



Optimization of headspace solid phase microextraction based on nano-structured ZnO combined with gas chromatography–mass spectrometry for preconcentration and determination of ultra-traces of chlorobenzenes in environmental samples

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ABSTRACT

In this study, a simple, novel and efficient preconcentration method for the determination of some chlorobenzenes (monochlorobenzene (MCB), three isomeric forms of dichlorobenzene (diCB), 1,3,5-trichlorobenzene (triCB) and hexachlorobenzene (hexaCB)) has been developed using a headspace solid phase microextraction (HS-SPME) based on nano-structured ZnO combined with capillary gas chromatography–mass spectrometry (GC–MS). ZnO nanorods have been grown on fused silica fibers using a hydrothermal process. The diameter of ZnO nanorods was in the range of 50–80 nm. The effect of different variables on the extraction efficiency was studied simultaneously using an experimental design. The variables of interest in the HS-SPME were stirring rate, desorption time and temperature, ionic strength, extraction time and temperature. For this purpose, a multivariate strategy was applied based on an experimental design using a Plackett–Burman design for screening and a Box–Behnken design for optimizing of the significant factors. The detection limit and relative standard deviation (RSD) ($n=5$) for the target analytes were in the range of 0.01–0.1 ng L⁻¹ and 4.3–7.6%, respectively. The developed technique was found to be successfully applicable to preconcentration and determination of the target analytes in environmental water and soil samples.

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1. Introduction

Chlorobenzene compounds, as a main class of environmental pollutants, have been widely used as industrial solvents, pesticides, dielectric fluids, deodorant and chemical intermediates [1,2]. They can enter the aquatic environment through solid and liquid effluents and atmospheric discharges [3]. They have toxic characteristics and potential harmfulness to the receiving aqueous environment [4]. Therefore, they are identified as priority pollutants by EPA [5]. The excessive exposure to these compounds can exert dangerous effects on the central nervous system, irritation of the eyes, irritation of the upper respiratory tract, hardening of skin, and hematological disorders including anemia [6]. Therefore, the separation and analysis of traces and ultra-traces of chlorobenzenes in environmental samples is important.

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Chlorobenzenes are usually determined by gas chromatography–electron capture detector (GC–ECD) or (GC–MS) gas chromatography–mass spectrometry [6–9]. However, low concentration and matrix interference are two problems in the determination of chlorobenzene compounds. Thus, beside of developments in modern analytical instruments, sample preparation processes are needed for the extraction and preconcentration of the desired components prior to determination. In the literatures, several sample treatment methods such as liquid–liquid extraction (LLE) [10], solid phase extraction (SPE) [11], liquid phase microextraction (LPME) [12–16] and solid phase microextraction (SPME) [17,18] have been developed to solve these problems. Each of them has advantages and disadvantages and should be chosen according to the analytical problem.

Solid-phase microextraction (SPME), introduced by Pawliszyn and co-workers [19,20], is a fast, simple, efficient, inexpensive and solvent free extraction technique [21]. SPME allows complete elimination of organic solvents in the pretreatment step, decreasing the steps for sample preparation and has become an accepted method for the determination of volatile and semi-volatile substances. Also, it could be easily coupled with different

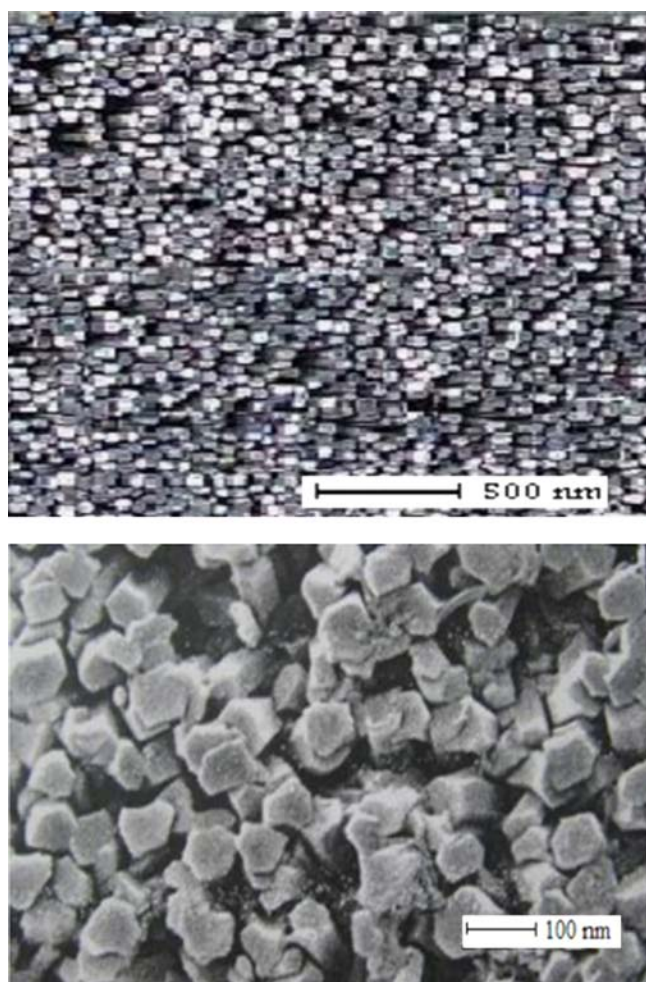


Fig. 1. Longitudinal SEM image of ZnO nanorod coated fused silica by hydrothermal process from solution containing of 0.01 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMT for 4 h at 80 °C.

determination techniques such GC and HPLC. There are different types of commercial SPME fibers; however, they usually have drawbacks of low thermal and chemical stability besides of the high cost and poor reusability. Recently some researchers have used nano-metal oxides as a coating of SPME fibers for analyte extraction and preconcentration in biological and environmental analysis [22–26]. Compared with traditional SPME fibers, nano-materials possess large surface area and high diffusion rate, which may result in high extraction efficiency and rapid equilibrium establishment. It was reported that ZnO nanostructured can be easily synthesized in various shapes and sizes using different chemical method [27–30]. The synthesized ZnO nanostructures as a coating of fibers in SPME have some advantages such as low cost, good conductivity, high stability in acidic media and proper adsorption properties [24]. Therefore, this fiber could be used to adsorption of a wide range of organic compounds with suitable sensitivity and high reproducibility.

The aim of this study was to develop a simple, highly effective and sensitive method for the preconcentration and determination of some chlorobenzene compounds in environmental samples. Therefore, the headspace solid phase microextraction based on the nanostructured ZnO as a coating followed by GC–MS was applied for this purpose. The experimental variables such as stirring rate, desorption time and temperature, ionic strength, time and temperature of extraction were optimized by a multivariate strategy based on an experimental design using a Plackett–Burman design

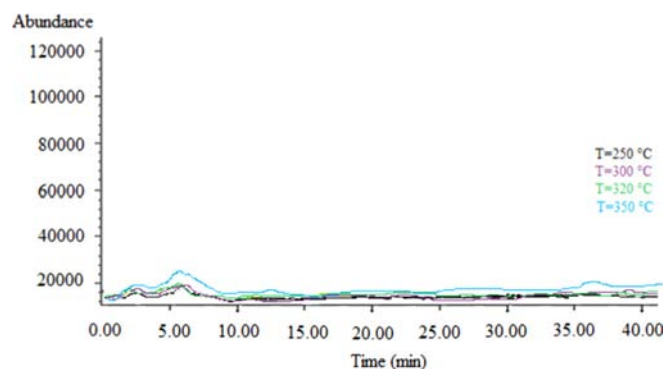


Fig. 2. Chromatograms showing baselines during conditioning of ZnO coating at 250, 300, 320 and 350 °C.

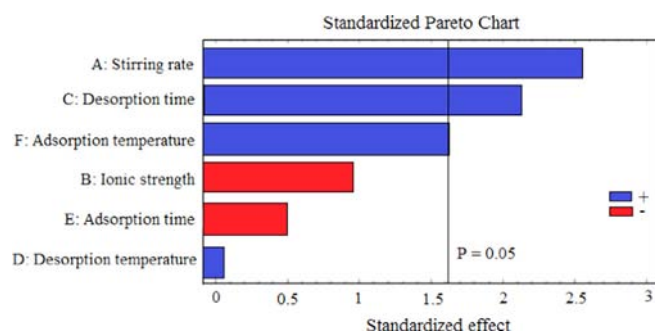


Fig. 3. Standardized ($P=0.05$) pareto chart, representing the estimated effects of parameters obtained from the Plackett–Burman design for CBzs compounds.

(PBD) for screening and a Box–Behnken design (BBD) for optimizing of the significant factors. The optimized procedure was applied to determine chlorobenzene compounds in environmental water and soil samples.

2. Experimental

2.1. Reagents and analytical standards

All chemicals were of analytical reagent grade. Reagent grade water was collected from a Milli-Q water purification system (Millipore, Bedford, MA, USA). The studied CBzs (monochlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,3,5-trichlorobenzene and hexachlorobenzene) were purchased from Sigma Aldrich (St. Louis, MO, USA). All of the organic solvents such as methanol and acetone were obtained from Merck (Darmstadt, Germany). Zinc Nitrate and hexamethylenetetramine (HMT) were also purchased from Fluka. Sodium chloride (Merck, Darmstadt, Germany) was used to adjust the ionic strength of the aqueous samples. The SPME syringe and fused silica optical fiber were purchased from Azar Electrode Company (Tabriz, Iran) and Poly micro Technologies Inc. (Tucson, USA), respectively. Standard stock solutions of 500 mg L^{-1} of target compounds were prepared in methanol. All solutions were stored in the dark at 4 °C. Working solutions were prepared by dilution of standard stock solutions with deionized water.

2.2. Instrumentation

GC–MS separations were carried out by an Agilent (Santa Clara, CA, USA) Technologies 6890N Network GC System and Agilent Technologies 5973 Network Mass Spectrometer. GC was equipped with DB-624 fused silica capillary column ($60 \text{ m} \times 0.25 \text{ mm}$

i.d. \times 1.40 μm film thickness). The column oven was initially held at 60 °C for 1 min, raised to 200 °C at a rate of 5 °C min^{-1} and finally raised to 250 °C at 10 °C min^{-1} and held for 10 min. GC–MS interface temperature was 250 °C, MS source temperature 250 °C and MS quadrupole temperature 150 °C, respectively. Scan m/z range was 30–300. Carrier gas was helium and its flow rate was 1.0 mL min^{-1} . Scanning electron microscopy (SEM) was employed to confirm the morphology of the coating as well as to ensure the required size of ZnO coatings on the surface of fused silica fibers. SEM micrographs were obtained using a Philips (Oregon, USA) XL30 instrument. Stirring of the solutions was carried out by a Heidolph MR3001 magnetic stirrer (Schwabach, Germany). A water bath was used for controlling the sample temperature.

2.3. Preparation of environmental samples

The environmental samples of well, river and tap water from the north of Iran, Caspian sea water, waste water and soil agricultural samples were analyzed by HS–SPME combined with GC–MS. Each water sample was filtered, in order to remove any suspended material. Before the analysis, the water samples were stored in a dark place at 4 °C in an amber glass bottle that was previously rinsed with ultra-pure water and methanol. All samples were stored at 4 °C in the darkness until analysis. To carry out the HS–SPME procedure, 10 mL of water or 2.0 g of soil samples were placed into a 15 mL glass vial. For soil samples, 10 mL distilled water were added, and the vial was then placed under magnetic stirring (1300 rpm) for 30 min for homogenization. The analytical method developed was directly applied for determination of CBzs compounds in water samples.

2.4. SPME fiber preparation

The fused silica fibers were cut into 40 mm lengths pieces followed by removing their polymeric cover by immersing them into acetone for 5 min. They were then sonicated in diluted hydrochloric acid (1 M), acetone and water, respectively. The growth solution was prepared by modifying the method reported by Vayssiers [30]. To obtain the desired morphology and alignment of ZnO nanorod, the effective parameters such as precursor concentration of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMT, the position of the substrate fiber, reaction time and temperature should be optimized during the synthesis process. Based on the previous reports [30–32] and our experiments in the lab to achieve the optimum condition, the fibers were vertically kept in a 100 mL aqueous solution of 0.01 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMT for 4 h at 80 °C. After completion of the growth, the prepared fibers were rinsed by Milli-Q water in an ultrasonic cleaner.

2.5. HS–SPME procedure

Extraction of CB compounds was performed by using the prepared SPME fibers via the headspace extraction method from a sample solution. The volume of 10 mL of working solution spiked with 10 ng L^{-1} of each analyte or aqueous samples were placed in a 15 mL conical flask together with a glassy stir bar. Then the vial was rapidly sealed with a silicon-rubber septum and an aluminum cap. The fiber was exposed to the headspace of solution by piercing the septum with the SPME needle assembly and then depressing the plunger. After the extraction, the fiber was transferred to the GC–MS port for desorption of analytes and further analysis.

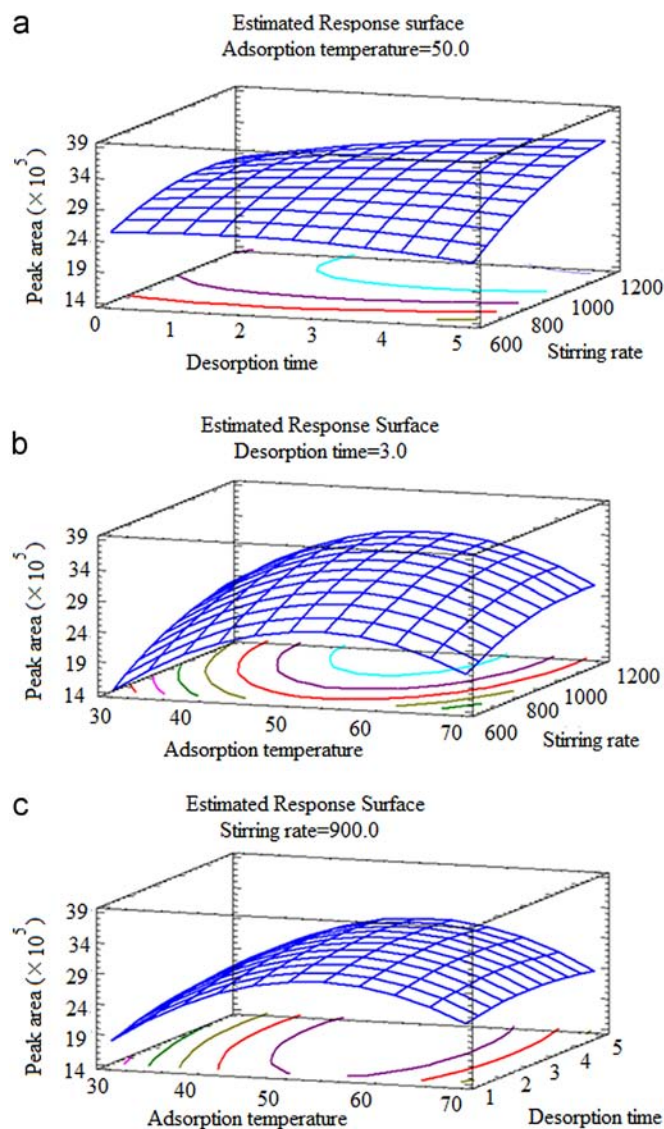


Fig. 4. Estimated response surface by plotting peak area versus (A) desorption time and stirring rate, (B) adsorption temperature and stirring rate, and (C) adsorption temperature and desorption time, with related contours.

Table 1

Analytical performance of the developed method for the preconcentration and determination of chlorobenzene compounds.

Analytes	LOD ^a (ng L^{-1})	R^{2b}	DLR ^c (ng L^{-1})	RSD ^d (%) ($n=5$)			
				Intra-day		Inter-day	
				One fiber	Fiber to fiber	One fiber	Fiber to fiber
MCB	0.01	0.99	0.05–1000	3.5	3.6	3.9	3.7
1,2-diCB	0.01	0.99	0.05–1000	4.8	4.1	4.0	4.2
1,3-diCB	0.012	0.99	0.05–1000	3.8	4.3	4.1	4.8
1,4-diCB	0.01	0.98	0.05–1000	4.2	4.6	3.6	4.0
1,3,5-triCB	0.015	0.99	0.06–1000	3.9	4.5	4.1	3.6
HexaCB	0.1	0.98	0.3–1500	4.4	4.1	3.8	3.9

^a Limit of detection.

^b Correlation of determination.

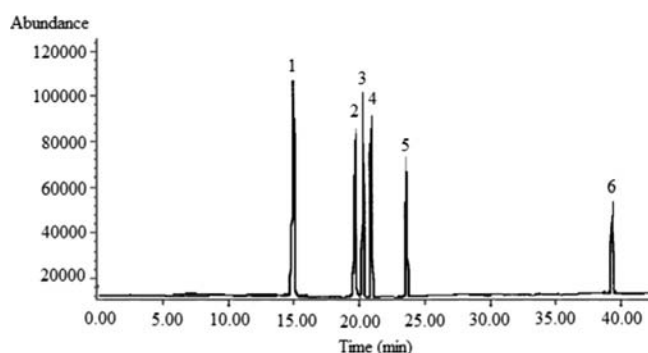
^c Dynamic linear ranges.

^d Relative standard deviation (spiked with 10 ng L^{-1} of each analytes).

Table 2The results of HS-SPME-GC-MS for analysis of CBzs in various environmental water samples ($n=5$).

Analytes	River water		Caspian sea water		well water		Waste water (1)		Waste water (2)		Soil sample (1)		Soil sample (2)	
	Found ^a	R (%) ^b	Found	R (%)	Found	R (%)	Found	R (%)	Found	R (%)	Found	R (%)	Found	R (%)
MCB	n.d.	102.7	n.d.	100.0	1.2	102.6	10.5	99.5	22.2	102.1	n.d.	98.3	9.8	100.4
1,2-diCB	n.d.	107.5	n.d.	98.3	1.8	98.6	18.0	103.2	27.9	99.9	n.d.	99.4	5.3	99.8
1,3-diCB	n.d.	99.4	n.d.	100.5	0.7	105.5	19.8	94.9	18.6	97.5	n.d.	105.4	n.d.	98.9
1,4-diCB	n.d.	101.1	n.d.	93.7	0.4	99.3	17.6	106.3	20.9	100.0	n.d.	100.8	1.7	97.9
1,3,5-triCB	n.d.	100.0	n.d.	91.0	0.6	99.8	9.3	104.1	14.3	98.4	n.d.	101.2	1.3	101.2
HexaCB	n.d.	98.8	n.d.	102.9	0.3	100.4	1.7	96.5	2.9	99.1	n.d.	106.7	n.d.	89.4

n.d.—Not detected.

^a The concentrations are as ng L^{-1} and ng kg^{-1} in water and soil samples, respectively.^b Recoveries were determined by spiking of 10^2 ng L^{-1} of standard solutions.**Fig. 5.** GC-MS chromatogram of Caspian Sea water sample spiked with 100 ng L^{-1} of CBzs after the HS-SPME at optimum conditions. (1) MCB, (2) 1,3-diCB, (3) 1,4-diCB, (4) 1,2-diCB, (5) 1,3,5-triCB and (6) hexaCB.

2.6. Optimization strategy of HS-SPME

There are several factors such as stirring rate, desorption time and temperature, ionic strength, time and temperature of extraction that affect the extraction process. In order to obtain the optimum conditions of HS-SPME for extraction of the CBzs from different samples, a Plackett–Burman design was applied for screening of the variables. After choosing the significant variables, in order to optimize and investigate the interaction between variables, a Box–Behnken design (BBD) was performed and a response surface equation was derived. The experimental design matrix and data analyses were performed using the STAT-GRAPHICS plus 5.1 software.

3. Results and discussion

3.1. Characterization of the fiber

3.1.1. Surface structure

Scanning electron micrographs (SEM) were used to investigate the surface characteristics of ZnO coating. The material was composed of arrayed ZnO nanorods coating on fused silica with diameter in the range of 50–80 nm. Therefore, applying this procedure resulted in the achievement of a high effective surface area for the remarkable capability for adsorbing analytes from the different matrix of samples [24,30,32,33]. Fig. 1 shows the longitudinal SEM image of ZnO nanorod coated fused silica.

3.1.2. Thermal stability and lifetime of the coating

Since the analytes extracted by the fiber are desorbed at an elevated temperature, the capability of resistance to high temperature is very important in terms of practical application.

In order to investigate the thermal stability of the ZnO coating, the baselines of the fiber were recorded at different desorption temperatures in the range of 250–350 °C. The obtained results showed that the coating of the fiber can withstand desorption temperatures up to 320 °C, which indicates that the ZnO coating is capable to analyze volatile and most of semivolatile compounds (Fig. 2). However, some further peaks were observed if the fiber was subjected to higher temperatures, which is due to the leakage of siloxane derivatives from the septum of injector port which was confirmed by the reported results in Mass library.

Lifetime is very critical for practical application of the fiber. For most commercial SPME fibers, the extracting efficiency decreases with extraction times increasing. The coating is damaged mainly due to exposure to high temperature, organic solvent, strong acidic or basic solution. In this study, the ZnO nanorods coating was used more than 150 times of adsorption and desorption cycle without significant decrement in the extraction performance.

3.2. Optimization of HS-SPME procedure

Since various parameters potentially affect the extraction process, these parameters have to be optimized in order to quantitatively extract the analytes of interest, in a short period of time. In this paper, the Plackett–Burman design was used for determination of the main effective factors. Then, the Box–Behnken design (BBD) and response surface methodology were applied to find the optimum levels of significant factors. At first, in order to select the variables having main effect on the HS-SPME, Plackett–Burman design was used as a screening method. Based on the preliminary experiments, the effect of six factors of stirring rate (600 and 1200 rpm), salt (0 and 20%), desorption time (1 and 5 min) and temperature (150 and 300 °C), time (10 and 30 min) and temperature (30 and 70 °C) of extraction or adsorption each of them at two levels, were investigated. The low and high values were selected from the results of previous experiments. The total design matrix showed 15 runs (12+3 centerpoints) to be carried out randomly in order to eliminate the effects of extraneous or nuisance variables. The ANOVA results were evaluated for determining the main effects. The results of 15 experiments by using a Plackett–Burman design for estimating the effects of the above factors at two selected levels for each parameter, show that the stirring rate (A), desorption time (C) and adsorption temperature (F) are most effective parameters. The analysis of the results is visualized using standardized main effect Pareto charts ($P=95\%$) as shown in Fig. 3. The results illustrated in Fig. 3 also confirm that the factors of A, C and F are the most effective factors on HS-SPME of CB compounds. A parameter is considered as significant when its value is higher than $\pm t$. All other variables are not significant factors in the studied range. According to Fig. 3, in this study, the stirring rate and desorption time were the most significant

Table 3
Characteristic performance data obtained by using HS-SPME-GC-MS and other techniques in preconcentration and determination of CBzs in environmental samples.

Method	Sample	LOD (ng L ⁻¹)	Recovery (%)	RSD (%)	Ref.
SPE-GC-MS	Water	10.0–42.0	59.1–96.1	3.3–12.2	[11]
^a DB-LPME-GC-ECD	Water	4.0–8.0	90–94	≤ 6	[12]
^b UAWE-SBME-GC-MS	Soil	0.7–27.3 ^g	93–105	≤ 6.8	[14]
^c SDME-GC-MS	Water	3.0–3.1	82–107	2.1–13.2	[15]
^d DLLME-GC-ECD	Water	0.5–50.0	71.1–81.3	0.52–6.0	[16]
^e HS-SPME-GC-IT-MS	Soil	0.03–0.1	–	3–5	[17]
HS-SPME-ECD	Water	0.32–2.25	–	≤ 5	[18]
HS-SPME-GC-MS	Water and soil	–	–	–	This work
– ZnO nanorods		0.01–0.1	91.0–107.5	3.5–4.8	
– ^f PDMS		100–10000	89.0–99.8	5.6–8.5	

^a Drop-based liquid-phase microextraction and gas chromatography-electron capture detection.

^b Ultrasonic-assisted water extraction and solvent bar microextraction.

^c Single drop microextraction.

^d Dispersive liquid-liquid microextraction.

^e Headspace solid-phase microextraction gas chromatography-ion trap mass spectrometry.

^f Polydimethylsiloxane.

^g ng g⁻¹.

variables having a positive effect on the extraction efficiency of the analytes. Adsorption temperature was the next most significant variable that also having the positive effect on the extraction efficiency. Based on the results of the screening study, to continue the optimization, three insignificant variables were fixed at appropriate amounts.

The Box–Behnken design (BBD) for the three significant factors of stirring rate, desorption time and adsorption temperature was performed to evaluate the optimum condition of HS-SPME. The Box–Behnken design has been carried out on fifteen randomized runs ($2 \times 3(3-1)+3$ centerpoints), using the STATGRAPHICS software. The number of experimental points (N) is defined by the expression:

$$N = 2K(K-1) + C_p$$

where K is the number of variables and C_p is the number of center points. In this study, K and C_p were set at 3 and 3, respectively, which meant 15 experiments had to be done. The normal probability graph and the histogram of residuals demonstrated that the residuals followed a normal distribution. It was therefore considered that the model provided a good description of the experimental data. The R -squared statistic indicates that the model as fitted explains 97.9% of the variability in relative area all were statistically acceptable at $P < 0.05$ levels. The 3D response surface plots and their related counters for the peak area were shown in Fig. 4. Estimated response surface for desorption time versus the stirring rate is shown in Fig. 4a. Stirring rate was an important factor that had a significant positive effect on the extraction efficiency. Increasing the speed of sample stirring is expected to enhance the rate of extraction of all target analytes because the equilibrium between the aqueous and vapor phases can be achieved more rapidly and it enhances the diffusion of the analytes towards the fiber. As can be seen in Fig. 4a and b, the extraction efficiency increased with increasing stirring rate up to 1100 rpm. However, when the stirring rate exceeded 1100 rpm, the stirring bar in the sample solution could not move steadily, and consequently lowered the extraction efficiency.

Desorption time was another important parameter that had a significant positive effect on the extraction efficiency of CBzs. As can be seen in the estimated surface for desorption time (Fig. 4a and c), the analytical signal increased until desorption time of 4.0 min, but kept almost unchanged above 4.0 min. Therefore, it was selected as optimum desorption time without carry-over effects.

The extraction temperature affects the efficiency of the extraction process by controlling the diffusion rate of CBzs into the coating of the fiber. Heating not only drives analytes from liquid

into headspace but also alters the partitioning of analytes between headspace and the fiber. As it was shown in Fig. 4b and c, increasing the adsorption temperature up to 50 °C causes to increase the extraction efficiency. When the extraction temperature exceeded 50 °C, a decrease in sensitivity was observed for the analytes.

According to the overall result of the optimization study, the following experimental conditions were chosen: stirring rate of 1100 rpm; desorption time of 4.0 min and adsorption temperature of 50 °C.

3.3. Analytical performance

The calibration curve was obtained after the standard series were subjected to the HS-SPME under optimum condition and then determined by GC-MS. The obtained calibration curve shows good linearity with correlation coefficient (r) of ≥ 0.98 . Under the optimized conditions, the analytical performance of the developed method was evaluated and summarized in Table 1. The LOD were calculated as the concentration of the analytes equal to three times of the standard deviation of the blank signal divided by the slope of calibration curve ($3S_b/m$). The reproducibility was estimated by the relative standard deviation (RSD, $c=10$ ng L⁻¹, $n=5$) of the peak areas of the HS-SPME of the analytes. The RSD values were evaluated for analysis by one fiber and two fibers (fiber-to-fiber).

3.4. Analysis of environmental water samples

Under the optimized conditions, the developed HS-SPME-GC-MS technique was applied to separation, preconcentration and determination of CB compounds in some environmental water and soil samples. In order to validate the proposed method, recovery experiments were also carried out by spiking the samples with different amounts of CBzs. The recoveries for the spiked samples varied from 91.0% to 107.5% for CBzs. Table 2 shows that the results of five replicate analysis of each samples obtained by the proposed method and the added amount of CBzs are in satisfactory agreement. Since the examined real samples include the salts, alcohols and some acids, it can be concluded that many interference problems are eliminated due to the fiber is not in contact with the samples. A chromatogram of Caspian Sea water sample spiked with CBzs after the HS-SPME shown in Fig. 5. A comparison of the represented method with other approaches reported in the literature for the determination of CBzs is given in Table 3. As can be seen, the LODs of this method are comparable with those obtained in the previous studies, and even lower than those

reported in the literatures. All the experiments for extraction of the desired components are also carried out by PDMS fiber at the optimized conditions obtained by the chemometric design for the fiber. The LODs for the extraction of the CB compounds by using ZnO nanorods SPME are 10^4 – 10^6 times lower than the LODs by using PDMS SPME fiber. It seems that the high surface area of ZnO nanorods increased the load capacity and sensitivity of the fiber in comparison to that of PDMS-SPME fiber. Finally, it is concluded that HS-SPME-GC-MS is an effective technique for the preconcentration and determination of CB compounds in different environmental water and soil samples.

4. Conclusion

The main goal of this study was to develop a simple and sensitive method by combining HS-SPME and GC-MS for the preconcentration and determination of ultra-trace amounts of some chlorobenzene compounds in environmental water and soil samples. Nano-rods zinc oxide as a stationary phase of SPME was synthesized and grown on fused silica fibers using a simple hydrothermal process. The nano-structured ZnO SPME fiber showed high temperature endurance, reproducible synthesis, chemical and mechanical resistance, easy preparation, affordable and relatively long life span. In addition, either the single fiber repeatability or fiber-to fiber reproducibility was satisfactory. In this study, the experimental parameters of HS-SPME were optimized using a Box-Behnken design after a Plackett-Burman screening design. The developed solvent free method proved to be a simple, fast, effective, sensitive and inexpensive method with high reproducibility and repeatability, and also applicable to the analysis of chlorobenzenes in environmental water and soil samples. In addition, due to the fact that the fiber is not in direct contact with sample solution, it can be successfully applied for samples with complex matrixes. Therefore, it seems that the results of nano-rods ZnO SPME are highly superior to those obtained by commercial PDMS-SPME fibers.

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