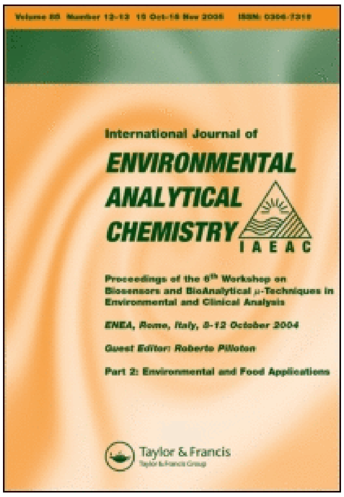

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In situ determination of organic compounds in liquid samples using a combined UV-Vis/fluorescence submersible sensor

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In order to improve the *in situ* evaluation and quantitative analysis of complex contaminations of liquid media such as ground-, surface, and wastewaters, an integrated submersible sensor probe has been developed. It is especially characterized by the option of simultaneously measuring ultraviolet/visible (UV/Vis) and fluorescence spectra. Owing to the compact construction with light sources, flow cell, detection system, and data acquisition/processing unit in the waterproof case, the data transfer to the surface can be realized electrically, and the operation depth is practically not limited. The variability in the measuring techniques allows a wide variety of chemical compounds to be analysed within a broad concentration range. The performance of the new submersible sensor probe was tested *ex situ* in laboratory scale, and the performance was comparable with that of stationary measuring instruments. As an example for an *in situ* application, the sensor probe was successfully used to monitor the migration of chemical substances during a tracer experiment in groundwater. The concentration of the tracer compound uranin (sodium fluorescein) was measured in the range of 5–500 $\mu g\,L^{-1}$ using fluorescence spectroscopy, while at the same time the contents of toluene were continuously detected in the same groundwater wells using the UV/Vis sensor channel.

Keywords: Submersible sensor probe; UV/Vis spectroscopy; Fluorescence spectroscopy; *In situ* measurements; Water analysis; Pollution control

1. Introduction

The *in situ* analysis of liquid samples, especially water as groundwater, surface water, and wastewaters, is a widespread problem in environmental science and technology. Very often, the composition and the spatial distribution of water components, namely pollutants, have to be estimated for risk assessment and evaluation of remediation necessity and success. The direct measurement in the field avoids a number of measuring errors such as undesirable transfer of volatile compounds into the gas phase, adsorption and reactions (e.g. oxidation) leading to non-quantifiable loss of the original substances. Another advantage of the application of sensor probes in comparison with

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conventional *ex situ* laboratory analysis is their suitability for long-term monitoring of the water quality in wells, natural waters, and industrial processes. Owing to the increasing relevance of low-invasive soil and water-cleaning techniques such as natural attenuation and enhanced natural attenuation in remediation practice, *in situ* sensing systems have attracted growing interest. Another important aspect of *in situ* analytical characterization is the inherent potential for process control especially for industrial purposes.

Optical methods such as ultraviolet/visible (UV/Vis) and fluorescence spectroscopy are suitable and established tools to measure a variety of unsaturated and aromatic compounds in liquid samples. Additionally, humic substances (organic polymers) and some inorganic species such as nitrate ions may be detected. Both methods are also successfully used for *in situ* sensors in process analysis and environmental chemistry [1–3]. In many cases, the determination of sum parameters can be used as an indicator for a possible contamination or as general parameter for water quality [4–7].

The application of fluorescence spectroscopy in environmental research (realized in various excitation and detection modes) has been described with various setups and devices representing a wide range of expenditure. The application of special techniques incorporating, for instance, the detection of the relaxation decay or the application of synchronous fluorescence spectroscopy, permits both the determination of distinct substances and the analysis of a spectrum of compounds [8–12]. However, such devices and especially the corresponding *in situ* sensor probes are usually expensive, and special methods of pattern recognition are necessary for evaluating the spectra. When the optical components, the data acquisition, and/or the complexity of the contamination prevent the analysis of distinct substances in the water, fluorometers can still be applied to monitor the water quality by determining various parameters, e.g. content of (aromatic) hydrocarbons, natural organic polymers, chlorophyll, colouring substances, or turbidity [13–15]. Compared with UV/Vis spectroscopy, fluorescence measurements are more sensitive and even allow traces of chemical substances to be detected in aqueous solution.

The light sources and the units for detection and data processing of such fluorometers are mostly positioned outside the *in situ* sensor probe. Therefore, the connection between the optical components in the probe and the detection unit has to be made using optical fibres. Owing to significant light absorbance and solarization in the UV range, the submergence of such *in situ* probes is considerably restricted.

Over the years, submersible sensor probes have been developed, permitting multiple wavelengths measurements for monitoring water quality. An overview is given in [16]. Such devices are available for fluorescence and UV/Vis spectroscopy. However, conventional sensing devices representing the state of the art include systems permitting the measurement of either absorbance or fluorescence. Therefore, they are often suitable only for certain purposes in environmental analysis and not applicable for the characterization of complex water pollution with different concentration ranges.

Taking this situation into account, the aim of this study was the development of an economical *in situ* measuring tool for long-term monitoring in groundwater wells or natural waters as well as for a process evaluation in environmental research in general with extended information yield in comparison with presently available measuring systems. The main principle of the new system is the combination of both measuring techniques (UV/Vis and fluorescence spectroscopy) within one single device. The sensor should be easy to handle and optionally applicable in depths of several hundred metres. These technical advantages can be realized using a cable joint for transfer of data and power supply. Therefore, all main components (light sources, detectors, microcomputer, additional sensors, e.g. for temperature and pressure) were placed in the probe in order to avoid the limitations related to the transmission of optical signals from the submersible sensor head to the detection system.

2. Description of the sensor and laboratory tests

The submersible sensor permitting simultaneous detection of UV/Vis and fluorescence spectra of liquid samples developed is shown schematically in figure 1. All the measurements presented here were performed using a prototype of the sensor probe developed.

In a preferred setup, the device enables the detection of UV/Vis transmission or absorption spectra in the spectral range of 200–800 nm. The usual operation conditions for the fluorescence measurements are excitation at a wavelength of 250 nm and detection of the emission in the range between 300 and 800 nm. The light sources, fibre optics, and detectors/spectrometers are positioned inside a compression-resistant case. The electronic data processing is also performed inside the submersible sensor head.

A miniaturized deuterium–halogen lamp (Ocean Optics, Duiven, Netherlands) is used as light source for the measurement of the UV/Vis spectra. The continuous spectra of deuterium (preferentially UV) and halogen (Vis) light sources are guided into a single optical pathway. The light source is connected to the measuring cell via an optical fibre without any additional optical filters. In order to reduce UV absorbance and aging, short solarization-resistant optical fibres with a diameter of 400 μm were employed. All these optical components were obtained from Ocean Optics (Duiven, Netherlands).

A quartz tube with a diameter of 14 mm is used as measuring cell. The tube is placed at the bottom of the sensor head. The liquid to be analysed flows through the cell during the movement of the sample. Alternatively, it can be pumped through the measuring cell. The quartz tube is separated (in a waterproof manner) from the electronic equipment of the sensor device.

The transmission measurement is made in the 180° configuration. A charge-coupled device (CCD) array with integrated grating and analogue/digital (AD) converter is utilized as detection system. The S2000 spectrometer was obtained also by Ocean Optics. For data processing including background correction and visualization, the OOI Base software from Ocean Optics (Duiven, Netherlands) was applied. Typical integration times were 300 ms, and in most cases the accumulation of five spectra was sufficient to achieve an adequate signal-to-noise ratio.

The performance of the sensor was comparable with that of conventional laboratory instruments (e.g. CADAS 200 from Dr. Lange, Düsseldorf, Germany), as shown in figure 2 for naphthalene in water. The sensitivity in the absorbance mode was practically identical when considering the different optical path lengths. The calibration curves of the submersible sensor show the expected linear behaviour in the whole concentration range of 1–30 mg L^{-1}.

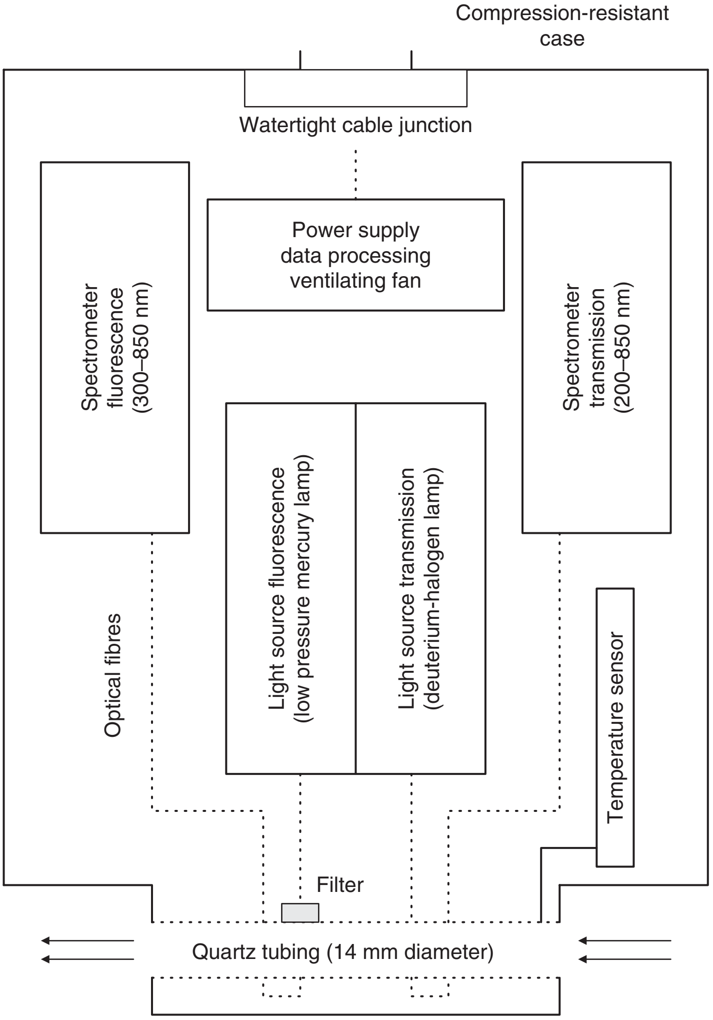

Figure 1. Operating principle of the submersible sensor.

For fluorescence spectroscopy, a low-pressure mercury lamp (Ocean Optics, Duiven, Netherlands) is used as light source. Using an optical filter, an excitation wavelength of 250 nm (±10 nm) is selected. Fluorescence emission is measured in 90° geometry, i.e. with a right angle between the incident and emission optical beams. The spectrometer (CCD array with integrated optical grating, also a S2000 from Ocean Optics) allows the emission to be detected in the spectral range of 300–800 nm. Typical measuring parameters are 3000 ms detection time and averaging over five spectra after background correction. As an example, figure 3 shows the fluorescence spectrum and the estimated calibration curve of pyrene in water. As is clear from the data, fluorescence spectroscopy with the submersible sensor probe permits the sensitive determination of an aromatic compound in the low $\mu g\,L^{-1}$ range, depending on the properties of the substance investigated. The spectrum and

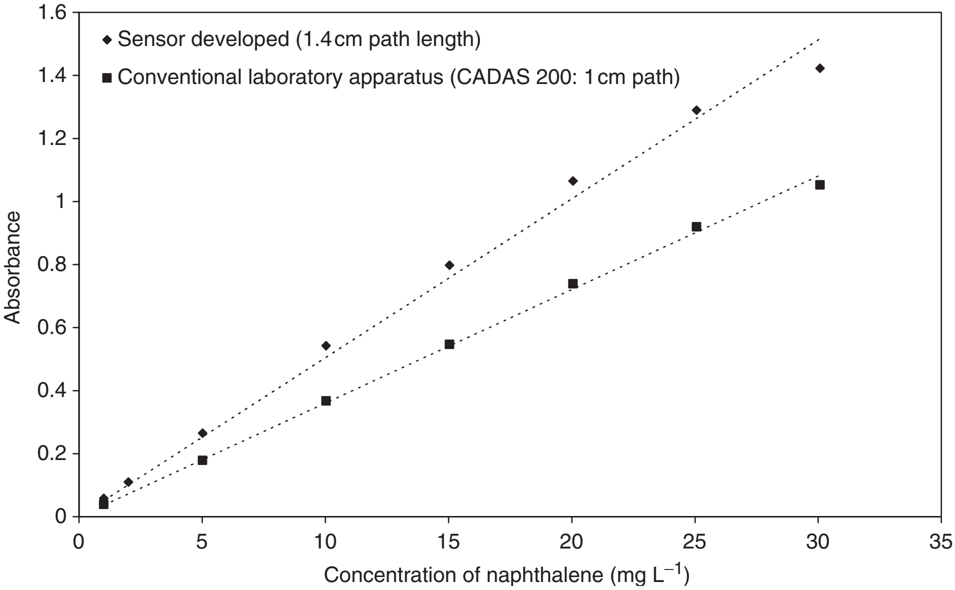

Figure 2. Calibration curves of naphthalene obtained by different spectrometers.

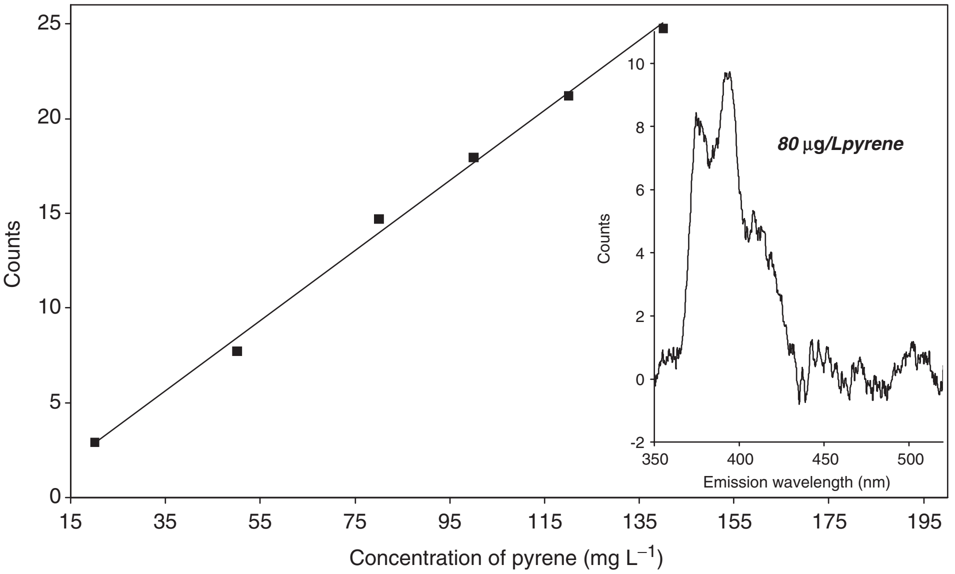

Figure 3. Fluorescence measurements of pyrene.

detectable concentration ranges are comparable with literature data obtained using laboratory instruments [17].

Similar tests have been performed with other substances relevant as water pollutants. Different polycyclic aromatic hydrocarbons (PAHs) were investigated using both UV spectroscopy (typically in concentrations of 0.5–20 mg L^{-1}) and fluorescence spectroscopy as shown in figure 3 for pyrene as an example. Further studies using fluorescence spectroscopy included the determination of different colouring substances (e.g. rhodamine) and technical mixtures of different mineral oil hydrocarbons. Furthermore, we studied the influence of possible matrix components on fluorescence spectra (salinity, humic acids). Calibration curves of different humic substances, BTEX-aromatics (benzene, toluene, ethylbenzene, isomers of xylene), nitrate, and colouring substances were determined using UV/Vis spectroscopy. Furthermore, gasoline and mineral oil hydrocarbons were investigated.

3. Field test of the sensor in the course of tracer experiments

The submersible sensor was successfully used during a tracer experiment in the frame of a groundwater remediation project. The site is a former hydrogenation plant in Zeitz (Saxony-Anhalt, Germany) where the groundwater is highly contaminated with benzene. Further details are given in [18]. In order to clarify the groundwater flow conditions (direction and velocity) as well as the potential for microbiological self-cleaning (natural attenuation), a number of test studies have been carried out.

Tracer studies with the model substances uranin (sodium fluorescein) and toluene which were injected into the aquifer and monitored at several wells were one objective of these investigations. Uranin is a commonly used fluorescent tracer because of its conservative behaviour and the low extent of sorption in the aquifer [18]. The formula of uranin is shown in figure 4. Compared with benzene and toluene (with water solubilities of 1.8 and 0.5 g L^{-1}, respectively), uranin (>600 g L^{-1}) is a hydrophilic compound. Therefore, the interaction of uranin with the aquifer

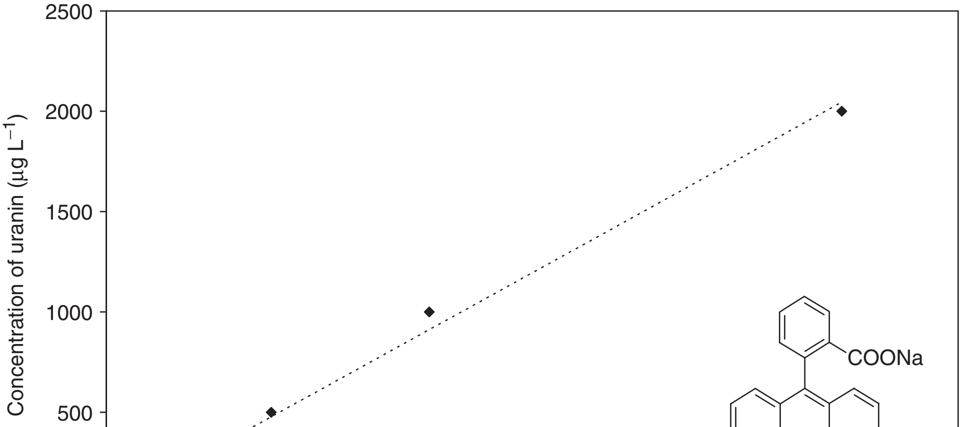

Figure 4. Calibration curve of uranin obtained by fluorescence spectroscopy.

(especially the organic matter in it) is much weaker, and the spread of this substance can be considered representative of the hydrological conditions [18]. Uranin can be determined very sensitively using fluorescence spectroscopy (emission wavelength 512 nm), and there is no background signal in natural waters. The calibration curve obtained with our sensor system (figure 4) shows that a quantitative analysis in the concentration range between (at least) $5\,\mu g\,L^{-1}$ and $2\,mg\,L^{-1}$ is permitted. In the case of the tracer experiment described, these ranges covered the expected values along the groundwater flow. A comparison with laboratory analysis (conventional fluorometers) for random samples showed an excellent agreement with results obtained by *in situ* monitoring. In principle, UV spectroscopy would also allow the determination of uranin in water. However, only concentrations $>200\,\mu g\,L^{-1}$ could be measured with satisfactory accuracy using this method. This detection limit was not suitable to characterize the spatial distribution in the tracer experiment sufficiently. Furthermore, fluorescence spectroscopy was found to permit a minimization of matrix effects for the complex measuring conditions present in the aquifer.

Simultaneously, the concentration of toluene was measured in various wells in the area of the test site using UV spectroscopy. For this, the intensity of the characteristic absorbance band at 254 nm was analysed. Possible matrix components (humic acids, salinity) do not influence this absorbance band within the concentration range as observed in the groundwater wells. Preliminary investigations had shown before that the concentration of the main pollution component benzene was comparatively constant, and other aromatic compounds occurred only in trace amounts. The initial concentrations of benzene were determined for each groundwater well before starting the tracer experiment. The values obtained ranged from 15 to $30\,mg\,L^{-1}$ and remained constant over several weeks. For each well, a calibration curve was determined by adding defined values of toluene to the originally present well-specific level of benzene. By using the obtained characteristic calibration curves for each well, toluene concentrations between 1 and $20\,mg\,L^{-1}$ could be measured *in situ*, thus giving the temporal expansion of the tracer compound in the aquifer. Again, a very good agreement between the sensor and the laboratory results (the latter obtained by headspace gas chromatography using a head-space sampler (DANI HSS 86.50, Cologno Monzese, Italy) coupled with a mobile gas chromatograph (ELEKTROCHEMIE HALLE ECH 87.20, Halle, Germany)) was proven by random tests (exemplarily shown for the sum signal of benzene and toluene in figure 5). This comparison indicates the capability of the new sensor for rapid *in situ* determination of monoaromatic compounds. For such substances, fluorescence spectroscopy would require excitation wavelengths below 200 nm [19] which would result in strong restrictions concerning the fibre material and the light sources.

A detailed *in situ* characterization (more than 1000 analyses using the sensor probe) of the concentration changes during a combined tracer experiment in a contaminated aquifer provided a unique insight into the hydrogeological conditions at the site. In particular, uranin and toluene were applied as hydrophilic and hydrophobic tracers, reflecting a different extent of interaction with the matrix. The two compounds could be simultaneously detected using both UV/Vis and fluorescence spectroscopy. The short duration (approximately 5 min) of the analysis provided a large number of analytical data within short time intervals, thus also allowing the detection of relatively fast

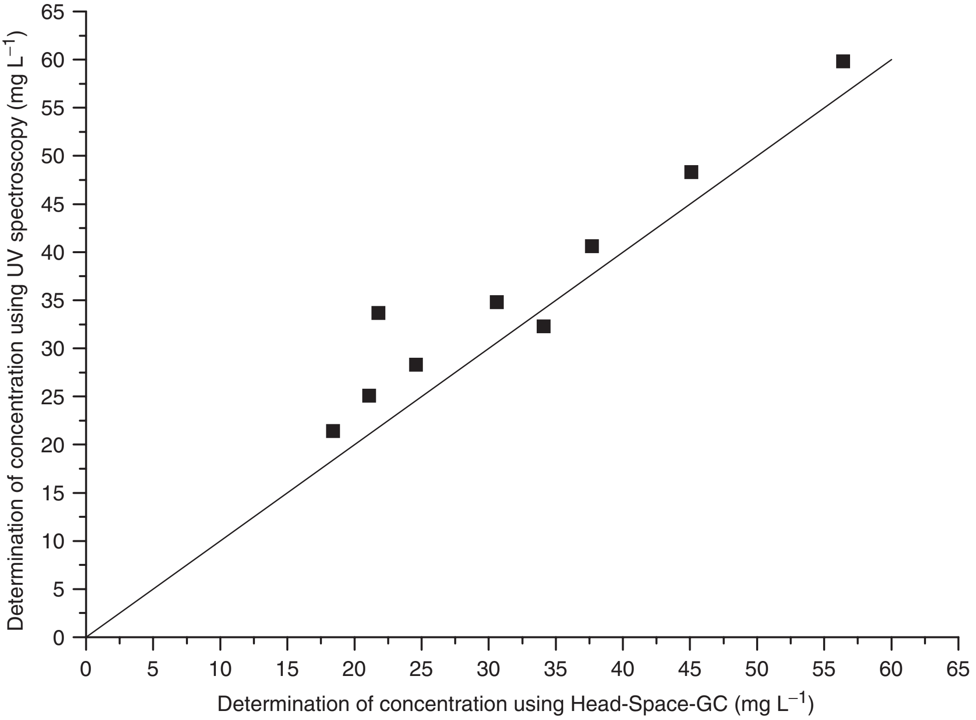

Figure 5. Comparison of analytical results of benzene and toluene obtained by UV spectroscopy and head-space gas chromatography.

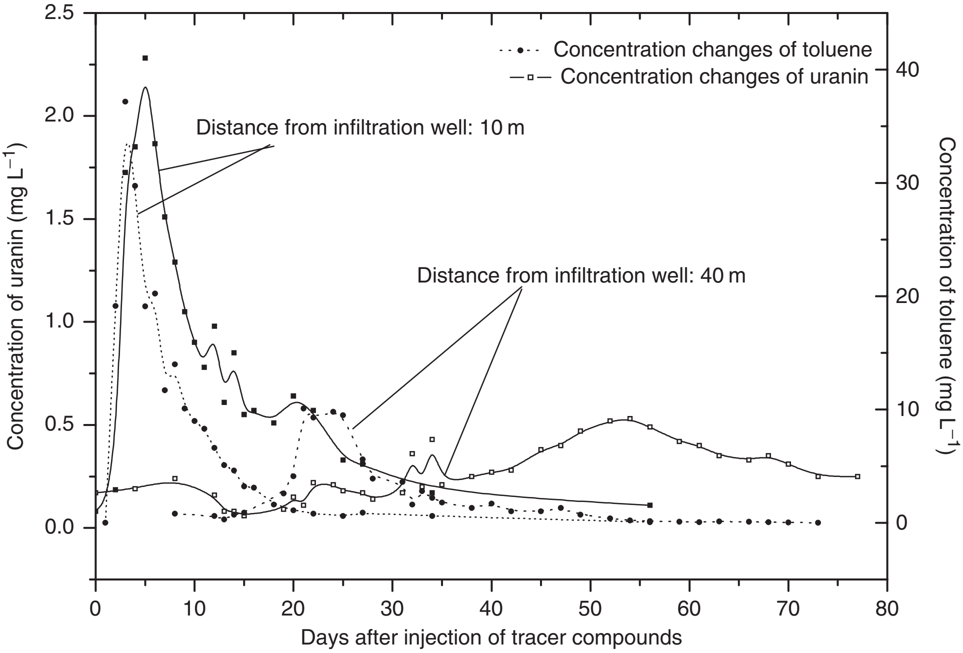

Figure 6. Concentrations of the two tracer compounds (toluene and uranin) depending on the time after injection and the distance of the monitoring well from the infiltration well.

groundwater flows. The *in situ* measurement provided a good basis for the modelling of the groundwater flows and for the prognosis of the natural attenuation process at the contaminated site [20].

The distribution of the two tracer compounds is exemplarily shown in figure 6. The concentrations of toluene and uranin are shown for two different monitoring wells in different distance to the infiltration well. In contrast to our expectations, toluene was only slightly retarded, whereas uranin was retarded much more so, possibly due to an interaction with clay minerals. A detailed discussion of this tracer distribution is given in [20]. Thus, the parallel measurement of both model components with different spectroscopic methods also allows information on the behaviour of pollutants in the groundwater flow to be obtained. Such results are essential for evaluating the processes of degradation and transport and, by combining rapid *in situ* analysis and modelling, for the selection of a remediation strategy [21].

4. Conclusion

A new submersible sensor was constructed. The device combines two measuring techniques: UV/Vis and fluorescence spectroscopy. Therefore, it can be applied to characterize a variety of substances in liquid, especially water samples. Excitation, detection of whole spectra and data processing are carried out in the sensor probe, thus avoiding limitations due to transmission losses in long optical fibres. The sensor can be applied for on-site and *in situ* environmental analysis, e.g. in the course of remediation projects, as well as for the control of industrial processes.

The sensor probe was successfully tested in the laboratory and in the field scale showing a sensitivity and accuracy comparable with those of stationary instruments. The potential for the characterization of transport and retardation of various pollutants with varying properties was shown exemplarily in a tracer experiment at a site with former industrial use, having led to a significant groundwater contamination.

References

[1] J. Workman, K.E. Creasy, S. Doherty, L. Bond, M. Koch, A. Ulman, D.J. Veltkamp. *Anal. Chem.*, **73**, 2705 (2001).
[2] W.R. Seitz. *Anal. Chem.*, **56**, 16A (1984).
[3] K.H. Koch. *Process Analytical Chemistry*, Springer, Berlin (1999).
[4] C.E. Del Castillo, P.G. Coble, J.M. Morell, J.M. Lopez, J.E. Corredor. *Mar. Chem.*, **66**, 35 (1999).
[5] R.E. Warnrock, W.W.C. Gieskes, S. van Laar. *J. Sea Res.*, **42**, 169 (1999).
[6] G. Abt-Braun, F.H. Frimmel. *Environ. Int.*, **25**, 161 (1999).
[7] K.S. Johnson, L.J. Coletti. *Oceanogr. Res. Pap.*, **49**, 1291 (2002).
[8] T. Baumann, S. Haaszio, R. Niessner. *Water Res.*, **34**, 1318 (2000).
[9] S. Rubino, A. Gomez-Hens, M. Valcarcel. *Talanta*, **33**, 633 (1986).
[10] C.L. Stevenson, T. Vo-Dinh. *Appl. Spectrosc.*, **47**, 430 (1993).
[11] R.D. Ji, G.A. Cooper, K.S. Booksh. *Anal. Chim. Acta*, **397**, 61 (1999).
[12] C.N. Ho, G.D. Christian, E.R. Davidson. *Anal. Chem.*, **52**, 1071 (1980).
[13] T. Ohno. *Environ. Sci. Technol.*, **36**, 742 (2002).
[14] J.F.R. Gower. *Int. J. Remote Sens.*, **25**, 1489 (2004).

[15] R.M.W. Amon, G. Budeus, B. Meon. *J. Geophys. Res. Oceans*, **108**, 3221 (2003).

[16] J. van den Broeke, G. Langergraber, A. Weingartner. *Spectrosc. Eur.*, **18**, 15 (2006).

[17] W. Karcher, F.J. Fordham, J.J. Dubois, P.G.J.M. Glaude, J.A.M. Ligthard (Eds), *Spectral Atlas of Polycyclic Aromatic Compounds*, Reidel, Dordrecht, The Netherlands, 1985.

[18] St. Gödeke, H. Weiß, H. Geistlinger, A. Fischer, H.H. Richnow, M. Schirmer. *Grundwasser*, **9**, 3 (2004).

[19] F. Lewitzka, U. Bünting, M. Niederkrüger. *GIT*, **3**, 283 (2003).

[20] St. Gödeke, H.H. Richnow, H. Weiß, A. Fischer, C. Vogt, H. Borsdorf, M. Schirmer. *J. Contam. Hydrol.*, **87**, 211 (2006).

[21] H. Borsdorf, C.P. Renschen, U. Roland. *Nachr. Chem.*, **53**, 203 (2006).