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Field Raman Spectrograph for Environmental Analysis

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PROJECT SUMMARY

The objective of this project was to develop a field portable Raman spectrograph and fiber optic probes that can be used to address DOE hazardous waste site characterization and monitoring needs.

A computer-controlled, near IR echelle Raman spectrograph has been assembled. The fieldable spectrograph is a compact instrument that rivals conventional laboratory instruments in terms of its performance. It provides high spectral resolution, and with a multichannel CCD detector, simultaneously collects a complete Raman spectrum at all wavelengths without repositioning the grating. The spectrograph is optically efficient (sensitive) and accepts a fiber optic input directly. A custom software package has been developed for data collection and spectral processing.

A series of field laser candidates were evaluated over the duration of this program. The ultimate choice for a laser was a wavelength stabilized diode laser. This device can be easily held in one's hand and consumes very little electrical power, yet it provides over 300mW optical power at 785nm - more than most other large laboratory systems.

Several unique fiber optic probes have been developed for particular DOE measurement scenarios. These hand-held probes are coupled directly to the laser and spectrograph through a duplex fiber optic cable. The probes employ distal filtering and other optical techniques to minimize the background generated in the optical fibers so that high quality Raman spectra are produced. Of particular note are end-viewing Raman probes that provide an "aim-and-shoot" type analysis capability which is well suited to rapidly identifying the contents of waste bottles, vials, and jars. A side-viewing design allows the probe to be inserted in protective housings such as a cone penetrometer rod where Raman analysis is performed through a window in harsh environments.

In support of field applications at DOE sites, a database of Raman spectra for 200 contaminants found at DOE sites has been compiled. Commercially available spectral search routines allow the database to be searched quickly for unknown compound identification. The feasibility for using the Raman instrument to analyze the contents of hazardous waste tanks and nonaqueous phase liquids in subsurface soil has been demonstrated in field demonstrations at an Oak Ridge National Laboratory radiation facility and in a cone penetrometer truck at the Savannah River Site, respectively.

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SECTION 1.0

INTRODUCTION

1.1 Introduction

The widespread contamination found across the U.S. Department of Energy (DOE) complex has received considerable attention from the government and public alike. A massive site characterization and cleanup effort has been underway for several years and is expected to continue for several decades more. The scope of the cleanup effort ranges from soil excavation and treatment to complete dismantling and decontamination of whole buildings. To its credit, DOE has supported research and development of new technologies to speed up and reduce the cost of this effort. One area in particular has been the development of portable instrumentation that can be used to perform analytical measurements in the field. This approach provides timely data to decision makers and eliminates the expense, delays, and uncertainties of sample preservation, transport, storage, and laboratory analysis.

In this program, we have developed and demonstrated in the field a transportable, high performance Raman spectrograph that can be used to detect and identify contaminants in a variety of scenarios. With no moving parts, the spectrograph is rugged and can perform many Raman measurements *in situ* with flexible fiber optic sampling probes. The instrument operates under computer control and a software package has been developed to collect and process spectral data. A collection of Raman spectra for 200 contaminants of DOE importance has been compiled in a searchable format to assist in the identification of unknown contaminants in the field.

1.2 Background

Vibrational spectroscopic techniques, such as Raman and infrared (IR) spectroscopies, are useful qualitative and quantitative analytical tools. For every molecule, both techniques produce a unique "fingerprint" spectrum consisting of a series of sharp lines (bands) at discrete wavenumber positions. The advantage of Raman over IR techniques in many situations is that measurements can be performed *in situ*, without sample preparation. Analyzing solid or aqueous samples is especially difficult by IR. Furthermore, IR optical fibers are expensive, transmit poorly at some wavelengths, tend to be hygroscopic, and are fragile - characteristics unsuitable for field deployment. Raman spectroscopy, on the other hand, works well with samples in any state and uses communications type optical fibers, which are optically efficient, rugged, and inexpensive.

The Raman experiment consists of exciting a sample with monochromatic laser light, collecting the scattered light, and analyzing the scattered light intensity as a function of wavelength. In most modern dispersive Raman systems, the analyzer is a grating spectrograph equipped with a multichannel detector positioned at the exit focal plane. This approach allows an entire region of the Raman spectrum to be collected without scanning the grating as required with single channel detectors. Raman spectra are presented with an ordinate calibrated in wavenumbers "shifted" from the exciting laser position (assigned the 0 wavenumber position). This allows Raman spectra to be

compared at different excitation wavelengths, since the wavenumber shift positions are independent of the excitation wavelength.

Typically, the Raman effect is about 10^{-8} of the incident laser intensity and Raman signals vary inversely by λ^4 , where λ is the laser excitation wavelength. Therefore, sensitive detectors, high laser powers, and short laser wavelengths are advantageous for Raman measurements. When considering the laser source, however, it is fluorescence "background" that often directs the choice of wavelength. Recently, most commercial Raman instruments have moved from visible to near IR laser sources, where fluorescence is generally less intense. For a Raman instrument that is going to be used in a variety of applications and a wide range of sample types, a near IR source is most practical.

The ultimate goal of this research program is the development of a compact, fieldworthy Raman instrument equipped with fiber optic probes that can be applied to DOE characterization problems. In order to achieve this goal, the project had the following major objectives:

1. To assemble and demonstrate a high performance, echelle grating Raman spectrograph with no moving parts in a configuration that can be transported and operated at DOE environmental restoration sites.
2. To develop and test a series of fiber optic probes that can be used to perform Raman measurements in specific applications including the identification of bottle contents, hazardous waste tank monitoring, and subsurface deployment in a cone penetrometer.
3. To develop a computer software package for the instrument which provides data collection, processing, and archiving of spectra in a searchable format. An operation manual for the instrument, including software documentation, was to be written for the instrument.
4. To compile a Raman spectral database of 200 DOE priority compounds to facilitate field identification of unknown contaminants.
5. To perform off-site evaluation of the instrument on real hazardous waste tank samples and in a cone penetrometer.

SECTION 2.0

RESULTS AND DISCUSSION

2.1 Development of a Prototype Spectrograph

2.1.1 Echelle Spectrograph Design

A field hardened Raman spectrograph designed for use with fiber optic probes has been fabricated. Figure 1 is a photograph of the instrument which is 24in (L) x 8in (W) x 6in (H) as shown. The compact size of the spectrograph allows it to be easily transported and operated in small trucks, vans, or automobiles at DOE sites and, at approximately 60 lbs., is light enough for a single person to carry for short distances.

Figures 2 and 3 show the optical layout of the echelle spectrograph designed for far visible and near IR operation. All components are positioned in the spectrograph on sturdy mounts that are secured firmly in position after alignment. This allows the instrument to be operated either in a flat position or on its side in a "tower" configuration as shown in Figure 1. There is no need for realignment or wavelength recalibration after changing positions. The spectrograph also avoids the use of delicate and optically inefficient slits at the entrance port. Simpler, more efficient, and more robust direct fiber coupling to the entrance is employed instead. For maximum optical throughput, the cross-dispersing SF-10 prisms and 150-mm camera lenses are antireflection coated with a near IR coating, and the 52.6 groove/mm echelle grating is coated with gold. The use of camera lenses rather than simple lenses provides superior imaging of the input fiber onto the detector, which results in higher resolution and peak intensity.

Although Figure 1 shows the instrument with a liquid nitrogen cooled CCD detector on it (most of the size of the detector is the liquid nitrogen dewar), Figure 3 depicts the current version of the instrument with an air-cooled CCD detector. This detector has recently become available from Photometrics, Ltd. (Tucson, AZ) and cools the CCD chip to -45°C , which introduces insignificant levels of dark noise into the Raman spectra. Air-cooling greatly enhances the fieldability of the instrument by eliminating the need for liquid nitrogen or recirculating glycol coolant. Detector testing is discussed further below.

The echelle spectrograph is compact and, at approximately 60 lbs, is light enough for a single person to carry for short distances. The size of the spectrograph is 16in (W) x 24in (L) x 8in (H) which allows it to be easily transported and operated in small trucks, vans, or automobiles at DOE sites.

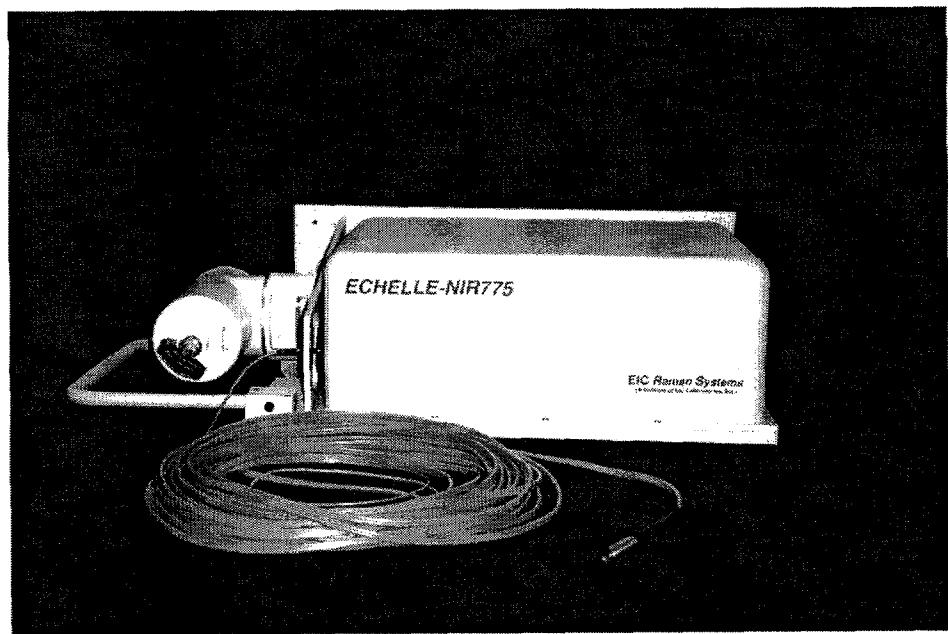


Figure 1. Photograph of the near IR echelle Raman spectrograph and fiber optic probe.

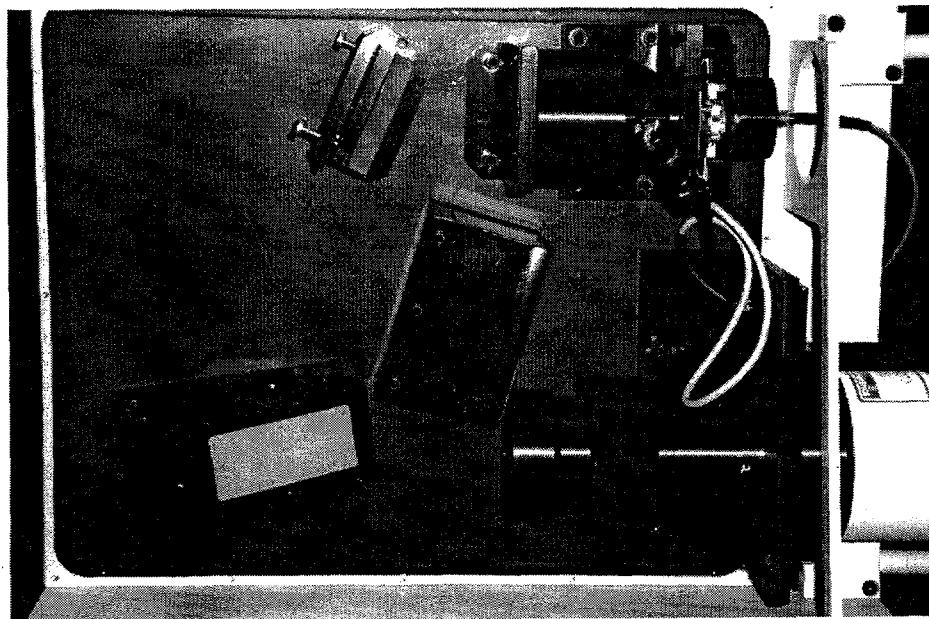


Figure 2. Internal view of the near IR echelle spectrograph.

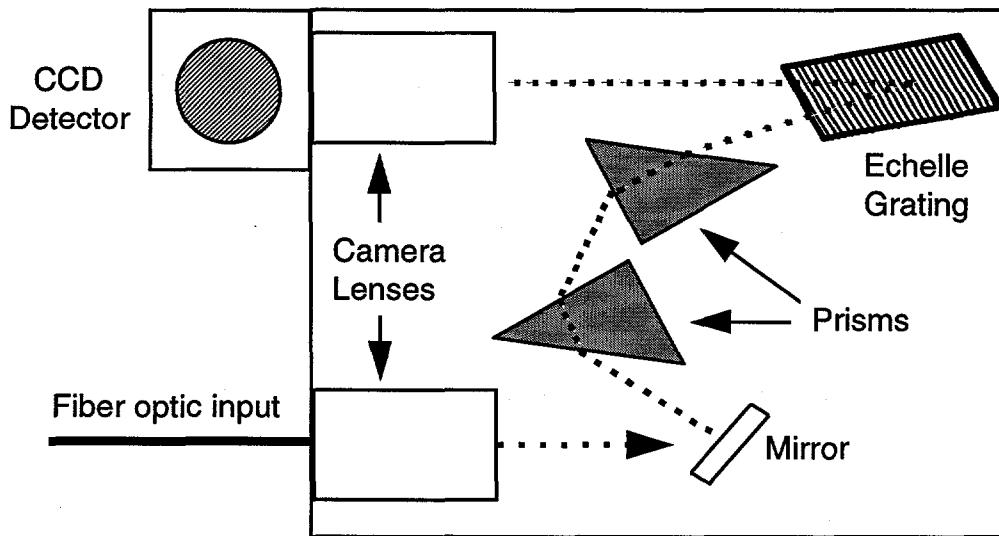


Figure 3. Optical layout of the near IR echelle spectrograph.

2.1.2 Spectrograph Performance

One of the key features of the spectrograph prototype is its high optical throughput, which in turn reduces spectral acquisition times. F-number is one measure of optical throughput. High f-numbers (e.g., f/5) indicate low throughput. In a direct fiber coupled spectrograph, maximum throughput is achieved when the f-number matches that of the optical fiber (ca. f/2 for all-silica type fibers). The echelle spectrograph was designed to be f/3, with low throughput losses. Also, as mentioned previously, all optical components used in the instrument were designed with antireflection coatings for maximum transmission of near IR light. The result is a spectrograph with throughput comparable to or better than conventional "fast" spectrographs which must sacrifice resolution and range in order to achieve high throughput.

A second important feature of the echelle spectrograph is its superior combination of spectral resolution and range. In all spectrographs, a compromise between spectral resolution and range must be reached. A resolution of 1cm^{-1} is adequate for nearly all Raman analyses. In order to achieve this resolution in any conventional grating spectrograph using one-dimensional dispersion of the Raman spectrum and a typical 25mm, 1024-element detector array, the range will be limited to just 1024cm^{-1} . The complete Raman spectrum covers over three times that range; however, the grating must be moved at least three times in order to acquire a full spectrum. This increases both the time and inaccuracy (unless the spectrograph is recalibrated after each grating movement) of the Raman analysis. The echelle spectrograph disperses the Raman spectrum in two dimensions onto the CCD detector array, spreading the spectrum over about 10,000 detector elements. This allows a full Raman spectrum to be collected without repositioning the grating and with much better than 1cm^{-1} resolution (about 0.3cm^{-1} theoretical per pixel element). Figure 4 is a Raman spectrum of naphthalene collected with the echelle spectrograph. The complete, high quality spectrum was acquired in just 10sec using a diode laser source (115mw at 785nm).

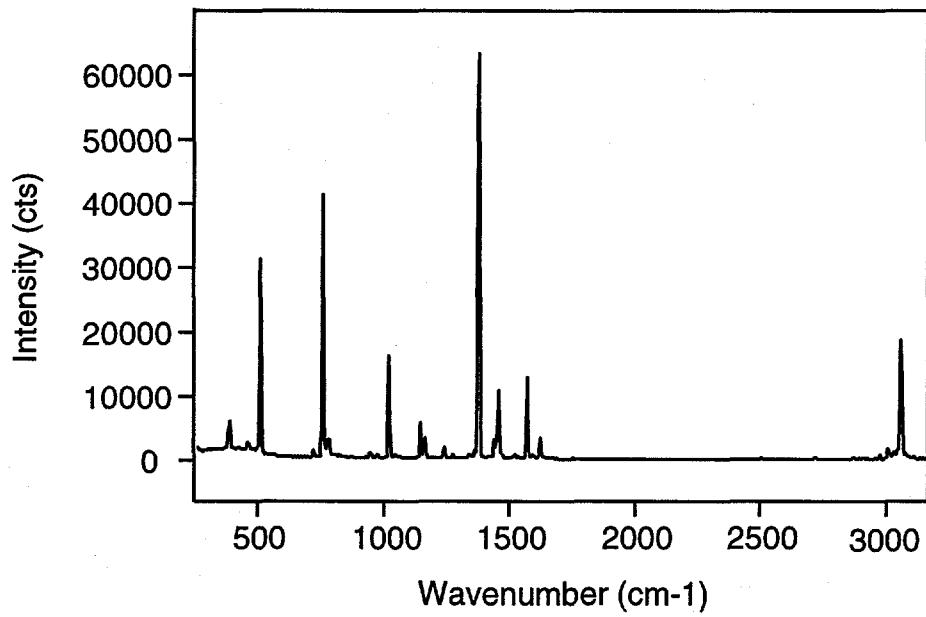


Figure 4. Raman spectrum of naphthalene collected with the near IR echelle spectrograph.

Figure 5 better illustrates the high resolution capabilities of the echelle spectrograph. Closely spaced emission lines from a neon lamp were resolved easily, even using a large, 200 μm core input fiber (resolution is optimum with a 25 μm core fiber). For comparison, the neon spectrum was also acquired with a more conventional plane reflection grating spectrograph. The spectrograph was operated under more favorable resolution conditions (100 μm fiber input). Taking into consideration the difference in the optical fiber core sizes, resolution was 4-5 times worse with the conventional spectrograph, which also had a range limited to about 1000 cm^{-1} .

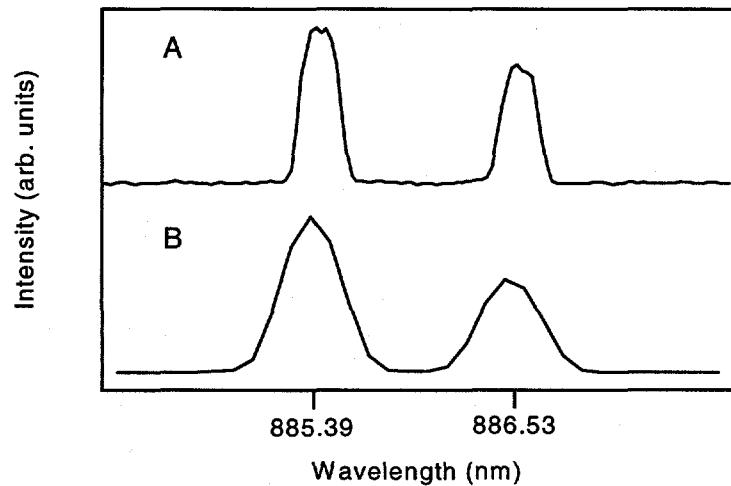


Figure 5. Neon lamp emission lines collected with (A) echelle, and (B) plane reflection grating spectrographs.

Three CCD detectors from Photometrics Ltd. were evaluated on the echelle spectrograph. The detectors differed in their mode of cooling and included liquid nitrogen, recirculating liquid, and air-cooled versions. The latter was a prototype unit for which EIC was selected as a test laboratory. All three detectors performed well, with low dark currents (backgrounds) at integration periods up to 10 minutes. On the basis of convenience, size, and weight we now use the air-cooled detector exclusively on the instrument. Only if long (e.g., half-hour or more) integration periods were required would a liquid nitrogen-cooled detector be used on the instrument.

2.2 Laser Testing

For field Raman applications, appropriate lasers are also needed. Typical laboratory lasers are wholly unsuited for field deployment as they are large, heavy, require high electrical power with extensive water cooling, and easily become "detuned." Table 1 lists several lasers which we identified early in this program as candidates for field deployment.

The lasers fall into two general categories: ion and solid-state. The main advantages of ion lasers are their frequency stability and proven, long-term utility in the laboratory environment. Reasonably portable ion lasers with air-cooling are available from several manufacturers and are at present a reasonable choice for visible Raman spectrometers. Low output intensity (<25mW) precludes their use in the near IR, however.

Solid-state lasers are attractive for field applications because of their potential for high output intensities in a compact unit. The diode pumped, frequency doubled Nd:YAG laser available from Coherent Laser Group is a good example of a solid-state device with these features. The laser, including power supply, is only 520mm (L) x 120mm (W) x 86mm (H) for the largest version (400mW optical output - lower intensity versions are even smaller) and weighs under 15lbs. Air cooling is provided by a 2-inch fan in the laser. We observed no change in emission frequency over a 10-hour period and output power stability from a 150mW version of the laser (Model DPSS- 150) was excellent as shown in Figure 6. Maximum long-term drift was about 5% for the DPSS laser, which is comparable to the short-term noise of many other lasers. Even higher power versions of the frequency doubled Nd:YAG laser will soon be available, whereas 200mW is a practical limit for competitive Ar ion lasers. At present, the major drawback of the Nd:YAG laser for visible wavelength Raman spectroscopy is its high price - about \$30,000 for a 200mW device.

In the near IR at wavelengths $<1\mu\text{m}$, solid-state laser technology is not so well developed. It was originally intended that diode lasers with moderate output intensities (100mW) at about 775nm be used with the echelle spectrograph. Diode lasers are the smallest of all lasers and are also among the least expensive (<< \$10K). Extensive testing in this program has shown, however, that lower cost diode lasers are not presently reliable enough for field use. The failure rate of the 100mW devices was extremely high - several lasers failed after less than 100hrs. of operation. Another difficulty encountered was "hopping" of the laser frequency. This problem, which requires recalibration of the spectrograph each time it occurs, was exacerbated when the laser emission was coupled into an optical fiber. Using an optical isolator to minimize reflections back into the laser (backreflections are one cause of the "hopping") improved frequency stability, but not to a degree acceptable for field implementation (<1 hop/hr.). The isolator also did not improve the failure rate.

Table 1. Candidate Lasers for Field Raman Applications

Type	Laser, Wavelength	mW	Advantages	Disadvantages
Ion	Ar, 488 or 514nm	200	Stable output frequency, simple operation and fiber optic coupling, low cost, high output intensity	Substantial air cooling necessary, limited tube life (<2000hrs.), large power requirement (20A @ 208Vac), bulky
	Kr, 647nm	100	Same except moderate output intensity	Same
	Kr, 752nm	25	Same except low output intensity	Same, low output intensity
Solid-State	Single Frequency Diode, 780-810nm	50	Very compact, low power requirement, theoretically long life (>10,000 hrs.)	Unstable output frequency, low output intensity, empirically short life (<<1000hrs.), difficult fiber optic coupling
	Tunable Diode, 770-780nm	500	Modest size, low power requirement, stable output frequency, theoretically long life, average fiber optic coupling, high output intensity	Higher cost, fragile construction
	Alexandrite, 750nm	>500	Stable output frequency, Very high output intensity	Large size, high electrical power requirement, pulsed output makes fiber optic coupling difficult, high cost
	Nd:YAG, Frequency Doubled to 532nm	Up to 400	Small size, low power requirement, stable output frequency, high output intensity, long life, facile fiber coupling	High cost

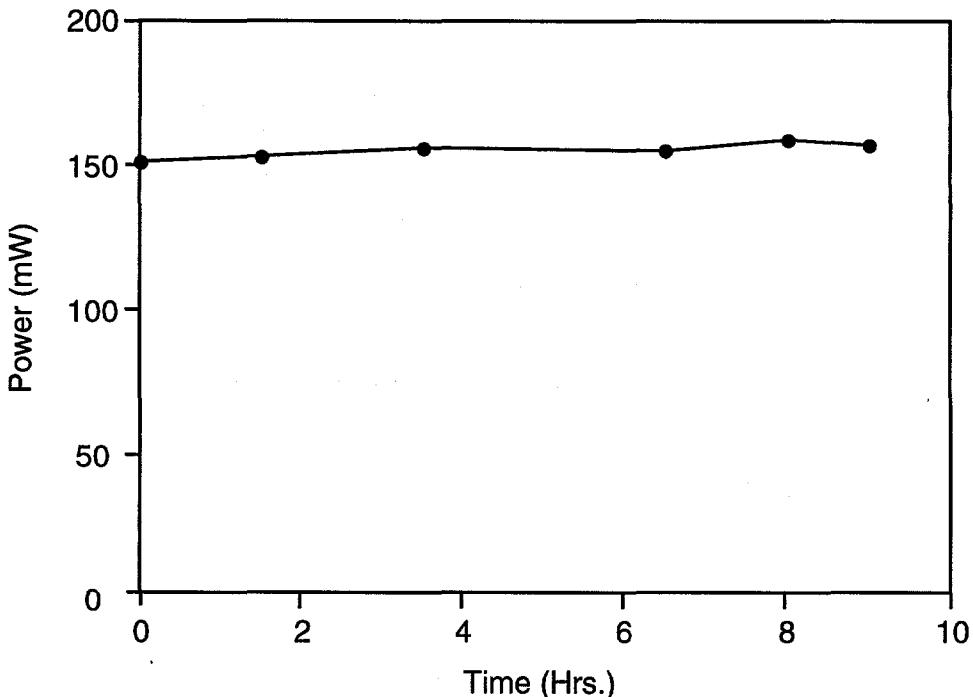


Figure 6. Output intensity of a 532nm Nd:YAG laser measured over nearly 10 hours.

A newer, and more expensive version of the diode laser, produced by Spectra Diode Laboratories (SDL, San Jose, CA), uses a grating to tune the laser wavelength (approximately \pm 5nm from the laser's center wavelength) and offers much better frequency stability than conventional diode lasers. Originally, this laser was offered with very high output intensity, 500mW, which is a desired target level for rapid, near IR Raman spectroscopy. The primary difficulty encountered during tests of one of these lasers was internal optical misalignment during warm-up. This resulted in large intensity losses (up to 450mW).

In the past 18 months, an advanced, ruggedized version of the external cavity, grating stabilized laser has become available from SDL. The device, including all temperature and control electronics, is housed in a unit the size of a child's shoebox (6in x 4in x 10in) weighing just 6 lbs. The former version of the laser consisted of two larger and heavier modules - a power supply and a laser head. The electrical requirement for the new laser is also low, typically about 25W to deliver 300mW of optical power at 785nm. Tests of the laser's stability showed almost no change in emission wavelength (\pm 0.05nm) over months of operation.

The final laser tested was a flash lamp-pumped alexandrite laser being developed jointly by EIC Laboratories and Big Sky Laser Technologies. Although the prototype laser was the largest and heaviest tested, it also provided the most output intensity (nearly 1W at 752nm). Full intensity could not be used when coupling to optical fibers, however, because the high energy pulses being delivered by the laser damaged the fibers. One improvement which was implemented was a reduction in pulse energy while maintaining average output intensity. With the production of the aforementioned stabilized diode laser by SDL, however, we decided not to pursue further the use of an alexandrite laser for field Raman spectroscopy.

2.3 Fiber Optic Raman Probes

Fiber optic probes are a key component of the field Raman system, providing flexible and safe sampling remote from the main instrument and operator. The probes also provide an *in situ* detection capability at difficult to access locations such as in hazardous waste tanks or underground.

2.3.1 Raman Probe Configurations

EIC has previously assembled prototype probes designed for 514.5nm argon ion laser excitation with an end-viewing geometry.¹ A schematic of the basic, end-viewing style probe is shown in Figure 7.

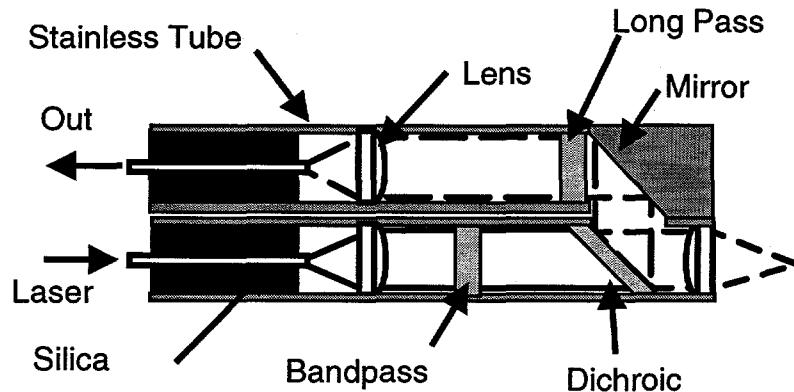


Figure 7. Schematic representation of an end-viewing fiber optic Raman probe.

During this program, probes designed for use with other laser sources were fabricated, incorporating several advanced features without altering the overall probe dimensions (0.5 in diameter x 3 in long). First, an epoxy is used to seal the probe cover, viewing lens, setscrews, fiber entry tubes, mirror holder, and internal components from water and water vapor. Second, hard-coated moisture-resistant filters are employed in place of conventional filters, which irreversibly lose optical transmission when exposed to water. The transmission of the new filters is also significantly higher than most conventional filters, providing more than twice the optical transmission through the probe. Third, improved collection efficiency is afforded by adding a fine adjustment capability to the collection fiber. Once optimum alignment is achieved the collection fiber ferrule is locked with a setscrew and epoxied in place. Fourth, stray light within the probe has been reduced by black anodizing some of the components.

The same advanced features have been incorporated into a "side-viewing" version of the Raman probe. Fabricated for the first time in this program, the side-viewing probe is well suited for direct Raman analysis when the probe is deployed through a solid medium such as soil or waste tank saltcake. Under these conditions an end-viewing probe could be easily damaged. A schematic of the side-viewing Raman probe is presented in Figure 8. Spectra collected with the probe are presented in later sections of this report.

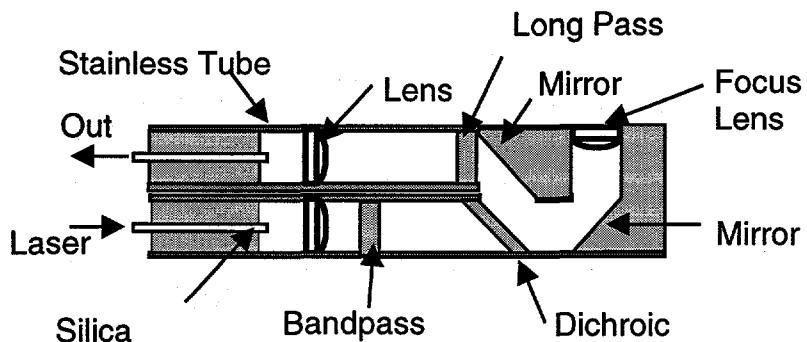


Figure 8. Side-viewing fiber optic Raman probe.

The side-viewing probe's small size allows it to be isolated and protected from the sample by placing it inside a rugged "punch-probe" designed to penetrate through solids during tank or drum inspections. We have designed and fabricated a punch-probe modeled after one of their standard penetrometer cones. A schematic of the punch-probe is shown in Figure 9. An interface module holds the side-viewing Raman probe and is used to position the probe at the face of a sapphire window. An appealing feature of the interface module is that it can also be used with a cone penetrometer. The sapphire window is employed because it is extremely durable and will not scratch during deployment. With the window removed, the viewing lens of the Raman probe can be adjusted in and out to position the focus for maximum sensitivity (this is usually achieved with the focal point just outside the outer window face). The sapphire window is sealed with Teflon or another suitable material after adjustment is complete. Note that the top of the punch-probe is threaded so that additional length(s) of pipe can be added to reach the desired tank or drum depth.

The final probe tested early in this program was a 752nm surface-enhanced Raman (SER) probe fabricated according to a design we had developed previously.² The probe worked well in aqueous solutions as shown in Figure 10 for 10ppm pyridine adsorbed from aqueous solution onto a roughened silver electrode at -0.6V. Further development of this probe was not pursued because our site contact left Oak Ridge and the cone penetrometer Raman evaluation was substituted for the SER field testing.

2.3.2 Radiation Testing of Raman Probes and Components

It has been proposed for some time to deploy Raman spectroscopy in DOE's hazardous waste tanks. Of primary concern is the effect of ionizing radiation on fiberoptic probes deployed in the tanks. To evaluate the effect of gamma radiation on our probe, as well as an all-silica probe (two optical fibers fused side-by-side in a silica tube) developed by Dr. Jack Young at ORNL for hazardous environments, we performed tests at the University of Massachusetts-Lowell radiation facility. Gamma radiation was produced by a Co⁶⁰ source. In the radiation chamber we placed an EIC Raman probe and the individual filters and lenses of which it is comprised, the ORNL probe, a sapphire window, some polymeric materials, and a short length of optical fiber.

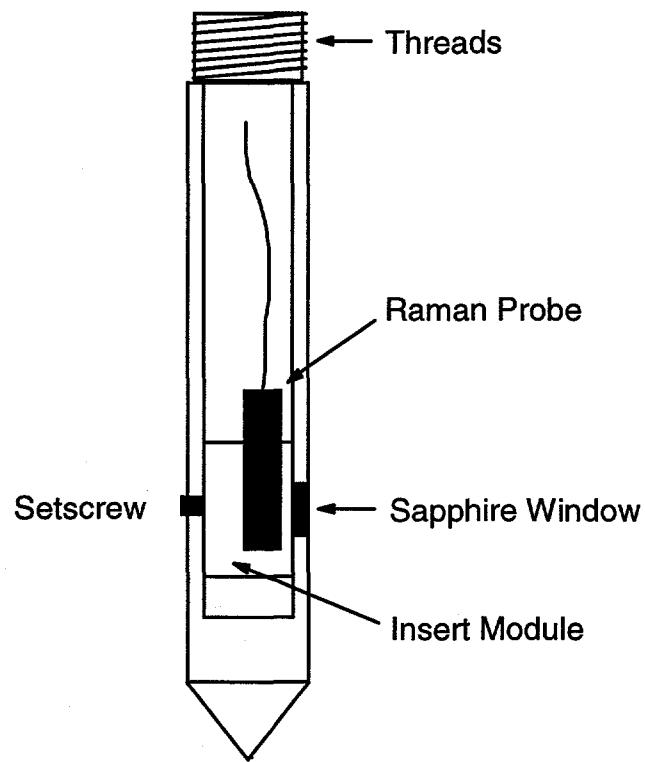


Figure 9. Punch-probe for Raman analysis in waste tanks and drums.

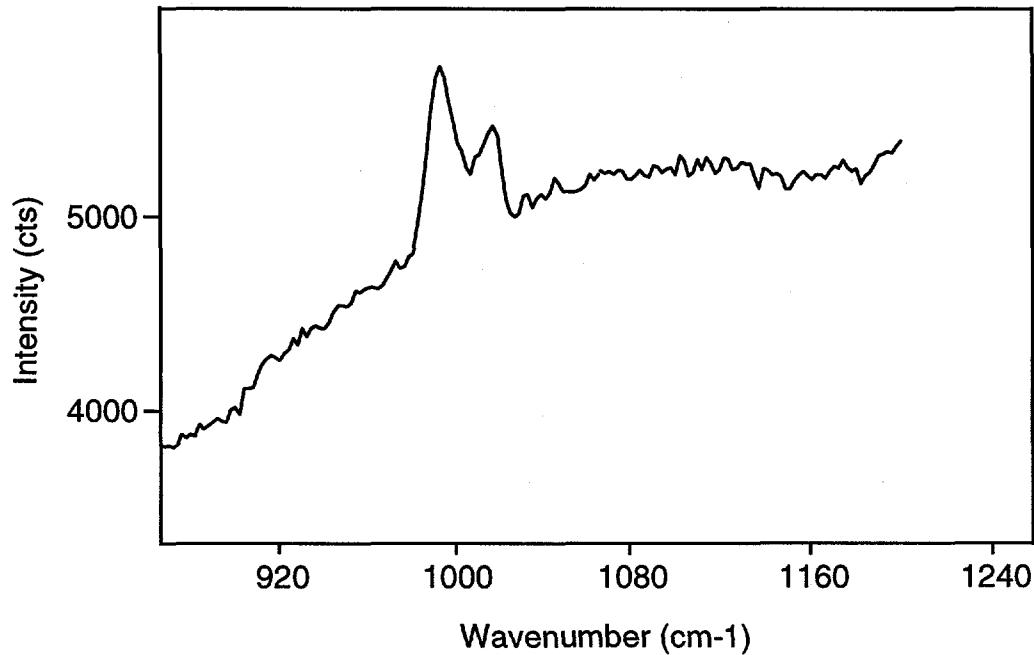


Figure 10. SER spectrum of pyridine collected with a fiber optic SER probe and 40mW of 752nm excitation.

The materials were subjected to a total dose of 450 krads with a peak dose of 12,000 rad/hr. At these levels, which exceed those found in most waste tanks, there was no visible change to the EIC or ORNL optical components. Optical transmission measurements performed on the components and probes confirmed that there was no appreciable change in optical properties. We attribute this success to the use of high purity quartz in all of the optical elements. Conventional glass components are known to darken when irradiated.

Figures 11 and 12 present Raman spectra before and after irradiation for the EIC and ORNL probes, respectively. In both cases it is clear that irradiation had little effect on probe performance. The broad bands near 800cm^{-1} and 1000cm^{-1} in Figure 12 are silica bands generated in the ORNL probe, which does not use optical filters to reduce this background.

2.4 Raman System Performance

The capabilities of the fiber optic echelle Raman spectrograph have been tested extensively using standard reference light sources and over 200 DOE contaminants. Important analytical parameters including wavelength calibration (accuracy and stability), spectral resolution, and sensitivity (determined as minimum detectable concentrations of analytes) have been measured.

2.4.1 Wavelength Calibration

Calibration accuracy can be tested with chemical compounds for which Raman shifts have been well established. Surprisingly, there are few such compounds. The ASTM committee on Raman spectroscopy has recently established Raman shift standards covering most of the Raman spectral range. Table 2 compares Raman shifts determined for solid naphthalene and a 50:50 (by volume) liquid mixture of toluene and acetonitrile using the echelle spectrograph (alexandrite laser excitation) with shifts established by ASTM.

Overall the values are in good agreement, matching to within 1cm^{-1} . The one peak in lesser agreement (the acetonitrile band near 380cm^{-1}) is quite broad, asymmetric and weak, making it difficult to positively assign peak position. Of all the values listed in Table 2, that one also showed the greatest variation between test instruments in the round-robin ASTM study. Long-term stability of the echelle's wavelength calibration was also excellent. The naphthalene calibration values were monitored over a several month period and no shifts were observed.

2.4.2 Resolution

Spectral resolution is most easily tested using narrow atomic emission lines from calibration lamps. The resolution of the echelle spectrograph was shown previously in Figure 3 for neon lamp emission lines. A $200\mu\text{m}$ core optical fiber was used as the input to the spectrograph. That core size is typical of fibers used in the fiber optic Raman probes with highest collection efficiencies, but reduces resolution by a factor of about 8 from optimum ($2.5\text{-}3\text{cm}^{-1}$ vs. $0.3\text{-}0.4\text{cm}^{-1}$). Nevertheless, the natural bandwidths for most condensed phase molecules we tested were considerably wider than 3cm^{-1} , so using a $200\mu\text{m}$ core collection fiber did not compromise resolution.

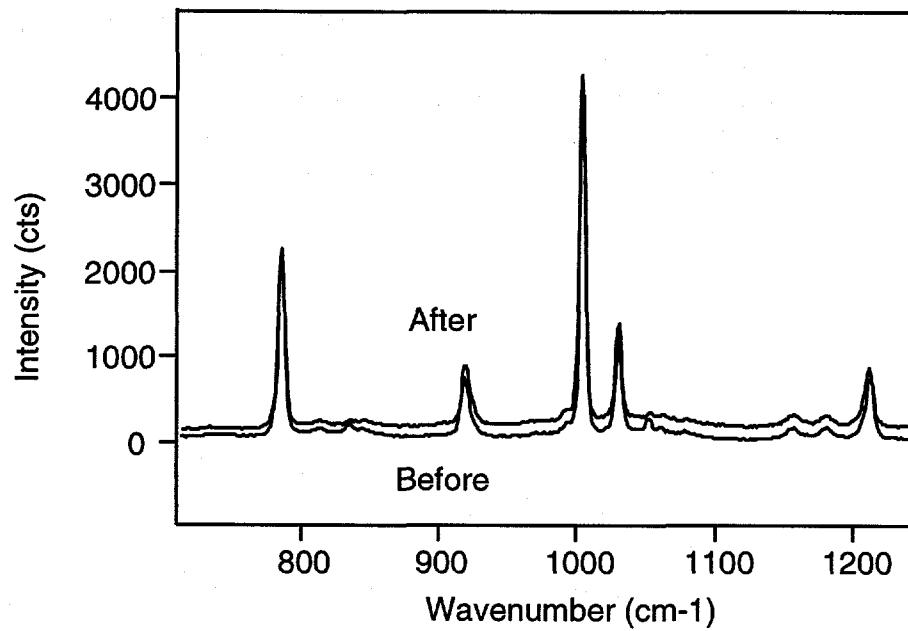


Figure 11. Raman spectra collected from a toluene:acetonitrile mixture with a filtered Raman probe before and after gamma irradiation. The spectra have been offset for clarity.

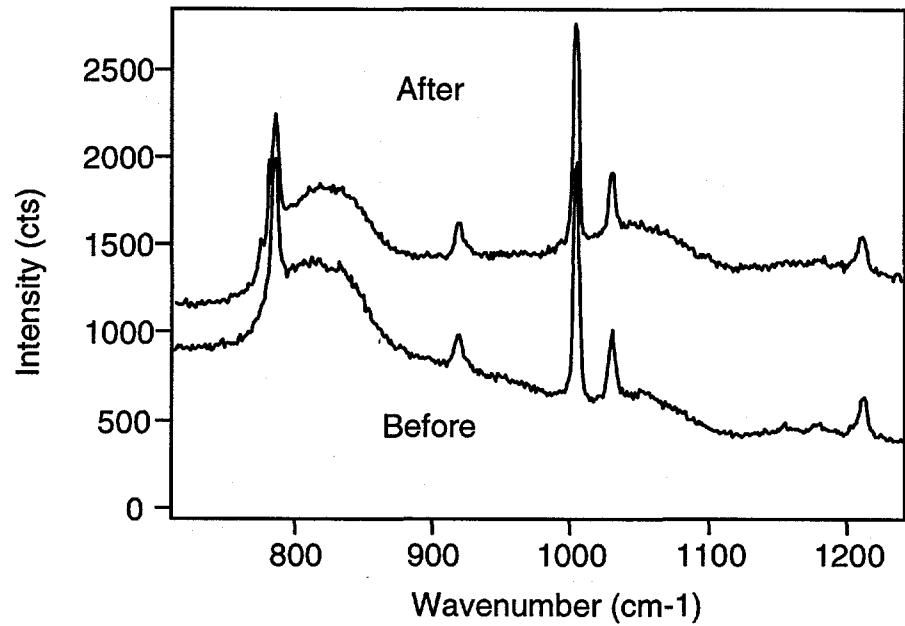


Figure 12. Raman spectra collected from a toluene:acetonitrile mixture with an ORNL all-silica Raman probe before and after gamma irradiation. The spectra have been offset for clarity.

Table 2. Calibration Testing of the Echelle Raman Spectrograph

ASTM T:A*	EIC T:A	Difference	ASTM Nap**	EIC Nap	Difference
378.5cm ⁻¹	376.8cm ⁻¹	-1.7cm ⁻¹	513.8cm ⁻¹	513.4cm ⁻¹	-0.4cm ⁻¹
521.7	521.2	-0.5	763.8	764.0	+0.2
786.5	786.1	-0.4	1021.6	1021.2	-0.4
919.0	919.1	+0.1	1147.2	1147.1	-0.1
1003.6	1003.8	+0.2	1382.2	1382.1	-0.1
1030.6	1031.2	+0.6	1464.5	1464.6	+0.1
1211.4	1211.4	0.0	1576.6	1576.8	+0.2
1605.1	1605.5	+0.4	3056.4	3056.0	-0.4
2253.7	2252.8	-0.9	* Toluene:Acetonitrile (50:50 by volume) ** Naphthalene		
2292.6	2292.3	-0.3			
2940.8	2941.5	+0.7			
3057.1	3056.3	-0.8			

2.4.3 Sensitivity

Sensitivity is an important issue for any instrument being considered for site characterization. Low sensitivity generally means that long, costly analysis times are required and, in the case of down-hole sensors, much of the *in situ* detection advantage is lost. Although the Raman effect is inherently weak, qualitative analysis of high concentration species can often be achieved in a few seconds. As a measure of instrument performance under conditions that could be routinely expected in the field (25 meter fiber probe, 125mW of 752nm alexandrite laser excitation at the sample), spectra were collected for neat solid and liquid samples as well as for dilutions of many of the compounds included in the Raman catalog. Water and/or carbon tetrachloride solvent was used as diluent depending on the solubility of the compound being studied. At the lowest concentrations, integration times ranged up to 10 min.

The sensitivity of the fiber optic echelle Raman system compared favorably with conventional laboratory Raman instruments. With the echelle system, minimum detectable concentrations were generally in the range of 1-10mM for both inorganic salts in aqueous solution and organic compounds in carbon tetrachloride. This level of sensitivity is suitable for the *in situ* identification

of major components in waste mixtures found in tanks or drums or as nonaqueous phase liquids underground. The sensitivity is also better, by as much as 10-fold, than we can achieve in the same analysis time using typical compact laboratory systems. In fact, based on our previous experience with conventional instruments, it was surprising that nearly all of the organic species could be readily detected at saturation levels in aqueous solution. An example is presented in Figure 13 where benzene, a carcinogenic solvent, is easily detected as a saturated aqueous solution (ca 10mM concentration).

In most field characterization scenarios, it is desirable to collect at least semi-quantitative analytical data in addition to qualitative information. Figure 14 shows that the Raman intensity is linear with respect to concentration and is typical of what we observed for organic compounds in carbon tetrachloride or water solvent and inorganic species in water. The slopes of the response "curves" for the potassium ferricyanide band at 2134cm^{-1} and the benzene band at 993cm^{-1} differ by less than 10% with correlation coefficients of 0.9997 and 0.9989, respectively.

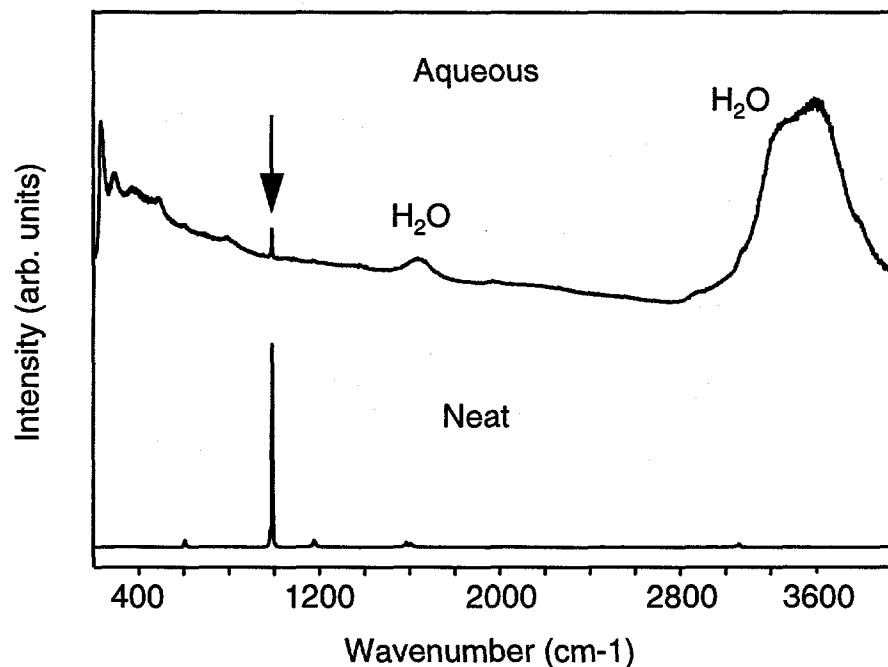


Figure 13. Raman spectrum of saturated aqueous benzene solution collected with the echelle spectrograph compared with a neat (100%) benzene reference spectrum.

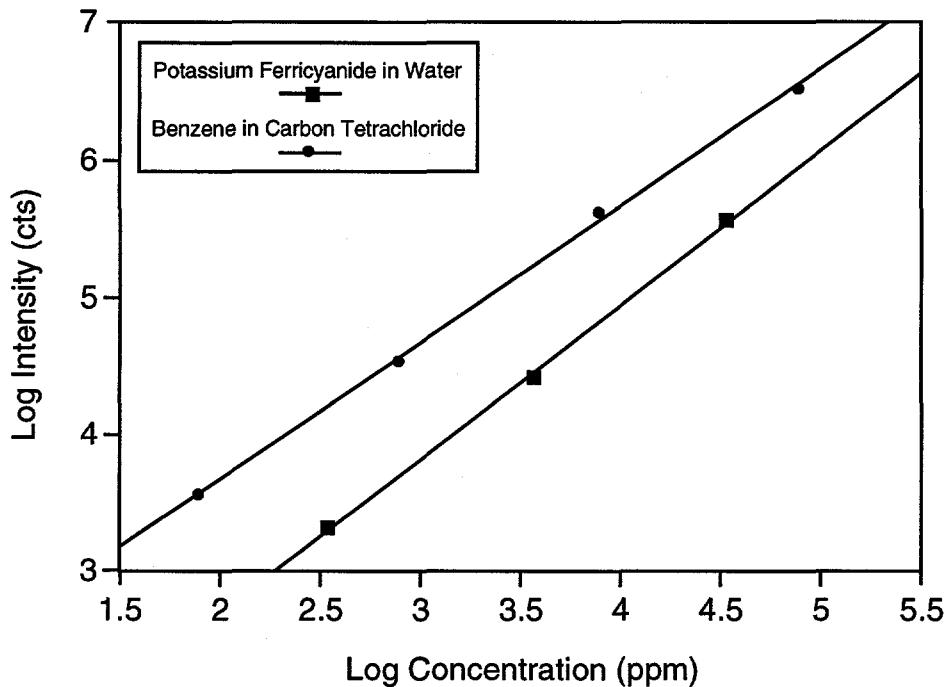


Figure 14. Raman response vs. concentration for potassium ferricyanide and benzene solutions.

2.5 Computer Software

Spectra such as the one shown for naphthalene in Figure 4 could not be collected and processed with computer programs supplied with the Photometrics detectors we tested. Therefore, we developed our own software, written in C++ using Microsoft® Foundation Class, to perform a number of key functions. The routines were object-oriented and operate in the Windows® environment. These functions include the following:

1. Splicing together the spectrum.
2. Performing an automatic wavelength calibration based on well-established atomic emission lines.
3. Applying an intensity correction (accounting for fiber, probe, and spectrograph transmission as well as detector quantum efficiency) vs. wavelength for the system.
4. Continuous data acquisition.
5. Direct generation of Windows® metafiles.

The wavelength calibration program is extensive and precise, using nearly 100 lines from four low pressure emission lamps. If frequent wavelength calibration by the user was required, this would be

a cumbersome and time-consuming task with so many points. However, because the optical system in the echelle is fixed, it is normally necessary to perform the wavelength calibration just once after assembly and alignment. Nevertheless, additional routines have also been written to automatically check wavelength calibration and recalibrate if necessary.

The intensity correction is not a common feature in Raman instruments but is especially important for the echelle because of the varying intensity profile within and between spectral orders. This is demonstrated in Figure 15 which shows uncorrected and corrected spectra for disodium phosphate after splicing. In the uncorrected spectrum, it is notable that the intensity is greatest near the center of each order (each "hump" in the spectrum is an order) and the overall intensity of the orders also varies. In addition to providing more accurate relative peak intensities, the flat baseline of the corrected spectrum also makes it considerably easier to locate peaks such as those found in the 600cm^{-1} region.

A more detailed description of the various software functions can be found in the Operations Manual for the instrument.

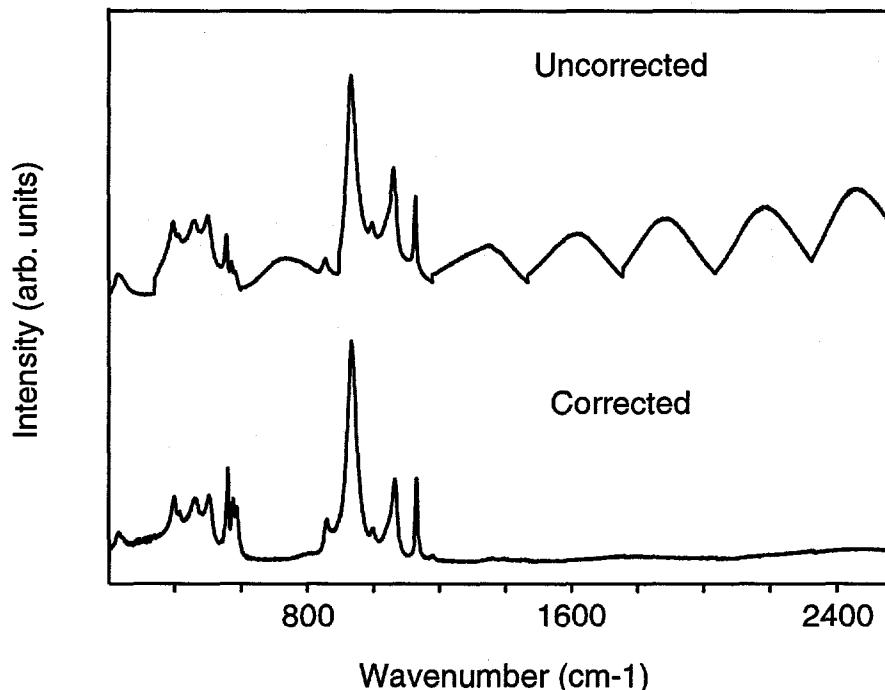


Figure 15. Uncorrected and corrected disodium phosphate spectra collected on the echelle Raman spectrograph.

2.6 Catalog of Raman Spectra

Qualitative Raman identification of sample components can be achieved by spectral interpretation, but this process is slow and prone to error, particularly when complex sample mixtures are

analyzed. Many analysis techniques (e.g., GC/MS and FTIR) now use libraries of standard compounds with sophisticated search and peak matching routines to facilitate analyte identification. For Raman spectroscopy, however, few libraries have been developed and they do not include many of the contaminants of concern to the DOE.

In this program a catalog of intensity corrected, wavelength calibrated Raman spectra for 200 compounds found as contaminants across the DOE complex has been compiled using the echelle spectrograph and end-viewing Raman probes. A listing of the compounds and experimental conditions under which the spectra were collected is included as Appendix A to this report. Individual spectra are stored as data arrays that can be processed and searched with Galactic Industries Corporation's (Nashua, NH) GRAMS/386® software. The Galactic software is versatile and is used by most Raman instrument manufacturers and users. Software we developed for our instrument archives all spectra directly in the Galactic.SPC array format so that file translation is not required when using GRAMS/386®. The 200 compounds in the database fall into the following categories:

1. Chlorinated hydrocarbons - 15 compounds
2. Benzene derivatives - 25 compounds
3. Polymers - 15 compounds
4. Chlorinated biphenyls/pesticides - 25 compounds
4. Other organics - 69 compounds
5. Inorganics - 51 compounds

2.7 DOE Site Applications

2.7.1 Hazardous Waste Tanks

2.7.1.1 Hanford Tanks

DOE's Hanford Nuclear Reservation in Richland, Washington has 149 single-shell and 28 double-shell underground tanks storing highly radioactive, heat-producing wastes. As residuals from the original liquid waste material that was pumped from the tanks or from the addition of chemicals intended to neutralize or precipitate out the most hazardous species, the tanks now contain a variety of nitrate and cyanide compounds that, under the right conditions, could explode. Another explosion hazard is hydrogen being generated in some of the tanks. There is particular concern over hydrogen buildup because the contents of some of the tanks are changing from sludge to a hard saltcake.

The hazards and changing nature of the materials in the Hanford tanks necessitates frequent characterization of the tanks. This is a dangerous and expensive process involving collection of core samples and analysis by laboratory methods. All work is conducted in special glove boxes and the cost for complete analysis of a single core sample can be up to \$1M. Methods which can rapidly profile the core samples in a hot cell can greatly reduce these costs. In order to reduce costs even further and improve worker safety, there is also a large effort underway to develop robotically

deployed sensors for characterizing *in situ* the distribution and concentration of key species in the tanks. For several years, Raman spectroscopy has been a leading candidate sensor for both *in situ* and *ex situ* analysis of tank materials because of its capability for high resolution analysis of mixtures of solid and liquid materials using fiber optic probes. Because the concentration of key components such as nitrates and cyanides is high (percent levels), the limited sensitivity of Raman is not problematic and samples can be analyzed in a few minutes or less.

We have evaluated the echelle Raman spectrograph for monitoring key species in hazardous waste tanks. As described in detail previously, a push-probe modification of a penetrometer cone employing a side-viewing Raman probe has been developed for *in situ* tank profiling. This design was judicious because cone penetrometers and robotic end-effectors based on them will be used for the in-tank inspection systems.

In order to test the capabilities of the echelle Raman system for the Hanford tanks, three waste tank simulants were provided by Dr. Fred Reich, a Raman spectroscopist at Hanford. The three samples represented different tanks and/or chemical processes and consisted of both liquid and solid materials. Aliquots were removed from each sample container and placed on glass microscope slides for analysis. Using an end-viewing fiber optic Raman probe and a krypton or alexandrite laser (100mW of 752nm excitation) with the echelle spectrograph, spectra were first collected for each sample wet and then again after up to an hour of air drying. The sample position was not moved during the drying period.

For comparison with the near IR echelle system, the Hanford samples were also analyzed with a visible Raman system consisting of an air-cooled argon ion laser operated at 514.5nm and a SPEX 270M spectrograph set for maximum resolution. The laser and spectrograph were coupled to an end-viewing fiber optic Raman probe. Again, 100mW of laser excitation was delivered at the sample.

Sample BY-104

Of the three tank simulants, the BY sample produced the simplest Raman spectra. Figure 16 presents spectra for dry and wet BY samples. The spectra were collected with the echelle spectrograph system in 60 and 600sec, respectively. The dry sample shows four bands at 725, 1070, 1386, and 1670cm^{-1} that correspond to Raman bands for solid sodium nitrate (see Figure 17). The major difference between the BY spectrum and a solid sodium nitrate spectrum is the twofold band broadening in the BY spectrum. This is due to the BY sample being in a partially hydrated state; the wet sample displayed even greater band broadening. The predominance of sodium nitrate in the sample is consistent with the known composition of the simulant, which was prepared with sodium nitrate at almost 90% of the sample's dry weight. Sodium nitrate is also a strong Raman scatterer, so its spectral dominance in this sample is not surprising.

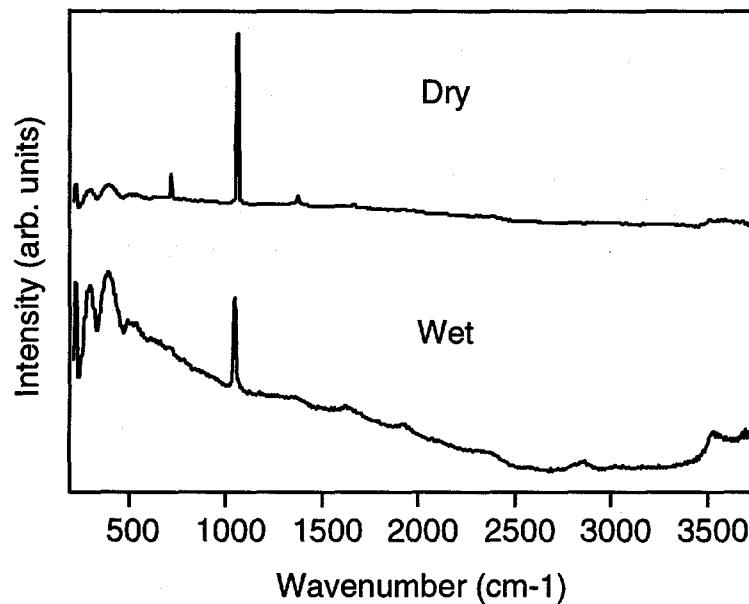


Figure 16. Raman spectra for dry and wet BY samples collected with the near IR echelle spectrograph.

Very different results were obtained for the wet BY sample. Only a single band was observed at a new position (1050cm^{-1}) with a much lower intensity relative to the background. Comparison with an aqueous nitrate standard showed that the band in the Raman spectrum corresponds to that of the nitrate ion (see Figure 17). These results are interesting in that no signal was obtained for solid material in the sample. This ability to discriminate between dissolved and solid materials can provide useful information about sample composition.

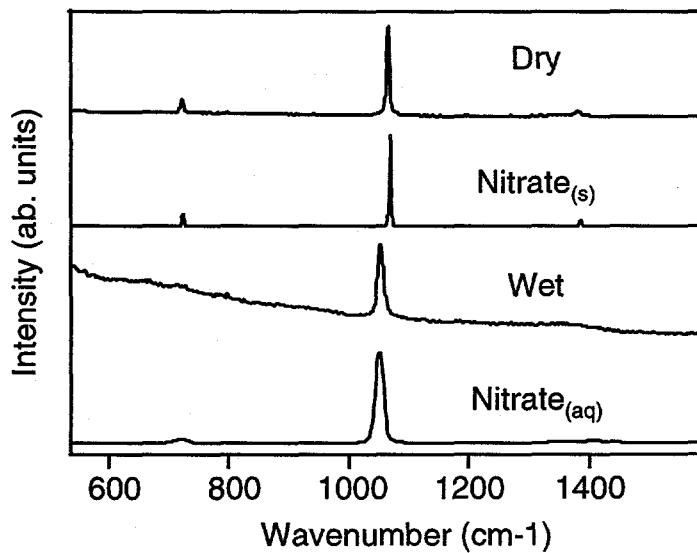


Figure 17. Raman spectra of BY samples and nitrates collected with the near IR echelle spectrograph.

With green illumination, similar trends in the Raman spectra were observed for the BY sample. Figure 18 shows a predominant nitrate ion band in the wet sample spectrum at 1050cm^{-1} , 20cm^{-1} below the major band in the dry spectrum (1070cm^{-1} , sodium nitrate). Close inspection also reveals a small band at the 1070cm^{-1} position in the wet spectrum for the solid sodium nitrate component of the sludge. With 514.5nm excitation, the background fluorescence for the wet sample was significant, limiting the detectability of the nitrate ion (integration time was confined to just 5sec).

The dry sample spectrum collected with green excitation was comparable to the one obtained with the near IR Raman system, indicating solely the presence of solid sodium nitrate. The major difference was that a comparable signal-to-noise ratio was achieved with the green system in about 25% of the time of the near IR system, with the trade-off of reduced spectral resolution and range.

Sample TPLANT-18

Like the BY sample, the TPlant sample gave very different results under wet and dry conditions. When dry, the sample charred under near-infrared laser illumination and no characteristic Raman bands were observed (see Figure 19). Using lower powers (25mW) and the pulsed alexandrite laser instead of the CW krypton laser did not improve spectral quality. When the sample was still wet, however, a strong Raman spectrum was collected. The wet TPlant spectrum is more complex than the BY spectra, with several prominent features in the oxyanion and cyanide spectral regions.

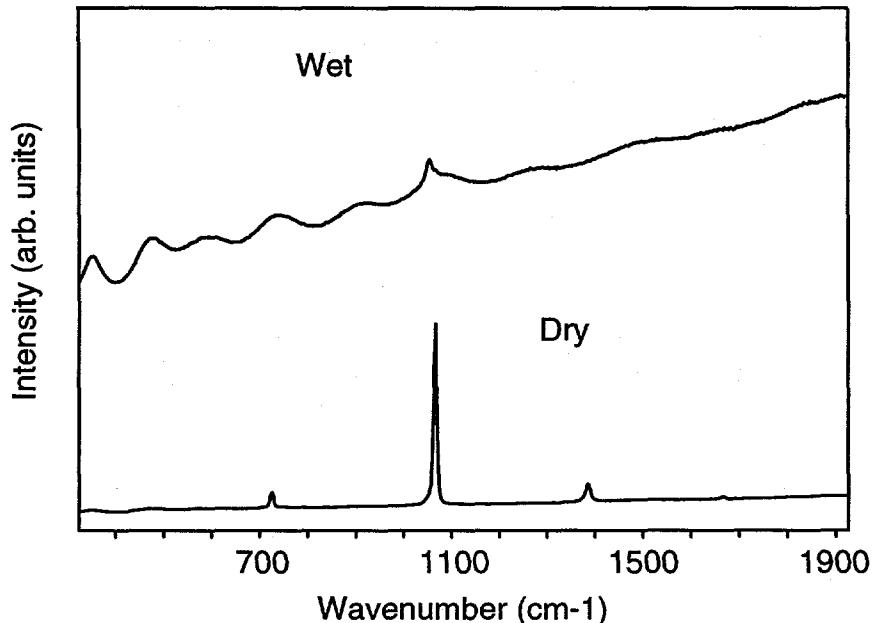


Figure 18. Raman spectra of dry and wet BY samples collected with the green Raman system.

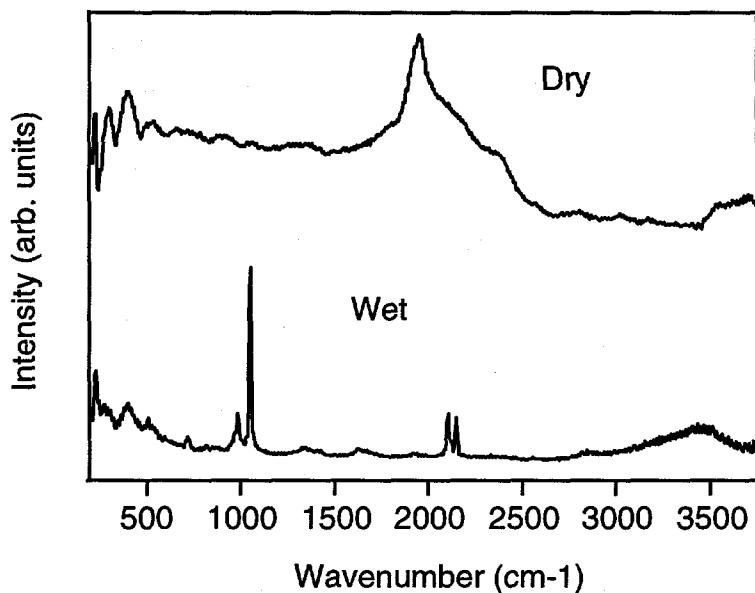


Figure 19. Raman spectra of dry and wet TPlant samples collected with the near IR echelle spectrograph.

Figure 20 focuses on the oxyanion region of the Raman spectrum for the wet TPlant sample. The predominant peak in the spectrum was again at 1050cm^{-1} (nitrate ion). There are other, more subtle features in the spectrum, however. For example, the peak at 1328cm^{-1} corresponds to the strongest band for aqueous nitrite ion (the broad band in the 1620cm^{-1} region is from water). There are also bands in the 990cm^{-1} region which can be attributed to sulfate species. Figure 21 shows more closely this region of the spectrum. The major peak in the triplet at 982cm^{-1} can be assigned to aqueous sulfate ion whereas the shoulder at higher wavenumber (994cm^{-1}) could be from a hydrated, solid sulfate. The remaining peaks in Figure 20 correspond to nitrate.

In the cyanide region of the wet TPlant spectrum are three bands at 2066 , 2105 , and 2144cm^{-1} . Figure 21 compares the sample spectrum with aqueous cyanide, ferrocyanide, and ferricyanide spectra. Clearly, there is no direct spectral match except perhaps for a very weak contribution of aqueous ferrocyanide (there appears to be a weak shoulder on the 2105cm^{-1} band which may correspond to the 2093cm^{-1} ferrocyanide band). There was also no correlation with dry, solid cyanide, ferrocyanide, and ferricyanide spectra in the catalog (sodium and potassium salts of iron cyanides produce sharp multiplets in this region). These results indicate that other, less common cyanide species may be present in this sample.

Using the green Raman system, the charring encountered with near IR excitation on the dry TPlant sample was not observed. In the oxyanion region of Figure 23, there is a transition from nitrate ion predominance in the wet sample to solid nitrate predominance in the dry sample, although nitrate ion is still visible in the "dry" spectrum. In the "wet" spectrum, the cyanide bands are nearly as intense as the nitrate peak. The positions and relative intensities of the two cyanide bands do not change with water content (or with sample positioning) which suggests that the two bands arise from a single species which is very hygroscopic.

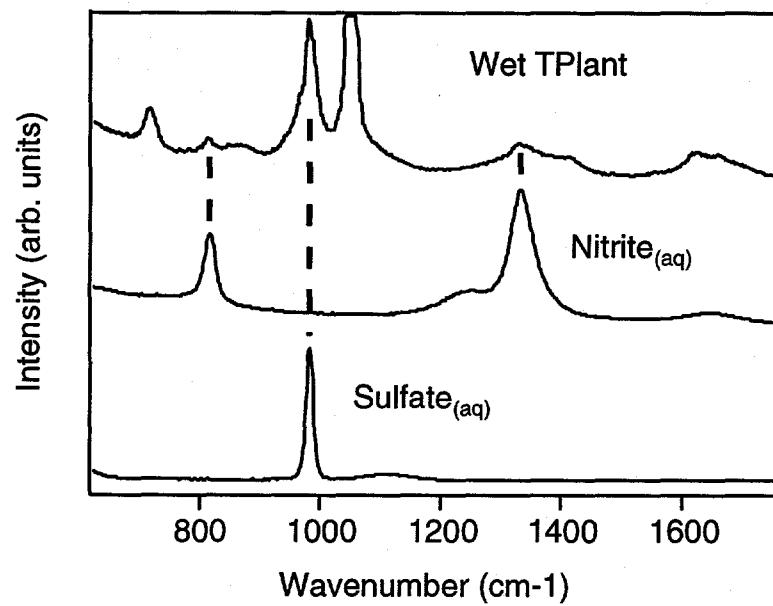


Figure 20. Raman spectrum of wet TPlant sample and inorganic ions collected with the near IR echelle spectrograph.

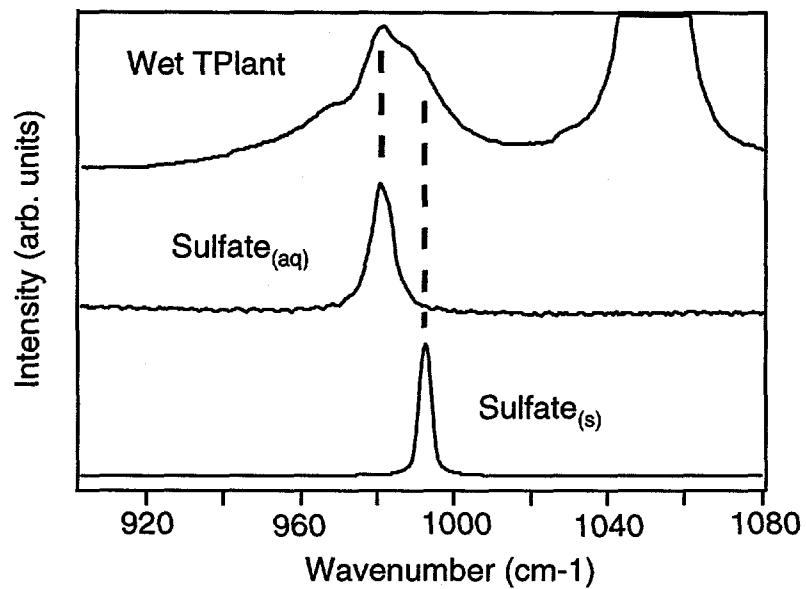


Figure 21. Sulfate region of the wet TPlant Raman spectrum.

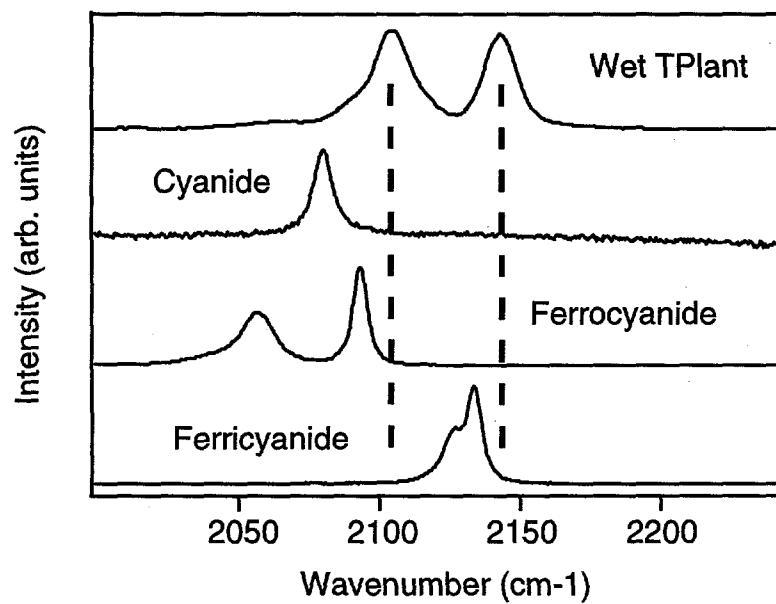


Figure 22. Cyanide region of the wet TPlant Raman spectrum and aqueous cyanide species.

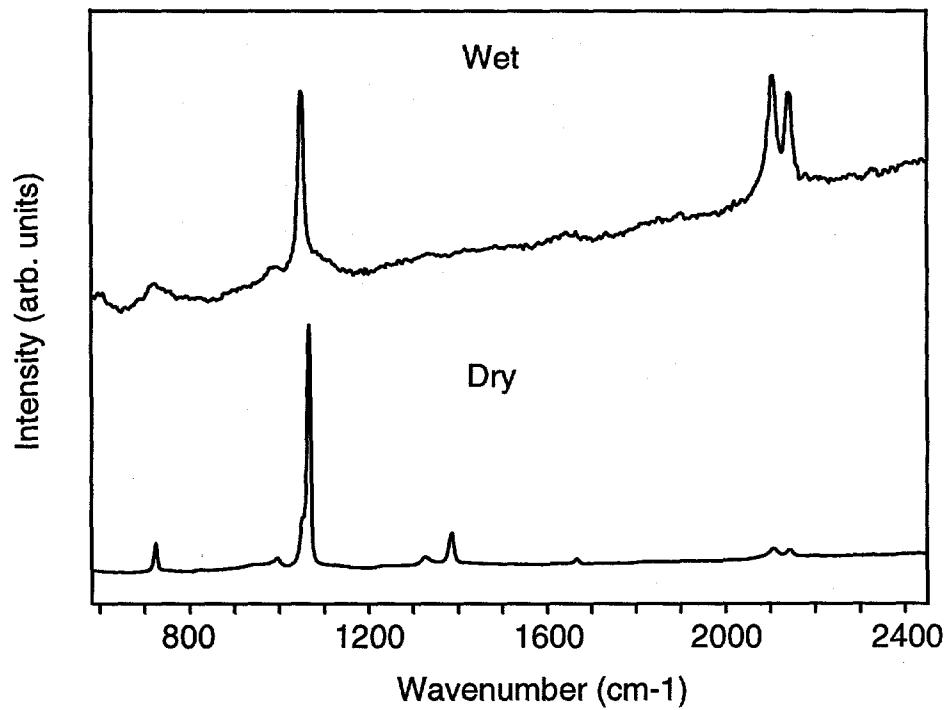


Figure 23. Raman spectra of the TPlant sample collected with the green Raman system.

Overall, the results with the green Raman system showed little qualitative difference from the near-infrared echelle spectra. The most notable exception was that the Czerny-Turner spectrograph could not resolve the three peaks in the 990cm^{-1} sulfate region as well as the echelle spectrograph.

Sample INFARM-1B

The species detected by Raman in the Infarm sample were nearly the same as those identified in the TPlant sample. Figure 24 is the salient portion of the spectrum collected with the echelle spectrograph. Again, the sample was "wet" because the dry sample was degraded under near IR illumination.

In the oxyanion region of the Raman spectrum, both nitrate ion (1050cm^{-1}) and sodium nitrate (725 , 1070 , 1386 , and 1670cm^{-1}) are observed along with lower levels of nitrite (815 , 1328cm^{-1}). Sulfate bands are also prominent at 453 , 619 , 635 , and 994cm^{-1} . The strong peak at 994cm^{-1} corresponds to the longer wavenumber shoulder on the 982cm^{-1} peak in the wet TPlant sample. The 994cm^{-1} peak is assigned to a solid sulfate species (probably hydrated, but not sulfate ion). This assignment is supported by the fact that this sample was drier than the TPlant sample and was formulated with more sulfate. The position of the band is closer to solid sodium sulfate, dibasic (993cm^{-1}) than either potassium sulfate, dibasic (984cm^{-1}) or ammonium sulfate (987cm^{-1}). The weaker sulfate bands do not match precisely the sodium sulfate peaks, however, perhaps due to broadening and shifting in the wet state.

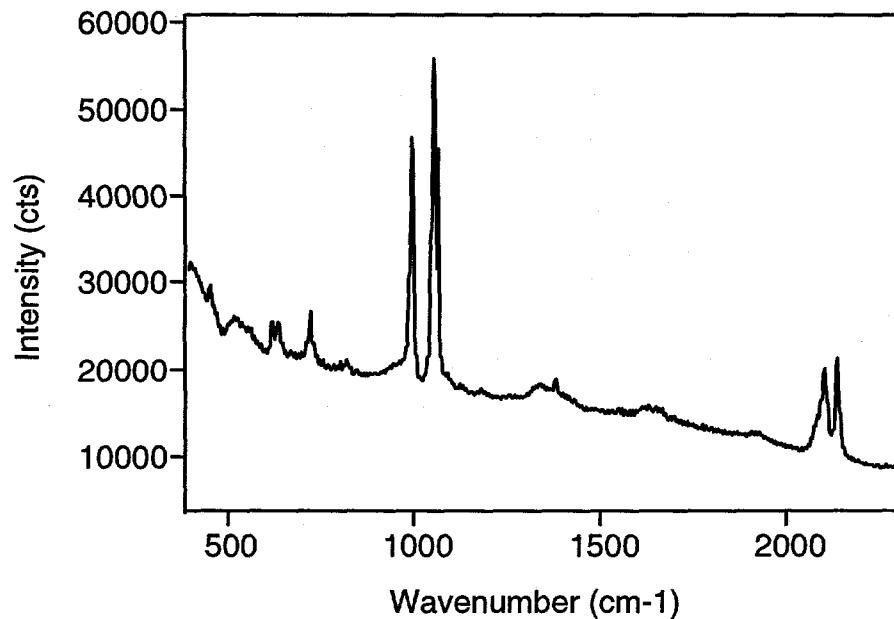


Figure 24. Raman spectrum of wet Infarm sample collected with the near IR echelle spectrograph.

There are two notable differences in the cyanide region of the Raman spectrum for the Infarm sample compared to the TPlant sample: (1) a shoulder at 2081cm^{-1} was clearly visible, and (2) the broad band at 2066cm^{-1} was not present. The shoulder is assigned to cyanide ion.

Results obtained for the Infarm sample using the green, Czerny-Turner Raman system are presented in Figure 25. Considerable fluorescence was observed for the wet sample. A much better spectrum was collected after the sample was air-dried. The inhomogeneity of the sample is clearly evident in that there is appreciably less sulfate and more cyanide (relative to nitrate) compared to Figure 26. The lower resolution of the Czerny-Turner spectrograph also makes it difficult to discern the cyanide band near 2080cm^{-1} .

In summary, the capability for using fiber optic probes to safely collect high quality Raman spectra of Hanford tank simulant samples remote from the spectrograph and operator has been demonstrated. The high resolution of the echelle spectrograph is advantageous for this application because the samples contain multiple components of similar chemical structure. There are also significant spectral changes associated with the degree of sample hydration. Lastly, it is evident that visible and near IR Raman systems can provide complementary characterization of tank samples - with green excitation, fluorescence sometimes interferes with the Raman signal while dry samples often charred under near-infrared illumination.

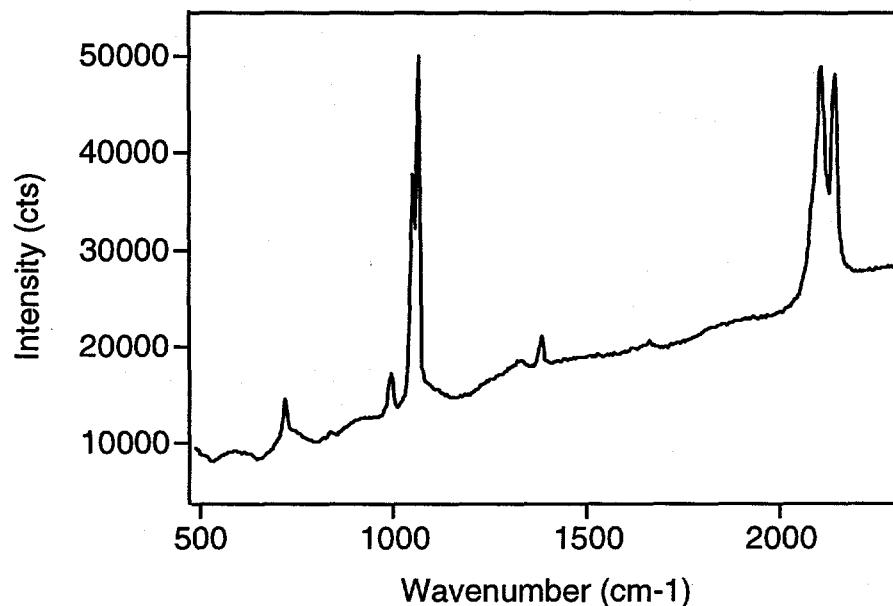


Figure 25. Raman spectrum of dry Infarm sample collected with the green Raman system.

2.7.1.2 Oak Ridge Tanks

It was initially planned that an off-site, follow-up demonstration to the Hanford simulant testing would be conducted in hot cells at Hanford. Logistical difficulties led to the tests being conducted in an Oak Ridge National Laboratory (ORNL) radiation facility instead. The near IR Raman system with 785nm diode laser was shipped to the ORNL site and set up in a room adjacent to the laboratory containing the samples. An end-viewing fiber optic Raman probe ran from the main instrument into a special, light-tight sample holder in the sample room. All samples were handled by ORNL personnel trained in working with radioactive materials, although the activity of the samples was known to be low.

The samples tested included 5 sludge samples, 2 liquid supernates, and a clear solid crystal. All samples had been collected previously from waste tanks at ORNL. Results for the sludge samples were somewhat disappointing, as Raman bands were observed in just one of the five samples. In the other cases, a strong fluorescence background was encountered. The background is also evident in Figure 26, which is the spectrum for the one sludge sample showing Raman bands. The two Raman bands weakly visible in the spectrum near 1050cm^{-1} and 1080cm^{-1} can be attributed to nitrate and phosphate species, respectively.

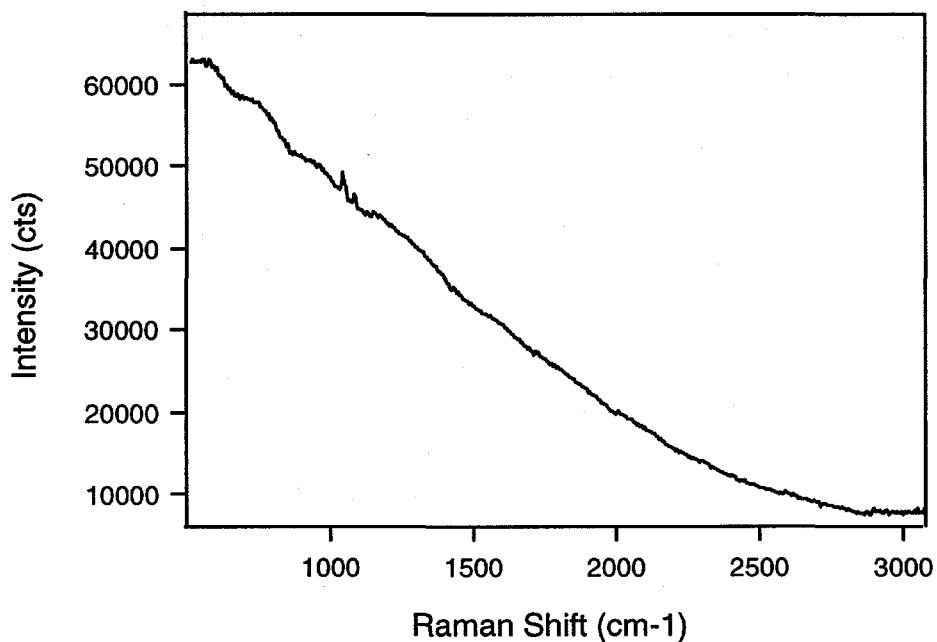


Figure 26. Raman spectrum collected from an ORNL waste tank sludge sample.

Raman bands were easier to detect in the two liquid supernate samples (Figure 27). In the first sample, the predominant species was sulfate detected at 982cm^{-1} . The second Raman band at 1068cm^{-1} we assign to carbonate. Both species have been commonly found when ORNL supernates are analyzed by laboratory ion chromatographic methods. In addition to sulfate and carbonate, nitrate is clearly present in the second supernate sample, as indicated by its strong, characteristic band near 1050cm^{-1} . Again, nitrate is a major species found in many ORNL tanks.

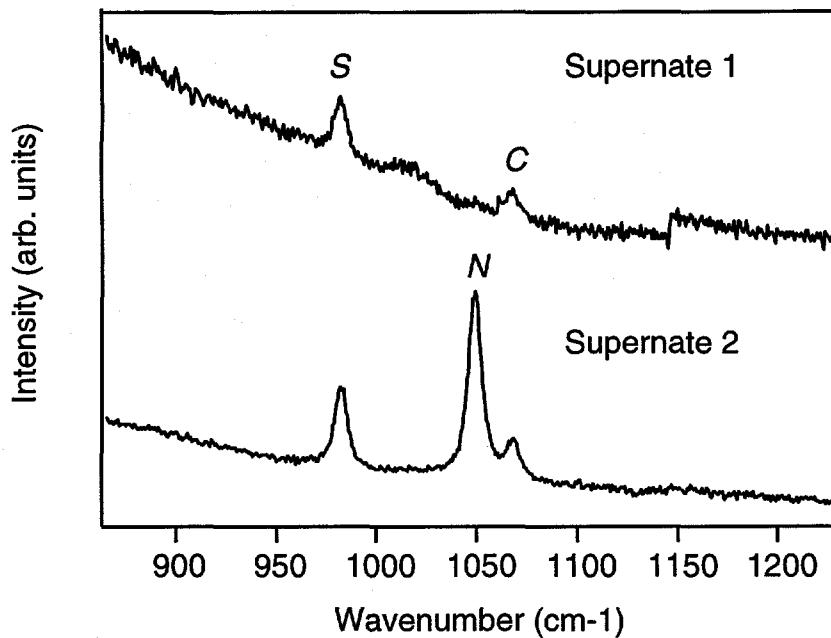


Figure 27. Raman spectra collected from ORNL waste tank supernate samples.
 S = sulfate, N = nitrate, and C = carbonate.

The final sample analyzed was a colorless crystal retrieved from a waste tank. The spectrum is presented in Figure 28. All of the major bands in the spectrum (934 , 412 , 543 , and 998cm^{-1}) are characteristic of solid phosphate. ORNL confirmed that independent analysis had also determined the crystal to be a phosphate.

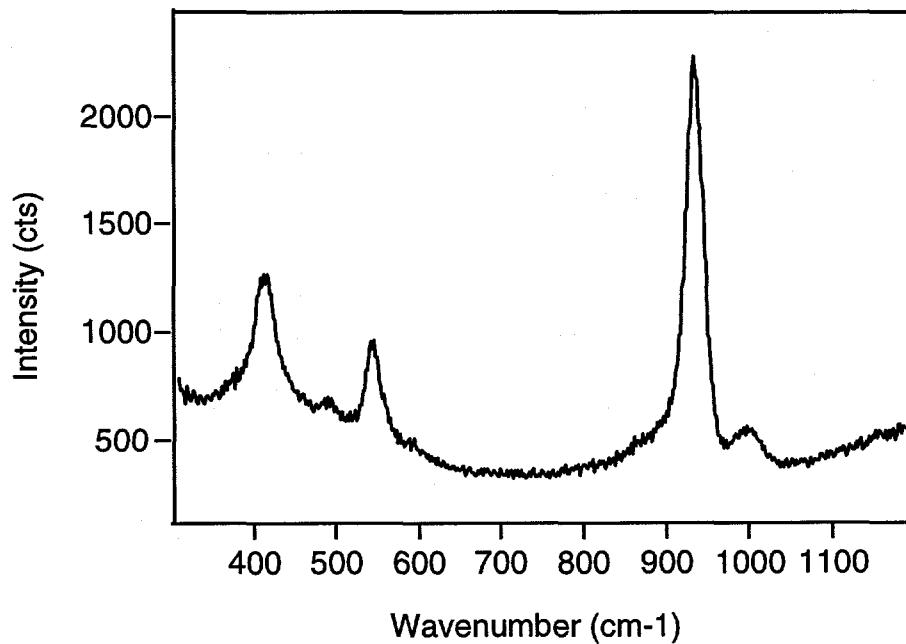


Figure 28. Raman spectrum collected from a waste tank solid.

2.7.2 Cone Penetrometer Raman

The second major DOE application considered in this program was identification of NonAqueous Phase Liquids (NAPLs) present in the subsurface. Dense NAPLs (DNAPLs) such as trichloroethylene (TCE) and perchloroethylene (PCE) have been found at several DOE sites and are a large concern. Among the most notable locations is the Savannah River Site (SRS). DNAPLs are often difficult to locate and identify, so we conducted a study to determine if Raman spectroscopy could be used in a cone penetrometer to detect DNAPLs *in situ*.

2.7.2.1 Laboratory Feasibility Studies

We first performed a study of Raman detectability in soils from SRS at different excitation wavelengths with the goal of determining the best operating wavelength(s) for cone penetrometer deployment. Three clean soils were obtained from SRS. The soils were collected from depths of 23.8, 105.2, and 130.2 ft and were red, gray-green, and light brown in color. Samples of each soil alone and spiked to saturation with PCE or TCE were excited with 35mW laser power at the following wavelengths: 364, 407, 521, 647, and 752nm. An ISA HR320 spectrograph outfitted with a CCD camera detector was used to collect the Raman spectra.

The results of the wavelength study using mid-visible wavelength excitation (521 and 647nm) were not encouraging - large fluorescence backgrounds were collected from all three soils in 1sec or less and Raman peaks could not be observed for PCE or TCE, even when spiked to saturation levels. Typical results are shown in Figure 29 and are compared with 752nm near IR excitation, which produces a significantly lower background.

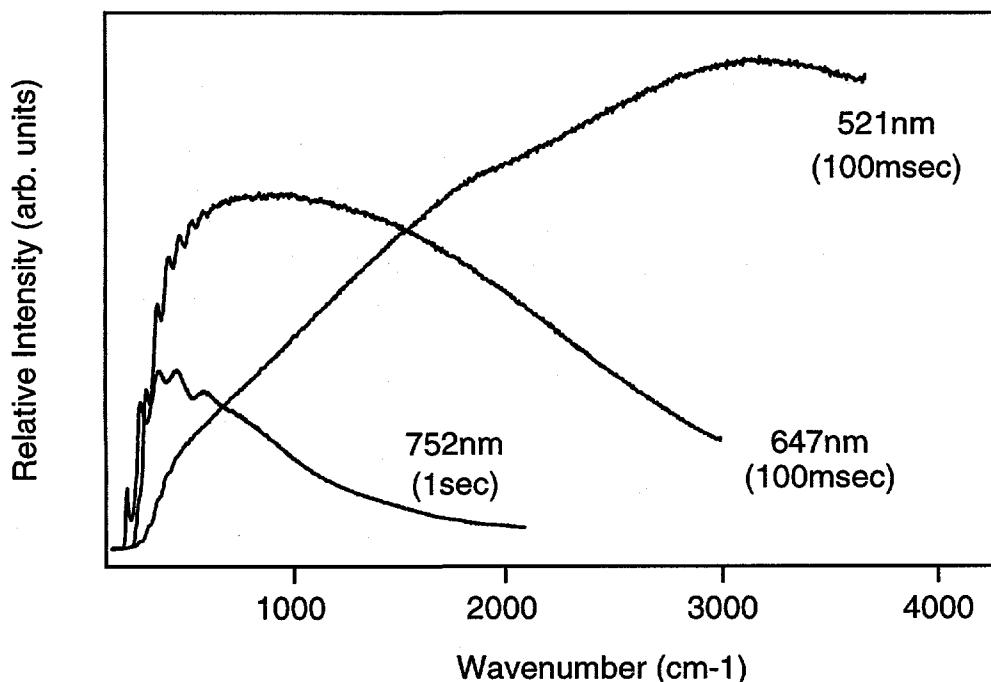


Figure 29. Comparative soil fluorescence backgrounds produced at three excitation wavelengths.

With 752nm excitation, PCE and TCE spectra could be observed in 10sec or less in all three soils. Figure 30 shows results obtained for TCE saturated SRS soil at 105.2 ft. The main TCE band near 635cm^{-1} is plainly visible and weaker bands near 780cm^{-1} and 840cm^{-1} are also detectable.

Excitation at the lower visible wavelengths (364nm and 407nm) gave somewhat better results overall. Figures 31 and 32 present the results for 364nm excitation. In contrast to 752nm excitation, the longer wavenumber PCE band at 1570cm^{-1} was detected more easily than the lower wavenumber band near 450cm^{-1} band. This is because the CCD detector is more sensitive at the longer wavenumber position. Another difference was that the 23.8 ft soil produced the highest backgrounds, making it difficult to detect the 450cm^{-1} band in that soil. With 752nm excitation, the 105.2 ft soil produced the strongest background.

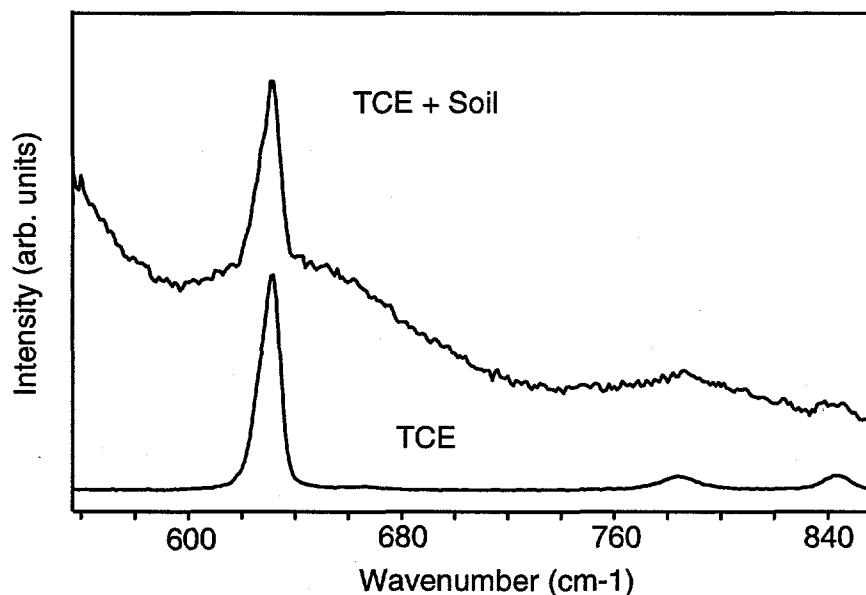


Figure 30. Spectra for 105.2ft SRS soil and TCE saturated soil collected with a 752nm Raman probe.

Based on the results of these tests, we conclude that lower visible and near IR excitation wavelengths are most suitable for detecting contaminants in soils. The best choice of laser wavelength is dependent on soil type. However, for field implementation in a cone penetrometer, the lack of a suitable laser emitting at lower visible wavelengths pointed to the use of a near IR laser for the SRS evaluation. Furthermore, it was expected that the use of a 785nm diode laser would produce even less background than the 752nm laser used in the laboratory studies.

2.7.2.2 Cone Penetrometer Field Evaluation

A one week field evaluation was conducted at DOE's Savannah River Site in February, 1998. Weather conditions were mild, but rainy after the first day of testing. The near IR echelle Raman system was set up in the DOE cone penetrometer truck. A 75 meter, duplex fiber optic cable was "pre-strung" through the penetrometer rods. One end of the cable was connected to the laser and spectrograph. The other end was coupled to the fibers of a side-viewing Raman probe like the

one shown in Figure 8. The probe was held inside the first section of penetrometer rod behind the tip and "looked out" through a sapphire window in the side of the rod (see Figure 10).

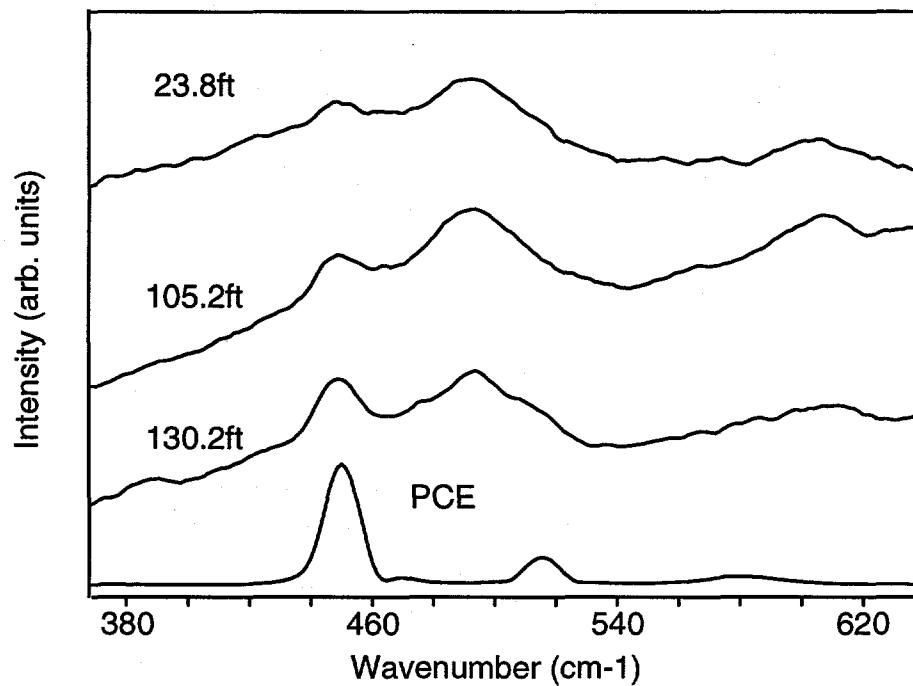


Figure 31. Raman spectra for PCE saturated SRS soils collected with 364nm excitation - low wavenumber region.

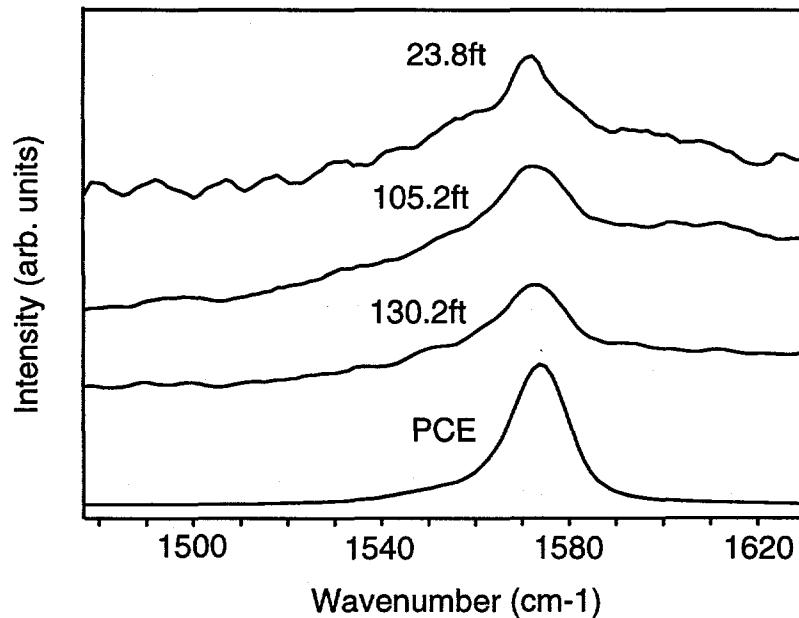


Figure 32. Raman spectra for PCE saturated SRS soils collected with 364nm excitation - high wavenumber region.

The first test location was a few meters from a groundwater well known to contain PCE DNAPL. During recent drilling operations, free PCE product had been removed from the ground at a depth of about 100 ft. Therefore, the cone was pushed to a depth of 95 ft and Raman measurements were begun. The results obtained between 101 ft and 104 ft are presented in Figure 33 and clearly show the presence of PCE at a depth of 102-103 ft. Strong, characteristic PCE bands at 236cm^{-1} and 448cm^{-1} are observed in the 102.5' spectrum shown in the figure. The PCE band near 1600cm^{-1} is also visible. The spectra also contain Raman peaks from the soil. Consistent with the cone penetrometer's geophysical measurements of soil type, the strong silicate Raman band at 465cm^{-1} disappeared as the cone traveled from sand into the clay layer where the PCE was detected. When the cone pushed through the clay layer into sand again, the silicate band returned. It is notable that the fluorescence background was lower and the Raman bands more pronounced in the field test than in the laboratory tests. We attribute this to the longer operating wavelength in the field (785nm vs. 752nm) and "pooling" of the DNAPL in front of the cone penetrometer window.

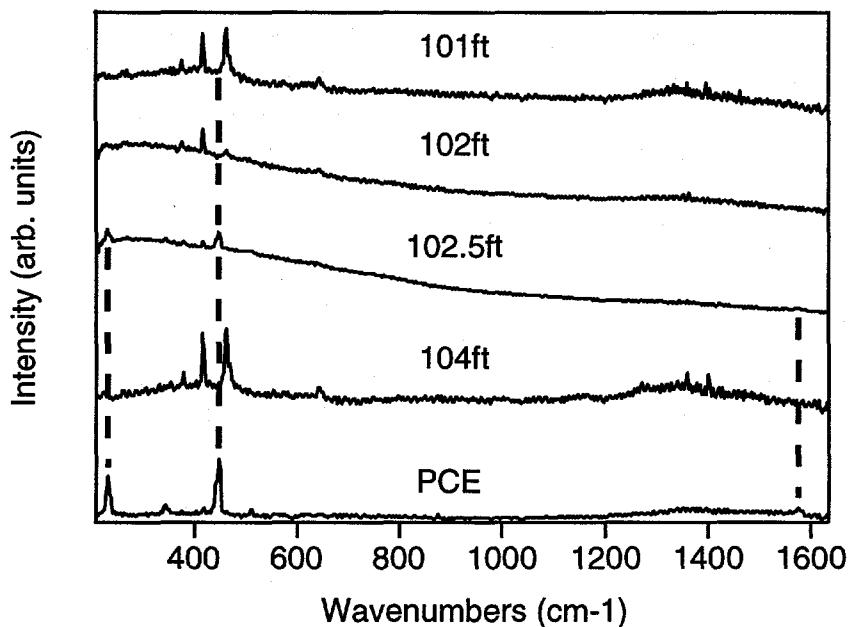


Figure 33. Raman spectra collected *in situ* with the cone penetrometer at SRS.

The cone was pushed in at an adjacent location and comparable results were obtained. When the cone penetrometer truck was moved a significant distance (about 50m) away from the known contamination spot, PCE was not detected. At a second site, also known to be heavily contaminated, PCE was detected at a depth of 28-29 ft. Again, moving about 25 meters away from the source produced "clean" spectra at all depths.

SECTION 3.0

CONCLUSIONS

A portable echelle Raman spectrograph prototype and fiber optic sampling probes have been developed in support of DOE waste site characterization. Using the latest developments in solid state detector and laser technologies, the new instrument represents a large reduction in size, weight, and energy consumption compared to conventional laboratory Raman instruments. With no moving parts, the instrument is rugged and well suited for field deployment. Indeed, the Raman system was used in two field evaluations without any problems.

The near IR echelle spectrograph developed in this program is an efficient device that combines high resolution (ca. 0.3cm^{-1} per detector element) and full Raman spectral coverage in a fixed optical configuration. At f/3 and with all antireflection coated optics, optical throughput of the echelle spectrograph is high. Using a small but powerful diode laser and a fiber optic probe, complete Raman spectra can be collected for parts-per-million level contaminants in water in 10 minutes. The Raman signal is linear with respect to concentration.

Fiber optic probes employing distal optical filtering and a 180° Raman backscattering geometry have also been developed to meet specific sensing needs. These probes afford both flexible and safe Raman sampling remote from the operator. The basic design of the probe is a cylindrical "end-viewing" configuration that provides a point-and-shoot analysis capability. This probe can be used to safely analyze the contents of waste bottles, sample vials, and other transparent containers without the need to open them. To facilitate the identification of unknown chemicals in these situations, a database of 200 Raman spectra has been compiled. All of the compounds in the catalog are contaminants which have been found at DOE sites. The Raman spectra are archived in an electronic format compatible with powerful, commercial spectral search routines.

A second fiber optic probe has been assembled in a side-viewing configuration. This configuration is useful in situations where the probe is being "pushed" (e.g., in a hazardous waste tank or underground). In the course of this program, we investigated the potential to use Raman spectroscopy in both of these applications. Laboratory testing with Hanford waste tank simulants and a field evaluation conducted in a radiation facility at ORNL with real samples has demonstrated that performing waste tank analysis with near IR Raman spectroscopy is feasible. Exposing the fiber optic probe to gamma radiation at and above the levels found in most tanks had no effect on performance, suggesting that *in situ* Raman spectroscopy in radioactive waste tanks should also be feasible. In a second field evaluation at SRS, we were able to positively identify PCE DNAPL in the subsurface at two different "spill" sites. Deployed in a cone penetrometer, the PCE was detected only at depths from which SRS personnel had previously collected DNAPL. At near IR wavelengths, the soil background was advantageously low and false positive responses were not observed at other depths. The results at SRS clearly demonstrate that near IR Raman spectroscopy can be used with a cone penetrometer to detect and identify DNAPLs in the subsurface.

Lastly, a custom computer software package and operations manual have been written for the instrument. The software operates in a user-friendly Windows® environment and performs all the functions necessary to produce intensity corrected, wavelength calibrated Raman spectra.

SECTION 4.0

REFERENCES

1. M.M. Carrabba and R.D. Rauh, "Apparatus for Measuring Raman Spectra Over Optical Fibers," U.S. Patent 5,112,127 (May 12, 1992).
2. M.M. Carrabba, K.M. Spencer, R.B. Edmonds, R.D. Rauh, and J.W. Haas III, "Spectroelectrochemical Technologies and Instrumentation for Environmental and Process Monitoring," SPIE Environmental and Process Monitoring Technologies, Vol 1637, 82-89 (1992).

APPENDIX A

Raman Spectral Catalog

Compound Listing

Library File Name(*.spc)	Compound	Wavelength of Excitation (nm)	Laser Power (mW)	Integration Time (s)	Original File Name(*.spc)
RLIBs001	Benzene	752	64	120	95342004
RLIBs002	Chlorobenzene	752	68	120	95346003
RLIBs003	m - Cresol	752	68	120	95346004
RLIBs004	o - Cresol	752	68	120	95346005
RLIBs005	p - Cresol	752	68	120	95347001
RLIBs006	1,2 - Dichlorobenzene	752	68	120	95349001
RLIBs007	1,4 - Dichlorobenzene	752	68	120	95349002
RLIBs008	2,4 - Dimethyl Phenol	752	68	120	96005004
RLIBs009	Ethylbenzene	752	68	120	96005006
RLIBs010	Pentachlorophenol	752	68	120	96015006
RLIBs011	Phenol	752	68	120	96015007
RLIBs012	Styrene	752	68	120	96016004
RLIBs013	Bromobenzene	785	50	120	brobenz
RLIBs014	2 - Chlorophenol	785	95	30	96326008
RLIBs015	Divinylbenzene	785	50	60	dvb
RLIBs016	1,3 - Dichlorobenzene	785	98	60	96087004
RLIBs017	Toluene	785	98	120	96089003
RLIBs018	m - Xylene	785	98	60	96089004
RLIBs019	p - Xylene	785	98	60	96089005
RLIBs020	o - Xylene	785	110	60	96094004
RLIBs021	Methyl Benzylamine	785	50	60	mbenz
RLIBs022	Benzyl Alcohol	785	120	5	96122007
RLIBs023	Benzaldehyde	785	120	3	96122008
RLIBs024	Benzoic Acid	785	50	60	Benzoica
RLIBs025	Sodium Benzoate	785	50	60	nabzoate
RLIBs026	1,2 - Dichloroethane	785	96	60	96085004
RLIBs027	cis - 1,2 - Dichloroethylene	785	96	60	96085005
RLIBs028	Dichloromethane	785	96	30	96085006
RLIBs029	1,2 Dichloropropane	785	96	60	96085007
RLIBs030	Hexachloroethane	785	96	60	96085009
RLIBs031	1,1,1,2 - Tetrachloroethane	785	96	60	96085010
RLIBs032	1,1,2,2 - Tetrachloroethane	785	96	60	96086003
RLIBs033	Tetrachloroethylene	785	96	40	96086004
RLIBs034	1,1,1 Trichloroethane	785	96	60	96086005
RLIBs035	1,1,2 Trichloroethane	785	96	60	96086006
RLIBs036	Trichloroethylene	785	98	60	96087005
RLIBs037	Carbon Tetrachloride	785	110	10	96094005
RLIBs038	Chloroform	785	110	15	96094006
RLIBs039	1,1 Dichloroethane	785	110	15	96094007
RLIBs040	1,2 - Transdichloroethylene	785	110	45	96094014
RLIBs041	Zinc Sulfate	785	116	30	96128004
RLIBs042	Ammonium Sulfate	752	110	240	95340001
RLIBs043	Magnesium Nitrate	752	110	120	95341004
RLIBs044	Manganese Nitrate	752	64	120	95341005

RLIBs045	Potassium Cyanide	752	64	120	95341006
RLIBs046	Potassium Ferrocyanide	752	64	120	95341007
RLIBs047	Potassium Nitrate	752	64	120	95341008
RLIBs048	Potassium Sulfate	752	64	120	95341009
RLIBs049	Sodium Cyanide	752	64	120	95341010
RLIBs050	Sodium Ferrocyanide	752	64	120	95341011
RLIBs051	Sodium Nitrate	752	64	120	95341014
RLIBs052	Sodium Phosphate Tribasic	752	64	120	95342001
RLIBs053	Sodium Silicate	752	64	120	95342002
RLIBs054	Sodium Sulfate	752	64	120	95342003
RLIBs055	Potassium Ferricyanide	752	64	120	96004004
RLIBs056	Cesium Nitrate	785	122	120	96051012
RLIBs057	Chromium(III) Nitrate	785	122	120	96051016
RLIBs058	Sodium Aluminate	785	122	120	96051017
RLIBs059	Ammonium Hexafluorosilicate	785	122	120	96051020
RLIBs060	Water	785	50	60	water
RLIBs061	Phosphorus Oxychloride	785	120	5	96081004
RLIBs062	Silver Nitrate	785	110	45	96094010
RLIBs063	Bismuth Phosphate	514	35	10	96094012
RLIBs064	Strontium Nitrate	785	120	10	96094013
RLIBs065	Sulfur	752	64	120	95352002
RLIBs066	Calcium Nitrate	785	118	60	96113002
RLIBs067	Ferric Nitrate	785	121	60	96117003
RLIBs068	Ammonium Tetrafluoroborate	785	116	60	96128003
RLIBs069	Bismuth Nitrate	785	116	30	96128005
RLIBs070	Sodium Phosphate Monobasic	785	118	60	96158001
RLIBs071	Potassium Phosphate Dibasic	785	118	60	96158002
RLIBs072	Sodium Phosphate Dibasic	785	121	60	96159004
RLIBs073	Potassium Metabisulfite	785	120	60	96162003
RLIBs074	Sodium Sulfite	785	118	20	96163002
RLIBs075	Potassium Sulfite	785	118	60	96163003
RLIBs076	NaHSO3 + Na2S2O5	785	125	60	96179001
RLIBs077	Sodium Hydrosulfite	785	125	60	96179002
RLIBs078	Aluminum Oxide	785	50	30	aluminab
RLIBs079	Sulfur Dichloride	785	100	60	96277004
RLIBs080	Phosphorus Pentachloride	785	98	60	96278003
RLIBs081	Phosphorus Pentasulfide	785	98	5	96278004
RLIBs082	Potassium Bifluoride	785	98	60	96278005
RLIBs083	Sodium Bifluoride	785	98	60	96278006
RLIBs084	Sulfur Monochloride	785	97	10	96281004
RLIBs085	Phosphorus Trichloride	785	96	15	96282003
RLIBs086	Arsenic(III) Trichloride	785	96	30	96282004
RLIBs087	Sodium Chromate	785	96	30	96282006
RLIBs088	Sodium Hydrogen Carbonate	785	97	120	96284008
RLIBs089	Ammonium Bifluoride	785	98	60	96283004
RLIBs090	Nickel Nitrate	785	95	60	96326003
RLIBs091	Sodium Sulfide	785	97	60	96284006

RLIBs092	Bis - 2 - Ethylhexylphthalate	752	64	120	95342005
RLIBs093	Disodium EDTA	752	68	120	95345001
RLIBs094	Trisodium EDTA	752	68	120	95345002
RLIBs095	Tripotassium EDTA	752	68	120	95346001
RLIBs096	Tetrasodium EDTA	752	68	120	95346002
RLIBs097	Di - n - Butylphthalate	752	68	120	95347002
RLIBs098	Diethyl Phthalate	752	68	120	96004005
RLIBs099	Di - n - Octylphthalate	752	68	120	96005005
RLIBs100	Thionyl Chloride	785	120	15	96081006
RLIBs101	2 - Propanol	785	50	60	propanol
RLIBs102	Ethanol	785	50	60	ethanol
RLIBs103	Dimethyl Phosphite	785	96	60	96082020
RLIBs104	Furan	785	96	60	96082022
RLIBs105	Acetone	785	98	60	96087006
RLIBs106	2 - Butanone	785	98	60	96087007
RLIBs107	Acetonitrile	785	98	60	96089006
RLIBs108	Triethanolamine	785	120	120	96108005
RLIBs109	Triethyl Phosphite	785	120	60	96120001
RLIBs110	Iso - Octane	785	120	20	96121003
RLIBs111	Decane	785	120	60	96121004
RLIBs112	Hexanes	785	120	60	96121005
RLIBs113	Pentane	785	120	60	96121006
RLIBs114	Acetic Anhydride	785	120	60	96121007
RLIBs115	Acetyl Chloride	785	120	15	96121010
RLIBs116	Butyl Acetate	785	120	60	96122005
RLIBs117	Tetrahydrofuran	785	120	20	96122009
RLIBs118	Cyclohexanone	785	120	20	96122010
RLIBs119	12 Crown 4	785	116	60	96128006
RLIBs120	18 Crown 6	785	116	60	96128007
RLIBs121	Acetaldehyde	785	115	60	96129004
RLIBs122	Ethylenediamine	785	115	60	96129005
RLIBs123	Tributyl Phosphine	785	115	60	96129006
RLIBs124	1,1,3,3 Tetramethylurea	785	115	15	96129007
RLIBs125	Dimethyl Sulfoxide	785	115	5	96129008
RLIBs126	Tributyl Phosphate	785	118	60	96163001
RLIBs127	Trimethyl Phosphite	785	80	60	96235005
RLIBs128	2 - Methyl Naphthalene	752	96	120	96015005
RLIBs129	Methyl Cyclohexanone	785	50	60	mcychex
RLIBs130	Naphthalene	785	115	10	96107003
RLIBs131	3,3 - Dimethyl - 2 - Butanol	785	120	30	96108004
RLIBs132	Diisopropylamine	785	120	60	96108006
RLIBs133	Phenolphthalein	785	50	60	phenol
RLIBs134	N,N Dimethylformamide	785	120	30	96121009
RLIBs135	N,N Dimethylacetamide	785	120	15	96122003
RLIBs136	Dimethyl Adipate	785	120	60	96122004
RLIBs137	Dimethyl Carbonate	785	120	20	96122006
RLIBs138	1,1 Dimethylhydrazine	785	120	60	96123003

RLIBs139	Triphosgene	785	115	60	96129003
RLIBs140	Diethyl Phosphite	785	80	60	96235006
RLIBs141	Dimethyl Methyl Phosphonate	785	80	60	96235007
RLIBs142	1 - Methyl Naphthalene	785	96	120	96015004
RLIBs143	3 - Hydroxy - 1 - Methylpiperidene	785	100	60	96277003
RLIBs144	Propylene Carbonate	785	50	60	propcarb
RLIBs145	Triethylamine Hydrochloride	785	98	60	96278002
RLIBs146	Lactic Acid	785	50	60	lactic
RLIBs147	2 - Chloroethanol	785	98	60	96278008
RLIBs148	2 - Diethylamino Ethanol	785	97	60	96281001
RLIBs149	Pyridine	785	96	30	96282005
RLIBs150	Methyl Sulfoxide	785	50	60	methsoxi
RLIBs151	Isoprene	785	50	60	isoprene
RLIBs152	50/50 Acetonitrile /Toluene	785	115	10	96107001
RLIBs153	alpha - Pinene	785	50	60	pinene
RLIBs154	Fluorene	785	50	60	fluorene
RLIBs155	Cyclooctane	785	95	30	96326009
RLIBs156	2 - Diisopropylaminoethanol	785	95	120	96326001
RLIBs157	Trimethyl Borate	785	95	30	96326010
RLIBs158	2 - Bromothiophene	785	50	60	BTP
RLIBs159	Propylene Oxide	785	50	60	po
RLIBs160	Vinyl Acetate	785	50	60	va
RLIBs161	2,2',3,3',4,5',6,6' - Octachlorobiphenyl	785	122	60	96052007
RLIBs162	beta - BHC	785	122	60	96052008
RLIBs163	alpha - BHC	785	122	60	96052011
RLIBs164	Manzeb	785	120	30	96080010
RLIBs165	Maneb	785	120	60	96080011
RLIBs166	Trifluralin	785	120	60	96080012
RLIBs167	Lindane	785	120	60	96081009
RLIBs168	Dieldrin	785	96	60	96082004
RLIBs169	2,4 D Acid	785	96	60	96082005
RLIBs170	2,2',3,4' - Tetrachlorobiphenyl	785	96	60	96082006
RLIBs171	Chlordimeform	785	96	60	96082007
RLIBs172	Captafol	785	96	60	96082009
RLIBs173	Linuron	785	96	60	96082010
RLIBs174	Benomyl	785	96	20	96082011
RLIBs175	Chlorthalonil	785	96	60	96082012
RLIBs176	Atrazine	785	96	60	96082013
RLIBs177	Cyanazine	785	96	60	96082014
RLIBs178	2,2',3,4',5',6 - Hexachlorobiphenyl	785	100	60	96095001
RLIBs179	Captan	785	120	60	96102003
RLIBs180	Folpet	785	120	60	96102004
RLIBs181	Metribuzin	785	120	60	96102005
RLIBs182	Butylate	785	118	60	96109001
RLIBs183	delta - BHC	785	80	60	96235008
RLIBs184	Silvex	785	97	60	96284004
RLIBs185	Zineb	785	98	30	96283003

RLIBs186	Teflon	785	115	180	96129009
RLIBs187	Polyvinylidene fluoride	785	115	60	96130003
RLIBs188	Polyvinyl Chloride	785	115	5	96130004
RLIBs189	Polyethylene Oxide	785	115	60	96130005
RLIBs190	Polyacrylic Acid	785	115	300	96130006
RLIBs191	Polyvinylpyrrolidone	785	115	60	96130007
RLIBs192	Polymethyl Methacrylate	785	115	60	96134003
RLIBs193	Poly Caprolactone	785	115	60	96134003
RLIBs194	Polyethylene	785	115	120	96134006
RLIBs195	Polyvinyl Alcohol	785	115	120	96134007
RLIBs196	Poly(4 - vinylpyridine)	785	115	30	96135003
RLIBs197	Polystyrene Chloromethylated	785	115	30	96135004
RLIBs198	Polyethylene Terephthalate	785	115	30	96135005
RLIBs199	Polyethylene Glycol	785	115	120	96135006
RLIBs200	Polystyrene	785	80	60	96235004

**INSTRUCTION MANUAL FOR THE EIC ECHELLE RAMAN
SPECTROGRAPH SYSTEM**

RS2000-1-785

EIC2000-1-785

(February, 1998)

EIC Raman Systems

(A Division of EIC Laboratories, Inc.)

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1. LASER OPERATIONS

CAUTION

The Model RS2000 laser systems are designed to be maintenance free and should not be opened by anyone other than EIC Laboratories, Inc. certified technicians. Opening the unit may result in hazardous radiation exposure. Please contact an EIC Laboratories, Inc. representative for any maintenance or service of the RS2000 system.

LASER SAFETY

The Model RS2000 Raman spectrophotometer system can contain both a SDL, SDL-8530 Wavelength-Stabilized High Power Laser (up to 0.5W at 785 nm) and a Coherent DPSS-523-150 Frequency Doubled, Diode-Pumped Nd:YAG Laser System (up to 150 mW at 532 nm). During normal operation and maintenance the system is designed to be CLASS I.

CAUTION

Use of controls or adjustments or performance of procedures other than those specified herein may result in hazardous laser radiation exposure.

Laser powers up to 0.5W at 785 nm and laser power up to 150 mW at 532 nm could be accessible if the protective housings are removed or the safety interlocks are intentionally defeated and the laser systems are operational. These conditions should exist only during service by factory trained technicians and are outlined below.

Precautions for Safe Operation of RS2000 Raman Spectrophotometer System

Do not under any circumstance remove the protective housing covers.

Do not under any circumstance operate the system with the protective covers removed.

The Model RS2000 laser Raman spectrophotometer complies with "Performance Standards for Laser Products", United States Code of Federal Regulations, 21 CFR 1040.10 and 21 CFR 1040.11. The product falls into Class I, and the appropriate warning labels are attached to the system (Figures 1-3). Prior to initial operation, annually or whenever the product has been exposed to adverse conditions, the user should have a factory trained service person verify the following to maintain compliance:

1. Safety Interlock on the sample chamber is operational.
2. Verify the integrity of the fiber optic cable.
3. Inspect all protective housings for possible adverse wear.
4. Inspect the condition of all protective housing labels.

Source for additional information on laser safety is:

"American National Standard for Safe Use of Lasers" (Z136.1)

American National Standards Institute (ANSI)

11th West 42nd Street

New York, NY 10036

INITIAL SETUP AND INSTALLATION

The Model RS2000 laser systems are designed to be installed only by EIC Laboratories, Inc. certified technicians. Installation by anyone other than EIC Laboratories, Inc. certified technicians may result in hazardous radiation exposure. Please contact an EIC Laboratories, Inc. representative for installation of the RS2000 system.

SYSTEM OPERATIONS

Start-up and Operation

1. PLUG POWER CORD INTO A PROPERLY RATED 110 VOLTAGE OUTLET. (Key switch should be "OFF".)
2. TURN ON THE POWER KEY SWITCH. (The indicator lamp will illuminate and the laser will start in ~15-20 seconds.)
3. LIFT COVER OFF SAMPLE CHAMBER/HOLDER.
4. INSERT SAMPLE INTO SAMPLE HOLDER.
5. REPLACE THE COVER OF THE SAMPLE CHAMBER/HOLDER.
6. ACQUIRE SPECTRUM.
7. LIFT COVER OFF SAMPLE CHAMBER/HOLDER.
8. REMOVE SAMPLE FROM THE SAMPLE HOLDER.
9. REPLACE THE COVER OF THE SAMPLE CHAMBER/HOLDER.
10. REPEAT STEPS 3-9 FOR ADDITIONAL SAMPLES.

Shutdown Procedure

1. TURN THE LASER KEY SWITCH TO THE OFF POSITION.

MAINTENANCE

WARNING: The laser portions of the RS2000 systems are designed to be maintenance free and should not be opened or adjusted by anyone other than EIC Laboratories, Inc. certified technicians. *Caution -* Opening of the laser protective housings may result in exposure to hazardous laser radiation (up to 0.5W) and/or dangerous voltages. Please contact an EIC Laboratories, Inc. representative for any maintenance or service of the laser systems.

No user maintenance of laser system or sample chamber/holder are required by the user. Annually it is recommended that a **factory trained service person** verify the following to maintain compliance with "Performance Standards for Laser Products", United States Code of Federal Regulations, 21 CFR 1040.10 and 21 CFR 1040.11:

1. Safety Interlock on the sample chamber is operational.
2. Verify the integrity of the fiber optic cable.
3. Inspect all protective housings for possible adverse wear.
4. Inspect the condition of all protective housing labels.

TROUBLESHOOTING

If the laser fails to turn on after following the start-up procedures, turn the key switch to "OFF". Then,

1. Check that the power cables and/or circuit breaker are operational.
2. Check the line voltage fuse.

If after checking steps 1 and 2 and the laser output is not present, contact the factory for servicing.

SERVICE

All service is to be conducted by factory trained personnel since laser powers up to 0.5W at 785 nm and laser power up to 150 mW at 532 nm could be accessible if the protective housings are removed or the safety interlocks are intentionally defeated and the laser systems are operational. These conditions should exist only during service by factory trained technicians and are outlined as follows:

1. Green (532 nm) laser output is emitted from the laser head and is present in the fiber interface housing. It would be accessible if that housing was removed from the green laser head during service.
2. Focused green (532 nm) is present in the fiber interface housing. It could be accessible during service if the interface cover was removed and the fiber connector was unscrewed from the coupler.
3. The green (532 nm) fiber output is emitted from the probe at the end of the fiber optic cable and would be present inside the sample chamber. It would be accessible during service if the fiber probe was removed from the probe holder on the chamber or if the chamber cover was removed and its interlock was defeated.
4. Red (785 nm) laser output is emitted from the laser head and is present in the fiber interface housing. It would be accessible if that housing was removed from the green laser head during service.
5. Focused red (785 nm) is present in the fiber interface housing. It could be accessible during service if the interface cover was removed and the fiber connector was unscrewed from the coupler.
6. The red (785 nm) fiber output is emitted from the probe at the end of the fiber optic cable and would be present inside the sample chamber. It would be accessible during service if the fiber probe was removed from the probe holder on the chamber or if the chamber cover was removed and its interlock was defeated.

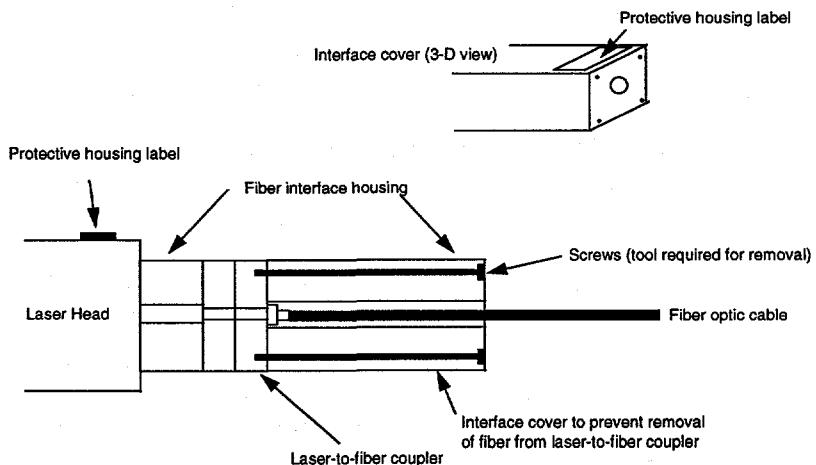


Figure 1. Illustration of the Laser Head Configuration.

DANGER
VISIBLE and/or INVISIBLE LASER
RADIATION WHEN OPEN
AVOID DIRECT EXPOSURE TO BEAM

**Protective Housing Label (Fiber Optic Interface)
DPSS 532 Laser System**

DANGER
VISIBLE and/or INVISIBLE LASER
RADIATION WHEN OPEN
AVOID EYE OR SKIN EXPOSURE TO DIRECT
OR SCATTERED RADIATION

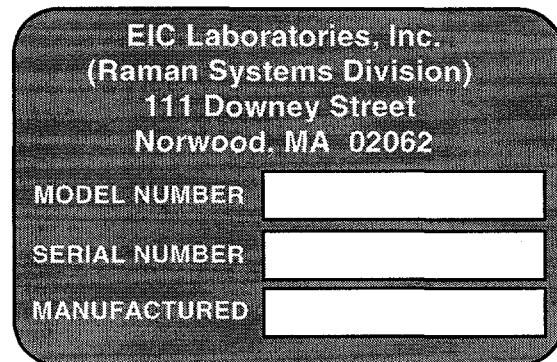
**Protective Housing Label (Fiber Optic Interface)
SDL-8530 Laser System**

DANGER
VISIBLE and/or INVISIBLE LASER
RADIATION WHEN OPEN
AVOID DIRECT EXPOSURE TO BEAM

Protective Housing Label (Probe Cover)

DANGER
VISIBLE and/or INVISIBLE LASER RADIATION
WHEN OPEN and INTERLOCK DEFEATED
AVOID DIRECT EXPOSURE TO BEAM

Protective Housing Label - Class IIIb (Defeat Tool)



Identification Label

PRODUCT CONFORMS TO 21 CFR 1040.10
AND 1040.11 AT DATE OF MANUFACTURE

Certification Label

Figure 2. RS2000 Labels.

2. RAMAN UNIVERSAL SAMPLE HOLDER OPERATIONS

CAUTION

The Model USH2000 Universal Sample is designed to be maintenance free and should not be serviced or installed by anyone other than EIC Laboratories, Inc. certified technicians. Servicing or installation of the unit may result in hazardous radiation exposure. Please contact an EIC Laboratories, Inc. representative for any maintenance or service of the Universal Raman Sample Holder.

LASER SAFETY

The Model USH2000 Universal Sample is designed to be used with the RS2000 Raman spectrophotometer system which can contain both a SDL, SDL-8530 Wavelength-Stabilized High Power Laser (up to 0.5W at 785 nm) and a Coherent DPSS-523-150 Frequency Doubled, Diode-Pumped Nd:YAG Laser System (up to 150 mW at 532 nm). During normal operation and maintenance the system, including the Universal Sample Holder, is designed to be CLASS I.

CAUTION

Use of controls or adjustments or performance of procedures other than those specified herein may result in hazardous laser radiation exposure.

Laser powers up to 0.5W at 785 nm and laser power up to 150mW at 532 nm could be accessible if the protective housings are removed or the safety interlocks are intentionally defeated and the laser systems are operational. These conditions should exist only during service by factory trained technicians and are outlined below.

Precautions for Safe Operation of RS2000 Raman Spectrophotometer System Universal Sample Holder

- Do not under any circumstance remove the protective housing probe cover.
- Do not under any circumstance operate the system with the protective probe cover removed.

The Model RS2000-TEAD Raman spectrophotometer system with the Universal Sample Holder complies with "Performance Standards for Laser Products" United States Code of Federal Regulations, 21 CFR 1040.10 and 21 CFR 1040.11. The product falls into Class I, and the appropriate warning labels are attached to the Universal Sample Holder (Figure A). Prior to initial operation, quarterly or whenever the product has been exposed to adverse conditions the user should have a factory trained service person verify the following to maintain compliance:

1. Verify that the safety interlock on the sample chamber is operational.
2. Verify the integrity of the fiber optic cable.
3. Inspect all protective housings for possible adverse wear.
4. Inspect the condition of all protective housing labels.

A source for additional information on laser safety is:

"American National Standard for Safe Use of Lasers" (Z136.1)
American National Standards Institute (ANSI)
11th West 42nd Street
New York, NY 10036

INITIAL SETUP AND INSTALLATION

The Model USH2000 Universal Sample Holder (configured for the RS2000 Raman spectrophotometer) is designed to be installed only by EIC Laboratories, Inc. certified technicians. Installation by anyone other than EIC Laboratories, Inc. certified technicians may result in hazardous radiation exposure. Please contact an EIC Laboratories, Inc. representative for installation of the Universal Sample Holder with the RS2000 Raman spectrophotometer.

UNIVERSAL SAMPLE HOLDER SYSTEM OPERATIONS

Operation

1. LIFT COVER OFF SAMPLE CHAMBER/HOLDER. (When the cover is removed, the shutter system automatically closes to prevent the laser light from entering the sample chamber.)
2. INSERT SAMPLE INTO SAMPLE HOLDER MODULE.
3. REPLACE THE COVER OF THE SAMPLE CHAMBER/HOLDER.
4. ADJUST THE HEIGHT OF THE SAMPLE WITH THE EXTERNAL LEVER. (Note there are no open beams present during this adjustment.)
5. ACQUIRE RAMAN SPECTRUM.
6. LIFT COVER OFF SAMPLE CHAMBER/HOLDER.
7. REMOVE SAMPLE FROM THE SAMPLE HOLDER.

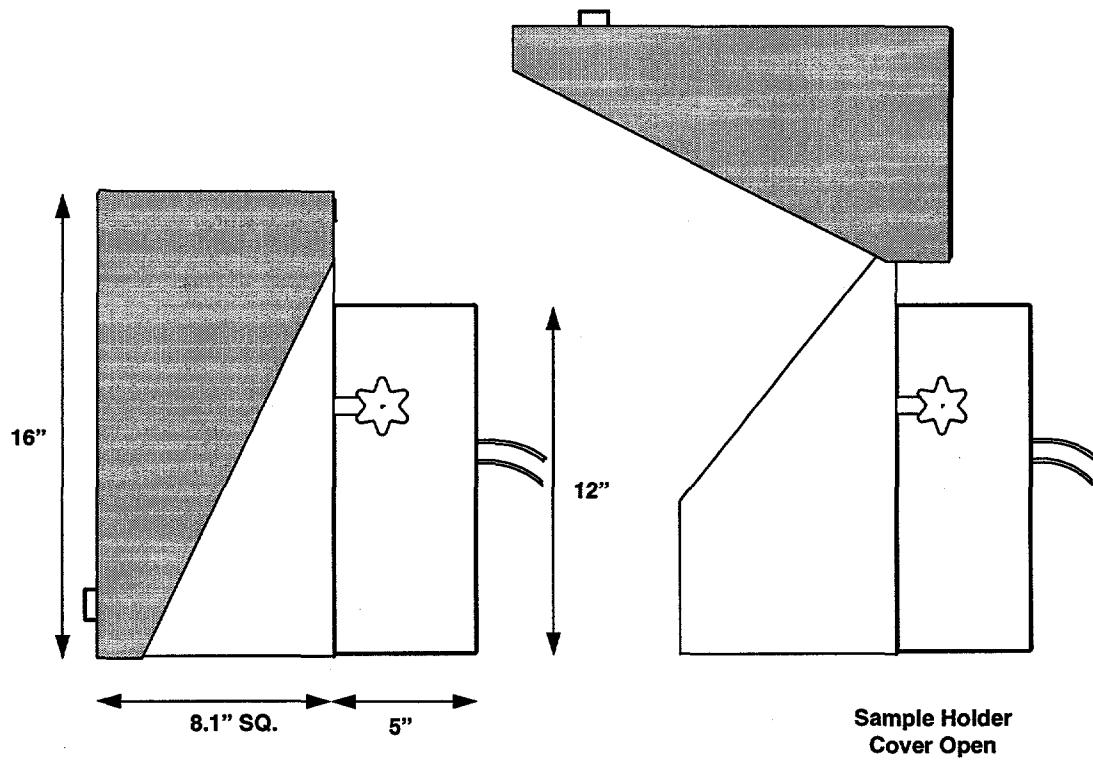
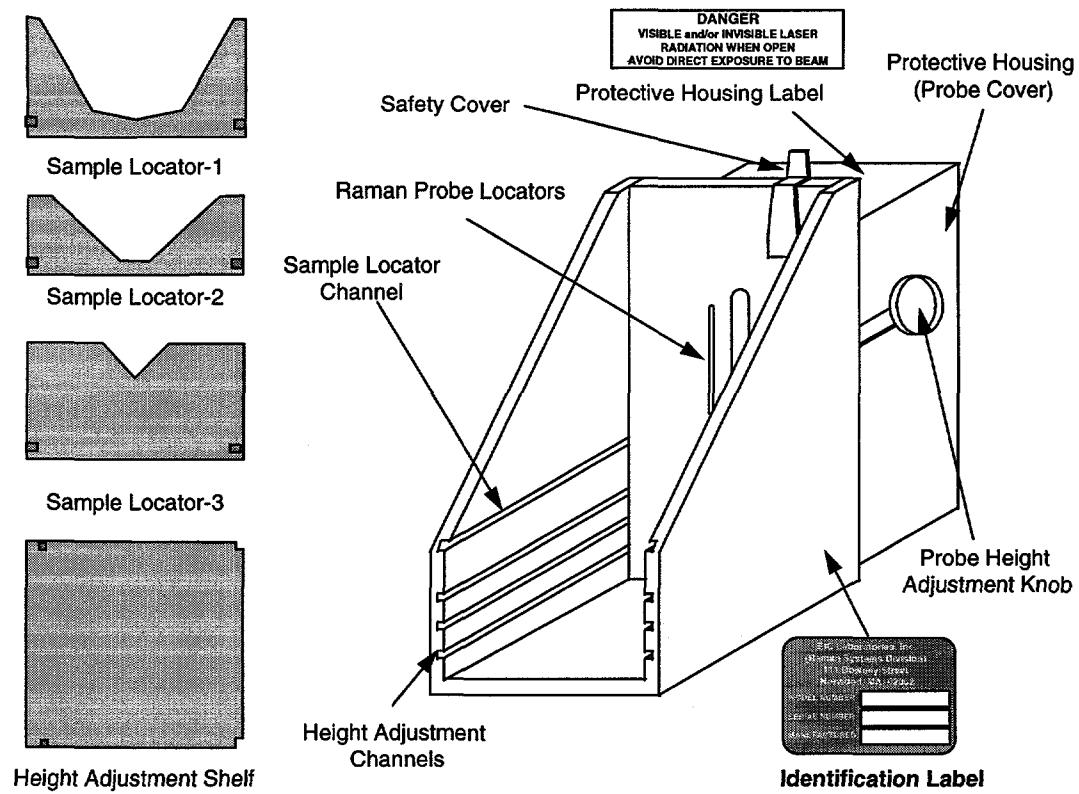


Figure 3 Illustration of Universal Sample Holder USH2000.

MAINTENANCE

WARNING

The Model USH2000 Universal Sample Holder (configured for the RS2000 Raman Spectrophotometer) is designed to be maintenance free and should not be serviced or adjusted by anyone other than EIC Laboratories, Inc. certified technicians. Caution - Removal of the laser protective housings may result in exposure to hazardous laser radiation (up to 0.5W). Please contact an EIC Laboratories, Inc. representative for any maintenance or service of the laser systems.

No maintenance of Universal Sample Holder is required by the user. Quarterly or whenever the product has been exposed to adverse conditions it is recommended that a **factory trained service person** verify the following to maintain compliance with "Performance Standards for Laser Products" United States Code of Federal Regulations, 21 CFR 1040.10 and 21 CFR 1040.11.

1. Verify that the safety interlock on the sample chamber is operational.
2. Verify the integrity of the fiber optic cable.
3. Inspect all protective housings for possible adverse wear.
4. Inspect the condition of all protective housing labels.

SERVICE

All service is to be conducted by factory trained personnel since laser powers up to 0.5W at 785 nm and up to 150mW at 532 nm could be accessible if the protective housing probe covers are removed or the safety interlocks are intentionally defeated and the laser systems are operational. These conditions should exist only during service by factory trained technicians and are outlined below.

The green (532 nm) fiber output is emitted from the probe at the end of the fiber optic cable and would be present inside the sample chamber. It would be accessible during service if the fiber probe was removed from the probe holder on the chamber or if the chamber cover was removed and its interlock was defeated.

The red (785 nm) fiber output is emitted from the probe at the end of the fiber optic cable and would be present inside the sample chamber. It would be accessible during service if the fiber probe was removed from the probe holder on the chamber or if the chamber cover was removed and its interlock was defeated.

USH2000-Universal Sample Holder

Service Procedure - USH-001

Removing a Raman Probe from the Universal Sample Holder

NOTE: THIS PROCEDURE SHOULD ONLY BE CONDUCTED BY FACTORY AUTHORIZED PERSONNEL OR INDIVIDUALS WHO HAVE COMPLETED A LASER SAFETY COURSE AND WHO HAVE BEEN TRAINED BY FACTORY AUTHORIZED PERSONNEL.

Reference Material

"RS2000 Raman Spectrophotometer User Manual.

"American National Standard for Safe Use of Lasers" (Z136.1), American National Standards Institute (ANSI), New York, NY (1993).

"Laser Safety Guide", Laser Institute of America, Orlando, FL (1989).

"Guide for the Selection of Laser Eye Protection", Laser Institute of America, Orlando, FL (1989).

Procedure:

- a. Establish a nominal hazard zone and take the appropriate laser safety precautions.
- b. Turn off laser system(s).
- c. Remove the four (4) screws that secure the probe holder cover and gently lift the cover off.
- d. Loosen the two (2) set screws which secure the Raman probe in the Probe Holder and gently remove the probe.
- e. Install the beam attenuator/cover onto the Raman probe.

Note: If the sample holder is to be operated with only one Raman probe, then a probe blank must be installed in the open hole of the probe holder.

- f. Reinstall the probe holder cover.

USH2000-Universal Sample Holder
Service Procedure - USH-002
Installing a Raman Probe from the Universal Sample Holder

NOTE: THIS PROCEDURE SHOULD ONLY BE CONDUCTED BY FACTORY AUTHORIZED PERSONNEL OR INDIVIDUALS WHO HAVE COMPLETED A LASER SAFETY COURSE AND WHO HAVE BEEN TRAINED BY FACTORY AUTHORIZED PERSONNEL.

Reference Material

"RS2000 Raman Spectrophotometer User Manual";
"American National Standard for Safe Use of Lasers" (Z136.1), American National Standards Institute (ANSI), New York, NY (1993).
"Laser Safety Guide", Laser Institute of America, Orlando, FL (1989).
"Guide for the Selection of Laser Eye Protection", Laser Institute of America, Orlando, FL (1989).

Procedure:

- a. Establish a nominal hazard zone and take the appropriate laser safety precautions.
- b. Turn off laser system.
- c. Remove the four (4) screws that secure the probe holder cover and gently lift the cover off.
- d. Remove the sample holder cover and insert the safety interlock defeat tool into the holder.
- e. Remove the beam attenuator/cover from the Raman probe.
- f. Insert the Raman probe slowly into the probe holder while observing the position of the probe face to the shutter mechanism. The probe should be positioned so that the lens is centered in the viewing area and the probe face should be as close to the shutter as possible without touching it. If the probe touches the shutter, it will not close. When the probe is properly positioned, tighten the two (2) set screws in the probe holder to secure the probe.

- g. Remove the safety interlock defeat tool and observe that the shutter closes properly. Repeat this process several times to confirm the proper operation of the shutter. If the shutter does not function properly, reposition the Raman probe.

Note: If the sample holder is to be operated with only one Raman probe, then a probe blank must be installed in the open hole of the probe holder.

- h. Once the probe is positioned properly, reinstall the probe holder cover.
- i. Remove the safety interlock defeat tool.
- j. Reinstall the probe holder cover.

3 Echelle Spectrograph General Overview

The EIC ECHELLE spectrograph is an especially designed unit that enables the end user to obtain the full Raman spectrum simultaneously while maintaining high resolution. Coupled to a fiber optic Raman probe, Raman spectra can be obtained rapidly by non-specialists through the use of a few simple computer keystrokes.

The ECHELLE spectrograph is able to concentrate most of the available light into multiple coincident spectral orders with high dispersion. The multiple spatially overlapping orders are separated by a predispersion element and projected as stacked segments onto the focal plane. Utilization of a two dimensional charge coupled device (CCD) detector with the ECHELLE theoretically allows the simultaneous acquisition of a complete ($0\text{-}4000\text{ cm}^{-1}$) Raman spectrum in a single measurement. The ECHELLE spectrograph is designed to have minimal optical aberrations so that the resolution of the system is limited only by the entrance aperture and the CCD pixel element density. For the current application where the sample is remote from the Raman system, the optical fiber core serves as the limiting aperture.

A schematic of an NIR echelle unit is shown in Figure 4 for the near-IR and visible echelles, respectively. A 50 to 200 μm core fiber optic from the Raman probes connectorized with an FC connector is coupled to the fiber optic entrance port of the echelle. The light entering the spectrograph from the optical fiber is collected and collimated by a f/2.0 lens for the near-IR echelle and a f/2.8 lens for the visible echelle.

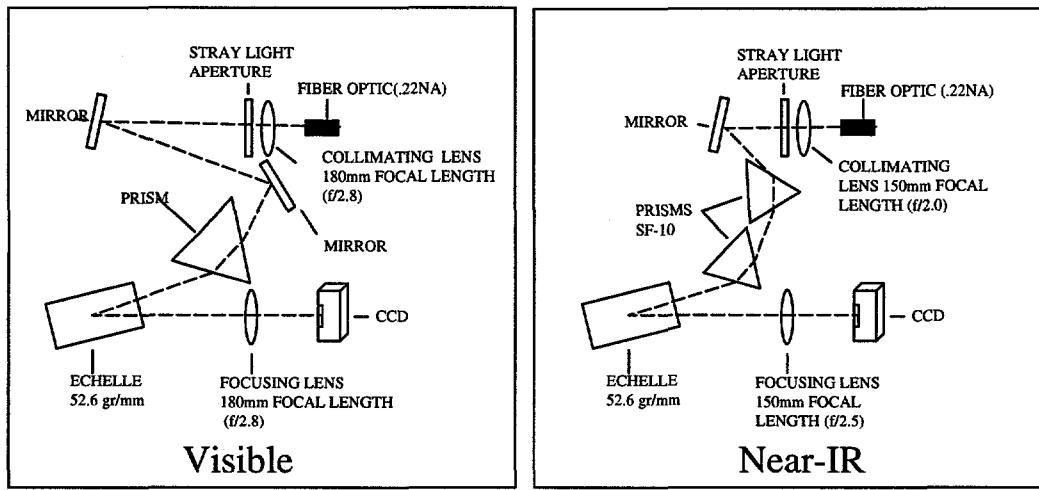


Figure 4. Schematic diagram of a visible and NIR Raman echelle spectrograph.

Between the fiber optic and the lens is an electronic shutter that allows Raman signals to enter into the echelle when desired. The collimated light passes through a mask (stray light aperture) to remove unwanted background scattered light. The collimated light is then reflected off a pair of turning mirrors into the prism before being dispersed into different orders by the echelle grating. In the near-IR echelle, the two dimensional array of collimated light is focused by a f/2.5 lens onto the CCD chip. With the visible echelle, the focusing lens is a f/2.8 lens.

The tilt of the echelle grating and the echelle spectral order range are determined by the wavelength of the light employed for the Raman scattering measurement. For excitation wavelength range of 750 to 785 nm, the echelle orders collected are 45 through 33 (742 to 1027 nm). On the other hand, for a green excitation (514-532 nm), the echelle orders collected are 66 through 52 (510 to 650 nm). The lower number echelle orders have the largest Raman shift from the excitation frequency. The EIC echelle spectrograph can theoretically collect from 0-3500 cm^{-1} in a single scan. In practice, filtering of the excitation line limits the collection range to 225-3500 cm^{-1} .

System Alignment

The EIC echelle spectrograph was aligned, calibrated, and tested prior to shipping. The mounts in the echelle system are designed to withstand vibration and should not change alignment during shipping. The echelle system is calibrated using emission lines from mercury, neon, argon, krypton, and xenon lamp sources.

Hardware Installation

The EIC echelle uses a Photometrics, Ltd. CH250 CCD detection system with a CH250/A style detector. Proper operation of the detector and software requires a 486DX PC with at least 16MB Ram, a Bus Based Video Card and one PCI expansion slot. The expansion slot is used for the controller board for the CCD camera. This board and the associated cables should be installed according to procedures for the CH250/A style head

described in the Photometrics *CCD Camera System Hardware Reference Manual*. The operational temperature of the CH250 camera is factory set for optimum performance near -50.0°C. Please note that the cooling fan power supply must be on when operating the CCD. Operation of the CH250 without the fan on will result in damage to the detector head.

Software Installation

The EIC echelle uses the following software systems that need to be installed on a 486 PC with 16MB Ram, Bus Based Video Card and One Expansion Slot:

GRAMS/386™ or GRAMS/32™ - Galactic Industries

RS2000 - EIC Laboratories, Inc. (Raman Systems Division)

The RS2000 software routines control the Photometrics CH250 air cooled CCD camera, and also calibrate, splice, and convert the echelle spectrum into a GRAMS/386™ or GRAMS/32™ file format. Proper operation of this software requires a controller board (see Photometrics manual) to be installed in the system computer.

If the software has not been preinstalled, then do the following installation procedures:

Install the GRAMS™ software first as described in the installation procedure in the GRAMS™ Manuals. GRAMS must be installed in the following directory C:\GRAMS. Once GRAMSTM is installed make sure that the Auto DDE Server mode is on under the Parameter. Next, install the RS2000 software using the specifically marked RS2000 software diskettes. To install the RS2000 software, follow the procedure outlined below:

Installation Procedure for EIC Raman System's RS2000e Program

The host computer should be a 486 or better IBM-compatible with at least 16 megabytes of RAM. Load a graphics driver (for your particular graphics card) capable of 256 colors at a resolution of 800 x 600. The indicated directory creation and file copying operations can be accomplished from the Windows File Manager.

Load the main program & support files

1. Create the directory c:\RS2000e
- 2.. Load the following files into c:\RS2000e:

RS2000e.exe	RS2000e.bmp	rs2000.ers	ersedit.exe
at200.dll	at200.ini	chartcur.cur	qcbasef.dll
*.eic(calibration file(s))			

Create the EIC Raman Systems program group

1. From the File menu in Program Manager, choose New
2. Select the Program Group option button, then OK
3. In the Program Group Properties dialog box, set Description as "EIC Raman Systems"
4. Press OK

Create RS2000e Program Item in EIC Raman Systems

1. Open (maximize) the EIC Raman Systems program group
2. Open File Manager
3. Resize/reposition File Manager so that EIC Raman Systems is also visible
4. From File Manager, drag the RS2000e.exe to the EIC Raman Systems program group
5. From File Manager, drag the ersedit.exe to the EIC Raman Systems program group

Run RS2000e Program

1. Open (maximize) the EIC Raman Systems program group
2. Double-click the RS2000e icon
3. RS2000e should start (perhaps taking several seconds to load and set up).

Changing the Calibration File and Startup Parameters for EIC Raman System's RS2000e Program

To change the *calibration file, laser wavelength, camera ID or the initial plot limits* on startup, you must run the Ersedit.exe program. The ErsEdit program makes changes to a file named RS2000.ers. Any changes made to the parameters must be stored under the file name RS2000.ers to take effect. See later section for more details about Ersedit.exe.

Software Features

In the RS2000 software, spectra can be acquired, viewed, and stored in a compact format. Key RS2000 software features utilized with the EIC echelle will be discussed here.

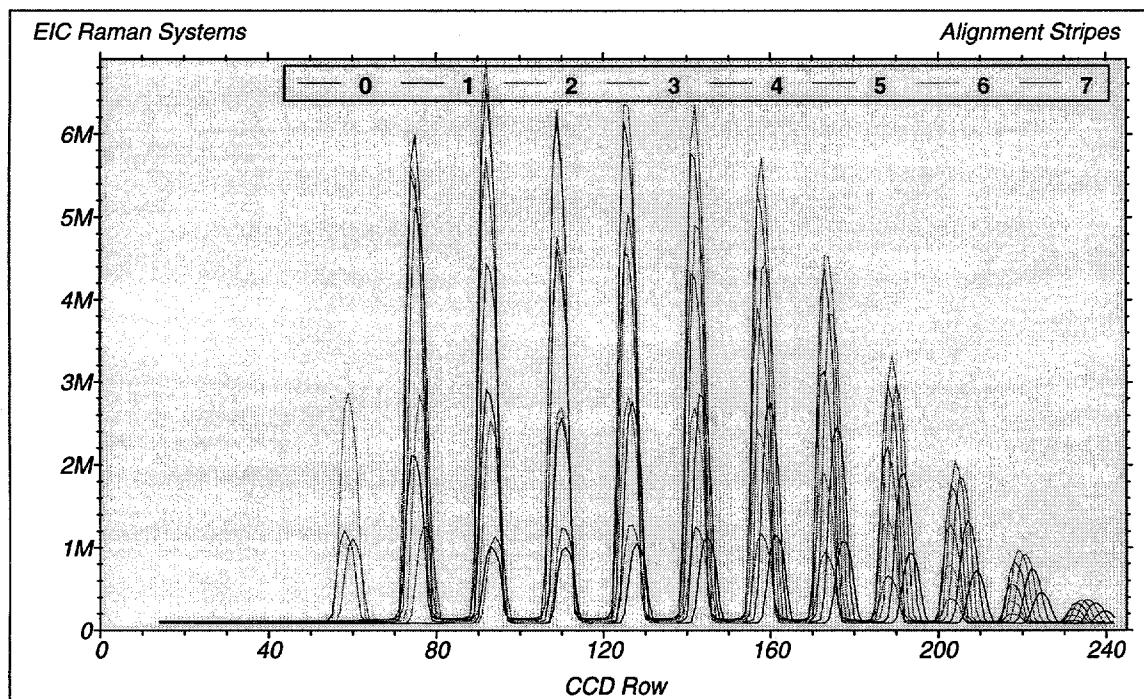
RS2000e Graph Types

RS2000e can display six distinct graphs. The purpose of each should be understood by the user. The six supported graph types are:

Alignment: The Alignment graph is provided as a check on the alignment of the track/camera/spectrograph combination. Eight (8) plots are displayed on the Alignment graph. Each plot represents the intensity of a vertical stripe as a function of row number. The Alignment graph is used only for initial setup or service and is not used during normal operation.

Alignment

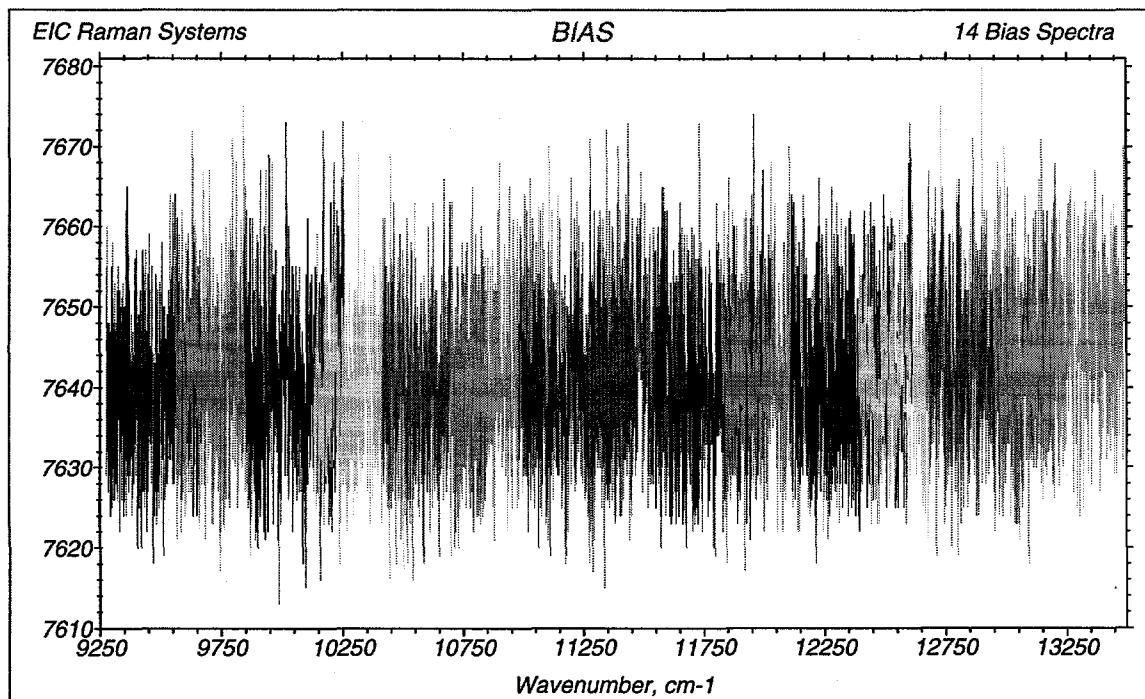
(Used only for initial setup or service.)



Bias: The Bias graph appears whenever a bias spectrum is acquired. A bias spectral acquisition is performed using a zero-second exposure time for the CCD camera without opening the shutter. The Bias graph displays the intensity of each track as a function of absolute wavenumber. There are as many plots (distinguished by color) on the Bias graph as there are tracks defined for the system camera. The bias serves as an indicator of camera performance. The bias data is saved within the running RS2000e program. There is no provision for saving or recalling bias data. However, The Bias plot can be saved in a Windows metafile if desired. The bias will change whenever the temperature of the camera changes significantly. A bias acquisition is performed automatically upon RS2000e startup. **Note that the bias changes significantly with camera temperature. For this reason, a new Bias should be acquired when the camera reaches its equilibrium operating temperature.**

Bias

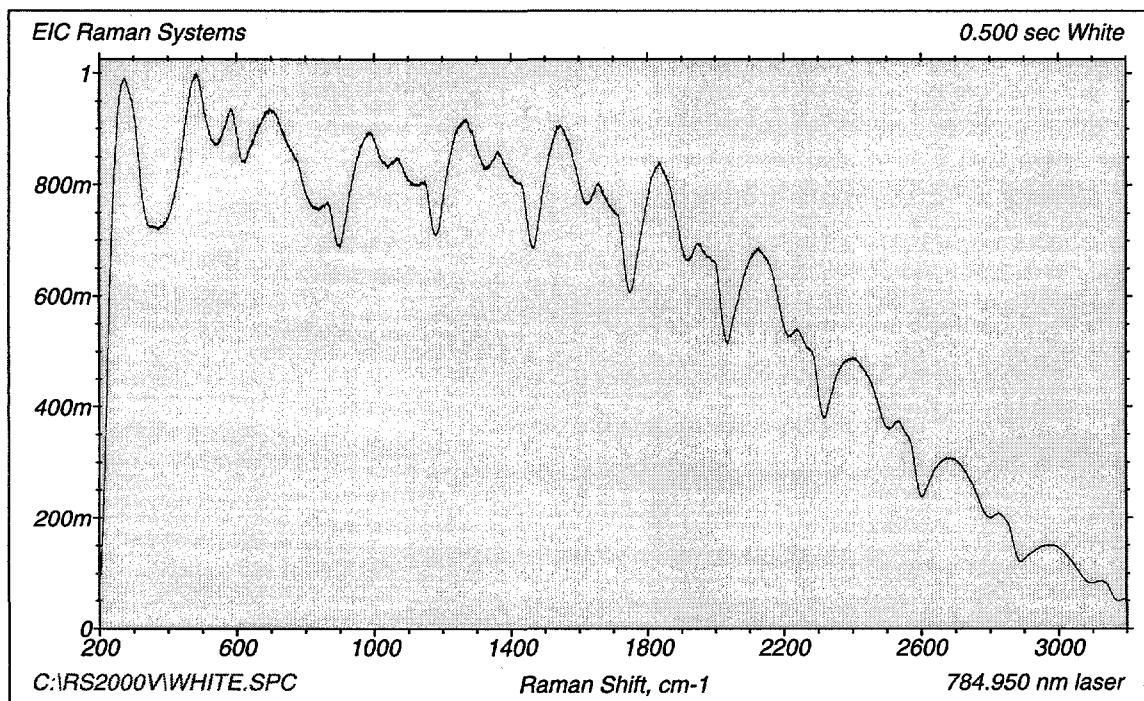
(Closed shutter, zero-time, track-by-track CCD readout.)



White: The White graph displays the White spectral intensity as a function of Raman-shifted wavenumber. The White spectral data is essential to the acquisition of meaningful Raman spectra. It is used as a means for correcting for the response characteristics of the probe, the spectrograph, and the CCD camera. The White spectrum is displayed in normalized form with a range of zero to unity. A White spectrum should be acquired from a white light source through the probe with a short exposure time. It is essential that cosmic occurrences or saturation of the CCD not be in the White spectrum. Normally, a White spectrum is acquired once, stored to a file (with filename **WHITE.SPC**), and recalled automatically upon system startup.

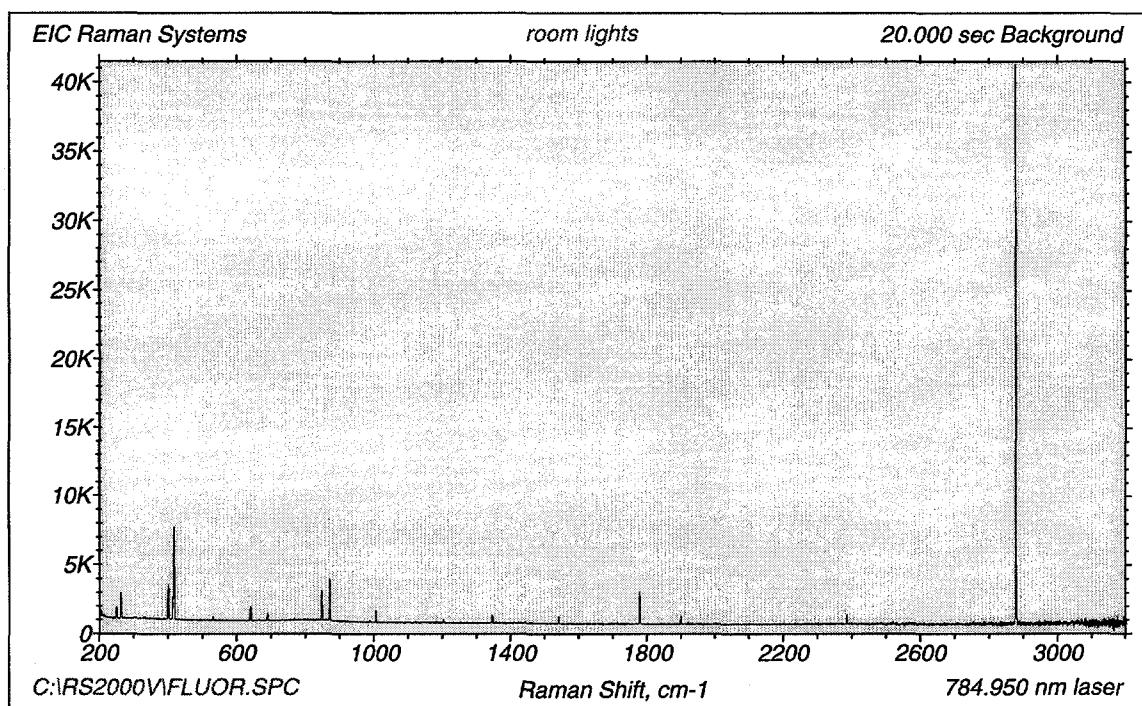
White

(White light spectrum to define system response function.)



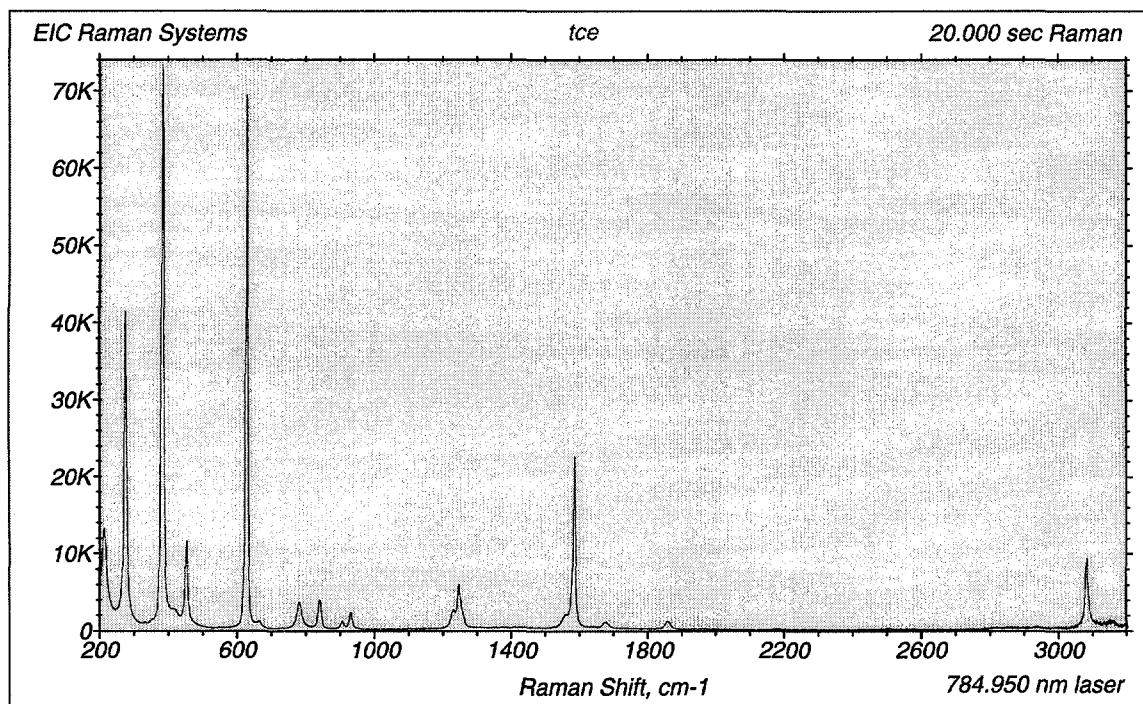
Background: The Background graph displays the Background spectral intensity as a function of Raman-shifted wavenumber. If Background Removal is toggled OFF, the Background spectrum has no effect on the Raman spectrum. If Background Removal is toggled ON, the Background spectrum is subtracted from the Raman spectrum before the Raman spectrum is displayed. Background use is optional.

Background
(Spectrum for Background removal.)



Raman: The Raman graph displays the Raman spectral intensity as a function of Raman-shifted wavenumber. If Background Removal is toggled ON, the Background spectrum is subtracted from the Raman spectrum before the Raman spectrum is displayed. NOTE: Once the Background spectrum has been subtracted from the acquired spectrum and displayed as a Raman spectrum, the removed spectral information cannot be restored within RS2000e.

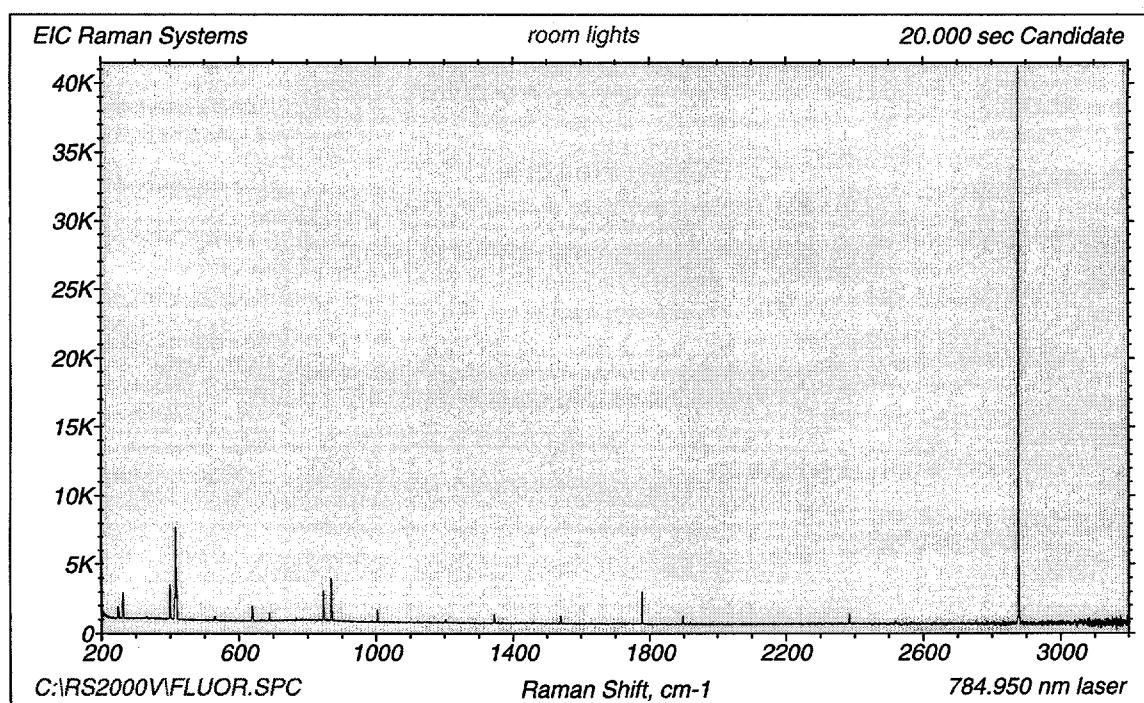
Raman
(Sample spectrum (w/ or w/o Background removal.))



Candidate: The Candidate graph is provided as a utility for spectral acquisition and recall. Candidate data is valid only when the Candidate graph is displayed. For this reason, there is no provision for returning to the Candidate graph without overwriting its data. The Candidate appears under three circumstances. Whenever spectral data is recalled from a file, the corresponding spectrum is temporarily displayed as a Candidate graph. Upon switching to White (or Background), you will be prompted for the choice of overwriting the currently stored White (or Background) spectrum. Whenever a White or Background spectrum is acquired, the spectral data is initially stored in the Candidate. RS2000e will then prompt you to overwrite the previous (White or Background) spectrum.

Candidate

(Temporary (acquisition or file recall) spectrum.)



Summary of Controls

Main Menu ("EIC Raman Systems-RS2000e" Window)

<u>MENU ENTRY</u>	<u>RESULTING ACTION</u>
<u>File</u>	
<u>Open</u>	Recall a spectrum from an spc file
<u>Save</u>	Save a spectrum to an spc file.(GRAMS 386 format)
<u>Print</u>	Print the current RS2000e graph.
<u>Print Preview</u>	Screen preview of graphics output.
<u>Print Setup</u>	Configure the active Windows hardcopy device.
<u>Save as Metafile</u>	Save the current RS2000e graph to a Windows metafile.
<u>Background Removal</u>	Toggle removal of Background from Raman on/off.
<u>Dark Removal</u>	Toggle removal of Dark from Raman on/off.
<u>Cosmic Filter</u>	Toggle application of Cosmic Filter on/off.
<u>Alignment</u>	Acquire an image and display an Alignment graph.
<u>Recalibrate vs. Lamp</u>	Recalibrate the spectrograph (single track systems only)
<u>Autodetect Camera</u>	Detects camera ID address (installation/service only)
<u>Exit</u>	Close the RS2000e program.
<u>Exposure</u>	Invoke the exposure time dialog box.
<u>Spectra</u>	
<u>Bias</u>	Acquire or access Bias spectrum.
<u>White</u>	Acquire or access White spectrum.
<u>Background</u>	Acquire or access Background spectrum.
<u>Raman</u>	Acquire or access Raman spectrum.
<u>Dark</u>	Acquire or access Dark spectrum.

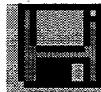
<u>Comment</u>	Invoke the comment dialog box.
<u>Halt</u>	Terminate current spectral acquisition.
<u>Grams/386</u>	Send current spectrum to GRAMS/386. DDE serve in GRAMS must be toggled on.
<u>Limits</u>	Set user-defined plot abscissa limits.
<u>View</u>	
Toolbar	Toggle the toolbar on/off.
Status Bar	Toggle the status bar on/off.
<u>Help</u>	
About RS2000e	Invoke the About RS2000e dialog box.

Toolbar

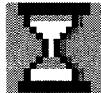
The Toolbar is a convenient means of accessing RS2000e control operations. It is only a convenience. All Toolbar operations can be accessed through Main Menu entries or pulldown menus. The Toolbar buttons displayed are:



Open (same as File/Open) Recall a spectrum from an spc file.



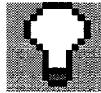
Save (same as File/Save)
Save a spectrum to an spc file.



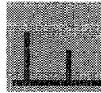
Exposure (same as File/Exposure) Invoke the exposure time dialog box.



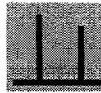
Bias (same as Spectrum/Bias)
Acquire or access Bias spectrum.



White (same as Spectrum/White) Acquire or access White spectrum.



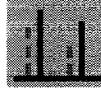
Background (same as Spectrum/Background) Acquire or access Background spectrum.



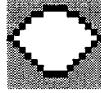
Raman (same as Spectrum/Raman) Acquire or access Raman spectrum.



Halt Acquisition
Terminate current spectral acquisition.



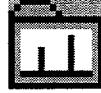
Background Remove (same as File/Background Remove) Toggle removal of Background from Raman on/off.



Filter (same as File/Cosmic Filter) Toggle application of Cosmic Filter on/off.



Print (same as File/Print)
Print the current RS2000e graph.



Metafile (same as File/Save Metafile) Save the current RS2000e graph to a Windows metafile.



Grams (same as File/Grams)
Send current spectrum to Grams/386.



About (same as Help/About RS2000e) Invoke the About RS2000e dialog box.

NOTE: RS2000e Controls are CONTEXT-SENSITIVE.

The same control action may produce different results if initiated under different circumstances. For example, if either File/Bias or the Bias Toolbar button control is selected, any of three actions may occur:

1. If there is not yet a bias spectrum in memory, a new Bias spectrum will be acquired and displayed.
2. If there is a Bias spectrum in memory AND the (preexisting) Bias spectrum is currently displayed, a new Bias spectrum will be acquired and displayed.
3. If there is a Bias spectrum in memory AND the (preexisting) Bias spectrum is NOT currently displayed, the preexisting Bias spectrum will be displayed.

At first, such context-sensitive controls may seem unnatural. However, the underlying logic is intended to permit examination of current Bias, White, Background, and Raman spectra while allowing spectral acquisition with a minimum number of keystrokes.

Special protection is afforded to preexisting White and Background data. Both White and Background acquire into the Candidate spectrum. An explicit operator decision is required to overwrite the Candidate or Background data.

Data is stored and recalled using the **Files** menu. The stored data in RS2000 is in a standard SPC format (GRAMS/386™ software from Galactic Industries). Spectral manipulation is accomplished using GRAMS/386™ software from Galactic Industries. GRAMS/386™ is a sophisticated software routine that allows the end user to perform spectral subtraction, baseline correction, smoothing, spectral comparisons, spectral storage in a variety of user friendly formats, annotation of spectral data, and plotting of the spectral data. A more thorough discussion of the capabilities of GRAMS/386™ is done in the Galactic Industries manual.

Acquiring Spectra

Run RS2000e Program

1. Open (maximize) the EIC Raman Systems program group.
2. Double-click the RS2000e icon.
3. RS2000e should start (perhaps taking several seconds to load and set up).

Acquiring BIAS Spectrum

Once the CCD has cooled to its operating temperature, Raman spectra may be collected with the RS2000 program. It is recommended that, prior to collection of Raman spectra, a Bias be collected and stored. The bias command is a record of the signal detected at the face of the camera when no light is present. In effect, it is a measure of the electronic noise of the camera. On the computer screen, the collected bias spectrum will appear as a noisy line in each echelle order. The bias is stored as a reference spectrum which allows for the subtraction of the electronic noise of the camera from the Raman spectrum. Collection and storage of the bias as the reference file is accomplished by clicking the mouse on the following toolbar icon:

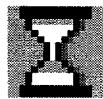


Bias (same as Spectrum/Bias) Acquire or access
Bias spectrum.

Acquiring White Light Spectrum

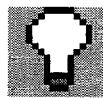
During the collection of Raman signals a combination of several instrumental factors, including each echelle order efficiency, the efficiency of the edge filters as a function of wavelength, and the efficiency of the CCD detector as a function of wavelength may be observed. This "instrument factor" can be removed by normalizing the data against a white light efficiency spectrum. Thus, before acquiring Raman spectra with a new probe, a white light spectrum of the probe should be acquired and saved as **WHITE.SPC**. Normally, this is only done once for each probe. The white light spectrum corrects for instrument response function and probe function which are present in every Raman spectra acquired with the echelle system. A bias reference spectrum must be obtained first and automatically subtracted from the white light spectrum. Follow the procedure described above to obtain the bias spectrum.

A white light spectrum is obtained by shining a diffuse white light into the face of the Raman probe (note the excitation source should be **OFF**). A white light spectrum is accomplished by clicking the mouse on the following toolbar icon first to set the exposure time.



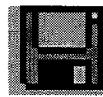
Exposure (same as File/Exposure) Invoke the exposure time dialog box.

Select an exposure time that will give a smooth spectrum **without** saturation occurring. The program will query you if saturation occurs. Then click the mouse on the following toolbar icon to acquire the white light.



White (same as Spectrum/White) Acquire or access White spectrum.

The program will query you as to whether to overwrite the existing white light spectrum or if saturation has occurred. **When an acceptable spectrum is obtained, it should be saved as WHITE.SPC.** Save the spectrum by clicking the mouse on the following toolbar icon.

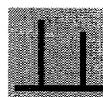


Save (same as File/Save)
Save a spectrum to an spc file.

It should be noted that every time a new probe is connected to the echelle spectrograph, a white light spectrum must be obtained for the new probe and saved.

Acquiring Raman Spectra

Raman spectra are collected by utilizing the **Raman** option in the **Spectra** menu or by clicking the mouse on the toolbar icon. The exposure time should be set prior to clicking the Raman icon.



Raman (same as Spectrum/Raman) Acquire or access Raman spectrum (RED).

ErsEdit Program for Echelle-based Raman Spectroscopy

ErsEdit was developed to provide users access to system data for EIC Raman Systems spectral acquisition programs, specifically RS2000e. The system file is named RS2000.ers. Only this name will be detected by the RS2000e spectral acquisition program. RS2000.ers contains the ERSHDR data structure in binary format. Any attempt to alter its data by programs other than ErsEdit may result in data corruption that could render your spectral acquisition system inoperable until restored.

Run ErsEdit Program

1. Open (maximize) the EIC Raman Systems program group
2. Double-click the ErsEdit icon
3. Ersedit should start

To make any changes to the file

1. Click with the mouse ERS
2. Click Open
3. Double click RS2000.ers
4. Edit the various parameters

To save any changes to the file

1. Click with the mouse ERS
2. Click Save
3. Double click RS2000.ers

The editable data fields of the ERSHDR data structure are:

Camera ID: The Camera ID is an integer flag for the address of the data acquisition card inside your computer. If this address is incorrect, the RS2000e data acquisition program will be unable to access the CCD camera.

Laser Wavelength: The vibrational data comprising a Raman spectrum are displayed in terms of a wavenumber offset from the excitation laser. As such, any error in the wavelength of the excitation laser will cause an erroneous shift in the spectrum abscissa. The floating point laser wavelength is given in nanometers.

Lower Plot Limit: An Echelle spectrograph acquires data over a wide wavenumber range. You may prefer to limit the screen display of data to a narrower region. The lower plot limit is a user-defined value for the left side of the plotting abscissa. The floating point lower plot limit is given in wavenumber shift.

Upper Plot Limit: An Echelle spectrograph acquires data over a wide wavenumber range. You may prefer to limit the screen display of data to a narrower region. The upper plot limit is a user-defined value for the right side of the plotting abscissa. The floating point upper plot limit is given in wavenumber shift.

Banner: The banner appears in the EIC Raman Systems plots. Altering this text string will change the banner displayed in the plots.

Eic Filename: The calibration data for your spectrograph is contained in a binary calibration file (*.eic). This text string must contain the full path to the *.eic calibration file. An example is "c:\RS2000e\yourcal.eic".

of Gratings: This integer value has no significance to your system.

Startup Grating: This integer value has no significance to your system.

ErsEdit Summary of Controls

Main Menu (“EIC Raman Systems-ErsEdit” Window)

<u>MENU ENTRY</u>	<u>RESULTING ACTION</u>
<u>File</u>	
<u>Print</u>	Print the current ErsEdit data.
<u>Print Preview</u>	Screen preview of ErsEdit data output.
<u>Print Setup</u>	Configure the active Windows hardcopy device.
<u>Exit</u>	Close the ErsEdit program.
<u>ERS</u>	
<u>Reset</u>	Set ERSHDR data to default values.
<u>Edit</u>	Edit ERSHDR system data.
<u>Open</u>	Open ERS system file.
<u>Save</u>	Save ERSHDR data to ERS system file.
<u>View</u>	
<u>Toolbar</u>	Toggle the toolbar on/off.
<u>Status Bar</u>	Toggle the status bar on/off.
<u>Help</u>	
<u>About ErsEdit</u>	Invoke the About ErsEdit dialog box.

Toolbar: The Toolbar is a convenient means of accessing ErsEdit control operations. It is only a convenience. All Toolbar operations can be accessed through Main Menu entries or pulldown menus. The Toolbar buttons displayed are:



Reset (same as ERS/Reset)

Set ERSHDR data to default values.



Edit (same as ERS/Edit)

Edit ERSHDR system data.



Open (same as ERS/Open)

Open ERS system file.



Save (same as ERS/Save)

Save data to ERS system file. on/off.



Print (same as File/Print)

Print the current ErsEdit graph..



About (same as Help/About ErsEdit)

Invoke the About ErsEdit dialog box.

4. FIBER OPTIC RamanProbe™

CAUTION

The EIC RamanProbe™ can be operated with a laser source. Visible and/or invisible laser radiation can be emitted from the probe aperture. Appropriate laser safety procedures should be observed when operating the probe with a laser source. See laser manufacturer's manual for precautions.

Raman Probe Overview

The patented EIC fiber optic Raman probe utilizes micro-optic components for delivering the laser excitation source to the sample and for collection of scattered light resulting in a compact probe head that is fiber optically coupled to the laser source and spectrograph. Figure 5 shows a schematic diagram of the EIC RamanProbe™.

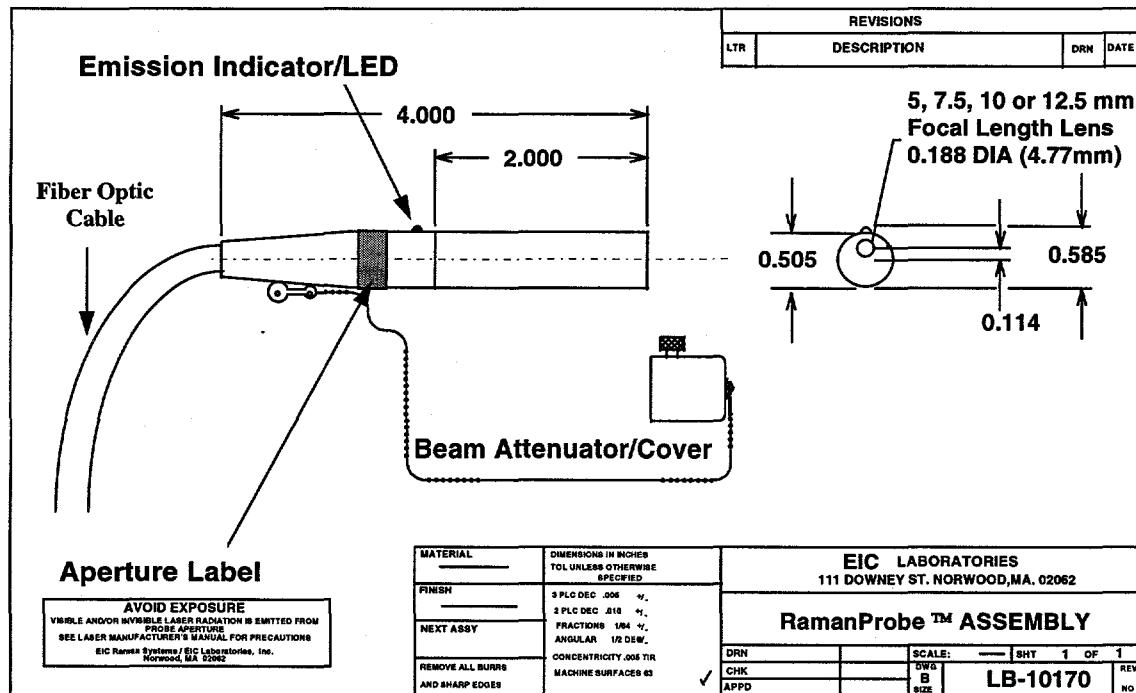


Figure 5. Schematic diagram of the EIC RamanProbe™.

Through the efficient use of dichroic and edge filters for separating the excitation and scattered light, respectively, the EIC probe utilizes a backscattering ($\theta=180^\circ$) sampling geometry. The RamanProbe™ backscattering collection geometry allows easy sample alignment and provides optimum throughput because of the total overlap between the excitation and collection cones. In addition, the EIC RamanProbe™ also incorporates laser safety features such as the beam attenuator/cover and the LED emission indicator. The LED emission indicator at the probe head can be configured by the user so that when the laser source is turned on the LED lights up indicating that laser radiation is emitted from the probe aperture. The LED emission indicator is also visible through laser safety glasses.

The EIC RamanProbe™ is coupled to the excitation source and the spectrograph via optical fibers to allow remote measurements of samples. Because of the delicate nature of fiber optics, it is necessary to encase the fiber optics in a protective jacket. A specially designed fiber optic cable was built for the RamanProbe™ that provides both protection to the optical fibers and also integrate electrical wires necessary to power up the probe LED safety. Figure 6 shows the various components of the RamanProbe™ fiber optic cable.

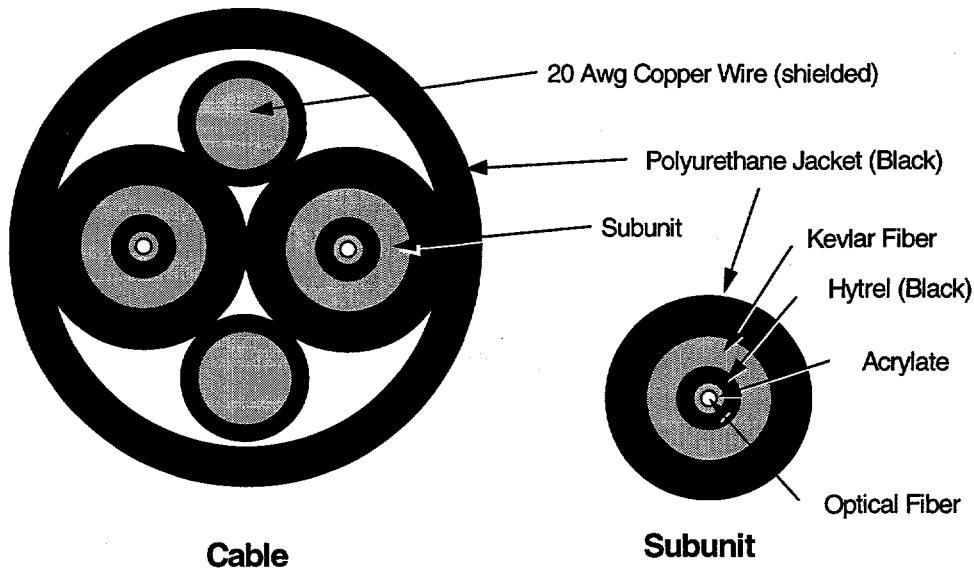


Figure 6. Components of the EIC RamanProbe™ fiber optic cable.

As shown in Figure 6, the RamanProbe™ collection and excitation fibers are bundled separately in a protective jacket of hytrel, kevlar fibers, and polyurethane. The fiber optic subunits and two 20 gauge hookup wires for the LED indicator are then woven together and encased in a polyurethane protective jacket. The resulting cable has a diameter of ~0.25" and fairly flexible. The probes are available in various fiber optic connectors such as FC, ST, and SMA connectors.

The EIC RamanProbe™ can be used with a laser source, primarily with a cw laser source. It is possible to interface the RamanProbe™ with a pulse laser; however, extreme care is required in coupling the probe optical fiber with the laser since the energy delivery per pulse can be extremely high and may cause damage to the fiber optic. If the user requires a pulsed laser source for excitation with the RamanProbe™, consult EIC Laboratories to properly configure the fiber optic connectors for high power applications. Figure 7 shows a schematic diagram of how a RamanProbe™ can be interfaced with a laser source.

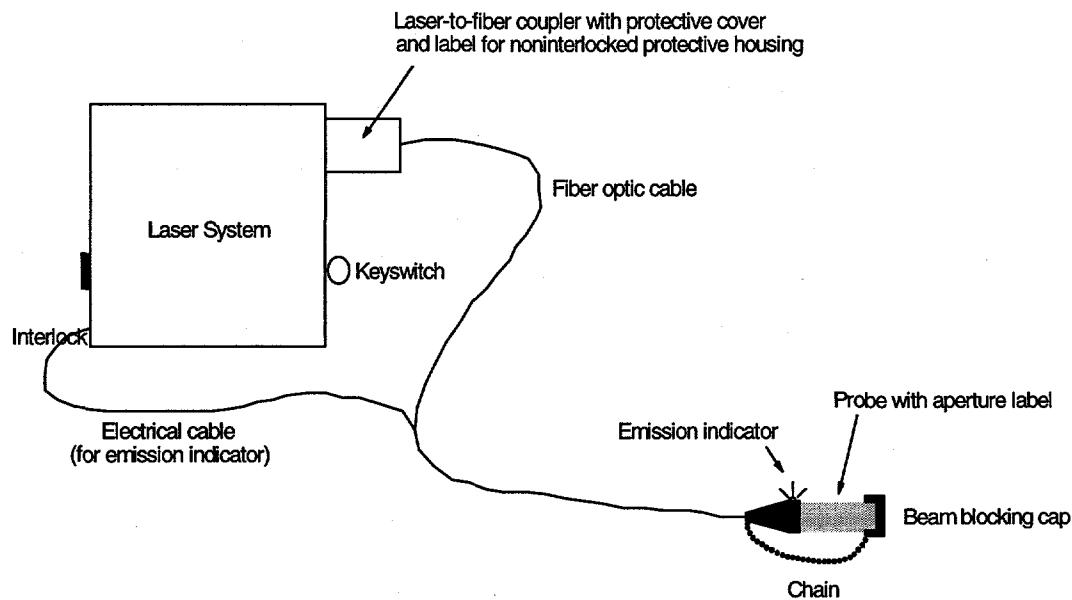


Figure 7. Integration of the RamanProbe™ with a laser source.

RamanProbe™ Operating Instructions

1. Remove the protective cover of the probe fiber optic connectors and make sure that the fiber face and connector endface are clean by wiping the connector end face with an alcohol soaked cotton swab.
2. After making sure that the laser source is either turned off or the shutter mechanism is engaged and that the probe beam attenuator/cover is in place, connect the appropriately labeled excitation leg of the probe cable connector into the laser source fiber optic cable coupler or receptacle. For FC or ST connectors make sure that the key in the connectors engages with the slot in the fiber optic adapter.
3. Connect the appropriately labeled optical fiber collection leg of the probe cable into the spectrograph fiber input.
4. If available, connect the electrical connector of the LED emission indicator into a power source. The LED emission indicator requires 3-5 V @ < 200mAmps. See Figure 8 or consult EIC for powering up the RamanProbe™ emission indicator.
5. After making sure that appropriate laser safety precautions are in place, turn on the laser source and set the power to the lowest possible setting. Open the laser shutter if available.
6. Remove the probe beam attenuator/cover and position the probe onto the sample so that the sample is at the probe focus. The probe is focused onto the sample when the laser spot at the sample is at the smallest.
7. Adjust the laser power to the desired setting and obtain Raman spectra.

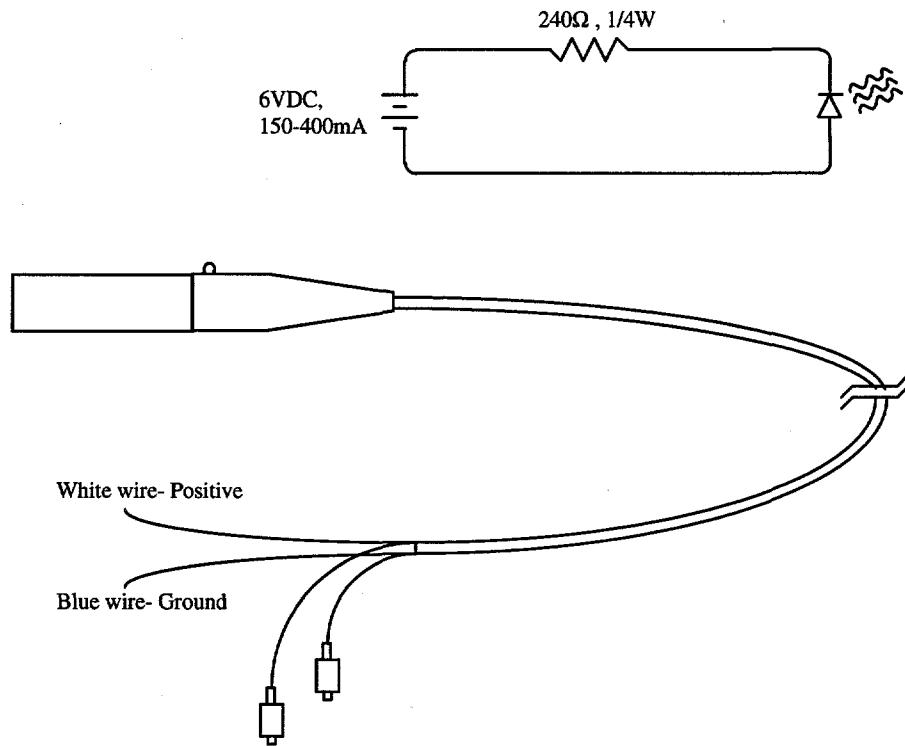


Figure 8. Illustration of attaching the LED to a power source for the RamanProbe™.

Sample Calculation of Nominal Hazard Zones of the RamanProbe™

The following example show how the nominal hazard zone of the RamanProbe™ is calculated using the formulas described in the “American National Standard for the Safe Use of Lasers” (ANSI Z136.1-1993). Figure 9 shows the various probe parameters required in calculating the nominal hazard zone values.

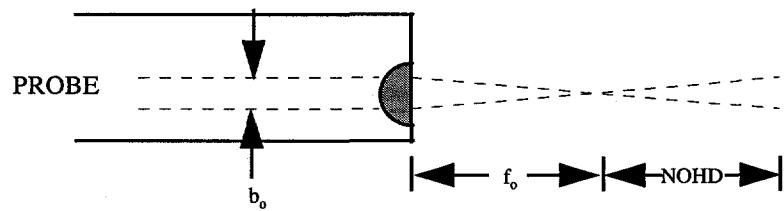


Figure 9. Probe parameters used in calculating nominal hazard zone values.

The equation for focused beam as given in Figure B5 in ANSI Z136.1-1993 is used to calculate the nominal ocular hazard distance (NOHD) for the RamanProbe™. The equation is as follows:

$$NOHD = \left(\frac{f_o}{b_o} \right) \left(\frac{4\Phi}{\pi \cdot MPE} \right)^{1/2}$$

where: f_o = probe focal length (cm)

b_o = diameter of laser beam incident on a focusing lens (cm)

Φ = total radiant output of the laser (watts)

MPE = Maximum Permissible Exposure (J•cm⁻²)

For the RamanProbe™, b_o is 0.254 cm. Therefore, the above equation can be simplified to the following equation.

$$NOHD = 4.442 \cdot f_o \left(\frac{\Phi}{MPE} \right)^{1/2}$$

For a typical aversion response time of 0.25 seconds, the MPE for wavelength range 400-700 nm is 6.36×10^{-4} J•cm⁻² or 2.55×10^{-3} W•cm⁻². For wavelength range from 700-1050 nm, the MPE for a 10 s typical aversion response time can be calculated from

$$MPE = \left(10.1 \cdot 10^{2.0(\lambda-0.7)} \right) \times 10^{-4} \text{ J•cm}^{-2}$$

where λ is the laser wavelength in nm . For example, a laser wavelength at 785 nm (0.785 m) will have an MPE value of 1.49×10^{-2} J•cm⁻² or 1.49×10^{-3} W•cm⁻² for a 10 seconds aversion response time. The table below shows the calculated nominal ocular hazard distance for several types of RamanProbe™ and different focal lengths

Table 1

Nominal ocular hazard distance for a 0.25 second aversion response at 532 nm and a 10 second aversion response at 785 nm to the RamanProbe™ operating at 100 mW exiting the probe.

fo (mm)	NOHD (cm) at 532 nm	NOHD (cm) at 785 nm
	100mW	100mW
5	13.9	18.2
7.5	20.9	27.3
10	27.8	36.4
12.5	34.8	45.5

For further discussion and more detailed description in calculating nominal hazard zone values for the RamanProbe™, refer to ANSI Z136.1-1993.

Precautions for Safe Operation of the RamanProbe™

If the input laser source is operated at 500 mW or less, the focusing and diverging nature of the probe would allow a maximum radiant power (as defined by US 21 CFR 1040.10 (e)(3)(i)) from the end of the probe of ~ 25 mW or less. With this maximum radiant power, the system is considered a Class IIIB device. The following precautions should be observed if the probe is operated in a Class IIIB system:

- Never look directly into the laser beam or at laser light scattered from a reflective surface which exceeds the accessible emissions limits listed in "Performance Standards for Laser Products" United States Code of Federal Regulations, 21 CFR 1040.10 and 21 CFR 1040.20.
- Avoid physical contact with the laser light.
- Do not under any circumstance remove the protective covers on the laser head.
- Do not under any circumstance operate the laser with the protective covers removed.
- Post warning signs near the laser operation areas.
- Controlled access areas, limited individuals trained in the safe operations of laser, are suggested for laser operations.
- Use protective eyewear, as precaution to accidental exposure to the direct or reflected laser light.

For additional source on laser safety, consult the laser manufacturer and the following literature from ANSI:

"American National Standard for Safe Use of Lasers" (Z136.1)
American National Standards Institute (ANSI)
11th West 42nd Street
New York, NY 10036

MAINTENANCE

WARNING

The RamanProbe™ is designed to be maintenance free and should not be opened or adjusted by anyone other than EIC Laboratories, Inc. certified technicians. Please contact an EIC Laboratories, Inc. representative for any maintenance or service of the RamanProbe™.

5. CUSTOMER SERVICE

EIC Laboratories, Inc. takes great pride in their products. Should there be any problems with the laser system, please call us at 781-769-9450. We will do our best to get your system operational as soon as possible.

WARRANTY

EIC Laboratories, Inc. warrants the Raman spectrophotometer system, exclusive of the laser unit*, to be free of defects in materials and workmanship for 12 months following the date of shipment. The warranty is limited to the original purchaser of the Raman systems and is not transferable. The warranty does not extend to any Raman system which has been damaged as a result of accident, neglect, misuse or as a result of service or modification by anyone other than EIC Laboratories, Inc.

* The laser systems are covered by the original laser manufacturer warranty.

EIC Laboratories, Inc. warrants the Universal Sample Holder to be free of defects in materials and workmanship for 12 months following the date of shipment. The warranty is limited to the original purchaser of the Raman systems and is not transferable. The warranty does not extend to any Raman system which has been damaged as a result of accident, neglect, misuse or as a result of service or modification by anyone other than EIC Laboratories, Inc.

EIC Laboratories, Inc. warrants the RamanProbe™ to be free of defects in materials and workmanship for 90 days following the date of shipment. The warranty is limited to the

original purchaser of the RamanProbe™ and is not transferable. The warranty does not extend to any RamanProbe™ which has been damaged as a result of accident, neglect, misuse or as a result of service or modification by anyone other than EIC Laboratories, Inc.

CUSTOMER SERVICE

EIC Laboratories, Inc. takes great pride in their products. Should there be any problems with the laser system, please call us at 781-769-9450. We will do our best to get your system operational as soon as possible.

WARRANTY

During the warranty period, EIC Laboratories, Inc. will repair or replace, at our option, any defective parts at no additional charge, provided that the buyer notify EIC Laboratories, Inc. of any warranty claim, obtains a return authorization, and ships the equipment prepaid to EIC Laboratories, Inc., 111 Downey Street, Norwood, MA 02062.