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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

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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^{-1}. 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.

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^{-1} for toluene, 0.7 mg L^{-1} for ethylbenzene, 0.1 mg L^{-1} for chlorobenzene, 0.6 mg L^{-1} for o-dichlorobenzene and 0.07 mg L^{-1} 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^{-1}, 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^2 g^{-1}) [20] endows it with a possibly high

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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 π-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 μm) and 5 μL 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-μm 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 × 0.32 mm × 0.25 μm) 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 radio 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.

For the preparation of the sol solution of PEG-g-G, 100 μL of MTMOS, 20 mg PEG-g-G and 100 mg PEG were added in an Eppendorf tube and mixed thoroughly by ultrasonic stirring for 5 min. Afterwards, 70 μL of TFA containing 5% water was added to the mixture, which was then sonicated for 5 min. After that, the sol solution of PEG-g-G coating material was obtained.

2.4. *Preparation of PEG-g-G coated fibers*

A stainless steel wire (o.d. 310 μm) was immersed in nitrohydrochloric acid for 2 cm until the wire was etched to the diameter of 140 μm. The etched stainless steel wire was washed gently by double-distilled water and dried in a desiccator at room temperature for 24 h. The etched surface would increase the contact area between the wire and sol–gel coatings.

The etched wire was vertically dipped into the sol solution 1.5 cm deep for 30 min and a gel coating was formed on the etched surface. After about 30 min drying, the coated wire was re-immersed into the sol solution and pulled out. This coating process was repeated until the desired thickness of the coating was obtained. Then, the coated fiber was put in a drier at room temperature for 24 h. Prior to use, the coated fiber was assembled to a 5 μL microsyringe [50] and conditioned at 100 °C for 1 h, 200 °C for 1 h and 280 °C for 1 h under nitrogen in the GC injector.

The PEG-coated fiber was prepared with the same procedures as the PEG-g-G-coated fiber except that PEG was used instead of PEG-g-G.

2.5. *Headspace SPME procedure*

To carry out headspace SPME (HS-SPME) for the analytes, 25 mL of water sample containing the seven compounds at each of 10 μg L^{-1} was placed in a 34 mL glass vial together with 9 g NaCl and a magnetic stirring bar. The vial was immediately sealed with a Teflon-lined cap to prevent sample evaporation. The needle of the SPME device, where the fiber was housed, was passed through the vial septum and then the fiber was pushed out from the needle and exposed to the atmosphere above the sample. After the extraction under stirring at 1000 rpm for 30 min, the fiber was withdrawn into the needle, removed from the vial and the needle was immediately pierced to the GC injection port and the fiber was pushed out for analysis. The fiber was kept in the injection port at 250 °C for 8 min. Prior to first use each day, the fiber was first activated by keeping it in the injection port at 250 °C for 30 min and then a blank analysis was made to verify that no interference peaks exist in the fiber.

3. Results and discussions

3.1. *Characterization of PEG-g-G coating*

The thermal properties of the PEG-g-G coating were analyzed by TGA (Fig. 1). Fig. 1a was the TGA curve of the PEG-g-G coating without heat treatment and Fig. 1b was the one of the coating after its being heat-treated at 100 °C for 1 h, 200 °C for 1 h and 280 °C for 1 h under nitrogen in the GC injector. The PEG-g-G coating was scanned within the temperature range investigated at a rate of 10 °C min^{-1} under N_2 atmosphere protection. Fig. 1a shows that the TGA curve of the PEG-g-G coating gave about 6% weight loss from 30–240 °C, which might be caused by the removal of the adsorbed water and the partial decomposition of the oxygen-containing functional groups of GO [51] which had not been involved in the sol–gel reaction. Fig. 1b shows that the TGA curve of the heat-treated coating has a platform between 50 °C and 450 °C. In other words, the heat-treated PEG-g-G coating had almost no weight loss in the temperature range from 50 to 450 °C. This means that the coating has a good thermal stability in that temperature range, which can satisfy the conditions for the determination of the seven aromatic compounds at 250 °C.

The coating thickness and surface morphology of the PEG-g-G coated fiber was characterized by SEM under different magnifications (Fig. 2). As illustrated in Fig. 2a, the diameter of the fiber was about 217 μm and the diameter of the etched wire was about 140 μm. So, the thickness of the coating was about 40 μm. Fig. 2b shows that a rough and highly porous structure existed on the surface of the entire coating, which would greatly increase the surface area and enhance the extraction capacity of the fiber [31].

The lifetime of the SPME coating is very important for its practical applications. In this study, the effect of the extraction times with the fiber on the peak areas of the analytes was investigated and the results are given in Fig. 3, which shows that the extraction efficiencies of the PEG-g-G coated fiber had no obvious decline even after 200 times HS-SPME extractions. The long lifespan of the coating is possibly due to the strong chemical interactions between PEG and graphene, the heat-resistant properties of the coating and the large contact area between the coating and the etched surface of wire.

3.2. *Optimization of extraction and desorption conditions*

Several parameters that could influence the SPME efficiency and analysis, such as desorption temperature and time, water sample volume, extraction time and salt addition, were investigated and optimized for their effects on the HS-SPME of the seven VACs.

3.2.1. *Desorption mode*

The desorption temperature and time were optimized. Giving an overall consideration of the thermal stability of the fiber coating, the volatility of the analytes and the maximum allowed temperature of the capillary column, the desorption temperatures between 150 and 250 °C were investigated. As a result, at 250 °C, the peak areas of the seven analytes reached the highest values. So, 250 °C was chosen as the desorption temperature.

The desorption time was investigated from 1 to 8 min at the desorption temperature of 250 °C, and the carry-over of compounds was checked after each desorption. As a result, after 8 min of the desorption at 250 °C, no carry-over of the compounds was observed when the fiber was desorbed for a second time. Therefore, 8 min of desorption at 250 °C was selected.

3.2.2. *HS-SPME time*

The HS-SPME process relies on the partition equilibrium of the analytes in the sample solution, the headspace of the aqueous sample solution and the fiber. Therefore, the extraction time is one of the crucial parameters which could affect the extraction efficiency. The effect of the HS-SPME time for the VACs was investigated by exposing the PEG-g-G fiber to the headspace of 25 mL of water solution containing each of the seven analytes at 10 μg L^{-1} for 10, 20, 25, 30, 50 and 120 min, respectively. Fig. 4a shows that the peak areas of the compounds increased with increased extraction time from 10 to 30 min and then remained almost constant. That is to say, the analytes could reach the extraction equilibrium at about 30 min. The short equilibrium time could be ascribed to the porous structure and the thin thickness of the coating (about 40 μm). Based on the above experimental result, the HS-SPME time was selected at 30 min.

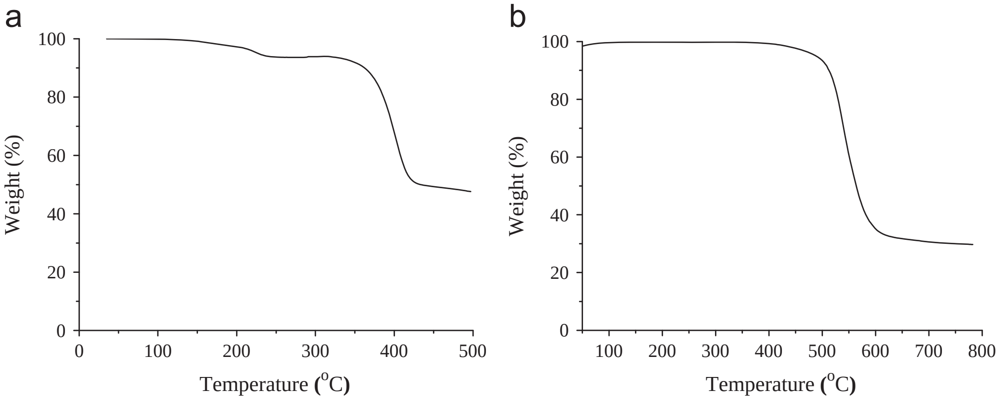

Fig. 1. TGA curves of the PEG-g-G coating before (a) and after heat-treatment (b).

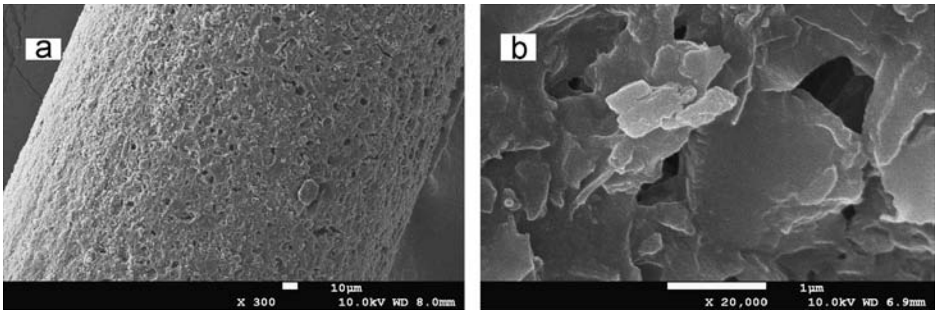

Fig. 2. Scanning electron microscopy images of the PEG-g-G coated fiber at a magnification of (a) 300-fold and (b) 20,000-fold.

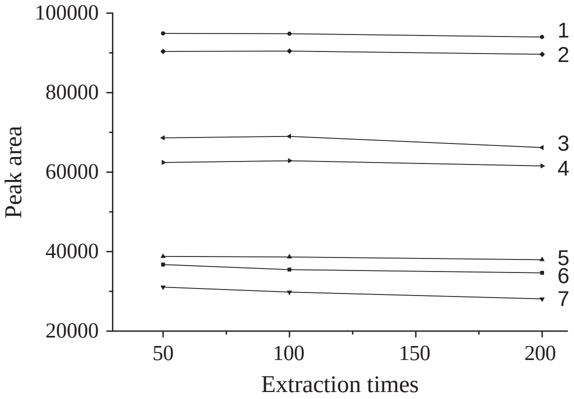

Fig. 3. Effect of the extraction times with the fiber on the peak areas of the analytes. Peak identifications: (1) ethylbenzene; (2) trichlorobenzene; (3) m-dichlorobenzene; (4) o-dichlorobenzene; (5) chlorobenzene; (6) toluene; and (7) bromobenzene.

3.2.3. The volume ratio of water to headspace

The volume ratio of the aqueous sample to headspace is another important parameter impacting the mass distribution equilibrium. Increasing the headspace would move the analytes partition equilibrium from liquid phase to gas phase, which could lead to more VACs being evaporated to headspace. However, large headspace would dilute the analyte concentration and therefore decrease the analytical sensitivity. In this study, the effect of water sample volume was investigated by changing the water volumes from 10 to 28 mL with the extractions being performed in a 34 mL glass vials at the same concentrations of the analytes in the water samples. Fig. 4b shows that the peak areas of the seven compounds first increased with the water volume being increased from 10 to 25 mL (the headspace volume was decreased from 24 to 9 mL), and then decreased from 25 to 28 mL (the headspace volume was decreased from 9 to 6 mL). Consequently, the volume of water samples was selected to be 25 mL, which corresponded to the volume ratio of 25:9 between water sample and the headspace.

3.2.4. Ionic strength

For most of organic compounds, their aqueous solubility will decrease with increased ionic strength. Increasing the salt content would enhance the analyte transfer rate from water to the headspace due to the salting-out effect. NaCl is the most commonly used inorganic salt for adjusting the ionic strength for an aqueous solution. The effect of the ionic strength was studied in the present work by changing the NaCl concentration in the range from 0 to 35% to the sample. Fig. 4c shows that for all the analytes studied, an increase in peak area was observed as the concentration of NaCl was increased in concentration range investigated. Therefore, 35% NaCl, i.e., 9 g NaCl in 25 mL water sample, was chosen.

3.3. Comparison of PEG coating and PEG-g-G coating

In this study, the extraction capabilities of both PEG and PEG-g-G coatings were investigated and compared for the HS-SPME of the VACs. As can be seen from Fig. 4d, the peak areas of all the compounds extracted by PEG-g-G coating were higher than those by the PEG coating. This could be because the large delocalized π-electron system of graphene can provide a strong affinity for carbon-based ring structures and increase the interactions between the aromatic compounds and the graphene.

3.4. Method validation

Under the above optimized experimental conditions, the parameters that show the analytical performance of the method, including the linear range (LR), correlation coefficients (r), limits of detection (LODs), and the intraday, interday and fiber-to-fiber

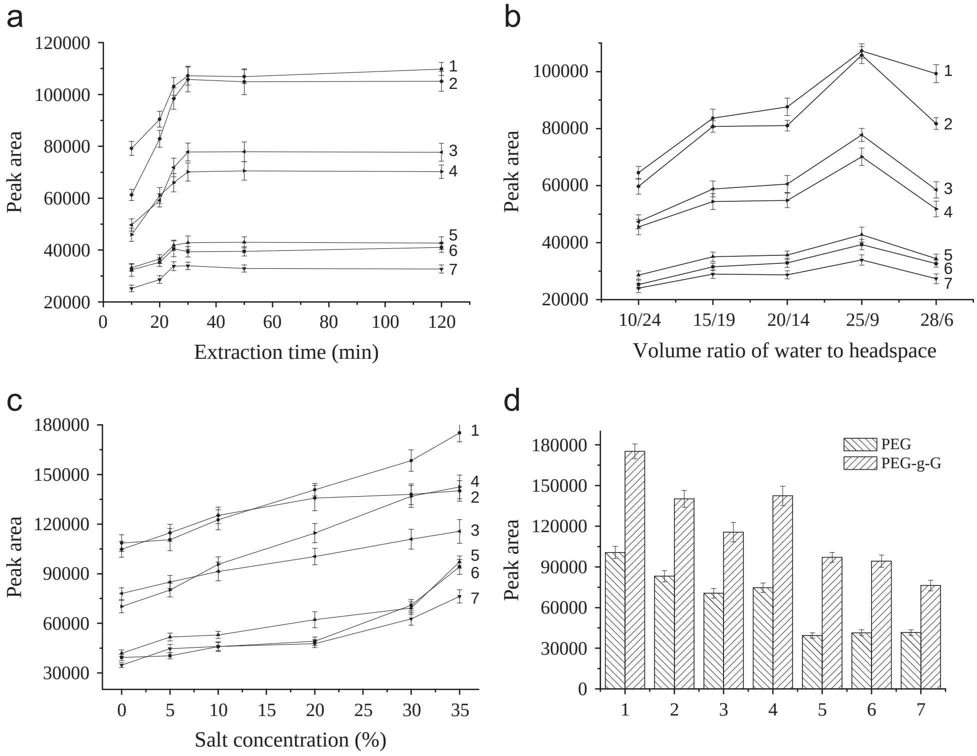

Fig. 4. Effect of extraction conditions on SPME efficiency. (a) the influence of extraction time; (b) the volume ratio of water to headspace; (c) the influence of salt concentration; (d) comparison of PEG coating with PEG-g-G coating. Peak identifications: (1) ethylbenzene; (2) trichlorobenzene; (3) m-dichlorobenzene; (4) o-dichlorobenzene; (5) chlorobenzene; (6) toluene; and (7) bromobenzene.

Table 1
Analytical performance data for the VACs by the SPME method.

Aromatic compounds	LR[a] (μg L^{-1})	*r*	LOD (ng L^{-1})	RSD (%)		
				Intraday	Interday	Fiber-to-fiber
Toluene	0.01–10.0	0.998	1.5	1.8	5.1	6.5
Ethylbenzene	0.01–10.0	0.998	1.0	4.7	6.0	8.7
Chlorobenzene	0.01–10.0	0.996	2.0	5.8	7.2	9.8
Bromobenzene	0.05–10.0	0.996	6.0	5.1	6.4	8.4
m-Dichlorobenzene	0.01–10.0	0.998	4.0	4.5	7.6	9.5
o-Dichlorobenzene	0.01–10.0	0.997	4.0	5.2	8.3	11.9
1,2,4-Trichlorobenzene	0.01–10.0	0.991	1.0	3.4	6.2	9.9

[a] LR, linear range.

variations of the method were investigated. The relevant experimental results are listed in Table 1.

The calibration curve was established in the range of 0.05–10.0 μg L^{-1} for bromobenzene and 0.01–10.0 μg L^{-1} for the others with the correlation coefficients (*r*) ranging from 0.991 to 0.998. Based on a signal-to-noise ratio (*S*/*N*) of 3, the LODs for the seven analytes were in the range from 1.0 to 6.0 ng L^{-1}. The intraday and interday precisions (RSDs, $n=5$) for the analytes at the concentration of 10 μg L^{-1} were in the range of 1.8–5.8% and 5.1–8.3%, respectively. The PEG-g-G fibers were prepared using the same method to test the fiber-to-fiber reproducibility (RSD, $n=5$). The fiber-to-fiber RSDs for the seven compounds ranged from 6.5% to 11.9%. In addition, there was no obvious decline for the extraction efficiencies with the PEG-g-G fiber after 200 times extractions, which indicated that the fiber had a long lifetime. These results show that the HS-SPME method using PEG-g-G fibers has a high extraction power and good repeatability for the seven VACs. The LODs of the current method are much lower than the maximum admissible concentration for each compound in water set by EPA [2] and SEPA [3].

3.5. *Analysis of real environmental water samples*

To determine the performance of the current method with the PEG-g-G fiber, the analysis of the seven VACs in tap, river and mineral water samples was preformed. As a result, no VACs was detected in the water samples. The recoveries for the water samples with the seven VACs being spiked at 1.0 and 10.0 μg L^{-1}, repectively, are listed in Table 2. The resultant recoveries of the method expressed as the percentage between the amounts found and the ones spiked were in the range from 83.2% to 111.8% with RSDs between 3.6% and 5.9%. Fig. 5 shows the typical chromatograms of the extracted seven VACs from river water sample.

3.6. *Comparison with other SPME coatings*

The performance of the current HS-SPME method with PEG-g-G fibers for the determination of VACs was compared with other SPME fibers such as PDMS [52], anilinemethyltriethoxysilane/polydimethylsiloxane (AMTEOS/PDMS) [53], single-walled carbon nanotubes (SWCNTS) [54], PEG-g-MWCNTs (multi-walled carbon

Table 2
Determination of the aromatic compounds and recoveries for tap, river and mineral water samples.

Aromatic compounds	Spiked (μg L^{-1})	Tap water (n=5)		River water (n=5)		Mineral water (n=5)	
		R[a] (%)	RSD (%)	R[a] (%)	RSD (%)	R[a] (%)	RSD (%)
Toluene	0.00	nd[b]		nd[b]		nd[b]	
	0.10	103.0	4.6	109.4	5.0	108.5	4.1
	10.0	91.2	3.7	102.2	5.9	89.8	4.0
Ethylbenzene	0.00	nd[b]		nd[b]		nd[b]	
	0.10	101.6	4.7	106.3	5.8	83.8	4.3
	10.0	111.8	4.1	109.7	4.5	106.0	3.6
Chlorobenzene	0.00	nd[b]		nd[b]		nd[b]	
	0.10	94.1	4.6	100.7	5.2	95.5	4.0
	10.0	86.7	4.9	90.1	5.0	87.6	4.4
Bromobenzene	0.00	nd[b]		nd[b]		nd[b]	
	0.10	100.8	4.2	95.0	4.6	94.7	4.5
	10.0	83.2	4.9	85.5	5.2	84.0	4.3
m-Dichlorobenzene	0.00	nd[b]		nd[b]		nd[b]	
	0.10	96.9	4.5	93.4	5.0	105.6	4.2
	10.0	88.9	4.8	104.9	5.6	102.3	4.0
o-Dichlorobenzene	0.00	nd[b]		nd[b]		nd[b]	
	0.10	108.0	4.7	92.4	4.9	102.6	4.4
	10.0	88.9	4.4	94.4	5.2	89.8	4.6
1,2,4-Trichlorobenzene	0.00	nd[b]		nd[b]		nd[b]	
	0.10	100.2	5.0	102.3	5.2	108.8	5.0
	10.0	101.3	4.4	100.8	4.6	98.2	4.3

[a] R, recovery of the method.
[b] nd, not detected.

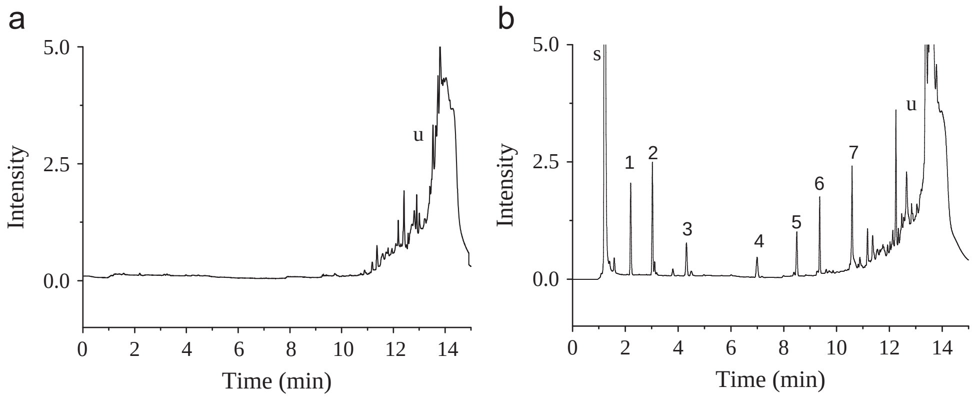

Fig. 5. Chromatograms of (a) river water sample and (b) the sample spiked with each compound at 1.0 μg L^{-1}. Peak identifications: (s) acetone; (1) toluene; (2) ethylenzene; (3) chlorobenzene; (4) bromobenzene; (5) m-dichlorobenzene; (6) o-dichlorobenzene; (7) 1,2,4-trichlorobenzene; and (u) unidentified peak from the fiber coating.

Table 3
Comparison with other fiber coatings for SPME methods.

Detection	Materials thickness	Analytes	LODs (μg L^{-1})	Extraction time (min)	Ref.
GC–MS	PDMS	m-Dichlorobenzene	0.006	30	[52]
	100 μm	o-Dichlorobenzene	0.006		
		1,2,4-Trichlorobenzene	0.004		
GC-FID	AMTEOS/PDMS	Toluene	1.2	20	[53]
	85 μm	Chlorobenzene	1.5		
		o-Dichlorobenzene	3.8		
GC-FID	SWCNTS	Toluene	0.013	20	[54]
	–	Ethylbenzene	0.011		
GC-FID	PEG-g-MWCNTs	Toluene	0.002	30	[31]
	–	Ethylbenzene	0.0007		
GC-FID	PEG-g-G	Toluene	0.0015	30	This method
	40 μm	Ethylbenzene	0.001		
		Chlorobenzene	0.002		
		Bromobenzene	0.006		
		m-Dichlorobenzene	0.004		
		o-Dichlorobenzene	0.004		
		1,2,4-Trichlorobenzene	0.001		

nanotubes) [31] from the viewpoint of the thickness of the coating, analytes, LODs and extraction time. As listed in Table 3, the LODs of the seven VACs with the current method are lower than that with the other methods, only with the exception of that for ethylbenzene by PEG-g-MWCNTs coated SPME fiber. In addition, the starting material of natural graphite and all the other reagents involved for the preparation of the PEG-g-G SPME fiber coating are commercially available and inexpensive, which makes the PEG-g-G SPME fiber cheap and economical.

4. Conclusions

In this study, a HS-SPME method using PEG-g-G fiber for the extraction of some VACs from real water samples was established. The PEG-g-G was successfully coated on the etched stainless steel wire using the sol–gel technology and the PEG-g-G fiber was successfully used for the HS-SPME of seven VACs. The developed PEG-g-G-coated SPME fiber exhibited high extraction efficiencies, low LODs and wide linear range, which benefited from the unique properties of the *G* and the porous structure of the fiber coating. The fiber coating demonstrated a good stability and durability, and the fiber can be reused more than 200 times for the current HS-SPME method without a significant loss of extraction efficiency.

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