



Carbon Nanotube/Polypyrrole Composites as a Novel Solid Phase Microextraction Fiber Coating for the Preconcentration of n-Alkanes from Aqueous Media

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ABSTRACT

In this paper, the electrochemical fiber coating (EFC) technique was used for the preparation of oxidized multiwalled carbon nanotubes–polypyrrole composite (MWCNTs–PPy) and applied as a new fiber for solid-phase microextraction (SPME) procedures in the gas chromatographic (GC) determination of n-alkanes in aqueous samples. The effects of various parameters on the efficiency of SPME process such as extraction time, extraction temperature, ionic strength, stirring rate and desorption time were studied. Under optimized conditions, the linear dynamic range of developed SPME-GC for the selected n-alkanes spanned 0.5-500 ngmL⁻¹ with R² larger than 0.996 and the limits of detection (N= 3) were in the range of 0.010–0.050 ngmL⁻¹. The method displayed good repeatability by using a single fiber (RSD<2.14%) and good fiber-to fiber reproducibility (RSD<7.65%). All of these characteristics demonstrate that the proposed SPME is an efficient, flexible and versatile sampling and extraction tool which is ideally suited for use with chromatographic methods.

KEYWORDS: Solid-phase microextraction; n-Alkanes; Composite polymer; Carbon nanotube Polypyrrole.

1. INTRODUCTION:

Sampling and sample preparation are important steps in the process of analysis. The techniques of sampling and sample preparation have been developed in recent years to meet the demands of fast analysis to locate problems as soon as possible. Solid-phase microextraction (SPME) is a relatively recent sample preparation technique that was introduced by Pawliszyn and co-workers [1-3]. To this day, SPME has been successfully applied in numerous environmental, food, flavor, pheromone, pharmaceutical, clinical, and forensic applications [4,5].

The key part of the SPME fiber is of course the fiber coating; however, in the present the number of different commercially available fiber coatings is still restricted, only including polydimethyl-siloxane (PDMS), PDMS/divinylbenzene (DVB), poly-acrylate (PA), carboxen/PDMS, carbowax (CW)/DVB, CW/template resin and DVB/carboxen/PDMS, etc. [4]. Silica rods are mainly used as SPME support for these commercial coatings. Silica fibers are expensive, fragile, and can easily be broken [5]. In order to overcome these problems, a large number of metallic fibers were reported in the literature; for example, pencil lead [6], anodized aluminum [7], anodized zirconium [8], and copper coated with copper(I) chloride [9] have been developed and used as SPME fibers. These metallic fibers showed improved mechanical stability and extraction

Performances Recently, there has been increasing interest in the use of conducting polymers as the extraction

phase [10–12]. Conducting polymers are multifunctional materials with various

Interesting properties such as their extraordinary stability, simplicity of synthesis from an inexpensive monomer, and unique electrochemical properties [13,14]. These properties make them easy to be electrodeposited on metal wire for SPME application [15]. Electrodeposition has rigid ability to control the film thickness formed, uniformity, and deposition rate [16].

Among various conducting polymers studied, polyaniline, polypyrrole, and their derivatives, have been successfully applied as SPME coating materials [17,18]; however, these polymeric materials are usually brittle, intractable, and often decompose before melting, which brings some disadvantages for real application [19]. The preparation of conducting polymers with great strength and flexibility is highly desired in this area.

Carbon materials have long been used as adsorbents for trapping or separation of organic compounds. In SPME, carbon materials such as polycrystalline graphite, low-temperature

Glassy carbon and activated carbon have been successfully used as the coating or fiber material. Carbon nanotubes (CNTs) are a kind of novel and interesting carbon material first found in 1991 by Iijima [19]. CNTs are divided into single-wall nanotubes (SWNTs) and multi-wall nanotubes (MWNTs) according to their numbers of the graphite sheets. The unique electrical, mechanical, and chemical properties of CNTs have aroused great interest of

research workers [20-26]. CNTs have curved surface (composed of two fullerene halves and a cylinder made of a rolled up graphite sheet), thus are expected to show a stronger binding affinity for hydrophobic molecules compared with a planar carbon surface. Furthermore, the internal pores of the CNTs are large enough to allow molecules to penetrate. The adsorption can occur on the inner hollow cavity of CNTs, on the outside surface, and on the interstitial spaces between the nanotube bundles. All these indicate that CNTs have strong physical adsorption ability to hydrophobic compounds.

With the great progress in the methods of preparing CNTs, large efforts have been devoted

To the fields of application, such as gas storage[27], preconcentration of volatile organic compounds, [28] removal of chemical and toxic wastes from water,[29] and GC,[30] etc. It is therefore conceivable that CNTs may have great analytical potential as an effective solid-phase microextraction adsorbent for some suitable compounds.

In recent years, environmental pollution by petroleum-type materials has increased with the growth of industries and increased demand for energy. The nature of petroleum hydrocarbon contamination is highly variable. Petroleum hydrocarbons themselves are diverse mixtures of chemical components. The more common functional categories of compounds found in petroleum products are *n*-alkanes, branched alkanes, cycloalkanes and aromatic compounds. Several studies have reported the use of SPME to detect trace amounts of *n*-alkanes in different samples using several SPME fibers such as [31-32].

In this work, for the first time carbon nanotube and polypyrrole composite on a tungsten fiber was used for preconcentration of *n*-alkanes (C₁₀-C₁₈) from the headspace of aqueous solutions and determined by gas chromatography technique.

2. EXPERIMENTAL:

2.1. REAGENTS:

n-Alkanes were purchased from Merck (Darmstadt, Germany). The mixed stock standard solution was prepared in methanol with the concentration of 1000 mg/l. Then, the working standard solutions were freshly prepared by diluting the mixed standard solution with doubly distilled water to the required concentration. Pyrrole (≥97% pure) was obtained from Merck (Darmstadt, Germany). Multiwalled carbon nanotubes were purchased from Iran petroleum research center (Tehran, Iran). Tungsten wire (300 μm O.D.) was used as SPME fiber. Methanol and nitric acid was purchased from Merck

(Darmstadt, Germany). Other reagents used were of the highest purity available. Double distilled water was used in all experiments.

2.2. APPARATUS:

The SPME holder for manual sampling is obtained from Azar Electrode (urmia, Iran). A magnetic stirrer (Heidolph MR 3003) was employed for stirring of the solution. An ultrasonic bath, model LBS2 from Euronda (Italy) was used for sonication purposes. The scanning electron micrographs of the fiber surface were obtained. Electrochemical polymerization of pyrrole was carried out using a Potentiostat/Galvanostat, micro Autolab, type III (The Netherlands). The chromatographic analyses of *n*-Alkanes were performed by a model 7890A gas chromatograph from Agilent (Wilmington, DE, USA), equipped with a split-splitless injector and a flame ionization detector (FID). Chromatographic separation was accomplished with a HP-5 column (30 m×0.32 mm. I.D.×0.25 μm). The column temperature was initially kept at 30 °C for 5 min, then increased at 15 °C min⁻¹ to 220 °C and kept for 5 min. Injector and detector temperatures were adjusted at 250 °C and 270 °C, respectively.

2.3. PREPARATION OF COMPOSITE COATING:

MWCNTs (100 mg) were refluxed in 7 mL of concentrated nitric acid at 115 °C for 3 h. The oxidized-MWCNTs were filtered and washed with deionized water for several times to pH 7. The composite coating of pyrrole and MWCNTs was synthesized electrochemically via in situ polymerization from a solution containing both the acid treated CNTs and the pyrrole monomer. Tungsten wire, platinum electrode and Ag/AgCl electrode were used as working electrode, counter electrode and reference electrode, respectively. Wire coating procedure was as follows: 40 mg of the oxidized-MWCNTs were ultrasonically dispersed in 20 mL water for 1 h and then 0.5 mL of pyrrole was added to the solution and sonicated for 15 min. The composite polymer coating was directly deposited from this solution on the tungsten wire by applying a constant potential of 0.9V for 1000 s. The coated fiber was placed in an oven at 100 °C for 30 min, and then at 250 °C for 2 h in the GC injector port to remove any volatile compound remaining in the fiber and obtain a smooth chromatographic baseline.

2.4. SPME PROCEDURE:

A standard solution of the mixture of *n*-alkanes at the concentration 0.1 μg mL⁻¹ was prepared from the stock solution by doubly distilled water. 50 ml of standard solution was pipetted into a 60 ml vial with a PTFE septum

cap and a 2-cm long stirring bar was placed into the solution. Then the sample vial capped with septum and magnetic stirring was used to agitate the sample. A simple water bath, placed on a magnetic stirrer, was used for controlling the temperature of the samples. The composite-coated fiber was housed in manual SPME holder and put into a vial, above the sample solution while 1.5 cm length of the fiber exposed to the sample solution. 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.

3. RESULTS AND DISCUSSION:

3.1. CHARACTERIZATION OF MWCNTS–PPY COMPOSITE FIBER:

The surface characteristic of the composite polymer was investigated using scanning electron microscope (SEM). It is seen from Fig. 1. that the surface of the polymer coating is rough with large effective surface area, which is favorable for the adsorption/extraction of analytes. The inclusion of the MWCNTs in the composite polymer is observed in the high resolution SEM shown in Fig. 1b. The diameter of the composite fiber is 343 μm , average thickness of the coated layer is 20 μm and size of particles is between 70 and 90 nm.

3.2. SPME OPTIMIZATION:

In order to obtain high extraction efficiency of the analytes using this microextraction technique, the main parameters such as extraction time, extraction temperature, ionic strength, stirring rate, desorption time, and temperature program were optimized.

3.2.1. TEMPERATURE PROGRAM:

In order to decrease of time of analysis and complete separation of peaks from each other, choosing of a suitable temperature program is necessary. For this purpose, four temperature programs according to table 1 were examined. The selected program as follows: The column temperature was initially kept at 30 $^{\circ}\text{C}$ for 5 min, then increased to 220 $^{\circ}\text{C}$ at 15 $^{\circ}\text{Cmin}^{-1}$ and kept for 5 min.

3.2.2. STIRRING RATE:

Agitation of the sample enhances the extraction rate and therefore reduces the extraction time because the equilibrium between two phases can be achieved more rapidly [32,33]. In this study, the effect of stirring speed on the extraction of the analytes was assessed for a period of 100-900 rpm. According to Fig. 2, the relative peak area increased with increasing stirring rate up to 350 rpm.

Faster stirring rates did not have significant effect on extraction efficiency. Hence, a stirring rate of 350 rpm was chosen for further studies.

3.2.3. DESORPTION TIME:

In order to ensure complete desorption of analytes from the fiber, suitable desorption time is critical. After adsorption of the analytes, desorption time was optimized by placing the fiber inside the GC injection port for a period of 1.0–20.0 min at 250 $^{\circ}\text{C}$. As Fig. 3 shows, desorption is complete within 5 min for all of the n-alkanes. Hence, desorption time of 5.0 min was chosen in this step.

3.2.4. 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 reaching the equilibrium [34]. For this purpose, HS-SPME was performed at different times between 10 and 70 min and the variation of peak area as a function of the extraction time was plotted. As Fig. 4 shows an extraction time of 20 min was sufficient to reach equilibrium for all n-alkanes and with increasing extraction time, the peak areas did not change. Hence, for saving time, 20 min was chosen for the extraction time.

3.2.5. EXTRACTION TEMPERATURE:

Extraction temperature should be optimized because it plays very important role in the extraction process by controlling the diffusion rate of analytes into the coating. The effect of temperature in the extraction yield was investigated varying the temperature between 20 and 70 $^{\circ}\text{C}$ with a constant extraction time of 20 min. As Fig. 5 shows, an increase in temperature from 20 $^{\circ}\text{C}$ to 25 $^{\circ}\text{C}$ increased peak areas and better recoveries were obtained, but at higher temperatures the ability of the SPME fiber to adsorb the n-alkanes decreased. This is because adsorption is an exothermic process and therefore, disfavored at high temperature. Thus by increasing the temperature, the distribution constant at equilibrium and thereby, the extracted amount decreases. Thus room temperature was chosen for the extraction temperature .

3.2.6. IONIC STRENGTH:

In SPME procedure, the matrix can be modified by adding salts, e.g. NaCl. In the presence of salts, the ionic strength of the water increases so as the solubility of the non-polar organic solutes in water decrease and more analytes release into the headspace, thereby, adsorption on the fibre enhances. Thus, the effect of this parameter on extraction efficiency was investigated. As Fig. 6 shows,

adding NaCl to extraction vial enhanced extraction efficiency. Thus, the extractions were carried out from the samples containing 2% NaCl.

3.3. VALIDATION PARAMETERS:

Figures of merit including linear range (LR), limits of detection (LOD) and limits of quantification (LOQ) were evaluated and summarized in Table 2. Calibration graphs were linear in the concentration range of 0.5–500 ngmL⁻¹ for all analytes with correlation coefficients (R²) of larger than 0.996. Precision in terms of reproducibility and repeatability (RSD %) was calculated. Three replicate determinations have been carried out using a single fiber and the results show that the RSD% of the method is less than 2.14% for all compounds, which indicates that the proposed method is repeatable. Also reproducibility studies performed on three different fibers show that the fiber-to-fiber RSD% is less than 7.65% for all compounds (Table 2). It is mentioned that although fiber-to-fiber reproducibility is relatively good, there is no need to use different fibers in a single analysis. Table 1 also presents LOD and LOQ in the present HS-SPME method. The limits of detection, based on S/N = 3, vary between 0.01 and 0.05

ngmL⁻¹ and limits of quantification, based on S/N = 10, vary between 0.03 and 0.15 ngmL⁻¹. In Table 3, a comparison has been made between the LODs, RSDs, and LR obtained in the present work and similar results reported by other research groups. The LODs and RSDs found in the present work are better than the values reported for other methods.

3.4. REAL SAMPLE:

To apply the proposed method in real sample analysis, three samples including paint waste from Arko paint factory (Tabriz, Iran), antiknock from Behran oil company (Tehran, Iran) and gas oil from National Iranian Oil Company (Tehran, Iran) were prepared. 1 ml of a sample and 100 ml of distilled water were poured into separating funnel and was placed for 1 hour on shaker. After extraction of compounds into distilled water, two phases were separated. Then, 50 ml of aqueous phase was pipetted into a vial and under optimized conditions was subjected to HS-SPME and GC analysis. The results found for these analyses were shown in Table 4 and chromatograms were shown in Fig.7.

Table 1: Examined temperature programs

Sr. No.	Examined temperature programs
1	50°C (2min) 40 °C/min 140 ° 10° C/min 220°C (2 min)
2	50°C (2min) 15 °C/min 220°C (4 min)
3	50°C (1min) 5 °C/min 220°C (2 min)
4	30°C (5min) 15 °C/min 220°C (5 min)

Table 2: linear range (LR), Correlation coefficient (r), Limit of detection (LOD), Limit of quantification (LOQ) and precision (RSD%).

Compound	Linear range (ngmL ⁻¹)	Correlation coefficient (r)	LOD (ngmL ⁻¹)	LOQ (ngmL ⁻¹)	RSD% (N=3)	
					Single fiber	Fiber-to-fiber
n-Undecane	0.5-500	0.998	0.05	0.15	1.72	3.64
n-dodecane	0.5-500	0.998	0.02	0.06	1.33	3.87
n-Tetradecane	0.5-500	0.996	0.01	0.03	0.47	7.65
n-Hexadecane	0.5-500	0.996	0.02	0.06	1.15	6.95
n-Octadecane	0.5-500	0.996	0.05	0.15	2.14	7.21

Table 3: Comparison of linear range (LR), limit of detection (LOD) and relative standard deviation (RSD%) of the present SPME-GC with other works for determination of n-alkanes.

Method	Detection technique	Linear range (ngmL ⁻¹)	Detection limit (ngmL ⁻¹)	R.S.D.% Single fiber	Reference
Headspace solvent microextraction	GC-FID	0.5–400 to 5–200	0.1–4	2.3–7.2	27
Headspace SPME	GC-FID	150-3000	50-150	2.3-8.6	28

Direct SPME	GC-FID	0.5-30	0.1-0.3	4.78-9.54	29
Headspace SPME	GC-FID	0.5-500	0.01-0.05	0.47-2.14	This work

Table 4: Determination of *n*-alkanes in real samples.

Sample	<i>n</i> - Undecane	<i>n</i> -dodecane	<i>n</i> -Tetradecane	<i>n</i> -Hexadecane	<i>n</i> -Octadecane
paint waste	ND*	1302±4.9**	ND	756±5.8	642±3.7
Antiknock	6235±7.3	1235±5.5	ND	ND	ND
gas oil	ND	ND	1104±4.6	13512±8.2	2144±9.6

* ND = Not detected.

** Concentration ($\mu\text{g mL}^{-1}$) ± Relative standard deviation (n = 3).

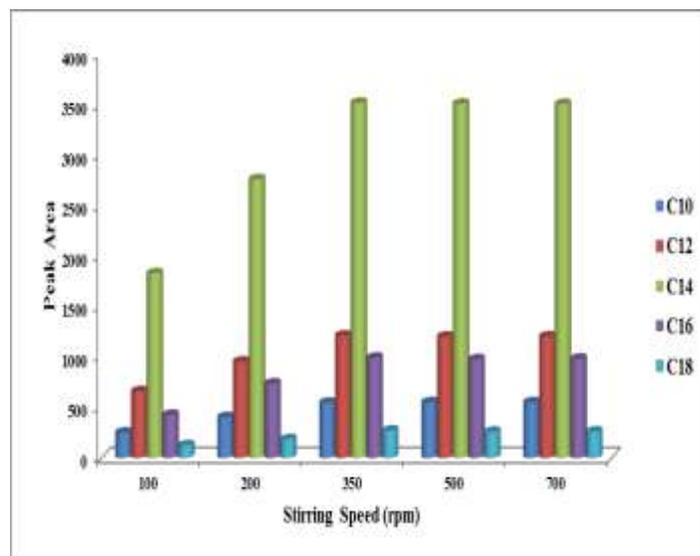
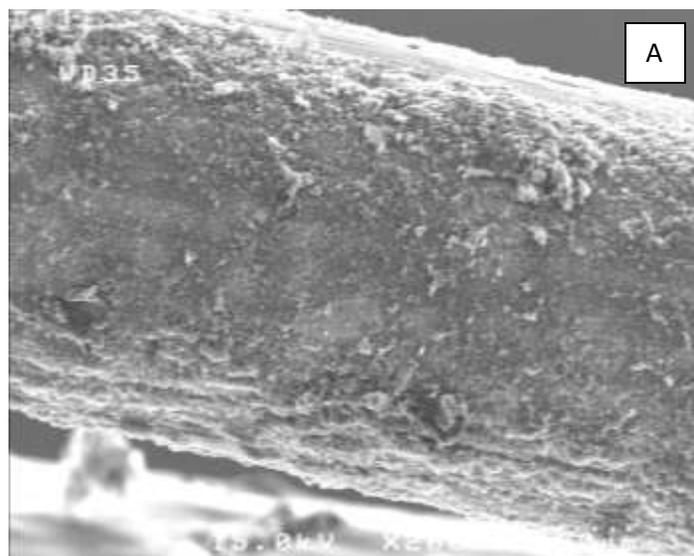


Figure 2: Effect of stirring rate on the SPME efficiency of *n*-alkanes.

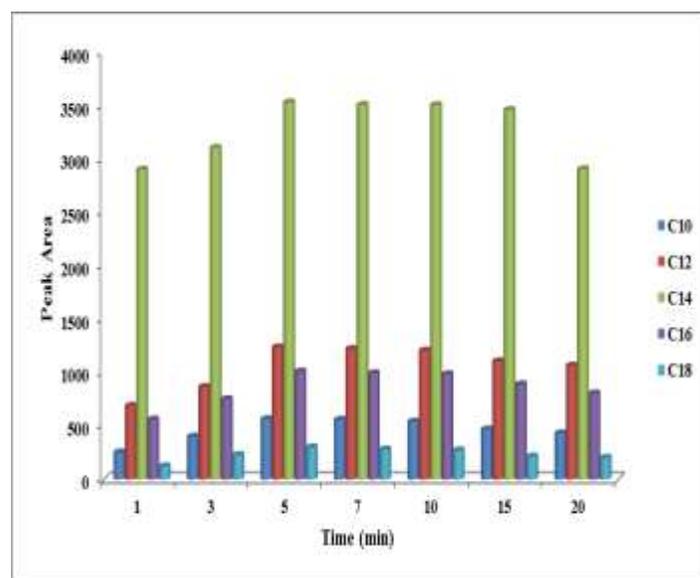
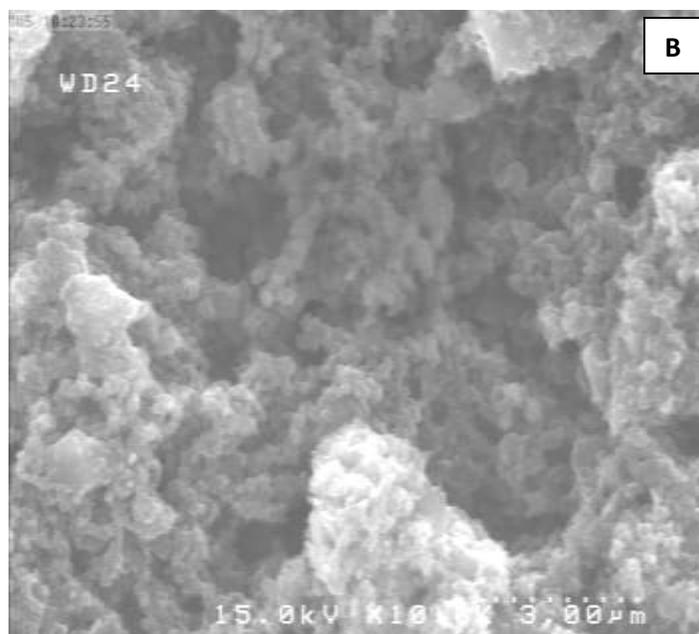


Figure 3: Effect of desorption time on the SPME efficiency of *n*-alkanes. Conditions: [*n*- alkanes] = $0.1\mu\text{g mL}^{-1}$ each, stirring rate = 350 rpm.

Figure 1: Scanning electron micrograph images of the surface of MWCNTs-PPy composite film. (a) Magnification 200×, (b) magnification 10000×.

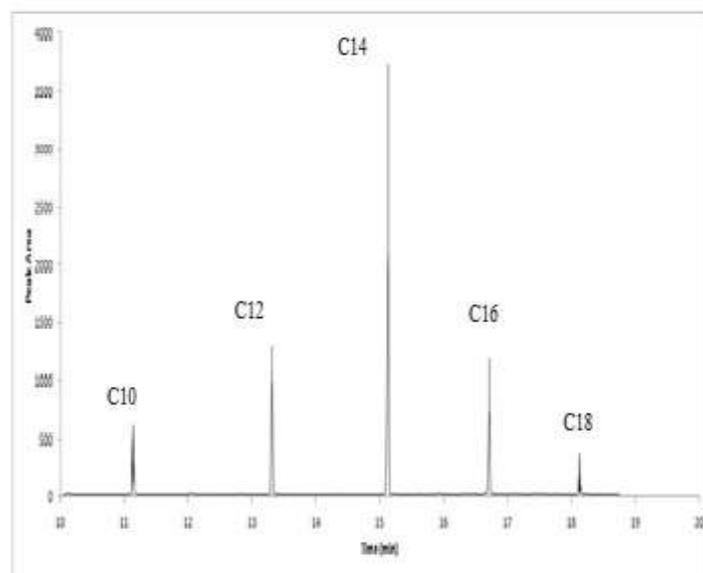
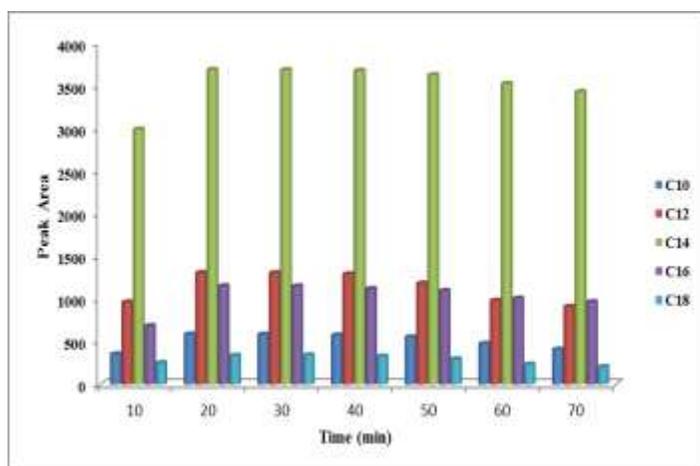


Figure 4: Effect of extraction time on the SPME efficiency of n-alkanes. Conditions: [n- alkanes] = $0.1\mu\text{g mL}^{-1}$ each, stirring rate = 350 rpm, desorption time=5 min.

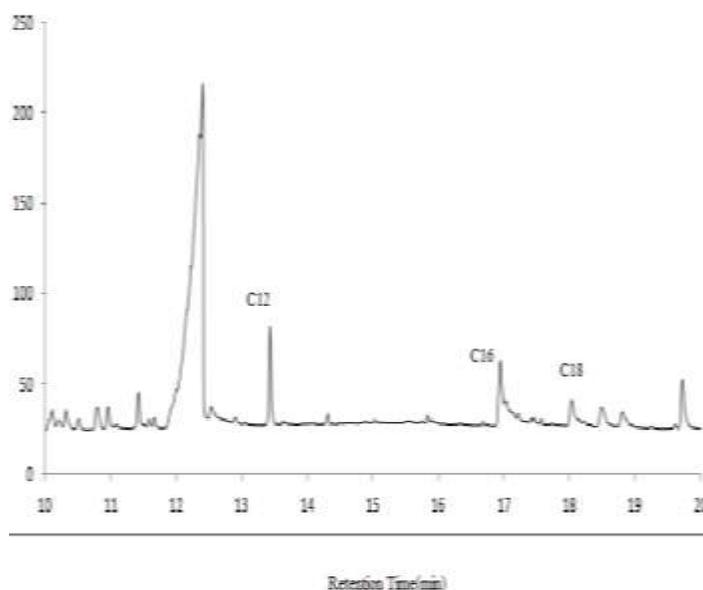
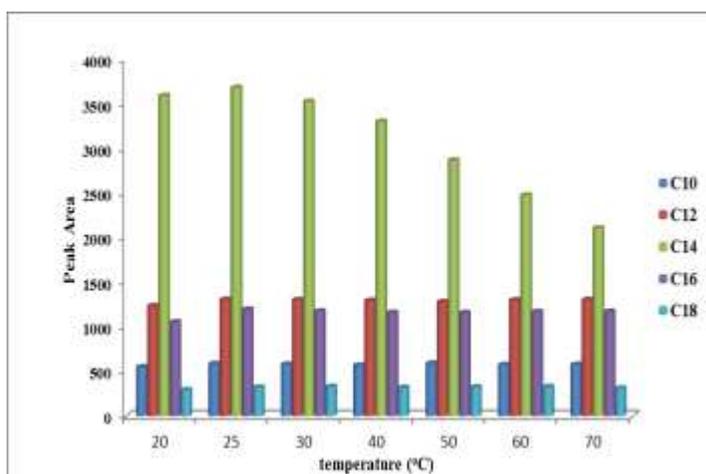


Figure 5: Effect of extraction temperature on the SPME efficiency of n-alkanes. Conditions: [n- alkanes] = $0.1\mu\text{g mL}^{-1}$ each, stirring rate = 350 rpm, desorption time=5 min, extraction time=20 min.

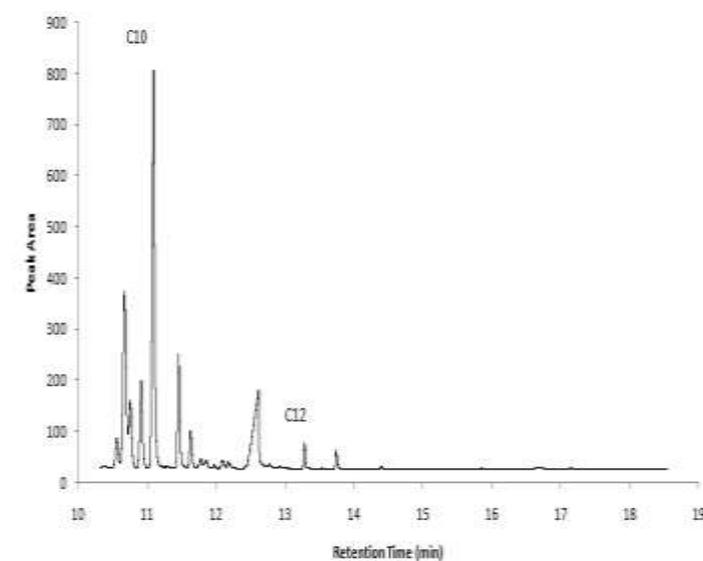
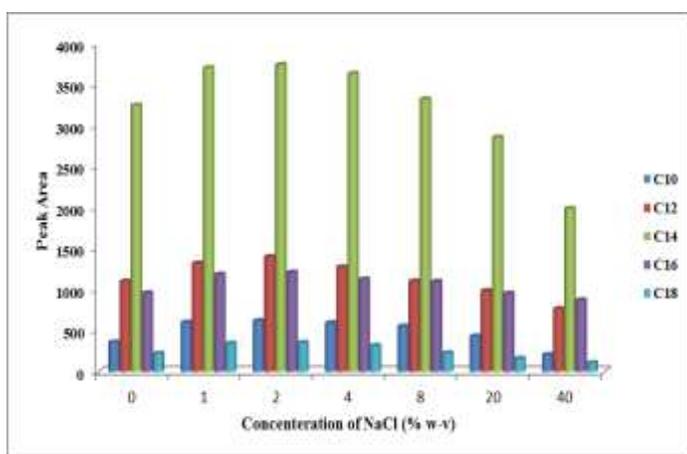


Figure 6: Effect of extraction temperature on the SPME efficiency of n-alkanes. Conditions: [n- alkanes] = $0.1\mu\text{g mL}^{-1}$ each, stirring rate = 350 rpm, desorption time=5 min, extraction time=20 min and extraction temperature=25 °C.

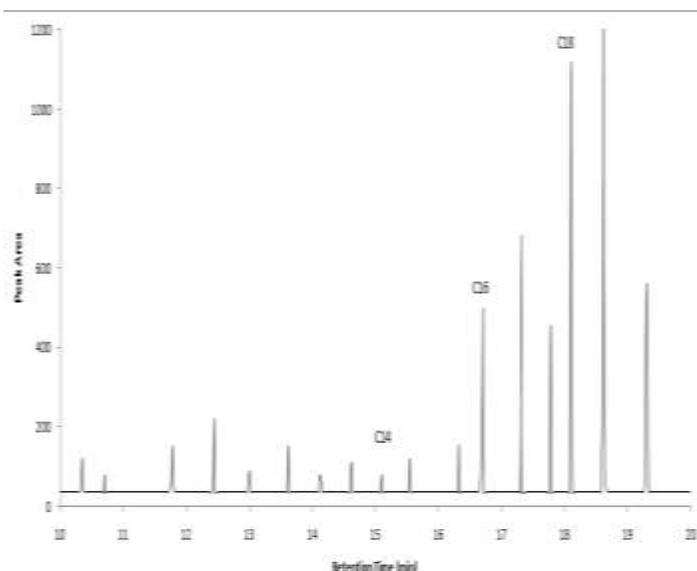


Figure 7: a) A chromatogram of standard solution (0.1 μ g/mL) and chromatograms of real samples for b) paint waste c) antiknock d) gas oil after HS-SPME under optimized conditions.

4. CONCLUSION:

In this study, an oxidized-MWCNTs–PPy SPME fiber was fabricated by electrochemical polymerization for the preconcentration of n-alkanes from aqueous media. 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, and reproducible preparation are among the clear advantages of the proposed fiber coating. The presented experimental results clearly demonstrate that oxidized-MWCNTs–PPy fibers are suitable for HS-SPME of n-alkanes and gas chromatographic (GC) determination of them in aqueous samples.

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