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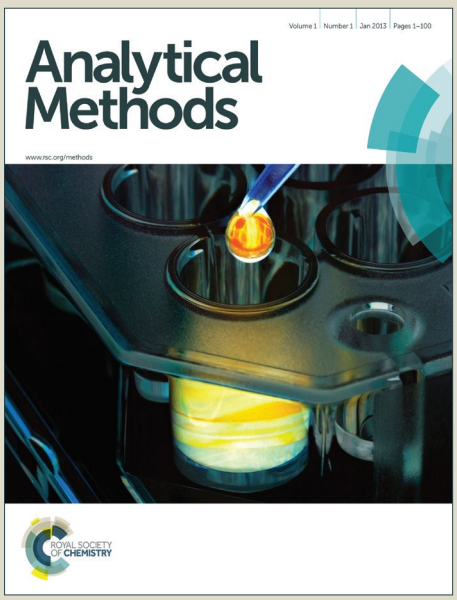

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ARTICLE

The headspace solid-phase microextraction of polycyclic aromatic hydrocarbons in environmental water samples using modified silica fiber by self assembled gold nanoparticles

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Fahimeh Zare[a], Mehrorang Ghaedi[a,*], Ali Daneshfar[b]

The headspace solid phase microextraction method with modified silica fibers prepared based on self assembled gold nanoparticles and sol-gel method is described for the determination of trace amount of polycyclic aromatic hydrocarbons in environmental water samples using high performance liquid chromatography-UV detection. Extraction parameters such as extraction time, extraction temperature, desorption time, type and volume of desorption solvent, sample volume and ionic strength were evaluated and optimized by experimental design. At optimum specified conditions, high characteristic performance such as reproducibility and repeatability and linear range (1-500 ng mL^{-1}) along the reasonable determination coefficient up to 0.995, presence of low limit of detection (from 0.10 to 0.89 ng mL^{-1}) suggest good and efficient applicability of method for estimation and quantification of understudy analytes. The proposed method was successfully applied for the extraction of polycyclic aromatic hydrocarbons in various environmental samples with relative recoveries for the spiked samples at 50 ng mL^{-1} of analytes in the range of 84 to 106% and RSDs below 5.1%. Also, reproducibility of fiber were in the range of 1.2-3.9, reproducibility of proposed fiber were in the range of 3.6-6.7.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) (containing two or more fused aromatic rings) are environmental pollutants which detected in various samples such as food and natural waters [1-6]. Their significant toxicity, potential mutagenicity and carcinogenicity enable them as priority pollutants in the European Union and U.S.Environment Protection Agencies [7-9]. Many studies have already been conducted for preconcentration and determination of PAH_S by solid phase extraction (SPE) [10-12], solid phase microextraction (SPME) [13-15], and dispersive liquid-liquid microextraction (DLLME) [16-18].

Solid-phase microextraction (SPME) is simple, fast, sensitive and convenient sample preparation technique, which minimizes solvent usage, while sampling and sample preparation is in one step [14]. This technique is based on the partition equilibrium of target analytes between the sample matrix and a polymeric stationary phase coated on the surface of fused silica fiber.

[a] Department of chemistry, Faculty of sciences, Yasouj University, Yasouj 75918-74831, Iran.
[b] Department of chemistry, Faculty of sciences, Ilam University, Ilam 69315-516, Iran.
Corresponding author: Tel./Fax: + 98 743 222 3048.
E-mail: m_ghaedi@yahoo.com

In spite of the advantages of this technique, commerically available SPME fiber suffer from drawback concern to the lack of proper chemical bonding of the stationary-phase coating, the relatively high thickness of the conventional fibers, instability with high temperature, carry over and incompatibility with organic solvents. Recently, research has been focused on the development of new coating protocol possible solving these problems.
The type of coating strongly affect the distribution constant of analytes among different phases, i.e. immobilized phase. In literatures, metal nanoparticles widely applied in different scientific fields [19-22], especially in solid phase microextraction because of their adsorption capacity [23]. Among the metals, gold nanoparticles (Au NPs) possess qualified merits such as well-defined structure and self-assembly capability for a wide range of functionalization procedures, as well as the proper stability [10].

Organic molecules containing thiol (SH) group can be bonded with of gold (Au), palladium (Pd) or silver (Ag) nanoparticles to form a self-assembled monolayer (SAM).

The sol-gel approach, commonly based on the hydrolysis and condensation of mixture containing polysiloxanes and alkoxysilanes by providing efficient incorporation of organic components into the inorganic polymeric structure in solution under quite mild thermal conditions that represent the largest category of coating development [24-26]. Sol-gel composed of organic-inorganic hybrid media is an economic and efficient SPME fiber preparation pathway. The porous

structure of the sol–gel coating offers a high surface area; allowing high extraction efficiency and the coating composition can be altered with a relative ease to give different selectivity characteristics. Strong adhesion of the coating on the support due to chemical bonding is a very important characteristic which increases the coating stability toward organic solvents [5].

The present study focus on design of a simple, robust and sensitive HS-SPME method coupled with HPLC-UV for the determination trace levels of PAHs in environment samples using modified silica fiber by self -assembled gold NPs as stationary phase.

The self-assembled monolayer (SAM) approach based on sol-gel method was proposed for the fabrication of fiber of solid-phase microextraction (SPME). After SAM of Au-NPs with 3-(trimethoxysilyl-1-propanthiol) via Au-S bonding, finally, chemically–bonded hybrid coating with unique structure and extremely large surface area was obtained using sol-gel technique.

The modified silica fiber using gold nanoparticles provides a much higher response to PAHs than other modified fiber with palladium or silver nanoparticles, owing to extraction ability of the gold nanoparticles based sol–gel coating and because of the better ability of gold nanoparticles for performing the self assembly monolayer reaction and so, production of porous fiber with high adsorption capacity.

The fiber coating plays a key role in SPME, and development of new fiber coatings with high extraction efficiency for the target analytes is an important research direction in this field. Although, various home-made SPME fibers are reported [2, 13-18], but these fibers coated with nonpolar poly(dimethylsiloxane) (PDMS) stationary phases. A significant drawback of such fibers is the absence of proper chemical bonding of the stationary phase coating with the fused-silica surface, which is responsible for their low thermal or chemical stability.

On the other hand, the high standard deviations, high extraction time (even to 120 min for achievement of lower LOD) of these fibers is still cahllenge, therefore the research in this area for the presentation of new coating is continued in order to achievement of wide dynamic range and higher sensitivity (lower LOD). The proposed fiber (coating) in this work have advanced selectivity and sensitivity which is mainly due to two reasons: (a) sol–gel coatings possess poros structures which should significantly increase the surface area availability on the fibers and (b) using self assembled gold nanoparticles with high surface area as a sorbent modifier will also able to provide enhanced adsorption efficiency for target analytes. It can be observed that the acuuracy and precision of proposed fiber is higher than other reported HS-SPME and SPME with the home-made fiber.

In the present work, new technique for preparation of an solid-phase microextraction (SPME) fiber, using sol–gel technology and self-assembly mono layer reaction is developed by hydrolysis of 3-(trimethoxysilyl)-1-propanthiol selfassembled monolayer bonded onto gold nanoparticles, then stationary phase by sol-gel reaction of precursor and polyethylene glycol as a coating polymer was produced. The applicability of the prepared fiber coating in conjunction with high performance liquid chromatography UV detection was examined by SPME of polycyclic aromatic hydrocarbons, as model analytes, from aquatic media.

Many inherent advantages of suggested fiber are the following: (i) porous structure which leads to high surface area and possibility of the use of coatings to achieve acceptable stationary-phase loading, sample capacities and fast mass transfer characteristics, (ii) high degree of flexibility in coating composition and selectivity, by varying the proportion of the sol solution ingredients or using a deactivation reagent (iii) self-assembled monolayer (SAM) of 3-(trimethoxysilyl)-1-propanthiol (3-TMSPT) was bonded on an Au nanoparticles lead to high selectivty for the extraction of target analytes. It can be clearly observed that the present method has better or comparable performance with other reported methods in extraction time, detection limit and cost of preparation.

Experimental section

Chemicals and reagents

Naphthalene, fluorene, pyrene, anthracene, acetone, ethanol, sodium chloride, sodium hydroxide, hydrochloric acid, trifluroacetic acid (TFA), methyltrimethoxysilane (MTMOS), 3-(trimethoxysilyl-1-propanthiol) (3-TMSPT), ethyl benzene, acetophenone and phenol were obtained from Merck (Darmstadt, Germany). Polyethylene glycol (PEG) (6000 g mol^{-1}) was purchased from Fluka (Buchs, Switzerland). Acetonitrile, water and methanol (HPLC-grade) were supplied by Sigma-Aldrich (St. Louis, USA). Stock standard solution of PAHs (100 mg L^{-1}) was prepared in methanol. In addition, working standard solutions were prepared daily in deionized water and stored in 4 ^{o}C.

Instrumentation

An ultrasonic bath alongside a heating system was used (Tecno-GAZ, Italy) with a frequency and power of 40 KHz and 130 W. The pH was controlled using pH/Ion meter model-686 (Metrohm, Switzerland, Swiss). Fourier transform infrared spectroscopy was recorded by FT-IR spectrophotometer (Model: FT-IR JASCO 460 Plus), while fiber morphology was studied through scanning electron microscopy (SEM; Hitachi S-4160, Japan). The chromatographic analyses were carried out via the use of an Agilent Technologies (Wilmington, DE, USA) 1100 HPLC system equipped with Micro Vaccum Degasser (model G 1379A), Quaternary Pump (model G 1311A), a Zorbax SB-C8 (Agilent) column and series Multiple wavelength Detector (model G13658). The chromatographic calculations were performed by Chemstation data handling system. Analytes were eluted with the following binary solvent (acetonitrile-water) gradient programme: initial 30% acetonitrile for 2 min and subsequent linear ramp to 50% (5 min), another linear ramp to 70% (5 min), and finally to 100% (5 min) with flow rate of 1 mL min^{-1}.

Preparation of fiber

The synthetic procedure for the preparation of gold, silver and palladium nanoparticles was replicated from our previous reports [27-29].

For preparing 3-TMSPT-Au, (3-TMSPT-Ag or 3-TMSPT-Pd), 100 mg gold (silver or palladium nanoparticles) nanoparticle were added to 1 mL of 3-(trimethoxy silyl-1-propanthiol) in 3 mL vial and thoroughly dispersed in ethanol following ultrasonication exposure for 5 min and stirring for 12 h. Subsequently, 100 mg polyethylene glycol was dissolved in chloroform, then, 200 μL of MTMOS and 50 mg 3-TMSPT-Au (in an Eppendorf tube) was added and dissolved thoroughly by ultrasonic agitation for 5 min. Then, around 500 μL of TFA was gradually added to the solution under ultrasonic exposure for another 5 min (All reaction steps for the preparation of fiber are presented in Fig. S1).

At this stage, treated fused silica (fused silica dipped into 1 mol L^{-1} sodium hydroxide solution for 1 h to expose the maximum number of silanol groups on the silica surface of the fibers, and then into 0.1 mol L^{-1} HCl for 30 min to neutralize the excess sodium hydroxide) was dipped vertically into the sol-solution by using the chemical bath technique in order to achievement of high homogenity film (20 min) and gel coating was formed on the activated outer surface of the fused silica. Then, the fiber was removed and placed into the desicator for 24 h. The fiber was then conditioned at as follows to remove any fiber contaminations: the fiber was put into oven and conditioned at 100, 200 and 250 °C for 1 h, respectively.

Extraction procedure

Aqueous solution of PAHs (7 mL of 200 ng mL^{-1}) was placed in 10 mL vial. During the extraction, the fiber was placed directly in the headspace of sample solution for 20 min at 45 ^{0} C (in ultrasonic bath). The extracted analytes were eluted ultrasonically with 50 μL of methanol for 5 min and the preconcentrated analytes were injected into HPLC/UV system for further analysis. Possible carry over was eliminated by ultrasonically cleaning the fiber in acetone for 10 min before using for another extraction.

Results and discussion

Characterization of fiber

The sol solution was characterized using FT-IR analysis. The absorption peak at ~600 cm^{-1} is concerned with Au-S band. The absorption peak at ~ 1630 cm^{-1} is attributed to the silanol groups (Si-OH), while the peak at 3424 cm^{-1} indicates O–H band while the sharp peak around 1120 cm^{-1} emerged from the Si-O-Si NPs stretching. Stretching vibration peak around 1500 cm^{-1} emerges from cross-linked polymerization of PEG (Fig.1a).

Scanning electron microscopy (SEM) technique was employed in order to study the surface characteristics of fiber. As can be seen from the image (Fig. 1b), the fiber have porous structure which increase the surface area on the surface of fiber, it was able to provide higher extractive capacity.

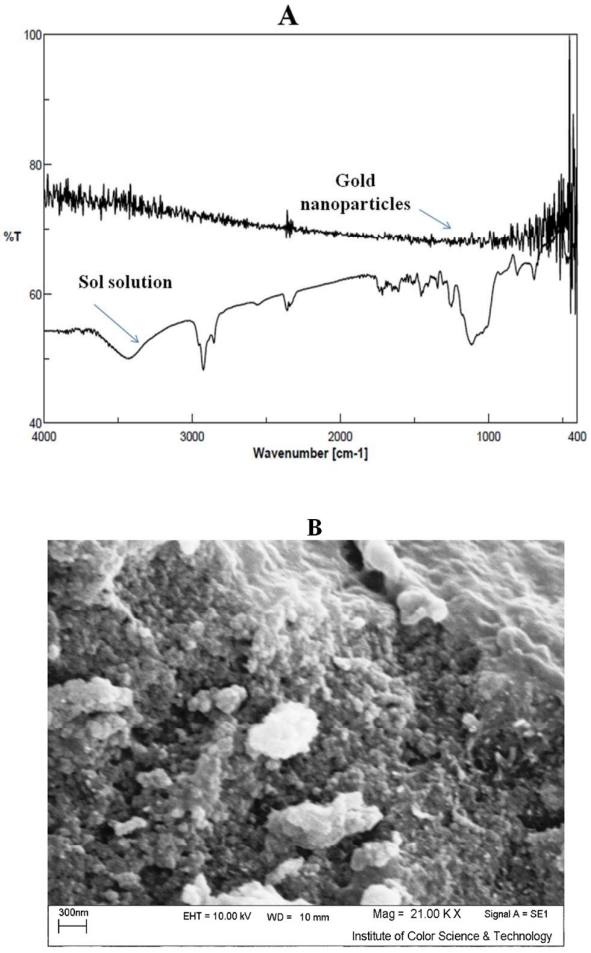


Fig. 1 (a) FT-IR spectrum of nanoprticle and sol solution; **(b)** The scanning electron microscopy images of fiber.

Optimization of method

Among three SPME pathway, headspace extraction due to lower matrix interferences and no diverse sample pH is prefered. Therefore, the headspace mode was selected for all experiments. Although sample pH has no effect, the pH 7 was selected for all experiments. Among various applied desorption solvents (acetone, acetonitrile and methanol), the best extraction efficiency were obtained using methanol (Fig.S2).

A fractional factorial design was selected to screen the relative main and interaction of variables including extraction time and temperature, salt concentration, desorption solvent, time of desorption and sample volume. The effect of the studied variables in the screening experiment are shown in Fig. 2a, the form of a Pareto chart. It is observed that desorption volume, extraction temperature and sample volume have critical effect on the response. The optimum value of variables set as: pH 7, 7 mL sample volume at 45

℃, 20 min ultrasonic time, 5 min desorption time, 50 µL methanol as eluent (Fig. 2 b,c).

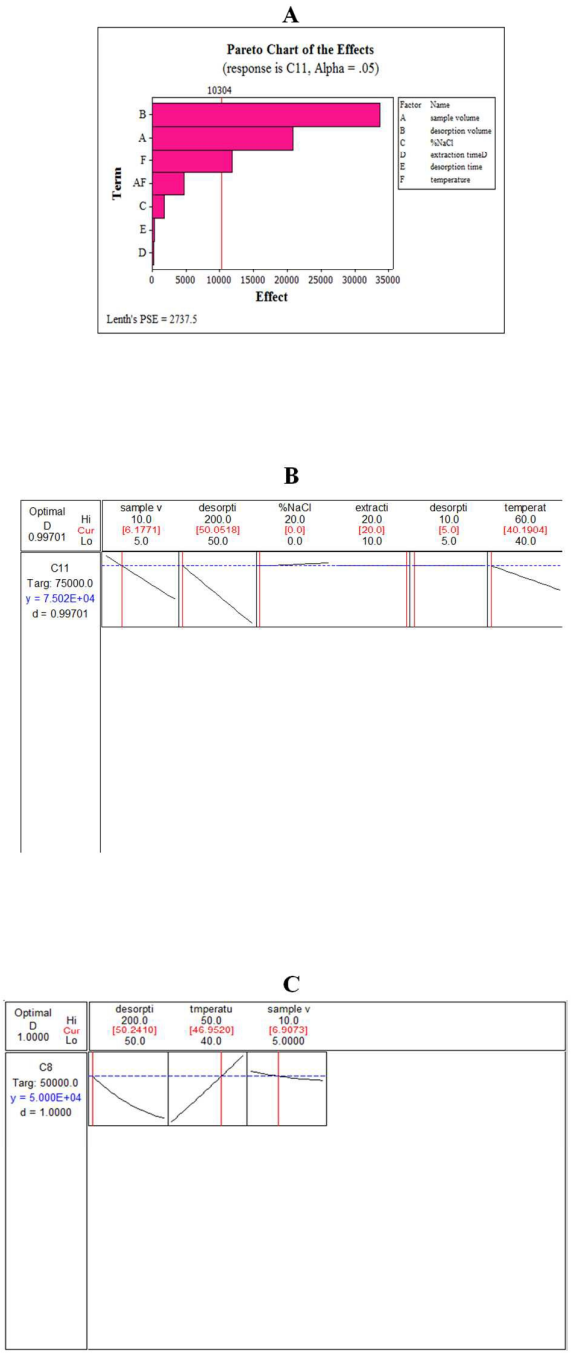


Fig. 2 (a) Standardized main effect Pareto chart of fractional factorial design for screening ; **(b)** Optimum plot of fractional factorial design; **(c)** Optimum plot of central composite design.

The type of stirring affected on the extraction efficiency due to change the mass transfer rate, therefore, for the strring the solution, ultrasnoic waves, agitation using stirrer and shaker were examined, the result was shown that agitation using ultrasonic waves lead to reducing the required time to reach thermodynamic equilibrium.
Generally ultrasonic agitation accelerates mass transfer of sample molecules from bulk solution to fiber coating and thereby greatly improves HS-SPME performance. The amount of analytes extracted depends strongly on extraction time. In this study, HS-SPME was performed from 5 to 40 min to examine the effect of extraction time. The maximum extraction efficiency was nearly achieved within 20 min. The extraction efficiency of the method is enhanced with ultrasonic agitation due to increasing the mass transfer rate. In addition, the time required to reach thermodynamic equilibrium is reduced [2]. Exposure of the fiber in gaseous sample is an important parameter in achieving distribution equilibrium of the analyte between the fiber and the sample. During extraction, analytes migrate between all three phases (fiber coating, the gas phase or headspace, and a homogeneous matrix) until equilibrium is reached. The equilibration time was proportional with analyte distribution constant.

In the extraction process, the desorption time had an obvious effect on the extraction efficiency of analytes. The desorption process should equilibrate for a sufficient time to achieve satisfactory extraction efficiency. As a result, 5 min was an efficient time for desorption of analytes, therefore selected as optimum value for further experiments.
Therefore, subsequently three factors influence (main and interaction) was optimized by central composite design using 20 run. In this study STATISTICA 7.0 package was used for regression analysis of the experimental data and to plot response surface.

Analysis of variance (ANOVA) was used to estimate the statistical parameters. A p-value less than 0.05 in the ANOVA table indicates the statistical significance of an effect at 95% confidence level [31-33]. On the basis of evaluating p values, an empirical relationship between the peak area values and the variables is the following regression equation:

$$Y \text{ (peak area value)} = 11977.3 - 9393.1\ X_1 + 8747.0\ X_2 - 2527.3\ X_3 + 2725.9\ X_1^2 + 194.7\ X_2^2 + 569.7\ X_3^2 - 8300.0\ X_1 X_2 - 450.0\ X_1 X_3 - 1800.0\ X_2 X_3 \quad (1)$$

The results of analysis of variance for the quadratic regression model are shown in Table 1. According to the analysis of variance, the model F-value (F_{model}=3.68) concluded that model is applicable for accurate and repeatable prediction of real behavior of present extraction method. The quality of fit of the polynomial model equation was expressed with the coefficient of determination (R^2 = 0.96 and adjusted R^2 = 0.90).

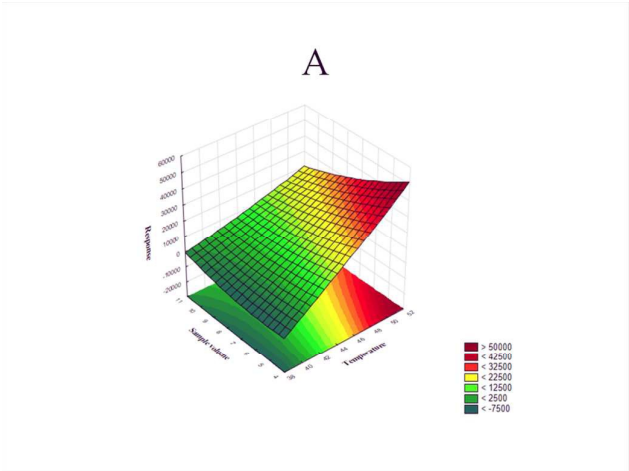
Table 1 A summary ANOVA table for obtained experimental responses.

Source	Degree of freedom	Sum of square adjusted	Mean square adjusted	F	P
interaction	3	578660000	192886667	12.29	0.002
Residual Error	8	125545513	15693189		

Lack of fit	5	107925513	21585103	3.68	0.157
Pure Error	3	17620000	5873333		
Total	19	3132769500			

The final optimized conditions of the variables to obtain maximum response was calculated. The interaction effects and optimal levels of the variables were determined by plotting the response surface curves. The curvatures of plots represented in Fig. 3 (a-c) support the presence of interaction between the variables.

In HS-SPME, the use of high temperature is suitable for increasing volatility of analytes and establishing the sample solution and gaseous phase. Therefore, the optimization of the extraction temperature is necessary. The results (Fig. 3a,c) show that the microextraction of analytes reach to maximum value at 45 ℃. Temperature has kinetic and thermodynamic effect on HS-SPME. Elevated temperature is favorable for the diffusion of analytes from bulk phase to the fiber coating and shortens the equilibration time. On the contrary, it also reduces the distribution coefficients of analytes between the fiber coating and aqueous phase because surface adsorption is generally an exothermic process [2]. In addition, temperature higher than 45 ℃ usually increases the solubility of analytes in aqueous phase and results in the decreased extraction efficiency accordingly. Fig. 3b shows the comprehensive effect of temperature on the extraction. The best extraction efficiencies were achieved at 45°C. In addition, further increase in temperature accelerates the evaporation of liquid into headspace and hence the sorption on the surface of sorbent. This process leads to blocking of the sorptive sites on the sorbet surface and decreasing effective surface area of sorbent. Based on our evaluation, a temperature of 45 ℃ was chosen as the optimized extraction temperature for further experiments.



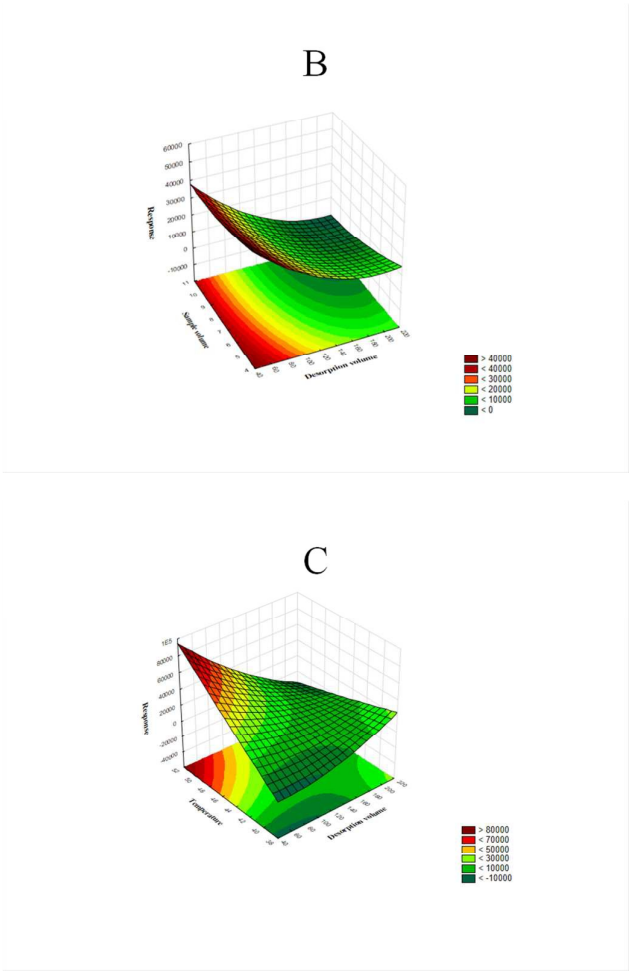


Fig. 3 Three dimentioanl response surface plot for **(a)** Sample volume - Temperature; **(b)** Sample volume-Desorption volume; **(c)** Desorption volume-Temperature.

In two liquid phase systems, the enrichment factor can be improved by increasing the volume ratio of acceptor to donor phases according to the following equation [30]:

$$Response = \left(\frac{C_f \times V_f}{C_{aq} \times V_{aq}}\right) \times 100 = EF \times \frac{V_f}{V_{aq}} (2)$$

where V_{aq} and V_f are the volume of the aqueous and organic phase, respectively. Therefore, it is reasonable that higher sample volume lead to higher extraction efficiency. So, 7 mL of sample volume was used to obtain high EF.

At higher volume of eluent, a significant decrease was observed that is probably due to change of extraction efficiency according to equation 2 significantly affect the enrichment factor.

Therefore, 50 µL of desorption volume was optimum for further work (Fig.3b).

Comparison of three kind of fibers

To study the extraction efficiency of the sol–gel fiber coatings, a comparison between 3 different fiber (by application of Au, Ag and Pd nanoparticles for SAM reaction and preparation of three kind of fibers) were conducted (Fig. S3). The chromatographic peak area for three kinds of fibers were compared together and results shown that modified fiber with gold nanoparticles was better than Ag and Pd nanoparticles fibers regards to the existence of gold nanoparticles due to the increasing of the surface area, additionally the coating has the porous surfaces that increase considerably the surface area.

The high extraction capability of gold nanoparticles in sol–gel SPME coatings to PAHs is due to the π-π interactions and hydrophobic interactions. And additionally, high surface area of the sol–gel coating should also provide enhanced extraction efficiency in SPME.

Selectivity of coating

To evaluate the selectivity of the suggested coating for HS-SPME of PAHs, a series of organic compounds with different physical-chemical properties (e.g. hydrophobicity, π-π interaction and polarity) were examined (ethyl benzene, acetophenone and phenol). The coating had much higher affinity to PAHs (Relative recovery; %RR >90) than to other analytes studied (%RR <70).

The result revealed that the presence of delocalized π system in the target molecules also played an important role in the selectivity of coating for HS-SPME. The π-system of PAH compounds and immobilized Au nanoparticles on the surface of the sorbent can cause the electron donor–acceptor interactions [10]. This improvement can be attributed to the relativistic effects of Au via notable electronic mobility. Au atoms utilize their empty valency shells to form coordination bonds with atoms having lone pair or delocalized electrons [10]. Since PAHs employed electron donor–acceptor interactions with the other compounds, beyond their hydrophobic effects, the increase in the extraction efficiency can be related to the interaction of Au NPs with target analytes.

Ethyl group was strongly electron donor, which could not interact with the π-electron-rich region of coating as π-electron donor via π-π interaction. Ketone group was weak electron-acceptor, so they had relatively low adsorption affinity. Furthermore, phenol was not electron acceptor, hence it had relatively lower relative recovery value compared with ketone group. Therefore, π-π interaction could enhance the adsorption affinity and selectivity of polycyclic aromatic compounds [24].

Quantitative characteristics of the method

The quantitative characteristics of the method such as linear dynamic ranges (LDR) and limits of detection (LOD) were studied. The results are summarized in Table 2. The proposed method has linear response over 10-500 ng mL^{-1} with limits of detection of 4.6-12.6 ng mL^{-1} and conduction of five replicate determinations at optimum specified conditions using a single fiber reveal that the relative standard deviation (RSD%) values were below 4% for all analytes, which indicates that the proposed method is repeatable. Also, reproducibility studies were performed on three different fibers, and fiber-to-fiber RSDs at the concentration 50 and 200 ng mL^{-1} were in the range of 3.6-6.7%, while each of fiber can be used up to 20 experiments without considerable change in extraction efficiency (Table 3). Finally, a comparison of this method with the reported methods (Table 4) demonstrates the feasibility of SPME fiber in terms of characteristic performance [2,4-6,34].

Table 2 Analytical performance data for the PAHs in HS-SPME method.

Analytes	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	DLR (ng mL^{-1})
Nap	0.89	2.96	2-500
Flu	0.46	1.53	1-500
Ant	0.12	4.20	3-500
Pyr	0.10	3.49	5-500

Table 3 Repeatability and reproducibility of HS-SPME.

Compound in concentration of 200 ng mL^{-1}	One fiber RSD (%)	Fiber-to-fiber RSD (%)	Compound in concentration of 50 ng mL^{-1}	One fiber RSD (%)	Fiber-to-fiber RSD (%)
Nap	1.5	3.6	Nap	2.9	4.1
Flu	1.2	3.8	Flu	2.7	4.8
Ant	3.0	4.2	Ant	4.0	6.7
Pyr	2.6	4.6	Pyr	3.9	5.5

Table 4 Comparison of sol-gel based fiber with other suggested fibers and other extraction methods in the literatures for determination of PAHs.

Method	LOD(ng mL^{-1})	DLR (ng mL^{-1})	RSD (%)	RR (%)	Extarction time (min)	Detection system	Refs
commercial polymer fiber	0.09	0.5-5	2.9-12.1	49-70	30	HPLC-FLD	6
PEG and PDMS fiber	0.05	0.01-500	2.5-9.6	85-101	40	GC-FID	2
Carbon nanotube sol-gel fiber	0.01	0.01-50	4.8-11.2	74-114	30	GC-MS	4
In tube SPME	0.003	0.05-2.00	5.1-7.6	Above 70	15	HPLC-FLD	5
ISDME	0.02	0.1-300	1.9-4.1	Above 85.5	1	HPLC-UV	34
HS-SPME	0.10-0.89	1-500	1.2-4	84-106	20	HPLC-UV	Present work

Analysis of real samples

The proposed method was applied for estimation of PAHs level in various environmental water samples. The results are shown in Table 5. There samples were prepared according to the procedure extensively described elsewhere [4,6]. A small portion of eluent solution was injected into HPLC and analyzed. Due to the absence of any analytes in the above mentioned real samples, standard addition method was applied after spiking known values (50 and 200 ng mL^{-1}), so as to estimate the accuracy and precision of the method. Fig.4 illustrates the chromatogram of the river water sample that indicate the reasonable and acceptable relative recoveries (RR, %) in the range of 84-106% along with RSD% from 2.9 to 5.1%. HPLC

chromatogram demonstrated a proper limit of detection with no extra peak indicating the efficiency of SPME method.

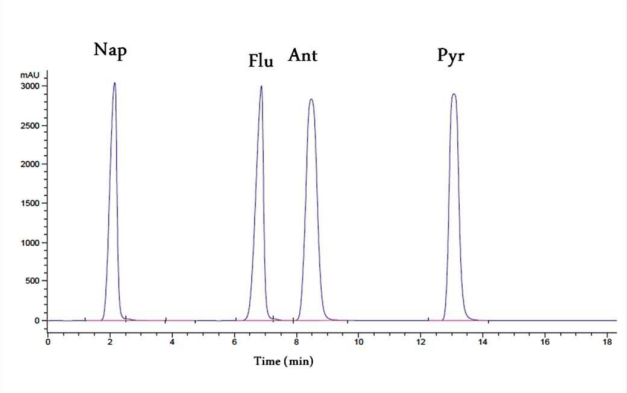


Fig. 4 Chromatogram of river water sample spiked with 100 ng mL^{-1} of PAHs.

Table 5 Relative recoveries obtained in the determination of PAHs in spiked river, mineral and waste water samples.

		River water (n=5)	Waste water (n=5)	Mineral water (n=5)
Analytes	Spiked (ng mL^{-1})	RR (RSD) %	RR (RSD) %	RR (RSD) %
Nap	0	-	-	-
	50	106 (3.8)	102 (4.4)	96 (2.9)
	200	102 (2.9)	96 (3.7)	92 (3.1)
Flu	0	-	-	-
	50	97 (4.3)	85 (4.8)	88 (3.6)
	200	93 (3.9)	94 (3.9)	93 (3.8)
Ant	0	-	-	-
	50	86 (4.4)	105 (5.3)	84 (4.1)
	200	94 (3.6)	98 (4.9)	89 (3.6)
Pyr	0	-	-	-
	50	85 (5.1)	106 (5.6)	86 (4.3)
	200	92 (3.8)	95 (4.8)	95 (4.1)

Conclusions

In this study, modified silica fiber using self-assembled Au-NPs with a reasonable selectivity for PAHs was prepared and applied as the coating for HS-SPME method. Owing to sol gel method, the synthesized sorbent benefit from advantages such as homogenity and high porosity. The present work describes the possibility of using SPME method for the microextraction and preconcentration of polycyclic aromatic hydrocarbons in environmental water samples prior to analysis by HPLC-UV system. The good linearity, enrichment factor and reasonable relative recovery have been also obtained.

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