

# Chemometrics Optimization of Volatile Organic Compounds Analysis in Water by Static Headspace Gas Chromatography Mass Spectrometry

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## Abstract

Static headspace coupled with gas chromatography-mass spectrometry was applied to extraction and analysis of volatile organic compounds in water samples. The effects of various factors affecting on the extraction efficiency including: the extraction temperature, extraction time, salt concentration and stirring speed were carried out by means of a 2<sup>4</sup> full factorial design. It was found that the effects of extraction temperature and salt concentration were significant. Then, a central composite design was performed to optimize the level of these factors. The optimal headspace conditions were achieved when the vials were heated under 88°C and 29% w/w addition of salt. At optimum operating conditions, analytical figures of merit of method such as linearity (0.9962-0.9996), repeatability (1.2-12.13%), detection limits (0.1-4.9 µg.L<sup>-1</sup>) and linearity dynamic range (10-1000 µg.L<sup>-1</sup>) were determined. The proposed methods can be used to direct investigation of the presence of Volatile organic compounds in environmental samples without pre-treatment of samples. Finally the optimized method was used to investigate the existence of volatile organic compounds in Babolroud River in the north of Iran.

**Keywords:** Optimization; Volatile organic compounds; Static headspace; Experimental design

## Introduction

Volatile organic compounds (VOCs) represent a class of organic substances characterized mainly by high volatility under environmental conditions. The main subgroups of these priority pollutants are halogenated volatile organic compounds (HVOCs), chlorinated short-chain hydrocarbons (CHCs) and monocyclic aromatic hydrocarbons (MAHs) [1,2]. Benzene, toluene, ethyl benzene and xylene (BTEX) are widespread pollutants of which the main source in the outside environment is vehicle traffic and indoor the cigarette smoke. They are also present in small quantities in drinking water and food, in painting substances or adhesives [3].

The main anthropogenic sources of VOCs to aquatic environments are the effluents of urban and industrial activities, including wastewater, atmospheric deposition, urban and rural runoff, extraction accidents, transport and/or transformations of fossil fuels, and natural sources (petrogenic and biogenic) [1,2]. The main reason for assessing VOCs in aquatic environments is their neurotoxic and carcinogenic effects (Huybrechts et al., 2005) [2]. Because of their toxicity, some VOCs have been included in the US Environmental Protection Agency (EPA) list of priority pollutants [4-6]. Also the European Union (EU) has classified several VOCs as priority contaminants (E.U. Directive 2004/42/CE) [7].

There are many reports about determination VOCs in environmental samples. For example, Safarova et al. [8] used headspace analysis combined with gas chromatography mass spectrometry for the analysis of 53 volatile organic compounds in river waters, waste waters and treated water samples down to 0.1 µg.L<sup>-1</sup> concentration levels. They concluded that the content of VOCs in river water mainly correlates to the content of these compounds in waste waters, which shows the anthropogenic character of the pollutions. Schmidt et al. applied HS-SPME with a Combi-PAL auto sampler to the pre-concentration of waters to obtain good reproducibility. Their method had sample-recovery values of 105–110% with good sensitivity and reproducibility [9]. For the quantitative work, the methods were validated and showed good linearity, precision, accuracy and limit of detection

(LOD) for the compounds studied. Sample preparation may largely influence the sensitivity and accuracy of measurements of VOCs due to their physico-chemical properties. Several sample introduction modules were coupled to chromatographic systems to improve the measurement quality (e.g., headspace sampling, solid phase micro extraction, purge and trap) [9,10]. Headspace analysis is a technique that separate and collect volatile compounds (in the gas phase) from different sample matrices such as water, solids, and foods [11,12]. Static or dynamic headspace gas chromatography (GC) analysis is the most adopted methods used by environmental agencies to determine VOCs from solid and liquid matrices [13]. However, direct aqueous injection (DAI) [14], liquid-liquid extraction (LLE) [14], membrane techniques, solid-phase extraction (SPE), solid-phase micro extraction (SPME) [8,15] and distillation techniques are also used as sample preparation techniques in analysis of VOCs. A primary benefit of using headspace GC is that one can analyze small amounts of analytes buried in a large amount of matrix without having to inject the matrix into the chromatography column. This technique results in clean, easy sample preparation coupled with less wear on the chromatography columns and the GC instrument. The static headspace (SHS) technique presents a wide linear dynamic range (with a limit of detection of up to 100 mg.L<sup>-1</sup>) [15], simpler instrumentation [8,9], good repeatability (coefficient of variation 4–10%) and high recuperation [15-17].

Static headspace is a sampling technique based on physicochemical processes of equilibrium between the solution and the headspace. The success of its use depends on factors such as the chemical nature of the

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compounds to be extracted, the temperature used during extraction, extraction time and amount of added salts [18]. Studies considering the variables one by one to obtain the best possible conditions of SHS sampling have been followed by Gaines et al. [19] and Atchen et al. [20], but these procedures requires a lot of experiments and are also time consuming.

In cases such as this, where many factors influence the response of the system, optimization of the extraction procedure can be carried out using multivariate statistical tools. These provide secure information concerning the best analytical conditions, the existence or otherwise of experimental errors, as well as showing any interactions that might exist between the factors involved. While traditional methods of optimization experiments, where only one variable is analyzed at a time, leaving the others fixed, require a large number of experiments, and do not allow investigating possible interactions between variables, and not explore fully the solution space for optimization [21].

Experimental design, that takes into account simultaneously several variables, seems the most convenient approach searching for the optimal operational conditions in a reasonable number of experiments [22-24]. The principles behind these techniques (known as Design of Experiments (DoE)), encompass the use of experimental design and the generation of mathematical equations and graphic outcomes [24]. Employing various rational combinations of factors, statistical experimental design fits experimental data into mathematical equations (known as models) applied in order to predict and optimize the examined responses. This methodology can be used for optimization of SHS conditions to determine VOCs in water. Examples of GC development and optimization attempts with the aid of DoE have shown important advantages [25-28].

The aim of the present paper was to develop and optimize a static headspace gas chromatography-mass spectroscopy method for the determination of VOCs, using experimental design. The significance of the studied factors was evaluated with the aid of a full factorial design (full FD) whilst the optimum SHS conditions were estimated by a central composite design (CCD) using both a graphical and a mathematical global optimization approach. Finally, the proposed method was tested for linearity, specificity, precision, accuracy and robustness (using experimental design).

## Reagents

The standard compounds benzene (99.9%), ethyl benzene (99%), xylene (99%), naphthalene (GC-grade) were taken from Fluka (Buchs, Switzerland) and toluene (99.9%) were purchased from Aldrich (Milwaukee, USA). 1,2-Dichlorobenzene (99%) as internal standards and sodium chloride (extra-pure grade) were purchased from Merck (Darmstadt, Germany). Helium gas was 99.999% pure and obtained from Sabalan Co. (Iran).

A mixed solution of each individual standard in methanol (250 mg.L<sup>-1</sup>) was prepared as the stock standard solution and kept at 4°C. Working solutions were prepared by diluting appropriate volumes of the stock solution with distilled water.

## Instrumentation

The chromatographic system used was an Agilent model 7890A gas chromatograph equipped with an Agilent model 5975C mass spectrometric detector. This instrument was coupled with a static headspace auto sampler (PAL System). A PC interfaced to the GC using Chemstation software (Agilent Technologies, USA) was used for data

acquisition and processing. The chromatographic separations were carried out on a DB-35MS capillary column (Agilent Technologies, USA), 60 m×0.25 mm i.d., 0.25 μm d.f., with 0.5 μm film thickness. All statistical calculations were carried out using the Design Expert 8 and the Statgraphics 5.1 softwares for Windows.

## SHS extraction procedure

Ten milliliter aliquots of water samples containing target VOCs and appropriate amount of NaCl were placed in a 22 mL headspace vials (Supelco, USA). These vials were sealed with rubber septa faced with PTFE (polytetrafluoroethylene) and then were constantly stirred by an agitator in a controlled temperature for 5 min before carrying out the SHS.

## Gas chromatography-mass spectrometry analysis

For chromatographic analysis of VOCs, 500 μl of the headspace vapor in the vials was removed with a gas-tight syringe and then injected immediately to the GC-MS. The carrier gas was helium and adjusted at a constant flow-rate of 1.0 mL.min<sup>-1</sup> and the split ratio was 5:1 Oven program temperature was 40°C (hold 2 min), rate 7°C/min up to 150°C (hold 1 min), and then rate 15°C/min raised to 200°C (hold 2 min). The ionization energy was 70eV, the source and quadrupole temperatures were 230°C and 150°C, respectively. The ionization mode was positive ionization. The mass spectra of the sample constituents were compared with a spectra library (Wiley) compatible with chemical classes of the components under study.

## Sampling

The samples were obtained from Babolroud River in the Babolsar city in the northern of Iran. Babolroud is one of the major rivers in the northern of Iran. It originates from Alborz Mountain and flows to the north to discharge in the Caspian Sea. The sampling sites on the Babolroud Rivers were established from the areas of intense port activity, and sink of urban runoff and refinery wastes. Surface water samples were collected during a two-day period in November 2011. Samples were collected in 40–120 ml glass vials and in duplicates. Each vial was filled to capacity to avoid any headspace. All the samples were kept at 4°C in the dark. VOCs determinations were accomplished in the laboratory less than 12 h after the sampling.

## Results and Discussion

### Screening design

Factors that can affect the extraction efficiency of SHS were; extraction temperature, sample salt concentration, stirring speed and extraction time. The particular value for a factor at which an experiment is run is called factor level. The levels of these factors were chosen based on previous experiments [9-12,28]. These factors and their levels are shown in Table 1. A 2<sup>4</sup> factorial design was applied to evaluate the main effects of these factors. The obtained design matrix is shown in Table S1 (of supplementary material). The proposed 16 experiments were run in random manner to minimize the effect of uncontrolled variables. The sum of chromatographic peak areas in analyzing of BTEX samples were considered as experimental response. Then the analysis of variance (ANOVA) was performed on the results by using the Design Expert 8 software to calculate the values of effects and interactions of factors. The results of ANOVA are shown in Table 2. A p-value less than 0.05 in the ANOVA table indicate the statistical significance of an effect at 95% confidence level. As can be seen in this table, the most significant variables are: extraction temperature (T) and amount of

Factor	Factor notation	Levels	
		-1	+1
Sample temperature (°C)	T	40	80
NaCl in sample (w/w, %)	S	5	29
Extraction time (min)	t	5	15
Stirring speed (rpm)	V	350	650

**Table 1:** Factors, factor notations and their levels for the 2<sup>4</sup> full factorial design.

Source	Sum of squares	d.f. <sup>a</sup>	Mean squares	F-value <sup>b</sup>	p-value <sup>c</sup> prob>F
t	4.13×10 <sup>15</sup>	1	4.13×10 <sup>15</sup>	3.31	0.0961
T	5.21×10 <sup>16</sup>	1	5.21×10 <sup>16</sup>	41.77	< 0.0001
S	3.58×10 <sup>16</sup>	1	3.58×10 <sup>16</sup>	28.70	0.0002
V	2.98×10 <sup>15</sup>	1	2.98×10 <sup>15</sup>	3.61	0.1505
tT	2.35×10 <sup>15</sup>	1	2.35×10 <sup>15</sup>	60.35	0.0815
tS	3.15×10 <sup>15</sup>	1	3.15×10 <sup>15</sup>	80.91	0.0705
tV	2.31×10 <sup>15</sup>	1	2.31×10 <sup>15</sup>	59.24	0.0823
TS	4.61×10 <sup>13</sup>	1	4.61×10 <sup>13</sup>	1.18	0.473
TV	1.85×10 <sup>12</sup>	1	1.85×10 <sup>12</sup>	0.05	0.8634
SV	1.09×10 <sup>15</sup>	1	1.09×10 <sup>15</sup>	28.09	0.1187
tTS	2.94×10 <sup>15</sup>	1	2.94×10 <sup>15</sup>	75.41	0.073
tTV	2.17×10 <sup>14</sup>	1	2.17×10 <sup>14</sup>	5.58	0.2549
tSV	1.36×10 <sup>15</sup>	1	1.36×10 <sup>15</sup>	34.85	0.1068
TSV	2.31×10 <sup>14</sup>	1	2.31×10 <sup>14</sup>	5.93	0.2481
Residual	1.37×10 <sup>16</sup>	11	1.25×10 <sup>15</sup>		

<sup>a</sup>Degrees of freedom.

<sup>b</sup> Test for comparing model variance with residual(error) variance.

<sup>c</sup> Probability of seeing the observed F-value if the null hypothesis is true.

**Table 2:** The results of analysis of variance for the 2<sup>4</sup> factorial design.

salt in sample solution (S). The extraction time and stirring speed and interactions terms had no significant effect on the response. Important factors can also be detected by plotting the Pareto chart (Figure S1) and normal probability plot (Figure S2). These figures confirm that two main factors are the extraction temperature and the salt concentration. The stirring speed and extraction time had no significant effect on the extraction recovery and was eliminated for further studies.

### Optimization design

In the next step, a rotatable, orthogonal central composite design (CCD) was employed to determine the optimal level for the important factors. In statistics, CCD is an experimental design, useful in response surface methodology, for building a second order (quadratic) model for the response variable without needing to use a complete three-level factorial experiment. This design permitted the response surface to be modeled by fitting a second-order polynomial with the number of experiments equal to (2<sup>f</sup>+2f+n), where f is the number of factors and n is the number of center runs. In this study, f and n were set at 2 and 5, respectively, which meant that 13 experiments had to be run, out of which 5 are replicate experiments carried out in the center of the design. Eq. (1) was used to calculate the axial spacing, a, for a rotatable and orthogonal CCD design:

$$a^2 = \frac{\sqrt{(N_c + N_a + N_0)N_c} - N_c}{2} \quad (1)$$

For a design with f factors, N<sub>c</sub>, N<sub>a</sub> and N<sub>0</sub> are the number of factorial points (2<sup>f</sup>), the number of star points (2f), and the number of runs at the center of design, respectively. Using Eq. (1), the axial spacing of a = ± 1.414 was calculated to satisfy rotatability and orthogonality of the design. The factor levels used in the CCD and the corresponding design matrix and responses are shown in Tables 3 and 4, respectively. The

13 experiments found above were run in a random manner, in order to minimize the effect of uncontrolled variables on the response. The Statgraphics 5.1 software was used to analyze the experimental results. To investigate the effects and interactions terms, the Pareto chart and analysis of variance were applied on the results. Figure S3 shows the Pareto chart of standardized effects for CCD design. To evaluate the effects of factors and their interactions, an ANOVA test was performed on these data. The results of ANOVA test on CCD data are shown in Table S2. Then a response surface model was developed by considering all the responses of CCD experiments. The model with the most reasonable statistics, that is, higher F- and R-values and low standard error was considered as the satisfactory response surface equation. The statistics for linear and a second-order models are listed in Table S3, which indicated that the linear model, with P values less than 0.05 was the best model. This linear model is shown in Eq. (2):

$$\text{Response} = 1.35 (\pm 0.29) \times 10^9 + 3.06 (\pm 0.38) \times 10^8(T) + 1.49 (\pm 0.38) \times 10^8 (S) \quad (2)$$

$$r = 0.94 \text{ SE} = 1.22 \times 10^8 \text{ F} = 41.23$$

where r is the correlation coefficient, SE is the standard errors or residuals and F is the Fisher statistics values. In Eq. (2), the coefficients for salt concentration and extraction temperature are large and positive. This shows that the chromatographic peak areas increase extensively with increasing these variables. The mathematical linear model describing the response surface for the CCD. An analysis of variance table has been constructed to examine whether the model accounts for a significant proportion of the total variance in the data (Table 5). The sum of square due to the factors as a percentage of the total sum of squares is 89.2%, showing that a reasonably large proportion of the variance is explained by the model. The variance ratio of the model mean square to the residual mean square gives a value of 41.23, which is significant at a probability level of P< 0.0001, indicating that the regression model accounts for a reasonable proportion of the variance in the responses.

Figure 1 shows the response surface developed by this model. The maximum response was reached when the temperature was close to 88°C and the salt concentration was 29% (w/w). The factor levels

Factor notation	Levels				
	-1.414	-1	0	1	1.414
T (°C)	32	40	60	80	88
S (w/w, %)	1	5	15	25	29

**Table 3:** Factor levels used in the central composite design.

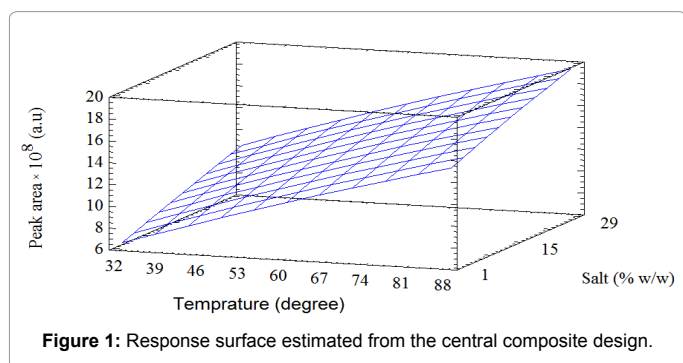
Experimental numbers	T	S	Response (a.u)
1	-1	-1	8.64×10 <sup>8</sup>
2	1	-1	1.44×10 <sup>9</sup>
3	-1	1	1.06×10 <sup>9</sup>
4	1	1	1.64×10 <sup>9</sup>
5	1.414	0	1.82×10 <sup>9</sup>
6	-1.414	0	9.15×10 <sup>8</sup>
7	0	1.414	1.67×10 <sup>9</sup>
8	0	-1.414	1.11×10 <sup>9</sup>
9	0	0	1.27×10 <sup>9</sup>
10	0	0	1.24×10 <sup>9</sup>
11	0	0	1.38×10 <sup>9</sup>
12	0	0	1.53×10 <sup>9</sup>
13	0	0	1.28×10 <sup>9</sup>

**Table 4:** Design matrix and responses for the central composite design experiments.

Source	Sum of squares	d.f.	Mean squares	F-value	p-value prob>F
Model	9.205×10 <sup>17</sup>	2	4.603×10 <sup>17</sup>	41.23	< 0.0001
T	7.426×10 <sup>17</sup>	1	7.426×10 <sup>17</sup>	66.53	< 0.0001
S	1.779×10 <sup>17</sup>	1	1.779×10 <sup>17</sup>	15.94	0.0025
Residual	1.116×10 <sup>17</sup>	10	1.116×10 <sup>16</sup>		
Lack of Fit <sup>a</sup>	5.524×10 <sup>16</sup>	6	9.207×10 <sup>15</sup>	0.65	0.6951
Pure Error	5.637×10 <sup>16</sup>	4	1.409×10 <sup>16</sup>		
Total	1.032×10 <sup>18</sup>	12			

<sup>a</sup>The variation of the data around the fitted model.

**Table 5:** The results of analysis of variance for obtained model.



**Figure 1:** Response surface estimated from the central composite design.

corresponding to the maximum response are considered as optimum conditions. It is interesting to note that the optimum conditions found above were not among the ones chosen during the experiments. In other words, the optimum conditions are not found in the design matrices. At higher temperatures (>90°C), the vapor pressure of water increases in the headspace vials (gas phase) and decreases the amount of the analytes of interest. In addition, there is a possibility of accidents with the syringe, once the pressure is increased under higher temperatures [16,29]. To evaluate the accuracy of improved SHS method, some experiments were carried out under optimum conditions. The results of three replications of experiments in these conditions indicated that, there is a good agreement between the predicted (1.96×10<sup>9</sup>) and experimental (1.88×10<sup>9</sup>) responses (95.92%). The closeness of predicted and experimental responses in optimum conditions reveals the credibility of obtained response surface model.

### Real samples analysis

The calibration curves of VOCs studies were performed at optimum conditions. The resulting calibration curves were linear with mean coefficients of determination (R<sup>2</sup>) 0.9988. The limit of detection range was 0.1-4.9 µg.L<sup>-1</sup>. Table 6 show the statistical parameters including limit of detection, linear range, and relative standard deviation calculated for improved procedure. The percent recoveries of the VOCs used in the present study were measured by spiking 50µg.L<sup>-1</sup> of standard VOCs to water samples. The percent of recoveries varied between 88 to 103%. The characteristics performance of this method was compared with other methods in Table 7, which indicated that the detection limits and the linear ranges found in the present work are comparable with the ones found by other researchers who used the SPME [30,31] or SHS [32,33] for analysis.

The optimum SHS conditions were used to analyze of real samples. Figure 2 shows the total ion chromatograms of a Babolroud river water sample. The main organic chemicals in river water were; ethylbenzene (48.03µg.L<sup>-1</sup>), toluene (33.04µg.L<sup>-1</sup>), naphthalene (8.54 µg.L<sup>-1</sup>), xylene (6.08 µg.L<sup>-1</sup>) and benzene (3.79 µg.L<sup>-1</sup>).

The maximum contaminant level (MCL) of ethyl benzene (700 µg.L<sup>-1</sup>), toluene (1000 µg.L<sup>-1</sup>), xylene (10000 µg.L<sup>-1</sup>) and benzene (5 µg.L<sup>-1</sup>) is established by EPA [4-6]. Even though the environmental quality standards list comprises naphthalene, maximum permissible limits have not been mentioned for these compounds. The VOC levels found in Babolroud river water samples were lower than the maximum allowable concentration, reported at EPA. Moreover the names,

Analyte	Regression equation <sup>a</sup>	Correlation coefficient (R <sup>2</sup> )	LOD (µg.L <sup>-1</sup> )	Linear range (mg.L <sup>-1</sup> )	R.S.D. (%) (n =7)
Benzene	y = 0.0152x + 0.0035	0.9996	0.6	0.02-1	12.13
Toluene	y = 0.0123x - 0.0694	0.9993	0.8	0.01-1	8.14
Ethyl benzene	y = 0.0020x - 0.0051	0.9993	4.9	0.01-0.75	9.56
m/p-Xylene	y = 0.1312x + 0.0742	0.9996	0.1	0.01-0.75	1.20
Naphthalene	y = 0.0111x - 0.1268	0.9962	0.9	0.02-0.75	1.47

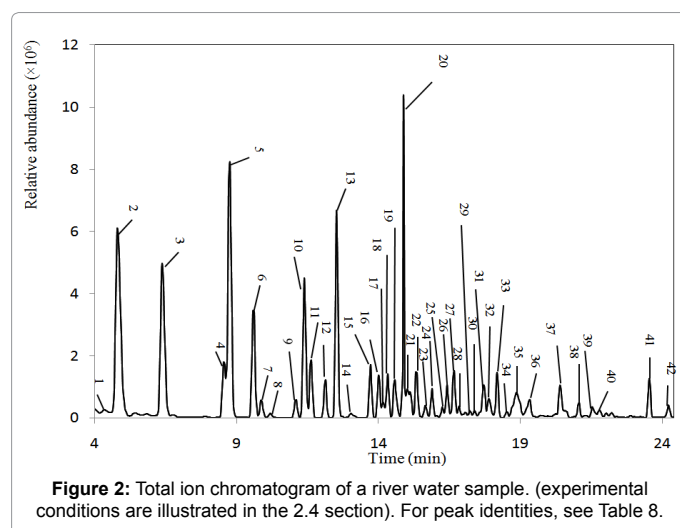
<sup>a</sup> y is the peak area and x is the analyte concentration in µg.L<sup>-1</sup>.

**Table 6:** Some analytical data obtained for VOCs analysis by SHS-GC-MS.

Methods	Sample/ Matrix	Limit of detection (µg.L <sup>-1</sup> )	Linear range (µg.L <sup>-1</sup> )	R.S.D. (%)	Recovery (%)	Ref
SHS-GC-MS	VOCs/river water	0.1-4.9	10-1000	1.20-12.13	90-108	<sup>a</sup>
SPME-GC-MS	VOCs/well water	0.2, 03	0.001-1.0	5.4, 6.4	---	[30]
HS-SPME-GC-FID <sup>b</sup>	VOCs/ marine water	1.3-12.8	0.01-5	2.2-5.3	88-103	[31]
SHS-GC-PID <sup>c</sup> -FID	VOCs/ seawater	0.22-7.48	0.05-0.5	5.6-9.8	---	[32]
GC-µECD <sup>d</sup>	Pesticides/ soil	0.004-1.2	0.5-200	0.5-14.1	66-147	[33]

<sup>a</sup>The presence method  
<sup>b</sup>Flame ionization detector  
<sup>c</sup>Photo ionization detector  
<sup>d</sup>Micro electron capture detector

**Table 7:** Comparison of figures of merits and recoveries of the presence method with other works.



**Figure 2:** Total ion chromatogram of a river water sample. (experimental conditions are illustrated in the 2.4 section). For peak identities, see Table 8.



number	Compound name	Characteristic ion (m/z)	Retention time (min)	Relative abundance (%)
1	1-Methyl- cyclopentene	67	4.756	0.31
2	Benzene	77	5.221	13.89
3	Toluene	91	6.791	9.39
4	Ethylbenzene	91	8.972	2.31
5	m/p-Xylene	91	9.164	13.49
6	o-Xylene	91	10.004	5.19
7	Styrene	104	10.281	0.84
8	(1-methylethyl)-benzene	120	10.597	0.23
9	Propyl benzene	91	11.495	0.79
10	1-Ethyl-3-methyl benzene	120	11.799	6.30
11	1,3,5-Trimethyl benzene	105	12.031	2.43
12	1-Ethyl-2-methyl benzene	120	12.534	1.57
13	1,2,3-Trimethyl- benzene	105	12.939	8.49
14	1-Methyl-2-(1-methylethyl)- benzene	119	13.44	0.29
15	1,2,4-Trimethyl- benzene	105	14.126	2.11
16	1-Methyl-3-propyl- benzene	105	14.42	1.68
17	(1-Methylpropyl)- benzene	173	14.575	0.51
18	2-Ethyl-1,4-dimethyl- benzene	119	14.734	1.79
19	Indane	117	14.979	1.83
20	1,4-Dichloro- benzenea	146	15.284	2.26
21	2-Ethyl-3,4-dimethyl- benzene	119	15.426	1.98
22	2-Ethyl-1,3-dimethyl- benzene	119	15.745	1.95
23	2-Butenyl- benzene	117	16.062	0.56
24	1-Ethenyl-3-ethyl- benzene	117	16.295	1.21
25	2-Ethyl-1,4-dimethyl- benzene	119	16.661	0.39
26	1,2,4,5-Tetramethyl- benzene	134	16.829	1.30
27	1,2,3,5-Tetramethyl- benzene	134	17.07	1.93
28	(1,1-Dimethylpropyl)- benzene	119	17.243	0.45
29	1-Methyl-3-(1-methyl-2- propenyl)- benzene	119	17.632	0.30
30	2-Ethyl-1,3-dimethyl- benzene	119	17.797	0.31
31	1H-Indene, 2,3-dihydro-5-methyl-	117	18.12	1.67
32	2-Ethyl-1,3-dimethyl- benzene	119	18.301	0.96
33	1-Methyl-4-(1-methylethenyl) benzene	117	18.594	1.75
34	1H-Indene, 1-methyl-	132	18.928	0.24
35	2,3-dihydro-4,7-dimethyl-1H-Indene	131	19.272	2.41
36	1H-Indene, 2,3-dihydro-1,6-dimethyl-	131	19.726	1.22
37	Naphthalene	128	20.811	2.06
38	1H-Indene, 2,3-dihydro-4,7-dimethyl-	131	21.467	0.64
39	2-Ethenyl-1,3,5- trimethyl- benzene	131	21.946	0.57
40	Ethanone, 1-(4-ethylphenyl)-	133	22.191	0.40
41	Naphthalene, 1-methyl-	142	23.95	1.43
42	Naphthalene, 2-methyl-	142	24.628	0.60

<sup>a</sup>Internal standard

**Table 8:** Major VOCs identified in Babolroud river water samples.

retention times, characteristics ions and relative abundance of other identified chemicals in river water sample are listed in Table 8.

## Conclusion

In this work, the effect of different factors on the SHS extraction efficiency of VOCs was studied by performing a 2<sup>4</sup> full factorial experimental design. The results showed that the percent of NaCl in the water samples and the extraction temperature were dominant factors in extraction efficiency of SHS. The results of VOCs analysis in optimum conditions indicated that the analytical figures of merits of the proposed method are comparable with other methods.

The main advantage of proposed protocol is that greatly decreased the risk of contamination or sample loss that can occur in other processes. No potential interferences are introduced, minimizing the

problems associated with the sample matrix. The sampling is fast and does not require expensive materials or extensive laboratory work. In addition, it does not use solvents, concentrating samples instead of diluting them, as it often happens when solvent extraction is used.

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