

Ordered Nanoporous Carbon Based Solid-Phase Microextraction for the Analysis of Nitroaromatic Compounds in Aqueous Samples

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ABSTRACT: *In this paper, the possibility of using a new ordered nanoporous carbon as a new fiber in headspace solid phase microextraction (HS-SPME) to determine of mononitrotoluenes (MNTs) in waste water is demonstrated. The structural order and textural properties of the ordered nanoporous carbon were studied by X Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) images and nitrogen adsorption isotherms. The analysis was done on a gas chromatograph equipped with flame ionization detector and capillary column. The main factors affecting the MNT compounds extraction such as rate of stirring sample solution, sample solution volume, ion strength of sample solution, extraction time and temperature have been investigated and established. Optimization of these parameters was done by Taguchi method and Orthogonal Array Design (OAD). The effects of these parameters were investigated using the analysis of variance (ANOVA). Under the optimum conditions, recovery values were between 87.1% and 106.2%, Limit Of Detections (LODs) ranged from 0.01 µg/L to 0.16 µg/L and Linear Dynamic Range (LDR) of 0.5–400 µg/L was obtained. Relative standard deviation of single fiber and fiber-to-fiber (n=4) was in the range of 3.7-4.2% and 7.3-8.9%. Performance of the present method was evaluated for extraction and determination of nitroaromatic compounds in wastewater samples in the range of microgram per liter and satisfactory results were obtained.*

KEY WORDS: *Gas chromatography, Mononitrotoluenes, Headspace solid phase microextraction, Ordered nanoporous carbon, Taguchi method.*

INTRODUCTION

Mononitrotoluenes (MNTs) are a group of explosive compounds that due to their broad application are widely present in aquatic environment [1]. MNTs are used in the synthesis of intermediates for production of dyes, rubber chemicals, pesticides and several other industrial applications [2-3]. The widespread use, mobility and

harmfulness of nitroaromatics and their degradation products demand rapid analysis in environmental matrices [4].

Capillary gas chromatography is the conventional technique for detection and identification of volatile compounds. However a proper isolation and

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pre-concentration technique should be applied before the chromatographic analysis. A number of separation/preconcentration procedures have been used for nitroaromatics and related compounds in aqueous samples include Liquid Liquid Extraction (LLE) [5], Solid Phase Extraction (SPE) [6] and microextraction. LLE based methods are time consuming labour intensive and require large amounts of organic solvents [7]. SPE method has the advantage of lower solvent consumption but is also time-consuming due to the numerous steps involved including conditioning, sample application, washing and elution of the SPE columns [8]. Microextraction techniques used are including Dispersive Liquid Liquid Micro Extraction (DLLME) [9], Homogeneous Liquid Liquid Micro Extraction (HLLME) [10], Headspace Solvent Micro Extraction (HSME) [11] and Solid Phase Micro Extraction (SPME) [12,13]. SPME method developed by Pawliszyn *et al.* in 1989 to redress the need for fast, solvent-free, sample preparation and has a number of advantages over many conventional sample preparation techniques [14]. SPME has been coupled with various analytical techniques such as Gas Chromatography (GC), GC-Mass Spectrometry (GC-MS), High Performance Liquid Chromatography (HPLC), Raman spectrometry [15] and capillary zone electrophoresis [16]. SPME process is carried out in some modes. Each of these methods has its own advantages and disadvantages. Among the possible alternatives, Headspace SPME (HS-SPME) which fiber is exposed into the headspace of the sample suitable for volatile analytes is presently considered as the best choice [17].

In SPME method, selection of appropriate SPME fiber coatings is important and the best fiber must be selected. Since the discovery of the ordered nanoporous silica materials including MCM-48, MCM-41, MCM-50, SBA-3 and SBA-15 [18], interest has been focused on them to serve as sorbents and separation materials [19-23]. Recently, ordered nanoporous carbons (CMK x) that is prepared from mesoporous silica templates are an area of extensive research, particularly with regard to potential applications as adsorbent for environmental remediation. The first nanoporous carbon material was prepared employing the MCM-48 type nanoporous silica as the hard molecular template and named as CMK-1. This was a beginning to synthesize other types of

nanoporous carbon materials such as CMK-3, CMK-5 [24-27]. CMK x can be prepared from a wide variety of low-cost precursors, typically biocompatible, quite chemically stable under nonoxidizing conditions, mechanical stability and is easily handled [28]. Large surface area (1000-1500 m²/g), pore volume higher than 0.5 cm³/g, high adsorption capacity and high thermal stability are the significant characteristics of these materials which enable them to be used in the catalyst industry [29], adsorbent of the organic or metallic pollutants from the industrial waste waters, and biomedical engineering Applications of these materials as SPME fiber coatings has been studied. For example, ordered nanoporous silica materials including, phenyl functionalized MCM-41 [30-31] and amino ethyl-functionalized SBA-15 [32].

In our previous work, [33] we used CMK-1 as a new fiber in SPME for pre-concentration of BTEX compounds for the first time. In this study CMK-1 adsorbent efficiency as SPME fiber for separation and microextraction of MNT compounds from aqueous samples has been studied and parameters that have some effect on microextraction process were optimized by Taguchi method and orthogonal array design (OAD). The resulting method was validated for quantitative purposes and then was applied to real sample analysis in combination with Gas Chromatography-Flame Ionization Detection (GC-FID).

EXPERIMENTAL SECTION

Reagents and solutions

Stock standard solution of MNT at the concentration of 1000 mg/L was prepared by dissolving appropriate amount of MNT in methanol or acetonitrile. The working standard solutions were prepared by serial dilutions of the stock solution with ultrapure water right before analyzing them. All solutions were prepared with ultrapure water.

P-nitrotoluene, *m*-nitrotoluene and *o*-nitrotoluene were from E. Merck (Darmstadt, Germany). Methanol and acetonitrile as the solvents (suprasolv or gas chromatography); tetraethyl orthosilicate (TEOS) as the silica source; cetyltrimethylammonium bromide (CTAB) as the surfactant; sodium hydroxide (NaOH), sodium fluoride (NaF) and deionized water for the synthesis of

nanoporous silica (MCM-48); sucrose as the carbon source and finally sulfuric acid as the catalyst for synthesis of nanoporous carbon were all obtained from E. Merck (Darmstadt, Germany).

Apparatus

Gas chromatographic analyses were made using Shimadzu (Japan) GC 2010 equipped with a flame ionization detector, hydrogen generator Model OPGU-2200s, and split/splitless injector. The GC apparatus was equipped with a BP-5 capillary column (30 m×0.25 mm i.d, 0.25 μm film thickness, 95% methyl-5% phenyl) from SGE (Victoria, Australia).

A SPME device was used in all experiment supplied by Azar Electrode Co., (Oroumie, Iran). The X-ray powder diffraction patterns were recorded on a Philips 1830 diffractometer using Cu -K_α radiation. The diffractograms were recorded in the 2θ range of 0.8–10 with 2θ step size of 0.01° and step time of 1 s. Adsorption-desorption isotherms of the synthesized samples were measured at 77 K on micromeritics model ASAP 2010 sorptometer to determine average pore diameter. Pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method [34], while surface area of the sample was measured by Brunauer-Emmet-Teller (BET) method[35]. SEM images were obtained with JEOL 6300F SEM.

Synthesis of nanoporous silica (MCM-48)

MCM-48 was prepared according to the synthesis procedure described by *Shao et al.* [36]. In a representative synthesis, the MCM-48 molecular sieves were prepared as follows: 10 mL of TEOS was mixed with 50 mL of deionized water and the mixture was vigorously stirred for 40 min at 35°C then 0.9 g of NaOH was added to it, and at the same time 0.19 g of NaF was added to the mixture. After another 60 min of vigorous stirring, 10.61 g of CTAB was added to the mixture, and stirring continued for 60 min. The mixture was heated for 24 h at 120°C in an autoclave under static conditions. The resulting product was filtered, washed with distilled water, and dried at 120°C. The as-synthesized samples were then calcined in air for 4 h at 550°C, increasing the temperature to 550°C at 18°C min⁻¹ of the heating rate.

Synthesis of CMK-1

CMK-1 was prepared according to the synthesis procedure described by *Ryoo et al.* [25]. In a representative synthesis, the CMK-1 molecular sieve was prepared as follows: 1 g MCM-48 was added to a solution obtained by dissolving 1.25 g sucrose and 0.14 g H₂SO₄ in 5.0 mL H₂O. The resultant mixture was dried in an oven at 100°C and then temperature was increased to 160°C. After 6 h at 160°C, the MCM-48 silica containing the partially carbonizing organic masses was again added to an aqueous solution consisting of 0.75 g sucrose, 0.08 g H₂SO₄ and 5.0 mL H₂O to assure carbonization. The resultant mixture was dried again at 100°C, and subsequently the oven temperature was increased to 160°C. The color of the sample turned dark brown or nearly black. This powder was heated to 900°C under vacuum using a fused quartz reactor equipped with a fritted disk. The carbon-silica composite obtained was washed with 1M NaOH solution in 1:1 EtOH-H₂O mixture (twice) at 90 °C to dissolve the silica template completely. The carbon samples were filtered, washed with ethanol and dried at 120 °C.

Fiber preparation

First, 0.08 g of CMK-1 powder was poured into a solution of 0.04 g Styrene-Acrylonitrile Copolymer (SAN) powder in 3 mL acetone and well-mixed. After a few minutes, acetone was evaporated to form a viscose suspension. A silver wire (1 cm) was introduced into the above-mentioned suspension. After evaporation of acetone at room temperature, a very firm porous coating of the sorbent in a SAN matrix was formed on the silver wire. The fiber was then conditioned in injection port of a GC at 240°C for 30 min to remove any fiber contaminations.

GC operating conditions

The GC operating conditions were as follows. The column temperature program was 60°C with a 2 min hold, rising at 10°C/min to 200°C and then rising at 20°C/min to 250°C, 5 min hold. Carrier gas velocity and makeup gas flow rate were 2 mL/min and 30 mL/min, respectively. The analytes were injected in the splitless mode at 230°C and the splitter was opened after 1 min. Detector temperature was 300 °C.

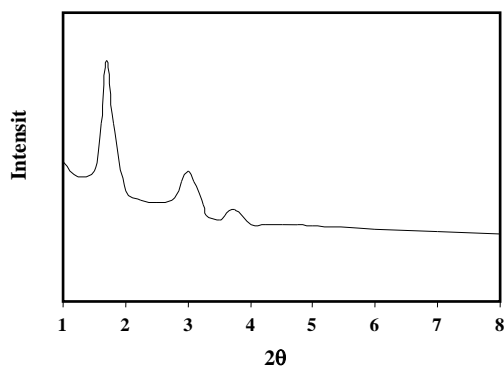


Fig. 1: XRD pattern of CMK-1.

Headspace sampling of MNTS from aqueous samples

12 mL of an aqueous solution of MNT compound with specific concentration (50 $\mu\text{g/L}$) was transferred to a 15 mL vial with silicon septum. After addition of proper amount of sodium chloride salt (196 mg) and magnetic stirrer, vials were closed by aluminium cover. Vials were put in water bath and then were transferred on to magnetic stirrer. After bath water temperature fixation (60 $^{\circ}\text{C}$), nanoporous carbon coated on silver wire was exposed to headspace of sample solution. After proper time (30 min), fibers were taken out from sample solution and for thermal desorption they were transferred to gas chromatography injection port.

RESULTS AND DISCUSSION

Characterization of the CMK-1

The quality of the nanoporous carbon samples prepared in this study was examined by nitrogen adsorption-desorption analysis, X Ray Diffraction (XRD) techniques and SEM image.

XRD patterns

In order to check the structural degradation, XRD data of nanoporous carbon were obtained on Philips 1830 diffractometer using $\text{Cu-K}\alpha$ radiation of wavelength 0.154 nm. Fig. 1 shows the XRD peaks of the CMK-1 sample. The XRD patterns of CMK-1 showed three diffraction peaks that can be indexed to (1 1 0), (2 1 0) and (2 2 0) in the 2θ range from 0.8 to 10, representing well-ordered cubic pores. The observation data from the original sample of CMK-1 are in good agreement with that previously reported [25].

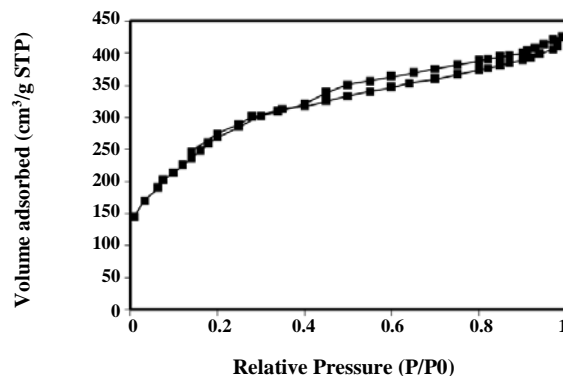


Fig. 2. Adsorption-desorption isotherms of nitrogen at 77 K on CMK-1.

N_2 adsorption-desorption analysis

Nitrogen physisorption is the method of choice to gain knowledge about nanoporous materials. This method gives information on the specific surface area and the pore diameter. Calculating pore diameters of nanoporous materials using the BJH (Barrett, Joyner, and Halenda) method is common. Former studies show that the application of the BJH theory gives appropriate qualitative results which allow a direct comparison of relative changes between different nanoporous materials. Fig. 2 shows nitrogen adsorption and desorption isotherms measured at 77 K by using a Micromeritics ASAP 2010 automatic analyzer. BET surface areas and the pore size determined by BJH method for the synthesized nanoporous sorbents were determined by the adsorption branches of the isotherms. Both of nanoporous materials show a type IV isotherm. The type IV isotherm (IUPAC classification) is typical for mesoporous systems. The surface area of CMK-1 samples was 1010.5 m^2/g and the average pore size was 26 Å . It should be noted that obtained results are in good agreement with previous reported results [25].

SEM Images of adsorbents

The surface morphology of the obtained CMK-1 and CMK-1 coated on silver wire was observed by SEM. As shown in Fig. 3, SEM pictures of the samples are in good agreement with previous results [25].

Optimization of the coating composition of fibers

To optimize the coating composition of fibers, various fibers of different composition of the coats were prepared

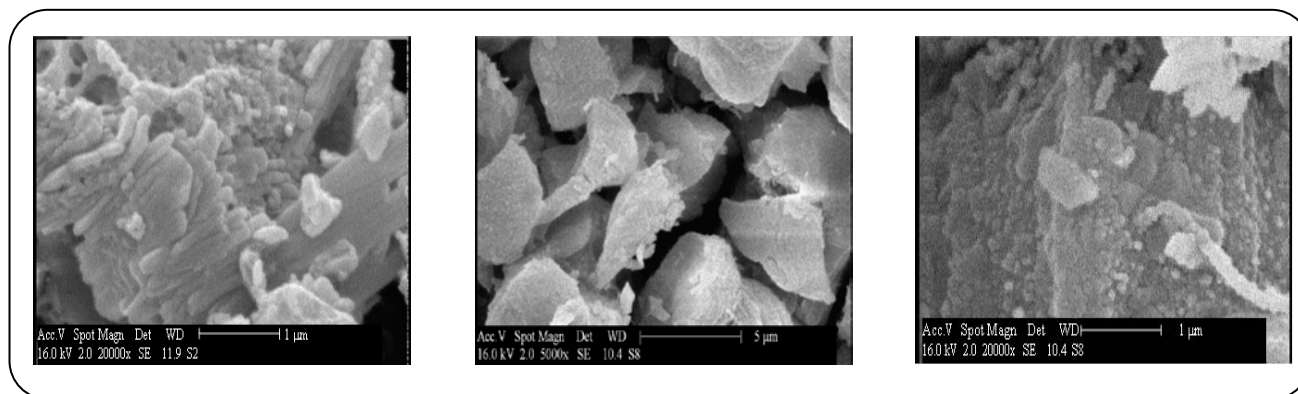


Fig. 3: SEM photographs of (A) CMK-1 powder and (B) CMK-1 coated of silver wire.

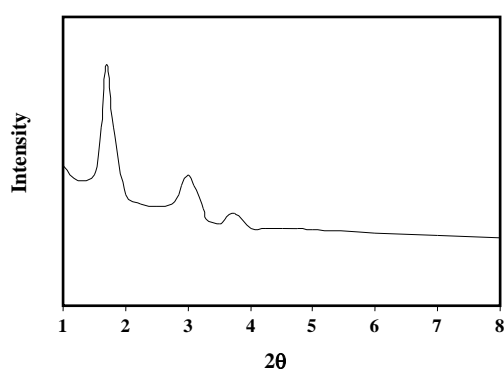


Fig. 4: Optimization of the fiber composition.

and tested. Fibers with coating compositions of 0.15, 0.25, 0.5, 0.75 and 0.85 (CMK-1/SAN) (wt %) were used to extract from solution samples containing 100 $\mu\text{g} / \text{L}$ of the MNT compounds. As illustrated in Fig. 4 increasing the (CMK-1/SAN) ratio promoted the extraction efficiency. Coatings having the ratio of (CMK-1/SAN = 0.85) had the highest extraction efficiency, but these fibers did not show a good mechanical stability, consequently coating with the composition of (CMK-1/SAN=0.75) was selected as the optimum one and used for the experiments, afterwards.

Taguchi design

The Taguchi method [37-39] has been generally adopted to optimize the design parameters, because this systematic approach can significantly minimize the overall testing time and the experimental cost. Using the orthogonal array specially designed for the Taguchi method, the optimum experimental conditions can be easily determined. This study considers five controllable

factors and each factor has four levels. Therefore, an OA_{16} (4^5) orthogonal array is chosen and the experimental conditions (Table 1) can be obtained. In order to estimate the best conditions for the extraction of MNTs 16 experiments were performed. ANOVA (analysis of variance) technique was used to assess the results and showed that the most important factor contributing to the extraction efficiency was extraction time (42.2%) followed by % salt (25.3%)

Effect of stirring rate

Agitating the solution can promote the mass transfer in the aqueous phase and induce the convection in the headspace. This phenomenon can be facilitating the equilibrium between the aqueous phase and headspace. Extraction in rates of stirring of 100, 600, 900 and 1200 rpm was tested. As can be seen in Fig. 5, the most extraction was at 600 rpm. At higher rates the extraction amount did not change. ANOVA results shows that percentage effect of stirring rate of sample solution on MNT compounds extraction is insignificant.

Effect of salt addition

It is well known that the water solubility of an organic compound is reduced by adding salt to an aqueous solution of the analytes. Salt addition increases the extraction efficiency for some analytes especially polar compounds and volatiles. However, it is not necessary for analytes with high distribution constants [40]. To study the salting-out effect, the extraction is performed in the presence of different concentrations of NaCl (0-16 wt%). The results (Fig. 5) showed that by increasing salt concentration from 0 to 16%, extraction amount increases, too.

Table 1: The OA_{16} (4^5) matrix for optimization of HS-SPME-GC-FID of MNT.

Trial no.	Factor A ^a	Factor B ^b	Factor C ^c	Factor D ^d	Factor E ^e
1	12	30	200	8	35
2	4	30	1200	16	60
3	7	30	900	4	23
4	12	20	600	16	23
5	4	20	900	8	45
6	10	30	600	0	45
7	12	10	900	0	60
8	10	10	1200	8	23
9	10	20	200	4	60
10	4	5	200	0	23
11	7	10	200	16	45
12	12	5	1200	4	45
13	7	20	1200	0	35
14	4	10	600	4	35
15	7	5	600	8	60
16	10	5	900	16	35

^a Factor A: sample volume, level 1:4 mL; level 2:7 mL; level 3:10 mL; level 4:12 mL.

^b Factor B: extraction time, level 1:5 min; level 2:10 min; level 3:15 min; level 4:20 min.

^c Factor C: rate stirring, level 1:200 rpm; level 2:600 rpm; level 3:900 rpm; level 4:1200 rpm.

^d Factor D: % salt (w/v), level 1:0(w/v); level 2:4 (w/v); level 3:8(w/v); level 4:16 (w/v).

^e Factor E: temperature, level 1: 23 °C; level 2:35 °C; level 3:45 °C; level 4:60 °C.

Consequently, succeeding experiments were carried out using samples solution containing 16 wt% of the sodium chloride salt. ANOVA results reported that percentage effect of salt concentration on MNT compounds extraction is 25.3%.

Effect of extraction time

Because SPME is an equilibrium method, extraction time as a parameter effective on microextraction process should be optimized. The optimal time for extraction should be the time of equilibrium since the mechanism of SPME is based on the equilibrium between analyte and the nonporous phase of the fibre. The effect of the extraction time on the extraction of the MNT compounds is illustrated in Fig. 5. The result reveals that increasing the extraction time from 5 to 30 min increased the efficiency of the extraction. The time required for equilibrium is 30 min. Therefore the extractions were done in 30 min. ANOVA results reported percentage

effect of extraction time on MNT compounds extraction is 42.2% which is the highest among all the parameters.

Effect of sample volume

Since the vial is of constant volume, the head space volume depends on the volume of the solution samples for the HS-SPME method; exchanging the sample volume will change its head space volume. An increase in the sample volume and consequently a decrease in the head space volume enhanced the extracted amount of analytes, while increased the sensitivity. All the experiments were carried out using vials of 15 mL and sample volumes of 4, 7, 10 and 12 mL. As can be seen in Figure 5, by increasing solution volume (or decreasing head space volume) a rather linear increasing in extraction amount was obtained, consequently the sample volume of 12 mL was selected as the optimum volume. ANOVA results showed that percentage effect of sample solution volume on MNT compounds extraction is 12.5%.

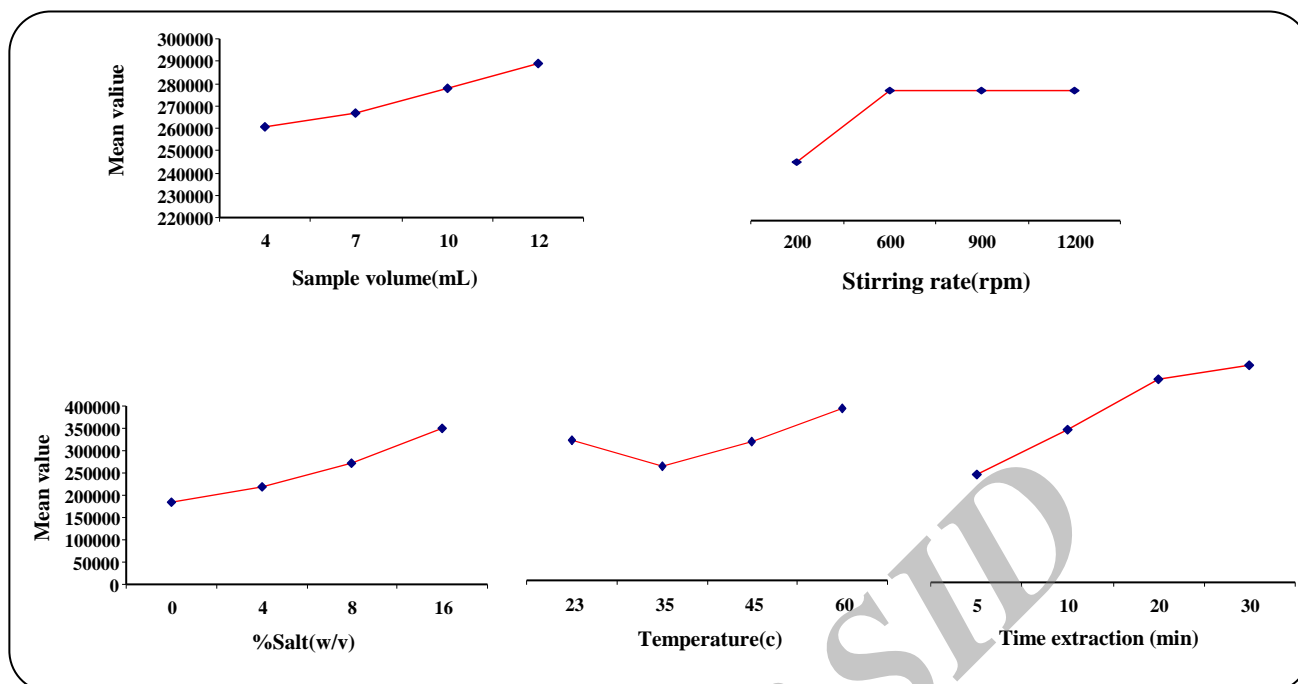


Fig. 5: Effect of sample volume, extraction time, temperature, rate stirring and % salt (w/v) on the HS-SPME-GC-FID of MNT.

Effect of extraction temperature

In headspace SPME, temperature has a dual effect. The use of high temperature is suitable for increasing volatility of analytes and establishing the analyte distribution equilibrium between the sample solution and gaseous phase but adsorption of the analytes on the fiber is undesirable at high temperatures. However, optimization of the extraction temperature is necessary. To study this effect, the extraction of the MNT compounds were carried out at different temperatures including 25, 35, 45 and 60 °C and the results are presented in Fig. 5. The maximum extraction was obtained at 60 °C. Therefore, other experiments were carried out at 60 °C. ANOVA results showed that percentage effect of sample solution temperature on MNT compounds extraction is 15.7%.

Optimization of desorption time and desorption temperature

After optimization of all parameters by Taguchi method, desorption time and temperature were investigated. Desorption tests were conducted at temperatures of 200, 210, 220 and 230 °C and the highest efficiency was achieved at 230 °C. It should be noted that the SAN adhesive was totally stable at this temperature and did not produce any additional peaks, while exceeding this temperature resulted in degradation of the adhesive.

On the other hand, the fiber residence times of 0.5, 1, 1.5 and 2 min in the injection port (splitless mode) were investigated to determine the optimum desorption time. These tests showed that desorption was complete at 1 min. So, it was determined that optimum desorption time is 1 min.

Fiber regeneration

One of the important features of the SPME systems is the regeneration ability of the fiber which greatly reduces the process cost. In this study, more than 60 experimental trials were carried out with one unique fiber and recovery values were evaluated by observing the changes in the recoveries of analytes. The results indicate that the fiber is stable in operation process. After 60 cycles, recovery of MNT compounds was stable to over 87%.

Analytical performance

In order to investigate the applicability of the proposed method for determining MNT in water samples, several factors including Limits Of Detection (LOD), Dynamic Linear Range (DLR), regression equation, correlation of determination (r^2) and Relative Standard Deviation (R.S.D.) (single fiber and fiber-to-fiber) were evaluated.

Calibration curves for the MNTs were tested in the concentration range of 0.1-1000 $\mu\text{g L}^{-1}$. The Limit Of Detection (LOD) was calculated as the concentration of

Table 2: Quantitative result of SPME-GC-FID of MNT from water sample.

Analyte	LOD ^a	R ^b	Regression equation	LDR ^c	%RSD _{fiber-to-fiber}
O-NT	0.04	0.998	Y=2233x + 7402 ^d	0.5-400	7.3
m-NT	0.16	0.999	Y=2182x + 10934	0.5-400	8.7
p-NT	0.01	0.998	Y=4560x + 3900	0.5-400	8.9

a) Limit of detection ($\mu\text{g} / \text{L}$). b) Correlation coefficient. c) Liner dynamic range ($\mu\text{g} / \text{L}$).
d) Y and x are peak area and concentration of the analytes ($\mu\text{g} / \text{L}$), respectively.

Table 3: Comparisons of LODs, RSDs, Matrix and LDR for extraction of MNTs from aqueous sample using DLLME, HLLME, HSME, HS-SPME

Extraction methods	LDR $\mu\text{g} / \text{L}$	LOD $\mu\text{g} / \text{L}$	RSD%	Matrix	Reference
DLLME	0.5-300	0.09-0.1	4.5-5.6	Water	[9]
HLLME	1-500	0.09-0.1	5.4-8.0	Water	[10]
HSME	3-600	0.02-0.06	2.6-6.6	Water	[11]
HS-SPME	0.5-400	0.01-0.16	3.7-4.3	Water	This work

Table 4: Determination of the MNT in different real sample by SPME-GC-FID.

Sample		<i>o</i> -Nitrotoluene	<i>m</i> -Nitrotoluene	<i>p</i> -Nitrotoluene
River water	Non-spiked	N.D	N.D	N.D
	Spiked ^a	54.4±1.7 ^b	52.5±3.5	53.4±2.7
	Recovery (%)	108.8	105.1	106.8
Sea water	Non-spiked	N.D	N.D	N.D
	Spiked	51.9±3.2	49.1±4.2	44.8±3.9
	Recovery (%)	103.7	98.2	89.6
Waste water of (P.C.I. Co.)	Non-spiked	15.5±1.2	N.D	N.D
	Spiked ^c	41.6±2.1	23.4±1.7	26.5±1.1
	Recovery(%)	104.4	93.7	106

a) 50 $\mu\text{g} / \text{L}$ of the MNTs were added to 12 mL of river water sample and sea water sample.
b) Mean value of three replicate measurements with relative standard deviations.
c) 25 $\mu\text{g} / \text{L}$ of the MNTs were added to 12 mL of waste water sample.

the analyte equal to three times of the standard deviation of the blank signal divided by the slope of calibration curve in the range of 0.01-0.16 $\mu\text{g} / \text{L}$ for different MNT. The analytical performance of the proposed method is summarized in Table 2.

The analytes calibration curve showed a good linearity (0.5-400 $\mu\text{g} / \text{L}$) with a correlation of coefficient of 0.998-0.999. The relative standard deviation of single fiber and fiber to fiber (n=4) was obtained in the ranges of 3.75-4.27 and 7.3-8.9, respectively.

In this study, we compared the proposed method with other microextraction methods to show its efficiency. Results of these comparisons are summarized in Table 3. As evident that, this method compared to other microextraction methods such as DLLME, HLLME

and HSME has provided good and acceptable results.

Natural sample analysis

The HS-SPME method was employed on the real samples to measure the extraction amount of MNT compounds. The real samples included river water (Tejen river), sea water (caspien sea) and a sample from waste water of P.C.I. Company (all are located in Iran). In order to evaluate matrix effect, all above samples were spiked with a standard MNT solution with the concentration of 25-50 $\mu\text{g} / \text{L}$ and three replicate desorption analysis were carried out after fiber exposure with the samples.

The results are summarized in Table 4. Fig. 6 shows the chromatogram of the standard samples of 50 $\mu\text{g} / \text{L}$ after HS-SPME process at the optimum conditions.

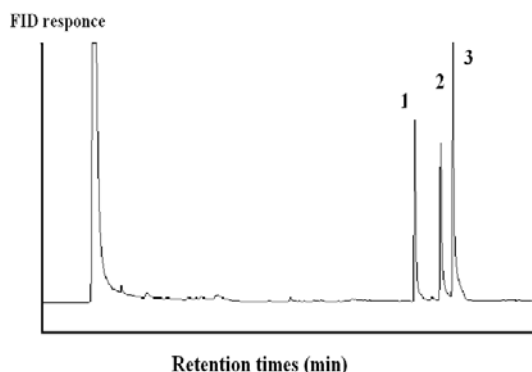


Fig. 6. Chromatogram of standard solution (50 µg/L) of MNTs after HS-SPME at optimum conditions. Peak: (1) *o*-nitrotoluene, (2) *m*-nitrotoluene, and (3) *p*-nitrotoluene.

CONCLUSIONS

In this study we have investigated the efficiency of HS-SPME method for measuring MNT pollutants. A new carbon nanoporous based SPME fiber was coated on silver wire has been used. Structural properties of this adsorbent (CMK-1) was studied by XRD, SEM images and nitrogen adsorption-desorption. The achievements of this method are very low detection limit, good linear range, high mechanical stability and rather high thermal resistance of this fiber is other advantage of this method. Every fiber is usable for 60 extractionextractions.

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