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Determination of methyl tert-butyl ether (MTBE) in Chinese fuels by gas chromatography/mass spectrometry and gas chromatography/flame ionization detector

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Abstract: A method was developed to determine the concentration of methyl tert-butyl ether (MTBE) in gasoline, diesel and heating oil by gas chromatography (GC) with mass spectrometry (GC-MS) or flame ionization detection (FID). The diluted gasoline was directly injected into the GC, and the complete separation of MTBE from co-eluting hydrocarbons was not required. GC/MS or GC/FID method can be used to analyze MTBE in different concentration range and have good consistency.

Keywords: methyl tert-butyl ether (MTBE); GC/MS; GC/FID

Introduction

Methyl tert-butyl ether (MTBE) has been widely used in many countries as an oxygenated additive and octane enhancer to reduce air pollution in unleaded gasoline. In America, the concentration of MTBE in gasoline has been increased to as high as 15% in response to the 1990 Clean Air Act and to meet the requirement of the USEPA's Reformulated Gasoline and Oxygenated Fuel Programs (USEPA, 1998), while the unleaded gasoline containing MTBE has just been used for only a few years in China. However, MTBE need also to be specified and controlled not only for fuel-quality reasons but also because they can pollute the environment as well. It is now a matter of concern that these compounds, under the engine internal combustion conditions, form ozone, and their emissions also contain NOx and form-aldehyde (Garcia, 1993). The tumorigenicity of MTBE has also been studied in long-term bioassays (Bird, 1997; Rudo, 1995). It has been found that MTBE exposure increased the incidence of liver tumors in female mice and testicular tumors in male rats (Belpoggi, 1995).

In an attempt to accurately determine MTBE that would comply with trade and government parameters, analytical methods for the unambiguous identification and quantification of the MTBE present in complex gasoline mixture have been developed. Spectrometric techniques, including fourier transform infrared method (Guardia, 1993) and nuclear magnetic resonance method (Meusinger, 1996), have applied for the determination of MTBE in gasoline. Recently, gas chromatography and other chromatographic techniques have been extensively employed for the determination of MTBE in gasoline (Kanal, 1994), water (Halden, 2001; Church, 1997), urban air (Pankow, 1997). However, complex column switching or troublesome extraction procedure was generally required to isolate MTBE from the interfering hydrocarbons. In addition, the linear response range and detection limit were not satisfying.

A method was developed to determine the concentration of MTBE in gasoline, diesel and heating oil in this paper. The diluted gasoline was directly injected into the gas chromatograph. Because the base ion in the electron impact mass spectrometry of MTBE is m/z 73, but m/z 73 ion are not the common fragment ions of the alkanes, alkenes and naphthenes of the fuel samples, a complete separation of MTBE from co-eluting hydrocarbons was not required. GC/MS or GC/FID method can be used to analyze MTBE in different concentration range and have good consistency.

1 Materials and methods

1.1 Reagents

MTBE standard was obtained from Acros Company. All solvents and reagents used were of analytical reagent grade or better.

1.2 Sample preparation

MTBE standard, gasolines (90 #, 93 #) and other fuels were directly dissolved into isooctane for the determination. For GC-MS, the gasolines were diluted 10000 times, and for GC-FID, the gasolines were diluted 40 times because of the relatively lower sensitivity. All MTBE standard solutions were prepared by spiking MTBE standard to the isooctane. The solutions were kept in refrigerator avoiding the evaporation of MTBE and isooctane.

1.3 GC-MS operating conditions

MTBE was analyzed with a Shimadzu GC/MS-QP5050A system. Operating conditions were as follows: DB-1 capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm), helium carrier pressure, 70.0 kPa; injector temperature, 230℃; split ratio, 10:1; interface temperature, 230℃;

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oven temperature programme, 40℃ for 4 min, then ramped at 20℃/min to 250℃ for 10 min. The detector was operated in the selective ion monitoring (SIM) for m/z = 73 ion. Because MTBE eluted earlier than isooctane and other ingredients in gasoline, the filament had to be shuts down before the elution of isooctane. The acquisition time ranged from 1.10 min to 2.50 min. Concentrations were determined from integrated peak areas. Injections of 1.0 μl were used by hand. Calibration curves for MTBE were prepared in the range of 0.1—10 μg/ml.

1.4 GC-FID operating conditions

An HP 6890 GC system(Hewlett-Packard) with FID was used. The optimized conditions for the HP-1 capillary column (30 mm × 0.25 mm i.d., film thickness 0.25 μm) were as follows: the injector port was held at 200℃ with a split ratio of 10:1, injections of 1.0 μl were used by hand; column head pressure 91.2 kPa; flow rate of N_2 carrier gas 1.3 ml/min. The flame ionization detector temperature 250℃; oven temperature was maintained at 40℃ for 4 min, then ramped to 250℃ at 30℃/min, and held for 5 min.

2 Results and discussion

2.1 GC-MS

Electron impact fragmentation of MTBE yielded an abundant m/z = 73 ion, due to the loss of a methyl group (CH_3 = 15 amu) from the compound. This highly stable ion fragment was almost unique to the ether in the gasoline mixture and was, therefore, a suitable candidate for SIM studies.

As this technique was extremely selective and sensitive, some test samples were pre-diluted in order to prevent overloading of the detector and thereby producing a non-linear response. And because MTBE eluted from the capillary column very quickly, it was difficult to find an appropriate reagent that could elute earlier than MTBE. Isooctane was chosen as the diluent, as it did not co-elute with MTBE(t_R > 3 min) and had no background using this type of capillary column. To prevent the overloading of the betatron, the filament must be turned off before the elution of isooctane. The turn-on time of the filament was between 1.10 min and 2.50 min, during which MTBE eluted at 1.73 min and could be fully detected. Fig. 1 shows the elution of MTBE using SIM model. There was no other intervene during this period of time. To make the high-boiling point ingredients of gasoline elute easily and decrease the overall analysis time, after the elution of MTBE the oven temperature was rapidly heated to bring off the remaining hydrocarbon components.

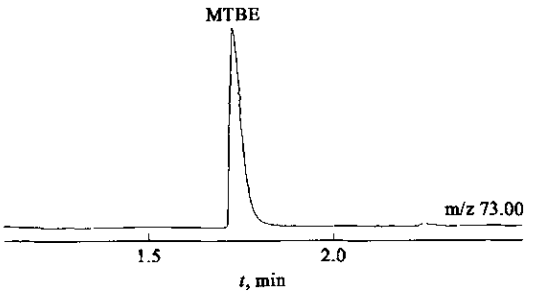

Fig.1 Chromatogram of MTBE in SIM model

It was possible to accurately determine the concentration of MTBE, as it was clearly resolved with the retention time in 1.73 min. Further confirmation of the presence of MTBE may be made by obtaining full scan mass spectra shown in Fig. 2.

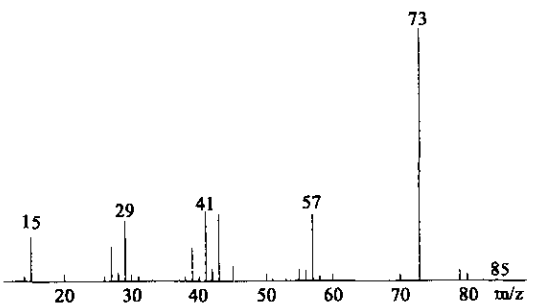

Fig.2 Full scan mass spectra of MTBE

Calibration standards of 0.1—10 μg/ml MTBE were prepared in isooctane without internal standards. In previous work, tertiary butyl alcohol, isopropyl alcohol or *n*-propyl alcohol was used as internal standards, and the ethers were separated from the gasoline by using a large amount of acetonitrile. The linear response ranged from 0.2 to 1.2 μg/μl, so the detection limit was relatively high and the linear response range was narrow(Kanal, 1994). However, in this experiment, the gasolines were diluted 10000 times and were directly injected into the gas chromatograph. The data showed no significant background interference from hydrocarbon components of the diluted gasolines in the retention time interval where MTBE eluted from the chromatograph. The ionizing voltage was 0.95 kV, which greatly contribute to the low detection limit(0.1 μg/L). A wide linear range of 0.1—

Table 1 The GC/MS determination of MTBE in Chinese fuels

Samples	Mean concentration of MTBE, vol% (n = 5)	RSD, % (n = 5)	Spike, vol% (n = 5)		Recovery, %
			Real value	Determined value	
90# gasoline	3.240	0.4234	0.600	0.664	110.7
93# gasoline	2.004	0.3036	1.000	1.087	108.7
Diesel	0	-	2.500	2.736	109.4
Kerosene	0	-	2.500	2.849	113.9
Heating oil	0	-	2.500	2.765	110.6

10 μg/ml was obtained and the linear regression coefficient was 0.9994.

The amount of MTBE in several commercial fuels sold in China was determined. It was found that there was no existence of MTBE in diesel, kerosene and heating oil. The results obtained are given in Table 1.

2.2 GC-FID

The parameters of inlet and detector were optimized. Different split ratio, flow rates of H_2, air and makeup gas were tested to determine the effects on detector signal. The optimized conditions were as follows: split ratio 10:1, H_2 flow rate 30 ml/min, air flow rate 400 ml/min, makeup gas flow rate 20 ml/min.

FID detector has a relatively low sensitivity to MTBE. Gasoline samples were diluted in isooctane 40 times for the determination. Because most hydrocarbon compound can get signals on FID, it is imperative to separate MTBE from other ingredients in gasoline. In this experiment, a low initial oven temperature 40℃ was kept for 3 min, MTBE got a good separation from other compounds and eluted at 2.08 min shown in Fig.3, which could be validated on MS detector by full scan mode. The integrated peak areas were used to determine the concentration and got a wide linear response curve between 10—1000 μg/ml, the linear regression coefficient was 0.9989.

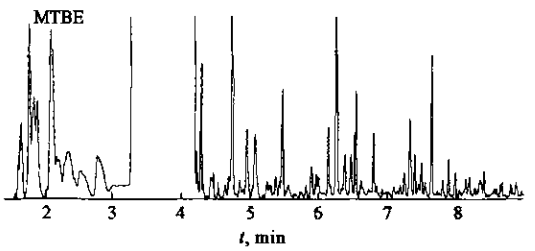

Fig.3 Chromatographic separation of MTBE by GC/FID

Table 2 summarized the comparison of concentrations of MTBE in gasoline samples by GC/MS and GC/FID. As can be seen, the concentrations obtained by GC/FID were in good agreement with the results obtained by GC/MS.

Table 2 GC/FID determination of MTBE in Chinese gasolines

Type of gasoline	Mean concentration of MTBE, vol% (n = 5)	RSD, % (n = 5)	Results by GC/MS, vol% (n = 5)	Relative deviation, vol% (n = 5)
90#	3.447	0.100	3.240	0.207
93#	2.674	0.135	2.004	0.670

3 Conclusions

The methods of GC/MS and GC/FID were developed to analyze percent quantity of MTBE in unleaded gasolines sold in China, since the use of unleaded gasoline containing MTBE is being developing and the oncogenicity of MTBE has been found. Direct injection of diluted sample using optimized GC/MS conditions made the analytical method in this research accurate, simple, fast and reproducible for the analysis of MTBE. There was almost no interference in the chromatographic retention intervals of the diluted gasoline sample where MTBE eluted. The linear range for the SIM mode(m/z = 73) under optimized conditions were 0.1 to 10 μg/ml. The detection limit was 0.1 μg/L. When using FID to replace MS detector, a wider linear response range was got from 10 μg/ml to 1000 μg/ml. GC/MS or GC/FID can be used to determine different concentration ranges of MTBE sample with consistent results.

References:

Belpoggi F, Soffritti M, Maltoni C, 1995. Methyl tertiary-butyl ether(MTBE)—a gasoline additive-causes testicular and lymphohaematopoietic cancers in rats [J]. Toxicol Ind Health, 11:119—149.

Bird M G, Burleigh-Flayer H D, Chun J S *et al*., 1997. Oncogenicity studies of inhaled methyl-tertiary-butyl ether(MTBE) in CD-1 mice and F344 rats[J]. J Appl Toxicol, 17: S45—S55.

Church C D, Isabelle L M, Pankow J F *et al*., 1997. Method for determination of methyl tert-butyl ether and its degradation products in water[J]. Environ Sci Technol, 31: 3723—3726.

Garcia F X, Lima L D, Medina J C, 1993. Determination of methanol and methyl tert-butyl ether in gasoline by infrared spectroscopy using the circle cell and multivariate calibration[J]. Appl Spectr, 47: 1036—1039.

Guardia M, Gallignani M, Garrigues S, 1993. Flow-injection derivative Fourier transform infrared determination of MTBE in gasoline[J]. Anal Chim Acta, 282:543—550.

Halden R F, Happel A M, Schoen S R, 2001. Evaluation of standard methods for the analysis of methyl tert-butyl ether and related oxygenates in gasoline-contaminated groundwater[J]. Environ Sci Technol, 35:1469—1474.

Kanal H, Inouye V, Goo R *et al*., 1994. GC/MS analysis of MTBE, ETBE, and TAME in gasolines[J]. Anal Chem, 66: 924—927.

Meusinger R, 1996. Gasoline analysis by ^{1}H nuclear magnetic resonance spectroscopy[J]. Fuel, 75: 1235—1243.

Pankow J F, Thomson N R, Johnson R L *et al*., 1997. The urban atmosphere as a non-point source for the transport of MTBE and other volatile organic compounds(VOCs) to shallow, groundwater[J]. Environ Sci Technol, 31: 2821—2828.

Song H, Duttweiler C M, Lemley A T, 1999. Analysis of methyl tert-butyl ether and its degradation products by direct aqueous injection onto gas chromatography with mass spectrometry or flame ionization detection systems [J]. J Chromatogr A, 857: 205—216.

Rudo K M, 1995. Methyl tertiary-butyl ether (MTBE)-evaluation of MTBE carcinogenicity studies[J]. Toxicol Ind Health, 11:167—173.

US Environmental Protection Agency, 1998. Questions & answers about methyl tert-butyl ether(MTBE)[R]. Office of Air and Radiation, Office of Mobile Sources, Fuels and Energy Division. July 29, 1998.

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