Rapid and Simultaneous Determination of Tetrabromobisphenol A and Hexabromocyclododecane Diastereoisomers in Soil by Matrix Solid-Phase Dispersion with Bamboo Charcoal as Dispersive Adsorbent

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A rapid and simple analytical method based on matrix solid-phase dispersion combined with liquid chromatography coupled with tandem mass spectrometry has been developed by using bamboo charcoal as a dispersive adsorbent to simultaneously determine tetrabromobisphenol A (TBBPA) and hexabromocyclododecane diastereoisomers (HBCDs) in soil. The factors influencing the performance of the proposed method were investigated and optimized in detail, and the matrix effects were evaluated. Under optimum conditions, the proposed method showed good linearity within the range of 0.8–80 ng g^{-1} and limits of detection of 4–75 pg g^{-1} (S/N = 3). The satisfactory recoveries of TBBPA ranging from 72.8% to 92.5% and HBCDs ranging from 76.8% to 102.2% were obtained with relatively standard deviation (RSD) ranging from 3.4% to 9.8%. The proposed method has been successfully applied to analyze TBBPA and HBCDs in actual soil samples from the Yellow River Delta in China.

Keywords: Tetrabromobisphenol A, hexabromocyclododecane diastereoisomers, matrix solid-phase dispersion, bamboo charcoal, soil

Introduction

Tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD), two kinds of high-production-volume brominated flame retardants (BFRs), are widely used for building materials, polymers, and electronic appliances to increase fire resistance [1]. Commercial HBCD mainly consist of γ-HBCD (75%–89%), while α-HBCD and β-HBCD are present in lower amounts (10%–13% and 1%–12%, respectively). Over the past decade, these fire retardants have received considerable attention because of their characteristics similar to persistent organic pollutants and ubiquity in many environmental components, such as water, sediment, air, soil, and living organisms [2]. Soil matrix is a major reservoir and sinks for hydrophobic organic pollutants because of its sorption quality and holding capacity. TBBPA and HBCDs tend to accumulate in soil through the utilization of sewage sludge as fertilizer [3]. Therefore, it is important to develop a rapid and sensitive analytical method in soil in order to understand their fate and behavior of these retardants in the environment.

Various analytical methods for TBBPA and HBCDs determination have been described [4, 5]. For instrumental analysis, liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) is preferred rather than gas chromatography (GC). The former is preferred because a compulsory derivatization of TBBPA prior to GC analysis likely produces poor accuracy and few errors; individual HBCD diastereoisomers cannot also be separated through GC because of thermal rearrangement and decomposition [6, 7]. For soil and sediment sample pretreatment, Soxhlet extraction (SE) [8], accelerated solvent extraction (ASE) or pressure liquid extraction (PLE) [9], and ultrasonic-assisted extraction (UAE) [10] have been successfully applied to extract TBBPA and HBCDs. However, crude extracts obtained from these techniques require a multistep cleanup, which requires time-consuming processes and large amounts of organic solvent.

Matrix solid-phase dispersion (MSPD), a rapid and efficient sample preparation technique, was first described in 1989 [11]. In this technique, analyte extraction and eluate cleanup are combined in one step that can be completed in several minutes and cost several milliliters of solvent. In MSPD, the selection of an appropriate dispersive sorbent is an important factor to obtain a satisfactory analytical performance [12, 13]. For example, Florisil, C18, and modified silica have been successfully used as dispersive sorbents to determine TBBPA and HBCDs in sewage sludge, sediment, and channel catfish [14, 15]. In recent years, bamboo charcoal (BC) as an effective and good alternative sorbent has attracted great attention. A scanning electron microscopy (SEM) image of BC (Figure 1) is obtained using SUPPATM 55 (Zeiss, Germany). Numerous unique micropores with an average length of 3–15 μm are clearly found on the surface. The special microporous structure and biological characteristics result in greater surface area and better absorption rate. Moreover, BC is an inexpensive material (approximately US $0.002 per gram), which is much lower than the price of other adsorbents, such as Florisil, polymers, and carbon nanotubes. These merits including its low price, extremely large surface area, and unique microporous structure imply that BC must be a promising adsorbent material. The applications, based on BC as sorbent in solid-phase extraction (SPE) to enrich four phthalate esters, TBBPA, and HBCDs in water samples and as dispersive sorbent in MSPD to determine PBDEs in soil, were successfully developed in our laboratory [16–19]. SPE is often applied to analysis of water or liquor sample as BC acts the function of sorption and enrichment. Nevertheless, MSPD is suitable for pretreatment of solid or semi-solid sample as BC conducts both effective dispersion and

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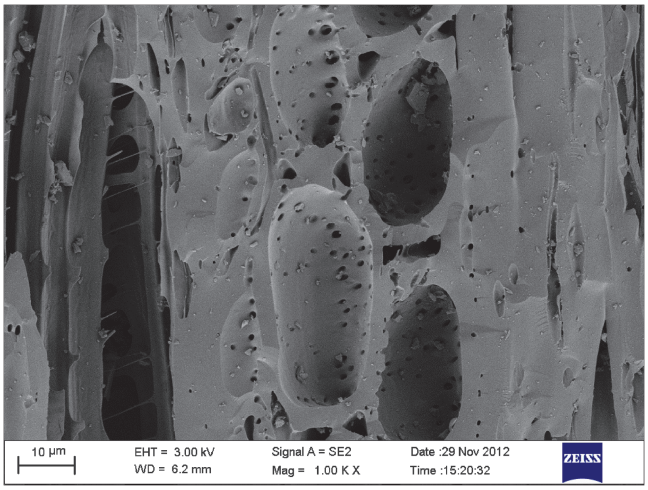

Figure 1. Scanning electron micrograph of bamboo charcoal

primary purification. However, MSPD technique with BC as a dispersive adsorbent has not yet been developed to simultaneously determine HBCDs and TBBPA in soil sample.

This research mainly aimed to develop a fast and sensitive MSPD-based method combined with LC–MS/MS by using BC as a dispersive sorbent to determine TBBPA and HBCDs in soil simultaneously. Factors possibly affecting the performance of the proposed method were also investigated and optimized in detail. The proposed method was validated and applied to actual soil samples collected from the Yellow River Delta in China.

Experimental

Chemicals and Materials. Pesticide residue-grade solvent, dichloromethane (DCM), *n*-hexane, and acetonitrile (ACN) were obtained from Oceanpak Company (Sweden). Methanol and acetone (Duksan, HPLC grade) were purchased from JieTeAo Trade Company, Beijing, China. Silica gel (70–230 mesh, Yudong Company, Qingdao, China), Florisil (60–100 mesh, Sigma-Aldrich, Beijing, China), alumina (Sinopharm Chemical Reagent Co., Ltd., China), and anhydrous sodium sulfate (Guangfu Company, Tianjin, China) were washed in DCM through Soxhlet extraction for 6 h. Cleanert ODS C18 was obtained from Agela Company (Tianjin, China). Unlabeled TBBPA, γ-, β-, and γ-HBCD (purity, >99%; 100 μg mL^{-1} in toluene) were procured from Accustandard (New Haven, CT, USA). The $^{13}C_{12}$-labeled TBBPA, γ-, β-, and γ-HBCD (purity, >98%; 50 μg mL^{-1} in toluene) as internal standards were obtained from Cambridge Isotope Labs (Andover, MA, USA). All standard stock solutions (1.0 μg mL^{-1}) were prepared with methanol and stored against light at −20 °C.

Rough Mao bamboo (5 years old, Shaoxing, Zhejing, China) was washed several times with distilled water and dried in an oven at 105 °C for 8 h. The dried bamboos were cut into smaller pieces and then were heated in muffle furnace at 800 °C for 3 h excluding oxygen. The resulting rough BC was boiled for 1 h with 10% HCl solution, washed several times with distilled water, and dried in the oven at 105 °C overnight. The purified BC was triturated, sieved through a 200-mesh sieve, and stored in a brown bottle. Before BC was used to develop MSPD, it was dried at 80 °C for 2 h.

Apparatus. An Agilent 1200 rapid resolution liquid chromatography equipped with an autosampler, a binary pump, and a temperature-controlled column compartment was used. Separations were carried out using a Zorbax Eclipse XDB-C18 column (i.d., 50 mm × 2.1 mm; particle size, 1.8 μm), and the column was kept at 50 °C. The flow rate of the mobile phase consisting of 90% methanol and 10% water was maintained at 0.5 mL min^{-1}. The injection volume was 10 μL.

An Agilent 6410 triple quadrupole mass spectrometer equipped with an electronic spray ionic source (ESI) was operated in negative ion mode. Nitrogen gas was used as drying gas with flow rate of 10 L min^{-1} and a temperature of 280 °C. The capillary voltage was 4000 V. The target compounds, internal standards, and relevant parameters, including fragmentor voltage, collision energy (CE), dwell time, precursor, and product ion, are listed in Table 1.

Sample Preparation and MSPD. Laboratory blank experiments were run with each solvent, glass syringe cartridge, and polyethylene frit to check contamination and to demonstrate laboratory background levels. The background levels of the laboratory blanks were below the detection limits when the following MSPD procedure was used. The blank soil sample was analyzed with the reported method [20]. No targets were detected in the blank soil. Blank soil spiked with the unlabeled standard of 10 ng g^{-1} and $^{13}C_{12}$-labeled standard of 20 ng g^{-1} was prepared, homogenized, covered, and stored in a refrigerator at −20 °C for more than 24 h to allow sufficient dispersion and equilibration. Screening experiments were carried out using the blank spiked soil.

In this study, MSPD procedure was used in accordance with previously described methods [21] with slight modifications. In brief, 0.5 g of soil sample and 0.5 g of BC were gently ground in an agate mortar with a pestle to yield an apparent homogeneous blend. Afterward, the mixture was transferred to a 5-mL glass syringe filled with 1.0 g of anhydrous Na_2SO_4 and a frit at the bottom. Another frit was used on the top of the syringe before compression to form a column packing. A 10 mL mixture of DCM and ACN (9:1, *v*/*v*) was used to elute the column at a flow of 1 mL min^{-1}, and the eluate collected in a glass conical tube was evaporated to dryness under a gentle stream of nitrogen. The residue was reconstituted in 0.2 mL of methanol for LC–MS/MS analysis.

Results and Discussion

Optimization of Chromatographic and MS/MS Conditions. In a previous study, the responses of γ-HBCD increase when ACN is used as a mobile phase instead of methanol in LC–MS/MS [22]. By contrast, the responses of α-HBCD and TBBPA decreased significantly when ACN was used in this study. TBBPA and three HBCD diastereoisomers could be separated completely in 5.5 min less than the time in the previous study when methanol and water were employed. Column temperature could also influence the responses of analytes. At column temperatures of 20 °C to 60 °C, the peak area of HBCDs increased remarkably. The highest response of TBBPA was obtained at a column temperature of 50 °C. Thus, 50 °C was used in the subsequent experiment.

The optimum temperature of dry gas may be inconsistent because of different instruments. Budakowski et al. [23] and Dodder et al. [24] reported that the optimum temperatures of turbo gas for HBCDs are 500 °C and 450 °C, respectively; column temperatures of 160 °C and 250 °C have also been used [10]. In this study, TBBPA and HBCDs showed different

Table 1. MS/MS parameters of the developed method

Compounds	Prec. ion	Prod. ion (P1/P2)	Group	Dwell time (ms)	Frag. (V)	CE (P1/P2)
Unlabeled TBBPA	542.8	418.1/78.9	1	120	220	45/50
$^{13}C_{12}$-TBBPA	554.8	428.9/78.9	1	120	220	45/50
Unlabeled HBCD	640.7	80.8/78.9	2	30	90	5/10
$^{13}C_{12}$-HBCDs	652.8	80.8/78.9	2	30	90	5/10

sensitivities when temperature was increased from 100 °C to 340 °C. TBBPA exhibited the highest response as temperature increased to 300 °C. The maximum sensitivities of α-, β-, and γ-HBCD were observed at 280 °C, 280 °C, and 260 °C, respectively. The compromised temperature was set at 280 °C to enhance their sensitivity.

Optimization of MSPD Conditions. The sensitivity and selectivity of MSPD largely depend on the dispersive and elution procedure. Therefore, the type and amount of dispersive sorbent and the type and volume of elution solvent should be investigated and optimized.

Dispersive sorbent is an important factor in MSPD similar to SPE. Many dispersive sorbents, including C18 [14], Florisil [25], silica gel [26], and alumina [27], are usually employed in MSPD. In this experiment, these dispersive sorbents, BC, and BC and Florisil mixture (1:1, *m*/*m*) were investigated, and 10 mL of DCM was used as an eluent. BC was the optimum choice for TBBPA, and Florisil was satisfied with HBCDs (Figure 2a). Blanco et al. [14] developed MSPD by using Florisil and acidic acetonitrile to determine phenolic compounds in sewage sludge and sediment sample. However, the recovery of HBCDs remarkably decreased by 50% of previous conditions, and the mechanism of which needs to be further studied. Therefore, BC was considered a satisfactory dispersive sorbent.

The ratio of dispersive sorbent to soil is also an important factor affecting recovery. A series of experiments was performed to investigate the effect of different BC-to-soil ratios with 1:5, 1:2.5, 1:1, 2:1, 3:1, and 4:1 when 0.5 g of soil and 10 mL of DCM were fixed. The results indicated that a ratio of 1:1 was the optimum choice. It could be explained that soil matrix could not be dispersed fully as ratio of 1:5 and 1:2.5; however, excessive BC could absorb the analytes. Therefore, a 1:2 ratio of BC to soil was chosen for further experiments.

In MSPD, the appropriate elution solvent is also a significant factor. In general, a nonpolar substance can be recovered using apolar solvents, such as DCM and *n*-hexane or mixtures of both [12]. ACN, acetone, and methanol as polar solvents are suitable for polar compounds. Six types of solvents, namely, acetone, DCM, methanol, ACN, *n*-hexane, and a mixture of DCM and ACN (9:1, *v*/*v*) with the same volume of 10 mL, were investigated. In Figure 2b, the highest recoveries of analytes were obtained when the solvent mixture was used, although other solvents except *n*-hexane exhibited a similar extraction capability. However, methanol and acetone produced yellow extractants, and the floc was separated during the concentration process. Furthermore, a series of experiments was designed to optimize the volume (2, 4, 6, 8, 10, and 12 mL) of the solvent mixture. The results showed that the recoveries of analytes increased as the volume increased from 2 mL to 10 mL and remained almost constant when the volume continuously increased to 12 mL. A 10-mL volume of the solvent mixture was chosen for the following experiments to save the elution solvent and time. The following MSPD conditions were obtained: extraction solvent containing 10 mL of DCM and ACN mixture (9:1, *v*/*v*) and a 1:2 BC-to-soil ratio.

Evaluation of Matrix Effect. The matrix-matched standards ranging from 0.8 to 80 ng g^{-1} were prepared with blank soil

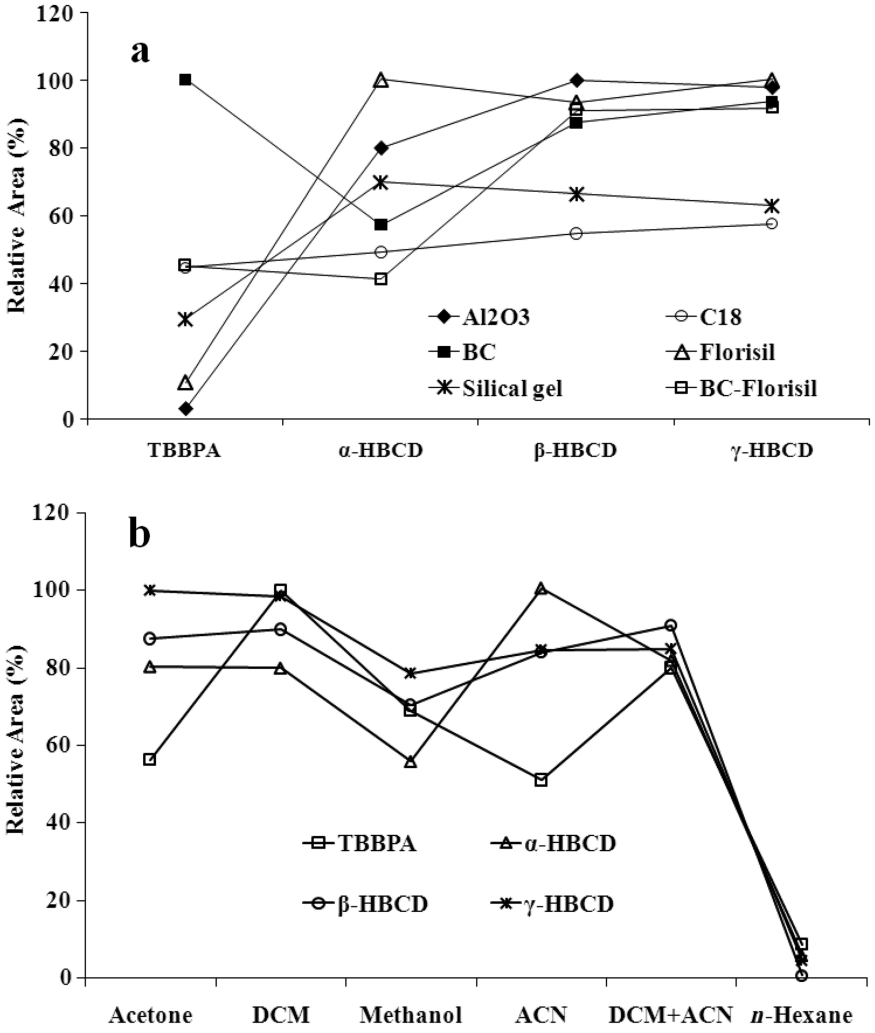

Figure 2. Optimization of different dispersive adsorbents (a) and elution solvent (b)

extracts to determine the matrix effect, and their responses were compared with those of the standards prepared in pure solvent (methanol). Several calibration curves were obtained, and the matrix effect was prominent. The signal suppression indicated a somewhat lower matrix effect on TBBPA (76%–83%), α-HBCD (61%–79%), β-HBCD (27%–35%), and γ-HBCD (29%–36%), and these findings are consistent with those in a previous report [10]. A mixture of isotope-labeled TBBPA and HBCDs was used as an internal standard to compensate for the matrix effect. The calibration curves with similar slopes were obtained for matrix-matched standards and standards in methanol. Therefore, the matrix effect was completely eliminated, and the isotopic internal standard should be added in the following experiments.

Method Validation. The analytical performance parameters are very important for their feature widespread use. Under the optimum conditions, the linearity, spiked recovery, limits of detection (LODs), and repeatability were measured (Table 2). Excellent linearity with correlation coefficients (r^2) of 0.996–0.999 was obtained over the concentration range of 0.8–80 ng g^{-1}. The LODs based on an *S*/*N* of 3 ranged from 4 pg g^{-1} to 75 pg g^{-1}. Spiked recoveries were examined by using blank soil samples fortified with TBBPA and HBCD standard solution at 4, 20 and 80 ng g^{-1} levels. The recoveries ranging from 72.8% to 92.5% for TBBPA and 76.8% to 102.2% for HBCDs were within the average recovery of 70% to 120%. The relative standard deviation (RSD) ranged from 3.4% to 9.8% with less than 20% at three spiking levels. These results indicated that the proposed method is consistent with the acceptance criteria of EU SANTE/11945/2015 [28].

The comparison between the proposed method and the other methods for the determination of TBBPA and HBCDs in different matrices [9, 10, 20, 29–33] is shown in Table 3. The proposed method is more efficient than other methods in terms of LODs and pretreatment time. MSPD is comparable with UAE and more efficient than SE and ASE techniques in terms of organic solvent consumption. Although a low amount of solvent is used in UAE, a cleanup procedure is required. Therefore, MSPD-LC–MS/MS with BC as a sorbent is a rapid, simple, and sensitive method to determine TBBPA and HBCDs in soils.

Analysis of TBBPA and HBCDs in Actual Soil Samples. The applicability of the proposed method was evaluated by analyzing six actual soil samples collected from Yellow River Delta located in Shandong province, which is the main production area of BFRs in China. The actual soil samples were freeze-dried, ground, and sieved. The 80-mesh fraction of the actual soil samples was collected and maintained at −20 °C until analysis. Before extraction was conducted, the samples were spiked with $^{13}C_{12}$-labeled TBBPA and HBCD mixture, and three replicates of each sample were analyzed. In Table 4, the concentrations of TBBPA, α-, β-, and γ-HBCD ranged from <LOD–0.53ng g^{-1}, <LOD–18.38 ng g^{-1}, <LOD–16.49 ng g^{-1}, and <LOD–16.93 ng g^{-1} (dry weight), respectively. The level of TBBPA in this study was lower than that in typical electronic waste-polluted soils in South China (1400–1800 ng g^{-1}) [34] and similar regions (1.64–7758 ng g^{-1}) [35], comparable with the soil obtained in Beijing (<LOD–0.12 ng g^{-1}) [36], and with the sediment (0.1–3.2 ng g^{-1}) in Western Scheldt, UK [37]. The concentrations of individual and total HBCDs were far lower than those in the surface soil from a manufacturing company in Sweden (23,000 ng g^{-1}) and comparable with nonpoint polluted soil (<10 ng g^{-1}) [38]. However, the concentration was higher than that in Chongming Island, China (<LOD–0.094 ng g^{-1}) [8]. The typical chromatograms of blank soil, blank soil spiked analytes, and actual soil sample are shown in Figure 3.

The actual soil sample was subjected to a repeat analysis on the basis of a reported analytical method [20] to validate the proposed method. In brief, 20 g of soil sample was Soxhlet extracted for 24 h with acetone–hexane, and the obtained crude extracts were further purified with concentrated H_2SO_4 and a silica SPE column. The final eluate was displaced in methanol and used for LC–MS/MS analysis. The results

Table 2. Characteristics of the proposed MSPD–LC–MS/MS method for the determination of TBBPA and HBCD diastereoisomers in soil

Analytes	Linear range (ng g^{-1})	Coefficient (r^2)	LODs (pg g^{-1})	Spiked level (ng g^{-1})	Recovery (%)	RSD (%, n = 6)
TBBPA	0.8–80	0.996	11	4	72.8	8.4
				20	98.0	5.7
				80	92.5	4.7
α-HBCD	0.8–80	0.998	75	4	76.8	9.8
				20	91.5	4.3
				80	96.4	6.9
β-HBCD	0.8–80	0.999	10	4	101.9	8.9
				20	102.2	3.4
				80	102.1	4.5
γ-HBCD	0.8–80	0.999	4	4	78.1	8.0
				20	87.9	4.3
				80	100.0	3.4

Table 3. Comparison of the proposed method with previously reported methods for the determination of TBBPA and HBCD diastereoisomers

Compounds	Samples	Extraction	Cleanup	Instrumental analysis	LODs (pg g^{-1})	Consumption of solvent (mL)	Ref.
HBCDs	Sediment	ASE for 5 min	Packed column	LC–MS/MS	25	200	[9]
HBCDs	Sludge	UAE for 15 min	DSPE[a]	LC–MS/MS	200–300	5	[10]
TBBPA and HBCDs	Soil	SE for 24 h	Acidic washing and SPE	LC–MS/MS	TBBPA: 600 HBCDs: 1200	200	[20]
HBCDs	Fish tissue	Shaking 1 h	GPC[b]	LC–MS/MS	100	40	[29]
HBCDs	Soil	SE for 48 h	Packed column	LC–MS/MS	3–5	200	[30]
TBBPA	Soil	SE for 24 h	SPE and derivatization	GC–MS	190	150	[31]
TBBPA	Sediment, sludge	UAE for 30 min	SPE	LC–MS/MS	2830	10	[32]
TBBPA&HBCDs	Sludge, Sediment	UAE and agitation for 4 h	SPE	LC–MS/MS	HBCDs: 1400–12,000 TBBPA: 2700	10	[33]
TBBPA&HBCDs	Soil	MSPD for 10 min		LC–MS/MS	TBBPA: 11 HBCDs: 4–75	10	This study

[a]DSPE, dispersive solid-phase extraction.
[b]GPC, gel permeation chromatography.

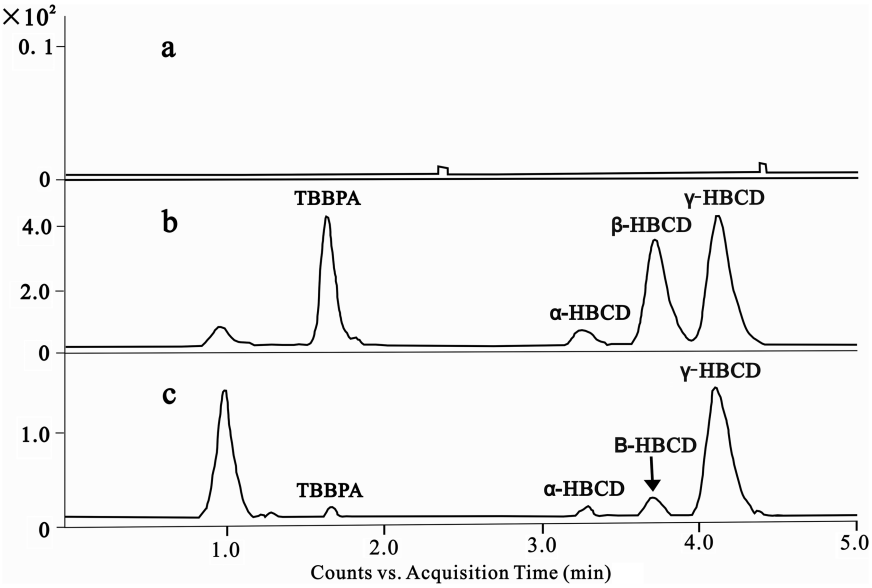

Figure 3. Typical total ion chromatograms of blank soil (a), blank soil spiked analytes (b) and actual soil sample (c)

Table 4. Concentrations of TBBPA and HBCDs in actual soil samples from the Yellow River Delta, China (ng g^{-1})

Sampling site	Proposed method				Method of Ref. [20]			
	TBBPA	α-HBCD	β-HBCD	γ-HBCD	TBBPA	α-HBCD	β-HBCD	γ-HBCD
S1	<0.011	<0.075	<0.01	<0.004	<0.03	<0.06	<0.06	<0.06
S2	<0.011	7.37	6.15	8.45	<0.03	7.01	6.11	8.07
S3	<0.011	7.86	4.02	14.5	<0.03	7.10	4.01	14.1
S4	0.12	<0.075	<0.01	<0.004	0.13	<0.06	<0.06	<0.06
S5	0.35	12.2	4.05	37.8	0.37	11.4	4.05	36.3
S6	0.53	18.4	6.49	16.9	0.57	17.1	6.51	16.4

shown in Table 4 demonstrated that the accuracy of the proposed method is in accord with or more efficient than the reported method, especially on β-HBCD, probably because the labeled HBCD diastereoisomers used in the proposed method can compensate mostly for the matrix effect of isotopic dilution.

Conclusions

In this paper, a rapid and simple analytical method has been developed to simultaneously determine trace levels of TBBPA and HBCD diastereoisomers in soil. The method is based on MSPD using BC as dispersive adsorbent and LC–MS/MS. The characteristics of this method showed that BC is a potential material for the effective dispersed solid sample pretreatment and primary purification. The results of the analyzed actual soil samples revealed that the proposed method is highly suitable for routine monitoring of low levels of TBBPA and HBCD diastereoisomers in soil because of rapidity, convenient operation, cost effectiveness, and low LODs.

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