

APPLICATION OF REMOTE RAMAN SCREENING TO PROCESSING OF MIXED WASTES IN DRUMS

B. A. Crawford, J. R. Jewett, K. E. Parker, and C. A. Petersen
Westinghouse Hanford Company
Richland, Washington 99352

ABSTRACT

Disposal of transuranic and low-level drum waste involves decisions based on transportation restrictions, Waste Isolation Pilot Project - Waste Acceptance Criteria, and regulation resulting from the Resource Conservation and Recovery Act of 1976 and the Washington State Department of Ecology. To support the decisions made concerning final disposition of these wastes, characterization protocols must be established that ultimately aid in defining the environmental impact. Under current methods, intensive and expensive laboratory analyses are requested to support these decisions. Alternative screening analyses have been investigated to support characterization and reduce costs and sample turn-around times. One promising screening technique involves application of remote Raman spectroscopy for identification of unknown salts, sludges, and solids in wastes. Raman spectroscopy when used with real-time radiography and visual documentation expands the information base available for making real-time decisions for treatment of diverse drummed radioactive solid waste in a waste processing facility. Fourier Transform Raman spectroscopy has been successfully employed to identify oxidizing reagent waste solutions disposed on vermiculite. In addition, it has been proven that low concentrations of material in binary salt mixtures can be detected by using fiber optic remote Fourier Transform Raman spectroscopy. Development of an extensive solid waste library is a key element in the deployment of this technology in the process environment of solid waste drums and barrels.

INTRODUCTION

The Environmental Protection Agency has accepted field screening methods as a means to provide real-time data and to assist in the optimization of sampling point locations for health and safety decisions (1). Furthermore, the Environmental Department of the states of New Jersey and Kentucky are advocating field screening for all remediation analyses except final certification (2). Even during certification, some states are recommending 50 percent of the final sample analyses proceed via sample screening.

The issue of dealing with thousands of drums of buried waste at the U.S. Department of Energy Hanford Site in Richland, Washington, is conducive to the application of remote screening technology to expedite and reduce the costs of characterization associated with remediation. The situation at the Hanford Site is induced by lack of offsite analysis capabilities for TRU (transuranic) contaminated wastes and low-level radioactive wastes. Transportation and storage of these wastes is not trivial and turn-around times through the laboratory often exceed 30 days. Requested analyses also are expensive.

The typical solid waste matrix encountered in drummed wastes at the Hanford Site consists of cellulose materials, latex gloves, ashes, concretes, failed equipment Pu residues, processing salts, and powders. Sludges, ashes, salts and adsorbed solvents on these materials cannot be visually characterized. Therefore remote analytical methods have been suggested to expand the characterization methods that are available to the processing environment.

EXPERIMENTAL

An analysis of samples was performed by Nicolet Corporation to examine the viability of library searching in reasonably large (i.e. in excess of 300 components) spectral libraries. In addition, observations of detection capabilities have been made for remote spectroscopic identification of binary salt mixtures. These techniques of library searching and remote spectroscopy couple to provide a system that can be used in

gloveboxes during the processing and characterization of TRU wastes.

The samples were run by both direct surface sampling in a sample cup and remote sampling with a six-around-one silica fiber optic probe. The six-around-one fiber optic configuration provides a single center fiber for light delivery to the sample surface and scattered light collection by six peripheral fibers. A Nicolet Raman 910 Fourier Transform Raman spectrometer (3) was used for sample excitation, data acquisition, and analysis. Samples were probed via an adjustable Nd:YAG laser with laser power adjusted between 60 mW and 1.0 W at the sample. Spectra were obtained over 2 to 90 seconds with the longest acquisition times being used in obtaining spectra via the fiber optic.

Three samples were analyzed. The first sample was pure reagent grade NaNO_3 salt. The second sample was a 50 weight % sample of NaNO_3 mixed with 50 weight % NaNO_2 . The first two samples were added to the Nicolet spectral database resident on the system used to run the samples. The third sample was a mixture of 2.0 M NaNO_3 and 2.0 M NaNO_2 dispersed on vermiculite.

Each sample was analyzed and additional comparisons were made of data acquisition times, system operation, and comparison of data that was obtained in the conventional vs. remote configuration. A spectral library search was performed for the vermiculite sample using peak recognition capabilities on the Raman 910 system.

RESULTS

Spectra of pure sodium nitrate are provided in Fig. 1. These spectra illustrate the quality of data obtained in the conventional sampling mode at 60 mW and 250 mW of laser power in the sample compartment. High quality spectra are obtainable at 250 mW of 1064 nm excitation without evidence of sample heating and associated background. At lower powers, such as those expected with excitation through a fiber optic, good quality spectra also are obtainable with a slight decrease in signal to noise.

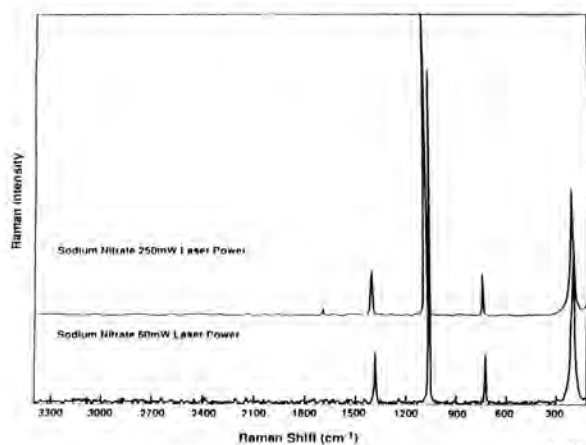


Fig. 1. Dry sodium nitrate.

Spectra shown in Fig. 2 illustrate the results of the Nicolet library search on the Raman 910 system. A positive identification was made to the 50 weight % mixture of NaNO_3 and NaNO_2 . A second match was found with pure sodium nitrate salt. Other matches found that had low-match ratings were the sodium salts of cellulose sulfate and 1-heptanesulfonic acid. Both of these chemical species show prominent features in the 800 to 1600 cm^{-1} range, where all peaks from the vermiculite sample were found.

Figure 3 provides a comparison of sulfur samples obtained with direct sampling in a pressed solid and with a fiber optic probe. Comparable signal to noise is observed in both sampling configurations. Normalizing the 8925 and 9245 cm^{-1} to the 9180 cm^{-1} peak and comparing spectra for both sampling configurations shows a peak intensity loss of 42 percent and 18 percent for the 9245 cm^{-1} and the 8925 cm^{-1} peaks, respectively.

Figure 4 shows results obtained from direct analysis of 52, 10 and 0.5 weight % potassium ferrocyanide in pure sodium nitrate

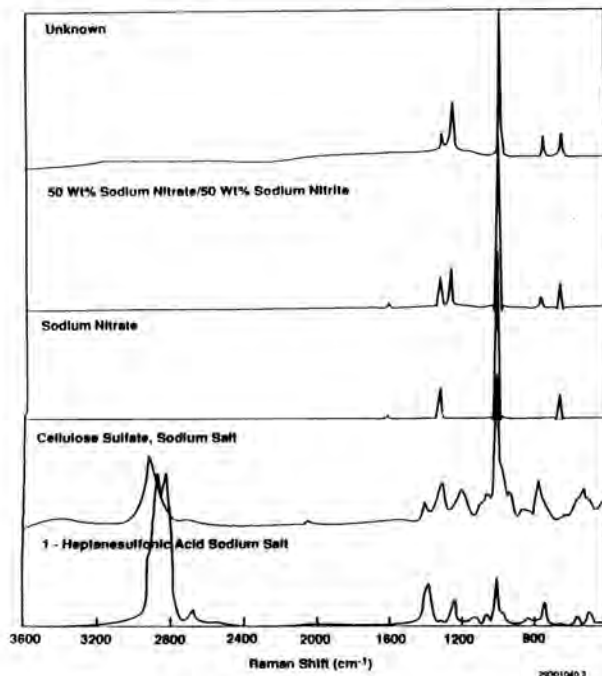


Fig. 2. Fourier Transform Raman spectral library search.

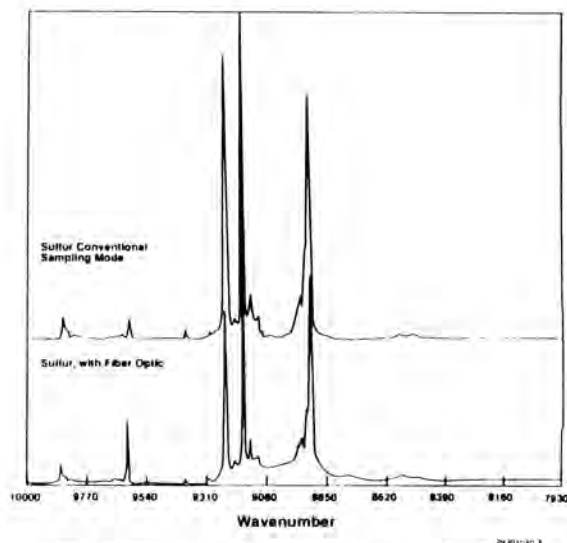


Fig. 3. Direct and remote spectra of sulfur.

nitrate salt. The spectra are shown over the 900 cm^{-1} to 2200 cm^{-1} range where it is useful to make comparisons between the 1060 cm^{-1} major nitrate peak and the peaks at 2100 cm^{-1} assigned to potassium ferrocyanide. Normalization to the 1060 cm^{-1} peak yields ratios of 0.09, 0.18 and 1.55 for the 0.5, 10.0 and 52.0 weight % samples, respectively. While linearity is not expected over a concentration difference of three magnitudes of ten for these solid samples, detection of ferrocyanide salts well below that shown at 0.5 weight % is achievable.

Figure 5 is provided for comparison with Fig. 4. Spectra are displayed as obtained after 90 seconds of data acquisition time. Results can be obtained at 0.5 weight % ferrocyanide using remote sample analysis.

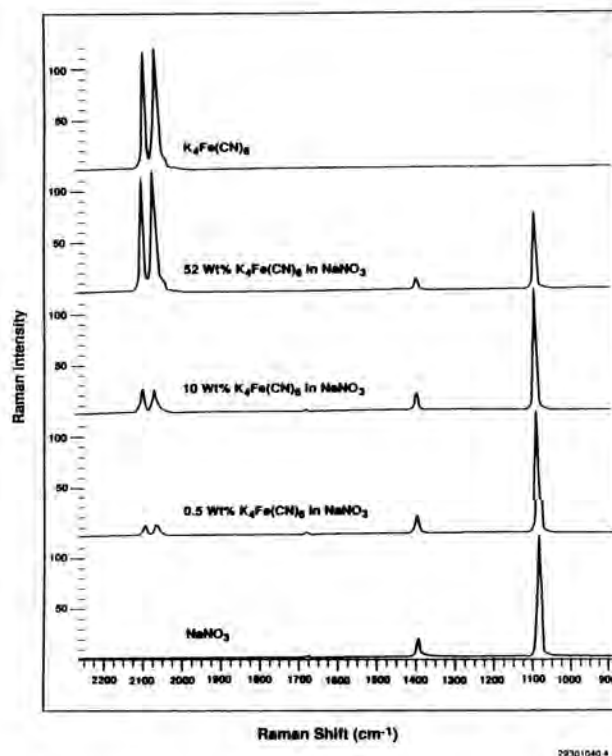


Fig. 4. Direct analysis of ferrocyanide in sodium nitrate.

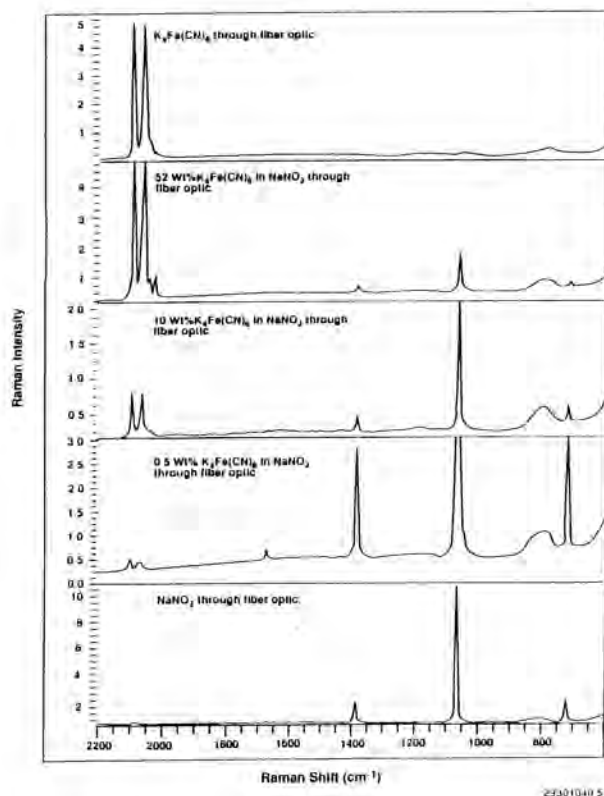


Fig. 5. Remote analysis of ferrocyanide in sodium nitrate.

DISCUSSION

The current Waste Receiving and Processing project design assumes the primary mechanism for characterization of solid waste will use offsite laboratories during initial phases. However, no commercial laboratories have been identified to handle TRU waste samples. The current cost for sample analyses certified according to protocols required by the Resource Conservation and Recovery Act of 1976 certified samples is \$9,000 per sample. The costs for noncertified samples are \$3,000 per sample.

Remote Raman spectroscopy can be used to a powerful advantage in analyses of drummed waste in gloveboxes at the Hanford Site. Statistical analyses indicate that the expected sample load to adequately characterize solid waste streams will exceed 2,000 samples per year. Characterization costs per sample using Raman screening methods have been calculated

to be \$3 per analysis with a sample turn-around time of 5 minutes. Overall savings have been estimated to exceed \$7 million annually.

Many samples have been studied, ranging from dry sodium nitrate and sodium nitrite mixtures to sample solutions dispersed on vermiculite. No evidence of sample heating or black body background is evident in any spectra obtained from these samples with up to 1.0 W of laser power delivered to the sample.

Some attenuation of peak intensities was observed for sulfur samples. However, this does not diminish the utility of the Raman instrument for drum processing as qualitative instrument. Therefore, these discrepancies should have negligible results during spectral library comparisons between spectral obtained directly and those obtained with fiber optics.

A system of quality control checks has been proposed to examine the ability of the system to positively identify unknowns. This will be performed by introduction of blind samples during library development. In addition, selected samples will be analyzed in the laboratory by conventional protocols.

CONCLUSION

To support process characterization in gloveboxes, remote Raman spectroscopy can be readily used. Not only can high quality spectra be obtained, using fiber optics on solid samples without sample preparation, but analysis can be completed in less than 2 minutes. Positive sample identification can be achieved readily via peak identification protocols in which spectral libraries in excess of 300 components or more can be searched within this 2 minute data acquisition time. Quantitative analysis of dry salt mixtures is also possible. Samples in which mixtures of salts at less than 1 weight % can be easily detected using fiber optic sampling.

REFERENCES

1. "Data Quality Objectives for Remedial Response Activities," Environmental Protection Agency (March 1987).
2. "Field Screening for Environmental Pollutants: Defining User Instrumentation Needs," Cambridge, Massachusetts, October 26 and 27, 1992, MIT (1992). Sponsored by US EPA Northeast Hazardous Substances Research Center, MIT Sea Grant College Program, MIT Technology, Business and Environment Program and Environmental Business Council.
3. "Nicolet Raman 910 Spectrometer," Nicolet Corp. Technical Note 169-710000 (November 1991).