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COMPARATIVE STUDY OF DIFFERENT APPROACHES FOR THE FLOW INJECTION-FOURIER TRANSFORM INFRARED DETERMINATION OF TOLUENE IN GASOLINES

M. GALLIGNANI,[1] S. GARRIGUES,[1] M. DE LA GUARDIA,[1]* J. L. BURGUERA,[2] and M. BURGUERA[2]

[1]Department of Analytical Chemistry, University of Valencia, 50 Dr. Moliner St. 46100 Burjassot, Valencia, Spain
[2]University of los Andes, Mérida, Venezuela

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Summary—A single channel flow injection manifold has been employed to carry out the direct determination of toluene in gasolines by FT–IR without any sample pretreatment and by using different strategies. Toluene can be directly determined by measuring the absorbance at 728 cm^{-1}, using a base line established between 835 and 575 cm^{-1}; and in this case a limit of detection of 0.01% (v/v) can be obtained with a dynamic range up to 2% (v/v). In some cases it could be convenient to determine toluene by derivative flow-injection FT–IR in order to avoid matrix interferences in the analysis of some types of gasolines. Carrying out the first order derivative FI–FT–IR measurements on the 728 cm^{-1} band between the peak at 731 and the valley at 725 cm^{-1} toluene can be determined without problems in establishing the base line and with a limit of detection of 0.01% (v/v). On the other hand, the use of the quotient between the first order derivative absorbance values of toluene, at the 728 cm^{-1} band, and benzene, at the 675 cm^{-1} band, can be applied for the determination of toluene in gasolines in which benzene has been previously analyzed, avoiding problems related to the determination of the base line and making measurements independent of the spacer employed.

The determination of toluene in gasolines is currently carried out by gas chromatography (GC)[1–4] and high performance liquid chromatography (HPLC).[5]

Infrared spectrometry has been used as detector in the chromatographic determination of toluene in gasolines, by using GC,[6] supercritical fluid chromatography[7] and HPLC,[8,9] but in the latter case mixtures of solvents, instead of real gasoline samples, were analyzed.

There are only few precedents on the use of IR spectrometers for the quantitative analysis of toluene, this technique being applied to the analysis of gas mixtures[10] and hydrocarbon oils in waters after *a priori* solvent extraction with CCl_4.[11] However, until now, we have not found any paper concerning the quantitative determination of toluene in gasolines by FT–IR.

The recent development of flow injection procedures for quantitative analysis by infrared spectrometry[12–28] has improved this kind of determination thus, contributing to the development of direct procedures for the analysis of real samples of pharmaceuticals,[21,25] pesticide formulations,[24] and paint solvents.[19,22]

For the direct analysis of gasolines we have proposed simple FI procedures for the direct determination of benzene,[23] and also for the FI derivative-FT–IR determination of methyl tert-butyl ether (MTBE)[26] which have shown that *a priori* dilution of samples with hexane is sufficient as a sample preparation step.

The aim of the present paper is to develop a direct, fast and simple procedure for the quantitative FT–IR determination of toluene in real gasoline samples and for this purpose three different approaches have been assayed: (i) one simple FI procedure, based on the use of absorbance values (working at different wavenumbers), (ii) a FI–FT–IR derivative procedure and (iii) a method based on the use of band quotient between the first order derivative values at the wavenumber characteristics of toluene and benzene. The analytical figures of merit of the above mentioned procedures are compared and these procedures applied to the determination of toluene in commercially available gasolines.

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*Author to whom correspondence should be addressed.

EXPERIMENTAL

Apparatus and reagents

A Perkin-Elmer Fourier Transform Infrared Spectrometer model 1750, with a temperature stabilized coated detector DTGS and equipped with a data station model 7700, was employed to carry out all the absorbance measurements using a nominal resolution of 4 cm^{-1}. A micro-flow cell SPECAC (Orpington, U.K.) with KBr windows and a pathlength of 0.117 mm was employed to carry out the FI–FT–IR measurements.

The manifold employed was essentially the same described for the determination of benzene in gasolines[23] and for the simultaneous determination of *o*-xylene, *m*-xylene and *p*-xylene in xylol samples.[22] It is a single channel manifold with a Gilson P2 Minipuls peristaltic pump and a Rheodyne Type 50 injection valve with a 320 μl loop. Pump tubing employed to transport the carrier are of Viton^R (Iso-Versinic) with 0.15 mm internal diameter and the connecting tubes are made of Teflon^R with an internal diameter of 0.8 mm.

A series of computer programs, developed by us[19,26] provide the continuous monitoring of absorbance and the different order derivative spectra, as a function of time, and also the mathematical treatment of the IR spectra.

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

General procedure

Direct FI–FT–IR analysis. Inject 320 μl of sample, previously diluted 1:9 with hexane, into a hexane carrier stream (0.28 ml/min) and obtain the corresponding FT–IR spectra as a function of time. These spectra are stored in the hard disk of the data station. From the peak height of the absorbance bands at 728, 695 and 464 cm^{-1}, using a base line between 835 and 575 cm^{-1}, and in the last case between 575 and 425 cm^{-1} the corresponding absorbance values are recorded as a function of time. Standard solutions of toluene in hexane are employed in all cases.

Derivative FI–FT–IR analysis. The same amount of samples, diluted in the same way as previously indicated, are injected into the hexane carrier and interferogrammes stored as before. However the FI recordings are established from the first and second order derivative spectra, measured in the wavenumber ranges previously mentioned. In this case it is not necessary to establishing a specific based line. Hexane solutions of pure toluene can be employed as standards.

Determination of toluene by using benzene as internal standard. For this purpose FI measurements were carried out in the first order derivative mode using the same procedure described before for sample preparation and sample injection. Data found for toluene (between 731 and 725 cm^{-1}) were divided by those found for benzene (between 678 and 672 cm^{-1}) and, taking into account the benzene concentration of samples previously analyzed by a simple FI–FT–IR procedure developed by us,[23] the toluene concentration can be establishing without requiring to determine a specific base line, the measurements being also independents of the spacer of the measurement cell (or the sample dilution).

Gas chromatography analysis. A standard test method,[3] based on the use of gas chromatography, was employed as a reference method and applied by the British Petroleum laboratory of Castellón (Spain) to the determination of toluene in two samples, also analyzed by us, using the developed FI–FT–IR procedures.

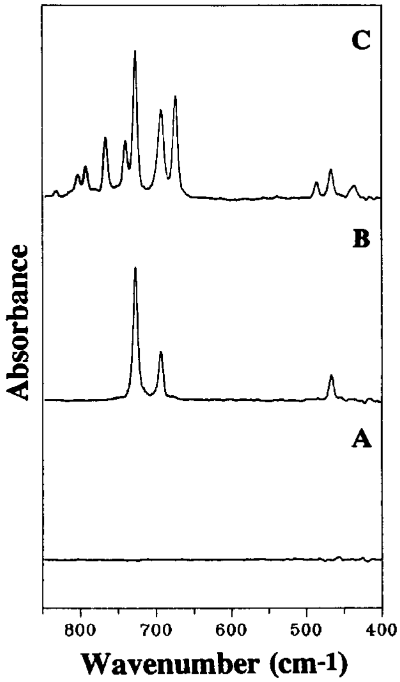

Fig. 1. FT–IR absorbance spectra of (a) pure hexane, (b) a 1% (v/v) toluene solution, and (c) a real gasoline sample containing 11.6% (v/v) of toluene diluted 1 + 9 in hexane.

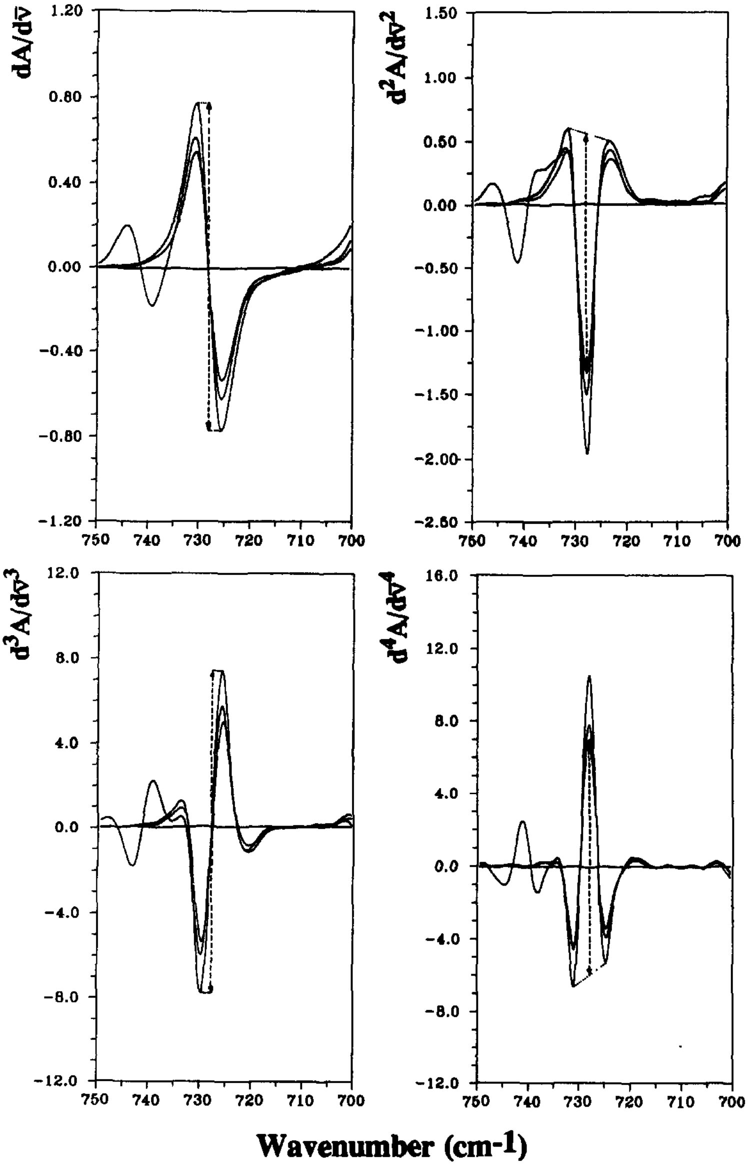

Fig. 2. Derivative FT–IR spectra of toluene standard solutions prepared in hexane with 1% and 1.5% (v/v) concentration and a real gasoline sample containing a 11.6% (v/v) of toluene diluted 1 : 9 with hexane.

RESULTS AND DISCUSSION

FT–IR spectra of toluene in gasolines

Toluene presents three well defined bands at 728, 695 and 464 cm^{-1} which could be employed for the quantitative determination of this compound in different types of commercial gasolines (see Fig. 1).

The band at 728 cm^{-1} is the most intense and in real samples it is only interfered with the presence of another band at 740 cm^{-1}. For the toluene band, an appropriate base line can be established between 835 and 575 cm^{-1} The band at 695 cm^{-1} seems to be common to different mono and di-substituted compounds and so it can be affected by the different composition of aromatic hydrocarbons in gasolines. The aforementioned base line, between 835 and 575 cm^{-1}, also seems appropriate for this band.

The band at 464 cm^{-1} has been reported as a characteristic band of toluene,[31] but at this wavenumber KBr windows have a poor transparency and because of that for the determination of toluene using the 464 cm^{-1} band a sample dilution of the order of 40% (v/v) must be employed instead of the 10% (v/v) dilution which can be recommended for the use of the other two bands. A spectral base line between

495 and 425 cm^{-1} can be recommended in this latter case.

Derivative FT–IR spectra of toluene in gasolines

The derivative spectra of toluene standards and that of gasolines containing toluene, obtained for different derivative orders, provide a convenient base line for the three bands considered for this determination and, in some cases, good agreement has been obtained between the spectra of pure toluene standards, dissolved in hexane, and diluted gasoline sample as it can be see in Fig. 2 for the band at 728 cm^{-1}. The same figure also shows the criteria employed to carry out the measurements of $dA/d\bar{\nu}$ in each case in order to obtain the most accurate results. The first and second order derivative spectra were obtained by using a derivative window of five points but in the case of third and fourth derivatives a window of nine points was employed.

Direct FI–FT–IR determination of toluene in gasolines

Based on previous studies, carried out for the determination of MTBE and benzene in gasolines,[26,23] an injection volume of 320 μl of sample and a carrier flow of 0.28 ml/min were selected as operation conditions to obtain the highest sensitivity with an appropriate sample throughput in flow injection. With the above conditions, and using a 4 cm^{-1} resolution, FT–IR spectra can be obtained and stored in the hard disk of the Perkin-Elmer 7700 data station in 17 sec; but when a more appropriate instrumentation can be used the data acquisition time can be tremendously reduced and so a higher carrier flow could be employed, providing a very fast analysis.

We have tried to determine directly toluene in gasolines by using the three characteristic bands of toluene at 728, 695 and 464 cm^{-1} and Table 1 summarizes the typical analytical figures of merit obtained from the calibration lines established for absorbance values at each wavenumber. However, when real gasoline samples were analyzed, accurate results were obtained only by using the most sensitive band at 728 cm^{-1} and also using the second order derivative values measured at the band of 695 cm^{-1} as can be seen in Table 2 in which results found by using the absorbance and the first four derivative values measured at 728 and 695 cm^{-1} have been included. So, for the determination of toluene in gasolines it must be recommended the use of the band at 728 cm^{-1}. In our case we have employed a 1:9 dilution of samples in hexane and standards dissolved in hexane.

Derivative FI–FT–IR determination of toluene in gasolines

The use of derivatives provides an interesting tool for increasing the selectivity of the spectrometric determinations, both in ultraviolet–visible and infrared spectrometry,[29,30] and it has been proved[26] that the use of derivative values in FI–FT–IR provides a better base line than the use of absorbance values and it avoids a series of interferences.

Toluene can be directly determined in gasolines after a sample dilution in hexane by using the derivative spectra in the previously indicated wavenumber range.

Table 3 summarizes the analytical figures of merit of the derivative FI–FT–IR determination of toluene by using different derivative orders. All these parameters were obtained from calibration lines of toluene in hexane and it can be seen that the use of derivative spectra provides, higher intercept values of the corresponding calibration lines than those found for the absorbance measurements. On the other hand the variation coefficient obtained from five independent measurements of a same solution, in

Table 1. Analytical figures of merit of the direct FI determination of toluene in gasolines by using different bands

	Band		
Parameter	728 cm^{-1}	695 cm^{-1}	464 cm^{-1}
Base-line (cm^{-1})	835–575	835–575	495–450
Dynamic range/up to	2.0% (v/v)	2.5% (v/v)	7.5% (v/v)
Equation line C in % (v/v)	$A = 0.001 + 0.3285C$	$A = 0.001 + 0.1238C$	$A = 0.004 + 0.0613C$
Regression coefficient	0.99997	0.99988	0.99960
VC (%), $n = 5$	0.5	0.7	2
LOD, $k = 3$	0.01	0.01_5	0.1

VC: Variation coefficient in percentage.
LOD: Limit of detection in % (v/v) for a probability level of 99.6%.

Table 2. Determination of toluene in gasoline samples using different approaches

		Toluene concentration % (v/v)										
		Band at 728 cm^{-1}					Band at 695 cm^{-1}					
Sample	Type	Direct absorbance analysis	First derivative analysis	Second derivative analysis	Third derivative analysis	Fourth derivative analysis	Direct absorbance analysis	First derivative analysis	Second derivative analysis	Third derivative analysis	Fourth derivative analysis	Internal standard
1	Unleaded	11.50 ± 0.07	11.6 ± 0.1	11.7 ± 0.2	11.7 ± 0.2	11.6 ± 0.3	22.8 ± 0.1	16.7 ± 0.1	11.8 ± 0.2	10.9 ± 0.8	9 ± 1	11.6 ± 0.2
2	Unleaded	10.00 ± 0.08	10.4 ± 0.1	10.1 ± 0.2	10.1 ± 0.2	10.1 ± 0.2	20.0 ± 0.1	15.8 ± 0.2	10.3 ± 0.2	9.8 ± 0.7	10 ± 1	10.0 ± 0.2
3	Normal	6.50 ± 0.04	6.6 ± 0.1	6.5 ± 0.2	6.4 ± 0.2	6.5 ± 0.2	13.50 ± 0.09	10.1 ± 0.1	6.7 ± 0.1	6.4 ± 0.5	6.3 ± 0.7	6.3 ± 0.1
4	Premium	11.20 ± 0.07	11.3 ± 0.2	11.3 ± 0.2	11.2 ± 0.3	11.4 ± 0.3	20.0 ± 0.2	14.9 ± 0.1	11.6 ± 0.2	11.0 ± 0.7	11.1 ± 0.5	11.4 ± 0.2
5	Unleaded	11.2 ± 0.9	11.2 ± 0.1	11.1 ± 0.2	11.0 ± 0.2	11.4 ± 0.2	19.5 ± 0.1	15.0 ± 0.1	11.3 ± 0.2	9.5 ± 0.7	10 ± 1	11.1 ± 0.2
6	Unleaded	16.7 ± 0.2	16.60 ± 0.09	16.6 ± 0.2	16.5 ± 0.3	16.6 ± 0.4	27.1 ± 0.1	19.5 ± 0.1	16.8 ± 0.2	14.9 ± 0.3	13.1 ± 0.3	16.6 ± 0.3
7	Unleaded	16.25 ± 0.08	16.2 ± 0.1	16.1 ± 0.1	15.9 ± 0.2	15.8 ± 0.3	25.0 ± 0.6	18.80 ± 0.09	15.95 ± 0.07	13.7 ± 0.2	13.5 ± 0.3	16.0 ± 0.3

general increases when the derivative order increases. The use of high orders of derivation also increases the background for a fixed sensitivity level and so, high derivative orders can not be employed for bands with a low sensitivity because it provides inaccurate results (see Table 2). However the use of derivative FI–FT–IR permits us to determine accurately toluene in gasoline samples in the wavenumber range of 695 cm^{-1} by using the second order derivative spectra and it avoids problems in the determination of the base line in the range of 464 cm^{-1}. In this latter case, due to the problems related to the determination of toluene, using KBr windows only the use of the first order derivative can be recommended (results not shown).

Table 2 summarizes results found in the analysis of gasolines by using derivative spectra and also by the internal standard method.

Determination of toluene by using benzene as internal standard

Benzene is present in real gasoline samples in a concentration level from 2.5 to 5% (v/v). This compound can be directly determined by using the band at 675 cm^{-1} which is not overlapped with other gasoline components, especially when derivative spectra are employed.[23]

For the determination of toluene, the band of benzene can be used as an internal reference. The ratio between the slopes of the calibration lines, in the first derivative order, found for toluene and benzene standard solutions provides a constant value of 2.37. This value can be employed to obtain the toluene concentration in a sample in which benzene has been previously determined.

The above mentioned strategy, described in the experimental part, avoids problems in the establishment of the base line and provides results in a good agreement with other based on direct absorbance at 728 cm^{-1} and derivative measurements (see Table 2).

Comparison between the different strategies employed

From the analytical figures of merit summarized in Tables 1 and 3 and from results obtained in the analysis of real samples it can be concluded that the use of the internal standard method provides results coincident with those found by direct FI–FT–IR determination using the band at 728 cm^{-1} and also by derivative FI–FT–IR at 695 cm^{-1}. However, in order to

Table 3. Analytical figures of merit of the determination FI–FT–IR of toluene in gasolines

			Band	
Derivative order	Parameter	464 cm^{-1}	695 cm^{-1}	728 cm^{-1}
First	Calibration line	$\frac{dA}{d\bar{v}} = 0.008 + 0.205C$	$\frac{dA}{d\bar{v}} = 0.010 + 0.375C$	$\frac{dA}{d\bar{v}} = 0.008 + 0.983C$
	Regression coefficient (r)	0.9994	0.9998	0.9998
Window: 5 points	V.C. (%)	1.0	0.9	0.9
	L.O.D. (% v/v)	0.1	0.015	0.01
Second	Calibration line	$\frac{d^2A}{d\bar{v}^2} = 0.016 + 0.309C$	$\frac{d^2A}{d\bar{v}^2} = 0.018 + 0.545C$	$\frac{d^2A}{d\bar{v}^2} = 0.010 + 1.678C$
	Regression coefficient (r)	0.9993	0.9997	0.9996
Window: 5 points	V.C. (%)	1.0	0.9	0.8
	L.O.D. (% v/v)	0.1	0.015	0.01
Third	Calibration line	$\frac{d^3A}{d\bar{v}^3} = 0.080 + 1.900C$	$\frac{d^3A}{d\bar{v}^3} = 0.090 + 3.301C$	$\frac{d^3A}{d\bar{v}^3} = 0.100 + 10.24C$
	Regression coefficient (r)	0.9990	0.9993	0.9988
Window: 9 points	V.C. (%)	2.0	0.8	1.5
	L.O.D. (% v/v)	0.2	0.025	0.02
Fourth	Calibration line	$\frac{d^4A}{d\bar{v}^4} = 1.010 + 16.10C$	$\frac{d^4A}{d\bar{v}^4} = 0.950 + 30.50C$	$\frac{d^4A}{d\bar{v}^4} = 0.900 + 115.2C$
	Regression coefficient (r)	0.9991	0.9993	0.9990
Window: 9 points	V.C. (%)	2.5	0.8	1.2
	L.O.D. (% v/v)	0.2	0.025	0.02

V.C. Variation coefficient in % (v/v).
LOD limit of detection for a probability level of 99.6%.

obtain the best sensitivity the 728 cm^{-1} band must be recommended. On the other hand, the use of benzene as internal standard is a convenient method to obtain a reference value but can not be proposed as an effective method for toluene determination because it involves the previous determination of benzene.

The use of derivative FI–FT–IR provides a good sensitivity and an appropriate limit of detection and avoids difficulties in establishing the spectral base line. So, both the absorbance FI–FT–IR measurements and also the use of derivative spectra can be recommended for the determination of toluene in gasolines without requiring any chemical pretreatment of samples after a 1:9 dilution with hexane.

To establish the accuracy of the developed procedure toluene has been determined in two real samples of gasolines, previously analyzed by Gas Chromatography by an independent laboratory, and results found are summarized in Table 4. As can be seen both, gas chromatography and derivative FI–FT–IR provide results of the same order, thus indicating the accuracy of the method developed.

The FI–FT–IR procedures permits us to carry out more than 20 injections/hr and, taking into account the simple pretreatment required, it can be concluded that this methodology is very convenient for the control analysis of gasolines.

Table 4. Analysis of real samples by both FI–FT–IR and gas chromatography

	Toluene content % (v/v)	
Sample	FI–FT–IR*	Gas chromatography
1	16.5 ± 0.2	16.75
2	16.2 ± 0.1	15.92

*Results obtained by first order derivative FI–FT–IR carrying out the measurements at the band of 728 cm^{-1} with a window of five points.

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REFERENCES

1. J. Sevcik, *J. High Resolut. Chromatogr. Commun.*, 1980, **3**, 166.
2. A. H. H. Tameesh, A. M. Lafta, K. R. Hammed and T. M. Sarkissian, *Fuel*, 1985, **64**, 1170.
3. Annual Book of ASTM Standard, American Society for Testing and Materials, Philadelphia, 1986, D-4053-86.
4. S. K. Poole, K. G. Furton and C. F. Poole, *J. Chromatogr. Sci.*, 1988, **26**, 67.
5. R. E. Pauls, *J. Chromatogr. Sci.*, 1985, **23**, 437.

6. M. Deveaux and J. P. Huvenne, *Chromatographia*, 1987, **23**, 626.
7. P. Morin, M. Caude, H. Richard and R. Rosset, *Analusis*, 1987, **15**, 117.
8. V. V. Volkov, V. N. Grechushnikov, I. N. Kalinkina, V. A. Nemtsev and I. P. Petrov, *Zh. Prikl. Spektrosk.*, 1983, **39**, 800.
9. C. C. Johnson, J. W. Hellgeth and L. T. Taylor, *Anal. Chem.*, 1985, **57**, 610.
10. S. Ripperger and R. Germerdonk, *Chem. Ing. Tech.*, 1983, **55**, 558.
11. Department of the Environment and National Water Council (U.K.), *Methods Exam. Waters Assoc. Mater.*, 1984, 21.
12. D. J. Curran and W. G. Collier, *Anal. Chim. Acta*, 1985, **177**, 259.
13. D. K. Morgan, N. D. Danielson and J. E. Katon, *Anal. Lett.*, 1985, **18**, 1979.
14. S. V. Olesik, S. B. French and M. Novotny, *Anal. Chem.*, 1986, **58**, 2256.
15. B. E. Miller, N. D. Danielson and J. E. Katon, *Appl. Spectrosc.*, 1988, **42**, 401.
16. M. Guzman, J. Ruzicka and G. D. Christian, *Vib. Spectrosc.*, 1991, **2**, 1.
17. P. T. McKittrick, N. D. Danielson and J. E. Katon, *Microchem J.*, 1991, **44**, 105.
18. M. Gallignani, S. Garrigues, M. de la Guardia, J. L. Burguera and M. Burguera, paper presented at the XXVII CSI, Bergen, Norway, June 1991, paper B-PO-29.
19. M. de la Guardia, S. Garrigues, M. Gallignani, J. L. Burguera and M. Burguera, *Anal. Chim. Acta*, 1992, **261**, 53.
20. M. Gallignani, S. Garrigues, M. de la Guardia, J. L. Burguera and M. Burguera, paper presented at the WCFIA '92, January 1992, Scottsdale, U.S.A., paper P-12.
21. S. Garrigues, M. Gallignani and M. de la Guardia, *Talanta*, 1993, **40**, 89.
22. S. Garrigues, M. Gallignani and M. de la Guardia, *Analyst*, 1992, **117**, 1849.
23. M. Gallignani, S. Garrigues and M. de la Guardia, *Anal. Chim. Acta*, 1993, **274**, 267.
24. M. Gallignani, S. Garrigues, A. Martínez-Vado and M. de la Guardia, *Analyst*, 1993, **118**, 1043.
25. S. Garrigues, M. Gallignani and M. de la Guardia, *Talanta*, 1993, **40**, 1799.
26. M. de la Guardia, M. Gallignani and S. Garrigues, *Anal. Chim. Acta*, 1993, **282**, 543.
27. M. Gallignani, S. Garrigues and M. de la Guardia, paper presented at XXVIII CSI, York, U.K., June–July 1993, paper FP2.24.
28. S. Garrigues, M. T. Vidal, M. Gallignani and M. de la Guardia, *Analyst*, 1994 (in press).
29. F. Rández-Gil, J. A. Darós, A. Salvador and M. de la Guardia, *J. Pharm. and Biomed. Anal.*, 1991, **9**, 539.
30. M. Gallignani, S. Garrigues and M. de la Guardia, *Analyst*, 1993, **118**, 1167.
31. Annual Book of ASTM Standard, American Society for Testing and Materials, Philadelphia, 1987, D-3606-87.