Au nanoparticles as a novel coating for solid-phase microextraction

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ABSTRACT

A novel solid-phase microextraction fiber based on a stainless steel wire coated with Au nanoparticles was prepared and has been applied, coupled with gas chromatography, to the extraction of aromatic hydrophobic organic chemical pollutants in rainwater and soil extract. The solid-phase microextraction fiber exhibited excellent extraction efficiency and selectivity. Effects of extraction time, extraction temperature, ionic strength, stirring rate and desorption conditions were investigated and optimized. Single fiber repeatability and fiber-to-fiber reproducibility were less than 7.90% and 26.40%, respectively. The calibration curves were linear in a wide range for all analytes. Correlation coefficients ranged from 0.9941 to 0.9993. The as-established SPME-GC method was used successfully to two real natural samples. Recovery of analytes spiked at $10 \mu g L^{-1}$ and $100 \mu g L^{-1}$ ranged from 78.4% to 119.9% and the relative standard deviations were less than 11.3%.

1. Introduction

Solid-phase microextraction (SPME), firstly introduced by Belardi and Pawliszyn [1], has got many applications in food [2,3], environment [4], biochemistry [5,6] and medicine [7] because of its sensitivity, rapidity, simplicity and free of solvent [8]. It has been coupled with various instruments and analytical technologies such as GC [9], HPLC [10,11], CE [12], UV [13,14] and MS [15]. Further development of SPME related intimately to the preparation and characterization of new sorbent materials. Molecular imprinted polymer [16], mesoporous materials [17], nanomaterials [18,19] and some organic polymers [20] have been used successfully as functional coatings over fused-silica fiber or metal wire supports.

Nanomaterials possessing excellent physical and chemical properties have attracted great attention lately in the separation science. Carbon nanotubes [8], fullerenes [21], nanoporous silica [18] and some nano-structured metal oxides [19,22] have been successfully used as SPME fiber coatings. Au nanoparticles (Au NPs) share many important properties with materials mentioned above and keep some special properties such as long term stability, easiness in chemical modification, compatibility with biomolecules

[23], and so on. Organic molecules containing thiol (SH) or amino (NH_2) groups can be adsorbed spontaneously onto the Au surface to form a well organized self-assembled monolayer (SAM) [24]. Researchers have made use of these properties to develop applications of Au NPs in analytical and separation science for a long time. Chi et al. [25] used a sensitive and simple colorimetric visualization method to detect melamine easily with citrate stabilized Au NPs, in which trace melamine of 25 ppb in real milk samples was quickly detected. Au NPs have been widely used in capillary electrochromatography and capillary electrophoresis as pseudo-stationary phase or stabilized on modified fused-silica capillary to separate neutral steroid drugs [7], polycyclic aromatic hydrocarbons (PAHs) [26] and biomolecules [5,6]. Currently available utilization in the sample preconcentration is mainly focused on solid-phase extraction [27], nanoparticle-single drop microextraction [28] and solid-phase nanoextraction [29]. Extraordinary properties of Au NPs deserve further investigations in other sample preparation method such as in SPME.

Based on these considerations, we prepared a novel Au NPs/SPME fiber through a simple layer by layer (LBL) self-assembly process. A new way to extract and preconcentrate PAHs, diphenyl and terphenyls in aqueous solution was developed using the physicochemical affinity between aromatic hydrophobic organic chemicals (HOCs) and Au NPs. The inherent chemical stability of gold makes the novel Au NPs/SPME fiber show high stability and durability towards acid, alkali and high temperature. The single fiber repeatability and fiber-to-fiber reproducibility are both satisfactory. The as-prepared fiber also has remarkable selec-

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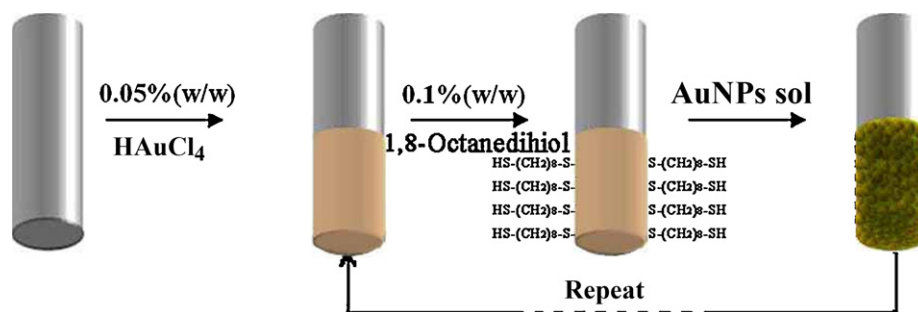E-mail address: sxjiang@lzb.ac.cn (S. Jiang).

Fig. 1. Schematic diagram of Au NPs/SPME fiber preparation process.

tivity towards compounds with high hydrophobicity and large π-electron systems.

2. Experimental

2.1. Instruments

An Agilent 7890A series gas chromatograph (Agilent Technologies, USA) equipped with a flame ionic detector was used. Chromatographic separation was carried out on an AT.SE-54 capillary column (30 m × 0.32 mm id. × 0.33 μm film thickness).

Ultrapure nitrogen (>99.999%) was used as the carrier and make-up gas at 1 ml min^{-1} and 30 ml min^{-1}, respectively. Both the injector and detector temperatures were fixed at 300 °C. Separation was achieved using temperature programs as follows: for PAHs, diphenyl and two terphenyls, the column temperature was initially held at 100 °C, and programmed at 5 °C min^{-1} to 215 °C, being held for 5 min, then at the rate of 1 °C min^{-1} to 223 °C, finally at 15 °C min^{-1} to 260 °C; for n-alkanes, phenols and amines, the column temperature was initially held at 50 °C, and programmed at 5 °C min^{-1} to 300 °C.

Scanning electron microscope micrographs of the Au NP fiber were obtained on a field emission scanning electron microscope (FESEM, JSM-6701F, Japan). Energy dispersive X-ray fluorescence (XRF) analysis was performed on a XRF spectrometer (EDAX-Genesis XMZ, USA) with a 20 kV of applied voltage and 10 μA of current.

2.2. Chemicals and solutions

The stainless steel wire (SUS304, Φ140 μm) was purchased from the Yixing Shenglong Metal Wire Net Co. (Jiangsu, China). Naphthalene, anthracene, fluorene, fluoranthene, 1-bromonaphthalene, diphenyl, m-terphenyl and p-terphenyl were obtained from the Shanghai Chemical Reagent Factory (Shanghai, China); n-hexane, n-octane, n-nonane, n-undecane, n-tridecane, n-hexadecane and n-heneicosane were purchased from the Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China); aniline, 4-toluidine, 4-chloroaniline and 1-naphthylamine were purchased from the Tianjin Chemical Reagent No. 1 Plant (Tianjin, China); phenol, 4-methylphenol, 4-chlorophenol, and 1-naphthol were purchased from the Beijing Chemical Reagent Factory (Beijing, China); 1,8-octanedithiol was obtained from the Alfa Aesar, chloroauric acid (HAuCl$_4$·4H$_2$O) was purchased from the Shenyang Keda Chemical Reagent Factory (Liaoning, China); trisodium citrate (C$_6$H$_5$Na$_3$O$_7$·2H$_2$O) was purchased from the Wuxi Minfeng Chemical Reagent Factory (Jiangsu, China). All chemicals were of analytical grade. 1,8-Octanedithiol was dissolved in ethanol with concentration of 30% (w/w) as stock solution. HAuCl$_4$·4H$_2$O of 1% (w/w) was prepared using distilled water as solvent. Analytes were dissolved in ethanol with concentration of 250 mg L^{-1}. All the stock solutions were stored at 4 °C for use.

2.3. Preparation procedures

2.3.1. Preparation of Au nanoparticles

Au nanoparticles were prepared through the reduction of HAuCl$_4$ by trisodium citrate as described by Frens and Kolliod [30]. Briefly, 30 mL of HAuCl$_4$ aqueous solutions (0.01%, w/w) was heated at 115 °C under vigorous stirring. While boiling, 0.6 mL of trisodium citrate aqueous solution (1%, w/w) was added very quickly. The solution turned to wine red in 2 min. After a 15 min reaction, the heating was stopped but the stirring was kept until the solution was cooled to room temperature. Nanoparticles prepared under these conditions were proved to be more regular and stable. The product was stored at 4 °C.

2.3.2. Preparation of Au NPs/SPME fiber

Preparation steps of Au NPs/SPME fiber are shown in Fig. 1 briefly and detailed as follows: (1) One end of the stainless steel wire (2 cm) was firstly washed with acetone, ethanol and distilled water in an ultrasonic bath for 10 min respectively and then dried at room temperature. Secondly, the wire was dipped in a HAuCl$_4$ solution (0.05%, w/w) for 3 h and then washed with deionized water. (2) The stored dithiol solution (30%, w/w) was diluted to 0.1% with ethanol. The pretreated stainless steel wire was then put into it for 12 h to form a SAM of dithiol; the excess 1,8-octanedithiol was removed through washing with ethanol. Afterwards, the fiber was immersed in the Au NPs gel (as prepared in Section 2.3.1) for another 48 h to absorb Au NPs onto the SAM; the excess Au NPs
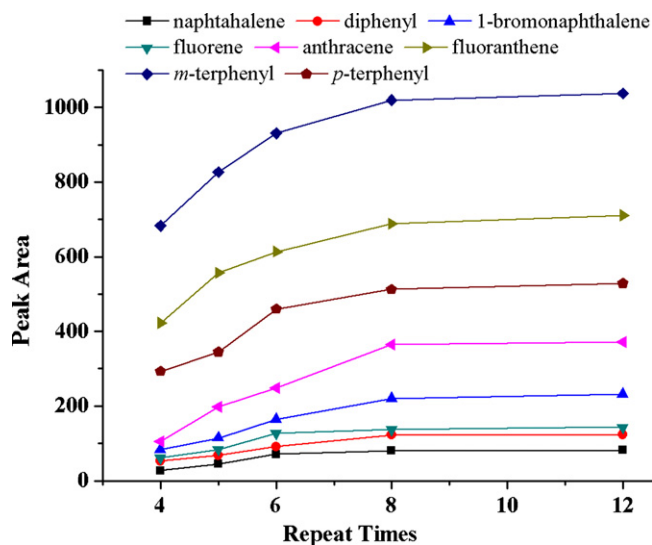

Fig. 2. Effect of repeat times on extraction capability. Conditions: concentration, 200 μg L^{-1}; extraction time, 50 min; extraction temperature, 60 °C; NaCl content, 20% (w/w); stirring rate, 800 rpm; desorption temperature, 300 °C; desorption time, 6 min.
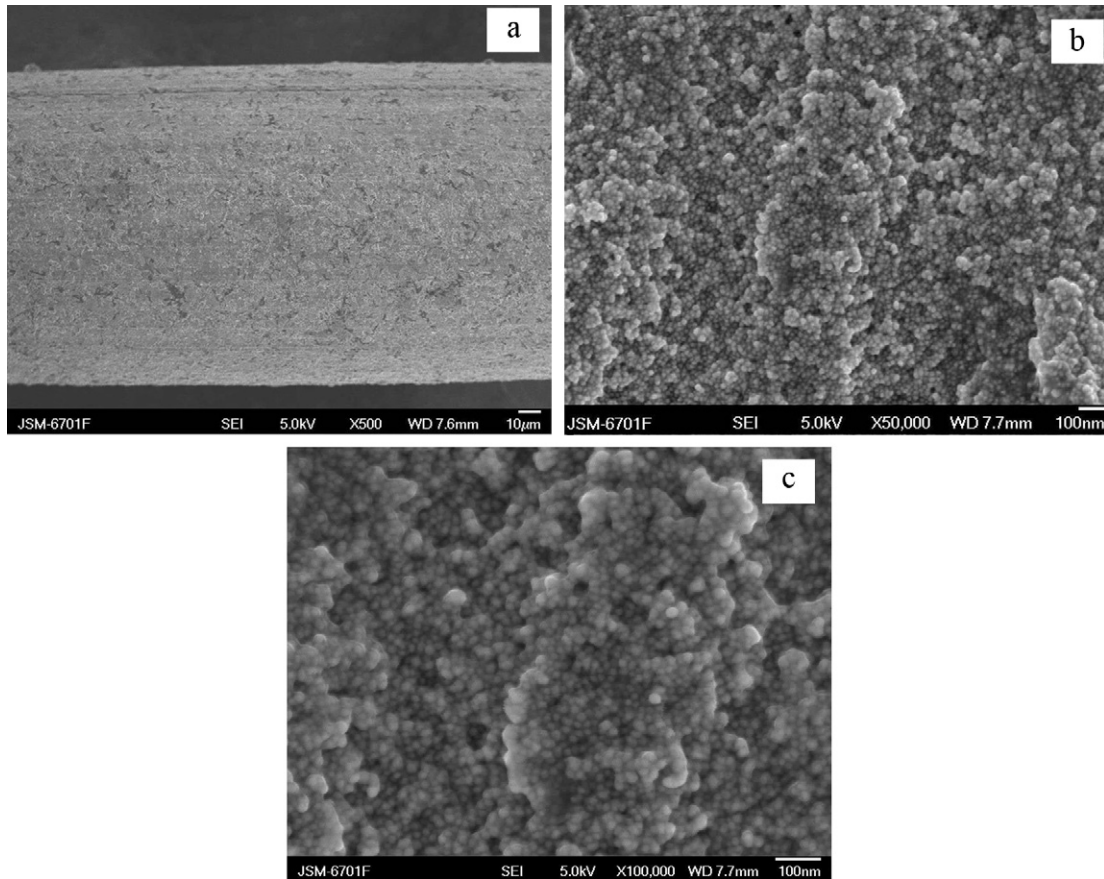
Fig. 3. FESEM images of stainless steel wire after modification by Au NPs at magnification of 500 (a); 50,000 (b); 100,000 (c).

were removed by washing with deionized water. This procedure was repeated for about eight times. The color of stainless steel wire was turned to dark bluish-grey after the entire preparation procedures.

2.4. Solid-phase microextraction

Before the SPME experiment, the Au NPs/SPME fiber was aged at 300 °C for 0.5 h under nitrogen. The fiber was installed into a homemade SPME device which was a modification of a 5 μm syringe [31]. 20 mL of sample solution (0.2 μg mL^{-1}) was put in a 25 mL glass vial with a rubber cork. The modified syringe was placed into the sample vial and the fiber was dipped in the sample solution directly. A magnetic agitator was used to accelerate the extraction. The extraction was performed under optimized conditions (temperature, time, ionic strength, and stirring rate). After the extraction, the fiber was withdrawn into the needle and
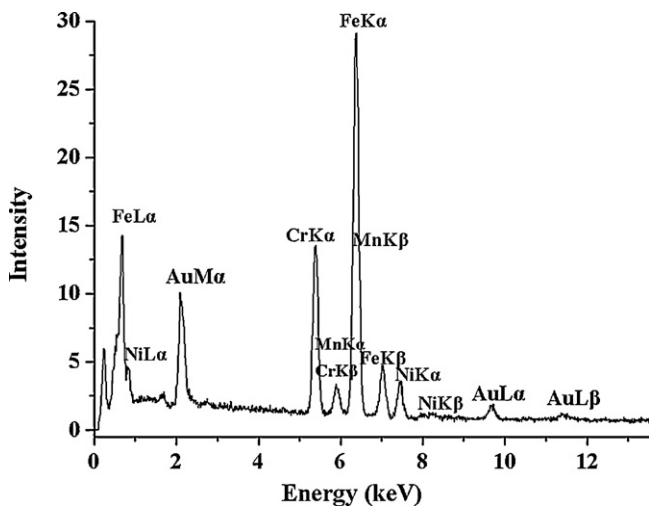

Fig. 4. Energy dispersive XRF analysis of Au NPs/SPME fiber.
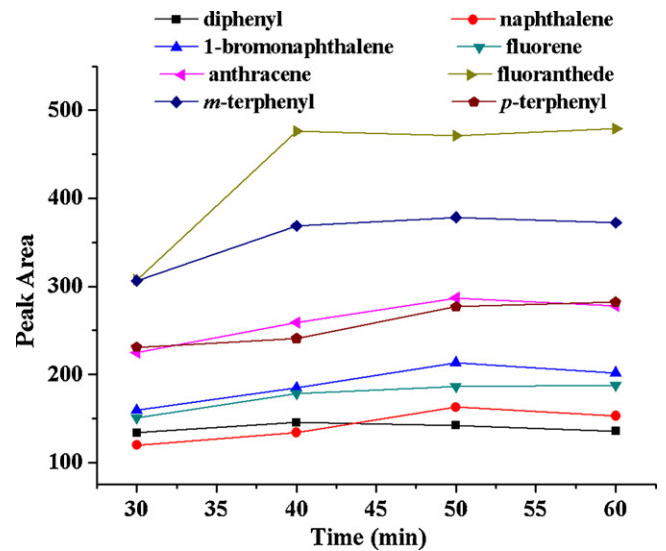

Fig. 5. Effect of extraction time on peak area of analytes. Conditions: concentration, 200 μg L^{-1}; extraction temperature, 60 °C; NaCl content, 20% (w/w); stirring rate, 800 rpm; desorption temperature, 300 °C; desorption time, 6 min.
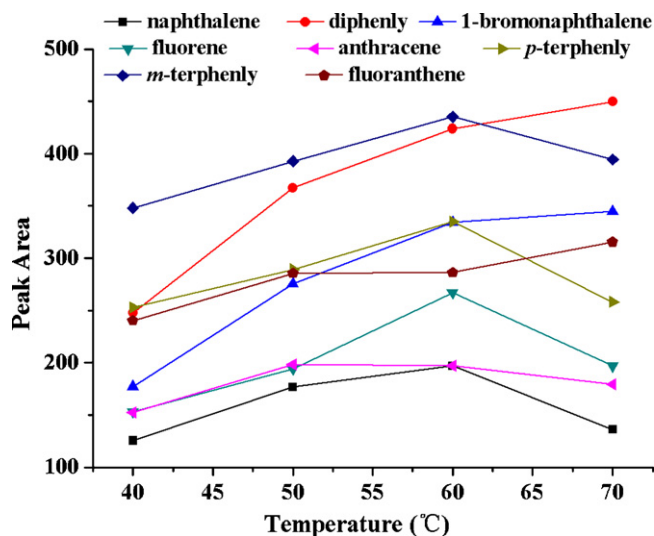
Fig. 6. Effect of extraction temperature on peak area of analytes. Conditions: concentration, 200 μg L^{-1}; extraction time, 50 min; NaCl content, 20% (w/w); stirring rate, 800 rpm; desorption temperature, 300 °C; desorption time, 6 min.

introduced into the GC inlet [32]. Desorption conditions were also optimized.

3. Results and discussion

3.1. Preparation of Au NPs/SPME fiber

Fig. 1 shows the preparation process of Au NPs/SPME fiber. It mainly included two sections.

3.1.1. Pretreatment of the stainless steel wire

Purpose of this procedure was to form an Au film on the wire surface through a reduction reaction between chloroauric acid (HAuCl$_4$) and the wire. HAuCl$_4$ is high caustic and the stainless steel wire easily broke in a concentrated HAuCl$_4$ solution or after a long-time reaction. The optimum HAuCl$_4$ concentration was investigated: we immersed the stainless steel wire in HAuCl$_4$ solutions with concentrations at 1%, 0.5%, 0.1%, 0.05%, 0.005% and 0.001%,
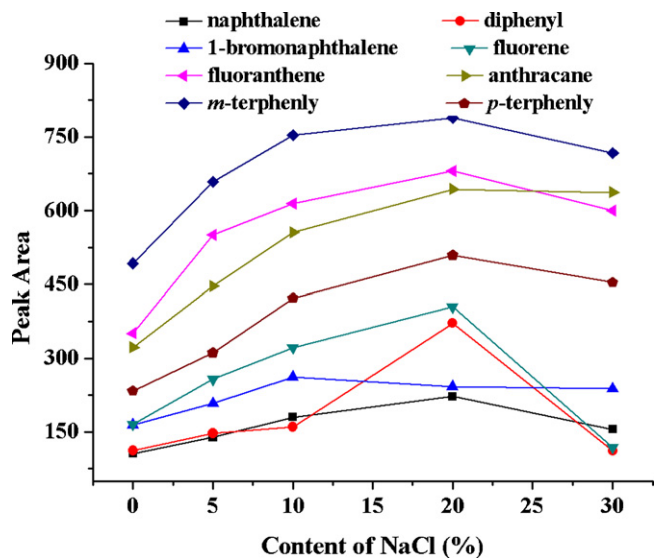

Fig. 7. Effect of NaCl content on peak area of analytes. Conditions: concentration, 200 μg L^{-1}; extraction time, 50 min; extraction temperature, 60 °C; stirring rate, 800 rpm; desorption temperature, 300 °C; desorption time, 6 min.
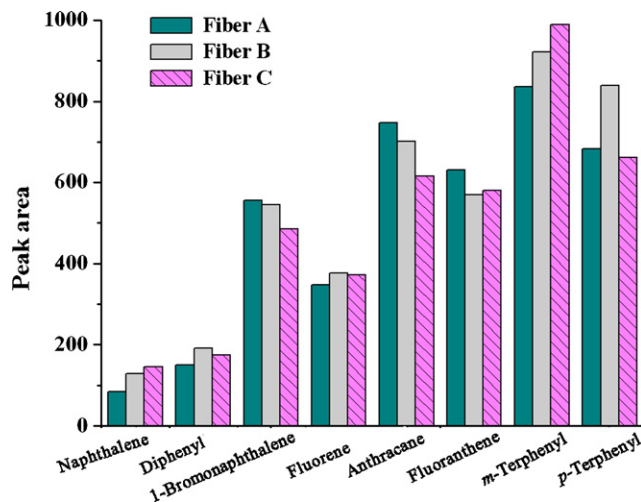

Fig. 8. Fiber-to-fiber reproducibility for Au NPs/SPME fiber preparation. Conditions: concentration, 200 μg L^{-1}; extraction time, 50 min; extraction temperature, 60 °C; content of NaCl, 20% (w/w); stirring rate, 800 rpm; desorption temperature, 300 °C; desorption time, 6 min.

respectively. As the experiment shows, more diluted solution (≤0.005%, w/w) needed a longer time reaction and more concentrated solution (≥0.1%, w/w) strongly corroded the stainless steel wire in a short time. So we chose 0.05% as the final concentration and the time was fixed at 3 h to obtain a satisfactory coverage of Au film and avoid mortal damage of stainless steel wire at the same time. Reaction between the wire and HAuCl$_4$ is shown as follows:

$$Fe + AuCl_4^- \rightarrow Fe^{3+} + Au + Cl^- \tag{1}$$
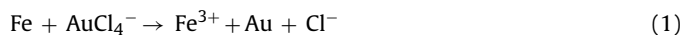
After the reaction, the surface of the stainless steel wire was covered with a thin film of Au and the color turned into pale pink. Untreated stainless steel wire could not form SAM of 1,8-octanedithiol and no Au NPs could be coated on it. So the process of reduction reaction was necessary and crucial.

3.1.2. Assembly of Au NPs onto the pretreated stainless steel wire

Concentration of dithiol in SAM formation was usually millimolar [33], so we dipped the pretreated fiber into the 0.1% (w/w) solutions of 1,8-octanedithiol and the time was fixed at 12 h according to some reports [34,35]. To obtain a higher Au NP immobilization efficiency on the SAM, the fiber was immersed in Au NP sol for 48 h. Thickness of the Au NP coatings determined the extraction efficiency to a great extent. As shown in Fig. 2, peak areas increase greatly with repeat times from four to eight. After eight times assembly, extraction efficiency increases slightly. In the view of saving preparation time, preparation of Au NPs/SPME fiber completed after eight times assembly of Au NPs.

Fig. 3 shows the FESEM images of the stainless steel wire after modification. It can be clearly seen that Au NPs are immobilized on the wire surface tightly. Au NPs are extremely uniform and the grain size is about 20 nm. Surface area of the fiber was very large because of the tiny nanoparticles, and this was favorable for efficient extraction. Tiny grain size also made the coating too thin to be measured by our available method. Energy dispersive XRF was used to verify the adsorption of Au NPs onto the fiber. As shown in Fig. 4, 2.1 keV is an M$_{\alpha 1}$ peak of gold [36]. Peaks at 9.6 and 11.3 keV are assigned to the L$_\alpha$ and L$_\beta$ of gold respectively [7]. These results clearly demonstrated the successful immobilization of Au NPs on the stainless steel wire. Since the detection depth of XRF analysis is about 1 μm, peaks of the matrix elements (Fe, Cr, Ni, and Mn) can also be seen in Fig. 4.

Table 1
Enhancement factors (EFs) and log$P$[a] for different analytes extracted on Au NPs/SPME fiber.

Compounds	ACD[b]/log$P$	EF ($n=3$)	Compounds	ACD/log$P$	EF ($n=3$)	Compounds	ACD/log$P$	EF ($n=3$)
Naphthalene	3.45	39.4 ± 1.3	n-Hexane	3.94	Not detected	Phenol	1.48	Not detected
Diphenyl	3.98	66.1 ± 4.1	n-Octane	5.01	Not detected	4-Methylphenol	1.94	Not detected
1-Bromonaphthalene	4.22	77.6 ± 13.6	n-Undecane	6.60	11.4 ± 3.0	4-Chlorophenol	2.43	Not detected
Fluorene	4.16	58.0 ± 4.4	n-Tridecane	7.66	27.7 ± 6.7	1-Naphthol	2.71	Not detected
Anthracene	4.68	105.2 ± 7.14	n-Hexadecane	9.26	170.9 ± 9.0	Aniline	0.94	Not detected
Fluoranthene	5.17	202.5 ± 10.6	n-Octadecane	10.32	189.7 ± 2.2	4-Methylamine	1.40	Not detected
m-Terphenyl	6.02	256.3 ± 7.2	n-Heneicosane	11.91	222.2 ± 9.1	4-Chloroaniline	1.76	Not detected
p-Terphenyl	5.63	158.0 ± 13.5				1-Naphthylamine	2.17	Not detected

[a] Octanol/water partition coefficient, measurement of how hydrophilic or hydrophobic a chemical substance is.
[b] Advanced Chemistry Development, maker of related database. Conditions: for aromatic HOCs, sample concentration, 200 μg L^{-1}; extraction time, 50 min; extraction temperature, 60 °C; NaCl content, 20%; desorption temperature, 300 °C; desorption time, 6 min. For n-alkanes, sample concentration, 200 μg L^{-1}; extraction time, 40 min; extraction temperature, 60 °C; NaCl content, 30% (w/w); desorption temperature, 300 °C; desorption time, 6 min.

Table 2
Analytical parameters of the Au NPs/SPME-GC method for the determination of analytes under the same conditions as in Table 1 and comparisons of the LODs with other methods.

Compounds	Linear range (μg L^{-1})	Linearity/R^2	LOD (ng L^{-1})	Repeatability ($n=3$, %) (single fiber)	Reproducibility ($n=3$, %) (fiber-to-fiber)	LODs[a] with commercial fiber [42] (ng L^{-1})		LODs[a] of Xu's method (ng L^{-1}) [43]	LODs of EPA method 601 (ng L^{-1}) [44]
						PDMS	PA		
Naphthalene	1–300	0.9984	250	2.49	26.40	150	220	240	1800[b]
Diphenyl	0.5–300	0.9987	50	4.27	12.27	–	–	–	–
1-Bromonaphthalene	0.5–300	0.9968	50	5.72	7.3	–	–	–	–
Fluorene	0.5–250	0.9948	50	4.27	4.28	80	80	300	210[b]
Anthracene	0.5–250	0.9993	25	6.42	11.13	180	110	–	660[c]
Fluoranthene	0.05–200	0.9964	25	7.90	5.6	250	170	580	210[c]
m-Terphenyl	0.05–200	0.9971	12.5	4.24	8.34	–	–	–	–
p-Terphenyl	0.05–200	0.9941	12.5	3.55	13.58	–	–	–	–

[a] SPME-GC-FID.
[b] LLE-HPLC-UV.
[c] LLE-HPLC-FLD.

3.2. Optimization of SPME parameters

3.2.1. Extraction time

The absorption and desorption of sample molecules on SPME fiber is a dynamic equilibrium. Normally, the time needed for equilibrium is the best for the extraction. As can be seen from Fig. 5, peak areas increase as the time increase from 30 to 50 min and reach a relatively stable stage after a 50 min extraction. So 50 min was chosen as the suitable extraction time.

3.2.2. Extraction temperature

Temperature has double influence on the SPME extraction: a higher temperature increases the values of diffusion coefficient and Henry's constant but decreases the distribution coefficient. Elevated diffusion coefficient is favorable for the diffusion of analytes to the fiber coatings and decreases the time for equilibrium, while decrease of the distribution coefficient reduces the adsorption capacity of the coating. So there will be a platform or a summit on the temperature–extraction capability curve. From the correlation studies on temperature and peak areas shown in Fig. 6, for most of analytes, the highest extraction efficiency is reached at 60 °C while some of them need a long time to reach equilibrium. Under the comprehensive consideration on analytical time and extraction capability, 60 °C was chosen as the optimum temperature.

3.2.3. Ionic strength

Ionic strength also has double effects on the extraction. With the increase of ionic strength, salting-out effect and procompetitive effect will influence the extraction diversely. We used NaCl to change the ionic strength of the sample solution in the range of 0–30% (w/w). As shown in Fig. 7, when the content of NaCl is lower than 20%, salting-out effect plays the major role and peak area increases with the increase of NaCl content. When the content of NaCl is higher than 20%, procompetitive effect is principal, and peak areas decrease with the increase of NaCl content. So, 20% was selected as the suitable content of NaCl.
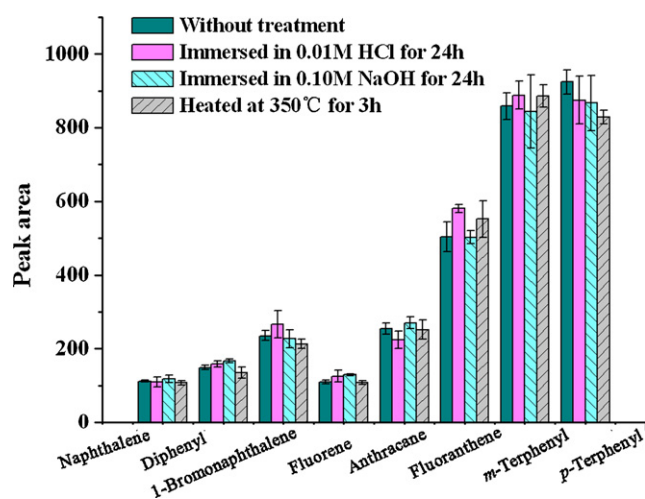

Fig. 9. Stability of Au NPs/SPME fiber. Conditions: concentration, 200 μg L^{-1}; extraction time, 50 min; extraction temperature, 60 °C; content of NaCl, 20% (w/w); stirring rate, 800 rpm; desorption temperature, 300 °C; desorption time, 6 min.

Table 3
Aromatic HOC concentration and recovery in real samples (n = 3) under the same conditions as in Table 1.

Compounds	Rainwater			Soil extract		
	Concentration (μg L^{-1})	Recovery (%)		Concentration (μg L^{-1})	Recovery (%)	
		Spiked 10 μg L^{-1}	Spiked 100 μg L^{-1}		Spiked 10 μg L^{-1}	Spiked 100 μg L^{-1}
Naphthalene	Not detected	110.1 ± 5.7	98.6 ± 5.0	84.0 ± 10.0	111.4 ± 6.8	119.9 ± 3.0
Diphenyl	Not detected	92.4 ± 6.3	84.5 ± 0.75	Not detected	87.3 ± 4.7	76.8 ± 2.4
Fluorene	Detected but not quantified	86.1 ± 2.5	102.4 ± 10.2	Not detected	94.8 ± 1.9	85.5 ± 3.3
Anthracene	17.2 ± 1.5	86.6 ± 9.2	113.9 ± 4.0	40.5 ± 3.7	98.6 ± 4.9	108.8 ± 4.4
Fluoranthene	18.1 ± 2.3	101.2 ± 10.7	96.8 ± 1.6	15.3 ± 3.6	106.0 ± 9.9	80.7 ± 1.4
m-Terphenyl	20.8 ± 4.0	99.5 ± 6.9	110.2 ± 4.9	24.0 ± 1.5	98.3 ± 10.5	87.8 ± 5.7
p-Terphenyl	18.8 ± 7.7	88.0 ± 6.2	78.4 ± 5.7	20.2 ± 2.1	114.2 ± 11.3	114.3 ± 6.5
Total	54.1			184.0		

3.2.4. Effect of stirring rate

Stirring, improves the extraction through accelerating the transference of sample molecules from the solution to the fiber, thus improves the extraction. As our experiment showed, extraction efficiency increased with the stirring rate. However, a stirring rate above 800 rpm caused the bubble formation in the solution. So the magnetic agitator was fixed at 800 rpm during the extraction.

3.2.5. Effect of desorption conditions

Complete desorption of analytes from the fiber enhances the sensitivity of the method as well as ensures that no crossover pollution for the next GC analysis [32], so we investigated the effects of injector temperature (from 250 to 300 °C) and desorption time (from 4 to 7 min) carefully. Based on these results, desorption at 300 °C for 6 min was chosen as the optimum desorption conditions.

3.3. Extraction selectivity studies of Au NPs/SPME fiber

Four types of organic compounds including aromatic HOCs (naphthalene, diphenyl, 1-bromonaphthalene, fluorine, anthracene, fluoranthene, m-terphenyl, and p-terphenyl), n-alkanes (n-hexane, n-octane, n-undecane, n-tridecane, n-hexadecane, n-octadecane, and n-heneicosane), phenols (phenol, 4-methylphenol, 4-chlorophenol, and 1-naphthol) and amines (aniline, 4-toluidine, 4-chloroaniline, and 1-naphthylamine) were chosen to test the extraction selectivity of the Au NPs/SPME fiber. The results are shown in Table 1. In this work, the novel SPME fiber could not extract phenols and amines from aqueous solutions no matter what extraction conditions were used, but it had a preconcentration effect on aromatic HOCs and n-alkanes ($n_c \geq 13$). Comparisons among the octanol/water partition coefficient (log Ps) of these compounds were carried out in order to find the relationship between their hydrophobicity and the enhancement factor
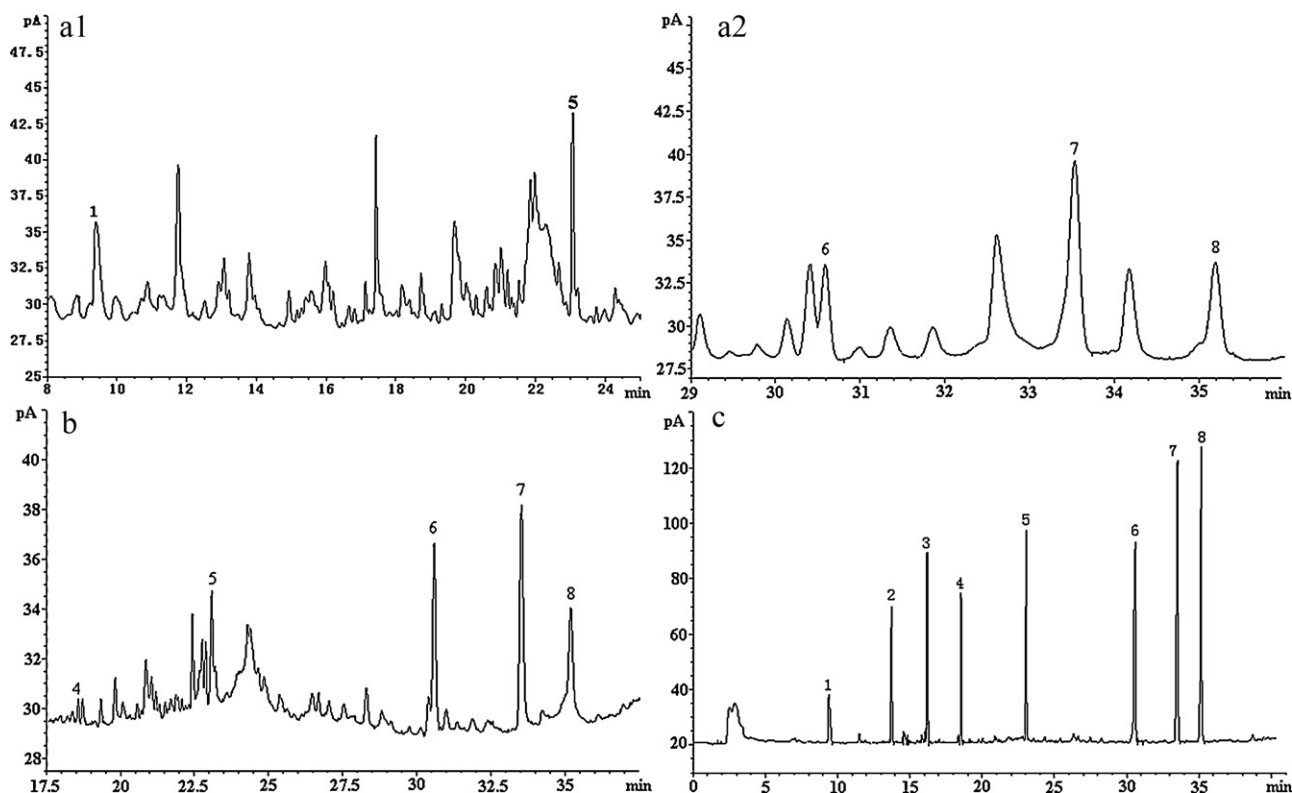

Fig. 10. GC chromatograms of aromatic HOCs in soil extract (a), rainwater (b) and standard solutions (c) extracted by Au NPs/SPME fiber. (1) Naphthalene, (2) diphenyl, (3) 1-bromonaphthalene, (4) fluorene, (5) anthracene, (6) fluoranthene, (7) m-terphenyl, (8) p-terphenyl. Conditions: concentration, 200 μg L^{-1}; extraction time, 50 min; extraction temperature, 60 °C; content of NaCl, 20% (w/w); stirring rate, 800 rpm; desorption temperature, 300 °C; desorption time, 6 min.

values [37] (EF, the ratio of the final concentration to the original). From Table 1, it is seen that only analytes with large log Ps (except phenols and amines) can be extracted by the fiber, and larger log Ps give bigger EFs among the same kind of compounds. These results can be attributed to the hydrophobic characteristic of the Au surface [38]. Analytes with higher hydrophobicity have stronger affinity with the Au NPs/SPME fiber, which is favorable to the extraction. It seemed that hydrophobicity was the dominative factor to be extracted by the fiber. Meanwhile, the Au NPs/SPME fiber gave much bigger EFs for PAHs with larger π-system. This suggested the existence of an additional interaction between aromatic HOCs and the Au NP surface.

In theoretical and computational chemistry, gold is "anomalous" due to its very large relativistic effects [39]. The relativistic effects lead to excellent electronic mobility, which makes it easier to use its empty valency shell to form coordinate bond with atoms having lone pair electrons, or use its valency electrons to form feedback-coordinate bond with atoms having unoccupied orbital. Hoffmann [40] modeled the chemisorptive molecule–surface interactions and explained the molecule–metal interaction in terms of the interaction of the frontier orbits, HOMO and LUMO. Pérez-Jiménez et al. [41] found the occurrence of electron transference from Au to the fullerene LUMO by a scanning tunneling spectroscopy experiment. Based on these theories and researches, we ascribed the selective extraction of PAHs on the Au NPs/SPME fiber to the interaction between π-system of PAHs and Au. There may be an electron transference between PAHs (π-donor system) and Au which strengthened the affinity beyond the hydrophobic effect, thus the extraction capacities were improved.

To sum up, the Au NPs/SPME fiber exhibited superb selectivity to some aromatic HOCs, which was favorable to its practical utilization.

3.4. Analytical evaluation

The analytical evaluation parameters for the Au NPs/SPME-GC method were studied under optimized conditions and results are shown in Table 2. Solutions used in linearity studies were prepared by diluting the stored solution with distilled water with concentration from 0.01 to 500 µg L^{-1} for each analyte. As can be seen from Table 2, good linearity is achieved in a wide range for all analytes with correlation coefficients (R^2) ranging from 0.9941 to 0.9993. Determination limits are in the range of 12.5–250 ng L^{-1}, which is defined as three times the baseline noise. These are relatively lower than the commercially available fiber and other method as shown in Table 2. The relative standard deviations (RSDs) for single fiber are from 2.49% to 7.90%. The fiber-to-fiber reproducibility was also evaluated using three fibers prepared in the same procedure and the results are shown in Fig. 8. RSDs for all the compounds are in the range of 4.28–26.40%.

3.5. Durability and stability

Durability and stability of the SPME fiber correlate to its lifetime and are very important for its practical applications. The fiber was exposed overnight in solutions of 0.1 mol L^{-1} NaOH and 0.01 mol L^{-1} HCl respectively. Thermal stability of the fiber was evaluated through heating the fiber at 350 °C for 3 h in the GC inlet. We compared the peak area before and after the treatment to evaluate the fiber stability and the results are shown in Fig. 9.

As can be seen from Fig. 9, no significant peak area change is observed after the treatments. Au NPs/SPME fiber shows well durability and stability towards harsh conditions. These characteristics can be ascribed to the chemical stability of gold and the strong Au–S bond. Furthermore, since the support of the novel Au NPs/SPME

fiber is the flexible and strong stainless steel wire, thus prolonging the lifetime at the same time.

3.6. Application to real samples

Aromatic HOCs are important environmental contaminants in air, soil and water. Many national organizations and government departments have developed laws and regulations to set limits of them to protect public health. For example, United States Environmental Protection Agent (US EPA) has provided estimates of levels of total cancer-causing PAHs (16 kinds of PAHs, including naphthalene, fluorene, anthracene, fluoranthene and so on) and the total maximum contaminant level is 0.2 mg L^{-1}. The as-established Au NPs/SPME-GC method was applied for the analysis of PAHs, diphenyl, and two terphenyls in rainwater and soil extract. Rainwater was collected in Lanzhou, China on May 20, 2010. The soil extract was obtained from the garden of Lanzhou Institute of Chemical Physics and was treated using the following procedure: put 335 g of soil in 335 mL of water and stirred dramatically for 60 min; keep still and the supernatant was transferred to another vessel. Both water samples were filtered through ordinary filter paper and 0.45 µm membranes and stored at 4 °C. The experimental results are shown in Table 3. Anthracene, fluoranthene, m-terphenyl, and p-terphenyl are detected and quantified in rainwater and soil extract and the concentrations in soil extract are higher than those in rainwater. This dropped a hint of enrichment effect of these compounds in soil. Total amount of the pollutions in the two samples was 54.1 and 184.0 µg L^{-1} respectively, which was lower than the regulation limits. Fluorene in rainwater is detected but the quantity is not in the linear range. The recoveries spiked in two samples at 10 and 100 µg L^{-1} are in the range from 78.4% to 119.9%. Chromatograms of the real samples and standard solution are shown in Fig. 10.

4. Conclusion

A novel Au NPs/SPME fiber has been prepared using a simple layer by layer self-assembly method. Coupled with GC analysis, the fiber exhibits fine extraction efficiency and selectivity. The established Au NPs/SPME-GC method has been used to extract several aromatic HOC pollutants in aqueous solutions, which achieved a wide linearity ranges and low LODs. The method was then applied to two real natural samples; four analytes were detected and quantified. The novel Au NPs/SPME fiber showed high stability and durability towards acid, alkali and under high temperature. Both the single fiber repeatability and fiber-to-fiber reproducibility were satisfactory. Au NPs can be a good sorbent for SPME.

References

[1] R.P. Belardi, J. Pawliszyn, Water Pollut. Res. J. Can. 24 (1989) 179.
[2] A.A. Boydboland, J.B. Pawliszyn, J. Chromatogr. A 704 (1995) 163.
[3] L.M. Ravelo-Pérez, J. Hernández-Borges, M.Á. Rodríguez-Delgado, J. Chromatogr. A 1211 (2008) 33.
[4] L. Pan, J.M. Chong, J. Pawliszyn, J. Chromatogr. A 773 (1997) 249.
[5] M.R. Ivanov, H.R. Bednar, A. Haes, J. ACS Nano 3 (2009) 386.
[6] C.Y. Lin, C.H. Liu, H.C. Chang, W.L. Tseng, Electrophoresis 29 (2008) 3024.
[7] F.K. Liu, Y.T. Hsu, C.H. Wu, J. Chromatogr. A 1083 (2005) 205.
[8] H.M. Liu, J.B. Li, X. Liu, S.X. Jiang, Talanta 78 (2009) 926.
[9] C.L. Arthur, L.M. Lillam, K.D. Buchbolz, Anal. Chem. 64 (1992) 1960.
[10] J. Chen, J.B. Pawliszyn, Anal. Chem. 67 (1995) 2530.

[11] A.A. BoydBoland, J.B. Pawliszyn, Anal. Chem. 68 (1996) 1521.
[12] A.L. Nguyen, J.H.T. Luong, Anal. Chem. 69 (1997) 1726.
[13] B.L. Wittkamp, S.B. Hawthorne, D.C. Tilotta, Anal. Chem. 69 (1997) 1197.
[14] B.L. Wittkamp, S.B. Hawthorne, D.C. Tilotta, Anal. Chem. 69 (1997) 1204.
[15] Z. Mester, R.E. Sturgeon, J.W. Lam, J. Anal. At. Spectrom. 15 (2000) 1461.
[16] X.G. Hu, Y.L. Hu, G.K. Li, J. Chromatogr. A 1147 (2007) 1.
[17] J.G. Hou, Q. Ma, X.Z. Du, H.L. Deng, J.Z. Gao, Talanta 62 (2004) 241.
[18] P. Hashemi, M. Shamizadeh, A. Badiei, P.Z. Poor, A.R. Ghiasvand, et al., Anal. Chim. Acta 646 (2009) 1.
[19] H.M. Liu, D.A. Wang, L. Ji, J.B. Li, S.J. Liu, X. Liu, S.X. Jiang, J. Chromatogr. A 1217 (2010) 1898.
[20] J.C. Wu, J. Pawliszyn, Anal. Chim. Acta 520 (2004) 257.
[21] C.H. Xiao, S.Q. Han, Z.Y. Wang, J. Xing, C.Y. Wu, J. Chromatogr. A 927 (2001) 121.
[22] D. Budziak, E. Martendal, E. Carasek, J. Chromatogr. A 1164 (2007) 18.
[23] M.C. Daniel, D. Astruc, Chem. Rev. 104 (2004) 293.
[24] A. Ulman, An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly, Academic Press, Boston, MA, 1991.
[25] H. Chi, B.H. Liu, G.J. Guan, Z.P. Zhang, M.Y. Han, Analyst 135 (2010) 1070.
[26] L. Yang, E. Guihen, J.D. Glennon, J. Sep. Sci. 28 (2005) 757.
[27] H.Y. Wang, W.B. Wilson, A.D. Campiglia, J. Chromatogr. A 1216 (2009) 5793.
[28] L. Chastri, S.K. Kailasa, H.F. Wu, Talanta 81 (2010) 1176.
[29] H.Y. Wang, A.D. Campiglia, Anal. Chem. 80 (2008) 8202.
[30] G. Frens, Z. Kolliod, Nature 241 (1973) 20.
[31] J.F. Liu, N. Li, G.B. Jiang, J.M. Liu, J.A. Jonsson, et al., J. Chromatogr. A 1066 (2005) 27.
[32] J.B. Zeng, B.B. Yu, W.F. Chen, Z.J. Lin, L.M. Zhang, et al., J. Chromatogr. A 1180 (2008) 26.
[33] J.H. Fendler, Chem. Mater. 13 (2001) 3196.
[34] L.M. Molina, B. Hammer, Chem. Phys. Lett. 360 (2002) 264.
[35] Y. Yourdshahyan, A.M. Rappe, J. Chem. Phys. 117 (2002) 825.
[36] D. Sýkora, V. Kašička, I. Mikšík, P. Řezanka, K. Zárba, et al., J. Sep. Sci. 33 (2010) 372.
[37] H.L. Xu, Y. Li, D.Q. Jiang, X.P. Yan, Anal. Chem. 81 (2009) 4971.
[38] K. Kobayashi, S. Kitagawa, H. Ohtani, J. Chromatogr. A 1110 (2006) 95.
[39] P. Pyykkö, Angew. Chem. Int. Ed. 43 (2004) 4412.
[40] R. Hoffmann, Rev. Mod. Phys. 60 (1988) 601.
[41] A.J. Pérez-Jiménez, J.J. Palacios, E. Louis, E. SanFabián, J.A. Vergés, ChemPhysChem 4 (2003) 388.
[42] R.A. Doong, S.M. Chang, Y.C. Sun, J. Chromatogr. A 879 (2000) 177.
[43] H.L. Xu, Y. Li, D.Q. Jiang, X.P. Yan, Anal. Chem. 81 (2009) 497.
[44] Method 610: Polynuclear Aromatic Hydrocarbons, Appendix A to Part 136, US EPA, Washington, DC, 2005.