

# A sol–gel based solid phase microextraction fiber for analysis of aromatic hydrocarbons

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## Abstract

A sol–gel based solid phase microextraction fiber for headspace sampling (HP-SPME) and GC determination of benzene, toluene, ethylbenzene and xylenes (BTEX) is introduced. The influences of fiber composition, microextraction conditions such as temperature and time on the fiber performance and desorption temperature and time were investigated. Under optimal conditions, the use of proposed fiber was thermally stable up to 250 °C and demonstrated high sensitive and fast sampling of BTEX from gaseous phase. Depending on the analysed substance, the linear range for a selected fiber and the applied GC-FID technique was from 4 to 80 ng mL<sup>-1</sup> with limit of detection (LOD) 0.2–0.7 ng mL<sup>-1</sup> and 100–1000 ng mL<sup>-1</sup> with LOD 8–20 ng mL<sup>-1</sup> for gaseous and soil samples, respectively. HP-SPME–GC analysis was highly reproducible—relative standard deviations (R.S.D.) were between 5.0 and 7.9%. The proposed fiber was successfully used for BTEX sampling from indoor air and headspace of soil samples. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Sol–gel fiber; Solid phase microextraction; BTEX; Soil analysis

## 1. Introduction

Aromatic hydrocarbons, in particular benzene, toluene, ethylbenzene and xylenes (BTEX) have acquired great relevance as ubiquitous pollutants of the outdoor and indoor human environment. Due to the toxicological properties of BTEX compounds, they were analyzed in blood and exhaled breath, urine and contaminated water as environmental pollution indicator [1,2]. Therefore, several analytical methods for determination of BTEX have been reported in literature [1,3–9].

Solid phase microextraction (SPME) is highly promising environmentally friendly sample preparation technique of target analytical potential. An important factor contributing to the rapid growth and popularity of SPME is its ability to perform sample extraction and preconcentration without requiring the use of hazardous organic solvents. In SPME, a sorptive stationary phase coating, either on the outer surface of a fused silica fiber and/or on the inner surface of a capillary, plays a vital role in analyte extraction. Due to importance of sta-

tionary phase coating, future developments and further SPME applications will greatly depend on new break through in the areas of coating technology. SPME coatings were devolved and evaluated based on polydimethylsiloxane (PDMS) [10], polyacrylate (PA) [11,12], carbowax:template resin [13], carbowax:divinilybenzene, nafion per fluorinated resin [14], and polyvinyl chloride (PVC) [15,16]. Sol–gel coatings have been used for preparation of SPME fibers with high thermal stability in development of methodology for volatile and semi-volatile organic compounds analysis [17–22].

We have recently introduced a PVC based SPME fiber for analysis of ethanol and methanol in human body fluids [16]. In this work, the preparation of a new SPME fiber based on sol–gel is described and it was successfully used for development of headspace solid phase microextraction and gas chromatographic determination of BTEX in indoor air and soil samples.

## 2. Experimental

### 2.1. Apparatus

A Chrompack Gas Chromatograph equipped with a FID detector, data processor (mosaic), and split/splitless injector

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was used for this study. A CP-WAX 52CB capillary column (50 m × 0.32 mm i.d., film thickness 1.2 μm) was utilized. A laboratory made SPME device was used in all experiments.

## 2.2. Reagents

Benzene, toluene, ethylbenzene, xylene isomers, Tetra-*n*-buthylorthotitanat (TBOT), pure graphite and other chemicals were all from E. Merck (Darmstadt, Germany). Helium and hydrogen 99.999% purity was from Roham Gas Co. (Midde East Dubai, United Arab Emirates).

## 2.3. Preparation of SPME fiber

The sol–gel coating material was prepared by 75:25 (%w/w) mixtures of TBOT and graphite. After a few seconds from mixing the mentioned materials, a viscose suspension was formed. A 1 cm length of silica rod (total length 2 cm) which was placed in a laboratory-made SPME device introduced into the above-mentioned suspension for several times and sol–gel/graphite coating (thickness 30 μm) was formed on a silica rod. The proposed SPME fiber was then conditioned in 240 °C for 8 h to remove any fiber contaminations.

## 2.4. GC operating conditions

The initial column temperature was maintained at 60 °C for 5 min and then raised at 5 °C min<sup>-1</sup> to 120 °C and held for 5 min. Helium was used as carrier and makeup gas, which their flow rates are 1.0 and 20 mL min<sup>-1</sup>, respectively. The injector and detector temperature were held at 240 and 250 °C, respectively. Injections of analytes were made in splitless mode.

## 2.5. Analytical procedure

### 2.5.1. Headspace sampling of BTEX from soil samples

An accurately weighed 2.0 g of soil sample was placed in a 25 mL vial then the vial sealed with a silicone septum and solid phase microextraction from headspace of the sample was carried out at 80 °C. After 10 min, the SPME fiber was removed from the vial and was immediately inserted into the hot injection port of GC in splitless mode and stayed for 10 s. The analytes were thermally desorbed and moved through the capillary column by helium as carrier gas and finally detected by FID.

### 2.5.2. Sampling of BTEX from indoor air

Volatile solvents and chemicals are measured in indoor air for health and environmental purposes or to monitor workplace exposure. It is well established that headspace SPME is ideal technique for sampling of analytes from gaseous phase. The proposed SPME fiber was placed at chemicals store in Petrochemical Co. (Bandar Emam, Iran), for 24 h at 25 ± 2 °C and then it was introduced in injection port of gas chromatograph.

## 3. Results and discussion

### 3.1. Effect of fiber composition

In SPME, sample analytes are extracted and concentrated by fiber coating. The efficiency of the coating for an analyte is the most important factor in the successful use of SPME. Selection of the coating is based on the polarity and volatility of the analytes. Therefore, it is important to use the appropriate coating for a given applications [23,24].

For the selection of suitable composition, fibers with various compositions (weight percent) were prepared, and extraction of BTEX from gas phase was performed. The obtained results are shown in Fig. 1. As can be seen among three prepared compositions, fiber no. 3 has maximum extraction efficiency in comparison to the other compositions. However, due to formation of a homogenous coating layer on fiber no. 2 (75% TBOT and 25% graphite) which provides excellent reproducibility for microextraction of BTEX, it was selected as optimum fiber in all experiments.

### 3.2. Effect of the microextraction temperature

Generally in such studies, high temperature is suitable for increasing volatility of analytes until they are achievable to the fiber. On the other hand, high temperatures are favorable for establishing the analytes distribution equilibrium between the fiber and gaseous phase but adsorption of the analytes on the fiber is undesirable at high temperatures [25]. Therefore, the effect of extraction temperature was investigated. For this purpose, extraction of BTEX was performed from 2.0 g soil samples containing 3000 ng g<sup>-1</sup> of each compound at various temperatures. The obtained peak areas were plotted *versus* temperature, and are presented in Fig. 2. As can be seen the adsorption of BTEX was increased up to 80 °C and then leveled off. Therefore, 80 °C was selected as a suitable experimental temperature for further studies.

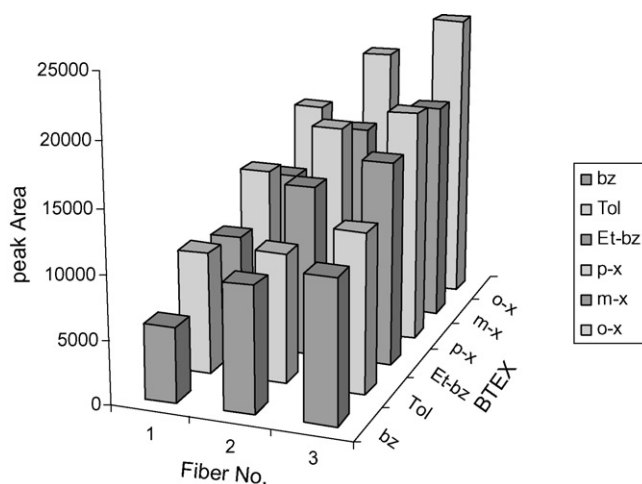


Fig. 1. Effect of fiber composition on BTEX extraction (fiber 1 = 15% (w/w) graphite:85% (w/w) sol–gel; fiber 2 = 25% (w/w) graphite:75% (w/w) sol–gel; fiber 3 = 30% (w/w) graphite:70% (w/w) sol–gel).

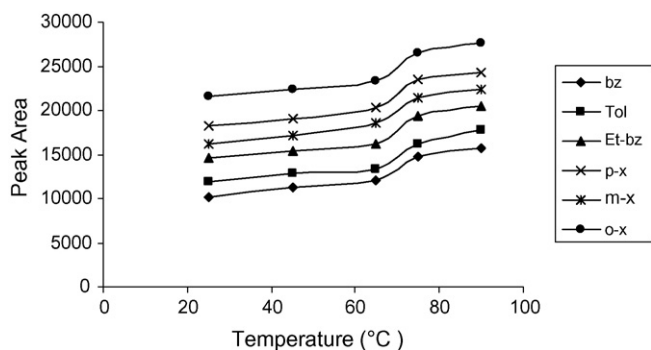


Fig. 2. Effect of temperature on the transfer of BTEX to headspace of soil samples.

### 3.3. Effect of microextraction time

Exposure time of the fiber in gaseous samples is an important parameter in achieving distribution equilibrium of analytes between fiber and sample; it is a decisive factor for improving the extraction efficiency [24]. Therefore, the proposed extraction procedure was carried out at different times, ranging from 2 to 40 min. Fig. 3 shows the plot of peak areas versus exposure times. From these results, it was concluded that equilibrium was reached during 10 min. Thus, in further extractions the fiber was exposed to headspace of sample for 10 min.

### 3.4. Effect of desorption temperature and time

After extraction of BTEX from headspace of soil samples, the fiber was immediately transferred to the injection port of the gas chromatograph. For selection of desorption temperature, injections were carried out at various temperatures ranging from 100 to 260 °C. As it was shown in Fig. 4, analytes completely desorbed at 240 °C, so it was selected as suitable desorption temperature. Experimental studies showed that the time required to complete desorption is less than 10 s for all analytes (Fig. 5). This was very short time and provided very rapid desorption of extracted compounds from the proposed fiber and led to sharp chromatographic peaks which was very effective in obtaining high peak capacities in chromatographic separations.

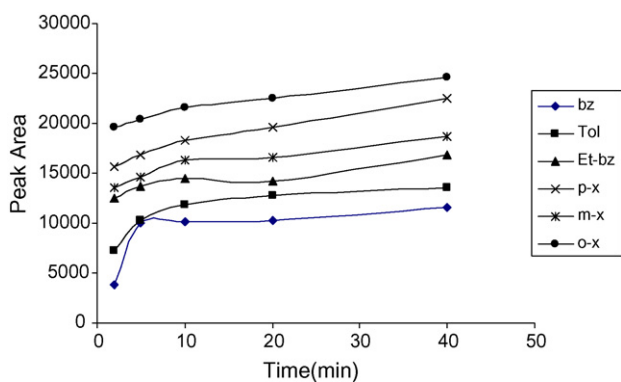


Fig. 3. Effect of time on BTEX extraction.

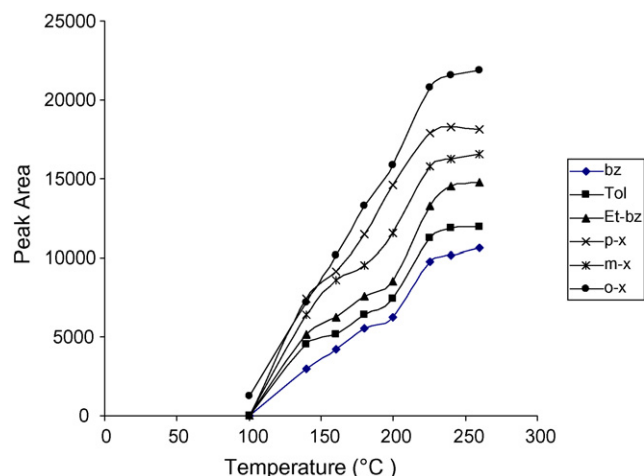


Fig. 4. Effect of desorption temperature.

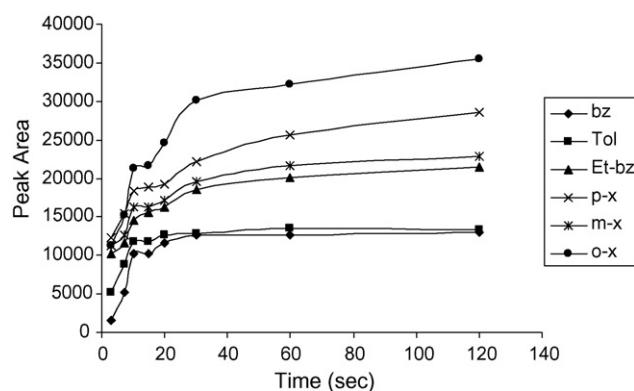


Fig. 5. Effect of time on desorption of the analytes from the fiber at 240 °C.

### 3.5. Study of the microextraction efficiency from the gaseous phase

In this case, 14 sequential extractions were performed on a single sample (see Fig. 6). The extraction efficiency of the analytes was calculated between 9 and 14.5% in the first extraction of BTEX compounds. It should be mentioned that, SPME is an

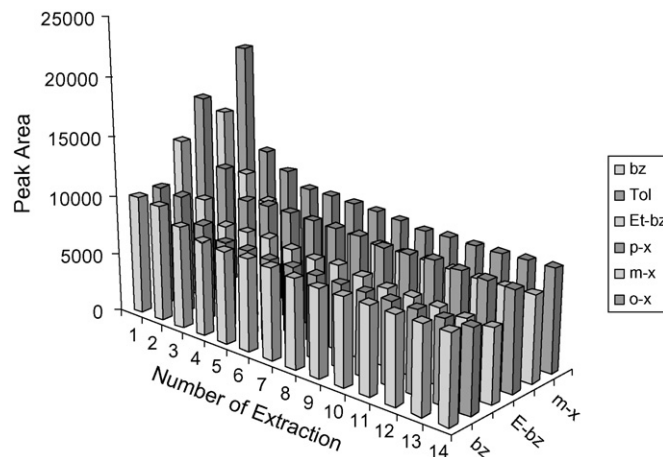


Fig. 6. Extraction efficiency of the SPME fiber. Fourteen sequential extractions were performed.

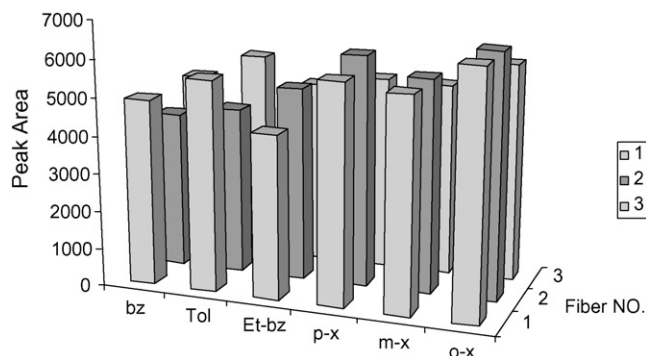


Fig. 7. Study of reproducibility of three laboratories made SPME fiber.

equilibrium method and quantitative extraction of the analytes lead to low detection limits. In most cases, commercial SPME fibers have very low capacities but good selectivity and reproducibility made them valuable analytical tools for sampling in chromatographic analysis.

### 3.6. Reproducibility of the proposed method

Further experiments have been performed to assess the repeatability of the method. Thus, five replicate determinations were carried out using a single fiber and the relative standard deviations were calculated. The obtained results showed the R.S.D. about 2.44% for all BTEX compounds, which indicates that the proposed method is repeatable. Also reproducibility studies performed on three different fibers, and relative standard deviations ( $1.95 \pm 0.21\%$  for all compounds) showed that fiber to fiber reproducibilities were excellent too (Fig. 7).

### 3.7. Quantitative characteristics of the proposed method

To demonstrate the suitability of proposed method for the quantitative analysis of BTEX in soil samples, we studied recovery of BTEX compounds from soil samples. The obtained results clearly showed that the matrix effect was negligible, so quantitative characteristics of the proposed method such as calibration curve equations, correlation coefficients, limit of detection (LOD) and linear dynamic ranges in sampling of BTEX samples were studied and the results are summarized in Tables 1 and 2. The high correlation coefficients ( $>0.995$ ) and low detection limits are advantages of the proposed method. The correlation coefficients were higher than 0.995 for all compounds in gaseous and soil samples. Detection limits ( $S/N=3$ ) were  $0.2\text{--}0.7\text{ ng mL}^{-1}$  and  $8\text{--}20\text{ ng g}^{-1}$  for gaseous samples and soil samples, respectively.

Table 3  
Comparison of proposed fiber and other fibers reported in the literature

Ref.	Kind of fiber	LOD	LDR	Matrix
1	Modified polyrrrole with tetrasulfanated nickel phthalocyanine	$20\text{--}50\text{ pg mL}^{-1}$	$0.06\text{--}50\text{ ng mL}^{-1}$	Water
2	Carbon-coated	$0.01\text{--}0.94\text{ ng mL}^{-1}$	–	Water
3	Activated-charcoal-coated fused silica	$1.5\text{--}2\text{ pg mL}^{-1}$	$5\text{--}10\text{ pg mL}^{-1}$	Water
4	This work	$8.0\text{--}20\text{ ng g}^{-1}$	$100\text{--}1000\text{ ng g}^{-1}$	Soil

Table 1  
Quantities characteristics of the proposed method for gaseous samples

Compound	Calibration curve equation	$R^a$	LOD <sup>b</sup>	LDR <sup>c</sup>
Benzene	$Y = 47.627x + 173.22^d$	0.996	0.7	10–80
Toluene	$Y = 44.813x + 703.69$	0.995	0.4	5–80
Ethylbenzene	$Y = 71.815x + 970.41$	0.998	0.2	4–80
<i>para</i> -Xylene	$Y = 76.277x + 1230.5$	0.999	0.2	4–80
<i>meta</i> -Xylene	$Y = 75.402x + 1222.1$	0.996	0.2	4–80
<i>ortho</i> -Xylene	$Y = 99.057x + 1235.1$	0.997	0.2	4–80

<sup>a</sup> Correlation coefficient.

<sup>b</sup> Limit of detection ( $\text{ng mL}^{-1}$ ).

<sup>c</sup> Liner dynamic range ( $\text{ng mL}^{-1}$ ).

<sup>d</sup>  $Y$  and  $x$  are peak area and concentration of the analytes ( $\text{ng mL}^{-1}$ ), respectively.

Table 2  
Quantities characteristics of the proposed method for soil samples

Compound	Calibration curve equation	$R^a$	LOD <sup>b</sup>	LDR <sup>c</sup>
Benzene	$Y = 4.5557x - 854.71^d$	0.995	20	300–1000
Toluene	$Y = 3.6367x + 286.33$	0.996	12.0	100–1000
Ethylbenzene	$Y = 5.0122x + 698.78$	0.997	8.0	100–1000
<i>para</i> -Xylene	$Y = 6.1889x + 792.11$	0.995	8.0	100–1000
<i>meta</i> -Xylene	$Y = 5.3256x + 787.44$	0.996	8.0	100–1000
<i>ortho</i> -Xylene	$Y = 7.3822x + 834.78$	0.998	8.0	100–1000

<sup>a</sup> Correlation coefficient.

<sup>b</sup> Limit of detection ( $\text{ng g}^{-1}$ ).

<sup>c</sup> Liner dynamic range ( $\text{ng g}^{-1}$ ).

<sup>d</sup>  $Y$  and  $x$  are peak area and concentration of the analytes ( $\text{ng g}^{-1}$ ), respectively.

### 3.8. Comparison of the proposed method with other methods

Efficiency of the proposed method was evaluated by comparing the LOD obtained by SPME-GC using proposed fiber and other fibers reported in the literature. The obtained results are summarized in Table 3. As it is seen the proposed SPME-GC method has a wider linear dynamic range (LDR) with a comparable LOD. On the other hand, simple and fast fabrication, no sample pretreatment as well as higher thermal stability are the main advantages of the proposed sol–gel based fiber in comparison to other reported SPME fibers for the determination of BTEX samples.

## 4. Analysis of real samples

To evaluate the efficiency of the proposed method in real samples, it was successfully applied to assay of BTEX in indoor air of chemical store as well as soil samples. Due to daily use of various BTEX compounds in our laboratory,

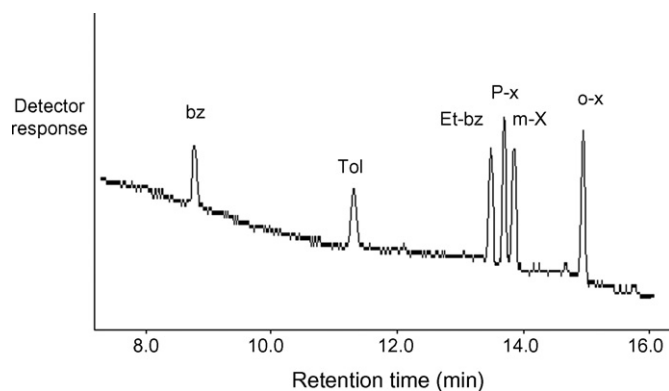


Fig. 8. Typical gas chromatogram of BTEX assay in headspace of soil sample.

Table 4  
Results obtained from the analysis of real samples

Compound	Concentration in soil sample (ng g <sup>-1</sup> )	R.S.D.%
Benzene	434 ± 26	5.99
Toluene	215 ± 17	7.91
Ethylbenzene	196 ± 14	7.14
<i>para</i> -Xylene	199 ± 10	5.03
<i>meta</i> -Xylene	204 ± 15	7.35
<i>ortho</i> -Xylene	163 ± 11	6.75

the concentration of BTEX components in indoor air is very unstable. However, the proposed fiber uses as an excellent sampling device for HS-SPME-GC determination. A typical chromatogram obtained from an indoor air sample is shown in Fig. 8.

To demonstrate the performance of the optimized SPME method, several polluted soil samples from ground of aromatic—Xylene plant in Bandar Emam Petrochemical Company (IRAN) were collected, and BTEX determination was done using proposed method. The obtained results are shown in Table 4. As can be seen, the amount of BTEX components can be accurately determined from proposed method with very low R.S.D. values.

## 5. Conclusions

In this study, a novel SPME fiber based on graphite (as solid sorbent) in inorganic polymeric matrix (sol-gel) coated on silica rod, is introduced and used for solid phase microextraction of BTEX from headspace of soil samples prior to capillary gas chromatographic analysis. A completely homogenous coating layer is easily formed on silica rod using 75% TBOT and 25% graphite. By applying 80 °C as microextraction temperature, 10 min as microextraction time and 240 °C as desorption temperature, excellent reproducible signals with R.S.D. about 2.44% for all BTEX compounds were obtained. The proposed SPME fiber has high thermal stability and can be used for more than 30 samplings. Proposed fiber affords a number of advantages in simplifying sample preparation, preconcentration and increasing reliability.

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