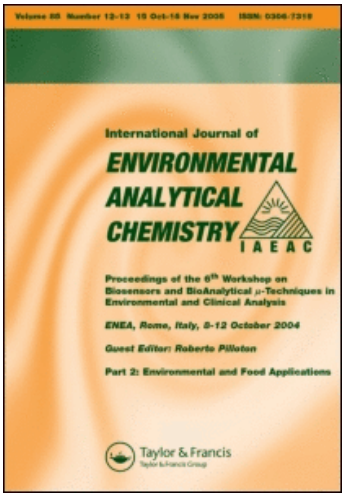

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DETERMINATION OF METHYL TERT-BUTYL ETHER (MTBE) IN AQUEOUS SAMPLES BY PURGE AND TRAP-GAS CHROMATOGRAPHY-FLAME IONIZATION DETECTOR

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A purge-and-trap method was developed for sensitive and fast determination of trace MTBE in aqueous samples. The sample solutions were added with 10% (w/w) sodium sulfate and adjusted to pH 4 by acetic acid and sodium acetate buffer solution to improve the purge efficiency before the analysis. A CP-4010 purge-and-trap injector (PTI) was used to purge MTBE from water and cool it in the cold-trap kept at −75°C, then the cooled trap was flash heated to release the analytes onto a HP-1 capillary column and detected by gas chromatography-flame ionization detector (GC-FID). A good linear response was obtained and the detection limit was $0.1\,\mu g\,L^{-1}$. This method has been successfully applied to the determination of MTBE in several Chinese river samples.

Keywords: MTBE; Purge-and-trap; GC-FID; River samples

INTRODUCTION

The environmental fate of methyl tert-butyl ether (MTBE) has become a subject of renewed interest due to the large quantities of this compound that is now being used to oxygenate gasoline to improve combustion and reduce the levels of atmospheric carbon monoxide, hydrocarbons and ozone [1]. The contamination of MTBE to the environment mainly comes from leakage of underground tank and discharge from cars [2]. MTBE dissolves readily in groundwater and moves faster than benzene, toluene, ethyl-benzene, xylene (BTEX) or any other fuel component. The leakage from tanks would easily contaminate the underground drinking water sources. In the atmosphere, MTBE would dissolve in rainwater and contaminate surface water or

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shallow ground water [3–5]. It has been reported that the detection of MTBE in groundwater and surface water was on a dramatic upswing in recent years [6].

The tumorigenicity of MTBE has been studied in long-term bioassays [7–9]. MTBE and its metabolite *t*-butanol are negative in standard genotoxicity studies [10]. It has been found that renal tumor induction by MTBE may be mediated by the accumulation of $\alpha_{2\mu}$-globulin [11,12]. An impaired degradation of this protein induced by bound metabolites of MTBE may cause renal toxicity, cell proliferation, and finally renal tumors in male rats [13]. MTBE exposure increased the incidence of liver tumors in female mice and testicular tumors in male rats [14]. Testicular tumors in male rats were also observed following oral administration of MTBE [15].

Trace levels of ether in water samples have been successfully analyzed by direct aqueous injection (DAI) methods [16,17]. Church *et al.* [17] described a DAI-GC-MS method for the determination of MTBE and related compounds with a MTBE detection limit near $0.1\,\mu g\,L^{-1}$ by maximizing the amount of sample injected ($10\,\mu L$) and venting the water after injection. However, general use of this method in commercial laboratories is unlikely, because of difficulties in adapting it to benchtop spectrometers and because of the series of bulky high-efficiency diffusion pumps that are required in the handling of large injection volumes to achieve low detection limits.

Solid-phase microextraction (SPME), a relatively new form of SPE, has been successfully utilized to rapidly concentrate MTBE and related oxygenate compounds in aqueous matrices [18,19]. SPME is a solventless extraction technique that relies on direct partitioning of analytes in either sample headspace or matrix to a small amount of stationary phase bonded to a fused-silica fiber. The selectivity and sensitivity of SPME is highly dependent upon the composition of the stationary phase. When the equilibrium between headspace and stationary phase is reached or the stationary phase is saturated, no more analytes can be absorbed on the fiber. Another solventless extraction technique, purge-and-trap, is free from this restriction. Three purge-and-trap gas chromatography methods [20], USEPA method 8240B/60B (mass spectrometry), USEPA method 8020A/21B (photoiozination detection), ASTM method D4815 (flame ionization detection), most commonly were employed for monitoring of oxygenate compounds in groundwater at leaking underground storage tank sites. All three methods were suitable for detecting ether oxygenate compounds at a concentration of 1 μg/L in reagent water. USEPA method 524.2 [21], which is a laboratory analytical method for the determination of volatile organic compounds (VOCs) in water, uses a purge-and-trap technique to isolate VOCs from water matrix, and capillary column gas chromatography-mass spectrometry (GC-MS) for the identification and measurement of the analytes. This method has been used for the determination of MTBE in estuarine water, sediments and human blood [22,23], and got detection limits of nanogram per liter levels.

This work presents a simple and fast purge-and-trap method for the analysis of MTBE in water samples. MTBE and other VOCs purged from water were directly cooled in a cold-trap maintained at desired low temperature by an electrically operated cryo-valve that introduced liquid nitrogen at an appropriate rate to cool the trap. After that, the cooled trap was flash heated to 200°C to release the analytes onto the analytical column and the GC program is started by the purge-and-trap injector (PTI) simultaneously. No adsorbent tube packed with sorbents was needed in this method, and the detection limit $0.1\,\mu g\,L^{-1}$ was obtained.

EXPERIMENTAL

Material and Reagents

MTBE standard was obtained from Acros Company and was directly weighed and dissolved in de-ionized water to form a concentration level of 0.1 mg mL^{-1} as the stock solution, and stored in refrigerator. Working standard solutions 10 μg mL^{-1} were obtained by diluting the stock solution with de-ionized water.

Buffer solution with pH 4 was the mixture of acetic acid and sodium acetate solutions. All solvents and reagents used were of analytical reagent grade or better.

Instrumentation

A Model CP-4010 PTI (Chrompack, Middleburg, The Netherlands) was used to purge the analytes from liquid phase. A 40-mL purge vessel for sample pretreatment was used throughout the experiment, which was kept at a constant temperature in a TB-B5 Thermo bath (Shimadzu, Japan). Carrier gas N_2 was led through this purge vessel and the volatile components purged from the sample were transported to the cooled trap via a condenser, which froze out excess moisture so as not to block the trap. The cold trap was a piece of CP-Sil 5 CB fused silica capillary column (30 cm × 0.53 mm, film thickness 0.50 μm) and maintained at desired low temperature by an electrically operated cryo-valve which introduced liquid nitrogen at an appropriate rate to cool the trap. At the point of injection, the cooled trap was flash heated to release the analytes onto the analytical column and the GC program is started by the PTI simultaneously.

The analysis was operated on an Agilent-6890 gas chromatograph (Agilent, USA) fitted with a HP-1 capillary column (30 m × 0.25 mm, film thickness 0.25 μm). The detector (FID) temperature was maintained at 250°C. The flame was supported by a mixture of H_2 50 mL min^{-1}, compressed air 400 mL min^{-1}, and N_2 (makeup gas) 20 mL min^{-1}.

Sampling Procedure

Water samples were collected in 10 L vessels at several typical points from Yongding river near Beijing, the downriver of Guanting reservoir in October 2000. The water (5–10 cm below the surface) was collected and immediately adjusted to pH 2–3 by 6 mol L^{-1} hydrochloric acid. They were stored in the dark at 4°C and analysis was usually carried out within a week.

Analytical Procedure

MTBE water samples were adjusted to pH 4.0 with HAc-NaAc buffer solution and were added 10% (w/w) Na_2SO_4 before analysis. A 15 mL sample was placed in the purge vessel, which was purged for 10 min with nitrogen gas at a pressure of 50 kPa. The purged analytes were trapped in the capillary cold-trap at −75°C. After purging, the trap was flash heated to 200°C and the gaseous analytes were released onto the analytical column and followed the gas chromatographic separation and determination. The column head pressure was kept at 50 kPa and the oven temperature was programmed at 140°C for 4 min, then ramped to 200°C at 10°C min^{-1}, and held at 200°C for 8 min.

RESULTS AND DISCUSSION

Selection of Trap Temperature

As shown in Figure 1, MTBE could be separated from other interference entirely ($t_R = 4.7$ min) and responded by FID. Although the boiling points of MTBE 55.2°C are not very high, it is necessary to keep a relative lower trap temperature of the cold trap, so that MTBE could be highly accumulated in this step. Accordingly, the trap temperature could firsthand dominate the efficiency of analytes' cooling and accumulation. The effect of trap temperature was studied and results showed that the trap efficiency could be improved by dropping the trap temperature and the chromatographic peak became sharper as well. When the trap temperature was below −75°C, MTBE could be trapped onto the cold trap completely. Thus, in this article −75°C was selected as the trap temperature for MTBE.

Effect of Purge Time and Purge Flow

The effects of purge time and purge flow were shown in Figures 2 and 3. It showed that improving purge flow-rate and purge time could bring more MTBE out of the water samples. A flow-rate of 30 mL min^{-1} for 10 min could get maximum purge efficiency. However, a shorter purge time could not offer the complete purge of the MTBE due to its high water-solubility, higher purge flow-rate or longer purge time may contribute to part loss of MTBE, which has already being trapped in the cold-trap. A lower purge flow could not efficiently carry MTBE out of the sample matrix, while a higher purge flow could also do harm to the adsorption and accumulation of MTBE in the cold trap. Therefore, a purge at 30 mL min^{-1} for 10 min was preferred.

Effect of pH Value

Optimum pH value was determined by varying the pH of MTBE standard solutions. The effect of pH value on the purge efficiency (reflected by the response peak area)

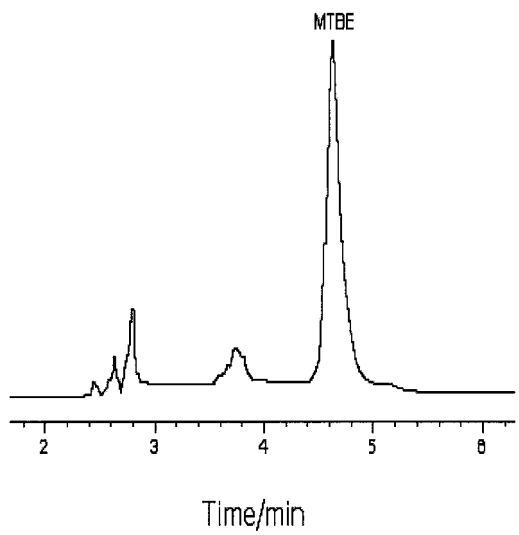

FIGURE 1 Separation of MTBE, 20 μg L^{-1} standard MTBE.

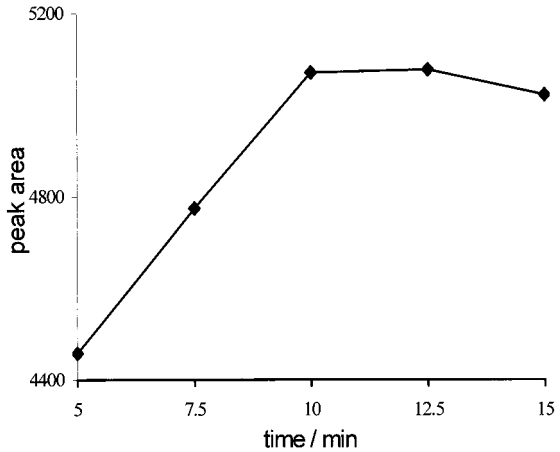

FIGURE 2 Effect of purge time, $10\,\mu g\,L^{-1}$ standard MTBE.

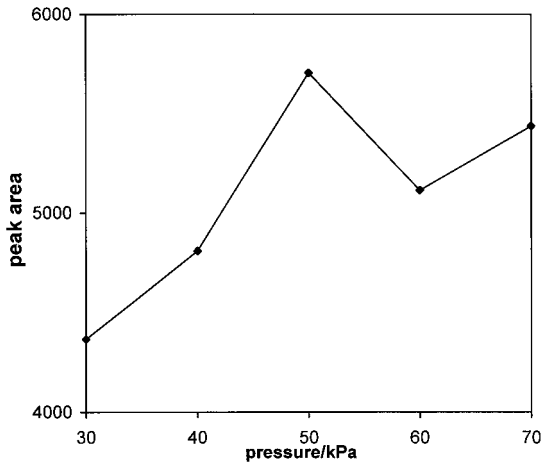

FIGURE 3 Effect of purge flow, $10\,\mu g\,L^{-1}$ standard MTBE.

is shown in Figure 4. Small amounts of HCl or NaOH were added to the solutions to adjust the pH value. It was found that the purge efficiency was highest when pH = 4.0. In lower pH value solution, an H–O bond may be formed easily and prevent the escaping of MTBE from the solution. In this experiment, HAc-NaAc buffer solution was chosen to keep the pH value stable.

Effect of Salts

The addition of salts to the sample increases greatly the efficiency of purge for MTBE. Three kinds of salts: NaCl, Na_2SO_4 and Na_2SO_3 were used to choose an appropriate one by comparing the results (as shown in Figure 5). When added 10% (w/w) to the solution, all three salts can improve the purge efficiency at the greatest degree. Na_2SO_3 could result in a highest sensitivity, then followed by Na_2SO_4, and NaCl.

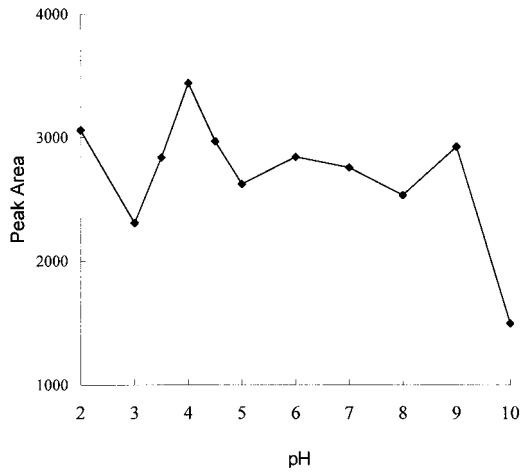

FIGURE 4 Effect of pH value, 10 μg L^{-1} standard MTBE.

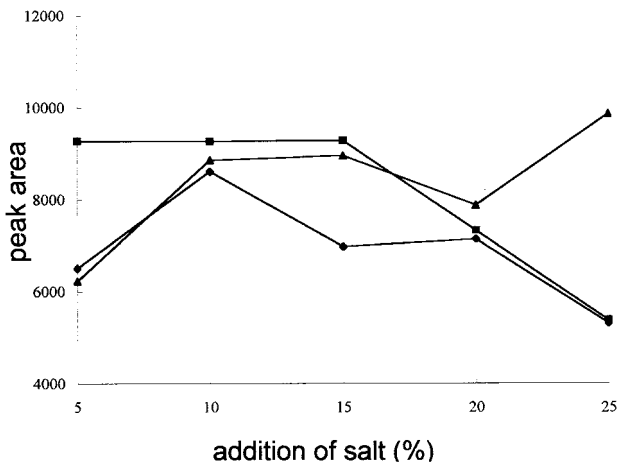

FIGURE 5 Effect of salts, NaCl(◆), Na_2SO_3(■), Na_2SO_4(▲), 10 μg L^{-1} standard MTBE.

However, the MTBE response peak area had best recurrence and accuracy when using Na_2SO_4. Thus a Na_2SO_4 concentration of 10% (w/w) was chosen to ensure that high and stable MTBE responses could be maintained.

Effect of Temperature

It was supposed that the escaping ability from water of MTBE would increase with the sample temperature increasing. While 30°C was a turning point in this experiment, the response peak area increased when the temperature was lower than 30°C; after that, it began to decrease greatly in spite of the increasing temperature (shown in Figure 6(a)). The same occurrence was confirmed by using headspace solid-phase microextraction method (Figure 6(b)). A quartz fiber coating with 100 μm thickness

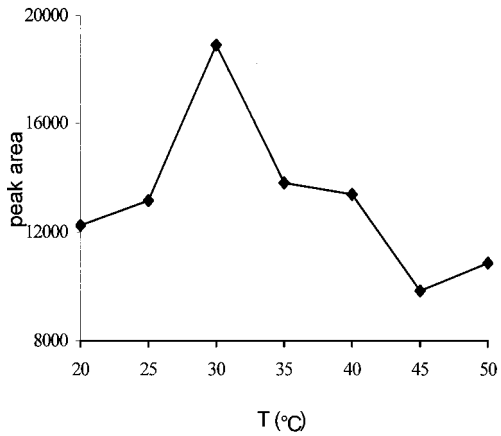

FIGURE 6(a) Effect of temperature/PTI, 10 μg L^{-1} standard MTBE.

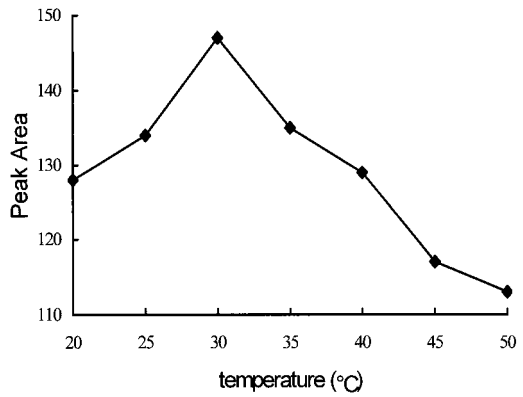

FIGURE 6(b) Effect of temperature/SPME, 10 μg L^{-1} standard MTBE.

polydimethylsiloxane was used to extract MTBE for 10 min under different temperatures. It was also found MTBE could be extracted at greatest degree at 30°C.

The purge efficiency could be affected mainly by two factors: sample temperature and solubility of MTBE. Improving the sample temperature could accelerate the molecular kinetic energy and help MTBE escape from the water solution. At the same time, however, the solubility of MTBE increased as well, which might prevent the escaping of MTBE. When the temperature was lower than 30°C, the former predominate the later so that the purge efficiency increased. After 30°C, the higher solubility outweighed the increasing escaping ability and made the escaping of MTBE more and more difficult. Thus the purge vessel was kept at 30°C in a thermal bath to improve the purge efficiency and sensitivity.

Linearity, Precision and Detection Limit

A series of standard samples 1, 10, 20, 30, 40, 50 μg L^{-1} were analyzed under optimized conditions. Satisfying correlation equation was obtained and the correlation coefficient

TABLE I Analysis of river water samples

Sampling points	*MTBE concentration* ($\mu g\,L^{-1}$) ($n=5$)	*RSD* (%)	*Spike* ($\mu g\,L^{-1}$)	*Analyzed concentration* ($n=5$)	*Mean recovery* (%)
1#	ND	–	20.00	18.90	94.5
2#	10.97	3.0	30.00	42.29	104.4
3#	ND	–	30.00	31.40	104.7
4#	ND	–	30.00	31.52	105.1
Tap water	ND	–	50.00	53.73	107.5

ND = Not detected.

was 0.9964. The detection limit, defined as three times of the background noise, was $0.1\,\mu g\,L^{-1}$. Replicate analyses ($n=5$) of a mixed standard solution were carried out to evaluate the precision of the method; the relative standard deviation was 3.2%.

Application to Aquatic Environmental Samples

The proposed method was applied to the analysis of the river water of Yong Ding River near Beijing, the lower reaches of Guan Ting Reservoir that once was the main source of drinking water for Beijing. 15 mL samples were directly used to determine the amount of MTBE. To test the possibility of matrix effects in this method, each sample was fortified with some MTBE standard. Table I summarizes the analysis results. MTBE were not detected in most of the samples except for sample 2#, which is very close to the underground storage tanks and may be impacted from the tanks leakage. Recoveries from these fortified samples were quantitative between 94.5 and 107.5%.

CONCLUSION

A fast and sensitive method PTI-GC-FID was demonstrated to determine the amount of MTBE in water samples. The analytes were directly purged from the water and then trapped in a capillary column by cooling the temperature to $-75^{\circ}C$ quickly. The sample temperature, the amount of salt added to the water sample, the purge time and the purge flow influence the purge efficiency of MTBE. This method can ensure enough volatile analytes to be trapped in the cold-trap so as to enhance the sensitivity and selectivity.

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