



# Application of polydimethylsiloxane rod extraction to the determination of sixteen halogenated flame retardants in water samples



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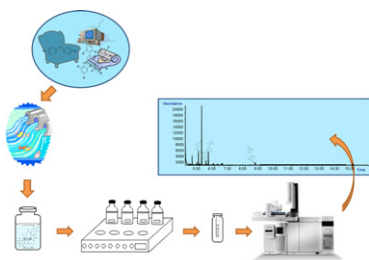
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## HIGHLIGHTS

- ▶ Simultaneous determination of nine BDEs and seven non-BDE flame retardants.
- ▶ Disposable polydimethylsiloxane (PDMS) is an efficient tool for flame retardants extraction.
- ▶ Enrichment factors between 108 and 840 were obtained.
- ▶ Detection limits obtained were in the range from 0.4 to 10 ng L<sup>-1</sup>.
- ▶ The method has been successfully applied in the analysis of complex matrix waters.

## GRAPHICAL ABSTRACT



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## ABSTRACT

An extraction and preconcentration procedure for the determination in water samples of several halogenated flame retardants (FRs), nine brominated diphenyls ethers (BDEs) and seven non-BDE FRs, was developed and validated. The optimised procedure is based on polydimethylsiloxane (PDMS) rods as sorptive extraction material, followed by liquid desorption and gas chromatography coupled to negative chemical ionisation–mass spectrometry (GC–NCI–MS) determination, rendering an efficient and inexpensive method. The final optimised protocol consists of overnight extraction of 100 mL of sample solutions containing 40% MeOH and 4% NaCl, followed by a 15-min sonication-assisted desorption with 300  $\mu$ L of ethyl acetate, solvent evaporation and GC–NCI–MS analysis. Under these conditions, extraction efficiencies in the 9 to 70% range were obtained, leading to enrichment factors between 108 and 840, detection limits in the range from 0.4 to 10 ng L<sup>-1</sup> and RSD values in the 2–23% range. After method validation, different real water samples, including river, ria, sea, landfill leachate, influent and effluent wastewater from an urban sewage treatment plant (STP) and effluent wastewater from a textile industry, were analysed. BDE-47, BDE-99, BDE-100 and BDE-197 were detected in wastewater and landfill leachate samples at concentration levels up to 2887 ng L<sup>-1</sup>. Among the non-BDE FRs, bis (2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (DEHTBP) was detected in surface water samples (sea, river and ria) between 1.3 and 2.2 ng L<sup>-1</sup> and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) in the landfill leachate (64 ng L<sup>-1</sup>).

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## 1. Introduction

Brominated flame retardants (BFRs) are a group of chemicals, used in many commercial products (such as televisions, computers,

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textiles, building insulation and furniture, etc.) to slow down or suppress the combustion process. They can be either aromatic, aliphatic, or cycloaliphatic compounds and can contain between 50% and 85% bromine by weight. Although at least 75 different BFRs have been commercially produced [1], the most frequently used and studied BFRs are brominated diphenylethers (BDEs), tetrabromobisphenol A (TBBP-A) and hexabromocyclododecanes (HBCDs) stereoisomers. The three major commercial mixtures of BDEs that have been produced were the deca-BDE mix (mostly BDE-209 with some nona and octa-BDE congeners), the octa-BDE mix (mostly hepta and octa-BDE congeners) and the penta-BDE mix (mostly penta and tetra-BDE congeners) [2]. Penta-BDE and octa-BDE mixtures have been banned in new products for European markets since 2004 and the use of the deca-BDE mix was also banned in 2008 [3,4]. Hence, the main manufacturers (Chemtura and Albemarle) have declared that by the end of 2012 they will have finished their production, importation and sale of deca-BDE for most uses [5]. Moreover, BDEs are listed as Priority Substances within the European Union Water Framework Directive [6]. In spite of these facts, the global consumption of BFRs increased in 2008 to 410,000 tons [5], simply because new flame retardants (FRs) have been marketed. These novel FRs, also called non-BDE FRs, include 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) and bis (2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (DEHTBP) which are used in replacement of penta-BDE; decabromodiphenyl ethane (DBDPE), as a substitute of deca-BDE; and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) replacing octa-BDE, among others [7,8]. Dechlorane plus (DP) can also be included in the term non-BDE FRs because, despite being a chlorinated FR used for over 40 years, it has only recently arisen as a relevant environmental and biota pollutant [9].

The lipophilic and bioaccumulative nature, the increasing evidence of persistence in the environment and humans, and epidemiological studies on BFRs explain the necessity to develop sensitive methodologies that can cope with the determination of these compounds in the environment at trace concentration levels. Thus, in recent years, a large number of studies have investigated the development of analytical methods and occurrence of BFRs in several matrices such as biological samples [10–12], air and dust [13–15], sediments and sewage sludge [16–18], but few studies have reported the presence of these compounds in aqueous samples [15,19].

Direct determination of BFRs in aqueous matrices is not possible due to their trace level and thus, a sample extraction/preconcentration step is required. Yet, it should be noted that most of the existing methods were exclusively developed for BDEs extraction and only very few of them consider some non-BDE FRs, resulting in a lack of ensemble extracting methods. In general, extraction of these compounds from water is performed by solid-phase extraction (SPE) [8,20,21]. Alternatively, and in order to reduce sample manipulation and organic solvent consumption, sorptive extraction techniques, such as solid-phase microextraction (SPME) [22–24] and stir-bar sorptive extraction (SBSE) [25,26] have been reported, but only for some BDEs. In this context, SBSE Twisters capacity is higher than that corresponding to SPME fibers, since a larger volume of sorbent is employed. Moreover, SBSE allows concentrating many samples simultaneously using different Twisters. On the other hand, other non-commercial (for analytical purposes) devices based on bulk materials, such as polydimethylsiloxane (PDMS) rods or tubes, present the same advantages of SBSE while being inexpensive in comparison to SPME fibers or SBSE Twisters. Therefore, they can be used as disposable devices [27], an attractive feature when determining hydrophobic analytes, such as BDEs and non-BDE FRs, since carry-over problems can be easily avoided. To date, disposable PDMS rods have only been employed for the determination of the penta-BDE mix using the headspace

sampling mode [28]. However, to the best of our knowledge, neither application to the determination of octa- and deca-BDE mix, nor to non-BDE FRs has been reported.

In this work, a new analytical method based on disposable PDMS rod extraction followed by liquid desorption and gas chromatography (GC) coupled to negative chemical ionisation–mass spectrometry (NCI–MS) is developed and validated for the simultaneous determination of nine BDEs and seven non-BDE FRs. Target compounds were selected in order to cover the most representative BDEs and their recent replacement chemicals, plus DP. Finally, different real water samples were analysed.

## 2. Materials and methods

### 2.1. Chemicals and extraction sorbent

Standard solutions of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) 100%, 2,2',3,4,4'-pentabromodiphenyl ether (BDE-85) 98.5%, 2,2',4,4',5-pentabromodiphenyl ether (BDE-99) 99.2%, 2,2',4,4',6-pentabromodiphenyl ether (BDE-100) 100%, 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153) 99.3%, 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154) 100%, 2,2',3,4,4',5',6'-heptabromodiphenyl ether (BDE-183) 100%, 2,2',3,3',4,4',6,6'-octabromodiphenyl ether (BDE-197) 98.1% and decabromodiphenyl ether (BDE-209) in isooctane, 50  $\mu\text{g mL}^{-1}$ , were provided by AccuStandard (New Haven, CT, USA). Solid standards of EHTBB 97.3%, DBDPE technical grade, DEHTBP 99.5%, BTBPE 100% and tris(tribromoneopentyl)phosphate (TTBPP) 97.3% were provided by AccuStandard and the two isomers of DP (*syn* and *anti*), 100  $\mu\text{g mL}^{-1}$  each in isooctane, were acquired from Cambridge Isotope Laboratories (Andover, MA, USA). As internal standards (IS), 3,3',4,4'-tetrabromodiphenyl ether (BDE-77) 100% and 2,2',3,4,4',5,6'-heptabromodiphenyl ether (BDE-181) 98%, 50  $\mu\text{g mL}^{-1}$  in isooctane, were obtained from AccuStandard and [ $^{13}\text{C}_{12}$ ]decabromodiphenyl ether ( $^{13}\text{C}$ -BDE-209) >98%, 25  $\mu\text{g mL}^{-1}$  in toluene, was purchased from Wellington Laboratories (Guelph, Canada). Diluted solutions of analytes and IS were made in acetone, when used to prepare spiked water samples, and in isooctane, when injected directly in the GC–MS. Isooctane, hexane, cyclohexane, toluene and methanol, chromatographic analysis grade, were purchased from Merck (Darmstadt, Germany). Acetone pestinorm, ethyl acetate and sodium chloride were acquired from VWR Prolabo (Mollet de Vallès, Spain). Deionized water was obtained with a Milli-Q Gradient A-10 system (18.2  $\text{M}\Omega\text{ cm}^{-1}$ , Millipore, Bedford, MA, USA).

Polyethersulfone (PES) and PDMS cord with a diameter of 0.7 mm (PES) and 2 mm (PDMS) were obtained from Membrane GmbH (Wuppertal, Germany) and GoodFellow (Huntingdon, England), respectively. Rods of these polymers with a length of 10 mm were prepared simply by cutting the PES or PDMS cord with a scalpel. Then, they were cleaned and stored in ethyl acetate and just prior to their use, they were dried with a lint-free tissue.

### 2.2. Samples

Several different water samples have been considered in this study: river, ria, sea, landfill leachate and wastewater samples. Ria and sea water were taken from a coastal area on the north-western coast of Spain. Urban influent and effluent wastewater samples were taken from an urban sewage treatment plant (STP) located in the northwest of Spain and receiving the discharges from a ca.100,000 inhabitants city. Industrial wastewater samples were obtained from a textile industry located in Catalonia (Spain) and landfill leachate water samples were taken in the Valencian Community (Spain).

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