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Determination of hexabromocyclododecane diastereoisomers in air and soil by liquid chromatography–electrospray tandem mass spectrometry

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ABSTRACT

Hexabromocyclododecanes (HBCDs), used as additive brominated flame retardants, are of high concern due to their widespread use and increasing levels in various environmental systems. High-performance liquid chromatography coupled with electrospray ionization tandem mass spectrometry (LC–MS/MS) was developed for the determination of HBCD diastereoisomers. A detailed study was carried out to optimize the composition of the mobile phase involving methanol/acetonitrile/water, and the values of MS/MS parameters. It was found that the mobile phase could simultaneously affect the chromatographic separation and sensitivity. The instrumental limits of detection (LODs) on column in this study were 0.5, 0.3 and 0.3 pg for α-HBCD, β-HBCD and γ-HBCD, respectively. The effects of extracted matrix components on HBCD determination were investigated by spiking air and soil sample extracts with three ^{13}C-labelled individual stereoisomers. The results indicated that the responses of the HBCD analysis in air and soils were not significantly affected by matrix effects. The method reported here was further applied to the air and soil samples. Three HBCD diastereoisomers were detected in all the air and soil samples, with levels ranging from 1.2 to 1.8 pg/m^3 and 1.7 to 5.6 ng/g dry weight, respectively.

1. Introduction

Hexabromocyclododecanes (HBCDs) are additive brominated flame retardants (BFRs) and are mainly used as thermal insulation in buildings, in upholstery textiles and in electronics [1]. Since the production and use of penta- and octabromodiphenyl ethers has been banned in Europe, HBCDs might become the replacement for polybrominated diphenyl ethers (PBDEs) in some applications [2] and slight increases in their concentrations have been found in various environmental systems [3]. Recent studies indicated that HBCDs are ubiquitous organic contaminants and share the major characteristics of persistent organic pollutants (POPs): persistency, bioaccumulation, long-range transport, and toxicity [3]. They have been included on the OSPAR (The Convention for the Protection of the Marine Environment of the North-East Atlantic) list of chemicals for priority action [4].

Technical grade HBCD mixtures are produced via bromination of cyclododecane-1,5,9-triene isomers. The commercial HBCDs on the market mainly consist of α-HBCD, β-HBCD and γ-HBCD. Although HBCD concentration can be determined as the total concentration of three diastereoisomers by gas chromatography (GC) with electron-capture detection (ECD) or mass spectrometry (MS), these techniques cannot separately measure different stereoisomers due to thermal rearrangement at temperatures above 160 °C and thermal decomposition at temperatures above 240 °C [5–7]. Further details regarding GC and GC–MS analysis can be found in recent reviews [8,9]. Liquid chromatography coupled to mass spectrometry (LC–MS) or tandem mass spectrometry (LC–MS/MS) is currently the preferred method for determining diastereoisomers in environmental samples and biota [10]. Signal intensity improvements gained using quadrupole and ion-trap mass spectrometry in different ionization modes such as atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) have been discussed previously [10,11]. Using LC–MS/MS and multiple reaction monitoring for $[M-H]^-$ (m/z 640.6) → $[Br^-]$ (m/z 79 and 81), Budakowski and Tomy [11] developed a sensitive method with the instrument limit of detection (LOD) of 4–6 pg for on column for a standard solution of γ-HBCD. Comparison of the results of different ionization modes indicated that ESI has a greater signal intensity than the APCI mode. Janak et al. [12] further reported a baseline separation method using an RP-C18 column and methanol/acetonitrile/water as the mobile phase. The LOD, defined as three times the noise level, was 0.5, 1 and 5 pg for γ-HBCD, α-HBCD and β-HBCD, respectively. Although most studies have used the ESI ionization mode of HBCDs, Suzuki and Hasegawa [13] first reported the HBCDs diastereoisomers and tetrabromobisphenol A (TBBPA) in water and sediment samples by using LC–APCI–MS. Their results showed that ionization of HBCDs by APCI led to a 2–5 times higher S/N ratio compared with ESI. They also concluded that ESI was more sensitive to matrix components. In addition,

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atmospheric pressure photoionization (APPI) was also compared with the ESI and APCI modes for HBCD analysis [14]. Although APPI can better resolve common problems in ESI and APCI such as matrix effects, the APPI signal intensities were approximately 10 times lower compared with ESI.

Many researchers [15–17] have reported that matrix effects might adversely affect the reproducibility and quantification of target analyte when developing an LC–MS/MS method, especially when using ESI as the ionization mode. For HBCD diastereoisomer analysis, different studies have presented contrary results. Budakowski and Tomy [11] confirmed the existence of the "ion suppression phenomenon" when determining HBCD diastereoisomers in both biotic and sediment samples using LC–ESI–MS/MS. Dodder et al. [18] developed a baseline separation method for HBCD diastereoisomer determination in the biological tissues. Investigation of the matrix effect showed that potential matrix interference did not significantly influence the LC–MS/MS analyses of the diastereoisomers, whereas the response of the HBCD enantiomers in tissue samples were greatly influenced by matrix effects and other changes to the ionization conditions.

As we know, HBCD can be analyzed using the same protocols as those reported in the PBDE study [12,19]. After finishing the PBDE measurements, the solvent was exchanged to methanol or acetonitrile for further HBCD analysis. Therefore, it is necessary to investigate whether the sample preparation and clean-up procedure can fulfill the determination requirements of diastereoisomers. In this study, a widely used clean-up procedure for soil and air samples was investigated for matrix effects by spiking ^{13}C-labelled HBCDs before injection. Also the optimization of MS/MS parameters for improving signal responses and the effects of mobile phase on the chromatographic separation and sensitivity are discussed in detail. The method developed in this study obtained completely baseline chromatographic separation and lower LODs.

2. Experimental

2.1. Chemicals and solvents

Unlabelled and $^{13}C_{12}$-labelled α-, β-, γ-HBCD were purchased from Cambridge Isotope Labs. (Andover, MA, USA) and used as received. The HPLC-grade methanol and acetonitrile were obtained from Merck (Darmstadt, Germany). Ammonium acetate and acetic acid were acquired from J.T. Baker (Phillipsburg, NJ, USA). Analytical grade hexane and methylene chloride were redistilled by a glass system.

2.2. Liquid chromatography

An Agilent 1100 series HPLC system (Agilent Technologies, Palo Alto, CA, USA) equipped with a vacuum degasser, quaternary pump and autosampler was used. The separation was performed on a Zorbax SB-C18 reversed-phase column (250 mm × 4.6 mm I.D., 5 μm, Agilent). The gradient mobile phase consists of methanol (A)/acetonitrile (B)/water with 10 mM ammonium acetate (C). The flow rate was set at 0.5 mL/min. The gradient program started at an initial composition of 80:10:10 A/B/C (v/v) and was ramped to 50:40:10 A/B/C in 18 min, followed by 30:70 A/B at 23 min, and was held for 7 min, then returned to 80:10:10 A/B/C in 8 min. The column was equilibrated for a further 6 min. The detailed program is listed in Table 1.

2.3. Mass spectrometry

An Applied Biosystems-Sciex API 4000 (Applied Biosystems, Foster City, CA, USA) triple quadrupole mass spectrometry equipped with a TurboIonSpray ionization interface was used. The Q1 scan range was m/z 630–660, operated with unit resolution for a scan time of 0.5 s. The quantities of the three diastereoisometric HBCDs were detected in electrospray ionization negative ion mode using multiple reaction monitoring (MRM) for $[M-H]^{-1} \rightarrow Br^-$ (m/z 640.6 → 79 and 652.6 → 79 for native and ^{13}C-labelled HBCD, respectively), utilizing unit resolution and a 200 ms dwell time per transition. Details of the optimized MS/MS parameters are listed in Table 2.

Table 1
Gradient mobile phase program for the separation of α-, β- and γ-HBCD

Time (min)	Methanol	Acetonitrile	Water (10 mM ammonium acetate)
0.0	80	10	10
18.0	50	40	10
23.0	30	70	0
30.0	30	70	0
37.0	80	10	10
43.0	80	10	10

2.4. Sample collection

Four air samples were collected during 11–15 November 2006 from the Tianhe district, Guangzhou. The sampling procedure was described elsewhere [20,21]. Before sampling, glass fiber filters (GFFs, Whatman, Maidstone, UK) were baked at 450 °C for 4 h to remove any organic contaminant, and polyurethane foam (PUF) plugs were Soxhlet extracted for 48 h with each of following solvents:methanol and 1:1 acetone–hexane. Air volumes of 800–860 m^3 were drawn at 0.3–0.5 m^3/min for 32–35 h using a high-volume air sampler. After sampling, loaded GFFs were wrapped with prebaked aluminum foil and sealed with double layers of polyethylene bags, and PUFs were placed in solvent rinsed glass jars with aluminum foil-lined lids and stored at −20 °C until extraction.

Three surface soils were sampled from the Tianhe, Huangpu and Liwan districts in the Guangzhou urban areas in December 2006. Each of the surface soil samples was collected using a pre-cleaned stainless steel scoop, and mixed with 5 cores from 0 to 10 cm depth. The soil samples were kept at −18 °C until analysis. Before extraction, soil samples were freeze-dried for 24 h and sieved through a 10-mesh stainless steel mesh.

2.5. Sample extraction and preparation

The sample extraction and preparation procedures have been described elsewhere [20,21] and modified in this paper. In brief, soil and air samples (including PUF plugs and GFF glass fiber filters) were extracted with a mixture of acetone and hexane (1:1) for 72 h with a Soxhlet extractor. Activated copper granules were added into the extractor flask to remove elemental sulfur. After extraction, the concentrated extracts from the soil and air samples were cleaned

Table 2
Optimised MS/MS parameters for the determination of α-, β- and γ-HBCD

Parameter	Optimised value
Source temperature, TEM (°C)	300
Ionization voltage (V)	4500
Ion source (GS1) setting	50
Ion source (GS2) setting	55
Curtain gas settings	10
CAD gas setting	25
Declustering potential (V)	−100
Entrance potential (V)	−8
Collision energy (V)	−50
Collision cell exit potential (V)	−6