Table 2.

2.2 Validation of the method

In order to investigate the recoveries of the target compounds, 2 g subsample of a BP-free soil (Alfisols) collected from an agricultural field in Beijing were added with 0.2 mL of BPs at two different concentrations dissolved in ethyl acetate to reach the final concentration of 2 and 40 ng/g and the solvent was evaporated before extraction. The blank and the control groups were also analyzed.

Fig. 2 Separation of dibromophenol isomers by chromatography.

Fig. 3 Chromatogram of the BPs in a mixture of standard compounds at 50 µg/L (a) and a spiked soil at 10 ng/g (b).

The results are shown in **Fig. 4**. The recoveries of the BPs were satisfactory ranging from 84.3% to 121.6% with the relative standard deviations of 0.04%–12.7% with the sole exception of 2-MBP which had a little poor recovery (44.6%–55.7%). The relatively low recovery of 2-MBP was attributed to its poor stability in the treatment process. Compared to the other BPs, 2-MBP had the lowest melting and boiling points (Howe et al., 2005) and a relative weak intermolecular hydrogen bonding interaction. Therefore, it had a weaker stability and a stronger evaporation potential than the others. During preconcentration treatment with nitrogen flow, the loss of 2-MBP was much heavier than other BPs. The average recovery of each analyte from the spiked soils experiencing the whole sample treatment procedure was higher than the one from the cartridge

cleanup treatment alone (**Fig. 1**). This phenomenon was possibly ascribed to the protective effect of the soil matrices on lessening the loss of the target compounds. Overall the recoveries of BPs for the whole procedure were satisfactory.

The detection limits of the method for the target compounds were obtained according to the concentrations of signal to noise equal to three, and the results are listed in **Table 3**. ^{13}C -PCB-208 (25 ng/mL) was used as the internal standard to correct the response deviation caused by the instrumental instability. Under the optimized conditions, the response was found to be linear in the validated range from 0 to 200 ng/mL with the correlation coefficient (R^2) higher than 0.9960 (**Table 3**), which demonstrates the robustness and reliability of the method established.

Table 2 Characteristic ions, relative abundances and retention time of the target compounds

Compound	Characteristic ions (m/z) (abundance, %)	Quantitative ion (m/z)	Retention time (min)
2-MBP	231 (94), 229 (99), 246 (30)	231	6.38
3-MBP	231 (99), 229 (99), 244 (51)	231	6.54
4-MBP	231 (99), 229 (91), 246 (70)	231	6.91
2,5-DBP	309 (99), 307 (51), 322 (14)	309	11.13
3,5-DBP	309 (99), 307 (52), 324 (46)	309	11.29
2,6-DBP	309 (99), 311 (50), 324 (16)	309	11.60
2,4-DBP	309 (99), 311 (52), 324 (27)	309	12.13
TBP	387 (97), 389 (99), 404 (22)	389	14.62
TBBPA	673 (99), 675 (71), 688 (25)	673	21.43
^{13}C -TBBPA	685 (99), 687 (71), 700 (12)	685	21.43

Table 3 Linear equations and detection limits

Compound	Regression equation	Correlation coefficient (R^2)	Method detection limit (ng/g)
2-MBP	$Y = 0.0004X + 0.9778$	0.9990	0.05
3-MBP	$Y = 0.0003X + 0.5363$	0.9993	0.04
4-MBP	$Y = 0.0004X + 0.8032$	0.9992	0.05
2,5-DBP	$Y = 0.0005X - 0.3868$	0.9996	0.05
3,5-DBP	$Y = 0.0006X - 0.2779$	0.9996	0.07
2,6-DBP	$Y = 0.0006X + 0.0092$	0.9998	0.06
2,4-DBP	$Y = 0.0006X + 0.5482$	0.9995	0.06
TBP	$Y = 0.0007X + 0.7903$	0.9991	0.05
TBBPA	$Y = 0.0042X + 1.7159$	0.9960	0.19

Table 4 Concentrations of the BPs in the e-waste contaminated soils (unit: ng/g)

Soil	2-MBP	3-MBP	4-MBP	2,5-DBP	3,5-DBP	2,6-DBP	2,4-DBP	TBP	TBBPA
1	—	—	—	—	—	—	0.17	0.72	6.07
2	1.12	—	1.69	—	0.07	1.78	1.99	0.64	5.05
3	0.14	—	—	—	—	0.86	2.10	2.64	15.34
4	—	—	—	—	0.13	0.47	1.97	0.94	16.98
5	—	—	—	—	—	0.07	—	0.85	5.15

“—”: below the limit of detection.

Fig. 4 Recoveries of the BPs from a spiked soil at the concentrations of 2 and 40 ng/g.

2.3 Application of the method to real soil sample analysis

The developed method was applied to analyze BPs in the soils collected from e-waste sites. The results (**Table 4**) suggest that e-waste dismantling and recycling activities resulted in contamination of BPs in the soils. TBBPA and TBP were found in all the soil samples while MBPs and DBPs were only found in some of the soil samples. In addition, TBBPA showed a higher concentration than the others probably owing to its larger usage in electronic devices and appliances (Covaci et al., 2009) than the other BPs. Whereas, 3-MBP and 2,5-DBP in the soils were below the detection limits.

3 Conclusions

A method for simultaneous analysis of nine BPs in soils was successfully developed. Florisil cartridge was adopted in sample purification and DB-XLB GC column was selected for BPs separation. The limits of detection and the recoveries for the compounds were satisfied. Moreover, the linearity of the calibration curves and the repeatability were also robust. The developed method was successfully applied to determine BPs in the soils collected from e-waste sites. The method developed for BP analysis is of great significance for the investigation of environmental behavior and fate of BPs.

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