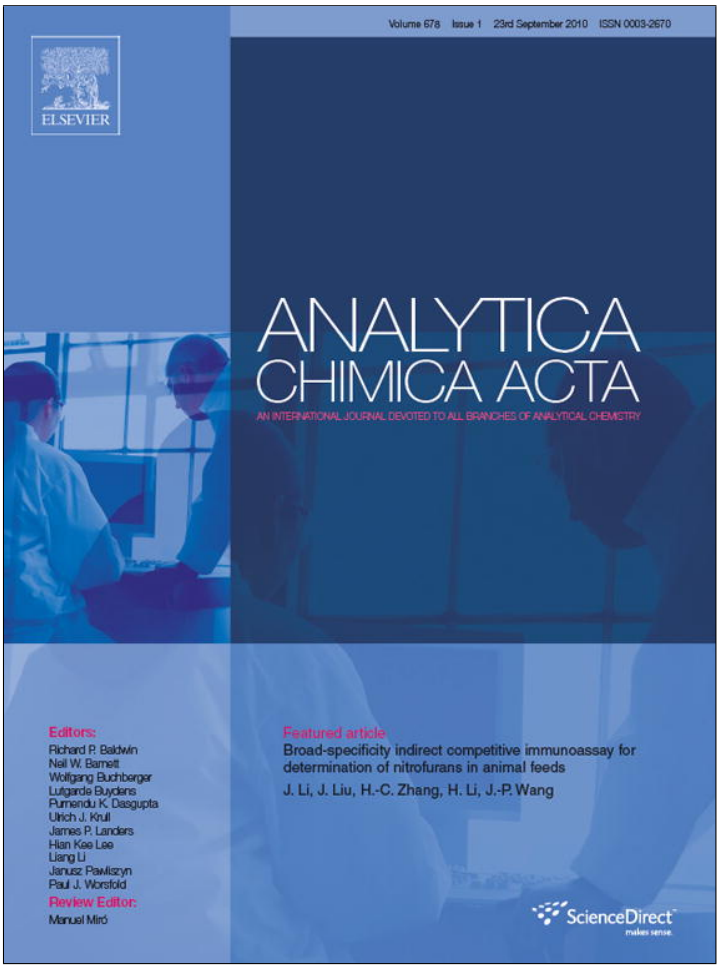

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Preparation and evaluation of graphene-coated solid-phase microextraction fiber

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ABSTRACT

In this paper, a novel graphene (G) based solid-phase microextraction (SPME) fiber was firstly prepared by immobilizing the synthesized G on stainless steel wire as coating. The new fiber possessed a homogeneous, porous and wrinkled surface and showed excellent thermal (over 330 °C), chemical and mechanical stability, and long lifespan (over 250 extractions). The SPME performance of the G-coated fiber was evaluated in detail through extraction of six pyrethroid pesticides. Although the thickness of G-coated fiber was only 6–8 μm, its extraction efficiencies were higher than those of two commercial fibers (PDMS, 100 μm; PDMS/DVB, 65 μm). This high extraction efficiency may be mainly attributed to huge delocalized π-electron system of G, which shows strong π-stacking interaction with pyrethroid pesticide. The G-coated fiber was applied in the gas chromatographic determination of six pyrethroids, and their limits of detection were found to be ranged from 3.69 to 69.4 ng L^{-1}. The reproducibility for each single fiber was evaluated and the relative standard deviations (RSDs) were calculated to be in the range from 1.9% to 6.5%. The repeatability of fiber-to-fiber and batch-to-batch was 4.3–9.2% and 4.1–9.9%. The method developed was successfully applied to three pond water samples, and the recoveries were 83–110% at a spiking of 1 μg L^{-1}.

1. Introduction

The solid-phase microextraction (SPME) technique was first introduced in 1989 [1], and has been proved to be a powerful sampling preparation technique with simple, fast, sensitive and solvent-free characteristics. SPME can be easily coupled with gas chromatography [2] or high performance liquid chromatography [3], and has been successfully applied to food [4], environmental [5,6], pharmaceutical [7], clinical [8], biological [9], and forensic analysis [10,11]. In general, fiber coating is considered to be the key factor in the SPME technique. Although several commercial SPME fibers with different coatings, such as non-polar polydimethylsiloxane (PDMS), carboxen/PDMS, semi-polar PDMS/divinylbenzene (PDMS/DVB) and polar polyacrylate, carbowax/PDMS, polyethylene glycol and carbowax/templated resin, have been applied in many fields, they still face disadvantages, such as cost, short lifespan, nonresistance to high temperature and breakage of the fiber, and these drawbacks limit their application. To meet the needs of complex analysis, new SPME coatings with remarkable properties, such as enhanced sensitivity [12], high thermal [13], mechanical and chemical stability, and low cost, have been developed continually using new preparation methods [14] or new materials [15,16].

Carbon materials are known for their high adsorption capacity for organic compounds, and some of them, such as single-walled carbon nanotubes [17], multi-walled carbon nanotubes [18,19], activated carbon [20] and glassy carbon [21,22] have already been used in SPME. Graphene (G), which is considered as the basic building block of all graphitic forms (including carbon nanotubes, graphite and fullerene C_{60}), is a single-atom-thick, two-dimensional carbon material [23]. Compared with other graphitic forms, G shows many outstanding advantages, such as its high surface area to weight (2630 $m^2 g^{-1}$), remarkable thermal and chemical stability, ultra-high mechanical strength, low production cost [24–26]. To date, G-based materials are applied in many fields, such as sensors and biosensors [27], energy storage [28,29], drug delivery [30,31], catalytic [32,33] and gas separation [34]. As the large delocalized π-electron system of G can form strong π-stacking interaction with the benzene ring [35], it might be also a good candidate as a SPME coating for the extraction of benzenoid-form compounds. Furthermore, the remarkable thermal, chemical and mechanical stability of G probably makes it a robust SPME

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coating. However, as far as we know, there is still no report of the application of G as a SPME coating.

In this study, graphene oxide (GO) was synthesized through chemical exfoliation of graphite, and graphene (G) was prepared by the reduction of the GO with *p*-phenylene diamine. The synthetic product was successfully characterized using atomic force microscopy (AFM) and transmission electron microscopy (TEM). Next, we immobilized the prepared G onto a stainless steel wire to obtain a novel SPME coating. In order to evaluate the extraction performance and stability of the G-coated fiber, six pyrethroid pesticides were selected as typical hydrophobic and benzenoid-form compounds. Several factors related to the extraction efficiency such as extraction time, stirring rate, desorption temperature and time were studied and optimized. The analytical characteristics of the SPME–GC method was then investigated under these optimized conditions. Finally, the G-coated fiber was applied to the extraction of pyrethroid pesticides in natural water samples to test its applicability in real sample analysis.

2. Experimental section

2.1. Materials and reagents

Stainless steel wires (O.D., 0.15 mm) were purchased from the AnTing Micro-Injector Factory (Shanghai, China); graphite powder and *p*-phenylene diamine (PPD) were purchased from the Lvyinhuabo Co., Ltd. (Xiamen, China); phenvalerate, cypermethrin, bifenthrin, permethrin, deltamethrin and cyhalothrin were purchased from the Agro-environmental Protection Institute, Ministry of Agriculture (Tianjin, China); potassium permanganate, concentrated sulfuric acid and sodium nitrate were obtained from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); and pesticide residue grade acetone was purchased from Tedia (OH, USA). 10 mg L^{-1} stock solutions of the six pesticides were prepared by diluting 100 mg L^{-1} of each compound with acetone, and a 1 mg L^{-1} mixture of the pyrethroid pesticides was prepared by further diluting the stock solution with acetone. All the above solutions were sealed with sealing rubber and stored at 4 °C in a refrigerator. The standard working solutions were prepared by diluting the mixture with deionized water to the required concentration, as required.

2.2. Equipment

Commercial manual sampling SPME devices with 100 μm PDMS and with 65 μm PDMS/DVB fiber were obtained from Supelco (Bellefonte, PA, USA). SPME–GC experiments were carried out on a Shimadazu GC-2010 GC system equipped with an electron capture detector (ECD) system. Separation was performed on a 30 m × 0.25 mm I.D. and 0.25 μm DB-1 capillary column (J&W Scientific, CA, USA). Operating parameters for the analysis of the pyrethroid pesticides were as follows: injector temperature held at 270 °C, splitless 2 min; column flow, N_2 1.40 mL min^{-1}; column temperature program: held at 170 for 2 min, then increased from 170 to 260 °C at 30 °C min^{-1} and maintained for 1 min, finally the temperature increased by 5 °C min^{-1} to 280 °C and held at 280 °C for 4.5 min; and detector temperature held at 300 °C. An LEO 1530 (LEO, Oberkochen, Germany) was used to obtain the scanning electron microscope (SEM) morphology of the G coatings and the elemental composition of GO and G; a TECNAI F30 (Philips-FEI, Netherlands) was used to obtain the TEM morphology of the G coatings; the AFM morphology of GO was obtained using an AFM 5500 (Agilent, USA); the thermogravimetric analysis of G was carried out on a simultaneous thermogravimetric analyser/differential scanning calorimeter (TA Instruments-Waters LLC, USA) from room temperature to 550 °C in flowing N_2 at a heating rate of 10 °C min^{-1}; and a TG16-WS (XiangYi Centrifuge Instrument Co., China) and a Branson 200 ultrasonicator (Danbury, CT, USA) were also used in this study.

2.3. Synthesis of GO and G

GO was prepared from graphite powder by chemical exfoliation [36–38]. 0.5 g graphite powder, 0.5 g $NaNO_3$ and 23 mL concentrated H_2SO_4were stirred together in an ice bath for 1 h. Next, 3.0 g of $KMnO_4$ was added slowly. Once these were mixed, the ice bath was removed and the suspension was stirred for 2 h at room temperature. Next, 46 mL of water was slowly transferred to the suspension using a dropper, and it was heated in an oil bath at 98 °C for 30 min. After another 100 mL of water was added, 10 mL H_2O_2 (30%) was slowly added. The mixture was centrifuged at 4000 rpm and washed six times with 10% HCl (v/v) aqueous solution to remove metal ions. Subsequently, the sediment was washed with deionized water and centrifuged at 8000 rpm to remove acid. The final sediment was dried at 40 °C for 72 h and redispersed in water with ultrasonication for 1 h to make a 1 mg mL^{-1} GO solution.

G was synthesized by reducing the GO with PPD [36]. To do this, 1.2 g of PPD was dissolved in 100 mL DMF, and then 100 mL of the 1 mg mL^{-1} GO solution was added. The mixture was refluxed in an oil bath at 98 °C for 36 h, forming a red solution. The solution was filtered and washed with acetone. Subsequently, the filter cake was redispersed in ethanol with ultrasonication for 30 min, giving a stock solution of G.

2.4. Preparation of G-coated fibers

The stock solution of G was filtrated again, and washed with acetone to remove PPD until the filtrate was colorless. The filter cake was redispersed in a 5-mL plastic centrifuge tube with 2 mL ethanol, to form a concentrated G ethanol solution. The solution was centrifuged at 8000 rpm for 10 min, and the sediment was transferred to a 0.5-mL plastic centrifuge tube.

Prior to coating, stainless steel wire (17 cm) was sequentially cleaned with acetone, then methanol and finally distilled water in an ultrasonicator for 5 min each, and then air-dried at room temperature. The coating was prepared by immersing the steel wire into the 0.5-mL plastic centrifuge tube filled with the G sediment. Subsequently, the fiber was drawn out and dried in air for 30 s. This procedure was repeated until the thickness of the coating met the requirement (6–8 μm). The length of the G coating was controlled at 1.5 cm by carefully scraping from the top with a knife. The new fiber was preheated in an oven at 100 °C for 24 h, and further heated in the GC injector port at 240 °C under nitrogen for 30 min.

2.5. Solid-phase microextraction

For SPME, a 10 mL 10 μg L^{-1} pyrethroid pesticide solution was placed in a 15-mL glass vial. SPME was performed by direct immersion of 1.5 cm of the fiber into this solution under stirring at 1000 rpm for 15 min. After extraction, the fiber was pulled out and inserted into the inlet of the GC, and desorbed at 270 °C for 2 min.

2.6. Real sample analysis

Three pond water samples were collected from the Xiamen University campus. The samples were filtered to remove any solid particles and then transferred to clean glass vials. Water samples and spiked water samples were tested immediately after sampling without any other pretreatment.

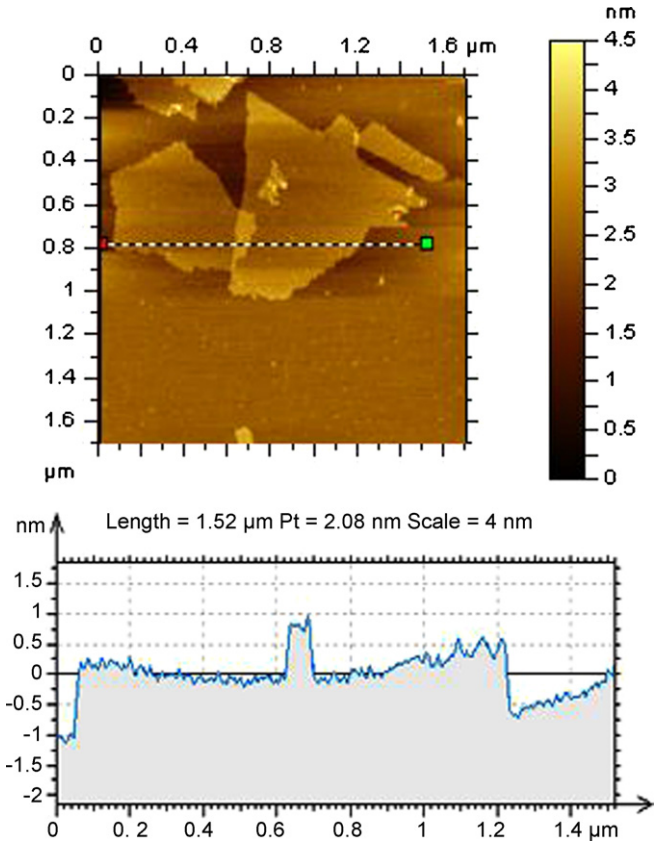

Fig. 1. AFM image of graphene oxide (GO) on isinglass (upper) and the height data along the line displayed in the upper figure (lower).

3. Results and discussion

3.1. Characterization of the prepared GO and G

As shown in Fig. 1, based on the AFM measurement results, the GO surface morphology is very flat, and its thickness is around 1 nm. From Fig. 1, we can see that there was an overlapping edge of the two pieces of GO around the middle of the image, and the thickness of the overlapped part was 1 nm thicker than that of the non-overlapped part, which further proved that the thickness of the GO was about 1 nm. This result is consistent with a report [39], which suggests that the prepared GO is a monolayer.

The TEM image (Fig. 2) of G prepared by the reduction of GO shows that the G sheet was a thin and transparent layer. The thermogravimetric analysis result showed that only very little weight loss of the G occurred between 100 and 300 °C. Even at 550 °C, about 80% of the weight remained, which indicated that G is a thermally stable material. Furthermore, in order to confirm that the prepared G was sufficiently deoxidized, element compositions of the GO and the G were determined using Auger electron spectroscopy. The results showed that the content of oxygen in the GO and G was 36% and 12%. These results approximate closely to previous reports [36,40], indicate that the GO had been sufficiently reduced by PPD.

3.2. Characterization of the G-coated fiber

3.2.1. Surface morphology of the coating

SEM images of the G coating are presented in Fig. 3. Fig. 3a shows that the coating possessed a homogeneous, porous and wrinkled structure. The porous and wrinkled structure of the coating could have increased the available surface area of the fiber, as well as its extraction ability. The inset image in Fig. 3a shows that the thickness of the coating was about 7.3 µm. The thicknesses of the other fibers we prepared were between 6 and 8 µm. In the high magnification SEM image of the coating (Fig. 3b), G sheets interlocking together to form a compact film can be observed, which indicated that the fiber would be mechanically stable.

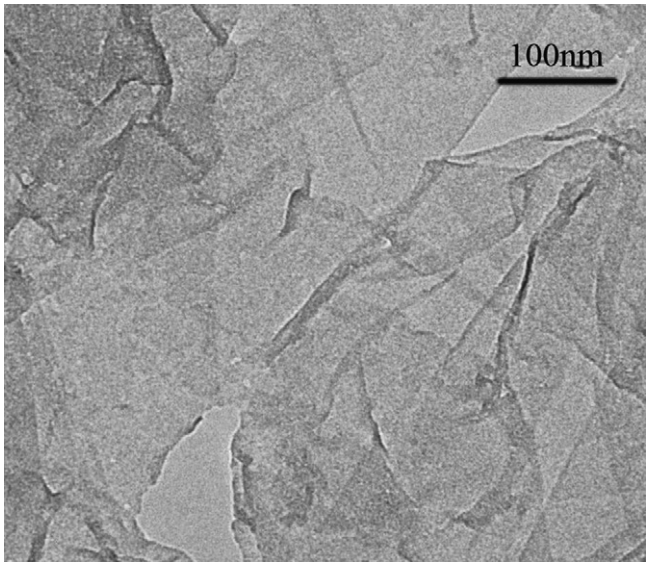

Fig. 2. TEM image of G.

3.2.2. The extraction efficiency of the G-coated fiber

To investigate the extraction ability of the G-coated fiber, six pyrethroid pesticides were selected as target compounds. Commercial PDMS (100 µm) fiber and PDMS/DVB (65 µm) fiber were selected for comparison since they are reported to have high affin-

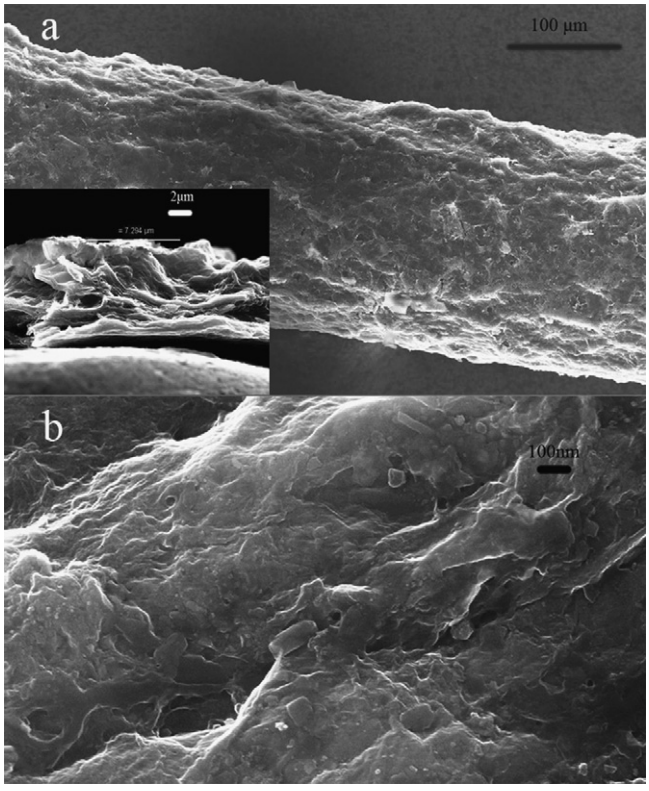

Fig. 3. SEM images of G coating at (a) 200× and (b) 30,000× magnification.

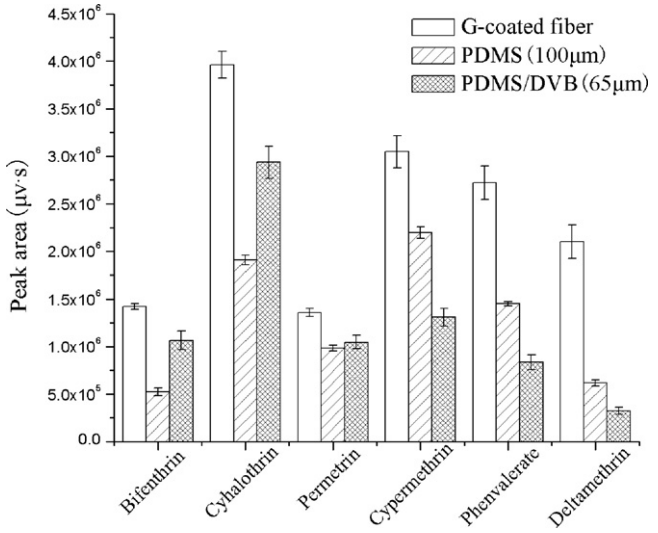

Fig. 4. Comparison of extraction amounts using the G-coated fiber and two commercial fibers. Conditions: sample volume, 10 mL; stirring rate, 1000 rpm; extraction time, 2 min; desorption temperature, 270 °C; and desorption time, 2 min. Concentration of each pesticide, 10 μg L^{-1}.

ity for pyrethroid pesticides [41,42]. Compared to the commercial fibers selected, G-coated fiber presented the best extraction results among all fibers for the six pyrethroid pesticides (Fig. 4). It should be noted that although the thickness of the G coating used in this study is only 6–8 μm, its extraction efficiency is still about 1.5-fold higher than those of the two commercial fibers (100 μm or 65 μm in coating thickness). It was estimated that a higher extraction efficiency of the G-coated fiber could have been attained with an increase of the G coating thickness. The high extraction efficiency of G-coated fiber towards the pesticides may have been due to porous and wrinkled structure, and the very large delocalized π-electron system of the coating. The porous and wrinkled structure increased the available surface area and thus increased the available adsorption sites of the fiber. The very large delocalized π-electron system can form a strong π-stacking interaction with the benzene rings in the pyrethroid pesticides. The results indicated that the G-coated fiber could be a good choice for SPME of non-polar pyrethroid pesticides.

3.2.3. Fiber stability

During the application and life span of an SPME fiber, the thermal, solvent and mechanical stabilities of the fiber are important characteristics. A G-coated fiber was conditioned at 250, 270, 290, 310 and 330 °C for 1 h in order to investigate the thermal stability of the fiber. After treatment, the extraction efficiency of the fiber was studied and, subsequently, the solvent stability of the G-coated fiber was evaluated. In the test, the fiber was immersed into different solvents including methanol, hexane, acetone, acetonitrile, HCl solution (0.1 mol L^{-1}) and NaOH solution (0.1 mol L^{-1}) for 1 h. After this, the fiber was washed with deionized water and dried at 100 °C. The ratio (r) of the fiber extraction efficiency after treatment to that before treatment is shown in Table 1. Based on the r values obtained (between 0.83 and 1.09), the fiber extraction efficiency remained almost unchanged after treatment, the G-coated fiber possessed high thermal (over 330 °C) and solvent stability. Next, the extraction efficiency of the G-coated fiber after 250 extractions was investigated and the result shown in Table 1 indicates that no obvious extraction efficiency change was found after 250 extractions, indicating the remarkable mechanical stability of the fiber. This result may have benefitted from the compact structure of the G coating, as well as the high mechanical strength of G and stainless steel wire, which together ensured a long lifespan (more than 250 extractions) for the fiber.

Table 1
Stability of G-coated SPME fiber.[a]

Analyte	r[b]			
	Before treatment	After thermal treatment	After solvent treatment	After 250 extractions
Bifenthrin	1	0.94	0.83	1.02
Cyhalothrin	1	0.88	0.93	0.96
Permethrin	1	0.87	1.08	0.94
Cypermethrin	1	0.83	0.92	0.95
Phenvalerate	1	0.90	0.88	0.93
Deltamethrin	1	0.91	1.09	0.90

[a] Conditions: sample volume, 10 mL; stirring rate, 1000 rpm; extraction time, 2 min; desorption temperature, 270 °C; and desorption time, 2 min. Concentration of each pesticide, 10 μg L^{-1}.
[b] The ratios (r) of extraction efficiencies are obtained by division of the peak areas after treatment with that before treatment.

3.3. Optimization of extraction performance

To achieve the best extraction efficiency of the G-coated fiber, several factors affecting the extraction efficiency, such as extraction time, stirring rate, desorption temperature and desorption time, were investigated and optimized.

3.3.1. Extraction time

The effect of extraction time on the extraction efficiency was investigated at 2.5, 5, 15, 30, 60 and 90 min. Theoretically, the equilibrium time of G-coated fiber should be very short, because the G coating thickness was only 6–8 μm. However, the extraction equilibrium of the G-coated fiber for pyrethroid pesticide was not completely reached until after 90 min, although a high extraction efficiency had been achieved (Fig. 5). This result indicated that the G-coated fiber had notable extraction capacity for the six pyrethroid pesticides [43]. Although the maximum extraction efficiency for the analytes would be obtained at equilibrium, the analysis time would be unduly prolonged. According to the non-equilibrium theory of SPME [44], SPME quantitative analysis can be utilized in a non-equilibrium situation if the extraction conditions are held constant. In this study, an extraction time of 15 min was selected as a compromise between analysis time and method sensitivity.

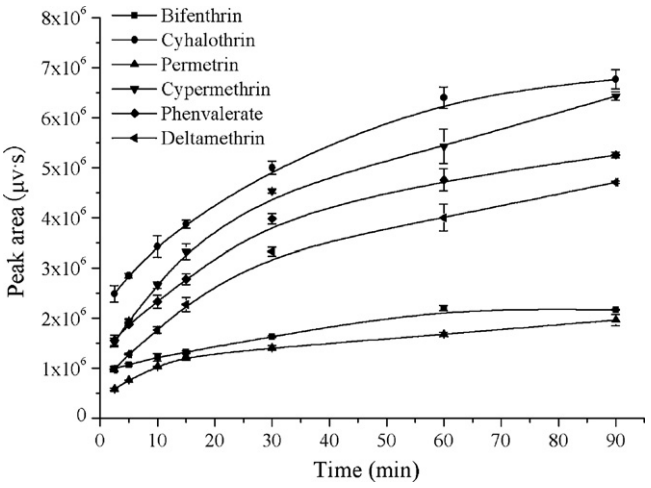

Fig. 5. Extraction time profiles for pyrethroid pesticides. Conditions: sample volume, 10 mL; stirring rate, 1000 rpm; desorption temperature, 270 °C; and desorption time, 2 min. Concentration of each pesticide, 10 μg L^{-1}.

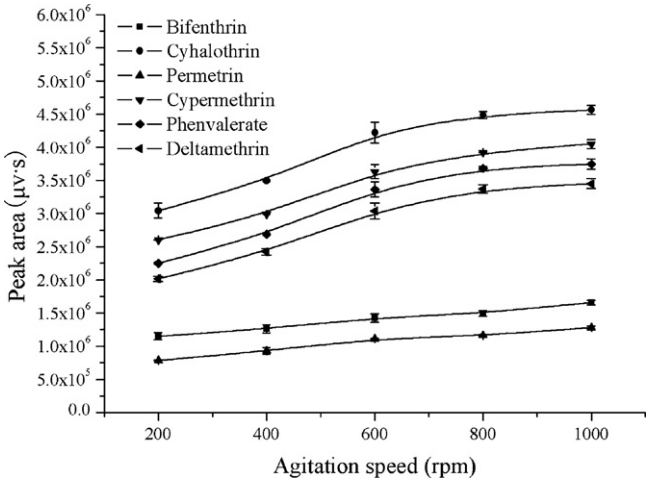

Fig. 6. Effect of stirring speed on the extraction efficiencies of pyrethroid pesticides. Conditions: sample volume, 10 mL; extraction time, 2 min; desorption temperature, 270 °C; and desorption time, 2 min. Concentration of each pesticide, 10 μg L^{-1}.

3.3.2. Stirring rate

Generally, increasing stir rate can effectively accelerate mass transfer of an analyte to the solid coating and thus enhance the extraction efficiency. Stirring rates ranging from 200 to 1000 rpm were used to investigate this effect. The results (Fig. 6) show that the extraction efficiencies of the analytes increased with a higher stirring rate, and the highest extraction efficiency was achieved at a stirring rate of 1000 rpm. Consequently, 1000 rpm was chosen as the optimum stirring rate for subsequent experiments.

3.3.3. Desorption temperature

Desorption temperature must be high enough to effectively release analytes from the coating and, consequently, a desorption temperature range from 250 to 310 °C was investigated. The peak area of all six pyrethroid pesticides remained unchanged above 270 °C. Although a higher desorption temperature can reduce desorption time, the high temperature may damage the coating and injector, and so the desorption temperature for subsequent experiments was set at 270 °C.

3.3.4. Desorption time

Desorption times of 1, 2, 3 and 4 min were used. The peak areas of the analytes increased from 1 to 2 min and reached equilibrium after 2 min. The analytes remaining in the coating after desorption at 270 °C for 2 min were checked and none were found, indicating that they had been released completely. The rapid desorption of analytes was mainly attributed to the thinness of the coating, and thus the desorption time was set at 2 min.

3.4. Evaluation of method performance

The G-coated fiber was used for SPME determination of the pyrethroid pesticides and the analytical characteristics under optimized conditions are shown in Table 2. The linear ranges of the method were from 0.05 to 100 μg L^{-1} for bifenthrin, cyhalothrin and deltamethrin, and from 0.1 to 100 μg L^{-1} for permethrin, cypermethrin and phenvalerate, with all the correlation coefficients being larger than 0.99. The limits of detection (LODs), defined as three times the baseline noise, were in the range 3.6 ng L^{-1} (bifenthrin) to 69.4 ng L^{-1} (phenvalerate). The reproducibility for each single fiber was evaluated by extracting aqueous samples spiked at 10 μg L^{-1} of each analyte (seven replicates), and the relative standard deviations (RSDs) were shown to be 1.9–6.5%. The fiber-to-fiber repeatability for the four fibers prepared in the same batch was in the range 4.3–9.2% (RSDs), and the batch-to-batch repeatability for four fibers prepared in different batches was 4.1–11.0% (RSDs).

3.5. Application to water samples

To test the fiber's applicability for the analysis of water samples, it was used to determine pyrethroid pesticides in pond water. As shown in Table 3, no pyrethroid pesticides were found in the three original pond water samples. The recovery of the six pyrethroid pesticides spiked at 1 μg L^{-1} in the pond water samples ranged from 83% to 110%, and the precision for all samples was below 9%. Fig. 7 shows a typical chromatogram of a pond water sample with and without pyrethroid pesticide spiking obtained using the G-coated fiber.

Table 2
Enrichment factor, detection limits, linear range linearity and repeatability of the proposed method.

Analyte	LOD ($S/N = 3$) (ng L^{-1})	Linearity correlation (r^2)	Linear range (μg L^{-1})	Precision (RSD%, $n = 7$)	Repeatability (RSD%, $n = 4$)[a]	
					Fiber-to-fiber	Batch-to-batch
Bifenthrin	3.6	0.9914	0.05–100	6.5	9.2	9.9
Cyhalothrin	5.6	0.9983	0.05–100	4.7	6.3	4.1
Permethrin	29.0	0.9915	0.10–100	4.8	7.9	11.0
Cypermethrin	42.2	0.9939	0.10–100	3.6	6.3	7.1
Phenvalerate	69.4	0.9921	0.10–100	5.0	4.9	9.8
Deltamethrin	18.6	0.9921	0.05–100	1.9	4.3	4.7

[a] The concentration of the standard solution was 10 μg L^{-1} for each compound, and other conditions were the optimized conditions.

Table 3
Analytical results for the determination of pyrethroid pesticides in pond waters.

Analyte	Pond water 1		Pond water 2		Pond water 3	
	No spiking	Recovery[a] (%)	No spiking	Recovery[a] (%)	No spiking	Recovery[a] (%)
Bifenthrin	ND[b]	99 ± 2	ND	104 ± 3	ND	83 ± 5
Cyhalothrin	ND	94 ± 4	ND	95 ± 2	ND	89 ± 6
Permethrin	ND	108 ± 7	ND	86 ± 2	ND	105 ± 6
Cypermethrin	ND	109 ± 9	ND	87 ± 7	ND	110 ± 7
Phenvalerate	ND	104 ± 5	ND	93 ± 4	ND	90 ± 5
Deltamethrin	ND	107 ± 9	ND	88 ± 4	ND	99 ± 4

[a] Recovery of the pyrethroid pesticides spiked at 1 μg L^{-1} in these water samples.
[b] Not detected.

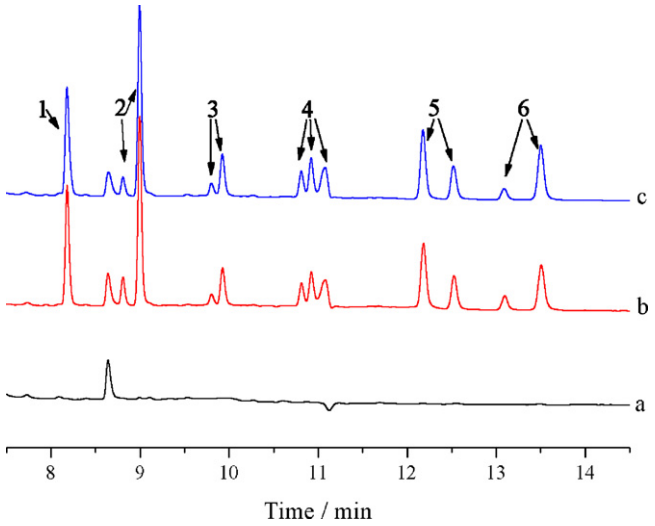

Fig. 7. GC chromatograms obtained using the method developed for (a) pond water 2, (b) pond water 2 spiked with 1 μg L^{-1} of each target, and (c) a mixture of standard solution with each target at 1 μg L^{-1}. Experiment conditions as in Fig. 4. Peak identity: 1, bifenthrin; 2, cyhalothrin; 3, permethrin; 4, cypermethrin; 5, phenvalerate; and 6, deltamethrin.

4. Conclusions

In this paper, we coated the synthesized G onto a stainless steel wire to construct a SPME fiber. The extraction efficiencies of the G-coated fiber towards six selected pyrethroid pesticides were compared with the commercial SPME fibers, PDMS and PDMS/DVB, and the G-coated fiber exhibited higher extraction efficiency than those of the commercial fibers. The main features of the G-coated fiber were its high extraction efficiency, low cost, good reproducibility, long lifespan (more than 250 extractions), good thermal (above 330 °C), chemical and mechanical stability. Combined with GC-ECD detection, the G-coated fiber was successfully applied to analyze pyrethroid pesticides in pond water samples, and the recovery for the samples ranged from 83 ± 5% to 110 ± 7%. These results indicated that the G-coated fiber offers a good alternative for the SPME of pyrethroid pesticides. It could be predicted that G-coated fiber would also show high affinity towards other benzenoid-form compounds via strong π-stacking interaction. Additionally, the potential of G as an SPE adsorbent is being exploited in our laboratory.

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