# VAPOUR GENERATION-FTIR DETERMINATION OF BUTYLGLYCOL IN WATER-BORNE PAINT SOLVENTS.

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## ABSTRACT

A simple and fast procedure is proposed for the direct determination by Fourier transform infrared spectrometry of butylglycol in water-borne paint solvents. The method is based on the injection of 2 μl of untreated paint solvent into an electrically heated Pyrex glass reactor in which the sample is volatilized at 150 °C. The vapour phase generated is transported by means of a nitrogen carrier flow of 400 ml min$^{-1}$ into an IR multiple pass gas cell and the spectrum in the mid infrared is recorded between 2500 and 600 cm$^{-1}$ as a function of time. Data found for samples are interpolated in two calibration curves obtained by injecting different volumes of pure butylglycol and pure water. The measurement of the area of the flow injection recording obtained from the absorbance of the transient signals in the range 1137-1131 or 1071-1065 for butylglycol and 1660-1640 cm$^{-1}$ for water allows the direct determination of these two compounds in a same sample. The method provides relative standard deviation values around 1%, a limit of detection of the order of 2.7-4.5 μg, recovery percentage values from 96 to 104 % and a sampling frequency of 65 h$^{-1}$. A commercial water-borne paint solvent containing butylglycol and water was analysed obtaining comparable values with the declared ones and with those obtained by a reference method based on ATR-FTIR measurements.

KEYWORDS: Infrared Spectrometry, Flow Analysis, Paints, Butylglycol and Water determination, Vapour phase.

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# 1. INTRODUCTION

Fourier transform infrared (FTIR) spectroscopy has been traditionally used to obtain qualitative information of organic samples (1-3) but in the last years it has been demonstrated that FTIR spectroscopy is also an excellent tool to obtain accurate quantitative results (4-6). However, some problems remain in the general applicability of FTIR spectroscopy for quantitative analysis due to solvent and window material transparency (7).

For the analysis of aqueous samples by FTIR it is necessary the use of adequate transmittance or reflectance cells with water resistant windows. The use of transmittance measurements requires very small pathlengths of the order of 25 μm due to the strong water absorption and the use of attenuated total reflectance (ATR) cells involves a poor sensitivity. Vapour or gaseous state is very useful for carrying out determinations by FTIR due to the high transparency of gases, the low background obtained for this kind of systems and the possibility of the use of multiple pass gas cells which can provide good sensitivity (8-9). For these reasons, FTIR spectrometry has been extensively used for detection in gas chromatography (10-12) and also in combination with sample pyrolisis (13-15). The only drawback is the fact that gaseous state is not so frequent in real samples to be analysed.

In the last few years, our research group has developed a new strategy for FTIR analysis based on the vapour generation from small injected volumes of liquid samples. This technique was firstly applied to the quality control of solvent additives (16) and gasoline components (17) and recently to the determination of alcohol in aqueous samples like alcoholic beverages (18) and blood (19).

Vapour generation FTIR technique presents an excellent linearity between the analytical signal and the sample volume injected in the system (16,18) and, because of that, the injection of discrete amounts of pure compounds opens exciting possibilities for the development of new analytical procedures in which the mass of an analyte, present in a sample, can be directly determined from the height or area of flow injection (FI) recording obtained by monitoring the FTIR spectra at an appropriate wavenumber range.

The aim of this work is to develop a simple method for the FTIR determination of solvents in water-borne paints by means of the injection of discrete volumes of samples and pure compounds into a volatilisation reactor. So, a new procedure has been developed for the

direct determination of butylglycol and water in water-borne paint solvents based on the use of vapour generation FTIR spectrometry.

Solvents are necessary in paint formulations in order to improve the solubility of resins and polymers and to improve the fluidity of the final product. Organic solvents have been employed traditionally in paint manufacture, the carbonyl and aromatic compounds being the most commonly employed. However, the use of water as a paint solvent has always been attractive for reasons of low cost and absence of toxicity risks (20). Water-borne paints need a minimum application temperature of 5 °C to made an adequate film formation and because of that, atmospheric conditions can delay its drying time. For this reason these paints need the addition of a co-solvent at low concentrations, the butylglycol being one of the most commonly employed (21).

The analysis of solvents employed in paint industry is usually carried out by gas chromatography (22-23). However, the chromatographic procedures are slow and time consuming and they are not very appropriate for the direct analysis of aqueous samples.

## 2. EXPERIMENTAL

### 2.1 Apparatus and reagents.

A Magna 750 Nicolet FTIR spectrometer (Madison, USA), equipped with a temperature stabilized DTGS detector, a long-lasting 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 Wilmad ultramini long-path cell (Buena, USA) with a volume of 100 ml and a permanently aligned multiple pass of 3.2 m equipped with a ZnSe window. The OMNIC[TM] software was employed to control the instrument, for data acquisition and also for processing the analytical data by means of the *Series* application.

The manifold employed for vapour generation FTIR measurements is the same as previously reported (16). It is a single-channel assembly with a nitrogen carrier flow that includes a volatilization reactor of 2.5 ml internal volume with gas inlet and outlet. Samples were injected inside the reactor through a septum using Hamilton gas-tight syringes (Reno,

NY, USA) of 0.5 and 5 µl. The temperature inside the reactor, which includes a thermic insulating coating, was controlled by means of a thermocouple and operated using a home made electrically controlled heater. The reactor was connected with the IR gas cell using Viton (Isoversinic) tubes of 4 mm i.d. The vapour generated inside the reactor was passed through the IR gas cell in which the spectra of the transient signals were obtained as a function of time.

Additionally, in order to obtain reference data for samples, a Specac-Graseby ATR cell model Specaclamb (Orlando, FL, USA) with ZnSe window and a Mattson (Madison, USA) Research 1 spectrometer were employed to carry out ATR-FTIR measurements.

Analytical reagent grade butylglycol from Panreac (Barcelona, Spain) was employed as standard and nitrogen C-45 (99.995 % v/v) from Carburos Metálicos (Barcelona, Spain) was used as carrier gas for FTIR measurements

## 2.2 General procedure

### 2.2.1 Vapour generation FTIR determination of butylglycol and water.

Two µl aliquots of untreated sample were injected into the reactor, previously heated to 150 °C, and the vapour phase generated transported into the gas cell using a carrier nitrogen flow of 400 ml min$^{-1}$. The FTIR spectra between 2500 and 600 cm$^{-1}$ were recorded as a function of time using a nominal resolution of 8 cm$^{-1}$ and accumulating 2 interferograms for each spectrum. The spectrum obtained from 10 interferograms of a pure nitrogen flow was used as background. The Gram-Schmidt plot, which is a representation of the infrared radiation arriving at the detector as a function of time, was obtained for the transient signals generated after the injection of samples. Each Gram-Schmidt point corresponds to a FTIR spectrum in which appropriate spectral ranges for the absorption of butylglycol and water can be selected. With the absorbance data found in the wavenumber ranges 1071-1065 and 1137-1131 cm$^{-1}$ for butylglycol and 1660-1640 cm$^{-1}$ for water, Chemigrams corresponding to butylglycol and water signals can be constructed. Chemigrams provide flow injection (FI) recordings which correspond to the absorbance of butylglycol and water in the selected wavenumber ranges. The area of these FI recordings was employed as the quantitative analytical variable, taking into consideration baseline corrections established between 1190

and 1005 cm$^{-1}$ for butylglycol and between 1730 and 1590 cm$^{-1}$ for water. Data obtained for commercial samples were interpolated using two external calibration curves prepared from injected volumes of pure solvents ranging from 0.05 to 0.40 µl for butylglycol and from 0.5 to 5 µl for water.

### 2.2.2 FTIR determination of butylglycol using ATR measurements.

An alternative FTIR procedure was used for the determination of butylglycol in paint solvents using ATR measurements. Samples were placed in the ATR cell plate and the spectrum between 2000 and 600 cm$^{-1}$ was recorded using a nominal resolution of 4 cm$^{-1}$ and accumulating 100 scans for each spectrum. Butylglycol was determined by measuring the absorbance peak height values at 1112 cm$^{-1}$ with a baseline correction established between 1323 and 954 cm$^{-1}$. Solutions of butylglycol in water were used as standards and measured in the same conditions than samples.

## 3. RESULTS AND DISCUSSION.

### 3.1 FTIR spectra obtained in vapour phase.

Figure 1.a depicts the maximum intensity FTIR spectrum generated in the vapour phase by injection of 0.4 µl of pure water and pure butylglycol, the nitrogen carrier flow rate being 406 ml min$^{-1}$ and the volatilizer temperature 100 °C. As it can be seen butylglycol is a compound which presents intense absorption bands in the mid infrared at 1068, 1134 and in the region between 2800 and 3000 cm$^{-1}$. These bands are unaffected by the presence of water, thus offering interesting possibilities to carry out its determination in water-borne paint solvents. On the other hand, water has a more complex spectrum in which the regions between 3500 and 4000 cm$^{-1}$ and between 1300 and 2000 cm$^{-1}$ present the main absorption.
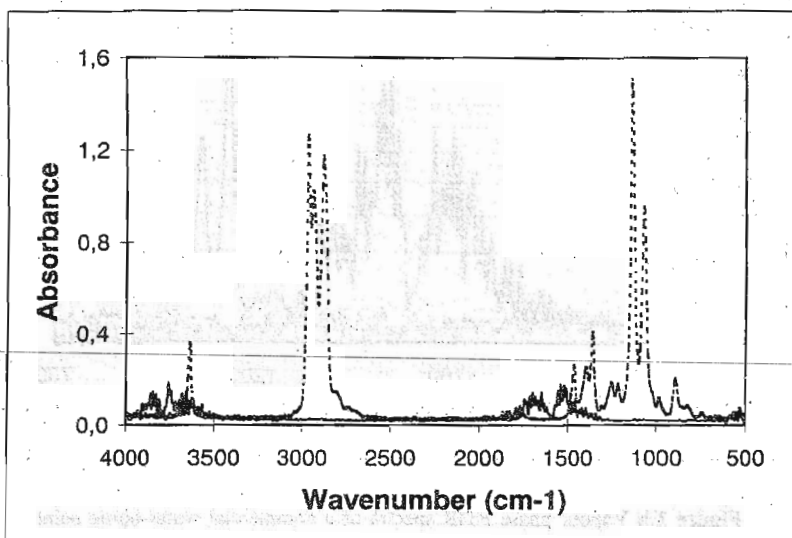
**Figure 1.a** Vapour phase FTIR spectra of pure butylglycol (......) and pure water (———). For experimental conditions: see the text.

Figure 1.b shows the maximum absorbance vapour phase spectrum between 2200 and 700 cm$^{-1}$ obtained by injection of 0.4 μl of a commercial paint solvent containing butylglycol and water in a composition of 5.9 : 94.1 (w : w). In this spectrum butylglycol bands can be clearly assigned as discussed above and, because of that, through this study, Chemigrams of butylglycol were obtained from the absorbance area under the spectra in the wavenumber range around the maxima of 1068 and 1134 cm$^{-1}$ using a baseline correction established between 1190 and 1005 cm$^{-1}$. For water determination, the infrared region between 1660 and 1640 cm$^{-1}$ with a baseline established between 1730 and 1590 cm$^{-1}$ was employed having not observed interferences from butylglycol.
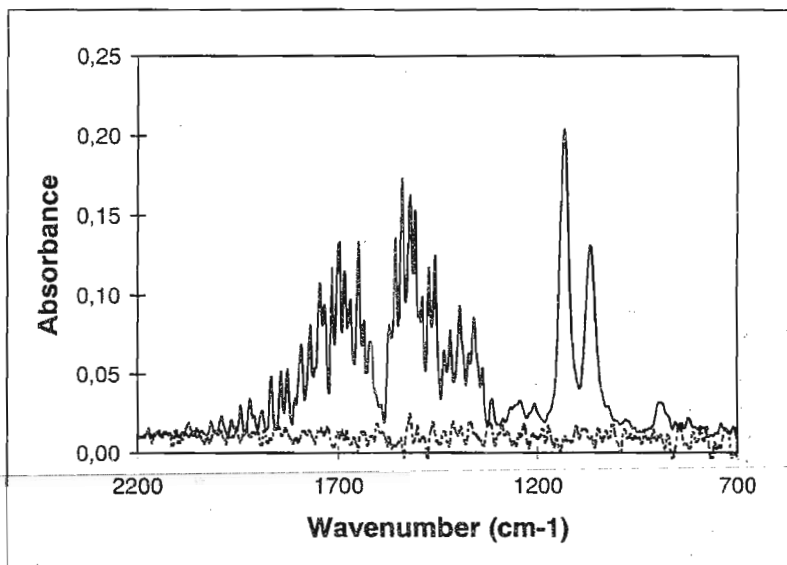
**Figure 1.b** Vapour phase FTIR spectra of a commercial water-borne paint solvent (———) and the nitrogen blank (......). For experimental conditions: see the text.

## 3.2 Effect of experimental parameters.

Reactor temperature is a new parameter introduced by vapour generation FTIR technique. The appropriate selection of volatilisation temperature provides the best sensitivity owing to the complete volatilisation of the analyte in the shortest time and it clearly influences the sampling frequency of the methodology developed. Figure 2.a depicts the effect of the volatilisation temperature on the butylglycol and water Chemigram peak area measurements obtained from the injection of 0.4 µl of pure compounds. This figure shows that temperature is not an important parameter for water determination because sensitive measurements can be obtained in the whole temperature range assayed from 70 to 210 °C. However, this parameter has a critical effect on the determination of butylglycol which has a volatilisation temperature of 171.5 °C. Figure 2.b shows the effect of temperature on the peak area measurements of butylglycol and water in a real paint solvent sample containing both components in a 5.9 : 94.1 (w : w) proportion, the injection volume being 1.0 µl. We can observe practically the same thermal behaviour noticed for pure compounds. So, for butylglycol determination it is necessary to work up to a critical temperature in order to obtain an adequate sensitivity of the

analytical measurements and, because of that, a temperature of 150 °C was selected to achieve the total volatilisation of both components in the same sample.
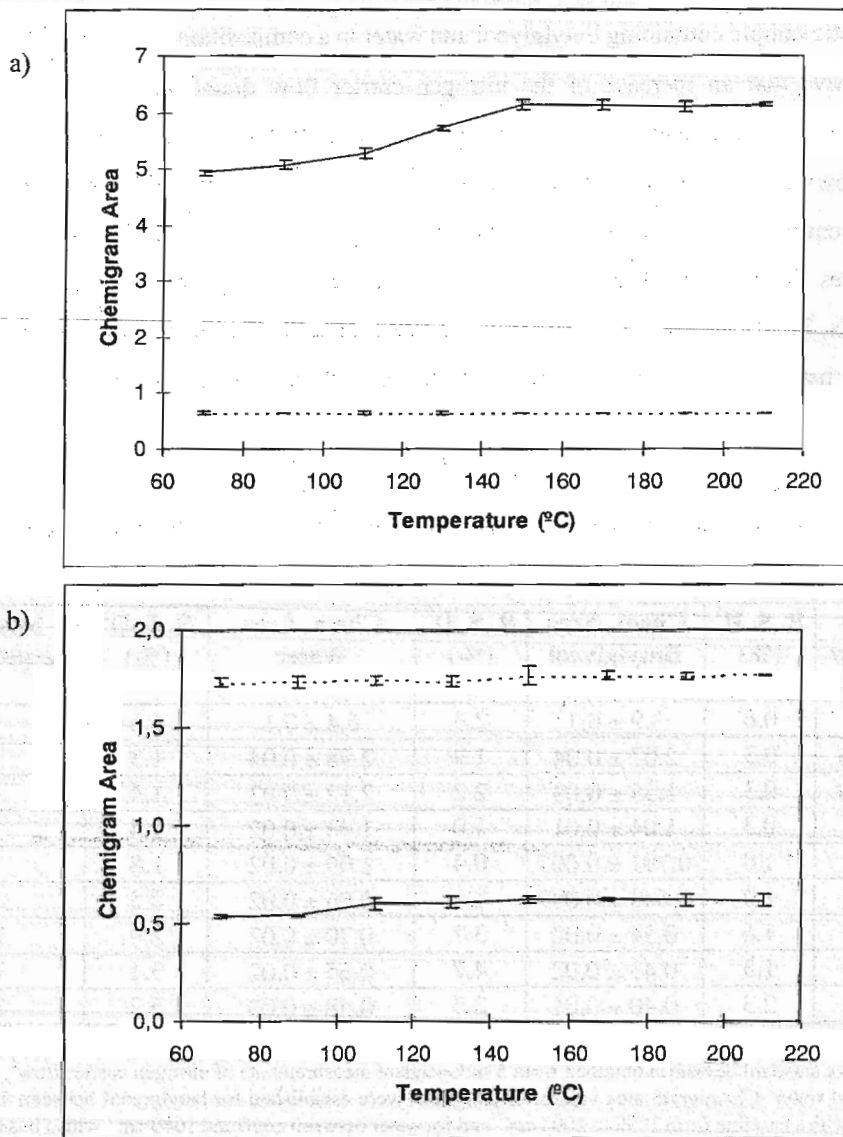


**Figure 2.** Effect of the volatilisation temperature on Chemigram area measurements. a) (———) pure butylglycol, (......) pure water. Experimental conditions: Injection volume = 0.4 μl, $N_2$ flow rate = 230 ml min$^{-1}$. b) Water-borne paint solvent containing butylglycol (———) and water (......). Experimental conditions: Injection volume = 1μl, $N_2$ flow rate = 230 ml min$^{-1}$. Standard deviations values are the mean of 5 independent measurements.

The carrier gas flow rate is a parameter which clearly influences the speed of sample introduction into the measurement cell, thus determining the sampling frequency of the methodology developed. Table 1 shows the peak area values obtained from the injection of 2 µl of a synthetic sample containing butylglycol and water in a composition of 6.0 : 94.0 (w :w). We can observe that an increase of the nitrogen carrier flow dramatically decreases the sensitivity of the vapour generation FTIR measurements for both components. However, the use of very low carrier gas flows involves an increase of the volatilisation time thus reducing the sample frequency. Regarding precision, the use of carrier flows between 200 and 500 ml min$^{-1}$ provides the best analytical precision for both, carrier flow and Chemigram area measurements. Therefore a nitrogen carrier flow rate around 400 ml min$^{-1}$ was chosen as a compromise between sensitivity, speed of analysis and precision, obtaining a sample frequency of 65 h$^{-1}$.

**Table 1.** Effect of the nitrogen carrier flow rate on the analytical sensitivity and sampling frequency

| Nitrogen carrier flow (ml min$^{-1}$) | R. S. D[1] (%) | Chem. Area Butylglycol | R. S. D[2] (%) | Chem. Area Water | R. S. D[3] (%) | Sampling frequency (h$^{-1}$) |
|---|---|---|---|---|---|---|
| 87.0 ± 0.5 | 0.6 | 3.9 ± 0.1 | 2.6 | 6.4 ± 0.1 | 1.6 | 14 |
| 194.5 ± 0.5 | 0.3 | 2.07 ± 0.04 | 1.9 | 2.98 ± 0.04 | 1.3 | 29 |
| 290.7 ± 0.9 | 0.3 | 1,35 ± 0.03 | 2.2 | 2.12 ± 0.03 | 1.4 | 40 |
| 388 ± 1 | 0.3 | 1.04 ± 0,01 | 1.0 | 1.43 ± 0.02 | 1.4 | 57 |
| 535 ± 5 | 1.0 | 0.791 ± 0.003 | 0.4 | 1.09 ± 0.02 | 1.8 | 75 |
| 675 ± 7 | 1.0 | 0.643 ± 0.009 | 1.4 | 0.86 ± 0.02 | 2.3 | 92 |
| 813 ± 13 | 1.6 | 0.54 ± 0.02 | 3.7 | 0.70 ± 0.02 | 2.9 | 109 |
| 936 ± 12 | 1,3 | 0.43 ± 0.02 | 4.7 | 0.65 ± 0.02 | 3.1 | 130 |
| 1091 ± 25 | 2.3 | 0.40 ± 0.01 | 2.5 | 0.58 ± 0.03 | 5.2 | 150 |

R.S.D = Relative standard deviation obtained from 5 independent measurements of nitrogen carrier flow[1], and butylglycol[2] and water[3] Chemigram area values. Chemigrams were established for butylglycol between 1137 and 1131 cm$^{-1}$ with a baseline from 1190 to 1005 cm$^{-1}$ and for water between 1660 and 1640 cm$^{-1}$ with a baseline from 1728 to 1590 cm$^{-1}$.

In previous studies about vapour phase FTIR spectrometry (16-18) we demonstrated that it is possible to find an excellent linearity between analytical signal 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 a new standardisation strategy in vapour phase procedures by means of the injection of different volumes of a single standard or a pure compound. In this sense, Fig. 3 shows the FI recordings obtained by injecting different volumes of pure butylglycol and the calibration curve which can be constructed by measuring the corresponding Chemigram area values. As it can be seen good linearity was obtained up to 0.36 mg for butylglycol with a correlation coefficient of 0.9999. The possibility to standardize vapour phase FTIR measurements by using pure compound injections provides a simple and fast method to evaluate the amount of butylglycol present in a water-borne paint solvent independently of the presence of other compounds if the selected bands remain unperturbed.
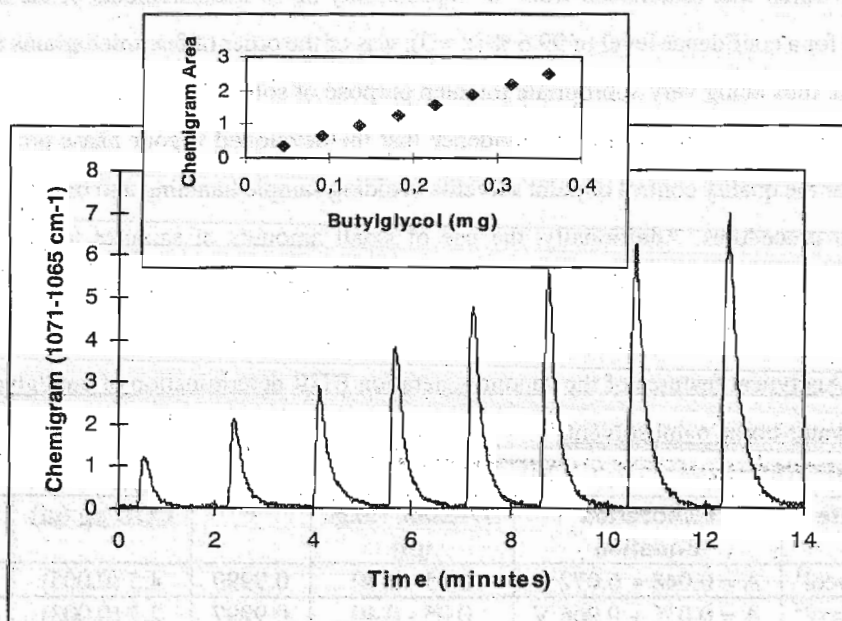


**Figure 3.** Effect of the injection volume on the Chemigram maximum values of butylglycol. Injected volume of pure butylglycol (in µl): 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40. Inset: Calibration curve obtained by measuring Chemigram area values for each injected mass. Calibration data presented are the mean of 5 independent measurements. Experimental conditions: T = 150°C, $N_2$ flow rate = 398 ml min$^{-1}$.

## 3.3 Analytical features of the vapour generation FTIR procedure for water-borne paint solvent determination.

Table 2 shows the main analytical features of the methodology developed for the direct determination of butylglycol and water using vapour generation FTIR measurements. In this table calibration curves were obtained by injecting different volumes of pure butylglycol and pure water using Hamilton micro syringes of 0.5 and 5 µl respectively. Regarding correlation coefficient values it is possible to conclude that the proposed standardization procedure works correctly. The repeatability, established from five injections of 0.2 µl of butylglycol and 2 µl of water, provides in all cases relative standard deviation values lower than 1 %. 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), was of the order of few micrograms for each compound, thus being very appropriate for such purpose of solvent analysis.

These analytical features give evidence that the developed vapour phase 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.

**Table 2.** <u>Analytical features of the vapour generation FTIR determination of butylglycol and water in water-borne paint solvents</u>

| Analyte | Calibration Equation | Dynamic range (µl) | r | LOD µg (µl) | R. S. D (%) |
|---------|----------------------|--------------------|----|-------------|-------------|
| Butylglycol[1] | A = 0.048 + 6.072 V | 0.05 - 0.40 | 0.9999 | 4.5 (0.005) | 0.9 |
| Butylglycol[2] | A = 0.055 + 9.906 V | 0.05 - 0.40 | 0.9997 | 2.7 (0.003) | 1.0 |
| Water | A = 0.073 + 0.627 V | 0.5- 4.0 | 0.9994 | 24 (0.024) | 0.7 |

Chemigram area values were obtained: for butylglicol[1] between 1071 and 1065 $cm^{-1}$ (baseline: 1190-1005 $cm^{-1}$); for butylglicol[2] between 1137 and 1131 $cm^{-1}$ with the same baseline correction; for water between 1660 and 1640 $cm^{-1}$ (baseline: 1728-1590 $cm^{-1}$).**A**: Chemigram area; **V**: injection volume of pure compounds.

## 3.4 Analysis of real samples.

A commercial water-borne paint solvent containing butylglycol and water in a manufactured composition of 5.9 : 94.1 (w : w) was analysed using the methodology described through this study. Results found are summarised in Table 3 also including values found by ATR-FTIR spectrometry which has been employed as reference method. It can be seen that comparable results for the proposed procedure and reference method were obtained.

Comparing both strategies, vapour phase generation and ATR-FTIR measurements, it is clear that the productivity of the vapour generation technique is higher than that of ATR providing a more sensitive analytical method and a very high sampling frequency.

**Table 3.** Analysis of a commercial water-borne paint solvent sample.

| Compound | Vapour phase-FTIR[1] (% w : w) | Vapour phase-FTIR[2] (% w : w) | ATR-FTIR (% w : w) |
|---|---|---|---|
| Butylglycol | 5.76 ± 0.05 | 5.83 ± 0.07 | 5.91 ± 0.02 |
| Water | 94.30 ± 0.06 | 94.17 ± 0.07 | ----------- |

Values indicated are the mean of 5 independent measurements ± the corresponding standard deviation. Chemigram area values were obtained in vapour phase technique: [1] for butylglycol between 1071 and 1065 $cm^{-1}$ (baseline: 1190-1005 $cm^{-1}$); [2] for butylglycol between 1137 and 1131 $cm^{-1}$ with the same baseline correction.

In order to test the applicability of the vapour phase technique, the recovery percentage of butylglycol spiked in a real sample at four different concentration levels was studied. Table 4 shows data obtained for recovery studies indicating that butylglycol is quantitatively recovered from spiked samples thus providing exciting possibilities for the direct analysis of this compound in paint solvents.

**Table 4.** Recovery studies on the butylglycol determination by vapour phase FTIR on spiked paint solvent samples.

| Added (% w : w) | Found (% w : w) | Recovery (%) |
|---|---|---|
| 4.32 | 4.24 | 98 |
| 8.20 | 8.5 | 104 |
| 12.70 | 13.1 | 103 |
| 15.85 | 15.2 | 96 |

Results were obtained from Chemigram area values measured between 1071 and 1065 cm$^{-1}$, baseline correction established between 1190 and 1005 cm$^{-1}$.

## 4. CONCLUSIONS.

The vapour phase FTIR procedure proposed in this study provides a fast and very simple analytical method for the direct determination of butylglycol in water-borne paint solvents. The use of calibration curves obtained by injecting different volumes of the sample components provides an evaluation of the mass of each compound present in the same sample when bands employed remain unperturbed. This method does not need any sample preparation step, avoiding the use of tedious separation procedures and providing an easy way for the quality control of paints with regard to solvent composition. On the other hand, the use of sample volumes of the order of microliter reduces analytical wastes.

## ACKNOWLEDGEMENTS

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