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Plunger-in-needle solid-phase microextraction with graphene-based sol–gel coating as sorbent for determination of polybrominated diphenyl ethers

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ABSTRACT

A solid-phase microextraction (SPME) device, assembled with a commercially available plunger-in-needle microsyringe, with the plunger coated with graphene via a sol–gel approach, was developed for the gas chromatographic–mass spectrometric determination of polybrominated diphenyl ethers (PBDEs) in environmental samples. This is the first application of graphene-based sol–gel coating as SPME sorbent. Parameters affecting the extraction efficiency were investigated in detail. The new coating exhibited enrichment factors for PBDEs between 1378 and 2859. The unique planar structure of graphene enhanced the π–π interaction with the aromatic PBDEs; additionally, the sol–gel coating technique created a porous three-dimensional network structure which offered larger surface area for extraction. The stainless steel plunger provided firm support for the coating and enhanced the durability of the assembly. The plunger-in-needle microsyringe represents a ready-made tool for SPME implementation. Under the optimized conditions, the method detection limits for five PBDEs were in the range of 0.2 and 5.3 ng/L (at a signal/noise ratio of 3) and the precision (% relative standard deviation, $n = 5$) was 3.2–5.0% at a concentration level of 100 ng/L. The linearities were 5–1000 or 10–1000 ng/L for different PBDEs. Finally, the proposed method was successfully applied to the extraction and determination by gas chromatography–mass spectrometry of PBDEs in canal water samples.

1. Introduction

Solid-phase microextraction (SPME) has been widely used as an effective sample preparation approach in the environmental, food, pharmaceutical, toxicological and forensic fields since it was first developed in 1990 by Pawliszyn's group [1]. SPME exhibits many advantages over conventional sample preparation methods by integrating sampling, extraction and introduction (generally to GC or HPLC) into a single step. It is based on the distribution of analytes between the matrix and a fiber coated with a stationary phase. As the fiber coating plays a key role in SPME, development of fiber coating for highly efficient extraction of the analytes has attracted much attention. Commercial available SPME fibers consist of an extracting phase deposited on fused-silica fibers possessing different selectivities: nonpolar coating (poly(dimethylsiloxane) (PDMS); carboxen/PDMS), semipolar coating (PDMS/divinylbenzene (DVB)), and polar coating (polyacrylate (PA); Carbowax/DVB; Carbowax/templated resin).

Although SPME is very popular, commercial fiber coatings present some drawbacks such as low recommended operating temperature (usually 240–280 °C), possibility of swelling in some organic solvents, risk of being stripped off under some extraction conditions, fragility and relatively high cost. To address some of these problems, a number of novel coatings have been developed for the extraction of different kinds of compounds. In addition, different kinds of coating support such as stainless steel, platinum, and titanium wires have been explored to replace silica rods [2–7]. To enhance the adhesion between the coating and the support, several coating approaches based on vapor deposition [8], electrochemical deposition [5], and sol–gel technology [9] have been proposed for the production of SPME fibers.

Carbonaceous materials such as polycrystalline graphite [10], low-temperature glassy carbon [11], activated carbon [12] and carbon nanotubes (CNTs) [13,14] as well as their functionalized forms have been successfully applied as SPME coatings. Quite recently, graphene, the first two-dimensional atomic crystal, since it was experimentally produced in 2004 [15], has emerged as a conceptually new class of carbon material. It is a monolayer of sp^2 hybridized carbon atoms packed into a dense honeycomb crystal structure. Graphene sheets can be prepared by various techniques including mechanical exfoliation of graphite [15], and reduction of exfoliated graphite oxide [16], etc. As the basic structural element of CNTs, graphene has been reported to possess a theoretical high specific surface area (2630 m^2/g) [17], which may make them suitable

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as sorbents if a sufficiently stable dispersion of graphene sheets is available [18]. Some exploration of this potential has appeared in the literature. For example, graphene-based gas sensors were reported to be capable of detecting individual gas molecules [19]. In addition, graphene-based composites have been successfully used to fabricate an electrochemical glucose biosensor [20]. Also, as the large delocalized π-electron system of graphene can form strong π–π interaction with the benzene ring [21], this material has great potential to serve as sorbent for extraction of benzenoid compounds. One study reporting the use of graphene as an SPME sorbent is noted [22]. Even so, to the best of our knowledge, no reports have been published on the application of graphene as an SPME fiber coating via sol–gel approach.

Polybrominated diphenyl ethers (PBDEs) have been commonly used as flame retardants in various products such as computer plastics, furniture, foams, textile and other materials [23]. Some brominated flame retardants are not chemically bound to the plastic or textiles and can eventually be released into the environment. In recent years, increasing levels of PBDEs have been detected in the global environment as well as in human tissue and other biota. Epidemiological studies have shown that PBDEs are causing health risks, such as endocrine disruption and adverse neurobehavioral effects, and they are also probable carcinogens [24,25]. Structurally similar to dioxin and the polychlorinated biphenyls, PBDEs are known to be persistent and can be easily bio-accumulated and difficult to eliminate [26]. Therefore, it is crucial to develop a simple, efficient and sensitive preconcentration technique for their determination at trace levels. The extraction of PBDEs from environmental water samples has been carried out by using liquid-liquid extraction (LLE) [27], stir bar sorptive extraction [28,29], cloud point extraction [26] and SPME [13,14] coupled with gas chromatography (GC) with electron-capture detection (ECD) or mass spectrometric (MS) detection. Although SPME is a fast, simple, solventless, and an efficient extraction technique, reports on its application for PBDEs are limited due to the low operating temperature of commercial SPME fibers, which is not high enough for complete desorption of these compounds which have high boiling points.

The purpose of the present work was to develop a novel SPME technique based on a plunger-in-needle microsyringe using the plunger wire as coating support and graphene as sorbent. The applicability of this novel SPME was evaluated by extracting and determining, by GC–MS, five PBDEs in water samples. The sol–gel technique was used as the coating method to create a porous structure and enhance thermal stability of the coating. The SPME technique developed was applied to the determination of trace PBDEs in canal water.

2. Experimental

2.1. Chemicals and materials

The five PBDE standards (50 mg/L in isooctane for each) were purchased from AccuStandard (New Haven, CT, USA) and stored in amber bottles in the refrigerator at −20 °C. They were 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). The structures of the five PBDEs are given in Table 1. HPLC-grade methanol and n-hexane were purchased from Tedia Co. (Fairfield, OH, USA). Isooctane was supplied by Merck (Darmstadt, Germany). Dimethylformamide (DMF) was bought from J.T. Baker (Phillipsburg, NJ, USA). Fluka Analytical (Buchs, Switzerland) was the supplier of the hydrofluoric acid (HF) (47–51%). Tetraethoxysilane (TEOS) and trifluoroacetic acid (TFA) (99%) were bought from Alfa Aesar (Ward Hill, MA, USA). Hydroxy-terminated PDMS was obtained from Sigma–Aldrich (St Louis, MO, USA). Silicon oil (350-CS) was applied by Sino Chemical (Singapore). Ultrapure water was obtained from an ELGA Purelab Option-Q (High Wycombe, UK) water purification system.

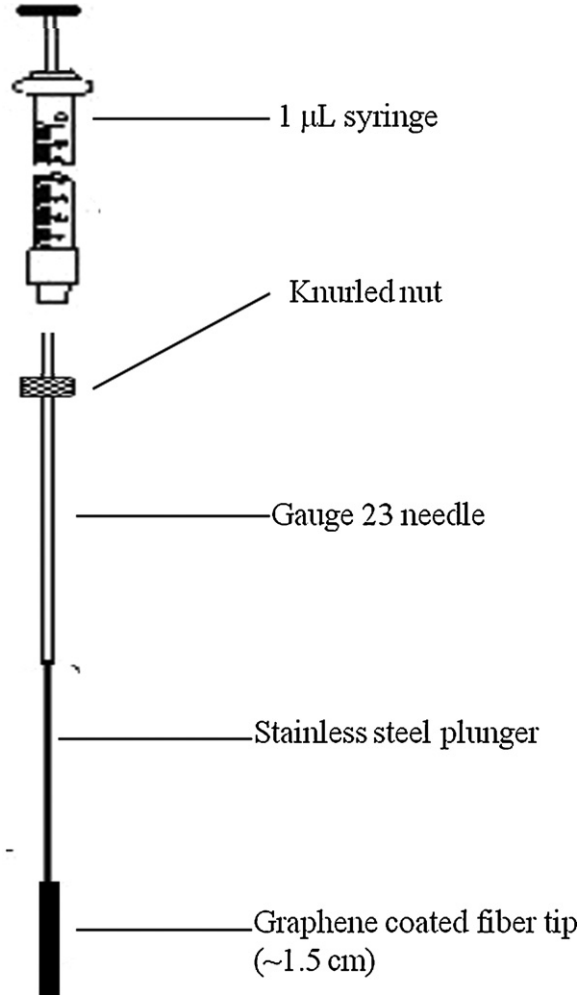


Fig. 1. Schematic of the home-assembled SPME device.

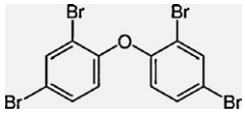
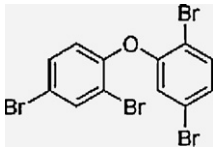
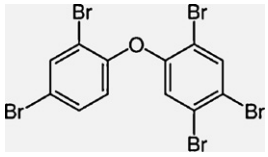
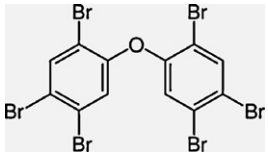
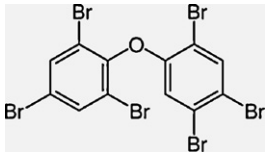
A manual SPME holder, and commercial SPME fibers with PDMS (100 μm and 7 μm) and PA (85 μm) coatings were purchased from Supelco (Bellefonte, PA, USA) for comparison with the plunger-in-needle device in terms of extraction performance.

2.2. Apparatus and instrumentation

The plunger-in-needle (with replaceable 26-gauge, 70 mm long needle, 0.47 mm internal diameter (I.D.)) microsyringe (1-μL capacity) was purchased from SGE (Ringwood, Victoria, Australia). For SPME applications, a replacement needle (23-gauge, 50 mm long needle, 0.63 mm I.D.) (SGE) was necessary. The latter shorter needle allowed the plunger, particularly the graphene-coated tip (of *ca.* 1.5 cm length), to be withdrawn into it for protection (during SPME operations, and GC/MS analysis) (see Fig. 1).

A Shimadzu (Kyoto, Japan) QP2010 GC–MS system equipped with a DB-5 MS UI (Ultra Inert) fused silica capillary column (20.0 m × 0.18 mm I.D., film thickness 0.18 μm) (J&W Scientific, Folsom, CA, USA) was used for analyses. Helium was employed as the carrier gas, at a flow rate of 1.7 mL/min. SPME was performed under splitless mode and 1 min sampling time. The injector port temper-

Table 1
Structures of PBDEs considered in this work.

Abbreviation	Name	Structure
BDE-47	2,2′,4,4′-Tetrabromodiphenyl ether	
BDE-49	2,2′,4,5′-Tetrabromodiphenyl ether	
BDE-99	2,2′,4,4′,5-Pentabromodiphenyl ether	
BDE-153	2,2′,4,4′,5,5′-Hexabromodiphenyl ether	
BDE-154	2,2′,4,4′,5,6′-Hexabromodiphenyl ether	

ature was set at 300 °C. The GC oven was initially held at 60 °C for 2 min, and then increased to 220 °C at a rate of 40 °C/min, and then further increased to 300 °C at a rate of 10 °C/min, and held for 7 min. The MS ion source and interface temperatures were set at 260 °C and 300 °C, respectively.

In order to mix the various ingredients in solution thoroughly, an Ultrasonic Cleaner (Elma LC30, Darmstadt, Germany) was used. A Vibramax 100 (Heidolph, Kelheim, Germany) magnetic stirrer was employed for stirring the sample during extraction. Thermogravimetric analysis (TGA) was performed using a Model SDT 2960 Simultaneous DTA-TGA instrument (TA Instruments, New Castle, DE, USA). A JSM-6701F Field Emission Scanning Electron Microscope (JEOL, Tokyo, Japan) was used for the investigation of the surface morphology of the sol–gel graphene fiber. The fiber was fixed on the stub by a double-sided sticky tape and then coated with platinum by a JFC-1600 Auto Fine Coater (JEOL) for 30 s.

2.3. Plunger-in-needle SPME fiber preparation

Graphite oxide, which was prepared based on modified Hummer's method [30], has been previously described in detail [31]. The modification was basically on smaller amounts of reagents used. The sol–gel mixture was prepared as follows: 2 mg of graphite oxide was dissolved in 100 μL of DMF in a 1.5 mL micro-centrifuge tube. The mixture was then sonicated for 2 h by ultrasonic agitation. This process would result in the formation of dispersed graphene oxide (GO) from the dissolved graphite oxide. Then, 350 μL of TEOS, functioning as sol–gel precursor, and 50 μL of hydroxy-terminated PDMS were added and sonicated for 20 min. The hydroxy-terminated PDMS serves to enhance the sol–gel network. Finally, 50 μL of TFA (acid catalyst, 95% water solution) was added and mixed thoroughly for another 5 min. The final mixture was then used for coating the fiber.

The stainless steel plunger was first cleaned with a lint free tissue and immersed in HF for 15 min at room temperature. The process of etching is to create a rough and porous surface so as to allow the formation of a stable network of sol–gel coating. The etched part of the plunger was washed gently with ultrapure water and dried under room temperature for 1 hour. The etched stainless steel plunger was then dipped vertically into the sol solution to a depth of *ca.* 1.5 cm and held for 1 h for the formation of sol–gel coating. The thickness of the sol–gel film can be controlled by varying the duration of coating as well as of the etching. The coated plunger was then dried at room temperature for 24 h. The fiber was initially conditioned by placing it in a GC injector at 100 °C for 1 h, and then conditioned at 300 °C for another 2 h. At this high temperature, the oxygen functional groups present in graphene oxide were removed [31,32], thereby forming the homogenous graphene-based fiber. The final thickness of the fiber was approximately 8 μm.

2.4. Sample preparation

A mixed standard solution (containing 10 mg/L of each analyte) was prepared by combining the five PBDE standards (each at 50 mg/L in isooctane). The standard mixture was used for the preparation of subsequent standards (using hexane as solvent), and a stock solution of 0.1 mg/L (in methanol). Water samples were prepared by spiking the latter solution into ultrapure water at different known concentrations.

Genuine water samples collected from a canal in Singapore was first filtered with 0.22 μm glass microfiber filter papers (Whatman, Maidstone, England) to remove any particulate matter and stored

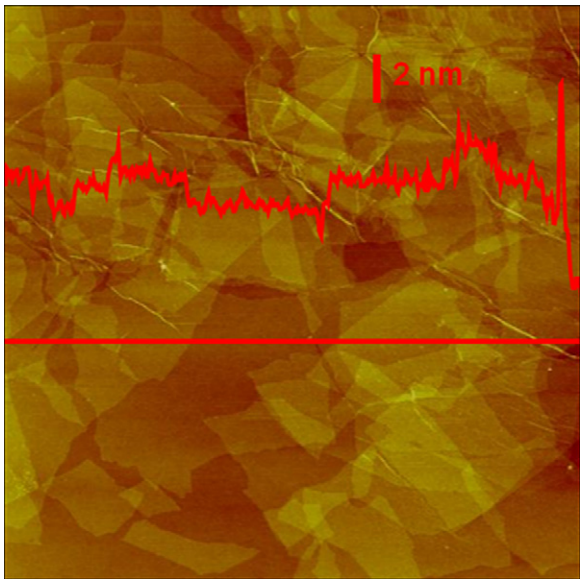


Fig. 2. AFM image of dispersed GO on a SiO_2/Si wafer, displaying a relatively smooth planar structure.

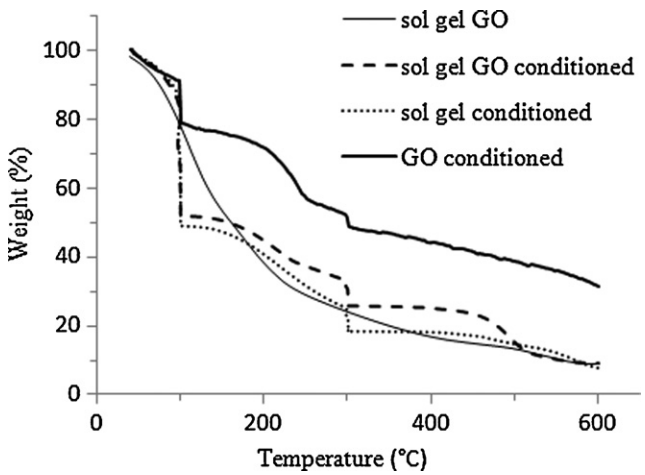


Fig. 3. Thermogravimetric analysis (TGA) curves of sol–gel GO at heating rate 10 °C/min under nitrogen gas. To condition the materials, they were heated at 100 °C for 1 h, and at 300 °C for another 2 h.

in an aluminum-wrapped glass bottle. It was then kept in the dark at 4.0 °C before analysis.

2.5. SPME procedure

A volume of 7 mL of sample solution was placed in an 8 mL glass vial with a stir bar. The vial was then immersed in a thermostatic silicon oil bath at 60 °C. During the extraction, the fiber was directly exposed to the aqueous sample for 20 min at 1000 rpm stirring rate. After SPME, the fiber was retracted into the needle and inserted into the GC injector at 300 °C for analyte desorption for 5 min. Conventional SPME with commercial fibers was carried out the same way.

3. Results and discussion

3.1. Characteristics of the sol–gel graphene fiber

The dispersed GO was characterized by atomic force microscopy (AFM, Veeco, NY, USA) as shown in Fig. 2. The thermal degradation characteristics of GO and sol–gel GO were evaluated by TGA. As can be seen from Fig. 3, the weight losses of GO at 100 °C and 200 °C are attributed to the removal of water and the decomposition of GO functional groups. After GO was conditioned at 100 °C for 1 h and at 300 °C for another 2 h, the weight loss of GO was ~50%. As reflected in Fig. 3, the conditioning of sol–gel GO at 300 °C for another 2 h resulted in much increased thermal stability. There was no significant loss detected when this material was heated up to 500 °C. This is consistent with the fiber's thermal stability (see below).

The morphological structure of the original stainless steel plunger wire is shown in Fig. 4a and b. The longitudinal surface (Fig. 4b) was smooth. After etching by HF, there was an obvious reduction in diameter (Fig. 4c) and a porous structure of the plunger wire was obtained (Fig. 4d). The SEM micrograph in Fig. 4e provided an estimated film thickness of 8 μm after coating of the sol–gel material. It is also evident that the coating possessed a porous network (Fig. 4f), which should significantly increase the available surface area on the fiber, thus enhancing extraction efficiency.

3.2. Operational stability

The sol–gel graphene fiber's thermal stability was investigated by performing extraction after it had been conditioned in the GC injector for 1 h at 300, 320, and 340 °C, respectively. The results (Fig. 5) indicated that sol–gel graphene coating can withstand a temperature of up to 340 °C without loss of extraction efficiency. Such a high operating temperature achieved is due to the thermal stability of graphene and the strong chemical bonding provided by sol–gel technology, which can be confirmed by thermogravimetric analytical results of sol–gel GO, as discussed above. The enhanced thermal stability allowed the use of a higher injection port temperature for efficient desorption of semivolatile analytes and thus extended the range of analytes. The fiber lifespan was studied by monitoring the change of extraction peak areas during its use and no obvious decline was observed after it had been used for about 200 runs.

3.3. Optimization of direct SPME procedures

In order to achieve the best extraction efficiency of the new coating for 5 PBDEs (Table 1), several parameters, including salting-out effect, extraction temperature, extraction time and desorption time, were investigated. Water samples used for these studies were prepared containing 1.0 μg/L of each PBDE.

3.3.1. Salting-out effect

Addition of salt can affect the amount of analytes extracted, depending on the types of analytes, the type of SPME fiber and the concentration of salt. The presence of salt may change the activity coefficients of the analyte in the aqueous phase and thus alter extraction efficiency. Nevertheless, it could increase the viscosity and density of the aqueous phase and thus negatively affect the kinetics of the process and, consequently, the extraction efficiency. In summary, the addition of salt might be favorable from a thermodynamic point of view but unfavorable from a kinetic point of view [34]. Here, the salt effect on extraction was evaluated at various concentrations of NaCl (0, 5, 15, 30%, weight (g)/volume (mL)) in 7 mL of water containing PBDEs at 1.0 μg/L. Fig. 6 shows that salt addition had negative effect on extraction performance, corroborating the results of other researchers [13,33,34]. This might conceivably be due to the slower kinetics involved.

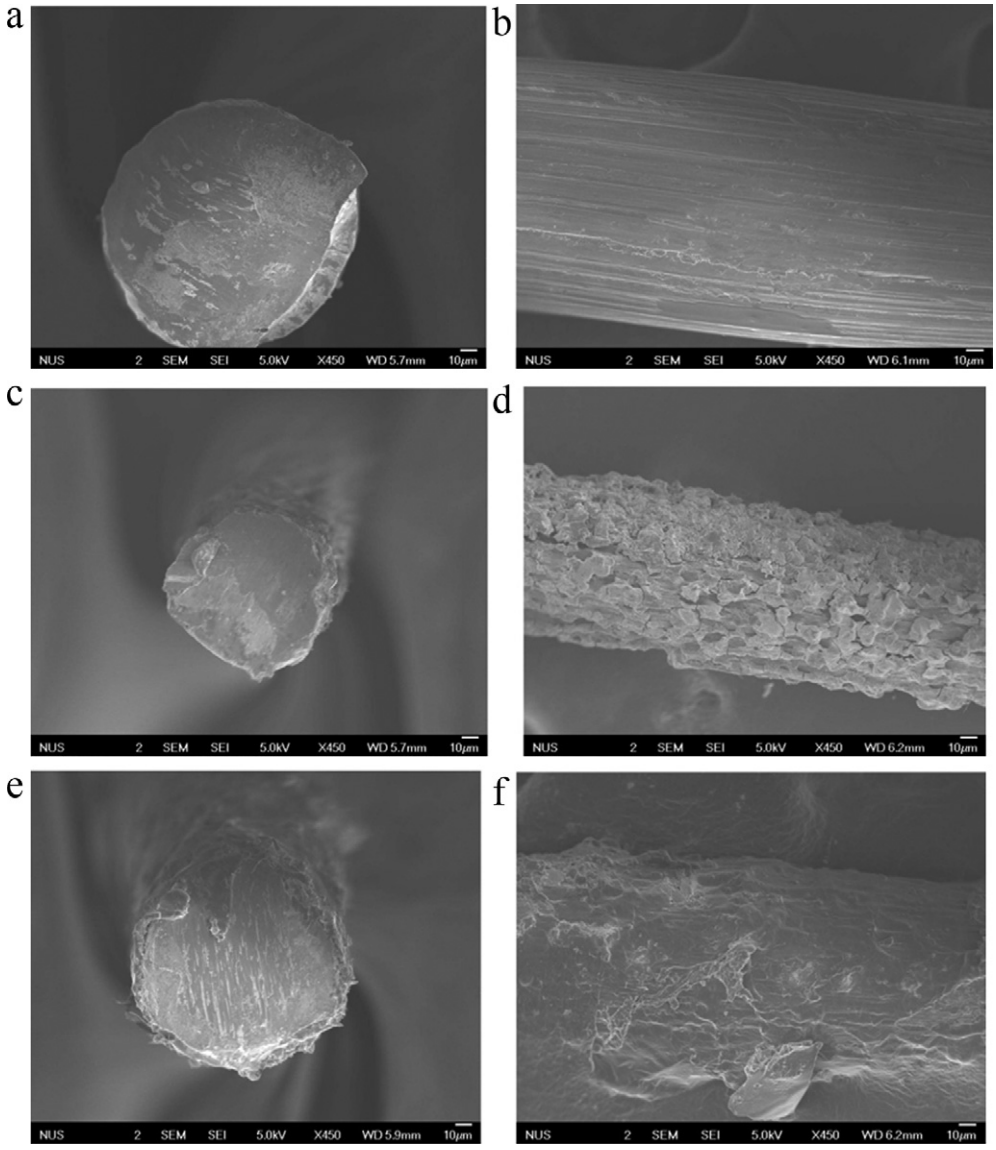


Fig. 4. SEM images of original stainless steel plunger wire, HF etched plunger wire and sol–gel graphene coated plunger wire: (a) cross-sectional view of original stainless steel plunger wire; (b) longitudinal view of original stainless steel plunger wire; (c) cross-sectional view of HF etched plunger wire; (d) longitudinal view of HF etched plunger wire; (e) cross-sectional view of sol–gel graphene coated plunger wire; (f) longitudinal view of sol–gel graphene coated plunger wire.

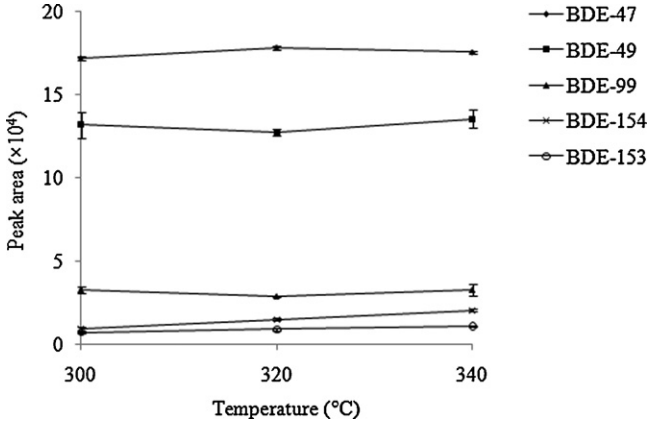


Fig. 5. Thermal stability of sol–gel graphene coated fiber. PBDEs at 1.0 μg/L. Conditions: NaCl addition, 0%; extraction time, 20 min; extraction temperature, 60 °C; stirring rate, 1000 rpm; desorption time, 5 min. Error bars show the standard deviation (n = 3).

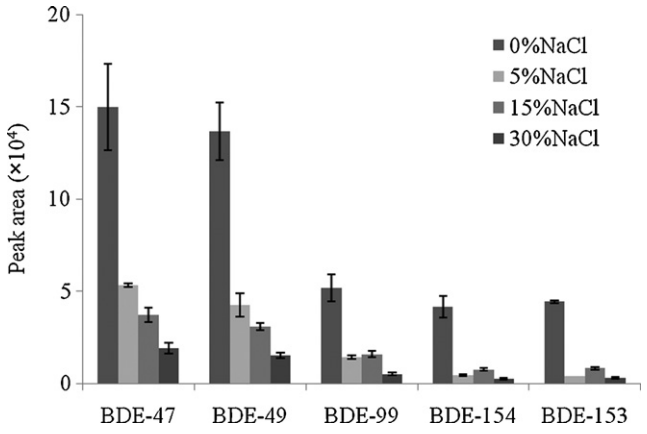


Fig. 6. Effect of NaCl addition. Conditions: extraction time, 10 min; extraction temperature, 60 °C; stirring rate, 1000 rpm; desorption time, 10 min. Error bars show the standard deviation of the mean (n = 3).

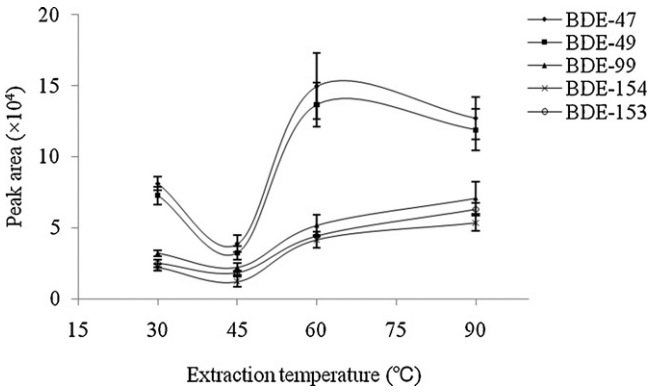


Fig. 7. Effect of the extraction temperature to 1.0 μg/L PBDEs in a water sample. Conditions: NaCl addition, 0%; extraction time, 10 min; stirring rate, 1000 rpm; desorption time, 10 min. Error bars show the standard deviation of the mean ($n = 3$).

3.3.2. Effect of the extraction temperature

The temperature effect on extraction was investigated within 30–90 °C as shown in Fig. 7. The highest extraction of BDE-47 and BDE-49 was reached at approximately 60 °C whereas the extraction efficiencies of BDE-99, BDE-154 and BDE-153 increased gradually as temperature increased, indicating a higher optimum temperature beyond 90 °C. Ideally, mass transfer occurs from the aqueous phase to sol–gel graphene fiber. This process is usually enhanced by high temperature and, in this way, improves extraction efficiency (subject to a certain maximum since the adsorption process is exothermic). However, the analytes are also in some degree distributed into the headspace of extraction vials under high temperature, due to the semivolatile properties of PBDEs. This may lead to reduced availability of these compounds to the fiber and consequently, resulting in decreased extraction efficiency. The lowest points at 45 °C might be a result of these conflicting effects. That is to say, the effect of analytes distributing to the headspace at this temperature is conceivably the dominant contributory factor compared to adsorption to the fiber. Considering the pressure limits of the glass vials and higher extraction efficiency for all the five PBDEs, an extraction temperature of 60 °C was chosen.

3.3.3. Effect of the extraction time

As mentioned above, SPME is an equilibrium-based extraction procedure and therefore a time-dependent process. The extraction times of these analytes were investigated from 10 to 60 min (at 20-min intervals) at 60 °C. PBDEs are semivolatile compounds. It is believed that with increasing extraction time, the probability of the semivolatile compounds partitioning to the headspace is enhanced at this high temperature, thus making them unavailable for extraction. As shown in Fig. 8, extraction efficiency decreased after 20 min. A reduction in extraction beyond a certain extraction time is a common observation in sorbent-based (e.g. SPME) and liquid-phase microextraction procedures. Therefore, 20 min was selected as extraction time.

3.3.4. Effect of the desorption time

Desorption time could affect the responses of the target analytes significantly, especially for compounds with high boiling point. A short desorption time could introduce carry over effect while a long desorption time could degrade the fiber and shorten its lifetime. In this work, the effect of desorption time was investigated at 1, 2, 4, 5 and 10 min at 300 °C. The chromatographic peak areas for all the five PBDEs reached their respective maxima (results not shown) after 5 min.

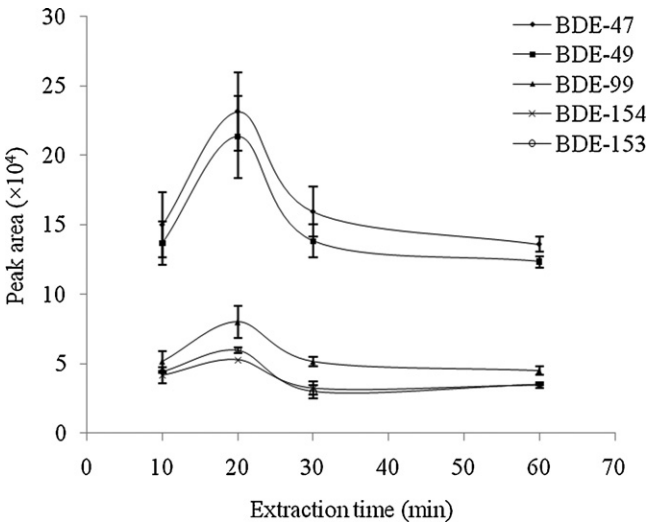


Fig. 8. Effect of the extraction time to 1.0 μg/L PBDEs in a water sample. Conditions: NaCl addition, 0%; extraction temperature, 60 °C; stirring rate, 1000 rpm; desorption time, 10 min. Error bars show the standard deviation of the mean ($n = 3$).

3.4. Comparison with commercial SPME fibers

The target analyte are aromatic compounds that are slightly polar and semivolatile. A commercially available 100 μm PDMS fiber has a low recommended operating temperature of 280 °C which was chosen as desorption temperature in this work. A PDMS-coated fiber (7-μm thickness) has a higher operating temperature (maximum: 340 °C) and is more effective for non-polar semivolatiles. On the other hand, PA is a polar coating; nevertheless, good results have been obtained previously in the extraction of low-polarity species by this fiber [34,35]. Thus, PDMS (100 μm and 7 μm thicknesses) and PA fibers were selected for comparing the extraction performance with the newly developed SPME fiber under the optimized conditions. Since the PA fiber and 7 μm PDMS fiber can stand higher desorption temperatures, 300 °C was selected for these fibers as well as for the sol–gel graphene fiber. The results are shown in Fig. 9. The figure shows that the sol–gel graphene fiber has superior extraction performance for PBDEs when compared to the commercial fibers. A chromatogram obtained by the sol–gel graphene fiber from an aqueous standard solution containing 1.0 μg/L of PBDEs is shown in Fig. S1 (Supplementary Material). The higher extraction efficiency could possibly result from carbon atoms present in the

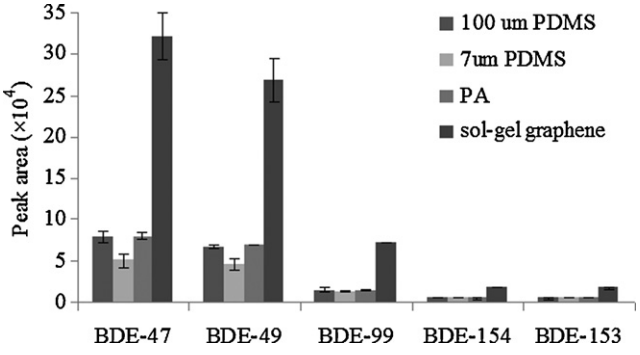


Fig. 9. Comparison of the extraction efficiency of the sol–gel graphene fiber with commercial 100 μm PDMS fiber, 7 μm PDMS fiber and PA fiber for PBDEs at 1.0 μg/L. Conditions: NaCl addition, 0%; extraction time, 20 min; extraction temperature, 60 °C; stirring rate, 1000 rpm; desorption time, 5 min. Error bars show the standard deviation of the mean ($n = 3$).

Table 2
Linear range, Regression data, Limits of detection (LODs) and Enrichment factors of PBDEs of the proposed method.

Analyte	Linear range (ng/L)	r^2	LOD (ng/L)	RSD[a] (fiber) (%, $n=5$)	RSD[b] (fiber to fiber) (%, $n=3$)	Enrichment factor[c]
BDE-47	5–1000	0.9934	0.2	3.2	7.7	2859
BDE-49	5–1000	0.9906	0.2	3.4	9.5	2812
BDE-99	10–1000	0.9937	1.0	5.0	14.9	1814
BDE-154	10–1000	0.9954	3.4	3.2	13.8	1529
BDE-153	10–1000	0.9964	5.3	4.2	11.4	1378

[a] Calculated from a sample spiked at a level of 100 ng/L.
[b] Calculated from a sample spiked at a level of 200 ng/L.
[c] Calculated from a sample spiked at a level of 1000 ng/L.

graphene surface possessing the effect of mixed sp^2 and sp^3 hybridization, which results in a highly delocalized conjugate system of π-electrons thus enhancing the π–π interactions with the aromatic PBDEs. Additionally, the porous structure of the 3D sol–gel silica network also provides larger surface area and thus improves extraction. Furthermore, the higher thermal stability of graphene may allow better desorption of PBDEs with relatively higher boiling points. These indicate that the sol–gel graphene fiber has conceivably strong binding affinity for the hydrophobic PBDEs.

3.5. Method evaluation

A series of experiments with regard to the linearity, limits of detection (LOD), repeatability, and enrichment factors was performed to validate the proposed method under the optimized extraction conditions. The results are listed in Table 2. The linear concentration range of the extraction method was tested over a range of 5 and 1000, or 10 and 1000 ng/L, depending on the analytes, with coefficients of determination (r^2) all greater than 0.990. The LODs for the PBDEs, calculated at a signal-to-noise ratio of 3, ranged from 0.2 to 5.3 ng/L. The results are comparable with the data obtained in a study in which polymer-functionalized single-walled carbon nanotubes were used for SPME-GC-ECD [13]. The present method showed higher sensitivity than that using multi-walled carbon nanotubes for SPME-GC-ECD [13]. The repeatability of one particular fiber and fiber-to-fiber reproducibility were studied at quintuplicate ($n=5$) and triplicate ($n=3$) analyses respectively to evaluate the precision of the extraction method. The relative standard deviation (RSD) of fiber repeatability ranged from 3.2 to 5.0% and the RSD of fiber-to-fiber reproducibility ranged from 7.7 to 14.9% which were satisfactory in both cases. Enrichment factors which are defined as the ratios of the final analyte concentrations after extraction and the initial concentrations of analytes in the standard sample mixture were assessed. The initial concentrations of analytes in the standard sample mixture were 1.0 μg/L. The final analyte concentrations after extraction were calculated by substituting the obtained peak areas into the standard calibration curve equations. As shown in Table 2, the developed method provided high enrichment factors ranging from 1378 to 2859.

Table 3
Analytical results for the determination of PBDEs in canal samples.

Analyte	Canal water without spiking		Canal water spiked at 100 ng/L	
	Concentration (ng/L)	RSD (%, $n=3$)	Relative recovery (%)	RSD (%, $n=3$)
BDE-47	6.70	0.7	77.9	5.1
BDE-49	7.19	2.8	79.5	6.2
BDE-99	n.d.[a]		81.9	3.6
BDE-154	n.d.		74.9	5.8
BDE-153	n.d.		74.8	7.8

[a] Not detected.

3.6. Application to water samples

The developed method was successfully applied to the analysis of trace PBDEs in water samples collected from a canal. The results are given in Table 3. Trace levels of BDE-47 and BDE-49 were detected at concentrations of 6.70 ng/L and 7.19 ng/L, respectively. Their presence was confirmed by spiking PBDE standards into canal water at a concentration level of 100 ng/L and reanalyzing the sample (Fig. 10).

To evaluate the accuracy of the method, the relative recovery test was performed by spiking PBDE standards into canal water at 100 ng/L. The relative recovery is defined as

$$\text{Relative recovery}\ (\%) = \frac{C_{\text{sample+s}} - C_{\text{sample}}}{C_s} \times 100$$

where $C_{\text{sample+s}}$ is the measured concentration of spiked canal water by external calibration method. C_{sample} is the measured concentration of canal water by an external calibration method and C_s is the spiked concentration. Results of relative recoveries and RSDs in triplicate are shown in Table 3. The data demonstrate that the relative recoveries ranged from 74.8% to 81.9%. The RSDs of target compounds were less than 8%, showing good reproducibility.

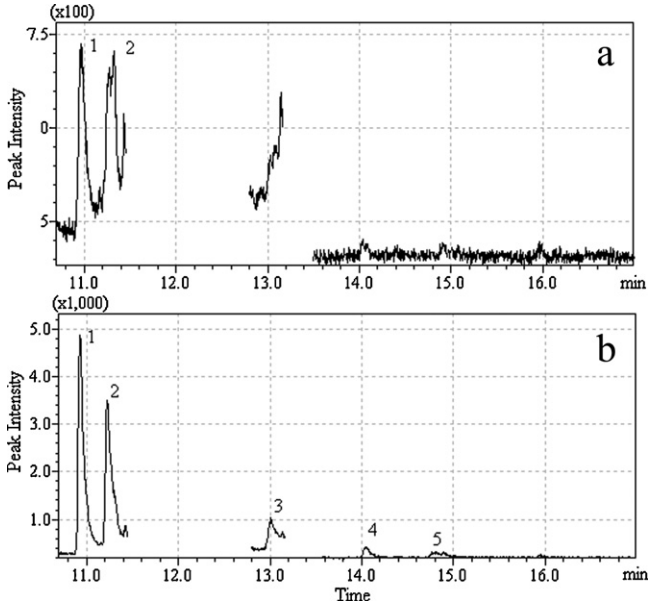


Fig. 10. GC–MS traces of canal water extracted by the developed method. (a) Canal water sample without spiking; (b) canal water sample spiked at 100 ng/L of PBDEs. Conditions: NaCl addition, 0%; extraction time, 20 min; extraction temperature, 60 °C; stirring rate, 1000 rpm; desorption time, 5 min. Peaks: 1: BDE-47; 2: BDE-49; 3: BDE-99; 4: BDE-154; 5: BDE-153. (Data were collected during the 10.70–11.45 min, 12.80–13.17 min and 13.50–17.00 min retention time windows.)

4. Conclusions

A novel sol–gel graphene-coated SPME approach using a commercially available plunger-in-needle microsyringe in conjunction with GC–MS, had been developed and applied to determine trace PBDEs in canal water samples. The graphene was coated on *ca.* 1.5-cm length of the plunger tip. Replacing the original needle with a shorter one permitted the implementation of a home-assembled SPME device. Compared with commercial SPME fibers such as 100 μm PDMS, 7 μm PDMS and 85 μm PA, the coated plunger showed higher extraction efficiency and selectivity for PBDE compounds. With GC–MS analysis, the procedure can achieve low detection limits ranging from 0.2 and 5.3 ng/L. Such a method offers a simple, rapid, sensitive and inexpensive tool for the determination of trace PBDEs in water samples.

This work has opened up the possibility of applying similar graphene-based sorbents for the extraction of other high boiling points compounds based on the high thermal stability of the coating. The thickness of the sol–gel film can be controlled by varying the duration of the coating process and therefore the extraction efficiency at different film thicknesses can also be evaluated. This sol–gel coating method together with the novel non-commercial microextraction setup described provide the foundation for future work in which in-house prepared sorbent materials in combination with a widely available and inexpensive plunger-in-needle microsyringe for SPME applications can be realized in a convenient and cost-effective manner.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.05.016.

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