



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.

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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 m²/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 isoctane 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

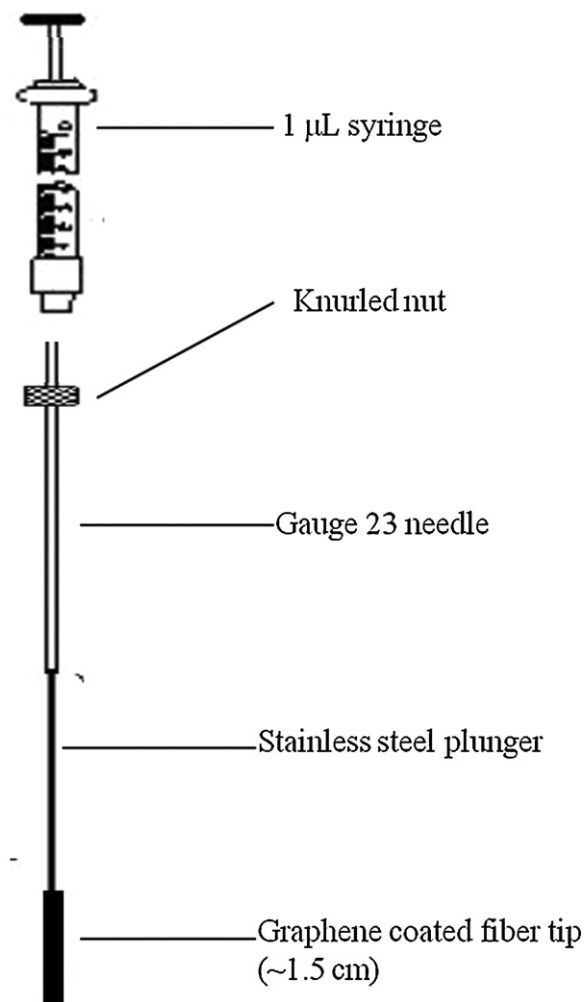


Fig. 1. Schematic of the home-assembled SPME device.

(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.

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 \times 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-

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