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Short communication

Trace analysis of methyl *tert*-butyl ether in water samples using headspace solvent microextraction and gas chromatography–flame ionization detection

Naader Bahramifar[a], Yadollah Yamini[a,*], Shahab Shariati-Feizabadi[a], Mojtaba Shamsipur[b]

[a] *Department of Chemistry, School of Sciences, Tarbiat Modarres University, P.O. Box 14115-175, Tehran, Iran*
[b] *Department of Chemistry, Razi University, Kermanshah, Iran*

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Abstract

In this study, a simple, rapid and efficient method for the extraction and determination of MTBE in water samples by the headspace solvent microextraction (HSME) and gas chromatography at sub (μg/l) level is described. Some significant variables such as type of solvent, extraction time, salt concentration, sample and microdrop volumes, stirring rate, sample and microsyringe needle temperatures were optimized. Using optimum extraction conditions (benzyl alcohol as extracting solvent, 4 M NaCl, sample temperature 35 °C, sample volume 6 ml, stirring rate 1000 rpm, microsyring needle temperature −6 °C, extraction time 7.5 min and micro drop volume of 2 μl) a detection limit of 0.06 μg/l and a good linearity ($R^2 > 0.999$) in a calibration range of 0.1–500 μg/l were achieved. This HSME method was applied to the analysis of MTBE in tap, well and spring waters and a groundwater sample contaminated by leaking gasoline from an underground storage tank (LUST) in a gasoline service station.

Keywords: Water analysis; Trace analysis; Headspace solvent microextraction; Methyl *tert*-butyl ether

1. Introduction

MTBE was introduced in 1979 as a fuel additive to increase the octane rating, but is now used at much higher concentrations (up to 15 wt.%) as a fuel oxygenate to reduce the atmospheric emissions of carbon monoxide and hydrocarbons. MTBE readily dissolves in water, moves rapidly through soils and aquifers, is resistant to microbial decomposition and is difficult to remove in water treatment. Its occurrence in the environment is of a great concern because of the toxicity of MTBE and its degradation products [1]. The United States Environmental Protection Agency (US-EPA) established a drinking water advisory for aesthetic concerns at 20–40 μg/l [2]. But, recently, California set a primary maximum contaminant level (MCL) of 13 μg/l for MTBE based on carcinogenicity studies in laboratory animals [3]. A secondary MCL of 5 μg/l was established in January 1999 for the taste and odor concerns [4].

MTBE and other oxygenates in ground waters are frequently measured using standard US-EPA approved methods (e.g., EPA 8021B, EPA 8260B, ASTM D 4815). These methods use purge and trap, headspace sampling techniques or direct aqueous injection (DAI), with gas chromatography–photoionization (GC–PID), flame ionization (GC–FID) or mass spectrometric (GC–MS) detection [5].

Recently, solid-phase microextraction (SPME), has been used to extraction and determination of many environmental pollutants [6] as well as MTBE content of ground water, surface water, industrial wastewater, drinking water and urban and rural precipitations [7–10]. However, despite several advantages of SPME [6], some practical drawbacks for the method have already been reported in the literature [11,12].

In the last few years, efforts have been directed towards miniaturizing the liquid–liquid extraction procedure by greatly reducing the solvent to aqueous phase volume ratio,

* Corresponding author. Fax: +98 21 8006544.
E-mail address: yyamini@modares.ac.ir (Y. Yamini).

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leading to the development of the solvent microextraction (SME) methodologies.

The methodologies that evolved from this novel approach fall into three categories:

(1) Direct single-drop microextraction, where the extractant phase is a drop of a water- immiscible solvent suspended in the aqueous sample [13,14].
(2) Microextraction using immiscible liquid films including liquid–liquid microextraction and liquid–liquid–liquid microextraction (back extraction) [15].
(3) Headspace solvent microextraction, where the extractant phase is a drop of solvent suspended in the headspace of sample [16,17].

Headspace solvent microextraction (HSME) is a novel method of sample preparation for chromatographic analysis. This system involves a microdrop of a high boiling point organic solvent extruded from the needle tip of a gas chromatographic syringe, which is exposed to the headspace above a sample. Volatile organic compounds are extracted and concentrated in the microdrop. Then, the microdrop is retracted in the microsyringe and injected directly into a chromatograph.

The high volatility and low polarity of MTBE lead the compound to have a fast diffusion to headspace and an enhanced distribution into the microdrop, respectively. These characteristics persuade us to study the determination of MTBE in water samples by a HSME method using a GC–FID equipment. Several experimental variables affecting the HSME procedure including the type of solvent, the stirring rate, the temperature and the volume of sample and microdrop and addition of a salt were optimized. Under the optimized experimental conditions, the detection limit and the dynamic linear range of the proposed method were then evaluated.

2. Experimental

2.1. Reagents and materials

MTBE (99.5%, Merck, Darmstadt, Germany) was used as received for the preparation of all standard solutions. Methanol (99.9%) and sodium chloride (99.5%) were obtained from Merck. Benzyl alcohol (99.0%) and toluene (99.8%) were obtained from Fluka. Double-distilled water was used for sample preparation. Helium (ultrapure carrier grade) was obtained from Roham Gas Company (Tehran, Iran).

Calibration stock solutions were prepared by adding 10 μl of pure MTBE to 10 ml of MeOH in a 10 ml vial with a PTFE-silicon septum (Supelco). The mixture was manually agitated for 5 min. The first dilution steps were performed with methanol whereas further preparation of the standard solutions was carried out with double distilled boiled water, which was cooled (to 1 °C) prior to use. The standard solutions were cooled at 4 °C and used within 4 weeks. All sample and standard vials were completely filled to eliminate headspace. The method was optimized with MTBE solutions of 100 μg/l concentration. A fixed concentration of toluene internal standard (5 mg/l) was prepared in the benzyl alcohol extracting solvent. It should be noted that, in this work, we used toluene as an internal standard because (1) its use resulted in an improved precision and accuracy and (2) there was no toluene in the real samples tested. However, in the presence of toluene in the samples, other internal standards (such as ethyl acetate) should be employed.

2.2. Instrumentation and analytical procedure

The extraction and injection procedures were carried out using a 5 μl SGE microsyringe (Code: 5B-7). A magnetic stirrer (Heidolph MR 3001 K) and an 8 mm × 1.5 mm stirring bar were used to stir the solution. Two circulating water bathes (Frigomix, B. Braun UM-S) were used for adjusting the temperatures of the syringe needle and the sample solution with an accuracy of ±0.1 °C. Detailed descriptions of the apparatus and extraction procedures were given in our previous paper [17].

The GC–FID analysis was performed using a Hewlett-Packard (5890 series II) gas chromatograph equipped with a flame ionization detector and a DB5 (5% biphenyl + 95% poly dimethyl siloxan) fused-silica capillary column with a 20 m × 0.53 mm i.d. and 1.5 μm film thickness (J & W Scientific, Folsam, CA). The injector and detector temperatures were 250 and 260 °C, respectively. The injection port was operated at a 1:1 split to allow for greater sensitivity. A constant flow (5 ml/min) of Helium was used as carrier gas. The analysis was performed with an initial column temperature of 40 °C held for 2 min followed by heating to 70 °C at 10 °C/min, and finally, heating to 250 °C at 45 °C/min, holding at 250 °C for 10 min to clean the column. MTBE eluted in 2.04 min, and the total time of analysis was 19 min.

All quantifications made in this study were based on the relative peak area of MTBE to the internal standard (toluene) from the average of three replicate measurements.

3. Results and discussion

Ai [18,19] proposed an equation to handle the situation of the non-steady state mass transfer for the headspace SPME that can be used for HSME. According to this improved model, a direct relationship exists between the amount of analyte extracted by HSME, and the initial concentration of analyte in the sample. This relationship indicates that HSME quantitative analysis is feasible in nonequilibrium situations once the HSME conditions and the sampling time are held constant.

3.1. Selection of extracting solvent

The extraction solvent has to satisfy the following three requirements: it should possess a low volatility, should conveniently extract the analytes and its peaks should be well-separated from the analyte peaks in the chromatogram. Thus, choosing the most suitable extracting solvent is very important for achieving good sensitivity, precision and selectivity of the target compounds. Five solvents differing in polarity and volatility, namely, 1-propanol, 1-butanol, toluene, *p*-xylene and benzyl alcohol were tested. Among different extracting solvents tested, the use of benzyl alcohol resulted in the best extraction efficiency, while its chromatographic peak was easily separated from the sample peaks. Thus, benzyl alcohol was chosen as an extracting solvent in this investigation.

3.2. Addition of salt

To study the salt effect on the MTBE extraction efficiency, water samples containing different concentrations of sodium chloride and potassium nitrate were analyzed. Results show that the headspace extraction efficiency of MTBE is increased with increasing concentration of both salts in the order of NaCl > KNO_3. A 4 M concentration of NaCl was chosen to provide the best results in further studies.

3.3. Sample temperature

The temperature of the sample influences the evaporation of MTBE into the headspace. We expected that an increase in sample temperature will result in improved the extraction efficiency, because of the increased evaporation of the analyte and analyte concentration in the headspace. The effect of sample temperature was studied by exposing a benzyl alcohol-extracting drop for 10 min in the headspace while changing the sample temperature from 15 to 45 °C.

The results are shown in Fig. 1. As it can be seen from Fig. 1, the amount of analyte extracted into the benzyl alcohol drop increases with increasing temperature up to 35 °C. This can be explained by the fact that at higher temperatures the vapor pressure of the analytes and their concentrations in headspace increase. However, the amount of analyte extracted decreases by further increase in temperature from 35 to 45 °C. It should be noted that, by increasing the sample temperature, the headspace temperature and, accordingly, the temperature of the microdrop would also increase. Since the analyte absorption on the microdrop is an exothermic process, the amount of analytes absorbed by the microdrop decreases upon a further increase in the sample temperature. Hence the optimum sampling temperature was 35 °C.

3.4. Sample volume

Sample volume plays an extremely important role in HSME analysis. In HSME the combination of K_{oh} (organic drop/headspace distribution constant) and K_{hs} (headspace/solution distribution constant) determines the magnitude of the sample volume effect on the amount of extracted analyte in the microdrop. An increase in sample volume and, consequently, a decrease in headspace volume enhance the extracted amount of analyte, which improves the sensitivity [20,21].

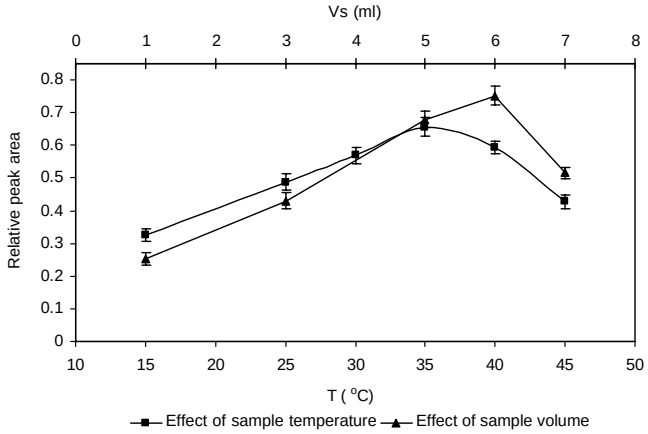

Fig. 1. Influence of sample temperature and sample volume on the relative peak area of MTBE. Extraction conditions: drop volume, 1 μl; extraction time, 10 min; microsyringe needle temperature, −4 °C; stirring rate, 500 rpm; NaCl concentration, 4 mol/l.

The optimal ratio of the aqueous volume to the headspace volume for headspace analysis in 10 ml vials was determined by varying the sample volume (amounts of 1, 3, 5, 6, 7 and 8 ml). The results are also shown in Fig. 1. The extracted amounts of MTBE increases continuously with increasing sample volume, reaches a maximum at an aqueous volume of 6 ml and then decreases at the sample volumes of 7 and 8 ml. Upon stirring the solution at a fixed rate, with a larger volume, the convection is not as good in the aqueous phase, resulting in less extraction. Moreover, when a volume of 8 ml is used the microdrop fall into the sample solution. This is because of the decreased volume of the headspace and increased induced agitation in the headspace.

3.5. Stirring rate

As demonstrated by Theis et al. [16], the overall extraction process has two rate determining steps, namely aqueous-phase mass transfer and diffusion of solutes into the extracting solvent. Although the diffusion of analyte into the extracting solvent cannot be easily enhanced in practice, the aqueous-phase mass transfer can be improved by stirring the sample solution. In fact, agitation of the sample solution enhances the mass transfer in the aqueous phase and induces convection in the headspace and, consequently reduces the time for reaching a thermodynamic equilibrium. Thus the equilibrium between the aqueous and headspace can be achieved more rapidly by stirring the aqueous sample. In this study, samples with a volume of 6 ml were

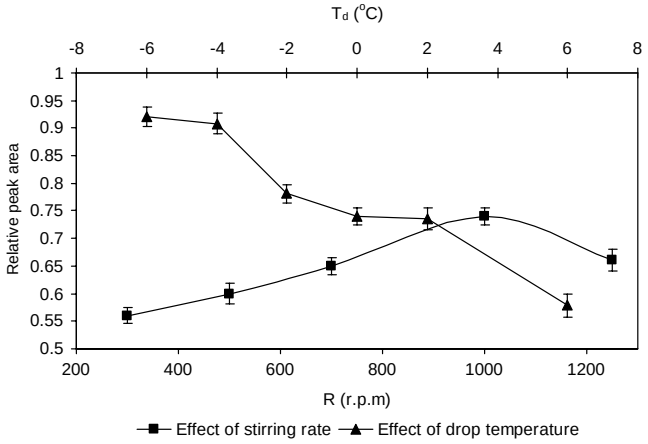

Fig. 2. Influence of stirring rate and microsyringe needle temperature on the relative peak area of MTBE. Extraction conditions: drop volume, 1 μl; extraction time, 10 min; sample volume, 6 ml; sample temperature, 35 °C; NaCl concentration, 4 mol/l.

continuously agitated at 35 °C at different stirring rates (300, 500, 700, 1000, 1250 rpm) with a 0.8 cm magnet on a stirrer plate (Fig. 2). According to Fig. 2, the relative peak area increases with increasing stirring rate up to 1000 rpm. Hence, a stirring rate of 1000 rpm was used for further works.

3.6. Microsyringe needle temperature

In the previous researches of HSME, the microsyringe was not cooled. In our previous works [17,22,23] we introduced a cooling system for the microsyringe needle, in order to cool the microdrop. It is well known that the organic drop/sample distribution coefficient decreases with increasing microdrop temperature, which results in the decreased sensitivity of the extraction process. To prevent this loss of sensitivity, the extracting phase can be cooled, while increasing the sample temperature. This "coldfinger" effect results in increased accumulation of the volatilized analytes on the extracting phase. This additional enhancement in the sample matrix-extraction phase distribution constant associated with the temperature gap present in the system can be described by the following equation [24]:

$$K_T = \frac{K_o T_h}{T_e} \exp\left[\frac{C_p}{R((\Delta T/T_e) + \ln(T_e/T_h))}\right] \quad (2)$$

where $K_T = C_e(T_e)/C_h(T_h)$ is the distribution constant of the analyte between the cold extraction phase (i.e., the microdrop having temperature T_e) and hot headspace at temperature T_h, C_p is the constant-pressure heat capacity of the analyte, $\Delta T = T_h - T_e$ and K_o is the organic drop/headspace distribution constant of the analyte when both drop and headspace are at temperature T_e, C_e and C_h are the concentrations of the solute in the microdrop and headspace, respectively.

The decreased needle temperature leads to the condensation of analyte on the cooled microdrop and, thus, increases the extraction efficiency. Thus the influence of needle temperature on the extraction efficiency of the system was studied from −6 to 6 °C and results are also shown in Fig. 2. The figure shows that the extraction efficiency increases with decreasing needle temperature. Hence, further extractions were performed at a microsyringe needle temperature of −6 °C. It is worth mentioning that, although the use of a separate water circulator for the needle cooling causes some increased cost of the system, the extraction efficiency of the system at a needle temperature of −6 °C, will be increased by factor of 50% (Fig. 2), as it compared with the results obtained at a temperature of 6 °C. Thus, at relatively high concentrations of MTBE (i.e., >0.01 mg/l) there is no need for such cooling system; while, at lower MTBE concentrations, the needle cooling seem to be necessary.

3.7. Extraction time

The optimum extraction time was determined by varying the time of exposing the microdrop in the headspace of a standard aqueous solution (from 2 to 15 min). A graph of extraction time versus relative peak area (Fig. 3) shows that the analytical signal increased with extraction time following a more or less exponential like behavior. This rapid initial increase in the amount of analyte extracted followed by a much slower increase lasting a long time reflects the processes taking place in the system [20,25].

The first stage corresponds to analyte extraction from the headspace only. As soon as the headspace concentration of the analyte falls bellow the equilibrium value with respect to the aqueous phase, the analyte molecules begin to diffuse from the aqueous phase to the gaseous phase, which is a rate-determining step. Since it is not practical to wait for equilibrium to occur, the extraction time should be just long enough for the extraction rate to slow down for an improved precision. An optimum sample extraction time of 7.5 min was therefore chosen for further studies.

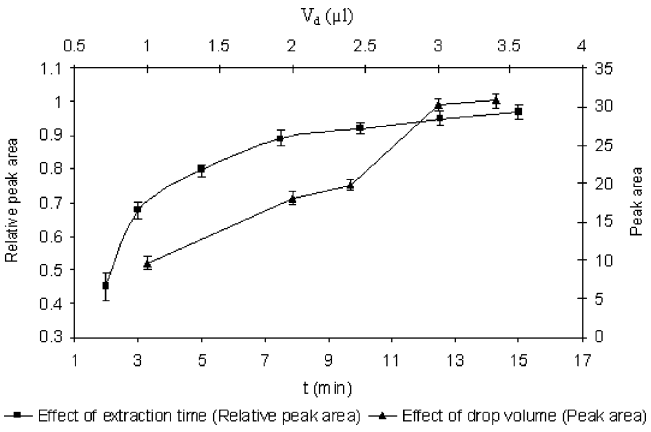

Fig. 3. Influence of extraction time and microdrop volume on the relative peak area of MTBE. Extraction conditions: microsyringe needle temperature, −6 °C; sample volume, 6 ml; stirring rate, 1000 rpm; sample temperature, 35 °C; NaCl concentration, 4 mol/l.

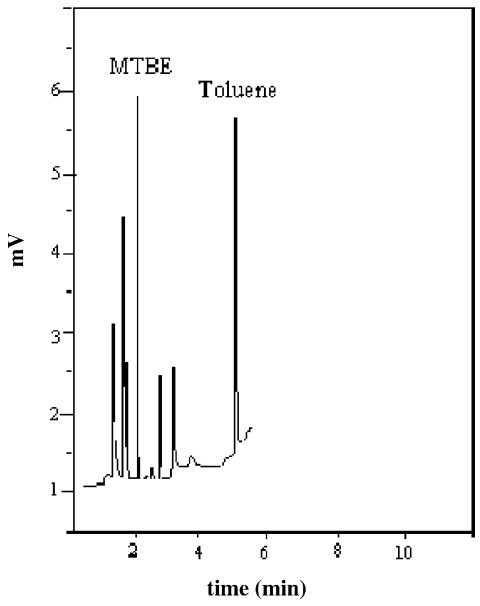

Fig. 4. FID chromatogram of a 100 μg/l MTBE solution extracted using headspace solvent microextraction. Extraction conditions: drop volume, 2 μl; extraction time, 7.5 min; microsyringe needle temperature, −6 °C; sample volume, 6 ml; stirring rate, 1000 rpm; sample temperature, 35 °C; NaCl concentration, 4 mol/l.

3.8. Organic microdrop volume

The amount of extracted analyte depends on the microdrop volume [17]. The effect of microdrop volume on the analytical signal is shown in Fig. 3.

As can be seen in Fig. 3, the use of a large organic drop results in an increased analytical response. However, larger drops are difficult to manipulate and are less reliable [26]. Additionally, the larger injection volumes result in band broadening in capillary GC. Thus, a microdrop volume of 2 μl was used as it ensured the formation of a stable/reproducible microdrop and allowed fast stirring speeds, albeit with some penalty in the form of loss of sensitivity.

3.9. Evaluation of the method performance

Fig. 4 shows the chromatogram of a standard solution containing 100 μg/l of MTBE after its headspace microextraction at optimum working conditions (i.e., extraction temperature, 35 °C; sodium chloride concentration, 4 M; extraction time, 7.5 min; stirring rate, 1000 rpm; drop volume, 2 μl; sample volume, 6 ml; microsyringe needle temperature, −6 °C). Under optimal experimental conditions, the linearity of the proposed HSME method, using GC–FID, for the determination of MTBE in water samples was evaluated. Calibration curves were prepared between 0.1 and 500 μg/l. At each concentration, three runs with independent samples were carried out. The calibration curve, with a regression equation $A_r = 0.0082C$ (μg/l) + 0.0158, where A_r is the relative peak area of MTBE to toluene as an internal standard, showed a correlation coefficient of 0.999.

The limit of detection (LOD), calculated based on the signal that differed three times from the blank average signal, was 0.06 μg/l. This value is better than the LOD obtained with DAI-GC–FID [27] and is more or less similar to that reported for the purge and trap with GC–FID [28], HS–SPME two dimensional GC–FID [29] and HS–SPME–GC–MS [7,10]. Table 1 compares the figures of merit of the present method with those reported in the literature for the determination of MTBE in water samples.

Analytical accuracy was assessed from the recovery of analyte spiked to various samples (Table 2). The recovery was 103–107% with a mean value of 105%. This obtained recovery is comparable with that achieved using the SPME in other studies [10,30]. The repeatability expressed as the relative standard deviation (R.S.D.) was obtained by carrying out five replicate assays on different water samples (Table 2), and gave a value less than 4.8%. These values were slightly better than the RSD obtained with HS–SPME–GC–MS [10].

In order to examine the enrichment factor of analyte, three replicate extractions were carried out at optimal conditions from aqueous solutions containing 100 μg/l MTBE. The enrichment factor, calculated as the ratio of the final concentration of the analyte in the microdrop and its concentration in the original solution, was found to be 1160. To obtain the final concentration of MTBE in the microdrop, it was injected to GC and the area of resulting signal was used to determine its concentration from a calibration graph obtained, from the direct injections of varying concentration of the sample under the same experimental conditions.

Table 1
Comparison of HSME with other methods for determination of MTBE in water samples

Method	Detection system	LOD (μg/l)	Dynamic linear range (μg/l)	R.S.D. (%)
Proposed method (HSME)	FID	0.06	0.1–500	4.8
Ref. [7] (HS–SPME)	MS	0.01	0.02–5	10
Ref. [9] (HS–SPME)	FID	0.45	5–500	6.3
Ref. [27] (static headspace)	MSD[a]	1.2[b]	–	4.5[b]
		2.0[c]		3.3[c]

[a] Mass-selective detection.
[b] Calculated by EPA method.
[c] Calculated by Hubaux and Vos.

Table 2
Determination of MTBE in water samples at optimum extraction conditions

Sample	Concentration (μg/l)	Added (μg/l)	Found (μg/l)[a]	Recovery (%)
Tap water	–[c]	20.0	21.2 (±2.2)	106
Spring water	–	10.0	10.2 (±4.5)	103
Well water	–	20.0	20.7 (±4.8)	104
Qhanat water[b]	6.8	4.0	11.6 (±1.9)	107

[a] Mean of triplicates with percent R.S.D.
[b] Qhanat water as a ground water sample was contaminated with leaking underground storage tank in gasoline service station.
[c] Not found.

Very recently, using a SPME method, Fang, et al., have shown that the presence of BTEX will result in the diminished extraction efficiency of MTBE [31]. In order to examine the influence of BTEX on the extraction of MTBE by the proposed method, the extraction of 20 μg/l of MTBE was performed in the presence and absence of 100 and 200 μg/l of *o*-xylene. The result indicated that, the presence of such amounts of *o*-xylene dose not affected the extraction efficiency of MTBE. This is most probably due to the fact that, in the proposed HSME method, the extraction inside microdrop is based on distribution while, in the SPME adsorption and distribution can occur, it is depend of the SPME coating. For instance, Crboxen-polydimethylsiloxane (CAR-PDMS) extracts MTBE via adsorption [31]. For adsorbent-type fibers, the number of sites or pores is limited. Analytes may compete for the same site. As the concentration of a mixture of analytes is increased, the sites will eventually become occupied. At this point no more samples will be adsorbed, or else displacement will occur [31].

4. Conclusions

Headspace solvent microextraction proposed in this work is attractive in terms of simplicity, analytical precision and accuracy, overall sample preparation time, cost and minimization of organic waste. In comparison with the purge and trap, the proposed method is advantageous in terms of its simplicity and low cost, while it has a limit of detection in the same range as purge and trap. Moreover, the limit of detection of the proposed method is much lower (of about three order of magnitude) than that of DAI method [5].

Since a fresh organic solvent is used for each extraction, there is no memory effect. Comparison of this technique with solid-phase microextraction for the determination of MTBE in water samples reveals that the two techniques are comparable in terms of precision, sensitivity and analysis time. While, HSME appears to offer three distinct advantages over headspace SPME. First, the choice of solvents is virtually unlimited, as compared to the number of phases currently available for SPME. Second, the cost of microliters of solvent for HSME is negligible compared to the cost of commercially prepared SPME fibers. It should be noted that, the apparatus involves a magnetic stirring, a glass vial, two circulating water baths and a microsyringe, which the water baths are the main costly parts. Moreover, in each extraction, only 2 μl of benzyl alcohol of a very low coast is necessary.

Third, the analyte desorption from the polymer in the GC injector is slower than the conventional solvent evaporation and leads to analyte peaks showing greater tailing. On the other hand, SPME offers the advantage that is no solvent peak in the chromatogram and splitless “injection” can be employed.

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