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Short communication

Optimization of headspace solid-phase microextraction by means of an experimental design for the determination of methyl *tert.*-butyl ether in water by gas chromatography–flame ionization detection

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Abstract

A procedure for determination of methyl *tert.*-butyl ether (MTBE) in water by headspace solid-phase microextraction (HS-SPME) has been developed. The analysis was carried out by gas chromatography with flame ionization detection. The extraction procedure, using a 65- μm poly(dimethylsiloxane)–divinylbenzene SPME fiber, was optimized following experimental design. A fractional factorial design for screening and a central composite design for optimizing the significant variables were applied. Extraction temperature and sodium chloride concentration were significant variables, and 20 °C and 300 g/l were, respectively chosen for the best extraction response. With these conditions, an extraction time of 5 min was sufficient to extract MTBE. The calibration linear range for MTBE was 5–500 $\mu\text{g/l}$ and the detection limit 0.45 $\mu\text{g/l}$. The relative standard deviation, for seven replicates of 250 $\mu\text{g/l}$ MTBE in water, was 6.3%. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Headspace analysis; Solid-phase microextraction; Experimental design; Water analysis; Methyl *tert.*-butyl ether

1. Introduction

Methyl *tert.*-butyl ether (MTBE) has been widely used as an oxygenate and octane intensifier in gasoline. However, it has become a known contaminant of aqueous systems due to its high solubility in water [1]. Its occurrence in the environment is a great concern because of the toxicity of MTBE and its degradation products. The US Environmental Protection Agency (EPA) has set an advisory level for taste and odor at 20–40 $\mu\text{g/l}$ [2].

Analytical methods used to determination MTBE include: purge and trap, headspace (HS) or direct aqueous injection (DAI) onto gas chromatography

(GC) [3–5]. A new extraction technique, solid-phase microextraction (SPME), has been used as an alternative. SPME does not require solvents, and it can be carried out directly from the liquid phase or from HS over the liquid samples [6]. SPME coupled with GC–MS has been used to determine MTBE in water [7,8] introducing the fiber in the aqueous phase. The time necessary for an effective extraction was fixed at 25 min [8] and 60 min [7]. In the first work, it was also indicated that added salt can cause problems due to salt crystallization on the fiber. The HS sampling is more advisable when the matrix could affect the determination of target analyte. On the other hand, HS versus direct sampling often shows an important reduction of extraction time.

There are several experimental variables affecting the HS-SPME procedure such as type of fiber, stirring rate, temperature, extraction time, and addi-

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tion of salt. Studies considering the variables one by one to obtain the best possible conditions have been followed by Gaines et al. [9] and Atchen et al. [10]. However, this procedure requires a high number of runs and is also time consuming. 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 runs [11,12]. This kind of methodology has been used for optimization of SPME conditions to determine pesticides in water [13,14]. Therefore, an experimental design can be the appropriate way to optimize the HS conditions to determine MTBE in water samples.

This work focused on the suitability of HS-SPME for determination of MTBE using GC–flame ionization detection (FID). The experimental design has been applied to determine the significant variables and to optimize the HS-SPME process of MTBE from water.

2. Experimental

2.1. Chemicals

MTBE (99.8% HPLC grade) was purchased from Sigma–Aldrich (St Louis, MO, USA). Methanol and sodium chloride were obtained from Panreac (Barcelona, Spain).

Standard solutions of MTBE in methanol were prepared (1000 mg/l), stored at 4 °C and used within 4 weeks. Working aqueous MTBE solutions, prepared just before use, were made from the stock methanolic solution and put into 40-ml vials sealed with PTFE-lined silicon septa. Vials and septa were purchased from Supelco (Bellefonte, PA, USA).

2.2. Equipment

SPME holders and fibers [100 µm thickness poly(dimethylsiloxane) (PDMS) and 65 µm poly(dimethylsiloxane)–divinylbenzene (PDMS–DVB)] were obtained from Supelco. A HP 6890 gas chromatograph equipped with a split-splitless injector and FID detector (Agilent Technologies, Wilmington, DE, USA) was used in all measurements. The injection port fitted with a 0.75-mm I.D. injection liner (Supelco) was operated in the splitless

mode, with the split/splitless purge valve opened 1 min after injection. The injection port temperature was 250 °C and helium served as carrier gas with a flow-rate of 2.2 ml/min. Chromatographic separation was accomplished with a fused-silica capillary column (HP-1, 30 m×0.32 mm, 0.25 µm film thickness, Agilent Technologies). The temperature program used was: 35 °C for 1 min, 20 °C/min up to 115 °C, hold 2 min, and then raised to 220 °C (2 min). The detector temperature was set at 280 °C. A PC interfaced to the GC using Chemstation software (Agilent Technologies) was used for data acquisition and processing.

A Heidolph MR 3003 magnetic stirrer (Heidolph Elektro, Kelheim, Germany) was used; 25-mm PTFE coated stir bars were put in the 40-ml vials just before runs.

The experimental matrix designs were carried out and evaluated using the STATISTICA software package (StatSoft, Tulsa, USA).

2.3. Analytical procedure

Sampling was carried out in the HS mode exposing the SPME fiber over stirred samples. The extraction was done for 5 min at 20 °C (using a constant temperature water bath). For all the runs, a stirring rate of 1000 rpm was used. After sampling the fiber was withdrawn into the needle of the holder and SPME was placed in the GC injector. The desorption temperature was 250 °C and 1 min was the desorption time for all the runs. No carryover was observed after this desorption time.

3. Results and discussion

The suitability of HS-SPME, using GC–FID, for the determination of MTBE in water was first checked. MTBE is a volatile compound with a boiling point of 53.6–55.2 °C. This ether is highly soluble in water (43–54.3 g/l) with an octanol–water partition coefficient ($\log K_{ow}$) of 1.20 [1]. These characteristics have to be taken into account before selecting the coating of the SPME fiber. Mixed phase coatings have complementary properties with respect to PDMS; and in general, they are more suitable for more volatile compounds showing higher distribution constants compared to PDMS.

For HS, stirring should be vigorous and has to be maintained constant in all experiments. The actual stirring rate required depends on the dimensions of the vial (40 ml) and the magnetic stir bar (25 mm). Hence, a stirring rate of 1200 rpm was chosen for all the preliminary runs. Several runs done under the same conditions (500 $\mu\text{g}/\text{l}$ aqueous solution of MTBE, room temperature, 1200 rpm) with different extraction times, showed that a 5-min time was sufficient to extract the MTBE by HS-SPME using PDMS–DVB fiber. The extraction efficiency of the two SPME fibers (65 μm PDMS–DVB and 100 μm PDMS) was also compared. Working under the same conditions (500 $\mu\text{g}/\text{l}$ of MTBE, room temperature, 1200 rpm, 5 min of extraction time) the efficiency was as much as 18 times better with a PDMS–DVB than with a PDMS stationary phase. Taking into account the latter results, PDMS–DVB fiber was selected for the screening and optimization designs trying to obtain the best experimental conditions.

3.1. Screening design

Considering the literature [6–10,13,14], five variables were selected to define the experimental field.

These variables affecting the extraction efficiency were: concentration of sodium chloride in water, extraction temperature, stirring rate, HS volume, and extraction time. The variables considered, the code used, and the low and high levels studied are shown in Table 1. The concentration of salt ranged from 0 (no addition) to 200 g/l (4 g of sodium chloride added to 20 ml of aqueous samples). The temperature, maintained by water bath, was from 24 to 60 °C. The stirring rate was from 800 to 1200 rpm. The HS volume varied from 10 ml (1/4 of total volume in 40-ml vial) to 20 ml (1/2 of total volume in 40-ml vial). The extraction time was considered from 2 to 20 min.

A 2^{5-2} fractional factorial design was applied to evaluate the main effects. This design, as a first step, is very useful since doing a few experiments it is possible to detect the most significant variables. In Table 1, are also shown the design matrix and the response (peak area in arbitrary units). The latter data are the average of two independent samples. In total, the design matrix had 11 runs, three of them in the central point. As the design shows, the runs were randomly carried out trying to nullify the effect of extraneous or “nuisance” variables.

Table 1
Experimental variables, levels, design matrix and results (peak area arbitrary units) in the 2^{5-2} fractional factorial design for MTBE determination with HS-SPME

Variable	Coded	Level		HSvol	Time	Peak area
		Low	High			
Salt concentration (g/l)	Salt	0	200			
Temperature (°C)	Temp	24	60			
Stirring rate (rpm)	Stir	800	1200			
Headspace volume (ml)	HSvol	10	20			
Extraction time (min)	Time	2	20			
Run	Salt	Temp	Stir	HSvol	Time	Peak area
3	200	60	800	10	2	532
5	0	24	1200	20	2	426
10 (C)	100	42	1000	15	11	566
4	0	60	800	20	20	234
9 (C)	100	42	1000	15	11	626
8	200	60	1200	20	20	446
7	0	60	1200	10	2	136
1	200	24	800	20	2	1730
2	0	24	800	10	20	458
6	200	24	1200	10	20	1697
11 (C)	100	42	1000	15	11	621

(C), central point.

An analysis of variance (ANOVA) was performed on the design to assess the significance of the model. The analysis of the results from the ANOVA showed that the significant variables were extraction temperature and salt concentration. The pareto chart of effects is shown in Fig. 1. In this chart, the bar lengths are proportional to the absolute value of the estimated main effects. This figure also includes a vertical line corresponding to the 95% confidence interval. An effect, which exceeds this reference line, may be considered significant with regard to the response. In this study the factors which gave significant effects in the signal were extraction temperature and sodium chloride concentration. The sign of the main effects showed that the response would be improved or not on passing a given factor from the lower to the high level.

The results of this first step led to the elimination of three variables: stirring rate, extraction time, and HS volume. Hence, the fixed values of 1000 rpm, 5 min, and 20 ml were chosen for the following step.

3.2. Optimization design

In order to optimize the variables that had significant influence, a central composite design (CCD) was carried out. The two variables and its low, central, and high levels were the followings: ex-

traction temperature (20–27.5–35 °C), and concentration of sodium chloride (150–225–300 g/l). These values are indicated in Table 2.

The CCD consists of the points of factorial design (2^N) augmented with $(2N+1)$ star points. In this work, 2^2 was augmented with $(2 \times 2 + 1)$. The star points are located at $+\alpha$ and $-\alpha$ from the centre of the experimental domain. An axial distance α was selected with a value of 1.414 in order to establish the rotatability condition. With the inclusion of this condition, the design generates information equally in all directions, i.e. a rotation of design about the origin does not alter the variance contours. The runs at the centre of the experimental field were performed three times more. Therefore, in total the matrix of CCD design involved 12 experiments. The values corresponding to every factor in each experiment are shown in Table 2. The experiments were randomly carried out, and each run was done with two independent samples. The average values of data (in arbitrary units of peak area) are shown in Table 2.

Fig. 2 shows the response surface developed by the model. The maximum was reached when the temperature was close to 20 °C and the salt concentration was slightly higher than 300 g/l. However, saturation problems appeared when salt concentration was over 300 g/l. Hence, trying to avoid

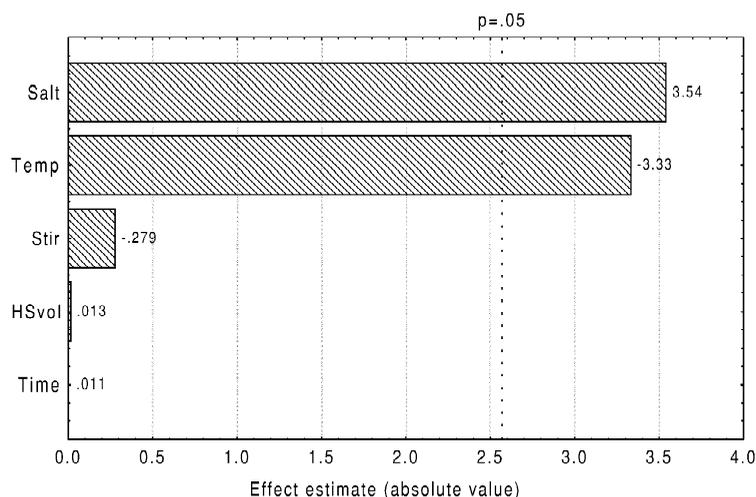


Fig. 1. Pareto chart of the main effects obtained from 2^{5-2} fractional factorial design.

Table 2

Experimental variables, levels, design matrix and results (peak area arbitrary units) in the central composite design (CCD) for MTBE determination with HS-SPME

Variable	Coded	Level		
		Low	Centre	High
Temperature (°C)	Temp	20	27.5	35
Salt concentration (g/l)	Salt	150	225	300
Run	Temp	Salt	Peak area	
11 (C)	27.5	225	1746	
1	20	150	1197	
5	18.5	225	1695	
8	27.5	315.8	2325	
10 (C)	27.5	225	1769	
2	20	300	2737	
4	35	300	1799	
9 (C)	27.5	225	1621	
12 (C)	27.5	225	1623	
6	36.5	225	1474	
3	35	150	871	
7	27.5	134.2	1130	

(C), central point.

saturation problems, a sodium chloride concentration of 300 g/l was chosen.

Resulting from this study, the optimum working conditions to obtain the best response were: extraction temperature, 20 °C; sodium chloride concentration, 300 g/l; extraction time, 5 min; stirring

rate, 1000 rpm and HS volume, 20 ml (in a 40-ml glass vial).

With these conditions, the linearity of the HS-SPME method, using GC-FID, for MTBE in water was evaluated. Calibration samples were prepared between 5 and 500 µg/l (5, 10, 25, 50, 100, 250, 500 µg/l). For each concentration, three runs with independent samples were carried out. The calibration curve, $y=5.7967x+174.440$, showed a correlation coefficient of 0.9953. The repeatability expressed as the relative standard deviation (RSD) was obtained by carrying out seven replicate assays at a level of 250 µg/l, and gave a value of 6.3%. This value was slightly better than the RSD obtained working with SPME-GC-MS [7] and HS-SPME-GC-MS [10].

The limit of detection (LOD), calculated considering the signal that differed three times from the blank average signal, was 0.45 µg/l. This value is better than the LOD obtained with DAI-GC-FID [3] and is similar to others obtained working with purge and trap with GC-FID [5] and HS-SPME-two-dimensional GC-FID [9]. The use of a more specific detection method, such as MS, results in a better LOD. Using SPME-GC-MS, the LOD was around 10 ng/l [7,8,10].

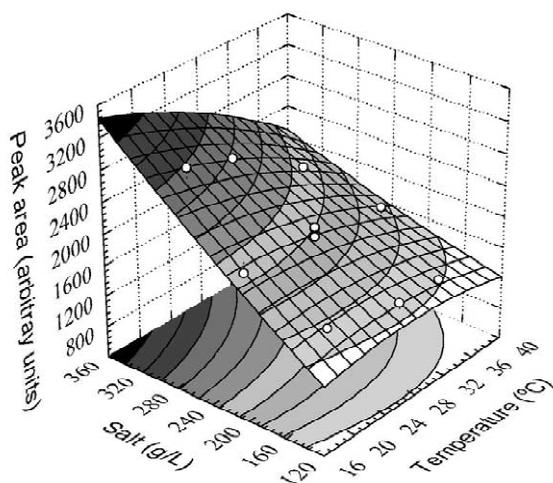


Fig. 2. Response surface estimated from the central composite design for temperature versus salt concentration.

The main advantages of the method are based on the simplicity of the equipment and rapidity. A time of 5 min was enough for the extraction. In a recent study [10] working with HS-SPME–GC–MS, the extraction time proposed was 30 min.

Considering the results, the proposed method could be suitable for screening, and also for determining the content of MTBE in contaminated waters (levels over 1 $\mu\text{g/l}$). Samples with low levels could be analyzed by means of more sensitive detectors.

4. Conclusions

This study proposes a simple HS-SPME method for the determination of MTBE in water that could be suitable for a screening method. The usefulness of experimental design is also shown in the optimization of extraction conditions for the HS-SPME method.

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