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Development, comparison and application of sorbent-assisted accelerated solvent extraction, microwave-assisted extraction and ultrasonic-assisted extraction for the determination of polybrominated diphenyl ethers in sediments

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ABSTRACT

Fast and selective analytical methods were developed based on sorbent-assisted mechanism and microwave-assisted extraction (SA-MAE), accelerate solvent extraction (SA-ASE) and ultrasonic-assisted extraction (SA-UAE) for the determination of polybrominated diphenyl ethers (PBDEs) in sediments. The experimental parameters, such as extraction conditions and sorbent amounts, were optimized according to Taguchi Orthogonal Arrays. The accuracy of developed SA-methods was a satisfactory ranging from 71% to 118%. The inter/intra-day RSDs were <10% indicating a good method precision. The limits of quantification (LOQ) for target BDEs were ≤1.0 ng/g dry weight (dw) with an exception of BDE 209 which was 10.0 ng/g dw. The proposed methods were validated by the analysis of PBDEs in standard reference materials (SRM 1944) and the method performances were compared with each other. The results approved the feasibility of SA-methods for PBDEs analysis in sediments. Meanwhile, the optimization processes indicated the mixed sorbents mainly worked on matrix effects elimination. The compositions of sorbents deserved careful optimization because different characteristics of the matrix and extraction intensity may produce various matrix effects. In addition, the developed SA-ASE method was successfully applied on real environmental samples collected from a typical polluted area. The data and calculation suggested local environmental contamination pattern and potential pollution source.

1. Introduction

PBDEs are mainly applied as brominated flame retardants (BFRs) with three commercial formulations: Penta-, Octa-, and Deca-BDE. Owing to their environmental persistence, bioaccumulation, and adverse health effects, Penta-BDE and Octa-BDE have been banned by the Stockholm Convention [1,2]. Recently, the environmental behaviors of PBDEs in soils and sediments are still under scrutiny by the society [3]. Wang et al. investigated 55 PBDEs in river sediments from Shanghai and 10 most frequently detected PBDE congeners (BDE 28, 47, 66, 85, 99, 100, 138, 153, 154, and 183) were detected at concentrations ranging from 0.042 to 21.7 ng/g dry weight (dw) with a median value of 0.475 ng/g dw [4]. PBDEs were also detected up to several ng/g dw in lake sediments and surface soils at remote areas as Antarctic ice-free areas and Tibetan Plateau [5,6]. Another work concerning the occurrence of PBDEs in North Sea sediments found low concentrations of PBDEs (< 1.0 ng/g dw) with an exemption of BDE 209 at concentrations up to 7.0 ng/g dw. The relative low detection frequency was explained as extremely low concentrations compared to method detection limits and replacement of PBDEs by Dechlorane Plus and other alternatives [7]. And PBDEs found far from manufacturing facilities/application zones indicated their long range transport ability and environmental persistence [6,8]. The levels near the manufacturing plant could reflect the potential pollution to local environment aroused by the production and usage which are considered as important emission sources for pollutants reaching into the environment [9].

To further understand the behaviors of PBDEs in different environmental matrices, various extraction methods such as Soxhlet extraction (SE), solid phase extraction (SPE) ultrasonic-assisted extraction (UAE), microwave-assisted extraction (MAE) and accelerated solvent extraction (ASE) have been developed [10–12]. Among these methods, ASE, MAE and UAE have been approved for extraction of organic pollutants from solid environmental matri-

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ces for their high extraction rate, automation of extraction and availability for wide range of different chemicals [13–15]. UAE was used because the energy provided by ultrasound could disperse the solid matrices and enhance the mass transfer to increase extraction efficiency [16]. Elevated temperature and pressure were key modifications of ASE to break down the correlation between matrices and analytes [17]. The energy of micro-wave caused rapid increase of solvent and sample temperature which also promoted the mass transfer between matrices and solvents [18]. A research concerning application of MAE for PBDEs in soils and fishes suggested MAE could provide sufficient efficiency comparable with ASE [19]. ASE, UAE and SE for PBDEs analysis in house dusts were also compared and the results suggested comparable extraction efficiencies [20].

On the other hand, with enhanced extraction capacity, co-extracts were unavoidable for UAE, MAE and ASE. To improve the analysis sensitivity and accuracy, clean-up procedures (chromatographic adsorption, SPE, and gel permeation chromatography, etc.) became essential [10,21]. Modified pretreatment methods have been developed based on classical extraction methods and sorbent-assisted (SA) matrix solid-phase dispersion of extraction (MSPD) to integrate sample dispersion, extraction and clean-up into one single step [22]. This combination could lead to minimum consumption of solvents and materials which complied with “Green analytical chemistry” guidelines [12]. However, to our knowledge, limited studies focused on the evaluation and comparison of these three significant SA-methods for PBDEs determination.

This study aimed to investigate the efficiencies of the emerging modified methods, SA-MAE, SA-ASE and SA-UAE, for the determination of PBDEs from real sediments. The key parameters have been optimized individually for each SA- methods based on references about PBDEs extraction using ASE, UAE and MAE. The method performances of SA-ASE, SA-MAE and SA-UAE were validated by SRM-1944. Soils and sediments from an area around a flame retardant manufacturing plant in Shandong province of China were collected and analyzed using developed SA-method to provide the information on environmental levels and profiles of PBDEs.

2. Material and methods

2.1. Chemicals and materials

Chemical names, structures and related information are shown in Fig. S1. PBDEs standards (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-85, BDE-183 and BDE-209) were obtained from Accustandard (New Hevan, CT). ^{13}C-labelled standards (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209) were purchased from Cambridge Isotope Laboratories (Andover, MA). HPLC-grade dichloromethane (DCM), isooctane, acetone and hexane were supplied by J.T. Baker (Phillipsburg, NJ). Ultrapure water (18.3 MΩ) was generated by a Milli-Q system (Millipore, Billerica, MA). Florisil, aluminia and silica gel were obtained from Sigma-Aldrich (St. Louis, MO). All sorbents were preheated at 150 °C for 12 h or 450 °C for 8 h separately followed by 5% water-deactivation. SRM 1944 (Table S1) were purchased from NIST (National Institute of Standards and Technology, MD) for method validation.

2.2. Sample collection

All samples were collected around a flame retardant manufacturing plant in Shandong province located at east coast of China. Detailed sampling information is presented in Fig. S2. The plant lies in a valley with hills around making the surrounding environment suitable for point source contamination research. According to local environment, seven sampling sites were located around the plant with another sludge sample collected from the local wastewater treatment plant (WWTP) about 20 km away. This WWTP site was marked as site G. Site A is the sewage outfall leading to a wastewater treatment unit which was enabled less than 2 years ago. Sediments were collect from this treatment unit which was marked as site B. Site C is local water reservoir supplying water consumption for an apple plantation (site F). Site D is an abandoned pool used for the storage and treatment of the wastewater from the plant before site B was enabled. Site E was an area of wetland which was a former drainage channel connecting local water reservoir and Site D. At each site, five separate samples were collected and mixed into one composite samples. Surficial soils (0–20 cm, site F) and sediments (site A-E) were collected with a stainless steel scoop and packed with aluminum foil. After transported to laboratory, all samples were freeze-dried and sieved through a stainless steel 2-mm sieve, stored at −20 °C until analysis. For method optimization, background sediment was also collected from upstream of the river far from the plant.

2.3. Sample preparation

An aliquot of 1.0 g solid sample was spiked with 20 ng ^{13}C-labelled standards as surrogate standard for each method optimization.

SA-UAE was carried out based on reported method with little modifications[23]. Briefly, extraction was using 5 mL hexane/acetone (1:1; v/v) in an ultrasonic bath for 20 min which were repeated for 3 times. An aliquot of 3.0 g pretreated Florisil were mixed with spiked sample to remove undesired interferers. The extracts were then concentrated under gentle flow of nitrogen gas, filtered with a 0.2 μm GHP membrane and re-dissolved with 200 μL isooctane for instrument analysis.

SA-ASE employed a Dionex ASE 350 Accelerated Solvent Extractor (Dionex, USA). Spiked sample was well mixed with 2.0 g Florisil, 1.0 g alumina and 2.0 g acidic silica, then placed in an extraction cell. The extraction employed a mixture of hexane and dichloromethane (1:1, v:v) as solvent and proceeded at 100 °C, 1500 psi and repeated for 3 cycles. The extracts were collected and concentrated to about 2.0 mL with a rotary evaporator. After filtration with a 0.2 μm GHP membrane, the liquid was concentrated to dryness under gentle nitrogen stream and re-dissolved with 200 μL isooctane.

SA-MAE procedure was applied with a microwave assisted extraction system SP-X (CEM Corp., Matthews, N.C., USA). The spiked sediment sample was mixed thoroughly with 3.0 g Florisil, 3.0 g alumina and 1.5 g acidic silica loaded into a 35 mL glass vessel. 10 mL acetone/hexane (1:1) mixture was added as an extraction solvent and pre-stirred for 2 min before extraction. The extraction temperature ramped to 130 °C in 5 min and held for 20 min. Irradiation power parameter was set as 150 W. When the extraction was complete, the vessels were moved and opened after cooling down to room temperature. The supernatant was collected and filtered through a glass fiber filter (CEM Corp., Matthews, N.C., USA). The filter system was washed with extraction solvent 3 times and all collected liquids were concentrated under gentle N_2. The residues were subsequently re-dissolved in 200 μL isooctane for further instrument analysis.

2.4. Instrument analysis

PBDEs were analyzed on an Agilent 7000 B Triple Quadrupole GC–MS/MS in MRM mode (EI–MS/MS, BDE-28, 47, 99, 100, 153, 154, 85, and 183) and an Agilent 5975C NCI GC–MS in SIM mode (BDE-209). A capillary GC column (DB-5, 15 m × 0.25 mm × 0.10 μm) was equipped in each system to achieve chromatographic separation. Each 2 microliters of sample were loaded onto capillary column in splitless injection mode.