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ORIGINAL

HP-SPME of Volatile Polycyclic Aromatic Hydrocarbons from Water Using Multiwalled Carbon Nanotubes Coated on a Steel Fiber through Electrophoretic Deposition

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Abstract A headspace solid-phase microextraction (SPME) method using a stainless steel wire electrophoretically coated with dodecylsulfate modified multiwalled carbon nanotubes was used for the gas chromatographic (GC) determination of polycyclic aromatic hydrocarbons (PAHs) in aqueous samples. Electrophoretic deposition was easily carried out from an aqueous sodium dodecylsulfate medium. The effects of various parameters on the efficiency of SPME process, such as extraction time, extraction temperature, ionic strength, desorption time, and desorption temperature were studied. Under optimized conditions, the detection limits for the various PAHs studied varied from 0.03 to 0.07 ng mL^{-1}. The inter-day and intra-day relative standard deviations at a 10 ng mL^{-1} concentration level ($n = 7$) using a single-fiber were from 5.5 to 9.7 and 4.1 to 8.5 %, respectively. The fiber-to-fiber RSD% ($n = 3$) was between 7.3 and 11.1 %. The linear ranges were between 0.1 and 100 ng mL^{-1}. The method was successfully applied to the analysis of a real sample with the recoveries from 88 to 105 % for 5 ng mL^{-1} and 89 to 101 % for 0.5 ng mL^{-1} samples.

Keywords Gas chromatography · Headspace solid-phase microextraction · Electrophoretic deposition · Carbon nanotube · Polycyclic aromatic hydrocarbon · Sodium dodecylsulfate

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds comprising two or more fused benzene rings. They are considered as pollutants of major environmental concern. Such molecules are primarily formed by incomplete combustion of fossil fuels such as wood, coal tar, diesel, and oil spills [1]. They are also present in cigarette smoke and some industrial effluents. They can enter the body through atmosphere, drinking water, food and smoking. As some PAHs are known or suspected to be carcinogenic or mutagenic to humans and other living organisms, they are potentially dangerous to human health. At present, these compounds are widespread in all parts of the environments; therefore, great attention has been paid to identification and quantitation of PAHs in environmental samples [2–5]. However, due to their low concentration and complex matrices, sample cleanup and preconcentration are usually necessary for the analysis of PAHs in environmental samples. Hence, the search for a simple, fast, and effective sample pretreatment has become an important issue in analytical chemistry [2, 6, 7].

Various methods have been used for the extraction of PAH, including liquid–liquid extraction (LLE) [8], microwave-assisted extraction (MAE) [9], solid-phase extraction (SPE) [10], ultrasonic extraction (UE) [11], head-space single-drop microextraction (HS-SDME) [12], and ionic liquid extraction [13]. Most methodologies for the analysis of PAHs are laborious, time consuming and need organic solvents.

Solid-phase microextraction (SPME), however, is an alternative technique which overcomes many of the above drawbacks. This method which was introduced by Pawliszyn [14] in 1989 is a preconcentration technique with many advantages. It is a simple, practical and solventless,

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yet sensitive technique for the determination of trace contaminants in many environmental samples. It also combines sampling, sample clean-up and preconcentration into a single step. In practice, the analytes of interest are initially extracted and concentrated by a sorbent material coated on a piece of silica fiber, which is then introduced into the analytical instrument for separation and determination. It is a technique which has been used by various researchers for a variety of environmental applications, including the analysis of PAHs [2], pesticides [15], and substituted benzene compounds [16] in aqueous samples.

Although various commercial coatings are available, the search for new advanced materials for SPME coatings is an important area of contemporary research. In recent years, great attention has been paid to nano-structured materials of different chemical composition, produced as nanoparticles, nanowires or nanotubes. There has also been great interest in their preparation, properties and applications in various fields. Among these have been an increasing number of applications of carbon nanotubes (CNTs) in chemical analysis.

Carbon nanotubes, which were discovered by Iijima [17], were produced through a carbon-arc discharge method similar to that used for preparing fullerenes. They exhibit the most extreme diversity in structure and structure-dependent properties [18, 19]. CNTs exhibit excellent mechanical and thermal properties, and although they are generally of inert structures, their electrical properties are sensitive to chemical doping by various molecules. Surface modification can afford CNTs some new functions, such as –OH, –COOH, and –NH$_2$ [20–22]. Carbon nanotubes have been successfully used for fabricating SPME fibers for the analysis of organic compounds such as, phenols [23], polybrominated diphenyls [24], and organochlorine pesticides [25] and PAHs [26].

One very promising technique being developed for manipulating CNTs is electrophoretic deposition (EPD). In EPD, charged powder particles, dispersed or suspended in a liquid medium are attracted and deposited onto a conductive substrate of opposite charge on application of a DC electric field. The principal driving force for electrophoretic deposition is the charge on the particle and the electrophoretic mobility of the particles under the influence of an electric field.

Preparation of a stable dispersion of CNTs in a suitable solvent is a necessary prerequisite for successful EPD. The most common strategy is the production of an electrostatically stabilized dispersion, which, in general terms, requires the preparation of a solvent medium in which the particles have a high f-potential, while keeping the ionic conductivity of the suspensions low. The stability of CNT suspensions, determined by f-potential measurements, has been studied mainly in aqueous and ethanol-based media [27–29].

Recent efforts on the development of efficient and facile methods of dispersing CNTs in aqueous media have been focused on the hydrophilization of CNT with molecules that bind to the CNT surface non-covalently [30, 31]. Such non-covalent functionalization has great promise as the modification-induced changes in the electronic and mechanical properties of CNTs are minimized [32]. Dispersion via non-covalent functionalization is based on the direct contact between a CNT and a dispersant molecule [31, 33]. Such modification of the CNT surface facilitates the disaggregation of CNT bundles into smaller diameter bundles [33] or even individual CNTs [30] and leads to the stabilization of suspended CNTs via steric or electrostatic repulsion mechanisms or both. Various surfactants, such as sodium dodecylsulfate (SDS) and materials like poly(ethylene glycol) [34] and carbohydrates (e.g., cyclodextrins) [35] have been evaluated as dispersants for CNTs.

Electrophoretic deposition from an organic medium has already been used to prepare CNT coatings for SPME of phenols from aqueous solutions [36]. However, the purpose of the present work was the electrodeposition of modified CNTs from water, which is a more environmentally friendly medium. Using such a medium, attempts were made to prepare a modified carbon nanotube-coated stainless steel fiber for the head-space solid-phase microextraction (HS-SPME) of PAHs from water.

Experimental

Chemicals

Polycyclic aromatic hydrocarbon standards including acenaphthylene (ACL), fluoranthene (FA), fluorene (FL), naphthalene (NA), phenanthrene (PHE) and biphenyl (BPH) were supplied by Fluka (Buchs, Switzerland). Sodium dodecylsulfate was purchased from Alfa Aesar (Karlsruhe, Germany). Multiwalled carbon nanotubes (MWCNTs) purchased from PlasmaChem GmbH (Darmstadt, Germany) were 20–40 nm in diameter and 1–10 μm in length. Stainless steel wire (type 100-014, 350 μm OD) was obtained from Ortho Organizers (CA, USA) and used as the SPME fiber. A 200 μg mL^{-1} stock solution of the mixture of PAHs was prepared in acetonitrile. Working solutions of these compounds were prepared by appropriate dilution of the stock solution with water. All solutions were stored in the dark at 4 °C. Helium gas (≥99.999 %) used as the GC carrier gas and N$_2$ gas (≥99.5 %) used as the make-up gas were obtained from Sabalan Co. (Tehran, Iran). HPLC grade acetonitrile was purchased from Merck (Darmstadt, Germany). Other reagents used were of highest purity available. Double distilled water was used in all experiments.

Apparatus

The SPME device (Fig. 1) was home made. It consisted of a 23-gauge, 9.0-cm stainless steel spinal needle purchased from Dr. Japan Co. (Tokyo, Japan) and housed in a 6.0-cm hollow cylinder of Al with two nuts and two pieces of rubber septum. A 17-cm piece of the stainless steel wire passing through the septum acted as the SPME fiber. One end of the fiber was attached to a cap and 3 cm of the other end was coated with MWCNTs. Electrophoretic deposition of MWCNTs onto the stainless steel SPME fiber was carried out with a Behpajuh potentiostat/galvanostat, model BHP 2061-C (Esfahan, Iran). The Pt counter electrode and the Ag/AgCl reference electrode used in the electrochemical process were from Azar Electrode (Urmieh, Iran). An IKA heater–stirrer, model RH basic 2 (Staufen, Germany) was used for stirring and heating the samples during the SPME process. An oven (WTE binder, Tuttlingen, Germany) was used for drying the coated fiber. All glasswares were cleaned thoroughly by soaking overnight in acetonitrile and rinsing with double distilled water. Vial caps and septa were also rinsed with acetonitrile and dried before use. Real samples were filtered by 0.45 μm Millipore filters, type HV (Schwalbach, Germany).

The chromatographic analysis of PAHs was performed by a Unicam model 4600 A gas chromatograph (Cambridge, UK) equipped with a split–splitless injector, flame ionization detector (FID), and a CBP-10 (25 m × 0.33 mm. I.D. and 0.5-μm film thickness) capillary column purchased from Shimadzu (Kyoto, Japan). The column temperature was initially kept at 60 °C for 1 min, increased at 15 °C min^{-1} to 175 °C, then increased at 1 °C min^{-1} to 185 °C, increased at 15 °C min^{-1} to 250 °C, and finally kept at 250 °C for 2 min. Injector and detector temperatures were adjusted at 250 and 300 °C, respectively. The scanning electron micrographs of the fiber surface were obtained using Philips XL30 (Eindhoven, The Netherlands) and Hitachi S4160 (Tokyo, Japan) scanning electron microscopes. A Bandelin Sonorex Super ultrasonic bath (Berlin, Germany) was used for sonication purposes. A Varian CP-3800/Saturn 2200 GC/MS instrument (Milgrave, VIC, Australia) equipped with quadrupole analyzer and electron impact ion-source (EI) was used for the identification of PAHs in real samples. The MS conditions were: mass range 50–300, electron energy 70 eV, GC/MS interface and ion source temperatures 250 °C.

Preparation of MWCNT-coated Fiber for HS-SPME

MWCNTs (100 mg) was refluxed in 7 mL of concentrated nitric acid at 110 °C for 1 h. The resultant MWCNTs was collected on a filter paper (Whatman 41, pore size 20 μm) and washed with distilled water until neutral and then dried overnight at room temperature. Then, 40 mg of the acid-treated with MWCNTs and 30 mg SDS was ultrasonically dispersed in 20 mL of water. The temperature of sonication was controlled and contained at 30 °C (±2 °C). The SDS combined with ultrasonication is used as a dispersion medium to debundle carbon nanotubes by steric or electrostatic repulsions. SDS also acts as a bonding material when the film is sintered in the furnace.

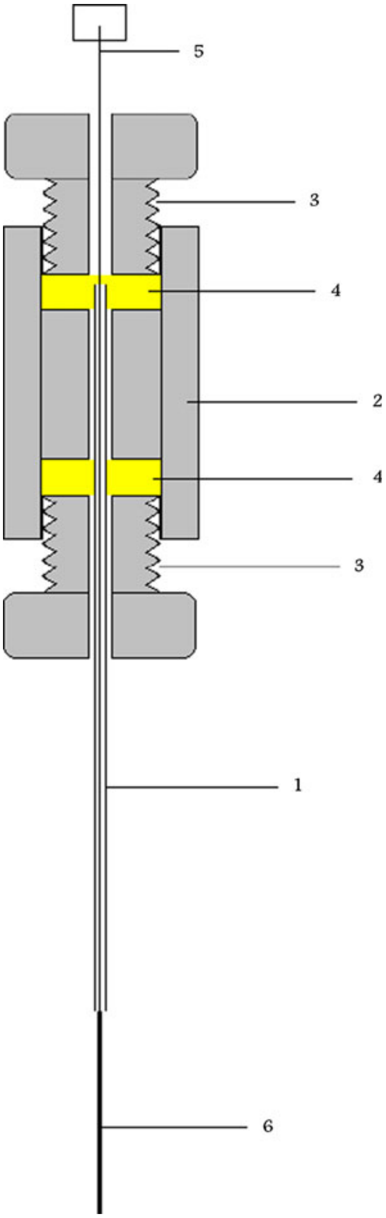

Fig. 1 Schematic of the home made SPME device. *1* Stainless steel needle, *2* hollow Al cylinder, *3* Al nuts, *4* rubber septum, *5* stainless steel fiber, *6* electrophoretic deposited MWCNTs

The electrophoretic deposition was carried out at room temperature. To make the coating adhere firmly to the surface of the wire, the wire surface was first roughened by a smooth sand paper and then washed in water followed by acetone while sonicating. The stainless steel wire, platinum electrode and Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. During the deposition process, a 3 cm length of the fiber was immersed in the suspension in such a way that the working electrode was kept at a distance of 1 cm from platinum electrode. The MWCNTs coating was directly deposited on the stainless steel wire from the above aqueous suspension by applying a constant potential of 8.0 V for 200 s. The coating conditions were optimized to get the maximum amount of the coating with favorable adhesion onto the substrate. The coated fiber was dried at 100 °C for 3 min in the oven, and the deposition process was repeated three more times until a desired thickness was obtained. To remove the SDS remaining in MWCNT-coated fiber, the prepared fiber was immersed in distilled water for an hour while stirring. The washing process was repeated for a second time. Thermal conditioning of the coated fiber was carried out by heating at 100 °C for 1 h in an oven, and then at 280 °C for 2 h in the GC injector port under a helium atmosphere. This was to remove any volatile compound remaining in the fiber.

HS-SPME Procedure

A 0.05 µg mL^{-1} working solution of the mixture of PAHs in distilled water was prepared from the stock solution on a daily basis. HS-SPME extractions were performed by placing 5.0 mL samples into a 12.0 mL sample glass vial capped with a septum. Magnetic stirring with a 1-cm long Teflon-coated stirring bar was used to agitate the samples at the highest but constant possible rate. Extractions were carried out by exposing the coated fiber above the sample solution. The extraction temperature was adjusted by placing the extraction vial in a water bath placed on the magnetic stirrer. After the extraction, the fiber was withdrawn into the needle, removed from the sample vial and immediately introduced into the GC injector port for thermal desorption. All experiments were carried out in triplicate.

Results and Discussion

Characterization of the MWCNTs Fiber

The surface characteristic of the coating was investigated using a scanning electron microscope (SEM). As seen in Fig. 2, the surface of the coating is rough with large effective surface area, which is favorable for the sorption/extraction of analytes. The thickness of coating measured by SEM was approximately 200 µm. The coating produced showed excellent stability in water samples.

To investigate the swelling and adhesion behavior of the coating in organic solvents, the coated fiber was immersed in hexane, acetone, methanol and acetonitrile for more than 3 h. No visible swelling of the coating was observed in these organic solvents. This is in contrast to major swelling of most commercial coatings after such treatment. For the study of the mechanical adhesion of the coating, the fiber was rubbed against a piece of white paper and it was observed that no black particles detached from the fiber. This was an indication of the favorable mechanical strength of the coating.

HS-SPME Optimization

There are a number of factors that may influence the efficiency of the HS-SPME technique including extraction temperature, extraction time, desorption temperature, desorption time, ionic strength, and whether or not samples

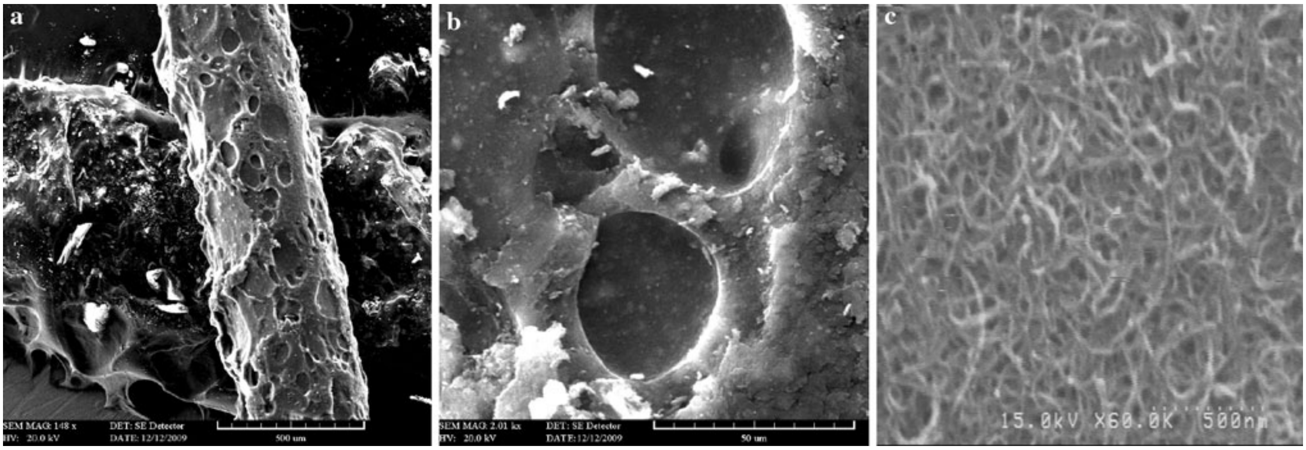

Fig. 2 Scanning electron micrograph images of the surface of the CNTs coating. **a** ×150, **b** ×6,000, **c**×60,000

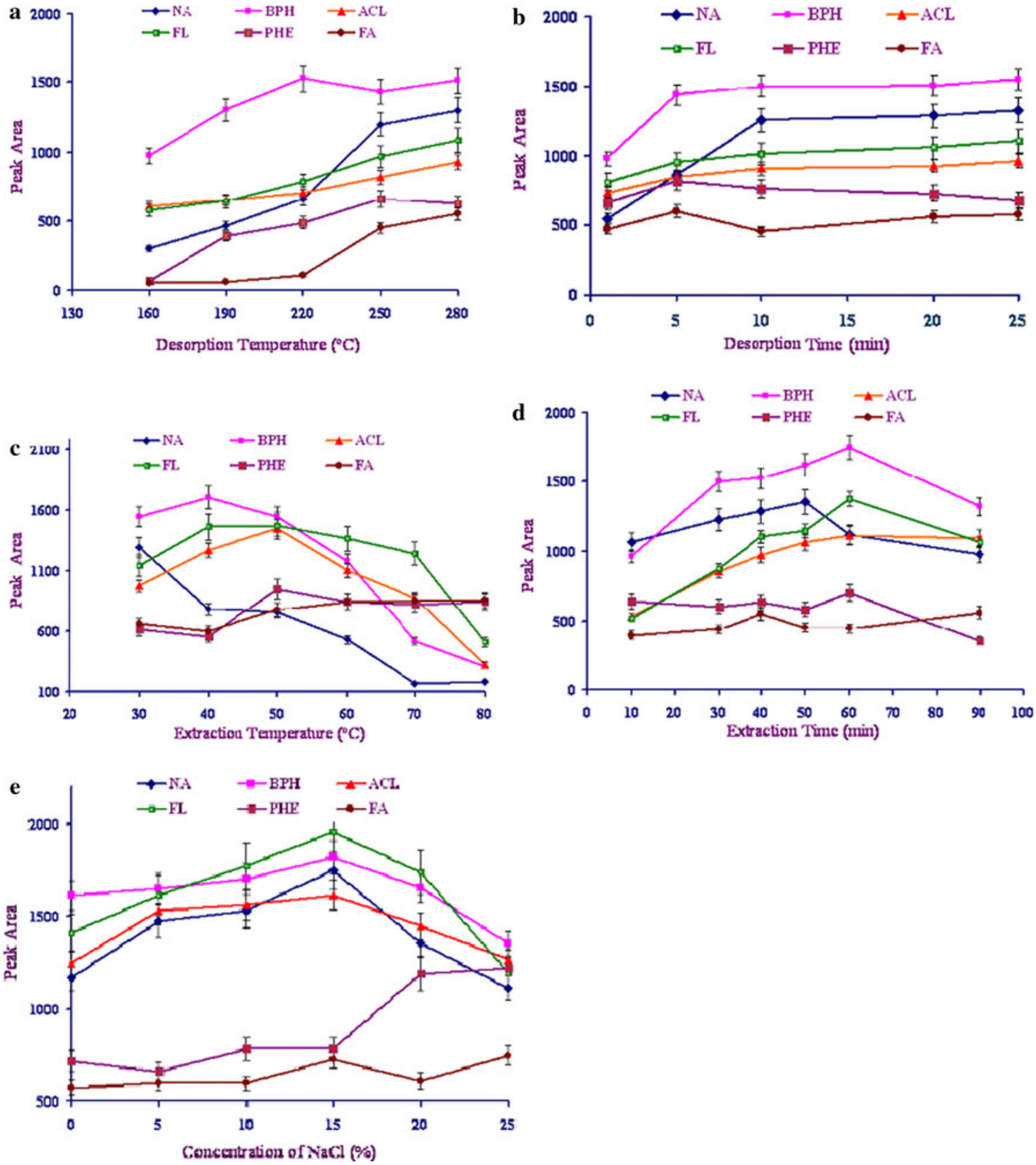

Fig. 3 Effects of desorption temperature, desorption time, extraction temperature, extraction time, and ionic strength on the SPME efficiency from 0.05 μg mL^{-1} each PAH. Conditions: **a** extraction temperature = 50 °C, extraction time = 50 min, desorption time = 20 min, no salt addition; **b** desorption temperature = 280 °C, other parameters the same as **a**; **c** desorption time = 15 min, desorption temperature = 280 °C, other parameters the same as **a**; **d** extraction temperature = 50 °C, desorption time = 15 min, desorption temperature = 280 °C, other parameters the same as **a**; **e** extraction time = 60 min, extraction temperature = 50 °C, desorption time = 15 min, desorption temperature = 280 °C

are agitated during the extraction. As agitation of the sample during fiber exposure has been shown to enhance analyte extraction and to reduce extraction time [14], and magnetic stirring is most commonly used in HS-SPME experiments to accelerate extraction, therefore all the experiments were performed under maximum but constant stirring rate.

Effect of Desorption Parameters

To ensure the complete desorption of analytes from the fiber and to avoid any memory effect or carryover, suitable desorption temperature and time are critical. For this reason, desorption of extracted analytes was carried out in the GC injection port at temperatures in the range of

Table 1 Limit of detection (LOD), percentage recovery (Recovery %), linear range (LR), coefficient of determination (r^2) and precision (RSD%) for the present method

Compound	LOD (ng mL^{-1})	Recovery (%)[a]		LR (ng mL^{-1})	Coefficient of determination r^2	RSD%[b]		
		5 ng mL^{-1}	0.5 ng mL^{-1}			Intra-day ($n = 7$)	Inter-day ($n = 7$)	Fiber-to-fiber ($n = 3$)
Naphthalene	0.06	94 (6.9)	93 (10.4)	0.1–100	0.9830	6.7	7.6	8.4
Acenaphthylene	0.05	96 (5.3)	91 (9.8)	0.1–100	0.9928	5.7	5.5	7.3
Fluorene	0.04	88 (3.9)	94 (5.8)	0.1–100	0.9835	4.1	6.3	6.7
Phenanthrene	0.03	105 (8.7)	101 (9.6)	0.1–100	0.9907	8.5	9.2	10.2
Fluoranthene	0.07	92 (7.2)	97 (11.3)	0.5–50	0.9678	7.8	9.7	11.1
Biphenyl	0.07	91 (5.5)	89 (6.9)	0.1–100	0.9898	5.4	6.3	6.8

[a] The values in parentheses are percent standard deviation for triplicate measurements

[b] Measured at 10 ng mL^{-1} level

Table 2 Comparison of linear range (LR), limit of detection (LOD) and relative standard deviation (RSD%) of the present HS-SPME/GC-FID method using MWCNTs with non-commercial coatings and other techniques

Compound	References			
	Present work	1-Butanol [6][a]	AMTEOS/PDMS [40][b]	SDS/PPy [42][c]
Naphthalene	0.1–100[d]	20–240	1–500	0.9–5
	0.06[e]	4	0.5	0.27
	6.7[f]	5.6	3.6	1.1
Acenaphthylene	0.1–100	–	–	0.2–5
	0.05	–	–	0.06
	5.7	–	–	4.2
Fluorene	0.1–100	10–240	2–1000	0.4–5
	0.04	7	1.5	0.11
	4.1	7.5	2.8	2.9
Phenanthrene	0.1–100	16–160	1–500	0.4–5
	0.03	6	0.2	0.12
	8.5	7.0	8.9	5.3
Fluoranthene	0.5–50	80–240	2–1000	0.3–5
	0.07	27	0.8	0.07
	7.8	12.9	6.3	10
Biphenyl	0.1–100	–	–	–
	0.07	–	–	–
	5.4	–	–	–

[a] HS-solvent microextraction, GC-FID (160 ng mL^{-1})

[b] HS-SPME/GC-FID, sol–gel aniline methyltriethoxysilane/polydimethylsiloxane (AMTEOS/PDMS) (5 ng mL^{-1})

[c] HS-SPME/GC–MS, dodecyl sulfate-doped PPy coating (10 ng mL^{-1})

[d] The first row of figures for each compound indicates linear range (ng mL^{-1})

[e] The second row of figures for each compound indicates detection limit (ng mL^{-1})

[f] The last row of figures for each compound indicates RSD%

160–280 °C. Higher temperatures were not used due to the thermal instability of the septum, which would cause noticeable blank signal and also gas leak due to boring of the septum by the SPME needle and reducing the septum lifetime. Figure 3a shows that larger peak areas are obtained at a desorption temperature of 280 °C. Desorption times were also optimized by placing the fiber in the GC injection port for a period of 1.0–25.0 min. The result showed that between 80 and 95 % of analytes was desorbed after 10 min. However, to eliminate any sample carryover, 5.0 min extra time was considered in this step, after which no carry over was observed. Therefore, a desorption time of 15.0 min was used in all experiments (Fig. 3b).

Effect of Extraction Temperature

PAHs show a wide range of volatility, and the release of those with lower volatility to the headspace during extraction is limited. In general, increasing the temperature could enhance the Henry's constants and diffusion coefficients of PAHs, and consequently the vapor pressure and the concentration of the analytes in the headspace increase [37]. Figure 3c shows the effect of extraction temperature in the range between 30 and 80 °C. As this figure shows, increasing temperature produces a negative effect on the extraction of naphthalene which is the most volatile PAH. However, the extraction of other PAHs increases up to a temperature of 50 °C, but due to the exothermic nature of the sorption process, beyond this temperature the extraction efficiencies almost invariably decrease. Therefore, 50 °C was chosen as the optimum extraction temperature.

Effect of Extraction Time

Since the HS-SPME technique is an equilibrium process of the analytes between the vapor phase and the fiber coating, it is important to determine the time required for reaching the equilibrium state [38]. In this work, six different extraction times were examined, the results of which are shown in Fig. 3d. As this figure shows, the extraction efficiencies reach a maximum at 60 min, after which they decrease. Therefore, an extraction time of 60 min was selected as the optimum time.

Ionic Strength

Enhanced ionic strength through addition of a salt is reported to increase extraction efficiencies and is known as the "salting-out" effect [39]. In this study, sodium chloride (NaCl) was used for adjusting the ionic strength. Although PAHs are considered as semi-polar compounds, increased ionic strength of the solution is reported to enhance PAHs sorption. In this respect, extractions were carried out from 0.05 μg mL^{-1} mixed PAHs solutions in the presence of

Table 3 Comparison of linear range (LR), limit of detection (LOD) and relative standard deviation (RSD%) of the present HS-SPME/GC-FID method using MWCNTs with similar works using commercial coatings

Compound	Present work	PDMS [2][a]	PA [2][b]	PDMS/DVB [41][c]	PA [43][d]
Naphthalene	0.1–100[e]	–	–	0.5–100	1–100
	0.06[f]	0.15	0.22	0.1	0.2
	6.7[g]	7	3	7	9.6
Acenaphthylene	0.1–100	–	–	0.5–100	10–100
	0.05	0.21	0.13	0.1	0.17
	5.7	3	10	9	8.3
Fluorene	0.1–100	–	–	0.5–100	10–100
	0.04	0.08	0.08	0.08	0.15
	4.1	2	10	6	12.8
Phenanthrene	0.1–100	–	–	0.1–20	10–100
	0.03	0.12	0.08	0.04	0.09
	8.5	3	8	8	10.1
Fluoranthene	0.5–50	–	–	0.1–20	10–100
	0.07	0.25	0.17	0.03	0.14
	7.8	8	11	8	11.4
Biphenyl	0.1–100	–	–	–	–
	0.07	–	–	–	–
	5.4	–	–	–	–

[a] HS-SPME/GC-FID (10 ng mL^{-1}), 100 μm PDMS coating

[b] HS-SPME/GC-FID (10 ng mL^{-1}), 85 μm PA coating

[c] HS-SPME/GC-FID, microwave-assisted extraction (10 ng mL^{-1}), 65 μm PDMS/DVB coating

[d] HS-SPME/GC-FID (10 ng mL^{-1}), 85 μm PA coating

[e] The first row of figures for each compound indicates linear range (ng mL^{-1})

[f] The second row of figures for each compound indicates detection limit (ng mL^{-1})

[g] The last row of figures for each compound indicates RSD%

0–25 % (w/v) NaCl. The results found are shown in Fig. 3e. As this figure shows, maximum extraction was obtained at 15 % (w/v) NaCl concentration. It seems that the salting-out effect lowered the solubility of PAHs in water and forced them to enter the vapor phase and be extracted by the fiber. Therefore, increased efficiency of extraction is resulted.

Validation Parameters

After optimizing the SPME procedure, figures of merit including linear range (LR), precision in terms of reproducibility and repeatability (RSD%) and limit of detection (LOD) were evaluated. The linear ranges determined for various PAHs were, in most cases, between 0.1 and 100 ng mL^{-1}. The coefficients of determination (r^2) obtained were between 0.9678 and 0.9928, as shown in Table 1. The precision of the method reported in Table 1 was determined by seven replicate analyses from mixed aqueous solutions containing 10 ng mL^{-1}of each PAHs. As this table shows, intra-day relative standard deviations (RSD%) varied between 4.1 and 8.5 %, while inter-day relative standard deviations were between 5.5 and 9.7 %. Also, the fiber-to-fiber precisions determined at 10 ng mL^{-1} level ($n = 3$) varied between 7.3 and 11.1 %. Table 1 also presents the detection limits based on S/N = 3 ratio in the present HS-SPME method, which are in the range 0.03–0.07 ng mL^{-1}.

In Table 2, a comparison is made between the LOD, RSD%, and LR values obtained in the present work and similar work reported by other research groups using non-commercial coatings or other techniques. As this table shows, the LOD and RSD% values found in the present work are better or comparable with the values reported for other methods. A comparison between the performance of the prepared fiber and different commercial fibers is also shown in Table 3. It is clearly seen that the performance of the present fiber coating is better than these PDMS and PA commercial fibers.

Real Sample

To confirm the applicability of the present HS-SPME method to extract PAHs from real samples, extraction recoveries were determined by extracting a tap water sample collected from the university campus and spiked with PAHs at a 5 and 0.5 ng mL^{-1} concentration level. Before analysis, the sample was filtered through 0.45 μm Millipore filter to ensure that the PAHs were present in a dissolved form. Three replicate analyses were performed on the sample using the MWCNT-coated fiber at optimal HS-SPME conditions. The recovery values at 5 and 0.5 ng mL^{-1} were between 88–105 % and 89–101 %, respectively (Table 1). The recovery values were in a satisfactory range, which demonstrated the suitability of HS-SPME method for extracting PAHs from water. As a real sample suspected of containing PAHs, the analysis of a sample of well water collected from the vicinity of a coal industry in Zarand (Iran) was also carried out. The analysis confirmed the presence of two PAHs, i.e. fluorene and phenantherene, present at 2.4 and 3.1 ng mL^{-1}, respectively. Compound identification was performed using GC–MS technique. The chromatograms showing the results obtained for the well water sample along with the results obtained for a standard sample and the tap water sample are shown in Fig. 4.

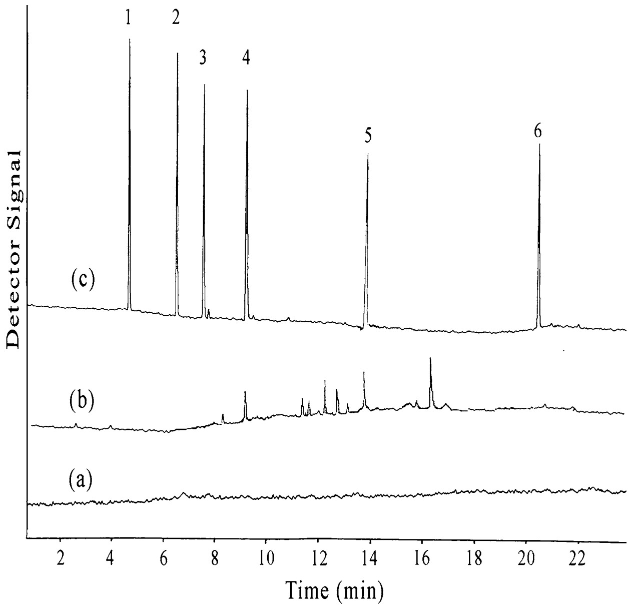

Fig. 4 The chromatogram obtained after HS-SPME-GC analysis of 5.0 mL *a* blank, *b* Zarand well water sample, *c* 10 ng mL^{-1} standard solution of each PAH. SPME conditions: extraction temperature 50 °C; extraction time 50 min; desorption time 15 min; desorption temperature 280 °C; salt concentration 15 % NaCl. Peak assignment: *1* naphthalene, *2* biphenyl, *3* acenaphthylene, *4* fluorene, *5* phenanthrene, *6* fluoranthene

Conclusion

In this study, a novel HS-SPME device was fabricated by electrophoretic deposition of modified MWCNTs from aqueous media on the surface of a stainless steel fiber. The aqueous medium made it possible to carry out the electrophoretic deposition at a lower potential and lower sonication time compared to organic media reported earlier [36]. The device showed high extraction efficiency toward PAHs in water. The coating had a porous structure, with high specific surface area and sorption capacity, and thus its high extraction efficiency. It was also stable enough to carry out at least 30–40 SPME extractions before being discarded. The proposed method showed good precision, wide linear range, low detection limits and high recoveries. Also, using SDS as the modifier of the surface of MWCNTs lowers the carbonyl content of the MWCNTs surface, making it more suitable for the extraction of less polar compounds. It is expected that this coating has considerable potential for the preconcentration and determination of other analytes from aqueous media.

Acknowledgments This paper is dedicated to the late Mrs. Fakhereh Saba, who without her support the Shahid Bahonar University of Kerman would not have been established.

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