EPA/600/A-96/120

A fiber optic multichannel laser spectrometer system for remote fluorescence detection in soils

Sean J. Hart, Yu-Min Chen, Bob K. Lien, and Jonathan E. Kenny*

Tufts University, Department of Chemistry, Medford, MA 02155
BL, U.S. EPA National Risk Management Research Lab, Ada, OK 74820

ABSTRACT

Fiber optic probes employing single channel laser excitation and fluorescence collection have been seeing increasing use for remote sensing applications. However, multi-channel systems offer enhanced capacity for qualitative and quantitative determination of analytes. We describe a system which employs simultaneous delivery of laser excitation wavelengths arising from stimulated Raman scattering (SRS). Separate fluorescence responses for each excitation channel are imaged through a spectrograph onto a CCD array detector. Each channel has a dedicated fiber optic pair to deliver and collect light. Results will be presented which evaluate the capabilities of this type of spectrometer for determination of organic contaminant mixtures in various sample matrices.

Keywords: Fluorescence, remote sensing, fiber optic, laser, soils, *in-situ*, field test, EEM, LIF

1. *IN SITU* FLUORESCENCE SENSING

In situ soil monitoring via fiber optics using laser induced fluorescence has become popular in recent years with the advent of CPT (Cone penetrometer technology) vehicles. Several groups have demonstrated and continue to develop systems capable of being installed in a CPT vehicle for onsite, *in-situ* measurements of fluorescent contaminants.[1,2,3] The ROST (Rapid optical screening tool) system, developed by Gillispie et al., has been commercialized and represents the advanced state of in-situ LIF measurement technology.[4] In earlier systems[1,2] only one pair of optical fibers is used: one for the delivery of laser excitation light and the other for the collection of contaminant fluorescence. The lack of other excitation wavelengths to measure the contaminant's absorbtion profiles imposes a limit on the amount of analyte speciation that can be accomplished. Often the calibration procedure employs a known contaminant mixture as a standard such as DFM (Diesel fuel marine) or a standard jet fuel.[4] While this allows the soil contamination measured with a system to be expressed as equivalents of the calibrant, it does not normally identify or quantify particular species. In some applications, the identity of the fluorescent species in a mixture is as important as knowing the relative total concentration.

The ROST system offers a way to further characterize a particular contaminant plume by stopping the advancement of the probe to scan the emission wavelengths and collect lifetime data at many emission wavelengths. Such data is organized into a WTM (Wavelength time matrix) which aids in the identification of species when the lifetimes of species in a mixture are different.[4]

Our system for in-situ remote sensing simultaneously delivers up to ten different excitation wavelengths to the sample and collects and disperses the emission due to each. Thus, three dimensional data, i.e. excitation-emission matrices or EEMs, are collected in real time during a push. This system offers more complete real-time screening capabilty than earlier systems, as well as the possibility of at least partial speciation without stopping the push to scan.

There are several different analyte / media systems in which our instrument must be able to function. These include aqueous systems, organic liquids such as LNAPL (Light non aqueous phase liquid) and DNAPL (Dense non aqueous phase liquid), and a myriad of soil types. In this communication we report laboratory and field measurements of analytes in different media and solvent systems, including ethanol, cyclohexane, and aqueous solutions, Ottawa sand and a silty clay type soil. In addition, selected results from a recent field test conducted at Hanscom Air Force Base in Lexington, MA will be discussed.

2. MULTICHANNEL REMOTE SENSING SYSTEM

2.1 Excitation source

The use of multiple channels without the need to stop and scan a light source allows the rapid excitation and collection of fluorescence from *in-situ* contaminants. Our system employs a Nd:YAG laser with second and fourth harmonic generating crystals. The output of the fourth harmonic generating crystal, at 266.0 nm, is used to pump a Raman shifter filled with methane and hydrogen gas (45:55 ratio). Most of the beams generated are Stokes shifted (longer wavelengths) but a few are anti-Stokes shifted (shorter wavelengths). The simultaneous generation of multiple excitation wavelengths using this source has been described in detail.[5,6]

2.2 Light delivery and collection

The light generated with the laser/Raman shifter combination is launched into 400/440/470mm diameter core/cladding/jacket silica-clad-silica fiber optics. There are two main sections to the fiber optic bundle: one contains fibers for the delivery of the ten excitation wavelengths to the soil through sapphire windows and the other contains fibers for the collection and return of contaminant fluorescence to the detection sub-system. The fibers are divided into two sections (10 and 20 meters respectively), for modularity, and are connected by standard ST-style fiber optic connectors.

To reduce scattered excitation light, a different cutoff filter (Schott WG series) is used for each channel. Due to the small core diameter (400μm) of the fiber optics, arranging 10 filters at the spectrograph entrance slit (commonly done with a single filter) is highly

impractical. Our solution was to cut and file the filters into circles small enough (diameter ≤ 2 mm) to fit into a fiber optic connector between the fibers. The details regarding the use of filters in fiber optic connectors can be found elsewhere.[7]

At the probe end, the fiber tips (light delivery and collection) are fixed at 16.4°, and are epoxied (Tra-con, Bedford, MA) inside a stainless steel tube, and then the fiber ends are polished flat on lapping paper.[8] The polished fibers (in stainless steel tubes) are spring mounted so that they push out against the sapphire window holders. The details of the probe body design have been given elsewhere.[5]

2.3 Detection subsystem

The fibers returning from the probe, propagating fluorescence from analytes, are interfaced to an imaging spectrograph (Acton Spectropro 150, Acton Research Corp., Acton, MA) via a fiber optic plug. The fluorescence is detected with a CCD detector (Princeton Instruments, Princeton, NJ) interfaced to a PC for data acquisition and analysis. The CCD integration time for all measurements was 1-2 seconds and the spectrograph resolution was 2.4 - 3.6 nm.

3. PROBE MEASUREMENTS

3.1 Lab measurements

The performance of the probe can be assessed by examining the EEMs (Excitation emission matrices) of several analytes and mixtures taken in several different media. A variety of samples have been measured and will be discussed in order to understand the probe's performance in a wide range of media. All lab measurements utilized ten excitation channels, with wavelengths: 257.7, 266.0, 278.4, 288.5, 299.1, 314.5, 327.3, 341.6, 362.1, 378.8 nm, the full capacity of the instrument.

For solution measurements, the sample container used was a tube with one end capped. The probe was inserted into the solution contained within. For solid sample measurements, the probe was laid in a trough style container with the sapphire windows in contact with the sample.

3.1.1. 3-component mixture in cyclohexane

An important measurement made was a 3 component mixture of representative 1, 2, and 3 ring compounds. This measurement allows us to clearly examine the instrumental response from three important classes of compounds. The standard mixture measured contained: 3 % (v/v) benzene, 86 ppm (w/w) naphthalene and 86 ppm (w/w) anthracene in cyclohexane.

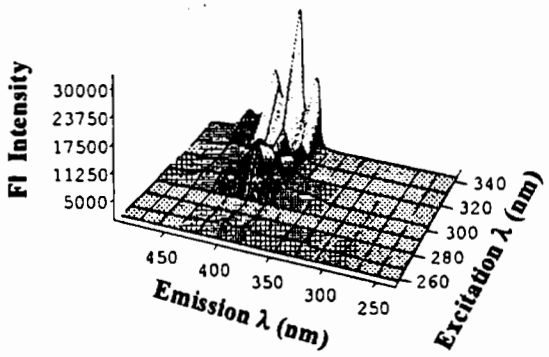

Figure 1. EEM of 3% Benzene, 86 ppm naphthalene, 86 ppm anthracene mixture

The EEM of the 3-component mixture measured is shown in figure 1, with the characteristic quadruplet of anthracene dominating and to shorter excitation and emission wavelengths the naphthalene doublet (330 nm peak) and finally the emission of benzene (280 nm peak) can be seen in the 266.0 nm excitation channel. The single spectrum for the 266.0 nm excitation channel for the standard mixture is shown in figure 2. While the anthracene fluorescence in the long wavelength excitation channels of the EEM in figure 2 is still the most intense, the smaller naphthalene and benzene signals can clearly be seen.

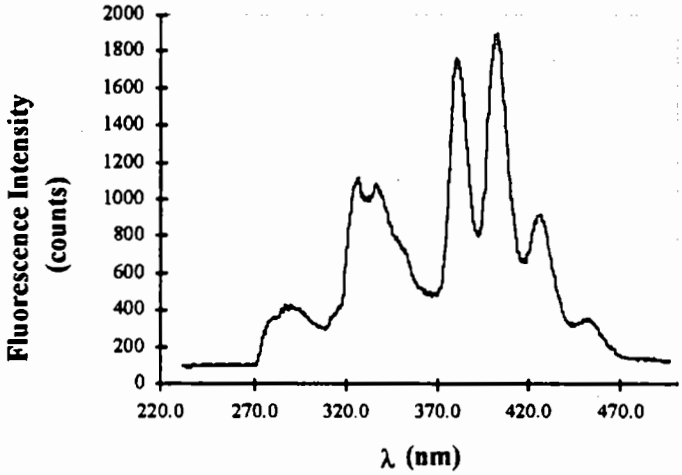

Figure 2. Fluorescence spectrum (266.0 nm excitation) from 3 % benzene, 86 ppm naphthalene, 86 ppm anthracene mixture EEM

3.1.2. Measurement of jet fuel in soil

In preparation for our field work at Hanscom AFB, lab measurements of JP8 were made in soil samples taken from the site. Pure JP8 was mixed with the soil samples (silty clay). The EEM of this mixture is shown in figure 3, with the large fluorescence intensities expected for pure fuel product even with a small particle size soil system such as silty clay.[8]

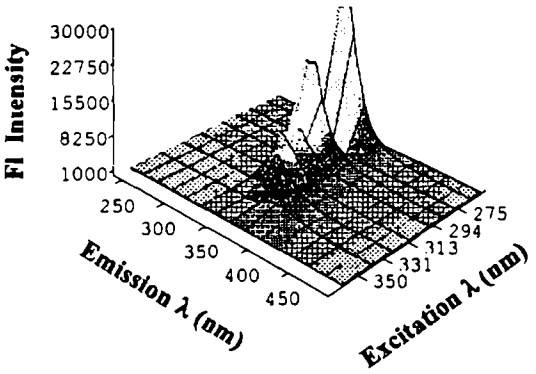

Figure 3. EEM of silty clay from Hanscom AFB mixed with JP8.

3.1.3 Aqueous phenol: linearity and detection limits

The measurement of truly aqueous aromatic compounds is an important goal towards successful *in-situ* measurement of groundwater plumes. Toward that goal we have begun work on probe measurements of species in water. The most simple starting point is phenol due to its high solubility in water. Figure 4a is an EEM of aqueous phenol (940 ppm) made using the tube container described above.

The upper limit of phenol's concentration signal response linearity was determined to be 471 ppm. By extrapolation with the minimum detection signal set to baseline counts plus 3 times the baseline standard deviation, the LOD (limit of detection) for phenol in water was determined to be 9.7 ppm.

3.1.4. Aqueous phenol in Ottawa sand

The aqueous phenol solution was also measured in Ottawa Sand (EM Science, Gibbstown, NJ). The EEM of phenol in Ottawa sand is shown in Figure 4b. The absolute peak signal in solution was 860 counts vs. 554 counts when the phenol solution was mixed with sand. This 36 % loss of signal is at least partly due to the excitation light penetration depth being reduced in Ottawa sand (particle size 420-595 μm) vs. that in solution.[2,8]

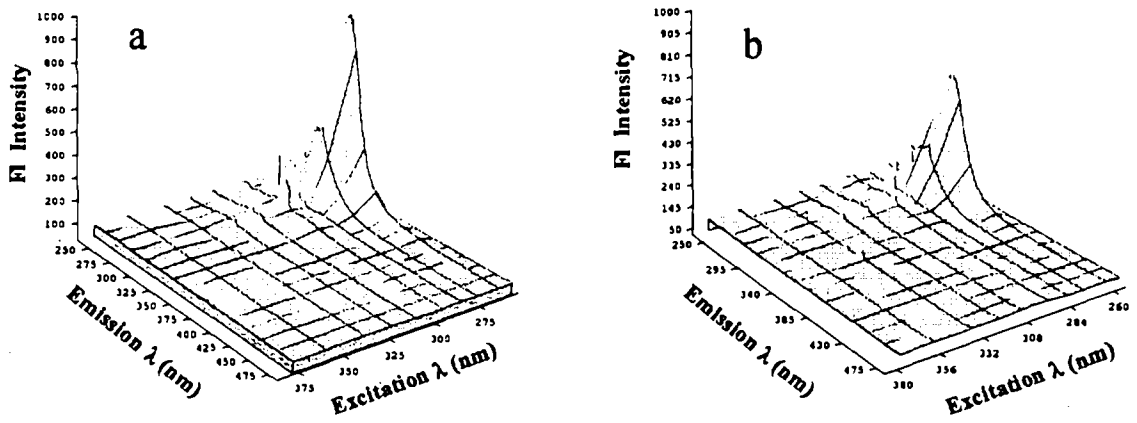

Figure 4. a) Aqueous phenol (940 ppm), b) Aqueous phenol (940 ppm) mixed with Ottawa sand.

3.2. Field measurements

Field measurements have recently been made at Hanscom AFB (6/28/96 - 6/30/96). During the field test, 14 pushes were made in a 2.5 day period with successful system operation and data collection using 8 channels in all cases. The two excitation wavelengths not used were 362.1 and 378.8 nm. The average depth pushed was approximately 17 feet with the deepest hole at 21 feet. While the system was configured to allow pushes to 30 feet, an exceptionally hard glacial till prevented us from pushing deeper. Future publications will discuss the work done at that site in more detail.

3.2.1. Quinine sulfate for calibration and power normalization

A system calibration was performed before each push to accomplish two goals: 1) confirm system operation and channel integrity and 2) act as a measurement of beam energy for power normalization. The compound used was quinine sulfate, well known as a fluorescence standard and to a lesser extent as a quantum counter. This calibrant was dissolved in ethanol and not the usual dilute H_2SO_4 due to damaging reaction of the latter with the steel probe body.

All of the probe channels report fluorescence, although not uniformly. This is due to several factors including the fiber optic attenuation of the strongest UV beams, and the small energy (before fiber optic launch) of the high order Stokes and first anti-Stokes beam. The net result is that the central channels (288.5 nm - 314.5 nm) have the largest signal. The emission spectra at the excitation wavelengths measured for standard quinine sulfate solution in ethanol (0.2 g/L) is shown in Figure 1.

According to Kasha's rule, fluorescence emission is independent of excitation wavelength and therefore the wavelength of fluorescence peaks of quinine sulfate at the different excitation wavelengths should be identical. This is not the case for the spectra

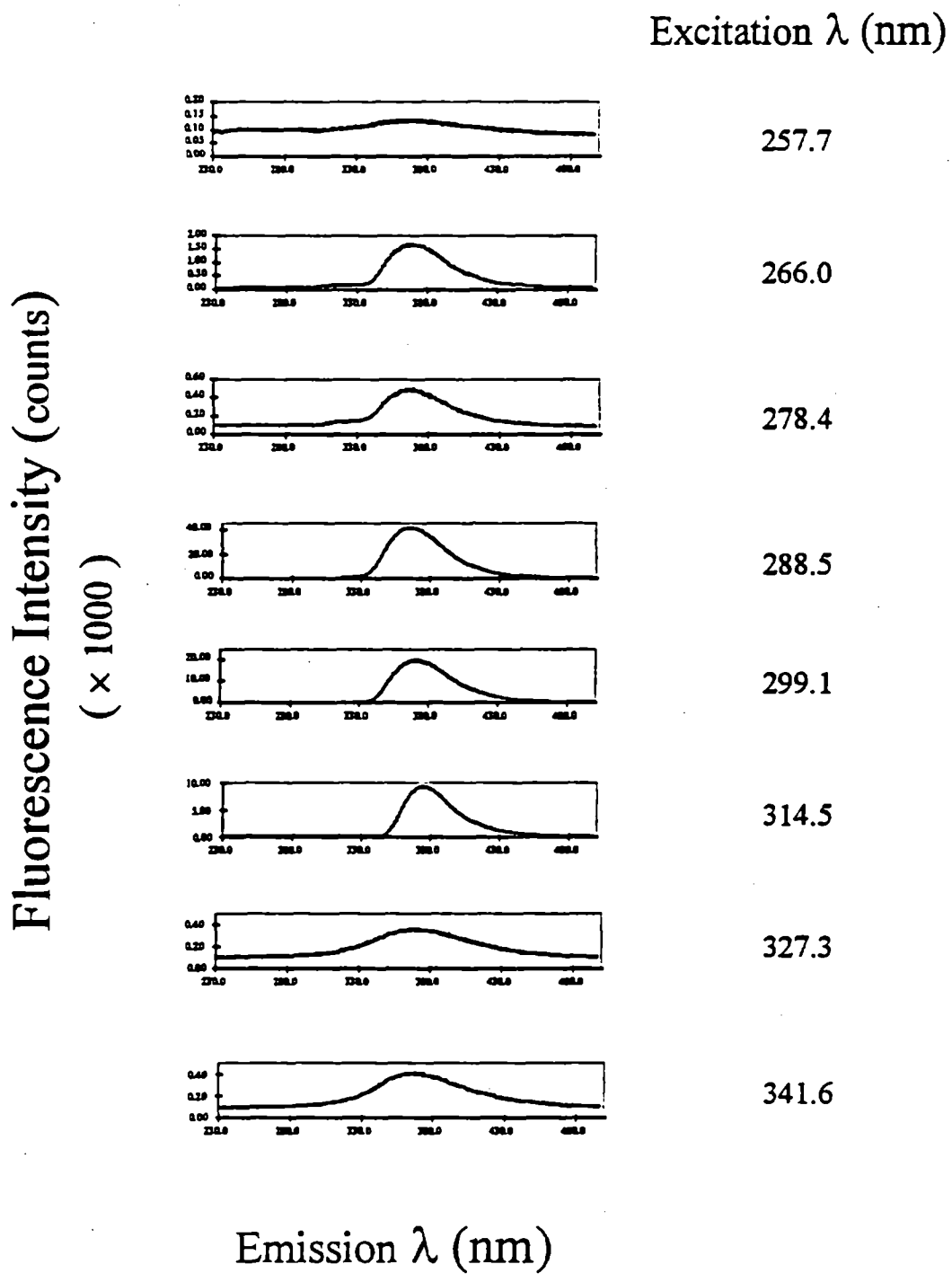

Figure 5. Emission spectra of quinine sulfate in ethanol, 0.2 g/L for the 8 excitation wavelengths used in the field.

shown in figure 5, where there are apparent shifts in the emission maxima. The spectral shifts are due to the different cutoff filters used in each channel to reject scattered light.

3.2.2. Pushes at Hanscom AFB

The summed fluorescence signal vs. cone tip depth for a typical push is shown in figure 6. One can see two depth regions of fluorescence, with peaks at 9 feet and 15 feet. Also shown in figure 6 is the EEM corresponding to the summed fluorescence maximum. The EEM in figure 6 has all channels reporting fluorescence with the highest intensity in the central excitation wavelength channels. Qualitatively this may indicate the presence of more two ring class compounds at this particular depth. In addition, the lower fluorescence signals extending off the long wavelength emission scale may indicate the existence of smaller amounts of three and possibly four ring species.

As an initial verification of our *in situ* measurements, the groundwater and fuel depth were measured with an oil / water interface probe (ORS Co.) immediately after the push in a nearby monitoring well (MW-9). The fuel depth measured from the ground surface was 14 feet and the top of the water table was 17.0 feet. The monitoring well was approximately 15 feet down gradient from the push site and therefore the amount of fuel product and the actual depths may differ. Nevertheless, the LIF depth profile contains signal from 11 to 14 feet (the probe windows begin 1 foot above the cone tip and are 1.5" apart) with a maximum signal seen at 14 feet which correlates well with the measurement of fuel product at 14 feet. From 11 to 14 feet, the LIF signal increases gradually and this may be due to contamination in the unsaturated zone or capillary fringe above the free fuel product. In addition, there is a small amount of signal at 18 feet which may be due to species in the groundwater at much lower concentration than in the fuel product layer.

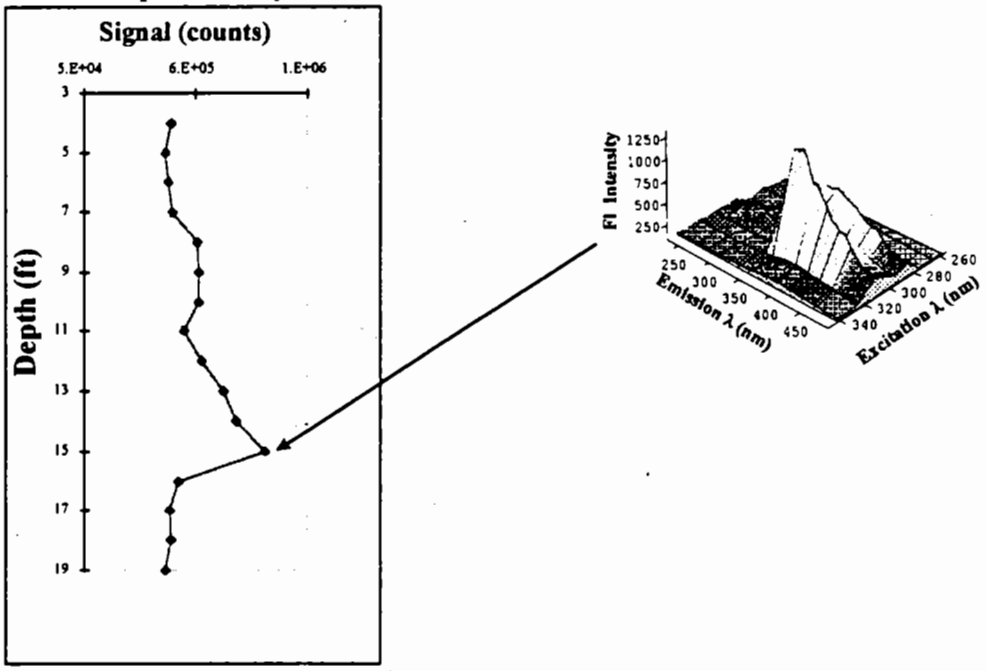

Figure 6. Summed fluorescence depth profile and EEM for the peak. LIF data taken at Hanscom AFB.

4. CONCLUSION

We have described and demonstrated our multichannel laser spectrometer system and probe in a variety of media. Lab measurements have been made for a three component mixture (Benzene, naphthalene and anthracene), jet fuel in silty clay, and aqueous phenol neat and in Ottawa sand. Field measurements have been made for quinine sulfate in ethanol as a standard calibrant and finally, we have presented the results for a selected push location from our recent field work at Hanscom AFB with a summed fluorescence depth profile and an EEM from that push. We have demonstrated the capacity of our system to measure fluorescent analytes in several media including water, NAPLs such as jet fuel, cyclohexane and ethanol. The simultaneous detection of our 3 component mixture demonstrates our system's ability to discriminate among 1, 2 and 3 ring aromatics. The calibration procedure using quinine sulfate has been tested in the field and has proven to be quick and convenient to implement. Finally, the operation of the system and the collection of field data has been demonstrated with a sample from our very recent field work.

5. ACKNOWLEDGEMENTS

This project was funded by the Robert S. Kerr Laboratory of U.S. Environmental Protection Agency. Additional support was provided by the Northeast Hazardous Substance Research Center at New Jersey Institute of Technology (NJIT project number R-43). Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement No. CR-821856 to Tufts University and agreement No. R-819679 to New Jersey Institute of Technology, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement should be inferred. The authors would like to extend thanks to John Macey and Jane Pepper for their help with the lab measurements and Susan Mravik and John Hoggatt for their roles in operating the CPT vehicle and handling the probe during the field measurements. The authors would like to extend special thanks to Tom Best, site manager, at Hanscom AFB for all of his efforts to accommodate us during the field work. In addition, the fuel and water depth data presented were taken by him during the site investigation.

6. REFERENCES

1. R. W. St.Germain, G. D. Gillispie, "Transportable tunable dye laser for field analysis of aromatic hydrocarbons in groundwater," *Proc. Second International Symposium of Field Screening Methods for Hazardous Waste Site Investigations*, Las Vegas, NV, Feb. 11-13, 1991.

2. S. H. Lieberman, S. E. Apitz, L. M. Borbridge, G. A. Theriault, "Subsurface screening of petroleum hydrocarbons in soils via laser induced fluorometry over optical fibers with a cone penetrometer system", *International Symposium on Environmental Sensing, EOS/SPIE Proceeding, Vol. 1716*, 1992.

3. J.E. Kenny, A.H. Kinney, "Spectroscopy in the field", *Spectroscopy*, 10, 7, 32, 1995.

4. Gregory D. Gillispie and Randy W. St. Germain, "Performance characterization of the rapid optical screening tool (ROST™), preprint from author.

5. J. Lin, S. J. Hart, T. A. Taylor, J. E. Kenny, "Laser fluorescence EEM probe for cone penetrometer pollution analysis", *A&WMA/SPIE Symposium on Optical Sensing for Environmental and Process Monitoring*, Vol. 2367, 70-79, 1994.

6. J. Lin, S. J. Hart, W. Wang, D. Namytchkine, and J. E. Kenny, "Subsurface contaminant monitoring by laser fluorescence excitation-emission spectroscopy in a cone penetrometer probe", *A&WMA/SPIE European Symposium on Optics for environmental and public safety*, Vol. 2504, 59-67, 1995.

7. S. J. Hart, J. Lin, J. E. Kenny, "Filters in fiber-optic connectors", to be submitted to *Applied Spectroscopy*, 8/96.

8. J. Lin, S. J. Hart, J. E. Kenny, "Improved two-fiber probe for *in-situ* spectroscopic measurements", to be published in *Analytical Chemistry*, Sept. 15 or Oct. 1, 1996.

TECHNICAL REPORT DATA

1. REPORT NO. EPA/600/A-96/120	2.	3. RI
4. TITLE AND SUBTITLE A FIBER OPTIC MULTICHANNEL LASER SPECTROMETER SYSTEM FOR REMOTE FLUORESCENCE DETECTION IN SOILS		5. REPORT DATE
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) SEAN J. HART[1], YU-MIN CHEN[1], BOB K. LIEN[2], JONATHAN E. KENNY[1]		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS TUFTS UNIVERSITY, DEPARTMENT OF CHEMISTRY, MEDFORD, MA 02155[1] USEPA NATIONAL RISK MANAGEMENT RESEARCH LAB, ADA, OK 74820[2]		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS USEPA NATIONAL RISK MANAGEMENT RESEARCH LAB, SUBSURFACE PROTECTION AND REMEDIATION DIVISION, PO BOX 1198 ADA, OK 74820		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE EPA/600/15
15. SUPPLEMENTARY NOTES		

16. ABSTRACT: Fiber optic probes employing single channel laser excitation and fluorescence collection have been seeing increasing use for remote sensing applications. However, multichannel systems offer enhanced capacity for qualitative and quantitative determination of analytes. We describe a system which employs simultaneous delivery of laser excitation wavelengths arising from stimulated Raman scattering (SRS). Separate fluorescence responses for each excitation channel are imaged through a spectrograph onto a CCD array detector. Each channel has a dedicated fiber optic pair to deliver and collect light. Results will be presented which evaluate the capabilities of this type of spectrometer for determination of organic contaminant mixtures in various sample matrices.

17. KEY WORDS AND DOCUMENT ANALYSIS

A. DESCRIPTORS	B. IDENTIFIERS/OPEN ENDED TERMS	C. COSATI FIELD, GROUP
Fluorescence, remote sensing, fiber optic, laser, soils, in-situ, field test, EEM, LIF		

18. DISTRIBUTION STATEMENT RELEASE TO THE PUBLIC	19. SECURITY CLASS(THIS REPORT) UNCLASSIFIED	21. NO. OF PAGES 10
	20. SECURITY CLASS(THIS PAGE) UNCLASSIFIED	22. PRICE

EPA FORM 2220-1 (REV.4-77) PREVIOUS EDITION IS OBSOLETE