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# FIBER OPTIC RAMAN SPECTROGRAPH FOR IN SITU ENVIRONMENTAL MONITORING

Final Report, Contract No. 02112402

By

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# PREFACE

Currently available technology is not adequate to assess environmental contamination at Department of Energy (DOE) sites, take permanent remedial action, and eliminate or minimize the environmental impact of future operations. Technical resources to address these shortcomings exist within the DOE community and the private sector, but the involvement of the private sector in attaining permanent and cost-effective solutions has been limited.

During 1990, on behalf of DOE's Office of Technology Development, Argonne National Laboratory (ANL) conducted a competitive procurement of research and development projects addressing soil remediation, groundwater remediation, site characterization, and contaminant containment. Fifteen contracts were negotiated in these areas.

This report documents work performed as part of the Private Sector Research and Development Program sponsored by the DOE's Office of Technology Development within the Environmental Restoration and Waste Management Program. The research and development work described herein was conducted under contract to ANL.

On behalf of DOE and ANL, I wish to thank the performing contractor and especially the report authors for their cooperation and their contribution to development of new processes for characterization and remediation of DOE's environmental problems. We anticipate that the R&D investment described here will be repaid many-fold in the application of better, faster, safer, and cheaper technologies.

Details of the procurement process and status reports for all 15 of the contractors performing under this program can be found in "Applied Research and Development Private Sector Accomplishments - Interim Report" (Report No. DOE/CH-9216) by Nicholas J. Beskid, Jas S. Devgun, Mitchell D. Erickson and Margaret M. Zielke.

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## ABSTRACT

This report discusses the development and testing of a small laboratory prototype, field Raman spectrometer which can be used with a fiber optic sampling probe incorporting substrates tailored for surface enhanced Raman spectroscopy (SERS) for low level detection of chemical species. The report also discusses the demonstration of the apparatus for both laboratory and field environmental samples typical of DOE environmental restoration sites. The preliminary results discussed in the report establish a new technique which can be used in the field to identify and profile *in situ* a wide variety of pollutants at the action levels required for remediation.

# FIBER OPTIC RAMAN SPECTROGRAPH FOR IN SITU ENVIRONMENTAL MONITORING

## EXECUTIVE SUMMARY

The objectives of this program were to develop and test in the laboratory a prototype of a small, fieldable Raman spectrometer that can be used with a fiber optic sampling probe over >50 meters of silica optical fiber; to develop a probe incorporating substrates tailored for surface enhanced Raman spectroscopy (SERS) for low level detection of chemical species; and to demonstrate the apparatus for both laboratory and field environmental samples typical of DOE environmental restoration sites. The overall goal was to establish a new technique which can be used in the field to identify and profile *in situ* a wide variety of pollutants at the action levels required for remediation.

### Technical Description

EIC has developed a Raman spectrograph based on a unique design which occupies less than 10% of the volume of a conventional Raman instrument. It is the initial prototype of an instrument that can be deployed to DOE environmental restoration sites for immediate chemical characterization of a variety of samples: soil, groundwater, storage tank contents, waste spills, etc. The instrument, which contains no internal moving parts, employs a coarse echelle diffraction grating and divides the spectrum into segments which are projected in stacked fashion onto the focal plane of a two dimensional charge coupled device (CCD) detector array. The spectrograph is designed to have both a low f/# (high light collection efficiency) and small size, without sacrificing resolution, an impossible feat for traditional spectrographs with linear dispersion and reflective optics. The optics are matched to a fiber optic input and 1:1 imaging at the focal plane. The spectrograph employs no slits, which, combined with the shorter light paths, fewer optical surfaces and high echelle efficiency makes the optical throughput of the instrument more than 10-fold higher than conventional Raman spectrographs. This fact, combined with the exceptional sensitivity of a new generation of CCD detector arrays, means that low power laser sources can now be used for conducting Raman spectroscopy. As a result, a self-contained Raman spectrograph which operates using two-phase wall or generator current and requires no flowing water for cooling is now possible.

In addition, the resolution of the system allows for complex mixtures to be analyzed such as mixture of chlorinated hydrocarbons (TCE, DCE, PEC etc.) and a component mixtures of gasoline type component (hexane, pentane, etc.). The ability to observe and resolve the chlorinated and light hydrocarbon type compounds is important since these compounds cannot be observed with other standard spectroscopic techniques (fluorescence, adsorption, IR) via fiber optics.

In environmental site characterization, the ability to probe samples remotely from the instrument will be very important. For example, spectroscopic probes deployed through cone penetrometers can be used to map chemical concentrations as a function of depth and to identify pockets of high pollutant concentration (e.g., dense nonaqueous phase liquids). Through the use of fiber optic probes, EIC has also made several breakthroughs in the area of Raman sampling which enable remote sampling over long distances while having the additional benefit of eliminating much of the prefiltering and sampling optics found in conventional instruments. It has been recognized for some time that silica optical fibers can be used to deliver the excitation light to the sample and return the scattered Raman spectrum from the sample to the spectrograph. However, although Raman spectra of strong Raman scatterers may be easily obtained over short fiber lengths, long fiber paths or long detector integration times will always result in the spectrum being "swamped out". For environmental analysis, capabilities of remote sampling over substantial distances and of long integration times for detection of dilute or weakly scattering pollutants will be absolutely essential.

We have employed micro-optical components and techniques currently used in medical endoscopy to construct a multifunctional stainless steel probe head 1-2 cm in diameter that perform most of the bulky prefiltering functions found in conventional Raman instruments. The laser light is launched into a first optical fiber which extends to the input of the probe head, which is positioned at the sample. This excitation light will contain unwanted frequencies arising from the laser itself and from Raman scattering generated within the silica fiber. These are removed by passage through a first set of filter micro-optics mounted in the head. The filtered, highly monochromatic light then illuminates the sample through the end of the probe. The collected scattered light is passed through a second micro-optical filter, also contained in the head. This second filter set removes most of the Rayleigh line, sending only the Raman spectrum into a second optical fiber which extends to the input of the spectrograph. The probes can accommodate a variety of end accessories, including filters, permiselective membranes and electrochemical cells for conducting SERS. A prototype Raman probe has been delivered to LLNL for testing at the mock-up waste storage tank at Los Alamos National Laboratory.

Raman spectroscopy is a relatively insensitive analytical method unless it is "enhanced" in some way. It becomes experimentally very difficult to measure spectra at concentrations below ~10 ppm. This sensitivity is sufficient for many types of pollutant and waste characterization. The application of an enhanced Raman technique such as surface enhanced Raman spectroscopy (SERS) is practical for low level analysis and has been demonstrated in our laboratory using fiber optics for the detection and analysis of organic constituents in aqueous environments at the parts per billion level.

SERS-based chemical sensing probes developed on this program incorporate a substrate with a general affinity for the class of molecules to be sensed. As an example, copper oxide-based Raman substrates have been developed for sensing and identification of dilute chlorinated hydrocarbons in water, while roughened silver substrates show affinity for aromatic and aliphatic hydrocarbons such as benzene and methyl ethyl ketone which are ubiquitous groundwater pollutants. The highly structured Raman spectra then are used for speciation. Spectra of ketones and of mixed chlorinated hydrocarbons, including trichloroethylene (TCE), have been obtained using actual environmental groundwater samples from the Bear Creek Burial Grounds at ORNL. The substrate will eventually be incorporated into the fiber optically coupled probe head, enabling *in situ* analysis of groundwater via small diameter (<5 cm) drilled wells or cone penetrometers.

EIC and Oak Ridge National Laboratories have established a Collaborative Research Agreement (CRA) which will allow the exchange of technology and facilities in order to develop and conduct on site testing protocols using fiber optic Raman spectroscopy, in accordance with the long term RDDT&E objectives. EIC has also expanded the program to fabricate fiber optic probes for testing at the Los Alamos mock-up waste storage tank, with subsequent demonstration at Hanford. EIC has also established collaborative agreements with other contractors involved in soil and groundwater mapping and sampling technology, in order to provide means for deploying the spectroscopic probes. The deployment methods include the use of cone penetrometers.

## Technology Status

The program has taken the Raman technology to the component level through development of laboratory prototypes of the spectrograph and probes and preliminary testings of the components have been completed. The DT&E phase will require development of a field hardened instrument package and refinement of field analytical protocols for identification, quantitation and mapping of specific pollutants. In addition, the DT&E phase will entail integration of the spectroscopic sample probes with appropriate sampling accessories. Once developed, this technology will obviate much of the expensive and time consuming laboratory analyses of environmental samples. It is therefore estimated that the payback of the original contract cost will be achieved rapidly through savings in analytical costs. In addition, more rapid and specific chemical characterization of a site will permit remediation activities to occur at a faster pace and be to be aimed only at contaminated locations.

## 1.0 INTRODUCTION

The objectives of this applied research program were: to develop and test in the laboratory a prototype of a small, fieldable Raman spectrometer that can be used with a fiber optic sampling probe over >50 meters of silica optical fiber; to develop a probe incorporating substrates tailored for surface enhanced Raman spectroscopy (SERS) for low level detection of chemical species; and to demonstrate the apparatus for both laboratory and field environmental samples typical of DOE environmental restoration sites. The overall goal was to establish a new technique which can be used both in the field to identify and profile *in situ* a wide variety of pollutants at the action levels required for remediation and waste storage tank characterizations. The packaging, electronics and software development along with the field demonstration of the spectrometer would encompass the DT&E phase of the project, which would follow based on the research results.

### 1.1 Technology Scope

The Department of Energy and the Nation are facing a problem of monumental proportions relating to waste and contamination of the environment at nuclear processing facilities generated over the last 40 years. The cost of site characterization and remediation is estimated to be about $85 billion [1]. Before remediation can begin, waste sites must be characterized both chemically and geologically. Presently, samples are collected and removed to laboratories for analysis, but this approach is both costly (up to several thousand dollars/sample), frequently negative, and subject to errors due to the changing nature of samples exposed to air or permitted to volatilize. In addition, the safety of sample collection activities is a serious concern, as is waste generation by standard sampling methods. These factors limit the extent and frequency of analysis conducted at any site as well as the adequate characterization of hydrologic migration of pollutants in groundwater and soil surrounding leaking containments. For these reasons, it is imperative to develop *in situ* screening methods to determine chemical composition of a variety of waste types and also to provide for remote sampling and monitoring capabilities.

There are numerous types of wastes and pollutants that require characterization at DOE nuclear processing and weapons facilities, but they can generally be grouped as concentrated/contained and as dilute/migrating [2-4]. The concentrated waste sites include underground storage tanks, 55 gallon drums and landfills. Of primary concern are 149 single walled underground storage tanks at the Hanford facility which have the highest potential for leaking hazardous waste into the environment.

Dilute waste plumes originate from the concentrated sources leaking into the soil and contaminating the surface and groundwater. These dilute contaminants require more sensitive analytical methods. Concentrated waste plumes also represent a hazard at certain DOE sites. These dense nonaqueous phase liquids (DNAPLs) are agglomerations of water insoluble, high density contaminants (e.g., chlorinated solvents, PCBs, creosote and motor and lubricating oils).

#### Baseline Technologies

Raman spectroscopy, including surface enhanced Raman spectroscopy (SERS), has several unique features which set 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. UV and visible absorption monitoring of pollutants [5], 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. Laser induced fluorescence 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 [6-8]. 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 [9-11]. Unlike Raman or the other direct spectroscopic techniques, these "optrodes" tend to be specific to one compound or compound group. For example, Angel and co-workers have reported an optrode for chloroform and TCE in the low ppb range [11]. Optrodes tend to be consumable and nonrenewable, and equilibrium with the environment is often slow to attain.

Normal and surface enhanced Raman spectroscopy have the potential of being a general method for the detection of a wide variety of molecules and ions [12- 22]. In addition, the Raman signal may be obtained from the Raman scattering off the substrate using a visible or near infrared (NIR) laser source. Since the transmission of relatively inexpensive optical fibers in these regions is very high, the use of inexpensive solid state laser diodes is very favorable for remote applications of Raman.

## Current Technology

During this program, we developed and tested both direct Fiber Optic Raman Spectroscopy and Fiber Optic Surface Enhanced Raman Spectroscopy as a general technique and instrument for environmental analysis. Using fiber optic Raman techniques it should be possible to obtain, through *in situ*/field measurements, highly specific chemical characterization and mapping of field sites and waste storage containers. Raman spectroscopy is suitable both for highly concentrated materials and also for sub-ppb detection levels under the appropriate conditions. Since the technique yields a multiline fingerprint of the waste products or polluting species, it can be used not only for sensing and monitoring, but also for identification.

The concentrated wastes that are found in underground storage tanks tend to be heterogeneous; thus, they cannot be characterized unless multiple samples are taken. An *in situ* technique employing a movable sample probe would be invaluable in this regard. The history of any one of these tanks is generally unknown. However, the types of compounds found to date span a range of gases, liquids, and solids in various physical forms, such as hydrogen, cyanides, oils and oil-based solvents, chlorinated hydrocarbons, organic chelating agents such as EDTA and oxalic acid, and complex inorganic ions, some associated with radioactive elements. Most of the substances found to date have characteristic Raman spectra and can be observed by direct fiber optic Raman methods. In addition to characterizing the contents of waste storage tanks, direct fiber optic Raman spectroscopy can also be used to detect corrosion on the interior surface of the tanks which would indicate areas of weakness or leakage.

Raman spectroscopy is a relatively insensitive analytical method unless it is "enhanced" in some way. It becomes experimentally very difficult with unenhanced Raman to measure spectra at concentrations below ~10 ppm. However, this sensitivity is sufficient for many types of pollutant and waste characterization. The application of an enhanced Raman technique are required for dilute waste plumes originating from the concentrated sources leaking into the soil and contaminating the surface and groundwater. One such technique is surface enhanced Raman spectroscopy (SERS) which is practical for low level analysis and has been demonstrated in our laboratory using fiber optics for the detection and analysis of organic constituents in aqueous environments at the parts per billion level [13-18]. The potential value of SERS has been underscored in two recent DOE reports on site characterization and remediation [1,10].

As part of this project and an ongoing Collaborative Research Agreement (CRA-90-003) with ORNL, we have detected and characterized chlorinated hydrocarbons in actual environmental groundwater samples obtained from the Bear Creek Burial Grounds at Oak Ridge Reservation. Acquisition of the SERS spectrum of the actual environmental groundwater sample required no preparation and the actual acquisition took less than five minutes.

Concentrated waste plumes from dense nonaqueous phase liquids (DNAPLs) should also give unique Raman spectra. They will form concentrated sludge areas in existing wells, or could be directly accessed through minimally intrusive cone penetrometers. Baseline experiments conducted during this program indicate that DNAPLs in soil and clays could be identified and characterized with unenhanced Raman techniques (e.g., direct fiber optic Raman techniques) combined with a cone penetrometer.

## Application of the Technology

The anticipated end product at the completion of the DT&E phase is a commercial field portable fiber optic Raman system. Using the field portable instrument, Raman spectroscopy can be applied to several site characterization problems. First, Raman probes can be introduced into waste storage tanks with unknown contents, and the major chemical species can be identified and their distribution mapped within the container. Second, high sensitivity Raman probes can be introduced into wells and the groundwater sampled and characterized *in situ.* Eventually, this same approach could be employed with rapidly deployed cone penetrometers for a more complete and cost-effective site mapping than possible with drilled and excavated wells.

A key feature of the DT&E program will be the field testing of a field hardened unit. These testings should include *in situ* Raman characterization of 1) the contents of a waste storage tank and 2) groundwater contamination, particularly by chlorinated hydrocarbons, at a site such as the Bear Creek Burial Grounds at Oak Ridge Reservation (ORR). The DT&E program would also involve making modifications to the instrument, based on the outcome of field tests, to ready the instrument for commercial availability to DOE in a form customized for the environmental restoration program. A second aspect of DT&E Phase is the further refinement of the instrument-computer interface to automate and improve field analyses and to provide enhanced, user-friendly spectral searching.

Advantages of the technique for DOE would include increased efficiency of environmental characterization and mapping, reduced costs associated with field sampling, and *ex situ* laboratory analysis, less direct exposure of personnel to polluted samples (e.g., in pump and fill operations), cost savings over more complex analytical instrumentation, and more effective real-time monitoring of remediation activities.

### 1.2 Technology Programmatic Requirements

The total program (R&D and DT&E Phases) will give us the necessary experience with applying Raman to site characterization to develop a line of user-friendly instruments keyed to environmental characterization and restoration which can be supplied on a commercial basis. It is only through the general availability of cost-effective instrumentation, operable by field technicians, that Raman can make an impact on the massive environmental restoration effort. Ongoing collaborations with groups at the national laboratories also investigating Raman for site characterization will ensure that the commercial instruments will reflect their relevant research results.

No such instrument currently exists. The increased efficiency of site characterization and monitoring compared to present sampling and laboratory analyses operations will greatly increase the rate at which hazardous regions can be selected for remediation or isolated. In addition, pollution-free areas abutting DOE sites or near underground storage tanks may be monitored to detect spreading via transport in the underground aquifer.

The further developments, under DT&E Phase, of the Raman technology and instrument 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 the number of more expensive analytical instruments necessary to maintain the DOE environmental activity.

The advantages sited 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. In addition to the DOE community, several other Federal agencies such as the Department of Defense (DOD), the Environmental Protection Agency (EPA), and the U.S. Geological Survey, as well as the commercial sector, will benefit from the introduction of a low cost commercial instrument.

## 2.0 METHODOLOGY AND APPROACH

### 2.1 Facilities and Equipment

Founded in 1971 and privately owned, EIC Laboratories, Inc. specializes in the applied physical sciences and conducts research and development in diverse areas of chemistry, physics, and materials science. All of the program work was conducted in our Norwood, Massachusetts facility, which includes 40,000 square feet for offices, research laboratories, engineering, design and manufacturing. These facilities comply with the Federal, Massachusetts, and Norwood environmental laws and regulations.

Research equipment utilized during the program included the following:

- **Analytical Instrumentation**. Scanning electron microscope with energy dispersive x-ray analysis; X-ray diffractometer with Debye-Scherrer and Laue capability; Fourier transform IR, UV-VIS-NIR, total luminescence and atomic absorption spectrometers; Raman spectrometer with variable wavelength laser excitation capability and optical multichannel analyzer and CCD detection; gas chromatographs; differential scanning calorimeter.

- **Electrochemical Instrumentation**. Computerized electrochemical impedance spectrometers, potentiostats, function generators, constant current sources, pH meters, and specialized test equipment.

- **Laser and Optics Laboratory**. Argon laser, Krypton laser, tunable pulsed and cw dye lasers, He-Cd and He-Ne lasers; optical tables and accessories; lock-in amplifiers, boxcar integrators, optical multichannel analyzer, several charge coupled device detectors for signal processing, monochromators, Raman spectroscopy systems, radiometers and thermopiles; fiber optics.

### 2.2 Experimental

#### 2.2.1 Small Spectrograph Development

EIC has developed for this program a Raman spectrograph based on a unique design which occupies less than 10% of the volume of a conventional Raman instrument. It is the initial prototype of an instrument that can be deployed to DOE environmental restoration sites for immediate chemical characterization of a variety of samples: soil, groundwater, storage tank contents, waste spills, etc. The instrument, which contains no internal moving parts, employs a coarse echelle diffraction grating and divides the spectrum into segments which are projected in stacked fashion onto the focal plane of a two dimensional charge coupled device (CCD) detector array. The spectrograph is designed to have both a low f/# (high light collection efficiency) and small size, without sacrificing resolution, an impossible feat for traditional spectrographs with linear dispersion and reflective optics. The optics are matched to a fiber optic input and 1:1 imaging at the focal plane. The spectrograph employs no slits, which, combined with the shorter light paths, fewer optical surfaces and high echelle efficiency make the optical throughput of the instrument more than 10-fold higher than conventional Raman spectrographs. This fact, combined with the exceptional sensitivity of a new generation of CCD detector arrays, means that low power laser sources can now be used for conducting Raman spectroscopy [18-22].

During this program, we completed the design, specified the parts, and fabricated a "breadboard" version of a spectrograph/monochrometer that had both high resolution and covered the entire Raman spectral range without the necessity of moving or changing the grating or other optical elements. We chose to develop a dispersive as opposed to a Fourier transform instrument, since the former can be built in a very rugged configuration without moving parts. A conventional high resolution dispersive spectrograph typically requires long internal focal lengths, multiple dispersive elements and scanning mechanisms. Thus, these units are usually very large and somewhat complex. Previous results in our laboratory prior to this program established the feasibility of using compact spectrographs while still allowing for the identification and quantification in the region of 200 to 4000 cm$^{-1}$ from the excitation line. Because of the reduction of optical elements, these compact spectrographs have throughputs up to 100 times greater than achieved in large research units.

The spectrograph design (Figure 2.1) utilizes a high efficiency echelle diffraction grating, which enables both high resolution and a large spectral range in a very compact package with essentially no moving parts. The coarse grating is used in relatively high orders and large angles of incidence. When used in this configuration, the multiple diffracted orders are spatially overlapping. Thus, a secondary dual dispersive element (two prisms) is used in an orthogonal direction to separate the orders. A lens set is then used to image the 2-dimensional spectral image onto the focal plane, which contains the detector.

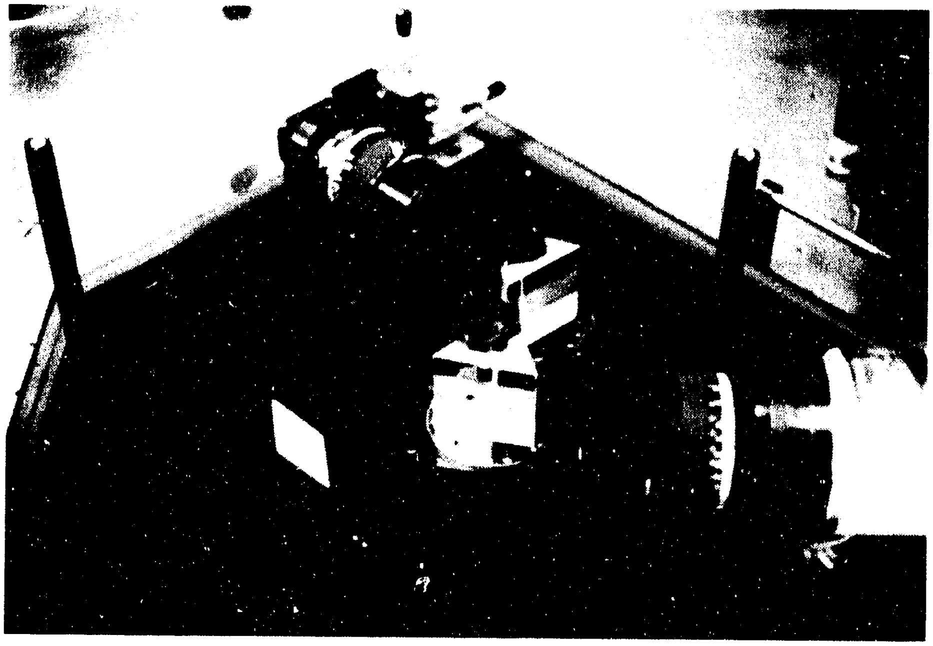


Figure 2.1. Photograph of breadboard prototype.

The actual system (Figure 2.1) incorporates a commercially available 52.65 groove/mm echelle grating (Milton Roy Corp.), which is operated at an incident angle of 63.4 degrees. The secondary dispersion element is a dual prism system which allows the Raman spectrum (200 - 4000 $cm^{-1}$) to be obtained in approximately 14 orders. The actual order numbers depend on the wavelength region. An analysis of this design at 780 nm is summarized in Table 2.1.

Table 2.1

Specifications of Echelle Raman Spectrometer in the 780 nm Region

| | |
|---|---|
| Configuration | Echelle grating with dual prism system for cross dispersion |
| Orders | 34 to 43 |
| Excitation Source | 780 nm diode laser |
| Spectral Range | 9320 to 12620 $cm^{-1}$ |
| Spectral Resolution | ~1-2 $cm^{-1}$ with fiber optic input - no slit |
| Focal Plane | Within 25.0 x 7.0 mm |
| Acceptance NA from fiber optic input | 0.2 |
| Imaging NA | 0.2 |

The spectrum presented in a flat field at the output of the spectrometer is imaged onto a CCD detection system. The CCD imaging system is a thermoelectrically cooled CCD9000L Raman Detection System supplied by Photometrics Ltd., Tucson, Arizona. The spectrum presented by the echelle was imaged onto the EEV P88130 charge coupled device (CCD) detector array (~25 x 7 mm) with a lens set specifically designed and coated for this application. The array has 1152 x 298 pixels. An approximately 300 $cm^{-1}$ spectrum per order is dispersed across the 25 mm detector width, giving rise to a detector limited resolution of 300/1152 = 0.3 $cm^{-1}$. However, the spectrograph entrance optics (i.e., fiber optic) limits the resolution to ~1-2 $cm^{-1}$. Pixels along the height dimension of each order are binned or connected together to yield the total accumulated photon flux. The CCD9000L incorporates a direct AT computer interface for acquiring data. A commercial software package by Photometrics and Galactic Industries was employed for manipulation and storage of spectral information and maintaining a spectral database which can be used with spectral matching algorithms.

### 2.2.2 Fiber Optic Raman Probe Development

We have employed micro-optical components and techniques currently used in medical endoscopy to construct a multifunctional stainless steel Raman probe head 1.25 cm in diameter that perform most of the bulky prefiltering functions found in conventional Raman instruments. The laser light is launched into a first optical fiber which extends to the input of the probe head, which is positioned at the sample. This excitation light will contain unwanted frequencies arising from the laser itself and from Raman scattering generated within the silica fiber. These are removed by passage through a first set of filter micro-optics mounted in the head. The filtered, highly monochromatic light then illuminates the sample through the end of the probe. The collected scattered light is then picked up by a second optical fiber or fiber array and passed through a second micro-optical filter, also contained in the head. This second filter set removes most of the Rayleigh line, sending only the Raman spectrum into a second optical fiber which extends to the input of the spectrograph. The probes can accommodate a variety of end accessories, including filters, permiselective membranes and electrochemical cells for conducting SERS. An illustration of the Raman probe is shown in Figure 2.2.

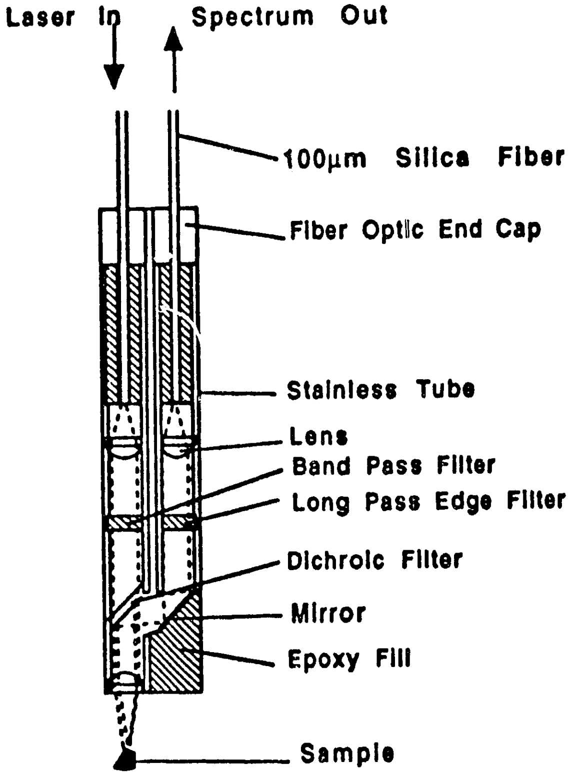


Figure 2.2. Illustration of fiber optic Raman probe.

### 2.2.3 SERS Substrate Development

Surface enhanced Raman spectroscopy (SERS) can be a general technique for environmental analysis. Typically in unenhanced Raman spectroscopy, about $10^{-3}$% of the intensity of visible light impinging on a molecule will be scattered, mostly elastically at the excitation frequency. However, about 1% of the scattered light will be at frequencies corresponding to combinations of the exciting light and the molecular vibrational frequencies (the Raman effect). Spectral resolution of the visible scattered light will yield a "fingerprint" of the molecule consisting of sharp lines which, like the infrared spectrum, give information about the bonding and structure. The main disadvantage of unenhanced Raman spectroscopy is its insensitivity. It becomes experimentally very difficult to measure spectra at concentrations below 0.01% (100 ppm). Thus, it is unlikely that Raman itself could ever approach the detection limits necessary for low level analysis. The application of an enhanced Raman technique such as SERS is practical for low level analysis and has been demonstrated in our laboratory using fiber optics for the detection and analysis of organic constituents in aqueous environments [14-18].

The SERS phenomenon was first reported by Fleischmann and co-workers in 1974 [23], who described a very large enhancement of the Raman signal from pyridine when adsorbed onto an electrochemically roughened Ag surface. Quantitative studies of Raman scattering from molecules adsorbed onto electrochemically roughened substrates of highly reflective metals or in solutions of their metal colloids indicate that the SERS enhancement factor can be as high as $10^7$ compared to the signal of adsorbates on nonactive or smooth surfaces. Although SERS has been observed on many metallic substrates, the most active appear to be Ag, Au, and Cu. Several excellent reviews detailing the theory of SERS have been published recently [24-26].

In many real environmental restoration locations there will be a mixture of pollutants which may adsorb, multiply and/or competitively onto the SERS-active sites. We have shown that the selectivity of the technique for environmental analysis can be augmented by several strategies. For example, the wavelength of excitation or the electrode potential may be used to "highlight" the SERS spectrum of one adsorbate over another, thus allowing a means of discrimination of multiple adsorbates [14,27]. A key factor, however, is the affinity of the metal surface for the adsorbate, given by the free energy of adsorption. This dependance results in a chemical selectivity in the adsorption process that is related to chemical structure [28,29].

Of particular significance to current DOE problems is the development of SERS substrates for small molecule chlorinated hydrocarbons such as $CCl_4$ and TCE. These molecules are difficult to detect with normal SERS techniques, apparently due to a low free energy of adsorption onto most metals. We have previously discovered, however, that a Cu electrode covered with a thin film of electrochemically formed copper oxide (biphase SERS substrate) gives a SERS signal for a variety of these chlorinated solvents in water, and that the adsorption process is activated by the light used for Raman excitation [13,18,30,31].

The laboratory SERS cell was fabricated from a 3 x 6 x 3 cm quartz cuvette with O-ring joints fused into three sides and the top. Electrodes were fed into the cell through O-ring joints and consisted of Pt counter, Ag/AgCl reference, and copper working electrodes. The working electrode was placed about 2 mm from the (large) face of the cell between the two electrodes. This orientation minimized the path length of incident and scattered light through the sample solution and simplified alignment of the electrode in the optical system. For transport/concentration studies, a membrane could be sandwiched between the spectroelectrochemical cell and a second cuvette with matching O-ring joint fused into the bottom.

The electrochemical procedures were previously developed at EIC [13,30]. Electrochemical roughening of polished copper electrodes, consisting of high purity 1.0 mm copper wire, was achieved with an oxidation/reduction cycle (ORC) from -0.6 to +0.2V in a 0.1M KCl electrolyte at 25 mV/sec using a Pine Instruments potentiostat. Actual environmental samples or laboratory solutions of the chlorinated hydrocarbon (carbon tetrachloride, 1,2-dichloroethane (DCE), chloroform and trichloroethylene (TCE), perchloroethylene (PCE)) and nonchlorinated hydrocarbon solvents in distilled water or 100 µg/ml solutions of 0.1M KCl were cycled several times under -1.0 to +0.3 V. The 0.3 V produces the photoactive copper oxide coating. Optimum SERS spectra were acquired at -0.2V on the cathodic sweep. All cycling occurred under laser illumination of 647 nm or 676 nm Krypton illumination. The use of the slightly different wavelengths for illumination and Raman spectroscopy did not produce significantly different results.

## 2.3 Data Reduction and Interpretation

EIC utilized a commercial spectroscopic software package for data analysis. The software package was Spectra-Calc/Lab Calc from Galactic Industries. This software is used to convert information from the CCD detection system to plots and graphs of the Raman spectra.

## 2.4 Quality Assurance

EIC Laboratories, Inc. carries out numerous research and development contracts for government and commercial clients in applied chemistry and materials science. Quality is maintained through a variety of internal procedures outlined below.

1. All members of the scientific staff have a scientist supervisor with whom they meet to evaluate the general quality of their work and to provide guidance. Supervisory roles within the company expand with experience and performance.

2. All members of the scientific staff maintain a scientific notebook on each contract to which they are assigned. Notebooks are generally kept according to procedures detailed in Writing the Laboratory Notebook by H.M Kanare (American Chemical Society, 1985).

3. Programs with a multiplicity of parallel tasks and detailed reporting requirements will typically include a Program Manager. The Program Manager is typically a company officer with a scientific background in the specific project area. Time is included in the contract for a weekly meeting with the Program Manager, Principal Investigator, and other members of the program team. The purpose of these meetings is to evaluate data, notebook entries, patentability, budget expenditures and reporting schedules.

4. The Principal Investigator on each program witnesses all notebook entries of others contributing to that program. The Principal Investigator's notebook is witnessed and reviewed by the Program Manager.

5. All reports are organized by the Principal Investigator and reviewed by the Program Manager, if one is designated, or by a company officer, before submission.

During this program, contributions of a Program Manager (Director of Research), a Principal Investigator (Group Leader, Ph.D. level), a Senior Scientist (Ph.D. level) and a Staff Scientist (Bachelor's level), followed the procedures outlined above. In addition, there were several consultants on the project involved in the design of specialized optical components. The Program Manager and Principal Investigator established and evaluated their work and compensation in accordance to EIC quality control procedures.

## 3.0 RESULTS AND DISCUSSIONS

### 3.1 Small Spectrograph Development

The optics of our echelle Raman spectrometer were planned so that the resolution is dependent only on input slit size (negligible blur). We developed the system so that it would require no slit with a fiber optic coupled (NA = 0.2) directly to the input with a diameter meeting the proper f/# (f/# = 2) match of the echelle spectrograph. Testing and characterization of the breadboard has indicated that the spectrograph has a resolution of ~1-2 wavenumbers. This resolution was obtained with a 100 $\mu$m diameter fiber optic as the entrance slit. In addition, the spectrograph has a range of almost 3700 $cm^{-1}$. To obtain this resolution with a conventional triple spectrograph system would require slits of 25 $\mu$m and movement of the grating 5 times to obtain the range. A comparison of the EIC echelle Raman spectrograph and a conventional system is shown in Figure 3.1.

The range of the echelle permits the instantaneous collection of Raman spectra without moving parts. In addition, the fiber optic probes allow for easy sampling capabilities. Figures 3.2 shows representative spectra from the system. The result from the diode laser system required a longer integration time to acquire the data. This is due to three factors. The first is the standard $1/\lambda^4$ dependence of the Raman signal. The second is the response curve of the CCD detector is decreasing toward the end of the Raman region with 784 nm excitation. The third and most significant is the optics used in the imaging components, and prisms need to have specialized coatings in the NIR to increase the throughput.

The resolution of the system allows for complex mixtures to be analyzed. An example of the resolution of an eight (8) component mixture of chlorinated hydrocarbons (TCE, DCE, PEC etc.) and a four component mixture of gasoline type components (hexane, pentane, etc.) are shown in Figure 3.3. The ability to observe and resolve the chlorinated and light hydrocarbon type compounds is important since these compounds cannot be observed with other standard spectroscopic techniques (fluorescence, adsorption, IR) via fiber optics.

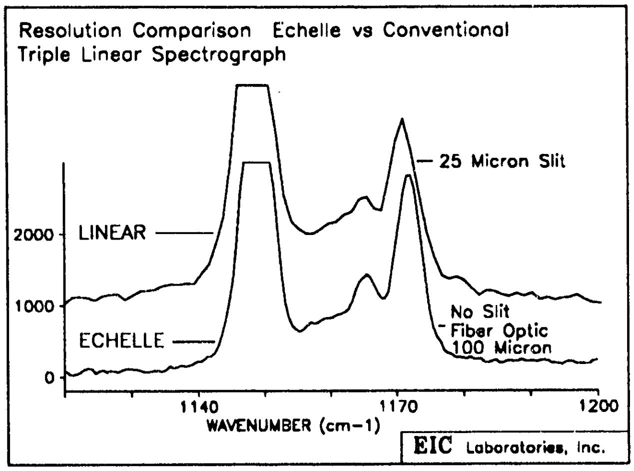


Figure 3.1. Comparison of the EIC compact fiber optic Raman echelle spectrograph for *in situ* monitoring and a conventional Spex's triplemate. The Raman sample is naphthalene and the laser power was 100 mW.

The results from the fiber optic Raman echelle spectrograph have indicated that the system has a significant improvement over conventional Raman systems in throughput, acquisition time, resolution and range. The results also indicate that a lens set specific to NIR/diode laser excitation will be required for future instruments.

## 3.2 Fiber Optic Raman Probe Development

In environmental site characterization, the ability to probe samples remotely from the instrument is very important. For example, spectroscopic probes deployed through cone penetrometers can be used to map chemical concentrations as a function of depth and to identify pockets of high pollutant concentration (e.g., dense nonaqueous phase liquids). During this program, EIC has also made several breakthroughs in the area of Raman sampling which enable remote sampling with fiber optics over long distances while having the additional benefit of eliminating much of the prefiltering and sampling optics found in conventional instruments. It has been recognized for some time that silica optical fibers can be used to deliver the excitation light to the sample and return the scattered Raman spectrum from the sample to the spectrograph. However, although Raman spectra of strong Raman scatterers may be easily obtained over short fiber lengths (<2 meters), long fiber paths or long detector integration times will always result in the spectrum being "swamped out". For environmental analysis, capabilities of remote sampling over substantial distances and of long integration times for detection of dilute or weakly scattering pollutants is absolutely essential. We have employed micro-optical components and techniques to construct a multifunctional stainless steel probe head 1-2 cm in diameter that perform most of the bulky prefiltering functions found in conventional Raman instruments.

Prototype Raman probes have been developed at several important Raman wavelengths during this program. The main focus was a probe at 514.5 nm which was fabricated for testing by LLNL at the Los Alamos mock-up waste storage tank. This prototype probe was fabricated and tested at EIC for the design and performance capabilities prior to delivery to LLNL. Figure 3.4 compares a 5 meter in-house probe and the 30 meter probe which was delivered to LLNL. A Raman spectrum of TCE obtained from these probes were obtained in only 10 seconds with a laser power of 50 mW. The signal to noise ration indicates the rapid collection capabilities of the probe.

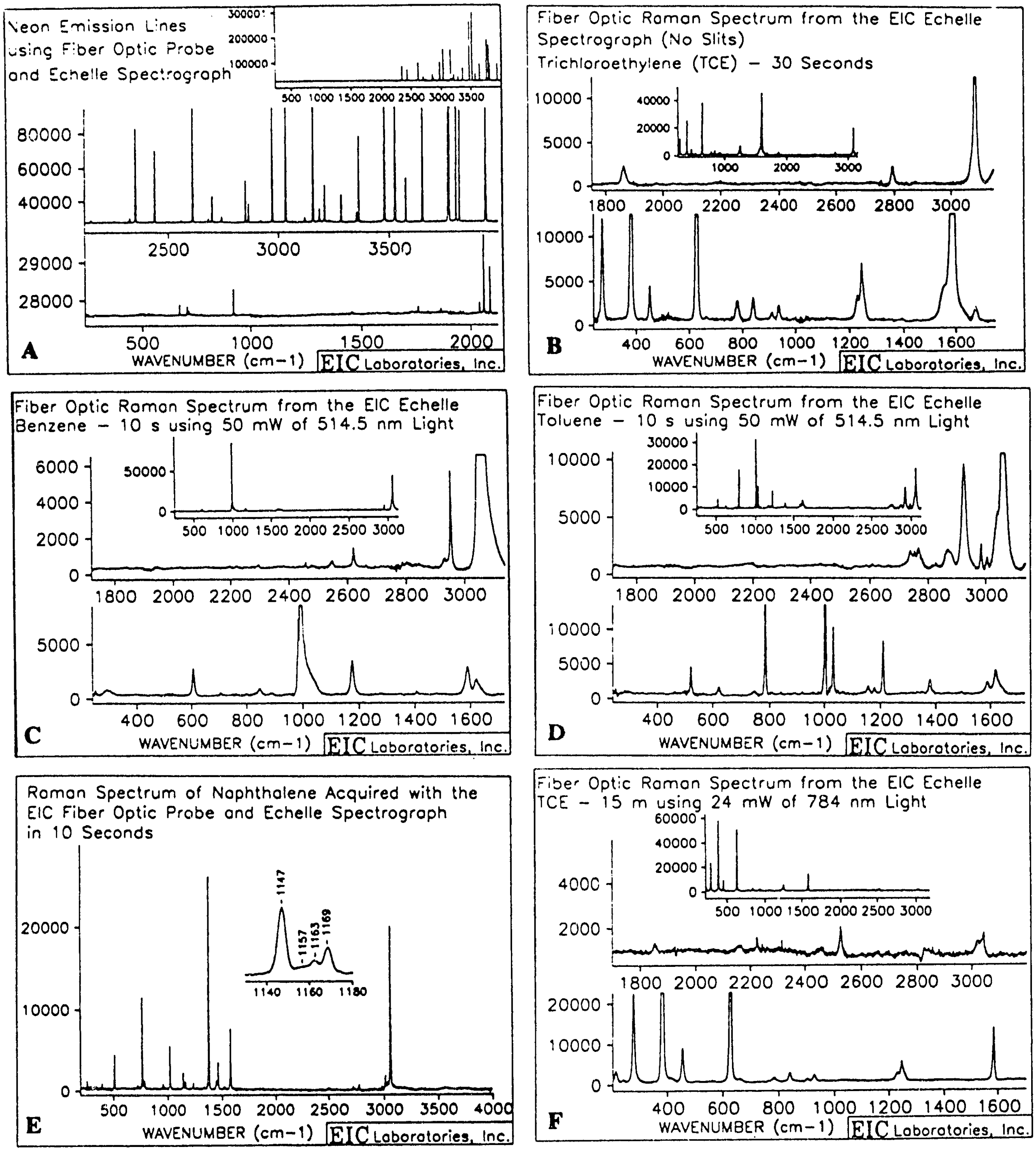
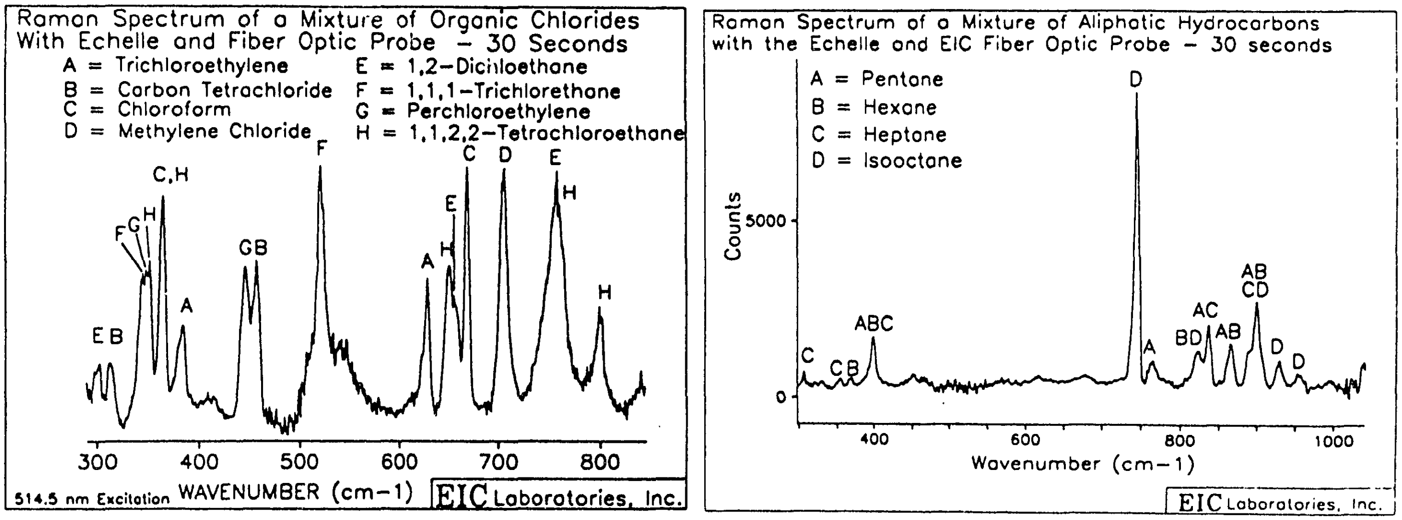
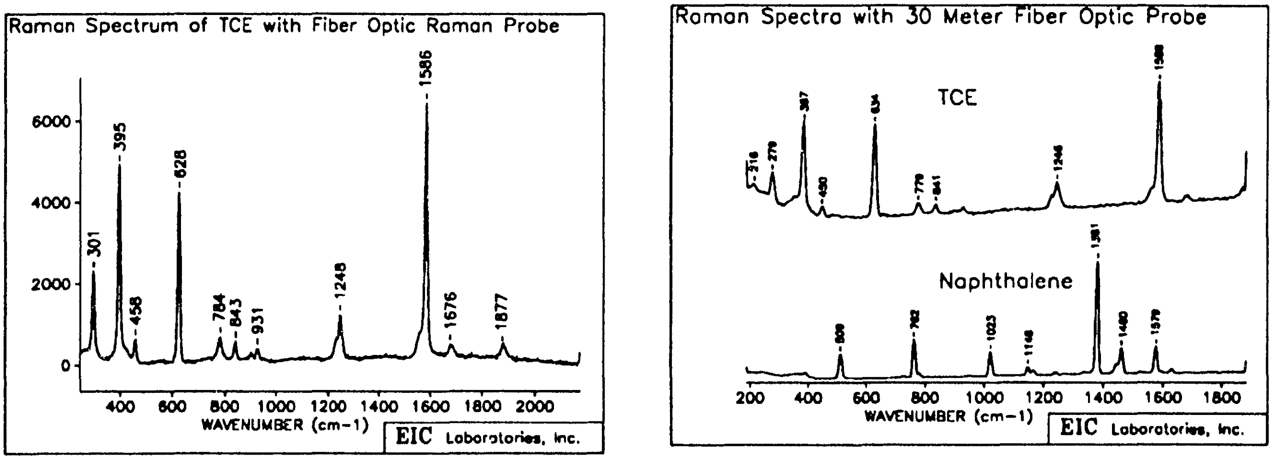


Figure 3.2. Fiber optic (5 meter) Raman spectra from the echelle spectrograph. The entrance aperture was a 100 μm fiber optic with no slit. A - Neon Calibration; B - TCE; C - Benzene, D - Toluene, and E - Naphthalene. A through E laser power and wavelength were 50 mW and 514.5 nm, respectively. F - TCE with Diode Laser at 784 nm with 24 mW of power.



**A** **B**

Figure 3.3 Fiber optic Raman spectra from the echelle spectrograph. (A) - An eight component mixture of chlorinated hydrocarbons; (B) - A four component mixture of hexane, heptane, pentane and isooctane. The entrance aperture was a 100 μm fiber optic with no slit. Laser power and wavelength were 50 mW and 514.5 nm, respectively.



**A** **B**

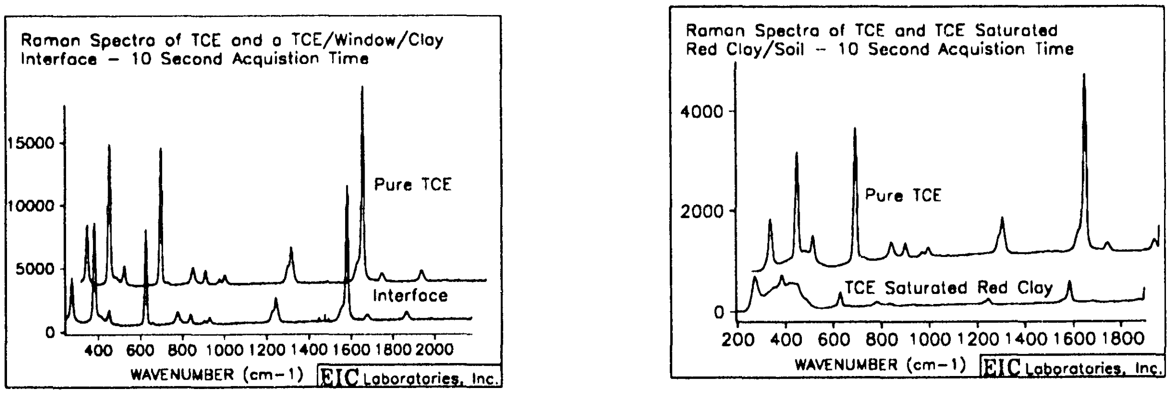
Figure 3.4. Raman spectra of TCE obtained in 10 seconds with the fiber optic Raman probe. A - 5 meter probe; B - 30 meter probe delivered to LLNL for testing at the Los Alamos mock-up waste storage tank compared to naphthalene.

A prototype Raman probe has been delivered to LLNL for testing at the mock-up waste storage tank at Los Alamos National Laboratory. The outcome of the Los Alamos testing will be used to further refine the probe design for a joint EIC/LLNL fiber optic Raman demonstration at the Hanford site. Field results from the Los Alamos testing were not available for this report.

Raman-Cone Penetrometer Probes - The 5 meter probe was also used to test the concept of using a Raman and Cone Penetrometer (CPT) system for environmental monitoring/field screening of concentrated waste plumes from dense nonaqueous phase liquids (DNAPLs) such as trichloroethylene (TCE) and tetrachloroethylene (PEC). Since tetrachloroethylene and trichloroethylene both have very low solubilities in water (200 parts per million and 1100 parts per million, respectively), and are denser than water, these two compounds are generally present as a separate liquid phase. For this reason, these compounds are referred to as dense nonaqueous phase liquids (DNAPLs). As DNAPLs are denser than water and air, they tend to migrate downward through the subsurface until they reach an impermeable layer. Then they will migrate laterally, following the structure of the impermeable layer.

The DNAPLs at DOE sites have proved difficult to locate and characterize due to the nature in which they migrate. For this reason it is highly desirable that a tool be developed which would characterize the DNAPLs in both a continuous (versus the current discrete sampling methods) and a minimally invasive manner.

With the 5 meter fiber optic probe developed in this program, a series of laboratory Raman experiments were conducted with soils typical of the DOE site. The soil was saturated with TCE or perchloroethylene. These experiments were conducted to determine the depth of focus of the Raman probe at the clay/DNAPL interface. The results are shown in Figure 3.5. The results indicate that the Raman spectra of the TCE can be obtained at all of the possible interfaces encountered with a CPT including TCE in the clay. The physical design of the current EIC probe will need to be modified for future side view CPT applications. An illustration of a possible Raman-CPT probe is shown in Figure 3.6.



A

B

Figure 3.5. Fiber optic Raman spectra through a window of (A) a clay/DNAPL interface and (B) in DNAPL saturated clay/soil. Spectra were collected with 50 mW @ 514.5 nm in 10 seconds.

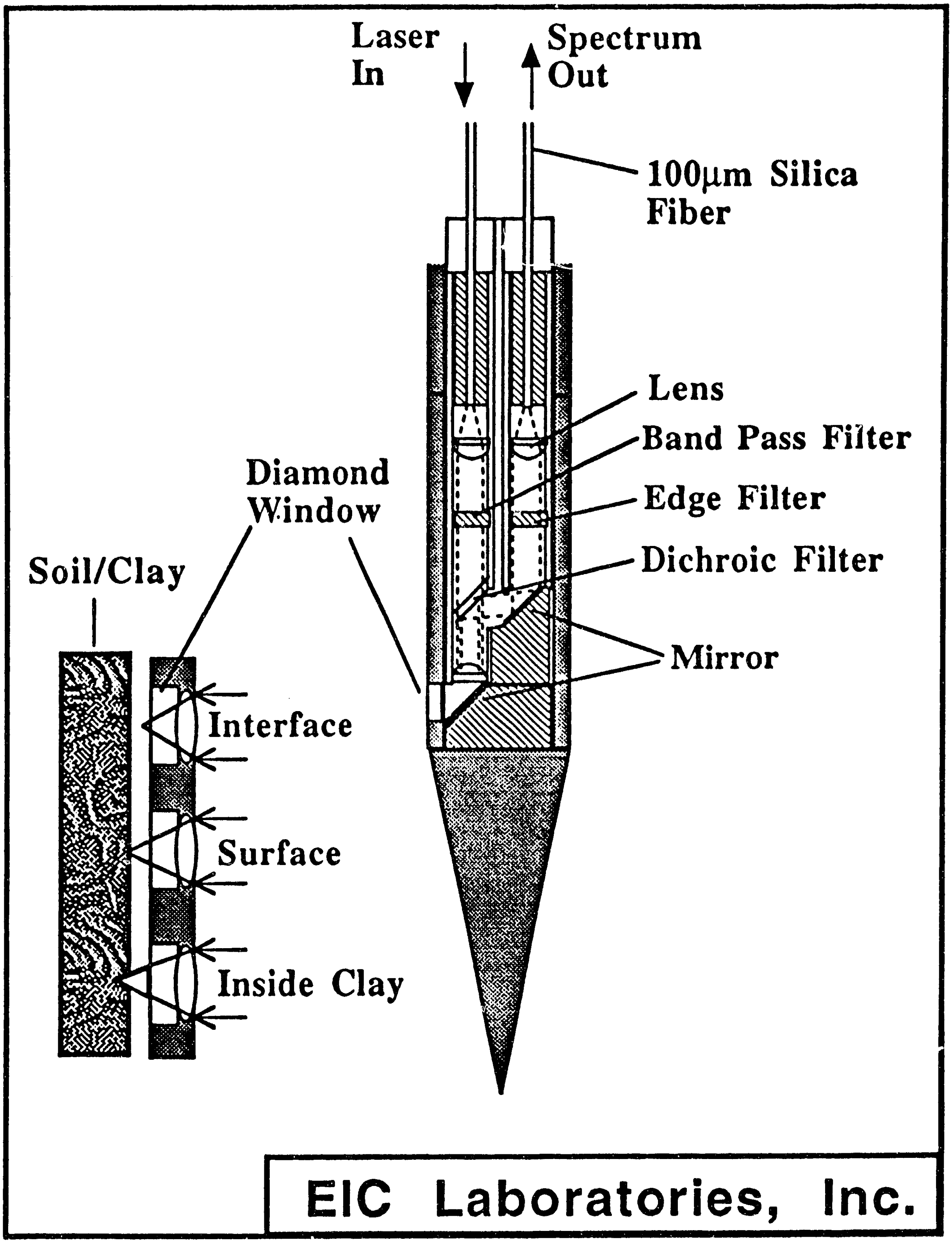


Figure 3.6. Illustration of a Fiber Optic Raman-Cone Penetrometer Probe and possible interface scenarios.

Fiber Optic SERS Probes - The fiber optic SERS probe is illustrated in Figure 3.7. The first SERS probe had the housing made of Teflon. This material was chosen based on previous probes for aromatic type compounds such as benzene and pyridine. Initial testing with the Teflon probe for the examination of chlorinated hydrocarbons indicated that material is unacceptable. The Teflon was adsorbing the small chlorinated compounds. This probe was refabricated with a stainless steel housing. The mechanical drawing and a photograph of the SS-SERS probe are shown in Figure 3.8. The probe is currently under continued testing and evaluation. After laboratory testing, the SERS probe will be field tested at the Oak Ridge Reservation under our existing collaborative research agreement (CRA-03-90) with ORNL.

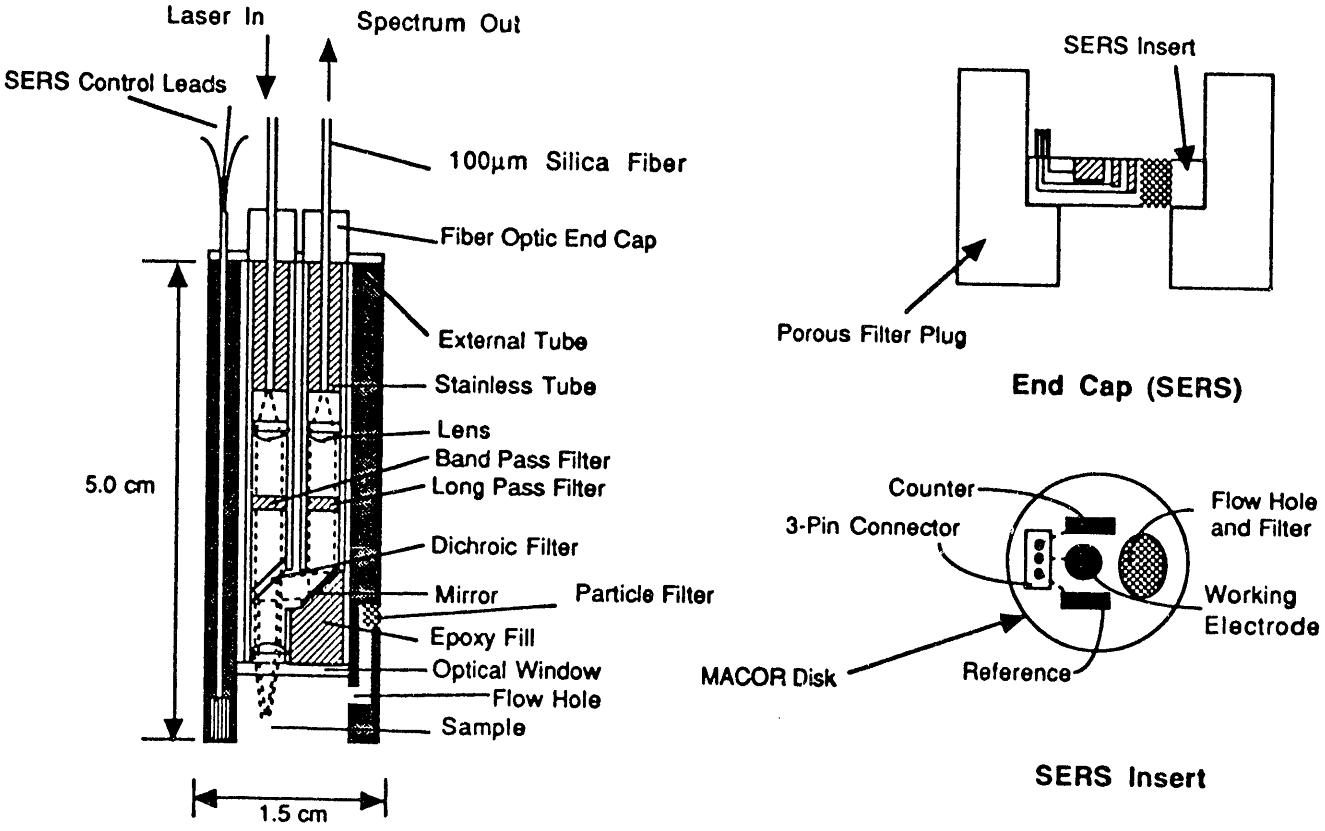
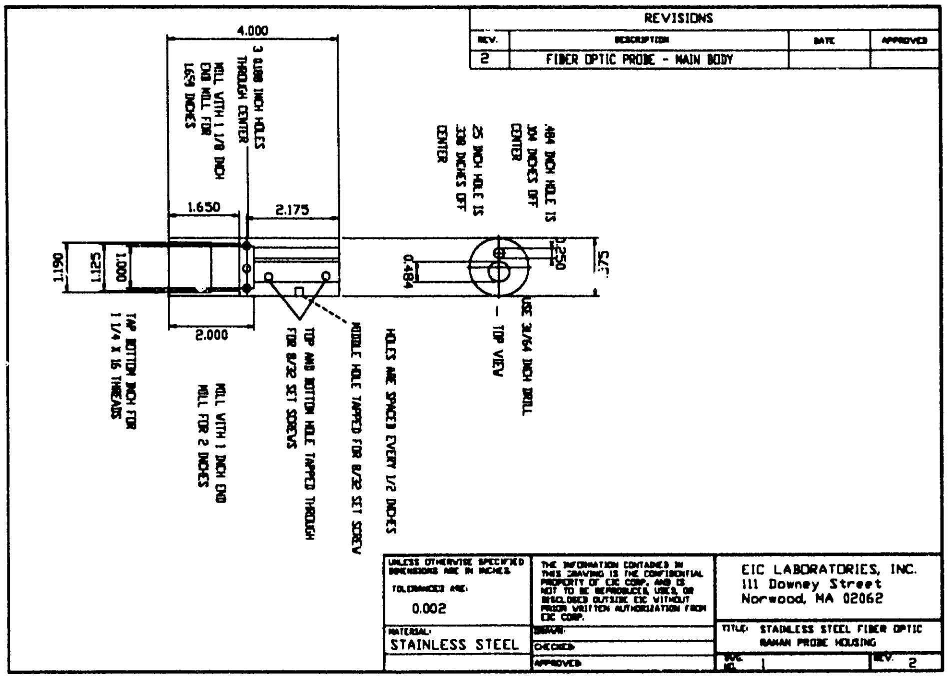


Figure 3.7. Illustration of the Fiber Optic SERS probe.



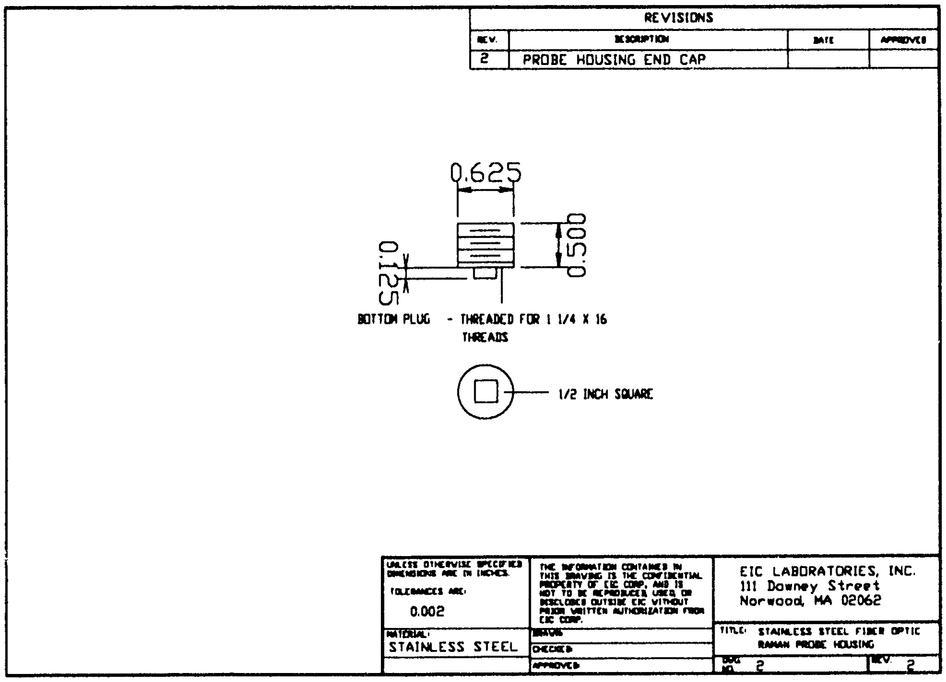


Figure 3.8a. Mechanical drawings of the fiber optic stainless steel SERS probe.

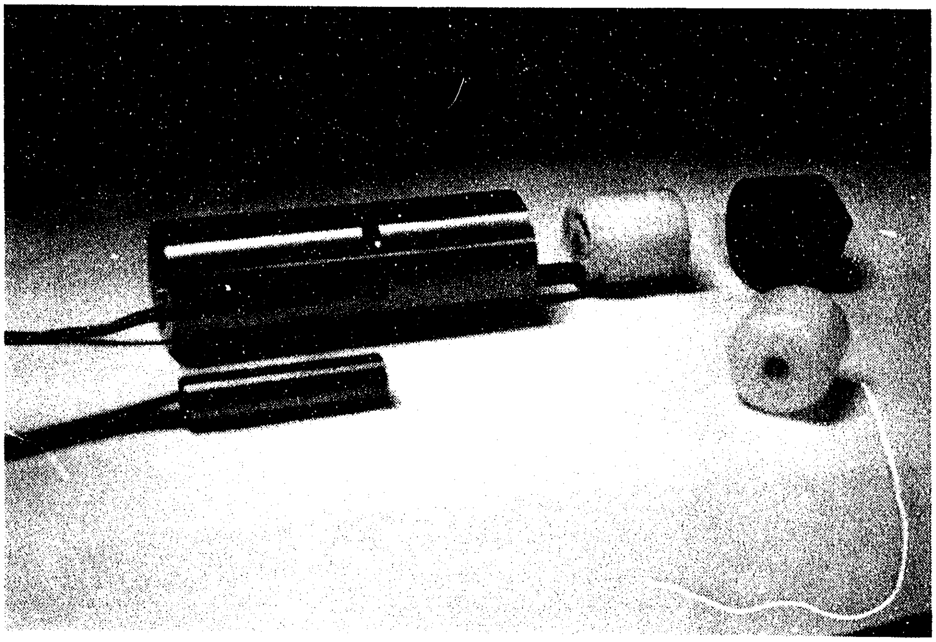


Figure 3.8b. Photograph of the prototype SS SERS probe.

## 3.3 SERS Substrate Development

Raman spectroscopy is a relatively insensitive analytical method unless it is "enhanced" in some way. It becomes experimentally very difficult to measure spectra at concentrations below ~10 ppm. This sensitivity is sufficient for many types of pollutant and waste characterization. The application of an enhanced Raman technique such as surface enhanced Raman spectroscopy (SERS) is practical for low level analysis and has been demonstrated in our laboratory using fiber optics for the detection and analysis of organic constituents in aqueous environments at the parts per billion level.

<u>Silver Based SERS Substrates</u> - SERS substrates for the detection of aromatic hydrocarbons, such as benzene, have been tested with diode laser excitation. The results shown in Figure 3.9 indicate only 4 mW of 670 nm light is necessary to detect a 400 ppm solution of benzene. A major series of experiments were conducted to determine the reproducibility of fabrication and the renewability of the electrochemical SERS substrates. Four hundred (400) separate SERS spectra of benzene in the ppm range were obtained with 10 different Ag SERS electrodes. Figure 3.10 shows an example from one Ag SERS substrate. The results indicate that a particular SERS substrate can be renewed without a significant loss of sensitivity (~5% reproducibility). This result is very important since it indicates the SERS probe can be continuously renewed *in situ*. However, the result between the different electrodes indicate that there is a variability of approximately 10 to 20%. This can easily be circumvented by calibrating each SERS substrate prior to use with a known standard.

SERS substrates for the detection of inorganic ions, such as nitrate, have been tested. Figure 3.11 shows an example from one Ag SERS substrate at ~10 ppm. The result is significant since the action level for nitrate is 45 ppm.

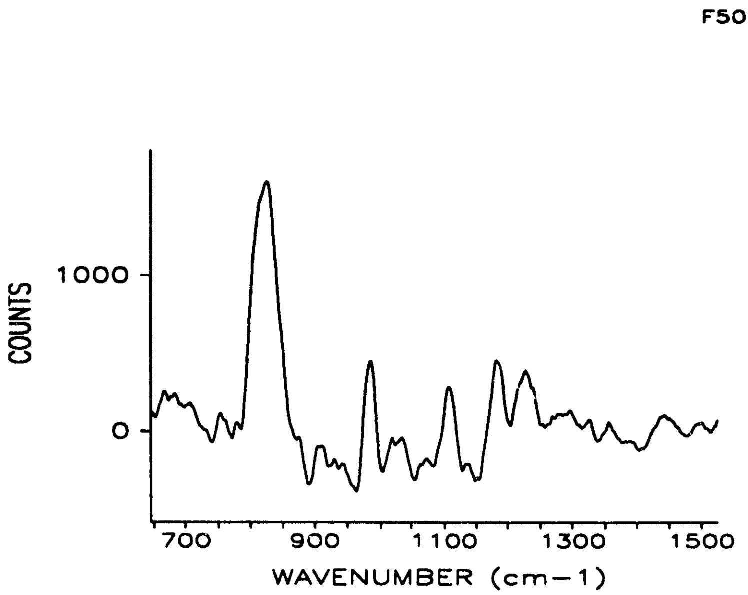


Figure 3.9. SERS spectrum of 400 ppm benzene on a Ag electrode. Laser power was 4 mW at 670 nm.

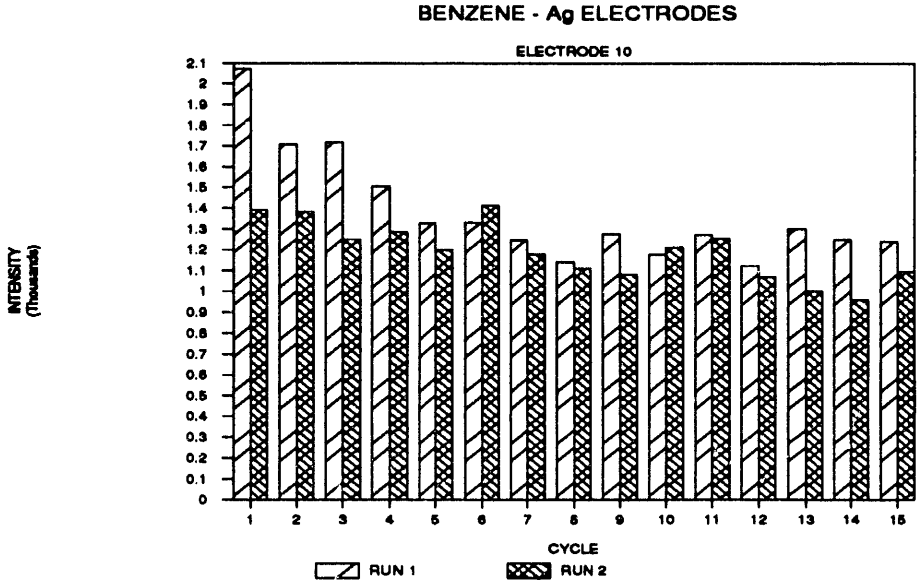


Figure 3.10. Intensity of the 986 $cm^{-1}$ SERS band of benzene on a Ag electrode as function of electrochemical cycles. Run 1 is a virgin electrode. Run 2 is the same electrode polished then roughened again by an oxidation/reduction cycle (ORC).

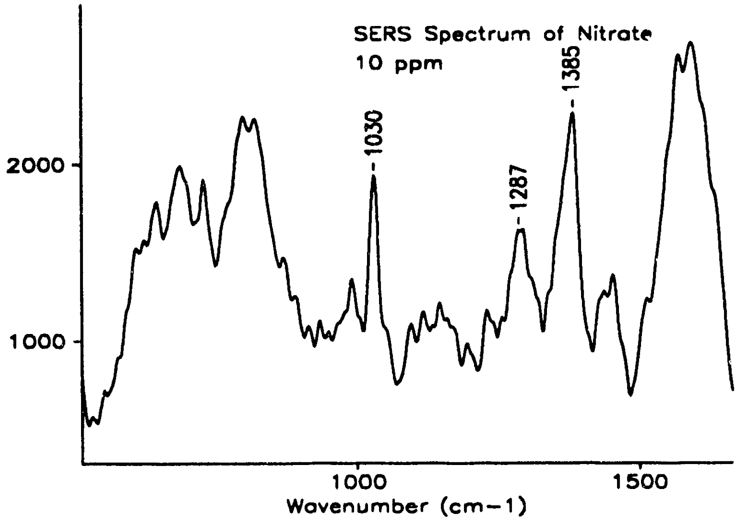


Figure 3.11. SERS spectrum of 10 ppm nitrate on a Ag electrode.

SERS-based chemical sensing probes developed on this program incorporate a substrate with a general affinity for the class of molecules to be sensed [18]. As an example, copper oxide-based Raman substrates have been developed for sensing and identification of dilute chlorinated hydrocarbons in water, while roughened silver substrates show affinity for aromatic and aliphatic hydrocarbons such as benzene and methyl ethyl ketone which are ubiquitous groundwater pollutants. The highly structured Raman spectra can then be used for speciation.

Photo-SERS of Chlorinated Hydrocarbons - As part of this program we broadened our investigation of oxidized copper substrates for detecting chlorinated hydrocarbons. Our previous results have shown that spectra of aliphatic chlorinated hydrocarbons and/or their reaction products are obtained when the Cu substrate is subjected to an oxidation/reduction cycle (ORC) under illumination. Since the chlorinated hydrocarbons are all electrochemically reducible in aqueous electrolytes, it was possible that we were observing a photoinduced electron transfer from a Cu oxide species to an adsorbed chlorinated hydrocarbon, resulting in reaction products formed adjacent to highly dispersed SERS-active Cu. There was also some visual evidence for polymeric products on the Cu electrodes when the reaction was carried out in saturated aqueous solutions of TCE. As described in previous reports [13,18], there are marked differences between the SERS spectra and the normal Raman spectra of the neat chlorinated hydrocarbons. Thus, it is likely that we observed the spectra of these polymeric products which, of course, can also be used to uniquely identify the parent compound.

Experiments to optimize the detection of chlorinated hydrocarbons using "photo-SERS" indicated that the best SERS spectra for TCE (Figure 3.12) were obtained when the ORC cycle was stopped during the reduction step at the potential of zero charge for Cu (-0.2V) [32]. The observation of the SERS spectra was also highly dependent on illumination during the cycling. Previous work by Thierry and Leygraf [33] has indicated the importance of illumination during the electrochemical roughening of Cu electrodes to produce Raman active sites.

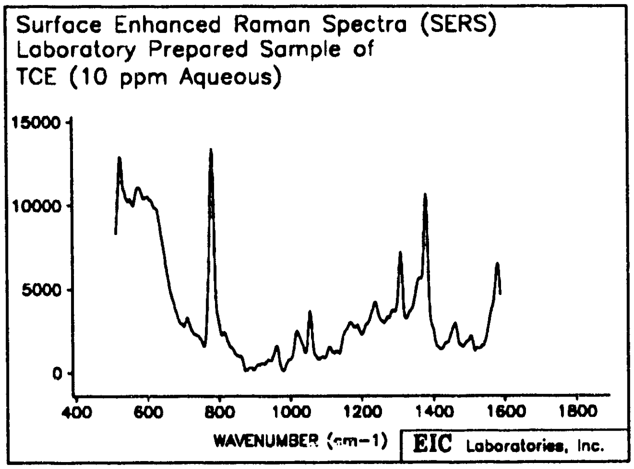


Figure 3.12. SERS spectrum on biphase Cu electrode of a laboratory prepared TCE aqueous (10 ppm) sample.

The vibrational features in Figure 3.12 indicate that a reaction is occurring on the electrode surface (see Appendix for vibrational assignments for carbon tetrachloride, 1,2-dichloroethane (DCE), chloroform and trichloroethylene (TCE)). From the results, it appears that ring formation is occurring due to an electrochemical and/or photochemical process. However, in our experiments no SERS spectra of the chlorinated hydrocarbons were observed unless the electrode was illuminated during the reduction step and thus a strictly electrochemical reaction can be ruled out.

This "photo" induced result indicates the possibility of a photoelectrochemical process. Copper oxides are known to be p-type semiconductors which eject electrons under illumination (Equation 1) [34]. The band gaps for the two possible copper oxides are 2.0-2.6 eV (620-477 nm) for $Cu_2O$ and 1.7 eV (730 nm) for CuO. These electrons can then electrochemically reduce the chlorinated hydrocarbon solvents.

$$Cu_2O + \lambda \rightarrow Cu_2O(h^+,e^-) \tag{3.1}$$

This electrochemical reduction is similar to a reaction scheme for the electrochemical reduction of chloroform which has been determined by Fritz and Kornrumpf [34] to be :

$$CHCl_3 + 2e^- \rightarrow CHCl_2^- + Cl^- \tag{3.2}$$

$$CHCl_2^- + CHCl_3 \rightarrow CH_2Cl_2 + CCl_3^- \tag{3.3}$$

$$CCl_3^- \rightarrow :CCl_2 + Cl^- \tag{3.4}$$

The formation of the dichlorocarbene during the electrochemical reduction process would tend to form a ring type structure [34]. This ring type structure is indicated in our SERS spectra with the strong band at 1380 $cm^{-1}$.

The quantitative results have indicated that the chlorinated hydrocarbon such as TCE on the biphase are detectable down to ~100 ppb with a relatively short integration time of 60 seconds. Longer integration time plus some of the recent advancements in CCD technology should allow the detection in the 1 to 10 ppb range.

Experiments were conducted on chlorobenzene to determine if "chloro" type aromatic hydrocarbons are observable on our biphase SERS substrate for chlorinated hydrocarbons. Chlorobenzene is also believed to be present at numerous DOE sites. Figure 3.13 shows the SERS spectra on a biphase Cu electrode from the sample acquired in 30 seconds. The results indicate that the chlorinated aromatic compound react similarly to the TCE type compounds. However, unlike the small chlorinated hydrocarbons, the chlorobenzene did have a potential dependent spectra. The signal to noise ratio indicates that detection in the mid-ppb range should be possible.

The results with chlorobenzene suggest that the biphase substrates should detect a wide variety of chlorinated compounds. Note, benzene did not tend to react on the biphase substrates but other small aliphatic hydrocarbons such as methyl ethyl ketone and acetone, which are ubiquitous groundwater pollutants, were observable.

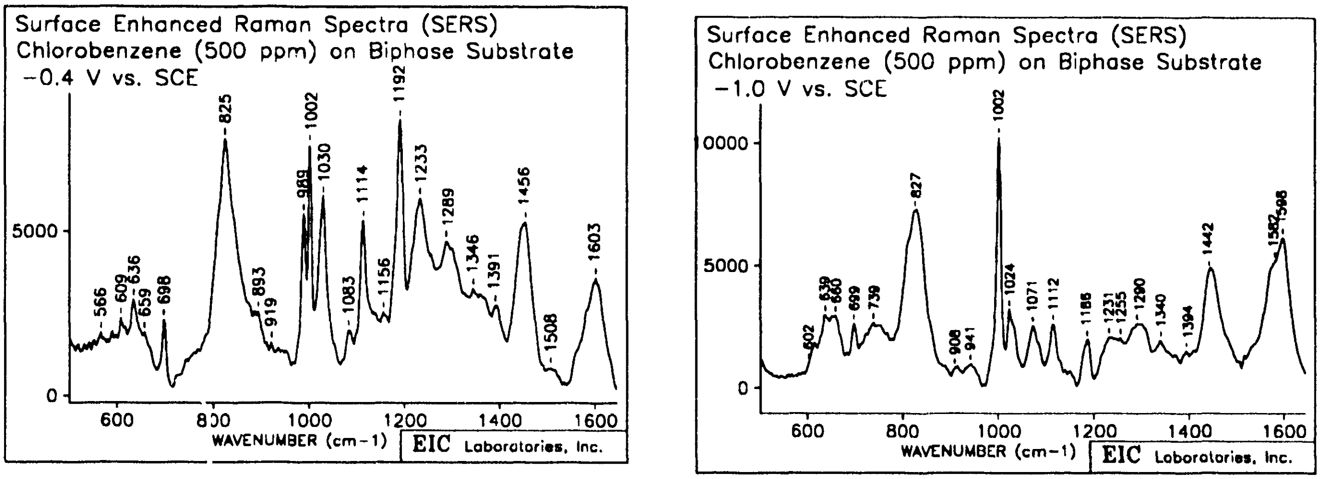


Figure 3.13. SERS spectra on biphase Cu electrode of chlorobenzene at two electrode potentials.

Concentration Cells - Several approaches were examined to enhance preconcentration of nonpolar species at the roughened SERS electrode surface, in order to extend the minimum detection limits. In one such approach, a microporous Teflon membrane was used which would preferentially pass nonpolar compounds such as chloroform to a nonaqueous electrolyte which contains the SERS electrode. In principle, the system will act as an accumulator for membrane permeable materials, which should result in a great increase in sensitivity. Probes of this design would be useful as monitors either directly in the groundwater or for volatile vapors in the headspace.

Experiments to optimize the detection of chlorinated hydrocarbons using concentration cells have indicated that the nonaqueous electrolytes interfere with the signal from the compounds of interest. The successful experiments in the detection with our biphase SERS substrates have deemphasized the need for this system, and the experiments with real environmental samples with the biphase SERS substrates were accentuated.

## 3.4 Analysis of Mixtures and Real Environmental Samples

Under our current Collaborative Research Agreement (CRA-03) with Oak Ridge National Laboratory we obtained in a groundwater sample from the Oak Ridge Reservation (ORR) Bear Creek Burial Grounds. Samples from wells GW-8, GW-12, GW-14, GW-15, and GW-46 were investigated. The majority of our work focused on the GW-15 sample since we had the largest quantity of this particular sample. The groundwater samples were stored in a refrigerated environment prior to the experiments. Previous testing at ORNL has indicated that the sample contained chlorinated hydrocarbons, aromatic hydrocarbons and aliphatic hydrocarbons. The actual samples were a murky brown solution that contained particulates.

The results of our analyses are very encouraging. Figure 3.14 shows the SERS spectrum on Ag electrode and normal Raman spectrum from the groundwater sample acquired in 60 seconds with no sample preparation. The solution was simply introduced into the SERS cell. The vibrational bands in the SERS spectrum seem to correspond to benzene or ketones. The position of the bands are slightly shifted from our laboratory experiments. This is probably due to the synergistic effects induced by the presence of chlorinated hydrocarbons.

We also examined the groundwater solution with our biphase copper based SERS substrate. Figure 3.15 shows the SERS spectrum on a biphase Cu electrode from the sample acquired in 1 second with no sample preparation. The solution was simply introduced into the SERS cell. When compared to a laboratory prepared sample of TCE (Figure 3.12), the peak positions and relative intensities are identical. **This result is the first positive identification of chlorinated hydrocarbons in a groundwater sample by a SERS/Raman based technique.**

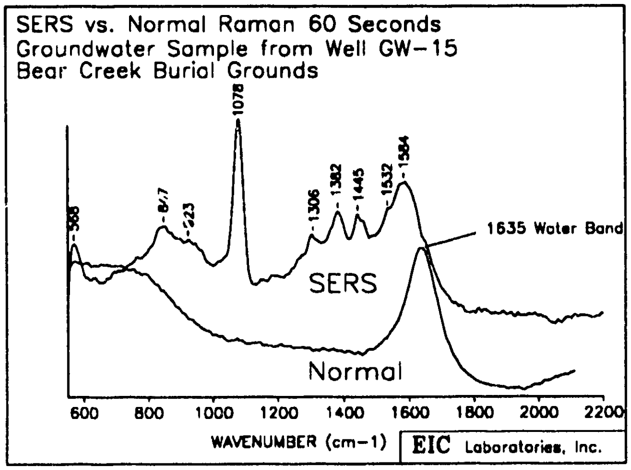


Figure 3.14. Normal Raman (Bottom) and SERS on Ag electrode (Top) of groundwater sample from the Bear Creek Burial Grounds at ORNL. Note the sample required no preparation before the analysis.

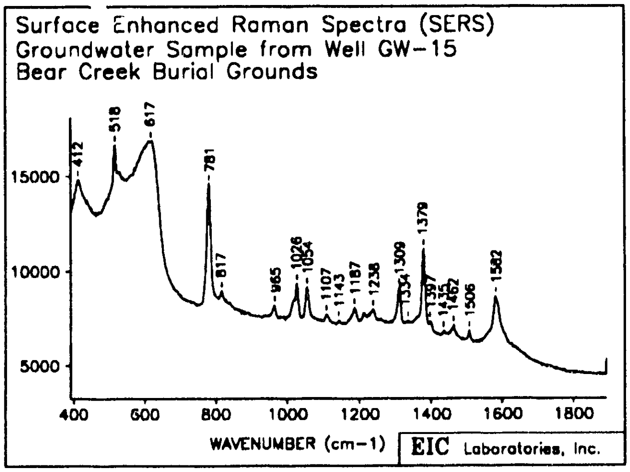


Figure 3.15. SERS spectrum on biphase Cu electrode of groundwater sample from the Bear Creek Burial Grounds at ORNL. Note the sample required no preparation before the analysis.

The results on the Ag substrate indicated that unidentified vibrational bands in the SERS spectrum may correspond to acetone or methylethylketone (MEK). Experiments were conducted to confirm this possibility on the biphase SERS substrates. Laboratory solutions of 0.05M acetone and 0.05M MEK were prepared. All data was acquired using 676 nm incident radiation at 100 mW. Spectra for these two solutions are shown in Figure 3.16. Similarities are apparent between the two spectra, although neither exhibits the 1070 $cm^{-1}$ band present in the Bear Creek Sample GW-15.

Bear Creek samples were reexamined at 676 nm laser radiation to determine any incident wavelength specificity on Ag for the chlorinated hydrocarbons. The band at 1070 $cm^{-1}$ was still present at a potential of -1.0 volts. At -0.2 volts, other weak bands appeared characteristic of chlorinated hydrocarbons. These spectra are presented in Figure 3.17. In this case, the biphase substrates were not employed. A comparison (Figure 3.18) between the spectra of the Bear Creek Burial Grounds sample and the MEK sample at -0.2 volts on the same type of substrate revealed that MEK is a constituent of the Bear Creek sample. It is believed that the presence of the 1070 $cm^{-1}$ band is due to a synergism between the chlorinated solvent and the ketone type solvents. Experiments to date have not confirmed or denied this hypothesis.

Spectra of ketones and of mixed chlorinated hydrocarbons, including trichloroethylene, have been obtained using actual environmental groundwater samples from the Bear Creek Burial Grounds at ORNL. The substrate will be incorporated into the fiber optically coupled probe head, enabling *in situ* analysis of groundwater via small diameter (<5 cm) drilled wells or cone penetrometers. Testing of the SERS probe with the biphase substrates will be conducted in conjunction with ORNL at the Oak Ridge Reservation under our existing collaborative research agreement (CRA-03-90) with ORNL.

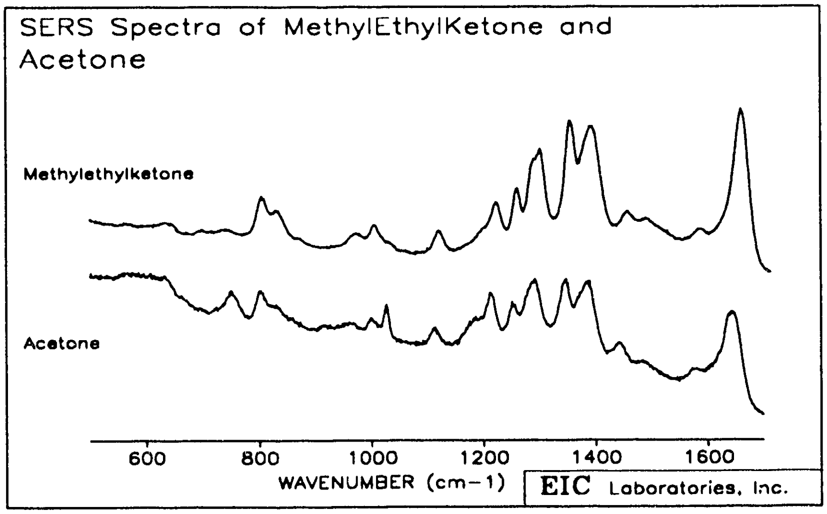


Figure 3.16. SERS spectra of 0.05M acetone and 0.05M MEK. Spectra were acquired in 10 seconds at 100 mW of 676 nm laser radiation. Copper SERS substrates were employed at -0.8 volts for acetone and -1.0 volts for MEK.

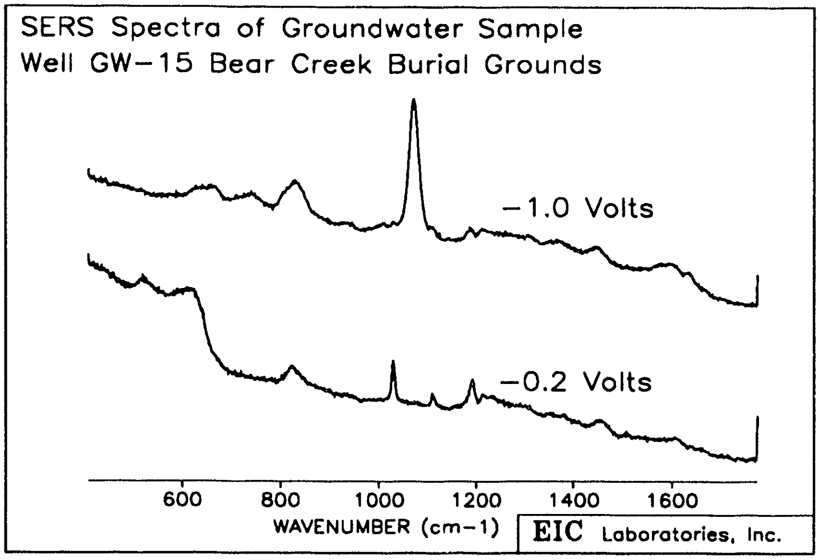


Figure 3.17. SERS spectra on Ag of Bear Creek Burial Grounds, Well GW-15. Laser excitation was 676 nm at 100 mW.

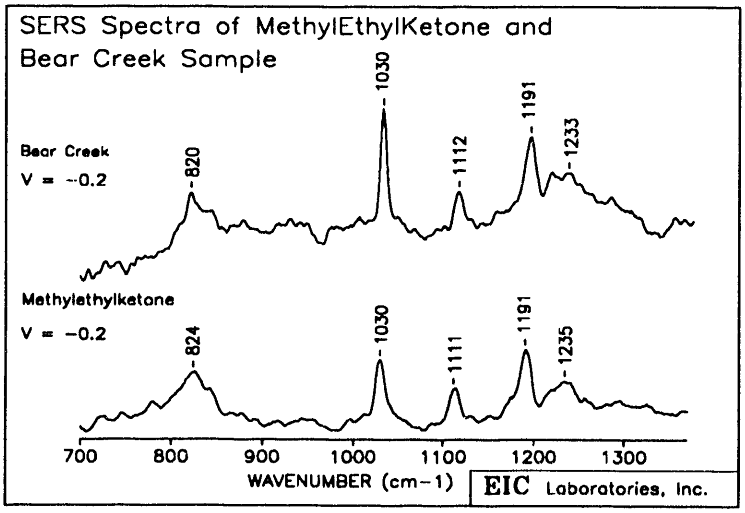


Figure 3.18. SERS spectra of 0.05M MEK and Bear Creek Burial Grounds, Well GW-15. Laser excitation was 676 nm at 100 mW.

# 4.0 TECHNOLOGY STATUS

## 4.1 Technology Development Evaluation

New *in situ* screening methods such as fiber optic Raman spectroscopic techniques developed during this program will be essential in reducing the cost of site characterization and remediation. Site characterization for chemical contamination must be accomplished prior to any adequate remediation can begin. The current approach of drilling wells and removing samples for laboratory analysis is costly and many times inefficient. Cost and efficiency factors will eventually limit the extent and frequency of analysis conducted at any site as well as the adequate characterization of hydrologic migration of pollutants in groundwater and soil surrounding leaking containments.

The fiber optic based Raman spectroscopy technologies developed during this program should be a useful general technique and instrument for environmental analysis. Using fiber optic Raman techniques it should be possible to obtain, through *in situ*/field measurements, highly specific chemical characterization and mapping of field sites and waste storage containers. Raman spectroscopy is suitable both for highly concentrated materials and also for sub-ppb detection levels under the appropriate conditions. Since the technique yields a multiline fingerprint of the waste products or polluting species, it can be used not only for sensing and monitoring, but also for identification.

There are numerous types of wastes and pollutants that require characterization at DOE nuclear processing and weapons facilities, but they can generally be grouped as concentrated/contained and as dilute/migrating [2-4]. The concentrated waste sites include underground storage tanks, 55 gallon drums and landfills. Of primary concern are 149 single walled underground storage tanks at the Hanford facility which have the highest potential for leaking hazardous waste into the environment. The concentrated wastes that are found in underground storage tanks tend to be heterogeneous; thus, they cannot be characterized unless multiple samples are taken. An *in situ* Raman technique employing a movable sample probe would be invaluable in this regard. Most of the substances expected to be found in waste storage tanks have characteristic Raman spectra and can be observed by direct fiber optic Raman methods. In addition to characterizing the contents of waste storage tanks, direct fiber optic Raman spectroscopy can also be used to detect corrosion on the interior surface of the tanks which would indicate areas of weakness or leakage.

Concentrated waste plumes also represent a hazard at certain DOE sites. These dense nonaqueous phase liquids (DNAPLs) are agglomerations of water insoluble, high density contaminants (e.g., chlorinated solvents, PCBs, creosote and motor and lubricating oils). As DNAPLs are denser than water and air, they tend to migrate downward through the subsurface until they reach an impermeable layer. Then they will migrate laterally, following the structure of the impermeable layer. The DNAPLs at DOE sites have proved difficult to locate and characterize due to the nature in which they migrate and to the difficulty of using a technique such as fluorescence or UV absorption. For this reason it is highly desirable that a tool be developed which would characterize the DNAPLs in both a continuous (versus the current discrete sampling methods) and a minimally invasive manner.

Concentrated waste plumes from dense nonaqueous phase liquids (DNAPLs) should also give unique Raman spectra. They will form concentrated sludge areas in existing wells, or could be directly accessed through minimally intrusive cone penetrometers. Baseline experiments conducted during this program indicate that DNAPLs such as trichloroethylene (TCE) and tetrachloroethylene (PEC) in soil and clays could be identified and characterized with unenhanced Raman techniques (e.g., direct fiber optic Raman techniques) combined with cone penetrometer.

The application of enhanced Raman technique will be required for dilute waste plumes originating from the concentrated sources leaking into the soil and contaminating the surface and groundwater since it becomes experimentally very difficult with unenhanced Raman to measure spectra at concentrations below ~10 ppm. Surface enhanced Raman spectroscopy (SERS) has been demonstrated during this program to detect a variety of contaminants including the chlorinated hydrocarbons in aqueous environments at the parts per billion level. As part of this project and an ongoing Collaborative Research Agreement (CRA-90-003) with ORNL, we have detected and characterized chlorinated hydrocarbons in actual environmental groundwater samples obtained from the Bear Creek Burial Grounds at Oak Ridge Reservation.

Further developments, under DT&E Phase, of the Raman technology and instrument 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.

Advantages of the fiber optic Raman technique for DOE would include increased efficiency of environmental characterization and mapping, reduced costs associated with field sampling, and *ex situ* laboratory analysis, less direct exposure of personnel to polluted samples (e.g., in pump and fill operations), cost savings over more complex analytical instrumentation, and more effective real-time monitoring of remediation activities. These advantages all relate to improvements in efficiency. In addition to the DOE community, several other Federal agencies such as the Department of Defense (DOD), the Environmental Protection Agency (EPA), and the U.S. Geological Survey, as well as the commercial sector, will benefit from the introduction of a fiber optic Raman spectroscopy field screening instrument.

## 4.2 Technology Integration Evaluation

EIC and Oak Ridge National Laboratories have established a Collaborative Research Agreement (CRA) which will allow the exchange of technology and facilities in order to develop and conduct on site testing protocols using fiber optic Raman spectroscopy, in accordance with the long term RDDTE objectives. EIC has also extended the program to fabricate fiber optic probes for testing at the Los Alamos mock-up waste storage tank, with subsequent demonstration at Hanford are planned with LLNL. EIC has also established collaborative agreements with other DOE contractors, including Science and Engineering Associates (SEA) and Applied Research Associates (ARA) involved in soil and groundwater mapping and sampling technology, in order to provide means for deploying the spectroscopic probes.

The total program (R&D and DT&E Phases) provides the DOE a line of user-friendly, cost effective, commercially available instruments keyed to environmental characterization and restoration. It is only through the general availability of cost-effective instrumentation, operable by field technicians, that Raman can make an impact on the massive environmental restoration effort. Ongoing collaborations with groups at the national laboratories also investigating Raman for site characterization will ensure that the commercial instruments will reflect their relevant research results.

The anticipated end product at the completion of the DT&E phase is a commercial field portable fiber optic Raman system. Using the field portable instrument, Raman spectroscopy can be applied to several site characterization problems. First, Raman probes can be introduced into waste storage tanks with unknown contents, and the major chemical species can be identified and their distribution mapped within the container. Second, high sensitivity Raman probes can be introduced into wells and the groundwater sampled and characterized *in situ*. Eventually, this same approach could be employed with rapidly deployed cone penetrometers developed by ARA for a more complete and cost-effective site mapping than possible with drilled and excavated wells. The increased efficiency of site characterization and monitoring compared to present sampling and laboratory analyses operations will greatly increase the rate at which hazardous regions can be selected for remediation or isolated.

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# APPENDIX

## Major Raman/SERS Peak Positions (cm$^{-1}$) and Vibrational Assignment for the Chlorinated Hydrocarbon Solvents

| $CCl_4$ | | $CHCl_3$ | | DCE | | TCE | | Vibrational Assignment |
|---|---|---|---|---|---|---|---|---|
| Raman | SERS | Raman | SERS | Raman | SERS | Raman | SERS | |
| 227 s | 220 w | | | | | | | Cu-C ? |
| | 261 w | | | | | | | Cu-C ? |
| | 288 w | | | | | | | Cu-C ? |
| 319 s | | | | | | | | "Chain expansion" |
| 462 s | | | | | | | | Symmetric $CCl_4$ str. |
| | 521 w | | 526 m | | 521 m | | 524 m | CCl str., Cu-C stretch? |
| | | | | | | 628 s | | CCl str. - secondary CA |
| | | 689 s | 670 w | 656 s | | | | CCl str. - primary CA symmetric $CCl_3$ str. |
| | | | | 674 m | | | | CCl str. - primary CA |
| 762 w | | | | | | | | CCl str. - primary CA |
| 787 w | 791 m | 760 m | 783 s | 755 s | 782 s | 780 m | 781 s | CCl str. - primary CA |
| | | | | 882 w | | 842 w | 862 w | CC skeletal str. |
| | | | | 944 w | 965 w | 930 w | 963 w | CC skeletal str., ring "breathing" |
| | | | 1021 w | | 1024 w | | 1018 w | In-plane CH deformation, CC str., ring "breathing" |
| | 1051 w | | 1056 m | 1055 w | 1058 m | | 1055 m | CC str., ring "breathing" |
| | 1089 w | | | | 1101 w | | 1105 w | CC str., ring "breathing" |
| | | | 1151 w | | 1148 w | | 1167 w | Ring "breathing" - cyclopropane type |
| | | 1218 w | | 1209 w | | | | $CH_2$ twist and rock |
| | | | 1234 w | | 1239 w | 1247 m | 1237 w | $CH_2$ twist and rock, in-plane CH deformation |
| | | | 1313 m | 1306 w | 1312 m | | 1312 m | $CH_2$ in-phase twist, $CH_2$ twist and rock, in-plane CH deformation |
| | | | 1352 m | | | | 1356 m | CH deformation |
| | | | 1381 s | | 1379 s | | 1379 s | Ring str. |
| | | | | 1433 w | | | | $CH_2$ deformation |
| | | | 1465 w | | 1464 w | | 1463 w | $CH_2$ deformation |
| | | | | | 1509 w | | 1505 w | Symmetric C=C str. - cyclo |
| | | | 1550 w | | | | | C=C str. - cyclobutene |
| | | | 1581 w | | 1582 m | 1585 s | 1580 s | C=C str. CA, 3 or C=C couple str. - polyene |

s - strong intensity, m - moderate intensity, w - weak intensity
CA = Chloroalkane, str. = stretch

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# END

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