A novel solid-phase microextraction using coated fiber based sol–gel technique using poly(ethylene glycol) grafted multi-walled carbon nanotubes for determination of benzene, toluene, ethylbenzene and o-xylene in water samples with gas chromatography-flam ionization detector

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ABSTRACT

In this study, poly(ethylene glycol) (PEG) grafted onto multi-walled carbon nanotubes (PEG-g-MWCNTs) were synthesized by the covalent functionalization of MWCNTs with hydroxyl-terminated PEG chains. For the first time, functionalized product of PEG-g-MWCNTs was used as selective stationary phase to prepare the sol–gel solid-phase microextraction (SPME) fiber in combination with gas chromatography-flame ionization detector (GC-FID) for the determination of ultra-trace levels of benzene, toluene, ethylbenzene and o-xylene (BTEX) in real water samples. The PEG-g-MWCNTs were characterized by Fourier transform infrared spectra and also thermo-gravimetric analysis, which verified that PEG chains were grafted onto the surface of the MWCNTs. The scanning electron micrographs of the fiber surface revealed a highly porous structure which greatly increases the surface area for PEG-g-MWCNTs sol–gel coating. This fiber demonstrated many inherent advantages, the main being the strong anchoring of the coating to the fused silica resulting from chemical bonding with the silanol groups on the fused-silica fiber surface. The new PEG-g-MWCNTs sol–gel fiber is simple to prepare, robust, with high thermal stability and long lifetime, up to 200 extractions. Important parameters influencing the extraction efficiency such as desorption temperature and time, extraction temperature, extraction time, stirring speed and salt effect were investigated and optimized. Under the optimal conditions, the method detection limits (S/N = 3) were in the range of 0.6–3 pg mL^{-1} and the limits of quantification (S/N = 10) between 2 and 10 pg mL^{-1}. The relative standard deviations (RSDs) for one fiber (repeatability) (n = 5) were obtained from 4.40 up to 5.75% and between fibers or batch to batch (n = 3) (reproducibility) in the range of 4.31–6.55%. The developed method was successfully applied to real water samples while the relative recovery percentages obtained for the spiked water samples at 20 pg mL^{-1} were from 90.21 to 101.90%.

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1. Introduction

BTEX is the collective name of benzene, toluene, ethylbenzene, and the xylene isomers (p, m, and o-xylenes), all being harmful volatile organic compounds (VOCs). Human exposure to these compounds can have serious damaging effects on the kidneys, heart, lungs, and the nervous system [1].

BTEX are emitted to the environment from an extensive variety of sources including combustion products of wood and fuels, industrial paints, adhesives, degreasing agents and aerosols [2]. On the other hand, BTEX have been widely used in the manufacturing of paints, synthetic rubber, agricultural chemicals and chemical intermediates. BTEX compounds are also abundant in petroleum products, such as fuel oil and gasoline.

Exposure to BTEX can occur by ingestion (consuming contaminated water or food), inhalation (exposure to BTEX present in the air) or absorption through the skin.

Maximum contamination levels (MCLs) according to the U.S. Environment Protection Agency (EPA) for benzene, toluene, ethylbenzene, and xylenes are 0.005, 1, 0.7, and 10 mg L^{-1}, respectively, and concentrations above MCL in air and water seriously affect human health [3]. There is, therefore, a vital need to develop simple and cheap analytical methods with low detection limits for the quantification of BTEX.

In recent years, the development of fast, precise, accurate and sensitive methodologies has become an important issue. However, despite the advances in the development of highly efficient analytical instrumentation for the end-point determination of analytes in biological and environmental samples and pharmaceutical prod-

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ucts, sample pre-treatment is usually necessary in order to extract, to isolate and to concentrate the analytes of interest from complex matrices, because most of the analytical instruments cannot directly handle the matrix. Therefore a sample preparation step is commonly required [4].

Conventional sample-preparation techniques [i.e. liquid–liquid extraction (LLE) and solid-phase extraction (SPE)] have involved drawbacks (e.g., complicated, time-consuming procedures, large amounts of sample and organic solvents and difficulty in automation). Using harmful chemicals and large amounts of solvents causes environmental pollution, health hazards to laboratory personnel and extra operational costs for waste treatment. Ideally, sample-preparation techniques should be fast, easy to use, inexpensive and compatible with a range of analytical instruments, so the current trend is towards the simplification and miniaturization of the sample-preparation steps and decrease in the quantities of the organic solvents used [4].

Solid phase microextraction (SPME), a solvent-free technique developed by Pawliszyn et al. [5,6], is based on the establishment of the analyte equilibrium between the liquid or gaseous sample and a polymeric coating on a fused silica fiber, which is part of the syringe needle. Commercially available SPME fibers consist of polymer-coated fused silica rods, with coatings ranging from polydimethylsiloxane (PDMS) for nonpolar compounds to polyacrylate (PA) for polar compounds. Compared to conventional sample preparation methods, SPME provides many advantages including its speed, simplicity and ease of operation. In addition, SPME combines sampling and sample preparation into one step and can be readily automated and coupled with separation techniques such as gas chromatography (GC). In spite of the advantages of this technique, the lack of proper chemical bonding of the stationary-phase coating and the relatively high thickness of the conventional fibers seem to be responsible for some drawbacks of the commercial fiber such as low thermal and chemical stability, the stripping of coating and short lifetime [7].

Sol–gel coating technology, established by Malik and co-workers [8], has solved most of these problems. The distinguished character of sol–gel technique is that it can provide efficient incorporation of organic components into inorganic polymeric structures in the solution under extraordinarily mild thermal conditions.

The porous structure of the sol–gel coating offers a high surface area; allowing high extraction efficiency and the coating composition can be altered with a relative ease to give different selectivity characteristics. Strong adhesion of the coating onto the support due to chemical bonding is a very important characteristic which increases the coating stability toward organic solvents and high desorption temperatures [7].

Carbon nanotubes (CNTs), essentially an allotropic form of graphitic carbon, were first described in 1991 by Iijima [9].

CNTs, which include single wall carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), have captured the attention of researchers worldwide due to their unique properties. CNTs have high surface area, the ability to establish π–π interactions, excellent chemical, mechanical and thermal stability, etc., which make them very attractive as adsorbents in SPE and SPME devices for either non-polar (in the case of non-functionalized CNTs) and polar compounds for which functionalization of the tubes plays a key role in selectivity [10,11]. Only a few investigations have been published on the application of CNTs in the fiber coating for SPME [12–26].

However, despite excellent properties, owing to their rigidity, chemical inertness and self-aggregation of CNTs with strong van der Waals forces, CNTs are difficult to dissolve or disperse in common organic solvents or polymeric matrices. Great efforts have

been focused on applying the methods of covalent or non-covalent functionalization to improve the solubilization of CNTs.

The intersection of CNTs science with sol–gel chemistry essentially allows the prepared coatings to efficiently integrate the advantages both from the CNTs and sol–gel technology.

In the present work, for the first time, we prepared a novel SPME fiber coating containing new stationary phase, hydroxyl-terminated poly(ethylene glycol) grafted via covalent functionalization of multi-walled carbon nanotubes (PEG-g-MWCNTs) by sol–gel technology. During the course of sol–gel reactions, the created organic–inorganic hybrid sol–gel PEG-g-MWCNTs polymer became chemically bonded to the fused-silica fiber producing a surface-bonded stationary-phase coating, with inherently effective chemical immobilization, thermal stability and higher extraction efficiency.

The developed sol–gel coating was then used for the determination of BTEX in real water samples with gas chromatography-flame ionization detector (GC-FID).

2. Experimental

2.1. Chemicals and materials

The MWCNTs (outer diameter 10–20 nm, length range 5–15 μm, purity > 95%, special surface area > 40–300 m^2 g^{-1}) were purchased from Shenzhen Nanotech Port (Shenzhen, China). Methyltrimethoxysilane (MTMOS), trifluoroacetic acid (TFA, 99%), poly(ethylene glycol) (PEG, MW 6000), tetrahydrofuran (THF), thionyl chloride (SOCl2) and sodium chloride were purchased from Merck (Darmstadt, Germany).

Analytical reagents grade methanol, benzene, toluene, ethylbenzene and o-xylene were also purchased from Merck (Darmstadt, Germany). Toluene and tetrahydrofuran (THF) were dried, deoxygenated, and distilled from Na/benzophenone ketyl before use.

2.2. Instrumentation

Gas chromatographic analysis was carried out using a Chrompack CP9001 (Middelburg, the Netherlands) fitted with a split/splitless injector and flame ionization detector (FID). Helium (99.999%, Sabalan Co., Tehran, Iran) was used as the carrier gas and was set at 1 mL min^{-1}. The separation was performed with a CP-Sil 5CB, a WCOT Fused silica capillary column, 30 m × 0.25 mm i.d. with 0.25 μm stationary film thickness of 100% polydimethylsiloxane (Chrompack, Middelburg, the Netherlands).

The column temperature was programmed as follows: initial oven temperature 40 °C for 5 min, increasing to 100 °C at 10 °C min^{-1} and directly to 200 °C at 20 °C min^{-1} then holding for 1 min.

The injector temperature was set at 250 °C and fiber desorption was carried out in the splitless mode for 20 s, plus 5 additional minutes with the split valve on, to assure complete cleaning. The detector temperature was held at 300 °C.

A VELP Scientifica heating magnetic stirrer, model ARE (Milano, Italy) was employed for stirring and heating samples during the extraction. To mix various solution ingredients, an ultrasonic bath (Branson 1510, Branson Ultrasonics Co., Danbury, CT), was employed at a frequency of 42 kHz.

The chemical structures of the PEG, pristine and functionalized MWCNTs were identified by a Fourier transform infrared spectroscopy (FT-IR, Thermo-Nicolet AVATAR 350 spectrometer). Thermal gravimetric analyses (TGA) were made with a TGA-50 (Shimadzu, Japan) instrument under nitrogen at a heating rate of 10 °C min^{-1}.
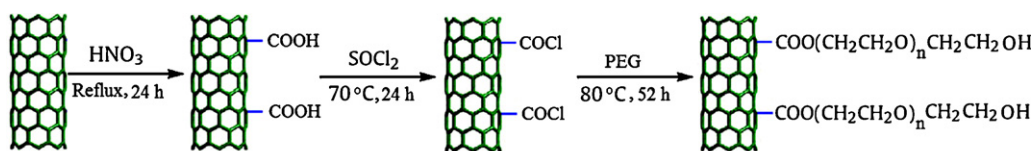
Fig. 1. Reaction scheme for the synthesis and preparation of PEG-g-MWCNTs.

Also the surface characteristics of the created sol–gel PEG-g-MWCNTs coating were studied by scanning electron microscopy (SEM) (LEO, model 1450VP, Germany).

2.3. Preparation of PEG-g-MWCNTs

A typical procedure for preparing MWNT-COCl is described as follows. The first step was to attach carboxyl groups onto the surface of nanotubes. In this carboxylation procedure, a 100 mL flask charged with 0.3 g of crude MWNTs and 50 mL of 60% HNO3 aqueous solution was sonicated in a bath for 30 min and stirred for 24 h at reflux. After having been cooled to the room temperature, the mixture was vacuum-filtered through a 0.22 μm membrane and washed with excess distilled water until the pH of the filtrate was 7.0. The filtered solid was then dried under vacuum for 12 h at 60 °C to give carboxylic acid-functionalized MWCNT (MWCNTs-COOH) [27]. Afterwards, 200 mg of MWCNT-COOH was stirred in 20 mL of SOCl2 at 70 °C for 24 h to convert the surface-bound carboxyl groups into acyl chloride groups. After centrifugation, the solid was rinsed repeatedly with anhydrous THF and then dried at the room temperature under vacuum [28].

After MWCNTs-COCl had been prepared, the dried solid was reacted with PEG as follows [29]. MWCNTs-COCl was mixed with 5 g of PEG (MW 6000) in 20 mL of toluene/THF solvent mixture (v/v 3/1) and 2 mL of triethylamine. The mixture was stirred for 52 h at 80 °C under a nitrogen atmosphere. The resultant solid was filtered, repeatedly washed with water to remove the unreacted PEG, and dried under vacuum. A typical procedure for synthesizing MWCNTs-g-PEG is illustrated in Fig. 1.

2.4. Fiber preparation

Before the coating process, in order to remove the polyimide layer from a 1 cm segment of the fiber at one of a 3-cm-long fused silica fiber ends, this layer was burnt off using a naked flame. Then the fiber was dipped into 1 M NaOH solution for 1 h, to expose the maximum number of silanol groups on the surface of the fiber, and cleaned with water. Then it was placed into 0.1 M HCl solution for 30 min to neutralize the excess NaOH. Then it was cleaned again and dried.

The sol solution was prepared as follows: 20 mg MWCNT-g-PEG and 100 mg PEG were added to 100 μL MTMOS in an eppendorf tube and dissolved thoroughly by ultrasonic agitation for 5 min. Then approximately 70 μL of TFA containing 5% water was sequentially added to the solution and the mixture was sonicated for another next 5 min. At this stage, treated fused silica was dipped vertically into the sol solution for an optimized time of 30 min and gel coating was formed on the activated outer surface of the fused silica. For each fiber, this coating process was repeated several times using a freshly prepared sol solution until the desired thickness of the coating was obtained. The fiber was placed in a desiccator at room temperature for 24 h. This was followed by the condition process. Conditioning of the fiber was as follows: the fiber was conditioned in a GC injection port under helium flow rate of 1 mL min⁻¹, at 100 °C for 30 min, then 200 °C for 1 h, and finally 300 °C for 1 h.

2.5. Preparation of aqueous standard solutions for extraction by SPME

Stock solutions (100 mg mL⁻¹) of BTEX were prepared in methanol and stored in the dark at 4 °C. Working solutions were prepared by the dilution of the stocks in the appropriate solvent. Tap water, mineral water, well water and wastewater samples were collected from Mashhad, Razavi Khorasan Province, Iran. Water samples were stored in amber-glass bottles without headspace and maintained in the dark at 4 °C until their analysis.

2.6. Headspace SPME procedure

For each HS-SPME analysis, 15 mL of water sample was placed into a 20 mL glass vial with 6 g of NaCl and a magnetic stir bar. The vial was sealed with rubber septa to prevent sample evaporation. Afterward, the stainless steel needle, where the fiber is housed, was pushed through the vial septum, and then the fiber was pushed out of the housing and exposed to the headspace above the sample at the optimal conditions. Extractions were performed in a water bath provided with a temperature control system in order to control the extraction temperature. Once the extraction period was over, the fiber was withdrawn into the needle, removed from the vial and then immediately inserted into the hot injection port of the GC at 250 °C for desorption. Each sampling was performed in triplicate. The fiber was cleaned everyday prior to the first extraction by leaving it in the injection port for 30 min at 300 °C to eliminate any carry-over of analytes from the previous extraction. Prior to starting a set of experiments, a blank analysis was performed to verify that no extraneous compounds were desorbed from the fiber.

3. Results and discussions

3.1. Characterization of PEG-g-MWCNTs

FT-IR was used to analyze the changes in the surface chemical bonding and structure, in the frequency range of 4000–400 cm⁻¹. FT-IR spectra can display that the PEG chains were chemically attached to the functionalized MWNT-COOH. To obtain these samples, CNTs were mechanically mixed to the KBr powder and pressed into disc shape. Fig. 2 shows the FT-IR spectra of the pristine MWCNTs, MWCNTs-COOH, PEG and PEG-g-MWCNTs.

Pristine MWNTs displays the weak signal at 1580 cm⁻¹, which is assigned to the stretching mode of the benzenoid ($\nu_{C=C}$) in the nanotube backbone [30]. Also the appearing of the band at 3400 cm⁻¹ is attributed to the presence of the hydroxyl groups (–OH) on the surface of the MWCNTs, which could appear either from ambient moisture bound to the MWCNTs or during the purification of the raw material (Fig. 2a) [31]. Moreover, pristine MWCNTs have some weak peaks between 3000 and 2800 cm⁻¹ which correspond to –CH stretching absorption band, indicating that pristine MWCNTs contain defects, which may be formed during their manufacture [32]. The presence of carboxylic groups after the oxidation step was confirmed with a C=O band stretching that appeared at around 1700 cm⁻¹ (Fig. 2b). The relative increase in the intensities of the bands about 3400 cm⁻¹ suggests that there could be possibly more –OH groups on the surface of the MWCNTs after oxidation. These
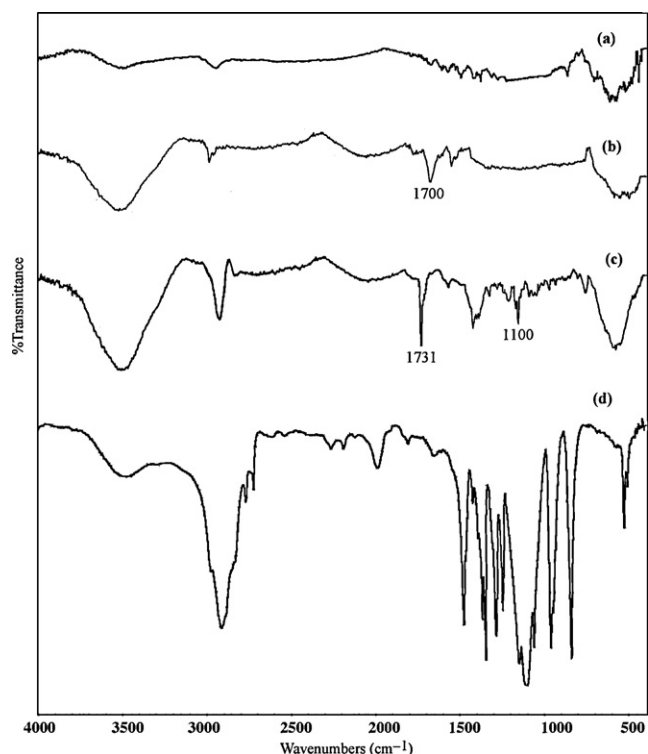
Fig. 2. FT-IR spectra of (a) pristine MWCNT, (b) MWCNT-COOH, (c) PEG-g-MWCNTs and (d) pure PEG.

Fig. 3. TGA curves of (a) pristine MWCNTs, (b) PEG-g-MWCNTs and (c) pure PEG.

observations clearly indicate the oxidation of the nanotube surface and the existence of –COOH groups attached to the surface of MWCNTs.

After the grafting of PEG, as shown in Fig. 2c, there appeared some new peaks in the region of 800–1600 cm^{-1} that are all characteristic of PEG and are not seen in the spectrum of pristine MWCNTs and MWCNTs-COOH. The C=O peak at 1731 cm^{-1} significantly appears after functionalization, which can be assigned to the carbonyl vibration of the ester bonding. The presence of ester bond can also be verified by the appearance of the C–O stretching at 1100 cm^{-1}. The peaks at 3000–2800 cm^{-1} also become more prominent when compared to those of pristine MWCNTs and MWCNTs-COOH, and are ascribed to the C–H stretching of CH$_2$ hydrocarbon chains of grafted-PEG. These results show that the PEG chains were chemically attached to the functional groups of MWCNTs.

The relative amount of the grafted-PEG and the thermal stability of the PEG-g-MWCNTs can be determined by the thermogravimetric analysis (TGA). The samples were scanned within the temperature ranging from 25 to 700 °C at a ramp rate of 10 °C min^{-1} under continuous N$_2$ flow. The weight loss curves of pure PEG, pristine MWCNT, and PEG-g-MWCNTs are presented in Fig. 3. Clearly, pristine MWCNTs have good thermal stability. When the temperature increases up to 700 °C, there is no obvious decomposition in pristine MWCNTs. The pure PEG completely decomposes in the temperature range between 380 and 560 °C with a weight loss over 99%. TGA traces of PEG-g-MWCNTs give considerable weight loss between 380 and 560 °C, corresponding to the decomposition of PEG covalently attached to MWCNTs. Neat MWCNTs hardly decomposed at the temperature below 600 °C. Therefore, the TGA results can be applied to estimate the relative amounts of the grafted PEG onto the MWCNTs. TGA of the PEG-g-MWCNTs showed a weight loss around 17 wt%, which demonstrates a moderate degree of the functionalization of PEG on MWCNTs.
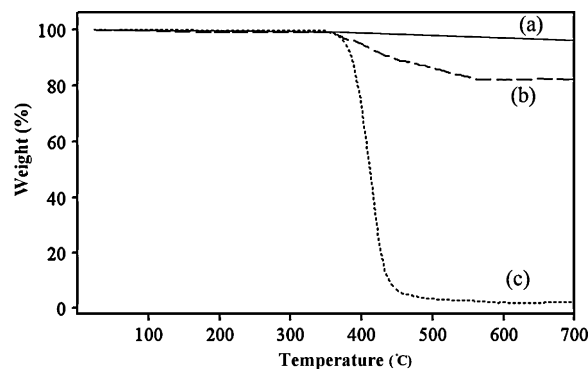
3.2. Sol–gel chemistry of the PEG-g-MWCNTs coating in SPME

In the sol–gel approach, four major sets of reaction occurred during the sol–gel processing: (1) hydrolysis of the precursor by TFA; (2) condensation of the hydrolyzed products with PEG-g-MWCNTs; (3) polycondensation of the condensation products into a three-dimensional sol–gel network and (4) chemical anchoring of the evolving sol–gel polymer to the surface of the fiber to create a surface-bonded polymeric coating. The sol solution was prepared by mixing appropriate amounts of methyltrimethoxysilane (a sol–gel precursor), PEG (a sol–gel active organic polymer), PEG-g-MWCNTs (stationary phase) and trifluoroacetic acid containing 5% water (a sol–gel catalyst). PEG was used to lengthen the sol–gel network and to help uniformly spread the stationary phase on the fiber. Fig. 4 represents the probable chemical structure of the PEG-g-MWCNTs fiber coating.

3.3. Surface structure of the coating

The morphology of the fiber was investigated by scanning electron microscopy (SEM) under different magnifications (Fig. 5). SEM analysis also revealed homogenously distributed coatings on the entire surface of the fiber. A lot of MWCNTs were observed on the surface of the PEG-g-MWCNTs sol–gel coating at high magnification.

The morphology of the fiber surface showed a rough and highly porous structure which greatly increases the surface area for PEG-g-MWCNTs sol–gel coating and further provide enhanced stationary phase loading and the extraction capacity and fast mass transfer. It increases the surface area on the fiber, therefore, even a thin coating will be able to provide enhanced stationary phase loading and high sample capacity. The porous structure also increases the speed of extraction and desorption.

3.4. Thermal stability

In order to obtain a complete desorption of the analytes from the fiber without carry-over effects and the spread of the SPME application, the thermal resistance is a very important parameter for SPME applications. The thermal stability of the PEG-g-MWCNTs fiber was studied by HS-SPME of BTEX in aqueous solution in NaCl saturated solution. The fibers were conditioned 1 h at different temperatures (ranging from 250 °C to 320 °C), and then were used to extract the analytes. The results indicated that PEG-g-MWCNTs fiber could withstand higher temperatures to 320 °C without loss of extraction efficiency. The results proved that the PEG-g-MWCNTs coating is thermally stable. Such a high operating temperature is due to strong
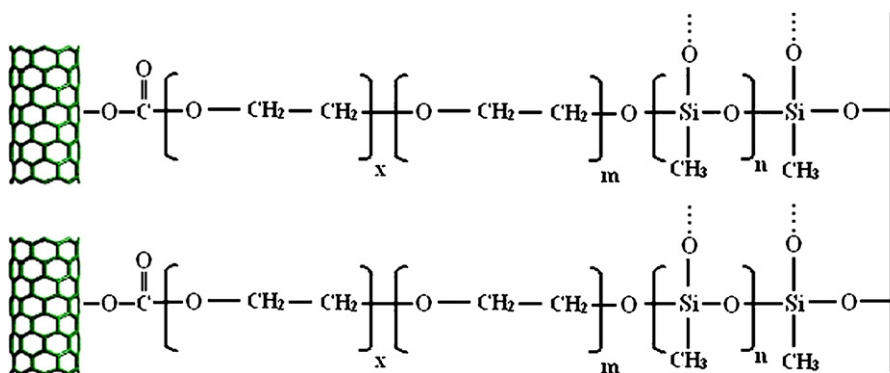
Fig. 4. Chemical structure of sol–gel PEG-g-MWCNTs fiber coating.

adhesion of the coating to the silica fiber surface through chemical bonding.

3.5. Lifetime of the coating

The lifetime of the coating layer of SPME is very important for practical applications. The coating is damaged mainly by its exposure to high temperatures, organic solvents, strong acidic and basic solutions [33]. The change of extraction efficiencies of PEG-g-MWCNTs fiber in extracting BTEX from the aqueous solution after being used for 30, 60, 90, 120, 150, 170 and 200 times is studied at 250 °C. No obvious decline was observed, which indicated that the fiber was still stable and usable at least for 200 times. However, the commercial fiber generally can be used for 50–100 times. Thus, the lifetime of the coating is prolonged. This long life span is because of the thinness of the coating and the heat-resistant properties due to strong chemical bonding between the sol–gel generated organic–inorganic composite coating and silica fiber surface.

3.6. Optimization of extraction and desorption conditions

Before performing the robustness test of an analytical procedure, it is necessary to carry out an optimization of the parameters that influence the process. The most important factors related to this extraction technique such as the desorption time and temperature, the extraction time and temperature, the agitation sample and the salting effect were investigated and optimized.

3.6.1. Desorption temperature and time

The desorption process is affected by the desorption time and temperature. Increasing the desorption temperature led to decreasing the partition coefficient of the analyte between the fiber coating and the gaseous phase. Using the highest possible temperature without damaging the fiber coating is a way of minimizing the desorption time of the analyte from the fiber surface. Regarding the high volatility of the compounds under study, only temperatures between 150 and 300 °C were tested. On the other hand,
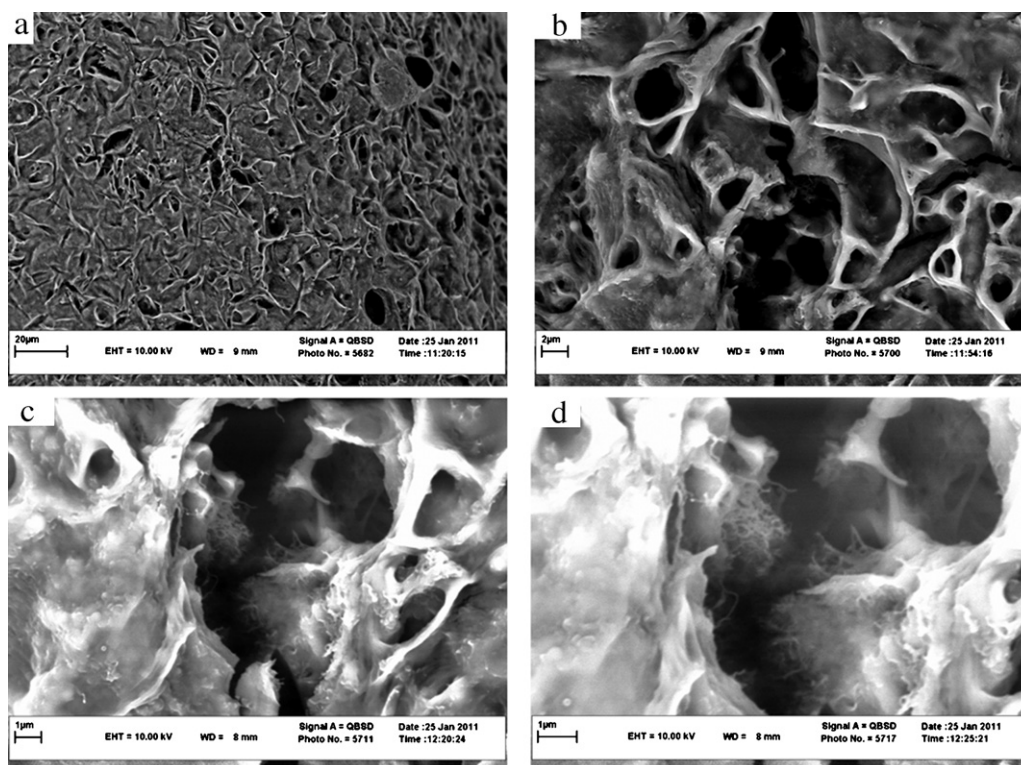

Fig. 5. Scanning electron micrograph images of the surface of PEG-g-MWCNTs SPME fiber at a magnification of (a) 2000-fold, (b) 10,000-fold, (c) 20,000-fold and (d) 30,000-fold.
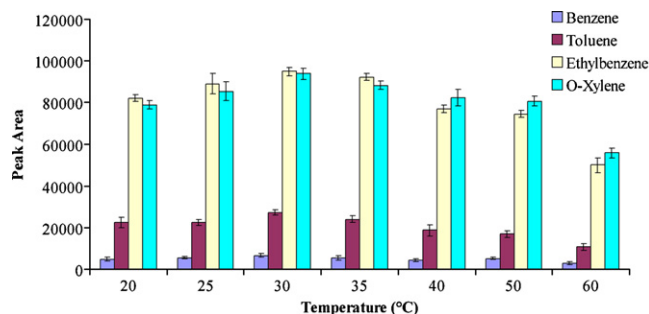
Fig. 6. Effect of extraction temperature on the extraction efficiency of BTEX.

Fig. 8. Typical chromatogram of BTEX in wastewater sample using PEG-g-MWCNTs coating fiber. Peak numbers correspond to (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene.

to avoid carry-over effect, desorption time should be sufficient for the quantitative desorption of the extracted analytes from the surface of the coating SPME fiber. For this reason, experiments were performed with various desorption times to test the effect of desorption time (0 up to 120 s) on the chromatographic peak areas of the analytes. All of the components are completely desorbed at 250 °C, so it was selected as the optimum desorption temperature and 20 s was selected as the optimal desorption time to eliminate any carry-over of analytes from the previous extraction. In addition, fibers were held for 5 min in the GC injection system to eliminate probable carry-over effects.

3.6.2. Extraction temperature

During the extraction, it was necessary for the solute to vaporize from the sample solution to the gas phase by heating the sample. On the other hand, increasing extraction temperature could increase the headspace/sample partition coefficient of the analyte. Also increase in the temperature leads to decrease of fiber coating/headspace partition coefficient. The first phenomenon leads to a higher concentration of the analyte in the headspace, and the second one results in the lowering of the equilibrium amount of the analyte that the fiber coating is able to extract. The optimal extraction temperature was investigated by exposing the fiber to the sample headspace for 30 min at temperatures ranging from 20 to 60 °C, which was illustrated in Fig. 6. As shown in Fig. 7, the extracted quantity of BTEX compounds increased up to 30 °C and decreased at higher temperature. Therefore, 30 °C was preferred as the optimum extraction temperature.

3.6.3. Extraction time

The extraction time is a critical parameter in the SPME procedure because it influences the partition of the target analytes between sample, headspace and SPME fiber coating. Extraction time also determines the sensitivity and reproducibility of the proposed method. The extraction time varied from 10 to 60 min for determination of the optimum extraction time (Fig. 7). It can be seen from Fig. 8 that extraction efficiencies for all BTEX compounds
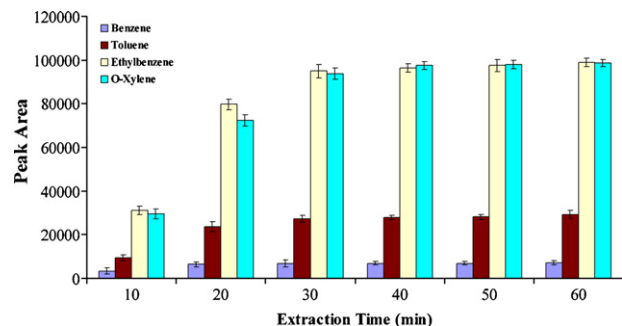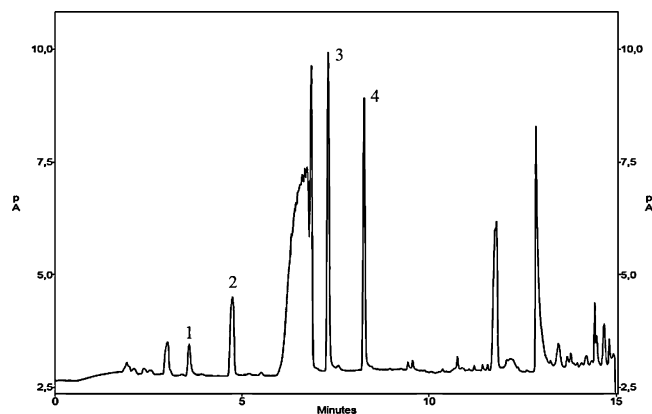
under investigation increased up to 30 min. After this time, the extraction efficiency did not change significantly for most of the analytes. Under these conditions, the analyte concentration equilibrium between headspace and fiber is reached.

3.6.4. Stirring speed

Agitation of samples increases the extraction efficiency and reduces the time required to reach thermodynamic equilibrium. The effect of the stirring speed on the responses of the target compounds was investigated in detail at the stirring speeds ranging from 200 to 1000 rpm. Our results showed that the peak area of the analytes increases with the increasing stirring rate. Hence, the stirring speed of 1000 rpm was used as the optimal value in further extractions.

3.6.5. Salt concentration

Addition of salt to the aqueous sample is usually made to improve the extraction of several analytes because the increase in ionic strength brings a reduction on the solubility of the hydrophobic analytes in the water solution and forces more of these analytes into the headspace and the extracting phase. The increase in the extraction extent can be explained by the engagement of water molecules in the hydration spheres around the ionic salt and hence in the reduction of the water concentration available to dissolve analytes. The salting-out effect was examined by monitoring the variation of peak areas in the presence of different concentrations of NaCl (from saltless up to saturation). Results show that the extraction efficiency of BTEX increased with the salt content in the range tested, and in the saturated salt concentration (6.0 g NaCl in 15.0 mL sample volume), maximum extraction efficiency was observed. Thus, in all extractions, 6 g NaCl was added to 15 mL sample solution to provide maximum salt effect.

4. Validation of the method

The analytical characteristics of the optimized HS-SPME method in terms of its linear range, repeatability, reproducibility, limits of detection (LODs) and limits of quantitation (LOQs) were investigated to estimate the efficiency and the feasibility for application to the analysis of environmental samples. In the optimum conditions, the calibration graphs were constructed for eight working aqueous standards containing all the analytes at different concentrations. For each point three replicate extractions were performed. The results are summarized in Table 1. Good linear relationship between the corresponding peak areas and the concentrations were obtained for all the analytes ($r^2 > 0.9961$). The limits of detection

Fig. 7. Effect of extraction time on the extraction efficiency of BTEX.

Table 1
Figures of merit of the proposed method.

Analyte	Linear range (pg mL^{-1})	LOD (pg mL^{-1})	LOQ (pg mL^{-1})	Correlation coefficient (r^2)	RSD (%) one fiber (repeatability) ($n=5$)	RSD (%) batch to batch (reproducibility) ($n=3$)
Benzene	(10–5) × 10^4	3	10	0.9979	4.40	4.31
Toluene	(7–5) × 10^4	2	7	0.9975	5.75	6.55
Ethylbenzene	(3–8) × 10^3	0.7	3	0.9961	4.90	5.07
o-Xylene	(2–8) × 10^3	0.6	2	0.9984	4.75	6.24

Table 2
Content of BTEX in real water samples and the accuracy of the established proposed method using the sol–gel PEG-g-MWCNTs coating fiber.

	Tap water			Mineral water			Wastewater			Well water		
	Mean (pg mL^{-1})	RSD (%)	Recovery (%)[a]	Mean (pg mL^{-1})	RSD (%)	Recovery (%)[a]	Mean (ng mL^{-1})	RSD (%)	Recovery (%)[a]	Mean (ng mL^{-1})	RSD (%)	Recovery (%)[a]
Benzene	76.50	5.50	100.90	6 × 10^2	4.56	97.20	3.15	10.72	92.05	2.07	6.63	95.21
Toluene	97.30	7.69	97.98	1.61 × 10^2	6.74	96.30	1.72	9.52	95.36	1.77	7.29	96.75
Eyhylbenzene	NQ	5.40	101.90	NQ	5.32	96.11	2.42	9.19	94.37	2.10	7.11	95.50
o-Xylene	NQ	5.29	95.60	65.00	4.93	95.21	1.82	9.57	90.21	1.61	6.94	94.15

NQ, not quantified.

[a] Relative recovery (%) = the amount found in the spiked sample – the amount found in the sample/the amount added × 100.

Table 3
Comparison of analytical characteristics for proposed fiber with other fibers in determination of BTEX compounds.

Reference	RSD (%)	LOD (ng mL^{-1})	Fiber
[34]	1.4–4.0	0.6–1.6	NiTi-ZrO$_2$-PDMS
[35]	3–7	0.08–0.6	PDMS (100 μm)
[36]	<8.2	5.6–12.4	Anodized aluminum coated with titania sol–gel
[37]	4.7–10.0	0.012–0.054	Lead dioxide
[38]	2.0–4.5	0.19–3.29	Graphite
[39]	3.5–10	100–800	Disposable ionic liquid (IL) coated fiber
[40]	6.6–9.8	1–13	HPTES–SBA-15
[41]	2.96–4.16	0.01–10	PDMS
[41]	3.44–4.57	0.002–0.8	PEG
[41]	5.87–8.42	0.001–0.8	PEG/CNTs
This study	4.40–5.75	0.0006–0.003	PEG-g-MWCNTs

(LODs) and quantification (LOQs), based on signal-to-noise ratio (S/N) of 3:1 and 10:1, were determined. Excellent results were obtained with LOD values in the low pg mL^{-1} range (Table 1), thus proving the potential of the method for the determination of BTEX compounds at ultra-trace levels. LODs and LOQs were obtained in the range of 0.6–3 pg mL^{-1} and 2–10 pg mL^{-1}, respectively. In order to assess the repeatability of the method, five replicate determinations (spiked at 20 pg mL^{-1} with each target analyte) were carried out using a single fiber and the relative standard deviations (RSDs) were calculated. The observed repeatability ranged 4.40–5.75% depending of the compound considered. The fiber-to-fiber reproducibility of three different fibers coated under the same conditions was also investigated, which ranged from 4.31 to 6.55%.

5. Real sample analysis

The proposed method was applied to the determination of BTEX in different water matrices such as tap water, mineral water, well water and wastewater samples.

The quantitative results of this water samples are listed in Table 2. BTEX compounds were detected in all the water samples but some of their concentrations were under their LOQs. As shown in this table, all BTEX compounds were found at ultra-trace levels in these water samples, indicating the high sensitivity of the sol–gel derived PEG-g-MWCNTs fiber. In order to investigate the performance of the established method, PEG-g-MWCNTs fiber was applied to extract these water samples spiked at 20 pg mL^{-1} for each compound. The recoveries and determination precisions are listed in Table 2. The results showed that the mean recoveries of

BTEX ($n=3$) ranged from 90.21% to 101.90% and the RSDs were between 4.56% and 10.72%.

These results clearly demonstrated that the accuracy of the developed method for the analysis of BTEX in real water samples was quite satisfactory. Fig. 8 shows a typical chromatogram obtained for BTEX in real wastewater sample with the sol–gel PEG-g-MWCNTs fiber.

6. Comparison with other related SPME methods

Some statistical data of the proposed method were compared the some reported SPME methods in literature (Table 3). The results showed that relative standard deviations values of the proposed method using sol–gel PEG-g-MWCNTs coating fiber were comparable with the other ones. It can be seen that this method has lower LOD than those of the other reported works. These advanced performances are mainly due to two reasons: (a) sol–gel coatings possess porous structures which should significantly increase the surface area availability on the fibers and (b) using MWCNTs with high surface area as a sorbent modifier will also be able to provide the enhanced adsorption efficiency for the analyte.

7. Conclusion

In this work, for the first time, chemically bonded sol–gel PEG-g-MWCNTs coating was prepared and then successfully applied for the analysis of BTEX at ultra-trace levels in four real water samples. Due to the unique properties of CNTs and the inherent advantageous features and also the performance of the sol–gel coating technology, this innovative fiber exhibited porous surface struc-

ture, good precision and accuracy, high selectivity and sensitivity, longer life span (over 200 times) and high thermal stability.

The porous structure of sol–gel coating increases the surface area on the fiber, the speed of extraction and desorption steps and sample capacity. An excellent thermal stability of at least 320 °C was obtained for the fiber coating, suggesting chemical bonding between the substrate and the polymeric coating, which will allow these fibers to be applied to a wider range of volatile compounds, especially less volatile compounds.

Based on these features, in this article, a rapid and facile method for routine ultra-trace analysis of BTEX in real water samples was introduced. Therefore, it could be expected to have a potential use in the other complex matrix samples. On the other hand, there are still some areas of research left to modify MWCNTs with other functional groups to increase coating fiber selectivity for highly complex samples.

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References

[1] R.J. Irwin, M. VanMouwerik, L. Stevens, M.D. Seese, W. Basham, Environmental Contaminants Enclyclopedia, National Park Service, Water Resources Division, Washington, DC, 1997.
[2] R.M. Alberici, C.G. Zampronio, R.J. Poppi, M.N. Eberlin, Analyst 127 (2002) 230.
[3] U.S. EPA. List of contaminants & their maximum contaminant level (MCLs) in drinking water. http://www.epa.gov/safewater/mcl.html#organic, 2004.
[4] A. Sarafraz-Yazdi, A. Amiri, Trends Anal. Chem. 29 (2010) 1.
[5] R.P. Belardi, J.B. Pawliszyn, Water Pollut. Res. J. Can. 24 (1989) 179.
[6] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[7] A. Kumar, Gaurav, A.K. Malik, D.K. Tewary, B. Singh, Anal. Chim. Acta 610 (2008) 1.
[8] S.L. Chong, D.X. Wang, J.D. Hayes, B.W. Wilhite, A. Malik, Anal. Chem. 69 (1997) 3889.
[9] S. Iijima, Nature (London) 354 (1991) 56.
[10] L.M. Ravelo-Pérez, A.V. Herrera-Herrera, J. Hernández-Borges, M. Ángel Rodríguez-Delgado, J. Chromatogr. A 1217 (2010) 2618.
[11] F. Augusto, E. Carasek, R.G.C. Silva, S.R. Rivellino, A.D. Batista, E. Martendal, J. Chromatogr. A 1217 (2010) 2533.
[12] R. Jiang, F. Zhu, T. Luan, Y. Tong, H. Liu, G. Ouyang, J. Pawliszyn, J. Chromatogr. A 1216 (2009) 4641.
[13] W. Zhang, Y. Sun, C. Wu, J. Xing, J. Li, Anal. Chem. 81 (2009) 2912.
[14] H. Liu, J. Li, X. Liu, S. Jiang, Talanta 78 (2009) 929.
[15] W. Du, F. Zhao, B. Zeng, J. Chromatogr. A 1216 (2009) 3751.
[16] N. Rastkari, R. Ahmadkhaniha, M. Yunesian, J. Chromatogr. B 877 (2009) 1568.
[17] J.-X. Wang, D.-Q. Jiang, Z.-Y. Gu, X.-P. Yan, J. Chromatogr. A 1137 (2006) 8.
[18] F. Wu, W. Lu, J. Chen, W. Liu, L. Zhang, Talanta 82 (2010) 1038.
[19] X. Liu, Y. Ji, Y. Zhang, H. Zhang, M. Liu, J. Chromatogr. A 1165 (2007) 10.
[20] Q. Li, X. Ma, D. Yuan, J. Chen, J. Chromatogr. A 1217 (2010) 2191.
[21] H. Asadollahzadeh, E. Noroozian, Sh. Maghsoudi, Anal. Chim. Acta 669 (2010) 32.
[22] X.-Y. Liu, Y.-S. Ji, H.-X. Zhang, M.-C. Liu, J. Chromatogr. A 1212 (2008) 10.
[23] J. Zeng, J. Chen, X. Song, Y. Wang, J. Ha, X. Chen, X. Wang, J. Chromatogr. A 1217 (2010) 1735.
[24] I. Minet, L. Hevesi, M. Azenha, J. Delhalle, Z. Mekhalif, J. Chromatogr. A 1217 (2010) 2758.
[25] H.H. See, M. Marsin Sanagi, W.A. Wan Ibrahim, A.A. Naim, J. Chromatogr. A 1217 (2010) 1767.
[26] W. Chen, J. Zeng, J. Chen, X. Huang, Y. Jiang, Y. Wang, X. Chen, J. Chromatogr. A 1216 (2009) 9143.
[27] G.-X. Chen, H.-S. Kim, B.H. Park, J.-S. Yoon, J. Phys. Chem. B 109 (2005) 22237.
[28] J. Liu, A.G. Rinzler, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, T. Iverson, K. Shelimov, C.B. Huffman, F. Rodriguez-Macias, D.T. Colbert, R.E. Smalley, Science 280 (1998) 1253.
[29] Y. Wen, H. Wu, S. Chen, Y. Lu, H. Shen, N. Jia, Electrochim. Acta 54 (2009) 7078.
[30] D.B. Mawhinney, V. Naumenko, A. Kuznetsova, J.T. Yates, J. Liu, R.E. Smalley, J. Am. Chem. Soc. 122 (2000) 2383.
[31] T. Ramanathan, F.T. Fisher, R.S. Ruoff, L.C. Brinson, Chem. Mater. 17 (2005) 1290.
[32] A. Nabipour Chakoli, J. Wan, J.T. Feng, M. Amirian, J.H. Sui, W. Cai, Appl. Surf. Sci. 256 (2009) 170.
[33] M. Liu, Y. Liu, Z. Zeng, T. Peng, J. Chromatogr. A 1108 (2008) 149.
[34] D. Budziak, E. Martendal, E. Carasek, J. Chromatogr. A 1187 (2008) 34.
[35] J.C. Flórez Menéndez, M.L. Fernández Sánchez, J.E. Sánchez Uría, E. Fernández Martínez, A. Sanz-Medel, Anal. Chim. Acta 415 (2000) 9.
[36] K. Farhadi, R. Tahmasebi, R. Maleki, Talanta 77 (2009) 1285.
[37] A. Mehdinia, M.F. Mousavi, M. Shamsipur, J. Chromatogr. A 1134 (2006) 24.
[38] F. Luo, Z. Wu, P. Tao, Y. Cong, Anal. Chim. Acta 631 (2009) 62.
[39] J.-F. Liu, N. Li, G.-B. Jiang, J.-M. Liu, J. Jönsson, M.-J. Wen, J. Chromatogr. A 1066 (2005) 27.
[40] R. Hashemi, M. Shamizadeh, A. Badiei, P. Zarabadi Poor, A.R. Ghiasvand, A. Yarahmadi, Anal. Chim. Acta 646 (2009) 1.
[41] A. Sarafraz-Yazdi, H. Piri Moghadam, Z. Es'haghi, S. Sepehr, Anal. Methods 2 (2010) 746.