Journal of Chromatography A, 1218 (2011) 3400–3406

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Optimization of a novel method for determination of benzene, toluene, ethylbenzene, and xylenes in hair and waste water samples by carbon nanotubes reinforced sol–gel based hollow fiber solid phase microextraction and gas chromatography using factorial experimental design

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ARTICLE INFO

Article history:
Available online 12 April 2011

Keywords:
Solid phase microextraction
Multi-walled carbon nanotube
Hollow fiber
BTEX
Sol–gel
Orthogonal array experimental design

ABSTRACT

A novel design of solid phase microextraction fiber containing carbon nanotube reinforced sol–gel which was protected by polypropylene hollow fiber (HF-SPME) was developed for pre-concentration and determination of BTEX in environmental waste water and human hair samples. The method validation was included and satisfying results with high pre-concentration factors were obtained. In the present study orthogonal array experimental design (OAD) procedure with OA_{16} (4^4) matrix was applied to study the effect of four factors influencing the HF-SPME method efficiency: stirring speed, volume of adsorption organic solvent, extraction and desorption time of the sample solution, by which the effect of each factor was estimated using individual contributions as response functions in the screening process. Analysis of variance (ANOVA) was employed for estimating the main significant factors and their percentage contributions in extraction. Calibration curves were plotted using ten spiking levels of BTEX in the concentration ranges of 0.02–30,000 ng/mL with correlation coefficients (r) 0.989–0.9991 for analytes. Under the optimized extraction conditions, the method showed good linearity (0.3–20,000 ng/L), repeatability, low limits of detections (0.49–0.7 ng/L) and excellent pre-concentration factors (185–1872). The best conditions which were estimated then applied for the analysis of BTEX compounds in the real samples.

1. Introduction

BTEX is the term which is applied for benzene, toluene, ethylbenzene, and xylene. These volatile, monocyclic aromatic compounds typically find in petroleum product, such as gasoline and diesel fuel, and various organic chemical formulations of products. These are the most soluble of the major gasoline compounds and, therefore, are common indicators of gasoline contamination. BTEX can have major effects on the central nervous system and may be important in the epidemiology of respiratory disorders and cancer too. The normalized quality limit for drinking water according EPA is for benzene; 5, toluene; 1000, ethyl benzene; 700 and for xylenes; 10,000 $\mu g L^{-1}$, respectively [1].

To gain knowledge about the behavior of BTEX in all fields of interest, precise and accurate analytical techniques are necessary.

Therefore, the pre-concentration and clean up of the samples has been performed using a number of different purification techniques such as solid-phase microextraction (SPME) and liquid phase microextraction (LPME).

The most common sample preparation technique is solid-phase microextraction, which is a solvent-less extraction procedure that involves the exposure of a coated fused silica fiber to a gaseous or liquid sample or the headspace above a liquid or solid sample. The fiber coating is typically an immobilized polymer, a solid adsorbent or a combination of the two [2–4].

It has been used routinely, in combination with GC and GC–MS, and successfully applied to a wide variety of compounds, especially for the extraction of volatile and semi volatile organic compounds from environmental, biological and food samples [5–7].

The solid phase technology for SPME fibers presents some serious problems such as fiber consubstantial properties and reduced the possibility of carry-over [8].

Among the different approaches to stationary phase development for SPME fibers, Malik and co-workers established a convenient pathway for surface coatings using sol–gel technology to overcome some important drawbacks of conventional SPME coatings such as; operating temperature problems, instability and swelling in organic solvents [9–11].

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doi:10.1016/j.chroma.2011.03.043

The objective of the work was improvement of previous works [9–12] and presents a simple and practical device that can overcome usual problems of ordinary SPME fibers such as sample carry over effects, breakage of the fiber and expensive cost.

In our previous work [12], we have proposed and studied the significant enhancement of analyte extraction which was performed in LPME and SPME by providing an integrated method of solid and liquid phase microextraction. Details of the method were described in that paper.

Following the previous work, we have considered the base of the last method more than the past and tried to develop it in order to innovate a more efficient method with lower detection limits.

In the previous work we have shown that the incorporation of bundles of chemically modified carbon nanotubes in organic solvent, 1-octanol that was supported by a piece of polypropylene hollow fiber improved extraction performance.

In this work, and almost simultaneously in other projects [13] we have focused on the different category and introduced a novel SPME technique namely; hollow fiber solid phase microextraction (HF-SPME). In this strategy, a nanocomposite containing carbon nanotubes that was prepared based on sol–gel technique was injected into a piece of polypropylene hollow fiber and the process of in situ gelation was occurred into the fiber.

It must be noted that; MWCNTs incorporation into extractor phase occurs more homogenous, number of active adsorbent sites is high, chemical bonds between analyte and extractor is stronger and thereupon, the enrichment factors are higher than what we previously reported, because of the different measurement setups which were used in the previous and current studies.

Since the hollow fiber segment exists as an individual device and is directly usable for extracting, handling is more convenient than the other traditional SPME fibers. In addition, disposable nature of the device totally eliminates the possibility of sample carry over and ensures high reproducibility.

The method validation was included and satisfying results with very high pre-concentration factor were obtained. It seems that online connection between the device and GC or HPLC is easily possible. Experiments in this area are ongoing. A simple heat trap was designed in our lab and is under consideration.

This device was applied for the microextraction and concentration of BTEX followed by gas chromatography. The results were evaluated using orthogonal array experimental design (OAD) with OA_{16} (4^4) matrix to study the effect of four factors influencing the HF-SPME method efficiency: volume of adsorption organic solvent, extraction and desorption time of the sample solution and stirring speed, by which the effect of each factor was estimated using individual contributions as response functions in the screening process. Analysis of variance (ANOVA) is employed for estimating the main significant factors and their percentage contributions. The optimized conditions were then applied for the analysis of BTEX compounds in the real samples and the data was compared with the experimental results.

2. Experimental

2.1. Chemicals and materials

The Accurel Q 3/2 polypropylene hollow fiber membrane used here was obtained from Membrana (Wuppertal, Germany). The wall thickness of the fiber was 200 μm, the inner diameter was 600 μm, and the pore size was 0.2 μm. The multi-walled carbon nanotubes (MWCNTs) were purchased from the Research Institute of the Petroleum Industry (Tehran, Iran). The mean diameter of the MWNTs was 10–15 nm, the length was 50–100 nm and purity >98%. Methyltrimethoxysilane (MTMOS, 97%), trifluoroacetic acid (TFA, 99%) and poly (methylhydrosiloxane) (PMHS) were purchased from Alfa Aesar (Ward Hill, MA, USA).

Methanol, 1-octanol, cyclohexan and acetonitrile with analytical quality (for organic trace analysis) were obtained from Merck (Darmstadt, Germany). Analytical reagents grade benzene, toluene, ethyl benzene and para-xylene also were purchased from Merck (Darmstadt, Germany). Stock solutions of BTEX (2000 μg/mL) were prepared by dissolving calculated amounts of each them in methanol. Fresh working solutions were prepared daily by diluting the stock solution in distilled water.

All experiments were carried out at room temperature, 22 ± 0.5 °C.

2.2. Instrumentation

The Varian 3800CP gas chromatography (Palo Alto, CA, USA) equipped with a flame ionization detector was employed for determination of the analytes. A DB-5 (5% biphenyl + 95% poly dimethyl siloxane) fused-silica capillary column (30 m × 0.25 mm i.d. and 0.25 μm film thickness) was applied for separation of the analytes.

The GC split valve was opened (split ratio: 1/20) and nitrogen was used as a carrier gas at the constant flow rate of 1.5 mL/min. The column oven was initially held at 50 °C for 2 min, programmed to 150 °C at a rate of 10 °C/min and then to 250°C at 20 °C/min.

The injections were carried out using a 10 μL Hamilton microsyringe (Bonaduz, Switzerland) and 10 mL extraction vial.

Stirring of the solutions was carried out by a Heidolph MR3001 magnetic stirrer (Schwabach, Germany) and a 8 mm × 1.5 mm magnetic stirring bar.

2.3. Fabrication of the HF-SPME fiber

2.3.1. Carbon nanotube functionalization process

In this work, MWCNTs were treated with acid as mentioned below; MWCNTs were dispersed into a flask containing concentrated nitric acid solution and refluxed at 140 °C for 2 h. After cooling, the MWCNTs were washed with the deionised water until the pH of the solution reached approximately 7. Then the solution was filtered and dried at 120 °C for 4 h to obtain the acidified MWCNTs.

2.3.2. Preparation of the sol solution

A 25-mg amount of functionalized CNTs was dissolved in 400 μL MTMOS. Then 50 μL distilled water and 50 mg PMHS were added. The mixture was agitated thoroughly by sonication for 30 min in a glass vial. Then 50 μL TFA was added to the resulting solution with ultrasonic agitation for 10 min and stable sol solution was formed.

The polypropylene hollow fiber was cut into small segments with a length of 2 cm. A disperse mixture (6 μL) of the MWCNTs reinforced sol solution was gradually injected into the hollow fiber using an HPLC syringe.

2.3.3. Aging of the sol and in situ gelation process

The prepared fiber was placed in a desiccator at room temperature for 24 h and the prepared fibers were conditioned at 50–150 °C for 6 h in the GC oven with gradually rising temperature program.

2.4. SPME procedures

Extractions were carried out according to the following steps:

Optimized volume of aqueous solution containing the BTEX compounds was added into the sample vial with a 8 mm × 4 mm magnetic stirring bar. The SPME hollow fiber was then placed in the aqueous solution. The vial was sealed and the stirrer turned on. At the end of the extraction for a prescribed period of time at room temperature the hollow fiber was taken out from the first vial and

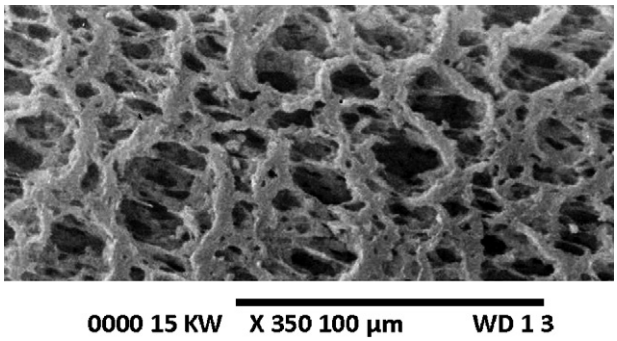

Fig. 1. (a) Scanning electron microscopy of the MWCNTs reinforced sol–gel and (b) SEM of polypropylene hollow fiber structure.

transferred into a second glass vial containing the optimal organic solvent (400 μL methanol) and the analytes were desorbed from fiber with ultrasonic agitation.

Finally, 1.00 μL of the organic solvent was withdrawn into the GC microsyringe and then injected into the GC-FID for further analysis. Due to the low cost, and to prevent the carryover effect, each hollow fiber piece only once was used in the experiments (see Fig. 1).

2.5. Screening procedure

For theoretical method evaluation the experimental matrix designs were carried out and evaluated using the STATISTICA 6 software package (StatSoft, Tulsa, USA). In this work, experimental design based on Taguchi's method was employed to screen the SPME conditions for the extraction and determination of the BTEX compounds.

To our knowledge, at least five factors might affect the experimental response in the HF-SPME method. These factors are type of organic solvent desorption, stirring speed, donor phase volume, extraction and desorption time. Except for the organic solvent type, assignments of other four factors and their levels in the OA_{16} (4^4) matrix are depicted in Table 1.

Assignments of factors and levels of screening between number of values using an OA_{16} (4^4) matrix and the results of OAD experiment trials along with the peak area responses were processed under direct observation analysis [14–16] which The levels along with the notation for the factors studied in the present study are given in Table 1.

2.6. Sample analysis

2.6.1. Paint wastewater treatment

Paint wastewater samples were filtered through a filter paper before analysis.

2.6.2. Hair samples treatment

A bulk of blank hair, necessary for method development and validation, was obtained from persons who referred to a male barber (in Mashhad, Iran). The absences of BTEX were verified using gas chromatography analysis.

Hairs of chemical store's men sellers were collected as the biological sample. Both Blank and sample, about 5 mm in diameter were cut with round-point scissors from the vertex posterior region of the scalp. Samples 2-4 cm long were selected for analysis.

Fat and surface contamination on the hair should be removed. Thus the hairs were washed with solvents as follow: 20 mL dichloromethane, 15 mL acetone, 15 mL methanol and 10 mL methanol, at room temperature for 5 min and then they were dried.

The washed and dried hairs were finally cut into approximately 1 mm pieces and digested by the following procedure:

2.0 mL methanol as an extracting solvent was added to 50 mg of hair, in a 10 mL screw-cap tube. The pH was adjusted to 7.4 by phosphate buffer solution. The samples were incubated at 50 °C for 5 h. Then remaining of solid hair matrix was filtered and rinsed with 0.5 mL ethanol [17].

Table 1
Factors and their notations together with their levels used in OA_{16} (4^4) matrix.

Variable		Coded levels			
		1	2	3	4
Extraction time (min)	E	10	25	35	45
Desorption time (min)	D	5	10	15	20
Stirring rate (rpm)	A	400	500	600	700
Donor phase volume (mL)	V	3.5	4	4.5	5

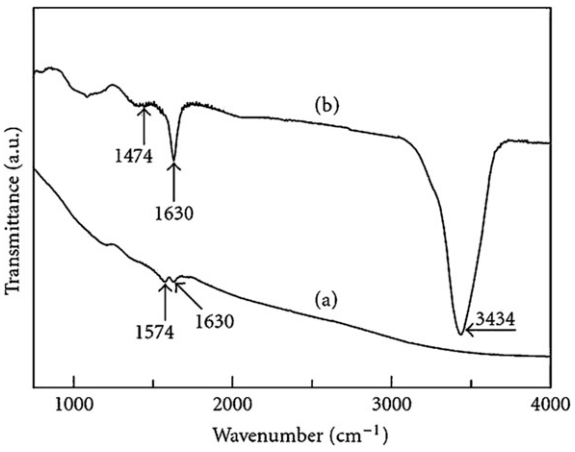

Fig. 2. FT-IR spectra of (a) untreated MWCNTs and (b) functionalized MWCNTs.

3. Results and discussion

3.1. Experimental optimization for the HF-SPME

In order to obtain high enrichment and extraction efficiency of the analytes using this microextraction technique (HF-SPME), the main parameters were optimized.

Fig. 2 shows the FT-IR spectra of untreated (a), and functionalized CNTs (b). FT-IR is mainly used to identify the presence or absence of functional groups. Region below 1400 cm^{-1} is named fingerprint region and is hardly used to identify compounds due its complexity.

The high symmetry presented on untreated CNTs generates very weak infrared signals due to the weak difference of charge state between carbon atoms. The weak difference of charge state leads to very small induced electric dipole, providing a silent spectrum. The peak related to C=C bonding at approximately 1630 cm^{-1} is seen very week in the spectrum of untreated CNTs, this effect can be explained by the very low formation of electric dipoles. This characteristic peak, however, can clearly be noticed on functionalized CNTs (F-MWCNTs). The functionalization breaks the symmetry of nanotubes, which enhances the generation of induced electric dipoles and signs as detected.

The peak appearance of F-MWCNTs in the 3434 cm^{-1} region indicates the stretching OH from carboxylic groups. Acid treatment also results in the appearance of a peak approximately at 1474 cm^{-1}, which corresponds to the C–O stretching indicating the introduction of carboxylic groups due to surface oxidation [18–20].

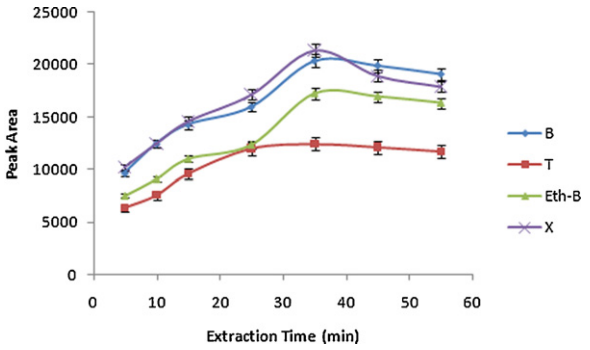

Fig. 3. The effect of extraction time on the extraction efficiency of BTEX compounds when using hollow fiber SPME with methanol as the desorption solvent. Other extraction conditions: analyst concentration 5 μg/L; stirring rate 600 rpm; desorption time 20 min.

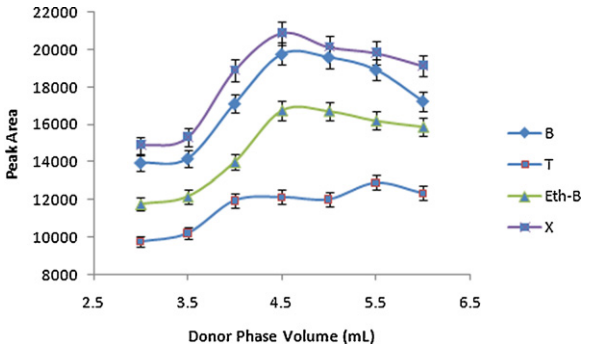

Fig. 4. The effect of donor phase volume on the extraction efficiency of BTEX compounds when using hollow fiber SPME with methanol as the desorption solvent. Other extraction conditions: analytes concentration 5 μg/L; stirring rate 600 rpm; desorption time 20 min; extraction time 35 min.

3.1.1. *Effect of the extraction time*

Extraction was performed from 5 to 55 min to determine the effect of extraction time.

Fig. 3 shows the peak area versus extraction time profiles for the analyst. It can be seen that equilibrium is attained after 30 min. However, the increase on the peak areas for these analytes after 35 min extraction can be considered as not significant, but the results shows that there is a degeneration on the method precision for longer extraction times. Therefore, the extraction time was fixed in 35 min.

3.1.2. *Solvent selection*

Accordingly, several desorption solvents such as 1-octanol, acetonitrile, methanol and cyclohexane were investigated. Based on the obtained results, methanol was found to get the best extraction efficiency, while its chromatographic peak was easily separated from the analyte peaks. Also because of its low vapor pressure at the extraction conditions the extract was stable at the extraction period. Therefore, methanol was selected as the desorption solvent.

It is noteworthy that an aqueous solution spiked into with the BTEX compounds (at the concentration level of 5 μg/L, was used in the extraction studies.

Certainly thermal desorption is more efficient method than solvent desorption for the HF-SPME. Therefore we have designed a simple device to online thermal desorption which is compatible with HPLC and GC. This is under further development and we will use it in the next researches

3.1.3. *Effect of the donor phase volume*

As the analytes are extracted from relatively large sample volumes into a very small volume of acceptor phase, most SPME applications provide substantial analyte enrichment. The preconcentration factor in HF-SPME is basically determined by the analyte recovery and by the phase's volume of the sample and the acceptor theoretically. As the volume of the sample increases, the pre-concentration factor also increases [21–23]. In HF-SPME, extraction is an equilibration process and, therefore the amount of analyte partitioning into the acceptor phase becomes independent of the sample volume when this volume is much higher than the product of the partition constant and the volume of the acceptor phase. Furthermore, the theoretical pre-concentration factor (CF) is given in the following equation:

$$\mathrm{CF} = 1\left(\frac{1}{k} + \frac{V_a}{V_d}\right)$$

where V_a and V_d are the acceptor and aqueous donor phase volumes, respectively and k is the distribution coefficient. This implies that increasing the CF requires V_a to be small and V_d to be large. On the other hand, a larger sample volume can even be disadvantageous due to poorer mass-transfer kinetics, resulting in worse extraction efficiency [24].

In the present work, the phase ratio of donor and acceptor solutions was optimized by changing the volume of the donor phase between 3 and 6 mL while the volume of acceptor phase was kept constant at 6 μL. Generally, the extraction efficiency can be improved by increasing the volume ratio of donor to acceptor phase. As seen in Fig. 4, however, the extraction results obtained for the analytes were most favorable to suggest a phase ratio of 750.0 (4.5 mL donor phase volume). Also, with an increase in the aqueous donor phase volume, gel phase dissolution may also be a concern. This would lead to a decrease in the extraction efficiency. Therefore, we selected a volume of 4.5 mL as the optimized donor phase volume.

3.1.4. *.Effect of the desorption time*

To reach the highest sensitivity, the desorption time was also evaluated to ensure that the analytes were completely desorbed from the fiber. Experiments showed that for all the studied four analytes, desorption was almost complete after 20 min. Thus, these conditions were chosen for routine analysis. This present procedure is applicable for high volatile analytes such as BTEX compounds. After isolation and pre-concentration in the hollow fiber, the analytes are directly move to the solvent desorption where they are desorbed from the fiber. But to be sure, that desorption was complete the fibers were checking-cleaned after each desorption.

3.1.5. *Effect of the stirring rate*

Stirring enhances mass transfer and reduces the time required to reach thermodynamic equilibrium. Since the analytes here are protected by the hollow fiber, faster stirring rates may be applied. The instrument's response was recorded for several stirring rates ranging from 0 to 1000 rpm for an extraction time of 35 min of 4.5 mL aqueous samples with each target analyte concentration of 5 μg/mL. The results confirmed that agitation of the sample enhances extraction. However, higher stirring rates (>600 rpm) resulted in massive air bubbles and decreased the preconcentration factors.

On the other hand, extraction recovery for benzene was decreased dramatically with increasing stirring speed because of its high vapor pressure and thus its evaporation during the procedure. Therefore, a 600 rpm setting was selected for the subsequent experiments.

3.1.6. *Effect of the concentration of MWCNTs on the extraction*

The influence of the amount of MWCNTs on the extraction capacity has been examined and 50 mg/mL was the optimal amount

Table 2
Figures of merit of the proposed method in the determination of the BTEX compounds in the paint wastewater.

Analyte	DLR (ng/L)	Regression equation	R^2	LOD (ng/L)	EF	%RSD (n = 5)
Benzene	1–20,000	Y = 16396.79+13138C	0989	0.61	1872	4.1
Toluene	0.3–20,000	Y = 16428.4+9629.6C	0.9985	0.50	532	4.5
Ethyl benzene	0.3–20,000	Y = 2188.74+2608C	0.9988	0.50	185	3.4
Xylene	3–20,000	Y = 8183.53+18243.6C	0.9991	0.49	1136	4.1

Table 3
Comparison of some methods which were used for determination of BTEX compounds.

No.	Date	Matrix	Extraction method	LOD	LDR	r	RSD	References
1	2004	Water	SPME	8.3–35.2 ng/L	1.5–1500 μg/L	0.999	3–8.3	[32]
2	2005	Paint waste water	SPME	0.1 mg/L	0.4–60 mg/L	0.997	8.3	[26]
3	2008	Water	SPME	0.6–1.6 μg/L	5–200 μg/L	0.999	–	[33]
4	2008	River water	LPME	0.03 μg/ml	0.05–20 μg/mL	0.997	4.61	[34]
5	2008	Soil	SPME	20 ng/g	100–1000 ng/g	0.995	2.44	[35]
6	2009	Water	SDME	0.8–7 ng/mL	0.01–20 μg/mL	0.998	1.8–2.47	[36]

of the CNTs (the range was between 10 and 100 mg/mL) in this work. The results confirmed that increasing of the amount of MWCNTs decreased repeatability. Since with increasing the amount of MWCNTs, the injection of massive reinforced composite into the fiber was difficult. Moreover the air bubbles occupied the fiber spaces.

3.1.7. Effect of pH and addition of salt into water sample solution

The solution pH was measured at the beginning of each experiment. Feed solution pH in range of 3–11 was tested. The changes in solution pH during BTEX adsorption on CNT reinforced sol–gel sorbent were insignificant implying that BTEX were in the molecular forms during adsorption process and that ion-exchange does not play a part in BTEX adsorption. And it was reflected high stability of CNT-sol–gel as BTEX adsorbents in a wide range of solution pH. Thus experiments were conducted without adjustment feed pH. The result agrees with the p-xylene adsorption on single-walled CNTs [25].

Addition of salt into water sample solution may have several effects upon extraction. Usually, depending on the solubility of the target analytes, adding salt to the sample enhances extraction of the more polar analytes. In the case of BTEX, salt addition was generally limiting the extraction of analytes. It was assumed that apart from the salting-out effect, salt addition causes a second effect named, salting-in effect. This phenomenon leads to changes in the physical properties of the Nernst diffusion film. So, target analyte's diffusion rate into the sorbent was reduced [26]. For the purpose of the present experiments, the influence of salt on the studied system was investigated by adding various amounts of NaCl in a series of concentrations (0%, 1%, 5%, 10%, w/v), and results shown the peak area decreased with increasing salt concentration in the aqueous sample. Therefore, no salt was added to the sample solution in further extractions.

3.2. Factor screening and discussion

In this study, ANOVA was applied to assess OAD results. According to the methods given [14,27–30], the results of the sums of squares (SSs) for different variables were calculated. Sixteen experimental trials were repeated three times. The error estimation of the experiments was calculated and used in ANOVA since no dummy columns (in which no actual factor is assigned) were assigned in OA_{16} (4^4) matrix.

The *SS (sum of squares)* is obtained by subtracting all the SS of the items from the total SS [31]. From the ANOVA results it can be seen that factor E (extraction time) is statistically significant at $P < 0.05$ while the remaining factors is not significant.

These conditions were different depending on the considered compounds, so the final selection should consider the purpose of the study. If the objective is mainly to analyze benzene and xylene, best conditions would include extraction time; 35 min, desorption time; 20 min, stirring speed; 600 rpm and volume donor phase; 3.5 mL. On the other hand, to analyze toluene and ethyl benzene these conditions are slightly different.

If simultaneous analysis of all compounds is required the most favorable conditions are: extraction time; 35 min, desorption time; 20 min, stirring speed; 600 rpm and volume donor phase; 4.5 mL. In fact, these conditions were employed for the rest of experiments in this study.

3.3. Method performance

3.3.1. Figures of merit

To evaluate the practical applicability of the HF-SPME technique, the figures of merit of this method including pre-concentration factor, the corresponding regression equation, correlation coefficient (r^2), limit of detection (LOD) and and linear dynamic range (LDR) were investigated under the best conditions. Calibration curves in paint wastewater and human hair samples were plotted against the concentration levels of the BTEX compounds. For each level, three replicate extractions were performed. The results are tabulated in Tables 2 and 4 (paint wastewater) and Table 5 (hair samples).

The pre-concentration factors (CF) were calculated based on the following equation:

$$\mathrm{CF} = \frac{A_{\mathrm{RP,final}}}{A_{\mathrm{SP,initial}}} \times \frac{V_{\mathrm{aq}}}{V_{\mathrm{ln}}}$$

where $A_{\mathrm{RP,final}}$ and $A_{\mathrm{SP,initial}}$ are the final and initial peak areas at after and before extraction of the BTEX compounds in the organic solvent respectively, that obtained based on direct injection of the BTEX solutions in methanol into the GC-FID for analysis. V_{aq} and V_{ln} are volume aqueous sample and internal volume of hollow fiber.

The method was compared with the other previous works (Table 3).

In comparison with the other conventional sample preparation methods, the developed method has the merits of considerable

Table 4
Results obtained for the analysis of the real sample;paint waste water.

Analyte	Concentration (ng/L)	%RSD (n = 5)
Benzene	1.7	2.80
Toluene	8.2	3.10
Ethyl benzene	7.4	3.00
Xylene	11.8	4.05

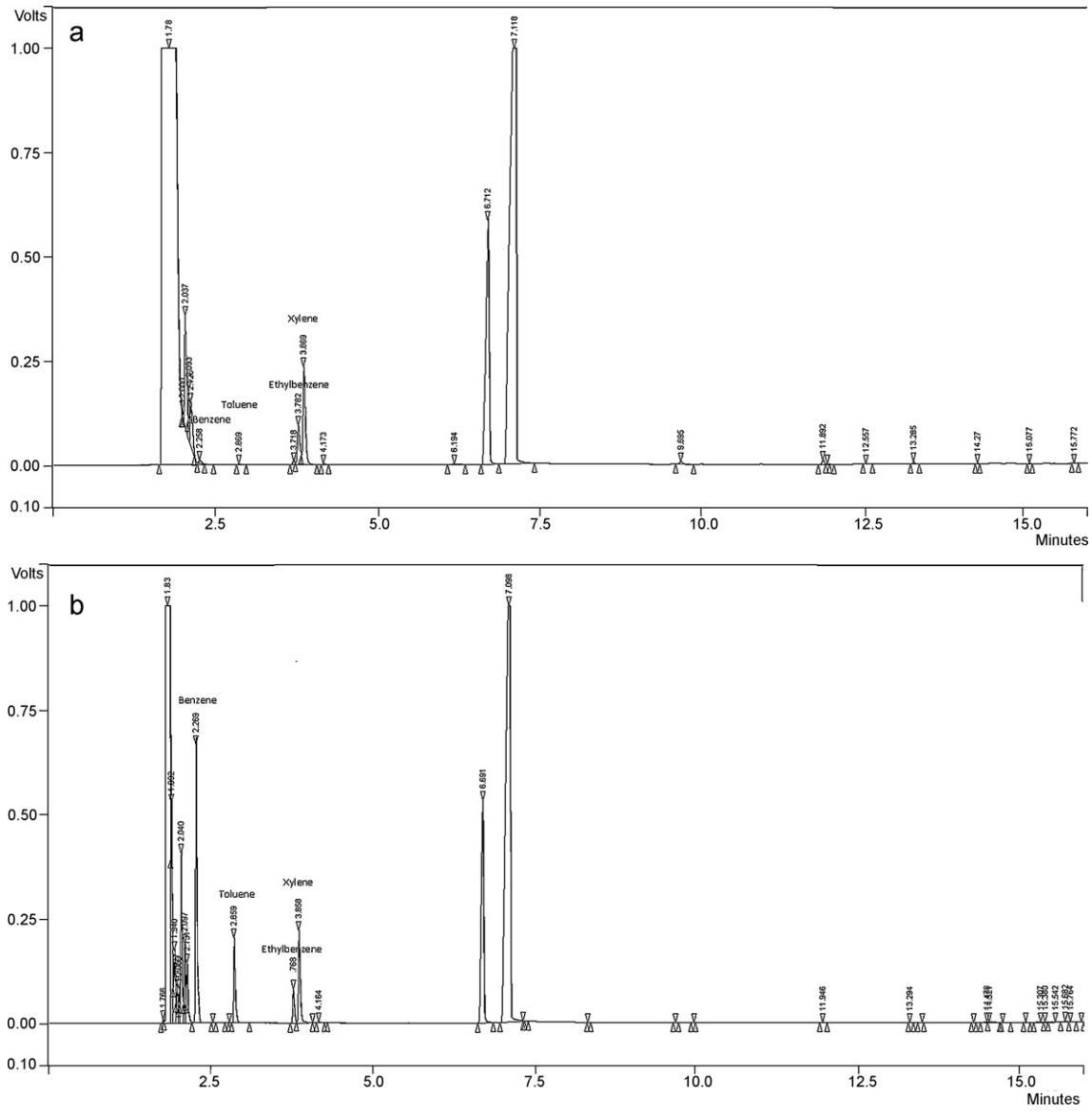

Fig. 5. GC chromatogram of hair sample, (a) before spiked, (b) after spiked (1 μg/L) and extracted dilution with 400 μL methanol.

analysis speed, good separation efficiency and elevated preconcentration, notable precision and high sensitivity.

3.3.2. Real samples

Applicability of the extraction method to extract the BTEX compound from paint waste water and hair samples was investigated. The analytical results of water matrix (waste water) is given in Table 3. The obtained results showed the R.S.D% about 2.80–4.05% for all BTEX compounds, which indicates that the proposed method is repeatable.

To evaluate the efficiency of the proposed method in real samples, it was successfully applied to assay of BTEX in human hairs of chemical store's men sellers as real sample.

Due to daily use of various BTEX compounds in the mentioned store the concentration of BTEX components in hair are possible.

Table 5
Figures of merit of the proposed method in the determination of the BTEX in the hair blank samples for validation.

Analyte	LDR[a] (ng/L)	Regression equation	r[c]	LOD[d] (ng/L)	Relative recovery (%100) 100 ng/L[e]	%RSD (n = 5)
Benzene	1.2–20,000	Y = 16396.79 + 13138C[b]	0989	0.7	87	5.2
Toluene	0.3–20,000	Y = 16428.4 + 9629.6C	0.99	0.6	79	4.7
Ethyl benzene	0.4–15,000	Y = 2188.74 + 2608C	0.997	0.5	82	5.0
Xylene	3–20,000	Y = 8183.53 + 18243.6C	0.998	0.5	74	5.1

[a] Liner dynamic range.
[b] Y and x are peak area and concentration of the analytes (ng/L), respectively.
[c] Correlation coefficient.
[d] Limit of detection.
[e] Recovery after spiked amount of analytes.

Table 6
Concentrations (ng/L) of BTEX compounds in the hair of chemical store's sellers.

Analyte	Concentration (mg/L)	%RSD (n = 5)	Relative recovery (%100)
Benzene	1[a]	2.80	84
Toluene	1[a]	3.10	91
Ethyl benzene	0.18[b]	3.00	–
Xylene	0.11[b]	4.05	–

[a] Spiked amount of analytes.
[b] Founded amounts without spiking of analytes.

No benzene and toluene were detected in real hair sample therefore real samples were spiked with these compounds to assess matrix effects. The chromatograms of hair sample before and after extraction was depicted in Fig. 5.

HF-LPME is a non-exhaustive extraction procedure and the relative recovery (determined as the ratio of the concentrations found in real and blank samples, spiked with the same amount of analytes), instead of the absolute recovery (used in exhaustive extraction procedures), was employed.

The blank human hair was collected from a local men barberry (Mashhad, Iran) that as a certified reference material of human hair was provided.

The proposed method was carried out for the analysis of the real human hair, and the analytical results together with the recovery for the spiked samples are given in Tables 4 and 5. It can be seen that the recovery for spiked samples was in the range of 74–87% (see Table 6).

4. Conclusions

For the first time, a novel disposable HF-SPME fiber based on carbon nanotube reinforced sol–gel technique was demonstrated for BTEX extraction and determination in the environmental and biological samples and orthogonal array designs were efficiently employed to screen the method. The proposed method has advantages such as simplicity, good accuracy and precision, relatively short extraction time, low cost, and minimum organic solvent consumption.

Conditions for the extraction and analysis of trace amounts BTEX compounds in different aqueous samples such as extraction and desorption time, stirring speed and volume of the donor phase, and extraction time were investigated and also screened using an OA_{16} (4^4) matrix. The hollow fiber SPME device is disposable, so the single use of the hollow fiber reduces the risk of cross-contamination and carry-over problems. This procedure can be successfully used for the analysis of organic analytes in aqueous and biological samples.

In addition, the experimental setup is very simple and highly affordable. Among the all reported microextraction techniques, this technique is an effective sample preparation/pre-concentration technique.

We recommended on the use of GC–MS detection for further studies, for achieve the selective and specific detection technique as for application to monitor samples.

Acknowledgements

The authors are thankful to the Birjand University, for supporting this research work.

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