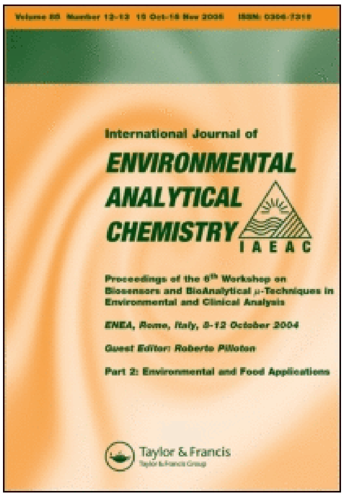

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Combination of a Mid-infrared Hollow Waveguide Gas Sensor with a Supported Capillary Membrane Sampler for the Detection of Organic Compounds in Water

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COMBINATION OF A MID-INFRARED HOLLOW WAVEGUIDE GAS SENSOR WITH A SUPPORTED CAPILLARY MEMBRANE SAMPLER FOR THE DETECTION OF ORGANIC COMPOUNDS IN WATER

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A Fourier transform infrared (FT-IR) spectroscopy based gas sensor for continuous analysis of liquid phase samples has been developed, coupling a short hollow waveguide (HWG) gas cell with a supported capillary membrane sampler (SCMS) probe. Passing an inert carrier gas through the thin-walled tubular silicon membrane enables the permeation of volatile organic compounds (VOCs) present in aqueous solution and facilitates their continuous and quantitative detection in the infrared hollow fiber by multiple internal reflection spectroscopy. The sensitivity of the sensor system has been determined at the ppb (μg/L) concentration level and the response time ranges from few minutes to 30 min, depending on the analyte and the permeation properties of the sampling membrane.

The experimental set-up consists of Bruker Vector 22 FT-IR spectrometer with an externally aligned 50 cm long silica HWG coupled to the SCMS, which is immersed into a glass flask filled with analyte solution and kept under constant stirring.

Aqueous solutions of benzene, toluene, xylene isomers and chloroform were qualitatively and quantitatively analyzed confirming the feasibility of this sensor approach for environmental analysis.

Keywords: IR sensor; FT-IR; Hollow waveguide; Capillary membrane sampler; Volatile organic compounds (VOCs); Water analysis

INTRODUCTION

Environmental monitoring situations demand the operation of *in-situ* analytical tools for direct continuous detection of hazardous contaminants in water, such as volatile

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organic compounds (VOCs). Sensor systems potentially provide real-time information, avoiding delicate sampling steps and extensive laboratory analysis. Monitoring of VOCs is required for the surveillance of drinking water resources (e.g. reservoirs and rivers), for wastewater discharges and for urban storm water, in order to estimate mass loadings and biological effects. In general, pollution analysis requires low detection levels in the sub-ppm concentration range along with sufficient substance specificity.

The combination of a hollow waveguide gas sensing technique coupled to Fourier transform infrared spectroscopy with a tubular capillary membrane sampling system detects trace amounts of organic compounds in aqueous solution, despite strong background absorptions of the water matrix. Short measurement times, rapid response, minute maintenance and unambiguous identification of individual species enable a wide range of applications. Initially developed for medical applications [1], hollow waveguides have been fabricated from different materials also for gas sensing applications [2,3], finding new applications for direct gas detection [4,5] and for analysis of volatile organic compounds in a soil, utilizing long hollow waveguides in a coiled geometry [6].

The developed optical sensor consists of several modules: a FT-IR spectrometer, a hollow waveguide sensing module, acting simultaneously as light transmitting device and as sampling/measurement cell, an extracting probe enabling analyte transfer from the liquid to the gas phase and a detector.

A hollow waveguide can be described as light pipe made from dielectric or metal materials, enabling propagation of infrared radiation in the hollow core due to reflection at the inside walls. Transmission losses are therefore determined by the reflectance of the waveguide walls. Hence, metal or metal-coated glass pipes do not transmit light very efficiently, since a small percentage of light energy is absorbed at each reflection at the metal surface.

Hollow waveguides may be differentiated into two categories: (i) Waveguides made from inner core materials with refractive indices greater than one transmit light via multiple internal reflections according to Snell's law (*leaky guides*); (ii) Waveguides made from inner wall materials with a refractive index less than one, which transmit light according to attenuated total reflection (*ATR guides*) [7].

Leaky guides largely increase the reflectance with an optical interference film coated onto the inner wall of the structural tube [8]. Therefore, dielectric internally coated metal waveguides, such as Ge, AgI, or ZnS coated Ag waveguides show excellent light transmission in the mid-IR range (3–15 µm). The thickness of the layer can be optimized for specific optical requirements [9].

Hollow waveguides are useful tools in chemical analysis, since liquid or gaseous samples can be presented in its bore. Furthermore, the internal hollow core is an efficient lightguide for remote sensing applications. Additionally, the mid-IR spectral range provides information with high molecular specificity, allowing clear distinction of classes of compounds and individual species. Due to multiple internal reflections, which enlarge the effective optical path length, the waveguide acts as a low-volume multi-pass gas cell with increased sensitivity. In addition, the optical efficiency, described by the ratio of the optical path to the cell volume, is substantially enhanced for a HWG in respect to a traditional gas cell. In case of a hollow waveguide, the optical efficiency is approximately 20 times better than for conventional gas cells of equal length [10].

Coupling of hollow waveguides to a conventional FT-IR spectrometer enables continuous gas monitoring with an on-line sensor system. The combination of the presented system with the supported capillary membrane sampler extends this measurement principle to liquid phase samples.

The membrane-sampling device coupled to the hollow waveguide/FT-IR spectrometer module enables quantitative detection of organic compounds in water with inexpensive maintenance utilizing commercially available components.

The SCMS (see Fig. 1) is in fact designed for continuous extraction of highly volatile organic compounds at equilibrium conditions from complex aqueous matrices into the gas phase [11]. The extraction module consists of a stainless steel probe with a length of 15 cm, with a thin-walled tubular silicone capillary membrane coiled around the support probe and connected to a gas inlet/outlet at the top.

The outer wall of the permeation tubing is in direct contact with the aqueous sample stream, allowing the analyte molecules to permeate from the bulk sample through the wall of the polymer membrane and to desorb into an inert carrier gas stream.

The permeation process is mainly governed by the permeability of the sample molecules through the polymer membrane and the vapor pressure of the analyte molecules.

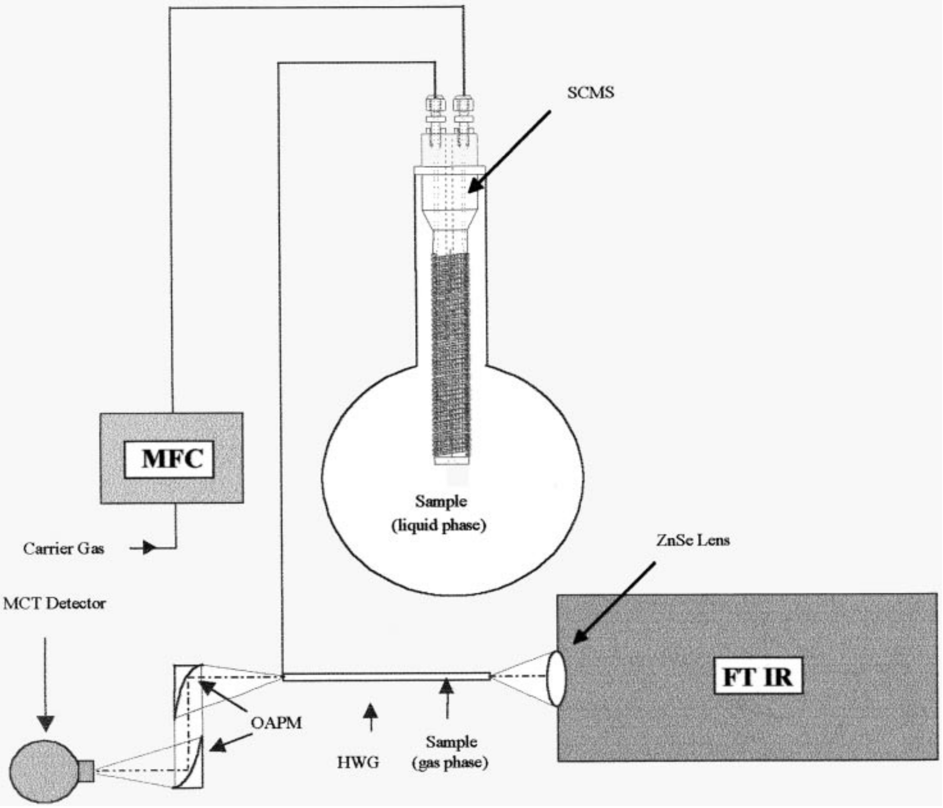

FIGURE 1 Experimental set-up including the SCMS probe, FT-IR spectrometer and hollow waveguide gas sensing module.

The length of the permeation tube and the flow rate of the carrier gas are adjusted, in order to ensure equilibrium conditions for the continuous extraction of analyte molecules from the aqueous phase into the gas phase.

The present work demonstrates the feasibility of continuous, accurate and reproducible measurements with the combination of a compact capillary extractor and a FT-IR based hollow waveguide gas sensing system.

The detection of an analyte mixture containing benzene, toluene and xylene isomers (BTX) clearly indicates that the investigated compounds yield different response times, depending on their specific permeability through the silicone membrane.

Moreover, the effect of the sample temperature has been investigated and it is shown that the capability of quantitative multi-component analysis is provided.

Finally, the determination of chloroform ($CHCl_3$) confirms a limit of detection down to the low (μg/L) concentration level.

EXPERIMENTAL

Equipment

The experimental set-up shown in Fig. 1 consists of a Vector 22 FT-IR spectrometer (Bruker Optik GmbH, Ettlingen, Germany), with an externally aligned straight HWG coupled to the SCMS probe by a set of stainless steel tubings.

A ZnSe lens ($f = 3.8$ cm, Macro Optica Ltd., Moscow, Russia) focuses radiation from the FT-IR spectrometer, equipped with a SiC light source, into the hollow core of the fiber. Two x, y, z-positioners (Newport, Irvine/CA, USA) hold a straight section of hollow waveguide and allow facile adjustment for efficient light coupling. The distal tip of the fiber is capped with a custom made connection module equipped with an anti-reflection coated ZnSe window, which allows simultaneous coupling of the radiation into the waveguide, while the gaseous sample is constantly transported through the hollow core of the fiber. Hollow waveguides applied during this study are made from silica structural tubes coated on the inside with an IR-reflective silver layer and protected with a dielectric silver iodine (AgI) coating [12]. The core diameter of the HWG is 1.1 mm and the length 510 mm [13,14]. This waveguide shows optimum transmittance in the mid-infrared spectral region from ~6.25 to 16.7 μm, a comparatively low attenuation of 0.5 dB/m (at 10.6 μm) and high transmission (70%) up to 240°C [15,16]. The waveguide length has been optimized for gas sensing purposes [10].

A LN_2 cooled mercury–cadmium–telluride (MCT) detector (D316, Infrared Associates, Stuart/FL, USA) detects the optical signal and a set of 2 off-axis parabolic mirrors (OAPM, $f = 4.6$ cm, Janos Technology Inc., Townshend/Vermont, USA) collects and focuses the radiation onto the 2 mm × 2 mm detector element.

The SCMS is immersed into a glass flask, filled with the analyte solution and kept under constant stirring. The carrier gas (air or nitrogen) stream is controlled via a mass flow controller (MFC 5850E, Rosemount Inc., Chanhassen/MN, USA) and a portable digital flow meter (Analyt GmbH, Wuppertal, Germany). Gas flows through the silicone permeation tube and exits the SCMS through a second 400 mm long stainless steel tube, which is directly connected to the HWG sensor module.

Absorption spectra are recorded with a spectral resolution of $4\,\mathrm{cm}^{-1}$, averaging during a measurement time of 30 s.

Materials and Detection Procedure

Benzene, toluene, *m*-xylene, *p*-xylene, *o*-xylene and chloroform were obtained from Sigma-Aldrich (Munich, Germany). Stock solutions were prepared by sampling the pure substances with 0.5–10 μL or 10–100 μL micropipettes, respectively, and further dilution for less concentrated samples. Between 0.3 and 3% (v/v) methanol (Sigma-Aldrich) has been added to the aqueous BTX solution, in order to ensure complete dissolution at high concentrations. Methanol does not spectroscopically interfere with the evaluated absorption bands of the analytes.

BTX compounds were detected immersing the SCMS probe through the neck of a 500 ml flask and keeping the bulk solution under constant stirring with a teflon stir bar. Nitrogen (99.99%) was used as carrier gas for the BTX determination and atmospheric compressed air for the chloroform detection.

For BTX measurements, a nitrogen flow rate of $200\,\mathrm{cm^3\,min^{-1}}$ was selected after optimization. For higher concentrations (0.05% – 50 mg/L) of chloroform solutions, a flow rate of $45\,\mathrm{cm^3\,min^{-1}}$ was established to be appropriate; for lower concentrations (50 mg/L–750 μg/L), a flow rate of $7\,\mathrm{cm^3\,min^{-1}}$ was selected in order to achieve maximum sensitivity.

Each measurement was made after purging the stainless steel tubings and the hollow waveguide with pure carrier gas, and verifying spectroscopically the absence of any analyte absorption with the probe immersed into water.

RESULTS AND DISCUSSION

Optimization of the System

Chemically similar compounds can be distinguished due to their characteristic absorption frequencies. Especially in the fingerprint region of the mid-IR classes of compounds and individual substances can be differentiated with superior discrimination power. Due to the transition from the liquid to the gas phase enabled by the membrane sampler, benzene, toluene, *m*-xylene, *p*-xylene and *o*-xylene (BTX) have been simultaneously analyzed in aqueous solution from the ppm region down to 750 μg/L. Therefore, the spectroscopic sensing method described here demonstrates multi-component analysis of one of the environmentally most relevant classes of pollutants. Due to their distinct vibrational spectra, benzene (absorption band at $674\,\mathrm{cm^{-1}}$), toluene ($728\,\mathrm{cm^{-1}}$) and *ortho*-, *meta*- and *para*-xylenes (742, 767 and $794\,\mathrm{cm^{-1}}$, respectively) have been simultaneously analyzed in an aqueous mixture.

Since the described sensing system is mainly sensitive to changes in temperature and stirring rate, influencing the permeation processes for each volatile organic compound, optimization of the measuring conditions and determination of suitable calibration procedures is required.

Permeation at Different Temperatures

Table I shows permeation times of five BTX compounds registered at different temperatures. It is evident that the time required for the permeation of each individual compound is strongly dependent on the temperature. Benzene permeates the applied silicone membrane before toluene, *o*-xylene, *m*-xylene and *p*-xylene.

TABLE I BTX permeation times (minutes) at six different temperatures, measured at t_{90} values. Concentration is 30 mg/L, flow rate 200 cm^3 min^{-1}, stirring velocity 750 rpm and the stainless steel connection tubing has a length of 40 cm

Temperature	*18*°C	*20*°C	*30*°C	*40*°C	*50*°C	*60*°C
Benzene	6	4	2	2	1	1
Toluene	17	12	2	2	1.5	1.5
Xylenes	22	19	5	5	3	2

TABLE II Sensitivity gain by evaluating peak areas at higher temperature compared to analysis at 20°C as reference

Temperature	*30*°C	*40*°C	*50*°C	*60*°C
Benzene	175%	183%	225%	284%
Toluene	274%	259%	353%	420%
o-Xylene	205%	260%	182%	173%
m-Xylene	259%	296%	198%	189%
p-Xylene	277%	311%	200%	186%

In order to determine the optimum working temperature for the calibration procedure, detection improvements for each aromatic compound were considered at different temperatures (Table II). Experiments have shown that an optimal temperature maximizing the sensitivity for each individual species during simultaneous determination is not achievable. Hence, 40°C was selected as compromise between the most significant detection improvements gained for the weaker spectral features of the xylenes and minute improvements gained for toluene and benzene at that temperature. For target analysis addressing individual species, the measurement conditions would be adapted accordingly.

In addition, previous experiments carried out with alcohols extracted from aqueous solution have shown that the sensor system operates more reliably at lower temperatures [17]. In case of ethanol, 40°C was determined to be the optimum temperature in order to obtain results with maximized reproducibility.

Furthermore, the overall sensitivity of the system is influenced by the stirring conditions. Increased stirring rates result in enhanced mass transport of molecules to the silicon membrane surface and consequently increase permeation efficiency. During the described experiments, the bulk solution was stirred via a magnetic stir bar. Positioning the SCMS module with an off-set from the flask center along with mechanical stirring has been confirmed as an alternative set-up creating turbulence more efficiently around the rod-shaped probe, which results in further sensitivity enhancement.

Multicomponent Diffusion Effects

Competitive effects have been observed due to multi-component permeation through the SCMS membrane. Continuous and undisturbed extraction of each individual compound is adversely affected by competitive permeation of other compounds. Resulting, the spectroscopic signal of each compound transported by the carrier gas into the hollow waveguide decreases, as shown in Fig. 2. Simultaneous detection of multiple compounds affects the overall stability of the system until the last component permeates through the membrane: only at that time an equilibrated mixture of all five components

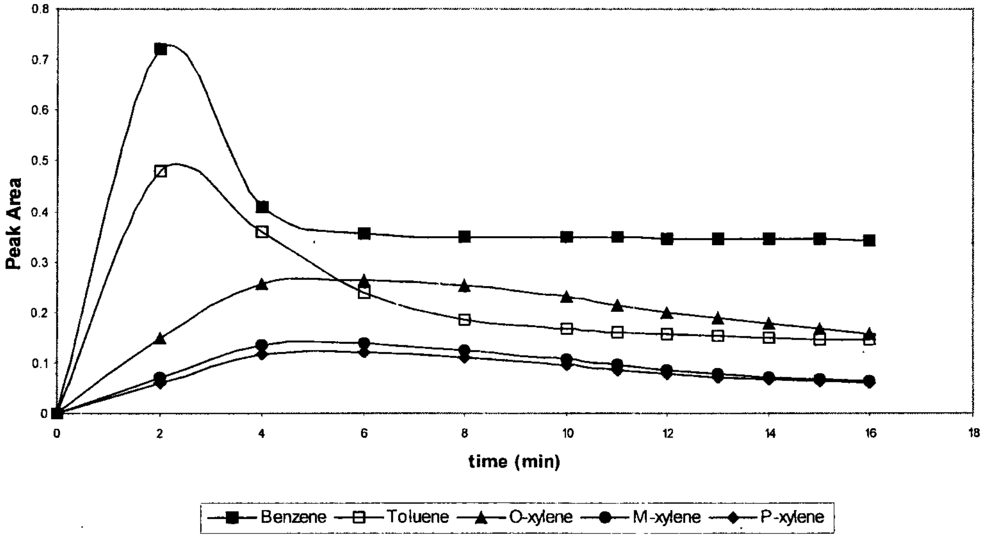

FIGURE 2 Simultaneous permeation of five BTX components at 30°C (flow rate 200 cm^3 min^{-1}, stirring velocity 750 rpm). Equilibrium curves are obtained integrating the peak areas of 11 different spectra acquired over a period of 16 min monitoring time.

will constantly permeate through the membrane. In case of the reported experimental examples, a mixture of BTX compounds reaches the optical gas cell after 15 min of continuous permeation of the multi-component standard at the described experimental conditions, producing a stable signal.

Response Time to Concentration Changes

The system response time to variations of the sample concentration from 4 to 5 mg/L was found to be few minutes (temperature 20°C, stirring rate 750 rpm, gas flow rate 200 cm^3 min^{-1}).

One ppm of each compound has been injected into the 4 mg/L solution, which was continuously stirred. The saturation values were determined to be reached at 3.5, 5, 7, and 9 min of continuous extraction for benzene, toluene, *m*-xylene simultaneously with *p*-xylene, and *o*-xylene, respectively (Fig. 3). These permeation times are in agreement with the results obtained during the calibration procedure.

System Calibration

Four different concentrated solutions have been analyzed: 30, 3 and 1 mg/L and 750 µg/L; the concentration values refer to each individual compound. All reported BTX measurements have been repeated at least three times, enabling statistical evaluation of the calibration curves. The obtained results are reported in Table III. Measurements have been carried out at the optimum operating temperature of 40°C, at constant stirring rate (750 rpm) and operating with a nitrogen flow of 200 cm^3 min^{-1}. The calibration curves show excellent correlation coefficients (in all cases > 0.99); the detection accuracy (see standard deviations in Table III) depends on the exact timing of the spectrum acquisition and on the competitive permeation efficiency during multi-component analysis, as

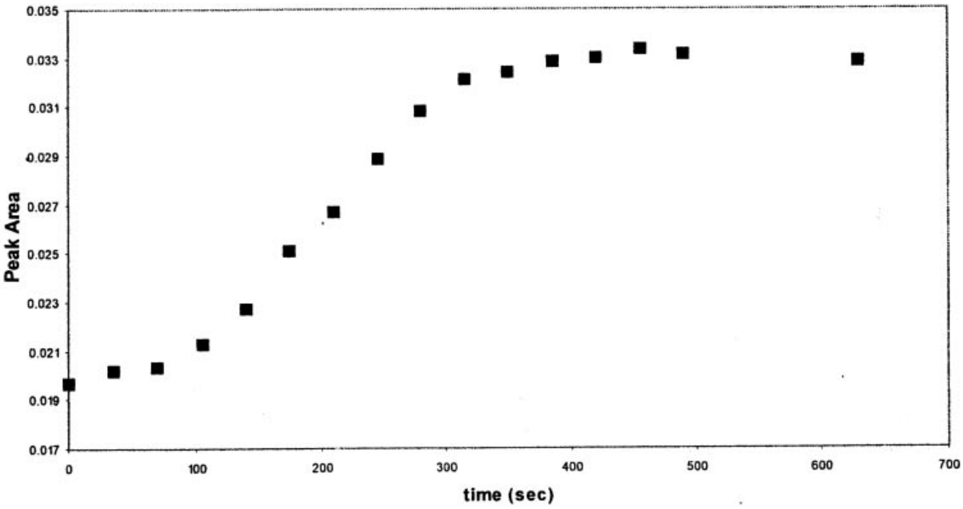

FIGURE 3 Equilibrium curve of toluene after injection of 1–4 mg/L BTX solution. It $t = 0$ is the time of the injection, toluene reaches the equilibrium value at approximately $t = 300$ s (t_{90} standard). Benzene and the xylene isomers show similar behavior.

previously described. Additionally, spectral interferences from CO_2 in the ppb range affect precise and reproducible analysis, particularly for benzene, especially at the lowest concentration level. In fact, the experimental set-up has an ~15 cm long unprotected optical path and atmospheric CO_2 bending vibrations create interferences with out-of-plane hydrogen vibrations of benzene and toluene. Hence, future sensor systems will emphasize reduction of CO_2 in the optical path ensuring constant measurement conditions. Operating with a high flow rate (200 cm^3 min^{-1}) efficiently reduces the influence of gaseous CO_2 between the open HWG tip and the ZnSe lens.

In case of chloroform detection, the system was operated at higher flow rates for data acquisition in the 500–50 mg/L calibration range, evaluating the peak areas at 1219 cm^{-1}. For the 5 mg/L–750 μg/L concentration range the peak area at 772 cm^{-1} has been evaluated at a lower flow rate for increased detection sensitivity (Fig. 4a). Chloroform measurements have been performed at a temperature of 20°C. Magnetic stirring at 750 rpm has been applied. For these conditions, the linear correlation coefficient between concentration and evaluated peak area is 0.98 (Fig. 4b) and confirms linear response of the developed sensor over more than two orders of magnitude.

With the application of novel IR light sources, such as quantum cascade lasers, further improvement of the detection limits can be expected [18].

CONCLUSION

We have investigated and demonstrated the application of a hollow waveguide IR sensor system for the determination of volatile organic compounds down to sub-ppm concentration levels. Combining the advantages of a hollow waveguide sampling cell, including enhanced optical efficiency and rapid response time due to the reduced sample volume with a supported capillary membrane sampler enables continuous monitoring of organic compounds in aqueous solution. Based on these results, it can

TABLE III Integrated peak areas of investigated BTX compounds, from 30 mg/L to 750 µg/L. Experimental points are evaluated as average of three different, integrated spectra at each concentration. Standard deviations range from less than 1% (30 mg/L solution) up to 50% at low concentrations of benzene. In case of the evaluation of benzene peaks at low concentrations, strong spectral interferences of CO_2 have been observed

Concentration (mg/L)	*Benzene*		*Toluene*		o-*Xylene*		m-*Xylene*		p-*Xylene*	
	Average	*St. deviation %*	*Average*	*St. deviation %*	*Average*	*St. deviation %*	*Average*	*St. deviation %*	*Average*	*St. deviation %*
0.75	0.000752	50.7	0.005856	18.7	0.001268	6.6	0.002561	15.7	0.004102	26.1
1	0.004896	7.7	0.004147	19.2	0.007569	10.5	0.001795	11.3	0.002960	7.0
3	0.013328	12.0	0.007805	5.8	0.011766	15.3	0.004453	44.6	0.004467	16.6
30	0.365	0.6	0.018852	19.3	0.266358	17.5	0.117602	28.1	0.104674	27.0

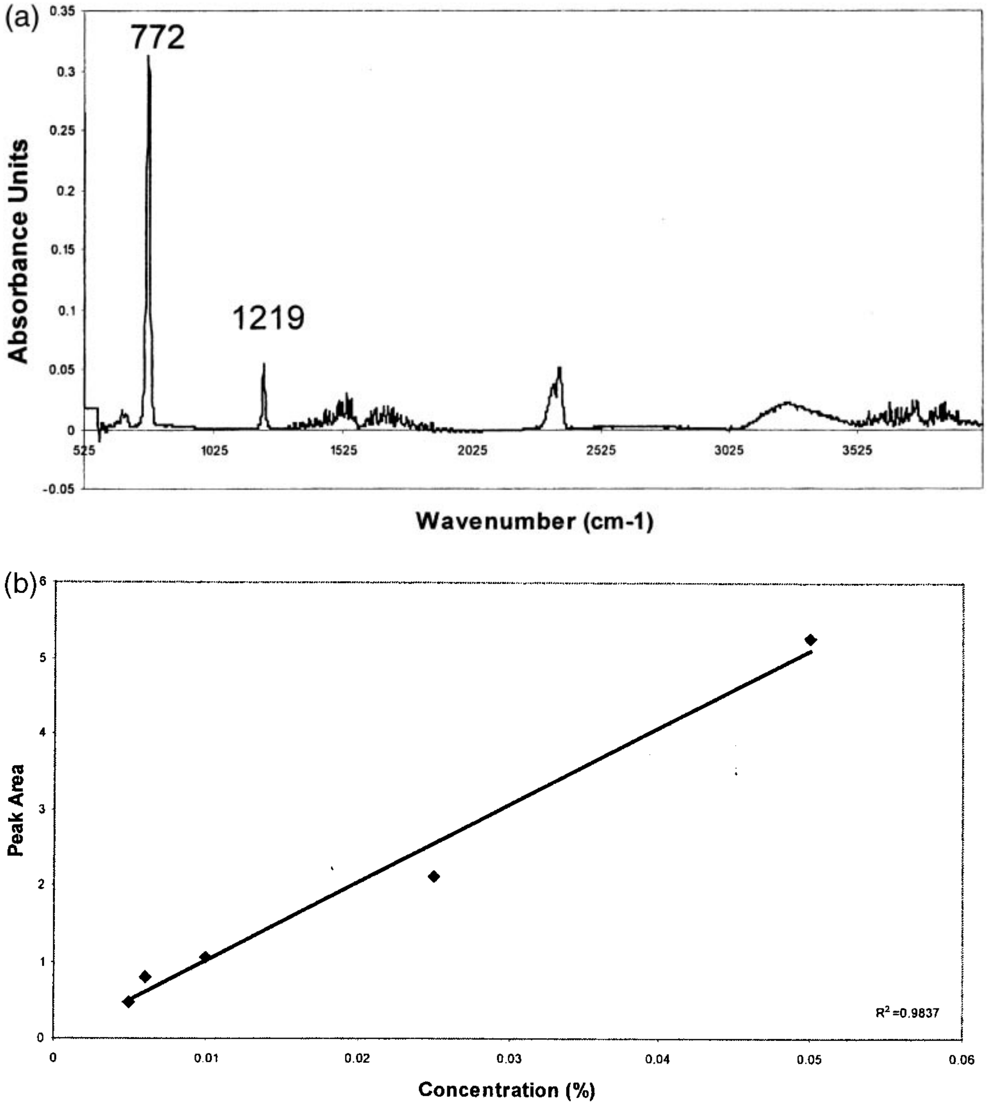

FIGURE 4 (a) Chloroform spectrum recorded with the HWG/FT-IR sensor system (500 mg/L, flow rate 45 $cm^3 min^{-1}$, temperature 20°C). (b) Chloroform calibration curve in the 50–500 mg/L concentration range obtained by five single measurements.

be concluded that the developed hollow waveguide IR gas sensing system provides high efficiency, reproducibility and rapid measurements for environmental monitoring of multiple organic compounds in aqueous solution.

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