Solid-phase microextraction with simultaneous oxidative sample treatment for the sensitive determination of tetra- to hexa-brominated diphenyl ethers in sediments

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a b s t r a c t

Solid-phase microextraction (SPME) is an effective technique for the extraction of polybrominated diphenyl ethers (PBDEs) from environmental water samples. Although it has been also applied to sediments, the organic content of this matrix causes an exponential decrease in the yield of the extraction. This work presents an improved SPME procedure for the sensitive determination of six PBDEs (tetra- to hexa-brominated congeners) in sediments containing up to 6% of total organic carbon (TOC). Samples (0.25–0.5 g) were accurately weighed in 22 mL glass vessels, mixed with a given amount of potassium permanganate, 0.5 mL of sulphuric acid and 5 mL of water. Extractions were performed at 100 °C, for 40 min, using a polyacrylate (PA) coated fibre in the headspace (HS) mode. Potassium permanganate showed a dramatic, positive effect on the yield of the extraction. Its optimum amount was related to the TOC of the sediment, with overall highest responses attained for 40 mg of oxidant per mg of organic carbon in the SPME vessel. Under final working conditions, the combination of SPME with gas chromatography coupled to tandem mass spectrometry (GC–MS/MS) provided relative standard deviations (RSDs) below 14%, relative recoveries from 76 to 111% and limits of quantification (LOQs) lower than 0.15 ng g^{-1} for all the investigated PBDEs in spiked river and marine sediments with different TOC. The performance of the method was also evaluated satisfactorily with a medium complexity (TOC 6.7%), real-life polluted sediment, previously analyzed in inter-laboratory comparison exercises.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are synthetic compounds used as flame retardant additives in a variety of products, such as building materials, electronic equipment, paints and textiles, in order to reduce the risk of ignition as well as the rate of combustion. Industrially, they have been produced as three technical formulations whose major components are tetra- to hexa-brominated congeners (penta-mix), hepta- to nona-brominated species (octa-mix) and decabromo diphenyl ether (deca-mix) [1,2]. Environmental evidences of the persistence, bio-accumulation and world-wide distribution of PBDEs, particularly in biota and solid samples, have led to the ban of most applications of penta- and octa-mix solutions in many countries [3]. Eventually, some manufacturers have also stopped the production of both mixtures. However, environmental benefits of above decisions are not immediate. On one hand, PBDEs are diffused out from everyday materials, formerly treated with these flame retardants. On the other one, PBDEs can be slowly released from polluted sediments to the water phase and then their concentrations be magnified in the trophic pyramid, particularly in the case of tetra- and penta-brominated congeners [4–6]. Consequently, the levels of PBDEs in sediments should be still monitored during coming years.

Methods for the determination of PBDEs in sediments normally involve the combination of an effective sample preparation strategy with their further sensitive and selective determination. Gas chromatography (GC) followed by mass spectrometry with negative chemical ionization (NCI-MS) [7–9], tandem mass spectrometry (MS/MS) after electron impact ionization [7,10–12] and high resolution mass spectrometry [12,13] are the most resorted approaches for the quantification of tetra- to hexa-brominated congeners. Sample preparation usually relies on exhaustive solid–liquid extraction techniques, such as Soxhlet [5,8], pressurized liquid extraction (PLE) [14,15] and microwave assisted extraction (MAE) [4], which are followed by one or several clean-up steps, based on the use of adsorption chromatography, activated copper powder for elemental sulphur removal, gel permeation chromatography and/or oxidative treatments. Sulphuric acid impregnated silica is the most popular of the oxidative treatments [5,8,16]; moreover, potassium permanganate ($KMnO_4$), in acidic conditions, can be also used as

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an effective clean-up strategy in the determination of persistent pollutants, e.g. polychlorinated biphenyls (PCBs), with the advantage of removing at the same time most of the co-extracted organic species as well as elemental sulphur [17,18].

Microextraction techniques, based on equilibrium processes, have been widely applied to the concentration of PBDEs in water samples [19–23]. Among them, headspace solid-phase microextraction (HS SPME) is particularly attractive since it combines high extraction efficiencies, selectivity and automation capabilities. HS SPME has been also proposed for the extraction of PBDEs (tetra- to hexa-brominated congeners) from sediment samples. Although it provided excellent limits of quantification (LOQs) in sandy matrices, the yield of the extraction underwent a dramatic reduction for more complex sediments [24], with LOQs above 1 ng g^{-1} (case of congeners 154 and 153) in samples containing around 2.0% of total organic carbon (TOC).

The aim of this research was to improve the sensitivity of SPME for the extraction of the major congeners in the technical penta-mix formulation from medium complexity sediments. In order to achieve this aim, without introducing a previous extraction step using an organic solvent, removal of most organic species contained in the sample and extraction of PBDEs were carried out simultaneously, by combining an oxidative sample treatment (based on the use of $KMnO_4$ under acidic conditions) with the HS extraction mode. The effects of several variables on the performance of the microextraction process are thoroughly evaluated and related to the TOC of the sample. After extraction, analytes were determined by GC–MS/MS. Performance of the proposed method was evaluated using spiked samples and also a marine sediment (TOC, 6.7%) with indicative values of target PBDEs.

2. Experimental

2.1. Solvents, standards and fibres

N-hexane and acetone, trace analysis quality, sulphuric acid (H_2SO_4, 98% purity) and potassium permanganate ($KMnO_4$, 99%) were obtained from Merck (Darmstadt, Germany). Individual standards (50 μg mL^{-1}, in nonane) of the six PBDEs considered in this study (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) were acquired from Wellington Laboratories (Guelp, Ontario, Canada). A standard of $^{13}C_{12}$ labelled BDE99 (50 μg mL^{-1}, in nonane) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). This species was used as internal surrogate (IS) in combination with GC–MS/MS detection. A pentaBDE standard mixture with a total PBDEs concentration of 10 μg mL^{-1}, in cyclohexane, was purchased from Dr. Ehrensdorfer (Augsburg, Germany). The relative abundances of above congeners in this mixture 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) [25]. Diluted solutions of the pentaBDE standard, the individual congeners and the IS were made in n-hexane and in acetone and used during optimization of GC–MS/MS determination conditions and to prepare the spiked sediment samples, respectively.

A manual SPME holder and fibres coated with different polymers: poly(dimethylsiloxane) (PDMS, 100 μm film thickness), polyacrylate (PA, 85 μm film thickness), PDMS-divinylbenzene (PDMS-DVB, 65 μm film thickness) and Carboxen-poly (dimethylsiloxane) (CAR-PDMS, 85 μm film thickness) were obtained from Supelco (Bellefonte, PA, USA). Before being used for first time, fibres were thermally conditioned following instructions provided by the supplier.

2.2. Samples and sample preparation

River and marine sediments were obtained from small rivers and marine harbours in Galicia (Northwest, Spain). All samples were freeze-dried and sieved. Fractions below 300 μm were retained for this study and their TOC content characterized. Discrete and pooled samples were fortified with PBDEs at different concentrations using either individual standards, or the commercial pentaBDE mixture. In both cases, 25 g of sieved samples were accurately weighed in glass jars and thoroughly mixed with 25 mL of acetone containing a known concentration of PBDEs. The resulting slurries were homogenized periodically and left in a hood until complete evaporation of the solvent. Then, samples were aged for at least 1 month before extraction. Spiked and non-spiked samples were stored at 4 °C in amber glass vessels. A real-life polluted marine sediment (code QBC005MS), which had been previously used in inter-laboratory comparison studies, was acquired from QUASIMEME (Wageningen, The Netherlands).

Under optimized conditions, samples (0.25–0.5 g) were accurately weighed in 22 mL SPME glass vessels. When GC–MS/MS was used as determination technique, 0.5 mL of the IS were added and vessels were left opened in a hood overnight. Salts, particularly in the case of marine sediments, were removed by shaking the sample with 10 mL of ultrapure water. After centrifugation, the aqueous supernatant was removed with the aid of a Pasteur pipette and 5 mL of water, 0.5 mL of H_2SO_4 (diluted 1:3 with water), a PTFE magnetic bar and a given amount of $KMnO_4$ were added to the solid residue. Vessels were closed and immersed in a water bath at 100 °C. After 5 min of equilibration, a PA fibre was exposed to the HS of the vial for 40 min. Finally, fibres were thermally desorbed at 300 °C for 2 min.

2.3. Equipment

Gas chromatography combined with tandem mass spectrometry (GC–MS/MS) was used for the selective determination of PBDEs. The employed system consisted of a Varian 450 model (Walnut Creek, CA, USA) gas chromatograph connected to an ion trap type mass spectrometer, Varian 240-MS, furnished with an electron impact (EI) ionization source in the external configuration mode. Analytes were separated in a Varian Factor Four capillary column (30 m × 0.25 mm i.d., d_f: 0.25 μm) operated at a constant helium flow of 1.0 mL min^{-1}. The GC oven was programmed as follows: 90 °C (held for 2 min), first rate 15 °C min^{-1} to 220 °C, second rate 8 °C min^{-1} to 290 °C (held for 8 min). The injector was maintained at 300 °C, with the solenoid valve changing from the splitless to the split mode after 2 min. Ion source, trap and transfer line temperatures were set at 180, 150 and 290 °C, respectively. The damping gas (helium) flow was fixed at 0.8 mL min^{-1}. Compounds were detected in the MS/MS mode using an electron multiplier offset of +200 V and a filament emission current of 80 μA. MS/MS parameters were adapted from those previously reported for an ion trap mass spectrometer furnished with an internal EI source [19]. Working MS/MS conditions and retention times of PBDEs are summarized in Table 1.

During the initial steps of this work, an Agilent 6890 (Wilmington, DE, USA) gas chromatograph furnished with a micro-electron-capture detector (micro-ECD) was also used. In this case, analytes were separated employing an Agilent HP-5 type capillary column (30 m × 0.25 mm i.d., d_f: 0.25 μm) operated at an helium constant flow of 1.2 mL min^{-1}. The micro-ECD detector was maintained at 300 °C, and the makeup nitrogen flow in the detector fixed at 60 mL min^{-1}. The temperature of the injector, the oven program and the injection mode were the same as in the GC–MS/MS system.

Table 1
GC–MS/MS detection parameters, linearity, repeatability (RSDs, $n = 5$ replicates) and instrumental LOQs.

BDE	Ret. time (min)	Parent ion (m/z)	Storage level (m/z)	Excitation voltage (V)	Quantification ions (m/z)	Linearity (R^2)	RSDs (%)[a]	LOQ (ng mL^{-1})
47	17.59	486	185	1.2	324 + 326 + 328	0.998	5.2	0.05
100	19.35	566	216	1.4	404 + 406	0.997	6.1	0.15
99 ($^{13}C_{12}$)	19.94	578	216	1.4	416 + 418	–	–	–
99	19.94	566	216	1.4	404 + 406	0.995	6.2	0.10
85	21.13	566	216	1.4	404 + 406	0.998	6.1	0.40
154	21.71	644	245	1.4	482 + 484 + 486	0.996	4.9	0.50
153	22.93	644	245	1.4	482 + 484 + 486	0.997	2.0	0.40

[a] Values for a standard solution containing 10 ng mL^{-1} of each BDEs.

Levels of PBDEs in sediment samples were quantified with the standard addition method. Once the accurately weighed samples were introduced in the SPME vessels, they were fortified with increasing levels of PBDEs, and a given amount of the IS (between 2 and 10 ng), both prepared in acetone. If necessary, a small volume of the same solvent (ca. 0.5 mL) was also added to guarantee the homogeneous distribution of the spiked compounds in the matrix. Vessels were left opened in a hood overnight and then extractions carried out as described in the previous section. Calibration curves were obtained by representing the response obtained for each compound (peak area), corrected with the signal for $^{13}C_{12}$ BDE99 in the case of GC–MS/MS detection versus the concentration added to the sample in the SPME vessel.

3. Results and discussion

3.1. Performance of determination techniques

Table 1 summarizes MS/MS detection parameters and some characteristics related to the performance of the GC–MS/MS system. The parent ion for each group of congeners was isolated in the trap with a window of 5 m/z units and further fragmented using a resonant wavelength. All PBDEs showed a common MS/MS transition reflecting the elimination of two atoms of bromine. Chromatograms were monitored using the sum of the two or three most intense product ions for each group of congeners, Table 1. Achieved limits of quantification (LOQs), defined as the concentration of compound given a signal 10 times higher than the baseline noise, ranged from 0.05 ng mL^{-1} for BDE47 to 0.5 ng mL^{-1} for BDE154, considering an injection volume of 2 μL. The linearity in the response of the GC–MS/MS system was evaluated with standards, at eight different levels of concentration, in the range from LOQs to 250 ng mL^{-1}. Within this interval, the correlation coefficients (R^2), corresponding to the plotting of peak areas versus concentration, were higher than 0.996 for all compounds, Table 1. The repeatability of the injection remained between 2 and 6%, without internal standard correction. On the other hand, the GC-micro-ECD system achieved LOQs between 0.2 and 0.4 ng mL^{-1}, depending on the compound and a slightly better linearity ($R^2 \geq 0.999$) and repeatability (RSDs 2–3%) than the GC–MS/MS instrument, data not shown. However, the limited selectivity of ECD detection impairs its applicability to real sediment samples. Particularly, the responses for BDEs 47, 100, 99 and 85 might be affected by the presence of PCBs in the sample, due to the risk of co-elution between above PBDEs and hepta- to deca-chlorinated PCBs [26,27].

3.2. Optimization of microextraction conditions

3.2.1. Preliminary experiments

Initially, SPME extractions were carried out with a river sediment (TOC 0.63%) fortified with the pentaBDE standard at 200 ng g^{-1}. Fractions of 0.5 g were introduced in 22 mL vials together with a PTFE coated magnetic bar. In a first series of experiments, samples were just moisturized with 5 mL of ultrapure water [24]; in the second one, 160 mg of potassium permanganate, 0.5 mL of sulphuric acid and 5 mL of water were added to the vessel [18]. In both cases, a PDMS fibre was exposed to the remaining HS for 30 min, at 100 °C. Significantly higher responses for the main components of the pentaBDE standard, particularly for penta- and hexa-brominated PBDEs, were attained under oxidative conditions, Fig. 1.

Further assays using marine sediments containing similar TOC values led to the same conclusion. However, for this latter matrix, corrosion of the metallic SPME needle was observed after a limited number of extractions. This effect was attributed to salts, particularly chlorides, contained in marine origin sediments. In presence of sulphuric acid, volatile acids, such as hydrochloride acid, were formed passing to the HS of the SPME vessel and reacting with the protective SPME needle and also with the metallic plunger attached to the core of the fibre. As a result, after 3–4 extractions, it was impossible to displace the fibre in and out of the protective needle. This problem was overcome shaking the sediment with 10 mL of water, for 2 min, in the SPME vessel. After centrifugation, the aqueous supernatant was discarded and the solid residue, containing the hydrophobic PBDEs, submitted to the oxidative treatment.

3.2.2. Fibre selection and sample treatment

Systematic optimization of SPME conditions was carried out using a sample (pool of river and marine sediments) with a TOC of 1.2%, spiked also with the pentaBDE mixture at 200 ng g^{-1}. Extractions were always performed in the HS mode, with the sample vessel immersed in a water bath at 100 °C, as recommended in previous works [19,24].

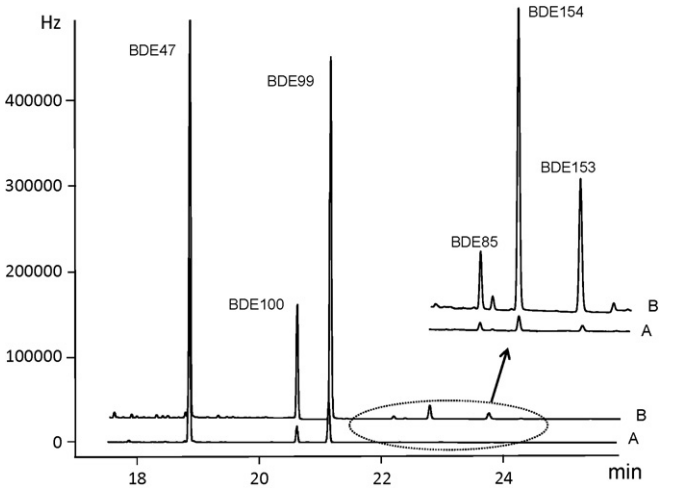

Fig. 1. Chromatograms (GC-micro-ECD) corresponding to the same river sediment (TOC 0.63%) spiked with the pentaBDE standard at 200 ng g^{-1}, without (A) and with oxidative treatment (B) during SPME extraction. HS SPME at 100 °C, for 30 min, using a PDMS fibre.

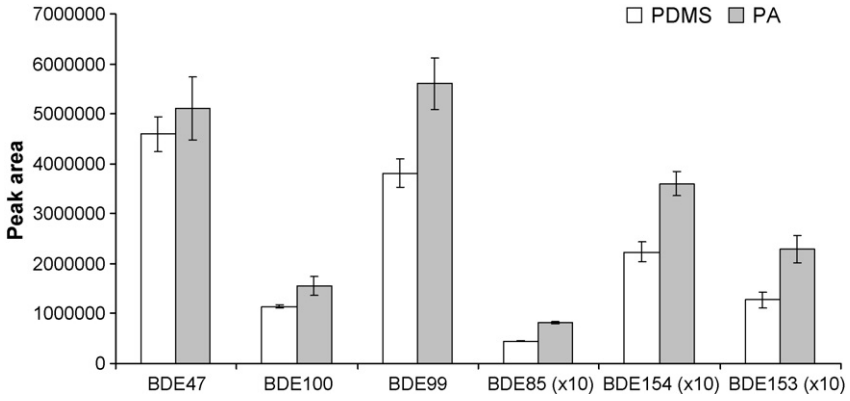

Fig. 2. Comparison of responses obtained with PA and PDMS coated fibres, $n = 4$ replicates.

Table 2
Experimental domain and standardized main effects of factors considered in the experimental factorial design.

Factor	Level		Standardized value					
	Low	High	BDE47	BDE100	BDE99	BDE85	BDE154	BDE153
$KMnO_4$ (mg)	40	160	0.06	3.3[a]	2.2	1.7	5.8[a]	4.9[a]
H_2SO_4 (mL)	0.2	1	−2.7	−0.5	−1.0	−1.4	0.8	0.2
Time (min)[b]	5	15	−0.5	−0.3	−0.3	−0.2	−0.3	−0.3

[a] Statistical significant factors at the 95% confidence level.
[b] Pre-heating time.

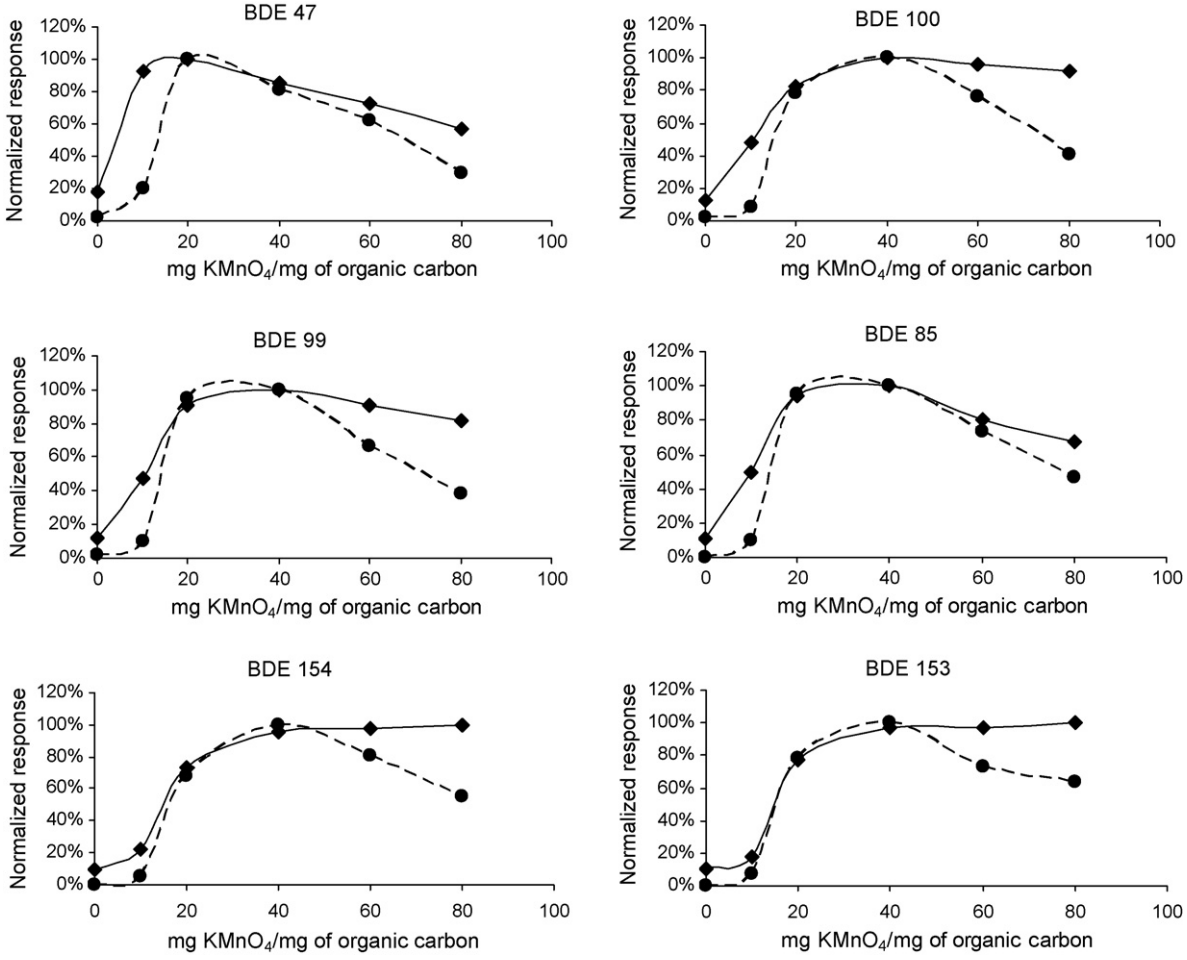

Fig. 3. Effect of $KMnO_4$ on the relative efficiency of the HS SPME. Solid line: river sediment, TOC 0.63%; dotted line: marine sediment, TOC 4.3%.

The SPME coating is a key factor controlling the efficiency of the extraction; therefore, it was the first of the investigated variables. Initial comparison among responses provided by PDMS, PA, PDMS-DVB and CAR-PDMS fibres (all new at the beginning of the study), considering two different sampling times (20 and 40 min), showed that the first two coatings performed better than PDMS-DVB and CAR-PDMS ones, data not shown. Fig. 2 compares the peak areas obtained using PA and PDMS fibres for a sampling time of 40 min, under oxidative conditions. With the exception of BDE47, considerably higher responses, with similar standard deviations, were noticed for the PA fibre. This result disagrees from previous data obtained for water samples [19]; nevertheless, it is in accordance to the moderate polarity of PBDEs, in comparison with other persistent pollutants, such as PCBs [28]. Obviously, in further extractions PDMS fibres were replaced by PA coated ones.

The effects of pre-heating time (5–15 min), volume of sulphuric acid (1:3) (0.2–1 mL) and amount of potassium permanganate (40–160 mg) on the efficiency of the HS SPME process were simultaneously evaluated using a 2^3 type experimental factorial design, with two central points. The sampling time was fixed at 40 min. Peak areas, obtained for each congener, were used as variable responses. Normalized values for the main effects associated with each factor, calculated with the Statgraphics Centurion XV software (Manugistics, Rockville, MD, USA), are summarized in Table 2. The absolute value of the main effect for a given factor is proportional to the variation in the response of the investigated PBDE when this factor changes from the low to the high level, within the domain of the design. A positive sign indicates an improvement in the efficiency of the extraction and a negative one the opposite effect. Neither the pre-heating time, nor the volume of sulphuric acid showed a statistically significant influence (95% confidence level) on the yield of the SPME process; however, the mass of $KMnO_4$ affected positively to the amount of PBDEs concentrated in the SPME fibre, being statistically significant for three (congeners 100, 154 and 153) of the six considered compounds. On the basis of these results, the pre-heating time was limited to 5 min and the volume of sulphuric acid was fixed at 0.5 mL, the central value within the explored range. Although 160 mg were adopted initially as the optimum mass of oxidant, further extractions, involving sediment samples with higher TOC values, showed that the above mass of $KMnO_4$ was entirely consumed before finishing the HS SPME step; therefore, a careful optimization of this factor using sediments with different organic matter contents was performed.

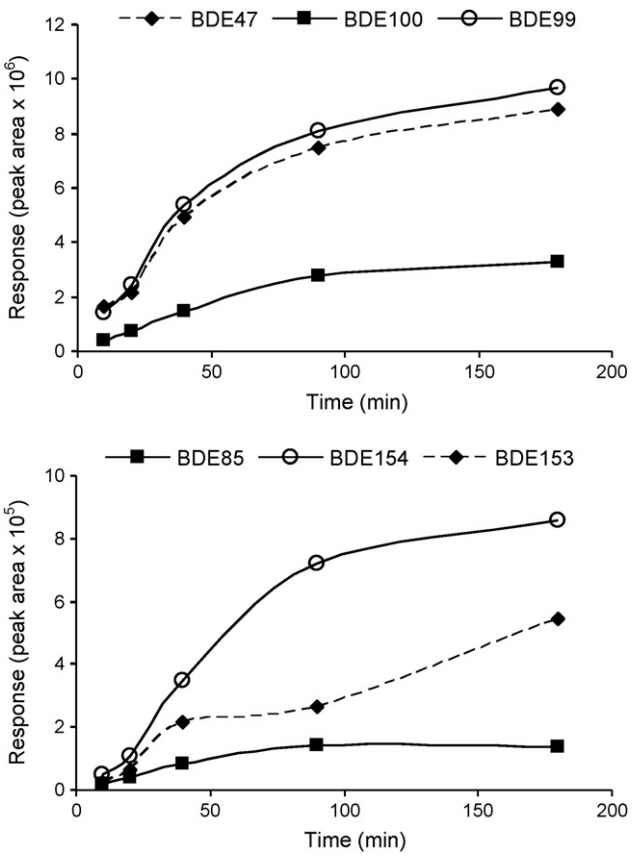

Fig. 4. Kinetics of the HS SPME under optimized conditions.

Table 3
Repeatability (RSDs, %) of the optimized SPME method for sediment samples fortified at different levels, $n = 4$ replicates.

BDE	River sediment, TOC 0.63%				River sediment, TOC 2.3%		Marine sediment, TOC 4.3%	
	GC-micro-ECD		GC–MS/MS		GC–MS/MS		GC–MS/MS	
	4 ng g^{-1} [a]	100 ng g^{-1} [b]	4 ng g^{-1} [a]	100 ng g^{-1} [b]	4 ng g^{-1} [a]	100 ng g^{-1} [b]	4 ng g^{-1} [a]	100 ng g^{-1} [b]
47	10.9	9.5	14.0	10.6	7.0	8.6	6.1	2.0
100	9.3	12.8	12.0	10.0	4.4	4.3	9.9	2.0
99	9.8	7.8	11.8	4.1	1.7	5.4	12.8	3.4
85	10.7	8.1	13.6	6.2	7.3	2.1	2.9	1.2
154	8.9	6.5	7.2	5.8	11.1	8.0	7.8	4.3
153	9.3	10.9	6.5	3.5	8.4	13.1	5.2	10.0

[a] Individual concentration of each BDE.
[b] Total concentration referred to the pentaBDE standard.

Table 4
Correlation coefficients (R^2) for sediments spiked at seven concentration levels in the range from 1 to 500 ng g^{-1}, referred to the pentaBDE standard. LOQs (ng g^{-1}), defined for S/N = 10, are given within parenthesis.

BDE	River sediment, TOC 0.63%		River sediment, TOC 2.3%	Marine sediment, TOC 4.3%
	GC-micro-ECD	GC–MS/MS	GC–MS/MS	GC–MS/MS
47	0.999 (0.02)	0.994 (0.01)	0.994 (0.02)	0.997 (0.03)
100	0.995 (0.04)	0.999 (0.02)	0.999 (0.04)	0.996 (0.05)
99	0.999 (0.04)	0.999 (0.02)	0.996 (0.06)	0.993 (0.05)
85	0.999 (0.06)	0.992 (0.06)	0.997 (0.08)	0.998 (0.12)
154	0.998 (0.06)	0.999 (0.05)	0.993 (0.07)	0.990 (0.10)
153	0.999 (0.06)	0.999 (0.06)	0.990 (0.1)	0.999 (0.15)

Table 5
Relative recoveries (as percentage, %) for two sediment samples. Added concentration 2 ng g^{-1} per compound, $n = 4$ replicates.

BDE	River sediment, TOC 0.63%		Marine sediment, TOC 4.3%
	GC-micro-ECD Mean ± SD	GC–MS/MS Mean ± SD	GC–MS/MS Mean ± SD
47	99 ± 12	110 ± 12	89 ± 6
100	103 ± 11	105 ± 10	96 ± 10
99	107 ± 11	103 ± 4	103 ± 12
85	90 ± 8	111 ± 6	97 ± 3
154	99 ± 8	96 ± 6	87 ± 8
153	83 ± 10	101 ± 4	76 ± 5

Fig. 3 depicts the normalized responses obtained for spiked river and marine sediments with TOCs of 0.63 and 4.3%, respectively. The *X*-axis represents the ratio between the masses of $KMnO_4$ and organic carbon in the extraction vessel. The addition of $KMnO_4$ led to a dramatic increase in the yield of the microextraction, with maximum responses attained between 20 and 40 mg of oxidant per mg of carbon, for all compounds in both matrices. At higher ratios, responses remained constant or started to decrease depending on the compound and the sample. It is worthy to note that, in absence of oxidant, congeners 85, 154 and 153 could not be extracted in a noticeable extension from the sediment with the higher TOC, Fig. 3. The initial improvement in the yield of the extraction with the amount of $KMnO_4$ is explained due to oxidation of the organic matter, which competes with the fibre for the PBDEs reducing the kinetics and the thermodynamic of their microextraction. For very high $KMnO_4$ masses, the increased viscosity and ionic strength of the slurry probably limit the evaporation rate of PBDEs resulting in lower responses. In view of data depicted in Fig. 3, 40 mg of $KMnO_4$ were added per mg of organic carbon in the extraction vessel. For sediments containing TOC values above 5%, it is recommended to reduce the sample intake (from 0.5 to 0.25 g) in order to avoid (1) the consumption of large amounts of oxidant as well as (2) the increase in the viscosity of the slurry.

3.2.3. *Stirring, cross-contamination and carry-over*

Sample stirring, with a PTFE bar, showed a positive influence in the efficiency of the extraction, particularly for penta- and hexabrominated congeners, data not given. It is assumed that stirring accelerates the destruction of the organic matter, which results in faster evaporation kinetics and higher partition coefficients between the PA fibre and the sample. However, the strong oxidative

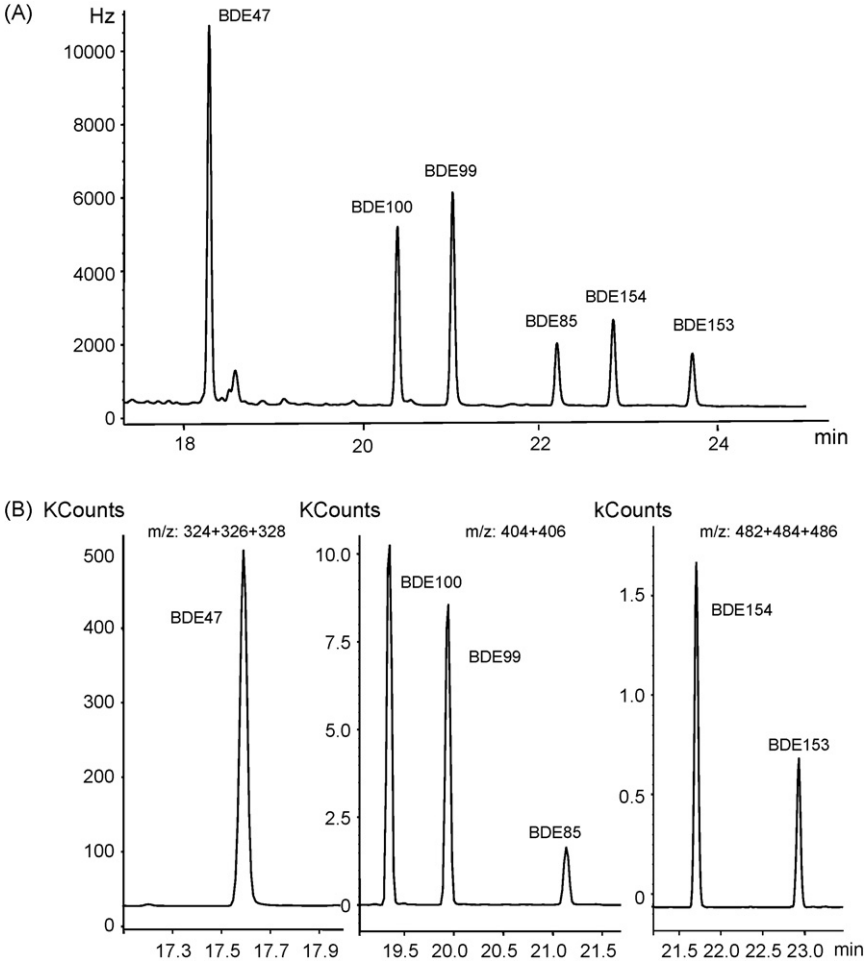

Fig. 5. Chromatograms obtained for a river sediment (TOC 0.63%) spiked at the 2 ng g^{-1} level. (A) Micro-ECD detection. (B) MS/MS detection.

Table 6
Concentrations of PBDEs in marine sediment *QBC005MS*, $n = 5$ replicates.

BDE	Measured concentration (ng g^{-1})		Assigned concentration (ng g^{-1})[a]	
	Mean	SD	Mean	SD
47	8.0	0.2	7.8	1.0
100	1.4	0.1	1.1	0.2
99	10.3	0.1	11.3	1.6
85	1.8	0.1	n.a.	n.a.
154	1.05	0.08	0.75	0.14
153	1.40	0.01	1.38	0.22

n.a.: not available.
[a] Average values for QUASIMEME inter-comparison exercise 618, round 37, year 2003–2004.

conditions eroded the surface of PTFE stir bars, leading to potential adsorptions of PBDEs in the generated pores. This fact might cause cross-contamination problems between samples. Wrapping the bars with PTFE tape, which is removed after each extraction, is an inexpensive solution to prevent cross-contamination problems associated with the re-use of stirrers.

Non-quantitative desorption of the analytes from the fibre is another source of cross-contamination in SPME based methods. This problem has a special relevance for low volatile species, as it is the case of PBDEs. The efficiency of the desorption step (2 min at 300 °C in the splitless mode) was evaluated by desorbing each fibre twice, after being exposed to samples spiked with relatively high concentrations of PDBEs. Responses observed in the 2nd desorption represented between 1 and 3% of those measured in the first one. Thus, PA fibres were left in the hot injector of the GC instrument for 5 additional min, after passing the solenoid valve from the splitless mode to the split one. The combination of high temperatures and a large helium flow (50 mL min^{-1}) along the body of the liner guaranteed the complete desorption of PBDEs preventing carry-over problems.

3.2.4. Extraction kinetics

Fig. 4 presents the responses (peak areas) obtained as function of the exposure time. The slow extraction kinetics matched with the trend reported for water samples using PDMS fibres [19]; moreover, they confirmed the stability of PBDEs under the strong oxidative conditions existing in the SPME vessel, since their amounts in the SPME fibre increased continuously with the exposure time, at least until 3 h. A sampling time of 40 min was adopted in order to speed up the sample throughput.

3.3. Performance evaluation

The proposed method was characterized in terms of precision, linearity, accuracy and LOQs, considering sediments with TOC values between 0.63 and 4.3%. Sieved samples were divided in several fractions, one was used as the blank and the others spiked with PBDEs at different concentration levels, either referred to total amount of the pentaBDE standard, or to individual concentrations of each species. All matrices were processed using GC–MS/MS as quantification technique; moreover, GC-ECD was also applied to the sample with the lower TOC. Relative standard deviations (RSDs) for extractions ($n = 4$ replicates) of samples spiked at different levels ranged from 1 to 14%, Table 3, which are values similar to those reported for SPME of water samples [19].

The linearity of the method was evaluated with samples spiked at different levels from 1 to 500 ng g^{-1}, referred to the pentaBDE standard. Plots of peak areas (corrected with the response of $^{13}C_{12}$ BDE99 when using GC–MS/MS detection) versus concentrations of each compound in the sample fitted a linear model, with correlation coefficients (R^2) from 0.990 to 0.999, Table 4. Quantification limits (LOQs) were estimated from the signal to noise ratios (S/N) of chromatographic peaks in the lowest levels of the linearity study. Although the obtained values increased with the TOC of the samples, the optimized method provided LOQs equal or lower than 0.15 ng g^{-1}, for all species, in the more complex of the investigated sediments (TOC 4.3%), Table 4. LOQs achieved for congeners 154 and 153 are 10 times lower than those previously reported for a soil sample with a twice lower organic carbon content (ca. 2.0%), using also SPME in combination with GC–MS/MS, but without considering the oxidative treatment optimized in this work [24]. Overall,

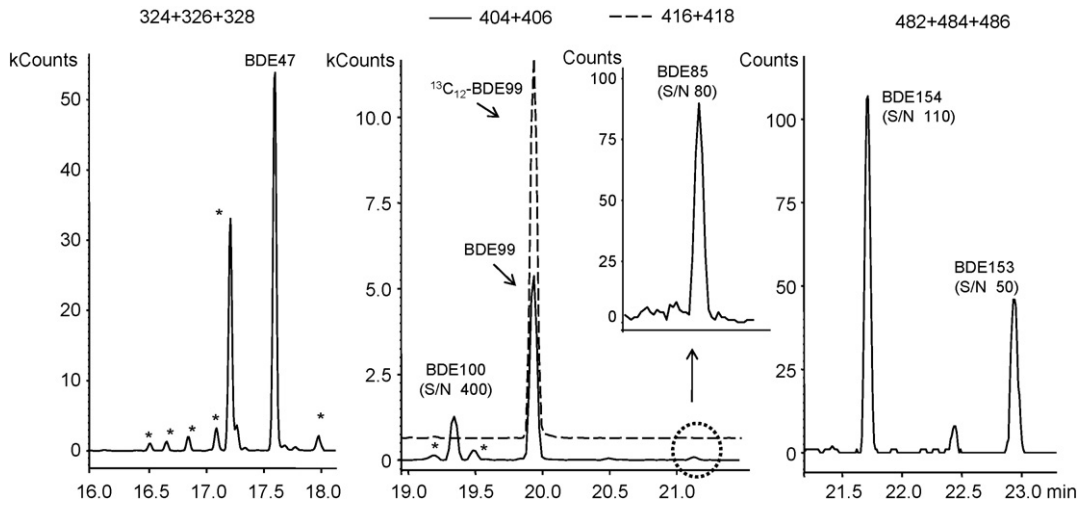

Fig. 6. GC–MS/MS chromatogram for a non-spiked marine sediment (TOC 6.7%), code QBC005MS, obtained from QUASIMEME. *Non-identified PBDEs.

LOQs presented in Table 4 are in the same order of magnitude than those reported by some authors using solid–liquid extraction methodologies followed by exhaustive clean-up of the extract [5,15]. They are also similar to those achieved combining extraction of soil samples with an organic solvent and further stir-bar sorptive extraction (SBSE) of the diluted extract for several hours [29].

Accuracy was assessed with two sediments, with low and medium TOC values, fortified with all PBDEs at 2 ng g^{-1}. Recoveries, evaluated with standard additions over each sample (three addition levels in duplicate were employed), ranged from 76 to 111% with standard deviations under 12%, Table 5. Fig. 5 shows the chromatograms obtained for the low organic matter content sample using micro-ECD and MS/MS detection. Even in ECD chromatograms, PBDEs peaks remained unaffected by co-eluting interferences. The oxidative sample treatment contributes also to increase the selectivity of the extraction, removing most organics, which are susceptible of being incorporated in the PA coating. Nevertheless, as commented previously, ECD detection is not recommended for the analysis of PBDEs in real-life samples due to the risk of species misidentification, particularly in PCBs containing sediments [18].

In addition to spiked samples, accuracy was also evaluated with a marine sediment (TOC 6.7%), naturally polluted with PBDEs and previously analyzed by several laboratories in the framework of an inter-comparison study. Concentrations determined by GC–MS/MS are summarized in Table 6. Overall, a good agreement was noticed between measured and assigned concentrations; although, the level found for BDE154 was slightly higher than the assigned one. Fig. 6 shows the GC–MS/MS chromatogram for this sample. In addition to target species, other PBDEs were detected in this sample, particularly in the time segments corresponding to tetra-and penta-brominated species, Fig. 6. The S/N values of chromatographic peaks for minor congeners in this sample, varied from 50 for BDE153 to 400 for BDE100 (Fig. 6), confirming the capability of the proposed method to quantify sub-ng g^{-1} levels of selected PBDEs in sediments with medium to high organic matter contents.

Under final working conditions, the average useful life of PA fibres was 50 extraction cycles. Although no problems were noticed with the mechanical stability of the coating, after the above number of extractions, the yield of the process underwent a reduction around 30%.

4. Conclusions

Sample treatment using $KMnO_4$ under acidic conditions enhances the applicability of HS SPME to the determination of tetra- to hexa-brominated PBDEs in sediments, lowering the limits of quantification of the method, without increasing significantly the complexity of sample handling and maintaining an acceptable stability of SPME fibres. The amount of $KMnO_4$ plays a major effect on the efficiency of the HS extraction, with the optimum mass being correlated to the content of organic carbon in the sample; moreover, PA fibres are a better alternative than the PDMS ones, recommended in previous studies. Under final working conditions, the optimized methodology constitutes a simple and straightforward approach to monitor the levels of tetra- to hexa-brominated PBDEs in sediments containing up to 6% of organic carbon, with LOQs in the sub-ng g^{-1} range, avoiding completely the use of organic solvents.

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