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Received April 1, 2011
Revised June 25, 2011
Accepted July 3, 2011

Research Article

Polypyrrole/graphene composite-coated fiber for the solid-phase microextraction of phenols

A polypyrrole (Ppy)/graphene (G) composite was developed and applied as a novel coating for use in solid-phase microextraction (SPME) coupled with gas chromatography (GC). The Ppy/G-coated fiber was prepared by electrochemically polymerizing pyrrole and G on a stainless-steel wire. The extraction efficiency of Ppy/G-coated fiber for five phenols was the highest compared with the fibers coated with either Ppy or Ppy/graphene oxide (GO) using the same method preparation. Significantly, compared with various commercial fibers, the extraction efficiency of Ppy/G-coated fiber is better than or comparable to 85 μm CAR/PDMS fiber (best extraction efficiency of phenol, *o*-cresol, and *m*-cresol in commercial fibers) and 85 μm polyacrylate (PA) fiber (best extraction efficiency of 2,4-dichlorophenol and *p*-bromophenol in commercial fibers). The effects of extraction and desorption parameters such as extraction time, stirring rate, and desorption temperature and time on the extraction/desorption efficiency were investigated and optimized. The calibration curves were linear from 10 to 1000 μg/L for *o*-cresol, *m*-cresol, *p*-bromophenol, and 2,4-dichlorophenol, and from 50 to 1000 μg/L for phenol. The detection limits were within the range 0.34–3.4 μg/L. The single fiber and fiber-to-fiber reproducibilities were <8.3 ($n = 7$) and 13.3% ($n = 4$), respectively. The recovery of the phenols spiked in natural water samples at 200 μg/L ranged from 74.1 to 103.9% and the relative standard deviations were $<3.7\%$.

Keywords: GC / Graphene / Phenols / Polypyrrole / Solid-phase microextraction
DOI 10.1002/jssc.201100303

1 Introduction

The solid-phase microextraction (SPME) technique, which was introduced in 1990, has proved to be an effective and powerful sample preparation technique in the recent years [1]. When coupled with gas chromatography (GC) [2] or high-performance liquid chromatography (HPLC) [3], it is widely applied in many disciplines due to its fast, sensitive, and solventless properties. To date, it is used for the extraction of various volatile and semi-volatile organic compounds from environmental [4], pharmaceutical [5], biological [6], and food samples [7], since it combines sample clean-up and preconcentration into one step. Based on the partitioning of analytes between the sample and the coating of the fiber, the latter is considered to be the most important part of the SPME technique. Currently, several kinds of SPME fibers such as non-polar polydimethylsiloxane (PDMS), carboxen/PDMS, semi-polar PDMS/divinylbenzene (PDMS/DVB) and polar polyacrylate (PA), carbowax/DVB, and polyethylene glycol are commercially available. Although these commercial fibers have been successfully applied in many fields, some of them still have drawbacks, such as high cost, nonresistance to high temperature and organic solvents, low extraction efficiency (especially for polar and ionic compounds), and selectivity, etc. To overcome these disadvantages, new SPME coatings with remarkable properties have been developed continually using new preparation methods, including direct use of uncoated fibers [8], sol–gel technology [9], epoxy-glued solid sorbents [10], electrochemical modification [11] and physical deposition [12], or new materials [13, 14].

Electrochemical preparations have been proved useful approaches for developing SPME coatings. A group of very promising SPME coatings using conductive polymers, such as polypyrrole (Ppy), polyaniline, polythiophene, and their derivatives, have been electrochemically prepared and applied for the extraction of polar and ionic compounds [15]. Ppy and its derivatives have been widely used for many

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Abbreviations: DVB, divinylbenzene; **GO**, graphene oxide; **G**, graphene; **PA**, polyacrylate; **Ppy**, polypyrrole; **SDBS**, sodium dodecylbenzenesulfonate; **SPME**, solid-phase microextraction

applications such as chemical sensors, electrochemically controlled devices, and stationary phases for separation and extraction [16] because of their good environmental stability, facile synthesis, and higher conductivity over many other conductive polymers. In the Ppy film preparation, a chemical [17] or electrochemical method [18] is available, but electrochemical synthesis is more convenient since Ppy film can be directly electrodeposited on the surface of a metal wire from an aqueous solution containing pyrrole and an electrolyte. In general, the Ppy-coating characteristics are strongly dependent on the polymerization conditions such as pyrrole concentration, counter-ion concentrations, and types, the voltage applied for electrochemical polymerization, the solvent, and the polymerization and reaction temperature. The electrochemical polymerization of pyrrole in aqueous solutions offers the possibility for a large number of anions to be applied as dopants [19]. The most common dopants or counter-ions used are oxalate, dodecylsulfate, perchlorate, chloride, and sulfate [20]. Ppy is synthesized on a surface of a metal wire using a potentiostatic method and the film applied for some alcohol SPME applications in the gas phase, but unfortunately, the coating could only be used at temperatures below 200°C [21]. However, an electrochemically deposited dodecylsulfate-doped Ppy film is used to determine phenolic compounds in water using headspace solid-phase microextraction, and the prepared coating is of good thermal stability, and can be applied at 300°C [22].

Graphene (G), with its extraordinary properties, was investigated and studied extensively in the recent years and, up to now, G-based materials are applied in many fields [23], such as sensors, biosensors, energy storage, drug delivery, catalytic, and gas separation. As we know, carbon materials have high adsorption capacity for organic compounds and some of them (such as single-walled carbon nanotubes [24], multi-walled carbon nanotubes [25], activated carbon [26], and glassy carbon [27]) have already been employed in SPME. Compared with other graphitic materials, G shows many outstanding advantages, such as high surface area–to-weight (2630 m^2/g), remarkable thermal and chemical stability, and ultra-high mechanical strength [28, 29]. Based on its large delocalized π-electron system, G can form strong π–π stacking interaction with the benzene ring [30], which indicates that it is a good candidate as an SPME coating material for the extraction of benzenoid compounds. In our previous work, G is shown to present its good characteristics in the SPME of six pyrethroid pesticides [31].

Phenols are bio-hazardous materials, which are widely used in various processes such as the manufacture of plastics, dyes, pesticides, papers, and petrochemical products. Now, as the most important contaminants in the environment, they are often found in waters, soils, and sediments. In this study, the Ppy/G coating fiber made using an electrochemical polymerization technique was applied for the SPME determination of phenols in aqueous solutions using gas chromatography coupled with a flame ionization detector (GC-FID). The effects of the main extraction parameters (including the extraction time and stirring rate of SPME, the desorption temperature and time) on the extraction efficiency were investigated in order to achieve the best experiment results.

2 Experimental

2.1 Materials and reagents

Graphite powder, phenol, *o*-cresol, and *m*-cresol used in this study were obtained from Lvyinhuabo (Xiamen, China); the ascorbic acid, pyrrole, sodium dodecylbenzenesulfonate (SDBS), and *p*-bromophenol from Sinopharm Chemical Reagent (Shanghai, China); 2,4-dichlorophenol from J&K Scientific (Shanghai, China); and the *n*-hexane, acetone, and methanol from Tedia (Fairfield, OH, USA). SDBS aqueous solution was used as an electrolyte in the polymerization of Ppy; 1 mg/mL stock solutions of the five phenols were prepared by dissolving 10 mg of each compound in methanol; and the working standard phenol solutions for the SPME procedures were prepared by diluting the mixed standard solution with methanol to the required concentrations. All the chemicals were of analytical reagent grade or HPLC grade. Pure water for solution preparation was from a Millipore autopure WR600A system (USA), and was used throughout the experiments. Stainless-steel wires (od, 0.15 mm) and a 10 μL micro-injector were obtained from the An Ting Micro-Injector Factory (Shanghai, China).

2.2 Equipments

An electrochemical analyzer (LabNet VA5021) was used for the coating preparation. A Hitachi S4800 scanning electron microscope (SEM, Tokyo, Japan) was used to obtain the coating SEM morphologies. A Branson 200 ultra sonicator (Danbury, CT, USA) was used to mix various solution ingredients. In order to compare extraction results, commercial manual sampling SPME devices with 85 μm PA, 75 μm Car/PDMS, 65 μm PDMS/DVB, 50–30 μm DVB/Car/PDMS, and 100 μm PDMS fibers were obtained from Supelco (Bellefonte, PA, USA). A Shimadazu GC-FID was employed for the SPME-GC experiments and a 30 m × 0.25 mm id, 0.25 μm DB-5 column (J&W Scientific) was applied to separate the extracted analytes. The instrumental parameters for the analysis of selected phenols were as follows: injector temperature (250°C), splitless mode (2 min); column flow, N_2 (1.32 mL/min); column temperature program: held at 60°C for 4 min, then at the temperature increased by 10°C/min to 90°C and held for 1 min, then the temperature increased by 10°C/min to 110°C and finally the temperature increased by 30°C/min to 260°C and held for 1 min; detector (FID), 30 mL/min for nitrogen (makeup gas), H_2 flow (40 mL/min), air flow (400 mL/min), temperature (300°C).

2.3 Synthesis of graphene oxide (GO) and G

GO was prepared from graphite powder by chemical exfoliation using the Hummers method [32, 33]. Graphite powder, $NaNO_3$, and concentrated H_2SO_4 were stirred together in an ice bath for 1 h, then $KMnO_4$ was added slowly as an oxidant and the suspension was stirred at room temperature. Wet GO was obtained by centrifugation and washing with pure water, and this was then dried at 40°C for 1 wk to give dry GO. Dry GO was dispersed in water with ultrasonication for 1 h to form GO solution at the selected concentration. The detailed synthetic method is described in our previous work [31]. The GO was characterized using AFM and the result proved that the thickness of the GO was about 1 nm.

Ascorbic acid was selected as a reducing agent for the G product [34]: 50 g ascorbic acid was added to a stirred yellow-brown dispersion of 3 mg/mL GO in 50 mL water, and the resulting mixture was heated to approximately 80°C for 1.5 h. The color of the dispersion changed to black, indicating the reduction of GO into G, accompanied by flocculation of the G. Gradually over a period of approximately 30 min, the reaction was completed. The G was centrifuged and washed with 150 mL deionized water for five cycles. Totally, 30 mL water was added to the residue and it was sonicated for 1 h to give G dispersion (5 mg/mL). Elemental compositions of the GO and the G were determined using Auger electron spectroscopy. The content of oxygen in the GO and the G was found to be 36 and 12%.

2.4 Preparation and characteristics of Ppy-, Ppy/GO- and Ppy/G-coated SPME fibers

Based on the laboratory-assembled SPME device and the position of the ''hot spot'' in the GC injector, the length of the stainless-steel wires was kept constant at 17.5 cm in this study. Prior to coating, the stainless-steel wire was cleaned with acetone, ethanol, and pure water in an ultrasonicator for 10 min each and then air dried at room temperature.

The polymerization process was carried out using a three-electrode system with stainless-steel wire (1.5 cm was immersed into solution) as the working electrode, a saturated calomel electrode as the reference electrode and a platinum wire as the counter electrode at room temperature [22]. A solution was prepared containing 0.10 M SDBS (SDBS as the electrolyte and DBS^- as the counter ion) and 0.050 mol/L pyrrole monomer at pH about 3.0 (a hydrochloric acid solution with concentration of 1.0 mol/L was used to adjust the pH value). The composite polymer coating was directly deposited from this solution onto the steel wire at a constant potential of 0.60 V for 900 s. The thickness of the Ppy coating obtained under this condition was 22 μm based on the SEM observation. The preparation procedures for Ppy/GO or Ppy/G-coated fibers were similar to those of Ppy, but for the addition of GO or G (the final concentration of GO or G was 3 mg/mL) to the solution and sonicating for 30 min to give fine dispersion. After polymerization, the fiber was immersed in pure water for 24 h to remove any deposit, heated at 100°C for 5 h in an oven, and finally conditioned at 260°C in a GC injection port under nitrogen gas for 1 h. Polymerization times from 300 to 1800 s were investigated in order to obtain different thicknesses of Ppy/G-coated fiber.

Figure 1 shows the SEM morphologies of the prepared fiber coatings, and indicates that the coating surfaces were very well distributed and became more rough and rugged from Ppy-coated fiber to Ppy/G-coated fiber. The average thickness of the Ppy and Ppy/GO-coated fibers was about 20 μm, and the thickness of the Ppy/G-coated fiber was about 30 μm when the polymerization time was 600 s.

2.5 SPME

The prepared fiber was assembled in a home-made SPME device [27] conditioned at 250°C for 1 h to remove any possible contaminants before use. A 15 mL glass vial was used as a sample container, and 10 mL of standard solution or sample was placed into the vial together with a spin bar. After homogenizing the vial solution, the needle of the SPME device was passed through the septum. The modified syringe was fixed at a suitable height above the sample vial, so that a 1.5 cm section of the coated fiber was completely

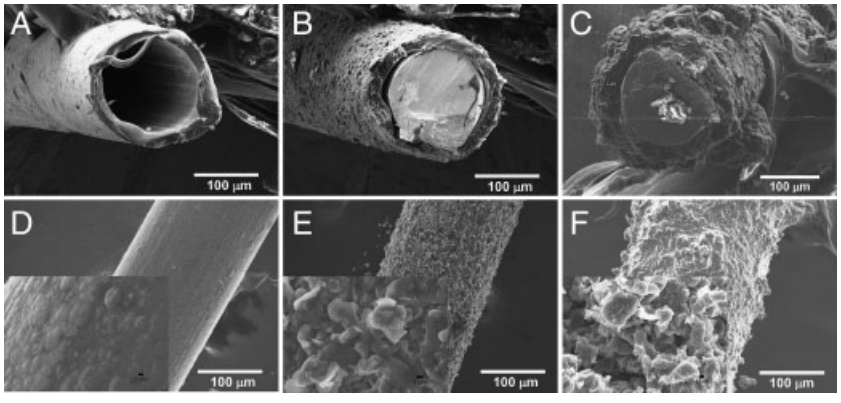

Figure 1. SEM images of Ppy, Ppy/GO and Ppy/G-coated fibers: (A, D) are Ppy-coated fibers at 300 × magnification and the small image in D is that at 3500 ×; (B, E) are Ppy/GO-coated fibers at 300 × and the small image in E is that at 5000 ×; (C, F) are Ppy/G-coated fibers at 300 × and the small image in F is that at 1500 ×.

immersed into the sample solution for 15 min at ambient temperature. After that, the fiber was removed from the sample vial and introduced into the GC injector at 250°C for 2 min desorption.

3 Results and discussion

3.1 Characterization of the prepared fibers

3.1.1 Extraction ability of the three prepared fibers

In this work, five phenols (phenol, *o*-cresol, *m*-cresol, 2,4-dichlorophenol, and *p*-bromophenol) were used as model compounds to evaluate the extraction performance of the prepared fibers. All the fibers were prepared by electrodeposition for 600 s. The extraction ability of the three prepared fibers was evaluated by extracting the five phenols under the same conditions. As shown in Fig. 2, the Ppy-coated fiber could hardly extract any analytes. Because of the strong polarity and the high hydrophilicity of phenol, the phenol extraction efficiency of the Ppy/G-coated fiber was comparable to that of the Ppy/GO-coated fiber. However, for the other four phenols, the extraction efficiency of the Ppy/G-coated fiber was obviously higher than that of the Ppy/GO-coated fiber, especially for the extraction of 2,4-dichlorophenol and *p*-bromophenol. From the SEM images (Fig. 1), it can be seen clearly that the surface of the Ppy-coated fiber was smoother than that of the Ppy/GO and Ppy/G-coated fiber, thus the available surface area was limited. Furthermore, the hydrophobicity of the Ppy/G-coated fiber was stronger than that of the Ppy/GO-coated one, which was good for the adsorption of organic compounds. Probably, with its large delocalized π-electron system, G was highly selective for electron-withdrawing organic compounds, which would explain its high extraction efficiency for 2,4-dichlorophenol and *p*-bromophenol as shown in Fig. 2. Therefore, in the following work, we mainly investigated the analytical performance and characteristics of the Ppy/G-coated fiber.

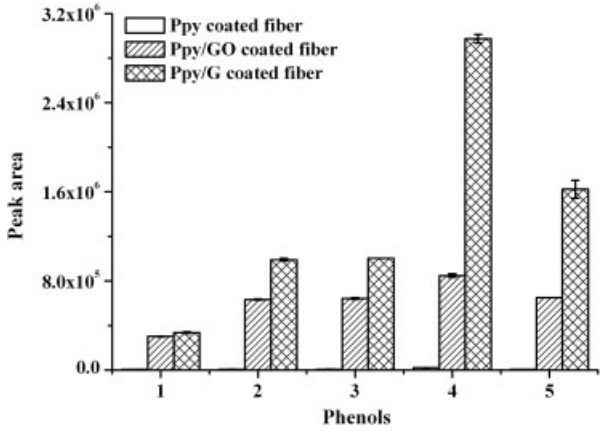

Figure 2. Comparison of the amounts extracted by a Ppy-coated fiber, Ppy/GO-coated fiber and Ppy/G-coated fiber. Peaks: 1, phenol; 2, *o*-cresol; 3, *m*-cresol; 4, 2,4-dichlorophenol; 5, *p*-bromophenol. Conditions: sample volume, 10 mL; extraction time, 15 min; stirring rate, 800 rpm; desorption temperature, 250°C; desorption time, 2 min. Concentration of each phenol, 1 μg/mL; $N = 3$.

3.1.2 Extraction ability of the Ppy/G-coated fibers with different polymerization times

At an applied potential of 0.60 V, the thickness of the coating depended mainly on the polymerization time when the pyrrole concentration, SDBS, and G were constant. Figure 3A shows the influence of polymerization time, since the extraction efficiency of the Ppy/G-coated fiber for phenols increased as the polymerization time increased from 300 to 1200 s. The fiber prepared with longer polymerization time possessed a thicker coating, and thus resulted in higher extraction capacity. However, a thicker fiber coating usually involves a longer balance time for the analytes during the SPME procedure. Considering both the extraction efficiency and balance time, a polymerization time of 600 s was selected for the following work.

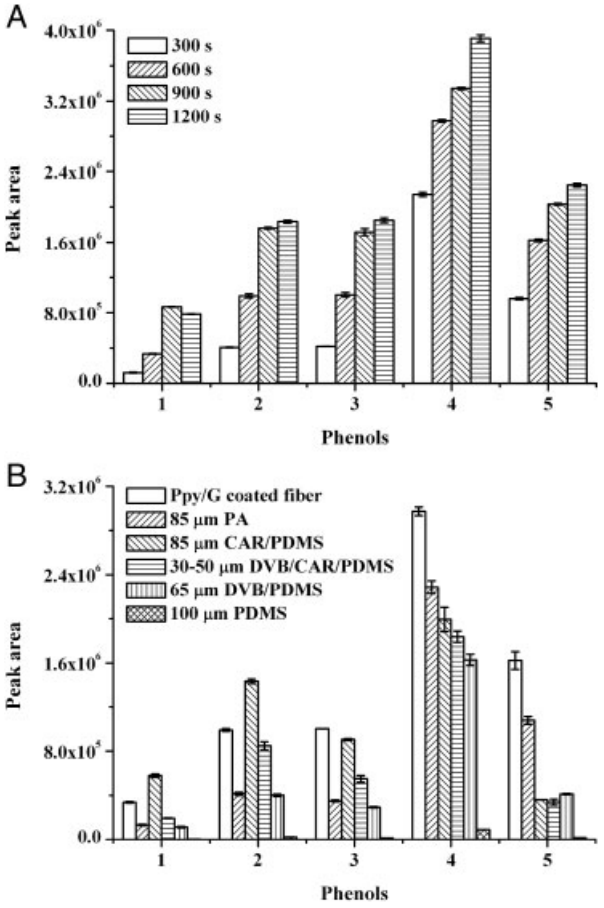

Figure 3. (A) Effect of polymerization time at constant potential 0.60 V during preparation of a Ppy/G-coated fiber on its extraction efficiency for phenols. (B) Comparison of extraction amounts of commercial SPME fibers and a Ppy/G-coated fiber. Peak marks and experimental conditions are the same as in Fig. 2.

3.1.3 Ppy/G-coated fiber compared with commercial fibers

To further evaluate the sensitivity and selectivity of the Ppy/G-coated fiber for the determination of phenols, five commercial fibers (85 μm PA, 85 μm Car/PDMS, 30–50 μm DVB/Car/PDMS, 65 μm PDMS/DVB, and 100 μm PDMS) were selected to compare the extraction efficiency. For phenol, *o*-cresol and *m*-cresol, as shown in the experiment results in Fig. 3B, the 85 μm Car/PDMS fiber gave the highest extraction efficiency among the selected commercial fibers, and was even slightly better than or comparable to that of our Ppy/G-coated fiber. The 85 μm PA fiber gave the highest extraction efficiency among the commercial fibers for 2,4-dichlorophenol and *p*-bromophenol but was not better than our Ppy/G-coated fiber. The experiment results demonstrated that the extraction ability of our Ppy/G-coated fiber for phenols was comparable to, or better than, that of the selected commercial fibers.

3.1.4 Chemical and mechanical stability of the Ppy/G fiber

As shown in the SEM images of the Ppy/G-coated fiber (Fig. 1), through electrochemical polymerization, Ppy could be firmly immobilized on the surface of the stainless-steel wire that was taken as a coating support. Although the G sheets on the coating surface may be scraped slowly during application, based on the experiment results, the fiber could be used more than 50 times without obvious decrease in extraction ability.

To investigate the chemical stability of the Ppy/G-coated fiber toward organic solvents, the fiber was immersed into different organic solvents (hexane, acetonitrile, and methanol) for 3 h, and then cleaned with pure water. Before extracting the analytes, the fiber was conditioned at 250°C for 30 min in an oven to remove any possible solvent residues. The experiment results shown in Fig. 4A indicate that no measurable change in the extraction ability was observed after the fiber was immersed into hexane or acetonitrile. When the fiber was immersed into methanol for 3 h, only slight degradation in the extraction ability could be found for *p*-bromophenol, indicating its good anti-organic solvent ability. As shown in Fig. 4B, the fiber extraction efficiency for the selected phenols was visibly degraded after being treated with strong acid or base (both 1 mol/L). Based on the results obtained, strong acid or base obviously affected the extraction ability of the fiber coating, and so we controlled the sample pH in the range 6–9 in the following work.

3.2 Optimization of the extraction performance

Commonly, experimental conditions such as extraction time, stirring rate, desorption temperature, and desorption time would affect the extraction efficiency. These conditions were investigated and optimized to achieve good extraction results in the experiments.

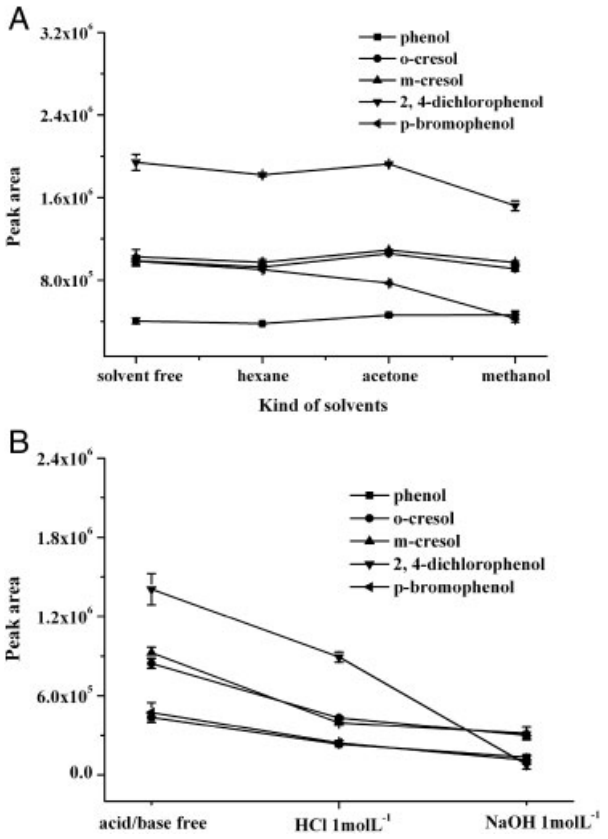

Figure 4. Influence of (A) organic solvents and (B) acid and base on the extraction ability of the Ppy/G-coated fiber. Experiment conditions are the same as in Fig. 2.

3.2.1 Extraction time

The extraction time was an important parameter related to extraction by the Ppy/G-coated fiber. In our work, the effect of the extraction time was investigated at 5, 10, 15, 25, and 35 min. As shown in Fig. 5, the adsorption quantity grows up with the extraction time and reaches an adsorption equilibrium after 25 min. In the routine analysis, it is not necessary to reach equilibrium if extracting conditions are maintained constant [35]. Experiment results revealed that 15 min extraction time was enough to achieve high extraction efficiencies for all phenols, and it was suitable for SPME-GC application. Therefore, in the following experiments, 15 min was selected as the extraction time.

3.2.2 Stirring rate

Generally, magnetic stirring accelerated the transfer of phenols from the water samples to the fiber, resulting in an increased extraction efficiency. The responses increased correspondingly as the agitation speed increased from 200 to 800 rpm in our experiment. Actually, magneton flutter

might lead to the breakage of SPME assembly and air bubbles when the stirring rate was 1000 rpm. Thus, a suitable stirring rate of 800 rpm was selected for further experimentation.

3.2.3 Desorption temperature

In SPME-GC experiments, the desorption temperature must be high enough to effectively release analytes from the coating. The temperature for desorption ranging from 220 to 300°C was investigated in this work. The chromatographic peak area of all five phenols was increased when the desorption temperature grows up from 220 to 250°C and slightly changed when the desorption temperature was above 250°C. Generally, a higher desorption temperature reduced desorption time, but was unfavorable for the lifetime of the coating. Thus, the desorption temperature for subsequent experiments was fixed at 250°C.

3.2.4 Desorption time

To ensure complete desorption and no crossover pollution for the following GC analysis, sufficient desorption time is another important factor. In this experiment, different desorption times of 1, 2, 3, and 4 min were selected to investigate its effect. The amount of desorption compounds increased with the desorption time but were constant after 2 min. No analytes remained after the fiber was desorbed at 250°C for 2 min. Based on these experiment results, the desorption temperature and time in the experiments which followed were set as 250°C and 2 min.

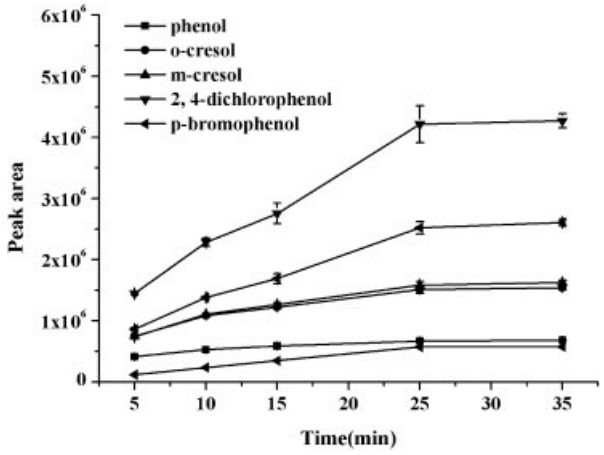

Figure 5. Extraction time profiles of a Ppy/G-coated fiber for five phenols at 1 μg/mL in aqueous solution. Conditions: sample volume, 10 mL; stirring rate, 800 rpm; desorption temperature, 250°C; desorption time, 2 min; $N = 3$.

3.3 Analytical evaluation

The analytical performance and characteristics of the proposed Ppy/G fiber under these optimized conditions were tested using spiked water samples, and the results are shown in Table 1.

The linear ranges of the calibrated curves were 50–1000 μg/L for phenol, and 10–1000 μg/L for the other four phenols, with all the correlation coefficients being larger than 0.99, which allowed the quantification of these compounds through the external standardization method. The limits of detection (LODs), which were defined as three times the baseline noise, were calculated to be 0.3–45 μg/L. The repeatability for each single fiber was performed by extracting aqueous samples spiked at 500 μg/L for each compound (seven replicates). The relative standard deviations were calculated in the range 5.9–8.3%. We also evaluated the fiber-to-fiber reproducibility using four fibers prepared in the same batch, and it was in the range 8.7–13.3%.

3.4 Real sample analysis

The developed method was used for the analysis of surface water samples and the results are shown in Table 2. Three water samples from Furong, Huaxue, and Yuandang Ponds around Xiamen University were collected, filtered, spiked, and analyzed within 24 h. The recovery of the phenol, *o*-cresol, and *m*-cresol spiked in the water samples at 200 μg/L ranged from 86.5 to 103.9% which was higher than that of 2,4-dichlorophenol and *p*-bromophenol (74.1–84.4%). No target analytes were detected in Furong and Yuandang

Table 1. Analytical merits of the proposed SPME-GC method for the determination of phenols[a)]

Compound	Linear range (μg/L)	R^2	LOD (μg/L)	Repeatability ($n = 7$, %)[b)] (single fiber)	Reproducibility ($n = 4$, %)[b)] (fiber-to-fiber)
Phenol	50–1000	0.9956	45.0	8.3	13.3
o-Cresol	10–1000	0.9989	0.9	7.4	8.9
m-Cresol	10–1000	0.9986	0.3	8.0	10.1
2,4-Dichlorophenol	10–1000	0.9966	4.1	6.5	9.1
p-Bromophenol	10–1000	0.9936	3.4	5.9	8.7

a) Experimental conditions: sample volume, 10 mL; extraction time, 15 min; stirring rate, 800 rpm; desorption temperature, 250°C; desorption time, 2 min; $N = 3$.
b) The concentration of the standard solution was 500 μg/L for each compound.

Table 2. Phenol concentrations and recovery in natural water samples using the SPME-GC method under the same conditions as in Table 2 ($N = 3$)

Compound	Furong Pond		Huaxue Pond		Yuandang Pond	
	Concentration (μg/L)	Recovery[b] (%)	Concentration (μg/L)	Recovery[b] (%)	Concentration (μg/L)	Recovery[b] (%)
Phenol	ND[a]	98.6 ± 2.7	ND[a]	102.4 ± 1.9	ND[a]	103.9 ± 1.2
o-Cresol	ND[a]	88.7 ± 0.2	ND[a]	93.8 ± 0.3	ND[a]	91.0 ± 0.1
m-Cresol	ND[a]	86.5 ± 2.7	ND[a]	94.6 ± 1.0	ND[a]	94.9 ± 0.8
2,4-Dichlorophenl	ND[a]	75.7 ± 3.3	ND[a]	81.4 ± 1.5	ND[a]	74.1 ± 1.6
p-Bromophenol	ND[a]	84.4 ± 3.7	22.9 ± 1.2	76.9 ± 1.7	ND[a]	82.1 ± 2.8

a) Not detected.
b) Spiked concentration of each compound was 200 μg/L.

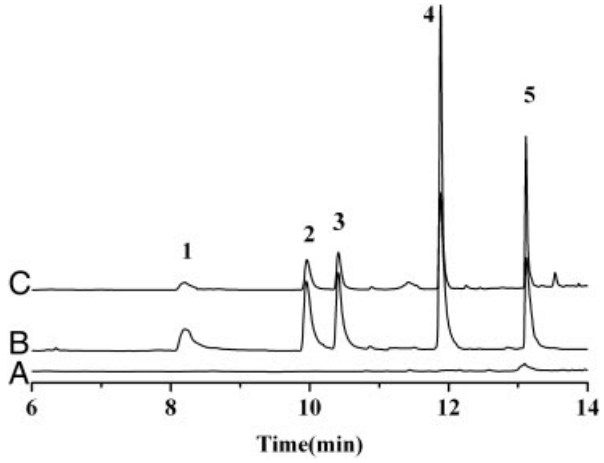

Figure 6. GC-FID chromatograms of phenols extracted using a Ppy/G-coated fiber from (A) Huaxue Pond sample, (B) Huaxue Pond sample spiked with 200 μg/L of each compound, and (C) a mixture of standard solution with each target at 100 μg/L. Peak identity: 1, phenol; 2, *o*-cresol; 3, *m*-cresol; 4, 2,4-dichlorophenol; 5, *p*-bromophenol. Experiment conditions are the same as in Fig. 2.

Ponds, whereas *p*-bromophenol was found at a concentration of 22.9 μg/L in Huaxue Pond. Figure 6 shows a typical chromatogram of a water sample from the Huaxue Pond with and without phenol spiking obtained using the Ppy/G fiber. In Fig. 6, the peak shape of phenols is wide and asymmetric, which shows the same problems of commercial fibers. In the splitless mode, during the sample desorption from the fiber coating, the compounds with lower boiling point would spread faster, which causes peak broadening seriously. Meanwhile, due to the adsorption effect between the fiber coating and phenols, the latter cannot be desorbed rapidly, leading to the peak broadening and tailing.

4 Concluding remarks

In conclusion, a novel fiber prepared by electrochemically polymerizing Ppy and G was developed and used. The extraction efficiency of the prepared Ppy/G-coated fiber for five phenols was highest compared with those obtained from Ppy or Ppy/GO fibers, and also better than or comparable to a number of commercial fibers. With good thermal and mechanical stability, the coating showed a long lifetime with excellent adhesion onto the steel surface. The Ppy/G-coated fiber was successfully applied to analyze phenols spiked into pond water samples at optimized conditions. The proposed method showed good precision, wide linear range, low detection limits, and high recoveries. This composite coating is expected to have considerable potential for preconcentration and determination of other analytes.

This research was financially supported by the Science and Technology Projects of Fujian Province (No. 2010Y0050), the Nature Scientific Foundation of Fujian (2009J01042), the Program of Science and Technology of Xiamen for University Innovation (3502Z20093004) and the National Nature Scientific Foundation of China-Korea Joint Research Project (No. 20911140274), which are gratefully acknowledged. Furthermore, we would like to extend our thanks to Professor John Hodgkiss of The University of Hong Kong for his assistance with English.

The authors have declared no conflict of interest.

5 References

[1] Arthur, C. L., Pawliszyn, J., *Anal. Chem.* 1990, *62*, 2145–2148.

[2] Oomen, A. G., Mayer, P., Tolls, J., *Anal. Chem.* 2000, *72*, 2802–2808.

[3] Wu, J. C., Pawliszyn, J., *Anal. Chem.* 2001, *73*, 55–63.

[4] Polo, M., Noya, G. G., Quintana, J. B., Llompart, M., Jares, C. G., Cela, R., *Anal. Chem.* 2004, *76*, 1054–1062.

[5] Camarasu, C., Madichie, C., Williams, R., *Trend Anal. Chem.* 2006, *25*, 768–777.

[6] Lambropoulou, D. A., Konstantinou, I. K., Albanis, T. A., *J. Chromatogr. A* 2006, *1124*, 97–105.

[7] Cao, C. F., Wang, Z., Urruty, L., *J. Agric. Food Chem.* 2001, *49*, 5092–5097.

[8] Sun, T. H., Jia, J. P., Fang, N. H., Wang, Y. L., *Anal. Chim. Acta* 2005, *530*, 33–40.

[9] Chong, S. L., Wang, D. X., Hayes, J. D., Wilhite, B. W., Malik, A., *Anal. Chem.* 1997, *69*, 3889–3898.

[10] Hou, J. G., MA, Q., Du, X. Z., Deng, H. L., Gao, J. Z., *Talanta* 2004, *62*, 241–246.

[11] Mehdinia, A., Mousavi, M. F., Shamsipur, M., *J. Chromatogr. A* 2006, *1134*, 24–31.

[12] Wang, J. X., Jiang, D. Q., Gu, Z. Y., Yan, X. P., *J. Chromatogr. A* 2006, *1137*, 8–14.

[13] Cui, X. Y., Gu, Z. Y., Jiang, D. Q., Li, Y., Wang, H. F., Yan, X. P., *Anal. Chem.* 2009, *81*, 9771–9777.

[14] Zhao, Q. C., Wajert, J. C., Anderson, J. L., *Anal. Chem.* 2010, *82*, 707–713.

[15] Wu, J., Mullett, W. M., Pawliszyn, J., *Anal. Chem.* 2002, *74*, 4855–4859.

[16] Lewis, T. W., Wallace, G. G., Smyth, M. R., *Analyst* 1999, *124*, 213–219.

[17] Zhong, W. B., Liu, S. M., Chen, X. H., Wang, Y. X., Yang, W. T., *Macromolecules* 2006, *39*, 3224–3230.

[18] Sakkopoulos, S., Vitoratos, E., Dalas, E., *Synth. Met.* 1998, *92*, 63–67.

[19] Waren, L. F., Anderson, D. P., *J. Electrochem. Soc.* 1987, *134*, 101–105.

[20] Tüken, T., Yazic, B., Erbil, M., *Prog. Org. Coat.* 2004, *50*, 115–122.

[21] Wu, J., Pawliszyn, J., *J. Chromatogr. A* 2001, *909*, 37–52.

[22] Alizadeh, N., Zarabadipour, H., Mohammadi, A., *J. Chromatogr. A* 2007, *605*, 159–165.

[23] Rao, C. N. R., Sood, A. K., Subrahmanyam, K. S., Govindaiaj, A., *Angew. Chem. Int. Ed.* 2009, *48*, 7752–7777.

[24] Lü, J., Liu, J., Wei, Y., Jiang, K., Fan, S., Liu, J., Jiang, G., *J. Sep. Sci.* 2007, *30*, 2138–2143.

[25] Zhang, W. Y., Sun, Y., Wu, C. Y., Xing, J., Li, J. Y., *Anal. Chem.* 2009, *81*, 2912–2920.

[26] Chai, X. L., He, Y., Jia, J. P., *J. Chromatogr. A* 2007, *1165*, 26–31.

[27] Zeng, J. B., Yu, B. B., Chen, W. F., Lin, Z. J., Zhang, L. M., Lin, Z. Q., Chen, X., Wang, X. R., *J. Chromatogr. A* 2008, *1188*, 26–33.

[28] Chen, H. Q., Muller, M. B., Gilmore, K. J., Wallace, G. G., Li, D., *Adv. Mater.* 2008, *20*, 3557–3561.

[29] Matthew, J. A., Vincent, C. T., Richard, B. K., *Chem. Rev.* 2010, *110*, 132–145.

[30] Cai, Y. Q., Jiang, G. B., Liu, J. F., Zhou, Q. X., *Anal. Chem.* 2003, *75*, 2517–2521.

[31] Chen, J. M., Zou, J., Zeng, J. B., Song, X. H., Ji, J. J., Wang, Y. R., Ha, J., Chen, X., *Anal. Chim. Acta* 2010, *678*, 44–49.

[32] Hummers, W. S., Offeman, R. E., *J. Am. Chem. Soc.* 1958, *80*, 1339–11339.

[33] Xu, Y. X., Bai, H., Lu, G. W., Li, C., Shi, G. Q., *J. Am. Chem. Soc.* 2008, *130*, 5856–5857.

[34] Dua, V., Surwade, S. P., Ammu, S., Agnihotra, S. R., Jain, S., Robert, K. E., Manohar, S. K., *Angew. Chem. Int. Ed.* 2010, *49*, 2154–2157.

[35] Ai, J., *Anal. Chem.* 1997, *69*, 1230–1236.

