



Graphene oxide based sol-gel stainless steel fiber for the headspace solid-phase microextraction of organophosphate ester flame retardants in water samples[☆]



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ARTICLE INFO

Article history:

Received 8 January 2016
Received in revised form 12 June 2016
Accepted 13 June 2016
Available online 16 June 2016

Keywords:

Stainless steel fiber
Graphene oxide
Headspace solid phase microextraction
Organophosphate ester flame retardants
Gas chromatography

ABSTRACT

In this paper, graphene oxide was coated onto a stainless steel wire through sol-gel technique and it was used as a solid phase microextraction (SPME) fiber. The prepared fiber was characterized by scanning electron microscopy (SEM), which displayed that the fiber had crinkled surface and porous structure. The application of the fiber was evaluated through the headspace SPME of nine organophosphate ester flame retardants (OPFRs) with different characteristics in water samples followed by gas chromatography and nitrogen-phosphorous detector (GC/NPD). The major factors influencing the extraction efficiency, including the extraction and desorption conditions, were studied and optimized. Under the optimum conditions, the proposed method was evaluated, and applied to the analysis of organophosphate ester flame retardants in real environmental water samples. The results demonstrated the HS-SPME method based on GO sol-gel fiber had good linearity ($R > 0.9928$), and limits of detection ($1.4\text{--}135.6\text{ ng L}^{-1}$), high repeatability ($\text{RSD} < 9.8\%$) and good recovery ($76.4\text{--}112.4\%$). The GO based sol-gel fiber displayed bigger extraction capability than the commercial PDMS fiber and the pure sol-gel fiber for both polar and apolar organophosphate esters, especially for the OPFRs containing benzene rings.

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1. Introduction

At present, brominated flame retardants are being banned or phased out owing to their persistence, bioaccumulation, and toxicity [1]. As a consequence, organophosphate esters which were regarded as the alternative of brominated flame retardants have increased dramatically to meet flammability standards and commercial needs. In most applications, organophosphate ester flame retardants (OPFRs) are used as additives which are just mixed and not chemically bonded with the materials, thus OPFRs can easily leach out of the material into the environment via volatilization, abrasion, and dissolution. Many OPFRs have been reported causing obvious nerve toxicity, carcinogenicity, genetic toxicity and dermatitis [2]. Additionally, halogenated OPFRs are supposed to be highly persistent in the environment and only slightly biodegrad-

able like some other lipophilic OPFRs [3]. Based on the growing hazard and persistence of OPFRs, more and more attentions have been paid for their distribution in the environment and the toxicity to the ecosystem, and OPFRs have been included in European lists of aquatic priority substances [4]. Therefore, the development of accurate, sensitive, simple methods for the analysis of trace level of OPFRs in environmental media is a hot topic currently.

Until now, a number of pretreatment techniques have attempted to extract OPFRs from environmental samples, including liquid-liquid extraction (LLE) [3], solid-phase extraction (SPE) [5], membrane-assisted solvent extraction (MASE) [6], dispersive liquid-liquid microextraction (DLLME) [7], microporous membrane liquid-liquid extraction (MMLLE) [8], hollow fiber liquid phase microextraction (HF-LPME) [9] and SPME [10,11]. LLE and SPE have been the most often used extraction methods. However, these methods are tedious, labor-intensive and consume large amounts of organic solvents, and suffer from poor recovery of tri (2-chloroethyl) phosphate (TCEP) (31%) [3] or tri (2-ethylhexyl) phosphate (TEHP) (50%) [5]. MASE employs a non-porous polypropylene membrane to improve the selectivity in the liquid-liquid extraction of OPFRs from water samples, but the

[☆] Selected paper from 17th International Symposium on Advances in Extraction Technologies, 7–11 November 2015, Sun Yat-Sen University, Guangzhou, Guangdong, China.

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extraction efficiency in MASE for the most polar TCEP only 5%, and MASE is also quite time-consuming (3 h) [6]. DLLME was introduced since it drastically reduces organic solvents consumption which usually happened in the classical large-scale methods. However, DLLME exhibited unsatisfactory recovery for TEHP (about 40%) [7]. Although MMLLE is simple, inexpensive and has no carryover problems, it is unsuitable for the determination of TCEP and TEHP in water samples. Additionally, the extraction efficiencies of HF-PLME for polar analytes of TEHP and TCEP were lower than other OPFRs and resulted in lower recoveries as well. The commercial PDMS/DVB fiber used in HS-SPME method, was still not suitable for extracting TEHP due to the low recovery (26.7%) and unacceptable deviation (64.8%) [10]. Very recently, a homemade ionic liquid-based sol-gel SPME fiber has been reported to extract OPFRs from environmental water samples and exhibited good extraction capability and precisions when it applied for the simultaneous extraction of different polarity OPFRs, even including TCEP and TEHP [11]. However, ionic liquid is expensive and adsorbs water so easily in the air that it is not suitable for practical application.

Graphene oxide (GO), as a graphene precursor, exhibits similar adsorption ability to graphene which shows excellent extraction performance as coating materials of SPME fiber [12–16]. Compared with graphene, GO abounds with many oxygen-containing chemical groups across the basal planes, such as epoxy groups, hydroxyl groups, and carboxyl groups, which indicates that it can be readily interacted with other materials [17]. Furthermore, GO is much cheaper than graphene, suitable for large scale production. Therefore, GO is more practical than graphene as an adsorbent material. Stainless steel wires have been reported as SPME fiber due to the rigidity, low cost, non-toxicity and durability compared to other metal wires and the commercial fused silica fibers. The sol-gel technology, which was established by Malik, et al., has been widely applied to synthesize coating in SPME [18–21]. The synthetic conditions of sol-gel are usually mild, and the materials prepared by the sol-gel technology are often of high purity and homogeneity, high thermal and solvent stability, and high surface areas with porous structure [18–21]. The integrated use of the sol-gel technology and the stainless steel wire for the preparation of SPME fibers would take the advantages of the both and possibly enhance the extraction capability and durability of the prepared fiber.

The present study aimed to prepare GO based sol-gel coating bonded on a stainless steel fiber which was used as the SPME fiber for the evaluating trace level of OPFRs in environmental water samples by the headspace mode coupled to gas chromatography and nitrogen phosphorus detector (GC/NPD).

2. Experimental

2.1. Materials

Graphite powder (50 meshes), Methyltrimethoxysilane (MTMOS, 97%) and poly (methylhydrosiloxane) (PMHS), et al., were all of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The commercial fibers coated with 100 μm PDMS on the fused silica were obtained from Supelco (Bellefonte, PA, USA). The stainless steel fiber (diameter: 0.2 mm) was obtained from Najing Wanbi Materials Co., Ltd. (Nanjing, China). The standard substances of nine OPFRs were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Their physicochemical properties are shown in Table S1 (See ESM)

Individual stock solutions of nine OPFRs were prepared in acetone at a concentration of 10 mg mL⁻¹ stored at 4 °C in darkness. A mixed standard solution of the nine compounds (0.5 mg L⁻¹ TnBP, TPrP, TPhP, EHDPP, TCrP, TEHP and 2.5 mg L⁻¹ TCEP, TCPP, TDCCP)

was prepared with acetone. A series of standard solutions were prepared by appropriate dilution from the stock standard solution with ultrapure water. All the working solutions were prepared just before use.

2.2. Instrument

Surface structure of the prepared fiber was investigated by JSM-6700 F scanning electron microscopy (SEM) (FESEM, JEOL, Japan). Fourier transform infrared spectroscopy was performed on Thermo Nicolet Is50 FT-IR instrument (Boston, MA, USA). The thermal stability of the developed fibers was investigated by an STA 409 PC thermogravimetric analysis (TGA) instrument. A magnetic stirrer (C-MAG HS7) purchased from Aika instrument equipment Co., Ltd (Guangzhou, China). Ultrasonic instrument KQ-100DE was purchased from Kunshan Ultrasonic Instrument Co., Ltd. (Jiangsu, China).

The analytes were separated and detected on a 6890N GC (Agilent Technologies, USA), equipped with a HP-5 capillary column (30 m \times 0.32 mm i.d., 0.25 μm film thickness) and nitrogen-phosphorous detector (NPD). Ultrapure nitrogen (>99.999%) was used as carrier gas at a constant head column pressure of 9.80 psi and it also used as make-up gas at 10 mL/min. Synthetic air (99.995%) and hydrogen (99.999%) were used as detector gases at flows of 60 and 3 mL/min, respectively. The oven temperature was programmed as follows: initial temperature from 80 °C (held for 1.0 min), heating at 20 °C min⁻¹ to 160 °C (held for 2.0 min), then at 4 °C min⁻¹ to 280 °C (held for 1.0 min). The injector and the detector temperatures were set at 270 °C and 320 °C, respectively.

2.3. Water sample

River water was collected from the Changjiang River (Wuhan, China). Pond water was collected from a pond near a farmland (Wuhan, China). Tap water was collected from Central China Normal University (Wuhan, China). All water samples were stored in amber glass bottles at 4 °C in darkness before use.

2.4. Preparation of GO based sol-gel stainless steel fiber and HS-SPME procedures

As shown in Fig. 1, the whole process of preparation of GO based sol-gel stainless steel fiber and its HS-SPME procedures were presented as follows:

Firstly, a stainless steel fiber was modified. 2.5 cm stainless steel fiber was washed with ethanol, acetone and again in ethanol to remove contaminants. 1.5 cm of the steel fiber end was dipping into 10⁻³ mol L⁻¹ MPTS ethanol solution for 3 h. Then, it was rinsed with ethanol and dried under nitrogen atmosphere. The modified stainless steel fiber was obtained after being immersed in 0.1 mol L⁻¹ hydrochloric acid solution for 1 h. Secondly, GO was obtained by the method introduced by Marcano et al. [22].

2 mg GO was dissolved in 100 μL DMF in a 1.5 mL micro-centrifuge tube, and the tube were sonicated for 2.5 h. Then, 350 μL MTMOS and 50 μL PMHS, used as sol-gel precursor and the deactivation reagent, respectively, were added to the above-mentioned micro-centrifuge tube and sonicated for 20 min. Finally, 50 μL of 95% TFA solution, used as the acid catalyst, was added and mixed for 10 min. The GO based sol-gel composite was obtained. Finally, the modified stainless steel fiber was vertically dipped 1.5 cm deep into the above GO based sol-gel composite for 10 min. Then, it was pulled out and dried at room temperature for 20 min. The whole coating process was repeated several times until the desired thickness of the GO based sol-gel coating (about 10 μm) was obtained (Fig. S1, see ESM). Then, the coated fiber was put in a drier for curing at room temperature for 24 h. Prior to use, the fiber was assem-

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