

Monitoring of pollutant in waste water by infrared spectroscopy using chalcogenide glass optical fibers

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Received 25 November 2003; received in revised form 5 February 2004; accepted 11 March 2004

Abstract

Infrared optical fibers based on chalcogenide glass are used as sensor for the determination of volatile organic pollutants in groundwater. The system work following the fiber evanescent wave spectroscopy principle, so-called **fiber evanescent wave spectroscopy (FEWS)**. It was tested in situ, in real time, under real-world conditions. The measurement set-up consisted of a FTIR spectrometer (BRUKER V22), coupled with the fiber (about 2 m), and a cooled mercury–cadmium–telluride detector. A special kit provided by Bruker was connected on the spectrometer to focus the infrared beam from the black body at the entry of the fiber. Some preliminary pilot scale tests, led in an artificial aquifer, show that the fiber permits access to the absorption line positions in a wide range from 4000 to 800 cm⁻¹. Moreover, it is shown that the original design of the fiber enables detection of weak concentrations of pollutants down to 1 ppm of C₂Cl₄. Then the experiments in “real-world” conditions are carried out after having applied a proper protection on the fibers. A comparison with the chemical analysis data shows that the optical fibers enable to follow the evolution of pollutant rates in water versus time. Finally, this work is promising in view of installing some permanent checking devices into wells to control the rate of pollutants in groundwater of landfill. © 2004 Elsevier B.V. All rights reserved.

Keywords: Sensor; Optical fiber; Chalcogenide glass; Pollutant; Waste water

1. Introduction

Most of the time, chemical analysis of waste water is carried out by chromatography. These technique is quite heavy to implement and need to take some ground water samples. Since the coming of the FTIR spectrometers, infrared spectroscopy has become an indispensable and efficient tool of analytical studies. Nevertheless, classical attenuated total reflection (ATR) or transmission registration need also to collect samples. An alternative method to acquire the infrared spectra consists of using some optical fiber, avoiding then the samplings. For this, the fiber is employed, on the one hand, to transmit the IR beams from the spectrometer to the sample, and on the other hand, as a probe by inserting a part of the fiber, called the sensing zone, into the studied environment. This technique is called fiber evanes-

cent wave spectroscopy (FEWS) for fiber evanescent wave spectroscopy because it is generally considered that the principle of the measurement is based on the presence of evanescent wave around the fiber during the propagation of light into the fiber. A new generation of optical fibers has been developed based on the large transparency domain of an original family of IR chalcogenide glasses transmitting from 2 to about 12 μm. These fibers have already been successfully used as chemical sensors in many fields of application: biology, medicine, food [1–8]. In all these cases, the experiments were carried out in a laboratory where the fibers were protected from “real-world” conditions.

The aim of the present work is to make a prototype mid-infrared sensor system for the determination of organic pollutants. For this, the role of the fiber is essential because we have to characterize some pollutants in groundwater remotely. This work took place in the framework of the IMSIS European contract of the fifth plan (in situ monitoring of landfill related contaminants in soil and water by infrared sensing). First results concerning this consortium

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works have been recently published [9,10]. The first paper [9] is related to the development of a miniaturized grating spectrometer made mainly by the Fraunhofer Institute of Physical Measurement Technique (Freiburg, Germany). The second paper [10] reports some preliminary results obtained using silver halide fiber optic sensor co-developed by the Tel Aviv University (Israel) and the Institute of Analytical Chemistry (Vienna, Austria). The present paper is devoted to presentation of the measurements carried out with the chalcogenide glass fiber made by our group. The abilities of the fiber have been improved because of a very precise schedule of conditions: long cables to transmit the beams, high sensitivity for the sensing zone, large transmission windows to detect simultaneously several chemical species, and an efficient device to protect the fiber. The pilot scale tests were carried out in an artificial aquifer system that simulated the landfill groundwater, and then the prototype was used outside in “real-world” conditions.

2. Experimental

2.1. Materials

The fibers were made using the $\text{Te}_2\text{As}_3\text{Se}_5$ glass, so-called TAS glass. This composition enables to obtain a large optical transmission window from 4000 to 900 cm^{-1} coupled to thermo-mechanical properties that permit to carry out the drawing process. The glass was prepared in a silica tube under vacuum following a well defined protocol as detailed in a previous paper [11]. The elements, Te, As, Se were firstly severely purified, then the mixture was distilled and maintained at 700°C for 12 h in a rocking furnace to ensure a good homogenization of the liquid. The silica ampoules were quenched in water and annealed near the glass transition temperature ($T_g = 137^\circ\text{C}$) to avoid permanent mechanical stresses on cooling. These successive steps are essential to avoid optical scattering losses mainly due to oxide chemical

bonds and scattering effects. Finally, the fibers were made from the glass cylinders thanks to a drawing tower built at the laboratory. The rods were drawn by selecting the best parameter combination of temperature and drawing speed. The appropriate diameter of the fiber is equal to $400 \pm 20\text{ }\mu\text{m}$. This value permit to inject the light beam into the fiber and to keep a good flexibility of the system. Moreover, it has been previously shown that the sensitivity of the sensor increases when its diameter decreases [12]. So, the diameter of the fiber was locally reduced to create a 20 cm long tapered sensing zone. This goal was achieved by two routes: on one hand by accelerating on line the speed during the drawing process, on the other hand, by using a chemical solution that congruently dissolve the glass. Typically, the fiber had a diameter of $100\text{ }\mu\text{m}$ in the sensing zone. Otherwise, a polymer coating was applied on the fiber to protect and prevent it from breaking. Of course, at the end, the protective polymer is removed from the sensing zone to enable a close contact between the sensor and the polluted water. Note that no hydrophobic selective polymer was applied on the fiber and the sensing zone was just constituted of a low diameter bare fiber.

2.2. Set up

Whatever the places where the experiments were conducted, the general set up was the same. The chalcogenide glass fiber aimed, on one hand, at transmitting the IR beams from the spectrometer to the polluted zone and, on the other hand at probing by dumping the fiber in the polluted zone as depicted in Fig. 1. For this, a unique fiber is used to avoid any loss due to connection between pieces of fibers. The measurement set-up consisted of a FTIR spectrometer (BRUKER V22), coupled with the fiber (about 2 m), and a cooled mercury–cadmium–telluride detector. A special kit provided by Bruker was connected on the spectrometer to focus the infrared beam from the black body at the entry of the fiber thanks to parabolic mirrors. Generally speaking,

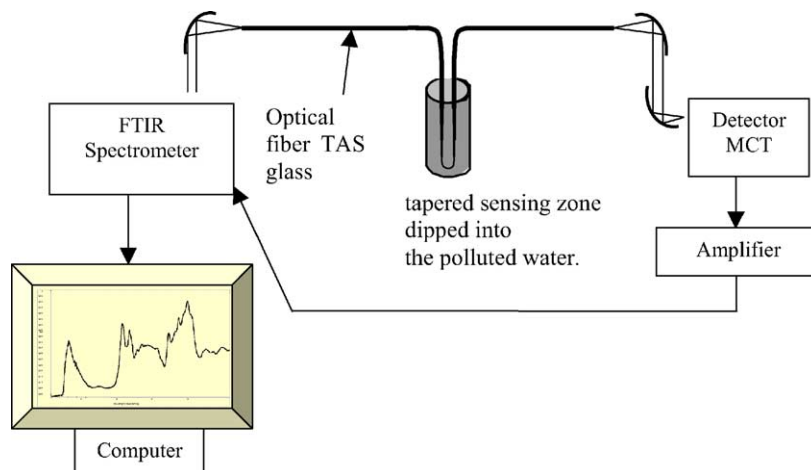


Fig. 1. Sketch of the experimental set up: an unique tapered chalcogenide glass fiber is used for the signal transportation and as sensing element.

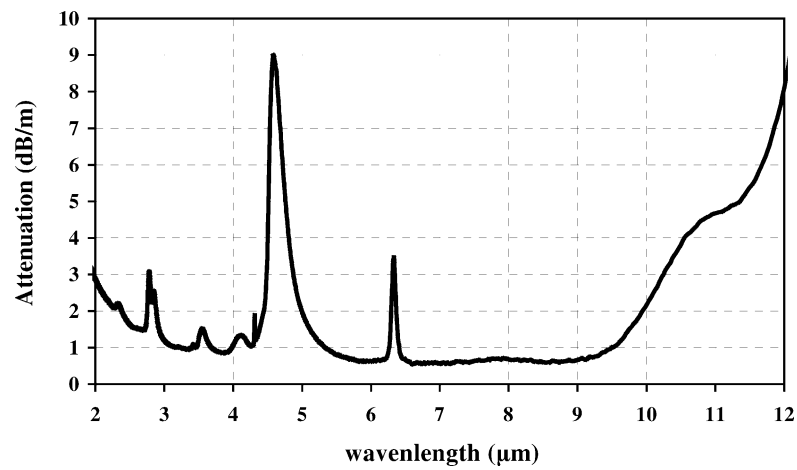
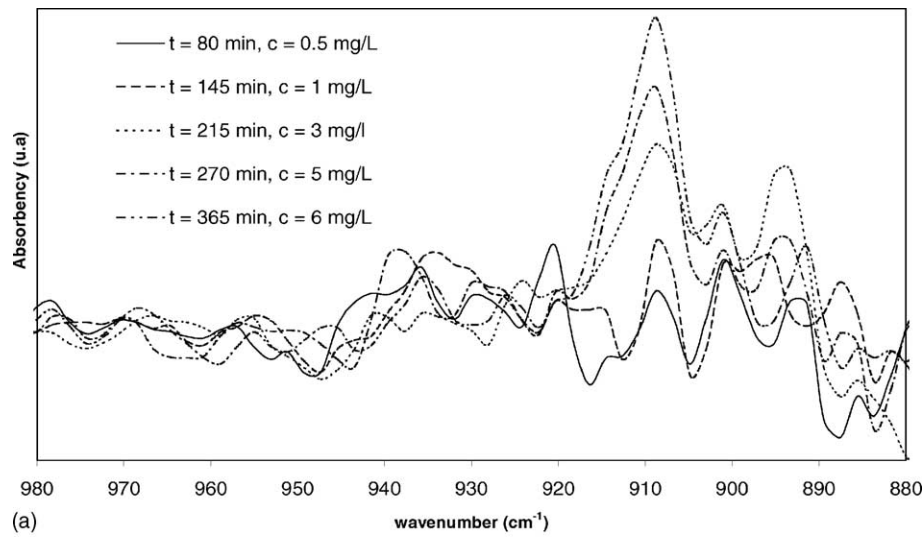
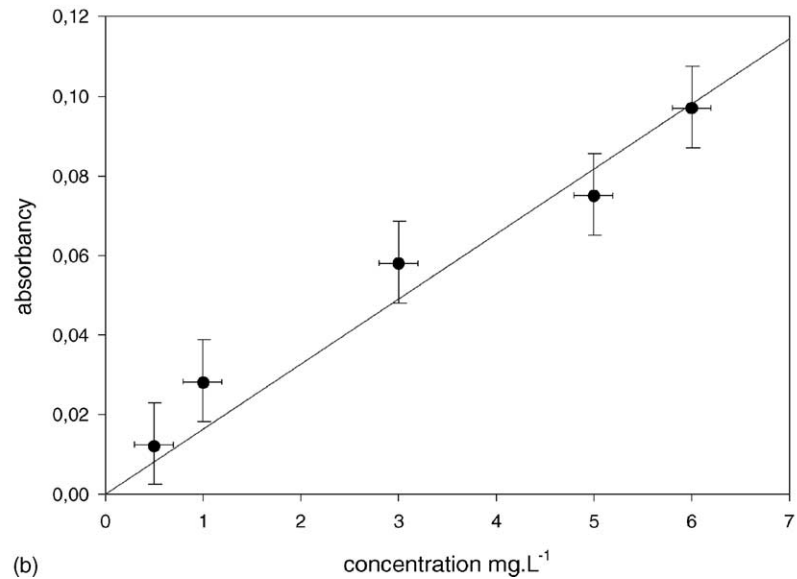


Fig. 2. Attenuation spectrum of a TAS glass fibers.



(a)



(b)

Fig. 3. (a) Spectrum recorded in Vienna in an artificial aquifer. The band at 910 cm⁻¹ is due to the C–Cl stretching vibration in C₂Cl₄. (b) Increase of the intensity of the line at 910 cm⁻¹ vs. the concentration of pollutant in the tank. This evolution agrees with the pseudo-Beer–Lambert law.

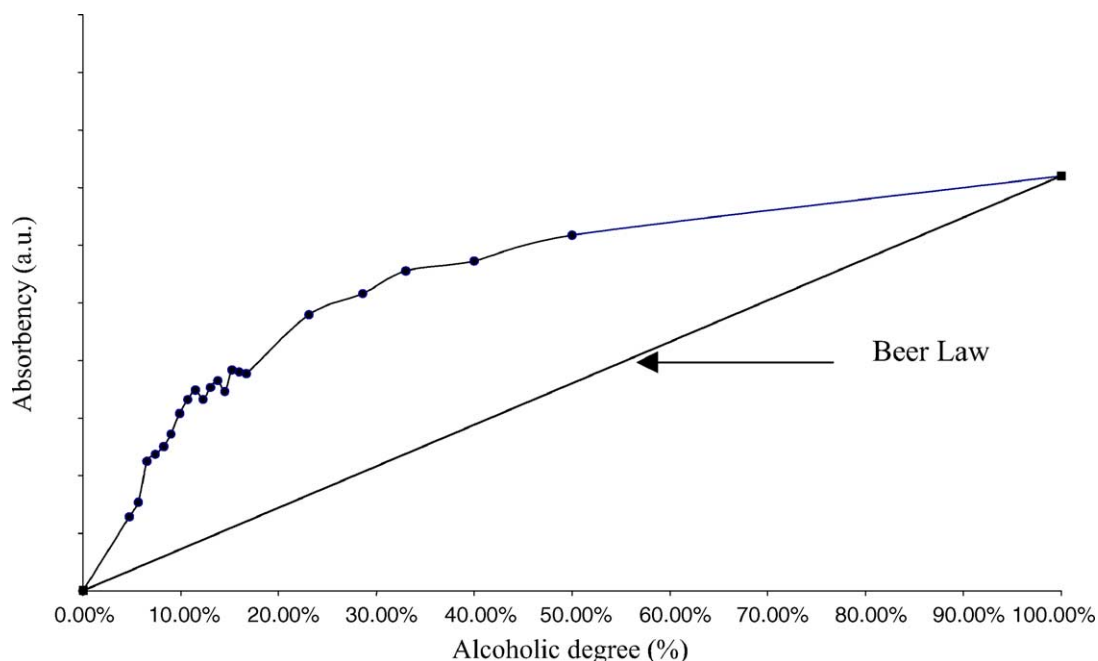


Fig. 4. Increase of the intensity of the ethanol line at 1050 cm^{-1} in water/ethanol mixtures, where the rate of alcohol varies from 0 to 100%. The straight line depicts the expected Beer–Lambert law. The large discrepancy observed between both lines is attributed to the TAS glass fiber hydrophobic behavior which enhance the signal of the ethanol to the detriment of the water absorption lines.

the light propagated in the multimode fibers by total internal reflection (TIR). TIR occurs at the interface, for the rays whose angles of incidence are over the critical angle, as long as the medium surrounding the fiber is weakly absorbent. When chemical species are brought into contact with the fiber, the IR optical rays are partially absorbed at the interface following the ATR rules. For optical fiber sensors, the FEWS is preferable to avoid confusion with ATR crystal probe devices. In any case, the optical signal is recorded at the ending extremity of the fiber, thus, providing the infrared single beam spectra. Fig. 2 displays the attenuation spectrum of the sensor measured by the cut-back method. The minimum losses are located in the $6\text{--}9\text{ }\mu\text{m}$ region and are just below 1 dB m^{-1} . The limits of transparency are around $2\text{ }\mu\text{m}$ in the near IR and $12\text{ }\mu\text{m}$ in the MIR with a few dB m^{-1} optical losses. Such attenuation are obviously far from silicate optical fiber which are suitable for long distance communication, but are largely sufficient for smaller scale application like remote spectroscopy with few meters of fibers. Indeed, as it is shown, the TAS glass fibers permit to record spectra in the range $4000\text{--}900\text{ cm}^{-1}$ with a good signal-to-noise ratio.

3. Results and discussion

3.1. Pilot scale tests

Pilot scale tests were conducted in an artificial aquifer system developed in Vienna at the IWGA institute. The tank contained 1 m^3 of simulated polluted water and was

filled with gravel. The measurement series was initiated using tetrachloroethylene (C_2Cl_4) as the pollutant. It was dissolved in 10 dm^3 of water using methanol as a dissolving agent. During the migration of the contaminants through the tank, the signals of the sensor systems were logged to a PC.

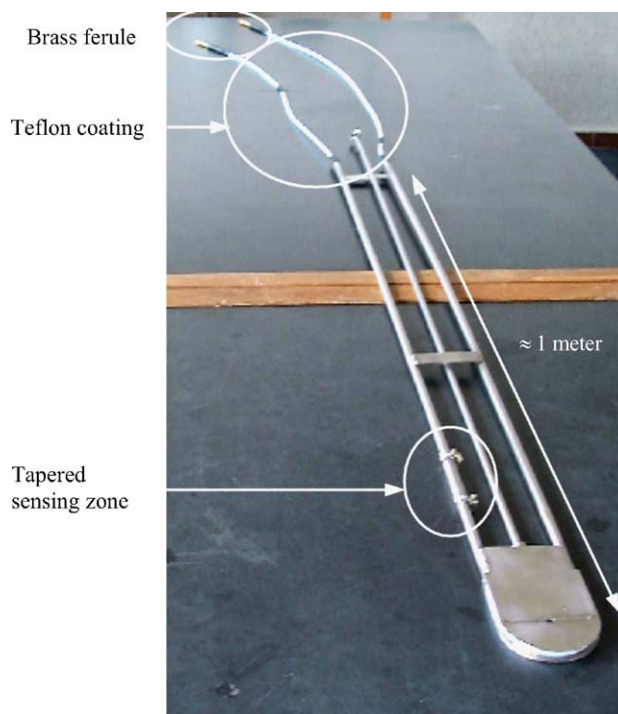


Fig. 5. Photography of the sensor used for the campaign of measurement in field.

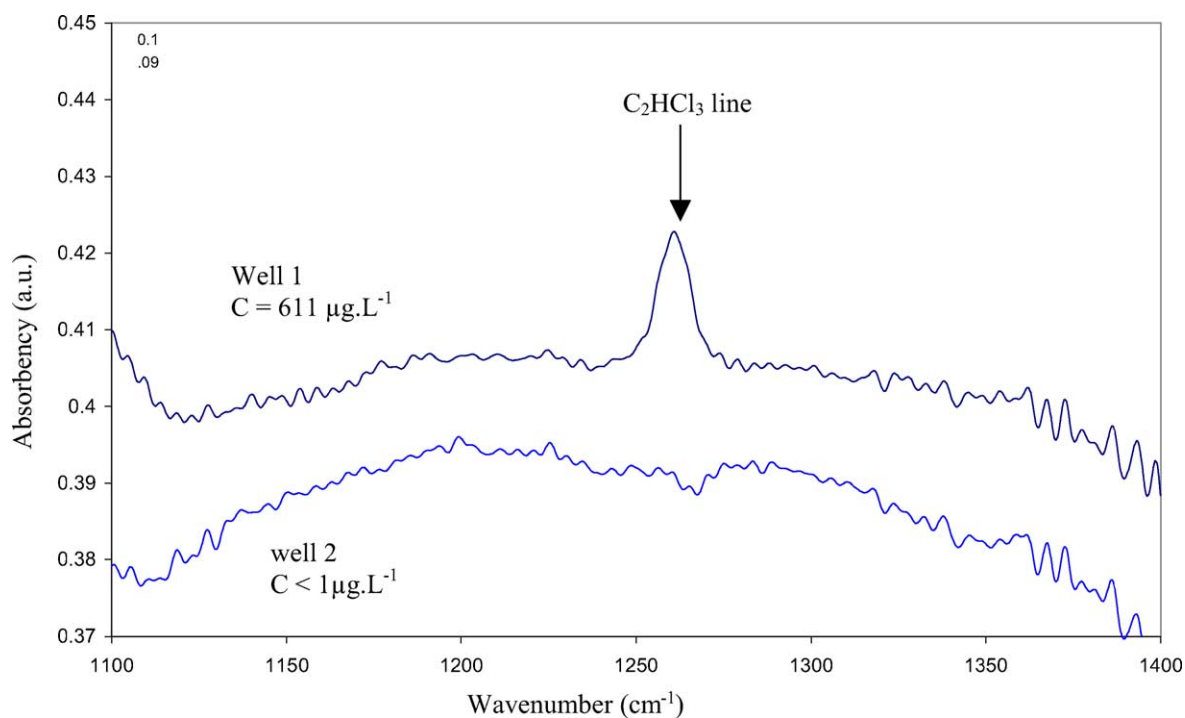


Fig. 6. Spectra recorded near Paris in an industrial fallow land mainly polluted by trichloroethylene (C_2HCl_3). The absorption band of C_2HCl_3 at 1255 cm^{-1} is clearly evidenced for the well 1 and not detectable for the well 2 in agreement with the chemical analysis results.

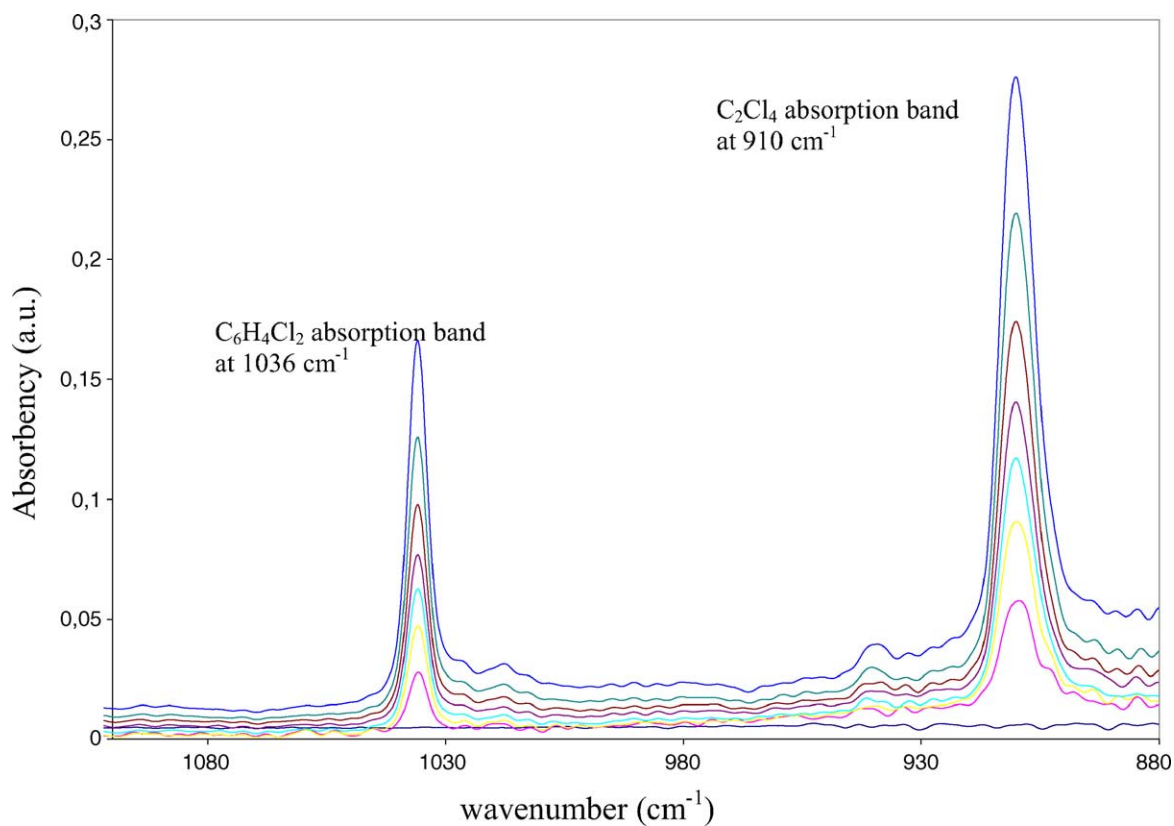


Fig. 7. Spectra recorded in Munich in a natural aquifer. It encompasses the both bands of C_2Cl_4 at 910 cm^{-1} and of $\text{C}_6\text{H}_4\text{Cl}_2$ at 1036 cm^{-1} showing that several pollutants can be detected simultaneously.

Simultaneously, samples for chemical analysis were drawn out from the wells at periodic intervals. The IR spectra (Fig. 3a), from 4000 to 900 cm^{-1} , encompass numerous absorption bands due to: the water of the solution, the carbon dioxide of the air, the Se–H and O–H residual bonds present in the TAS glass. Overall, the C_2Cl_4 is also identified using the absorption feature of the C–Cl stretching vibration at 910 cm^{-1} . In Fig. 3b, one can check that the absorbency of this absorption line increases linearly with the concentration of pollutant in agreement with the pseudo Beer–Lambert law

$$A = \varepsilon(\lambda)lc$$

where $\varepsilon(\lambda)$ is the extinction coefficient, l the length of immersion of the fiber, and c is the concentration. Note that this correlation cannot be generalized. Indeed, some experiments lead in the laboratory on ethanol/water mixtures showed that the increase of the ethanol line absorbency is not linear in the whole range of concentration (Fig. 4). This behavior is attributed to the hydrophobic property of the TAS glass which enhances the ethanol absorption lines to the detriment of the water ones. Nevertheless, for low concentration in aqueous solution, the Beer–Lambert law remains a good approximation.

From these pilot scale experiments, it appears that the sensor permits access to the absorption band positions of much

of pollutants thanks to the large window of transmission of the TAS glass from 800 to 4000 cm^{-1} . Overall, it has been proved that the original design of the tapered fiber enabled detection of weak concentrations down to about 1 mg dm^{-3} although no selective polymer was applied on the fiber. Nevertheless, these optical fibers should be durable under various natural working conditions in ground water and soil. At this time, the fibers, even protected by polymer, were not easily handled because of their weak mechanical properties.

3.2. On field experiments

For the experiments carried out in rougher real-world campaigns, a proper protection was applied on the sensor. Firstly, the fibers were coated, on line during the drawing process, with a polymer that make them easier to handle and reinforced their mechanical properties. Then the coated fibers were inserted into Teflon tubes. Finally, these tubes took place in a metallic housing, thus, constituting a complete captor (Fig. 5). The both fiber extremities were introduced into two brass ferules that permit a perfect aligning with the focus mirror of the spectrometer.

The first campaign of measurement was organized near Paris in an industrial fallow land. This industrial site was expected to be polluted mainly by trichloroethylene

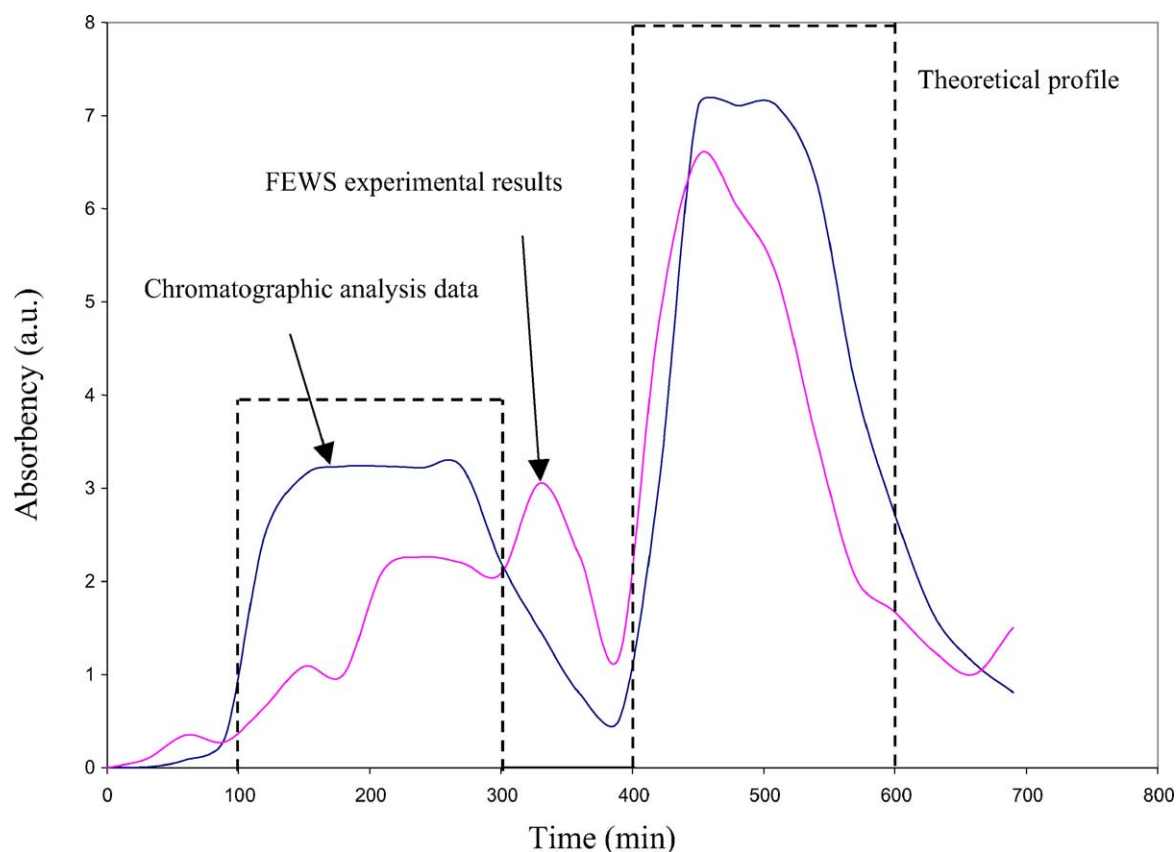


Fig. 8. Comparison between the evolution of the intensity of the $\text{C}_6\text{H}_4\text{Cl}_2$ line and the chromatographic analysis. The dotted line plot the profile of the pollutant concentration as introduced in the aquifer.

(C_2HCl_3). Chemical analysis measurements had shown that the C_2HCl_3 concentrations were $611 \mu\text{g dm}^{-3}$ in the monitoring piezometer well (labeled 1) and less than $1 \mu\text{g dm}^{-3}$ in the second one (labeled 2). The water of both wells was probed by the captor. In Fig. 6, the absorption band of C_2HCl_3 at 1255 cm^{-1} is clearly evidenced for the well 1 and not detectable for the well 2 in agreement with the chemical analysis. This experiment proved that the captor was a reliable tool to detect pollutant in real-world condition as soon as its concentration is high enough.

The second campaign took place outdoors in Munich at the Technique University where a natural aquifer system was built. This real-world conditions site enabled in situ studies of the sensor response and spreading of the pollutants injected into the system with controlled ground water flow. The sensor was immersed into a monitoring well at a distance of about 3 m downstream of the sample inlet and at a depth of 0.3 m. The dichlorobenzene ($C_6H_4Cl_2$) and the tetrachloroethylene (C_2Cl_4) were used as the pollutant analytes and injected in the inlet of the aquifer. Within 2 h, the pollutants were identified in the fingerprint region of the spectrum ($1100\text{--}800 \text{ cm}^{-1}$) as shown in Fig. 7. As already said, the absorption band at 910 cm^{-1} is due to the C–Cl stretching vibration, whereas $C_6H_4Cl_2$ exhibits a band at 1036 cm^{-1} , which is an aromatic C–Cl stretching vibration. In agreement with pilot scale experiments, the limit of detection is around 1 ppm (1 mg L^{-1}) for both pollutants. In order to check the ability of the sensor to detect a given evolution of the pollution rate, the analytes were introduced following a well-defined profile of concentration versus time. Simultaneously to the optical sensor measurements, samples were taken from the wells at periodic intervals for chemical analysis by head space gas chromatography. As shown in Fig. 8, the chemical reference analysis data are in agreement with the injected pollutant concentration profile. Concerning the optical fiber sensor the results are fairly good for $C_6H_4Cl_2$ (Fig. 8), nevertheless for C_2Cl_4 it was not possible to detect the drop of concentration induced after 350 min. Nevertheless, these measurements proved that such a sensor is able to discriminate simultaneously both pollutant in real-world conditions and permit to give the general evolution of their concentration versus time.

4. Conclusion

Due to its large window of transmission and their low optical losses, the TAS glass fiber permits access to the absorption bands positions of pollutants. The detection of weak concentrations of pollutants, down to 1 mg L^{-1} (1 ppm), was made possible, thanks to the original design of the fiber including a tapered sensing zone. Knowing that chalcogenide glass are very stable against water or air chemical aggression, these results are promising in view of installing some permanent checking devices into wells to control the rate of pollutants in waste water of landfill.

In the future, several improvements are expected concerning directly the sensor. Firstly, the use of an hydrophobic selective polymer on the sensing zone should enhance the infrared signal of pollutants. Secondly, a new drawing tower will be available in the laboratory within few months that will be able to play with the fiber diameter on line with a large accuracy. This new equipment will permit, on one hand to enlarge the fiber extremity diameter to facilitate the injection of the light into the fiber, on the other hand to reduce again the diameter of the sensing zone. Overall, it will be of great benefit to install the tower in a clean room or at least to use a class: 100 dust-free hood while drawing.

A FTIR broad band spectrometer, such as the Bruker 22, is a high-performance equipment since they permits to record the whole MIR spectra in no more than 1 min with a good sensitivity. Nevertheless, such equipment is large and heavy making the present set up quite uncomfortable to handle during in field experiments. No doubt that alternative methods have to be thought like in ref. [9], devoted to the development of a miniaturized spectrometer. From this point of view, the coupling of IR Laser diodes with TAS glass fibers, could be a promising track that we will explore in a next future.

Acknowledgements

This work is supported by the environment French agency (ADEME) and takes place within the framework of the European IMSIS contract (In-situ Monitoring of landfill related contaminants in Soil and water by Infrared Sensing).

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