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Gas Chromatographic Detection of Polycyclic Aromatic Hydrocarbons (PAHs) in Indoor Air After Direct Extraction by a Novel Monolithic Adsorbent

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Polycyclic aromatic hydrocarbons (PAHs) have been listed among the hazardous compounds according to the US environmental protection agency (USEPA) and the world health organization (WHO). Even low concentrations of PAHs have shown serious toxicity, highlighting the necessity of the measurement of these compounds which require highly sensitive and precise methods. In this study, for the first time, a solid phase microextraction (SPME) fiber was fabricated by a highly porous monolithic nanofiber nanocomposite based on polyethersulfone (PES)/multiwalled carbon nanotubes (MWCNTs) and used for direct sampling of indoor air before identification of polycyclic aromatic compounds by gas chromatography-flame ionization detector (GC-FID). A new homemade sampling chamber was also designed to increase the exposure of airborne PAHs to the proposed SPME fiber. The microextraction conditions were optimized. The correlation coefficients and the linear range (LDR) of the compounds ranged from 0.9991 to 0.9996 and from 0.02 to 10 mg m^{-3}, respectively. In addition, the limit of detection (LOD) varied in the range of 0.014-0.032 mg m^{-3}. The relative standard deviation (RSD) for single fiber and fiber-to-fiber was 2.95 and 5.95%, respectively. This method was successfully applied to measure some PAHs in indoor spaces.

Keywords: Monolithic fibers; Polyethersulfone, Solid-phase microextraction, Polycyclic aromatic hydrocarbons, Gas chromatography, Indoor air

INTRODUCTION

Volatile organic compounds (VOCs) refer to a class of environmental pollutants that can decrement the quality of indoor air. Indoor air pollution may cause serious diseases such as asthma, cancer, sexual disabilities, Parkinson's disease, brain tumors, and multiple chemical allergies. Air pollution is one of the causes of early death in children (50% of the deaths in children younger than five years old). Liver problems and dryness of the eyes are among the other complications caused by air pollution [1].

Polycyclic aromatic hydrocarbons (PAHs) are a group of toxic and potentially dangerous compounds formed by joining two or more benzene rings [2-6]. PAHs are inert and nonpolar molecules with low water solubility due to their oleophilic nature. Upon entrance into the body, they are mostly stored in the liver, lungs, and kidneys. PAHs can be decomposed into simpler compounds or other metabolites and excreted through urine, feces, and breast milk. Some of these metabolites are more toxic and harmful than their corresponding primary compound. Regarding the adverse effect of these compounds on humans and other living organisms, several studies have surveyed the presence of these compounds in food, drinking water, air, and other biological samples [7-16]. Natural activities, domestic heaters (charcoal and wood heaters, oil ovens), apparatus operating with natural gas, smoking, cooking evaporations, grilled meats, and frying foods are among the main sources of PAHs [17]. According to the literature, the smoke of cigarettes and hookah contains various toxic compounds such

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as heavy metals, carbon monoxide, and nicotine as well as diverse carcinogenic compounds such as PAHs. The mentioned compounds can enter the body through inhalation causing more than 5 million annual deaths [18,19]. US environmental protection agency (USEPA) has announced 16 PAHs compounds as distinct aromatic pollutants [20].

The release of PAHs in indoor spaces has further increased due to the rise in smoking cigarettes and hookah being unaware of its adverse consequences and the production of fruit-flavored tobacco with rising popularity among people (men and women, especially youth). In this case, Vu *et al.* identified 14 types of PAHs in the smoke of 50 different types of cigarettes [21]. Also, Sepetdjian *et al.* succeeded in identifying 16 types of PAHs in the smoke of cigarettes and hookah [22]. In addition, numerous studies have examined the PAHs in the smoke of cigarettes and hookah [23-25] all of which indicated the presence of a lot of PAHs in their smoke.

Measurement of PAHs in various matrices requires highly sensitive and accurate analytical devices. In all the mentioned studies, the PAHs were not addressed separately, therefore, gas chromatographic methods coupled with flame ionization detector (FID) and mass spectrometry (MS) have higher applications compared to other techniques [26-28]. On the other hand, due to the high toxicity of PAHs, the assessment of these compounds in low concentrations requires efficient concentrating approaches [29-31]. Our literature survey showed that all the developed methods for the assay of PAHs in air samples used a preconcentration or collection step (often solid phase extraction or liquid extraction) before gas chromatographic detection [32]. In most cases, a microextraction step preferably solid phase microextraction (SPME) has been performed after the first preconcentration step to increase the enrichment factor and sensitivity and there is no report about the use of direct SPME on initial air samples before the final detection probably due to the absence of high porous SPME sorbents. Therefore, introducing new SPME fibers to direct sampling of PAHs at trace concentration levels from air samples can reduce the multiple preconcentration steps, the expenses of the experiments as well as the analysis time.

Nanostructured carbon-based materials with high porosity have been used as a specific coating for SPME fibers [33,34]. In continuation of our research on SPME fibers, we have recently developed a novel monolithic mixed matrix membrane based on polyethersulfone (PES)/functionalized MWCNTs nanocomposite to serve as an SPME fiber in the determination of chlorophenols in various samples [35]. Further studies indicated that the porosity of this fiber can be increased by altering the temperature during the preparation of the polymeric membrane. Therefore, the present study introduces an improved monolithic polymeric SPME fiber for the adsorption of PAHs from indoor air before their detection by GC-FID. To the best of our knowledge, this report for the first time introduces the preparation and the application of monolithic polymeric SPME fiber for the direct sampling of PAHs without additional steps from air samples before their monitoring with GC.

EXPERIMENTAL

Reagents and Materials

All PAHs compounds (Naphthalene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene) were obtained from Merck (Darmstadt, Germany) and stored at 0-4 °C in a refrigerator. The standard solutions of the PAHs were prepared by dilution of the stock solution in deionized water. Multi-walled carbon nanotubes (MWCNTs) with an average outer diameter of 8-10 nm were synthesized by chemical vapor deposition of acetylene on Fe: CO catalyst at 720 °C followed by functionalization with the COOH group [36]. PES and N, N-dimethyl sulfamide were supplied from Fluka (Switzerland). Nitrogen and hydrogen at a purity of 99.999% were prepared from Sabalan Oxygen Company, Tehran, Iran.

Instruments

Agilent 6890N gas chromatography device made in the USA equipped with flame ionization detector and HP Chemstation software was employed in this research. This device had a split/splitless injection valve with an HP-5 capillary column with a length of 30 m and an inner diameter of 0.32 mm and a static phase thickness of 0.25 μm (95% dimethyl polysiloxane-cross bond 5% phenyl) supplied from Restek USA. Solid-phase microextraction (SPME) syringes were obtained from Azar Electrode Company, Urmia, Iran. A scanning electron microscope (model JXA-840 JEOL company; Japan, Tokyo) located in the Razi Metallurgical

Research Center of Karaj, Iran, was also applied to assess the morphology of the fibers. In all experiments, a magnetic stirrer-heater (ZMS74 of Zag Shimi Company; Iran, Tehran) was used to stir the sample at a specific temperature. A researcher-made glass chamber with a volume of 50 liters was also employed. A fan (Faran, Iran, model DOP-002 DC 12V_1.4 W) was utilized.

Preparation of the Integrated Fiber

The fibers were prepared according to our previous study with slight modifications [35]. Functionalized MWCNTs and PES were used to prepare monolithic fiber. First, functionalized MWCNTs (20 mg) were added to 250 µl of N, N-dimethyl sulfamide solvent and ultrasonicated for 5 min. After the formation of MWCNTs suspension, 250 µl of PES solution (45% (W/V) PES-N,N, dimethyl sulfamide) was added followed by 20 min of ultrasonication. The obtained viscose suspension was then transferred into a 2-ml syringe and injected into deionized water (1 l) as the coagulant solvent. To create high porosity in the fibers, the suspension was injected at 70 °C and under stirring (360 rpm) of coagulant solvent (Fig. 1). Then, to completely replace the initial solvent with the coagulant solvent and create sufficient porosity in the nanocomposite structure, the fibers were kept in water for 4 h. Finally, the fiber was dried at 80 ℃ for 8 h. The fiber was cut into a length of 2.5 cm and fixed in an SPME stainless steel syringe needle. The useful length of the fiber after installation on the needle was 2 cm. The fiber was attached to a 5-cm needle of the SPME device and then inserted into the GC injection port at 215 ℃ for 20 min to remove any fiber contamination before its application.

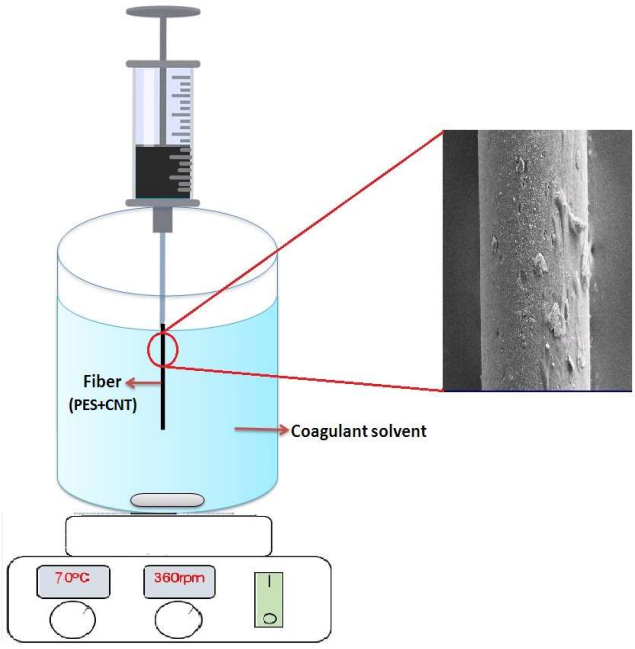

Fig. 1. Polymer injection into the coagulant solvent.

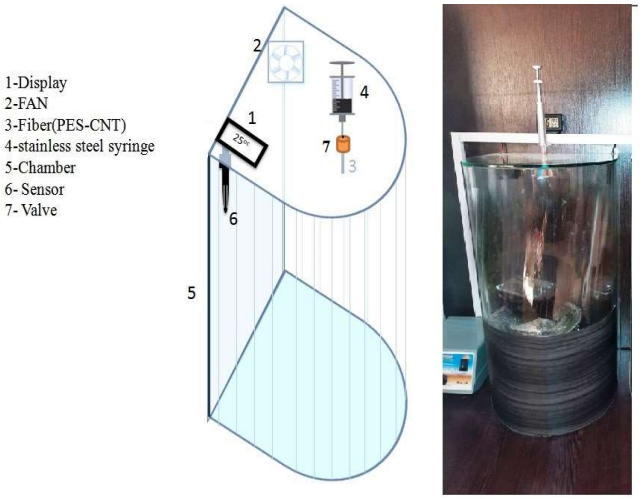

Fig. 2. SPME process from the headspace of indoor air. Experimental conditions: extraction time, 30 min; extraction temperature, 25 °C; fan rotation speed, 600 rpm; desorption temperature 215 °C; desorption Time 5 min.

Solid Phase Microextraction Procedure of PAHs from the Indoor Air and Chamber

To optimize the microextraction conditions of the proposed SPME technique for direct preconcentration of PAHs from indoor air, a glass chamber was designed as shown in Fig. 2. The volume of the chamber was 50 l (0.05 m^3) and a microextraction fiber mounted on an SPME syringe was placed in its upper interior. The concentration of the standards inside the chamber air (mg m^{-3}) was adjusted by injecting exactly a microliter volume of the prepared aqueous stock solution of PAHs using a microsyringe at the rate of 5 mg m^{-3}. For ventilation and immediate evaporation of the pollutants at the injection time, a fan was installed at the top corner of the chamber (see Fig. 2). To extract PAHs from indoor air, the microextraction fiber was placed in the

headspace of the environment for 30 min at room temperature (~25 °C). After extraction, the fiber was removed and placed on the injection valve of GC at 215 °C for 2 min to desorb the analytes.

After providing the optimal conditions for the SPME fiber and to obtain the quantitative characteristics of the proposed method, a calibration curve was made by adjusting the standard concentration of PAHs in the chamber air.

GC Analysis

Due to the wide range of the remaining time of the GC-separated analytes, a temperature program was utilized for separation. In the first stage, the column was kept at 100 °C for 1 min. Then, the temperature was raised at the rate of 30 °C min^{-1} to 300 °C and maintained there for 2.5 min. Nitrogen was utilized as the carrier and makeup gas with the respective flow rates of 1.1 and 45 ml min^{-1}. The temperature of the injection valve and FID detector was set at 310 °C. Analytes were injected in the splitless mode. The conditions of the GC analysis are summarized in Table 1.

Real Samples Detection Procedure

The efficiency of the proposed sample was explored by analyzing real samples from 4 possibly contaminated zones along with a sample from a place with a low probability of the presence of the studied analytes to serve as the control. To assess the efficiency of the proposed method in the analysis of PAHs in the real sample, places with the possibility of the presence of PAHs were chosen. As the smoke of cigarettes and hookah contain high levels of PAHs, four places containing cigarette and hookah smoke were selected. In all four indoor places, people smoked cigarettes and hookah for 2 h. A place was also considered as the control sample in which the probability of the presence of the analytes under study was zero. The specifications of the mentioned places are listed in Table 2.

To extract PAHs from the sampling places, the microextraction fiber was placed at the headspace for 30 min. After extraction, the fiber was transferred to the laboratory in an ice bath. For the desorption of analytes, the fiber was finally exposed to 210 °C (desorption temperature) for 1 min at the injection valve. Figure 3 demonstrates the SPME process from the sample space.

RESULTS AND DISCUSSION

Fiber Composition and Characterization

In SPME, the structure and chemical composition of the solid phase play a key role in extraction efficiency and selectivity. In this regard, the effect of the adsorbent composition on the extraction efficiency was examined to achieve better repeatability and higher sensitivity. To this end, fibers were prepared with various contents of functionalized MWCNTs and PES. The prepared adsorbent included PES and MWCNT. PES is a well-known commercial polymer that has found extensive applications in microfiltration, ultrafiltration, gas separation, and medical applications (hemodialysis membranes and artificial organs) due to its high mechanical and chemical stability in acidic and alkaline media [37,38]. Also, MWCNTs are of crucial significance due to their unique electrical, optical, mechanical, and thermal features [39]. The high strength and porosity of PES along with the high adsorption capacity of MWCNTs can provide a high-efficiency adsorbent for the SPME method. The thermal stability of the adsorbent was also assessed. As shown in the TGA scan plotted in the

Table 1. GC condition and Temperature Program for Analysis of PAHs

Inlet	Splitless, 215 °C. split vent: 10 ml min^{-1}, 0.5 min
Column	Const flow, pressure: 0.77 psi, flow: 1.1 ml min^{-1}
Oven	100 °C (hold 1 min) ramp 30 °C min^{-1} 300 °C (hold 2.5 min Runtime: 10.16 min
Detector	260 °C, Makeup flow: 45 ml min^{-1}

Table 2. Specifications of the Sampling Places (Iran, Urmia)

Station	A	B	C	D	E
Place	Closed gazebo of Ahoor restaurant	Cafeteria	Real estate agency	Real estate agency (2)	The control sample (blank)

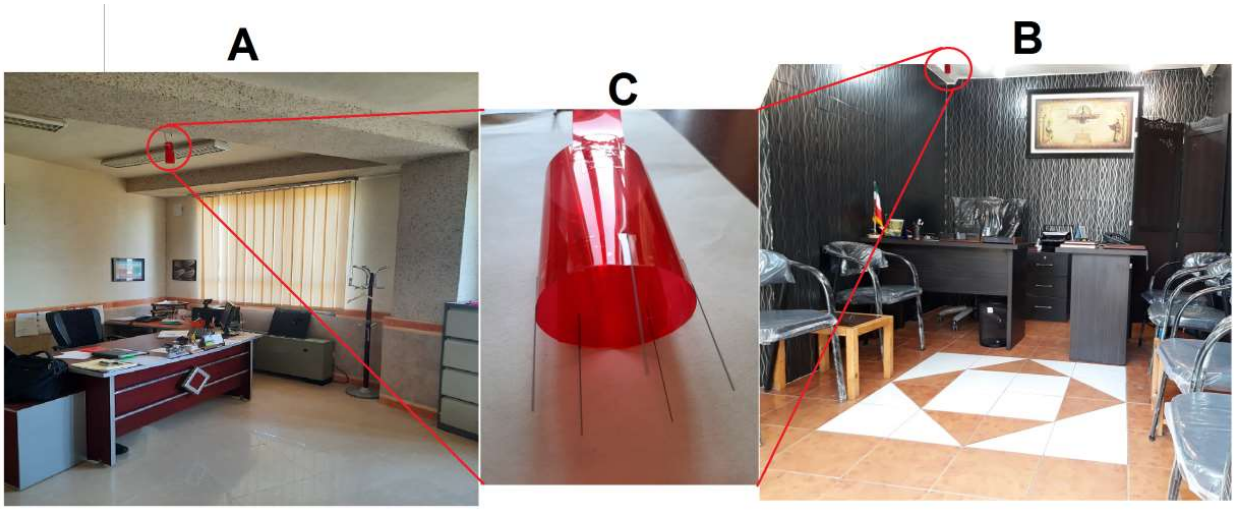

Fig. 3. SPME process from the (A) control sample (B) state office and (C) sampling device. Experimental conditions: Extraction time 30 min; extraction temperature about 25 °C; fan rotation speed, 600 rpm; desorption temperature 215 °C; desorption Time 5 min.

temperature range of 50 to 700 °C (Fig. 4), the prepared fiber only had 2% mass conversion up to 230 °C, suggesting its acceptable thermal stability.

Table 3 presents various compositions of prepared nanocomposites. Figure 5 illustrates gas chromatographic detection of a sample containing PAHs after SPME with the proposed fibers of various compositions. As can be seen, the fiber containing 15% functionalized MWCNTs and 85% polymer led to the highest extraction efficiency (Fiber M5). Therefore, this coating was considered the optimal one. Fibers containing more than 15% functionalized MWCNTs deviated from integrity, thus, they were excluded. SEM images of the selected fiber at different magnifications clearly show its high porosity (Fig. 6). The high porosity of the nanocomposite promotes its entrapment capability to be used as an SPME fiber.

Optimization of the Microextraction Temperature

In microextraction from headspace, the temperature may show a dual effect. Higher temperatures are in favor of the volatility of the analyte and can increase the distribution coefficients of the gaseous analytes. The adsorption of the analytes on the fiber is not, however, desirable at high temperatures. Anyway, the extraction temperature has to be optimized. As the standard temperature of the indoor spaces is 25 °C, all stages of the extraction were carried out at 25 °C.

Table 3. Various Composition of Prepared Nanocomposite

Name	Fiber composition	
	%MWCNT-COOH	%PES
M1	0	100
M2	1	99
M3	5	95
M4	10	90
M5	15	85

Optimization of Microextraction Time

Fiber exposure time is another important parameter in the equilibration of the analyte distribution between fiber and sample; therefore, it is a key factor in improving extraction efficiency. In this context, the extraction process was evaluated for different process times varying from 10 to 60 min. Figure 7 shows the peak area as a function of microextraction time. As can be seen, the equilibrium conditions are reached in 30 min and the extraction efficiency decreases with enhancing time, which may be due to the establishment of a new equilibrium or the desorption of analytes from the adsorbent surface. Therefore, the microextraction process was carried out for 30 min in the subsequent experiments.

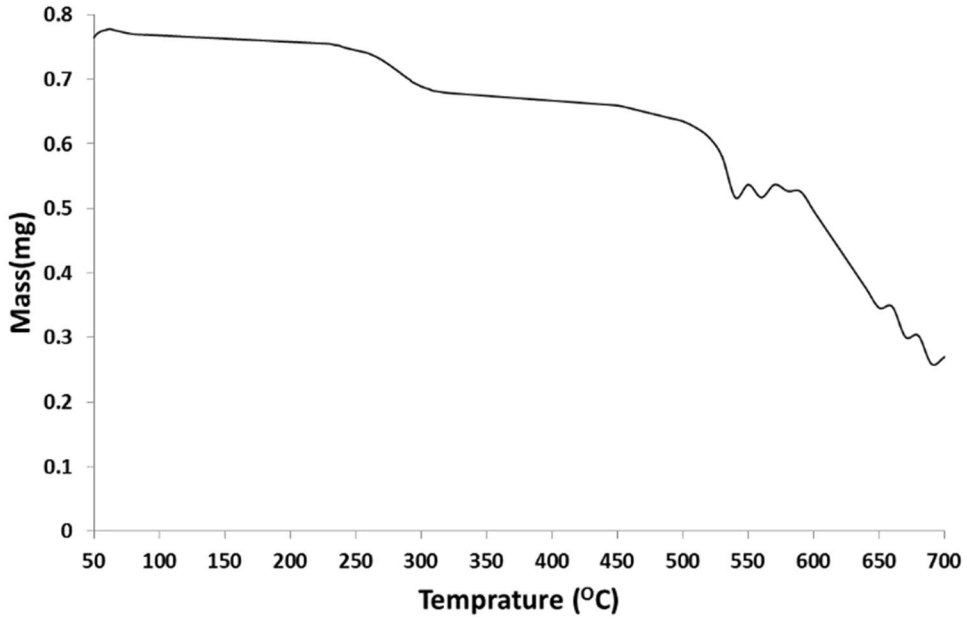

Fig. 4. Thermogravimetry analysis (TGA) of the fiber, (M5 = 15% MWCNT-COOH, 85% PES).

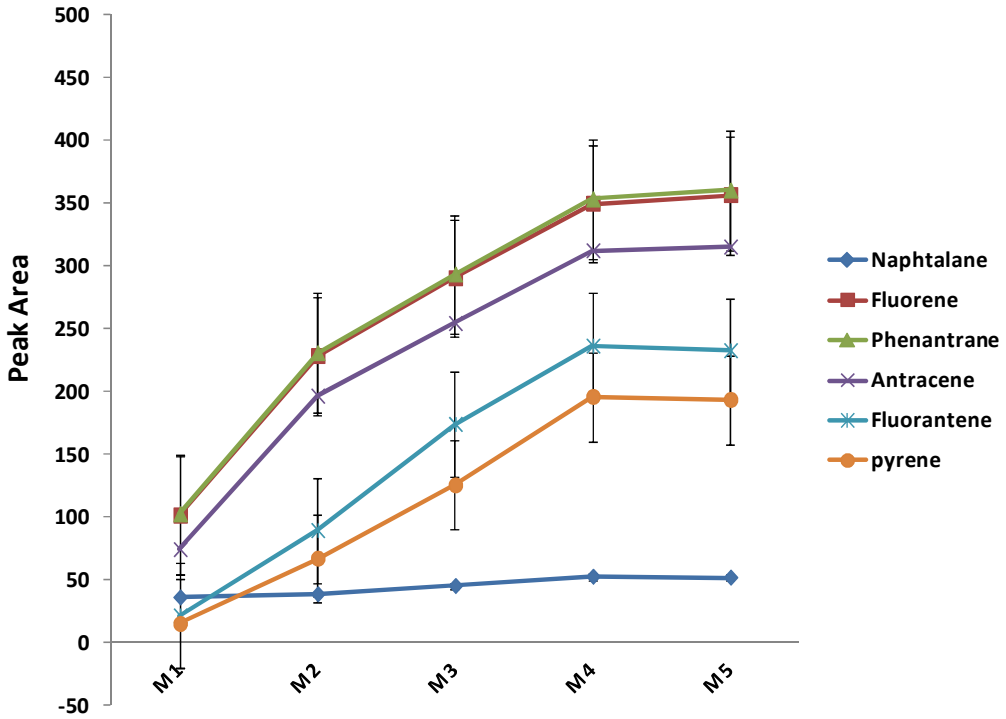

Fig. 5. Effect of the fiber composition on the microextraction of PAHs from indoor air (M1 = 0% MWCNT-COOH, 100% polymer M2 = 1% MWCNT-COOH, 99% polymer M3 = 5% MWCNT-COOH, 95% polymer M4 = 10% MWCNT-COOH, 90% polymer M5 = 15% MWCNT-COOH, 85% polymer). Experimental conditions: Naphthalene concentration 5 mg m^{-3} and other analytes 20 mg m^{-3}; extraction time 30 min; extraction temperature 25 °C; fan rotation speed, 600 rpm. desorption temprature 215 °C; desorption Time 5 min.

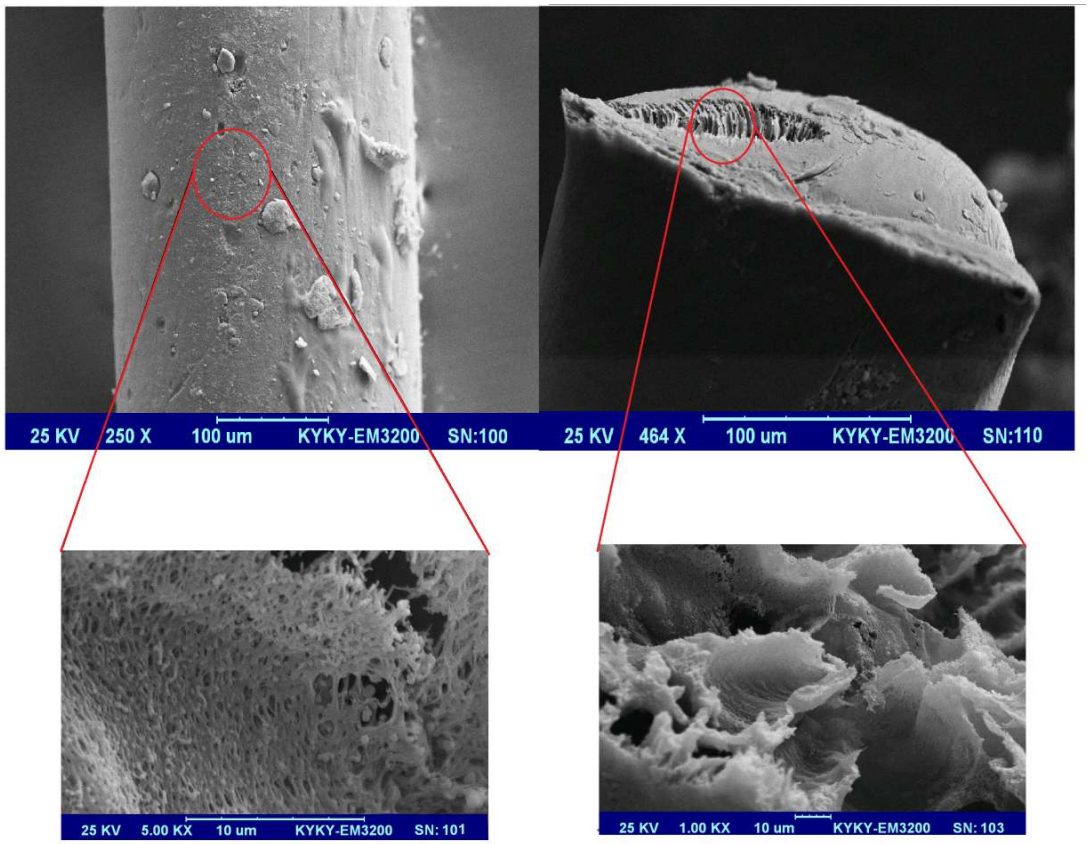

Fig. 6. SEM image of the optimal fiber containing 15% MWCNT and 85% PES.

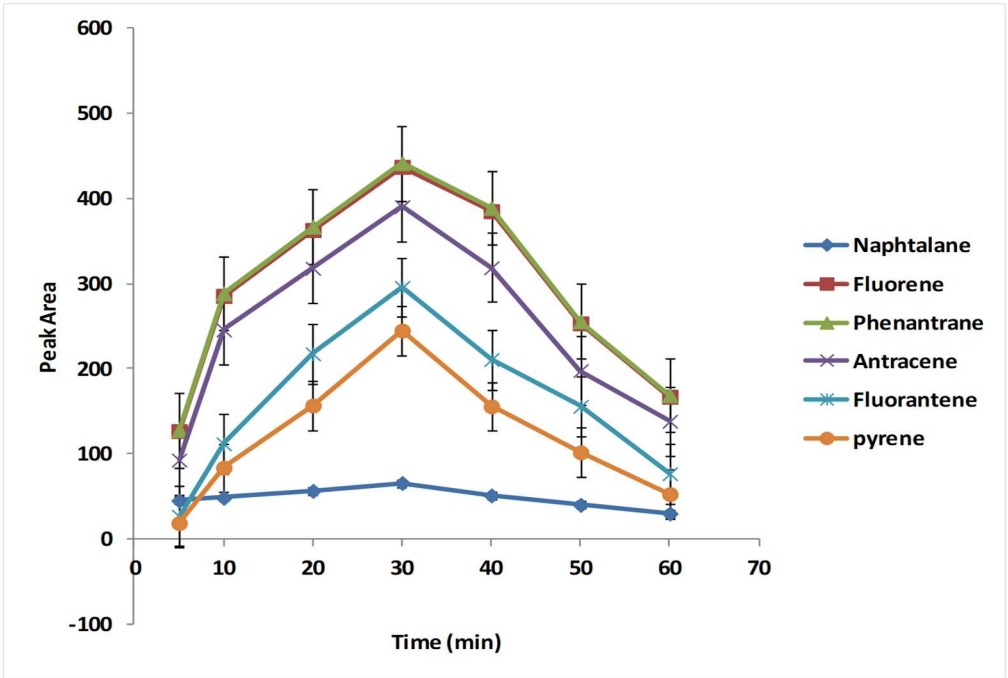

Fig. 7. Effect of the microextraction time on the extraction of PAHs from indoor air. Experimental conditions: Naphthalene concentration 5 mg m^{-3} and other analytes 20 mg m^{-3} extraction temperature 25 °C; fan rotation speed, 600 rpm. desorption temperature 215 °C; desorption Time 5 min.

Optimization of the Desorption Time and Temperature

Samples were injected at various temperatures (150-210 °C) to determine the optimal desorption temperature for gas chromatographic detection. As indicated in Fig. 8A, the maximum desorption occurred at 210 °C beyond which, the structure of the nanocomposite collapsed due to the thermal instability of PES. Therefore, the temperature of 210 °C was selected as the optimal desorption temperature. Desorption of analytes was performed at 210 °C for different times (0.5-6 min), whose results are shown in Fig. 8B. As can be seen, the desorption time of 1 min was sufficient for the complete desorption of the analytes. Therefore, the fiber was placed in the injection valve for 1 min.

Repeatability of the Proposed Method

Five successive tests were conducted to evaluate the repeatability of the method. The relative standard deviation (RSD) was calculated for the extracted analytes. Based on the results, the relative standard deviation of all analytes was below 4.11%, suggesting the acceptable repeatability of the method. The repeatability of the fiber preparation procedure

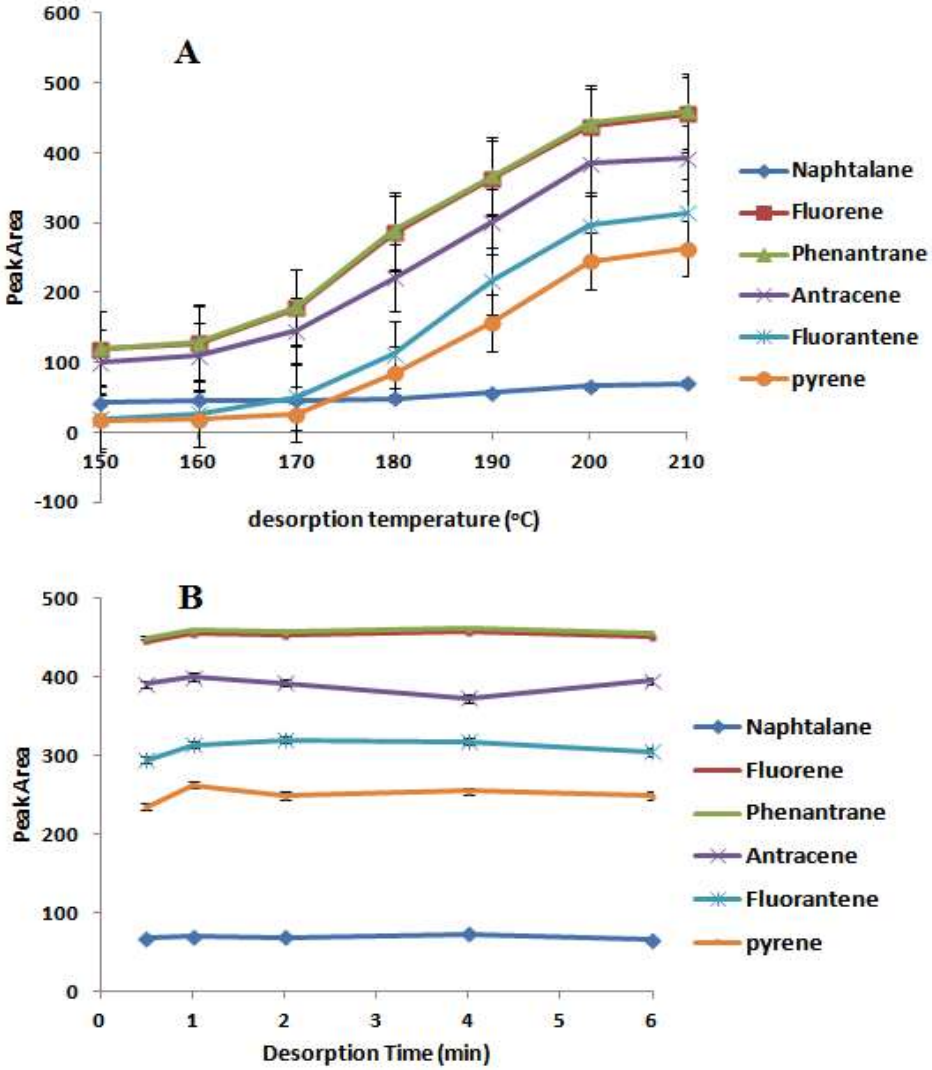

Fig. 8. Effect of desorption temperature (A) and desorption time (B) of PAHs. Experimental conditions: Naphthalene concentration 5 mg m^{-3} and other analytes 20 mg m^{-3}; extraction time 30 min; extraction temperature 25 °C; fan rotation speed, 600 rpm.

was also examined by conducting some tests on three fibers prepared under the same conditions. The relative standard deviation of the fibers fell below 5.95% for all fibers, indicating the suitability of the fiber fabrication process despite its manual nature. The results are depicted in Table 4.

Quantitative Specification of the Proposed Method

Quantitative specifications of the studied method including the calibration curve, correlation coefficients, limit of detection, and linear dynamic range were also assessed as presented in Table 5. The correlation coefficients were 0.9991-0.9996. The proper linear range (0.02-10 mg m^{-3}), as well as low detection limits (0.014-0.032 mg m^{-3}), are among the outstanding advantages of the proposed method.

Analysis of the Real Samples

The results obtained from the analysis of the real samples are presented in Table 6. Also, typically recorded chromatograms of a mixture of analytes from various samples are shown in Fig. 9. The high porosity and monolith membrane structure of the prepared nanocomposite led to its high adsorption capability. Thus, this nanocomposite offers a unique ability to measure trace amounts in indoor air. Another advantage of fiber preparation with the solvent replacement method was the production of fibers with a similar structure, which can be used to prepare commercial fibers in the future.

CONCLUSIONS

A novel nanocomposite adsorbent with high porosity was introduced based on functionalized MWCNTs and PES to be used as an SPME fiber for indoor air analysis. The high and unique adsorption features of MWCNTs, as well as the porous structure of the PES membrane and the high thickness of the proposed fiber (due to its integrity), provided the fiber with high adsorption capacity. Mechanical strength and chemical and thermal resistance of the fiber were in acceptable ranges. These properties of the designed fiber provide its direct application for one-step preconcentration of

Table 4. Relative Standard Deviation for 5 Successive Extractions Processed by One Fiber and 3 Extraction Procedures with Three Different Fibers under Similar Conditions

Compounds	Relative standard deviation (5 replications) One fiber	Relative standard deviation (3 replications) Fiber to fiber
Naphthalene	4.11	5.95
Fluorene	3.65	5.63
Phenanthrene	3.85	5.51
Anthracene	2.95	4.86
Fluoranthene	3.46	2.75
Pyrene	3.48	5.35

Table 5. Analytical Merits of the Proposed Method for the Determination of PAHs in Indoor Air

Compound	Calibration equation	R[a]	LOD[b]	LDR[c]
Naphthalene	$y^d = 9.5384x^e + 0.0472$	0.9995	0.032	0.04-2.5
Fluorene	y = 21.696x + 0.112	0.9993	0.016	0.02-5
Phenanthrene	y = 23.455x + 0.0212	0.9996	0.014	0.02-10
Anthracene	y = 19.551x + 0.0726	0.9991	0.014	0.02-5
Fluoranthene	y = 13.529 +0.0772	0.9996	0.020	0.04-5
Pyrene	y = 12.112x +0.0658	0.9994	0.023	0.04-5

a: Regression coefficient. b: LOD (mg m^{-3}). c: Linear dynamic range (mg m^{-3}). d: Peak area. e: Concentration of PAHs (mg m^{-3}).

Table 6. Results of Analyzing PAHs by SPME in Indoor Air

Compound	($mg\ m^{-3}$)				
	A	B	C	D	E
Naphthalene	0.686 ± 0.012	1.084 ± 0.014	ND	0.081 ± 0.003	ND
Fluorene	0.116 ± 0.004	0.066 ± 0.002	0.159 ± 0.001	0.04 ± 0.002	ND
Phenanthrene	0.06 ± 0.002	0.022 ± 0.001	0.032 ± 0.001	0.017 ± 0.001	ND
Anthracene	0.016 ± 0.001	0.019 ± 0.001	0.014 ± 0.001	0.011 ± 0.001	ND
Florentine	0.035 ± 0.003	0.024 ± 0.001	ND	ND	ND
Pyrene	0.028 ± 0.001	0.034 ± 0.002	ND	ND	ND

ND[a]: Non-detectable. Station A: Closed gazebo of Ahoor restaurant. Station B: Cafeteria. Station C: Real estate agency. Station D: Real estate agency (2). Station E: Control sample.

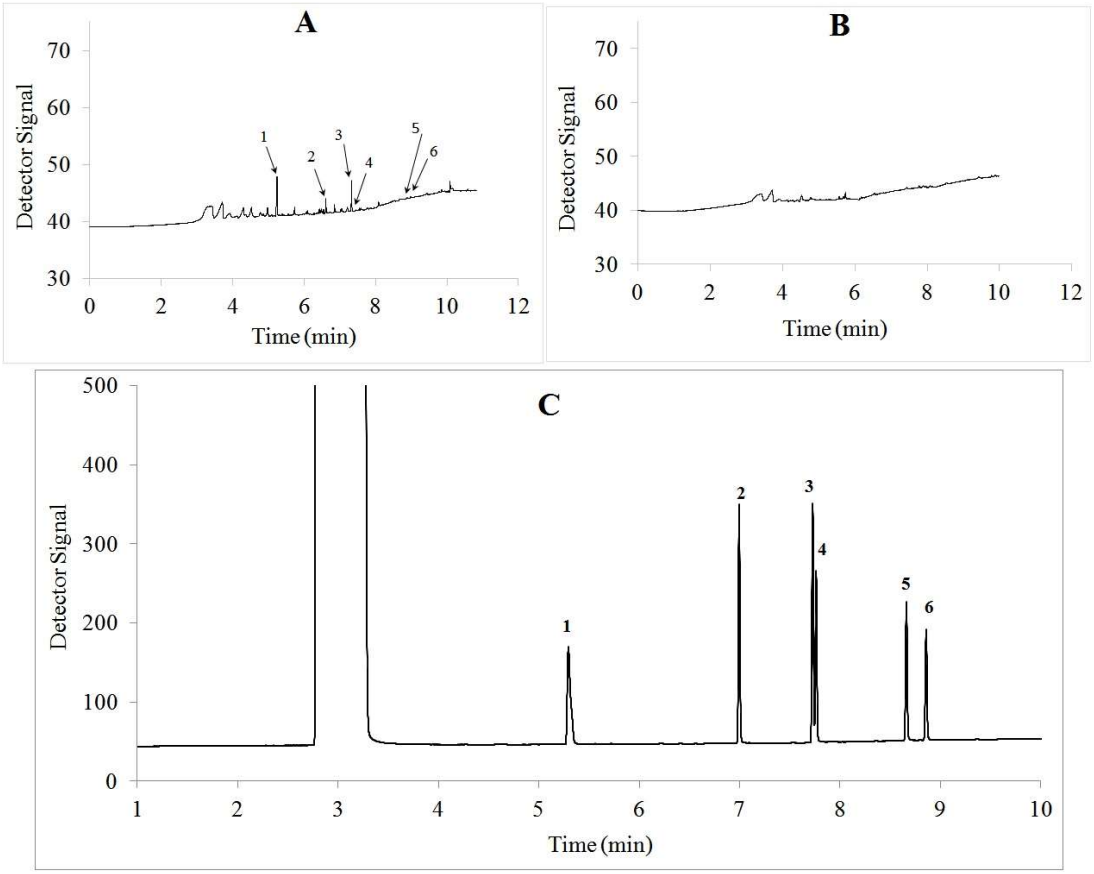

Fig. 9. Typical chromatograms of (A) Cafeteria, (B) Control sample; Experimental conditions: Extraction time 30 min; extraction temperature about 25 °C. (C) PAHs Standards; Experimental conditions: Naphthalene concentration 5 $mg\ m^{-3}$ and other analytes 20 $mg\ m^{-3}$; extraction time 30 min; extraction temperature 25 °C; fan rotation speed, 600 rpm; desorption temperature 215 °C; desorption Time 1 min.

PAHs by SPME from indoor air samples. The facile fabrication method and low cost are among the other advantages of the proposed fiber. The successful application of the fiber was reported in the SPME of PAHs compounds in the real samples. The quantitative features of the proposed method, its wide linear range, low LOD, and high repeatability further confirmed the suitability of the proposed method for the analysis of PAHs. The ability of this method to analyze these compounds in various samples is another benefit, further confirming the applicability of this method for the analysis of real samples.

REFERENCES

[1] M. Majd, S. Nojavan, Microchem. J. 171 (2021) 106852.

[2] A.A. Matin, P. Biparva, M. Gheshlaghi, J. Chromatogr. A 1374 (2014) 50.

[3] M. Guo, Z. Gong, X. Li, G. Allinson, J. Rookes, D. Cahill, Ecotoxicol. Environ. Saf. 140 (2017) 191.

[4] X. Zhang, J. Yang, X. Wang, C. Li, T. Peng, Q. Miao, X. Du, X. Lu, Talanta 243 (2022) 123385.

[5] B.B. Kefi, L.L. El Atrache, H. Kochkar, A. Ghorbel, J. Environ. Sci. 23.5 (2011) 860.

[6] J.C. Chuang, G.A. Mack, N.K. Wilson, Atmos. Environ. B, Urban Atmos 25.3 (1991) 369.

[7] Z. Feng, C. Huang, Y. Guo, W. Liu, L. Zhang, Talanta 209 (2020) 120541.

[8] N. Manousi, A. Kabir, K.G. Furton, E. Rosenberg, G.A. Zachariadis, Microchem. J. 166 (2021) 106210.

[9] M. Yazdanpanah, S. Nojavan, J. Chromatogr. A 1585 (2019) 34.

[10] X. Ma, P. Huang, X. Dang, Y. Ai, D. Zheng, H. Chen, Microchem. J. 146 (2019) 1026.

[11] J. Pang, D. Yuan, X. Huang, J. Chromatogr. A 1571 (2018) 29.

[12] N.A. El-Naggar, H.I. Emara, M.N. Moawad, Y.A. Soliman, A.A.M. El-Sayed, Egypt. J. Aquat. Res. 44 (2018) 9.

[13] K. Ravindra, R. Sokhi, R. Van Grieken, Atmos. Environ. 42 (2008) 2895.

[14] ATSDR, US. "Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs)." US Agency for Toxic Substances and Disease Registry, Atlanta, GA (1995).

[15] C. Anyakora, F. Babalogbon, U. Obiakor, I. Afolami, H. Coker, Sci. Res. Essay 3 (2008) 254.

[16] F.F. Karam, F.H. Hussein, S. J. Baqir, F.M. Abid, Asian J. Chem. 24 (2012) 5589.

[17] W. Jedrychowski, A. Galas, A. Pac, E. Flak, D. Camman, V. Rauh, F. Perera, Eur. J. Epidemiol. 20 (2005) 775.

[18] I.A. Fawzy, N.K. Nashwa, M.A. Ahlam, Res. J. Environ. Toxicol. 5 (2011) 282.

[19] K. Sun, Y. Song, F. He, M. Jing, J. Tang, R. Liu, Sci. Total Environ. 773 (2021) 145403.

[20] B. Munoz, A. Albores, Selected Topics in DNA Repair 201 (2011) 125.

[21] A.T. Vu, K.M. Taylor, M.R. Holman, Y.S. Ding, B. Hearn, C.H. Watson, Res. Toxicol. 28 (2015) 1616.

[22] E. Sepetdjian, A. Shihadeh, N.A. Saliba, Food Chem. Toxicol. 46 (2008) 1582.

[23] P. Jacob, A.H. Abu Raddaha, D. Dempsey, C. Havel, M. Peng, L. Yu, N.L. Benowitz, Cancer Epidemiol Biomarkers Prev. 20 (2011) 2345.

[24] A. Shihadeh, R. Salman, E. Jaroudi, N. Saliba, E. Sepetdjian, M.D. Blank, C.O. Cobb, T. Eissenberg, Food Chem. Toxicol. 50 (2012) 1494.

[25]J.A. Holme, H. Valen, B.C. Brinchmann, G.E. Vist, T.K. Grimsrud, R. Becher, A.M. Holme, J. Vrevik, J. Alexander, Toxicol. 473 (2022) 153206.

[26] O.S. Olatunji, O.S. Fatoki, B.O. Opeolu, B.J. Ximba, Food Chem. 156 (2014) 296.

[27] S.W. Wang, K.H. HsuShou, C.H. Su-H, T. Der, Y.W. Hwei, F. Cheng, J. Food Drug Anal. 27 (2019) 815.

[28] J. Jeffery, M. Carradus, K. Songin, M. Pettit, K. Pettit, C. Wright, Chem. Cent. J. 12 (2018) 27.

[29] C.M. McMahonb, C. Herbrandsonc, M.J. Kraused, C. M. Schmittd, C.J. Lipperte, G.C. Prattf, Environ. Pollut. 231 (2017) 487.

[30] M.C. Pietrogrande, G. Demaria, M. Russo, Environ. Sci. 124 (2023) 644.

[31] Y.H. Kim, K.H. Kim, Sci. Rep. 5 (2015) 11679.

[32] S.K. Pandey, K. Kim, R.J.C. Brown, Trends Anal. Chem. 30 (2011) 1716.

[33] A.A. Matin, P. Biparva, M. Gheshlaghi, K. Farhadi, Chemosphere 93 (2013) 1920.

[34] X.L. Song, Y. Chen, J.P. Yuan, Y.J. Qin, R.S. Zhao, X. Wang, J. Chromatogr. A 1468 (2016) 17.

[35] A.A. Matin, P. Biparva, M. Gheshlaghi, E. Marzi Khosrowshahid, K. Farhadi, J. Chromatogr. B 1150 (2020) 122190.

[36] E. Couteau, K. Hernadi, J.W. Seo, L. Thien-Nga, C.S. Miko, R. Gaal, L. Forro, Chem. Phys. Lett. 378 (2003) 9.

[37] Y. Manawi, V. Kochkodan, E. Mahmoudi, D.J. Johnson, A.W. Mohammad, M.A. Atieh, Sci. Rep. 7 (2017) 15831.

[38] M.S. Tijink, M. Wester, J. Sun, A. Saris, L.A. Bolhuis-Versteeg, S. Saiful, J.A. Joles, Z. Borneman, M. Wessling, D.F. Stamatialis, Acta Biomater. 8 (2012) 2279.

[39] M. Alimohammady, M. Jahangiri, F. Kiani, H. Tahermansouri, Carbon Lett. 29 (2019) 1.