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# A solid phase microextraction fiber coated with graphene–poly (ethylene glycol) composite for the extraction of volatile aromatic compounds from water samples

Zhi Li<sup>a,b</sup>, Ruiyang Ma<sup>a</sup>, Shasha Bai<sup>b</sup>, Chun Wang<sup>a</sup>, Zhi Wang<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry, College of Science, Agricultural University of Hebei, Baoding 071001, China

<sup>b</sup> College of Food Science & Technology, Agricultural University of Hebei, Baoding 071001, China

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## ABSTRACT

Poly(ethylene glycol)-grafted graphene (PEG-g-G) was prepared and used as the solid phase microextraction (SPME) fiber coating for the extraction of seven volatile aromatic compounds (VACs) from water samples followed by the determination with gas chromatography–flame ionization detection. The PEG-g-G coating was characterized by both the thermal gravimetric analysis and scanning electron microscopy. The results verified that the PEG was successfully grafted onto the surface of graphene and the coating had a highly porous structure. Several important experimental parameters that could influence the SPME efficiency were investigated and optimized. Under the optimized conditions, the limits of detection were in the range from 1.0 to 6.0 ng L<sup>-1</sup>. The relative standard deviations for intraday and interday variations were in the range of 1.8–5.8% and 5.1–8.3%, and for fiber-to-fiber variations, were between 6.5 and 11.9%, respectively. The results indicated that the PEG-g-G fiber had the advantages of high extraction efficiency and good thermal stability and durability. It can be reused more than 200 times without a significant loss of extraction efficiency. The method was successfully applied to the analysis of seven VACs in tap, river and mineral water samples.

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## 1. Introduction

Aromatic compounds are a class of chemical substances that contain one or more benzene rings. Many of these compounds are hazardous for human health; they are carcinogenic, neurotoxic, and can cause birth defects [1]. The maximum contaminant level (MCL) in drinking water [2] established by the US Environmental Protection Agency (EPA) is 1.0 mg L<sup>-1</sup> for toluene, 0.7 mg L<sup>-1</sup> for ethylbenzene, 0.1 mg L<sup>-1</sup> for chlorobenzene, 0.6 mg L<sup>-1</sup> for o-dichlorobenzene and 0.07 mg L<sup>-1</sup> for 1,2,4-trichlorobenzene. The MCLs set by State Environmental Protection Administration (SEPA) in China National Standard GB3838-2002 [3] for toluene, ethylbenzene, chlorobenzene, o-dichlorobenzene and trichlorobenzene are 0.7, 0.3, 0.3, 1.0 and 0.02 mg L<sup>-1</sup>, respectively. Therefore, it is necessary to develop simple and effective analytical methods for the determination of aromatic compounds in drinking waters at low concentration levels. At present, several sample pretreatment methods have been used for the extraction of volatile aromatic compounds (VACs), such as dispersive liquid–liquid microextraction [4], single-drop microextraction [5], headspace solvent microextraction [6], solid phase extraction [7] and solid phase microextraction (SPME) [8]. Among them, SPME

has been most extensively used since it is solvent-free and integrates sampling and extraction into one step [9,10].

SPME is based on the partition equilibrium of the analytes between the liquid or gaseous sample and a thin layer of adsorbent material, which is generally coated onto the fused silica fiber or wire. The coating material of the SPME fiber plays a key role for the extraction since it affects the partitioning of the analytes between the coating and sample matrix, and consequently affects the extraction efficiency of the SPME method. An ideal fiber coating should have high extraction efficiency, high thermal and solvent stability, long lifetime and strong adhesion between the coating and a fused silica fiber or wire.

Up to now, many coating materials have been commercialized, such as polyacrylate (PA), polydimethylsiloxane (PDMS), carboxen/polydimethylsiloxane (CAR/PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), carbowax/divinylbenzene (CW/DVB), divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and carbowax/templated resin (CW/TPR). At the same time, many other novel materials for SPME coatings have also emerged, such as polypyrrole [11], polyaniline [12], polyurethane foam [13], polymeric ionic liquid [14], molecular imprinted polymer [15] and carbon based coatings [16–18]. Recently, a novel allotropic member of carbon named graphene (G), which was first reported by Geim and coworkers in 2004 [19], has gained great attention from many researchers. Graphene has displayed excellent optical, mechanical, thermal and electrical properties. Its high theoretical surface area (2630 m<sup>2</sup> g<sup>-1</sup>) [20] endows it with a possibly high

\* Corresponding author at: Department of Chemistry, College of Science, Agricultural University of Hebei, Baoding 071001, China. Tel./fax: +86 312 7521513.

E-mail addresses: [zhiwang2000@hotmail.com](mailto:zhiwang2000@hotmail.com), [wangzhi@hebau.edu.cn](mailto:wangzhi@hebau.edu.cn), [zhiwang2013@aliyun.com](mailto:zhiwang2013@aliyun.com) (Z. Wang).

adsorption capacity. Because graphene has an atomically thin honeycomb lattice of carbon atoms, which comprises a single layer of  $sp^2$ -hybridized carbon atoms arranged in six-membered rings, it possesses a rich stacking  $\pi$ -electron system and could have a strong affinity for aromatic compounds [21]. However, up to now, only a few articles have been published on the application of the graphene in the fiber coating for SPME. In this regard, Ke et al. prepared a graphene-coated SPME fiber for the extraction of some organochlorine pesticides [22]. Zhang et al. prepared a graphene-supported zinc oxide SPME coating for the preconcentration of sulfur volatiles [16]. Zou et al. developed a polypyrrole (Ppy)/graphene composite coating for the SPME of some phenols [23].

Currently, the SPME sorbent phases were mainly coated onto the fused silica fiber or wires through vapor deposition [24], physical deposition [25], molecular imprinting polymer (MIP) procedures [26], electrochemical procedures [27] and sol-gel technology [28–31]. Among them, the sol-gel technology, which was established by Malik and coworkers [32], has been widely applied to synthesize porous and dense coatings, ceramic thin films and organic-inorganic hybrid materials. The sol-gel process mainly involves the catalytic hydrolysis of the precursors and a polycondensation of the hydrolyzed products and other active components to form a macromolecular network structure [33]. The synthetic conditions 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 [34].

The commercial coatings are often immobilized on fused silica fibers, which are fragile and must be handled with great care. In addition, the coating materials often easily strip off from the fiber, which causes a short lifetime for some SPME fibers [35]. In order to overcome the fragileness of SPME fibers, several different kinds of mechanically resistant metal wires have been explored, such as copper wire [36], silver wire [37], Pt wire [38], Ni-Ti alloy wire [39], oxidized titanium wire [40], anodized aluminum wire [41], gold wire [42] and stainless steel wire [43–45]. Among them, stainless steel wire has recently gained more attention over fused silica fiber due to its rigidity, low cost, non-toxicity and durability [45]. When the stainless steel wire was etched, the surface between the coating and the substrate could be increased, which could strengthen the adhesion of the coating to the wire and then improve the lifetime of the fiber. The integrated use of the sol-gel technology and the etched stainless steel wire for the preparation of the graphene-based SPME fibers would take the advantages of the both and possibly enhance the durability of the prepared fiber.

In the present work, hydroxyl-terminated poly(ethylene glycol) was grafted onto graphene nanoparticles (PEG-g-G) via a covalent functionalization method. The PEG-g-G was coated on an etched stainless steel wire by the sol-gel technology and served as a SPME fiber coating material for the first time. The characteristics of the PEG-g-G coating, such as stability, surface morphology, coating preparation reproducibility and extraction efficiency were investigated. The prepared fiber was tested for the preconcentration of seven VACs (toluene, ethylbenzene, chlorobenzene, bromobenzene, m-dichlorobenzene, o-dichlorobenzene and 1,2,4-trichlorobenzene) from environmental water samples followed by gas chromatographic analysis with flame ionization detection (GC-FID).

## 2. Experimental

### 2.1. Reagents and materials

Toluene, ethylbenzene, chlorobenzene, bromobenzene, m-dichlorobenzene, o-dichlorobenzene, trichlorobenzene, acetone, hydroxyl-terminated poly(ethylene glycol) (PEG, MW 6000), methyltrimethoxysilane (MTMOS), tetrahydrofuran (THF), trifluoroacetic

acid (TFA, 99%), thionyl chloride ( $SOCl_2$ ), sodium hydroxide (NaOH), hydrochloric acid (HCl), graphite powder (50 meshes) and all other reagents were obtained from the Boaixin Chemical Reagents Company (Baoding, China). Toluene and THF were dried, deoxygenated and distilled before use. The stainless steel wires (o.d. 304, 310  $\mu m$ ) and 5  $\mu L$  microsyringe were bought from Shanghai Gaoge Industrial and Trade Co., Ltd. (Shanghai, China).

The standard stock solution of the seven aromatic compounds (toluene, ethylbenzene, chlorobenzene, bromobenzene, m-dichlorobenzene, o-dichlorobenzene and trichlorobenzene) was prepared in acetone at 1.0  $mg L^{-1}$  in a 100.0-mL brown volumetric flask. All the standard solutions were stored at 4 °C in the dark. The double-distilled water used throughout the work was prepared on a SZ-93 automatic double-distiller from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China).

Tap water sample was collected freshly from our laboratory (Baoding, China); mineral water sample was purchased from the local supermarket (Baoding, China); river water sample was collected from Tang river in Baoding (Hebei, China). All the water samples were passed through a 0.45- $\mu m$  pore size membrane filter to remove the particulate matters prior to use.

### 2.2. Apparatus

A FULI GC-9790II (Fuli, <http://www.cnfuli.com.cn/>) equipped with a split/splitless injector and a flame ionization detector (FID) was employed for the analysis of the aromatic compounds. The analytes were separated on a KB-Wax fused silica capillary column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu m$ ) coated with polyethylene glycol (Kromat, <http://www.kromat.com.cn/>) with ultra pure nitrogen (99.999%) as carried gas at a flow rate of 2.0  $mL min^{-1}$ . The oven temperature was programmed as follows: initial temperature from 50 °C (held for 1.0 min), heating at 5 °C  $min^{-1}$  to 80 °C, then at 30 °C  $min^{-1}$  to 255 °C. The injector and the detector temperatures were set at 250 and 270 °C, respectively. The SPME fiber desorption was carried out in the split mode with a split ratio of 1:10.

A magnetic mixer of model 85-2B (Jinyi, <http://jtyl.testmart.cn/>) was employed for stirring the sample during the extraction. An ultrasonic bath (SK5200H, KUDOS, <http://www.kudoschina.com/>) was employed at a frequency of 59 kHz for ultrasonication.

The thermal properties of the PEG-g-G coating were measured by thermal gravimetric analyses (TGA) with a TG209F1 instrument (NETZSCH, Germany). The samples were heated to 800 °C under a nitrogen atmosphere at a heating rate of 10 °C  $min^{-1}$ . The surface morphology of the coating was observed by scanning electron microscopy (SEM) on a JSM-7500F (JEOL, Japan).

### 2.3. Preparation of sol solution

First, natural graphite powders were oxidized to graphene oxide (GO) and then transformed into GO sheets. The surface of GO sheets would be covered with some epoxy, hydroxyl and carboxyl groups [46]. Then, graphene-COCl was prepared as follows. 200 mg of GO was stirred in 20 mL of  $SOCl_2$  at 70 °C for 24 h to convert the surface-bound carboxyl groups into acyl chloride groups. After centrifugation, the solid was rinsed repeatedly with anhydrous THF and then dried at room temperature under vacuum [47]. Afterwards, all of the dried solid graphene-COCl (about 160 mg) was reacted with PEG as follows [48,49]. The graphene-COCl was mixed with 5 g of PEG in solvent mixture of 2 mL triethylamine, 5 mL THF and 15 mL toluene. Under a nitrogen atmosphere, the mixture was stirred for 52 h at 80 °C. After that, the product was filtered, repeatedly washed with water to remove the unreacted PEG, and dried under vacuum. Then, the final PEG-g-G product was obtained.

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