Advances in Environmental Technology 1 (2018) 13-22

Advances in Environmental Technology

journal homepage: http://aet.irost.ir

Ordered nanoporous carbon (CMK-3) coated fiber for solid-phase microextraction of benzene and chlorobenzenes in water samples

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ARTICLE INFO

Article history:
Received 22 January 2017
Received in revised form
4 August 2017
Accepted 8 July 2018

Keywords:
Chlorobenzene Compounds
Solid-Phase Microextraction
Ordered Nanoporous Carbon
Orthogonal Array Designs

ABSTRACT

Nanoporous carbons (CMK-3) were prepared and have been used as a fiber coating for headspace solid phase microextraction (HS-SPME). The prepared materials were characterized by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and N_2 adsorption/desorption isotherms. The efficiency of the fiber was evaluated using a gas chromatography (GC) system for the extraction of benzene (B) and chlorobenzenes (CBs) from the headspace of aqueous samples. The prepared nanomaterial was coated onto a copper wire for fabrication of the SPME fiber. These fibers featured advantages like easy and fast preparation, high thermal and mechanical stability. To optimize different parameters which influence the extraction efficiency such as sample volume, extraction temperature, extraction time, ionic strength and stirring rate, a Taguchi OA_{16} (4^5) orthogonal array experimental design was used. Based on the results obtained from the analysis of variance (ANOVA), the optimum conditions for extraction were established as: 12 mL sample volume; laboratory temperature; 20 % (w/v) NaCl; 35 min extraction time and stirring rate of 600 rpm. Under the optimized conditions for B and CBs, the linearity was from 2.5 to 800 µg/L, the relative standard deviation (RSD %) of the method was between 5.2 and 9.3% and limit of detections (LODs) was between 0.09 and 0.28 µg/L. The recovery values were from 85.40% to 104.20 % in water samples. Finally, the applicability of the proposed method was evaluated by the extraction and determination of B and CBs in the water samples.

1. Introduction

Chlorobenzenes (CBs) which are widely used as pesticides, dielectric fluids, industrial solvents, deodorant and chemical intermediates can enter the aquatic environment through solid and liquid effluents and atmospheric discharges [1]. These compounds have high octanol–water partition coefficient [2], so biological agglomeration can be expected in the aquatic ecosystem. Due to their acute toxicity [3] and potential harm to the aqueous environment [4], these compounds have been ranked as undesired pollutants by United States Environmental Protection Agency (USEPA) [5]. Thus, excessive exposure to these compounds can exert effects on the central nervous system, irritation of the upper respiratory tract, irritation of the eyes, toughening of the skin and hematological disorders including anemia [6]. Therefore, research is directed towards developing inexpensive, simple and effective sample preparation and analytical techniques for the detection of trace quantities of these compounds in water samples [1,7]. In general, trace determination of CBs in water is usually performed by gas chromatography or high performance liquid chromatography coupled with a sample pretreatment step such as the routinely used solid-phase extraction (SPE) [4], liquid-liquid extraction (LLE) [8,9] or even the more recently introduced single drop microextraction (SDME) [10], dispersive liquid-liquid microextraction (DLLME) [1] and solid-phase microextraction (SPME) [5,11] techniques.

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DOI: 10.22104/AET.2018.1936.1094

SPME is a solventless sample preparation technique that was introduced by Pawliszyn at 1990 [12]. Integrating sampling, extraction, pre-concentration and sample introduction in a single process has been performed by solid-phase microextraction and is predominantly carried out on SPME fibers [13]. The use of metal wires as SPME supports with high mechanical stability makes this technique powerful for routine analysis. Several wires such as platinum, anodized aluminum, gold, stainless steel and copper have been used as SPME supports [14,15]. Carbon materials have long been used as adsorbents for separation of organic compounds. In SPME, carbon materials such as glassy carbon films, pencil lead, activated carbon and activated charcoal have been successfully used as the coating or fiber material [16,17]. In the early 1990's, new ordered nanoporous materials were synthesized by researchers at Mobil Oil Corporation [18]. Ryoo et al. (1999) have synthesized ordered nanoporous carbon using the nanoporous silica as the hard molecular template [19]. Nanoporous carbons have attracted widespread attention in many areas of modern science and technology, including catalysis, adsorption, and biomedical engineering [20,21]. The first nanoporous carbon material was prepared employing the MCM-48 type nanoporous silica as the hard molecular template and named as CMK-1 that was a beginning to synthesize other type nanoporous carbon materials such as CMK-3, CMK-5 [22]. Nanoporous carbons are of particular interest because of their remarkable properties, such as high surface areas, regular frameworks, good mechanical stability and narrow pore size distributions [23]. The first time, MCM-41 was synthesized as fiber coating in SPME for the extraction of aromatic hydrocarbons by Du et al. [20-22]. The use of phenyl functionalized MCM-41 particles were also reported from the same laboratory [2,25] and showed to have higher stability and better selectivity. Amino ethyl-functionalized SBA-15 have been used as fiber coating in SPME by Hashemi et al. [26]. In this study ordered nanoporous carbon (CMK-3) is synthesized and used for the first time as fiber coating of SPME onto copper wire and in combination with GC–FID for the headspace analysis of B and CBs compounds in water. The extraction ability of this kind of new fiber was investigated and extraction conditions were optimized using an OA_{16} (4^5) orthogonal array design.

2. Materials and methods

2.1. Reagents

Tetraethyl orthosilicate (TEOS from E. Merck (Germany) as silica source, poly(ethylene glycol)-block poly(propylene glycol)-block-poly(ethylene glycol) (P123 from Aldrich) as surfactant, sucrose as carbon source, sulfuric acid as a catalyst, hydrochloric acid, ethanol, methanol, sodium hydroxide and benzene (B), chlorobenzene (CB) , 1,2-dichlorobenzene (1,2-DCB), 1,4-dichlorobenzene (1,4-DCB) with maximum available purities were obtained from E. Merck (Germany). The stock standard solution was prepared in HPLC-grade methanol to get a concentration of 1000 µg/L for B, CB, 1, 2-DCB, 1, 4-DCB. Environmental water samples were collected from the Caspian Sea water in Sari city (North of Iran), drinking water and sewage water from Tehran and stored in 2 L pre-cleaned glass bottles without previous treatment until analysis.

All solutions and samples were stored at 4 °C in the dark place in sealed glass containers completely filled (without headspace) to avoid analyte losses and to ensure reproducibility.

2.2. Instrumentation

An SPME syringe (Azar Electrode Co, Oroumie, Iran) was utilized for holding and injection of the CMK-3 fiber into the GC injection port. The analysis of CPs was performed by a Shimadzu GC-2010 GC-FID system. The GC was fitted with a BPX5 capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness, 95% methyl–5% phenyl) from SGE (Victoria, Australia). The injection port was held at 240°C and used in the splitless mode with a splitless time of 4 min. Ultra pure helium (99.9999%, Air Products, West Sussex, UK) was used as the carrier gas and column flow was adjusted to 1 mL/min. The analysis was performed with an initial column temperature of 90 °C, held for 5 min and followed by heating to 150 °C at 6 °C/min (held 3 min) and then increased to 250 °C with 40 °C/min (held 8 min). The FID temperature was maintained at 290 °C. The chromatographic conditions were previously optimized and validated for the analysis of these compounds. Ultra pure nitrogen (99.9999%, Air Products), as makeup gas for FID, was passed through a molecular sieve trap and an oxygen trap (Chromatography Research Supplies) at the flow rate of 30 mL/min. The porosity characteristics of the mesoporous carbon were determined by N_2 adsorption–desorption experiments performed at 77 K on micromeritics model ASAP 2010 sorptiometer. The specific surface area (S_{BET}) was determined from the linear part of the Brunaure–Emmet–Teller (BET) equation. Pore size distribution was estimated from the adsorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) method. The X-ray powder diffraction pattern was conducted on a Philips 1830 diffractometer using Cu -K_α radiation. XRD pattern was obtained from 1° to 10° of 2θ, with a 2θ step size of 0.018° and a step time of 1 s. The surface features and morphologies of the samples were investigated by scanning electron microscopy (SEM JEOL 6300F). The samples were coated with gold to improve their conductivity before scanning.

2.3. Preparation of SBA-15

Ordered mesoporous silica SBA-15 was prepared by using the P123 as the surfactant and TEOS as the silica source. The preparation procedure was taken from the literature [27].

The preparation procedure of mesoporous silica was as follows: First, 4.0 g of P123 was dissolved in 130 mL of deionized water and 20 mL of concentrated HCl (37 wt%) with stirring at 38 ˚C. Then, 8.50 g of TEOS was added and the resulting mixture was stirred at 38 °C for 20 h. The mixture was transferred into an autoclave and left at 100 ˚C for 48 h. The solid was separated by filtration, washed with deionized water, dried at room temperature, and calcined in air at 550 ˚C for 6 h to obtain the SBA-15 samples.

2.4. Preparation of CMK-3

Mesoporous carbon, CMK-3, was prepared according to the process described in the literature [28]. Typically 1 g of SBA-15 was mixed with 5 mL of aqueous solution containing 1.25 g of sucrose and 0.14 g of H_2SO_4. The resulting sludge was placed into an oven at 100 ˚C for 6 h. Subsequently, the oven temperature was increased to 160 ˚C for 6 h. In order to obtain fully polymerized and carbonized sucrose inside the pores of the silica template, 0.8 g of sucrose, 0.09 g of H_2SO_4, and 5 g of water were added to the pretreated sample again and the obtained mixture was subjected to the thermal treatment as described above. The composite was then pyrolyzed under nitrogen flow at 890 ˚C and kept under these conditions for 6 h to carbonize the polymer. The mesoporous carbon (CMK-3) was obtained by removing the silica matrix using a 4 mol/L NaOH solution at room temperature followed by filtration, washing, and drying at 120 ˚C for 4 h.

2.5. Preparation of the SPME fiber

The surface of a copper wire was polished and then cleaned with acetone in an ultrasonic bath for 30 min, followed by drying at 30 ˚C. Typically, 0.35 g of epoxy glue and 0.65 g nanoporous carbon powder as sorbent was added to 10 mL of THF solution under stirring. The heating temperature was adjusted at 70 ˚C to turn the THF into vapor until a viscous suspension was formed. 1.2 centimeter of the copper wire was successively introduced into the viscous suspension. The prepared nanoporous SPME fiber was heated at 60 ˚C for 24 h in an oven and then mounted at the SPME syringe. It was then inserted into the GC injection port to be conditioned at 250 ˚C for 4 h to remove any fiber contamination [29].

2.6. GC operating conditions

The GC operating conditions were as follows: column temperature program of 60 ˚C with a 2-min hold, rising at 10 ˚C /min to 150 ˚C and then rising at 15 ˚C /min to 220 ˚C, 2-min hold. Carrier gas (Ultra pure helium) velocity and makeup gas (pure nitrogen) flow rate were 10 cms^{-1} and 30 mL/min, respectively. The analytes were injected in the splitless mode at 230 ˚C and the splitter was opened after 2 min. Detector temperature was 290 ˚C.

2.7. The headspace SPME procedure

A SPME device (Azar Electrode Co., Oroumie, Iran) was used for holding and injection of the proposed fiber into the GC–FID injection port. A 15 mL vial containing a magnetic stirrer bar and 12 mL of water sample, 2.4 g NaCl was added. The vial was rapidly sealed with a rubber septum cap, and the fiber was exposed to the headspace of the aqueous phase while the solution is being stirred by a magnetic stirrer. The vial was heated at laboratory temperature with stirring for 20 min. After 20 min the fiber withdrawn from the bottle and immediately transferred to the injection port of a gas chromatograph and thermal desorption of analytes is performed for 2 min at 230 ˚C.

3. Results and discussion

3.1. Characterization of the CMK-3

The quality of the samples prepared in this study was tested by XRD, SEM and nitrogen adsorption–desorption analysis.

3.2. XRD analysis

The quality and structural ordering of CMK-3 were assessed by powder X-ray diffraction. The XRD pattern of the mesoporous carbon CMK-3 is shown in Figure. 1. The XRD pattern for CMK-1 exhibits an intense diffraction peak and two weak peaks indexed as (1 0 0), (1 1 0), and (2 0 0) crystal facets in the 2θ range from 0.8 to 10, which belong to two-dimensional hexagonal structure. The observed data from the original sample of nanoporous carbon are in good agreement with that previously reported [24,25].

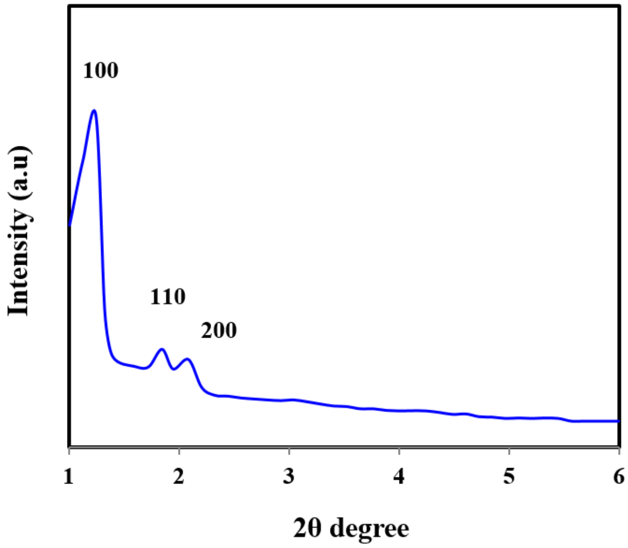

Fig. 1. XRD pattern of CMK-3

3.3. Nitrogen adsorption–desorption analysis

A nitrogen adsorption-desorption technique was used to determine the surface porous textural properties of the synthesized nanoporous material. This method provides information on the specific surface area, the pore volume and the pore diameter. Brunauer–Emmett–Teller (BET) equation was used to calculate specific areas and Barret–Joyner–Halenda (BJH) equation was applied to evaluate pore size distributions and total pore volumes. Figure 2 shows the nitrogen adsorption and desorption isotherm measured at 77 K by using a Micromeritics ASAP 2010 automatic analyzer. It can be seen that the CMK-1 exhibiting a typical type IV curves. The isotherm showed a distinct hysteresis loop, which is characteristic of mesoporous materials [30]. The textural properties of mesoporous carbon are collected in Table1.

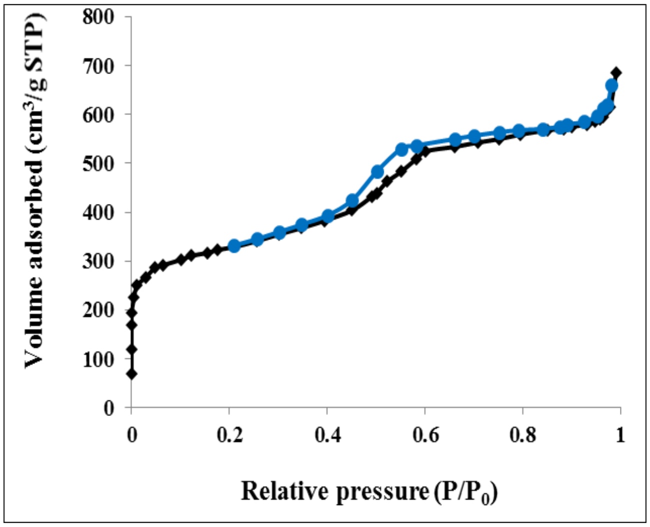

Fig. 2. Adsorption–desorption isotherms of nitrogen at 77 K on CMK-3

Table 1. Textural parameters of the CMK-3 employed in this study

Sample	V_p (cm^3 g^{-1}) ^{a}	D (nm) ^{b}	S_{BET} (m^2 g^{-1}) ^{c}
CMK-3	0.68	3.6	997

^{a} total pore volumes, ^{b} pore diameter, ^{c} Specific surface area

3.4. SEM analysis

SEM instrument was employed to characterize the morphology of the synthesized nanoporous carbon. SEM images of CMK-3 and nanoporous adsorbent coated on copper wire are shown in Figure 3. It is clear from Figure 3 that, samples have a spherical morphology of mesoporous materials.

3.5. Optimization of fiber composition

For this purpose fibers with the following compositions (percent by weight) are prepared: (CMK-3:epoxy glue) (85:15), (75:25), (65:35), (55: 45). The extraction procedure is performed as mentioned section 2.7 at 100 μg/L and the best composition is selected. The coating composition CMK-3:epoxy glue (85:15) has maximum extraction efficiency in comparison with other compositions in the adsorption of the analytes, but these fibers did not show a good mechanical stability, consequently coating with the composition of CMK-3: epoxy glue (65:35) was selected as the optimum one and used for the experiments, afterwards.

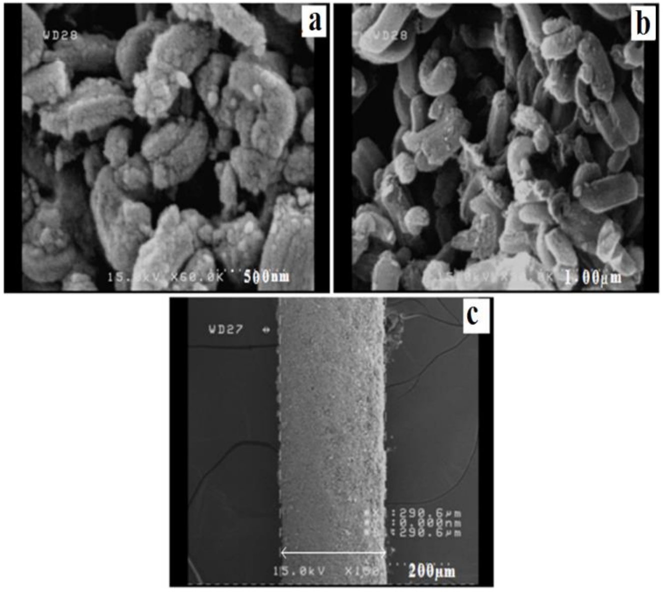

Fig. 3. SEM photographs of (a and b) CMK-3 powder and (c) CMK-3 coated copper wire

3.6. Taguchi method

The Taguchi method is a statistical methodology for designing an experiment and analyzing data such that an investigation can be conducted more effectively. Using the orthogonal array specially designed for the Taguchi method, the optimum experimental conditions can be easily determined. In the present work, five controllable factors and each factor at four levels on the HS-SPME of B and CBs were considered (Table 2). Therefore, an OA_{16} (4^5) orthogonal array was chosen, and the experimental conditions (Table 3) can be obtained by combining Table 2 and the OA_{16} (4^5). The peak areas for the analytes were considered as the experimental response. The OA_{16} orthogonal array scheme was adapted, which requires 16 experiments to complete the optimization process. ANOVA was used to assess the OAD results [31] and the obtained data after calculation is tabulated in Table 4.

3.7. Study of the HS-SPME system variables

To gain full advantage of the procedure, several experimental parameters must be studied to obtain an optimized system. These parameters were optimized in this research by a five-factor four level factorial design and the experimental data were calculated using Qualitek 4 Software. The mean values of the four levels of each factors showed how the extraction efficiency changes when the level of that factor changes. Fig. 4 illustrates the mean of the integrated peak area as a function of the levels of the studied factors.

Table 2. Coding of factors and levels of the orthogonal test

Level	Factors				
	A **sample volume (mL)**	**B** **extraction time (min)**	**C** **rate stirring (rpm)**	**D** **% salt (w/v)**	**E** **temperature (°C)**
1	3	5	0	0	Lab.tem[a]
2	7	10	600	5	35
3	10	20	900	10	45
4	12	35	1200	20	60

[a] laboratory temperature (23 ˚C)

Table 3. The OA_{16} (4^5) matrix for optimization of HS-SPME of B and CBs

Exp. No.	Factor				
	A	**B**	**C**	**D**	**E**
1	12	35	0	10	35
2	3	35	1200	20	60
3	7	35	900	5	lab.tem[a]
4	12	20	600	20	lab.tem
5	3	20	900	10	45
6	10	35	600	0	45
7	12	10	900	0	60
8	10	10	1200	10	lab.tem
9	10	20	0	5	60
10	3	5	200	0	lab.tem
11	7	10	0	20	45
12	12	5	1200	5	45
13	7	20	1200	0	35
14	3	10	600	5	35
15	7	5	600	10	60
16	10	5	900	20	35

[a]:laboratory temperature (23 ˚C)

Table 4. ANOVA result for experimental response in the $OA_{16}(4^5)$ matrix

Source	d.f	SS	V	F	SS″	PC (%)
sample volume (A)	3	5.66×1010	1.89×1010	24.51	5.43×1010	35.006
Temperature (B)	3	4.13×1010	1.38×1010	17.90	3.90×1010	25.153
rate stirring (C)	——	——	——	——	——	——
time extraction (D)	3	2.67×1010	0.90×1010	11.57	2.44×1010	15.732
% Salt (E)	3	1.58×1010	0.53×1010	6.86	1.35×1010	8.721
Error	19	1.46×1010	0.07×1010			15.388
Total	31	1.55×1011				100

d.f: degrees of freedom; SS: Sum of squares; V: Variance; SS″: purified sum of squares; PC: percentage contribution; F: Critical value is 9.27 ($P < 0.05$).

3.8. Effect of extraction volume

The head space volume and volume of the solution samples are dependent when using vials of a constant volume for the head space-SPME method, i.e. changing the sample volume changes its head space volume. In increasing the sample volume, the headspace volume is decreased and thus the amount of analytes present in the headspace phase is increased while enhancing the sensitivity. Therefore, the sample volume should be optimized as an effective parameter of the extraction process. All the experiments were carried out using vials of 15 mL and sample volumes of 3, 7, 10 and 12 mL. Results showed that increasing the sample volume from 3 to 12 mL increased the extraction and consequently the sample volume of 12 mL was selected as the optimum amount Figure 4.

3.9. Effect of extraction Temperature

In the head space-SPME process, temperature has a twofold effect. The use of high temperature is suitable for increasing volatility of analytes but at higher temperature, the distribution coefficients of analytes between gaseous phase and the fiber are generally decreased. To study this effect, the extraction of the B and CBs compounds were performed at different temperatures, including laboratory temperature, 35, 45 and 60 °C and the results are shown in Figure 4. The maximum extraction for all compounds was obtained at the laboratory temperature and extraction decreased at higher temperatures. Therefore, further experiments were performed at laboratory temperature. This may be due to two factors. First, at high temperatures the fiber coating can lose its ability to adsorb analytes due to the absorption of water vapor. The other reason is that the adsorption of analytes by the fiber is an exothermic process, which can decrease the partition coefficient at high temperatures.

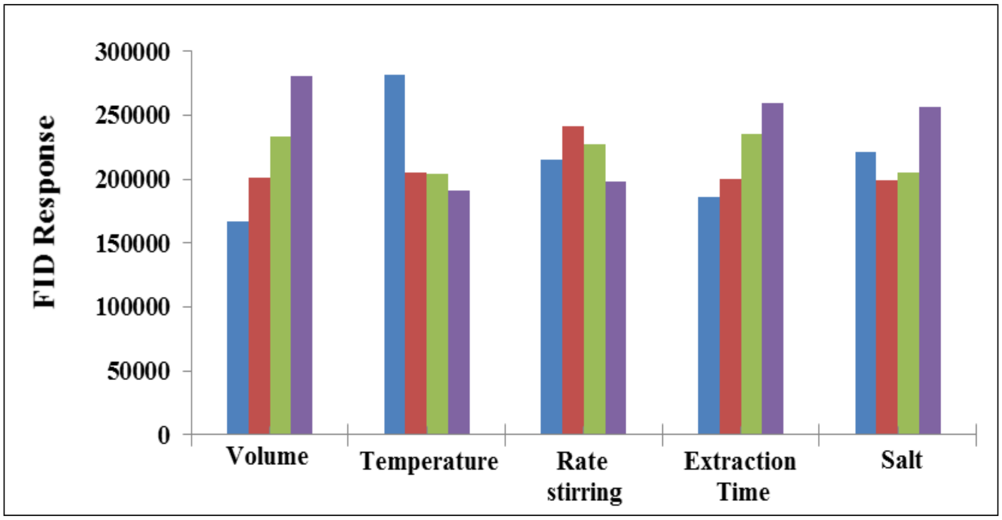

Fig. 4. The effect of the sample volume, extraction temperature, stirring rate, extraction time and salt % on the HS-SPME of CBs and B. Extractions were performed for a 12 mL aqueous sample solution under stirring (900 rpm) spiked with each analyte at 200 µg/L

3.10. Effect of stirring rate

Several studies have shown that, mass transfer from a liquid sample to the headspace can also be increased by stirring the sample. According to Figure 4, the maximum extraction capability was obtained at the stirring speed of 600 rpm for all B and CBs; therefore the stirring rate of 600 rpm was selected as the optimum rate for the experiments.

3.11. Effect of extraction time

To optimize the extraction time, the fiber is exposed to the headspace above the solution for 5, 10, 20, and 35 min. The effect of the extraction time on the extraction of the B and CBs compounds is shown in Figure 4. Increasing the extraction time from 5 to 35 min increased the efficiency of the extraction. It can be seen that 35 min was not enough for the extraction process to reach the equilibrium. The results obtained indicate that the time needed to reach the equilibrium state was at least 50 min. An extraction time of 20 min was finally chosen as the optimum time for the subsequent evaluation.

3.12. Effect of salt addition

By decreasing the solubility of the analyte in sample solution, the amount of analyte partitioned into the headspace and, finally, into the fiber coating will increase. In order to study this effect, the extraction of the B and CBs compounds was carried out after addition of the 0-20 wt% NaCl to the samples solution. This obviously indicates that the addition of NaCl improved the extraction and optimum adsorption on the fiber was observed when 20 wt% NaCl was added for all the analytes (Figure 4).

3.13. Reproducibility of the proposed method

Further experiments have been carried out to assess the repeatability of the method. Thus, four replicate (n = 4) determinations have been performed using a single fiber and the relative standard deviations calculated. The obtained results showed the RSD% between 5.2 and 9.3% for all B and CBs compounds, which indicates that the proposed method is efficient. Also reproducibility studies performed on four different fibers show that the fiber-to-fiber RSD% is less than 15% for all compounds. It is mentioned that although fiber-to-fiber reproducibility is relatively good, there is no need to use different fibers in a single analysis (Table 5).

Table 5. Limit of detection, correlation coefficient, dynamic linear ranges, relative standard deviations for HS-SPME of B and CBs

Analyte	LOD[a]	R[b]	DLR[c]	%RSD $_{\text{fiber-to-fiber}}$	%RSD $_{\text{single fiber}}$
B	0.24	0.995	2.5-400	14.4	9.3
CB	0.13	0.999	1-800	9.7	5.9
1,2 –DCB	0.09	0.998	1-800	10.9	6.4
1,4 –DCB	0.28	0.997	2.5-400	9.32	5.2

[a] :Limit of detection (µg/L), [b] :Correlation coefficient, [c]:Liner dynamic range (µg/L).

3.14. Evaluation of the method performance

Under optimum conditions, limit of detections (LODs), regression equations, correlation coefficient (R^2) and dynamic linear ranges (DLRs) were obtained (Table 5). Correlation coefficients were obtained in the range of 0.995–0.999. The LOD was calculated as the concentration of the analyte equal to three times of the standard deviation of the blank signal divided by the slope of calibration curve in the range of 0.07-0.28 µg/L. Efficiency of the proposed method was evaluated comparing the LODs obtained by SPME-GC using proposed fiber and other fibers reported in the literature. The obtained results are summarized in Table 6.

Table 6. Comparison of analytical characteristics for proposed fibers in determination of B and CBs compound

Analyte	This work			Reference [32]			Reference [33]			Reference [1]			Reference [34]		
	RSD[a]	LOD[b]	DLR[c]	RSD	LOD	DLR	RSD	LOD	DLR	RSD	LOD	DLR	RSD	LOD	DLR
B	9.3	0.24	2.5-400	<%8	7.2	20-800	%7.3	0.6	0.1-100	-	-	-	-	-	-
CB	5.9	0.13	1-800	-	-	-	-	-	-	-	-	-	-	1.9	5-20
1,2 –DCB	6.4	0.24	1-800	-	-	-	-	-	-	5.4	0.05	0.1-100	-	-	-
1,4 –DCB	5.2	0.28	2.5-400	-	-	-	-	-	-	4.6	0.02	0.05-100	-	-	-

[a]: Relative standard deviation, [b]: Limit of detection (µg/L), [c]: Liner dynamic range (µg/L).

3.15. Real sample analysis

During the present investigation, matrix effects in the extraction were also evaluated by investigating the applicability of the proposed method to determine B and CBs concentration in Sea water, potable and well water samples. Potable and well water were collected from Tehran, and sea water from the Caspian Sea (all are located in Iran). In order to evaluate the matrix effect, all above samples were spiked with a standard B and CBs solution with the concentration of 25 µg/L and three replicate desorption analysis were performed after fiber exposure to the samples. The results, summarized in Table 7, show that the relative recoveries for all samples were in the range of 85.40–104.20%. Figure 5 shows the chromatogram of the analytes from spiked tap water after the headspace-SPME process under optimized conditions.

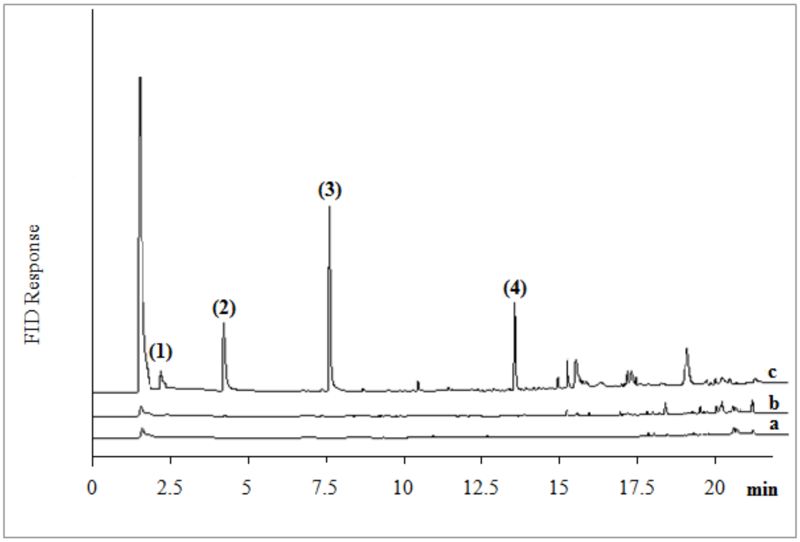

Fig. 5. HS-SPME-GC-FID chromatograms of background of fiber (a); non-spiked tap water (b) and spiked tap water (c) with 25 µg/Lof CBs and B. Peaks: benzene (1), chlorobenzene (2), 1, 2-dichlorobenze (3) and 1, 4-dichlorobenze (4)

Table 7. The results obtained for the analysis of spiked real water samples by the proposed method, under the optimized conditions

Sample	B	CB	1,2-DCB	1, 4-DCB
Well water				
Non-spiked[a]	–	–	–	–
Spiked	24.15±1.45[b]	22.07±2.60	21.35±2.79	21.59±2.35
Recovery (%)	96.60	88.30	85.40	86.36
Tap water 1				
Non-spiked	–	–	–	–
Spiked	23.82±2.14	21.65±2.25	23.03±1.32	21.69±2.41
Recovery (%)	95.31	86.60	92.12	86.79
Caspian sea water				
Non-spiked	–	–	–	–
Spiked	25.80±1.16	26.05 ±1.53	25.56 ±1.89	25.36±1.86
Recovery (%)	103.21	104.20	102.26	101.45

[a] 25 µg/L of the B and CBs were added to 12 mL of different samples, [b] Mean value of three replicate measurements with relative standard deviations

4. Conclusions

The HS-SPME-GC method with CMK-3 coated fiber for the determination of B and CBs have been developed and validated in this study. The experimental parameters for extraction of B and CBs were investigated and optimized by means of a Taguchi's OA_{16} (4^5) orthogonal array experimental design. The results showed that extraction volume was the most significant factor for B and all BCs in the HS-SPME procedure while extraction temperature offered secondary contribution. The prepared fibers present advantages like easy and fast preparation, good linear calibration range, low LOD, relatively good RSD together with high thermal and mechanical stability resulting in a long service time.

Acknowledgement

The authors are thankful to research council of Iran University of Science and Technology for the financial support.

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