Zeolite Imidazolate Framework Nanocrystals Electrodeposited on Stainless Steel Fiber for Determination of Polycyclic Aromatic Hydrocarbons

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ABSTRACT: *New Solid-Phase Microextraction (SPME) coating was made by electrodeposition of Zeolite Imidazolate Framework (ZIF-67) nanocrystals with the aid of polyaniline (PANI) on steel fiber. The SPME fiber was used to extract four Polycyclic Aromatic Hydrocarbons (PAHs) from the Head Space (HS) of tea infusions and determined by Gas Chromatography coupled with a Flame Ionization Detector (GC-FID). The coating of the SPME fiber was characterized by Fourier Transformed InfraRed (FT-IR) spectroscopy and Scanning Electron Microscopy (SEM). Vital parameters affecting extraction performance, including desorption conditions, salt concentration, extraction time, and temperature, have been evaluated and optimized. The validated method was specific for the PAHs analysis, with the Limit of Detection (LOD) as low as 20.0 to 50.0 ng/L. The linear range was relevant to 70.0-180.0 ng/L with a relative standard deviation (RSD) % of less than 12.8. The factor of enrichment was found to be 446.7-808.8. The synthesized coating was shown to be thermally and chemically stable. The recommended approach was successfully applied to quantify PAHs in some frequent tea infusions in the market. The fiber coating of ZIF-67 can be easily made and applied efficiently to detect PAHs pollution in the environment and food products.*

KEYWORDS: *Metal-organic framework; Solid-phase microextraction; ZIF-67; Gas chromatography; Tea infusion.*

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INTRODUCTION

PAHs are composed of two or more fused aromatic benzene rings. They are contaminants produced by the combustion of fossil fuels and are made up of individual compounds [1, 2]. PAHs easily enter the body by consuming contaminated food and, despite their high molecular weight, can penetrate the gastrointestinal tract due to its lipophilic properties [3]. PAHs are distributed widely throughout the atmosphere as a class of harmful organic contaminants. They can be transported in gaseous form or bound to particulate matter over long distances within the atmosphere. PAHs are well known to be considered endocrine disruptors, so prenatal and childhood exposure to PAHs may impair childhood growth. Contamination of foods by PAHs is related to the environment of their production and processing [4, 5]. Based on European Union [6], and the United States Environmental Protection Agency legislation, currently, sixteen PAHs are listed as priority contaminants. Tea is one of the most widely used drinks in many countries of the world. Tea leaves may become contaminated by the direct absorption of PAHs into the leaves during plant development, deposition of particulate matter, and smoke for drying purposes [7]. PAHs entry into the infusion depends on variables such as time to brew or the ratio of tea and water [8], which may lead to the development of certain cancers [9]. PAHs measurement was reported frequently in tea [10, 11] and herbal infusions [12, 13] that mostly are based on liquid chromatography with fluorimetric [2, 14] and ultra-violet [12] detection, and GC-mass spectrometry [10, 11]. These samples have trace amounts of PAHs which mean a preconcentration step must be included before analysis. New sample preparation methods such as microextraction techniques have received more attention than preconcentration techniques like solid-phase extraction [15] or liquid-liquid extraction [16, 17], due to their lower solvent consumption and simple, clean, and fast operation. Quantification of PAHs by microextraction methods such as liquid-liquid microextraction [18], and stir bar sorptive extraction [13] have been reported. *Pawliszyn et al.* in 1989 [19], for the first time, introduced SPME, which has many advantages, including simplicity, low solvent use, Less damage to the environment, and simple automation [16]. Significant SPME disadvantages are related to the properties of the fiber, such as brittleness, memory effect, high cost, short lifetime, low coating stability, and swelling quickly by organic solvents [20]. Some of these disadvantages can be eliminated by using new coatings to improve the SPME fibers' selectivity, stability, and lifetime. Thus, various coating materials for SPME fiber, including molecular imprinting polymers [21], porous and ionic liquid polymers [22, 23], covalent organic frameworks (COFs), and Metal-Organic Frameworks (MOFs) as a new class of crystalline porous materials [24-26] have been developed. MOFs are made by a metal or poly-nuclear metal clusters linked by organic connectors, with the ability to combine the essential advantages of organic electron donor linkers and metal cations as electron acceptors (oxides) creating a systematic lattice of canal and cavities on a nanoscale basis. By using appropriate linkers, the pore structure can be made for different applications. Zeolites are a group of crystalline microporous aluminosilicate minerals, both of natural and synthetic origin containing alkaline and alkaline-earth metals with a frame structure encompassing interconnected cavities [27, 28]. The general formula of zeolite compounds can be given as Mx/n $[(AlO2)x(SiO_2)y]\cdot mH_2O$. Here, the negatively charged structures of the alkaline or alkaline earth metals are generally balanced with n-valence M cations, but they can be able to change [29]. They have many advantages as supports because of their high surface area, shape/size selectivity, and easy separation from reaction mixtures. Zeolites have extensive applications in both pollution control and soil remediation, as adsorbents, molecular sieves, membranes, ion exchangers, and catalysts [30].

A new type of MOFs is a zeolite framework made by ZIFs in which all tetrahedral atoms and bridges are transition metals (Co, Cu, Zn, etc.) and imidazolate units, respectively. ZIF pore size is 0.7~13.1Å, and ZIF surface area is about twice as large as inorganic zeolites. Due to the exceptional properties of ZIF, such as thermal and chemical stability, zeolite, and MOF advantages, ZIFs are promising candidates for SPME coating. ZIF can be placed on the surface of metal wire as a novel SPME coating through a single-stage electrochemical polymerization [31, 32].

In this work, based on our knowledge, for the first time, ZIF-67 lonely was used as a fiber coating substance with the help of PANI to produce a novel fiber coating through electrodeposition-enhanced solid-phase microextraction (EE-SPME) coupled with GC-FID applicable to

preconcentration, extraction, and determination of certain PAHs in a few tea and infusion samples.

EXPERIMENTAL SECTION

Chemicals

Naphthalene (Nap), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), acetonitrile, aniline, sodium chloride, methanol, ethanol, cobalt(II) nitrate hexahydrate, and aniline with the highest available purity made by Merck (Darmstadt, Germany) were purchased. 2-methylimidazole was supplied from Sigma-Aldrich (Madrid, Spain). All solvents used to prepare the solution and chromatographic separation were high-performance LC grade.

Standard Solution

Individual stock solutions were prepared in acetonitrile for each PAH (10000 mg/L). Stock solutions were appropriately diluted to prepare simple and combined working solutions of Nap, Flu, Phe, and Ant in distilled water (each of them with a concentration of 4 μg/L). Until analysis, all stock and working solutions were stored at 4 °C while protected from light.

Instrumentation

An Agilent gas chromatograph 7890A manufactured by the USA, with an FID and split-splitless injector, was used. A HP-5 column (30 m × 0.32 mm i.d. × 0.25 μm) as stationary phase and ultra-pure N_2 (purity > 99.999%) as carrier gas was applied. At first, the column oven temperature was set at 40 °C, held for 3.5 min, raised to 220 °C at 30 °C 1/min, then held for 5 min at 220 °C. The total time for the analysis was 16.5 min. Detector and injector temperatures were adjusted respectively at 300 ° C and 280 ° C. Nitrogen flow rates, as the gas carrier and nitrogen adopting the role of make-up gas were modified to 0.8 mL/min and 30 mL/min, respectively. The splitless mode was utilized.

Nanocrystals of ZIF-67 were prepared and electrochemically deposited on stainless steel wires with the aid of aniline utilizing a Zagchemie Coulometer model ZCM761 (Tehran, Iran) to make a homemade SPME fiber. The SPME fiber was a piece of stainless steel wire (type 012, 355 × 0.3 mm) that passed through the septum. One of the ends of the fiber was coated with a thin film consisting of PANI/ZIF-67 nanocomposite, and the other end was connected to a metal cap of 15 mm.

In order to characterize the surface morphology of the assembled ZIF-67 nanocrystals, the SEM was prepared by KYKY SBC-12 A (China). FT-IR spectra were obtained from Brucker (Germany) using a Tensor 27 FT-IR spectrometer. An Ultrasonic cleaning bath with heating (J.P. Selecta, Spanish) was used to conduct sonication. A Heidolph 3001 series magnetic stirring hotplate MR 3001 K from GmbH & Co. KG, (Germany) was used to stir and heat samples.

ZIF-67 Nanocrystals Synthesis

The ZIF-67 was synthesized according to a previously published method [33]. Briefly, methanol and cobalt nitrate hexahydrate, 2-methylimidazole were used to synthesize ZIF-67 at room temperature. A precise quantity of 2-methylimidazole (246.0 mg) and cobalt nitrate hexahydrate (291.0 mg) were individually dissolved within 20 mL of methanol. Both solutions were mixed in the next stage, the mixture obtained was stirred for up to 30 min at room temperature. The resulting solution was kept at ambient temperature for 24 hours to complete the reaction. The precipitated violet powder was separated by filtration and washed cautiously using methanol and finally left overnight to dry at ambient temperature.

PANI/ZIF-67 Nanocomposite Preparation

Before electrodeposition, the surface of the stainless steel wire was made rough using smooth sandpaper and washed sequentially along with sonication by methanol, acetone, and distilled water. Suspension of nanocomposite containing ZIF-67 nanocrystals (0.02 g) in 20 mL distilled water, 2 mL ethanol, and 0.01 M aniline as a film former was deposited directly on the wire surface immersed in 20 mL distilled water via application of a constant 1.5 V potential for 30 min under ambient temperature. Before SPME, coated wires were heated for 2 h under 200°C and placed within a GC injector port for 1 h under 300°C amidst the flowing of nitrogen.

The EE-SPME Procedures

For EE-SPME experiments, a tri-electrode system was built using the ZIF-67 (Co) coated wire as the Working Electrode (WE), a saturated calomel electrode [21] as the reference electrode (RE), and a platinum wire as the Counter Electrode (CE).

Experiment Outline

Influential performance factors concerning the fiber preparing stage, consisting of aniline concentration (A), Ethanol volume (B), time (C), sorbent amount (D), and applied potential (E), were selected based on initial tests and literature. In order to optimize the factor values, the Central Composite Design (CCD) was used to achieve the most favorable response. Response surface methodology (RSM) adopts a critical role in the design, formulation, development, and analysis of novel scientific studies, in addition to the improvement of current products and research. Amidst the CCD tests, four PAHs were used (Nap, Ant, Phe, Flu) conducted by using the Design-Expert 10.0. 6.0 software package, USA.

SPME Procedure and Analysis

To perform headspace (HS)-SPME, to 20 mL glass vial, 10 mL sample solution, and 2.0 g of NaCl was added, and it was sealed immediately with silicon septum. The sample solution was stirred with a Teflon-coated stirring bar at 700 rpm, and over the sample solution, the PANI/ZIF-67 coated fiber was exposed to a headspace at 40°C for 40min for extraction. Following extraction, the fiber has been removed and promptly inserted into GC inlet at 280 °C for 5min for GC analysis.

HS–SPME Optimization

The analytes can be extracted from the liquid phase or headspace above the sample onto the fiber in the HS–SPME procedure and thermally desorbed in the gas chromatograph injector. Potential factors such as extraction time, extraction temperature, and salt affect the number of analytes extracted for the extraction process on the fiber. Appropriate injector temperature and exposure time can improve analyte thermal desorption efficiency for desorption processes. These factors have been studied and optimized to achieve the best ZIF-67-coated fiber extraction performance. An aqueous solution at 4 µg/L was used to optimize each of the PAHs.

Preparation of Real Samples

Different samples of tea infusions were purchased from local markets, including green and black tea, chamomile, borage, and relaxing herbal (borage, lavender, valerian, lime, and lemon verbena). Samples were prepared by pouring the bag content into 100 mL of hot water, filtering, and cooling to ambient temperature after 5 min. Then it was analyzed as described in section SPME procedure and analysis.

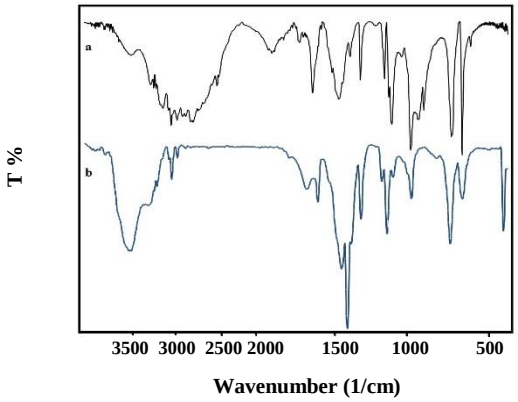

Fig. 1: FT-IR spectra of a) 2-methyl imidazole and b) ZIF-67.

RESULTS AND DISCUSSION

Characterization of ZIF-67 Nanocrystals

The molecular structure of the ZIF-67 has been confirmed using FT-IR spectroscopy. Fig. 1 depicts FT-IR spectra of 2-methylimidazole (a) and ZIF-67(b).

The broad and stable absorption of 2-methylimidazole has been shown within the 2200-3300 1/cm range because of hydrogen bond vibrations among the pyridinic nitrogen (N.H··N) and pyrrole group [34]. At 1851 1/cm, there is resonance among N.H stretching vibrations and N.H···N bending "out of plane", which disappear entirely within the ZIF-67 product spectrum, proving the complete deprotonation of the 2-methylimidazole linkers amidst the creation of the ZIF formation [35]. At 423 1/cm, the new absorption band is accredited to Co-N stretching, which is in accordance with the preceding ZIF-67 report [36, 37]. In the meantime, at 1588 1/cm, the C-N stretching vibration and 755 1/cm out of plane mode for 2-methlyimidazole are substantially weakened and emerged as a doublet that validates the presence of Co-N bond. Also, at 1303-1500 1/cm, the great bands are accredited to the total ring stretching.

Fig. 2a shows a general SEM image of the product ZIF-67. The product consists of a large number of regular particles with uniform and perfect dodecahedral rhombic shape. The SEM image of ZIF-67 illustrates a well-defined facet, rhombic dodecahedron shape straight edge, and

smooth surface.

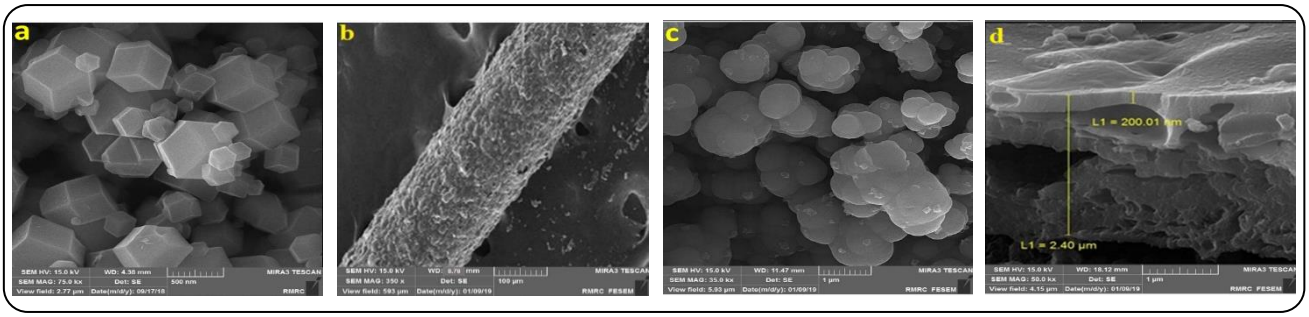

Fig. 2: SEM images of ZIF-67 product (a) SPME fiber (b) SPME fiber at 1000-fold magnification (c) and SPME fiber thickness (d).

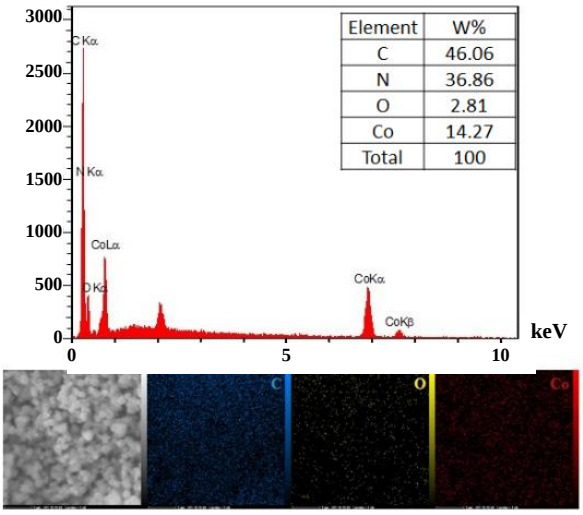

Fig. 3: EDX spectra and elemental mapping of ZIF-67.

The surface characteristics of the electrochemical coated fiber were further investigated by the SEM technique (Fig. 2b). It is seen from the SEM of the coated surface presented in Fig. 2c, that the electrochemical coatings possess porous structures together with nano-particles on the surface, which should significantly increase the surface area availability of the fiber [9]. Coating film thickness was estimated at 2.4 µm, as shown in the SEM image (Fig. 2d).

The results of energy-dispersive X-Ray Spectroscopy (EDX) used to detect the elemental composition of ZIF-67 were shown in Fig. 3 in order to assess the purity of the material. As in the ZIF-67 EDX spectrum displayed in Fig. 3, The presence of carbon, nitrogen, oxygen, and cobalt, without impurities, is apparent. The mapping images of ZIF-67 EDX are shown in Fig. 3, which confirms the presence of carbon, oxygen, and cobalt in the synthesized product.

Coating Preparation Optimization

CCD was used to optimize variables influencing PANI/ZIF-67 preparation. The impact of the extraction conditions concerning the response was significant ($p<0.05$) regarding the predicted p-value originating from the ANOVA result. The ANOVA regression equation resulted in a 0.9743 correlation coefficient (R^2). It guarantees favorable modification of the quadratic model relative to the empirical data. The modified R^2 was 0.8717, showing a high potential for the model in response prediction. Besides, the Model F-value was 9.5, suggesting the significance of the model. A p-value of 0.1215 for the lack-of-fit suggests its insignificance concerning the pure error.

Although, the quadratic impact of aniline concentration (A), ethanol volume (B), time (C), sorbent amount (D), and applied potential (E) did not exhibit any significance ($p<0.0001$) (Table 1).

The significance of A, BC, A^2, and C^2 interaction terms on the response ($p<0.05$) is summarized in Table 2.

Actual response vs. predicted response showed a favorable correlation between the predicted and actual values. A favorable fit to the model is proven by the points cluster in the vicinity of the sloping line and exhibit adequate variation among the predicted and empirical values within the chosen independent variables range. Moreover, the predicted vs. residual response plots were randomly dispersed, showing the eternal nature of empirical measurements' variance for all Y values. In order to assess the interactive impact of the two variables concerning response, 3D model graphs were utilized. The graphs display the impact of these independent variables and the interactive impact of every independent variable regarding the response variables. Fig. 4 depicts 3d plots of CCD in which the AUCs of the PAHs as responses were plotted against variables including time, ethanol, and aniline to obtain the optimum amount of the variables that affect SPME coating properties.

Table 1: Analysis of variance (ANOVA) of the CCD experiment for the extraction of PAHs by SPME.

C	Source	S P	LoF P	ARS	PRS	T	Const.	Lambda
Nap	Q	< 0.0001	0.0193	0.9633	0.8702	Square Root	-0.8	-
Flu	Q	0.0005	0.2263	0.8645	0.5809	Base 10 Log	0	-
Phe	Q	0.0006	0.1952	0.8594	0.5498	Power	3	0.3
Ant	Q	0.0015	0.0821	0.8322	0.4396	Square Root	0	-

C: Compound; Q: Quadratic; S: Sequential; LoF: Lack of Fit; P: P value; ARS: Adjusted R- Squared; PRS: Predicted R-Squared; T: Transform; Const: Constant

Table 2: Summary of analysis of variance (ANOVA) of the CCD experiment for the extraction variables of PAHs performed by SPME.

				p-value; Prob> F
Source	Nap	Flu	Phe	Ant
Model	< 0.0001	0.0007	0.0008	0.0016
A-Aniline	< 0.0001	0.0002	0.0012	0.0017
B-Ethanol	< 0.0001	0.0734	0.0132	0.0692
C-Time	0.0950	0.3072	0.0041	0.0031
AB	0.0004	0.0683	0.8970	0.5078
AC	0.0002	0.1260	0.0662	0.0356
BC	0.0023	0.0201	0.1393	0.4076
A2	< 0.0001	0.0002	0.0003	0.0004
B2	0.0009	0.9718	0.1246	0.9259
C2	< 0.0001	0.0028	0.0049	0.0117

A: Aniline; B: Ethanol; C: Time

It validates the presence of a substantial positive interaction among the applied potential and ethanol volume, implying optimal values of 1.5 V, 2 mL ethanol, and 30 min in the extraction procedure. There was significant interaction concerning applied potential and ethanol volume and sorbent amount, as shown in Fig. 4.

Effect of Desorption Conditions

To obtain accurate analysis, sufficient time is needed to desorb all analytes from the surface of the fiber. If the time for desorption is not enough, not only will the analyte tracking be inaccurate, but the residual analysis will also affect subsequent extractions. Differently, the fiber can be damaged at continuously high temperatures if the desorption time is extended. When time lasts up to 5 min, complete desorption will be obtained.

Effect of Salt Addition

Due to the salting effect, the solubility of PAHs will be reduced by adding electrolytes such as NaCl to the aqueous solution of PAHs, which in turn increases the efficiency of extraction. Fig. 5a shows the results of the effect of NaCl concentration on the efficiency of extraction.

The relationship between extraction efficiency and concentration of NaCl depends on the ionic strength. If the concentration of NaCl is less than 20 percent, the efficiency of extraction depends directly on the concentration of NaCl. In contrast, the efficiency of extraction of some analytes will be significantly reduced as the ionic strength continues to increase. This phenomenon may be associated with changing the partition coefficient in high concentrations of NaCl. The optimum concentration of NaCl was selected as 20 percent (w / v) according to the results obtained.

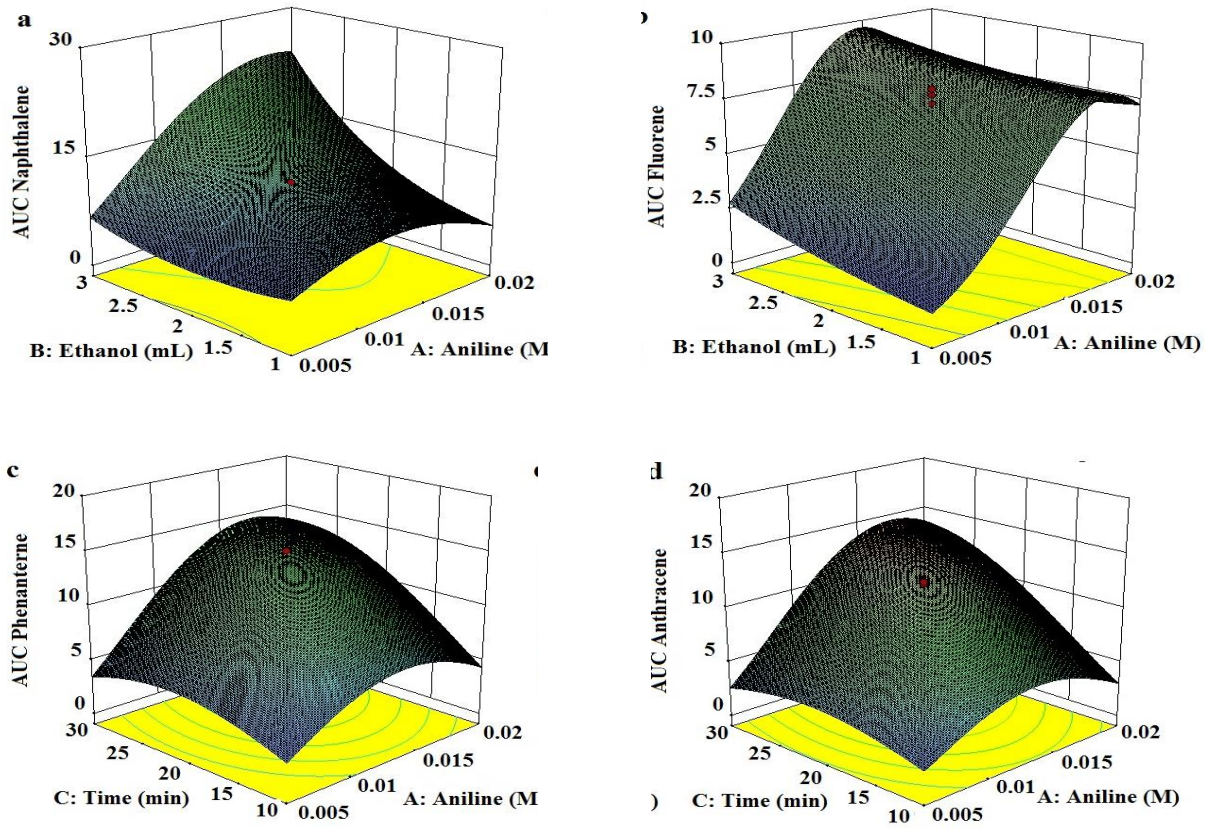

Fig. 4: 3D plot of PAHs' AUCs obtained at the various amounts of variables consisting of time, ethanol, and aniline using the CCD.

Extraction Temperature and Time

A high extraction temperature will generally increase the mass transfer of analytes from the sample to the SPME fiber coating; the rate of extraction will, therefore, be increased. The partition coefficient of the analytes between the coating and the headspace will be decreased by raising the temperature due to the exothermic process of absorption. The temperature effect was investigated in the 20–60 °C range on the extraction efficiency of the PAHs. The increase in temperature between 20 and 40 °C will increase the extraction of PAHs, as shown in Fig. 5b. PAH peak areas decreased at temperatures above 40 °C, as shown in Fig. 5b, so 40°C was selected as the optimum temperature. Fig. 5c shows the effect of time on analyte adsorption in the ZIF-67 coated fiber. Results show that the adsorption equilibrium time has been increased by increasing the molecular weight of PAHs and subsequently, relatively low diffusion coefficients. In the following experiments, the optimum time of 40 min was selected to achieve maximum extraction performance while saving time.

Evaluation of Method Performance

Analytical characteristics of the headspace SPME analysis of four PAHs by PANI/ZIF-67 coated fiber under optimized conditions have been summarized in Table 3.

For Nap, it was found a linear response in the range of 2-500 µg/L, 2-1000 µg/L for Flu, 2-1000 µg/L for Phe, and 2-100 µg/L for Ant, with the correlation coefficients (r) ranging from 0.9940 to 0.9996. The precision was evaluated by using the same fiber for four replicate extractions under the same conditions. Results showed that the relative standard deviation (RSD) was less than 12.8 percent for single-fiber repeatability.

Food Sample Analysis

PAHs in tea infusions were analyzed using the ZIF-67 coated fiber, followed by the developed SPME-GC

Table 3: Direct injection limit of detection (LOD) in µg/L, limit of quantitation (LOQ) in µg/L, LR in µg/L, correlation coefficient (r^2), IDP (%, n=3) and EF (%).

Analyte	CE	LR	R^2	LOD	LOQ	IDP	EF
Nap	y=0.788x + 22.60	2-500	0.9970	0.05	0.18	1.40-10.50	446.70
Flu	y=0.970x + 10.19	2-1000	0.9970	0.03	0.11	1.00-11.60	577.94
Phe	y=2.392x + 35.58	2-1000	0.9980	0.02	0.07	0.90-6.90	808.82
Ant	y=2.519x + 3.704	2-100	0.9950	0.04	0.14	1.90-12.80	545.59

CE: Calibration Equation; LR: Linear Range; IDP: Interday Precision; EF: Enrichment Factor

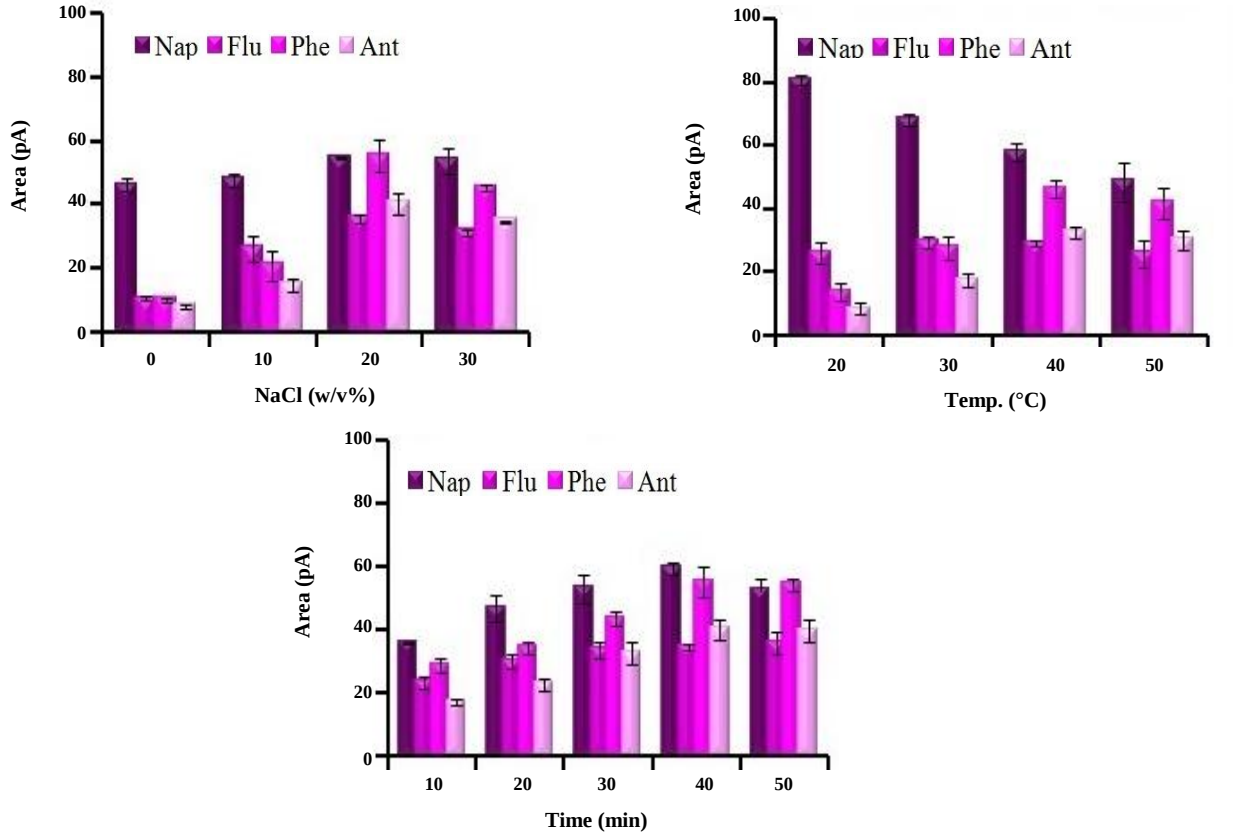

Fig. 5: Effect of NaCl% (a), extraction temperature(b), and extraction time(c) on the extraction efficiency (n=3).

method. The chromatograms and corresponding results are shown in Fig. 6 and Table 4, respectively.

The method recovery was determined in two different spiked levels (25 and 50 µg/L) of PAHs in order to estimate the accuracy of the method developed. Results Table 4 show that the recoveries range from 72.37% to 139.87%. It can be seen that, while Nap and Flu were present in all the samples, the concentration of Phe was not detectable in most samples. These results show that PAHs can occur in tea infusions so they can be dangerous, and consumers should be aware of their use.

CONCLUSIONS

PANI/ZIF-67 coated on steel wire as an SPME device can be prepared by a facile electrodeposition method. The fiber for adsorption of PAHs showed many advantages including easy preparation, low price, high resistance to temperature (~500°C), high adsorption affinity to PAHs, and efficient extraction. PAHs were desorbed from PANI/ZIF-67 coating in the injection port of GC, and estimated by a simple validated GC-FID method. Application of the method in the analysis of actual samples showed most of them are contaminated with some PAHs,

Table 4: The quantification parameters of the HF-SPME-GC-FID method for the determination of the PAHs in tea infusions.

Samples	PAHs	Conc. (µg/L)	Spiked Conc. 25 (µg/L)		Spiked Conc. 50 (µg/L)	
			Recovery (%)	RSD% (n=3)	Recovery (%)	RSD% (n=3)
Relaxing herbal	Nap	1.5	135.9	0.7	133.1	2.9
	Flu	2.1	92.2	2.1	117.5	10.7
	Phe	0.9	82.9	3.5	130.6	16.5
	Ant	4.0	124.5	7.1	139.9	7.3
Borage	Nap	2.3	103.6	2.8	110.6	8.9
	Flu	1.3	83.9	3.6	86.5	0.2
	Phe	ND	93.9	2.3	93.2	1.2
	Ant	3.1	117.3	5.3	95.2	13.1
Chamomile	Nap	3.3	120.2	2.9	125.2	0.9
	Flu	1.8	92.1	8.4	112.7	6.3
	Phe	ND	74.9	5.6	97.6	12.4
	Ant	ND	113.3	8.6	100.8	9.1
Black Tea	Nap	1.5	106.0	3.2	87.5	16.4
	Flu	0.3	82.8	5.7	72.8	4.3
	Phe	ND	74.4	6.7	76.1	3.3
	Ant	ND	96.5	3.13	101.7	3.4
Green Tea	Nap	3.3	105.0	15.1	86.3	16.4
	Flu	1.1	79.6	1.6	81.1	1.3
	Phe	ND	72.4	3.5	79.1	3.0
	Ant	2.6	128.0	2.9	105.2	9.0

ND: not detected; Conc.: Concentration

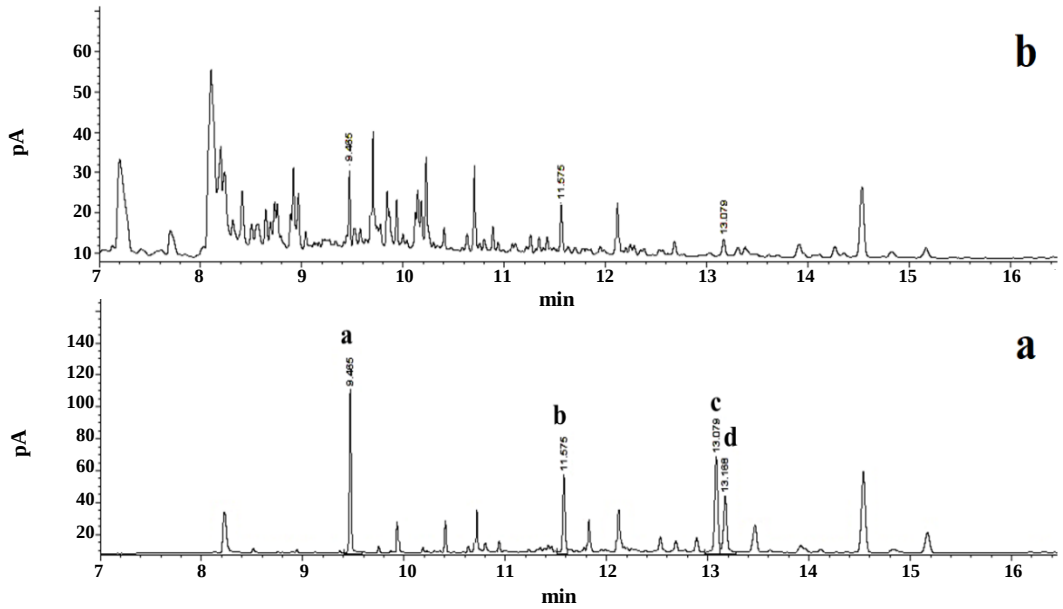

Fig. 6: Chromatograms of the standard solution of PAHs: Nap: a, Flu: b, Phe: c, Ant: d (a); real sample of black tea (b).

although their level may not exceed the maximum permitted level, it is worth noting that their monitoring and evaluation by a simple and reliable method are very important due to the hazardous effects of the PAHs on the human body and the environment.

Finally, it can be concluded that the PANI / ZIF-67 fiber is expected to have a wide application in the cleaning and preconcentration of trace PAHs from the aqueous samples, and is feasible for use in food and environmental analyses.

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