ELSEVIER

Journal of Chromatography A, 726 (1996) 153–159

JOURNAL OF CHROMATOGRAPHY A

Complementarity of purge-and-trap and head-space capillary gas chromatographic methods for determination of methyl-*tert.*-butyl ether in water

B. Nouri[a,b,*], B. Fouillet[a], G. Toussaint[b], R. Chambon[a], P. Chambon[a,b]

[a] *Department of Toxicology, Faculty of Pharmaceutical Sciences, University of Claude Bernard, 8 Avenue Rockefeller, 69373 Lyon Cedex 08, France*

[b] *Institut Pasteur de Lyon, Hygiène Appliquée à l'Homme et à son Environnement, Avenue Tony-Garnier, 69365 Lyon Cedex 07, France*

Received 28 July 1995; revised 7 August 1995; accepted 24 August 1995

Abstract

An improved method has been developed for the quantitative determination of traces of methyl-*tert.*-butyl ether (MTBE) over a large range of concentrations in water samples based on two complementary techniques: head-space capillary gas chromatography and purge-and-trap gas chromatography. The interesting aspect of this study lies in the complementary performances of these two methods, each in its specific range, for the analysis of MTBE in water samples. Head-space gas chromatography was used as a screening technique in routine analyses, while purge-and-trap gas chromatography was used as a confirmation method for the negative results. The analytical precision was good with both methods. Detection limits were 50 $\mu g\,l^{-1}$ for head-space gas chromatography and 2 $\mu g\,l^{-1}$ for purge-and-trap gas chromatography, with 90% calculated recovery. Choice of different parameters for the purge-and-trap method is discussed.

Keywords: Head-space analysis; Purge-and-trap methods; Methyl-*tert.*-butyl ether

1. Introduction

Alcohols such as methanol, ethanol and ethers such as methyl-*tert.*-butyl ether (MTBE) can be blended into gasoline to improve octane performance. MTBE is commonly added to gasoline in the USA and western Europe at up to 10% v/v. As the use of this blending agent becomes more widespread, suitable analytical procedures will be required for its determination. The determination of MTBE in vehicle exhaust samples, water, sediment and gasoline atmosphere by either high-performance liquid or gas chromatography has been reported in the literature [1–5]. In this paper, we report an improved method to analyse MTBE over a large range of concentrations. This method is based on both head-space and purge-and-trap capillary gas chromatography. Head-space gas chromatography (HSGC) is used as a routine technique for monitoring MTBE in water samples. Purge-and-trap (PTGC) is employed when improved sensitivity is required: it is used to assay for MTBE only on previously negative samples.

* Corresponding author. Address for correspondence: Department of Toxicology, Faculty of Pharmaceutical Sciences, University of Lyon, 8 Avenue Rockefeller, 69373 Lyon Cedex 08, France.

0021-9673/96/$15.00
SSDI 0021-9673(95)00929-9

Limits of detection have been determined at 50 $\mu g\,l^{-1}$ for HSGC and at 2 $\mu g\,l^{-1}$ for PTGC.

The aim of our study was to optimize PTGC with respect to sensitivity and to illustrate the complementarity of the performances of the two methods, each in its specific concentration range, for the determination of MTBE in water samples over a large range of concentrations.

2. Experimental

2.1. Reagents

MTBE was 99% pure analytical standard (Aldrich). Acetone was pure standard-grade chemical purchased from SDS (France). Water used for the preparations of standard solutions and for dilution of samples was distilled and degassed under a stream of nitrogen.

2.2. Apparatus

2.2.1. Head-space gas chromatography (HSGC)

GC analysis was carried out on a Perkin-Elmer Model Sigma-2000 gas chromatograph equipped with a flame ionisation detector (FID). An automatic head-space HS-100 (Perkin-Elmer) was used. GC separation was achieved with a capillary fused-silica column, 50 m×0.23 mm I.D. coated with CP-Sil 8 CB, 1.2 μm film thickness (Chrompack). The sample in the head-space autosampler was kept at 60°C and the transfer line temperature at 90°C. The apparatus was thermostatted for 60 min prior to analysis with a pressurization time of 2 min and an injection time of 0.08 min. The column temperature was programmed from 60°C (10 min isothermal) to 200°C at a rate of 20°C min^{-1}; this final temperature was maintained for 1 min. The detector temperature was 300°C. The helium carrier gas flow-rate was 2 ml min^{-1}. The data was processed with a Merck D-2000 reporting integrator.

2.2.2. Purge-and-trap gas chromatography (PTGC)

Analyses were performed on a Tekmar LSC-2000 purge-and-trap concentrator interfaced to a Varian 3400 gas chromatograph equipped with a FID. The stationary phase in the 50 m×0.53 mm I.D. fused-silica column was CP-Sil 8 CB methylsilicone with 5 μm film thickness purchased from Chrompack. The column temperature was programmed as follows: after an initial period of 1 min at 25°C, the temperature was increased to 200°C at a rate of 20°C min^{-1}; this final temperature was maintained for 2 min.

The FID temperature was 300°C. A constant carrier gas flow of 5 ml min^{-1} with ultra-pure helium was used for all analyses. A stainless-steel tube (12×1/8″) packed with a polymer of 2,6-diphenyl-*p*-phenylene oxide (Tenax) was used as an adsorbent trap. The physical properties of Tenax have been described by others [6–8]. The LSC-2000 was connected (through a capillary interface) to the capillary column via a fused-silica transfer line (0.32 mm) heated at 175°C. A Spectra-Physics SP-4290 reporting integrator was used to process the data.

2.3. Calibration solutions

A stock solution of MTBE standard in acetone was prepared at 5 g l^{-1} and stored at +4°C in glass sealed with PTFE-lined lids. Calibration standards were prepared in water at 1, 2, 5, 10, 20, 50 and 80 $\mu g\,l^{-1}$ concentrations for PTGC and at 50, 100, 200, 300, 500 and 1000 $\mu g\,l^{-1}$ for HSGC. These solutions were always made extemporaneously.

2.4. Procedure

A calculated amount of stock solution was added slowly with a microsyringe into 20-ml head-space vials (Perkin-Elmer) containing 10 ml of water. For HSGC the vial was immediately sealed with a Teflon-faced butyl rubber septum using an aluminium crimp top cap and transferred to a HSGC autosampler. For PTGC a 5-ml aliquot of the sample was immediately transferred to the purge vessel via a luer-lok fitting with a 5-ml syringe.

2.5. Sampling

Water samples were collected in 1-l sealed glass vessels and stored at +4°C until analysis.

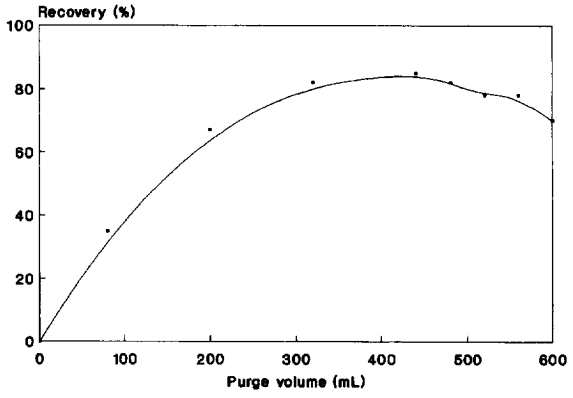

Fig. 1. Relationship between purge volume and recovery (%) of MTBE at 20 $\mu g\,l^{-1}$ (detector response) ($n=3$) on the Tenax trap at ambient temperature.

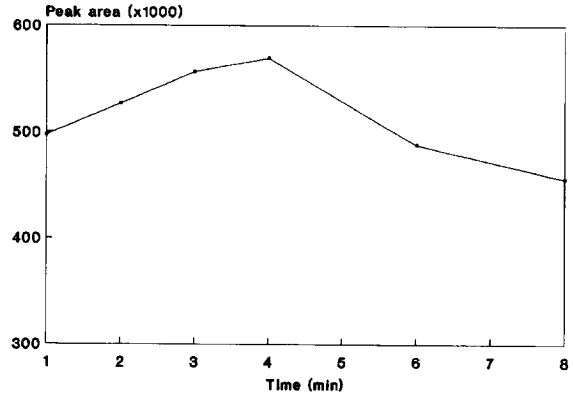

Fig. 2. Relationship between drying time and amount of MTBE at 20 $\mu g\,l^{-1}$ (detector response) ($n=3$) on the Tenax trap at ambient temperature.

3. Results and discussion

We have optimized the different steps of the PTGC procedure to lower the limit of detection because the health aspects of the incorporation of large amounts of MTBE in gasoline are still under investigation, and at present no recommended exposure limit has been approved. Our initial investigation was aimed at determining the optimal purge volume that gives the best recovery of MTBE. Fig. 1 shows that the recovery of MTBE improved by increasing the purge volume to 440 ml; however, a larger purge volume results in recovery loss of MTBE due to its premature elution from the Tenax trap. The volume of 440 ml obtained by setting the purge flow-rate at 40 ml min^{-1} and the purge time at 11 min was the purge volume giving optimum recovery of MTBE (90%) without breakthrough.

During sample purge water vapour can be adsorbed on the trap and introduced onto the GC column. To minimize water retention, Tenax was chosen as an adsorbent trap. The main advantages of this adsorbent over other porous polymers are its high temperature stability and extremely low affinity to water vapour [9]; thus only a short time is needed to remove water from the trap during the drying step. Fig. 2 shows that a drying time of 4 min gives satisfactory results; a longer time resulted in a slight loss of MTBE, probably due to desorption of MTBE.

Fig. 3 and Fig. 4 indicate that there was no desorption of MTBE from the Tenax trap within 1 min at 200°C, and that only 18% of the total quantity of MTBE was desorbed after 2.5 min at 100°C; therefore the Tenax trap was desorbed efficiently at 200°C over 2.5 min.

A capillary interface was used to refocus MTBE before transfer onto the column after the desorption step. A temperature of −60°C for the cold trap ensured that MTBE was trapped with high efficiency; this choice was in agreement with the diagram illustrating the approximate temperature at which breakthrough is experienced on various size

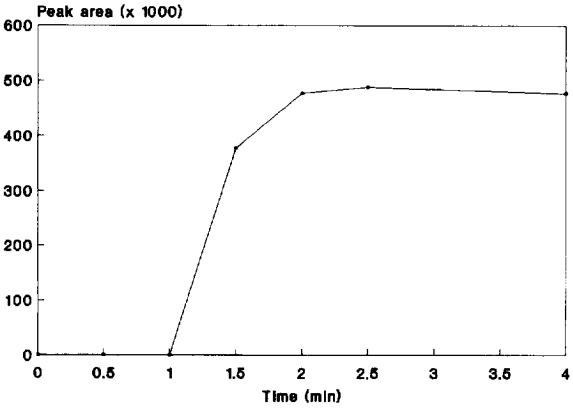

Fig. 3. Relationship between desorption time and amount of MTBE at 20 $\mu g\,l^{-1}$ (detector response) ($n=3$) on the Tenax trap at 200°C.

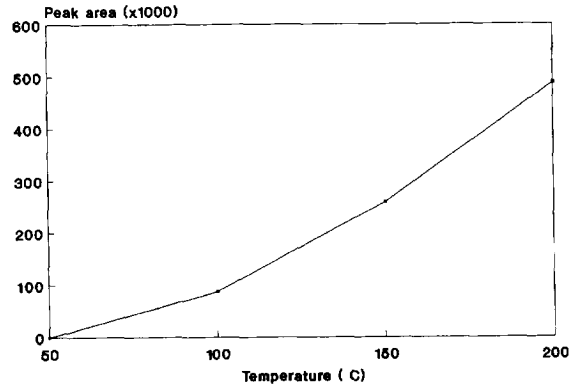

Fig. 4. Relationship between desorption temperature and amount of MTBE at 20 $\mu g\,l^{-1}$ (detector response) ($n=3$) on the Tenax trap during 2.5 min.

columns as a function of the solute boiling point [10].

The capillary interface coupled with a cryogenic GC oven improved the peak shape as illustrated in Fig. 5.

Table 1
Optimum conditions of purge-and-trap gas chromatographic parameters

Trap	Tenax
Sample volume	5 ml
Sample purge	
Gas	Helium
Flow	40 ml/min
Time	11 min
Temperature	Ambient
Dry purge	
Time	4 min
Temperature	Ambient
Desorption	
Preheat	175°C
Temperature	200°C
Time	2.5 min
Gas	Helium
Capillary interface	−60°C
Bake	
Temperature	225°C
Time	8 min

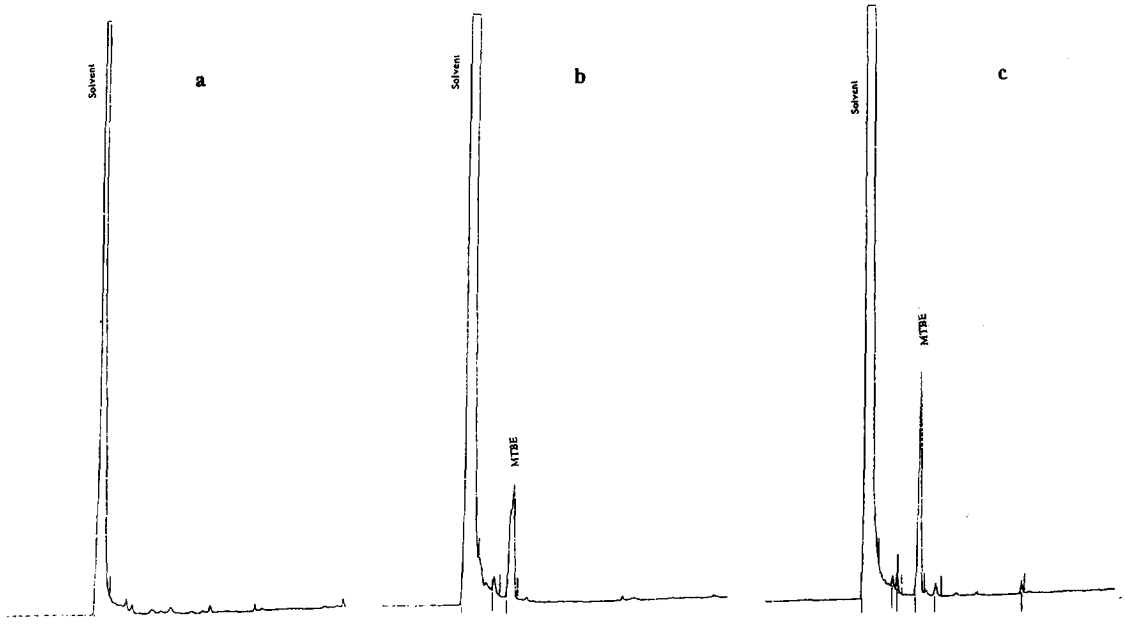

Fig. 5. Chromatograms of MTBE spiked in water at 20 $\mu g\,l^{-1}$ under optimum conditions. (a) Blank chromatogram. (b) Capillary interface temperature (CIT) −10°C, initial temperature of column (ITC) 25°C. (c) CIT −60°C and ITC 25°C.

Under optimum conditions (Table 1) the repeatability of the method was tested using water samples spiked at 5 and 60 $\mu g\,l^{-1}$. The repeatability at both levels was excellent, and the standard deviation was less than 2% ($n=6$). The limit of determination in water samples was 2 $\mu g\,l^{-1}$. Good linearity was obtained in the range 2–80 $\mu g\,l^{-1}$, the typical equation being $y=19\,603x+10\,882.58$ with a correlation coefficient of 0.999.

In January 1993 an accidental gasoline spill occurred in an area of southeast France. We were asked to analyse the quantities of MTBE in groundwater and to supervise the evolution of the pollution. The first analysed samples were contaminated by 1 to 2 mg l^{-1} MTBE. At these concentration levels the limits of PTGC appear to have been reached because the detector was saturated with all volatile purged compounds, and dilution series were necessary to quantify the MTBE, which increased the risk of errors in quantitation and the analysis time of each water sample.

We developed a HSGC method for the determination of MTBE in water samples to avoid problems met with PTGC. The HSGC method performance was found to be linear up to 1000 $\mu g\,l^{-1}$, with a relative standard deviation value of 7% at a concentration of 60 $\mu g\,l^{-1}$ in the water sample. The linear regression of the MTBE has a correlation coefficient of 0.999, with $y=-6.456x-10.075$, and a detection limit of 50 $\mu g\,l^{-1}$ in water samples.

This last method allowed us on the one hand to confirm results produced with PTGC and on the other to reduce interferences which mask the MTBE peak. Indeed, for the same water sample analysed directly with HSGC and diluted twice for PTGC analysis (Fig. 6), we noted a considerable decrease of the interfering matrix peaks in the head-space chromatogram without a preliminary dilution; in HSGC the water sample is thermostatted and the gas phase is injected onto the column, while in PTGC the sample is purged and the gas phase is concentrated on a trap before injection onto the column, thus increasing the interfering peaks.

Fig. 7 shows the correlation between the results for MTBE in samples from gasoline-contaminated groundwater obtained by both PTGC and HSGC. The correlation coefficient is 0.965 with a slope of 0.996.

The ratio of the concentrations obtained by PTGC and HSGC is given in Table 2. The difference between these ratios was attributable to errors associated with the numerous sample dilutions necessary for PTGC analysis as described previously or to possible matrix effects and not to imprecision of one or the other method. With the omission of the single absurd concentration value (ratio of 0.78), which disproportionately skews the linear regression, the correlation is 0.989 with a slope of 0.948. Clearly, there is good agreement between the two methods for the determination of MTBE in real water samples.

During supervision of the pollution over several months, the concentration of MTBE in groundwater samples decreased gradually. All analyses were confirmed by either one of the two techniques. However, when concentrations were between 10 and 40 $\mu g\,l^{-1}$, the analyses were done only by PTGC, since the detection limit of HSGC was 50 $\mu g\,l^{-1}$. This reflects the limitations of the latter method for the determination of MTBE in water samples at low concentration levels.

4. Conclusion

The results of our experiments show that both HSGC and PTGC are complementary for the determination and confirmation of high concentrations of MTBE in water samples. PTGC cannot quantify MTBE at concentrations higher than 50 $\mu g\,l^{-1}$; however, this can be done with HSGC without the need for a great number of dilutions. Moreover, using HSGC we noted a considerable decrease of the interfering matrix peaks.

Although the latter procedure minimized sample handling and run time, it was 25 times less sensitive than PTGC. Therefore, HSGC can be used in preliminary monitoring. Negative samples should then be further analyzed by PTGC.

There is good agreement between the two methods for the determination of MTBE in real water samples.

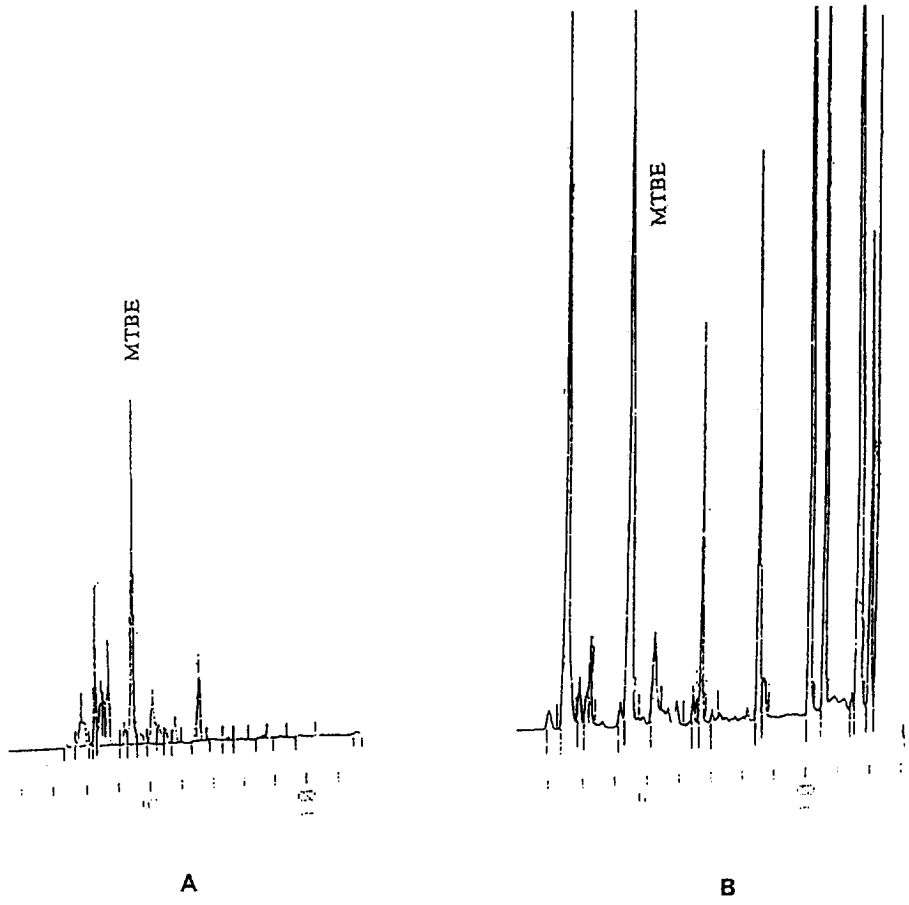

Fig. 6. Chromatograms of MTBE in gasoline-contaminated water. (A) Head-space gas chromatography; direct injection without preliminary dilution (sample volume 10 ml). (B) Purge-and-trap gas chromatography; diluted by half (sample volume 2.5 ml).

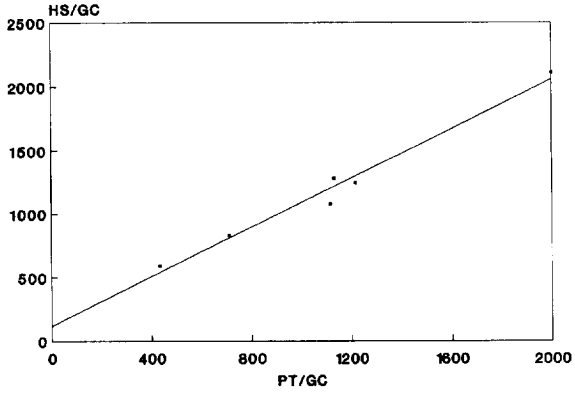

Fig. 7. Linear plot of mean MTBE concentrations ($\mu g\,l^{-1}$) in samples of gasoline-contaminated groundwater from southeast France. Slope and coefficient for all points, 0.996 and 0.965, respectively; single highest point omitted, 0.948 and 0.989.

With these techniques separation of MTBE from volatile organic carbon compounds was possible only with modified temperature-programmed chromatography.

Table 2
Ratio of the concentrations of methyl-*tert.*-butyl ether obtained by PTGC and HSGC in samples of gasoline-contaminated groundwater from southeast France

Samples	Ratio
1	1.36
2	1.17
3	0.78
4	1.13
5	0.92
6	1.02
7	1.05

References

[1] J. Sevcik, J. High Resolut. Chromatogr. Chromatogr. Commun., 3 (1980) 166.
[2] R.E. Pauls and R.W. McCoy, J. Chromatogr. Sci., 19 (1981) 558.
[3] J.P. Durand and N. Petroff, 6th AGELFI Eur. Symp., Cannes, November 26–27, 1981, Rev. Inst Fr. Pet., 37(4) (1982) 575.
[4] J.A. Price and K.J. Saunders, Analyst, 109 (1984) 829.
[5] A. Bianchi and M.S. Varney, J. High Resolut. Chromatogr., 12 (1989) 184.
[6] R. Van Wijk, J. Chromatogr. Sci., 8 (1970) 418.
[7] J.M.H. Daemen, W. Dankelman and M.E. Hendriks, J. Chromatogr. Sci., 13 (1975) 79.
[8] K. Sakodynskii, L. Panina and N. Klinskaya, Chromatographia, 7 (1974) 339.
[9] R.H. Brown and C.J. Prunell, J. Chromatogr., 178 (1979) 79.
[10] R.G. Westendorf, Performance of a Third Generation Cryofocusing Trap for Purge and Trap, The 39th Pittsburgh Conference, February, 1988, New Orleans, LA.