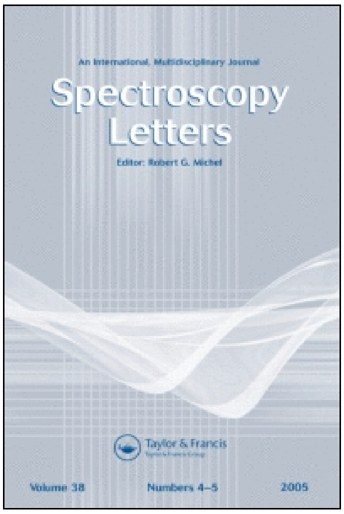

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Determination of Paint Solvents by Vapour Phase Fourier Transform Infrared Spectrometry.

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To cite this Article López-Anreus, Emilio , Garrigues, Salvador and de la Guardia, Miguel(1997) 'Determination of Paint Solvents by Vapour Phase Fourier Transform Infrared Spectrometry.', Spectroscopy Letters, 30: 8, 1629 — 1648

To link to this Article: DOI: 10.1080/00387019708006748

URL: http://dx.doi.org/10.1080/00387019708006748

SPECTROSCOPY LETTERS, 30(8), 1629-1648 (1997)

DETERMINATION OF PAINT SOLVENTS BY VAPOUR PHASE FOURIER TRANSFORM INFRARED SPECTROMETRY.

Keywords: Infrared Spectrometry, Flow Analysis, Paint Solvents, Vapour Phase, Methylisobutylketone, Toluene.

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ABSTRACT.

A fast procedure has been developed for the direct determination of paint solvents. The method is based on the injection of small volumes of untreated solvent mixtures into a heated Pyrex glass reactor in which the sample is volatilized and introduced by means of a flow of nitrogen into an IR multiple pass gas cell and the spectrum in the mid-IR region is registered as a function of time. Data found for samples are interpolated in calibration graphs obtained by injecting different volumes of pure compounds which constitute the solvent mixture. A methylisobutylketone (MIBK) toluene mixture was used as test system to develop the proposed procedure. The method provides a limit of detection of the order of 1-4 µg, a relative standard deviation of the order of 0.4 to 2% for five independent measurements, and recovery percentage values from 99.8 till 103.6 %. A commercial sample of polyurethane paint solvent has been analysed by the developed procedure.

1. INTRODUTION

Organic solvents are introduced in paint formulations to improve the solubility of binders (different types of resins and polymers) and to improve the fluidity of the final product in order to control the extent of paint coverage on a solid surface to obtain an homogeneous film. The most important properties of solvents employed in paint industry are: solvent power, rate of evaporation, boiling point, distillation range, flash point, inflammability and toxicity which must be carefully evaluated in order to select the appropriate solvent or solvent mixture for a specific paint (1-2). The most commonly used solvents in organic solvent based paints are carbonyl and aromatic compounds with a relatively high volatility. In this sense, MIBK and toluene are two typical solvents used in polyurethane paint manufacture (3).

The analysis of solvents employed in the paint industry is generally carried out by physical methods based on evaporation velocity and by gas chromatography, especially, with several compounds present in a paint formulation (2,4).

Infrared spectrometry is a well established analytical technique that provides interesting qualitative information about the composition of organic samples and chromatographic effluents (5-9) but it can also, as has been clearly established in recent years, be useful for accurate quantitative analysis, especially by using the flow analysis approach (10-11) which improves its application to the quality control of industrial products (12-14). The few applications of IR spectrometry for the analysis of paint solvents (15-16) are due to problems related to the solvent transparency in the infrared range, the appropriate selection of sample diluents, the determination of the cell thickness and the fast and reliable filling and cleaning of liquid cells (17).

Recently, our research group developed a new strategy for FTIR analysis which is based on vapour generation from small injected sample volumes. This technique has already been successfully applied for the determination of additives in pure organic solvents (18), alcohol determination in alcoholic beverages (19) and gasoline analysis (20). The vapour phase FTIR technique presents an excellent linearity of the analytical signal (Absorbance peak height, flow injection recording height or area) versus the volume injected in the system (18-19) and it reduces the matrix effect (20). On the other hand, the injection of discrete amounts of pure compounds or mixtures of compounds opens new possibilities for the development of analytical procedures in which the mass of an analyte, present in a sample, can be determined directly from the area of the FI recording obtained by monitoring the FTIR spectra within an appropriate wavenumber range.

In the present study the MIBK-toluene system, commonly employed in polyurethane paints, has been used as a test system to evaluate the applicability of vapour phase FTIR spectrometry for the quantitative analysis of paint solvents.

2. EXPERIMENTAL

2.1 Apparatus.

A Magna 750 Nicolet FTIR spectrometer (Madison, USA) equipped with a temperature stabilised DTGS detector, an Ever-Glo^{TM} source and a KBr beamsplitter was employed to carry out the spectral measurements at a nominal resolution of 8 cm^{-1} using a permanently aligned Wilmad ultramini long-path cell (Buena, USA) with a volume of 100 ml and an optical pathlength of 3.2 m, equipped with a ZnSe window. Omnic^{TM} software from Nicolet was used to control the instrument, for data acquisition and also for processing the analytical results using *Series* application. The apparatus employed for the vapour phase FTIR measurements (Figure 1) contained a volatilization reactor of total internal volume of 2.5 ml allowing a constant nitrogen flow to be swept through. The samples are injected through a septum using a Hamilton micro syringe of 0.5µl. The temperature inside the thermally insulated reactor was controlled by means of a thermocouple. Heating was done using a home made heater. The vapour generated by the reactor is passed through the IR gas cell and time dependent spectra are recorded.

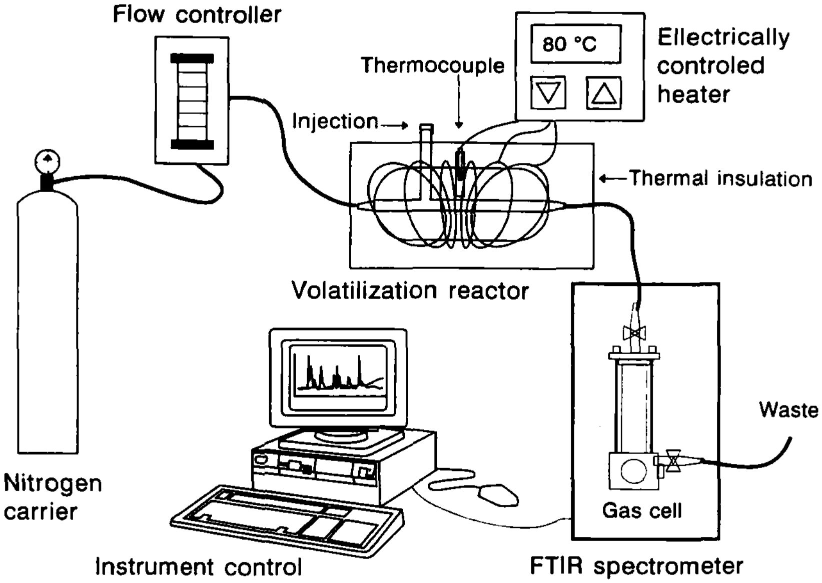

Figure 1. Apparatus employed for vapour phase FTIR analysis.

2.2 Reagents

Analytical reagent grade MIBK and toluene from Panreac (Barcelona, Spain) were employed for the experiments using N_2 C-45 (99,995% v/v) from Carburos Metálicos (Barcelona, Spain) as carrier gas.

2.3 General Procedure

A volume of 0.2 μl of untreated sample is injected into the reactor heated at 80°C using a nitrogen carrier flow of 350 ml min^{-1} The FTIR spectra between 2000 and 500 cm^{-1} are recorded as a function of time with a nominal resolution of 8 cm^{-1} and accumulating

2 interferograms for each spectrum. As background a spectrum obtained from 10 interferograms during the application of pure nitrogen at the same flow rate is used. The Gram-Schmidt trace, which is a representation of the radiation intensity arriving at the detector as a function of time, is obtained from the transient interferograms generated by injection of small volumes into the reactor. Each Gram-Schmidt data point corresponds to an FTIR spectrum from which an appropriate spectral range can be selected, corresponding to the specific absorption of MIBK and toluene. From these data chemigrams are obtained for either of the two compounds analysed. These chemigrams provide a flow injection (FI) recording of the absorbance in a selected wavenumber range as a function of time. The processing of the analytical signals is indicated in Figure 2.

For the chemigrams, the absorbance spectrum was integrated within the following intervals: for MIBK determination: i) between 1734 and 1730 cm^{-1} after baseline correction (reference points set at 1900 and 1650 cm^{-1}) or ii) between 1174 and 1170 cm^{-1} , after baseline correction established using data at 1650 and 875 cm^{-1}. For toluene determination, the selected wavenumber interval for chemigram construction was chosen from 731 to 727 cm^{-1} with a baseline fixed at 800 and 650 cm^{-1}. Data obtained for commercial samples were interpolated using two calibration curves prepared from injected standards of pure solvents with volumes ranging from 0.05 to 0.40 µl.

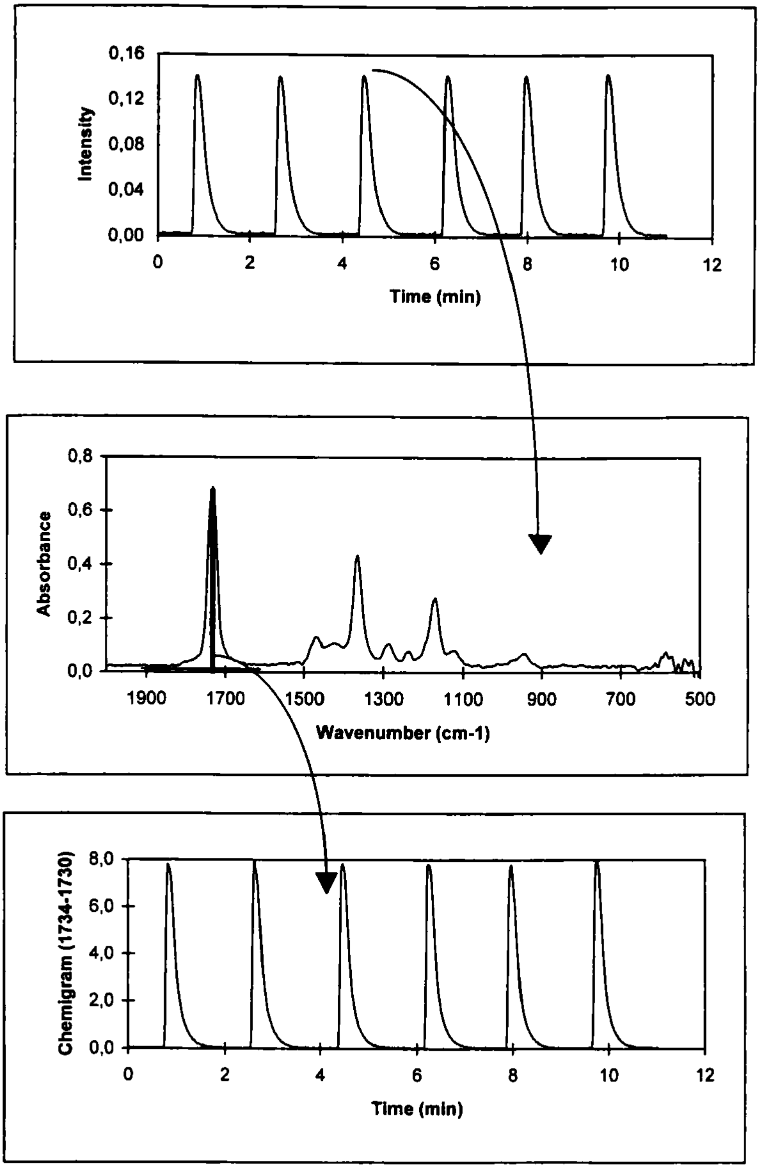

Figure 2. Processing of the analytical signals from the Gram-Schmidt recording of the whole injection to the analytical transient signal obtained by treating a reduced wavenumbers range of data. The recorded data corresponds to the injection of 0.2 μl of pure MIBK in a N_2 carrier flow of 400 ml min^{-1} and using a reactor temperature of 80°C. The spectrum corresponds to the maximum signal obtained and for processing the Chemigram, the area under the spectra for a wavenumbers range between 1734 and 1730 cm^{-1} was employed, using a base line established between 1900 and 1650 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1 FTIR Spectra Obtained in Vapour Phase.

Figure 3 shows the maximum absorbance vapour phase spectrum generated by injection of 0.2 μl of pure MIBK and pure toluene, respectively, with the carrier flow rate at 400 ml min^{-1} and the volatilizer temperature at 80 °C. As can be seen, toluene is a compound which has a few intense absorption bands in the mid infrared; an intense band at 729 cm^{-1} is characteristic of the monosubstituted benzene, which is not affected by the presence of MIBK, and further bands above 3000 cm^{-1} which correspond to the C-H stretching vibrations of the substituted benzene ring, are appropriate for quantitative analysis. On the other hand, MIBK possesses more absorption bands of analytical interest: three bands, at 1172 for the CH_3 symmetric bending, 1365 for the C-C skeletal stretching vibration in branched alkanes and 1739 cm^{-1} for the C=O stretching, offer opportunities to determine this compound in paint solvents.

The inset of figure 3 shows the maximum absorbance vapour phase spectrum between 2000 and 500 cm^{-1} obtained by injection of 0.2 μl of a commercial polyurethane paint solvent containing a 60:40 (w:w) mixture of MIBK and toluene. In this spectrum, MIBK and toluene bands can be clearly assigned as discussed above. The bands chosen in this study are the most intense and mutually unperturbed bands for each compound. The band of MIBK at 1365 cm^{-1} has not been considered because toluene shows some absorption in this

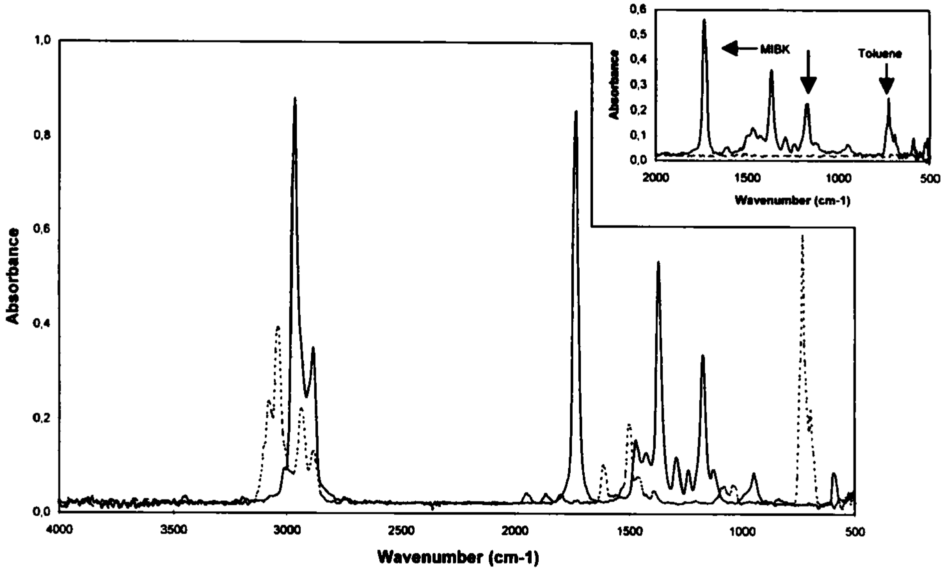

Figure 3. Vapour phase FTIR spectra of pure MIBK (—) and pure toluene (.....).
Inset: Wavenumber range from 2000 to 500 cm^{-1} for a commercial polyurethane paint solvent (—) and the nitrogen blank (.....).
Experimental conditions: T = 80 °C, Injection volume = 0.2 μl, Nitrogen flow = 350 ml min^{-1}, Resolution = 8 cm^{-1}.

region. To obtain the chemigrams of MIBK and toluene, the absorbance area under the spectra in the wavenumber interval around the maxima of the absorbance bands at 1739 cm^{-1} , 1172 cm^{-1} and 729 cm^{-1}, respectively, is calculated after appropriate baseline correction .

3.2 Effect of Experimental Parameters.

Reactor temperature, carrier gas flow rate and injection volume are the main experimental parameters which influence the size and shape of the peaks obtained for the analysis of MIBK and toluene using vapour phase FTIR spectrometry.

Although boiling temperature of MIBK and toluene are 119.0 °C and 110.6 °C respectively, reliable measurements can be obtained in the whole temperature range from 60 to 140 °C. Table 1 summarises data obtained for repetitive injections of 0.2 μl of pure MIBK and pure toluene and, as it can be see, the signals obtained using both, chemigram height or area, remain approximately constant in all the range assayed, showing that under these conditions it is possible to work below the boiling point of the compounds to be analysed. On the other hand, it has been observed that the temperature has no effect on the sampling frequency, and repeatability is also not affected by the temperature. From these studies a volatilization temperature of 80 °C has been chosen to carry out the analysis of polyurethane paint solvents.

The carrier gas flow is the most important parameter which affects sampling frequency. An increase of nitrogen carrier flow greatly decreases the sensitivity of the vapour phase FTIR determination of MIBK and toluene, as can be seen in Figure 4. Carrier flow rates lower or equal than 200 ml min^{-1} are most appropriate to obtain best results. However, the use of low carrier flow values leads to an increase of the volatilization time, thus reducing the sampling frequency. In the present study a flow rate of 350 ml min^{-1} has been chosen as a compromise between sensitivity and speed of the analysis providing a sample analysis frequency of one per minute.

TABLE 1.

Effect of the volatilization temperature on the analytical precision obtained for MIBK and toluene determination by vapour phase FTIR.

Temperature (°C)	Methyl iso-butyl ketone		Toluene	
	Height Chemigram *R.S.D (%)*	Area Chemigram *R.S.D (%)*	Height Chemigram *R.S.D (%)*	Area Chemigram *R.S.D (%)*
60	3.97 ± 0.02 *0.5*	2.69 ± 0.02 *0.7*	3.95 ± 0.06 *1.5*	2.96 ± 0.04 *1.4*
70	3.99 ± 0.05 *1.2*	2.60 ± 0.03 *1.1*	3.98 ± 0.04 *1.0*	2.94 ± 0.03 *1.0*
80	4.02 ± 0.03 *0.7*	2.70 ± 0.02 *0.7*	4.05 ± 0.07 *1.7*	2.93 ± 0.03 *1.0*
90	3.97 ± 0.02 *0.5*	2.66 ± 0.01 *0.4*	4.15 ± 0.03 *0.7*	3.04 ± 0.02 *0.7*
100	3.94 ± 0.02 *0.5*	2.63 ± 0.03 *1.1*	4.16 ± 0.03 *0.7*	3.06 ± 0.03 *1.0*
110	3.98 ± 0.02 *0.5*	2.70 ± 0.01 *0.4*	4.14 ± 0.01 *0.2*	3.06 ± 0.01 *0.3*
120	3.96 ± 0.02 *0.5*	2.68 ± 0.01 *0.4*	4.16 ± 0,02 *0.5*	3.01 ± 0.03 *1.0*
130	3.93 ± 0.02 *0.5*	2.65 ± 0.02 *0.8*	4.21 ± 0.03 *0.7*	3.05 ± 0.02 *0.7*
140	3.94 ± 0.03 *0.8*	2.62 ± 0.04 *1.5*	4.16 ± 0.02 *0.5*	2.96 ± 0.02 *0.7*

Chemigram area and height values were obtained for MIBK between 1734 and1730 cm^{-1} for a baseline set at 1900 and 650 cm^{-1}and for toluene between 731 and 727 cm-1, the base line set at 800and 650 cm-1. Values are mean of five independent injections ± standard deviation.R.S.D = relative standard deviation.

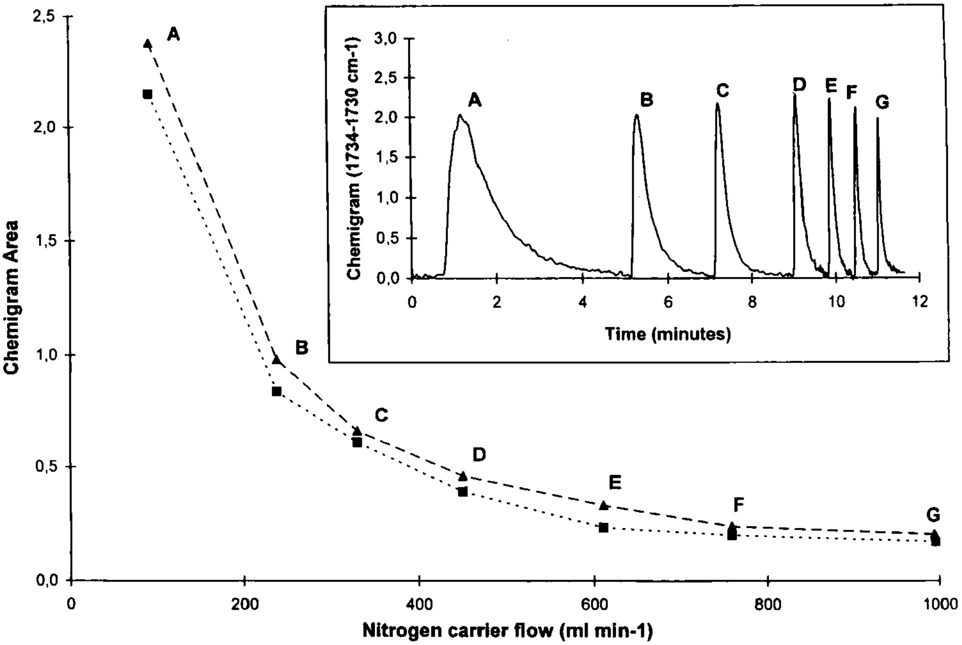

Figure 4. Effect of the nitrogen carrier flow rate on the Chemigram area values of a synthetic sample containing MIBK and Toluene at a composition of 60:40 (w:w). (-----) MIBK, (.....) Toluene. Data evaluation, see text.
Inset: Chemigrams obtained for MIBK, carrier flow rate (in ml min^{-1}) A: 93, B: 237, C: 329, D: 451, E: 611, F: 759, G: 996 .
Experimental conditions : T = 80 °C, Injection volume = 0.2 μl, Resolution = 8 cm^{-1}.

In previous studies on vapour phase FTIR spectrometry (18-19) we have demonstrated that it is possible to find good linearity between analytical signals (chemigram height or area) and injection volume. This fact can be used for improving the analytical sensitivity by increasing the sample volume injected but it also offers interesting possibilities to use an alternative standardisation strategy in vapour phase procedures by means of the injection of different volumes of a single standard or pure compound. Figure 5 shows the FI recordings obtained by injecting different volumes of pure toluene and the calibration curve which can be constructed from the corresponding chemigram areas. As can be seen, good linearity is obtained up to 0.26 mg for toluene with a correlation coefficient of 0.9998.

The possibility to standardise the vapour phase FTIR measurements by means of pure compound injections provides a method to evaluate the amount of toluene or MIBK in a sample independently of the presence of other compounds if the selected bands remain unperturbed.

3.3 Analytical features of vapour generation-FTIR spectrometry for MIBK and toluene determination in paint solvents.

Table 2 summarises the main analytical features of the methodology developed for the determination of MIBK and toluene in paint solvents. In this table calibration curves were obtained by injecting different volumes of pure MIBK and pure toluene. Regarding analytical performance, the best values were obtained using chemigram heights.

The repeatability, established from five injections of 0.2 µl of pure compounds, provides in all cases relative standard deviation values lower than 2 %. The limit of detection, which was established from the repeatability of 10 measurements of the nitrogen blank and for a confidence level of 99.6 % (k=3) is of the order of few

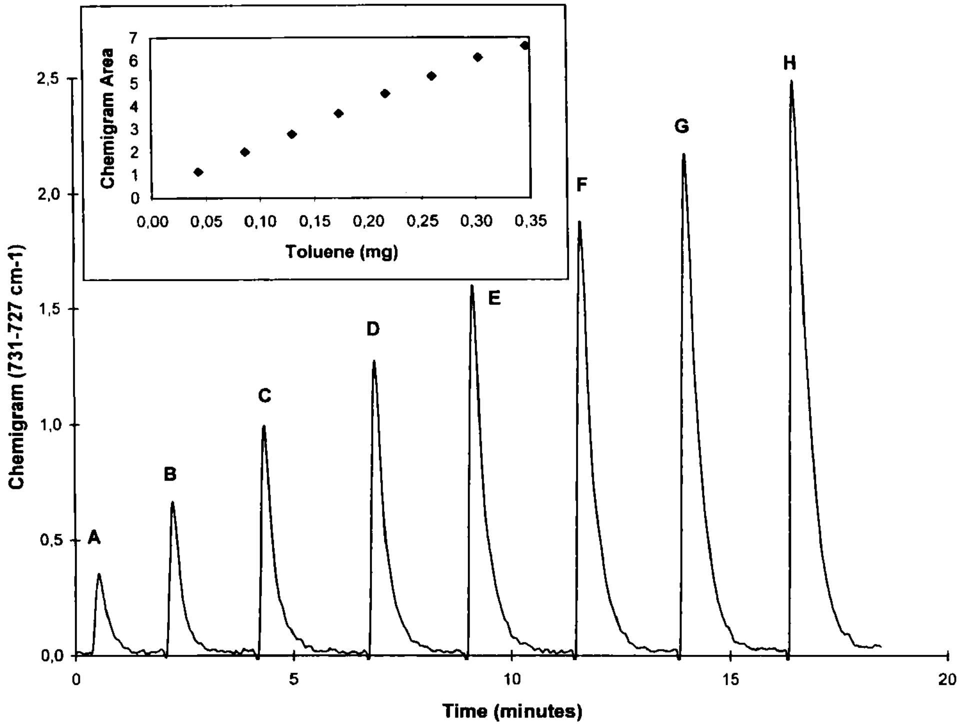

Figure 5. Effect of the injection volume on the chemigram maximum values of toluene.

Injected volume of pure toluene (in μl) A: 0.05, B: 0.10, C: 0.15, D: 0.20, E: 0.25, F: 0.30, G: 0.35, H: 0.40.

Inset: Calibration curve obtained by measuring chemigram area values for each injected mass. Calibration data presented are the mean of five independent measurements.

Experimental conditions: T = 80 °C, Nitrogen flow = 350 ml min^{-1}, Resolution = 8 cm^{-1}.

TABLE 2.

Analytical features of the vapour generation-FTIR determination of MIBK and toluene in paint solvents.

Analyte	Measurement criterion	Calibration Equation	r	Dynamic range (µl)	LOD µg(µl)	R.S.D (%)
MIBK^1	Chemigram Height	H = 0.183 + 15.702 V	0.9998	0.05-0.40	1.6 (0.002)	0.7
	Chemigram Area	A = -0.005 + 4.151 V	0.9989	0.05-0.20	1.6 (0.002)	2.0
MIBK^2	Chemigram Height	H = 0.043 + 6.158 V	0.9997	0.05-0.40	1 (0.001)	1.2
	Chemigram Area	A = 0.008 + 1.803 V	0.9997	0.05-0.30	4 (0.005)	0.4
Toluene	Chemigram Height	H = 0.330 + 16.664 V	0.9998	0.05-0.35	3 (0.004)	0.7
	Chemigram Area	A = 0.013 + 4.783 V	0.9998	0.05-0.30	3 (0.004)	0.5

Chemigrams were obtained for area values between 1734 and 1730 cm^{-1} (base line: 1900-650 cm^{-1}) for MIBK^1, between 1174 and 1170 cm^{-1} (base line: 1650-875 cm^{-1}) for MIBK^2 and between 731 and 727 cm^{-1} (base line: 800-650 cm^{-1}) for toluene. **H**, Chemigram height; **A**, Chemigram area; **V** injection volume in µl; **r**, correlation coefficient; **LOD**, limit of detection (k=3) for a probability level of 99.6% expressend in µg (in brackets it is indicated the corresponding volume of solvent in µl which corresponds to the LOD); **R.S.D**, Relative standard deviation calculated from five independent measurements.

micrograms of each compound, thus being appropriate for such purpose of solvent determination.

The aforementioned analytical features give evidence that the developed vapour phase FTIR procedure is suitable for the quality control of paint solvents avoiding sample handling and time consuming separation procedures. Additionally, the use of small amounts of samples to perform the analysis reduces the risks of operator poisoning and environmental pollution.

3.4 Analysis of a real paint solvent sample.

A commercial polyurethane paint solvent sample, containing MIBK and toluene with a manufactured composition of 60:40 (w:w) was analysed using different criteria. Results based on chemigram height and area from using different bands are summarised in table 3; the methodology provides in all cases accurate results.

To test the accuracy of the methodology developed for MIBK and toluene determination, a real sample of polyurethane paint solvent containing both components was spiked with the two compounds under study at different levels, and these samples were analysed using chemigram peak height values. Table 4 shows the data obtained. The deviations from the expected values for toluene and MIBK are given as relative values.

4. CONCLUSIONS.

The vapour phase FTIR procedure developed in this study provides a method for the determination of MIBK and toluene in polyurethane paint solvents. Calibration curves, obtained by injecting different volumes of the pure compounds to be analysed provide the

TABLE 3.

MIBK and toluene determination in a real polyurethane paint solvent sample containing 60% w/w MIBK and 40% w/w toluene.

ANALYTE (% w/w)	MEASUREMENT CRITERION	
	Chemigram Height	Chemigram Area
MIBK[1] Toluene	58.9 ± 0.4 41.1 ± 0.5	58.9 ± 0.4 41.1 ± 0.5
MIBK[2] Toluene	59.0 ± 0.5 41.0 ± 0.6	58.0 ± 0.6 42.0 ± 0.6

Chemigrams were obtained for a wavenumbers range between 1734 and1730 cm^{-1} (base line: 1900-650 cm^{-1}) for MIBK[1], between 1174 and 1170 cm^{-1} (base line: 1650-875cm^{-1}) for MIBK[2] and between 731 and 727 cm^{-1} (base line: 800-650 cm^{-1}) for toluene. Values are mean ± standard deviation of five independent measurements.

TABLE 4.

MIBK and Toluene recovery values found for spiked paint solvent samples.

Analyte	Present (% w/w)	Added (% w/w)	Found (% w/w)	Recovery (%)
MIBK	60	2.10	62.7	101.0
	60	4.98	67.3	103.6
	60	8.75	68.6	99.8
Toluene	40	2.25	42.8	101.3
	40	3.91	44.9	102.3
	40	6.15	46.2	100.1

Results were obtained from Chemigram height values measured for MIBK between 1734 and 1730 cm^{-1} for a base line between 1900 and 1650 cm^{-1}, and for toluene between 731 and 727 cm^{-1}, the base line being 800-650 cm^{-1}.

basis for the accurate evaluation of the mass of either compounds considered in a same sample, based on the use of specific bands. It does not need any sample preparation thus providing a fast and easy method for the quality control of paint products with regard to solvent composition. The use of small volumes of samples in the order of a microliter reduces waste and make FTIR measurements more environmentally friendly.

ACKNOWLEDGEMENTS.

The authors acknowledge the financial support of the Conselleria d'Educació i Ciència de la Generalitat Valenciana project GV 3218/95.

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Date Received: May 16, 1997
Date Accepted: June 18, 1997