Simultaneous Flow Analysis Fourier Transform Infrared Determination of Benzene, Toluene, and Methyl *t*-Butyl Ether in Petrol*

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A new procedure has been developed for the simultaneous flow analysis Fourier transform infrared (FTIR) determination of benzene, toluene and methyl *t*-butyl ether (MTBE) in real petrol samples. The method is based on the dilution of samples in hexane (1 + 9) and direct injection of 300 µl of the diluted samples into a 0.28 ml min^{-1} carrier flow of hexane. First-order derivative absorbance measurements are carried out by FTIR, in the wavenumber range 1350–400 cm^{-1}. The three compounds studied were determined simultaneously in the same sample without additional sample preparation. Benzene was determined by measurement of the first order derivative (dA/d$\bar{v}$, where A is the absorbance, and $\bar{v}$, the wavenumber) between the peak at 678 cm^{-1} and the valley at 672 cm^{-1} with a dynamic range between 0.005 and 0.8% v/v, being established as the limit of detection for a probability level of 99.6%. Toluene was determined by measuring dA/d$\bar{v}$ between 731 and 725 cm^{-1}, the dynamic range being from 0.01 to 2.0% v/v. Methyl *t*-butyl ether was determined by measuring dA/d$\bar{v}$ between 1209 and 1201 cm^{-1}, providing a dynamic range between 0.035 and 2% v/v. The method can be applied to the direct analysis of petrol; the results obtained in the determination of the three compounds in real samples agree with those found by gas chromatography.

Keywords: *Flow analysis; Fourier transform infrared; simultaneous analysis; petrol*

Introduction

Petrol is a complex mixture of volatile flammable liquid hydrocarbons containing hundreds of different natural components and some additives.

The determination of aromatic hydrocarbons, and methyl *t*-butyl ether (MTBE) in petrols is common in petroleum refinery plants, and in the petrochemical and related industries.[1] The determination of benzene is particularly common because European Community laws specify a maximum tolerated level of this compound in petrols of 5% v/v.

Gas chromatography and other chromatographic techniques have been extensively used for the determination of benzene,[2–10] toluene,[4,5,11–13] and MTBE.[5,13–18]

However, there are few precedents in the literature about the use of infrared (IR) techniques for the determination of benzene[19] and MTBE[20] in petrols. For the determination of toluene, IR has only been used as detector in liquid chromatography[21,22] and supercritical fluid chromatography[23] or for the analysis of gases[24] or hydrocarbons in oils after solvent extraction.[25]

The recent development of flow analysis procedures (FA)[26–30] in the field of infrared spectrometry has helped to solve some of the many drawbacks of quantitative determinations using this technique; (i) repeatability and accuracy of the determinations have been improved,[31] (ii) the possibility of direct analysis of real samples has been enhanced[32], (iii) easy and fast methods for the quantitative quality control of several compounds in the same sample have been provided[33], and (iv) the sensitivity of Fourier transform infrared (FTIR) determinations has been increased by means of on-line coupling and preconcentration techniques.[34]

One of the main advantages of FA FTIR methodology is that it permits the simultaneous determination of several compounds in the same sample[35,36] by means of measurements at different wavenumbers in the same interferogram. To determine each of the investigated compounds in the sample, spectra and not overlapped absorbance bands must be employed. However, in the analysis of complex materials this approach must be improved by using single mathematical procedures, which could help solve problems related to matrix interference. In this sense, the use of FA FTIR derivative spectrometry permits the direct determination of compounds in real samples without requiring previous separation or clean-up procedures and without problems in establishing the baseline.[37]

In a previous paper we proposed a single procedure for the direct determination of benzene in petrols by FA FTIR[38] based on the use of the band at 675 cm^{-1} with appropriate selection of the baseline between 1712 and 650 cm^{-1}. On the other hand, a comparative study of different approaches for the FA FTIR determination of toluene in petrols which was carried out concluded that in some instances toluene could be determined by measuring the absorbance at 728 cm^{-1} using a baseline established between 825 and 575 cm^{-1}, but that, in general, it might be convenient to carry out this type of analysis by FA FTIR derivative spectrometry.[39] The same approach can also be applied to the direct determination of MTBE in petrols.[37]

The main objective of this study was to develop an appropriate methodology for the direct and simultaneous determination of benzene, toluene, and MTBE in real petrol samples by means of derivative FTIR measurements in a flow system.

Experimental

Apparatus and Reagents

A Perkin-Elmer (Beaconsfield, UK) Fourier transform infrared spectrometer, Model 1750, with a temperature-stabilized coated detector (FR-DTGS) and equipped with a series 7700 data station was employed to carry out first-order derivative absorbance measurements with a nominal resolution of 4 cm^{-1}, using a Specac (Orpington, UK) micro flow cell with KBr windows and a pathlength of 0.117 mm.

A series of computer programmes, written in OBEY and in BASIC, were developed to store each of the interferograms obtained as a function of time, to establish from these the corresponding zero-order and first-order absorbance spectra, and to determine the corresponding FA peaks in the derivative mode.[32,37]

The manifold employed for the FA FTIR determination is basically the same as previously described for the determination of benzene in petrols.[38] It is a single-channel manifold with a Gilson P2 Minipuls (Villiers-le-bel, France) peristaltic pump and a Rheodyne Type 50 (Cotati, USA) injection valve with a 300 µl loop. The pump tubing used to transport the carrier was made of Viton (Iso-Versinic) with 0.15 mm internal diameter, and the connecting tubes were made of poly(tetrafluoroethylene) (PTFE) with an internal diameter of 0.8 mm.

The simultaneous determination of three components in the same sample does not require any additional modification of the manifold, and only requires that the data treatment is applied to different wavenumber ranges in the same spectrum.

Analytical-reagent grade benzene, toluene, and hexane (Panreac, Barcelona, Spain), and MTBE supplied by Repsol, (Cartagena, Spain) were employed without further purification.

General Procedure for the FA FTIR Derivative Determination of Benzene, Toluene, and MTBE in Petrol

Take 2.5 ml of gasoline and dilute to 25 ml with hexane. Inject 300 µl of this solution into a carrier stream (0.28 ml min^{-1}) of pure hexane, and store the corresponding interferograms, obtained as a function of time, for a nominal resolution of 4 cm^{-1}. Calculate from the stored data the first-order derivative spectra, and determine the derivative values between 1209 and 1201 cm^{-1} for MTBE, 731 and 725 cm^{-1} for toluene, and between 678 and 672 cm^{-1} for benzene. From these data, construct the FA peaks for each injected solution. Determine the peak height and, for measurements obtained for a series of standard solutions, containing the three components under study, adjust the corresponding calibration graph by least squares and interpolate the peak-height values of samples in the regression line.

Gas Chromatography Analysis

To determine the accuracy of the developed procedure, a series of real samples were analysed independently in our laboratory, using the FA FTIR procedure, and in the laboratory of British Petroleum (Castellon, Spain), using a standard gas chromatography procedure.[4,14]

Results and Discussion

FA FTIR Determination of Benzene

Benzene has a well defined and very strong band at 675 cm^{-1} [see Fig. 1(a)], which is well resolved in real petrol samples commercialized in Spain. However, it has been found that toluene and heavier aromatic compounds could interfere in the determination of benzene in American petrols.[19] In order to avoid matrix problems and to perform the most general analytical procedure possible, the first-order derivative spectra can be employed.

Using a procedure developed by us,[38] benzene can be determined by FA FTIR using absorbance measurements at 675 cm^{-1} with a baseline established between 712 and 650 cm^{-1}. Under these conditions, the following analytical parameters were found: a dynamic range between 0.002 and 0.8% v/v of benzene in 1 + 9 diluted petrol–hexane samples; a typical calibration equation of $A = 0.001 + 0.769\ C$, where A

is the absorbance and C the concentration, in % v/v with a correlation coefficient $R = 0.9994$; a sensitivity of 65.6 absorbance units C^{-1} cm^{-1}; a limit of detection of 0.002% v/v for $k = 3$; and a relative standard deviation of 1.0% for five independent analyses of a standard containing 0.4% v/v benzene.

When first-order derivative measurements were made, instead of zero-order values, the following parameters were found: a dynamic range between 0.005 and 0.8% v/v; a typical calibration line $\mathrm{d}A/\mathrm{d}\bar{v} = 0.004 + 2.335C$, where $\bar{v}$ is the wavenumber, with $R = 0.9993$; a sensitivity of 199.6 derivative units C^{-1} cm^{-1}; a limit of detection of 0.005% v/v for $k = 3$; and a relative standard deviation (RSD) of 1.0% for five independent analyses of a sample containing 0.4% v/v benzene.

Comparing the analytical characteristics of the absorbance FA FTIR and derivative procedures, it can be concluded that the derivative procedure is the more sensitive, because the derivative values were obtained between a peak and the adjacent valley and using an arbitrary scale. However, the limits of detection obtained by the two procedures are comparable. On the other hand, the well defined baseline found for derivative spectra provides good reproducibility for measurements made in real samples.

FA FTIR Derivative Determination of Toluene

In a previous paper,[39] different approaches for the FA FTIR determination of toluene in petrols were compared; it was found that toluene can be determined by measuring absorbance values at 728 cm^{-1} using a baseline established 825 and 575 cm^{-1} [see Fig. 1(b)]. However, in some types of petrol, matrix interferences occur; first-order derivative values, measured between the 731 cm^{-1} peak and the 725
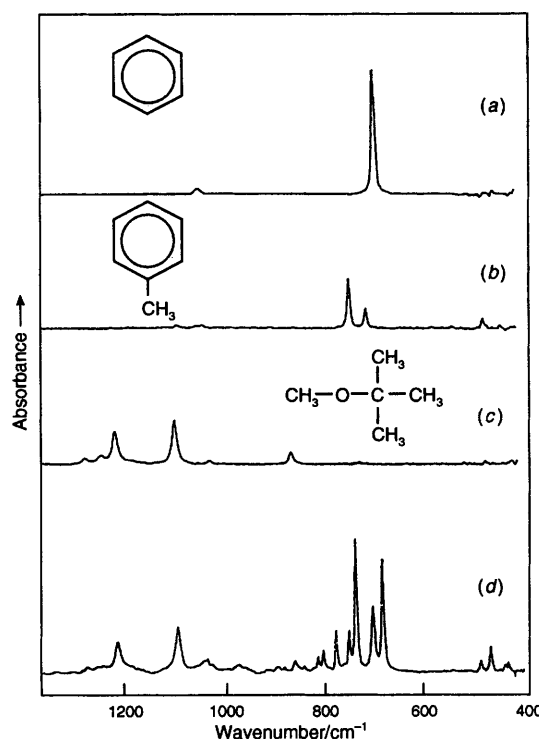

Fig. 1 FTIR Spectra of (a) 0.5% v/v benzene in hexane, (b) 0.5% v/v toluene in hexane, (c) 0.5% v/v MTBE in hexane, and (d) a petrol sample containing 3.20% v/v benzene, 15.7% v/v toluene and 4.6% v/v MTBE diluted 1 + 9 with hexane

cm^{-1} valley, are therefore employed to avoid this type of problem.

Under the conditions described earlier; a typical calibration line dA/d$\bar{v}$ = 0.001 + 0.9830C (C in % v/v) with R = 0.9993 can be established. This can provide a sensitivity of 84.0 (derivative units C^{-1} cm^{-1}), and a limit of detection of 0.01% v/v toluene in diluted petrols, the dynamic range of the procedure being from 0.01 to 2% v/v. A typical derivative value of 83.5 ± 0.8 (derivative units C^{-1} cm^{-1}) was obtained for a standard containing 1% v/v of toluene diluted in hexane, providing a relative standard deviation of 0.9%.

FA FTIR Derivative Determination of MTBE

Methyl t-butyl ether can be determined directly in petrol samples by FA FTIR using the first-order derivative spectra and carrying out the measurements between the peak at 1209 cm^{-1} and the valley at 1201 cm^{-1}, which corresponds to the band at 1205 cm^{-1} [see Fig. 1(c)]. Under the conditions described earlier, and with an injection volume of 300 μl and a carrier flow of 0.45 ml min^{-1}, hexane solutions of pure MTBE provided a typical calibration line of dA/d$\bar{v}$ = 0.0002 + 0.3524C (C in % v/v) with a regression coefficient, R = 0.9994. The sensitivity corresponded to 30.12 (derivative units C^{-1} cm^{-1}). The limit of detection for k = 3 corresponded to 0.035% v/v. For five independent measurements of a standard solution containing 1.0% v/v of MTBE, a derivative value of 30.0 ± 0.2 can be found, which corresponds to a relative standard deviation of 0.6%.

Simultaneous Determination of Benzene, Toluene, and MTBE

Fig. 2 shows the first-order derivative spectra of pure standards of benzene, toluene, MTBE, and a real petrol sample. Clearly, in the three different wavenumber zones defined for the FA FTIR derivative determination of each component, all the investigated compounds provide bands and do not contribute to increases in the background of the other compounds. So, it might be expected that the interferograms obtained for petrol samples diluted with hexane, and multicomponent standards containing all three components (benzene, toluene, and MTBE) could be used for the simultaneous determination of the three compounds in real samples without any prior sample extraction or clean-up. For this purpose, complete interferograms must be obtained for the injected sample or standards and stored as a function of time; these data are then used to establish the zero-order absorbance spectra and the first-order derivative.

It has been confirmed that MTBE solutions in hexane up to 1.5% v/v (which corresponds to a concentration in petrol of the order of 15% v/v) do not provide signals in the wavenumber range corresponding to the benzene and toluene determinations.

Solutions of benzene in hexane up to 1% v/v (which corresponds to a concentration of benzene in petrol of a 10% v/v, taking into account the dilution used in the FA FTIR determinations) do not modify the derivative signals obtained between 1209 and 1201 cm^{-1}, nor those found between 731 and 725 cm^{-1}; taking into account that the maximum tolerated level for benzene concentration in commercial petrols in the European Community is lower than 5% v/v, it can therefore be concluded that benzene does not interfere in the determination of MTBE and toluene.

Spanish petrol samples have a high concentration of toluene (of the order of 15–17% v/v),[39] hence the interference of toluene solutions from 0 to 2% v/v (which corresponds to a concentration in petrols of up to 20% v/v), was studied. The results obtained indicated that toluene does not cause interference in the determination of MTBE.

In the determination of benzene, the presence of high concentrations of toluene causes an increase in the absorbance at 675 cm^{-1}, which affects the peak-height values at 675 cm^{-1}; however, using the first-order derivative spectra, benzene can be determined by measuring the dA/d$\bar{v}$ values between 678 and 672 cm^{-1} without interference from toluene (see Table 1).

On comparing the slopes of the calibration graphs obtained for pure standards of each of the investigated compounds with those of multicomponent standards, it can be seen that the benzene pure standard provides a sensitivity of 199.6 (derivative units C^{-1} cm^{-1}), benzene–toluene–MTBE (1 + 1 + 1), a sensitivity of 200.2, and benzene–toluene–MTBE (1 + 5 + 1), a sensitivity of 199.4.

On the other hand, the sensitivity obtained for the toluene determination by derivative FA FTIR corresponds to 84.0 for pure standards of toluene, 85.9 for 1 + 1 + 1 toluene–benzene–MTBE, and 84.6 for 1 + 5 + 1 benzene–toluene–MTBE. The small interference observed in multi-elemental standards is due to the presence of MTBE, because high concentrations of benzene do not affect the derivative measurement at the toluene wavenumber. However, the interference of MTBE occurs only for MTBE: toluene ratios are ⩾1, which does not correspond to the real situation in commercially available petrols.

For MTBE, the sensitivity values corresponded to 30.12, 30.08, and 30.14 for pure MTBE standards, and 1 + 1 + 1, and 1 + 5 + 1 benzene–toluene–MTBE mixtures; this indicates that the simultaneous determination of the three investigated
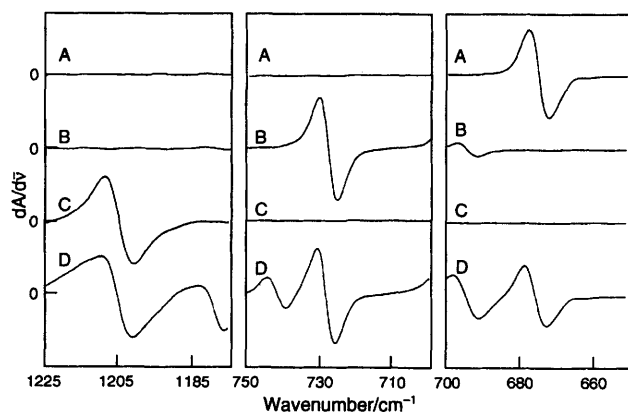

Fig. 2 First-order derivative spectra of: A, a 0.5% v/v benzene in hexane solution; B, a 1.5% v/v toluene in hexane solution; C, a 0.5% v/v MTBE in hexane solution; and D, a real petrol sample, containing 3.2% v/v benzene, 15.7% v/v of toluene, 4.6% v/v MTBE, diluted 1 + 9 with hexane

Table 1 Study of the interference of toluene in the determination of benzene ([benzene] = 0.2% v/v)

Toluene concentration (% v/v)	Benzene concentration found (% v/v)	
	A*	B†
0	0.201	0.200
0.5	0.203	0.199
1.0	0.208	0.201
1.5	0.212	0.199
2.0	0.218	0.203
3.0	0.224	0.199

* Values obtained by carrying out absorbance measurements using a baseline established between 825 and 575 cm^{-1}.

† Values obtained by first-order derivative analysis between the 678 cm^{-1} peak and the 672 cm^{-1} valley.
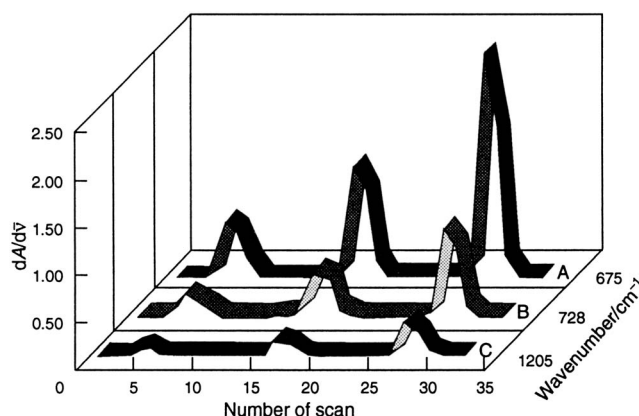
Fig. 3 FA recording obtained of absorbance derivative values for the simultaneous determination of benzene, toluene, and MTBE in petrols. A, Benzene, B, toluene, and C, MTBE

Table 2 Determination of benzene, toluene, and MTBE in real petrol samples by FA FTIR derivative spectrometry

	Benzene		Toluene		MTBE	
Sample	FA FTIR	GC*	FA FTIR	GC	FA FTIR	GC
1	3.20 ± 0.06	3.16	15.7 ± 0.1	15.92	4.6 ± 0.1	4.4
2	1.74 ± 0.03	1.70	16.2 ± 0.1	15.91	4.9 ± 0.1	5.0
3	3.26 ± 0.04	3.31	15.0 ± 0.05	—	<LOD†	0.0
4	1.80 ± 0.03	1.78	16.4 ± 0.1	16.71	<LOD	0.0
5	3.06 ± 0.06	3.00	12.60 ± 0.08	—	<LOD	0.0

* GC = Gas chromatography.
† LOD = Limit of detection.

compounds does not modify the analytical characteristics of the FA FTIR determination of each compound.

To obtain the derivative spectra, whilst taking into account that the use of derivative windows with high numbers of data points provides poorer sensitivity than the use of windows containing fewer points,[37] a window of five points was selected for a reading interval of 1 cm⁻¹ and a resolution of 4 cm⁻¹.

Fig. 3 shows that, by carrying out peak-height measurements in the three wavenumber intervals, benzene, toluene, and MTBE can be determined simultaneously. In comparison with the analysis by gas chromatography, the developed procedure permits the simultaneous determination of all investigated compounds without a prior separation step nor the need to wait for the consecutive elution of each of the chromatographic peaks.

Analysis of Real Samples

Five commercial petrols, two unleaded, premium petrols and three leaded petrols, were analysed by the proposed FA FTIR procedure and, independently, by gas chromatography. The results in Table 2 show that values of the same order were found using both methodologies, and that for the determination of MTBE in leaded petrol, which does not contain this additive, values lower than the limit of detection were found. So, it can be concluded that the FA FTIR methodology permits the accurate determination of benzene, toluene, and MTBE in real petrol samples, without necessitating prior sample extraction and only involving the prior dilution of samples with hexane.

The method has a sample throughout of 25 injections per hour, which provides a faster determination than other methodologies proposed in the literature.

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