

## Application of a fiber-optic NIR-EFA sensor system for in situ monitoring of aromatic hydrocarbons in contaminated groundwater

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### Abstract

Interaction of analyte molecules with the evanescent wave of light guided in optical fibers is among the most promising novel sensing schemes that can be applied for environmental monitoring and on-line process analysis. By combining this measuring principle with the solid-phase extraction of analyte molecules into the polymer cladding of a fiber, it is possible to perform direct absorption measurements in the cladding, if the fiber is adapted to a conventional spectrometer/photometer. A big advantage of this arrangement is that the measurement is scarcely disturbed by matrix effects (background absorption of water in IR measurements, stray light due to turbidity in the sample). By using near-infrared (NIR) evanescent field absorption (EFA) measurements in quartz glass fibers coated with a hydrophobic silicone membrane it is possible to design and construct sensors for monitoring apolar hydrocarbons (HCs) in aqueous matrices.

The paper presents a fiber-optic sensor system for the determination of aromatic HCs in groundwater or industrial wastewater. Generally, this instrument is suitable for quantitative in situ monitoring of pollutants such as aromatic solvents, fuels, mineral oils or chlorinated HCs with relatively low water saturation solubility (typically between 0.01 and 10 g l<sup>-1</sup>). The sensor probe is connected via all-silica fibers to a filter photometer developed at the IFIA, thus, allowing even remote analysis in a monitoring well. This portable instrument provides a total concentration signal of the organic compounds extracted into the fiber cladding by measuring the integral absorption at the 1st C–H overtone bands in the NIR spectral range.

In situ measurements with the sensor system were performed in a groundwater circulation well at the VEGAS research facility of the University of Stuttgart (Germany). The NIR-EFA sensor system was tested within the frame of an experiment that was carried through in a tank containing sandy gravel with a groundwater-saturated aquifer, where soil and groundwater were contaminated with

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technical grade xylene. The goal of this experiment was to model and optimize the groundwater circulation well used for the remediation of the aquifer and soil surrounding the well. The sensor proved to trace reliably the total hydrocarbon concentration in the process water pumped from the well to a stripper column. Measurements were performed continuously over 4 months with C8 HC sum concentrations in the process water between  $80 \text{ mg l}^{-1}$  down to the limit of detection, which is around  $200 \text{ } \mu\text{g l}^{-1}$ . It could be demonstrated that the fiber-optic sensor system is a valuable tool for near-real-time control of a remedial action technique and verification and documentation of its success. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Gasoline and other fuels as well as aromatic hydrocarbon solvents are produced and used in large quantities in many areas. An associated hazard in utilizing, storing and transporting these substances and other polluting compounds like chlorinated hydrocarbons, is the environmental impact of leaks and spills that can contaminate soil and groundwater at industrial sites. Due to this, there is a need for monitoring of these toxic compounds, e.g. in hydrocarbon (HC) remediation facilities at contaminated areas [1]. Furthermore, the treatment of discharged process waters of HC production and storage facilities on the one hand, or at industrial plants utilizing HC products on the other hand, has to be verified to meet regulatory discharge limits. Traditionally, discontinuous batch sample collection followed by laboratory analysis is used to demonstrate regulatory compliance. In Germany the threshold value for the discharge of HC containing wastewater into the sewer for the metalworking industry is  $10 \text{ mg l}^{-1}$  [2]. In the present standard procedure for HC analysis, the wastewater sample is extracted with 1,1,2-trichloro-trifluoroethane followed by IR spectrometric determination of the HC sum concentration [3]. Besides the ecologically doubtful use of an extractant, that destroys the ozone layer, this kind of analysis is time consuming, expensive and can only provide a brief, temporary ‘snapshot’ view of a treatment system’s performance. Therefore, fast, simple and inexpensive HC analysis techniques are needed which allow to monitor the pollutants continuously and in situ.

New spectroscopic sensing techniques for HC pollutants whose basic principles have been developed during the last years are now in a stage of development, which promises to fulfill these demands. These techniques that are all based on evanescent field absorption (EFA) measurements with optical fibers as sensing elements either work in the near-infrared (NIR) [4–6] or in the mid-infrared (MIR) spectral range [7,8]. Similar to solid phase micro-extraction (SPME) introduced by Pawliszyn [9], a polymer-clad fiber is used to obtain a solvent-free HC extraction and sample preparation. Instead of transferring the extracting fiber to a GC, the optical fiber is directly coupled to a spectrometer or photometer unit and the HC species extracted into the fiber cladding are monitored in situ by an absorptiometric measurement. This is possible due to the evanescent wave tail of the measuring light conducted in the fiber core, which extends into the fiber polymer cladding.

In contrast, to the very short fibers used in SPME (1 cm length), that are mounted in a syringe-like device, in NIR-EFA spectroscopy the interaction length of the quartz glass

sensing fiber with the sample has to be in the range of 10 to 30 m to get a suitable sensitivity. This is due to the fact that the intensities of C–H harmonics and combination absorption bands of HC molecules occurring in the NIR range are by a factor of 10–100 lower than the corresponding fundamental vibration bands in the MIR range. On the other hand, EFA measurements in the NIR have the advantage that quartz glass optical fiber technology can be applied, which is fairly advanced due to numerous applications in the telecommunications industry. In contrast to the silver halide fibers used in the MIR spectral range, these fibers have rather good mechanical properties, are stable against chemical attack and are able to transmit the light over distances of up to a few hundred meters between spectrometer and sensing element, i.e. even remote in situ analysis in deep wells of contaminated areas is possible.

In this paper basic principles of NIR-EFA sensing are presented in an exemplary fashion for the continuous monitoring of BTEX (benzene, toluene, ethylbenzene and xylene)-type aromatic HCs in contaminated groundwater. The instrumental setup of an EFA sensor element installed in a flow cell and combined with a NIR bandpass photometer as well as the performance of the sensing equipment during calibration and in situ field measurements of aromatic C8 HC isomers will be described.

## 2. Evanescent field absorption spectroscopy

The theory of internal reflection [10] and EFA spectroscopy [11] has been given in detail earlier and will only be discussed briefly in this paper. The measuring light transmitted in an optical fiber by total reflection at the core/cladding interface produces a standing wave whose evanescent field penetrates into the fiber cladding over some distance, which is in the range of the wavelength of light used for the measurement. The quartz glass fiber NIR-EFA sensor developed at our institute has a hydrophobic polysiloxane cladding that extracts apolar HCs from the aqueous phase [4]. For this extracting fiber all the fundamental principles and theoretical aspects of SPME are valid [9].

The apolar HC species that are enriched in the cladding, according to the Nernst distribution law, can absorb energy from the fraction of light in the evanescent field. Such interactions, illustrated schematically in a longitudinal section view of the fiber in Fig. 1, lead to a specific absorption of light intensity in the NIR spectral range at the corresponding C–H overtone and combination bands of HC compounds. Due to the extraction step and the direct absorptometric measurement in the cladding, interference from strong water O–H absorption bands or from turbidity in the solution is avoided. For low analyte concentrations ( $\ll$  saturation concentration) the absorbance signal  $A$  obtained from an evanescent field measurement at an absorbing wavelength can be approximated by the following equation [11]:

$$A = \log \frac{I_0}{I} = \varepsilon_e L K_{fw} C_w^\infty \quad (1)$$

where  $I_0$  is the transmitted light intensity with the sensor in pure water,  $I$  the transmitted intensity with the sensor in analyte solution,  $\varepsilon_e$  the effective absorptivity,  $L$  the length of the sensor fiber,  $K_{fw}$  is the fiber/water distribution constant, and  $C_w^\infty$  is the equilibrium concentration of the analyte in water.

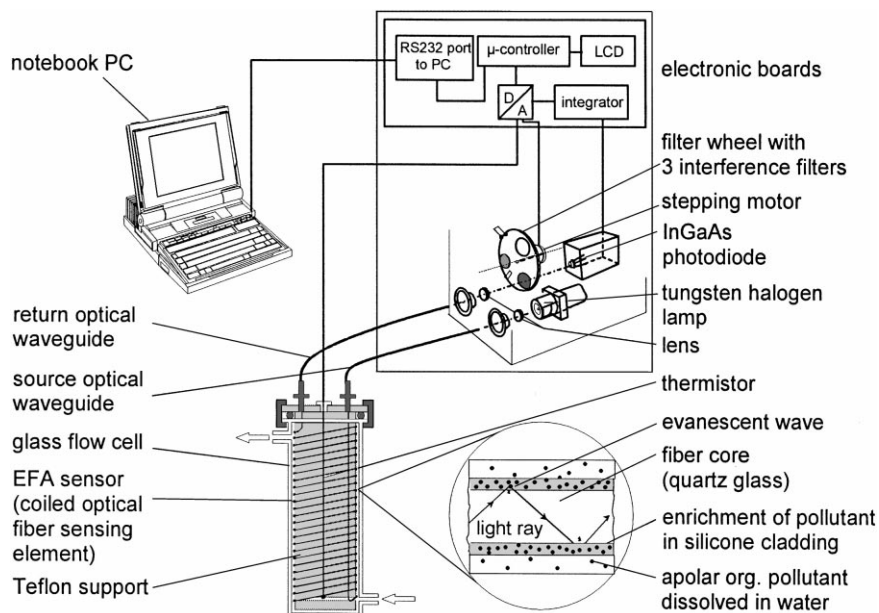


Fig. 1. Illustration of evanescent field absorption (EFA) sensing principle and instrumental setup of coiled fiber-optic sensor and NIR bandpass filter photometer unit (fiber sensor element installed in a flow cell).

Because of the linear dependence of absorbance on fiber length and analyte concentration the equation has a formal similarity with Beer's law. However, the effective absorptivity  $\varepsilon_e = \eta_m \varepsilon_m$  is dependent on  $\eta_m$ , which is the ratio of light intensity in the evanescent field to the total light intensity transported in the fiber core, and  $\varepsilon_m$  the molar absorptivity of the analyte species. Because  $\eta_m$  is influenced by refractive index changes in the cladding caused by analyte enrichment,  $\varepsilon_e$  can not be considered to be constant at higher analyte concentrations. Moreover, if the penetrating HC species induce a distinct increase of the refractive index in the silicone cladding, an additional decrease in light intensity is observed, which is caused by stripping of higher order modes from the fiber and a corresponding decrease in the numerical aperture. Both effects may lead to non-linearity of the absorbance/concentration data at higher analyte concentrations [5].

### 3. Experimental

#### 3.1. NIR-EFA fiber-optic sensor

An immersion-type probe for NIR-EFA sensing is built by coiling a multimode step-index optical fiber of 12–30 m length on a stainless steel support protected from sharp edges with Teflon<sup>TM</sup>. This support consists of four comb-like structures and the fiber is threaded through the teeth of these structures. Finally, it is fixed by four perforated Teflon<sup>TM</sup> strips, which are pressed on the teeth of the comb structures. To reach a compact geometry the fiber forms a

single or double coil on the support. The commercially available polymer-clad silica (PCS) fiber (Fiberguide Industries, NJ) has a low-hydroxide quartz glass core of 210  $\mu\text{m}$  diameter, a 10  $\mu\text{m}$  poly(dimethylsiloxane) (PDMS) coating and a 20  $\mu\text{m}$  nylon protective jacket. The procedure to turn the PCS fiber into a sensing element for non-polar hydrocarbons has been described earlier [11]. In this procedure the outer nylon protective jacket of the fiber is chemically removed by dissolving it with 1,2-propanediol at 160°C. A stainless steel protective casing with an open area of approximately 26% of the surface provides sufficient analyte flow to the sensor and physical ruggedness for in situ use. The sensor has final dimensions of a 5 cm  $\times$  14 cm cylinder.

The experiments described in this paper required a probe, which could be installed in a flow cell. Therefore, a sensor fiber of 30 m length was coiled as a single spiral on a Teflon<sup>TM</sup> support of cylindrical geometry with a notched surface. Here, the probe has final dimensions of a 4.5 cm  $\times$  25 cm cylinder and the sensing fiber is coupled to all-silica transmitting fibers with standard SMA connectors mounted on the top of the cylinder. The top of the cylinder has the shape of a flange and fits into a cylindrical glass flow cell with a similar flange. The probe is fixed in the glass flow cell by a locking ring and sealed by a Viton<sup>TM</sup> O-ring. The flow cell with the installed probe is shown in Fig. 1. It has a low dead volume of 35 ml and two hose couplings at the bottom (inlet) and the top (outlet). They can be connected to a volumetric flask with a calibration sample or to a bypass of a process water pipe by Teflon<sup>TM</sup> tubing.

### 3.2. Photometer unit of EFA sensor system

Fundamentally, the absorptometric measurement of the HC species enriched in the fiber cladding can be performed with each commercially available NIR (spectro)photometer that has fiber-optic adaptation. Up to now fiber sensor coils have been adapted to a GUIDEDWAVE model 260 grating spectrometer and to a BRUKER VECTOR 22/N FT-NIR instrument. Details of the instrumental setup used with the GUIDEDWAVE model 260 and the performance of the corresponding HC sensor system have been thoroughly described in earlier papers [4–6].

Fig. 1 depicts a schematic view of the sensor coil installed in the glass flow cell adapted with all-silica optical waveguides to the portable filter photometer developed at the IFIA. The measuring light of a tungsten halogen lamp first is conducted by an all-silica fiber to the sensor fiber. The light modified by the HC absorption in the sensing fiber is transferred via a second all-silica fiber into the spectral evaluation unit. Light coming back from the sensor element is focused on a wheel with three bandpass filters. While two filters select light in the wavelength range of the unsaturated and saturated 1st overtone C–H absorption bands of HC compounds around 1645 and 1715 nm, the third filter is transparent in the non-absorbing wavelength range around 1540 nm and provides the reference light. The three filters are positioned sequentially in the light beam by the stepping-motor driven, rotating wheel and the transmitted intensities are measured by an InGaAs photodiode. Automatic control of the filter wheel, stepping-motor, tungsten halogen source and InGaAs photodiode is provided by a micro-controller. This controller also calculates absorbance values from the intensities measured by the photodiode at the C–H ( $I_M$ ) and reference ( $I_R$ ) wavelengths according to:  $A = \log I_R / I_M$ . Due to the fact, that the wavelength ranges of the measuring and reference filters are close together, drifts in the intensity of the light source, in the

sensitivity of the photodiode and changes in the transmission of the optical components within the photometer are effectively compensated. According to Eq. (1) the absorbance  $A$  calculated by the micro-controller is — at least at lower analyte concentrations — linearly correlated to the HC concentration in the aqueous phase.

Up to 20 HC calibration functions (for single HC components or for mixtures) can be stored on the micro-controller. With the help of a stored calibration function the HC concentration is calculated directly from the corresponding absorbance value and indicated on the LCD display of the photometer. It is a stand-alone instrument, which can be easily operated by simple function keys. The absorbance zero-point is set by performing a measurement with the sensor head in pure water. Afterwards, periodic measurements are started (minimum interval is 30 s) and the sensor head is contacted with the aqueous HC solution. Data are collected and stored automatically by the system. Via an RS232 interface, stored data can be sent to a computer for graphical presentation as well as for evaluation and documentation purposes or new calibration data can be transmitted from the computer to the photometer.

The strong dependence of the penetration depth of the evanescent wave light field in the sensor fiber on temperature leads to an offset in the absorbance signals given by the system, if the sensor temperatures are different during zero-setting and sample measurement. This offset is automatically compensated by measuring the actual sample temperature by a thermistor attached to the sensor (cf. Fig. 1), whose signals are also transmitted to the micro-controller. From the difference of the sample temperature and the temperature stored during zero-setting the controller calculates the offset by using stored polynomial functions describing the absorbance/temperature curves relative to the measured wavelength range and corrects it.

### 3.3. Sensor calibration for aromatic compounds homogeneously dissolved in water

Before conducting in situ measurements of BTEX-type aromatic hydrocarbons homogeneously dissolved in water, the EFA sensor system with the 30 m sensing fiber was calibrated in the laboratory. The preparation of calibration standards was performed with the same technical grade xylene (purchased from Häfner, Asperg) that later was used in the soil and groundwater purification experiment. Analysis of this technical grade xylene with a GC/FID setup (HP 6890 gas chromatograph) showed that it contained a mixture of C8 HC aromatic compounds (14% *o*-xylene, 65% *m*- and *p*-xylene and 21% ethylbenzene). Two aqueous standard stock solutions were prepared by spiking the appropriate amount of the C8 HC mixture into methanol and then diluting with distilled water in a volumetric flask. The final methanol concentration did not exceed 0.4% of the solution volume. Calibration standards with concentrations ranging from around 200 to 1 50 000  $\mu\text{g l}^{-1}$  were prepared in volumetric flasks by further diluting aliquots from the stock solutions with distilled water. The volumetric flasks were filled to the stopper to avoid any headspace and losses due to evaporation of the volatile analyte. All solutions were used within 1 h to minimize evaporative loss. The sum concentration of aromatic compounds in the corresponding sample flask was determined by measuring an aliquot of the solution by GC/FID reference analysis (HP 6890 gas chromatograph) or by UV absorption spectrometry (Cary 2400).

During calibration the inlet and outlet of the flow cell with the sensor were connected by Teflon<sup>TM</sup> tubing to a piston-diaphragm-dosing pump and to a volumetric flask, which

was filled up close to the top with the aqueous sample. For circulating the sample through the flow cell the volumetric flask with the corresponding sample was closed with a special stopper. The Teflon™ tubing was passed through two holes in the polyethylene stopper and sealed with silicone glue. In this way, the sample could be pumped to the flow cell and back in a closed loop and evaporative losses were minimized. During the circulation the sample solution in the volumetric flask was stirred at  $\sim 500$  rpm by a stir bar and a magnetic stirrer to avoid any concentration gradient within the flask. The water flow rate in the cell was  $0.165 \text{ l min}^{-1}$ . Pumping deionized water through the flow cell and zero-setting of the absorbance signal started a measurement. After checking the baseline noise for a few minutes the sensor was contacted with the corresponding sample solution. Sensor signals were acquired in time intervals of 30 s until equilibrium was reached and the same procedure was used for all successive calibration samples. The equilibrium absorbance/concentration data were used for setting up the calibration function.

In situ monitoring of the mixture of C8 HC aromatic compounds with the EFA sensor system at the VEGAS facility was performed in a similar way. A photograph of the experimental configuration at the measuring point is shown in Fig. 2. Here, the flow cell was installed in a bypass of a pipe that transported contaminated process water from a groundwater circulation well to a stripper column. Zero-setting of the sensor absorbance signal was done with the bypass being connected to a jar with deionized water. Afterwards the two-way valve of the bypass was switched to the process water pipe and absorbance data were collected continuously in 1 min intervals. During the in-line measurements the water flow rate in the cell was  $0.5 \text{ l min}^{-1}$ .

### 3.4. HPLC/UV off-line analysis of aqueous solutions of aromatic HCs

In order to validate the data obtained by the NIR-EFA in situ measurements, at certain periods of time grab samples were drawn from the inlet pipe of the stripper column and off-line single sample analysis was performed by HPLC/UV. The method used for the determination of the aromatic HC concentration in the grab samples has been described earlier by Klaas et al. [12]. The separation of the different aromatic compounds was done by a Spherisorb ( $5 \mu\text{m}$ ) ODS II column with a length of 12.5 or 25 cm and an inner diameter of 4.6 mm. A 70:30 acetonitrile/water mixture with a flow rate of  $1 \text{ ml min}^{-1}$  was used as solvent (isocratic elution). UV detection of the xylene isomers and ethylbenzene was done at a wavelength of 195 nm. The integral area of the corresponding peaks in the chromatogram was used to calculate the C8 HC sum concentration.

## 4. Results and discussion

### 4.1. Specifications for EFA sensing of aromatic HCs

#### 4.1.1. NIR-EFA spectra

HC species dissolved in excess of water cannot be measured directly by NIR absorption spectroscopy using conventional transmission techniques due to the strong water O–H

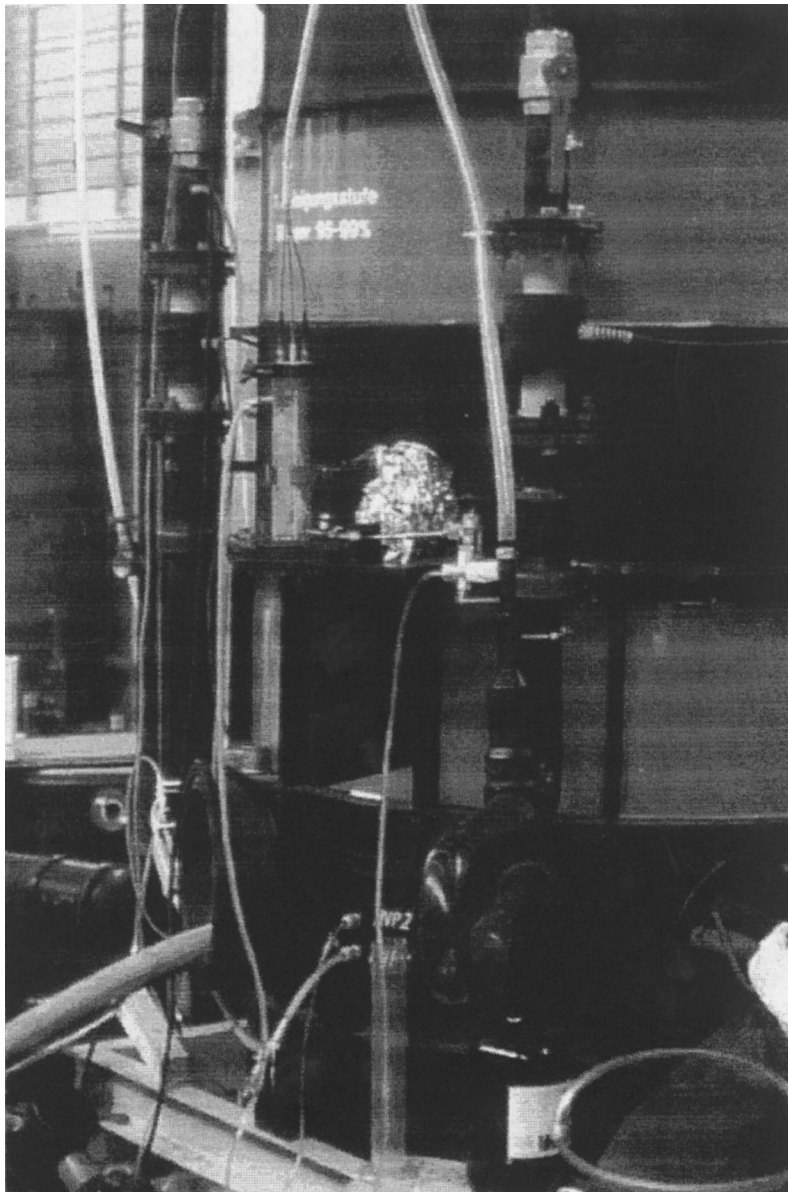


Fig. 2. Photograph of the in situ measuring point at the feed pipe of a stripper column (xylene remediation experiment at the VEGAS facility); the glass flow cell with the fiber-optic sensing element was installed in a bypass of the pipe.



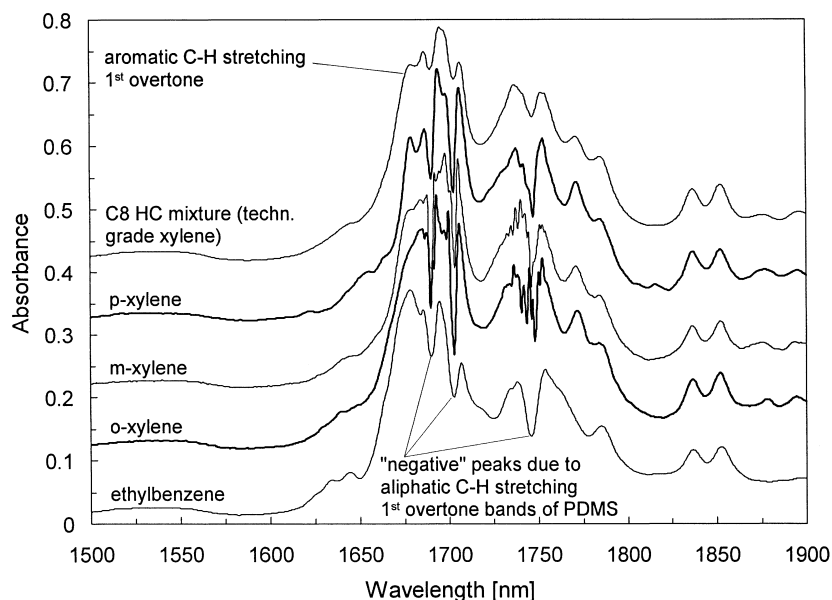


Fig. 3. Comparison of the NIR-EFA spectra of aqueous solutions of pure xylene isomers, ethylbenzene and a technical grade xylene; HC concentration:  $60 \text{ mg l}^{-1}$ ; spectra were recorded using a 12 m EFA sensor adapted to a BRUKER VECTOR 22/N FT-NIR spectrometer.

absorption bands at 1450 and 1940 nm, that overlap the much weaker C–H peaks in the 1600–1900 nm range [4]. For this reason NIR spectroscopy has not been applied directly to aqueous samples, e.g. in environmental applications. EFA-NIR spectroscopy overcomes this problem by extraction of the apolar species into the hydrophobic coating that is formed by the PDMS cladding of the fiber sensing element. If an EFA fiber-optic sensor is combined with a high-resolution spectrometer one can exploit the full spectral information.

In Fig. 3 NIR-EFA spectra of  $60 \text{ mg l}^{-1}$  aqueous solutions of the pure xylene isomers, of ethylbenzene and of a technical grade xylene used in the VEGAS remediation experiments are shown. These spectra have been recorded using a 12 m EFA sensor in combination with a BRUKER VECTOR 22/N FT-NIR spectrometer. Generally, due to the excellent spectral resolution of this instrument in all spectra the aromatic C–H stretching 1st overtone band around 1679 nm can clearly be distinguished from the aliphatic C–H stretching 1st overtone bands of the  $-\text{CH}_3$  (1704 nm) and  $-\text{CH}_2$  groups around 1730 and 1765 nm. Furthermore, these EFA spectra contain additional bands of the PDMS fiber cladding. “Negative bands”, which are caused by the swelling of the silicone polymer due to HC enrichment can be seen in the spectral range from 1675 to 1750 nm, while the “positive” silicone bands around 1850 nm originate from the refractive index increase in the cladding due to the aromatic HCs. The effects that lead to these additional bands of the silicone matrix in NIR-EFA spectra of HC analytes have been discussed in detail earlier [4,11,13]. As expected, the aromatic C–H 1st overtone stretch band is the most prominent band in every spectrum and shows a varying fine structure depending on the respective C8 HC compound. All the pure

aromatic HCs depicted in Fig. 3 are contained in the technical grade xylene and its spectrum is a superposition of the spectra of the single compounds. This example demonstrates that well resolved EFA-NIR absorption spectra — similar to conventional NIR spectra — allow extracting information about different compounds contained in a mixture. We have obtained quantitative multi-component analysis of three or four compounds in a HC mixture by applying partial least squares (PLS) calibration and data evaluation techniques to such NIR-EFA spectra [14].

However, in many applications it is not the surveillance of single HC species, but rather monitoring of a whole group of compounds which is required. Thus, for describing water quality often a sum parameter, e.g. the DOC value (concentration of dissolved organic carbon) or the AOX value (adsorbable organic halogen) is used [15]. Therefore, we have combined the sensor with a filter photometer (see Section 3 and [16,17]) that provides a sum signal (i.e. a kind of optical sum parameter) for the total amount of apolar HC compounds extracted into the silicone cladding of the fiber. Fig. 4 shows a comparison of the transmission spectra of the broadband measuring and reference bandpass filters installed in this instrument and the NIR-EFA absorption spectrum of the technical grade xylene that was used in the remediation experiments. From these spectra it is obvious, that the filter with 1715 nm central wavelength (CWL) and a 90 nm bandwidth covers the major part of the 1st overtone aromatic and aliphatic C–H stretch bands of this C8 HC mixture and allows to measure the integral light absorption induced by these compounds. Usually, the second measuring channel (filter with 1645 nm CWL) is intended to be used for measurements of olefinic HCs, e.g. trichloroethene and covers only the flank of the aromatic bands. Nevertheless,

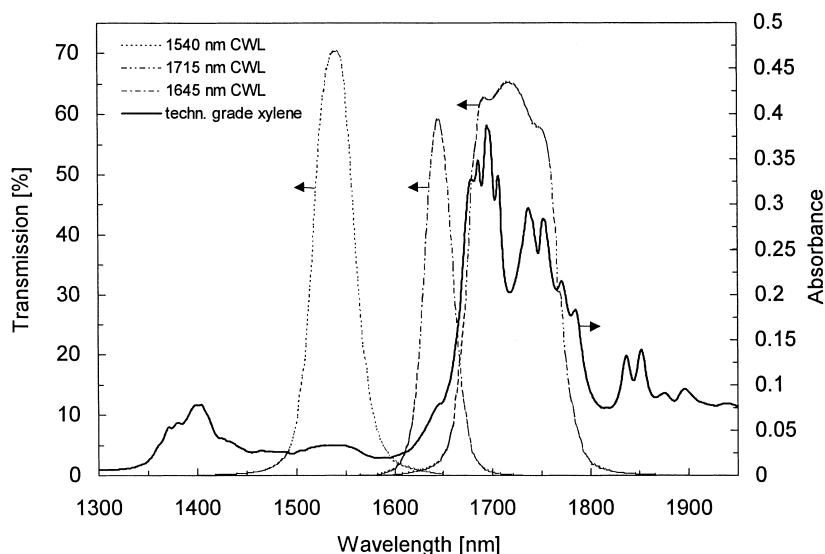


Fig. 4. Transmission spectra of the measuring and reference filters used in the photometer and NIR-EFA spectrum of a  $60 \text{ mg l}^{-1}$  aqueous solution of technical grade xylene; measurements are done in the spectral range of the 1st overtone C–H absorption bands.

for the C8 HC application it also delivered a (smaller) absorption signal that was useful for calculating the ratio of the two channels and thus, to identify whether strong changes in the composition of the HC mixture did occur in the course of the experiment.

#### 4.1.2. C8 HC calibration function

The EFA sensor calibration function for aqueous solutions of technical grade xylene to be used in the VEGAS field trials was determined before in the laboratory by linear regression of the experimental data obtained from xylene calibration samples with known HC sum concentration (see Section 3). Fig. 5 shows the calibration functions of the C8 HC mixture for both measuring channels of the photometer (1715 and 1645 nm CWL). The data have been determined from the equilibrium absorbance values of the corresponding calibration samples, which were recorded using a 30 m EFA sensor connected to the filter photometer. For automatic calculation of the C8 HC sum concentration the slope and intercept of the calibration function for the 1715 nm measuring channel, which are given in Fig. 5, were stored on the micro-controller of the photometer. The absorbance/C8 HC sum concentration data in the measured range from approximately 200 to 1 50 000  $\mu\text{g l}^{-1}$  show a rather good linearity ( $R^2 = 0.9966$ ). This is also true for the 1645 nm measuring channel, where an  $R^2$  of 0.9954 was obtained, but compared with the 1715 nm channel the sensitivity (slope) in this wavelength range is by a factor of approximately 2.75 lower. The limit of detection

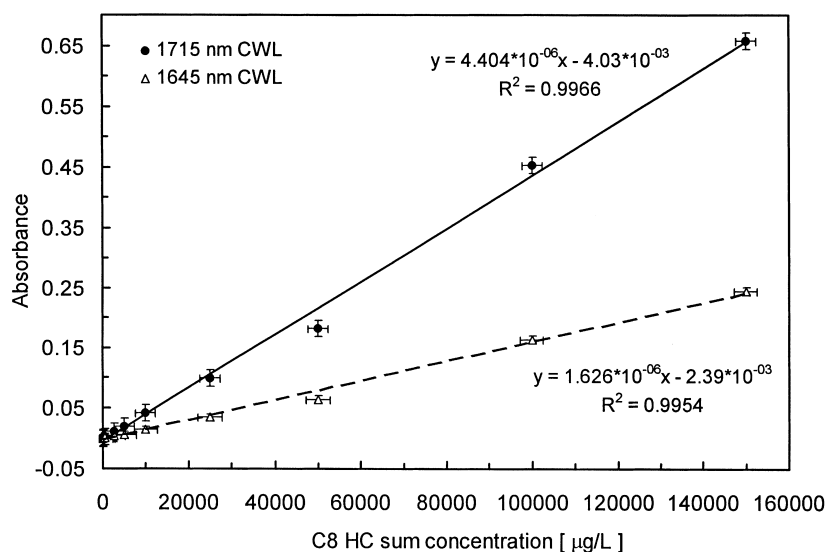


Fig. 5. EFA sensor calibration functions for aqueous solutions of technical grade xylene (C8 HC mixture) using the 30 m EFA sensor installed in a flow cell in combination with the NIR filter photometer; absorbance/C8 HC sum concentration data are given for both measuring channels of the photometer located at central wavelengths of 1715 and 1645 nm; error bars parallel to ordinate axis represent standard deviation of the residuals of the absorbance data (calculated according to [18]); error bars parallel to abscissa axis represent the standard deviation of the analytical results (C8 HC concentration data) obtained with the help of the corresponding calibration function (standard deviation calculated according to [18]).

(LOD) for the sum concentration of this C8 HC mixture in aqueous solution was calculated from the slope of the calibration function and the three-fold standard deviation of the photometric baseline noise at the 1715 nm channel to be  $200 \mu\text{g l}^{-1}$ . This value is in the order of magnitude of LOD values for other apolar hydrocarbons in aqueous solutions, which have been given for different combinations of EFA sensor and (spectro)photometer units [17].

#### 4.1.3. C8 HC sorption kinetics

Generally, the sensor response times for HC compounds in aqueous solution strongly depend on the HC species and the hydrodynamic conditions and typically are dominated by film kinetics, i.e. the diffusion of the HC analyte molecules through the aqueous Nernstian boundary layer at the sensor surface is the rate-determining step. This has been discussed in detail by Conzen et al. [5,11]. For volatile chlorinated hydrocarbons, e.g. 1,2-dichloroethene or trichloroethene and well-stirred solutions the  $t_{95\%}$  values (time to reach 95% of the equilibrium signal) are typically in the range of 2 to 5 min [17].

A longer equilibration time ( $t_{95\%} = 21$  min) is needed for aromatic molecules like the C8 HC isomers and non-turbulent hydrodynamic conditions, that arose from the design of the flow cell with a low dead volume and relatively low flow rate (cf. Section 3). In Fig. 6 the response curve of the 30 m sensor to solutions of increasing HC concentration is shown for both measuring channels of the NIR photometer. The increasing C8 HC sum concentrations and the corresponding equilibration steps are clearly traced by the sensor.

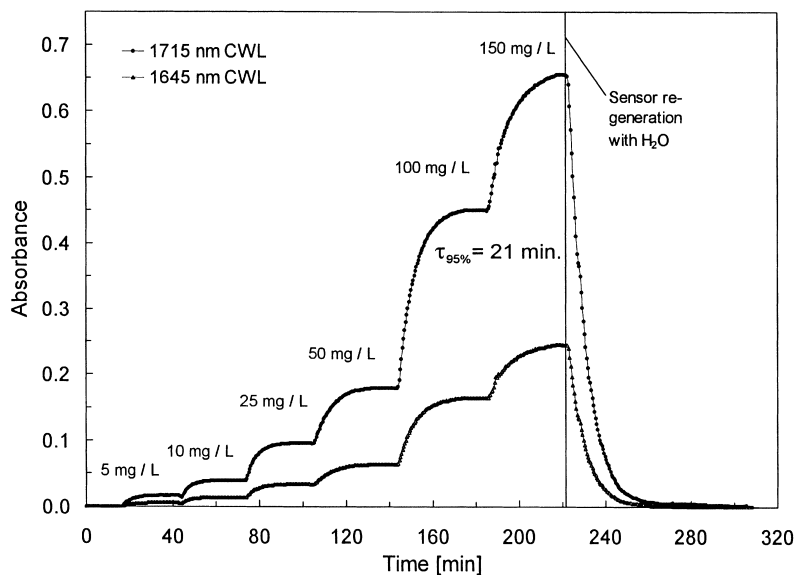


Fig. 6. Response signals vs. time obtained with the 30 m EFA sensor/NIR filter photometer system for measurements of aqueous solutions of technical grade xylene (laboratory calibration of sensor system); absorbance/time data are given for both measuring channels of the photometer located at central wavelengths of 1715 and 1645 nm; water flow rate in sensor cell:  $0.165 \text{ l min}^{-1}$ .

This curve also demonstrates that the sorption of low molecular weight HCs in the silicone cladding is completely reversible because the signal returns to the baseline if the sensor comes in contact with pure water. Another possibility to regenerate the fiber sensor is to put it in air for evaporation of volatile compounds and then immerse it again in pure water [16].

However, this full reversibility of the sensor in water is not valid for HC molecules with a chain length of  $\geq C_{12}$  contained, e.g. in mineral oils. These compounds have a very high affinity to the PDMS cladding and must be removed by swelling and washing the cladding with petroleum ether or acetone [13].

#### 4.2. Continuous field tests with the EFA sensor system in a xylene contaminated groundwater at the VEGAS facility

Field experiments for testing the performance of the EFA sensor/filter photometer system in a monitoring situation with process water containing homogeneously dissolved BTEX-type hydrocarbons were performed at the research facility for subsurface remediation VEGAS of the Universität Stuttgart, Germany. The research facility includes several large-scale tanks of various sizes with volumes up to 750 m<sup>3</sup>. The various test setups are filled with partially contaminated soils and aquifer material thus, simulating contaminated sites without the risk of uncontrolled spreading into the natural environment. This arrangement allows large-scale experiments on in situ groundwater and subsurface remediation techniques and application and testing of in situ monitoring systems under controlled and reproducible conditions [19].

In 1998 an experiment was carried through in a tank that contained natural sand and gravel from the Rhine valley (Baden-Württemberg, Germany) with a groundwater-saturated aquifer. Soil and groundwater were contaminated with technical grade xylene (mixture of C<sub>8</sub> HC isomers, see Section 3). The main goal of the experiment was the modeling and optimization of a vacuum vaporizer and groundwater circulation well [20] used for the remediation of the aquifer and soil surrounding the well. Within the frame of this experiment the EFA sensor/filter photometer system was tested in continuous in situ measurements over a period of 4 months to check the long-term performance. The sensor installed in a glass flow cell was positioned in a bypass of a pipe that transported contaminated process water to a stripper column (cf. Fig. 2).

In Fig. 7 the C<sub>8</sub> HC sum concentration measured by the sensor system in 1 min intervals is plotted versus time for the first hour of the remediation experiment. These data are shown in detail because at this initial stage of the experiment strong HC concentration changes occurred within minutes. On the other hand, it is a fact already discussed in the Section 4.1.3 (see also Fig. 6) that the sensor needs approximately 20–25 min to be in equilibrium with the aqueous HC solution under the hydrodynamic conditions given in the flow cell. Thus, for most periods of time within this first hour of the experiment the sensor could only deliver semi-quantitative results, because it had been calibrated in the laboratory with equilibrium data (cf. Fig. 5). Off-line data obtained by HPLC/UV laboratory analysis of grab samples taken from the process water at the feed pipe during this 1 h period and the corresponding stripper pump flow rate are also presented in Fig. 7. Due to the slightly different positions of the EFA sensor measuring point in the bypass and the sampling point at the feed pipe, the

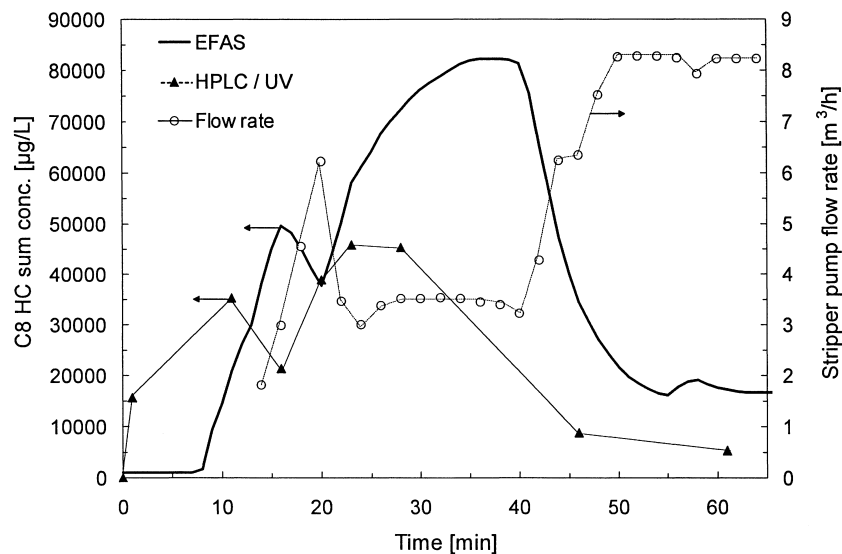


Fig. 7. Monitoring of C8 HC sum concentration in a bypass of the feed pipe of a stripper column connected to a groundwater circulation well at the VEGAS facility; comparison of EFA sensor in situ data and HPLC/UV off-line analysis data of grab samples for the first hour of the remediation experiment.

in situ curve and the HPLC curve show a time shift of a few minutes. The in situ HC sum concentration values measured by the sensor strongly increase 6 min after the start of the stripper pumping at 0 min (the flow rate of the pump in the first 15 min is not given because a water/air mixture was pumped in the pipe system leading to imprecise readings of the flow meter until the stripper column was filled up completely with water). The data clearly indicate that the EFA sensor though not being in equilibrium with the aqueous HC solution instantaneously traced the changes in the C8 HC sum concentration induced by variation of the pump flow rate. This can be seen especially after 15 and 40 min where the flow rate was strongly increased leading to a decrease in the HC concentration. This decrease is caused by the dilution effect induced by pumping larger amounts of low contaminated water from the outer surroundings of the well. The “pattern” of the EFA sensor in situ and the HPLC/UV off-line concentration curves clearly resemble each other, thus, indicating that the data agree from a qualitative point of view and in the order of magnitude.

However, the C8 HC sum concentrations given by the sensor are approximately by a factor of 2 higher than those measured by off-line analysis. And this was also found for the data collected during the following weeks of the experiment. Fig. 8 gives the same comparison over the period of 1 week after the beginning of the remediation experiment, where the concentration changes were much slower and the sensor was in equilibrium with the aqueous HC solution for most of the time. The rough pattern of both data sets is again similar and the increase of the C8 HC sum concentration in the time period between 34 and 52 h due to a decrease in the stripper pump flow rate is detected by both methods. But two features in Fig. 8 are evident: the offset in the concentration/time plots and the

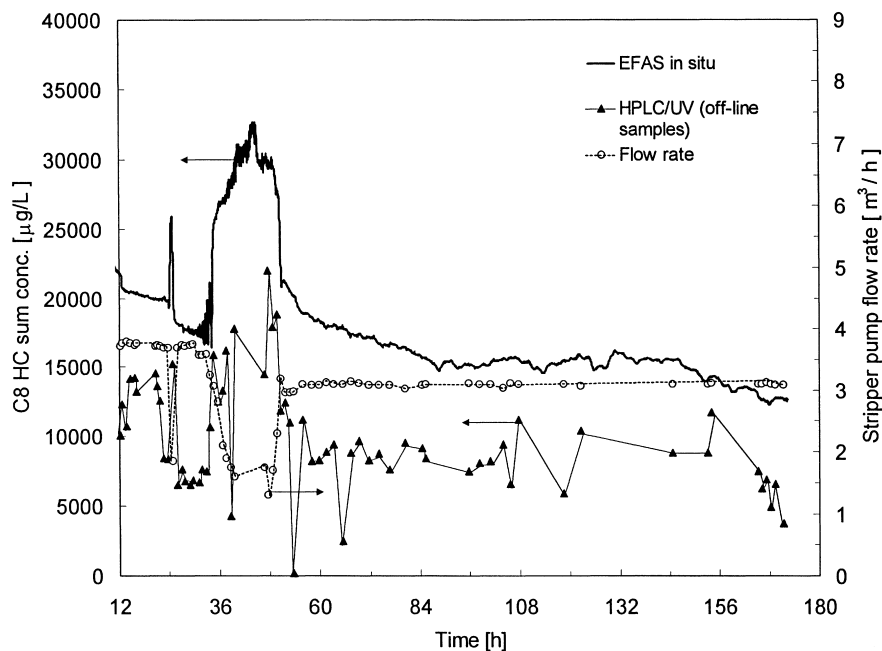


Fig. 8. Monitoring of C8 HC sum concentration in a bypass of the feed pipe of a stripper column connected to a groundwater circulation well at the VEGAS facility; comparison of EFA sensor in situ data and HPLC/UV off-line analysis data of grab samples for the first week of the remediation experiment.

large scattering of the off-line analysis data especially at times where no big and sudden concentration changes were expected because of a rather constant pump flow rate (time interval between 52 and 168 h). The EFA sensor in situ data for this period on the other hand seem to be more consistent with the experimental conditions because they indicate a relatively constant decrease in the C8 HC sum concentration values. This steady decrease for a constant stripper pump flow rate was also expected by the hydrogeologists conducting the experiments with the vacuum vaporizer and groundwater circulation well from similar experiments performed earlier.

Because both the calibration of the EFA sensor system as well as the calibration of the laboratory HPLC/UV instrument had been carried out with well-defined calibration samples and controlled by reference analysis it was improbable that a wrong calibration could have caused the offset in the data. Furthermore, losses of highly volatile C8 HCs in the grab samples could of course be a problem but were minimized by fast sampling in GC vials that were hermetically sealed by a septum and avoiding any headspace in the aqueous samples.

A strong change in the composition of the HC mixture due to some chromatographic effect within the soil matrix would have caused a change in the slope of the C8 HC sum calibration function of the EFA sensor system. But this point could also be ruled out as a source of error because GC reference analysis of some feed water samples showed a constant ratio of the compounds and also the EFA sensor system recorded a rather constant signal ratio of 2.78 for the two measuring channels over time (cf. Section 4.1.2).

In view of these considerations it seems rather likely for us that natural microbial organisms contained in the soil and groundwater used for the remediation experiment are the main reason for the general offset in both data sets, the strong “scattering” within the off-line analytical results and the tremendously lower HC analyte concentrations in some of the grab samples (cf. Fig. 8). During the experiments large amounts of bio-films appeared in the stripper column as well as in the pipes and after weeks even in the sensor flow cell indicating a lot of biological activity in the groundwater. This implies that degradation of xylene in the water samples could be of some importance. Biodegradation of BTEX-type HCs under aerobic and anaerobic conditions in contaminated sites has been described in the literature [21] and is known to be enhanced by groundwater circulation remediation procedures [20]. On the other hand, due to technical reasons the grab samples had to be stored >1 week before HPLC-UV analysis was performed. Because the off-line analysis was performed generally with some time delay after sampling, the micro-organisms contained in the samples could have been able to partially degrade and mineralize the aromatic HCs and thus, to decrease the concentration values especially for samples that were stored over longer periods of time. This possible interference due to the micro-biology in the samples had not been anticipated by the experimenters and made it difficult to do an exact validation of the in situ data.

In Fig. 9 the C8 HC sum concentration data of EFA sensor in situ analysis are plotted versus the HPLC/UV off-line analysis data of the grab samples (only samples where the

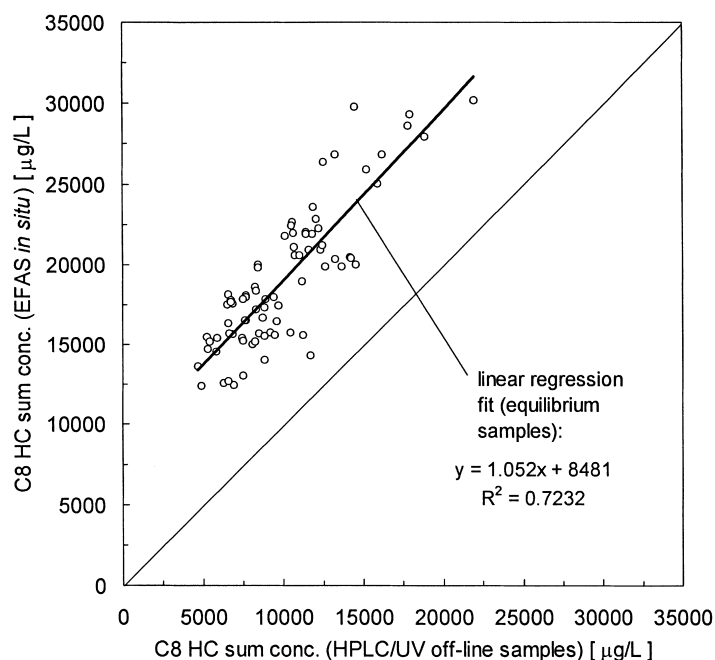


Fig. 9. Correlation of EFA sensor in situ data and HPLC/UV off-line analysis data of grab samples; xylene remediation experiment at the VEGAS facility.



sensor was in equilibrium with the aqueous phase have been taken into account). The data points are not lying on the diagonal — which would mean an “ideal” matching of both data sets — but are rather scattered around the regression line ( $R^2 = 0.7232$ ), which runs parallel to the diagonal with a slope close to one and a strong positive offset. The offset reflects the fact that the HPLC/UV concentration data have a relative mean deviation of –48% compared with the EFA sensor in situ concentration data. On the other hand, the plot also demonstrates that both data sets are correlated to each other in spite of the problems encountered with the degradation of the grab samples discussed above.

In any case, the results obtained show that near-real-time data provided by the EFA sensor technology (though being semi-quantitative for very fast concentration changes) allow a more reliable control of process conditions due to the higher information content achieved by a continuous monitoring technique compared to single sample laboratory analysis, where the results usually are obtained after delay times of hours or days. Moreover, especially samples containing organic analytes are prone to sampling errors (e.g. loss of volatile analytes) and possibly to micro-biological artifacts and interference that may occur during sample transport and storage.

During the continuous field measurements in the xylene remediation experiment the EFA sensor fiber proved to be stable from a chemical and mechanical point of view over the whole 4 month period of the experiment. The only maintenance operation that was necessary approximately 6 weeks after the start of the measurements was the removal of hydraulic lime and a bio-film of algae that were deposited on the sensing fiber. The lime was removed by circulating a 0.2 M formic acid solution through the flow cell and the bio-film by a 15% aqueous  $H_2O_2$  solution.

## 5. Conclusions

The feasibility of in situ chemical sensing of BTEX-type hydrocarbons with a compact EFA sensor/filter photometer system has been demonstrated in field trials. Continuous measurements at the VEGAS research facility were carried through in a tank containing sandy gravel and a groundwater-saturated aquifer that was contaminated with C8 HC isomers. The results obtained in a bypass stream of a pipe leading to a stripper column showed, that the sensor response to BTEX-type HCs in aqueous solution is fully reversible and that quantitative information about the HC sum concentration is provided in the low  $mg\ l^{-1}$  range. However, a prerequisite to obtain quantitative in situ information about the HC sum concentration is that the concentration changes in the process occur in time intervals that are compatible with the 20 min response time of the sensor to BTEX-type HCs and that now strong changes in the composition of the HC mixture occur. A frequent re-calibration is not necessary because the sensor system showed no drift of the absorbance values with time.

The validation of the in situ EFA sensor data described in this paper was not completely satisfying because of the problems encountered with the degradation of the grab samples. Future field experiments certainly have to focus on this point and to do an exact validation by comparing the sensor data to established laboratory methods, e.g. EPA methods for analysis of HCs in water and to carefully pay attention to minimize chemical and micro-biological artifacts in the samples.

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## References

- [1] R.O.G. Franken, in: F. Arendt, G.J. Annokée, R. Bosman, W.J. van den Brink (Eds.), Proceedings of the 4th International KfK/TNO Conference on Contaminated Soil, Berlin, Germany, Kluwer Academic Publishers, Dordrecht, 1993, pp. 845–851.
- [2] Rahmen-Verwaltungsvorschrift über Mindestanforderungen an das Einleiten von Abwasser in Gewässer, Anhang 40, "Mineralölhaltiges Abwasser", 1992, p. 809.
- [3] DIN (German Industrial Standard) 38409: Part 18 "Bestimmung von Kohlenwasserstoffen (Determination of Hydrocarbons)", Beuth Verlag GmbH, Berlin, 1981.
- [4] J. Bürck, J.-P. Conzen, H.J. Ache, *Fresenius J. Anal. Chem.* 342 (1992) 394.
- [5] J.-P. Conzen, J. Bürck, H.J. Ache, *Appl. Spectrosc.* 47 (6) (1993) 753.
- [6] J. Bürck, J.-P. Conzen, B. Beckhaus, H.J. Ache, *Sens. Actuators B* 18 (1994) 291.
- [7] R. Kellner, R. Göbel, R. Götz, B. Lendl, B. Edl-Mizaikoff, M. Tacke, A. Katzir, in: A.V. Scheggi (Ed.), Proceedings of the Conference on Optics for Environmental and Public Safety, Munich, Germany, SPIE, Bellingham, Vol. 2508, 1995, pp. 212–223.
- [8] B. Mizaikoff, M. Kraft, M. Jakusch, *Sea Technol. Mag.* 40 (2) (1999) 25.
- [9] J. Pawliszyn, *Solid Phase Microextraction — Theory and Practice*, 1st Edition, Wiley, New York, 1997.
- [10] N.J. Harrick, *Internal Reflection Spectroscopy*, Harrick Scientific, Ossining, New York, 1979.
- [11] J.-P. Conzen, Doctoral thesis, University of Karlsruhe, Germany, and KfK report No. 5302, 1994.
- [12] N. Klaas, B. Simmank, C. Rademacher, Determination of volatile compounds by HPLC — a fast and simple method, Jahrestagung der Fachgruppe Wasserchemie der GDCh, Koblenz, 1996.
- [13] E. Sensfelder, J. Bürck, H.J. Ache, *Fresenius J. Anal. Chem.* 354 (1996) 848.
- [14] J.-P. Conzen, J. Bürck, H.J. Ache, *Fresenius J. Anal. Chem.* 348 (1994) 501.
- [15] W. Guhl, U. Werner, *Nachr. Chem. Tech. Lab.* 45 (4) (1997) M15.
- [16] J. Bürck, M. Mensch, K. Krämer, *Field Anal. Chem. Technol.* 2 (1998) 205.
- [17] J. Bürck, in: J. Pawliszyn (Ed.), *Applications of Solid Phase Microextraction*, 1st Edition, The Royal Society of Chemistry, Cambridge, 1999, p. 638.
- [18] D.A. Skoog, J.J. Leary, *Instrumentelle Analytik (German version of 4th Edition of Principals of Instrumental Analysis)*, Springer, Berlin, 1996, p. 774.
- [19] B. Barczewski, H.-P. Koschitzky, in: G. Kreysa, J. Wiesner (Eds.), *Resumée Beitr. DECHEMA-11. Fachgespräch Umweltschutz, DECHEMA, Frankfurt / Main, Germany, 1996, DECHEMA, Frankfurt, 1996, pp. 79–101.*
- [20] B. Herrling, E.J. Alesi, G. Bott-Breuning, S. Diekmann, in: F. Arendt, G.J. Annokée, R. Bosman, W.J. van den Brink (Eds.), Proceedings of the 4th International KfK/TNO Conference on Contaminated Soil, Berlin, Germany, 1993, Kluwer Academic Publishers, Dordrecht, 1993, pp. 1083–1092.
- [21] T.B. Stauffer, E.L. Libelo, W.G. MacIntyre, J.M. Boggs, R. Stapelton, in: Proceedings of the 6th International FZK/TNO Conference on Contaminated Soil, Edinburgh, UK, 1998, Thomas Telford Publishing, London, 1998, pp. 95–100.