A Remote Fiber Optic Ground Water Monitoring System

Based on Surface Enhanced Raman Spectroscopy

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Abstract

Ground water quality is being threatened in many areas of the United States by the intrusion of toxic chemicals from industrial discharge; agricultural runoff; chemical spills; and leachate from landfills, storage ponds, and leaking underground storage tanks. Unlike surface contaminants, which are quickly diluted, chemicals in the ground water often remain highly concentrated for long periods of time. Some chemicals are so toxic that even trace concentrations, on the order of a few parts per billion, pose a danger to human health. An efficient and effective means of monitoring ground water is required to insure public safety. One approach is to develop a fiber optic system capable of measuring the presence and/or movement of ground water contaminants.

In an effort to develop such a system, an electrochemically aided surface enhanced Raman chemical sensor has been designed and tested. A description of the optrode along with supporting equipment, experimental procedures and preliminary spectroscopic performance is discussed. Tests were conducted using a deionized aqueous solution contaminated with pyridine.

1.0 Introduction

The availability and quality of surface water has become limited in many areas of the country. This has made ground water an important natural resource, and the focus of considerable public attention. Unfortunately, ground water quality is also being threatened in many regions of the United States by the intrusion of toxic chemicals from industrial discharge; agricultural run-off; chemical spills; and leachate from landfills, storage ponds, and leaking underground storage tanks. Since ground water moves at

1

a rate ranging from several feet per day to as little as inches per century, chemicals entering the system can have diverse effects on its composition. Unlike surface contaminants, which are quickly diluted, chemicals in the ground water often remain highly concentrated for long periods of time. Some chemicals are so toxic that even trace concentrations, on the order of a few parts per billion, pose a danger to human health.

Unfortunately, standard tracing techniques are often inadequate to define the flow and fate of chemicals in ground water systems. For example, current practice in monitoring the movement of leachate from landfills requires the driving of wells large enough to admit sample collectors, and the laboratory testing of water samples for contaminants at regular intervals. The physical removal of a sample from a well exposes it to air and temperature differences which may result in outgasing of volatile components, substantially altering the analytical results. Such sampling is labor intensive and therefore costly, requiring a larger lined bore hole and a capped opening for sample collection. Since most wells are tested at six month intervals, this approach is inadequate in terms of safety and modeling, allowing sufficient time for leachate to escape and spread throughout the system. In most cases, too little data is acquired to verify predictions. In other cases, toxic chemicals remain undetected, since laboratory samples are tested only for a limited number of specific compounds. Therefore, a more efficient and effective means of monitoring ground water is required to insure public safety.

Most of the recent related research in chemical monitoring of trace organic contaminants in ground water can be attributed to fluorescence spectroscopic techniques (Hirschfeld, et al., (1983, 1985); Milanovich, et al., (1983); Perry, et al., (1984); Kulp et al., (1987); Jones and Porter, (1988); and, Fuh et al., (1988)). Unfortunately only a small fraction of known chemical species are amenable to fluorescence techniques. This paper discusses an alternative approach to remote fiber optic ground water monitoring using a system based on surface enhanced Raman spectroscopy (SERS). Even though SERS is not a new technique, application of this spectroscopic technique conducted over fiber optics is indeed new. The following sections include a brief narrative of remote fiber spectroscopy (RFS) followed by a discussion of the equipment and procedures used to study monitor contaminants through fiber optics.

1.1 Remote Fiber Spectroscopy

Remote fiber spectroscopy (RFS) describes the process used in this paper to perform a preliminary investigation on pyridine-contaminated deionized water. Fluorescence, scattering, and absorption techniques are all amenable to RFS (where possible fluorescence is chosen because of its high sensitivity). In general, light of an appropriate frequency is launched into a single fiber, and coupled to the region of interest with a specially designed sensor. The return signal is collected and transmitted back to a spectrometer via a fiber link (in some cases the same fiber used for access) where it is spectrally sorted. In many cases, the loci of peaks vs. wavelength provides sufficient information to identify the nature and concentration of contaminants in the region of interest, since the intensity of the signal at particular wavelengths can be related to specific compounds.

This in-situ measurement can be accomplished using Remote Fiber Spectroscopy (RFS) or Remote Fiber Fluorimetry (RFF). The main elements

needed to perform RFS are shown in Figure 1. Several key components must
be integrated to produce an RFS system. These include a light source or
laser, couplers, fiber optics, fiber optic chemical sensors, conventional
optical elements, and a precision spectrometer with computer aided
analysis. In addition, a knowledge of spectroscopy, optics, chemistry,
data acquisition, and real time analysis are required to design, develop,
and apply such an approach. The following sections briefly discuss each
component required for RFS and highlight their operation.

1.1.1 Light Source

To perform RFS, many different excitation sources may be considered.
These include incandescent or gas discharge lamps, single line, tunable,
dye, and pulsed lasers, and other emitters outside the visible range.
Lasers may produce more power than required for analysis, so the beam must
be expanded, attenuated using a neutral density filter, and then focused
and launched into the optical fiber. For example, with a well designed
fluorescence chemical sensor, as little as 10 microwatts of power may be
required for accurate analysis (Hirschfeld et al., 1984). Raman scattering
techniques, however, require much higher excitation energies. By
comparison, the experiments described later in this paper use an argon-ion
laser which produces 1.2 watts at an excitation frequency of 514.5
nanometers. Any in-situ spectroscopic approach requires a sensor to be
coupled to the monitoring system.

1.1.2 Coupler

A mechanism is required to position the end of the optical fiber
relative to the incoming laser, and to collect the return signal. Several
approaches have been suggested for this operation (Perry et al., 1984).
One possible configuration is shown in Figure 2 where a perforated mirror
with a small aperture separates the highly focused excitation beam from the
divergent wavefront containing the return signal. The illuminating beam
passes through the aperture in the mirror, and the return signal is
reflected off the mirrored surface and directed to the spectrometer using a
conventional optical system. This approach is considered more efficient
and versatile compared to methods using either a beam splitter or a
dichroic mirror. The RFS apparatus used in this study employed the
mirror\aperture approach to couple laser light into and the return signal
out of the optical fiber.

1.1.3 Fiber Optics

Light can be forced to travel through a thin glass fiber whose cross
section and optical properties are designed based on the phenomena of total
internal reflection. By virtue of their flexibility and waveguide
properties, optical fibers can transport light from large, inconveniently
located or relatively immovable sources into remote or occluded areas and
then can bring the light back to conveniently placed instruments for
analysis.
The most common type of fiber used in RFS is a step-index fiber, in
which light travels through a core surrounded by a cladding of lower
refractive index. Those fibers which have a large numerical aperture, or
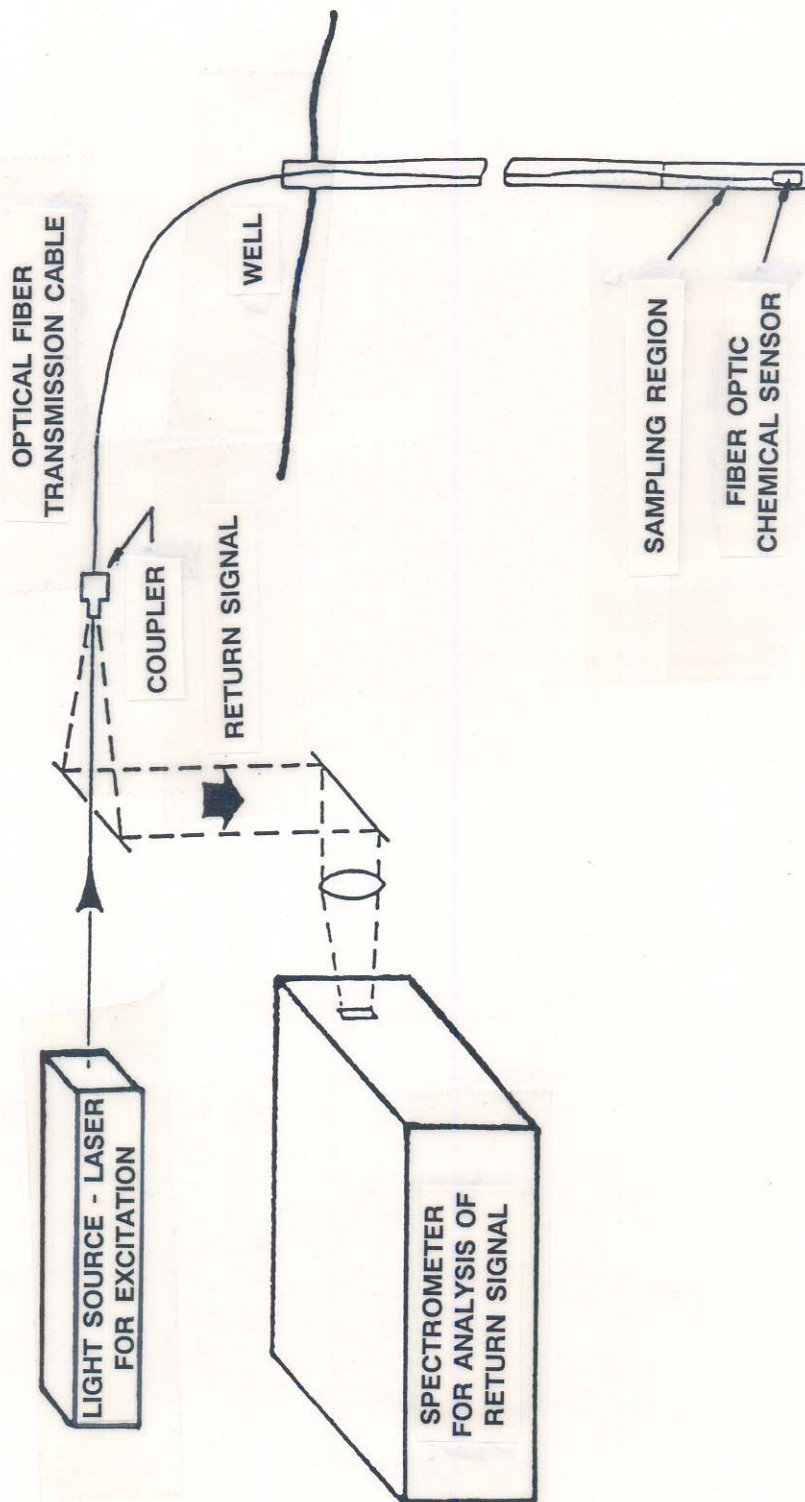
Figure 1. An overview of Remote Fiber Spectroscopy (RFS). Generally, light of an appropriate frequency is launched into the fiber at the coupler, to a desired sensor. The return signal is collected and transmitted back to a monochromator via a fiber link to be spectrally sorted. The loci of signal versus wavelength provides information on the identity and concentration of the particular chemical specie(s).
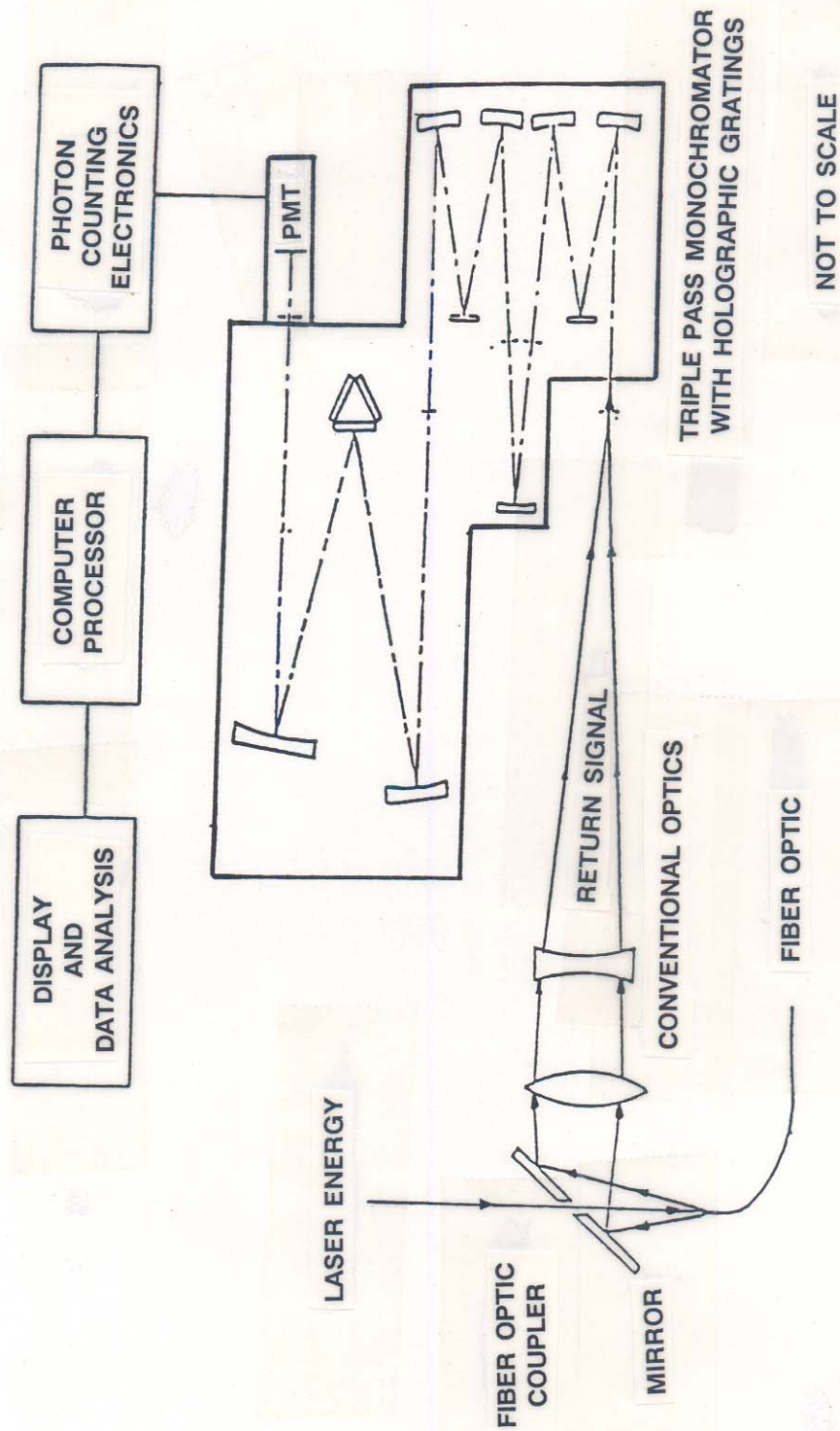
Figure 2. A detailed diagram of the individual components composing the remote fiber spectrometer. In this figure the fiber optic chemical sensor is not shown.

acceptance angle, are classified as multimode. In this case, some rays travel parallel to the longitudinal axis of the fiber; other rays periodically reflect off of the core/cladding interface, tracing more complex paths as they propagate through the fiber.

The ability to do some types of RFS depends on the use of low loss optical fibers for transmitting light energy at various frequencies. Fibers made from glass or fused silica transmit in the 300-1300 nanometer range, but transmission intensity varies as a function of frequency. In many cases, an optical fiber is unable to transmit light of a specific frequency. The large diameter, low loss multimode optical fiber used in this study was selected based on its spectral bandpass.

1.1.4 Spectrometer

A spectrometer is required to resolve the return signal into spectral frequencies which characterize specific chemical compounds. The spectrometer used for this research was a Spex 1877B Scanning TRIPLEMATE which is a state-of-the-art spectrograph specially tailored to provide the low-stray light and flat, undistorted focal plane ideal for sensitive work with optical multichannel detectors, or photomultiplying tubes (PMT). As shown in Figure 2, the unit has two mains sections. The first is an 0.22-m double monochromator with gratings locked in a subtractive-dispersion mode. It acts as a variable-wavelength, selectable bandpass filter that feeds a non-dispersed segment of radiation from a sample into the entrance slit of the second, or spectrograph, stage. It should be noted that the spectrometer used in this study was specially modified to permit scanning of the filter stage. The 0.6-m, single-monochromator spectrograph stage disperses the radiation over the detector. To vary this dispersion and the spectral coverage at the focal plane, the spectrograph has provisions for mounting three gratings, of different groove intensities, on a manually actuated turret. The optical path of the spectrometer is also shown in Figure 2. Analysis is by a GaAs cathode quantum counting end-on photomultiplier (RCA C3103406) connected to a high voltage power supply and a discriminator counter (Pacific Instruments Model No. 126D). The photomultiplier is operated in a thermoelectrically cooled mount and housing which minimizes dark current. The monochromator and photomultiplier are connected to a recorder, and to a real-time data processing system based on a Zenith XT Model No. 158-43.

1.1.5 Fiber Optic Chemical Sensor (FOCS)

Fiber optic chemical sensors are devices attached to the distal end of a fiber optic transmission line. They are used to position the incoming light into the sampling volume and collect the return signal for spectroscopic analysis. The geometric design of these sensors must match the geometry used with standard spectroscopic analysis techniques, such as, fluorescence, transmission, or Raman scattering. A great deal of research has focused on FOCS design, since it is the nucleus of any RFS technique. The fiber optic chemical sensor employed in this analysis uses surface enhanced Raman spectroscopy (SERS), in a back-scatter mode, to identify a chemical contaminant. The following section introduces the reader to Raman scattering and SERS.

1.2 An Overview of Raman Spectroscopy

Raman spectroscopy has important advantages which make it an important tool for surface analysis. In particular, researchers in surface science, corrosion, catalysis, and chemical analysis find this high resolution technique advantageous for surface characterizations (Wokaun et al., 1985; Chan and Bell, 1984). Raman spectroscopy enables one to observe molecular migrations on surfaces and, where surface or catalytic reactions are concerned, provides a means to study reaction intermediates that may only exist at the surface. Additionally, Raman spectra may provide information on the geometry and bonding of adsorbates and surface products, as well as phase changes that occur upon adsorption, surface reaction, desorption and thermal excursions. A brief overview of some of the principles important to Raman and SER spectroscopy are presented below.

When incident light of frequency ν_0 strikes a molecule, it may be scattered either elastically or inelastically. For elastic collisions, the photon's energy is unchanged resulting in Rayleigh scattering. Raman scattering arises from inelastic collisions. The imparted photon energy may cause the molecule to move to a higher energy level, resulting in a scattered photon of less energy and lower frequency producing "Stokes lines". If a photon strikes a molecule which is undergoing a transition to a lower energy level, the result is a scattered photon of increased energy and frequency producing "anti-Stokes lines". These frequency shift are associated with specific vibrational and rotational transitions of the molecule and thus permit specie identification. The intensity of the shifted frequency provides information on specie population.

Raman scattering may be better understood if one considers that photon frequency shifts are principally due to electron interactions, since the nuclei are much more massive. Suppose that the incident frequency of light ν_o is large compared to the nuclear frequencies. Considering the relative masses of the nuclei and electrons, only the electrons will be able to respond and follow the high frequency vibrations. Thus the polarizability of the nuclei is essentially constant for a given position and is approximately a function of nuclear position only. The nuclei are moving at a frequency ν_{mol} due to thermalization and so the polarizability must also depend on this frequency. As the electric vector polarizes the molecule, the "beat" frequencies $\nu_o + \nu_{mol}$ will arise for the induced electric moment P. This provides an explanation for the Stokes and anti-Stokes Raman shifts (Szymanski, 1967; Sudhanshu, 1985; Gardner, 1987).

It is generally agreed that at least two mechanisms (electromagnetic and chemical interactions) between the adsorbate (pyridine) and the substrate (silver) are responsible for surface Raman enhancements (Wokaun et al., 1985; Schatz, 1984). The electromagnetic contribution depends only on surface roughness and is therefore molecule independent. As the surface molecule radiates at its Raman frequency, a roughened surface will act to enhance the rate of emission. Enhancements are greatest for the first monolayer of adsorbed species with weaker enhancements resulting from additional physisorbed or chemisorbed layers (Wokaun et al., 1985; Schatz, 1984). Resonance effects are assumed responsible for signal amplification.

Unlike the electromagnetic interactions, chemical interactions are limited to the first monolayer. They involve adsorbate charge transfer to and from the metal surface. It has been postulated that upon adsorbate chemisorption or surface reaction, substrate electrons partially fill the lowest unoccupied level of the adsorbate setting up a resonance. The chemical contribution to SER spectroscopy depends upon both the environment and adsorption geometry of the surface. Chemical enhancements are highly

molecule specific, since they require particular donor/receptor energy levels (Wokaun et al., 1985; Schatz, 1984; Pockrand, 1984).

2.0 Experimental

The SER fiber optic chemical sensor used in this study is shown in Figure 3. The prototype sensor was made from a 1/4" stainless steel Swagelok union. A 500 micron diameter optical fiber and a rod lens were installed in access holes drilled in a 1/4" diameter teflon rod. The working electrode, discussed below, was also installed in a 1/4" diameter teflon rod which acted as an insulator between the working electrode and counter electrode. These holders were installed into the fitting, using nylon ferrules, to form a sampling cavity. Holes drilled in the fitting allowed the solutions to enter this cavity.

Electrode potentials were controlled in a conventional three electrode system using a Model 363 Potentiostat/Galvanostat (EG&G Princeton Applied Research). The working electrode was a 2 mm diameter silver wire that was externally connected to the potentiostat with another silver wire encased in plastic tubing and sealed with epoxy. Silver purity exceeded 99.999% in both cases. The target surface of the silver electrode was finely polished using standard metallurgical techniques, concluding with polishing on a fine felt wheel using a 0.05 micron Al_2O_3 polishing solution. The working electrode was then electrochemically cleaned for 5 minutes in a 0.1M NaCl solution at -0.5 volts vs. the silver\silver chloride reference electrode, following procedures discussed by Lee et al., 1988. After chemically cleaning the sensor, it was rinsed and immersed in deionized water for electrochemical roughening. To roughen the electrode, the electrochemical potential was slowly cycled four times between -0.9 to +0.4 volts D.C.; ending at the potential used in the analysis (-0.6 volts). These electrochemical procedures chemically decompose the organic residue between trials and physically roughen the silver surface to induce the surface enhancements discussed above.

Once cleaned, the SER sensor was immersed in a deionized aqueous solution of 10 ppm pyridine. Complete spectra were obtained on a Spex 1877B monochromator with an 1800 groove/mm grating in the spectrographic stage and 600 groove/mm in the filter stage. Data were collected using a data acquisition program developed by one of the authors (Bond) and were manipulated and plotted using specially developed programs and modules available in ASYST (McMillian Software).

3.0 Results

Spectroscopic results taken with the prototype sensor exposed to 10 ppm pyridine in deionized water are shown in Figures 4-7. These tests were conducted using a Lexel Model 93 Argon-Ion Laser with an excitation energy of 1.2 watts at 514.5 nm, and 15 meters of 500 micron diameter multimode fiber optic. Spectrometer settings were 2 mm on the inlet slit, 3 nm spectral bandpass on the filter stage, 3 mm on the spectrographic inlet, and .01 mm at the PMT. The figures show the difference-spectra of the 10 ppm pyridine contaminated solution referenced to pure deionized water. The difference-spectra were smoothed using cut filtering techniques prior to plotting. Even though the signal to noise ratio has not been optimized, many of the major peak locations reported by Carrabba, Edmonds and Rauh (1987) for pyridine on silver electrodes using conventional methods were identified. Their results have been converted from wavenumber to
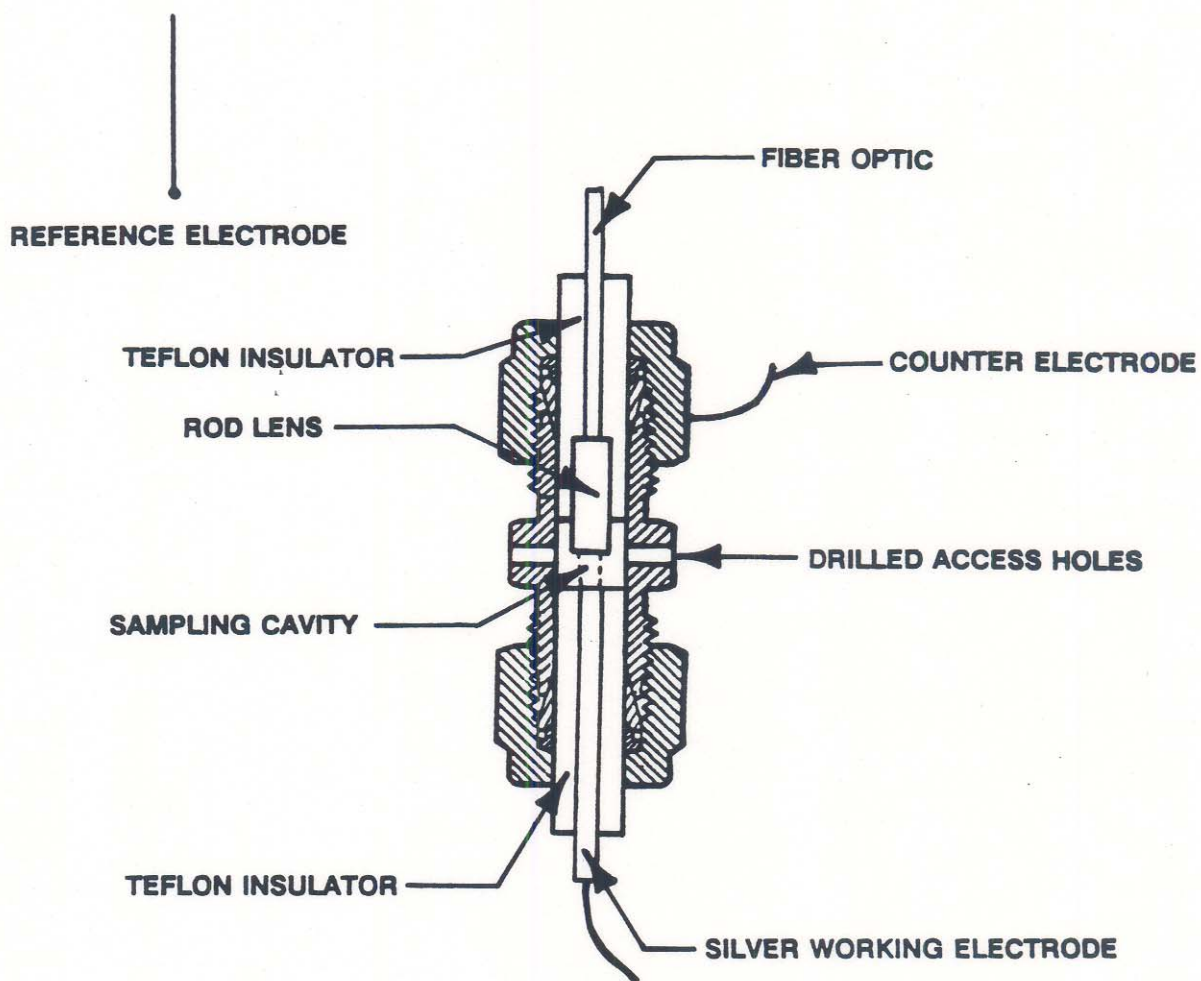
Figure 3. A schematic of the fiber-optic chemical sensor used in this study. The reference electrode has been included in this figure since this sensor's electrode potentials were controlled using the standard three-electrode system depicted above.
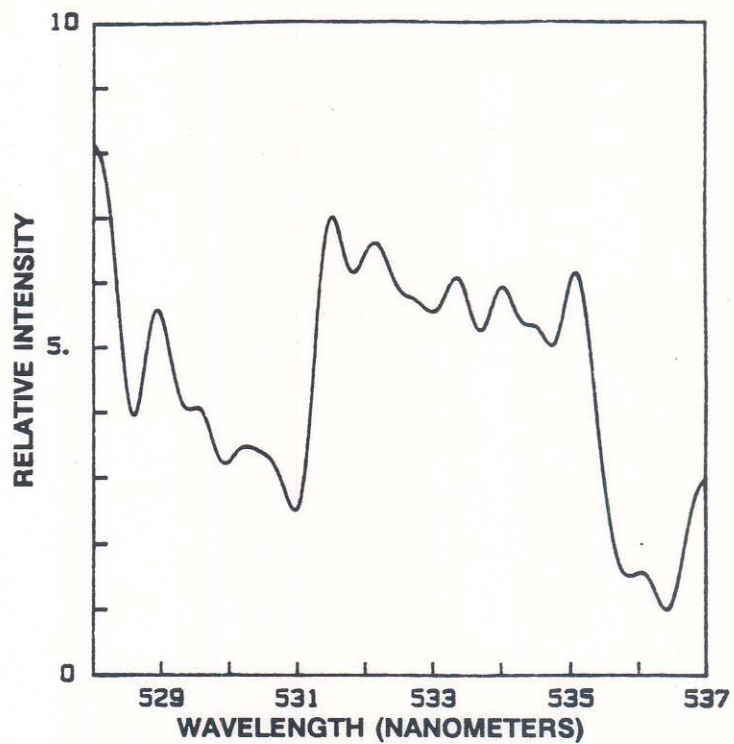
Figure 4.   SER spectra recorded for 10 ppm pyridine in deionized water over the 528-537 nanometer region.
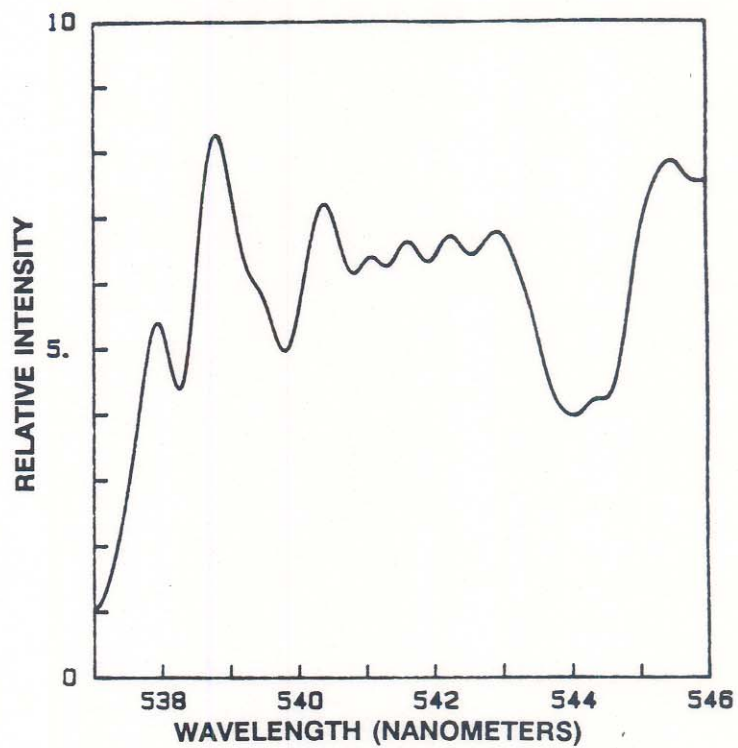

Figure 5.   SER spectra recorded for 10 ppm pyridine in deionized water over the 537-546 nanometer region.
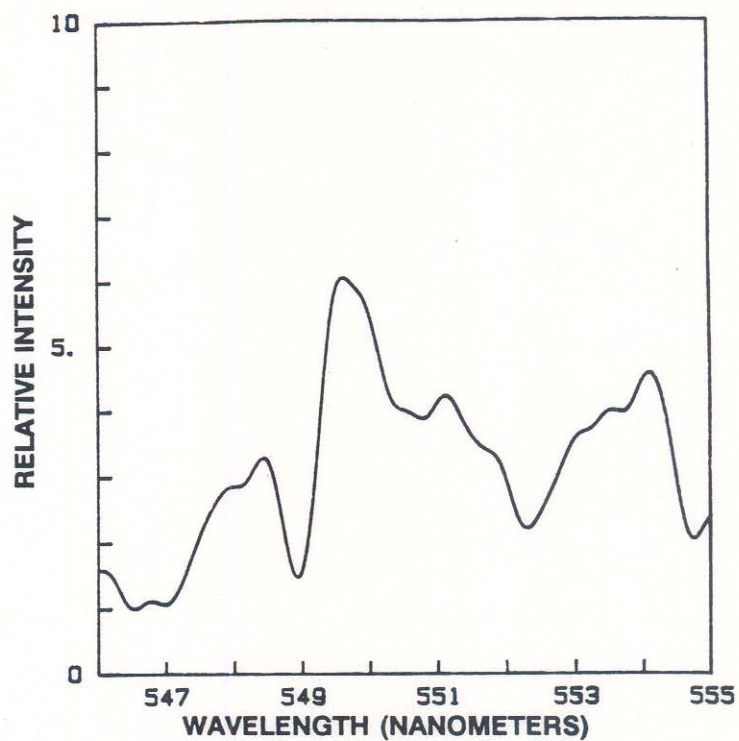
Figure 6. SER spectra recorded for 10 ppm pyridine in deionized water over the 546-555 nanometer region.
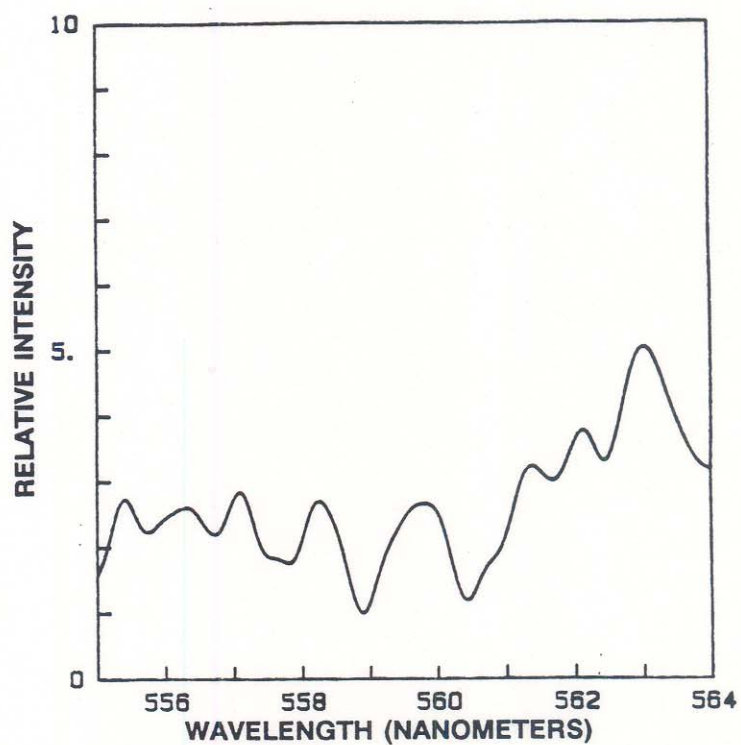

Figure 7. SER spectra recorded for 10 ppm pyridine in deionized water over the 555-564 nanometer region.

wavelength in Table 1 for comparison with the wavelength results taken through the fiber optic system.

It should be noted, however, that Carrabba, Edmonds and Rauh dissolved 0.1 M KCl in deionized water to form their solvent, as opposed to the pure deionized water used as a solvent for the fiber optic tests. Variations in the results shown in Table 1 may be attributed in part to the salt addition. Furthermore, the presence of the KCl electrolyte, in their study, acts to increase the surface roughness and thus the enhancement effects which produce stronger emissions. The absence of salt in the fiber optic tests may be partially responsible for the suppressed signal and resolution in peak identification.

The work by Carrabba, Edmonds and Rauh was performed at an excitation energy of 100 milliwatts as compared to the 1.2 watts used in this study. As noted by Lee et al., 1988, higher resolution spectroscopy can be obtained by increasing the excitation energy and slowing the data acquisition rate. Thus, the additional peaks shown in Figures 5-8, and not accounted for in Table 1, may have resulted from the higher excitation energy and data acquisition rate (5 Hz at a scan rate of 0.01333 nm/sec) used in the fiber optic tests. Another possible explanation may be associated with pyridine absorption and interaction with the coated surface of the rod lens.

4.0 Conclusions

This paper has introduced a remote fiber optic ground water monitoring system based on surface-enhanced Raman spectroscopy. A new electrochemical sensor has been described and used to identify pyridine-contaminated deionized water. The sensor design permits both electrochemical cleaning and conditioning of the optrode. Raman scattering measurements have been made and, even though the system and sensor were not fully optimized, results compared favorably with those measured by other investigators using conventional Raman scattering equipment.

Future research will focus on improving the optical design of the sensor, upgrading the signal to noise ratio, examining the influence of laser excitation energy levels, quantifying pyridine mixtures as a function of concentration and electrochemical potential, studying the influence of electrolyte additions, and finally examining solute/solvent interaction in drinking water and ground water.

5.0 References

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Table 1

A Comparison of Spectral Identification by Peak Position for Pyridine
at -0.6 V with Data taken by Carrabba, Edmonds, and Rauh (1987)

Carrabba, Edmonds, and Rauh Peak Location Wavenumber(cm^{-1})	Peak Location Wavelength (nm)	This Study Peak Location Wavelength (nm)
622	531.5093	531.558
650	532.3015	532.186
752	535.2074	535.120
764	535.5513	536.060
1004	542.5245	542.230
1032	543.3499	542.940
1064	544.2963	545.480
1140	546.5573	547.990
1212	548.7166	548.400
1370	553.5154	554.160
1477	556.8132	557.090
1564	559.5236	558.240
1593	560.4330	559.810
1620	561.2823	561.380