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Journal of Chromatography A, 910 (2001) 377–383

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Short communication

Method for determination of methyl *tert*-butyl ether in gasoline by gas chromatography

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Received 5 September 2000; received in revised form 29 November 2000; accepted 30 November 2000

Abstract

A simple method for the determination of methyl *tert*-butyl ether (MTBE) in gasoline has been developed. The separation of MTBE from other analytes was controlled by the use of gas chromatography–mass spectrometry in the full scan mode using the characteristic primary, secondary and tertiary ions m/z 73, 57 and 43. The sample mass spectrum did not show any superimposition of other analytes. The separation from the common gasoline component 2-methylpentane was sufficient for reliable quantitation. An application of the developed conditions using gas chromatography with flame ionization detection was performed by the analysis of regular, euro super, super premium unleaded and ‘Optimax’ gasoline from petrol stations in the area of Frankfurt/Main, Germany. Regular unleaded gasoline shows an average MTBE content of 0.4% (w/w), whereas the MTBE content in euro super gasoline varies between 0.4 and 4.2% (w/w). The blending of MTBE to super premium has increased from 8.2% (w/w) in 1998 to 9.8% (w/w) on average in 1999. The recently introduced gasoline ‘Optimax’ shows an average MTBE content of 11.9% (w/w). The presented method might also be used for the analysis of other ethers, such as ethyl *tert*-butyl ether, which requires the use of another internal standard. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gasoline; Methyl *tert*-butyl ether; Ethyl *tert*-butyl ether; Ethers; Methylpentanes

1. Introduction

The gasoline oxygenate methyl *tert*-butyl ether (MTBE) has been detected in the aquatic and atmospheric environment in many countries [1–6] which has led to concern about its environmental fate due to the large amounts that are now being produced. For example, in the USA 8.8×10^9 kg of

MTBE were produced in 1997 [1]. In Germany the use of MTBE as a fuel additive also significantly increased since 1985 and reached approximately 0.45×10^9 kg in 1997 [7–9].

In Germany little information has been published about the use of MTBE in gasoline so far. The methods used in order to analyse oxygenates in gasoline generally are complex. Among the methods used are gas chromatography (GC) [10,11], GC–mass spectrometry (MS) [12,13], high-performance liquid chromatography (HPLC) [14], nuclear magnetic resonance (NMR) spectroscopy [15,16], Fourier transform infrared (FTIR) spectroscopy [17–19] and total oxygen measurement [19]. The GC

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methods require single, dual or multicolumn column-switching and/or back-flushing systems, extraction of the oxygenates either with water or ethylene glycol or previous cleanup by acetonitrile prior to GC analysis and often an oxygen-specific detection method (oxygen-flame ionization detection, O-FID) was necessary. However, simple GC methods in combination with flame ionization detection (FID) have been developed using capillary columns of different polarities, both common columns for the analysis of gasoline [12,20] and columns with more polar stationary phases [21,22].

In this study a simple GC method by use of GC equipped with FID and a SE-54 capillary column for the improved separation of MTBE from hydrocarbons in gasoline was developed.

2. Experimental

2.1. Materials and methods

MTBE and ethyl *tert*-butyl ether (ETBE) standards were obtained in the highest commercially available purity (>97%, Fluka). Standard solutions of ETBE in distilled methanol (>99.9%, Fluka) were prepared to a concentration of 1 mg/ml, cooled at 4°C and used within 4 weeks.

Gasoline samples were collected in 10-ml vials at different gas stations of big companies in the Frankfurt area during filling a vehicle. The vials were completely filled and sealed. The samples were cooled, transported to the laboratory and were analysed within 24 h. For the analysis 1 µl gasoline was diluted by 500 µl methanol and 60 µl of the ETBE standard solution (1 mg/ml) was added. The method was developed by use of GC–MS and applied to GC.

2.2. Instrumental

The GC system (Thermo Quest Finnigan Trace GC 2000) coupled to the MS system (Thermo Quest Finnigan Voyager GC–MS) and the GC system (Fisons Instruments GC 8160) used for the application were adapted to the same conditions: the injector port was kept at 240°C and the split mode with a ratio of 1:20 was used. Liners with an inner diameter

of 0.75 mm and a 50-m SE-54 capillary column (Chromatographie Service, Langerwehe, Germany) with a film thickness of 5 µm were installed. The GC column temperature was first held at 30°C for 23 min, then increased to 240°C at a rate of 20°C/min and held for 40 min. Helium and hydrogen served as carrier gases at a flow of 0.8 ml/min for GC–MS and the GC system, respectively. The detector temperature of the GC was 300°C.

Peak detection and integration was carried out by use of XCalibur (Version 1.0, GC–MS) and ChromCard for Windows (1.19–7β, GC).

The scan range of GC–MS was m/z 40–600. The mass spectrometer was tuned to optimize signals from m/z 40 to 125. MTBE standards were used in order to determine the characteristic ions and the retention times used for identification of MTBE in the gasoline samples. Mass chromatography of m/z 73, m/z 57 and m/z 43 in full scan mode was used for qualifying MTBE. The MTBE signals could be checked with respect to superimposition by other compounds, especially by 2-methylpentane, since the analyses were carried out in the full scan mode. ETBE served as internal standard for quantification of gasoline samples analysed by GC.

3. Results and discussion

The GC method was developed by choosing an appropriate capillary column, liner and internal standard for the analysis from the literature. The carrier gas flow, split ratio and oven temperature program were adjusted in order to provide an optimal separation of MTBE from other analytes. It is known that particularly 2-methylpentane, which is a common compound in gasoline tends to superimposition with MTBE. By use of GC equipped with O-FID the alkanes are not detected and a clean MTBE peak can be quantified. However, in the present case a GC method for the analysis of MTBE in combination with the very common and versatile FID is described. Complex back-flushing and column-switching systems are not required.

Amongst the common capillary columns used for the analysis of gasoline [12,20] a SE-54 (94% methylsilicone gum, 5% phenyl and 1% vinyl) was

preferred to a 100% dimethylsilicone gum stationary phase because MTBE tends to superimposition with 2,3-dimethylbutane by use of the latter. The retention window between 2- and 3-methylpentane was chosen for the elution of MTBE due to the absence of superimposition with other hydrocarbons from gasoline.

The method was established using GC–MS in the full scan mode. The identification and quality of the separation of MTBE was controlled by use of its primary, secondary and tertiary ions m/z 73, 57 and 43, respectively. Separation of MTBE from 2-methylpentane is not reached completely but to an acceptable extent. Reasonably good separation was also reached by Hardman et al. [12] using helium as carrier gas and a low starting temperature of the GC oven (25°C). In the present study improvement of

the analytical conditions was achieved by the use of hydrogen instead of helium and an increase in the oven starting temperature to 30°C. Additionally the column length could be shortened from 60 m [12] to 50 m.

For the quantitation of MTBE, fluorobenzene [23,24], methyl propyl ketone or methyl ethyl ketone [25], diisopropyl ether (Dr. Thölmann, Infracor, Marl, Germany, personal communication), *tert*-butanol, butyl ethyl ether [11] and methyl [$^2\text{H}_3$]*tert*-butyl ether [26] have been used as internal standards. For the present study ETBE was used because of its physicochemical similarity with MTBE, its reasonably good stability and its clear separation from other analytes in the GC of all types of gasoline. Due to the possible use of ETBE as an octane enhancer in gasoline every sample was injected without internal

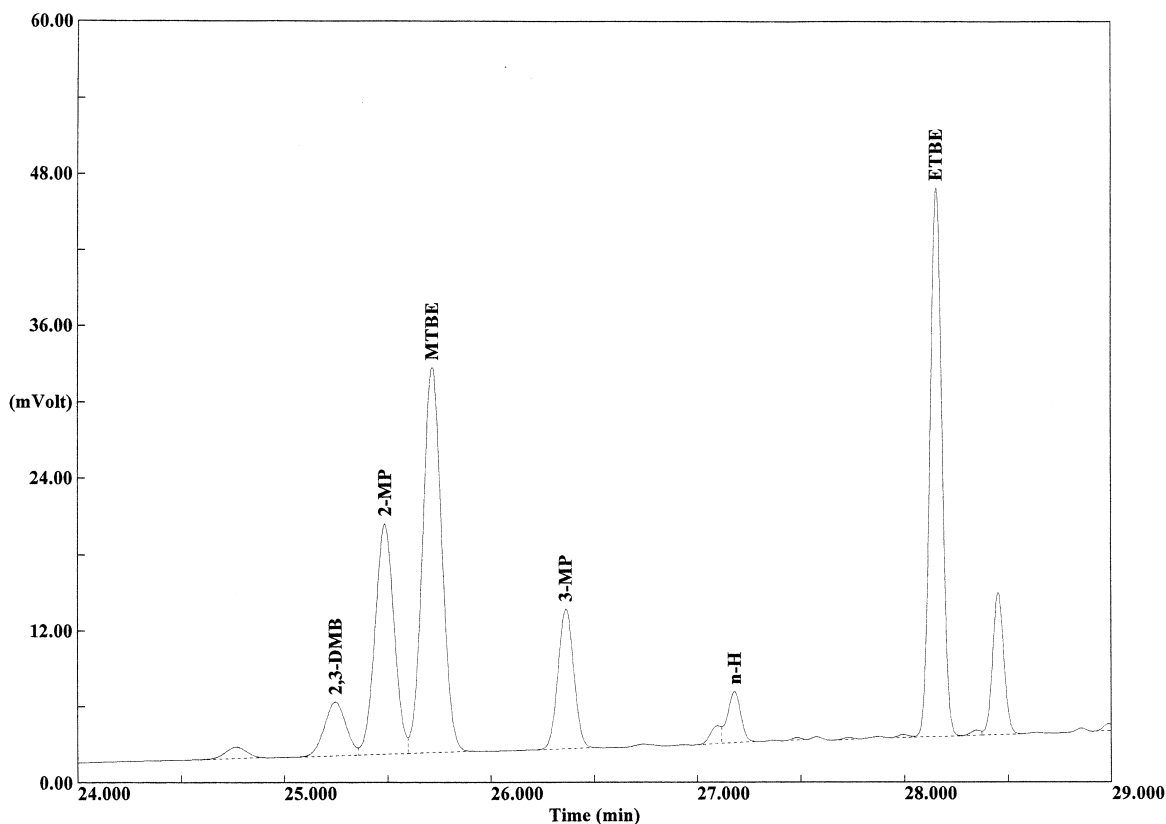


Fig. 1. Typical partial gas chromatogram of super premium unleaded gasoline. ETBE served as internal standard. 2,3-DMB, 2,3-dimethylbutane; 2-MP, 2-methylpentane; MTBE, methyl *tert*-butyl ether; 3-MP, 3-methylpentane; n-H, *n*-hexane.

standard prior to quantitative analysis to reassure that ETBE was not present in the sample. ETBE was not detected in any sample. However, it has to be considered that ETBE is used as gasoline additive in the USA, France and Italy [27].

Optimization of the temperature program showed best results when the temperature of 30°C was held as long as possible for the separation of MTBE from 2-methylpentane and when the temperature was increased at a high rate before the elution of MTBE in order to receive a narrow peak shape. The analysis time was set to 30 min and an analytical cycle including the cleaning of the chromatographic column was complete in 94 min. Due to the generally slow carrier gas flow velocity of 0.8 ml/min an analysis of MTBE was time-consuming. In order to

reduce the analysis time the carrier gas flow was accelerated to 1.5 ml/min once the conditioning temperature of 240°C was reached and faster reconditioning was received. Before the next sample analysis the gas flow was reset again to 0.8 ml/min.

After the optimizing procedure by GC–MS, the developed method was applied to the GC analysis of regular unleaded, euro super unleaded, super premium unleaded and ‘Optimax’ gasoline (Figs. 1–3 and Table 1).

The results of 39 analysed gasoline samples of different oil companies show average MTBE contents of 0.4% (w/w) for regular unleaded, 9.8% (w/w) for super premium unleaded and 11.9% (w/w) for the new ‘Optimax’ gasoline. The amounts of MTBE for euro super unleaded gasoline generally

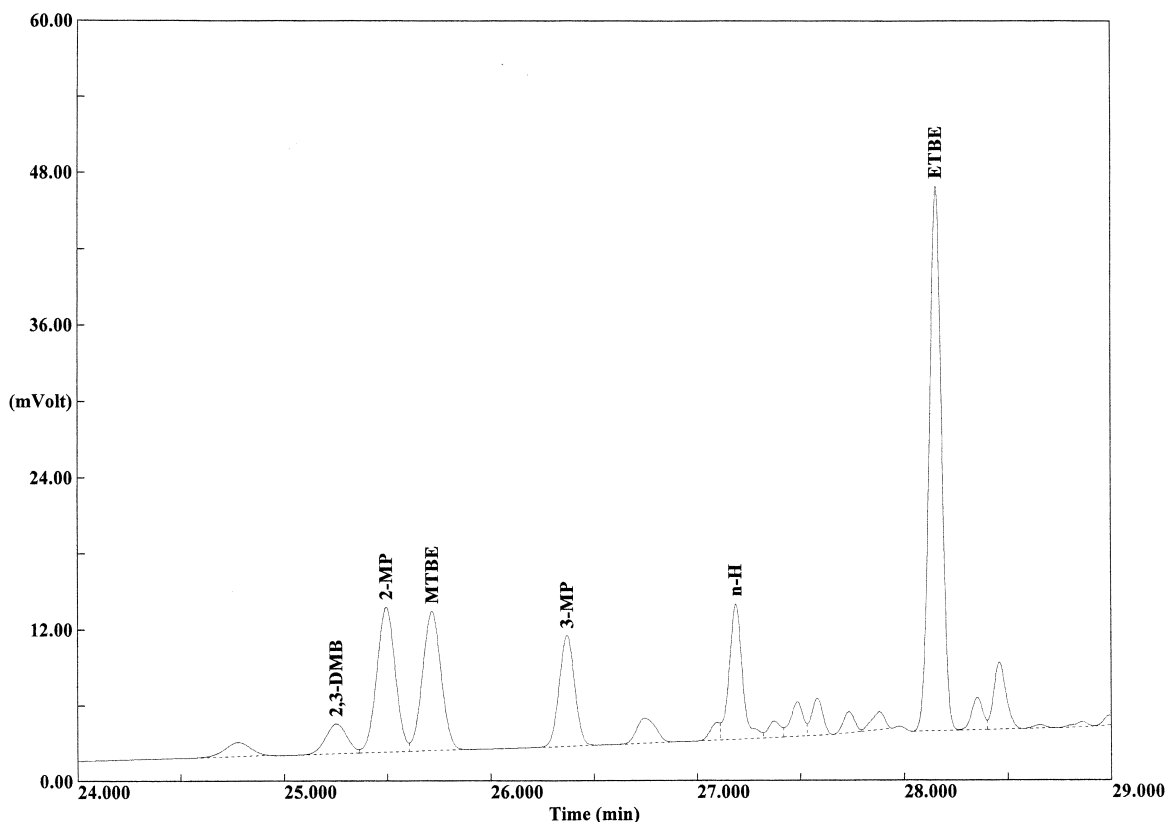


Fig. 2. Typical partial gas chromatogram of euro super unleaded gasoline. ETBE served as internal standard. 2,3-DMB, 2,3-dimethylbutane; 2-MP, 2-methylpentane; MTBE, methyl *tert*-butyl ether; 3-MP, 3-methylpentane; n-H, *n*-hexane.

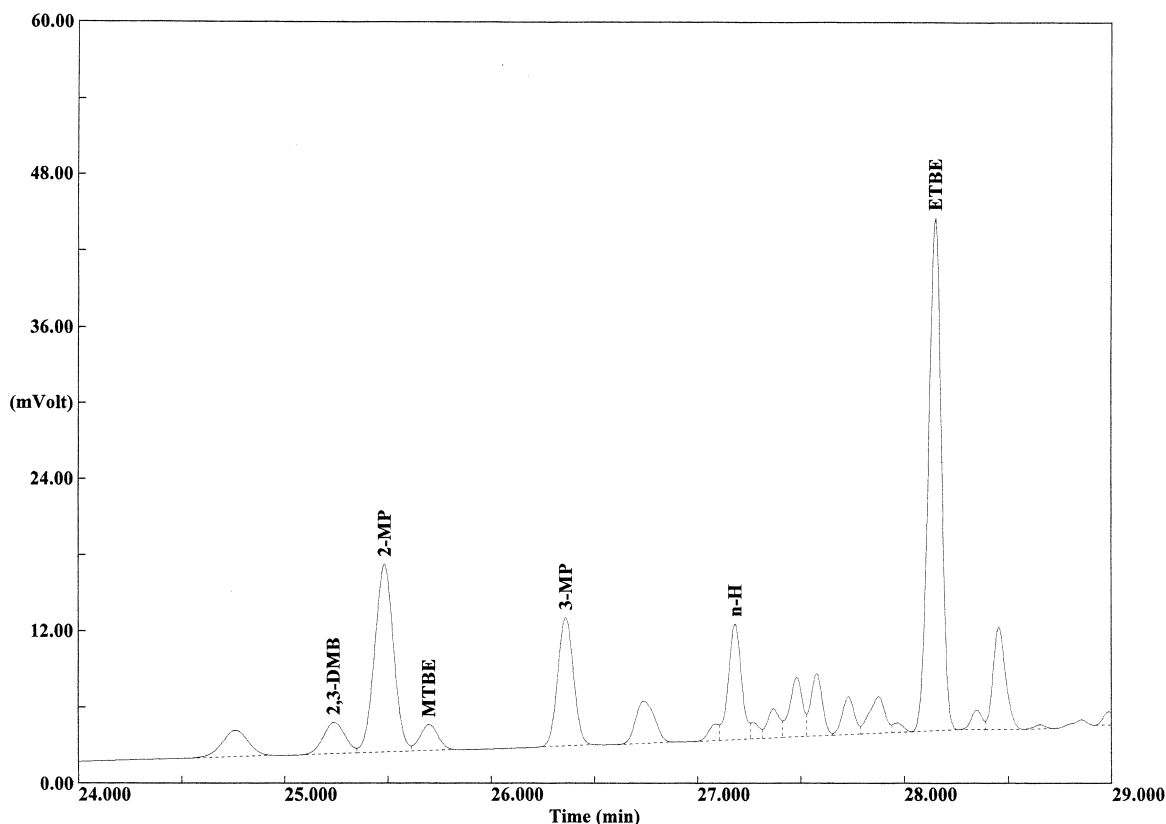


Fig. 3. Typical partial gas chromatogram of regular unleaded gasoline. ETBE served as internal standard. 2,3-DMB, 2,3-dimethylbutane; 2-MP, 2-methylpentane; MTBE, methyl *tert*-butyl ether; 3-MP, 3-methylpentane; n-H, *n*-hexane.

vary from 0.3 to 1.3% (w/w) although the amount in euro super from company 2 with an average of 3.5% (w/w) is remarkably higher.

The obtained data are comparable to other published data and show an increase in the use of MTBE in Germany in gasoline since 1992–1993. Average MTBE values of 0.2, 1.7 and 8.7% (w/w) in regular, euro super and super premium unleaded gasoline were measured in 1992–1993 [25] and 0.3, 1.6 and 6.0% (w/w) in 1996, respectively [7]. In 1998 super premium was blended by a few big companies with a median of 8.2% MTBE (w/w), whereas the value for all measured companies was 7.7% (w/w) [9]. It can be concluded that particularly the bigger companies offer ‘cleaner-burning’ gasoline and add higher amounts of MTBE to the fuel. The use of the

oxygenate in super premium has increased to 9.8% (w/w) in 1999. A slight increase to 0.4% (w/w) can also be observed regarding regular unleaded gasoline, whereas the source data for euro super fluctuate significantly. Therefore, the data basis is not sufficient for the development of an average value.

4. Conclusion

The developed GC method in combination with FID is a simple and reliable means for the determination of MTBE in gasoline. Optimal analysis was achieved by use of a 50-m SE-54 capillary column with a film thickness of 5 μm , a liner with an inner diameter of 0.75 mm and a low gas flow of

Table 1

Analysed samples of regular, euro super, super premium unleaded gasoline and Optimax gasoline^a

Company	Location	Date	Regular unleaded	Euro super unleaded	Super premium unleaded	Optimax
1	Stresemannalle	3 August 1999	0.3	1.3	12.2	–
1	Autobahn 66	26 August 1999	0.4	0.9	6.8	–
1	Sossenheim	26 August 1999	–	–	11.0	–
2	Kennedyallee	3 August 1999	0.5	4.2	10.8	–
2	Kennedyallee	24 August 1900	–	2.9	–	–
2	Friedberger Landstraße	19 July 1999	–	3.4	9.0	–
2	Autobahn 66	26 August 1999	0.6	3.5	10.2	–
3	Kennedyallee	3 August 1999	0.5	0.3	10.1	–
3	Kennedyallee	24 August 1999	–	0.6	–	–
3	Kelkheim	26 August 1999	0.5	–	10.7	–
4	Friedberger Landstraße	19 July 1999	0.3	0.4	9.5	–
4	Kennedyallee	3 August 1999	0.3	0.7	8.5	–
4	Kennedyallee	24 August 1999	–	0.4	–	–
4	Hansaallee	19 July 1999	–	–	9.1	–
4	Friedberger Landstraße	27 June 2000	–	–	–	13.6
4	Friedberger Landstraße	29 June 2000	–	–	–	10.4
4	Kennedyallee	29 June 2000	–	–	–	11.6
Average			0.4	–	9.8	11.9

^a The samples were taken at Frankfurt am Main in 1999 and 2000.

0.8 ml/min. The oven temperature program was set to 30°C for 23 min, then increased to 240°C at a rate of 20°C/min and held for 40 min. The achieved separation of the gasoline component 2-methylpentane from MTBE is sufficient for reliable quantitation. The method is also useful for the measurement of other ethers, for example ETBE when another internal standard is chosen.

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