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FIELD RAMAN SPECTROGRAPH FOR ENVIRONMENTAL ANALYSIS

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2.5 Field Raman Spectrograph for Environmental Analysis

CONTRACT INFORMATION

Contract Number	DE-AC21-92MC29108
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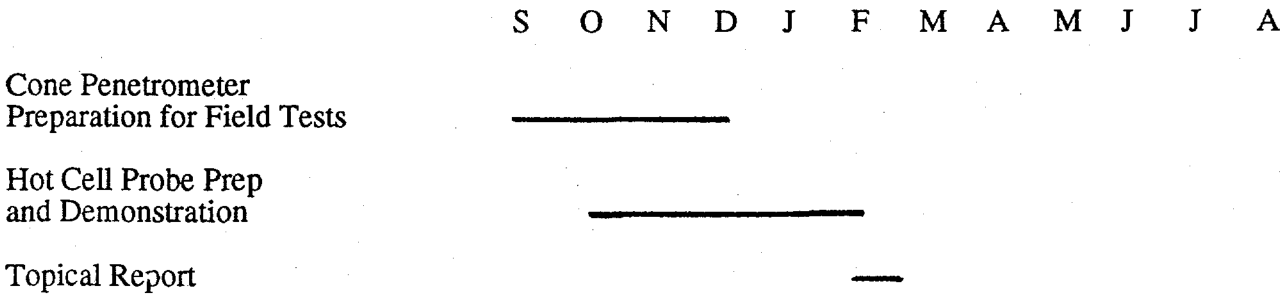
Principal Investigator	Dr. Michael M. Carrabba
METC Project Manager	Mr. Curtis V. Nakaishi
Period of Performance	September 29, 1992 to February 28, 1995
Schedule/Milestones	

FY95 Program Schedule (Phase I)



OBJECTIVES

The principal objective of the first Phase of the program is to take existing Raman technology demonstrated at the component level at EIC and to integrate it into a system of hardware, software and operational protocols which can be evaluated for *in situ* environmental analysis at DOE environmental restoration field sites. The Phase I program will increase the Maturity Level of this technology from III to IV. A Phase II program is anticipated in which actual field tests will be conducted and application-oriented software and hardware modifications will be developed.

BACKGROUND INFORMATION

Technology Requirements for DOE Site Characterization. Following identification of a potentially contaminated facility it is necessary to characterize the type of contamination and its extent before remediation can begin. In the case of soil and groundwater, it is important to limit remediation activities to contaminated locations. Thus, *in situ* techniques are extremely useful for mapping contaminant distribution as well as for measuring remediation effectiveness. The five-year (1992-96) Environmental Restoration and Waste Management Plan [1] recommends two types of *in situ* characterization technologies for development: 1) methods to assess hazardous contaminants in air, soil and groundwater before, during and after remediation; 2) probes for storage tanks, wastewater and other facilities in order to determine the chemical and radiological hazards in order to specify safety of entry and remedial action.

Raman Spectroscopy for Environmental Analysis. Raman spectroscopy, including Surface Enhanced Raman techniques, has several unique features which sets it apart from alternative approaches to *in situ* analysis. First, it is a direct spectroscopic technique with a very high information content that can be conducted remotely over optical fibers. The multiple sharp spectroscopic peaks contained in the Raman spectrum can frequently be used for conclusive identification of single compounds or of individual components in mixtures. Ultraviolet and visible absorption monitoring of pollutants [2], as well as laser induced fluorescence (LIF), tend to give broad, featureless responses. These may be useful as general warning techniques, but cannot be employed for identification. LIF can be very sensitive, but is applicable mostly to the detection of aromatic hydrocarbons such as may be found in leaks of gasoline storage tanks [3]. Since LIF of these pollutants requires ultraviolet excitation, transmission over optical fibers is compromised by fiber absorption. UV laser excitation is also difficult to implement in the field. Some pollutants such as volatile aliphatic chlorinated hydrocarbons are nonfluorescent and nonabsorptive in accessible wavelength ranges.

Direct infrared absorption gives vibrational spectral information similar to Raman spectroscopy. However, optical fibers spanning the infrared are made from esoteric materials that are not economical for this application. Furthermore, water is a very strong infrared absorber, so detecting dilute impurities in water by this method would be extremely difficult (water is only a very weak Raman scatterer).

Several optical fiber techniques for *in situ* environmental water analysis have recently been under investigation which are indirect in that they use a chemical indicator at the end of the optical fiber exposed to the polluted source [4-6]. Unlike Raman or the other direct spectroscopic techniques, these "optrodes" tend to be specific to one compound or compound group. For example, Angel and coworkers have reported an optrode for chloroform and trichloroethylene (TCE) in the low ppb range [6]. Optrodes tend to be consumable and nonrenewable, and equilibrium with the environment is often slow to attain.

Normal Raman spectroscopy is a relatively insensitive technique, with an analytical range down to approximately 0.1% in relatively clean samples with a low fluorescence background. Thus, its primary environmental application will be in characterizing concentrated samples, for example in the search and identification of dense nonaqueous phase liquids and other solvent agglomerations in soil. In this regard, combining fiber optic Raman spectroscopy with cone penetrometry or a similar rapid sampling method is the favored approach. Raman spectroscopy can be combined with various probe tools to provide access to underground storage tanks, where, for example, the composition of salt cakes and other components can be identified prior to entry. Normal Raman methods with fiber optic sampling probes can also be used to identify and classify unknown waste materials during cleanup, sometimes directly through the walls of glass or transluscent plastic containers.

There is considerable interest in *in situ* determination of dilute toxins in groundwater. Surface enhanced Raman techniques are potentially useful here. In this method, nanotextured surfaces of certain metals (e.g., Au, Ag, Cu) give Raman spectra of organic adsorbates with enhancement factors of up to 10^8. The selection and reproducible fabrication of substrates that are selective for priority pollutants such as TCE, and the extension of the technique down to regulatory levels, are issues that are currently being investigated.

Downsized Raman Instrumentation. Despite the recent availability of several small Raman spectrographs, there remains a requirement for high performance, rugged equipment that can withstand the field environment and that is generally portable and usable at remote sites. Furthermore, the technique benefits from high spectral resolution that is difficult to achieve in small spectrographs of conventional design. Pelletier [7] first described an echelle spectrograph with CCD detection for Raman spectroscopy. He was able to obtain an entire spectrum with a single measurement out to >4000 cm^{-1} from the laser exciting line (514.5 nm) with better than 2 cm^{-1} resolution. In such instruments, the spectrum is divided into pieces, which are then imaged onto the focal plane of a sensitive, low noise CCD detector array. The high efficiency of the grating, throughput of the spectrograph and sensitivity of the CCD detector enabled him to achieve comparable spectra with <1% of the total energy delivered to the sample compared to Fourier Transform Raman, after correction for the different wavelengths used for excitation. The feasibility of using diode laser excitation with CCD detection and a conventional limited range spectrograph was first demonstrated by Wang and McCreery [8]. EIC Laboratories pioneered the application of holographic filters to very efficiently separate the Raman spectrum from the intense Rayleigh line, thus eliminating the need for large pre-filtering monochrometers in many applications of Raman spectroscopy [11].

Fiber optic sampling for Raman spectroscopy has been considered by several research groups. Benner and Chang were the first to identify the problem of Raman scattering within the fiber for delivering the laser excitation to the sample as well as within the collection fiber arising from the intense Rayleigh line [10]. They suggested optical filters to remove the unwanted components. Later reports of fiber optic Raman sampling typically employed short fiber lengths, thus minimizing the contribution from the silica background (silica is a relatively weak Raman scatterer) [11-12]. Myrick and Angel [13] and work in this laboratory [14-15] demonstrated optical configurations for removing the silica background that could be incorporated into the sampling head. In particular, the micro-optical sampler developed in this laboratory permits the construction of a pen-type probe which addresses the gaseous, liquid or solid sample via the tip.

In a prior program under DOE sponsorship, EIC combined the echelle spectrograph approach and fiber optic Raman probes to produce a laboratory prototype of a novel compact Raman spectrograph [15]. The spectrograph employed commercial optics and performed well as a proof of principle, and was employed to record spectral signatures of several priority pollutants and mixtures. It was noted that the use of the instrument on site would require further engineering to produce a field hardened instrument package and to develop field sampling procedures and analytical protocols. These issues are addressed under the current program with METC.

PROJECT DESCRIPTION

The following specific Tasks have been set forth in this program to meet the stated objective: 1) to develop and test a small, field hardened, computer operated echelle Raman spectrometer that can be fiber optically coupled to a transportable compact laser source and probe over 50 meters; 2) to develop field-hardened probes incorporating optical components and substrates which can be used in field screening of soils and ground and surface waters for DOE priority pollutants, both for location of concentrated pollutant sources and also for determination at the action levels required for remediation; 3) using this spectrograph, to develop a database of Raman spectra of primary waste components to be found at DOE sites which can be used in field identification; and 4) through collaborations with National Laboratories to make onsite qualitative and quantitative assessments of waste storage tank composition, and groundwater and soil pollution.

ANTICIPATED BENEFITS TO DOE

Reduction of Health and Environmental Risks. The result of the program will be a new instrument with multiple capabilities for detecting, identifying and monitoring high and low level pollutants in the field setting. The increased efficiency of site characterization and monitoring compared to present sampling and laboratory analysis operations will greatly increase the rate at which hazardous regions can be selected for remediation or isolated. Combined with rapid sampling methods, the instrument will be useful in locating agglomorations of nonaqueous phases, resulting from leaks and spills, which act as sources for groundwater pollution. The use of Raman to identify remotely potentially hazardous materials will be used to avoid human exposure and to ensure safe access to waste repositories.

Reduction of Costs. Field Raman instruments and protocols are designed to minimize the number of labor intensive field sampling activities and analytical operations in the laboratory. As such, the instrument will save both manpower and in the number of more expensive analytical instruments necessary to maintain the DOE environmental activity.

Improved Operations. The advantages cited above all relate to improvements in efficiency. In addition, the technology can be used for monitoring water and possibly soil remediation efforts in real time and without the uncertainties of environmental sampling.

RESULTS

A major accomplishment of the program to date has been the construction of a prototype rugged field spectrograph based on an echelle diffraction grating for use in the near infrared spectral region. The echelle grating design allows a very high resolution (~1 cm^{-1}) to be achieved in a rack-mountable compact instrument. The detector is a low noise charge coupled device (CCD) planer array, whose two dimensional format is fully used in the echelle design. The spectrograph employs precision dispersive optical components which have been custom designed, fabricated and coated for achieving the highest possible throughput and image quality in the 600 to 1100 nm spectral range. Raman scattering excited by laser sources in this range typically have reduced interference from background fluorescence compared to visible laser excitation. A key component of the program has been the selection of fieldable laser sources for the near infrared region and the demonstration of their use in Raman applications. These include a proprietary solid state laser source operating at 752 nm that provides sufficient intensity (~500 mW) for weak Raman scatterers. Lower intensity laser sources may frequently be employed, however, for example diode lasers and compact gas lasers. One advantage of the CCD detector is its extremely low background noise, achievable now with thermoelectric air cooling (rather than liquid nitrogen or recirculating coolant). This low background permits extended periods of signal integration if necessary, and hence the use of very low power lasers for some applications. The spectrograph uses no slits, but rather is designed for direct fiber optic input which provides a significant advantage for light collection efficiency.

Several remote Raman probes have been developed which allow the laser light to be directed down one optical fiber, to illuminate the sample, to collect the scattered light, remove the Rayleigh scattering at the laser frequency, refocus the Raman scattered light into a second optical fiber, and direct the light back to the spectrograph/analyzer. The probe heads contain micro-optical components which perform all focusing, collection and filtering functions. A key feature of these probes is the removal of the Raman scattering generated within the optical fibers. The probes can accommodate a variety of sampling accessories. The probes have been modified with a novel side viewing port for incorporation into a cone penetrometer head, a robotically deployed arm in a waste tank inspection system, or similar application.

The performance of the spectrograph/laser/probe assembly has been outstanding. A comparison of the resolution of two closely spaced neon emission lines for the Echelle and a more conventional Czerny-Turner instrument is shown in Figure 1. The superior resolving power of the echelle is clearly demonstrated and is useful for multicomponent analysis. The instrument was recently introduced at the 1994 Pittsburgh Conference.

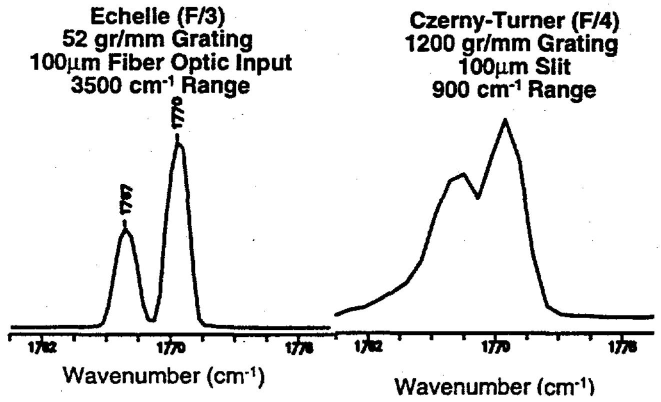


Figure 1. Comparison of the spectroscopic resolution of neon emission lines using an imaging Czerny-Turner spectrograph and the EIC Near Infrared Echelle spectrograph.

Laboratory tests of saturated soils using the Raman/penetrometer fixture have demonstrated the identification of trichloroethylene and other solvents. Figure 2 shows the spectrum of pure TCE, revealing the "fingerprint" obtainable for this ubiquitous priority pollutant that can be employed for identification. However, many soils tend to be highly colored, so that absorption of the excitation

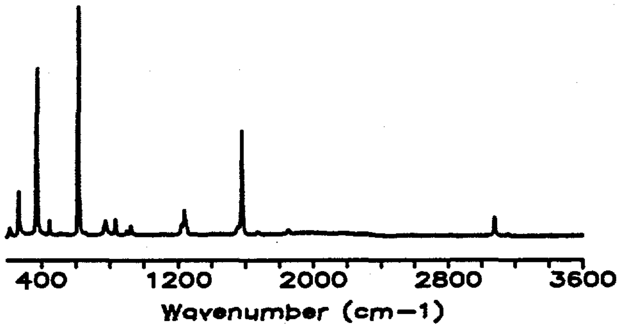


Figure 2. Raman spectrum of pure TCE obtained with EIC's echelle spectrograph. The full Raman spectral range (200-3600 cm^{-1} with respect to the exciting frequency) is obtained in a single image on the CCD focal plane without moving gratings or other optical elements.

light reduces the intensity of the Raman scattering compared to the pure sample and background fluorescence masks the Raman spectrum. Figure 3 shows Raman spectra obtained from typical red clay soil samples from the Savannah River site. The visible laser source gives rise to a broad fluorescent background. The TCE peaks can only be discerned using the longer wavelength 752 nm excitation, where the fluorescence background is lower. In general, the red sources and matched spectrographs have permitted the observation of Raman signatures in a wider variety of soil types than is possible with visible laser excitation.

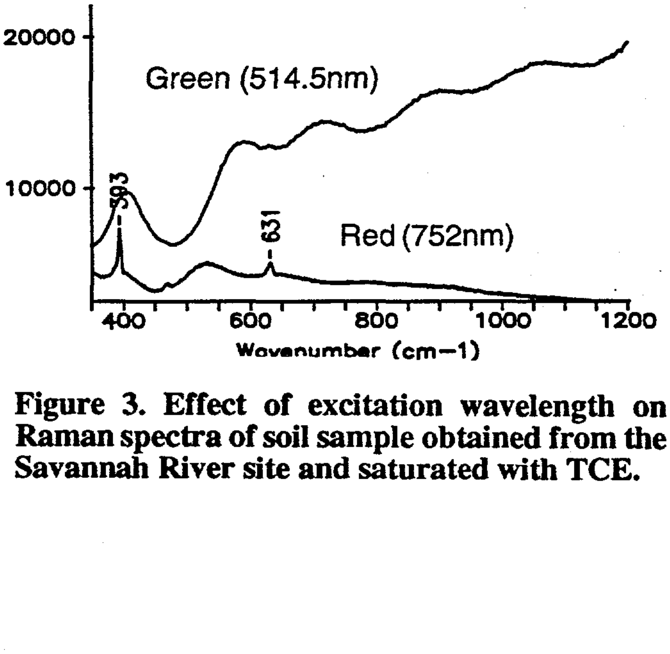


Figure 3. Effect of excitation wavelength on Raman spectra of soil sample obtained from the Savannah River site and saturated with TCE.

A probe accessory for conducting surface enhanced Raman spectroscopy has been refined and is undergoing testing for dilute chlorinated solvents and other waterborne contaminants. Substrates selective for TCE are based on a biphase surface concept developed and patented at EIC Laboratories [15-16]. Here, one layer traps or reacts with the compound of interest, bringing the products in contact with an underlying SERS-active metal. Copper with an oxide overlayer has been shown to be selective for TCE and related compounds at low levels in water.

To date the system has been used to assemble a comprehensive library of spectra of compounds found at DOE sites. The library currently includes over 75 of the most frequently encountered materials in waste storage tanks and in environmental matrices. All spectra are stored in digital form and are readily retrievable using spectroscopic software being configured for the echelle spectrograph. The spectra also include commonly encountered mixtures which can be resolved using the techniques. Included among the mixtures are simulants of the Hanford waste tanks analyzed in preparation for future field tests. Over 700 spectra have been employed to prepare the library documenting neat compounds, mixtures, and dilutions of significance to the DOE characterization and remediation effort.

FUTURE WORK

Near-term plans include refinement of analytical protocols and preparation for field testing at selected hazardous waste sites, including further refinement of cone penetrometer probes and development of methods for hot cell testing. Also in progress is the development of Operator and Field manuals for the instruments. Enhanced instrument automation, software development and accessories/protocols for sampling of radioactive environments are anticipated for Phase II. Also planned for Phase II is further testing at DOE field installations, including demonstration of near infrared Raman spectroscopy/cone penetrometry for locating dense non-aqueous phase liquid agglomerates in soils.

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