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

R. Montes, I. Rodríguez, E. Rubí, R. Cela.

Departamento de Química Analítica, Nutrición y Bromatología, Instituto de Investigación y Análisis Alimentario, Universidad de Santiago de Compostela, Santiago de Compostela 15782, Spain.

Abstract

The suitability of an inexpensive polydimethylsiloxane (PDMS) sorbent, produced at 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 ºC, 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 (eg. 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 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.

Nowadays, miniaturization, 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 customized 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 (GC).

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 ºC 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 x 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 ºC.

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 neither with the PDMS rod nor with the sample extract, avoiding cross-contamination problems.

Under optimised conditions, extractions were carried out at 95 ºC, for 14 hours (overnight) using 10 mm long PDMS rods exposed to the headspace of 110 mL vessels containing 80 mL of water and 24 g (p/v=30%) of sodium chloride. Diethyl ether (1 mL) was employed to recover analytes from the PDMS rod. The organic extract was evaporated to dryness, at room temperature, with a gentle stream of nitrogen and reconstituted using 25 μL of isooctane. Fig. 1 depicts graphically sample extraction and analytes desorption steps.

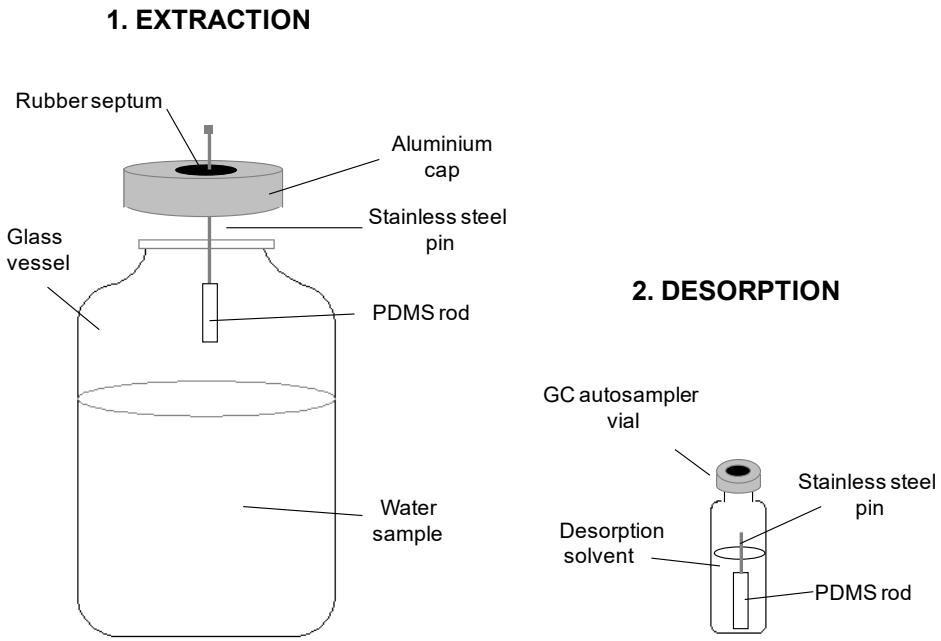

Fig. 1. Scheme of extraction and desorption steps in the HSSE of PBDEs from water samples using PDMS rods.

2.3. Equipment

An Agilent 6890 gas chromatograph (Wilmington, DE, USA) furnished with a split/splitless injection port and micro-electron-capture detection (micro-ECD) was employed to measure the concentrations of PBDEs in the final isooctane extracts from water samples, and thus, to assess the influence of different experimental conditions on the performance of PBDEs extraction with PDMS rods. Analytes were separated in an Agilent HP-5 type capillary column (30 m x 0.32 mm I.D., d_f: 0.25 μm) using a constant helium flow of 1.5 mL/min and the following oven temperature program: 90 ºC (2 min), first ramp at 15 ºC/min until 220 ºC, second ramp at 8 ºC/min to 290 ºC (held for 10 min). Standard solutions and sample extracts were injected in the splitless mode (2 μL, splitless time 2 min). Injector and detector temperatures were set at 270 ºC and 300 ºC, respectively. The makeup nitrogen flow in the micro-ECD system was fixed at 60 mL/min.

3. Results and discussion

3.1. Preliminary experiments

As a first step in the evaluation of PDMS rods suitability for the extraction of PBDEs from water samples, the variability of the proposed methodology was evaluated. This information is also required to determine whether a given variable plays a significant influence on the yield of the extraction or not. Working under repeatability conditions (n= 4 replicates), considering ultrapure water samples spiked at the 1000 pg/mL level (referred to the pentaBDE standard), and using PDMS rods with a length of 10 mm relative standard deviations below 12% were obtained for all species. These data were considered as acceptable to proceed with optimisation of the sorptive extraction method.

3.2. Desorption solvent

Extracted compounds can be recovered from PDMS sorbents, eg. coated stir bars or simply PDMS rods, by thermal desorption or using a small volume of an organic solvent. Although, the first option allows achieving lower detection limits, it requires the use of a thermal desorption unit in combination with the GC instrument. Moreover, only one chromatographic analysis can be performed per sample; therefore, the second possibility was considered in this work. On the basis of their high volatilities and medium polarities, similar to those of PBDEs, dichloromethane, acetone and diethyl ether were considered to recover target species from PDMS rods. After being exposed to spiked water samples, each rod (10 mm length) was soaked for 5 min with 3 consecutive fresh fractions (1 mL volume) of the same solvent in closed GC autosampler vials. Obtained extracts were dryness evaporated and reconstituted with 25 μL of isooctane. Recoveries between 77 and 86% were achieved with the first mL of dichloromethane and acetone; whereas, values from 86 to 89 % were obtained using diethyl ether. Percentages of PBDEs in second fractions varied from 12 to 16% for the first two solvents and from 10 to 11% for diethyl ether. Third fractions of acetone of dichloromethane contained also higher percentages of PBDEs (up to 6%) than in the case of diethyl ether (1-2%). Taking into account these results, and considering also its higher volatility, diethyl ether was chosen as extraction solvent. Its volume was limited to 1 mL, even assuming that a fraction of the compounds extracted from the water sample remained in the PDMS sorbent, in order to reduce solvent consumption and also to shorten the further dryness evaporation step. Obviously, rods were employed only once to avoid carry-over problems. From an economical perspective, this did not represent any drawback due to their very low cost (under 0.1 euros per 10 x 2 mm PDMS extraction element). Experimentally, it was also verified that PBDEs were not lost during dryness evaporation of primary diethyl ether extracts, data not given.

3.3. Optimisation of extraction conditions

Unless otherwise stated, optimisation of extraction conditions was performed using 10 x 2 mm PDMS rods and 110 mL vessels containing 80 mL of water spiked with the pentaBDE standard at the 500 pg/mL level. The percentage of acetone in the extraction vessel was maintained under 0.5%. Extractions were carried out overnight (14 hours) at 80 ºC. In order to simplify the experimental set up and to avoid cross-contamination problems, due to sorption of PBDEs on PTFE coated bars, sample stirring was not considered.

Effects of sampling mode and sample volume. Kinetics of sorptive extraction processes might change depending on the sampling mode: headspace or direct extraction. In spite of the very low vapour pressures of PBDEs, above 3 times higher signals were obtained for all congeners in the HS mode. This behaviour is in agreement with previous results obtained using SPME fibres [21]; moreover, it suggested that, under selected extraction conditions (80 ºC, 14 h), analytes have not reached the equilibrium among the three phases (water, headspace and PDMS) presented in the extraction vessel; otherwise, the efficiency of the process should be independent of the sampling mode. Other factors, such as the distance between the surface of the sample and the PDMS rod, or the orientation of the last, vertical or horizontal, versus the first, did not play any noticeable effect on extraction efficiencies.

Fig. 2 shows the influence of the sample volume on the responses obtained for target species. Extractions were carried out using aliquots of the same spiked water sample. Data for 10 mL of water corresponded to 22 mL volume vessels, the rest of experiments were performed using 110 mL ones. As observed, responses for all compounds increased steady with the sample intake, proving the high extraction capacity of PDMS rods. Considering these results, the sample volume was fixed at 80 mL and extractions were carried out in the HS mode.

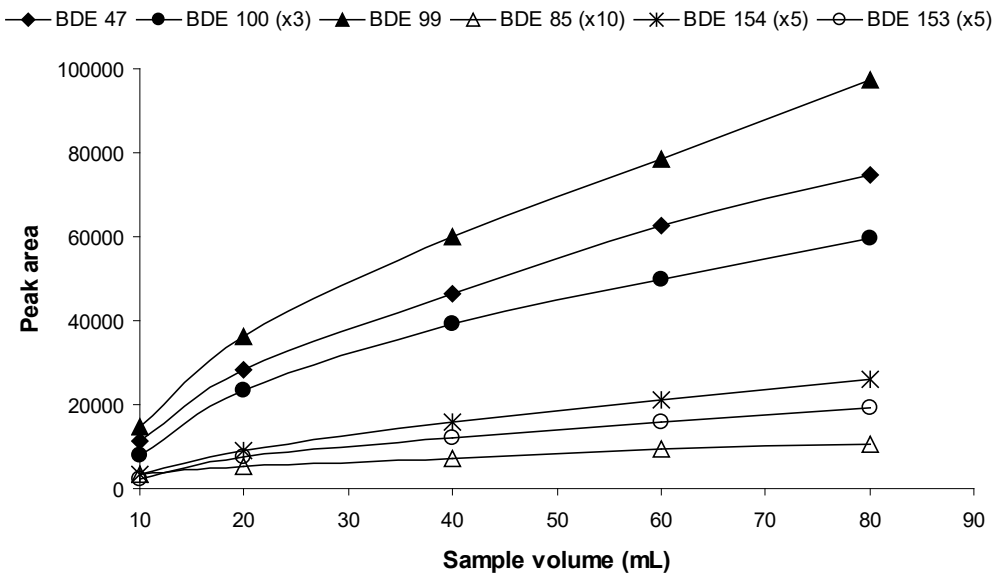

Fig. 2. Influence of sample volume on responses obtained for each BDE. HSSE at 80 ºC for 14 hours.

Temperature and ionic strength. Theoretically, both factors affect to kinetics and thermodynamics of sorptive extraction processes. Diffusion rates of analytes from the sample to PDMS rods rise with the temperature; however, their distribution constants between this polymer and the sample decrease [23]. On the other hand, for non ionic and moderate polar species, such as PBDEs, increasing the ionic strength of the sample, eg. using sodium chloride, it is expected to improve the efficiency of the extraction at the expense of slowing down its kinetics. In practise, the effects of both factors were evaluated simultaneously using a mixed mode $3^1 2^1$ experimental factorial design [24]. On the basis of previous results obtained for PDMS fibres [21], the factor temperature was evaluated in the range from 65 to 95 ºC, at three levels, and the concentration of sodium chloride at two, 0 and 30 %, Table 1. Extractions, under conditions defined for each of the six experiments comprised in the design, were carried out in duplicate following a randomised order. Table 1 shows the standardised main effects of both factors on the average response obtained for each analyte. Their absolute values are proportional to the variation in the efficiency of the extraction when the considered factor changes from the low to the high level defined in the domain of the design. The sign means if the extraction efficiency increases (positive sign) or decreases (negative sign). Temperature played a positive and statistically significant influence (95 % confidence level) on the extraction process for all species. The absolute value of its main effects rose with the number of bromine substituents in the molecule of each BDE. The effect of sodium chloride was positive and significant for tetra and penta-brominated congeners (BDEs 47, 100, 99 and 85), whereas, its influence was negligible for BDEs 154 and 153, Table 1. The interaction temperature-salt and the quadratic term associated to the first variable never achieved the statistical significant bound, data not shown. On the basis of these results, in further experiments 24 g of sodium chloride were added to 80 mL of water in the extraction vessel. The need for high extraction temperatures was also clear.

Factor	Range of values			Standardised main effects					
	Low	Medium	High	BDE47	BDE100	BDE99	BDE85	BDE154	BDE153
Temperature (ºC)	65	80	95	6.7*	9.1*	10.5*	11.1*	11.5*	12.5*
NaCl (%)	0	-	30	6.9*	4.2*	4.8*	8.8*	-0.1	1.0

Table 1. Experimental domain and standardised coefficients of main effects associated to factors considered in the experimental design. Data for 80 mL water samples and 14 hours of HSSE using 10 x 2 mm PDMS rods. *Statistically significant effects at the 95% confidence level

Time and extraction efficiency. The efficiency of the HSSE for a given compound was experimentally calculated as the ratio between the mass of this specie in isooctane extracts from PDMS rods and that added to the sample in the extraction vessel. The first was determined by external calibration, using diluted standards of the pentaBDE solution in isooctane, at five different concentration levels, analysed under same conditions as sample extracts. Fig. 3 depicts the efficiency of the extraction at two different temperatures: 80 and 95 ºC, considering sampling periods from 1 to 36 hours. Each point in the graph represents the average response of two replicates. Working at 80 ºC, none of the compounds achieved the equilibrium within the considered sampling interval. At 95 ºC, extraction efficiencies for BDEs 47, 100 and 99 reached a plateau after 14 hours of HS sampling, whereas longer periods were necessary for the rest of congeners. By convenience, an extraction step of 14 hours (overnight) at 95 ºC was fixed as working conditions. Although, the enrichment step is rather long, many samples can be extracted simultaneously using inexpensive, disposable PDMS rods. After that, the obtained liquid extracts can be loaded in the autosampler of the GC system; therefore, sample throughput is mainly controlled by the chromatographic separation step. Anyhow, the extraction step is still nearly twice shorter than that proposed for *Twisters* (PDMS volume 47 μL), when applied to the determination of PBDEs in water samples [22].

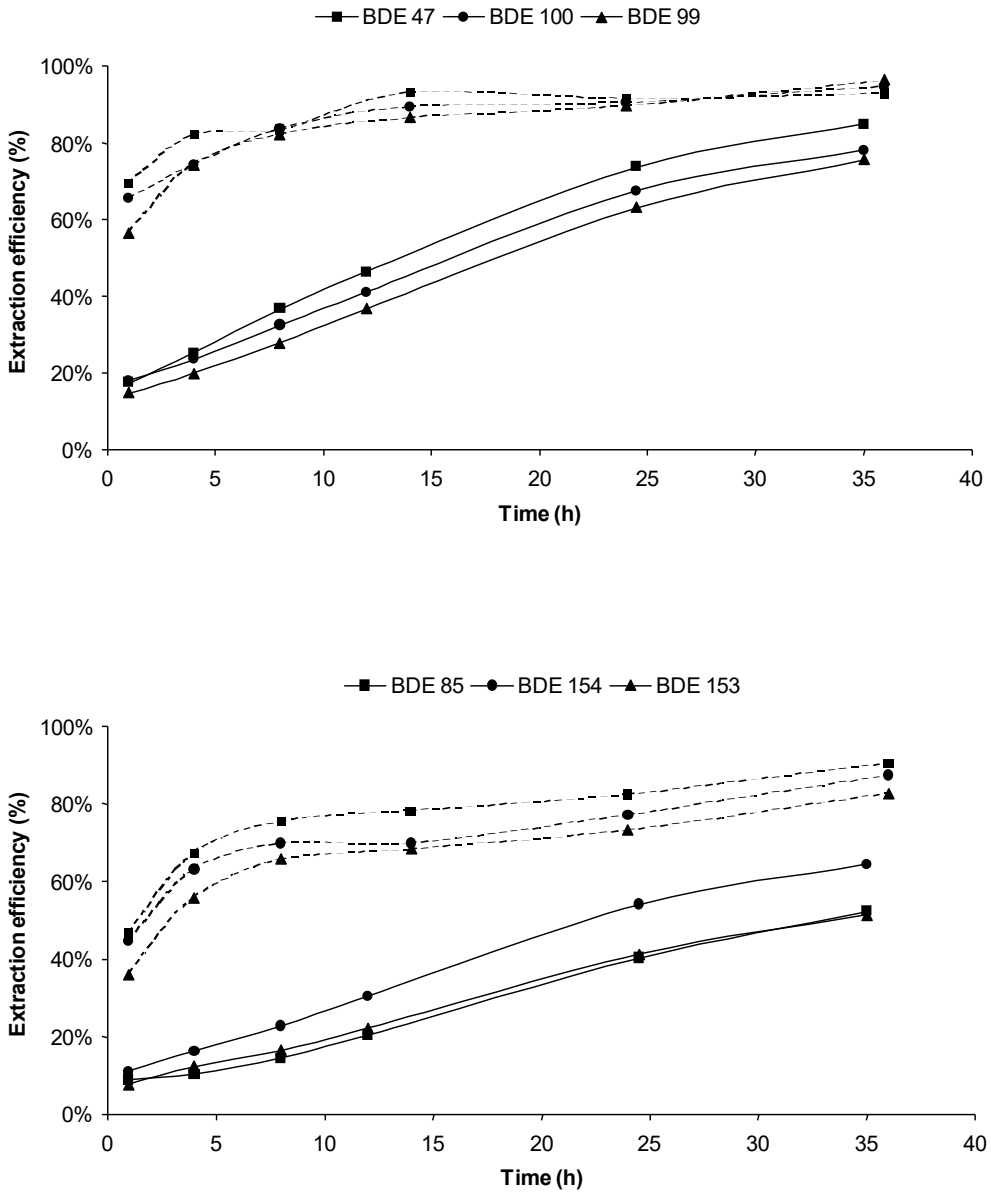

Fig. 3. Time-course of the HSSE at 80 (solid line) and 95 ºC (dotted line). Data for spiked, 80 mL volume water samples containing 300 mg/mL of sodium chloride. Average efficiencies for duplicate extractions

Enrichment factors and experimental extraction efficiencies achieved for 80 mL water samples (n= 4 replicates), under above conditions, are shown in Table 2. Theoretical extraction efficiencies are also provided. The last were calculated using the following equation [12]: $E\% = \frac{1}{\left(\frac{\beta}{K}+1\right)} x100$ (eq. 1). Although this expression has been developed for a system with two phases, it can be extrapolated to our case assuming that, in the equilibrium, amounts of PBDEs in the HS of the extraction vessel are negligible. In the above equation, the term β is the ratio between sample and sorbent volumes ($8x10^4$ and 31 μL, respectively), whereas K represents the distribution coefficient for each BDE between the PDMS rod and the water sample. The exact values of K under working conditions (referred to sample temperature and ionic strength) are unknown; however, the experimental data obtained at 100 ºC using PDMS SPME fibres were taken as a good approach [25]. The concordance between experimental and predicted extraction efficiencies, for those congeners which have

achieved the equilibrium (BDEs 47, 100 and 99), can be considered as acceptable; particularly, assuming that no correction was applied to compensate for the incomplete desorption of analytes from PDMS rods using only 1 mL of diethyl ether.

Congener	Log K[a]	Extraction efficiency (%)		Enrichment factor
		Theoretical	Experimental	
BDE47	4.47	92	93 ± 8	2976
BDE100	4.73	95	89 ± 9	2850
BDE99	4.81	96	87 ± 9	2780
BDE85	4.77	96	78 ± 6	2500
BDE154	5.21	98	70 ± 8	2240
BDE153	--	--	69 ± 10	2210

Table 2. Extraction efficiencies and enrichment factors obtained under final working conditions: HSSE at 95 ºC for 14 h using 80 mL of water containing 24 g of NaCl, n= 4 replicates.
[a] Values taken from reference [25];-- Not available

Organic modifiers. Addition of small percentages of water-soluble organic solvents to samples might modify the efficiency of sorptive extractions. Particularly, using PDMS coated stir bars for direct extraction of PBDEs from water samples at room temperature, it has been proved that methanol addition prevents the adsorption of penta- and hexaBDEs on the walls of glass vessels and improves significantly the efficiency of their extraction [22]. In our case, acetone was initially considered as the organic modifier since the pentaBDE standard mixture, employed to spike water samples, was prepared in this solvent. Several experiments were accomplished adding increased percentages of acetone to water samples (from 0.5 to 5%); however, significant variations on the efficiency of the extraction were not observed, data not shown. Further assays considering methanol as modifier led to similar results. Very likely, the responsible for the contradictory patterns between results obtained in this work and those corresponding to the application of Twisters to PBDEs determination [22] is the variable temperature. At 95 ºC, the extension of analytes losses due to adsorption processes is insignificant when compared to those occurring at room temperature.

Amount of PDMS. The effect of PDMS volume on the yield of the HSSE was assessed considering rods with two different lengths: 5 and 10 mm (PDMS volumes 16 and 31 μL, respectively) and two different extraction conditions: 14 h at 95 ºC and 12 h at 80 ºC. As expected, the yield of the extraction process decreased with the volume of PDMS. The extension of this diminution changed depending on sampling conditions and target species. The less volatile analytes (BDEs 85, 154 and 153) underwent the higher decrease in their extraction efficiencies (up to 50%), data not given. Moreover, for all congeners, at 80 ºC the reduction of extraction yield was more significant than at 95 ºC. These data suggest that the volume of the PDMS rod might affect not only to the yield but also to the kinetics of the extraction process. The 10 x 2 mm PDMS rods were kept for further studies.

3.4. Method performance

The linearity of the method was evaluated using water samples spiked with the pentaBDE standard mixture at six different concentration levels from 30 to 5000 pg/mL. Each level was processed in duplicate. Concentrations of individual congeners in the spiked samples were calculated using their relative abundance in this commercial mixture, see experimental section. Correlation coefficients (R^2) higher than 0.9983 were obtained, Table 3. Repeatability was

investigated using samples spiked at three different levels: 60, 120 and 500 pg/mL (values referred to the pentaBDE standard). Four replicates were processed per level. Relative standard deviations in the responses (peak areas) for all congeners remained under 12%. Obviously, the highest average variabilities corresponded to the most diluted samples, Table 3. Keeping on mind that: (1) a different rod is employed for each sample and (2) three stages (extraction, desorption and dryness evaporation) are comprised in the sample preparation method, its precision was considered as acceptable and similar to that reported for SPME fibres when applied to PBDEs analysis in water samples [21]. Quantification limits of the developed approach remained at the very low pg/mL level, in the same order of magnitude than those obtained using PDMS coated stir bars in combination with GC-MS detection [22]. In order to obtain a direct comparison between the sensitivity of the proposed enrichment method and that of the SPME technique, aliquots of the same spiked sample were processed using both approaches. SPME extractions were accomplished with 100 μm film thickness PDMS fibres under optimal conditions described elsewhere [21]. Fibres were thermally desorbed in the splitless injector of the GC-ECD. Extracts from PDMS rods were made up to 25 μL with isooctane and a fraction of 2 μL injected in the same GC system. For all congeners, between 2 and 5 fold higher responses were achieved using PDMS rods than employing SPME fibres.

In spite of the extraction capability of PDMS rods, it is evident that GC-ECD lacks of enough selectivity for the determination of PBDEs, at low concentrations, in real-life polluted samples. The combination of the proposed sample preparation approach with more selective determination techniques, eg. GC-MS using chemical ionisation in the negative mode, it is expected to improve the achieved quantification limits, particularly for congeners 47, 100 and 99, which elute in a relatively noisy region of GC-ECD chromatograms and they can be overlapped, partially o totally, with peaks corresponding to other persistent halogenated pollutants, eg. polychlorinated biphenyls [26,27].

Congener	Linearity		Repeatability for spiked samples (RSD %)			Q.L.(pg/mL)
	Interval (pg/mL)	R^2	60 pg/mL[a]	120 pg/mL[a]	500 pg/mL[a]	
BDE47	(11-1900)	0.9996	3.3	7.4	3.4	5
BDE100	(3-430)	0.9992	8.2	6.6	5.3	1
BDE99	(12-2000)	0.9994	6.4	8.0	5.2	3
BDE85	(0.4-55)	0.9992	11.1	9.9	5.5	0.3
BDE154	(0.8-130)	0.9990	7.7	3.3	5.8	0.5
BDE153	(0.8-135)	0.9983	12.4	6.3	5.2	0.4

Table 3. Linearity, repeatability (n= 4 replicates) and quantification limits (S/N=10) of the proposed method. [a] Concentration values referred to the pentaBDE mixture

Influence of the type of sample on the efficiency of the HSSE was evaluated by comparison of responses obtained for ultrapure (Milli-Q), ultrapure water fortified with 30 mg/L of humic acids, river, sea and treated wastewater samples spiked with the pentaBDE standard at two different levels (500 and 100 pg/mL). Data for raw wastewater fortified at the higher concentration level are also provided. Samples were first filtered and then submitted to optimised extraction conditions (HSSE at 95 ºC for 14 h using 10 mm x 2 mm PDMS rods after addition of 24 g of NaCl). In case of river, sea and wastewater non-spiked aliquots were also processed, Fig. 4; however, none of the analytes was detected in blank samples. In general, responses obtained for the six PBDEs in all samples were equivalent to those achieved using ultrapure water, Table 4. Therefore, efficiency of the HSSE method was unaffected by matrix effects; consequently, samples can be quantified using external calibration.

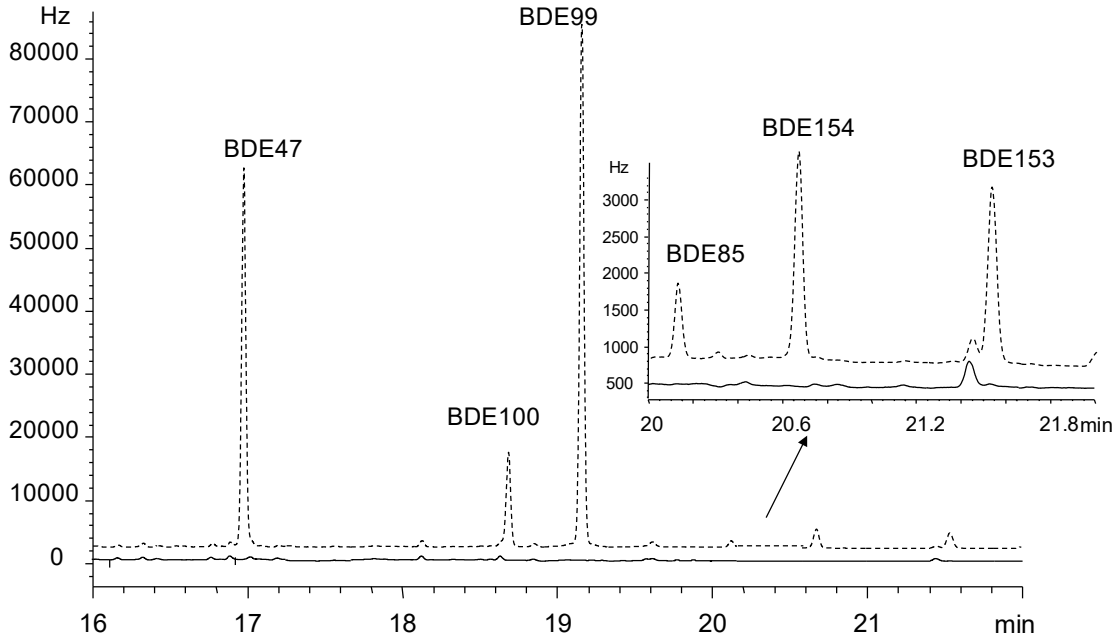

Fig. 4. Overlay of GC-ECD chromatograms for non-spiked and spiked aliquots (80 mL volume) of a raw wasterwater sample. Solid line, non-spiked aliquot; dotted line, same sample spiked with 500 pg/mL of the pentaBDE standard.

	Normalised responses with their RSD (%)								
Sample	Milli-Q with 30 mg/L of humic acids		River water		Seawater		Treated wastewater		Raw wastewater
Spiked level(pg/mL)[a]	100	500	100	500	100	500	100	500	500
BDE47	96 ± 6	103 ± 6	95 ± 6	98 ± 5	96 ± 6	95 ± 7	101 ± 9	89 ± 4	92 ± 10
BDE100	89 ± 10	105 ± 6	91 ± 8	97 ± 6	93 ± 8	92 ± 5	96 ± 8	90 ± 5	86 ± 9
BDE99	96 ± 8	103 ± 6	91 ± 2	95 ± 5	96 ± 13	95 ± 7	99 ± 8	95 ± 6	82 ± 8
BDE85	92 ± 6	93 ± 7	98 ± 10	91 ± 7	99 ± 5	87 ± 9	102 ± 11	102 ± 10	71 ± 7
BDE154	88 ± 9	100 ± 6	94 ± 4	94 ± 6	95 ± 13	90 ± 12	97 ± 9	98 ± 9	93 ± 8
BDE153	99 ± 7	103 ± 7	97 ± 9	94 ± 11	100 ± 9	90 ± 10	107 ± 7	100 ± 9	95 ± 8

Table 4. Evaluation of possible matrix effects. HSSE at 95 ºC for 14 h using spiked samples containing a 30% of NaCl. Normalised responses to those achieved for ultrapure water, n= 4 replicates. [a] Concentration values referred to the pentaBDE mixture.

4. Conclusions

An alternative method for the determination of PBDEs in water samples has been presented. PDMS rods are inexpensive and provide similar enrichment efficiencies to those reported for coated stir bars, containing a similar amount of PDMS. Despite rods were manually prepared in the laboratory, by cutting pieces of PDMS cord, and extractions were carried out using different PDMS units, an excellent precision was achieved. Moreover, the theory of sorptive extraction processes, previously developed for PDMS coated fibres and stir bars, can be employed to predict factors affecting to thermodynamics and kinetics of extractions with PDMS rods. The applicability of the HSSE method to the analysis of real-polluted water samples can be enhanced by using more selective determination techniques than GC-ECD.

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