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Suitability of polydimethylsiloxane rods for the headspace sorptive extraction of polybrominated diphenyl ethers from water samples☆

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Abstract

The suitability of an inexpensive polydimethysiloxane (PDMS) sorbent, produced on an industrial scale, for the extraction of polybrominated diphenyl ethers (PBDEs), from tetra- to hexabrominated congeners, from water samples was assessed. Experiments were carried out using samples spiked with a pentabromo diphenyl ether (pentaBDE) mixture, PDMS rods with a diameter of 2 mm and gas chromatography with micro-electron-capture detection (GC-micro-ECD). Influence of several variables on the efficiency of the enrichment step and the further desorption of the analytes was investigated in detail. The best performance was achieved in the headspace sorptive extraction (HSSE) mode, at 95 °C, using 80 mL water samples containing a 30% of sodium chloride. Extractions were performed overnight using disposable PDMS rods with a length of 10 mm (31 μL volume). Analytes were further recovered from the PDMS sorbent using just 1 mL of diethyl ether. This solvent was evaporated and extracts reconstituted with 25 μL of isooctane. Under final working conditions absolute extraction efficiencies from 69 to 93% and enrichment factors higher than 2200 folds were achieved for all species. The proposed method provided acceptable precisions (relative standard deviations values under 12%), correlation coefficients higher than 0.998 and the yield of the HSSE process remained constant for different water samples.

Keywords: Sorptive extraction; PDMS rods; PBDEs; Water analysis

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been employed worldwide as additive, not chemically bound, flame retardants in textiles, plastic and electronic devices. From these matrices, they can be released into the surrounding environment. This behaviour added to their environmental persistence, toxicity and bio-accumulation trend have caused a great concern about their potential impact in wildlife and human health. Excluding primary sources (host materials treated with these flame retardants additives), the highest concentrations of PBDEs have been found in particulate matter and dust from interior areas [1,2] and fatty tissues from top predator animals [3]. In addition, relevant concentrations have been measured also in human fluids [4].

On the other hand, levels of PBDEs in water samples are extremely low; however, water, and particularly wastewater, might contribute significantly to the discharge and spread of these pollutants in the biosphere [5–7]. On the basis of their octanol–water partition coefficients, only the less substituted PBDEs (up to six bromine atoms) are expected to be presented in the water phase. From a toxicological perspective, some of the most concerning congeners (e.g. BDE47, 100, 99, 154 and 153) belong to above described class [8]. These congeners are also the major components of technical pentaBDE formulations. Although, industrial production and commercialisation of pentaBDE mixtures has been forbidden in the European Union [9] and voluntary stopped in the USA [10]; tetra-, penta- and hexaBDE congeners will be still discharged in the environment for many years due to: (1) their continuous release from previously produced materials treated with pentaBDE flame retardant solutions, and (2) because of dehalogenation reactions of higher brominated congeners, e.g. BDE209, which use it is still allowed [11]. As a consequence, there is still a need for sensitive and reliable sample preparation methods allowing PBDEs determination in water samples at the very low pg/mL level.

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Nowadays, miniaturisation, reduction in sample manipulation and organic solvents consumption, as well as, time and cost effective sample preparation approaches are challenging issues in analytical chemistry. In the case of water analysis of low and medium polar analytes, sorptive extraction techniques (based on the use of PDMS sorbents), represent an important advance to achieve these aims [12–14]. PDMS is available in several formats, the most popular are solid-phase microextraction (SPME) fibres followed by coated stir bars (*Twisters*) and other non-commercialised devices such as PDMS thin-film [15], tube [16] and rods [17,18]. Particularly, bulk PDMS rods present very interesting characteristics. Their extraction capacity is higher than that corresponding to SPME fibres since a larger volume of sorbent is employed (in practise, it can be customised for each application since the sorbent is available in cords with different diameters); moreover, rods are inexpensive in comparison to fibres and *Twisters*; therefore, they can be used as disposable devices. This last feature is especially interesting in the determination of semi-volatile species such as PBDEs since: firstly, it avoids carry-over problems due to their incomplete desorption from the PDMS sorbent, and secondly, it allows considering long sampling periods, given that, at difference to SPME, many samples can be concentrated simultaneously using different rods. Up to now, PDMS rods have been employed for the extraction of chlorinated pollutants [17] and polycyclic aromatic hydrocarbons [18] from water samples; moreover, they have been proposed also as passive samplers for the determination of time-weighted average concentrations of environment relevant species [19,20]; however, from the best of our knowledge, applications to the determination of PBDEs have not been reported yet.

The aim of this work is to evaluate the possibilities of PDMS rods for the extraction of six PBDEs (the major components of pentaBDE formulations) from water samples. The influence of several variables on the efficiency of the extraction process is described in detail. Observed results are justified using the theoretical knowledge and basic principles of sorptive extraction techniques. Moreover, the performance of the optimised method is compared to that reported for PDMS coated SPME fibres [21] and stir bars [22], when applied to the determination of PBDEs in water samples.

2. Experimental

2.1. Solvents, standards and extraction sorbent

Acetone, isooctane, dichloromethane, diethyl ether and methanol, trace analysis quality, were obtained from Merck (Darmstadt, Germany). Sodium chloride and humic acids were acquired from Merck and Aldrich (Milwaukee, WI, USA), respectively. A pentaBDE standard mixture with a total PBDEs concentration of 10 μg/mL in cyclohexane was purchased from Dr. Ehrensdorfer (Augsburg, Germany). This commercial solution contains the following PBDEs at concentrations over 1%: 2,2′,4,4′-tetrabromodiphenyl ether (BDE47), 2,2′,4,4′,6-pentabromodiphenyl ether (BDE100), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE99), 2,2′,3,4,4′-pentabromodiphenyl ether (BDE85), 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE154) and 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE153). Their relative abundances, established using pure standards obtained from Wellington and injected under same conditions in the GC-micro-ECD system, were: 37.5 ± 1.5% (BDE47), 9.2 ± 0.6% (BDE100), 40.1 ± 1.8% (BDE99), 1.3 ± 0.1% (BDE85), 2.6 ± 0.2% (BDE154) and 2.7 ± 0.2% (BDE153). Diluted solutions of the pentaBDE standard were made in acetone, when used to prepare spiked water samples, and in isooctane, when injected directly in the gas chromatograph.

PDMS cord with a diameter of 2 mm was purchased from GoodFellow in 20 m rolls (Bad Nauheim, Germany). Rods of this polymer with different lengths (5 and 10 mm) were prepared in the laboratory simply by cutting the PDMS cord with a sharp blade. Resulting pieces were weighted accurately and only those, with the same nominal length, showing mass variations under 1% were considered for extraction experiments. Prior to their use, rods were first soaked for 15 min with a mixture of dichloromethane:methanol (1:1) and then thermally desorbed overnight at 250 °C under a nitrogen flow of 50 mL/min. Conditioned rods can be used immediately or stored, in closed glass vessels at room temperature, until needed.

2.2. Samples and sample preparation

Spiked and non-spiked samples (ultrapure, river, sea and wastewater) were considered in this study. Grab wastewater samples were taken in the influent and the effluent from an urban sewage water plant equipped with primary and secondary treatments. River, sea and wastewater samples were passed through 1 μm glass fibre filters when received and processed immediately.

Extractions of PBDEs were carried out using glass vessels furnished with PTFE layered rubber septa and aluminium caps. A conventional stainless steel pin (ca. 40 mm length × 0.7 mm diameter) with a flat head was passed through the septum and a PDMS rod was skewered at its tip. The rod was exposed directly to the water sample or maintained in the headspace (HS) of the vessel, depending on extraction conditions. Vessels were hermetically sealed using an aluminium cap. Extraction experiments were carried out in recipients with two different volumes: 22 and 110 mL. The influence of the temperature on the efficiency of the sorptive extraction process was evaluated by placing the whole system (extraction vessels with PDMS rods) in the interior of an oven with a temperature control precision of ±2 °C.

After an established sampling period, vessels were allowed to cool down and opened. The stainless steel pin, attached to the PDMS rod and the septum, was held with tweezers and cut using pliers to remove the last. The PDMS rod, still connected to approximately 0.5 cm of stainless steel pin, was dried using a soft tissue and introduced into a 1.5 mL GC autosampler vial containing 1 mL of a volatile organic solvent. This vial was capped and soaked for 5 min. After that, it was opened and the extraction polymer removed holding the stainless steel pin with tweezers. Operating in this way, tweezers never get in direct contact nei-