Novel Optical Detection Schemes for In-Situ Mapping of Volatile Organochlorides in the Vadose Zone

Project ID: 70050

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Research Objective

The long-term objective of this research is to develop a system for measuring and identifying a wide range of volatile organic hydrocarbons, including organochlorides, at ppb levels *in-situ* in the subsurface ("at-depth") using a fiber-optic REMPI probe in a cone penetrometer. And, to do this in a system that has a fiber-optic Raman probe and an image guide for simultaneous Raman and video imaging of the measurement area. The specific focus of much of the proposed work is to identify and optimize those experimental parameters which effect the *in-situ* determination of organic molecules in the subsurface using resonance-enhanced multi-photon ionization (REMPI). To accomplish this goal we will systematically investigate the dependence of REMPI on laser wavelength, power and other experimental parameters for a variety of high-priority groundwater and vadose zone contaminants to determine optimal measurement conditions. Emphasis will be placed on visible excitation so that the high transmission of fiber-optics at visible wavelengths can be fully utilized. A fiber-optic REMPI system will then be designed and integrated into an existing cone penetrometer system at LLNL. The design will be compatible with existing Raman and fluorescence probes. Fiber-optic probe designs will result from information gained in the first studies, and from previous experience by both the USC and LLNL groups. We will model the performance of different probe designs in a way similar to models we have developed for fiber-optic Raman and fluorescence probes. The specific studies that will be performed are described below. Finally, we will field test the probe in a cone penetrometer. LLNL has considerable experience in this area. This work will also be supported by a cone penetrometer experimentation group at SRL.

In this work we will study the use of both low-order (*e.g.*, 1+1, short wavelength) and high-order (*e.g.*, 2+2 visible-wavelength) REMPI excitation schemes, (described below), for some high priority volatile organic and VOC contamimants to learn the best way to measure these UV-absorbing molecules in the subsurface. This knowledge will be applied to optimization of REMPI for *in-situ* measurements using fiber optics. Also, we will investigate the best optical geometry for the fiber optic launch and collection probes to determine the effect on the signal-to-noise ratio (SNR) and how best to integrate REMPI into existing fiber-optic probes that are used for Raman and fluorescence measurements. Finally, we will study the REMPI 1+1 and 2+2 signals for different sample matrices as a function of excitation wavelength across a broad spectrum. A result of this study should be a determination of the optimal excitation and collection conditions and sampling methods for organic contaminants in different matrices, and an understanding of the strengths and limitations of using fiber optics for REMPI sampling.

Background

The long-term goal of this project is to develop a system to measure VOCs in the subsurface, *in-situ*, at both very low concentrations (vapor phase) and at high concentrations (liquid phase, NAPLs) using a fiber-optic probe. Visible wavelength REMPI will be developed for low level concentrations, whereas Raman scattering is already available for liquid phase measurements. REMPI has sensitivity

comparable to fluorescence but can be used to measure non-fluorescent compounds. However, it is more selective than fluorescence and has been used to measure trace levels of molecules in complex matrices such as flames and plasmas.

Volatile organic chemicals are found in almost every natural water source on earth. This is primarily due to the poor disposal practices of the past and accidental spills. For example, in 1988 it was estimated that 33.1 million pounds of benzene and 344.6 million pounds of toluene were released into the environment.[14] Once these chemicals have been introduced into the ground, they begin to partition into the water supplies and collect in wells and other storage areas. Since clean-up of contaminated water supplies is very expensive, it is desirable to develop techniques that can be used on-site to rapidly identify the organic pollutant as well as the amount of contaminant present.

Gas chromatographs (GC) are the most commonly used instruments for the detection of trace volatile organic compounds in water samples.[15,16] For these analyses, there is typically a preconcentration step that extracts the sample from the water and requires a great deal of time and effort. This extraction can be through various methods such as activated charcoal, liquid/liquid extraction, or solid phase microextraction (SPME).[17,18] Since both the preconcentration and GC separation steps require time and sample preparation, it would be favorable to have a fast, remote analysis capability.

REMPI Background

Resonance enhanced multiphoton ionization (REMPI) is a useful technique for obtaining both qualitative and quantitative information about volatile organic pollutants. In addition to the applications mentioned above this technique has been used extensively as a selective ionization source for mass spectrometers[6-12b] as well as in spectroscopic combustion analysis[13-16b] in the last couple of decades. In the REMPI technique, a tunable pulsed laser is used to electronically excite a specific molecule using one or more photons. A 1+1 excitation scheme refers to a two-photon process where one photon creates the excited molecule and another photon ionizes the molecule from the excited state. In a 2+2 excitation scheme two photons are used to excite then ioinize the molecule — a four-photon process. As shown in Fig. 1 the main difference between resonance ionization and laser ionization (LI) is that an electronic excited state is involved in REMPI. This not only results in very large enhancements but is also the reason REMPI can be used as a qualitative technique. While excited, the subsequent absorption of an additional photon(s) then ionizes the molecule. Ionization probability is much larger for REMPI than for LI because the "real" state in REMPI is much longer lived than the "virtual" state in LI. Also, because of the large enanecements in REMPI, even four-photon excitation schemes provide very high sensitivity. And, it is important to point out that REMPI requires low to moderate laser power.

Once ionized, an electrode that is biased at a high positive or negative potential is used for efficient electron or ion collection. The current created by these electrons/ions flowing to the electrode is then measured as a voltage drop across a "leak resistor," and the resulting voltage is therefore proportional to the concentration of the specific species being ionized. Due to the non-linear nature of this technique it is important to have high power densities, small focused beam, near the collection electrode. A higher power density increases the probability of ionizing the specific molecule of interest. Although the electrode is typically biased at 800-1000 V, the current is extremely low requiring only a very small relatively well-regulated power supply.

In the REMPI technique a relatively low power pulsed laser is focused to a small spot to induce molecular ionization in a multiphoton, **N**-photon, process where the multiphoton energy exceeds the ionization potential. In nonresonant multi-photon ionization (MPI), the ionization cross section, d_N, is low but increases with increasing photon flux, I, with d_N being proportional to I^N. By tuning the laser so that the energy sum of the **N** photons is in resonance with a *real* intermediate resonance state, E_f, (REMPI) the ionization cross section is enhanced by up to 10^6 if the $E_o \rightarrow E_f$ transition is an allowed transition of the molecule (E_o is the ground state, E_f is the energy of the resonant electronic state). This is shown schematically in Fig. 1. The greatly enhanced ionization cross section in REMPI results in extremely high ion yields and thus very high sensitivity. Because ions can be collected very efficiently this technique is one of the most sensitive *in-situ* methods for applications such as combustion diagnostics.[23-25]

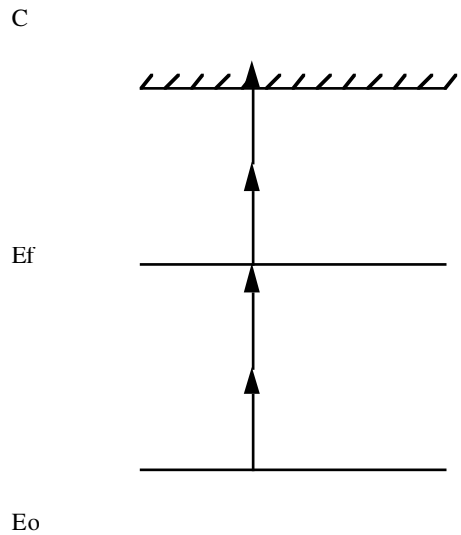

Fig. 1. Energy level diagram showing the resonant ionization of a molecule through a multi-photon ionization process.

REMPI is widely used to obtain multiphoton spectra because of its high sensitivity and simplicity. Although there have been a few reports of its analytical use most reports have focused on studying the resonance enhanced multiphoton ionization process itself rather than its use for quantifying chemical species. However, applications of this technique are beginning to appear. For example the spectral sensitivity and selectivity of resonance-enhanced multi-photon ionization spectroscopy for detecting various chloroethylenes has been demonstrated and REMPI has been used to measure many radical species including O, H, OH, CH, CO, HCO, CH_3 and chlorinated flame radicals.[23-31] REMPI has been used most widely for measuring gas-phase spectra of simple molecules, molecule fragments and radical species. However, as indicated above recent studies have used REMPI for organic molecules, and we recently demonstrated its use for measuring volatile organic molecules *in-situ*.

Due to its sensitivity and qualitative capabilities, REMPI, is an excellent technique for remote analysis of many types of volatile organics in the environment. In previous related work, we showed that by using optical fibers it is possible to introduce high power laser pulses to a remote area.[17c] A REMPI probe is made by simply placing a small biased electrode near the focus of this laser pulse, making it possible to make a simple and remote probe that can be placed down a well or other inaccessible area for remote trace analysis. Most organic contaminants absorb most strongly in the UV. For example, BTEX compounds (*e.g.*, benzene, toluene, ethylbenzene and xylenes) absorb strongly in the 240 to 280 nm range. In previous work we used 266 nm excitation in a 1+1 excitation scheme to measure toluene at ~1 ppb with a fiber-optic probe. However, in that work we also showed that four-photon REMPI, in a 2+2 excitation scheme at 532 nm, could be used to measure toluene at concentrations around 10 ppb. This result was achieved using a relatively small laser with ~25 mJ of power per pulse. This is an important result because it demonstrates that REMPI can be used to measure low levels of organic contaminants with a small visible-wavelength laser, and at wavelengths that are compatable with fiber-optic probes. The use of visible wavelengths also makes REMPI compatable with existing fiber-optic Raman and fluorescence probes, and thus compatable with cone penetrometry.

Before REMPI can be applied to the measurement of subsurface contaminants it is necessary to make fundamental measurements to characterize it for this purpose, especially comparing 1+1 and 2+2 excitation schemes. And, the optimal laser power for the analytes of interest. The optimal wavelength for a REMPI measurement does not always correspond to the maximum sample absorbance, because of lower background ionization in regions of lower absorbance,[33] or rapid relaxation

to spin-forbidden states[2]. Although these results were obtained at low pressure and the experiments aren't too related, it is not known if similar results, especially background ionization, might be observed in one-atmosphere experiments. As mentioned above, most applications of REMPI have been for molecular fragmentation in mass spectrometry. In this application systematic studies of laser wavelength have rarely been done. Most detailed excitation wavelength studies have been carried out for flame species.[19-22] Thus, an important part of this work is to study the excitation wavelength dependence of the REMPI signal for the contaminants of interest. We also need to determine what other experimental parameters can be optimized for an analytical measurement, and to evaluate potential interferences. The excitation wavelength dependence of REMPI signals will be determined for several high-priority pollutants using both 1+1 and 2+2 excitation schemes. REMPI signals as a function of sample matrix, sample state (dry, wet, etc.), and excitation wavelength have not been obtained in a systematic way for the compounds of interest and such studies are crucial to making this a reproducible analytical technique. No fiber-optic REMPI studies have appeared in the peer-reviewed literature. So, it is difficult to predict the limitations that might be caused by the use of fiber-optic probes.

We will investigate the use of fiber optics to deliver the laser to the sample and to collect the resulting ion emission using a small, ~1-mm diameter, bead electrode connected to the surface instrument by a small insulated wire. Recent results in our laboratory demonstrate that sufficient laser power can be delivered to the sample by a fiber optic to make very sensitive REMPI measurements without damaging the optical fiber. The technique has the potential for identifying subsurface organic contaminants at very low levels and rapidly. In combination with a fiber-optic Raman probe this allows organic contaminants to be measured and identified over a wide concentration range. The use of fiber optics for both REMPI and Raman spectroscopy could minimize the need for grab-sampling. In this work we will study the REMPI excitation wavelength dependence at UV and visible wavelengths for different matrices to better understand how to optimize the signal. Also, we will investigate fiber-optic probe geometries to determine the effects of the fiber on the SNR and optimal wavelength and power. Finally, we will investigate the incorporation of both REMPI and Raman into a cone penetrometer-compatable probe, that is also outfitted with an image guide for direct visualization of the sampling region. A result of this study should be a determination of the optimal excitation wavelengths and sampling conditions for organic contaminants in different matrices, and an understanding of the strengths and limitations of using fiber optics for REMPI sampling.

Our preliminary REMPI work is quite exciting.[12,13] The toluene detection limit measured *in-situ* with a fiber-optic REMPI probe is ~1ppb using a 1+1 excitation scheme at 266 nm, well below the regulatory limit. And, using a 2+2 excitation scheme at 532nm, the detection limit was ~10 ppb. A 90-s analysis was shown to be sufficient to identify and quantify toluene, even in a complicated sample like gasoline, and with little or no interference from benzene. The laboratory-built fiber-optic REMPI probe is a small hand-held device that is readily adaptable for field work.

REMPI Results

In recent work a simple fiber-optic probe suitable for remote measurements of ppb levels of aromatic hydrocarbons using resonance enhanced multi-photon ionization (REMPI) was developed.[12,13] Optical fibers transport the laser pulse to the sample and a small wire transfers the ion current to a digital oscilloscope. The measurement takes about one minute to perform, requires no sample preparation, and can be made through optical windows. The limit of detection for toluene was ~1.4ppb using 1+1, 266 nm excitation, and ~10 ppb using 2+2, 532 nm excitation. We are currently extending this to the measurement of compounds, such as VOCs, that absorb at even shorter wavelengths.

Fiber-Optic REMPI Probe. In preliminary work a simple fiber-optic probe suitable for remote analysis using resonance enhanced multiphoton ionization was developed and used to determine the toluene concentration in aqueous gasoline samples via a head space measurement. An optical fiber transmits a high power laser pulse (266 nm) to the sample, ionizing it, and the subsequent ions are collected with a platinum electrode. Measurements take approximately 1.5 minutes to perform, require no sample preparation, and have been demonstrated over distances of five meters. The limit

of detection for toluene in water using this probe is 1.54 ± 0.02 ppb (wt/wt). In addition to the 1+1 excitation, the feasibility of a 2+2 excitation scheme using 532 nm has been investigated.

Sample preparation: For this study, aqueous toluene and gasoline samples were prepared by placing equal volumes of toluene or gasoline (Shell 93 octane) and deionized water in a sealed container and stirring them vigorously for several days. The water portion of the sample was then extracted and placed in a sealed container. This solution was saturated with toluene, giving a concentration of 550 ppb toluene.[18h] To cover the concentration range of toluene that was measured in this paper, 0 ppb to 550 ppb, dilutions of this saturated solution were made using deionized water. For measurements using the fiber-optic REMPI probe, spiked water samples were placed in a petri dish and covered with a plastic air tight lid with a small hole in the center. The probe was placed over this hole and sealed and the headspace above the sample, and allowed to equilibrate for 20 minutes with the probe in place. For experimental optimization experiments of electrode bias voltage and laser power, neat toluene or toluene diluted in methanol was injected into the sealed cell and allowed to evaporate completely. For measurements of dry vapor in a sealed cell the concentration of toluene is reported in ppb (mol/mol) with respect to air. For measurements of aqueous solutions of toluene concentrations are reported as ppb (wt/wt).

All of the data are shown without averaging or smoothing. For all measurements, the intensity of the REMPI signal is based on peak height after a fixed delay time from the laser pulse, and all error bars displayed represent one standard deviation of five replicate measurements. A linear best fit of the data was calculated, and the detection limit is taken as 3 times the standard deviation of the blank divided by the slope (*e.g.*, a "3σ" detection limit).

Fiber launch conditions: One difficulty in using fiber optics for REMPI measurements is avoiding damage to the excitation fiber. Focusing the laser on the tip of the fiber can chip the face, or in some cases completely destroy the fiber's tip. In addition, it was also found that if too much power was launched into the fiber or into the cladding of the fiber, catastrophic damage to the core/cladding interface was observed. Since REMPI is a non-linear process it is important to launch as much power down the fiber as possible. By using a pinhole at the fiber tip, and placing the fiber just beyond the focus of the laser, it was found that optical fibers can withstand approximately 200 mJ/pulse at 532, and this launch worked very well for REMPI experiments.[32,37]

REMPI signal intensities for a particular sample depend on several different parameters such as electrode voltage, excitation fiber, laser power and excitation wavelength. As these parameters are sample dependent, there is no optimized setting for all measurements, but we have investigated these parameters for toluene and gasoline measurements. The first of these parameters, electrode voltage, is very important for signal collection, and is primarily dependent on the probe design. One of the main reasons for the great sensitivity of REMPI is the collection efficiency of the signal. Because the signal being collected is charged particles, it is possible to achieve a collection efficiency of approximately 100%.[13b (above)] Thus, it is important to optimize the bias voltage of the electrode to maximize signal while reducing error from small voltage fluctuations. This optimization was performed by injecting the equivalent of 1.78 ppth of toluene into the sealed cell, allowing it to evaporate, and then monitoring the ion signal as we varied the probe voltage from 500 to 1200 volts. Three distinct regions were evident from this data. At voltages lower than 800 V, there is a dramatic increase in signal due to enhanced collection efficiency and reduced electron/ion recombination. Between 800 and 1100 V, a plateau region exists where the maximum collection efficiency occurs. Above 1100 V, the ion signal once again increases dramatically with increasing probe voltage, because of the cascade effect. Based on the results of this experiment +1000 V was used for all remaining measurements.

Power density is crucial to obtaining quality REMPI signals and thus high sensitivity. It is important both to transmit the maximum amount of excitation light through the fiber, as well as to have a small spot size near the electrode tip. Optimizing the power density of the spot near the electrode is dependent on the diameter and type of excitation fiber used. Therefore we investigated using a low •OH content 1000 mm fiber, a high •OH content 910 mm fiber and a high •OH 550 mm fiber (Fig. 2). The low •OH content fiber, with a 1000 mm diameter, has its greatest transmission efficiency in the region of 350 nm to 800 nm. However, this fiber costs less than a fiber of comparable diameter that has a transmission maximum in the ultraviolet region. When using this fiber, 6.1 mJ of 266 nm

light were launched into the fiber and approximately 4.0 mJ were measured at the distal end. By injecting various amounts of toluene into the cell and monitoring the ion signal while using this fiber for excitation it was possible to obtain a calibration curve for toluene in the vapor phase. From this calibration, the sensitivity was found to be 0.045 ± 0.004 mV/ppb of toluene corresponding to a detection limit of 4.4 ± 0.4 ppb (mol/mol) of toluene in air. Next, we performed the same experiment using a high ∑OH content, 910 mm fiber with better UV transmission. For this experiment, 6.1 mJ of 266 nm light was launched into the fiber and 5.4 mJ was measured at the distal end. The sensitivity of the probe increased to 0.0636 ± 0.0006 mV/ppb of toluene with a limit of detection of 1.005 ± 0.009 ppb (mol/mol). Next experiments were done to determine the optimum fiber diameter. We found that a 550 mm fiber with a high •OH content could transmit the same amount of power as the larger fibers. Using this fiber allowed for a tighter focus near the electrode and therefore a greater power density. As a result, an increase in sensitivity to 0.0912 ± 0.0008 mV/ppb and a lower detection limit of 0.858 ± 0.0007 ppb (mol/mol) were obtained using the 550 mm fiber.

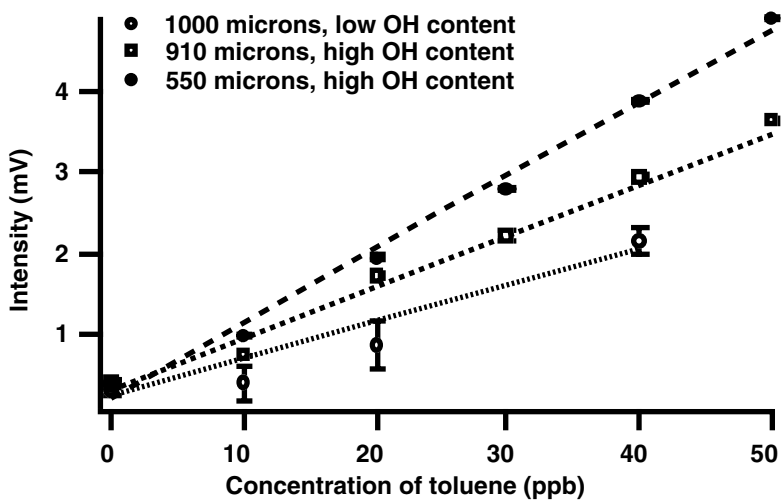

Fig. 2. The effect of optical fiber type and diameter on sensitivity of REMPI signal. Circles denote the 1000 μm low •OH content fiber, squares denote the 910 μm high •OH content fiber and triangles denote the 550 μm high •OH content fiber. Excitation of the sample was accomplished by launching 6.0 mJ/pulse of 266 nm light into the specific fiber. Each point represents the average of five measurements with error bars showing ± one sample standard deviation.

To determine the dynamic range different amounts of toluene were injected into the cell covering a concentration range from 1 ppb to 10 ppm (mol/mol). After the toluene evaporated, five measurements were made at each concentration. These results are shown in Fig. 3. From this plot it is evident that the REMPI signal remains linear over approximately 3.5 orders of magnitude of toluene in air. Therefore this is an excellent technique for remotely monitoring toluene concentrations over the ppb to a few ppm levels using fiber optics.

Calibrations experiments were also carried out for aqueous-phase toluene using the fiber-optic REMPI probe. Fig. 4 shows the calibration of toluene in spiked water samples using a 1+1 excitation scheme at 266 nm (open circles). For these measurements, the spiked water samples were placed in a petri dish so that the amount of liquid was equal in volume to the headspace volume above the sample. After approximately 10 minutes, equilibrium between the liquid toluene and the vapor toluene was reached and a measurement was taken. This was repeated for samples ranging in concentration from 5.5 ppb to 275 ppb (wt/wt) toluene. For this calibration we obtain a sensitivity of 0.137 ± 0.002 mV/ppb. This is significantly better than that obtained using the cell described earlier.

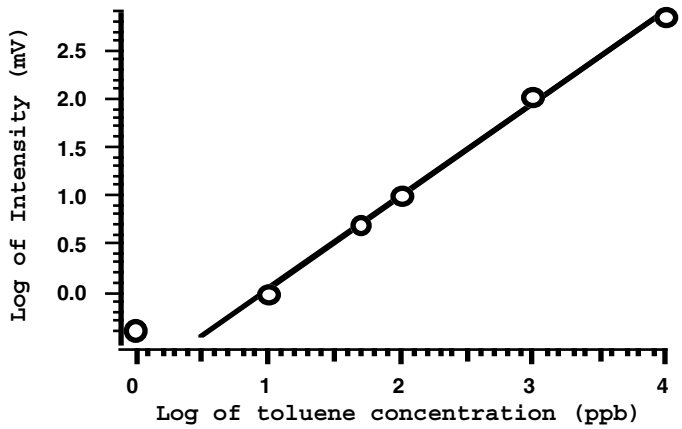

Fig. 3. Dynamic range of REMPI technique for measurement of toluene. A 550 mm high •OH content fiber was used for these measurements with the collection electrode biased at +1000 V and 266 nm excitation. Each point in this curve represents the average of five measurements with error bars showing ± one sample standard deviation.

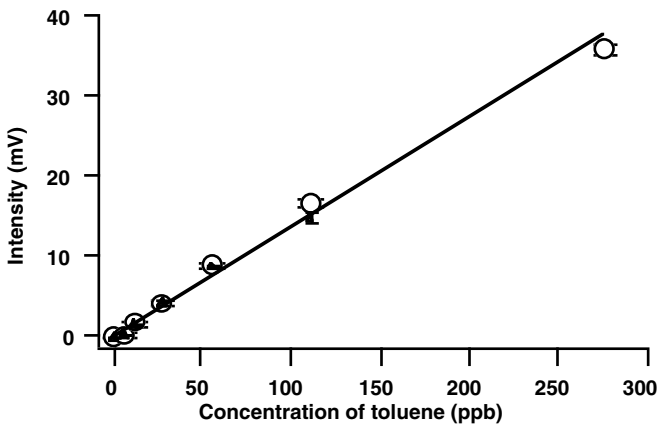

Fig. 4. Calibration of toluene spiked water samples (open circles), and the toluene from gasoline spikedwater samples (dark triangles). For both calibrations a 550 mm high •OH content fiber was usedfor these measurements with the collection electrode biased at +1000 V and 266 nm excitation.Each point in this curve represents the average of five measurements with error bars showing± one sample standard deviation.

While all the reasons for this enhancement have not been totally investigated, the primary reason for this difference is that the electrode in the probe has an additional insulating layer not present in the cell. This additional insulation prevents short circuiting of the probe and therefore both increases the ionization signal and decreases the background. From this increase in signal to background, we lower our detection limit of toluene to 1.54 ± 0.02 ppb of toluene in water.

Since gasoline is often found in ground water samples, and a major constituent of gasoline is toluene, we also tested our probe using water samples spiked with gasoline. These gasoline spiked samples were prepared by the same procedure used for the toluene, and therefore should have very similar concentrations of toluene in the saturated sample. This calibration is shown in Fig. 4 (dark triangles) and the concentration listed on the abscissa is the concentration of toluene in the water, based on a saturated concentration of 550 ppb. It is obvious from this calibration that the sensitivity and detection limit of toluene from the gasoline spiked samples is similar to toluene spiked water samples (0.132 ± 0.004 mV/ppb and 1.88 ± 0.06 ppb). This shows that there are no significant

interferences from the other constituents in gasoline. To verify this, we tested benzene, hexane, heptane, and methanol using our probe with 266 nm excitation and found no appreciable signal from neat solutions of these compounds. The lack of interference from these samples is explained by the fact that the resolution of the various vibronic bands that occurs in the vapor phase is sufficient to prevent significant ionization of these compounds. In addition to this, and maybe more importantly, the solubility of toluene in water is much greater than all other major constituents of gasoline except methyl tertbutyl ether, and benzene.[36]

2+2 Excitation, Preliminary Results. Even the best high •OH content optical fibers transmit more efficiently in the visible than in the ultraviolet. Because of this, we investigated the use of higher order excitation schemes using our probe. To do this 532 nm light was launched into the 550 mm fiber and approximately 20 mJ/pulse were measured at the distal end. This light was then excited and ionized the toluene from the spiked water samples via a 2+2 excitation scheme. The results are shown in Fig. 5 and demonstrate the feasibility of using this higher order excitation for much more distant measurements than five meters. While the sensitivity, 0.0139 ± 0.0005 mV/ppb, and detection limit, 8.6 ± 0.3 ppb (wt/wt), for this experiment are nearly an order of magnitude lower than for the 1+1 excitation scheme, these results are very promising. It is possible to launch much greater laser powers at 532 nm through fibers larger than 550 mm and could possibly allow for comparable sensitivity as well as increased measurement distances.

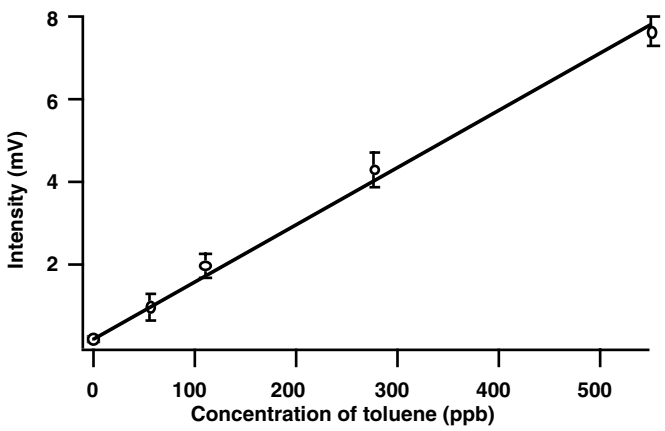

Fig. 5. Calibration of toluene spiked water samples with a 550 mm high •OH content fiber was used for these measurements with the collection electrode biased at +1000 V and 532 nm excitation. Each point in this curve represents the average of five measurements with error bars showing ± one sample standard deviation.

Pulsed Fiber-Optic Excitation. One difficulty in using fiber optics to measure LIBS spectra is avoiding damage to the excitation fiber. Focusing the laser to a tight spot on the fiber tip can chip the surface or in some cases completely destroy the fiber. Catastrophic damage at the core cladding interface was observed if the power were too high, if the fiber were misaligned, or if laser spots were too small. For the paint sample measurements, power levels of 4.2 mJ and 19.0 mJ were typically measured at the probe tip, the end nearest the sample, for the 600 mm and 1000 mm excitation fibers, respectively. In the case of a 600 mm excitation fiber, power levels as low as 1 mJ were observed to produce a plasma at the sample. To minimize fiber damage the laser was used at the lowest power possible and was loosely focused using an f/8 lens so that the spot was relatively large compared to the fiber tip. The decreased power density, together with the use of a small pinhole in front of the fiber tip, eliminated fiber damage for input powers as high as 200 mJ. This arrangement resulted in 40 to 50% throughput to the fiber-optic probe tip, depending on the size of the excitation fiber.

Recently we described the use of a LIBS probe for determining Pb in paint *in-situ*.[37] The probe used for this work was a modified fiber-optic Raman probe. Although it was not optimized for LIBS

measurements we were able to measure 0.014% Pb in latex paint, on a dry-weight basis, with relative sample standard deviations of 5 to 10%. The measurement takes less than one minute to perform, requires no sample preparation, and can be made through overlayers of non lead-containing paint. The use of a fiber-optic probe with separate excitation and collection fibers minimizes sample alignment and allows coupling of the probe to a conventional spectrometer using simple optics. The proposed research should provide the basis for designing much better LIBS probes.

REMPI System. The REMPI system (Fig. 6) consists of a Q-switched Nd:YAG laser operating at either the second or fourth harmonic (Continuum Model Surelite III operating at 532 nm, or New Wave Research Model MiniLase-20 operating at 266 nm), a high voltage power supply (Gamma High Voltage Model RC5-30P), the probe/collection electronics and a fast digital oscilloscope (LeCroy Model 9350L). The high power laser pulse is first launched into the optical fiber. This launch was described in detail in previous works.[17c] Laser light is transmitted through the fiber to the probe where it is focused to a point, ionizing the analyte. Electrons created from this ionization are then collected on a platinum electrode biased at +1000 V. The current created by the collection of these electrons is then run through a 250 kW resistor and the resulting voltage drop across the resistor is measured using a 1MW coupled 500 MHz digital oscilloscope. Data shown is the average signal from 1000 laser shots at 10 Hz for a total acquisition time of approximately 1.5 minutes. The laser power at the probe tip was typically 5.4 mJ/pulse (266 nm) or approximately 20 mJ/pulse (532 nm), depending on the excitation wavelength used.

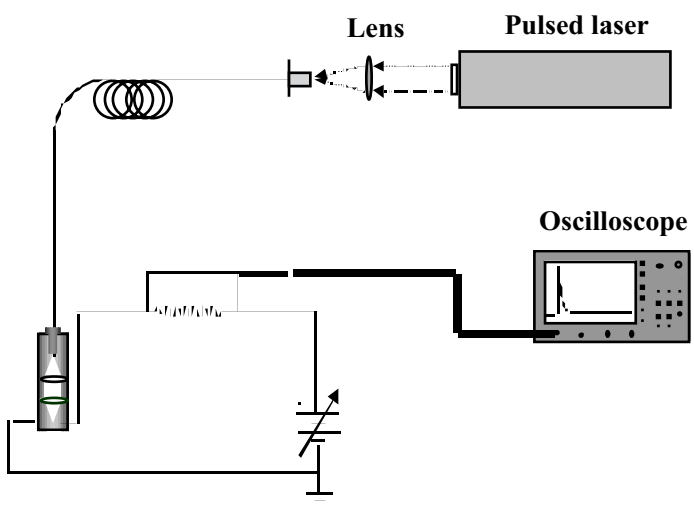

Fig. 6. Schematic diagram of REMPI apparatus showing fiber-optic launch and collection electrode

Fiber-Optic Probe

A unique aspect of our REMPI system is the use of a fiber-optic probe that delivers the laser beam to the sample, allowing remote measurements to be performed easily. The probes we have used thus far are simple modifications of existing designs that have been used in our group for Raman and LIBS spectroscopy.[35,37] The use of an optical fiber for laser excitation and a platinum electrode for signal collection gives the probe setup its simple and remote capabilities. In preliminary work, three different excitation fibers were tested, with core diameters of 1000 mm, 910 mm and 550 mm. Fibers were typically 5 m in length for UV measurements, and the effect of different •OH contents was also examined. Laser light was focused into the excitation fiber using a f/4 lens. Care is taken to eliminate damage to the input face of the fiber by placing a pinhole at the fiber tip that is just slightly smaller than the fiber core diameter (500 mm diameter in the case of a 550 mm fiber).

A cross section of the probe is shown in Fig. 7. The excitation fiber is located in the top of the probe housing, which is made out of aluminum, and the transmitted light is collimated using an f/1.5 fused silica lens. This collimated light is focused to a small spot within 1 mm of the electrode tip using another f/1.5 fused silica lens. Electrons created from the ionization of the sample are collected by the electrode that is biased at +1000 V with respect to the aluminum housing of the probe. The current created by the flow of electrons to the electrode is measured as a voltage drop across a "leak" resistor using a digital oscilloscope.

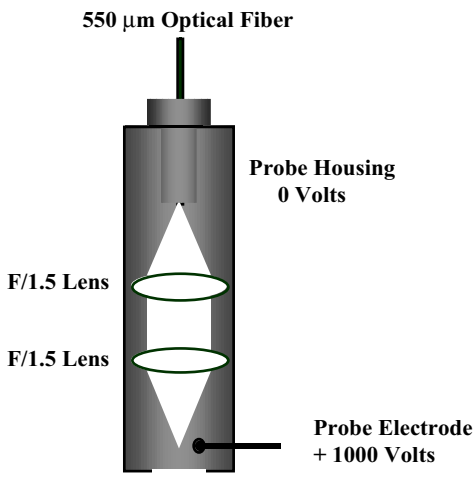

Fig. 7. Detail of the fiber-optic REMPI probe. The lens are 1-inch diameter f/1.5 plano convex, and the platinum electrode is biased at +1000 V with respect to the aluminum housing.

Penetrometer Compatible, Fiber-Optic REMPI Probe Design: LLNL

Background: LLNL has had considerable experience designing and fielding penetrometer deployable sensing technologies, including a chemical TCE sensor and Raman probe. These systems, although both capable of *in-situ* sampling from a cone penetrometer assembly, were significantly different in their base configuration. The TCE sensor operated on colorimetric principles. In the basic sensor design, optical fibers are used to remotely monitor a quantitative, irreversible chemical reaction that, upon exposure to TCE, forms products that absorb certain wavelengths of light. The sensor system has three major components: a miniature pumping and delivery system, an electro-optic readout device for monitoring the transmission of the sensor, and the sensor itself. The system design allows consecutive measurements to be taken at short intervals in and on-demand basis; control and monitoring are done remotely. The small reaction volume of the sensor allows a large number of measurements to be made before the reagent reservoir must be recharged. The reagent delivery system was designed to fit into a standard penetrometry cone (Fig. 11, next page). Two syringe plungers are fixed with respect to one another and simultaneously driven by a motor and a screw, allowing spent reagent to be captured in the empty syringe as fresh reagent is delivered to the sensor. The reagent delivery system and sensor housed in the penetrometer cone are isolated from the environment until a measurement depth is reached. The TCE sensor is then exposed to soil vapors by means of a removable and disposable ground-penetrating tip. The cone is driven to the desired depth and then retracted by 15 cm, leaving the removable tip behind. This creates a void, and exposes the sensor to soil vapors. An optical/electrical cable provides communication from the ground surface to the sensor. This system was successfully tested in multiple field tests at Savannah River Site, yeilding *in-situ* measurement of TCE in the parts-per-billion range (ppb). LLNL also designed and constructed a hardened fiber optic Raman probe and housing to provide *in-situ* characterization of underground storage tanks at the US Department of Energy Hanford site. The Cone Penetrometer

Fiber Optic Spectroscopy Probe Assembly consists of three major components: a penetrometer compatible probe housing, an optical Raman probe, and a window assembly The probe housing is designed to be an integral unit of the CP, supporting the load of a 40 ton vertical push. The probe housing provides a means of optically aligning and locking a fiber optic spectroscopy probe along its vertical axis and a housing for the window assembly along its radial axis. The probe housing also contains cable-way passages, providing a means for electrical cabling to additional sensors, such as the envisioned REMPI electrodes, in the penetrometer tip as needed. Optical communication between the vertically seated Raman probe and the environment is accomplished by the window assembly. The window assembly houses a sapphire window that provides optical access to hazardous sample material without compromising mechanical strength or chemical resistance. A focusing/collimating lens that is housed within the window assembly provides control over the field of view and the depth of penetration of the laser beam in the sample. A single fiber optic cable provides laser input to the probe. A seven fiber optic bundle collects the signal. Seven collection fibers are used rather than one both to increase the collection area and therefore efficiency of the probe and to allow for use of a larger laser spot size (4 mm) when interrogating the sample. A larger spot size results minimizes the efffect of inhomogeneous grain size, resulting in increased signal to noise. The collection fibers are filtered with a long pass filter to remove scattered laser light; the laser excitation fiber is filtered with a laser band pass filter to remove silica Raman generated in the optical fiber. The Raman cone penetrometer probe was successfully tested in a vessel containing tank waste simulant at Hanford.

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