

Extractive sampling methods to improve the sensitivity of FTIR spectroscopy in analysis of aqueous liquids

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Abstract. Several methods of extractive sampling based on solvent elimination have been used to determine the concentration of different substances such as a sugar and a volatile organochloride in aqueous solutions. A dry extract technique based on the use of thin microporous polyethylene films as sample support has been evaluated in comparison with the direct transmission measurement through the liquid samples. Afterwards the Attenuated Total Reflection (ATR) on ZnSe and Ge crystals with a polymer coating has also been tested. The highest signal-to-noise ratio was obtained with the dry extract technique for the determination of a non volatile sugar. On the other hand, the best signal, lowering the detection limits to the low ppm concentrations, was obtained with the liquid extractive sampling (LES) method using a polymer coating on an ATR crystal for the determination of organochlorides.

Key words. FTIR, IR, organochlorine compounds, organochlorides, ATR, coated ATR technique, aqueous solutions.

Introduction

Water is the most ubiquitous material in a lot of liquid and solid products. It is also a very strongly absorbing and temperature dependent material in both the near and mid infrared (IR) spectral regions. As such, water creates immense background problems for many infrared applications: hydrogen bonding alters the frequencies of stretching and bending vibrations, and bands move generally to lower frequencies (longer wavelengths) usually with increased intensity and larger widening. Thus water increases the background noise (standard deviation), reduces the accuracy, raises the detection limit significantly, and linearity according to Beer-Lambert law could not be achieved.

The most common approach to reduce or avoid the effect of water in infrared analysis has been to perform some sort of solvent elimination. One such solvent-elimination approach involves a two-step procedure [1]. In the first step the sample is sprayed onto a mesh-made cup filled with a non-absorbing salt such as KCl. In the second step the sample is dried by passing nitrogen or air through the mesh container holding the KCl. Unfortunately, this technique is only marginally suitable for aqueous samples as water dissolves the salt matrix. This limitation can be avoided by using a water insoluble material, such as diamond powder, as the drying support.

A variation on this approach involves first removing the analytes from their aqueous background via solvent extraction into a more volatile organic solvent [2,3]. When the analyte is present in an organic phase, it can be dried more efficiently. The disadvantages of this technique include the necessity for a high partition coefficient for the analyte, the extra time and mixing necessary to achieve equilibrium distribution between the phases, and the careful separation of the organic from the aqueous phase.

In the analysis of aqueous liquids, several methods of sample preparation based on solvent elimination have been proposed. Goulden [4] outlined for the first time the basic principles of application of infrared spectroscopy for the analysis of liquid milk. A method where the solvent of HPLC effluents is eliminated by evaporation of the mobile phase after eluate deposition on the surface of a heated mid-IR transmitting diamond powder has been described by Kuehl and Griffiths [1]. An approach for near infrared (NIR) spectroscopy where fiberglass advantageously replaces the diamond powder proposed for the aqueous liquids has been presented by Meurens [5] and Alfaro [6] who describe the performance of such a system on model sugar solutions representing fruit juices. In addition, infrared spectrometry was used to predict concentrations of individual sugars and acids of orange juice by Dupuy et al. [7]. The principle of using a dry extract has also been applied to mid IR spectroscopy by Gagnon et al. [8]. The dry extract system patented by these authors is based on the use of a thin, microporous polyethylene film as sample substrate.

Another technique frequently used in the analysis of liquids is the Attenuated Total reflectance (ATR) spectroscopy [9,10]. One of several applications of this accessory was made by Wong et al. [11] for antibiotic solutions analysis based on a cylindrical internal reflectance element. Moreover, in a previous work [12], this accessory was applied in the rapid analysis of fruit juice. ATR is a method of contact between a thinner optical medium with refractive index n_1 , usually the sample, and a crystal or internal reflection element (IRE) with a high refraction index n_2 and with a weak infrared absorption in the region of interest. The rays, once coupled into the IRE, are reflected on its inner surface. At each reflection, a standing evanescent wave exists when a portion of radiation energy penetrates a short distance into the thinner optical medium to interact with the sample molecules. The penetration depth (d_p) depends on the

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incidence angle and the refractive index of both materials ($n_1 > n_2$) and the wavelength (λ). Harrick [13] explains this depth by the following equation:

$$d_p = \lambda / (\eta_1 2\pi(\sin^2\theta - (\eta_2 / \eta_1)^2)^{0.5}).$$

Where θ is the angle of incidence of light beam. The $1/e$ penetration depth of the evanescent wave is typically on the order of the wavelength.

The main advantage of ATR is in the fact that it is able to obtain spectra from samples spectra covered by the broad and intense water absorption bands. This procedure consists of mathematically rationing the water spectrum out of the sample spectra [13,14]. Depending on the surface of contact between the IRE and the sample, three kinds of ATR accessories exist: cylindrical ATR (CATR), Squarecol parallelepiped ATR (PATR) and horizontal ATR (HATR). The PATR and CATR accessories have an effective surface several times greater than the HATR accessory [13], so the light is reflected more times against the axial wall of the crystal and, therefore, the pathlength and the optical density increase.

To further improve the sensitivity of this system, that is to easily reach detection limits in the low ppm concentrations, it is necessary to exclude water almost completely and concentrate the analyte. Water can be removed from the IRE surface allowing the organic compounds to be extracted. The application of a hydrophobic polymer membrane over the surface of the IRE impedes water molecules to interact with infrared radiation and makes possible the selective diffusion of organic molecules into the polymer where they are detected by the absorption of infrared (IR) radiation [15]. Thus, the detection limits are lowered, and measurements in the low ppm concentrations are possible.

In this paper, we describe the application of different techniques in determining the concentration of aqueous solutions:

- direct transmission measurement and attenuated total reflection (ATR) as direct techniques;
- solid extract sampling (SES) as a dry extract transmission technique, and liquid extract sampling (LES) as ATR technique with a selective polymer coating over the internal reflection element (IRE) as extractive techniques.

A volatile trichloroethylene (TCE) compound and a non volatile glucose compound are chosen for measurements with the different techniques for comparison in terms of signal-to-noise ratio.

Materials and methods

Preparation of solutions

Glucose and trichloroethylene (TCE) solutions are prepared from 1 to 10 000 ppm. TCE of analytical reagent grade (Janssen Chimica, 2340 Beerse, Belgium) ($\rho = 1.46 \text{ g/cm}^3$) is injected with a pipette into 10 mL methanol to generate a solution; this solution is transferred into a 1 L measuring flask, which is then filled up with distilled water, and stirred for about 30 minutes. A new solution is prepared just prior to each measurement in order to avoid evaporation of TCE. For the preparation of TCE solutions in concentrations

below 1 000 ppm, an initial solution (1 000 ppm) is first prepared in distilled water, and the final solutions are prepared by sequential dilution.

Spectra acquisition

All measurements are performed with an interferometer MIDAC (MIDAC Corporation, Costa Mesa, Ca, USA) coupled to a PC working with Spectra Calc (SC) software (Galactic Industries Corporation, Salem, NH 03079, USA). 10 scans of symmetrical interferograms are coadded at 4 cm^{-1} resolution for each spectrum and absorbance spectra are computed from 4000 to 400 cm^{-1} .

Direct transmission measurement

An SL-2 FTIR demountable cell kit from International Crystal Labs (Garfiels, NJ 07026, USA) with CaF_2 windows and a spacer of $25 \mu\text{m}$ are used for the direct transmission measurements through liquid samples. The liquid samples are placed in the transmission cell with a syringe, the cell is mounted on the sample holder of the spectrometer, and spectra are acquired directly without any sample preparation. The background spectra were obtained by using the empty transmission cell as a reference.

ATR measurement

HATR (horizontal ATR) and PATR (Squarecol parallelepiped ATR) accessories from GRASEBY-SPECAC Inc. (Orpington, Kent, England) with incidence angle of 45° are used. These accessories are equipped with zinc selenide (ZnSe) and germanium (Ge) crystals (GRASEBY-SPECAC) as internal reflectance elements (IRE). The samples are scanned directly on HATR or PATR crystal without any preparation like in the direct transmission measurement. The background spectra are pure water spectra on ATR crystal.

Solid extract sampling (SES)

This method uses a thin microporous polyethylene membrane (3M) as sample extract support. The polyethylene film is fixed with glue on a 1.5 cm diameter metal ring to form a rigid and transparent sample support, called «polyethylene disk».

The sample preparation consists of three operations: 1) Deposit of $100 \mu\text{L}$ sample on the polyethylene disk film; 2) drying of the sample by heating for 10 minutes in a microwave oven; 3) mounting the polyethylene disk in the holder of the spectrometer. The spectra are obtained by transmission measurement through the dry extract and the polyethylene film. The background spectra are acquired by using the empty spectrometer holder as a reference.

Liquid extract sampling (LES)

To exclude disturbing water from IR measurements and concentrate the chlorinated hydrocarbon, a solution of polycarbonate ($\rho = 1.25$) at 5% in dichloromethane is prepared and deposited homogeneously onto the HATR Ge crystal. After evaporation of the solvent, a polymer film remains on the surface. The coating has a thickness of about $10 \mu\text{m}$. The growth of TCE concentration in the polymer coating is studied during its diffusion in order to determine the response time of this method. All sample spectra are ratioed against

the dry polymer-coated HATR crystal. The polymer background spectra are obtained by using the coated HATR without sample as reference.

Noise

The noise spectrum represents the variation (standard deviation) of absorbance due to instrumentation and sample presentation, its value is calculated by the average of ten measurements (see Sect. "spectra acquisition") of the sample against itself.

Signal-to-noise measurements

The measurements of signal and noise are done with water, glucose (1000 ppm) and TCE (1000 ppm) aqueous solutions placed in a transmission cell, on a PATR crystal, on an HATR crystal on an HATR crystal covered with polycarbonate, and on the thin microporous polyethylene disk.

The signal value is the absorbance measured at a wavenumber chosen as representative of the considered substances.

The signal-to-noise ratio is calculated by dividing the signal values by the noise values at the same wavenumbers.

Determination of limit of detection

The limit of detection is the concentration of the analyte among the examined concentrations at which, at the position of the absorption band of interest, there is a signal that is 3 times stronger than the noise [15].

Results

The broad intense absorption bands of water: the O–H stretching region from 3 400 to 3 100 cm^{-1} , and the H–O–H bending mode at approximately 1 632 cm^{-1} are observed in figure 1. These absorption bands greatly disturb the analyte measurements. The full spectrum from 3 700 to 500 cm^{-1} of concentrated trichloroethylene and concentrated glucose compounds are respectively shown in figure 2 and figure 3.

Direct measurements

Direct transmission measurement

The spectrum from 4 000 to 400 cm^{-1} of distilled water obtained by direct measurement through the liquid sample in the transmission cell is presented in figure 1A. The spectrum from 1 179 to 988 cm^{-1} of glucose at 500 and 1 000 ppm obtained by ratioing out the water spectrum, and its noise spectrum are shown in figure 4. The spectrum from 2 865 to 2 800 cm^{-1} of TCE at 500 and 1 000 ppm and its corresponding noise spectrum are shown in figure 5. Table II shows the values obtained in measuring the signal, noise and signal-to noise values for water, glucose (1 000 ppm) and TCE (1 000 ppm), each at a selected wavenumber in direct transmission measurement.

Table I lists the limits of detection of glucose and TCE solutions for considered absorption bands.

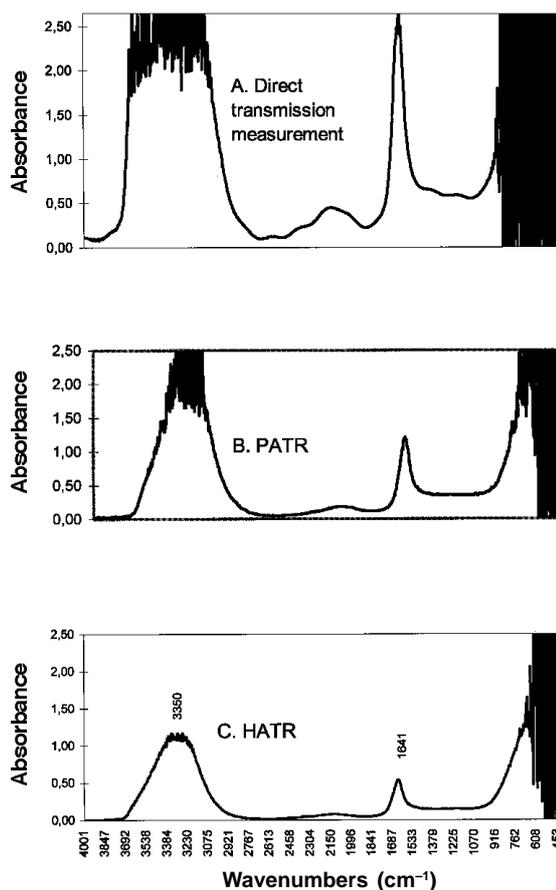


Fig. 1. Spectra of water from 4 000 to 400 cm^{-1} : A) Direct transmission measurement; B) PATR method (ZnSe IRE); C. HATR method (ZnSe IRE).

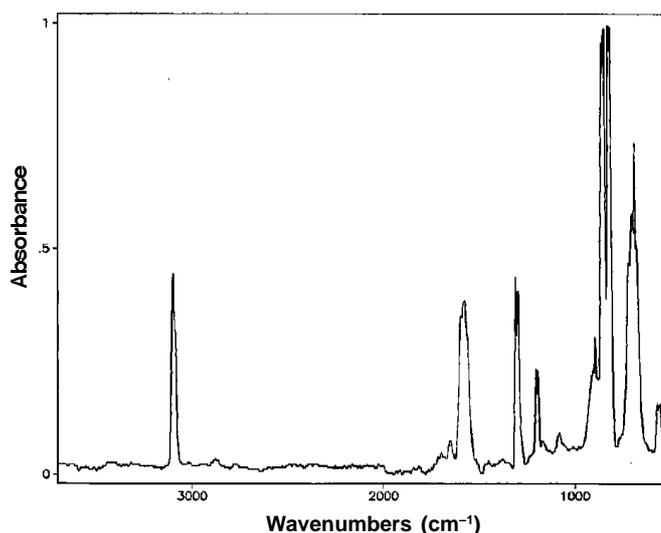


Fig. 2. Full spectrum of TCE from 3 700 to 500 cm^{-1} .

ATR measurement

Figure 1B and C shows the PATR and HATR spectra from 4 000 to 400 cm^{-1} of distilled water. The PATR spectrum from 2 994 to 2 802 cm^{-1} of glucose (1 000 and 100 ppm)

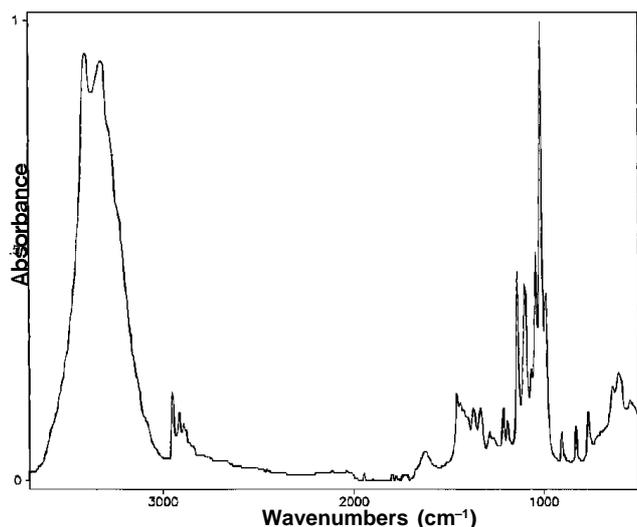


Fig. 3. Full spectrum of glucose from 3 700 to 500 cm^{-1} .

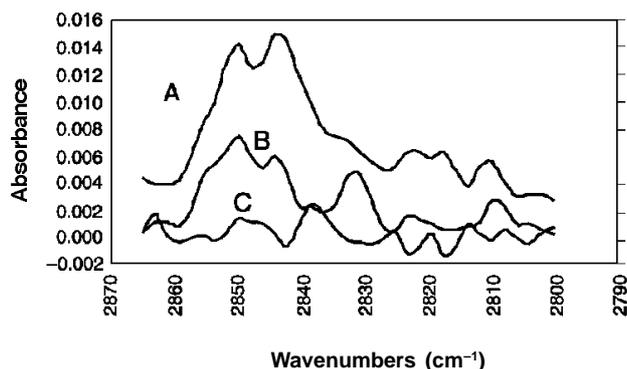


Fig. 5. Spectra of TCE from 2 865 to 2 800 cm^{-1} obtained by direct transmission measurement: A) TCE at 1 000 ppm; B) TCE at 500 ppm; C) Noise of TCE.

Table I. Limits of detection for glucose and TCE aqueous solutions using the direct transmission measurement, ATR: PATR (ZnSe), HATR (ZnSe), HATR (Ge); SES and LES techniques at selected wavenumbers.

Solution	Method (cm^{-1})	Wavenumber	Limits of detection (ppm)
Glucose	Direct transmission	1 038	500
Glucose	PATR (ZnSe)	1 072	100
Glucose	HATR (ZnSe)	1 072	100
Glucose	HATR (Ge)	1 072	300
TCE	Direct transmission	2 850	500
TCE	HATR	931	100
TCE	PATR	931	100
Glucose	SES	1 157	1
TCE	LES	931	10

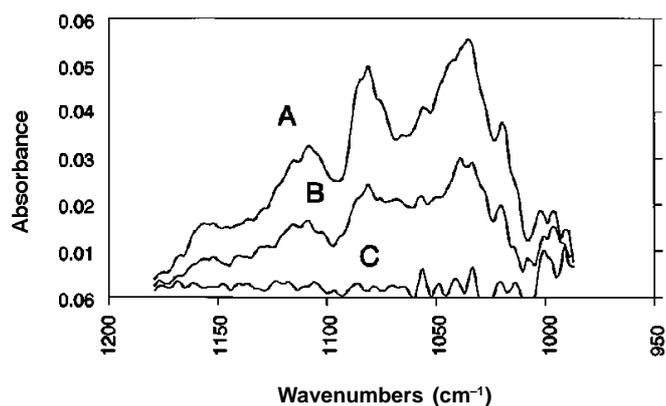


Fig. 4. Spectra of glucose from 1 179 to 988 cm^{-1} obtained by direct transmission measurement: A) glucose at 1000 ppm; B) Glucose at 500 ppm; C) Noise of glucose.

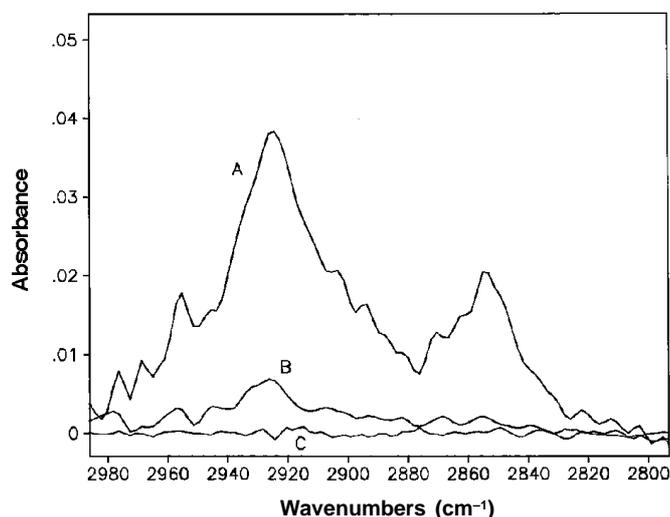


Fig. 6. Spectra of glucose from 2 994 to 2 802 cm^{-1} obtained by PATR measurement: A) Glucose at 1 000 ppm; B) Glucose at 100 ppm; C) Noise of glucose.

Table II. Signal, noise and signal-to-noise values for glucose (1000 ppm) and TCE (1000 ppm) using the direct transmission measurement, ATR: PATR (ZnSe), HATR (ZnSe), HATR (Ge); SES and LES techniques at selected wavenumbers.

Compound	Method (cm^{-1})	Wavenumber	Signal	Noise	Signal-to-noise ratio
TCE	Direct transmission	2 850	0.020	0.0018	11.1:1
TCE	PATR (ZnSe)	931	0.023	0.0020	11.5:1
TCE	HATR (ZnSe)	931	0.011	0.0020	5.5:1
TCE	HATR (Ge)	931	0.002	0.0010	2:1
TCE	LES	931	0.011	0.00091	12.4:1
Glucose	Direct transmission	1 038	0.057	0.0056	10.2:1
Glucose	PATR (ZnSe)	1 157	0.059	0.0021	28.1:1
Glucose	HATR (ZnSe)	1 157	0.010	0.0023	4.4:1
Glucose	HATR (Ge)	1 157	0.006	0.0015	4.0:1
Glucose	SES	1 157	0.090	0.0015	59.3:1

obtained by ratioing out the water spectrum, and its corresponding noise spectrum are shown in figure 6. The spectrum from 946 to 831 cm^{-1} of TCE (1 000 ppm) obtained with the HATR (Ge) coated by a polymer film, PATR (ZnSe), HATR (ZnSe), and HATR (Ge) accessories are shown in figure 7 (A, B, C and D respectively). HATR and PATR spectra are also taken for concentrations: 1 000, 500, 100 and 10 ppm of both products dissolved in water. The limits of detection for glucose and TCE solutions for these methods are listed in table I.

Table II shows the values obtained in measuring the optical signal, noise and signal-to-noise ratio for water, glucose (1 000 ppm) and TCE (1 000 ppm) using the ATR technique (respectively PATR with ZnSe crystal, HATR with ZnSe crystal, HATR with Ge crystal).

Extract measurements

Solid extract measurement (SES)

Figure 8 presents the spectrum of microporous polyethylene after water evaporation. Figure 9A shows the spectra from 1 248 to 900 cm^{-1} of glucose solutions at nine different concentrations from 100 to 1000 ppm, obtained after evaporation of the solvent from the microporous polyethylene disk. Figure 9B gives the absorbances at 1 076.3 cm^{-1} as a function of the concentration of these nine solutions. Figure 10A presents the spectrum from 1 740 to 950 cm^{-1} of glucose solution at 10 000 ppm in transmission mode obtained before the evaporation of water. Figure 10B shows the spectrum of water from 1 740 to 950 cm^{-1} . Figure 10C presents the SES (dry extract) spectrum from 1 740 to 950 cm^{-1} of glucose obtained after evaporation of water.

The signal, noise, and signal-to-noise ratio values for glucose (1 000 ppm) at 1 157 cm^{-1} using the solid extract measurement are respectively 0.090, 0.0015 and 59.3 (Tab. II). The limit of detection is 1 ppm (Tab. I).

Liquid extract measurement (LES)

Figure 7A shows the absorption from 946 to 831 cm^{-1} of TCE (1 000 ppm) after sample deposition over the Ge crystal coated by a polycarbonate film. The diffusion of organochloride molecules into the polymer coating is studied in order to know the time needed to obtain stable and constant values of absorbances. Spectra of TCE solution are taken every minute from the time of filling the coated HATR cell until 10 minutes (Fig. 11). Intensities of the absorption peaks of TCE at 931 cm^{-1} are shown in figure 12 as a function of time.

The signal, noise and signal-to-noise values for TCE (1 000 ppm) at 931 cm^{-1} using the LES method are respectively 0.011, 0.00091 and 12.4 (Tab. II).

Discussion

Direct measurements

The direct transmission measurement in the CaF_2 cell is not suitable for the determination of TCE solutions because the low frequency cutoff of CaF_2 is located at 960 cm^{-1} (Fig. 1A), where the most important peaks of TCE are situated (931 and 841 cm^{-1}). On the contrary, the effective use-

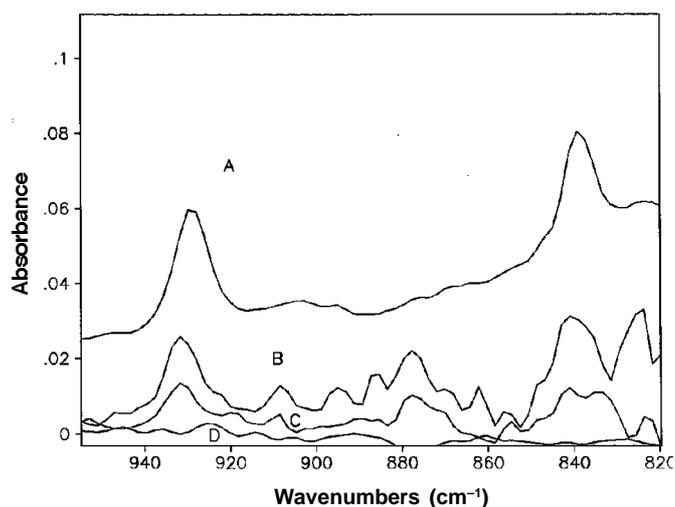


Fig. 7. Spectra of TCE from 946 to 831 cm^{-1} , at 931 and 841 cm^{-1} (1 000 ppm): A) With a polycarbonate coating on the HATR Ge crystal; B) Uncovered PATR ZnSe crystal; C) Uncovered HATR ZnSe crystal; D) Uncovered HATR Ge crystal.

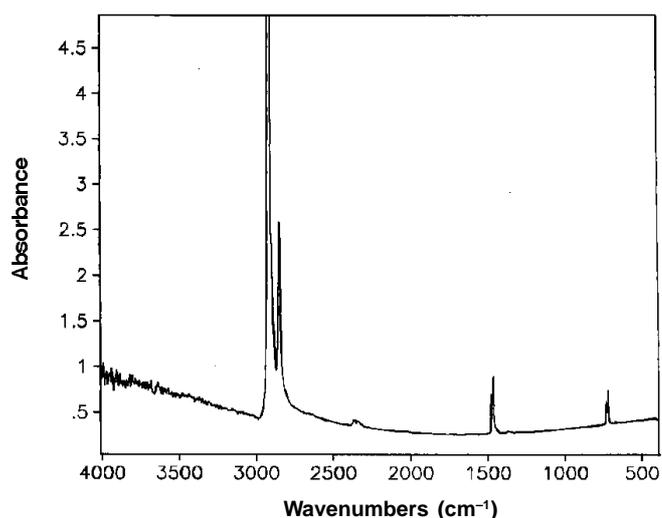


Fig. 8. Spectrum of a thin microporous polyethylene from 4 000 to 400 cm^{-1} .

ful spectral regions for PATR (ZnSe) and HATR (ZnSe) go respectively from 4 000 to 800 cm^{-1} and from 4 000 to 680 cm^{-1} .

For glucose and TCE, the PATR (ZnSe) optical signal (Fig. 7B) is more intense than the HATR (ZnSe) optical signal (Fig. 7C) and both are more intense than the HATR (Ge) optical signal (Fig. 7D) (Tab. II). This is explained by the fact that PATR has a much longer optical pathlength than HATR and that the Ge crystal gives a shorter depth penetration of light in the sample than the ZnSe crystal.

The comparison of limits of detection given in table I shows much better sensitivity for ATR methods than the direct transmission measurement on aqueous solutions of glucose and TCE. This is explained by the fact that the

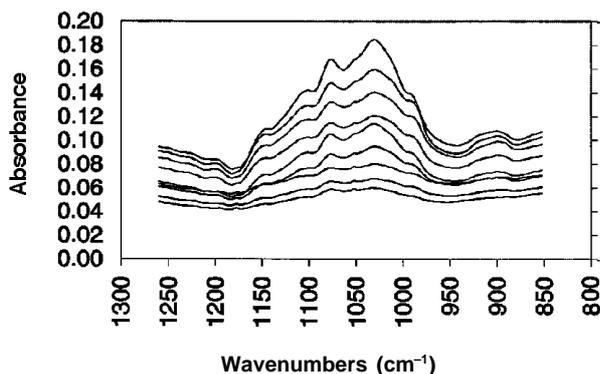


Fig. 9A. Spectra of glucose from 1 458 to 910 cm^{-1} obtained by SES (dry extract) method, at 100, 200, 300, 400, 500, 600, 800, 900 and 1 000 ppm.

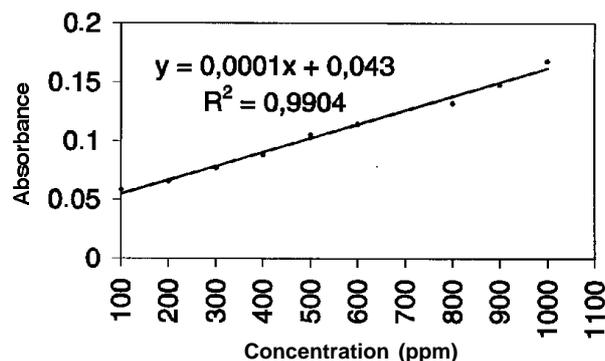


Fig. 9B. Glucose absorbances obtained by SES (dry extract) method at 1 076.3 cm^{-1} as a function of different concentrations.

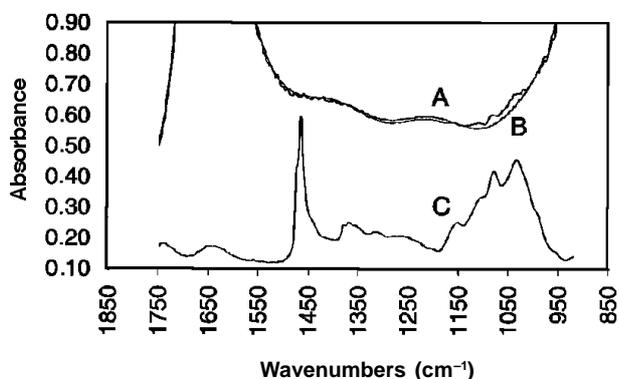


Fig. 10. Spectra of glucose from 1 740 to 950 cm^{-1} : A) Glucose at 10 000 ppm in transmission mode; B) Water spectrum in transmission mode; C) Glucose spectrum by SES (dry extract) method.

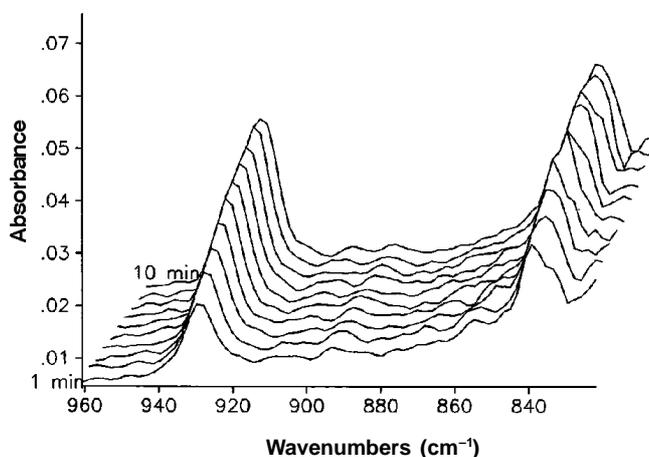


Fig. 11. LES method (polycarbonate coating over the HATR Ge crystal): Absorbance of TCE (1 000 ppm) from 960 to 820 cm^{-1} at 931 and 841 cm^{-1} as a function of time from 1 to 10 min.

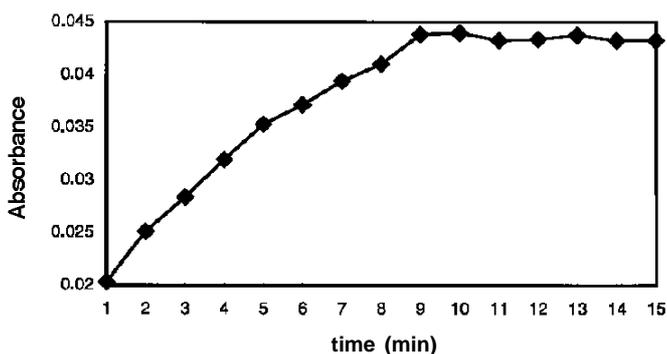


Fig. 12. LES method: Enrichment of TCE at 931 cm^{-1} in the polycarbonate coating of HATR Ge crystal over a period of 15 min.

optical pathlength is shorter in ATR than in direct transmission measurement, and, therefore, the absorbance and the noise levels are lower in the former technique. The better detection limits of ATR techniques can also be explained by their better signal-to noise ratios (Tab. II).

Extract measurements

The extractive methods are developed to solve the problem of water interference and analyte dilution.

The water removal and the analyte concentration by evaporation in the SES method allows more intense and clear signals to be obtained for dry extract than the aqueous solution of glucose (Fig. 9A, Fig. 10). The relationship between the intensity of these signals and the concentration of glucose follows the Beer-Lambert law (Fig. 9B).

The statistical performance of calibration obtained by linear regression ($R^2 = 0.9904$, $SD = 3.31\%$, 33.1 ppm) for sample glucose at concentrations from 100 to 1 000 ppm are better than those given by Wilson et al. (1995) [16] for aqueous solutions of glucose and citric acid ($R^2 = 0.988$ and 0.971 respectively). In addition, the signal-to-noise ratio of the SES method is equal to 59.3 at the maximum peak being better than the other methods experimented here, and the detection limit reaches 1 ppm of glucose in aqueous solution (Tab. I).

The selective diffusion of TCE molecules into the polymer coating over the ATR crystal allows more intense and clear signals to be obtained for coated HATR than for uncoated PATR and HATR (Figs. 7A, B, C, D). Furthermore, the noise corresponding to the LES method on coated HATR is as low as 0.00091 and the signal-to-noise ratio is equal to 12.4 whereas the signal-to-noise for uncoated HATR (Ge) is equal to 2 (Tab. II). In the same way the limit of detection of TCE by LES method is 10 ppm instead of 100 ppm by PATR (ZnSe) and HATR (ZnSe), and 300 ppm by the HATR (Ge) method (Tab. I). Thus, the improvement due to the polymer coating is of more than one order of magnitude. This is explained because the analyte molecules are concentrated in the hydrophobic polymer coating, impeding the interaction of water molecules with infrared radiation.

TCE molecules diffuse into the polymer until the tenth minute (Fig. 11). After that, an equilibrium in the enrichment process is observed (Fig. 12).

To perform quantitative measurements with the LES method it is possible to work on the rising curve (Fig. 12), taking spectra before the equilibrium point (constant absorbance). On the other hand, this method is completely reversible and reproducible after rinsing with water for a few minutes, therefore, it can be used repeatedly with other concentrations of aqueous solutions. For 10 repeated absorbance measurements at 931 cm^{-1} of a 1 000 ppm TCE solution, a relative standard deviation of 1.8% is obtained.

Conclusion

The results of the experiments performed with different methods allow some important facts to be elucidated in the determination of concentration of aqueous solutions:

- The direct transmission measurement presents an intense optical signal that is suited for concentrations higher than 500 ppm without any sample preparation.
- The solid extractive sampling (SES) results show the best signal-to-noise ratio for glucose compound and a lower detection limit for the same compound. However, this method is not appropriate for the study of TCE solutions because of the volatility of this compound and time consuming sampling.
- The results obtained with different extracting sampling methods indicate that the ATR method [PATR (ZnSe) and HATR (ZnSe)] is a worthy analytical tool to obtain IR spectra of aqueous solutions in the low ppm concentration.
- The potential of the ATR method is improved with the complete exclusion of water from the measurement,

obtained by coating the internal reflection element with a hydrophobic polymer. This Liquid Extractive Sampling (LES) method is suitable for the study of TCE solutions in lower ppm concentrations. This coating prevents the interaction of light with water molecules that is reflected in the considerable signal-to-noise ratio obtained with respect to the other methods. This technique could also be extended to other nonpolar organic water contaminants.

To further ameliorate the sensitivity of this LES system measurement, better penetration depths of the evanescent wave must be obtained. Results using a ZnSe crystal coated with other polymers and measurements of multicomponent aqueous solutions with multivariate statistical methods will be published at a later date.

References

1. Kuehl, D. T.; Griffiths, P. R. *Anal. Chem.* **1980**, *52*, 1394.
2. Duff, P. J.; Conroy, C. M.; Griffiths, P. R.; Karger, B. L.; Vouros, P.; Kirby, D. P. *Proc. Soc. Photo-Opt. Instrum. Eng.* **1981**, *289*, 53.
3. Conroy, C. M.; Duff, P. J.; Griffiths, P. R.; Azarraga, L. V. *Anal. Chem.* **1984**, *56*, 2636.
4. Goulden, J. D. S.; *Dairy Res.* **1964**, *50*, 273.
5. Meurens, M. *Achema Frankfurt, Germany* **1982**, *82*, 51.
6. Alfaro, G.; Meurens, M.; Birth, G. S. *Appl. Spectrosc.* **1992**, *44*, 979.
7. Dupuy, N.; Meurens, M.; Sombret, B.; Legrand, P.; Huvenne, J. P. *Appl. Spectrosc.* **1992**, *46*, 860.
8. Gagnon, J. E.; Povey, N. P.; Gagnon, D. R.; Midgley, R. R. International application published under the patent cooperation treaty PCT/US92/05350, 24 June (1992).
9. Mirabella, F. M. Jr.; Harrick, N. J. *Internal Reflection Spectroscopy: Review and Supplement*, Harrick Scientific, Corp., New York (1985).
10. Urban, M. *Attenuated total reflectance spectroscopy of polymers*, ACS, Washington DC (1996).
11. Wong, J. S.; Rein, A. J.; Wilks, D.; Wilks, P. JR. *Appl. Spectrosc.* **1984**, *38*, 32.
12. Meurens, M.; Li, W.; Foulon, M.; Acha, V. *Cerevisia* **1995**, *20*(3), 33.
13. Harrick, N. J. *Internal Reflection Spectroscopy*, Wiley, New York (1967).
14. Koenig, J. L. *Spectroscopy of Polymers*, ACS, Washington DC (1992).
15. Heinrich, P.; Wyzgol, R.; Schrader, B.; Hatzilazaru A.; Lybbers, D. W. *Appl. Spectrosc.* **1990**, *44*, 1641.
16. Bartl, F.; Delgadillo, I.; Davies, A. N.; Meurens, M.; Huvenne, J. P.; Volka, K.; Wilson, R. H. *Fresenius J. Anal. Chem.* **1996**, *354*, 1-5.