Contaminant Detection, Identification, and Quantification Using a Microchip Laser Fluorescence Sensor

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Abstract: This paper describes a series of laboratory tests conducted to assess the performance of a novel fluorescence-based in situ sensor for environmental contaminants. The sensor, which can be deployed downhole in a monitoring well, or incorporated into the shaft of a cone penetrometer, is less than 4 cm in diameter and uses a miniature microchip laser that produces ~200 ps pulses of ultraviolet radiation at a high repetition rate (~10 kHz) to excite fluorescence in a wide range of compounds. Results from laser induced fluorescence tests on single compound aqueous solutions of benzene, toluene, and o-xylene (BTX) demonstrate the sensor's ability to perform contaminant analyses on compounds with fluorescence lifetimes on the order of 1 ns. A linear relationship between contaminant concentration and fluorescence intensity was observed for concentrations over several orders of magnitude from the sensor's detection limit (<1 ppm for o-xylene) to solutions of pure BTX compounds at aqueous solubility. Owing to the microchip laser's short pulse length, fluorescence lifetimes were obtained directly from measurements without the need for spectral deconvolution. Analysis of data from these tests highlights the importance of differentiating a sensor's ability to detect, identify, and quantify compounds of interest—performance thresholds that ultimately define potential applications for the device.

Introduction

Most organic molecules, when excited with ultraviolet light, re-emit less energetic optical radiation. This emitted radiation is known as fluorescence and is characterized by its intensity as a function of both time (after excitation) and wavelength. Since this information is linked to the physical characteristics of an individual molecular species, it provides a powerful means to perform chemical analyses. The intensity information (as a function of wavelength) is typically referred to simply as the emission spectrum, and the term lifetime is used to indicate the time it takes for the intensity at any particular wavelength to fall to $1/e$ of its original value. Observation of these parameters may enable the detection, identification, and/or quantification of chemical species within an aqueous solution. However, each of these performance measures requires data of a different type and quality (e.g., signal to noise ratio) and creates a hierarchy of performance capabilities for a sensor.

The work presented here provides a detailed review of laboratory proof tests conducted to differentiate the ability of a novel in situ microchip laser induced fluorescence (LIF) sensor to detect, identify, and quantify benzene, toluene, and o-xylene (BTX compounds) levels in aqueous solutions, which are major components of fuels and therefore common environmental pollutants. The LIF sensor used in this investigation takes advantage of both time and wavelength information to investigate contamination in soil and groundwater. Several references provide a detailed review of its fundamental operating characteristics [Johnson and Zayhowski, "Sensor system for remote spectroscopy," U.S. Patent No. 5,483,546 (1996); Zayhowski and Johnson 1996], performance in laboratory prepared soil matrices (Sinfield et al. 1999; Sinfield 1997), and capabilities in actual field environments (Bloch et al. 1998). The device provides excitation using a passively Q-switched microlaser pumped by a fiber-coupled near-infrared diode laser, and generates short pulses (~200 ps) of 266 nm radiation at a repetition rate near 10 kHz. The microchip laser, focusing optics, and collection system are very compact, and the entire assembly can be placed in a monitoring well or contained within the shaft of a cone penetrometer (a standard geotechnical site exploration tool). Thus, ultraviolet (UV) radiation necessary to excite fluorescence in environmental pollutants such as gasoline is generated at the point of contamination, while the infrared diode pump laser remains above ground. This configuration takes advantage of the excellent transmission of infrared energy through fiber optic cable (attenuation<6 dB/km), and minimizes the ultraviolet attenuation (~20 dB/30 m of fiber) and nonlinear effects that characterize conventional fiber-optic-based LIF sys-

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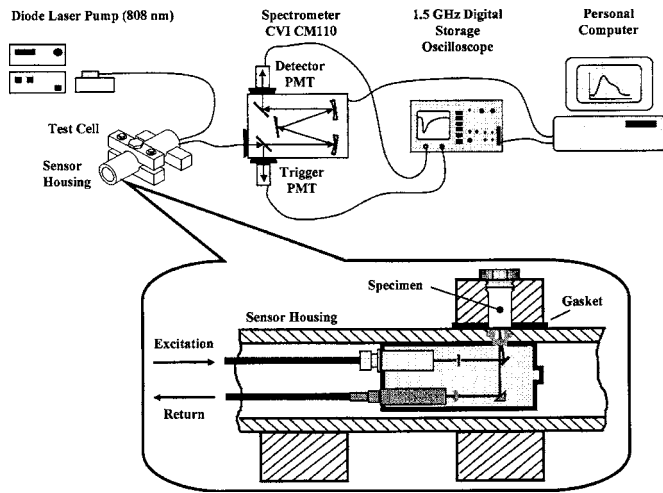
Fig. 1. Schematic of experimental apparatus

Scale: — = 2.0 cm

Fig. 2. Liquid test cell

tems (e.g., Pepper et al. 2002, 1998; Marowsky et al. 1998; Gillispie et al. 1993; Knowles and Lieberman 1995; Kenny et al. 1987).

Materials and Methods

Apparatus

The experimental apparatus used to evaluate the performance of the LIF probe includes spectroscopic hardware, a test cell, and a data acquisition system and has been described in detail in prior publications (e.g., Sinfield et al. 1999; Bloch et al. 1998). The experimental configuration employed here (see Fig. 1) is representative of a downhole monitoring well scenario in which the test probe is in direct contact with aqueous solutions and fluorescence observations are not obstructed by the presence of soil particles.

Spectroscopic Hardware

The microchip laser is pumped by a 1 W continuous wave 808 nm diode laser (SDL Inc. Model 2372-P3). The 808 nm output from the diode laser is used to pump, via fiber optic cable, a Nd:YAG microchip laser which is housed in a stainless-steel probe assembly. The microchip laser is mounted in the probe using a threaded fitting that contains a sapphire window and an UV silica focusing optic. This laser is passively Q switched and provides 200 ps pulses of 1,064 nm light at a repetition rate of approximately 10 kHz (Zayhowski and Dill 1994). After two stages of frequency doubling, and subsequent filtering to remove 1064 and 532 nm light, a fourth harmonic is generated in the UV at 266 nm which is focused just outside the probe's sapphire window. Molecular fluorescence excited by the UV microchip laser is imaged through the same window onto the tip of a 550 μm-diameter silica return fiber (note that the excitation and return radiation path angles shown in Fig. 1 are illustrative).

The output of the fiber is focused on the entrance slit of a 1/8 m scanning monochromator (CVI Inc. Model CM110) with an f number of 3.3 and a 2,400 line/mm grating blazed at 250 nm. A fast photomultiplier tube (PMT) (Hamamatsu H5783-03) is used to detect light intensity at the exit slit of the monochromator. A trigger signal is generated using an UV silica beam
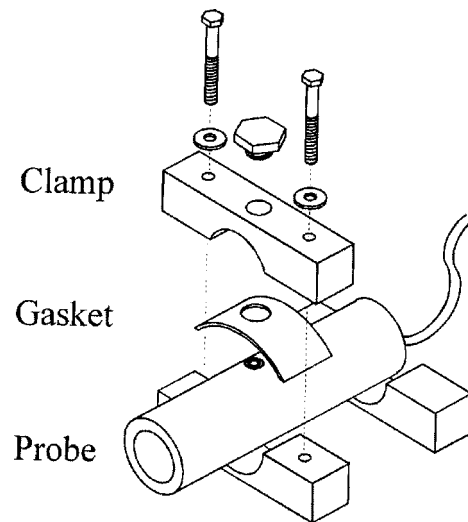
splitter mounted within the monochromator to direct a small fraction of the light entering the spectrometer onto a second PMT. The PMTs are operated at approximately 800 V and have a demonstrated fall time on the order of 1 ns.

Test Cell

The test cell employed in the laboratory experiments was used to simulate immersion of the probe in a liquid as if the probe were lowered into a monitoring well. The cell (Fig. 2) consists of a rectangular stainless-steel block clamp that is placed around the probe. The test sample is placed in a cylindrical hole in the clamp located directly above the laser output window of the probe. The hole contains approximately 1.5 cm^3 of sample solution, although only a small fraction of this volume is actually interrogated by the laser. Sample loss around the probe/clamp interface is prevented using a Teflon gasket; volatilization is prevented by a stainless-steel cap fitted with a fluorocarbon rubber o-ring.

Data Acquisition

A LeCroy 9362 1.5 GHz digital storage oscilloscope is used as a fast analog-to-digital (A/D) converter to acquire fluorescence signals at a sampling rate of 5 giga-samples per second (GSa/s) for a period of 50 ns referenced to the trigger; 500 traces are typically averaged for each measurement. The PMT output signal is measured across a 50 Ω load. A personal computer is used to control the monochromator grating and the oscilloscope.

Specimen Preparation

Test solutions were prepared by dilution of stock solutions, which comprised distilled demineralized water maintained in equilibrium with reagent-grade compounds. During each test, a volume of the desired sample was sealed in the test cell with zero headspace. This procedure minimized loss by leakage or volatilization throughout the duration of a LIF test. Fresh solutions were used for each test. In addition, blanks of distilled demineralized water were measured whenever test solutions were changed, to demonstrate that no residual contamination remained in the test cell.
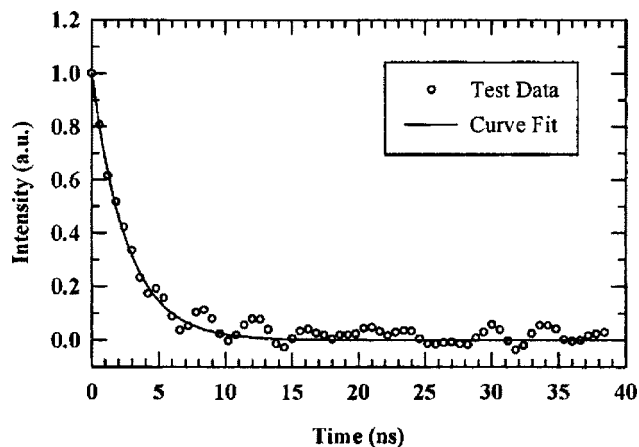
Fig. 3. Representative fluorescence decay curve for aqueous equilibrium solution of benzene at 300 nm

Data Analysis

A series of tests were performed to determine the sensor's sensitivity to BTX compounds and its time–response. Each test involved recording the time-dependent fluorescence spectrum (from 275 to 350 nm) of one of the BTX compounds at a particular concentration in water. The spectra from each test were analyzed to determine: (1) the total fluorescence signal gathered from the test medium; (2) the fluorescence lifetime of the compound in solution; (3) the wavelength of the peak fluorescence emission; and (4) the peak fluorescence intensity. The total fluorescence signal was determined by integrating over time and wavelength using trapezoidal integration; results are presented in arbitrary units (a.u.) due to corrections for the spectral response of the spectroscopic hardware. Absolute signal amplitudes were typically on the order of 10^1 mV at the oscilloscope input for peak concentration levels. After background subtraction, the fluorescence data were fit with a decay curve of the form $I(t)=ae^{-t/\tau}$ using a least-squares routine, where τ is an empirically derived fluorescence lifetime.

Results

The data acquired with this system are presented in several formats. A plot of the fluorescence signal, integrated in time, versus emission wavelength is referred to as an emission wavelength spectrum. A plot of fluorescence signal versus time, at any individual emission wavelength, is termed an intensity-time trace. The collection of all of the information available from a fluorescence test, in terms of both the time and wavelength, can be presented in a three-dimensional plot referred to as a wavelength–time–intensity (WTI) profile. Throughout the discussion that follows, the peak fluorescence signal is defined as the highest intensity observed at any wavelength. Further, the total fluorescence signal is the volume under the WTI profile.

Fluorescence Spectra, Lifetimes, and Linearity

Of the compounds tested, benzene has the shortest fluorescence lifetime; Fig. 3 shows the response at 300 nm from a 1,780 ppm aqueous (equilibrium) solution. A fluorescence lifetime of 2.6 ns was obtained by the fitting procedure described above, and agrees well with the lifetime of 2.4 ns obtained by Gillispie and St. Ger-
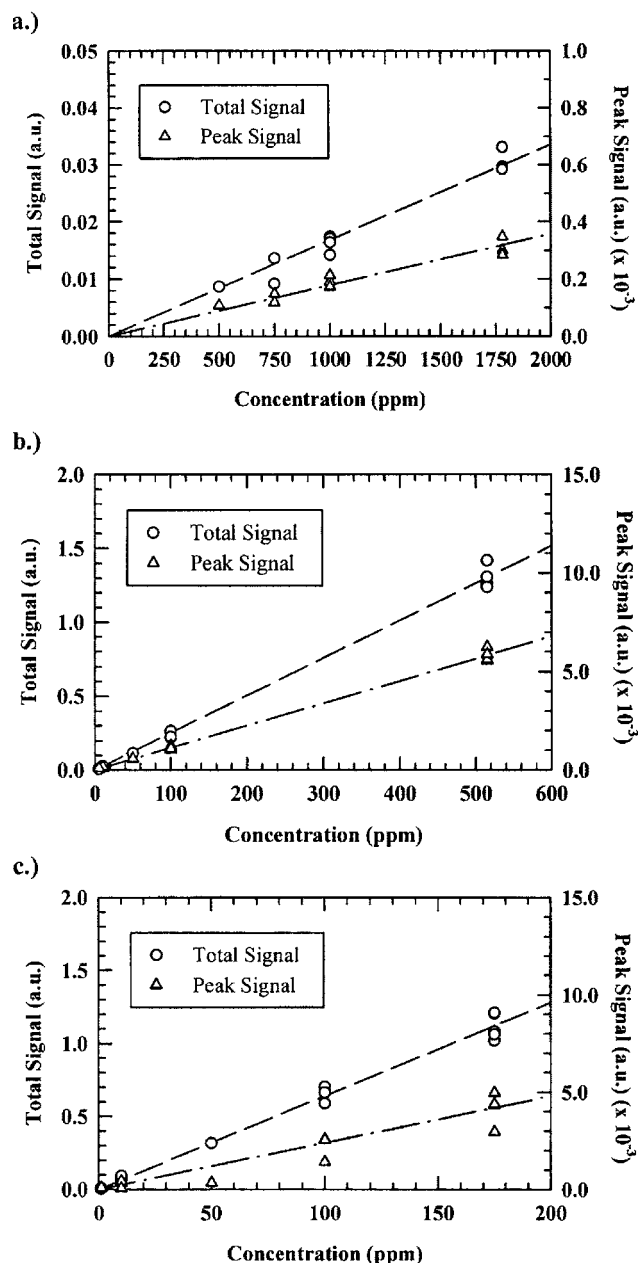

Fig. 4. Fluorescence signal and aqueous concentration for: (a) benzene; (b) toluene; and (c) o-xylene

main (1992) using 5–7 ns excitation pulses and deconvolution techniques for data analysis. A ten-test mean lifetime of 2.6±0.1 ns was measured using aqueous solutions of benzene having concentrations ranging from 500 to 1,780 ppm. Similar measurements on solutions of toluene and o-xylene gave fluorescence lifetime values of 6.2±0.2 ns ($n=13$) and 6.7±0.2 ns ($n=16$), respectively. Errors are 1 SD.

Over the majority of the concentration ranges considered, tests on each compound demonstrated a linear relationship among the peak signal, the total fluorescence signal, and the concentration of a compound in solution. However, the slopes of the lines relating compound concentration to either peak signal (the highest intensity observed at any wavelength) or total fluorescence signal (volume under the WTI profile) differ among the three compounds (Fig. 4). This results from the fact that the LIF probe is more sensitive to some compounds than others. The fluorescence-to-

concentration relationship, essentially a calibration factor, varies among compounds for two reasons. First, the UV absorptivity varies for different compounds. Under equivalent conditions, a solution of benzene, for example, absorbs an order of magnitude less at 266 nm than does an equimolar concentration of o-xylene (Berlman 1965). Second, the quantum yield (ratio of the number of emitted photons to absorbed photons) also differs among compounds (and can also be influenced by environmental factors). The quantum yield of benzene, for example, is less than one-third of that for o-xylene (Murov et al. 1993). Both of these considerations influence the magnitude of the fluorescence signal.

Discussion

The following discussion distinguishes among capabilities to detect, to identify, and to quantify contaminants in solution via fluorescence. These differences establish a hierarchy of performance that determines the potential applications for the sensor. For example, the ability to detect the presence of a compound in solution or simply recognize a change in state relative to background conditions has reconnaissance and monitoring value, and can help, for example, in finding leaks in landfill systems or indicating the presence of harmful agents in water supplies. Identification of compounds becomes important during site investigation activities where the nature of contaminants are unknown or in scenarios in which one contaminant must be distinguished from another to facilitate selection of the most appropriate treatment measures. Finally, quantification capabilities may be required when using a sensor to determine if treatment procedures at a contaminated site are necessary or if they have been effective given regulatory guidelines for allowable contaminant concentrations.

Detection of BTX Compounds

On the hierarchy of sensor performance outlined here, detection of the presence of a contaminant relative to a baseline or background is the least challenging operation for a sensor. To achieve this goal the sensor need only reliably indicate the presence of a signal in excess of the "uncontaminated" background.

For the experiments performed in this study, the criterion for the detection of a compound was defined to be a minimum signal level of approximately three times the standard deviation of the background (3σ), as sampled by the A/D converter of the oscilloscope. Assuming that the random noise component of the background, which cannot be effectively subtracted from the fluorescence signature, can be characterized by a normal distribution, the 3σ criterion should include approximately 99.9% of the noise. Thus any signal above this threshold could reasonably be interpreted as the product of fluorescence.

The background associated with this LIF system was evaluated from ten full-spectrum scans of water blanks (a data set containing the response to nearly 400,000 laser pulses). The ten background scans were carried out on different days over a period of 3 months, and thus represent long-term behavior of the system. The standard deviation of the background signal was 6.3 $\times 10^{-6}$ a.u.

The corresponding detection limits for benzene, toluene, and o-xylene were 100, 2, and 0.8 ppm, respectively. These values were obtained by dividing the 3σ minimum required signal level
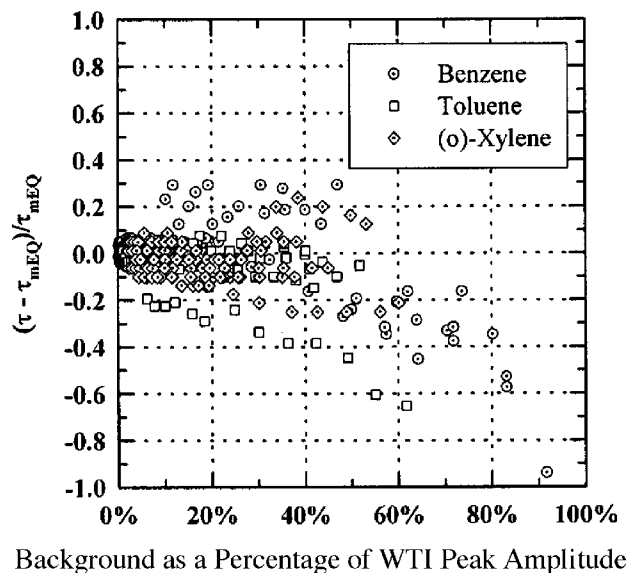

Fig. 5. Effect of background on fluorescence lifetime determinations

($3 \times 6.3 \times 10^{-6}$ a.u.) by the slope of the plot relating peak fluorescence signal to aqueous concentration for each of the BTX compounds.

Identification of BTX Compounds by Fluorescence Lifetime

Identification of a contaminant requires more information than is needed to simply confirm its presence in a sample. In some cases, the emission-wavelength (EW) characteristics of fluorescing compounds can be useful for identification purposes, especially when differentiating between light and heavy aromatics. However, BTX emission-wavelength spectra are broad, and although unique, tend to overlap considerably, thus limiting the value of the emission wavelength spectrum for chemical identification. Thus this research effort focused on fluorescence lifetime, which this LIF system is well suited to measure due to the fact that the pulses produced by the Q-switched laser can be regarded as essentially ideal impulses in the chemical systems of interest.

Signal to noise ratio (SNR) is a concern in the measurement of fluorescence lifetime, as with decreasing concentration, the overall shape of the fluorescence decay curve is increasingly affected by the noise in the measurement system. As a result, it is necessary to establish a minimum signal level above the noise that will facilitate reliable and repeatable calculations of fluorescence lifetimes. This signal level must exceed that required simply for detection of the contaminants. The signal level must also be great enough to include several reliable data points on the decay curve of the test compound which can be used to facilitate a curve fitting procedure. For the reported experiments, the minimum signal level required for repeatable determinations of fluorescence lifetimes was empirically determined by analyzing the sensitivity of the decay curve fitting procedure to different ratios of background to signal intensity.

Fig. 5 illustrates the relationship between the accuracy of the decay constant obtained from a curve fit and the assumed ratio of the background to peak fluorescence intensity. The curve fit accuracy is presented using a normalized lifetime ratio that illustrates the variation in the curve fit decay constant relative to the decay constant that was generated from maximum SNR experi-

ments on equilibrium solutions of the respective contaminants. The numerator represents the difference between the decay constant obtained from a particular test, τ, as determined by employing a given noise band assumption and the mean lifetime obtained from equilibrium data, τ_{mEQ}. The denominator is simply the mean equilibrium lifetime.

The points presented in Fig. 5 were obtained by subtracting different assumed background values from the data prior to fitting exponential decay curves. The background values were assumed to be constant as a function of both time and wavelength. Negative intensity values (data below assumed background levels) were ignored in the curve fitting operation. The rejected data varied in value over a range from 1 to 10 times the standard deviation of the actual background observed throughout the testing program.

Fig. 5 demonstrates the dependence of the fitted value of the decay constant on the background (and thus the fraction of the decay curve used in the fitting process). Reasonably repeatable fluorescence lifetimes were measured when the WTI curve's peak amplitude was at least four times the level of the background (background/WTI peak$\geq 25\%$ or SNR≥ 4). Within this range, lifetimes are determined within approximately $\pm 10\%$ of the values found for equilibrium solutions, with a confidence of approximately 70%. Note that, although sufficient to distinguish among many compounds, this level of error precludes effective discrimination between compounds such as toluene and o-xylene, whose lifetimes differ by less than 5%.

Given that the standard deviation of the background noise for tests performed in this program is approximately 6.3×10^{-6} a.u., and again assuming that the background noise is random normal in nature, a noise envelope can be established at a signal value of 1.6σ which includes approximately 90% of the noise signal. Therefore a minimum WTI peak amplitude of approximately 4.0×10^{-5} a.u. (i.e., $4 \times 1.6 \times 6.3 \times 10^{-6}$) is required to identify a compound on the basis of its fluorescence lifetime. Corresponding identification limits for benzene, toluene, and o-xylene were ~ 225, 4, and 2 ppm, respectively.

Quantification of BTX Compounds

Accurate contaminant quantification appears to require a greater signal to noise ratio than identification of compounds by fluorescence lifetime. This results from the fact that only a single, high quality intensity-time trace at a single wavelength is required to achieve a reasonable decay time estimate. In contrast, concentration measurements make use of the entire WTI profile; thus, a large portion of the WTI curve must lie above the background to yield accurate concentration measurements. As the concentration of a contaminant in solution decreases, the fluorescence radiation emitted by the material will decrease uniformly at all wavelengths. Therefore the general shape of the WTI profile would be expected to remain approximately the same, and would simply scale according to the peak height.

Since both the peak signal and volume of the WTI profile are proportional at higher concentrations of BTX, the quantification ability of the LIF sensor was assessed by comparing these two values as concentration decreased. When the magnitude of the WTI peak is no longer proportional to its volume, at least one of these metrics is no longer proportional to concentration, and quantification becomes less certain. Fig. 6 demonstrates that the relationship between WTI peak amplitude and the volume under the WTI curve becomes nonlinear as the peak signal approaches
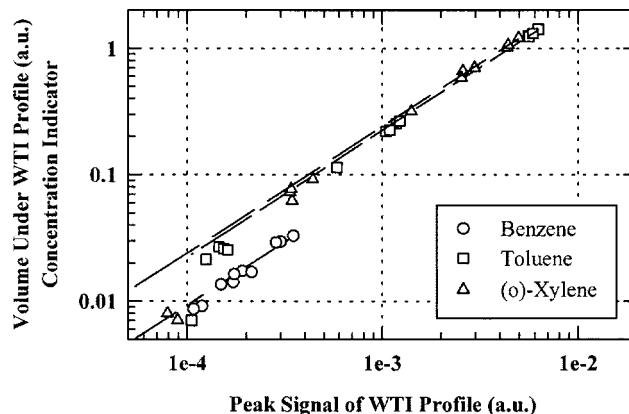

Fig. 6. Relationship between peak amplitude and volume of WTI profiles

$1-2 \times 10^{-4}$ a.u., where 2×10^{-4} a.u. corresponds to a SNR of approximately 20 [i.e., $(2 \times 10^{-4})/(1.6 \times 6.3 \times 10^{-6})$].

Combining the divergence point (2×10^{-4} a.u.) illustrated in Fig. 6 with the relationships between contaminant concentration and peak fluorescence signal (Fig. 4), lower limits for the quantification of BTX compounds using this LIF system are conservatively estimated to be approximately 750 ppm for benzene, 18 ppm for toluene, and 8 ppm for o-xylene.

Summary and Conclusions

Aqueous solution experiments demonstrated that the LIF probe can detect toluene and o-xylene at aqueous concentrations often found in the environment [noting that EPA National Primary Drinking Water Regulations define maximum contaminant levels (the highest level of a contaminant that is allowed in drinking water) of 1 ppm for toluene and 10 ppm for total xylenes, and thus concentrations in "contaminated settings" would clearly exceed these levels by definition (EPA 2003)]. While benzene is notably more challenging to detect, the presence of aromatics such as toluene or o-xylene is often a strong indicator of the presence of other aromatics and assessment of these compounds can enhance the efficiency of efforts to explore contaminated sites. Further, the LIF sensor can accurately measure fluorescence lifetimes as short as ~ 2.5 ns without a need for signal deconvolution. Results from single-compound aqueous solution tests also illustrated that there is a clear straight-line relationship between contaminant concentration and observed fluorescence intensity that can be used to calibrate the LIF sensor for quantitative analyses over environmentally relevant concentration ranges. While it is recognized that the performance of the LIF sensor will degrade in natural environments involving contaminant mixtures and nonaqueous media, the results presented herein show promise for the practical application of in situ remote optical spectroscopy in select applications.

These experiments also highlight that the capabilities of the LIF sensor are directly linked to the performance characteristics of the data acquisition system and, more importantly, illustrate the need to distinguish among a contaminant sensor's ability to detect, to identify, and to quantify chemical compounds. Each of these capabilities requires data of a different nature and quality, and success in achieving any of these levels of measurement can enable valuable practical applications. Recognition that the inabil-

ity of a sensor to achieve the level of performance required for quantification does not preclude its use for an array of other important identification or detection oriented applications can make the difference between rejection and continued pursuit of a new technology.

Acknowledgments

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