Online sensing of volatile organic compounds in groundwater using mid-infrared fibre optic evanescent wave spectroscopy: a pilot scale test


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Abstract A prototype sensing system for in-situ monitoring of volatile organic compounds in contaminated groundwater was tested at a pilot scale plant. The sensor consists of a commercially available Fourier transform infrared spectrometer, connected to a 6 m long infrared transparent silver halide fibre optic cable. A 10 cm long core-only section at the centre of the fibre is mounted on a sensor head and coated with a hydrophobic polymer layer, while the remaining fibre is protected by Teflon tubing and thus not in contact with the surrounding media. The sensor head was immersed into the monitoring wells of the pilot plant testing the sensor system under circumstances close to field conditions and typical for in-situ measurements. The pilot plant consists of a 1 m³ cubic tank filled with gravel. A pump is used to circulate water horizontally through the tank, simulating a natural aquifer. The evolution of the concentration of analytes injected into the system is monitored with time using the developed prototype sensing system. The results are validated by corresponding sampling and analysis with headspace gas chromatography.

Keywords IR sensor; landfills; poly(ethylene-co-propylene); polymer coating; silver halide fibre; volatile organic compounds

Introduction The analysis of organic pollutants in groundwater, landfill effluents and sewages mainly relies on discontinuous methods involving three phases: (i) on-site sampling, (ii) transportation of the sample to the lab and (iii) analysis of the sample (CEN, 1997; CEN, 1994). However, immediate action would benefit from an analytical device providing qualitative and quantitative information in-situ and close to real time (Holst and Mizaikoff, 2002; Mizaikoff, 1999). The IMSIS probe, developed during a European Union project (IMSIS, “In-Situ Monitoring of Landfill Related Contaminants in Soil and Water by Infrared Sensing”, EVK1-CT-1999-00042), combines the advantages of inherent selectivity in the mid-infrared (MIR) spectral region with molecular recognition based on enrichment of analyte molecules into hydrophobic polymer layers (Goebel et al., 1995; Jakusch and Mizaikoff, 2001; Mizaikoff et al., 1995). The envisaged application of this sensor system targets continuous monitoring of groundwater conditions at or near contaminated sites with particular emphasis on volatile organic compounds (VOCs). The developed sensor utilises evanescent wave spectroscopy (EWS) based on total internal reflection (TIR) as the measurement principle (Griffiths and de Haseth, 1986; Jakusch et al., 1997). TIR occurs when light from an optically denser medium is incident at the boundary to an optically thinner
medium at an angle greater than the critical angle (Harrick, 1967). At each reflection a standing wave ("evanescent wave") forms which penetrates exponentially, decaying into the adjacent optically thinner medium. Molecules within the penetration depth of the standing wave can absorb light from the evanescent field enabling optical measurements similar to conventional absorption spectroscopy. The hydrophobic polymer layer fulfils several tasks.

- Hydrophobic molecules (e.g. tetrachloroethylene (TeCE) or BTX compounds (benzene, toluene, xylene)) are enriched in the polymer coating by diffusion. The partition coefficient $\log K$ for the transition of molecules between the aqueous phase and the polymer layer typically varies between 2 and 3. Analyte molecules are enriched within the penetration depth of the evanescent field, leading to an enhanced characteristic absorption.

- Due to the hydrophobic nature of the polymer water, a strong absorber in the IR, is excluded to a great extent from the polymer layer. Varying water absorption is observed only when the dry polymer is brought into contact with water for equilibration. The polymer reaches an equilibrium state with the aqueous phase in less then 24 h.

- The polymer layer protects the fibre from physical, chemical and mechanical stress. Silver halide (composition: $\text{AgCl}_x \text{Br}_{1-x}$) is chemically unstable when exposed to UV radiation, base metals or chloride ions. Therefore, a homogeneous polymer coating without cracks or pinholes is a prerequisite.

**Methods**

The sensor prototype is based on a Bruker Vector 22 Fourier transform infrared (FT-IR) spectrometer (Bruker Analytische Meßtechnik GmbH, Germany), a 6 m long silver halide multimode fibre optic cable (Bunimovich and Katzir, 1993) with a diameter of 900 µm and a liquid nitrogen cooled mercury-cadmium-telluride (MCT) infrared detector (Infrared Associates, Florida, U.S.A.). Figure 1 shows a sketch of the optical setup. A 10 cm section in the middle of the fibre was dip coated with a thin layer (3 µm to 5 µm) of poly(ethylene-co-propylene) (E/PCo), in order to enrich volatile organic compounds (VOCs) within the penetration depth of the evanescent field emanating from the fibre surface. The fibre is

**Figure 1** Sketch of the optical system. FT-IR spectrometer with launching optics (left). A 6 m long silver halide fibre connects the spectrometer with the detector (right), where a mirror arrangement is used to focus the signal onto the detector element. The sensor head in the middle of the fibre protects the exposed section against mechanical damage and can be lowered into the monitoring well.
linked to the spectrometer and the detector by a custom made setup utilising off-axis parabolic mirrors aligned with conventional $x$–$y$–$z$ positioners.

Tetrachloroethylene and 1,2-dichlorobenzene (DCB) were selected as model analytes for their relevance at contaminated sites throughout Europe and for their strong and selective absorption in the fingerprint region of the MIR. TeCE and DCB show only very limited miscibility (~ 0.1 g/L) with water (Gujral, 1992; Horvath, 1985a,b; Shaw, 1989). Hence, methanol (MeOH) has been added as a solubility promoter. The analytes were first dissolved in 10 L of tap water at a concentration of 0.2 g/L each (MeOH concentration: 40 mL/L). A saturated sodium chloride (NaCl) solution was added to the analyte concentrate, which enables tracing the analytes by measuring the electrical conductivity, assuming that both NaCl and the analytes distribute homogenously within the plot. The analyte concentration was selected in such a way that the final concentration in the tank was in the low ppm (mg/L) concentration range.

The pilot plot (Figure 2) simulates a section of an aquifer with two groundwater monitoring wells for parallel testing of two sensor systems. Two vertical filter pipes (a) (type: = SBF pb GERMANY DN 150 165x7,5 = 31052 = 99 =) are placed in a 1 m$^3$ container (b) made of PVC filled with gravel (type: RIESL 4–8mm, Herzer Sand- und Kieswerk, A-1220 Vienna).

From the results from pre-tests the flow scheme through the pilot plant was altered twice. In the final setup the groundwater enters the plot at three inlets located at one side of the plot in three different depths and leaves the plot at three corresponding outlets in each of the two monitoring wells, which should result in a horizontal groundwater flow. This setup also ensures that water flows through the monitoring wells instead of circulating around. The velocity of flow is controlled by a multi-channel metering pump (d) connected with Tygon tubes pumping the water in a closed loop through the plot. From a storage tank (e) contaminants and tracer substances can be added to the loop. In each monitoring well sampling possibilities (f) are installed at 3 different depths. Additional sensors can be implemented for tracer experiments (e.g. electrical conductivity sensors). Flow velocity and water level are measured. All pipes are made of Teflon, all fittings of nickel-plated brass.

The pilot plant was filled with local groundwater or drinking water with the water table kept a few centimetres below the soil surface. Then the sensor system and conductivity meters were placed in the wells. Care has to be taken that the polymer coated section of the

Figure 2 Schematic drawing of the plot used for the experiments. The sensor head and the conductivity electrode are introduced into the monitoring well (a). A peristaltic pump (d) is used to circulate the water through the container (b). The container with the analyte solution (e) can be connected to the pump to inject the contaminants into the system. At position (f) reference samples can be drawn. Note that the water has to pass through the monitoring wells, although they have a higher hydraulic resistance than the surrounding gravel.
prototype sensor is exposed to air only for a short time, so that the equilibrium state described above is not disturbed. Therefore the sensor head is stored permanently under water. The multi-channel metering pump was adjusted to a flow volume of 51 L/h. Hence, the volume of water in the tank (350 L) is completely re-circulated once every 6.9 h. Considering the area of flow in the pilot plant with approximately 1 m² this corresponds to a velocity of flow of 1.2 m/d.

The analyte solution was not injected before the sensor readout showed a constant baseline, i.e. not before the polymer coating was in equilibrium with the aqueous phase. After the equilibrium state was reached the analyte solution was injected into the pilot plant through the 3 inlets within a short period of time (approximately 15 min) using the multi-channel metering pump. Subsequently recirculation was started.

During the migration of the contaminant plume through the tank, the signals of the sensor system and the conductivity meters have been logged to a PC. All spectra were recorded in the range between 4,000 cm⁻¹ and 400 cm⁻¹, although, due to the absorption of the materials used, useful information is only contained in the region between 1,550 cm⁻¹ and 650 cm⁻¹. For each spectrum 100 single scans at a resolution of 4 cm⁻¹ were averaged at time intervals of five minutes.

Simultaneously, samples for reference analysis have been collected from the wells in periodic intervals. The sensor head was immersed to a depth so that it was located next to one of the three outlets. Thus, it was ensured that the collected samples have the same properties as the aqueous phase surrounding the sensor head.

Results and discussion

Figure 3 shows the results of one experiment with the analytes TeCE and DCB. TeCE exhibits one spectral feature at 911 cm⁻¹, corresponding to a C-Cl stretching vibration and DCB shows two features in the observed spectral region: one aromatic C-Cl lattice vibration at 1,036 cm⁻¹ and one aromatic out of plane vibration at 748 cm⁻¹. The DCB feature at 1,036 cm⁻¹ is overlapped by the absorption band of MeOH (Hesse et al., 1995). In the beginning of the experiment all three applied measurement principles show the same tendency. Note that the signal rises immediately after the sensor is immersed into the plot, which is due to a residue of TeCE originating from a prior experiment. After the injection of the contaminants is completed the concentration rises steadily. It is also remarkable that the

![Figure 3](https://iwaponline.com/wst/article-pdf/47/2/121/423927/121.pdf)

**Figure 3** Evolution of the concentration of TeCE and DCB measured with the prototype sensor and the reference method, using HS-GC-FID. Note that the concentration rises immediately after the sensor is immersed into the plot, even before contaminants are added. This is due to the fact that the plot was still contaminated with analytes from previous experiments.
integration results from the two DCB bands do correspond very well with each other. However, the concentration measured with the sensor system is higher by a factor of two compared to the results from the reference analysis. This phenomenon is not yet fully understood and subject to further investigation. Previous experiments have demonstrated excellent agreement of TeCE and DCB data with corresponding reference analysis by HS-GC.

At the end of the experiment the sensor was removed from the plot and immersed into distilled water immediately. From Figure 3 it can be seen that it takes about one hour for the concentration to drop to 50% of the initial value.

**Conclusion**

The pilot scale tests have shown that the sensor principle is adequate for the task of on-line and in-situ sensing of VOCs in groundwater at simulated real world conditions. However, several issues still have to be addressed and improved: sensor response time, especially for decreasing concentrations, robust calibration of the sensor system, fibre stability, fibre handling, sensor coating, and alignment of the optical components. Ruggedness of the fibre with respect to physical and chemical factors needs to be improved to reach a state of true field capability. For a field ready system the fibre has to be protected by appropriate tubing, preventing strong bending, which could damage the fibre. Furthermore, fibre contact with base metals has to be avoided. However, these requirements mainly address engineering problems of the fibre connectors mounted at the fiber ends and appropriate sensor head design and polymer coating.

At this stage of development the spectrometer cannot be operated without a power supply and furthermore the detector has to be refilled with liquid nitrogen (LN) approximately every 6 to 8 hours. In a next step towards a more autonomous spectrometer a Peltier- or Stirling-cooled MCT detector or a deuterated triglycine sulphate (DTGS) detector will be implemented.

Sensor response time is a crucial factor. The system has proven that it can follow a rising concentration trend very well, but cannot follow a drop in concentration as fast. This is due to the intrinsic nature of the polymer enriching hydrophobic compounds. As a matter of fact there are analytes (such as perchlorobutadiene), which enrich almost irreversibly in E/PCo and cannot be purged just by means of water. In that case the polymer must be purged with air or a solvent (e.g. MeOH), to remove all traces of the analyte. However, for threshold alarm applications fast sensor response is more crucial than the recovery time. Hence, this concept is feasible for a wide range of continuous pollution monitoring situations.

**References**


