



Original Research Article

Simultaneous Extraction and Preconcentration of Benzene, Toluene, Ethylbenzene and Xylenes from Aqueous Solutions Using Magnetite–Graphene Oxide Composites

Mohammad Ameri Akhtiar Abadi¹, Mahboubeh Masrournia^{1,*}, Mohamad Reza Abedi²

¹Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

²Department of Applied Chemistry, Quchan Branch, Islamic Azad University, Quchan, Iran

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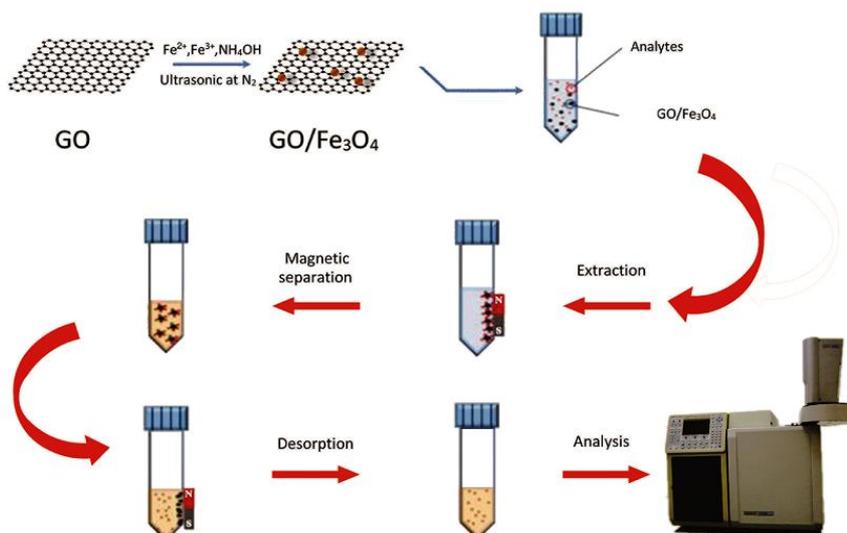
Magnetic dispersive micro-solid phase extraction

BTEX

ABSTRACT

For simultaneous extraction and determination of benzene, toluene, ethylbenzene, *m,p*-xylenes, and *o*-xylene (BTEX) gas chromatography -flame ionization detector (GC-FID) and magnetic dispersive micro-solid phase extraction were used for real water samples. To have an efficient sorbent, magnetic graphene oxide (Fe₃O₄@GO) was synthesized and utilized in the process of microextraction. The analytes were adsorbed by vortexing, supernatant was decanted using a magnet, and the sorbent was eluted using a proper solvent. Screening and optimizing significant variables in the process of microextraction were carried out following a two-stage approach, including Plackett-Burman screening design, and central composite design, accompanied by response surface analysis. The ranges of linear dynamic were 10 - 3000 ng mL⁻¹ and limits of detection were 3-10 ng mL⁻¹. The relative standard deviations of the intra-day and inter-day were blow 8.0 and 10.0% (n=5), respectively. The introduced technique was implemented in real water samples successfully, and the relative percentages of recovery determined for the spiked water samples at 200.0 ng mL⁻¹ ranged from 80.3 to 103.0%.

GRAPHICAL ABSTRACT



* Corresponding author: Mahboubeh Masrournia

✉ E-mail: masrour@mshdiau.ac.ir; mah.masrour@gmail.com

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Introduction

Among the most important aromatic hydrocarbons found in petroleum derivatives such as gasoline and other important industrial chemicals are benzene, toluene, ethylbenzene and three isomers of xylene (BTEX). They are extensively utilized for producing paints, rubber products, chemical intermediates, agricultural chemicals, etc. [1-3]. BTEX compounds affect the human body through gastrointestinal respiration and cause serious hazards such as mutagenesis causing skin cancer and kidney damage. [4-6]. Therefore, they are considered to be hazardous and priority compounds by the Environmental Protection Agency (EPA). They are also important pollutants of groundwater and surface water due to their high water solubility than other petroleum hydrocarbons and high shelf life in nature [7]. Therefore, developing simple, fast, and economic analytical methods with a small range of detection for measuring BTEX in nature is essential. The main step to analyze organic pollutants in environmental specimens is to extract the analytes from diverse matrices in an effective and rapid manner [8].

One of the best techniques is Solid phase microextraction (SPME) as it uses solvent-free, is simple, and well adapted to gas chromatography (GC) analysis of volatile and semi-volatile ingredients [9, 10]. However, this method has drawbacks such as stripping of coating, fiber breakage, and syringe needle [11]. Therefore, a novel solid phase micro extraction, like dispersive solid phase micro-extraction and magnetic dispersive solid phase micro-extraction, were produced to eliminate these drawbacks [12].

In the magnetic dispersive micro-solid phase extraction (MD- μ -SPE) method, magnetic adsorbent was dispersed directly in the sample solution using a vortex mixer. After the extraction of analytes, it is possible to separate the magnetic adsorbent from sample solution using an external magnet bare and then wash the analyte using a suitable solvent for further analysis [13]. This method provides a rapid and simple solution with a high extraction yield and pre-concentration.

Graphene is one of the carbon allotropes and a promising material in analytical chemistry [14]. Graphene oxide (GO) is one of the most important

graphene derivatives with significant characteristics including large surface, a chemical structure consisting of sp³ carbon domains surrounding the sp² carbon domain, and an easy and inexpensive production method [15-17]. Due to functional groups (e.g., hydroxyl, carboxylic) and epoxide groups on its surface, GO is highly hydrophilic and has good solubility and dispersion in any solvent, especially water [18]. Moreover, its surface can be modified to be used as an adsorbent and to increase the extraction efficiency by materials and other functional groups [19].

Today, many studies synthesize magnetic graphene oxide nano-composites (Fe₃O₄@GO) using the coprecipitation method or electrostatic interactions [20-22]. The Fe₃O₄@GO nanocomposite was prepared using the co-precipitation method. The magnetic adsorbent was readily collected by an external magnet. To find an optimum condition for experimenting with the proposed microextraction procedure, a design was implemented with two steps of experimental strategy, viz. (DOE) based Plackett-Burman (P-B) screening design and central composite design (CCD). The introduced technique was employed to extract and determine BTEX in real water samples. All processes were done using a gas chromatography-flame ionization detector (GC-FID).

Material and methods

Analytical reagents grade toluene, ethylbenzene, *o*-xylene, *m*-xylene, benzene, and *p*-xylene were procured from Merck (Darmstadt, Germany). Ferrous chloride tetrahydrate, ferric chloride, sodium hydroxide, sodium chloride, hydrochloric acid, and ammonium solution (25%) were supplied by Merck (Darmstadt, Germany) and 3 mg/mL GO dispersed solution was supplied by Rayan Fanavar Sina company (Tehran, Iran). Methanol and acetonitrile (HPLC grade) were supplied by Fluka (Buchs SG, Switzerland). To filter deionized water and other solvents, deionized water was supplied by Ghazi Company (Tabriz, Iran).

Stock and working Solutions

stock standard solution of BTEX (1000 mg L⁻¹) was obtained in methanol and kept at 4°C. The solutions needed for optimizing and calibrating the curves were obtained through diluting the stock standard

solutions using ultrapure water and kept at 40°C in dark.

Apparatus

To determine the analytes, the Varian 3800CP gas chromatography (Palo Alto, CA, USA) connected to a flame ionization detector was used. A DB-5 (5% biphenyl + 95% poly dimethyl siloxane) fused-silica capillary column (30 m × 0.25 mm i.d. And 0.25 m film thickness) was used to separate the analytes. Using the GC split valve (split ratio: 1/10) nitrogen was employed as a carrier gas with a constant flow rate (1.1 ml/min). At first, the column oven was at 45 °C for 1 min and then the column was heated until 90 °C at a rate of 10 °C /min. The temperature of the injector was 150 °C and the FID temperature remained at 200 °C. The total time for each GC run was 5.50 min.

Morphological examinations, were done using scanning electron microscopy (SEM, FESEM HITACHI S4160 Japan), and transmission electron microscopy (TEM) images were developed in TEM PHILIPS CM30 (Netherland). The GO and synthesized Fe₃O₄@GO were examined using a Fourier Transform Infrared (FT-IR) spectrometer (Bruker, Germany). The magnetic property was analyzed by a vibrating sample magnetometer (VSM) model AGFM (Alternating Gradient Force Magnetometer, Iran). The values of pH were modified and measured by a pH meter (Metrohm). A Vortex model 3 (IKA, Germany) was used for the desorption step.

Synthesis magnetic graphene oxide

To obtain the magnetic GO, chemical co-precipitation was carried out on Fe(III) and Fe(II) ions exposed to GO [23]. For this purpose, GO (0.9 g) was dispersed in 250 mL of water through sonication for 1 h so that the carboxylic acid groups were transferred to carboxylate anions. Afterwards, 0.04 mol of FeCl₃·6H₂O and 0.02 mol of FeCl₂·4H₂O were dissolved in 25 mL of water solution. The solution was added as drops to GO solution at ambient temperature in presence of nitrogen flow (40 mL/min) and fast vigorous stirring. Then, 25% ammonia solution was added using a droplet (10 drop per minute) so that the pH increased to 10. The stirring was performed at 65 °C for two extra hours. Afterwards, an external magnet was used to collect

the precipitate while decanting the solution. Doubled distilled water was used to wash the black precipitate and then the solution was dried in vacuum at 65 °C.

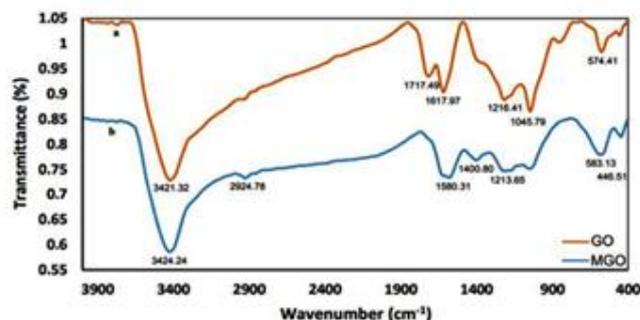


Figure 1: FTIR spectra of GO (a) and GO/ Fe₃O₄ (b)

Characterization of GO/Fe₃O₄

The FT-IR spectra were developed for both GO and Fe₃O₄@GO (Figure 1). The stretching vibrations of epoxy C-O (1216 cm⁻¹) and O-H band (3421 cm⁻¹) for GO appeared at 1213 cm⁻¹ and 3424 cm⁻¹ respectively for Fe₃O₄@GO. The band at 1717 cm⁻¹ is pertinent to the stretching of the C=O bond of carboxyl groups [24]. The peaks of Fe–O characteristic stretching vibration at 583 cm⁻¹ appeared in the curve b. The results indicated that the Fe₃O₄ NPs were properly decorated on surfaces of GO [25]. The morphology and structure of GO and Fe₃O₄@GO were studied using SEM and TEM. The images clearly showed Fe₃O₄@GO and deposition of Fe₃O₄ nanoparticles on the GO sheets (Figure 2). The magnetization hysteresis loop of the composite was an S-shape curve, suggesting the superparamagnetic nature of the composite (Figure 3). The saturation of the magnetization value of Fe₃O₄@GO nanocomposite (10.24 emu/g) was adequate to make sure that the separation of the compounds from solutions would be done easily and rapidly.

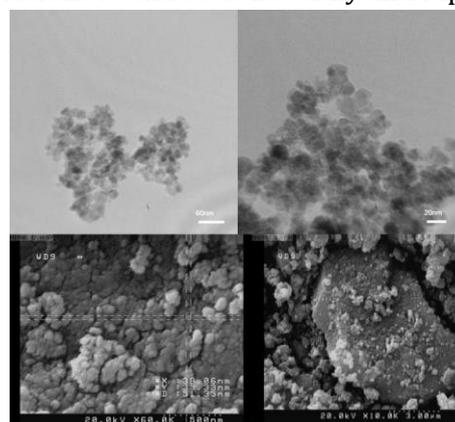


Figure 2: TEM (top) and SEM (bottom) images of GO/ Fe₃O₄ at different magnifications

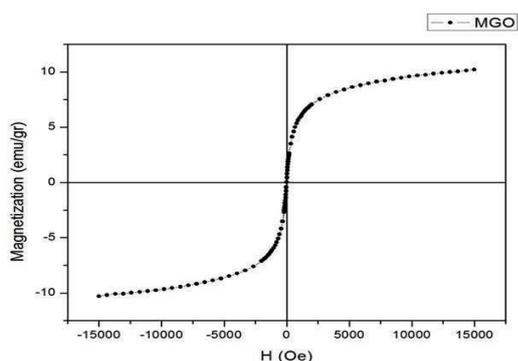


Figure 3: Hysteresis loops of GO/Fe₃O₄ anocomposite

Extraction procedure

The extraction process was as follows: An appropriate and optimized amount of Fe₃O₄@GO was permeated in test tube containing 20.0 mL of 1.0 µg/mL sample solution (with proper pH) and vortexed vigorously for 5.0 minutes. Then, an external neodymium magnet was brought near the tube wall to separate the analyte loaded Fe₃O₄@GO from the solution to cast off the supernatant. Then, 0.2 mL of methanol (desorption solution) was added to the tube and vortexed vigorously for 6.0 min to elute analytes. Moreover, magnetic nano sorbents were isolated by the magnet and eventually, 1.0 µL of the organic solvent was extracted into the GC microsyringe for reinjection into the GC-FID and analyses.

The average result obtained from the three repetitions of experiments was used in calculations.

Result and discussions

Optimization of the microextraction procedure

To obtain maximum efficiency of extraction and find out the best condition for measuring BTEX compounds, several effective parameters in the extraction were examined including the salt amount, extraction time, desorption solvent volume, desorption time, sorbent amount, the composition of desorption solution, and volume of the sample.

A key parameter in the extraction recovery is the choice of solvent elution type. For this reason, the desorption of the analyte from the magnetic absorbent was examined by different organic solvents, among which methanol was adopted as the desorption solvent for BTEX compounds extraction owing to its highest peak area (Figure 4).

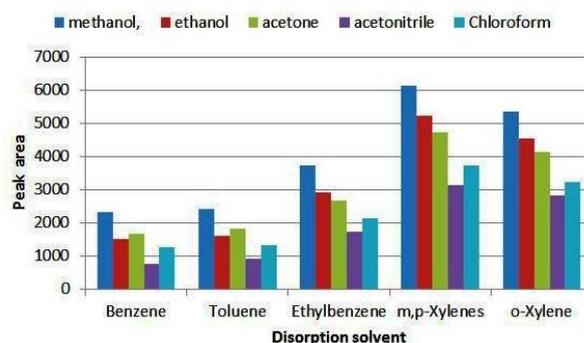


Figure 4: Effect of type of desorption solvent on the extraction

Table 1: Factors, codes, levels and symbol in the Plackett-Burman design matrix

Factors							Levels						
							Low (-1)		High (+1)				
(F1) Amount of sorbent (mg)							5		20				
(F2) Extraction time (min)							1		10				
(F3) Desorption time(min)							1		10				
(F4) Salt amount [% w/v]							1		20				
(F5) sample volume (mL)							5		25				
(F6) Desorption solvent volume (µL)							200		1000				
Runs	F1	F2	F3	F4	F5	F6	TCPA benzene	TCPA toluene	TCPA ethylbenzene	TCPA m,p-xylenes	TCPA o-Xylene		
1	-1	+1	+1	-1	+1	-1	3768.1	3928.5	7645.9	6833.2	4687.3		
2	-1	-1	-1	+1	+1	+1	5536.1	8232.5	13759.7	11702.4	8638.3		
3	+1	+1	-1	+1	-1	-1	5929.5	8912.4	13768.5	9303.5	10341.9		
4	+1	-1	+1	+1	-1	+1	8423.7	13889.5	20012.2	23841.4	21408.8		
5	-1	-1	+1	+1	+1	-1	4235.2	5270.1	11903.6	8821.1	5939.2		
6	-1	+1	+1	+1	-1	+1	6783.7	10479.5	16311.5	18468.3	14165.4		
7	+1	-1	+1	-1	-1	-1	8002.2	10126.2	17200.4	20143.3	15619.7		
8	+1	+1	-1	+1	+1	-1	4163.8	5431.8	11278.3	7926.8	6115.5		
9	+1	+1	+1	-1	+1	+1	7041.5	11377.3	17090.4	19704.4	14645.8		
10	+1	-1	-1	-1	+1	+1	6342.5	10072.5	16123.5	15697.6	11243.6		
11	-1	+1	-1	-1	-1	+1	6006.8	9496.2	15098.6	16566.2	11989.6		
12	-1	-1	-1	-1	-1	-1	4795.1	6541.5	11311.3	12489.3	8348.2		

Screening design

The design of experiment (DOE) was based on the Plackett-Burman (P-B) screening design and central composite design (CCD) was exerted to achieve significant parameters and interacting variables. Mini Tab 17.00 was used for the investigation of experimental data and generation of the DOE.

To find factors with the greatest impact on microextraction and to decrease the key factors count in the microextraction, P-B design, including 12 experiments, was randomly utilized to remove uncontrolled variables [26]. Six screened variables were salt amount, extraction time, desorption solvent volume, desorption time, sorbent amount, and volume of the sample. A matrix of the P-B design at three levels of low (-1), central (0), and high (+1) was determined for each variable based on initial experiments listed in Table 1. The total chromatographic peak area (TCPA) experiment with three replicates was performed as a response for each experiment. According to the result of ANOVA computation, when p-value of a main factor is less than 5% (at 95% confidence level), the factor is statistically significant. Moreover, Pareto chart was utilized to compare and examine the main factors where the results of the DOE normalization were analyzed at 95% confidence level (Figure 5 a–e). In this chart, the vertical line represents 95% confidence level and the bar length is proportionate to the absolute value of the main effect [27].

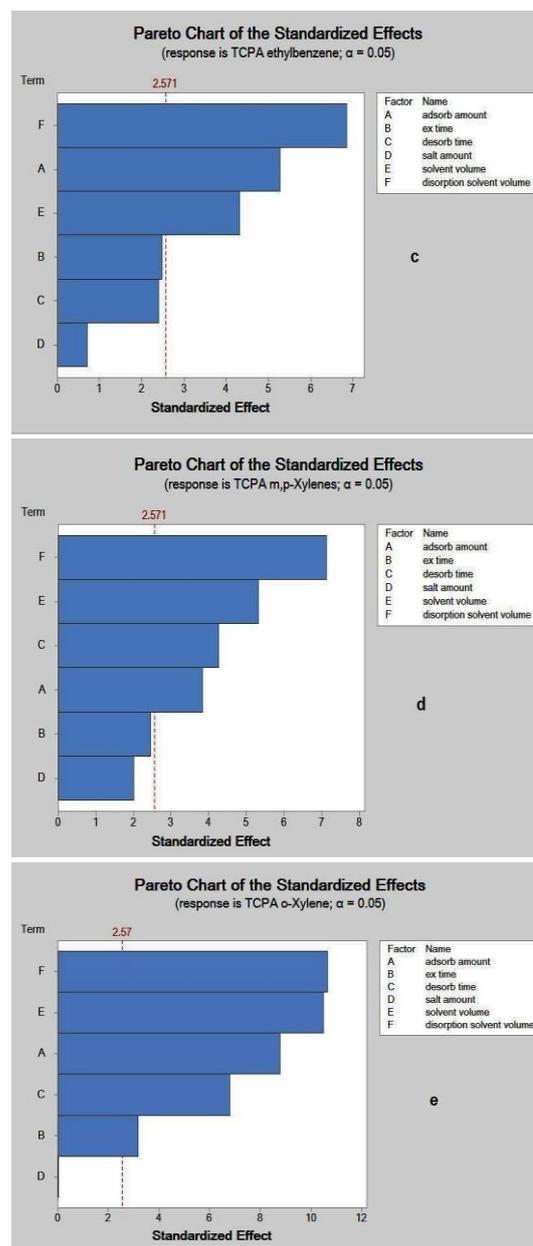
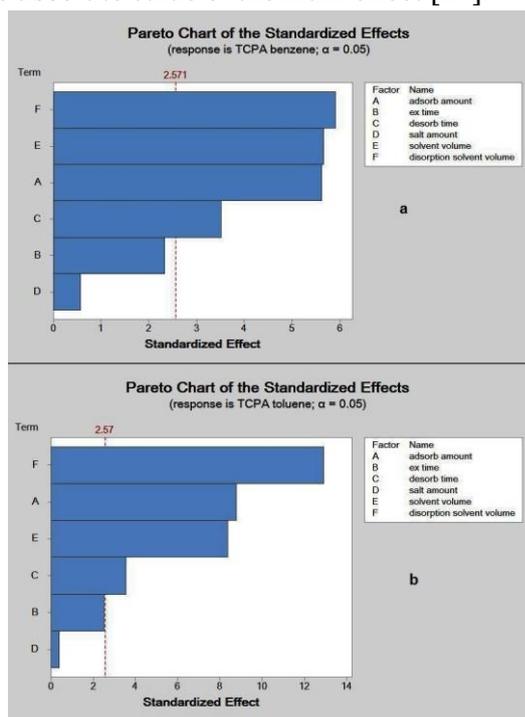


Figure 5: (a-e) Standardized main effect Pareto charts for the Plackett–Burman design for benzene, toluene, ethylbenzene, *m,p*-xylenes, and *o*-Xylene. Vertical line in the chart defines 95% confidence level.

In addition, a factor is significant when its bar length crosses the reference line (t-value) on the chart. Therefore, four factors including sample volume, desorption solvent volume, desorption time, and sorbent amount were recognized as significant factors in the MD- μ -SPE method, of which desorption solvent volume had the highest impact on the response relative to the other three factors. Other non-significant factors, including extraction time and salt amount, were fixed at 5.0 min., and 1.0% w/v, respectively.

Optimization design

P-B design, including the sample volume, desorption solvent volume, desorption time, and sorbent amount, as the significant variables, was used to make sure the optimization status of the four factors adopted from the first screening.

Second-order CCD was used to have more optimization by employing a response surface methodology (RSM). The points count in CCD is an axial runs of $2k$, factorial run of $2k$, and C_0 center point runs [27].

Thereby, $N=2k+2k+C_0$ yields the total experimental runs (N) of CCD, where k and C_0 represent the numbers of variables and the count of center points, respectively [27]. The CCD experiments were done randomly to reduce the influences of uncontrolled variables. The CCD design contains 16 cube points, seven center points in a cube, eight axial points, and zero center point in axial with $\alpha=2$ (selected to establish rotatability conditions), with 31 randomized runs in sum.

It is possible to create a second-order polynomial model through the analysis of variance, which demonstrates the interaction terms of the main factors and that of the first-order quadratic and response. The following represents the regression Equation (1):

$$R = \beta_0 + \beta_1 F_1 + \beta_2 F_2 + \beta_5 F_5 + \beta_6 F_6 + \beta_{11} F_1^2 + \beta_{22} F_2^2 + \beta_{55} F_5^2 + \beta_{66} F_6^2 + \beta_{12} F_1 F_2 + \beta_{15} F_1 F_5 + \beta_{16} F_1 F_6 + \beta_{25} F_2 F_5 + \beta_{26} F_2 F_6 + \beta_{56} F_5 F_6 \quad (1)$$

where β_0 stands for the intercept and β_1 - β_{56} represent the regression coefficients (non-coded units).

The adjusted R^2 values are 91.12, 90.38, 94.27, 93.88, and 91.72 for the extraction of toluene, ethylbenzene, benzene, *m,p*-xylenes, and *o*-xylene, respectively (at 95% confidence level), meaning that the polynomial model equation corresponds perfectly to the response variables.

An important part of the ANOVA result is the lack of fit (LOF) that can verify the suitability of the model for responses. According to the F-test, when the LOF is not a significant variable, the models have good fit with the responses, for which the P-value of LOF is above the selected α -level [28, 29]. For the extraction of toluene, ethylbenzene, benzene, *m,p*-xylenes, and *o*-xylene, the P-value of LOF were 0.21,

0.85, 0.20, 0.98, and 0.38, respectively ($0.05 < \alpha$), indicating that the models are well fit with the responses.

Desorption solvent volume (F_6) for *m,p*-xylenes, ethylbenzene, and *o*-xylene and the desorption time (F_3) for benzene and toluene has the highest regression coefficients. That is, the main factors are the most important variables with a negative value. Compared with the second order regression coefficients (interaction between the same factors), the interaction of $F_6 * F_6$ for benzene and *m,p*-xylenes have the highest positive values, and the interactions of $F_3 * F_3$ for toluene and $F_1 * F_1$ for ethylbenzene and *o*-Xylene have the highest negative values, respectively. In addition, quadratics regression coefficients (interaction between two different factors) demonstrated the interaction between the desorption time and sample volume ($F_3 * F_5$) for ethylbenzene, *m,p*-xylenes, and *o*-xylene. And the amount of sorbent and desorption solvent volume interaction ($F_1 * F_6$) had the highest negative values for benzene and toluene.

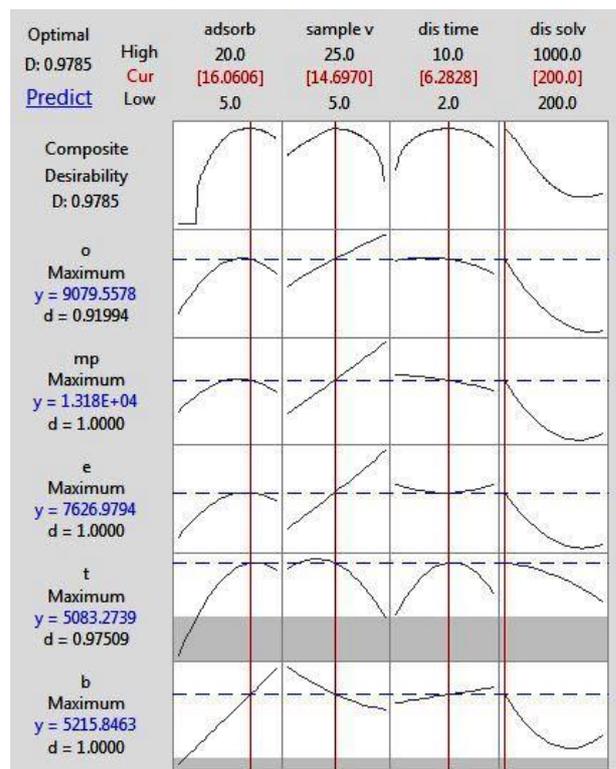


Figure 6: Optimization plot Profiles toluene, ethylbenzene, benzene, *m,p*-xylenes, and *o*-xylene, for predicted values for TCPA

By achieving the fitted model to extract toluene, ethylbenzene, benzene, *m,p*-xylenes, and *o*-Xylene, the optimization plot (Figure 6) can be employed to

find the effect of a change in each factor on the responses and composite desirability of responses. The highest response to the goal and the best response for the analytes were used to draw the optimization plots (Figure 6). Figure 6 shows that the maximum responses are 5083.2, 7626.9, 5215.8, 13180.04 and 9079.5, with desirability levels of 0.9, 1, 1, 1 and 0.9 for extraction of toluene, ethylbenzene, benzene, *m,p*-xylenes, and *o*-xylene, respectively. Based on Figure 6, desorption solvent volume (200.0 μ L), desorption time (6.0 min), sorbent amount (16.0 mg), and sample volume (15.0

mL) were selected as the optimum values for the significant factors.

Analytical performance of method

Analytical figures of merit for validation and the practical use of the MD- μ -SPE method with the optimum extraction conditions were calculated to find the analytes inclusive, enrichment factor (EF), limit of detection (LOD), linear dynamic range, limit of quantification (LOQ), and relative standard deviations (RSD%) (Table 2).

Table 2: Figures of merit for the developed method

Analyte	Linearity range (ng/ml)	R ²	LOD (ng/ml)	LOQ (ng/ml)	RSD% (n = 5)		EF ^a
					Inter day	intra day	
benzene	50-3000	0.9985	10	50	10.0	8.0	8.4
Toluene	50-3000	0.9971	10	50	6.3	5.0	7.5
ethylbenzene	10-3000	0.9974	3	10	7.0	5.1	7.6
<i>m,p</i> -xylenes	10-3000	0.9985	3	10	8.5	7.1	9.0
<i>o</i> -Xylene	10-3000	0.9981	3	10	8.0	6.2	8.0

^aEF was calculated at the concentration level of 2000 ng/mL for each analyte

The LOD and LOQ were obtained as $S/N = 3$ and $S/N = 10$, respectively. The values of LOD and LOQ were between 3–10 ng mL⁻¹ and 10–50. ng mL⁻¹, respectively. From the calibration curves, linearity was observed between range 10–3000 ng mL⁻¹ with $R^2 > 0.9971$. The precision of extractions (intraday and inter-day) was examined using five-replicate experiments for the samples spiked with 1000 ng mL⁻¹ of BTEX compounds on the same and three days afterward. The RSDs of the intraday and inter-days were less than 8.0 and 10.0 (n=5), respectively, for the analytes.

The enrichment factor (EF) is the ratio of the analyte concentration in the methanol phase (C_0) to the initial analyte concentration in the aqueous sample solution (C_{aq}), which was obtained as Eq.2.

$$EF = C_0 / C_{aq} \quad \text{Eq.2.}$$

where C_{aq} is the analyte concentration in the sample solution before the analyte extraction in the sample solution and C_0 was determined from calibration curves using the strand solution injected directly.

Comparison of the MD- μ -SPE and other extraction techniques

A comparison was made between the proposed technique and previous studies (Table 3) based on the BTEX analysis in water samples including headspace using a needle trap device (HS-NT) [34], solid phase extraction (SPE) [30], single drop microextraction (SDME) [31], direct immersion single drop microextraction (DI-SDME) [32], magnetic solid phase extraction (MSPE) [37], hollow fiber liquid phase microextraction (HF-LPME) [33], and solid phase microextraction (SPME) [3, 35, 36] procedures. Apparently, the LODs and RSDs found here were better than or comparable with those of the other methods. This is in spite of the point that some have used MS detection [3, 36, 37]. In addition, the linearity of the proposed technique is more than other MSPE [37], SPE [30], and SPME [35] procedures. However, the proposed technique is simpler, cheaper, and faster than the other methods.

Table 3: The comparison of the proposed method with other methods applied for the determination of BTEX in water samples

Extraction Procedure	Sorbent/fiber	Linearity (ng/mL)	LOD (ng/mL)	RSD (%)	Ref.
SPE-GC-FID ^a	C18	8000–35000	104–372	3.0–3.5	[30]
SDME-GC-FID ^a	2-octanone	10–20000	0.8–7	1.8–2.4	[31]
DI-SDME-GC-FID ^a	n-octanol	50-20000	5-10	5.0-8.0	[32]
HF-LPME-GC-FID ^a	1-octanol	50-20000	5-30	2.0-4.6	[33]
HS-NT-GC-FID ^a	carboxen/PDMS ^a	50-300	10-25	1.0-8.0	[34]
SPME-GC-MS ^a	Co ₃ O ₄ nanostructure fiber	10-500000	1-11	7.5-11.2	[3]
HS-SPME-GC-FID ^a	Anodized aluminum coated with titania sol-gel	10-800	5.6-12.4	4.0-8.2	[35]
HS-SPME-GC-MS	PDMS on titanium wire	10-25000	0.75-10	1.7-8.4	[36]
MSPE-GC-MS ^a	Zeolite/iron oxide	1-100	0.3-3	8.0-11.0	[37]
MD-μ-SPE-GC-FID	GO/Fe ₃ O ₄	10-3000	3-10	5.0-8.0	This work

^a SPE: solid phase extraction, SDME: single drop microextraction, DI: direct immersion, HF-LPME: hollow fiber liquid phase microextraction, HS-NT: headspace using a needle trap device, HS: headspace, SPME: solid phase microextraction, MSPE: magnetic solid phase extraction, PDMS: polydimethylsiloxane

Real sample analysis

The introduced technique was used to analyze BTEX in different water matrices including deionized water, wastewater samples, and river water. The deionized water sample was obtained

from Ghazi Company (Tabriz, Iran). The river water sample was supplied from a nearby river and wastewater was supplied by a research chemical institute, all located in Bojnourd, Iran.

Table 4: Analysis of real samples

Analyte	Deionized water sample			River water			Waste water		
	Mean ^a (ng mL ⁻¹)	RSD (%)	Relative recovery (%) ^{b,c}	Mean ^a (ng mL ⁻¹)	RSD (%)	Relative recovery (%) ^{b,c}	Mean ^a (ng mL ⁻¹)	RSD (%)	Relative recovery (%)
Benzene	NQ	8.1	98.3	NQ	9.0	92.2	3.5×10 ²	9.0	82.5
Toluene	NQ	5.4	101.0	NQ	5.2	96.4	3.2×10 ²	6.2	83.5
ethylbenzene	NQ	5.0	100.3	NQ	6.0	103.0	NQ	7.0	88.2
m,p-xylenes	NQ	7.3	99.1	78	8.3	87.3	3.3×10 ²	9.3	80.3
o-xylene	NQ	6.3	100.0	81	8.2	95.5	2.7×10 ²	7.1	84.5

NQ: not quantified.

^a Founded concentration (ng mL⁻¹).

^b Real samples spiked with 200.0 ng mL⁻¹.

^c Relative recovery (%) = (the amount found in the spiked sample – the amount found in the sample/the amount added) × 100

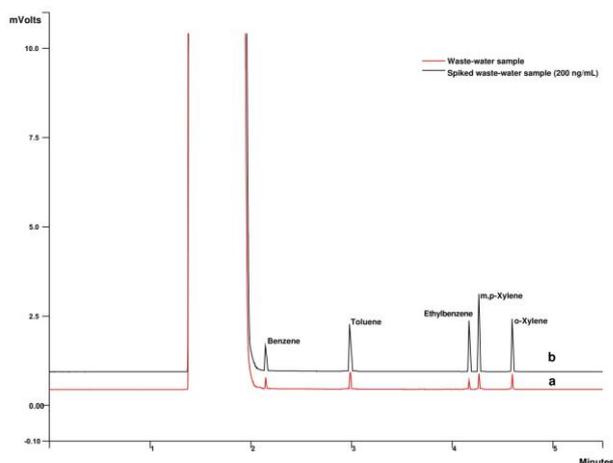


Figure 7: Chromatogram of BTEX compounds in (a) waste water sample and (b) waste water spiked with 200 ng mL⁻¹ of each analyte

The samples contained some of the BTEX compounds, while some were not found because of very low concentrations (lower than LOQs) (Table 4). To examine the established method performance, 200.0 ng mL⁻¹ of each BTEX compound was spiked in the water samples. Table 3 lists the mean recoveries (n = 3) and determination precisions. The recovery ranges were 80.3-103.0% and the precisions (RSD) were below 9.3%. The accuracy of BTEX analysis in the real water samples was supported with the proposed technique. A normal chromatogram developed for BTEX in the real wastewater sample is shown in Figure 7.

Conclusion

The MD- μ -SPE using Fe₃O₄@GO as a sorbent mixed with GC-FID was effectively used to separate and detect trace amounts of BTEX in real water samples. The Advantages of this proposed method include environmentally friendly one, cost-effectiveness, low detection limit, short extraction time, and simple operation with a high pre-concentration factor. Multivariate techniques including placket burman design and central composite design were utilized to check and optimize main variables affecting the micro-extraction of BTEX. Under adjusted conditions, the proposed MD- μ -SPE technique demonstrated high sensitivity, fast, simple, reproducible and accurate satisfactory recovery in spiked samples to analyze BTEX in real water samples.

Conflict of interest

The authors have no conflict of interests.

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