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Field Raman Spectrograph for Environmental Analysis

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PII.14 Field Raman Spectrograph for Environmental Analysis

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Introduction

The enormous cost for chemical analysis at DOE facilities predicates that cost-saving measures be implemented. Many approaches, ranging from increasing laboratory sample throughput by reducing preparation time to the development of field instrumentation, are being explored to meet this need. Because of the presence of radioactive materials at many DOE sites, there is also a need for methods that are safer for site personnel and analysts.

Objectives and Approach

For nearly a decade, our objective has been to pursue the development of fiberoptic spectroscopic instruments for *in situ* chemical analysis. Ultimately, this approach can provide the highest quality, most timely, and least expensive analytical data at a site. By making measurements remote from the analyst, this approach also virtually eliminates the risk of exposure to hazardous chemicals.

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Technology Description

This project entails the development of a compact Raman spectrograph for field screening and monitoring of a wide variety of wastes, pollutants, and corrosion products in storage tanks, soils, and ground and surface waters. Analytical advantages of the Raman technique include its ability to produce a unique, spectral "fingerprint" for each contaminant and its ability to analyze both solids and liquids directly, without the need for isolation or cleanup.

Technical Accomplishments

Spectrograph

We have assembled a Raman spectrograph that is unique in its optical configuration and, with no moving parts, is well suited for field work. The optical layout of the system is shown in Figure 1. Key components in the spectrograph are two prisms and an echelle grating which disperse the Raman spectrum from a sample in two-dimensions onto a CCD detector array. This allows a full Raman spectrum to be collected without repositioning the grating and with high resolution (better than 1 cm^{-1}). No other spectrograph provides this powerful combination of high resolution and wide spectral range. Furthermore, with no moving parts, frequent wavelength calibration

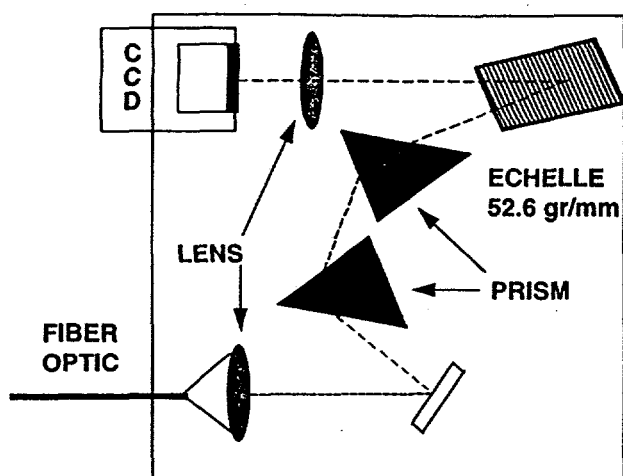


Figure 1. Optical Layout of the Near-IR Echelle Raman Spectrograph.

required with other spectrographs is not necessary with the echelle spectrograph. Using Raman shifts established by ASTM for naphthalene, the echelle spectrograph's calibration was measured to be accurate within 1 cm^{-1} over the whole Raman range and no change in wavelength calibration was observed over several months of operation.

The echelle spectrograph is also an optically efficient instrument, providing rapid detectability from ppm to percentage level concentrations. Figure 2 shows Raman response vs. concentration plots for potassium ferricyanide in water (a Hanford waste tank problem) and benzene in carbon tetrachloride (an Oak Ridge waste tank problem). Lower detection limits for most analytes are in the range 50-500 ppm. This level of sensitivity compares favorably with conventional laboratory Raman instruments and is suitable for *in situ* identification and monitoring of major components in waste mixtures found in tanks or drums or NonAqueous Phase Liquids (NAPLs) underground. Some of the throughput-enhancing (time-reducing) features of the instrument include direct fiber optic coupling

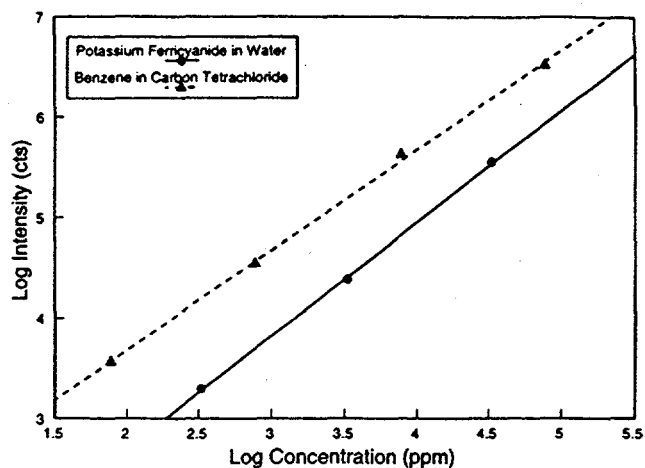


Figure 2. Raman Response vs. Concentration for Two Waste Tank Components.

(replacing slits), low f-number transmission ($f/3$), and extensive use of antireflection coatings.

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

Lasers

Another important component of a Raman system is the laser source. The echelle spectrograph assembled in this project is designed to be used with near-IR laser sources such as solid-state or ion lasers. The advantage of this approach is that for many samples interference from fluorescence is reduced in the near-IR. As part of this program, new high-power lasers are being evaluated for field use. To date, pulsed alexandrite and external cavity diode lasers providing 500mW or more optical power have been determined to be most useful for field Raman analysis.

Fiber Optic Probes

A significant part of this program has been directed to the development of fiber optic probes for use with the Raman spectrograph in specific field applications. These probes are much smaller than commercially available probes and utilize microfilters to provide "clean" spectra over long fiber lengths. One of these devices is a "side-viewing" probe that has been configured for deployment in a cone penetrometer to identify NAPLs in soil and groundwater. A schematic representation of the device is shown in Figure 3. The small, 0.5 in diameter of the EIC Raman probe is critical for this application because of the limited space available in the cone. Other commercial Raman probes do not come close to fitting in even the largest penetrometer cones. A slightly modified, lighter weight version of the cone penetrometer Raman probe is the "punch-probe" designed for Raman analysis in waste tanks and drums.

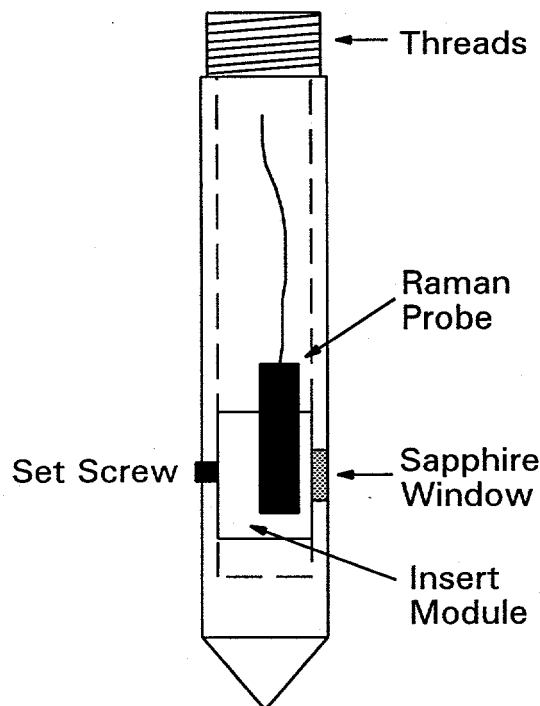


Figure 3. Cone Penetrometer Raman Probe.

A second, "end-viewing" probe designed to be pointed through the side of a bottle in order to identify the bottle's contents has also been assembled. Additional probes designed to profile the contents of Hanford's waste tanks and for other applications are currently under development.

Spectral Library

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. We have begun to create a Raman spectral library that includes chemicals of interest to the DOE. To date, a catalog of intensity corrected, wavelength calibrated Raman spectra for over 70 compounds found at DOE sites has been compiled. The bulk of the catalog consists of spectra for chlorinated and light aromatic hydrocarbon solvents found throughout the DOE complex, and inorganic salts found in Hanford's waste tanks.

DOE Applications

Waste Storage Tank Profiling. In order to test the capabilities of the echelle Raman spectrograph for rapidly profiling the contents of waste storage tanks, three simulants representing different tanks and/or chemical processes were obtained from Hanford and analyzed. Strong Raman signals were collected from inorganic species including nitrates, nitrites, sulfates, and cyanides in all three samples in just a few seconds, as shown in Figure 4. It is notable that the spectra are markedly different, clearly demonstrating the ability to detect compositional differences with the Raman technique. In the

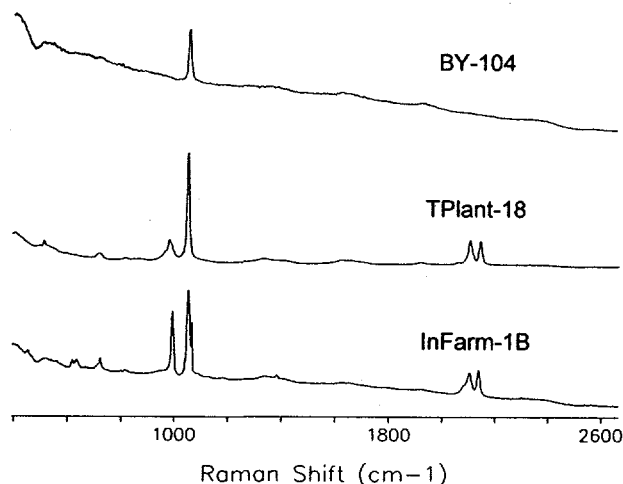


Figure 4. Raman Spectra of Hanford Waste Tank Simulants.

course of analyzing the samples, it also became evident that the high resolution capability of the echelle spectrograph is essential for this application because small spectral shifts were observed for closely related species (e.g., ferricyanides with different cations) or single species at different levels of hydration.

Searching for NAPLs. At many sites the most important goal of initial characterization is to locate and identify a high concentration NAPL pollution source so that immediate action can be taken. The most common NAPLs are Dense NAPLs (DNAPLs) such as trichloroethylene (TCE) and perchloroethylene (PCE) and Light NAPLs (LNAPLs) such as gasoline. Both types are projected to be present, for example, in locations at the Savannah River site (SRS). Figure 5 shows how even similar chlorinated hydrocarbon solvents can be differentiated and identified based on their Raman spectral "fingerprints."

We are exploring the use of the cone penetrometer Raman probe described earlier to identify NAPLs in soil and groundwater (i.e., "floating" on or below the water table). To test feasibility for detecting NAPLs in soil (the more challenging matrix), soils were collected from

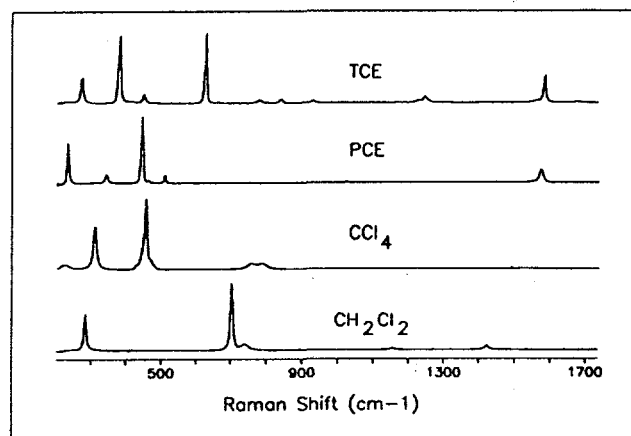


Figure 5. Raman Spectra of Four Common Solvents can be Differentiated Easily.

SRS at depths where PCE DNAPL might be expected to be found and analyzed with the cone penetrometer Raman probe. The samples collected were "clean," but when spiked to saturation, the PCE was detected readily. The spectrum for a 105.2 ft sample is shown in Figure 6.

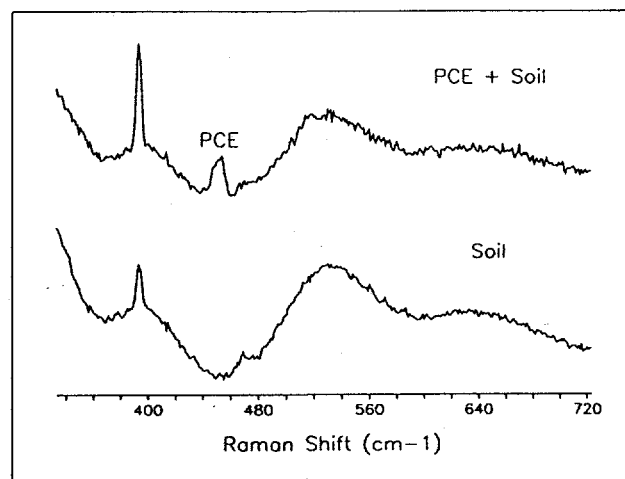


Figure 6. DNAPLs are Detectable in SRS Soil.

Based on the demonstrated feasibility for Raman detection of NAPLs, field testing with a cone penetrometer at SRS is scheduled for the next phase of the project.