ELSEVIER

Short communication

Determination of methyl *tert*-butyl ether in gasoline: a comparison of three fast methods based on mass spectrometry

José Luis Pérez Pavón*, Miguel del Nogal Sánchez, Carmelo García Pinto,
María Esther Fernández Laespada, Bernardo Moreno Cordero

*Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Ciencias Químicas,
Universidad de Salamanca, 37008 Salamanca, Spain*

Abstract

A high-speed quantitative analysis of methyl *tert*-butyl ether (MTBE) using three different methods with mass spectrometry detection has been performed. The first method is based on fast chromatography and required an analysis time of 5.23 min per sample, although a certain period (6 min) was necessary for the initial measurement conditions to be regained prior to analysing the next sample. The other two are non-separative methods and are based on direct injection and headspace generation. The analysis times were 1.5 and 3.5 min, respectively, although in the latter case an additional period of time was required to extract volatiles from the sample. The analytical characteristics of all three methods are highly satisfactory in terms of linearity, lack of fit, precision and accuracy. The methods were applied to the determination of MTBE in different gasoline samples. The non-separative methods afforded slightly higher concentrations than those found when fast chromatography was used; this is due to the presence of other minor components that contribute to the abundance of the ion at *m/z* 73, characteristic of MTBE. We propose a correction that removes this error very satisfactorily and allows the same results to be obtained with all three methodologies proposed.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Methyl *tert*-butyl ether; Gasoline; Direct injection; Chemometrics; Headspace analysis; Mass spectrometry

1. Introduction

Methyl *tert*-butyl ether is a volatile organic compound widely employed as an additive in gasolines. It was originally used to increase the octane index when tetraethyl lead was withdrawn from gasolines. Later, it was used to increase the efficiency of combustion and achieve a cleaner burning process and thereby reduce the emission of compounds such as carbon monoxide and ozone. Some other fuel oxygenates used as additives in gasolines are ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and diisopropyl ether (DIPE).

MTBE is highly soluble in water, is highly mobile, and is sparingly biodegradable. The combination of these proper-

ties together with the high content of this compound in some gasolines may account for the appearance of elevated concentrations of MTBE in surface waters, ground waters, and even in rain and snow. Some studies [1] have shown that gasoline spills and unburned fuel components used in boats are the main sources of pollution of surface waters.

The most widely used analytical methods include purge and trap [1,2,3], headspace generation [4], direct aqueous injection (DAI) [5] and solid-phase microextraction (SPME) [6–8], generally combined with gas chromatography and mass spectrometry detection (GC–MS) [3–9]. Choice of one method or another mainly depends on the concentration range to be determined. In this sense, the methodologies employing gas chromatography–mass spectrometry with some preconcentration step are the most sensitive.

Gas chromatography is one of the techniques most widely employed to quantify mixtures of organic compounds in

* Corresponding author. Tel./fax: +34 923 294483.
E-mail address: jlpp@usal.es (J.L. Pérez Pavón).

environmental samples. However, owing to its long analysis times it has not been possible to apply it as a screening technique or for rapid quantitative analysis. Nevertheless, the advent of microbore columns, together with the possibility of using shorter columns, high carrier gas flows and rapid temperature programming, allow the use of GC to achieve rapid separations [10–12].

The development of non-separative methods for the resolution of different analytical problems is currently of great interest, mainly owing to their fast analysis speeds. Sometimes, it is not necessary to obtain information about the individual compounds of a sample to resolve the analytical problem in hand, it sufficing to obtain a characteristic profile of the sample formed by all the components integrating it. Some methods based on this type of generation of signal corresponding to the whole set of components are near-infrared spectroscopy (NIR) [13–15], Membrane inlet mass spectrometry (MIMS) [16–18], pyrolysis mass spectrometry (Py-MS) [19–21], and headspace mass spectrometry (HS-MS) [22–27].

Here we propose three rapid methods for the determination of MTBE in gasolines with detection by mass spectrometry. One of them is based on fast gas chromatography and the other two are non-separative methods, with no chromatographic steps. One of them is based on direct injection of samples into the mass spectrometer and the other is based on headspace generation and later introduction into the spectrometer.

2. Experimental

2.1. Samples

MTBE was supplied by Acros Organics (Geel, Belgium). The different solutions of the compound were prepared by dilution of the commercial product in methanol (Merck, Darmstadt, Germany). Five different types of gasoline were used; they were suitably diluted for injection into the analysis system.

2.2. Procedure

2.2.1. Fast gas chromatography–mass spectrometry measurements

To perform the gas chromatographic measurements, a DB-VRX capillary column (20 m × 0.18 mm × 1 μm) was used. The carrier gas was helium N50 (99.995% pure; Air Liquide). 1 μL of sample was introduced through an integrated automatic liquid sample injection system (7683). The injection port was operated in the split injection mode (1:10) and the injector temperature was 250 °C. The column was used with the following temperature program: 50 °C for 0.5 min, 70 °C/min to 150 °C, 50 °C/min to 240 °C, and 240 °C for 0.5 min. These temperature ramps are the maximum ones permitted by the instrumental configuration employed. The detector was a quadrupole mass spectrometer (HP 5973 N).

The m/z range was 35–100 amu, and MTBE was identified by comparison of the experimental spectra with those of the NIST'98 database (NIST/EPA/NIH Mass Spectral Library, version 1.6). Data collection was performed with Enhanced ChemStation, G1701CA Version C 00.00 software [28] from Agilent Technologies.

2.2.2. Direct injection-mass spectrometry measurements

Using the same automatic injector described above, 1 μL of sample was injected into the system. In this case, the column was maintained at 240 °C throughout the time of analysis in order to minimise analyte retention. The same m/z range was used. Data collection was performed with the same software described above.

2.2.3. Headspace-mass spectrometry measurements

The apparatus used to measure the patterns of volatiles of the samples was a GERSTEL ChemSensor 4440 (Mülheim an der Ruhr, Germany). The samples (10 μL) were placed in a headspace sampler (HP 7694) at a temperature of 80 °C, for 20 min, where the headspace was generated. The headspace sampler was coupled to a GC–MS system by a transfer line (heated to 130 °C). In this case again, the column was held at 240 °C throughout the time of analysis. The total ion current signal was obtained in the same m/z range and data collection was performed with Pirouette® 3.0 software [29] from Infometrix Inc.

2.3. Safety precautions

MTBE is a suspected carcinogen and caution must be exercised with it. All samples were prepared in a cold chamber at 5 °C using latex gloves and a half-mask respirator.

3. Results and discussion

The signals generated by each of the three instrumental configurations used when one of the gasoline samples (gasoline 1) was analysed are shown in Fig. 1. The shape of the signals of the rest of the samples was similar. Fig. 1a shows the Total Ion Chromatogram (TIC) obtained when fast chromatography was used. MTBE had a retention time of 1.5 min. Fig. 1b was obtained when the characteristic ion of MTBE – $m/z = 73$ – was selected from the TIC. The mass spectrum recorded for this retention time is shown in Fig. 1c and was identical to that present in the database employed. The spectrum from this database is plotted in the upper part of Fig. 1c.

Fig. 1d shows the signal of the set of gasoline compounds analysed when the direct injection methodology was employed. Upon selecting the characteristic ion, $m/z = 73$, the result shown in Fig. 1e was obtained, from which it may be seen that the time elapsing between injection and the detection of MTBE with this methodology was 0.780 min. The mass spectrum corresponding to this time is shown in Fig. 1f.
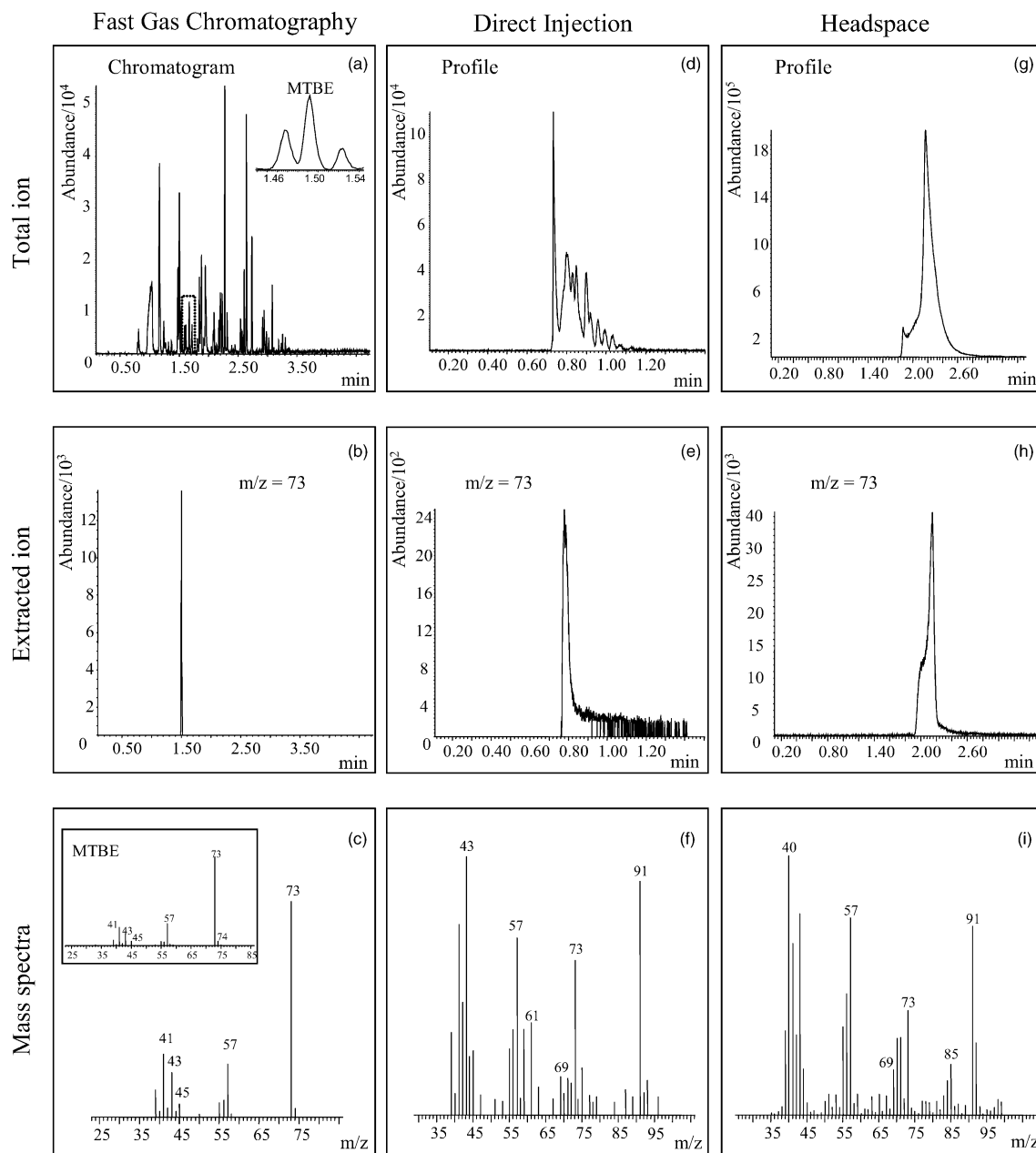
Fig. 1. Signals generated by each instrumental configuration when analysing a gasoline sample.

In this case, the spectrum selected was completely different from the MTBE spectrum from the database since the compounds of the sample were not subjected to any kind of separation and arrived at the spectrometer together. The *m/z* that appeared corresponded to the set of fragmentation patterns characteristic of linear and branched (57, 71, 85), cyclic (55, 69, 83) and aromatic (77, 78, 91, 92) hydrocarbons present in the gasolines. Fig. 1g shows the signal profile obtained when headspace generation was used and its shape can be seen to be similar to that shown in Fig. 1d, even though only the volatile compounds generated in the headspace after a process of heating to 80 °C were introduced into the mass spectrometer. Fig. 1i corresponds to the mass spectrum of all

the components present in the sample arriving at a given time (2.115 min) at the detector.

For this gasoline sample, 95% of the intensity of the *m/z* = 73 corresponded exclusively to MTBE; 5% was due to other compounds that contribute only a little to this *m/z*. This may allow quantification of this compound in the gasolines using univariate models in which only the *m/z* = 73 is included.

3.1. Linearity, lack of fit, precision and accuracy

The main characteristics defining an analytical method were assessed for the three instrumental configurations proposed. Three univariate calibration curves were constructed

Table 1
Analytical characteristics of the three methods proposed for the quantification of MTBE

Correlation coefficient, R^2	Fast gas chromatography	Direct injection	Headspace
Lack of fit ($F_{4,6}^{tab} = 4.53$)	0.9949 NO ($F_{4,6}^{cal} = 2.17$)	0.9955 NO ($F_{4,6}^{cal} = 1.79$)	0.9922 NO ($F_{4,6}^{cal} = 2.35$)
R.S.D.			
Level 0	–	–	–
Level 1	4.8	0.7	3.7
Level 2	0.4	1.0	2.0
Level 3	4.5	1.6	5.1
Level 4	1.0	3.3	4.1
Level 5	4.4	1.6	2.4
Validation step relative error			
Level 0	–	–	–
Level 1	0.1	14.8	6.8
Level 2	−2.3	0.9	4.2
Level 3	4.0	−3.3	3.2
Level 4	−5.2	−2.5	−4.1
Level 5	2.6	2.5	0.6

Level 0: only solvent (methanol).

with five levels of MTBE concentration uniformly distributed in the 0.00–20.5 mg/L range for the methods based on fast chromatography and on direct injection, and in the 0.00–586 mg/L range for the method based on headspace generation. Each concentration level was analysed in duplicate. The analytical characteristics of the three proposed methods are shown in Table 1.

It is important to check that the models generated do not present lack of fit [30]. The experimental value of F was lower than that tabulated for a significance level of 0.05, such that none of the three models showed lack of fit.

The precision of the methods was calculated through the relative standard deviation (R.S.D.) of the replicates measured for each of the concentration levels studied. The results obtained point to good reproducibility for the proposed methods. Accuracy was measured by leave-one-out internal validation. The value obtained in this prediction was compared with the added value of MTBE. Table 1 shows the mean relative error obtained for each concentration level. In all three cases, the results can be considered highly satisfactory. The positive and negative standard deviations indicate that there is no trend in the data.

3.2. Time of analysis

The three methods proposed required different times of analysis. The methodology based on fast gas chromatography required 5.23 min for the temperature program to be completed and to ensure complete elution of the compounds present in the sample injected. Additionally, about 6 min were necessary to re-establish the initial conditions, so the analysis time per sample was in the region of 11 min.

When direct injection was used, the time of analysis was 1.5 min. Immediately after analysing a sample, the injection system is ready for the next sample and its introduction into the device, because the column temperature remains constant throughout the period of sample analysis. Taking into account the time necessary for washing the injection syringe, sample capture and actual injection the interval between samples was 2 min.

The headspace generation method required an initial heating time for volatiles to be formed. The volatile generation time used in the present work was 20 min. However, since the instrumental configuration employed had an oven with 6 positions for heating samples simultaneously, this headspace generation time could be overlapped and the injection interval between samples was considerably reduced. With an analysis time of 3.5 min it was possible to achieve complete elution of the volatiles generated. An interval between sample injections of 3.90 min was chosen in order to avoid overlapping between the different measurements and operations of the equipment.

Whereas with conventional chromatography it is only possible to analyse two samples per hour [26], fast gas chromatography allowed the measurement of 6 samples. The non-separative methods based on headspace and direct injection allowed the analysis of 10 and 30 samples/h, respectively, implying an important increase in sample throughput.

3.3. Analysis of gasoline samples

The gasoline samples studied here were analysed in duplicate using the three methods proposed. Fig. 2 shows the chromatogram obtained for gasoline 2. Fig. 2a corresponds to the total ion chromatogram and Fig. 2b to the extracted ion at $m/z = 73$. Unlike gasoline 1 (Fig. 1b), where 95% of the abundance of the $m/z = 73$ ion corresponded to MTBE, in gasoline 2 this value was around 85%. The remaining 15% corresponded to minor compounds that also display this m/z. Among all the gasolines analysed, gasoline 1 was the one with the lowest abundance in $m/z = 73$, corresponding to different compounds of MTBE, and gasoline 2 was the one showing the greatest abundance. The other gasolines were in an intermediate position. Apart from MTBE, gasoline 1 did not display any compound with this m/z whose identification was possible. This is because of its low abundance. However, in gasoline 2 seven compounds were identified: isopentane ($t_R = 1.167$ min), ethyl *tert*-butyl oxide ($t_R = 1.670$ min), toluene ($t_R = 2.270$ min), ethylbenzene ($t_R = 2.598$ min), *m*-xylene and *p*-xylene ($t_R = 2.638$ min) and *o*-xylene ($t_R = 2.732$ min).

In light of these results, it is clear that the non-separative methods differ with respect to the chromatographic method in the quantification of MTBE in gasoline samples containing small amounts of other compounds that contribute to the $m/z = 73$. Thus, for example, this difference would be smaller in gasoline 1 (about 5%) and larger when gasoline 2 is employed (about 15%). The separative method is free of such interferences.

Table 2a shows the concentration of MTBE expressed in % (w/v) for the gasoline samples analysed with the three methods proposed. There are few differences in the concentrations

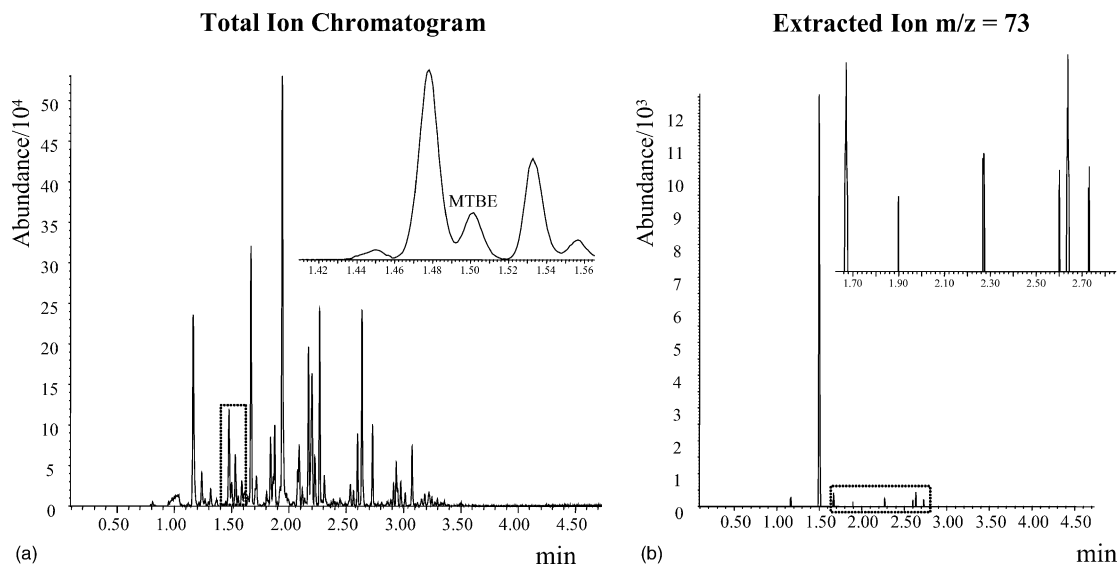**Total Ion Chromatogram**   **Extracted Ion m/z = 73**

Fig. 2. (a) Chromatogram obtained upon analysing gasoline sample 2. The upper part of the figure shows an enlargement of the zone close to the retention time of MTBE. (b) Chromatogram of the extracted $m/z = 73$ ion. In the upper part, most of the minor compounds contributing to this m/z can be seen.

found in gasoline 1 with the three methods. The relative errors of the direct injection and headspace generation methods with respect to the chromatographic procedure were 4.8 and 7.1%, respectively when this type of gasoline was analysed. Nevertheless, the differences were more pronounced for gasoline 2. The relative errors of the direct injection and headspace generation methods with respect to the chromatographic method were now 17.8 and 20.5%, respectively. The non-separative methods afforded very similar results for all types of gasoline analysed and, as is logical, the concentrations found were always higher than those obtained with fast gas chromatography since they included the whole of the $m/z = 73$ ion because it is not possible to assign the abundance corresponding exclusively to MTBE.

3.4. Mathematical correction of signals in non-separative methods

In order to eliminate the positive error obtained with the non-separative methods in the determination of MTBE, we propose a mathematical correction which somehow separates the contribution to intensity of the $m/z = 73$, typical of MTBE, from that arising from other compounds present in small amounts in most gasolines. It is based on the study of the

abundance relationships of the different ions recorded with fast gas chromatography for the different gasolines.

The $m/z = 91$ ion is not present in the mass spectrum of MTBE and, additionally, it is characteristic of most hydrocarbons that may produce interferences in the $m/z = 73$ with the compound studied. The intensity ratio for $m/z = 73$ (which does not correspond to MTBE) and $m/z = 91$ taking into account that whole analysis time was comprised in a range between 0.0023 and 0.0032 for most of the commercially available gasolines in Spain. With a view to proposing a single correction system that would be valid for different types of samples, we chose an intermediate value between both values as a compromise. In this way, it is possible to relate the intensity coming from the $m/z = 73$ that does not derive from MTBE to that corresponding to the $m/z = 91$. The differences between the total intensity recorded for the $m/z = 73$ and the previously calculated value allowed us to determine the intensity of the m/z associated with MTBE.

The following equation depicts the above calculations:

$$I^{new}_{(m/z=73)} = I_{(m/z=73)} - 0.0027 I_{(m/z=91)} \qquad (1)$$

where $I^{new}_{(m/z=73)}$ corresponds to the new abundance value of this ratio after performing the correction proposed; $I_{(m/z=73)}$

Table 2
Concentration of MTBE expressed as % (w/v) for the gasoline samples analysed before (a) and after (b) performing the proposed correction

Sample	Table 2a			Table 2b	
	Fast gas chromatography	Direct injection	Headspace	DI (corrected)	HS (corrected)
Gasoline 1	4.2 ± 0.4	4.4 ± 0.4	4.5 ± 0.4	4.2 ± 0.4	4.2 ± 0.4
Gasoline 2	0.73 ± 0.07	0.86 ± 0.06	0.88 ± 0.09	0.76 ± 0.06	0.74 ± 0.09
Gasoline 3	2.4 ± 0.2	2.6 ± 0.2	2.6 ± 0.3	2.4 ± 0.2	2.4 ± 0.3
Gasoline 4	3.1 ± 0.3	3.3 ± 0.3	3.3 ± 0.4	3.1 ± 0.3	3.2 ± 0.4
Gasoline 5	3.9 ± 0.4	4.1 ± 0.3	4.1 ± 0.4	3.9 ± 0.3	3.9 ± 0.4

and $I_{(m/z=91)}$ are the total abundance values for the 73 and 91 ratios, respectively, along the analysis time.

It should be stressed that all the values necessary to calculate $I^{new}_{(m/z=73)}$ can be obtained from the results of the non-separative methods since the variables involved correspond to the intensity of these m/z along the time of analysis. The results obtained after applying this correction are shown in Table 2b. Now, both the method based on direct injection and that based on headspace generation afforded results that were very similar to those obtained with the fast chromatographic method. In the case of gasoline 1, the results obtained were identical with all three proposed methods. The relative errors of the direct injection and headspace generation methods with respect to the chromatographic procedure were 4.1 and 1.4%, respectively, in the case of gasoline 2.

3.5. Comparison of proposed methodologies

In view of the results obtained, the three methodologies proposed can be said to afford similar results, suitable for the determination of MTBE in gasolines. The choice of one over another will depend, among other factors, on the type of information required and on the type of sample to be analysed.

If it is desired to obtain qualitative and/or quantitative information about the species present in gasoline samples it is necessary to use the technique involving a chromatographic separation although, as seen, this requires a relatively long analysis time. The great advantage of the direct injection method is that it is possible to determine MTBE in the presence of other components in the sample with errors of 5% or less without the need to perform chromatographic separation, such that the time of analysis per sample is reduced to only 2 min. The method based on headspace generation has the advantage that only the volatile components corresponding to the sample analysed are injected into the system. It is therefore a very suitable method for samples containing particles in suspension (which cannot be injected directly) or for those showing a matrix effect (which will be minimised because only the volatile compounds are injected). It is possible to attain good sampling speed, although the total time of analysis is slightly longer than with the direct injection method.

4. Conclusions

The proposed methods have been successfully applied to the rapid detection and quantification of MTBE in five different types of gasoline. The analysis times are considerably reduced when the non-separative methods are employed. Thus, using the chromatographic method, over a period of 1 h it is possible to analyse 5 samples whereas with the direct injection and headspace generation methods it is possible to analyse 30 and 10 samples, respectively, in the same time. However, when the non-separative methods are used, a certain error may arise due to the presence of other compounds that contribute to the intensity at the mass/charge character-istic of the compound studied. This positive systematic error in the determination of the concentration of MTBE can be satisfactorily corrected using the algorithm proposed here, enabling the use of all three methods and obtaining similar results in all cases. Choice of one method over another may therefore depend on factors such as the number of samples to be analysed, the time available for analysis and the nature of the sample.

References

[1] Y.J. An, D.H. Kampbell, G.W. Sewell, Environ. Pollut. 118 (2002) 331.
[2] M. Mezcua, A. Agüera, M.D. Hernando, L. Piedra, A.R. Fernández-Alba, J. Chromatogr. A 999 (2003) 81.
[3] M. Rosell, S. Lacorte, A. Ginebreda, D. Barceló, J. Chromatogr. A 995 (2003) 171.
[4] D.T. O'Neill, E.A. Rochette, P.J. Ramsey, Anal. Chem. 74 (2002) 5907.
[5] L. Zwank, T.C. Schmidt, S.B. Haderlein, M. Berg, Environ. Sci. Technol. 36 (2002) 2054.
[6] J. Dron, R. García, E. Millán, J. Chromatogr. A 963 (2002) 259.
[7] T.F. Lin, C.L. Liu, F.C. Yang, H.W. Hung, Water Res. 37 (2003) 21.
[8] F. Piazza, A. Barbieri, F.S. Violante, A. Roda, Chemosphere 44 (2001) 539.
[9] F. Fang, C.S. Hong, S. Chu, W. Kou, A. Bucciferro, J. Chromatogr. A 1021 (2003) 157.
[10] C.G. Fraga, B.J. Prazen, R.E. Synovec, Anal. Chem. 72 (2000) 4154.
[11] J.L. Hope, K.J. Johnson, M.A. Cavelti, B.J. Prazen, J.W. Grate, R.E. Synovec, Anal. Chim. Acta 490 (2003) 223.
[12] N. Wu, J.C. Medina, M.L. Lee, J. Chromatogr. A 892 (2000) 3.
[13] Z. Wang, T. Dean, B.R. Kowalski, Anal. Chem. 67 (1995) 2379.
[14] S. Macho, M.S. Larrechi, Trends Anal. Chem. 21 (2002) 799.
[15] L. Zhang, G.W. Small, M.A. Arnold, Anal. Chem. 74 (2002) 4097.
[16] M.B. Springett, V. Rozier, J. Bakker, J. Agric. Food Chem. 47 (1999) 1125.
[17] D. Lloyd, K.L. Thomas, G. Cowwie, J.D. Tamman, A.G. Williams, J. Microbiol. Methods 48 (2002) 289.
[18] C.S. Creaser, D.G. Lamarca, J. Brum, C. Werner, A.P. New, L.M.F. dos-Santos, Anal. Chem. 74 (2002) 300.
[19] R. Goodacre, D.B. Kell, Anal. Chem. 68 (1996) 271.
[20] B.S. Radovic, R. Goodacre, E. Auklam, J. Anal. Appl. Pyrol. 60 (2001) 79.
[21] C. Pérès, C. Viallon, J.L. Berdagué, J. Anal. Appl. Pyrol. 65 (2002) 161.
[22] J.L. Berdagué, C. Viallon, N. Kondjoyan, C. Denoyer, C. Thonat, Viandes Prod. Carnés 19 (1998) 78.
[23] I. Marcos Lorenzo, J.L. Pérez Pavón, M.E. Fernández Laespada, C. García Pinto, B. Moreno Cordero, J. Chromatogr. A 945 (2002) 221.
[24] C. Pérès, F. Begnaud, J.L. Berdagué, Sens. Actuators 87 (2002) 491.
[25] I. Marcos Lorenzo, J.L. Pérez Pavón, M.E. Fernández Laespada, C. García Pinto, B. Moreno Cordero, L.R. Henriques, M.F. Peres, M.P. Simoes, P.S. Lopes, Anal. Bienal. Chem. 374 (2002) 1205.

[26] J.L. Pérez Pavón, M. del Nogal Sánchez, C. García Pinto, M.E. Fernández Laespada, B. Moreno Cordero, A. Guerrero Peña, Anal. Chem. 75 (2003) 2034.

[27] J.L. Pérez Pavón, M. del Nogal Sánchez, C. García Pinto, M.E. Fernández Laespada, B. Moreno Cordero, Anal. Chem. 75 (2003) 6361.

[28] Enhanced ChemStation, G1701CA, Version C 00.00, Agilent Technologies, 1999.

[29] Pirouette®: Comprehensive Chemometrics Modeling Sofware, Version 3.0, Infometrix, Woodinville, WA, 2000.

[30] Analytical Methods Committee, Analyst 119 (1994) 2363.