Dodecylsulfate-doped polypyrrole film prepared by electrochemical fiber coating technique for headspace solid-phase microextraction of polycyclic aromatic hydrocarbons

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Abstract

The electrochemical fiber coating (EFC) technique was used for the preparation of dodecylsulfate-doped polypyrrole (PPy-DS), and applied as a new fiber for solid-phase microextraction (SPME) procedures. PPy-DS film was directly electrodeposited on the surface of a platinum wire from an aqueous solution containing pyrrole and sodium dodecylsulfate, using cyclic voltammetry (CV). The effect of polymerization conditions and type of dopants on the thermal stability, adhesion and extraction characteristics of the fiber were investigated. The electron microscopy imaging of PPy-DS film suggested that the surface fiber coating was well-distributed with a porous structure. The fiber coating can be prepared easily in a reproducible manner, and it is inexpensive and has a stable performance at high temperatures (up to the 300 °C). The extraction properties of the fiber to eight polycyclic aromatic hydrocarbons (PAHs) were examined, using a headspace-SPME (HS-SPME) device coupled with gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS). The results revealed study shows that PPy-DS as a SPME fiber coating is suitable for the successful extraction of PAHs. The effects of the extraction parameters including exposure time, sampling temperature, salt concentration, and stirring rate on the extraction efficiency have been studied. A satisfactory reproducibility for extractions from spiked water samples at PPb-level with R.S.D. < 7.6% ($n = 7$) was obtained. The calibration graphs were linear in the range of 0.5–100 ng ml^{-1} and detection limits for the selected PAHs were between 0.05–0.16 ng ml^{-1}. Comparing the HS-SPME results for extraction and determination of PAHs using PPy-DS fiber with the corresponding literature data using PDMS fiber shows that the proposed fiber has a better detection limit for low molecular weight PAHs. The life span and stability of PPy-DS fiber is good and it can be used more than 50 times at 250 °C without any significant change in sorption properties.
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1. Introduction

Pawliszyn and coworkers devised solid-phase microextraction (SPME) as a new extraction technique in 1989 [1]. This technique uses a thin polymer film coating to extract analytes from aqueous or gaseous samples. Then, the fiber is inserted directly into the injector of a gas chromatography system, and the extracted analytes are thermally des-

orbed and analyzed. SPME can integrate sampling, extraction, preconcentration and sample introduction into a single step. The technique is very simple, fast, solvent-free, inexpensive, easily automated, and reliable, and has been applied to both headspace and direct aqueous sample analysis with excellent sensitivity and good selectivity [2]. Nowadays, SPME is among the most recommended techniques, employed for the extraction and preconcentration of volatile and semi-volatile compounds at trace levels in variety of matrixes [3–7]. The introduction of new polymeric fibers, the development of new experimental configurations and the improvement of automatic devices will undoubtedly lead

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to the application of SPME to different fields of chemical analysis.

To achieve more selective determination of different classes of compounds, the number of available coating materials has increased in recent time. Up to now, only seven kinds of SPME coatings are commercially available: poly-dimethylsiloxane (PDMS), PDMS-divinyl benzene (DVB), polyacrylate (PA), carboxen-PDMS, carbowax (CW)-DVB, carbowax-templated resin, and stable flex DVB-carboxen-PDMS. The non polar PDMS fiber was the first polymer being used for SPME and, to date, this coating is the most used one, which extracts only non polar analytes very well [8–10]. However, according to the principle of a like dissolve like, the polar compounds are more likely to be extracted by polar coatings such as PA and CW-DVB [11,12]. The CW-DVB fiber is strongly polar, but its maximum temperature is only 265 °C which limits its application range.

In recent years, intrinsic conducting polymers with conjugated double bonds have attracted much attention as advanced materials. There has been growing interest in conducting polymers due to their multifunctional properties and potential applications, as ion exchangers, energy-storage materials, corrosion-resistant coatings, catalysts, chemical sensors and materials for separation [13–27]. They are versatile materials in which molecular/analyte recognition can be achieved in different ways, including: (i) the incorporation of counter ions; (ii) utilizing the inherent and unusual multifunctionality of the polymer (e.g., hydrophobicity, acid–base character, π–π interaction, polar functional groups, ion exchange property, hydrogen bonding, and electroactivity) and (iii) the introduction of functional groups to the monomers. Also, these materials have additional advantages as they can be easily synthesized in both aqueous and nonaqueous media, chemically and electrochemically. There are varieties in type of dopant and additives during synthesis. All these conditions and varieties affect the chemical, mechanical, morphological and electronic properties of the polymers.

Among those conducting polymers, polypyrrole (PPy) is especially promising for commercial applications because of its good environmental stability, facile synthesis and higher conductivity over many other conductive polymers. Pyrrole can be polymerized conveniently with oxidation reactions by either an electrochemical method or a chemical method. Chemical polymerization method is capable of producing polymers on a large scale. However, the flexibility of PPy is limited by the nature of oxidizing reagents used and the reaction conditions employed. Electrochemical synthesis is more convenient, because polymer film is directly electrodeposited on the surface of metal wires from an aqueous solution containing pyrrole and electrolyte, using one of the electrochemical techniques. The advantages of electrochemical method are that it can be controlled easily and it is more flexible, because polymers with different functional groups can be formed conveniently by changing dopant ions or using substituted pyrrole monomers under controlled electrochemical conditions. Moreover, the polymer film can be coated directly on the metal wires (such as Pt) which have better mechanical strength than silica fibers. The electrochemical polymerization of pyrrole in aqueous solutions has offered the possibility for a large number of anions to be applied as dopants [19]. Recently, Pawliszyn and co-workers synthesized PPy on the surface of metal wires by a potentiostatic method and applied this film for SPME of some alcohols in gas phase [24]. Thermal stability of this film was reported to be about 200 °C. Obviously the lower thermal stability of the film restricts the range of applications of this film in on-fiber SPME.

PAHs are the ubiquitous contaminants in the environments. These compounds are originally from both natural and anthropogenic sources that involve incomplete combustion, aluminum smelting or from the spillage of fossil fuels. On the basis of properties and molecular mass of PAHs, two classes of PAHs can be distinguished (i.e., the two- and three- rings and four- to six-rings, [28]. The low-molecular-mass two- and three-ring PAHs have a significant acute toxicity whereas some of the high-molecular-mass PAHs shows high carcinogenic and mutagenic potentials [29,30]. Due to their potential or proven carcinogenic effect, the US Environmental Protection Agency (EPA) has promulgated 16 unsubstantiated PAHs in their list of 129 priority pollutants [31].

In this paper, we present preliminary results on the electrochemical fiber coating (EFC) method for preparation of anion-doped polypyrrole and its application as a new fiber for headspace solid-phase microextraction (HS-SPME). The influence of dopant on morphology and thermal stability of the polymer prepared by cyclic voltammetry (CV) was investigated using scanning electron microscopy (SEM) and thermal gravimetric analyses. In addition dodecylsulfate-doped polypyrrole (PPy-DS), as a thermally stable and suitable fiber, was used for the extraction and determination of some PAHs by HS-SPME device coupled with gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS). To determine the amount of PAHs in water samples, the effects of main extraction parameters, such as exposure time, sampling temperature, salt concentration, and stirring rate on the extraction efficiency were also investigated. The resulting HS-SPME-GC-MS detection limits using PPy-DS as a new sorbent were compared with those obtained using commercial PDMS previously reported in literature.

2. Experimental

2.1. Reagents

Pyrrole (Fluka, Switzerland) was distilled before use. The polycyclic aromatic hydrocarbons (PAHs) including naphthalene (99%), acenaphthylene (98%), acenaph-

thene (99%), flurene (99%), phenanthrene (98%), fluoranthene (98%), pyrene (98%), and chryzene (97%) were obtained from Fluka and Merck (Darmstadt, Germany). The stock solutions of these compounds were prepared at a concentration of $2\,mg\,ml^{-1}$ in methanol–dichloromethane (50:50). These stock standard solutions were diluted with methanol–dichloromethane (50:50) to prepare a mixed stock solution with concentration of $0.1\,mg\,ml^{-1}$ for each PAH. The model solutions containing the required amount of each analyte ($0.5–200\,ng\,ml^{-1}$) were freshly prepared daily by diluting mixed standard solutions with double distilled water. Stock and working standards were stored at $4\,°C$ in the refrigerator. All solvents used in this study, were of analytical reagent grade or HPLC grade. Sodium dodecylsulfate (SDS), sodium chloride, sodium perchlorate, sodium sulfate, and sodium acetate were of the highest purity available and obtained from Aldrich and Merck.

2.2. Apparatus

The SPME holder for manual sampling was obtained from Azar Electrode (Ourumieh, Iran). A magnetic stirrer (Heidolph MR 3001 K) and a $8\,mm \times 15\,mm$ stirring bar were used to stir the solution. A laboratory-made two compartment-recirculating glass cell in conjunction with circulating water baths (Frigomix B. Braun UM-S) were used for adjusting the temperature of sample solutions with an accuracy of $±0.1\,°C$.

Electrochemical polymerization of pyrrole was carried out using a Behpajuh (BHP 2061-C model) potentiostat (Isfahan, Iran). An electrochemical cell including an extra pure platinum working electrode ($2\,cm \times 200\,\mu m$ I.D.), a Pt counter electrode and a double junction saturated calomel electrode (dj-SCE), as reference electrode were used for preparation of the polymer.

Separation and quantification of PAHs analytes were carried out using a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and a DB-5 (5% biphenyl + 95% methyl polysiloxane) fused-silica capillary column ($20\,m \times 0.53\,mm$ I.D. and $1.5\,\mu m$ film thickness, J&W Scientific, Folsam, CA). The injection port and detector were operated at 250 and $280\,°C$, respectively. Fiber was introduced into the chromatographic columns using splitless mode injection. The GC split valve was closed for 5 min, and helium was used as carrier gas with a flow rate of $6\,ml\,min^{-1}$. The detector gases flow rates were $300\,ml\,min^{-1}$ of air and $30\,ml\,min^{-1}$ of hydrogen. A Hewlett-Packard (HP, Palo Alta, USA) HP 6890 series gas chromatograph equipped with an split/splitless injector and a HP 5973 mass-selective detector was also used. The analytical column was a HP-5 with a $30\,m \times 0.25\,mm$ I. D. and $0.25\,\mu m$ film thickness. Chromatographic data were recorded using an HP Chemsation, which was controlled by Windows NT (Microsoft) and equipped with Wiley mass spectral library. Helium and nitrogen (99.999%) were used as carrier and make-up gas, respectively. The flow rate of carrier gas was adjusted at

$1\,ml\,min^{-1}$. The separation of PAHs on GC-FID and GC-MS was performed by a temperature program as follows: $50\,°C$ for 4 min, increased to $280\,°C$ at a rate of $10\,°C\,min^{-1}$ and held at $280\,°C$ for 10 min.

The scanning electron micrographs of the fiber surface were obtained using a Philips XL30 scanning electron microscopy (Holland). Thermal gravimetric analysis was performed using a PL-STA 1500 Thermal Science (England).

2.3. Electrochemical fiber coating

Polypyrrole film was prepared electrochemically using a three-electrode system. PPy-DS film was directly electrodeposited on the surface of a platinum wire (as working electrode) from an aqueous solution containing pyrrole (0.1 M) and SDS (7×10^{-3} M) using cyclic voltammetry (CV). Prior to electropolymerization, the solution was deoxygenated by purging with N_2 for 5 min, and the platinum wire surface was cleaned in acetone using ultrasonic bath for 15 min and was subsequently washed with distilled water. The experimental parameters for CV technique were scan rate, $20\,mV\,s^{-1}$; potential range 0.5–1.2 V; number of scans, 10 cycles. The metal wire coated with PPy-DS film was washed with methanol, acetone, water and then dried under nitrogen gas flow. The thickness of the coating obtained under this condition was $16\,\mu m$ according to the SEM study. The PPy-DS fiber was connected to the stainless steel tubing of SPME holder. Before its use for SPME experiment, the fiber was heated at $100\,°C$ for 20 min in oven, and finally conditioned at $280\,°C$ in a GC injection port under helium gas for 1 h until a clean blank was obtained. Moreover, blanks were run periodically during the analysis to confirm the absence of contaminants.

2.4. Headspace extraction procedure

A 10-ml aliquot of aqueous solution spiked with the PAHs was extracted with PPy-DS fiber using the HS-SPME mode. The PPy-DS fiber housed in manual SPME holder was used. The fiber was conditioned prior to use by inserting into the GC injection port for 5 min. Water (10 ml) containing the target PAHs was placed in a 25 ml glass vial with a PTFE-silicon septum. After the addition of sodium chloride and magnetic stirring bar, the vial was tightly sealed with a aluminum cap to prevent sample loss due to evaporation. During the extractions, the vials were thermostated using a heated circulating water bath, and the temperature was maintained at the desired value by circulating.

The PPy-DS fiber was exposed to the headspace over the stirring liquid sample for 10–120 min, depending on the experiment. After completion of sampling step, the fiber was withdrawn into the needle and removed from the sample vial. The fiber was then immediately inserted into the injection port of the GC.

3. Result and discussion

The quality and thickness of polymer film can be greatly influenced by experimental parameters such as type of the dopant ion, electrochemical conditions and reaction medium. Meanwhile, it is well-understood that the size, geometry and charge of counter ions have a significant effect on the property of PPy films. In this work, PPy was synthesized in the presence of different dopants such as chloride, perchlorate, acetate, sulfate, and dodecylsulfate ions in aqueous medium. Polymer films doped with chloride, perchlorate, and acetate anions showed weak adhesion on the Pt wire and were unstable at high temperatures (>200 °C). Therefore, the application of these three fibers for extraction were impossible. While, corresponding thermogravimetric curves revealed that the fibers coated with sulfate (PPy-S) and dodecylsulfate-doped PPy (PPy-DS) at 200–450 °C with ramp of 10 °C min^{-1} under argon atmosphere are thermally stable up to 300 °C In addition, the perfect adhesion of these films to Pt wires were established. The extraction properties of these two fibers to eight PAH were examined using a HS-SPME devise. The extraction abilities under the same experimental conditions are illustrated in Fig. 1. The results showed that PPy-DS possesses a better efficiency toward the PAHs than PPy doped with sulfate, PPy-S, (some three times). These results can be explained by the presence of a C12 chain alkyl group in DS ion increased the hydrophobic interaction of PPy-DS film with PAHs. It had been reported that the introduction of an anionic surfactant during the preparation of the PPy leads to improved properties of the polymers [32,33]. Thus, PPy-DS was employed as fiber coating at HS-SPME for further analyses of PAHs in water samples.

The thickness of fiber coating can be controlled by electrochemical conditions. Thus, effect of electrochemical conditions such as scan rate and cycle number on the extraction property of PPy-DS fiber was also investigated. The extraction ability of PPy-DS fibers prepared by CV at various cycle numbers and scan rates are shown in Figs. 2 and 3, respectively. Good extraction efficiency was observed for PPy-DS films prepared under a cycle number range of 10–20 and a scan rate 20 mV s^{-1}. However, the extraction efficiency diminished at higher scan rates.
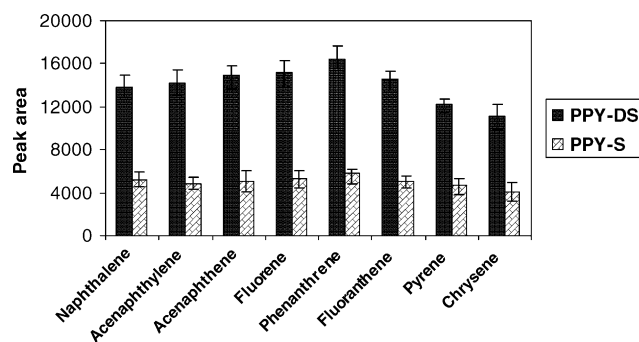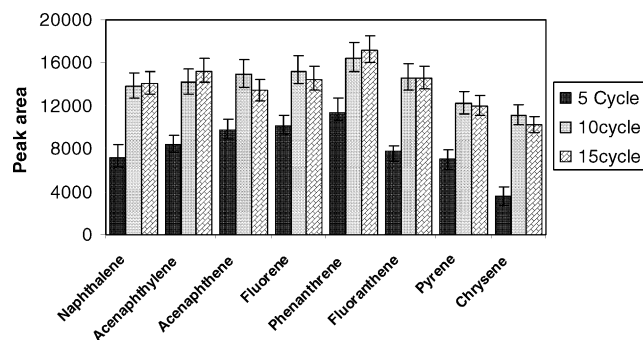
Fig. 2. Effect of cycle number during EFC of PPy-DS at 20 mV s^{-1} on the signal intensity of PAHs.

3.1. Characteristics of the PPy-DS fiber coating

The surface characteristics of the polymer films were investigated by scanning electron microscopy. Fig. 4 shows the micrographs of the PPy-DS fiber at 250 (A), 1000 (B), and 2500 (C) folds magnifications. As can be seen from Fig. 4, the electrochemical coating possesses a porous structure and the surface of the fiber is very-well distributed. A high surface area provides the fiber with large stationary phase loading and high extraction capacity. The thermal stability of fiber is an important parameter in SPME experiments. Usually, the coatings are mainly damaged at high temperatures of the injection port of gas chromatographs. While, the high thermal stability of fiber allows the use of high-injection temperatures for efficient desorption of less-volatile analytes, so that a great number of less-volatile compounds can be analyzed. The fibers coated with dodecylsulfate-doped PPy were found to be stable at high temperatures up to 300 °C. In fact, it was found that the extraction peak area remain more or less the same after the fiber was conditioned for 1 h at temperatures 200, 220, 250, and 280 °C, successively.

The coating lifetime is important for practical application. The life span of the PPy-DS fiber was also evaluated. We have used the PPy-DS fiber for extraction of PAHs from aqueous solutions more than 50 times at 250 °C. The extraction efficiency results show that it have no obvious decline after a

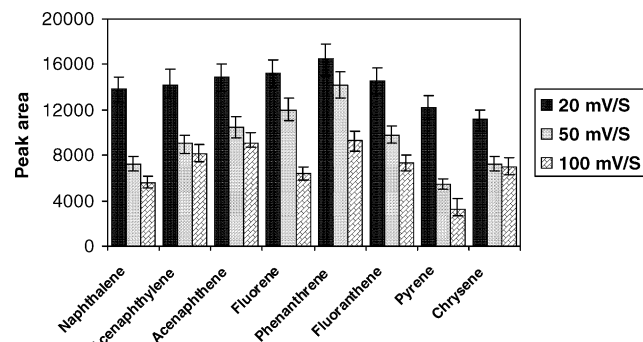Fig. 1. Comparison of the extraction abilities of PPy-DS and PPy-S coatings for the PAHs.

Fig. 3. Effect of potential scan rate during EFC of PPy-DS with 10 cycles on the signal intensity of PAHs.
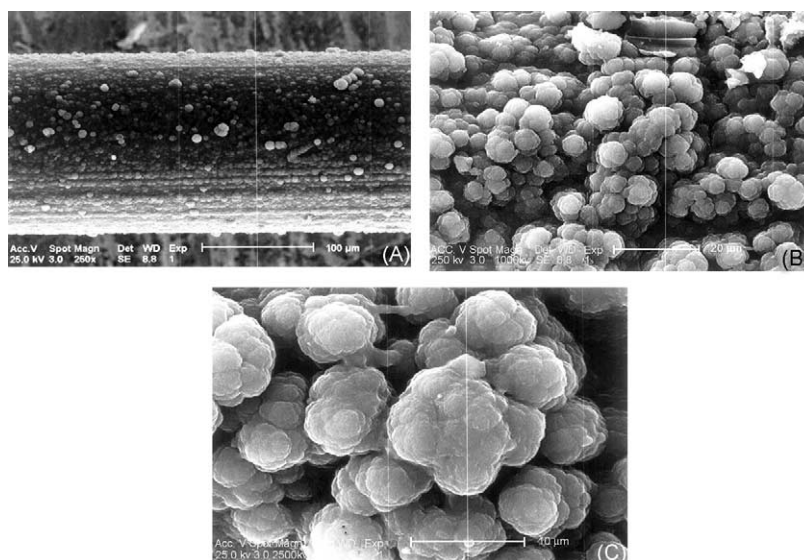
Fig. 4. The scanning electron micrograph of the dodecylsulfate-doped polypyrrole fiber at 250 (A), 1000 (B), and 2500 (C) folds magnification.

PPy-DS fiber being used for more than 50 times, so that it is still stable and reusable.

The fiber-to-fiber reproducibility was also investigated. To evaluate the reproducibility of the electrochemical coating procedure, three different fibers were coated under the same synthetic conditions, After performing microextractions under similar experimental conditions, the results were found to be almost identical within the precision of the method (R.S.D. = 3.3–7.4%). The results clearly indicate that the EFC technique possesses a good reproducibility for SPME fiber preparation.

The desorption time was studied by leaving the fiber in the injector for progressively longer periods of time, after it had been exposed to solutions of the same concentration, under identical adsorption parameters. Desorption times from 1 to 6 min were investigated. The carry over was measured with one blank injection following the initial desorption. At the desorption temperature of 250 °C, PAHs were fully desorbed from the fiber coating after 2 min and no carry over effect was observed in blank injections.

3.2. Analysis of PAHs compounds

A mixture of eight PAHs including: naphthalene, acenaphthylene, acenaphthene, flurene, phenanthrene, fluoranthene, pyrene, and chrysene were used as model compounds. The SPME of the selected analytes was performed from the headspace of water solution spiked with PAHs. The effect of main extraction parameters, such as exposure time, sampling temperature, salt concentration, and stirring rate of the sample were studied. The adsorption time profiles were studied by monitoring the GC peak area as a function of exposure time, while the fiber was exposed to standard solutions of the PAHs at a concentration of 10 ng ml^{-1} for time ranging

from 10 to 120 min (Fig. 5). All results were obtained from three replicates to ensure reproducibility. Fig. 5 shows that at constant temperature, the extraction efficiency increases with exposure time, and reaches a plateau when an equilibrium is established. The equilibrium times for the PAHs increased with increasing molecular mass. Fig. 6 presents the effect of solution temperature on the extraction ability of mixture, obtained by plotting the peak area as a function of temperature. As can be seen, the extraction ability increases, with increasing temperature, up to 45 °C, due to the increasing distribution constant of analytes between the aqueous phase and headspace. However, for most of the PAHs a slight decrease in adsorption capacity was observed when temperature increased up to 70 °C. This is most probably due to a decreased partition coefficient of analytes between headspace and fiber, because adsorption is generally an exothermic process.
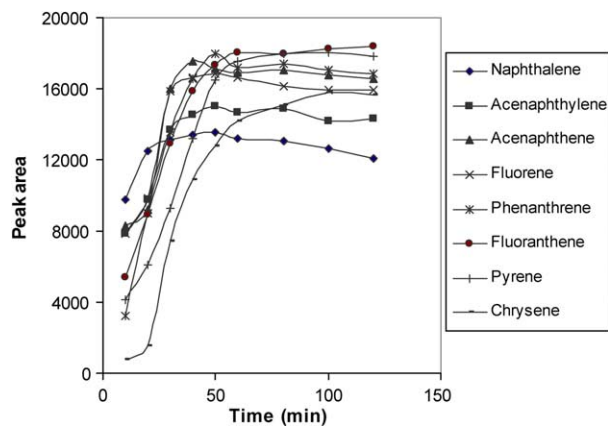

Fig. 5. Effect of the extraction time on the signal intensity of PAHs. Conditions: PAHs concentration: 10 ng ml^{-1}, extraction temperature: 45 °C, stirring speed: 500 rpm, NaCl: 3 M (R.S.Ds. were in the range of 3.5–9.5%).
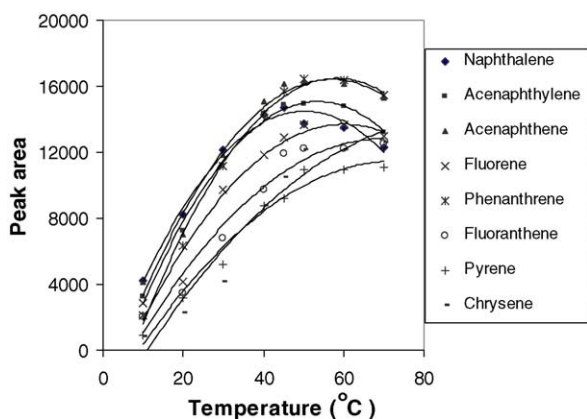
Fig. 6. Influence of the extraction temperature on the signal intensity of PAHs. Conditions: PAH concentration: 10 ng ml^{-1}, extraction time: 30 min, stirring speed: 500 rpm, NaCl: 3 M (R.S.Ds. were in the range of 2.6–9.1%).

The influence of NaCl concentration on the extraction efficiency was investigated by preparing solutions of PAHs in a range of 0–4 M. The results indicated that the extraction efficiency increases with increasing concentration of NaCl, reaches a maximum in the presence of 3 M NaCl and remains constant thereafter. The best results obtained for an aqueous sample containing 3 M NaCl, which was three to eight times greater than that obtained for an aqueous sample with no added NaCl. Therefore, all further extractions were conducted with 3 M NaCl added.

Agitation of the sample improve mass transfer in the aqueous phase and induces the convection in the headspace, and consequently, the between aqueous phase and headspace can be achieved more rapidly. In other words, sample stirring reduces the time required to reach the equilibrium and extraction time by enhancing the diffusion of the analytes towards the fiber, especially for higher molecular mass analytes. Extraction efficiency of the studied compounds was measured from 10 ml of the model sample solutions containing 3 M NaCl and 30 min extraction times at various stirring speeds.

The results revealed that extraction efficiency reaches a maximum and remains constant above 500 rpm.

3.3. Quantitative analysis

Figures of merit of the method including dynamic linear range (DLR), correlation coefficient of calibration graph, and relative standard deviation are listed in Table 1. Calibration curves were drawn using 10 spiking levels of PAHs in the concentration range of 0.5–200 ng ml^{-1}. For each level, three replicate extractions and determination were performed at optimal conditions. The values of correlation coefficient obtained, were between 0.985 and 0.998, showing an acceptable linearity in the dynamic ranges represented in Table 1. The relative standard deviations (R.S.Ds.) were between 2.6 and 7.6% for 5 replicate analyses of model aqueous solutions. Limits of detection (LODs) calculated as three times the baseline noise under MS-SIM conditions, were in the range of 0.05–0.16 ng ml^{-1} (Table 1). Comparing the HS-SPME results for extraction and determination of PAHs using PPy-DS fiber with literature data using PDMS [34] fiber shows that the proposed fiber has better detection limits for low molecular weight PAHs (Table 1).

3.4. Application to real samples

To evaluate the reliability of the proposed method, two real water samples, along the banks of the Caspian Sea (Rasht, Iran) and Zayandeh-rood river (Isfahan, Iran) were collected in amber glass bottles (1000 ml). The bottles were rinsed several times with the water to be analyzed and, afterwards, filled until overflow to prevent loss of volatile compounds in the presence of head space. The water samples were transported and stored at 4 °C until their analysis for PAHs (without any pre-treatment). No PAHs were found in samples under GC-FID analysis. Thus, the samples were spiked with 5 ng ml^{-1} of eight PAHs and five replicate HS-SPME analyses were performed for each water sample using the PPy-DS fiber at optimal conditions. The percent recoveries for samples obtained by GC-FID were between 83–108%, indicating that the process is not influnced by the matrix for the samples of the promulgated PAHs. Finally, the real samples were analyzed for PAHs by the proposed method using GC-MS. Fig. 7

Table 1
Dynamic linear range (DLR), correlation coefficient and relative standard deviation for the analysis of PAHs with HS-SPME-GC using PPy-DS fiber and comparison of the detection limits obtained by HS-SPME-GC-MS with 16 μm PPy-DS and 100 μm Poly dimethylsiloxane (PDMS) fibers (Ref. [34])

Compound	DLR (ng ml^{-1})	Correlation coefficient	R.S.D. %, $n = 7$ (2 ng ml^{-1})	LOD[a] (pg ml^{-1})	
				PPy-DS	PDMS
Naphthalene	0.5–100	0.981	6.8	160	180
Acenaphthylene	0.5–100	0.994	3.5	90	270
Acenaphthene	0.5–100	0.991	2.9	55	100
Fluoren	0.5–100	0.998	2.6	50	70
Phenanthrene	0.5–100	0.992	5.3	60	80
Fluoranthene	0.5–100	0.994	4.8	120	100
Pyrene	1–100	0.991	6.9	130	110
Chrysene	1–100	0.985	7.6	150	30

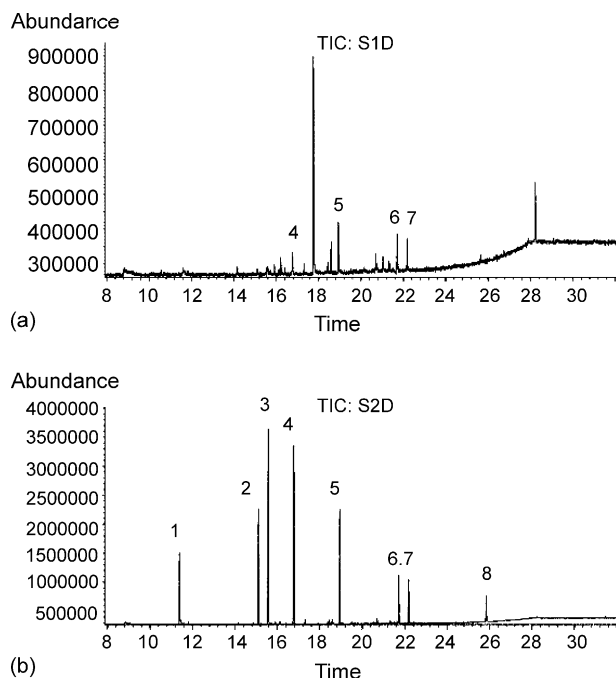[a] Limit of detection calculated as three times the baseline noise.

Fig. 7. The total ion chromatogram (TIC) obtained by SPME-GC-MS under full scan acquisition mode (20–500 Da) for a sea water in a extraction time of 30 min: (a) non-spiked and (b) spiked with 5 ng ml^{-1} of eight PAHs using a PPy-DS fiber. (1) naphthalene, (2) acenaphthylene, (3) acenaphthene, (4) flurene, (5) phenanthrene, (6) fluoranthene, (7) pyrene, and (8) chryzene.

illustrated total ion chromatogram (TIC) obtained under full scan acquisition mode for sea water spiked with 5 ng ml^{-1} PAHs and non-spiked samples. Some of the compounds included in this study were found at very low levels in the sea water sample and its concentration was evaluated using HS-SPME method. The data was further confirmed by the standard addition method. The analytical results are summerized in Table 2. These results show that GC-MS after SPME, using the proposed fiber, is a powerful method for monitoring PAHs at very low concentration in water samples.

Table 2
Headspace solid-phase microextraction by PPy-DS and capillary GC-MS determination of PAHs in real water samples

compound	Water sample	
	Caspian sea water[a]	Zayandeh-rood river water
Naphthalene	ND[b]	ND
Acenaphthylene	ND	ND
Acenaphthene	ND	ND
Fluoren	520 ± 49	ND
Phenanthrene	670 ± 41	ND
Fluoranthene	610 ± 52	ND
Pyrene	630 ± 61	ND
Chrysene	ND	ND

[a] Mean ± S.D. (pg ml^{-1}), $n = 4$.
[b] Not detected.

4. Conclusion

Electrochemical fiber coating offers a simple and convenient technique for the coating of SPME fibers. The porous structure, inexpensive and easy preparation, long lifetime, strong interaction, high thermal stability, reproducible preparation, and strong adhesion of the coating to the platinum wire are among the clear advantages of the proposed fiber coating. The thickness of the polymer film can be controlled by electrochemical conditions.

A dodecylsulfate-doped polypyrrole(PPy-DS), as a new fiber, was introduced and evaluated for extraction of PAHs from water samples. The presented experimental results clearly demonstrate that PPy-DS fibers are suitable for HS-SPME of PAH analytes. The combination of HS-SPME by PPy-DS fiber with GC-MS under full scan acquisition mode can achieve low LODs, and be applied to determine PAHs in real samples.

Acknowledgements

References

[1] R.P. Belardi, J. Pawliszyn, J. Water Pollut. Res. J. Can. 24 (1989) 179.
[2] J. Pawliszyn, Solid-Phase Microextraction: Theory and Practice, Wiley-VCH Inc., New York, 1997.
[3] R. Baciocchi, M. Attina, J. Chromatogr. A 911 (2001) 135.
[4] X. Yang, T. Peppard, LC GC 13 (1995) 882.
[5] X.-P. Lee, T. Kumazawa, K. Sato, O. Suzuki, Chromatographia 42 (1996) 135.
[6] N. Nagasawa, M. Yashiki, Y. Iwasaki, Forensic Sci. Int. 78 (1996) 95.
[7] M.R. Lee, Y.C. Yeh, W.S. Hsiang, C.C. Chen, J. Chromatogr. B 707 (1998) 91.
[8] V. Ignacio, C. Carolina, J. High Resolut. Chromatogr. 19 (1996) 472.
[9] L. Maria, P. Manuel, L. Pedro, C. Rafael, Anal. Chem. 73 (2001) 5858.
[10] G. Gmeiner, C. Krassnig, E. Schmid, H. Tausch, J. Chromatogr. B 705 (1998) 132.
[11] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160.
[12] S. Magdic, A. Boyd-Boland, K. Jinno, J. Pawliszyn, J. Chromatogr. A 736 (1996) 219.
[13] J.C. Vidal, E. Garcia, J.R. Castillo, Anal. Chim. Acta 385 (1999) 213.
[14] T.E. Campbell, A.J. Hodgson, G.G. Wallace, Electroanalysis 11 (1999) 215.
[15] C. Jerome, D. Labayc, I. Bodart, R. Jerome, Synth. Met. 101 (1999) 3.
[16] E. Smela, J. Micromech. Microeng. 9 (1999) 1.
[17] T. Ilo, P. Buhlmann, Y. Umezawa, Anal. Chem. 71 (1999) 1690.
[18] N. Alizadeh, H. Khodaei-Tazekendi, Sens. Actuators B 75 (2001) 5.
[19] L.F. Waren, D.P. Anderson, J. Electrochem. Soc. 134 (1987) 101.
[20] L. Shafiee-Dastjerdi, N. Alizadeh, Anal. Chim. Acta 505 (2004) 195.
[21] H. Bagheri, A. Mohammadi, J. Chromatogr. A 1015 (2003) 23.

[22] Dj. Djozan, S. Bahar, Chromatographia 58 (2003) 637.

[23] H. Bagheri, M. Saraji, J. Chromatogr. A 910 (2001) 87.

[24] J. Wu, Z. Dong, J. Pawliszyn, Presented at Extech'99 Symposium on Extraction Technology, Waterloo, 1999.

[25] J. Wu, J. Pawliszyn, J. Chromatogr. A 909 (2001) 37.

[26] J. Wu, X. Yu, H. Lord, J. Pawliszyn, Analyst 125 (2000) 391.

[27] J. Wu, H. Lord, J. Pawliszyn, H. Kataoka, J. Microcol. Sep. 12 (2000) 225.

[28] D. Bal, J. Li, S.B. Chen, Environ. Sci. Technol. 35 (2001) 3936.

[29] O.P. Heemken, N. Theobald, B.W. Wenclawiak, Anal. Chem. 69 (1997) 2171.

[30] R. Doong, S. Chang, Y. Sun, J. Chromatogr. A 879 (2000) 177.

[31] P.K. Wong, J. Wang, Environ. Pollut. 112 (2001) 407.

[32] J. Stejskal, M. Omastova, S. Fedorova, J. Prokes, M. Trchova, Polymer 44 (2003) 1353.

[33] P.S. Rao, D.N. Sathyanarayana, S. Palaniappan, Synth. Met. 128 (2002) 311.

[34] R. Doong, S. Chang, Y. Sun, J. Chromatogr. A 879 (2000) 177.