



# Micro-solid phase extraction followed by thermal extraction coupled with gas chromatography-mass selective detector for the determination of polybrominated diphenyl ethers in water



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## ABSTRACT

A method of analyzing environmental contaminants in water based on micro-solid phase extraction ( $\mu$ -SPE) followed by thermal extraction (TE) and a cold-trapping step, coupled with gas chromatography-mass selective detection (GC-MSD) was developed and validated.  $\mu$ -SPE-TE-GC-MSD was employed in the determination of five polybrominated diphenyl ethers. The  $\mu$ -SPE sorbent was chitosan-graphene oxide (CS-GO) composite, which was prepared by mixing CS and GO by means of ultrasonication. The CS in the composite was cross-linked with glutaraldehyde. After  $\mu$ -SPE, the analytes in the extract were extracted thermally in a thermal desorption unit tube combined with a cooled injection system, coupled to GC-MSD. The extraction conditions were optimized for the detection of the target compounds in water. This method provided linearity ranges of between 0.1 and 20  $\mu\text{g L}^{-1}$  (depending on the analytes), with coefficients of determination,  $r^2$ ,  $\geq 0.9982$ . The calculated relative recoveries were between 71.52 and 96.15% whereas precision (based on % relative standard deviations) was between 3.54 and 11.36%. The method showed limit of detection and limit of quantification ranges of between 0.007 and 0.016  $\mu\text{g L}^{-1}$ , and between 0.023 and 0.054  $\mu\text{g L}^{-1}$ , for the two groups of analytes, respectively. The method was applied to the determination of the target analytes in water.

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## 1. Introduction

The monitoring of contaminants in environment is required in order to estimate and manage the associated risks with the presence of these compounds in that environment. There are two types of sources from which contaminants may enter the aqueous environment. Sewage treatment plants and wastewater treatment plants are regarded as the major source. Urban storm water, agricultural runoff, and wet and dry deposition from the atmosphere represent the other. The determination of the hydrophobic organic compounds in the aquatic environment is challenging due to their trace concentrations in complex sample matrices [1,2].

Polybrominated diphenyl ethers (PBDEs), the anthropogenic chemicals widely applied as flame retardants, are used in polymers

for textiles, plastics, paints and electronic components [3,4]. They can leach from these manufactured products into the environment leading to their accumulation, and remain undegraded for several years [5]. Due to their highly hydrophobic character (high  $K_{ow}$ ), PBDEs can be accumulated in fats and proteins posing health risks such as endocrine disruption, reproductive toxicity, neurobehavioral effects and probable carcinogenicity [6–8]. Preconcentration techniques for PBDEs in environmental water that have been reported include stir bar sorptive extraction (SBSE) [9,10], solid-phase microextraction (SPME) [11,12], dispersive liquid-liquid microextraction (DLLME) [13] and dispersive solid-phase extraction [14]. Although, these techniques have obvious advantages over classical extraction methods such as liquid-liquid extraction (LLE), they do have some drawbacks. SBSE has a layer absorptive surface, but up to now, the commercially available coating for stir bars include only polydimethylsiloxane, ethylene glycol-silicone and polyacrylate, still a limited range [15]. In SPME, the extraction fibers are costly and fragile [16,17]. Furthermore, the adsorption capacity in SPME is limited by the low surface area of the sorbent phase.

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**Table 1**  
Some physicochemical properties of PBDEs considered in this work.

Name	Abbreviation	Empirical formula	Structure	Log $K_{ow}$ at 25 °C <sup>a</sup>
2,2',4,4'-Tetrabromodiphenyl ether	BDE-47	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O		7.3
2,2',4,5'-Tetrabromodiphenyl ether	BDE-49	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O		7.3
2,2',4,4',5-Pentabromodiphenyl ether	BDE-99	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O		7.6
2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE-154	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O		7.8
2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE-153	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O		7.9

<sup>a</sup>[30,31].

For DLLME, in general, only extraction of hydrophobic solutes is possible. Even then, the use of extraction solvents in this method is limited. In conventional DLLME, solvents with higher densities than water such as dichloromethane, chlorobenzene, chloroform and carbon disulfide are normally required. They are considered to be more toxic and environmentally unfriendly [18] than less dense solvents. Micro-solid-phase extraction ( $\mu$ -SPE), a relatively simple, fast sampling technique that requires minimal amount of solvents with good cleanup properties, was developed to overcome most of these problems. The  $\mu$ -SPE device consists of a porous polypropylene membrane envelope in which a few milligrams of sorbent were housed. The membrane in the device reduces to a significant extent of potential interferences in the sample, and hence the extraction can be accomplished without additional sample cleanup processes. A major advantage of  $\mu$ -SPE is that the cleanup and preconcentration during the extraction process take place in a single step.

Chitosan (CS), a natural polymer composed of partially acetylated glucosamine, has been attracted by numerous researchers due to its outstanding properties such as non-toxicity, biocompatibility, hydrophilicity and antibacterial activity [19,20]. The functional groups of the glucosamine (amine and hydroxyl groups) act as adsorption sites. The cross-linking is made between functional groups of CS and different agents (glutaraldehyde or epichlorohydrin) in order to make the compound stable in acidic solution [21,22].

Graphene, a monolayer of carbon atoms in  $sp^2$  hybridized honey comb crystal structure has attracted attention in the sample preparation field due to its huge surface area that allows a large adsorption capacity [23–25]. As the large delocalized  $\pi$ -electron system of graphene can form strong  $\pi$ - $\pi$  interaction with benzene ring [26], it can be used as sorbent for the extraction of benzenoid compounds. Moreover, graphene oxide (GO) possesses functional groups containing a large number of oxygen atoms such as hydrox-

yls, epoxides and carboxyls on its graphitic backbone [23]. Since GO can be dispersed in water containing a polymer matrix, the epoxy group in graphene oxide reacts favourably with the primary amine group of the polymer. This modification process of GO is commonly used to form a new mixed CS-GO composite [27–29].

In the present work,  $\mu$ -SPE with CS-GO as sorbent, was used to extract PBDEs in water. The extract was subjected to thermal extraction (TE) in a thermal desorption unit (TDU) of a commercial autosampler. The extract after this was adsorbed onto a Tenax TA liner in a cooling injection system (CIS) of the autosampler. The analytes were then desorbed from the CIS and channelled into a gas chromatography-mass selective detection (GC-MSD) system. The  $\mu$ -SPE-TE-GC-MSD procedure was applied to the determination of trace PDBEs in river water samples.

## 2. Experimental

### 2.1. Chemicals and materials

AccuStandard (New Haven, CT, USA) supplied the five PBDE standards (each at 50 mg L<sup>-1</sup> in iso-octane): 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,2',4,5'-tetrabromodiphenyl ether (BDE-49), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153) and 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154). Some physicochemical properties of these PBDEs are shown in Table 1 [30,31]. Stock solution containing mixed standards (10 mg L<sup>-1</sup> of each analyte) was prepared by combining five PBDE standards. The subsequent standards were prepared from standard mixture using *n*-hexane as solvent and a stock solution of 0.1 mg L<sup>-1</sup> was prepared using methanol (MeOH) respectively. They were kept at 4 °C in refrigerator. CS powder from crab shell and toluene, *o*-xylene, 1-octanol, and glutaraldehyde were bought from Sigma-Aldrich (St Louis,

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