Fiber Optic Lif-sensors for the Trace Analysis of Environmental Pollutants in Water and in the Soil

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ABSTRACT

Laser-induced fluorescence (LIF) spectroscopy and fiber optics are shown to be a promising tool for the diagnostics of environmental pollutants in water and in soil. Time-integrated detection of fluorescence in an "early" and in a "late" time window with respect to the excitation pulse simplifies the method so far that it becomes very attractive for practical applications. Results from field measurements are reported, when oil contaminations under a gas station are investigated. The specifity of this method can be improved, when multiwavelength laser excitation at 248 nm, 276 nm, and 317 nm is applied. This allows to separate between different components of aromatic hydrocarbons, like BTXE-aromates and PAH molecules. In the second part of the paper an example for the application of LIF spectroscopy in soil physics is described, when the flow paths of environmental pollutants in the ground are investigated. The results are discussed with respect to problems in the sealing of sanitary landfills.

INTRODUCTION

In the last years fiber optic sensors and laser-induced fluorescence (LIF) spectroscopy becomes very interesting in remote sensing of various environmental pollutants in air, water and in the ground. Besides measuring only fluorescence intensities, time-resolved recording of the fluorescence improves the sensitivity of the method considerably [1]. In most of the cases investigated so far, the LIF-decay spectra of pollutants and surrounding media, e.g. water or soil, show significant differences, when the excitation is performed in the ultraviolet (uv) spectral range [2-4].

In the first section of this paper, time-integrated fluorescence detection in an "early" and in a "late" time window with respect to the excitation pulse is shown to simplify the method so far that it becomes very attractive for practical applications. Results from field experiments are reported, when oil contaminations in polluted water and soil samples are investigated.

Since petroleum products are complicated mixtures of mono- and polycyclic aromatic hydrocarbons the excitation with laser light below and above 300 nm changes the intensity and the decay characteristics of the induced fluorescence spectra dramatically. Therefore, a compact multigas-excimer laser and a hydrogen Raman-shifter are applied to get laser radiation at 248 nm, 276 nm, and 317 nm, respectively. Then time-integrated LIF detection in four time gates with proper duration and delay times be used to seperate between different components of monocyclic aromatic hydrocarbons, like benzene, toluene, xylene, ethylbenzene (BTXE) and polycyclic aromatic hydrocarbons (PAH). First examples from laboratory measurements are given in this paper.

In the second section, fiber optics and LIF are used to measure accurate temporal and spatial distributions of tracers with water characteristics in different soil samples. These data give informations on the flow paths of environmental pollutants in the ground. They can be used by soil scientists to prove existing transport models, and to calculate mobilities of different pollutants in the ground. In addition, these results are discussed with respect to the problem of sealing sanitary landfills with natural materials.

1. TRACE-ANALYSIS OF OIL CONTAMINATIONS WITH TIME-INTEGRATED LIF-SPECTROSCOPY

Sensitive detection of oil contaminations in water or soil samples by LIF spectroscopy requires a separation between the fluorescence signal of aromatic hydrocarbons and organic components which simultaneously are excited by the

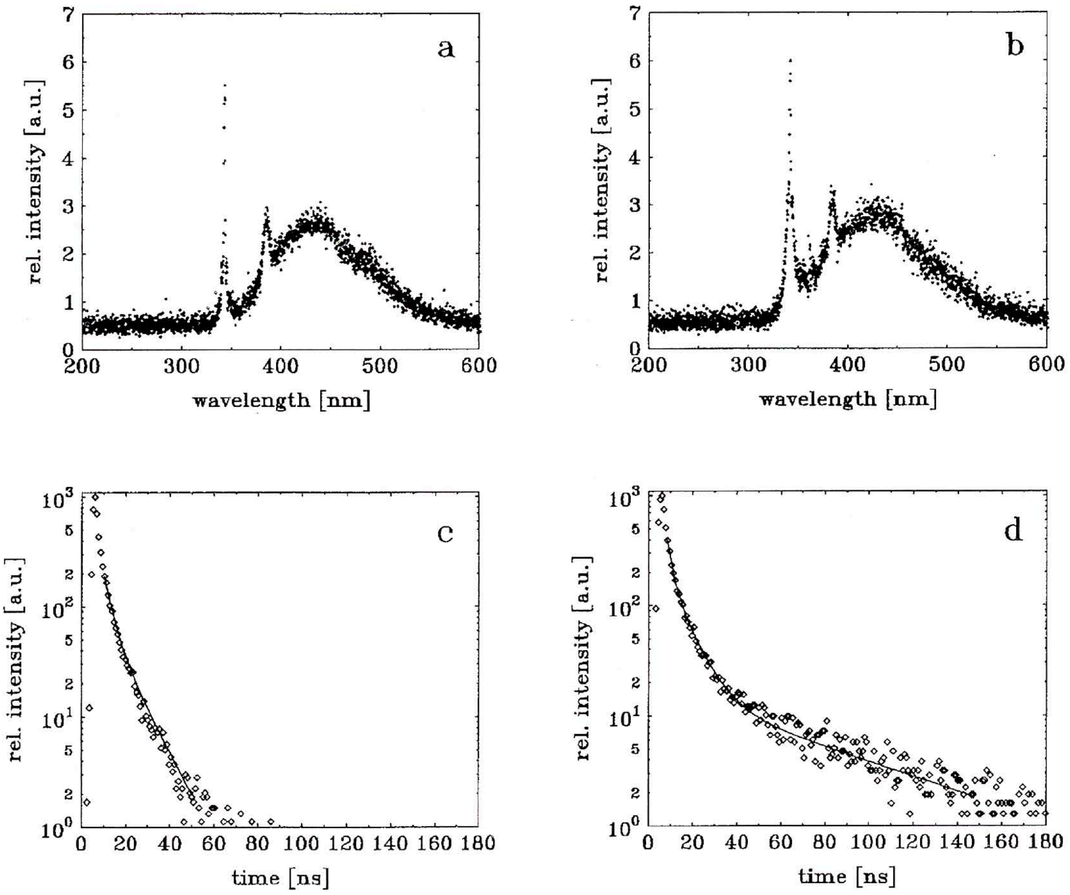

Fig. 1 - Competition of laser-induced fluorescence intensity spectra and time-resolved LIF decay spectra of (a,c) natural water and (b,d) a 10mg/l oil-water mixture. The excitation was performed with a nitrogen laser at 337 nm, the observation wavelength for the time-resolved measurements was 400 nm.

laser. In fig. 1 the fluorescence intensity- and the time-resolved LIF-spectra of pure water (a,c) and of oil polluted water samples (b,d) are shown, when a nitrogen laser at 337 nm is applied for the excitation.

In the case of the intensity spectra (a,b) two peaks at 337 nm and 380 nm from the elastic - and the Raman scattered laser light in water and a broad fluorescence band between 350 and 600 nm, which is emitted by dissolved organig matter (DOM) are obtained. There is no significant change in the fluorescence intensities in the spectra from a pure and an oil polluted water sample when the oil concentrations are below 10 mg/l. Therefore, only recording intensity spectra can not be used for qualitative and quantitative diagnostics. However, when time-resolved LIF is applied, oil concentrations below 1mg/l can be measured. This is shown in fig. 1c and d. After excitation at 337 nm with a laser pulse of 2 ns (FWHM) duration the time evolution of the LIF signal is recorded with a bandpass filter at 400 nm. For a pure water sample a LIF-signal is only obtained for times t < 80 ns after the laser pulse, while for oil water mixtures (c=10 mg/l engine oil in water) fluorescence can be measured for times up to 200 ns. Therefore, time-resolved laser spectroscopy is a promising tool for the trace analysis of oil polluted water or soil samples [1,2].

1.1 Theoretical considerations

For a rough theoretical approach, a homogenous mixture of one species PAH-molecules M with a concentration $[^1M]$ is assumed. After excitation with a short laser pulse (δ -pulse excitation) at the time t=0 the temporal derivative of the concentration of excited molecules for times t>0 is given by the rate equation [3]:

$$\frac{d\,[^1M^*]}{dt} = -\,(k_{SE} + k_{IQ} + k_{XM})\,[^1M^*] \qquad (1)$$

The rates k_{SE} for spontaneous emission, k_{IQ} for inter- and intramolecular quenching processes and k_{XM} for quenching by impurities like an additional molecular species X, are independent in time, providing that the viscosity of the solution is low. Then the differential equation (1) is solved by the "fluorescence response function"

$$I_F(t) = a \cdot e^{-\frac{t}{\tau_F}} \tag{2}$$

where τ_F is the "molecular fluorescence lifetime" of the species M:

$$\tau_F = \frac{1}{k_{SE} + k_{IQ} + k_{XM}} \tag{3}$$

Since petroleum products are mixtures of a large number of mono- and polycyclic aromatic hydrocarbons, their fluorescence decay spectra can be described by a sum of exponentials with characteristic intensities a_i and fluorescence lifetimes τ_i:

$$I_F(t) = \sum_{i=1}^{n} a_i \cdot e^{-\frac{t}{\tau_i}} \tag{4}$$

For example, a numerical evaluation of experimental time-resolved fluorescence spectra of pure engine oil (15W-40HD) leads to a sum of three exponentials with decay times $\tau_{o1} = 7$ ns, $\tau_{o2} = 27$ ns and $\tau_{o3} = 110$ ns, and corresponding intensities $\tau_{o3} = 730$, $a_{o2} = 240$, $a_{o3} = 30$ for excitation at 337 nm and observation of fluorescence at 400 nm. However, for the same experimental conditions, the fluorescence decay of natural water can be described by only two exponential functions with the parameters $a_{W1}= 650$, $\tau_{W1}= 4$ ns, $a_{W2}= 350$ and $\tau_{W2}= 10$ ns. With these experimental results a computer simulation is developed to describe the dependency of the temporal evolution of oil-water LIF-spectra on the concentrations of oil in the sample [1]. In figure 2a the results of the calculations are shown. The left curve corresponds to the fluorescence decay spectrum of pure water. With increasing concentration of engine oil in the water sample significant fluorescence intensities are obtained for times t>60 ns. This is in good agreement with the experimental results shown in figure 1d. In order to make this method attractive for practical applications, time-resolved recording of the fluorescence intensities is simplified to time-integrated detection of the fluorescence in only two time gates. One opens between 0 to 100 ns (I_1) and the other one between 100 and 200 ns (I_2) with respect to the laser pulse. In the "early" time window both, the laser-induced fluorescence from the DOM and from the PAH molecules are detected, while in the "late" window only fluorescence from PAH-components of the oil is obtained. The ratio I_2/I_1 is a sensitive indicator for the diagnostics and can be used for qualitative and quantitative determinations of sum-PAH concentrations in the samples under investigation.

In fig. 2b the results of numerical simulations for the ratios I_2/I_1 as function of the engine oil concentration are shown for an oil water mixture. These results are compared with the experimental data, which are measured with the time-integrated LIF detection method (refer to fig. 3a). A good agreement is obtained in the relative scale.

For excitation at 337 nm and observation of the fluorescence at 400 nm a typical detection limit for oil contaminations is 0.5 mg/l in water. In average most mineral oils have only 1% PAH-components and because excitation at 337 nm will only give fluorescence from the PAH molecules, this results in a detection limit of sum-PAH in the order of µg/l. The same method can also be adapted to the detection of oil pollution in the ground, providing that the unpolluted soil sample shows short fluorescence decay times with typical $\tau_i \leq 10$ ns, which results from organic materials in the soil. In figure 3b experimental ratios I_2/I_1 are shown for oil polluted quartz sand samples. The large uncertainties in the data are mainly caused by problems in the preparation of homogeneous distributions of oil in the sand samples. From the laboratory measurements the detection limit of oil contaminations is estimated to be 5 mg/kg soil for the present set-up. The average power of the nitrogen laser used during these measurements is about 0.2 mJ/pulse.

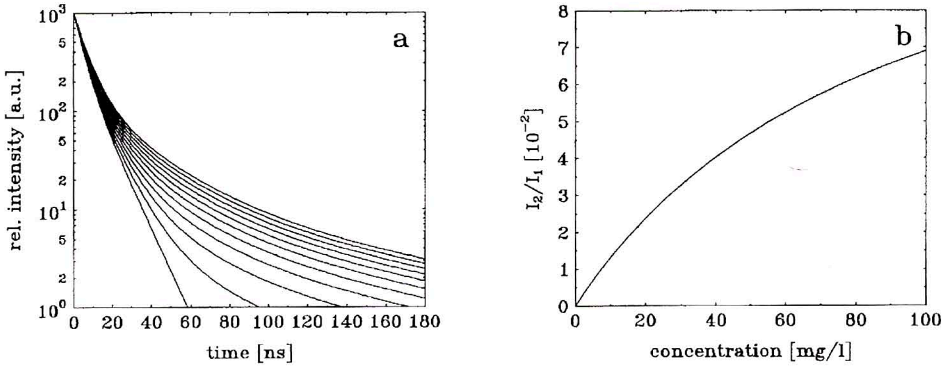

Fig. 2 - (a) Results of numerical simulations of time-resolved decay spectra for different concentrations of engine oil (PAH-molecules) in natural water. The left curve shows the decay of pure water. Then in steps of 2.5 mg/l the oil concentration is increased. The right curve shows the decay of an oil-water mixture with 25 mg/l oil. (b) Calculated ratio of time-integrated fluorescence intensities I_2/I_1 depending on the concentration of engine oil in the water sample.

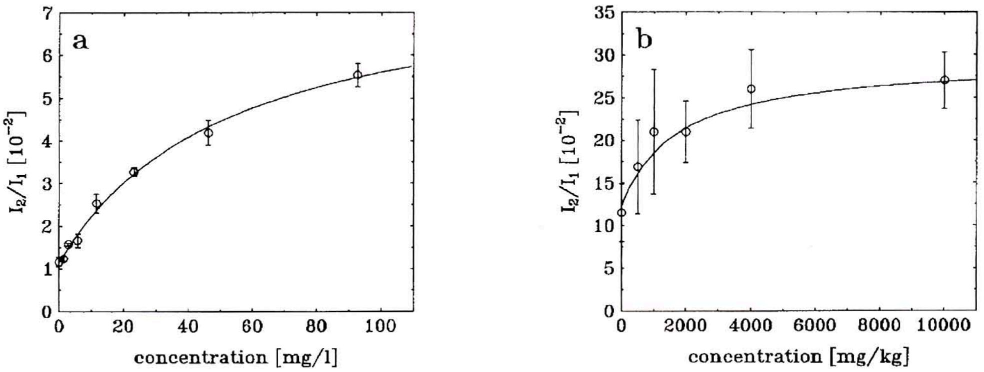

Fig. 3 - Ratio of the time-integrated fluorescence intensities I_2/I_1 in dependence on various engine oil concentrations (a) in natural water and (b) in sand.

1.2 Experimental set-up and field measurements

In figure 4 the present set-up for the field measurements is shown. It consists of a compact sealed-off multigas-excimer laser, which is operated with nitrogen (337 nm) or KrF (248 nm) at repetition rates up to 100 Hz, a fiber optic system with integrated detection head for the excitation and the observation of the fluorescence and an electronic section for data accumulation and processing. The LIF-signal is detected with a monochromator or bandpass filter and a photomultiplier. Two 100 MHz counters are applied for the time-integrated recording of the fluorescence intensities I_1 and I_2. A trigger unit controls the duration and the position of the gates for the counters with respect to the laser pulse. The first gate opens between t=0 and 100 ns (I_1), while the second counter is activated for the time interval t=100 to 200 ns (I_2). At t=0 the laser excitation is performed. The typical duration of a laser pulse is about 2 ns (FWHM) and the time for data accumulation is about 2 minutes. Then the measured intensities I_1 and I_2 are transferred to a personal computer for data processing. The whole system is computer controled.

The photon counting technique is applied to ensure best detection sensitivity. In case of low oil contaminations in water or soil samples this is most important for recording fluorescence intensities in the "late" time window. However, the accuracy of the data taken with this method depends very sensitively on the number of photons counted and on the ratio of counted photons to exciting laser pulses (refer to fig.4b and c). Therefore, these effects that limit the

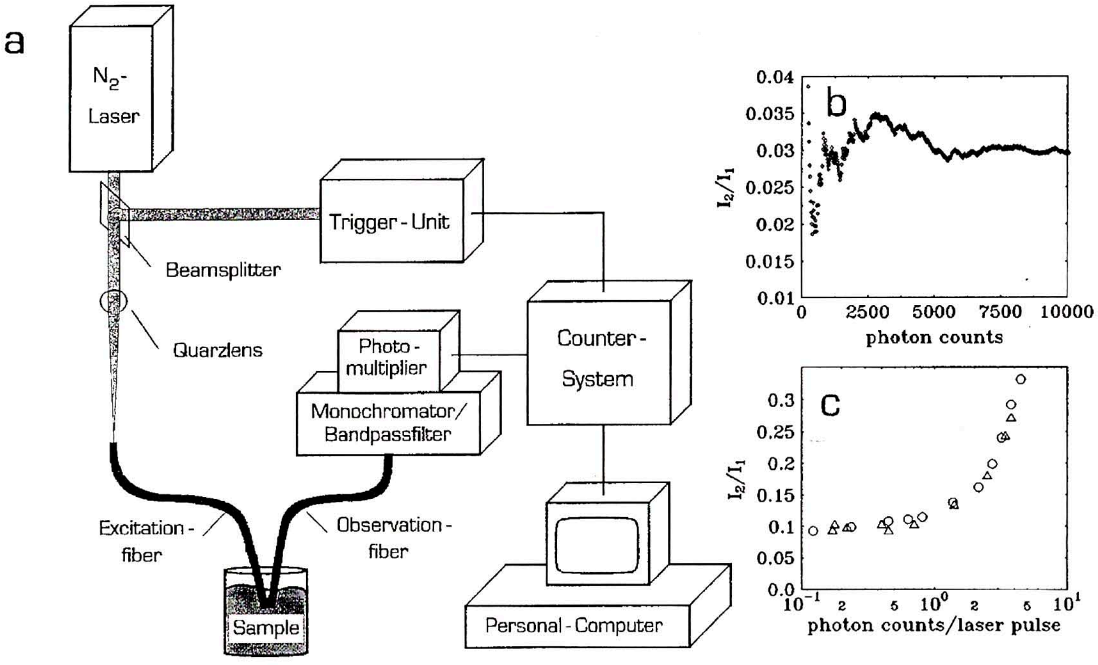

Fig. 4 - (a) Experimental set-up for time-integrated detection of polluted soil and water samples. (b) Accuracy of the ratio I_2/I_1 depending on the number of detected photons for an oil-water mixture of 10 mg/l. (c) Dependence of the ratio I_2/I_1 on the ratio of detected photons and laser pulses (Δ experimental data, O calculations).

accuracy in the determination of the time-integrated LIF intensities have to be considered. The results from a computer simulation in fig. 4b show that an accuracy in the ratio I_2/I_1 of better than 5% requires the registration of at least 6000 photons. On the other hand, because of the limited time resolution of the 100 MHz counters used in the present set-up makes it necessary to consider dead time effects. This is shown in figure 4c. Again a computer simulation is used to calculate the dependency of the ratio I_2/I_1 on the number of detected photons to excitation pulses. A very good agreement between the simulation and the experimental results is obtained. Therefore, in order to avoid systematic errors in the data, the ratio between detected photons and exciting laser pulses should be below 1:2 during the measurements. This gives about two minutes time for data accumulation when the repetition rate of the laser is 100 Hz and the number of detected photons is 6000.

Results from field measurements are shown in figure 5. Here diesel fuel contaminations in the soil near a leaking gas pump are analyzed with the fiber optic LIF-sensor. In a first step drillings are taken from the ground and then in a second step on-line the intensities I_1 and I_2 are measured. A vertical layer of 2 m depth and 6 m width is investigated. The positions of the boreholes are indicated in the site plan of figure 5. From the surface down to a depth of 1.5 m the soil consists of sand, followed by a 0.15 m thick layer of peat and then clay. The data from laboratory experiments (refer to figure 3b) are used as a calibration curve to converte the measured ratios I_2/I_1 from the field experiment into concentrations with units mg/kg soil. In figure 5 an isometric plot of the diesel fuel contamination in the soil is shown. Directly below the position of the leaking gas pump (arrow in fig. 5) the highest diesel concentrations of more than 10000 mg/kg are found in a depth of 0.8 m, while in the layers below 1.5 m the concentration decreases down to 100 mg/kg. Another interesting result of these measurements is that the peat layer acts as a "natural sealing" in the soil. In the clay directly below the leaking gas pump only concentrations between 100 and 2000 mg/kg are detected while it is about 10000 mg/kg in layers directly above the peat. The concentration drops down below 5 mg/kg when drillings are analyzed that are taken from the same layer but more far away from the gas pump. All data are compared with the results of the chemical analysis of the same samples (infrared spectros-

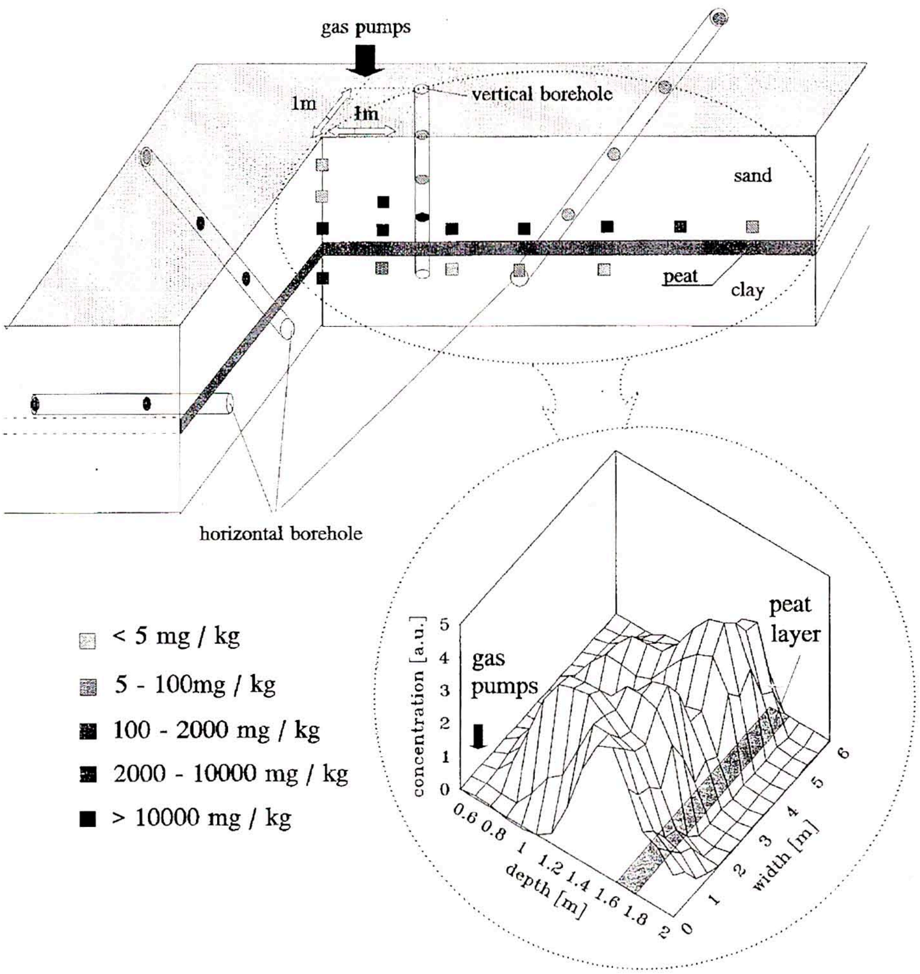

Fig. 5 - Site plan and experimental results of diesel fuel contaminations in a vertical soil layer near a leaking diesel gas pump.

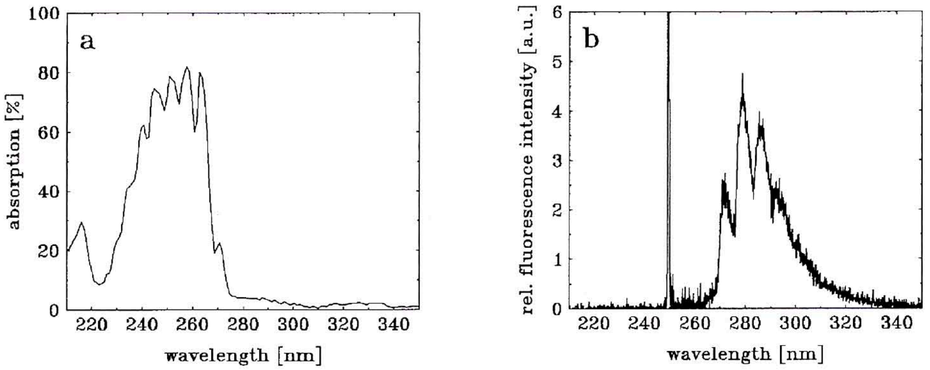

Fig. 6 - (a) Absorption spectrum of benzene. (b) Time-integrated fluorescence spectrum of benzene after excitation at 248 nm.

copic method "DIN 38409-H18"). In nearly all cases a very good agreement in the relative scale but also in the absolute values is obtained. The advantages of the time-integrated fiber optic LIF-technique compared to the chemical analysis are the on-line diagnostics of the samples and an improved spatial resolution in combination with a high sensitivity.

1.3 Multiwavelength excitation

Petroleum products are complicated mixtures of aromatic hydrocarbons in various compositions. Depending on the number of hydrocarbon rings the absorption spectra are shifted from the blue into the ultraviolet spectral range. Monocyclic aromatic hydrocarbons, e.g. BTXE show only strong absorption bands below 300 nm [5]. In figure 6 the absorption spectrum of benzene is shown. Only excitation with a KrF-excimer laser at 248 nm will induce fluorescence from this component, while this will not be possible when using a nitrogen laser at 337 nm. On the other hand, most PAH-molecules like phenanthrene or pyrene have more red shifted absorption bands in the spectral range between 300 and 500 nm [6].

Therefore, multiwavelength laser excitation and time-integrated detection of fluorescence at suitable wavelengths seems to be a promising method to select between different components of aromatic hydrocarbons. When applying a KrF-excimer laser and a hydrogen Raman-shifter it is possible to produce laser radiation at 248 nm, 276 nm and 317 nm simultaneously. Then the separation between mono- and polycyclic aromatic hydrocarbons in the samples under investigation is possible. Besides this, laser excitation at 248 nm will also increase the sensitivity of the method used so far. In figure 7 the LIF-intensity spectra of pure water (a) and a mixture of 10 mg/l oil in water (b) are shown for excitation at 248 nm. When comparing these spectra with the ones measured for excitation at 337 nm (refer to fig. 1) no differences in the LIF-intensities are observed in the case of natural water, while this is changed for the oil water mixture. For the 10 mg/l oil-water mixture and excitation at 248 nm the maximum of fluorescence intensity is obtained around 350 nm. However, the fluorescence intensity of a natural water sample at 350 is about a factor of 4.5 lower. Also the intensity of the Raman scattered laser light at 270 nm is changed, depending on the concentration of oil in the sample under investigation. This is due to the more efficient absorption of BTXE below 300 nm. The Raman scattered nitrogen laser light at 380 nm does not change the intensity in oil polluted compared to pure water samples (refer to fig. 1). More detailed experiments for using these effects in the diagnostics are in progress.

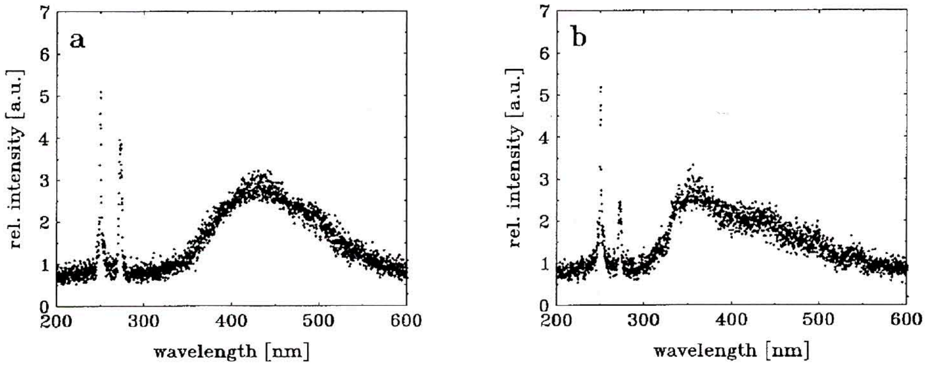

Fig. 7 - Laser-induced intensity spectra of (a) natural water and (b) a 10 mg/l engine oil water mixture. The excitation was performed with a KrF-excimer laser at 248 nm.

2. TEMPORAL AND SPATIAL DISTRIBUTION OF TRACERS IN THE GROUND

Informations on the flow path of environmental pollutants in the ground are not only of great interest in soil physics, but also necessary for well-aimed appraisals of damages, in cases of leaking oil tanks or gas pumps as well as the sealing of sanitary landfills. In soil science the investigations of the temporal and spatial distributions of suitable tracers are important for evaluating the validity of existing transport models, and in order to describe the mobility of different pollutants, e.g. plant-protective agents, radio nuclides or fertilizers in various soil systems. With conventional batch techniques, as shown schematically in figure 8, breakthrough curves (BTC) can only be determined without any information about the spatial distribution of the tracer in the sample. Usually a column of soil is eluted by a dye tracer solution of an initial concentration C_0 at the top, while the effluent is collected at the bottom in fractions after certain time intervals t. The temporal dependency of concentrations C(t) in the different fractions is determined photometrically in order to get a BTC of the soil sample (refer to fig.8) [7,8].

2.1 Experimental methods and results

The present experimental set-up consists of an Ar^+-laser with an emission wavelength at 488 nm, a fiber optic system and a CCD-camera (refer to fig 9a). The laser radiation is coupled into five identical glass fibers for the excitation of the tracer dye. Optrodes are applied in a way, that the excitation and the observation fibers of same diameter are fixed together in a parallel arrangement by means of plastic tubes. In order to minimize the disruption of the natural structure of the soil sample, an optrode diameter of less than 1 mm is used with fibers of 200 m in diameter. The LIF-intensity is detected by a CCD-line camera (1728 pixel), which is protected from backscattered or reflected laser radiation by a cut-off interference filter. The observation fibers are fixed directly on the surface of the filter. Then an area of about 85 pixels of the CCD-line is illuminated by the light coming out of a single observation fiber. The LIF-signal is recorded with the CCD-array. Exposure times between 10 ms and 10^6 ms are available. Then the data are transferred and analyzed by a personal computer, which also controls the CCD-camera.

The optrodes are positioned at well defined places in a soil column of 72 mm in diameter and 40 or 60 mm in height. This is shown in fig. 9a. For the first experiments quartz sand with a grain size distribution of less than 2 mm was used, because its chemical and physical properties are most suitable for these investigations.

The tracer dyes that can be used in these experiments have to fulfill some options. Their spectral characteristics should allow the excitation with an Ar^+-laser line and they should hold the standard requirements of soil physics. Because of its well known qualities in soil investigations through long standing applications in soil science and a good absorption at 488 nm, fluoresceine (Spiro[isobenzofuran-1(3H),9'-[9H]xanthen]-3-one,3',6'-dihydroxy-,disodiumsalt) is applied in these experiments. A major problem, especially for fluoresceine, is a dependency of the fluorescence yield on the pH-value of the surrounding medium. The fluorescence intensity decreases rapidly when changing from alkaline into acidic region. Beyond that, an adsorption of the dye molecules onto the sediment surface can be observed to a

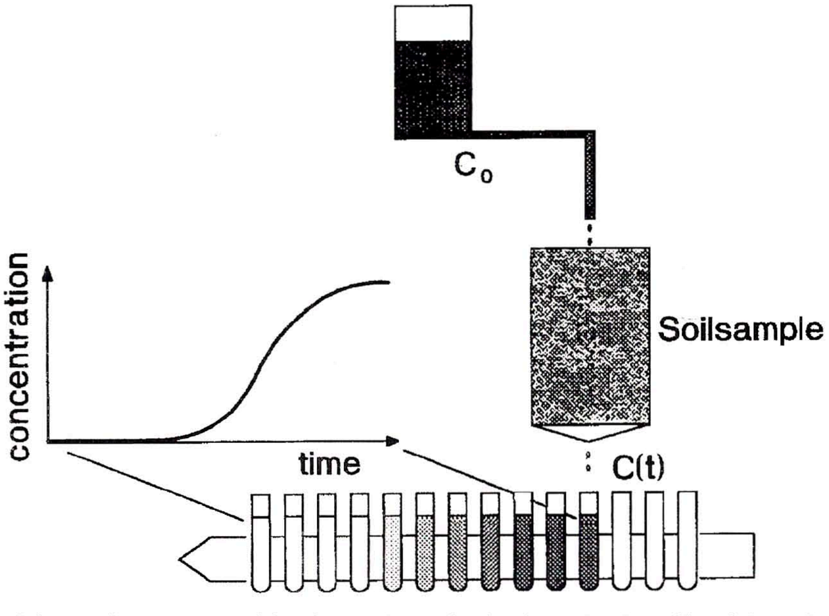

Fig. 8 - Scheme of a conventional batch experiment for the determination of breakthrough curves.

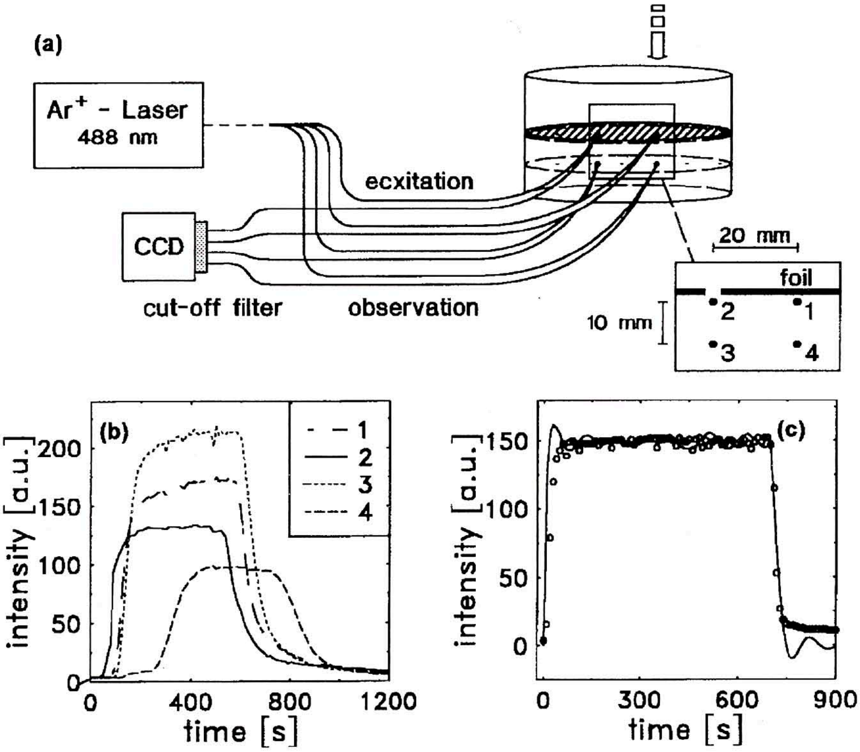

Fig. 9 - (a) Experimental set-up. (b) Time dependent distribution of a tracer in a simple model of a sanitary landfill with a leak in the sealing. (c) Experimental breakthrough curve (dots). The line is the result of a computer fit by a "finite element analysis" [9].

certain extent for clay samples [10]. By using quartz sand and dye solutions in the neutral pH-region these effects are negligible.

Before starting measurements the soil columns are saturated with water from the bottom. The dye solution is applied to the samples in drops with adjustable frequencies above the position of optrode 1 as indicated by an arrow (refer to fig. 9a). Directly after application of the dye, water is used in the same manner to rinse the soil column. A typical time dependent fluorescence signal, due to the variation of the fluoresceine concentration in front of the optrode in a quartz sand sample is shown in fig. 9c. This breakthrough curve was fitted by a transport model based on the "finite element analysis" [9]. The oscillations at the rising and falling edge of the BTC are due to numerical uncertainties of the calculation in the model. So this laser-induced fluorescence technique enables a verification and, if necessary a correction of existing transport models in soil science. Effects, like the dependency of the temporal shape of the breakthrough curves on the elution frequency or the position of the optrodes in the sample are obtained with this LIF-method, too. Both, lower frequencies, and a deeper positions in the soil column, give the BTC a smoother shape [10].

One example for the capability of this laser-induced fluorescence method in a practical application, concerning the problem of sealing sanitary landfills, is shown in fig. 9a. A light- and watertight plastic-foil with a hole of 1 mm in diameter above the position 2 is used as a simple, idealized model for a leak in the sealing. The time dependent distribution of the tracer in this experiment shows (refer fig. 9b), that the dye solution first arrives at optrode 2 after about 25 s. Remarkable is the hydrodynamic distribution with depth as well as in the layer below the foil. This is given by the signals of the optrodes 1 and 3 and they are starting nearly at the same time (50 s). At position four the fluoresceine arrives latest, about 225 s after starting the elution. This characteristic behaviour at the different positions is also obtained in the second part of the experiment, when water is applied to the soil column 500 s after starting the experiment.

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