TEST REPORT
for
REMOTE VS. CONTACT RAMAN
SPECTROSCOPY

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MASTER

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ABSTRACT

This report details the evaluation of two methods of spatially characterizing the chemical composition of tank core samples using Raman spectroscopy. One method involves a spatially-scanned fiber optic probe. The fiber optic probe must be in contact with a sample to interrogate its chemical composition. The second method utilizes a line-of-sight technique involving a remote imaging spectrometer that can perform characterization over an entire surface. Measurements using the imaging technique are done remotely, requiring no contact with the sample surface. The scope of this document studies the effects of laser power, distance from each type of probe to the sample surface, and interferences unique to the two methods. This report also documents the results of comparative studies of sensitivity to ferrocyanide, a key contaminant of concern in the underground storage tanks at DOE's Hanford site. The effect of other factors on signal intensity such as moisture content is explored. The results from the two methods are compared, and a recommendation for a Raman hot cell core scanning system is presented based on the test results.

This work is part of a joint effort involving several DOE laboratories for the design and development of Raman spectroscopy systems for tank waste characterization at Westinghouse Hanford Company under the auspices of the U.S. Department of Energy's Underground Storage Tank Integrated Demonstration.

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TEST REPORT for NON-CONTACT REMOTE IMAGING and FIBER OPTIC CONTACT PROBE RAMAN SPECTROSCOPY

1.0 INTRODUCTION

Lawrence Livermore National Laboratory (LLNL), in the Technical Task Plan (TTP) SF-2112-03 subtask 1, is responsible for the comparative study of two methods of Raman Spectroscopy that are compatible with the hot cell environment at Westinghouse Hanford Company (WHC) for the rapid scanning of core samples for the characterization of tank samples under the auspices of the U.S. Department of Energy (DOE) Underground Storage Tank Integrated Demonstration (UST-ID). LLNL is assigned the further responsibility of generating a report describing the results and analysis of the comparative study for delivery to WHC. This work is part of a joint effort involving several DOE laboratories for the testing and development of Raman systems for UST waste characterization.

1.1 PURPOSE

This report details the evaluation of two methods of spatially characterizing the chemical composition of core samples using Raman spectroscopy. One method involves a spatially-scanned fiber optic probe, depicted in Figure 1. The second method involves a line-of-sight technique involving a remote imaging spectrometer that can perform characterization over an entire surface, as illustrated in Figure 2. The results of this comparative study form the basis for recommending specifications for a core-scanning system.

1.2 SCOPE

The scope of this document includes studies detailing the effects of the following factors on the fiber optic and non-contact imaging techniques of remote Raman spectroscopy:

- Laser power
- Distance from each type of probe to the sample surface.
- Background lights.
- Glass fiber Raman.

This report also documents the results of comparative studies of sensitivity to ferrocyanide, a suspected key hazardous component in tank wastes.

Figure 1: Fiber optic Raman probe. a) Design of a two fiber probe. b) Illustration of fiber probe for core sampling in hot cell application.

Figure 2: Conceptual design of a non-contact imaging Raman core analyzer.

2.0 EXPERIMENTAL

2.1 GENERAL

Laser excitation was provided using the 514.5 nm line of either a Spectra Physics Model 2025-03 or 165-06 argon ion laser. The laser power used throughout this study was 100 mW, measured after a 514.5 nm band pass filter. Chemical samples were prepared in 1 cm quartz or glass cuvettes. These samples included dry solid sodium nitrate (NaNO_3), wet solid NaNO_3 with 20 weight percent (wt%) of water, potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) in sodium chloride (NaCl) to give solid mixtures of 12, 5.7, 0.95, 0.14, and 0.024 wt% of $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$ (1.8 wt%) in NaNO_3 with 21 wt% water added, and a layered sample of NaNO_3 , Na_2MoO_4 , K_2SO_4 , and 8.3 wt% $\text{K}_4\text{Fe}(\text{CN})_6$ in NaCl . A solid core sample of layered NaNO_3 and K_2SO_4 with approximately 15 wt% water was prepared and used on a motorized translation stage to simulate a core scanner. All Raman spectra were calibrated using the 546, 577, and 579 nm Hg lines from the fluorescent room lights as a wavelength standard. Unless otherwise stated, all Raman spectra were recorded in the absence of room lights. Data analysis was performed using IGOR graphing and data analysis software (Wavemetrics) on a Macintosh IIfx computer.

2.2 FIBER PROBE

The geometry of the fiber probe used in this study is illustrated in figure 1a. It consisted of two 200 μm core diameter glass clad glass core fibers arranged side by side in the tip of a Raman probe. One fiber was used to bring laser excitation to the sample (launch fiber), while the other served to collect Raman scattered light from the sample (collection fiber). The fiber NA was measured as approximately 0.125 giving an F number of 4. The length of fiber from the laser source or monochromator to the probe tip was 20 feet. The filtered output of an argon ion laser was focused onto the launch fiber using a 10x microscope objective. The probe itself was mounted vertically in a translational stage equipped with a micrometer. This configuration was used to give variable distances between the probe tip and the top surface of solid samples. Light from the collection fiber was collimated with a lens ($f/4$), passed through a Kaiser HNF-514-1.0 1 inch diameter laser notch filter, then focused onto the entrance slit of a CHROMEX IS-50 image corrected monochromator. A 600 groove/mm grating blazed at 500 nm was utilized. The wavelength was centered on 554 nm. The slits of the monochromator were held at 30 μm throughout this study. Raman signals were detected with a Princeton Instruments liquid nitrogen cooled 576x384 front illuminated EEV CCD camera. Data collection times ranged from 1 to 60 seconds.

2.3 NON-CONTACT REMOTE IMAGER

A schematic of the non-contact remote Raman imaging system is shown in figure 3. The output from an argon ion laser is directed through a band pass filter to a pair of x,y scanning mirrors. The mirrors, part of a General Scanning Inc. model 600-301003 line scanner, were used both to deliver a single point (mirrors stationary) or a vertical

Figure 3: Schematic of non-contact Raman imaging system.

Figure 4: Intensity verses distance of probe from sample surface. 1066 cm^{-1} band of NaNO_3 . Fiber optic probe.

stripe of laser light to the sample (x mirror stationary, y mirror scanned using a triangular wave from an SRS Model DS345 30MHz Synthesized Function Generator with an amplitude of 0 to 0.25 volts peak to peak). The rotating mirror was used to position the laser excitation on the sample within the line of sight field of view of the camera optics. The sample was held stationary at distances of 1.5, 2, 3, 4, 5, and 10 feet from the camera lens. The laser output was not focused at the sample, and the laser spot size was determined by the natural divergence of the laser. The camera lens was a Nikon AF Micro NIKKOR 195 mm 1:2.8 lens with a range of 1 to 10 feet. The output of the lens was f-stopped at 4, and was focused onto the slit of a CHROMEX IS-50 monochromator. A Kaiser HNF-514-2.0 2 inch diameter notch filter was used to remove the laser line prior to the monochromator. The monochromator settings were as described in section 2.2. Raman signals were detected using a Princeton Instruments liquid nitrogen cooled 512x512 back illuminated TKE CCD camera. Data collection times ranged from 1 to 60 seconds.

3.0 FIBER PROBE RESULTS

3.1 POWER

Laser power was measured prior to the microscope objective placed after a 514.5 nm band pass filter. The power was adjusted to 100 mW. The laser power actually delivered to the sample was measured at the fiber probe tip to be 50 mW. Similar results were observed using a 400 μ m fiber probe.

3.2 DISTANCE

The Raman spectrum of NaNO_3 was recorded at 1 second exposures at distances between the fiber probe tip and the solid sample surface of 0.0, 0.25, 0.5, 1, 1.5, 2, 2.5, 5, 7.5, and 10.0 mm. The intensity of the 1066 cm^{-1} peak, measured at each distance as the difference between the peak height and the baseline, is plotted verses distance in figure 4. This plot illustrates that errors in the placement of the fiber probe within 1 mm of the sample surface can result in a decrease in signal of up to 35%. The dependence of the Raman signal intensity on surface distance follows the double exponential fit shown in figure 4.

3.3 SENSITIVITY

The intensity of the 2064 and 2094 cm^{-1} Raman bands of $\text{K}_4\text{Fe}(\text{CN})_6$ in NaCl at various concentrations was measured at the optimal surface distance of 0.0 mm from the probe. Plots of peak intensity verses weight percent $\text{K}_4\text{Fe}(\text{CN})_6$ are shown for exposure times of 10 and 60 seconds in figures 5 and 6 respectively. At the shorter time, a limit of detection of 0.95 wt% was observed. The lower level of detection increased to 0.14% at times greater than 30 seconds. The signal to noise ratio was 1.5 at best at the lowest concentration level.

Figure 5: Peak intensity versus weight percent $K_4Fe(CN)_6$ in NaCl. 10 second exposure. Fiber optic probe.

Figure 6: Peak intensity versus weight percent $K_4Fe(CN)_6$ in NaCl. 60 second exposure. Fiber optic probe.

3.4 BACKGROUND LIGHTING

The ratios of the intensity of the 1066 cm^{-1} Raman band of NaNO_3 to the 546 and 579 nm Hg lines from fluorescent room lights are plotted in figures 7 and 8 respectively as a function of distance from the fiber probe tip to the sample surface.

3.5 GLASS FIBER RAMAN

The Raman spectrum of NaNO_3 at a probe distance of 0.0 mm from the sample surface is shown in figure 9. This spectrum illustrates the large contribution of the surface reflected Raman signals due to the glass optical laser launch fiber. The glass Raman is the dominant feature in the spectrum at frequencies below 900 cm^{-1} . The dependence of the signal due to reflected 445 cm^{-1} glass Raman band on probe surface distance is depicted in figure 10. This follows a similar double-exponential curve as the dependence of Raman signal on distance. The ratio of the 1066 cm^{-1} peak of NaNO_3 to the reflected 445 cm^{-1} glass peak as a function of probe distance is shown in figure 11. A simple single exponential curve fit is illustrated. If the concentration of NaNO_3 is taken to be a constant in a sample, then the ratio of the two peaks can be used to calculate the probe distance from the surface.

3.6 INTERFERENCES

Several phenomenon were observed that decreased the observed Raman signal of the 1066 cm^{-1} peak of NaNO_3 and the 2064 and 2094 cm^{-1} peaks of ferrocyanide by approximately 50%. In dry samples, crystals were observed to jump from the sample to the probe surface, both diffusing the laser excitation beam as it exited the probe, and blocking the field of view of the collection fiber. This was not observed with moist samples. However, sample was observed to adhere to the probe surface when it was placed in contact with the sample surface. This resulted in attenuation of the Raman signal from the sample, as well as contamination of the next location on the sample to be probed.

4.0 NON-CONTACT REMOTE IMAGING RESULTS

4.1 POWER

Laser power was measured prior to the scanning mirrors placed after the 514.5 nm band pass filter. The power was adjusted to 100 mW. The laser power actually delivered to the sample was measured at the sample to be 98 mW. Results were observed using the scanning mirrors in static mode to illuminate the sample at a single point, 1-2 mm beam diameter.

Figure 7: Ratio of Raman intensity versus room lights. 1066 cm⁻¹ band of NaNO₃. 546 nm Hg line from fluorescent lights. Fiber optic probe.

Figure 8: Ratio of Raman intensity versus room lights. 1066 cm⁻¹ band of NaNO₃. 579 nm Hg line from fluorescent lights. Fiber optic probe.

Figure 9: Raman spectrum of NaNO₃. Fiber optic probe. 0.0 mm from surface. 1 second.

Figure 10: Intensity versus distance of probe from sample surface. Reflected 445 cm⁻¹ band of glass Raman from launch fiber. 1 second. Fiber optic probe.

Figure 11: Intensity versus distance of probe from sample surface. Ratio of 1066 cm^{-1} band of NaNO_3 to 445 cm^{-1} band of reflected glass Raman from launch fiber. 1 second. Fiber optic probe.

Figure 12: Intensity versus distance. 1066 cm^{-1} peak of NaNO_3 . 1 second. Non-contact Raman Imaging system, single point mode.

4.2 DISTANCE

The Raman spectrum of NaNO_3 was recorded at 1 second exposures at distances between the sample and the camera optics of 1.5, 2.0, 3.0, 4.0, 5.0, and 10 feet. The sample was positioned so as to be directly along the optical axis of the camera lens at each distance. The sample is brought into focus by adjusting the effective collection f-number of the camera optics. The intensity of the 1066 cm^{-1} peak, measured at each distance as the difference between the peak height and the baseline, is plotted in figure 12. The signal falls off rapidly at first, then approaches a asymptotic value of approximately 2500 counts between 4 and 10 feet (the maximum distance available with the Nikon lenses). The intensity verses distance data is approximated by an $f(x) = a/x$ curve fit. Changes in the distance of the sample from the collection optics on the order of an ± 1 inch had little effect on the sample intensity at a given camera lens focus.

4.3 SENSITIVITY

The intensity of the 2064 and 2094 cm^{-1} Raman bands of $\text{K}_4\text{Fe}(\text{CN})_6$ in NaCl at various concentrations was measured at each distance listed in section 4.2. Plots of peak intensity verses weight percent $\text{K}_4\text{Fe}(\text{CN})_6$ at 1.5 feet are shown for exposure times of 10 and 30 seconds in figures 13 and 14 respectively. At the shorter time, a limit of detection of 0.14 wt% was observed with a signal to noise ratio of 12. The lower level of detection increased to 0.024% at times greater than 30 seconds. The signal to noise ratio was 3 during a 60 second exposure of the lowest concentration sample (0.024 wt%). The corresponding time yielded a signal to noise ratio of 40 for the 0.14% sample. A plot of Raman intensity verses distance for the 2065 cm^{-1} peak of the 0.14 wt% $\text{K}_4\text{Fe}(\text{CN})_6$ sample (figure 15) exhibits a $f(x) = a/x$ dependence similar to that noted for NaNO_3 . At 1.9 wt% $\text{K}_4\text{Fe}(\text{CN})_6$, the signal intensity of the 2065 cm^{-1} band is 1.7% of the intensity of the 1066 cm^{-1} band of NaNO_3 recorded under similar conditions.

4.4 BACKGROUND LIGHTING

The ratio of the intensity of the 1066 cm^{-1} band of NaNO_3 to the 579 nm Hg lines from fluorescent room lights is plotted verses distance in figure 16. The exposure time is 1 second. The 546 nm band is not included due to saturation of the 16 bit resolution of the CCD during the 1 second exposure.

4.5 MOISTURE CONTENT OF SAMPLE

The Raman spectra of both dry and moist (20 wt% H_2O) samples of NaNO_3 were recorded as a function of distance. The addition of moisture to the sample results in a decrease of 73% in the intensity of the 1066 cm^{-1} band of NaNO_3 , as seen in figure 17. This loss is presumably due to the concomitant decrease in sample reflectivity as the moisture content increases. The Raman spectra of $\text{K}_4\text{Fe}(\text{CN})_6$ (1.9 wt%) in moist NaNO_3 (21 wt% H_2O) were also recorded. The sample almost immediately showed evidence of oxidation to ferricyanide. The ratio of the 2065 and 2094 cm^{-1} bands of $\text{K}_4\text{Fe}(\text{CN})_6$ to the

Figure 13: Peak intensity versus weight percent $K_4Fe(CN)_6$ in NaCl. 1.5 feet. 10 second exposure. Non-contact Raman imaging system, single point mode.

Figure 14: Peak intensity versus weight percent $K_4Fe(CN)_6$ in NaCl. 1.5 feet. 30 second exposure. Non-contact Raman imaging system, single point mode.

Figure 15: Intensity versus distance. 0.14 wt% K₄Fe(CN)₆ in NaCl. 10 second exposure. 2065 cm⁻¹ K₄Fe(CN)₆ peak. Non-contact Raman imaging system, single point mode.

Figure 16: Ratio of Raman intensity / room lights vs distance. 1066 cm⁻¹ band of NaNO₃ versus 579 nm Hg room light. 1 second exposure. Non-contact Raman imaging system, single point mode.

Figure 17: Effect of moisture on Raman band intensity. Ratio of 1066 cm^{-1} band of NaNO_3 21wt% in H_2O versus dry NaNO_3 . Non-contact Raman imaging system, single point mode. 1 second exposure.

Figure 18: Effect of moisture on Raman band intensity. Ratio of 2065 and 2094 cm^{-1} bands of 1.9 wt% $\text{K}_4\text{Fe}(\text{CN})_6$ to the 1066 cm^{-1} band of NaNO_3 20wt% in H_2O versus distance. Non-contact Raman imaging system, single point mode. 5 second exposure.

1066 cm^{-1} band of NaNO_3 verses distance is plotted in figure 18. The ferrocyanide peaks represents approximately 2.3% of the signal NaNO_3 signal at any distance.

4.6 SCANNING IMAGING MODE

The non-contact imaging system can be run in a single point mode that emulates the operation of a contact fiber probe. In this mode the scanning mirrors are held at a constant DC offset to steer the beam like fixed, flat mirrors. Only the point where the laser beam impinges on the sample is probed. When an AC voltage is applied to the y-movable mirror, a vertical slit image of laser excitation is produced in the entire surface of the sample, the length of which is addressable by the volt-peak-to-peak (vpp) amplitude of the applied voltage, and the width which is due to the natural divergence of the laser. The stripe of laser light is imaged directly back to the slit of the monochromator, and subsequently onto the CCD detector. The two dimensional nature of the CCD in conjunction with the image corrected monochromator results in the spatial preservation of the Raman scattering originating at unique sites along the stripe of laser excitation. The result is a system that can image an entire surface cross-section of a sample at once. If the optics, or the sample, are translated in the plane perpendicular to the laser stripe and parallel to the front surface of the collection optics, the entire surface of the sample can be scanned in minutes or less.

The scanning imaging capabilities are illustrated in figures 19 and 20. The sample under investigation was layered with 4 inorganic salts with disparate Raman signatures placed 2 feet from the spectrograph. Spectra obtained when running under single point conditions yield only information about the point of illumination at the center of the sample, and suggest the presence of K_2SO_4 and Na_2MoO_4 (figure 19). When the y-mirror is scanned at 0.25 vpp, the spectrum reveals all of the components present along the front face of the sample with a single exposure time of 1 second. The components of the sample can be spatially resolved if the CCD chip is partitioned into 10 read-out stripes 51 pixels in height. Figure 21 shows the spatially resolved sample and the corresponding Raman spectra, all recorded simultaneously with an exposure time of 1 second.

The scanning imaging Raman spectrograph can also be designed without the use and expense of scanning mirrors. If the mirrors are held static, a negative cylindrical lens can be used to generate the vertical laser stripe on the sample. Results of such a lens system were comparable to those of the scanning mirror system.

Figure 19: Non-contact Raman imaging system. Mixed component sample. Single point mode. 1 second exposure. Full CCD chip bin.

Figure 20: Non-contact Raman imaging system. Mixed component sample. Scanner mode, 0.25 Vpp. 1 second exposure. Full CCD chip bin.

Figure 21: Non-Contact Imaging Raman Spectroscopy. Four Component Sample. Scanning mode. 1 second exposure. CCD Chip Partitioned into 10 Stripes

5.0 COMPARISON OF FIBER PROBE AND NON-CONTACT IMAGER

The intensity of the Raman signal from a sample is given by the following relationship:

$$\frac{S}{N} \propto [\Theta_M] \left[\frac{1}{\lambda^4} \right] [G][P][\epsilon_D]$$

where Θ_M is the spectrograph efficiency, λ is the laser wavelength, G is the efficiency of the collection geometry, P is the laser power, and ϵ_D is the detector efficiency. In the present study, Θ_M , λ , and ϵ_D are constants. P is also held constant at the laser source. The collection geometry G is therefore the primary source of any differences in the signal observed for identical samples by the single point fiber probe and the single point non-contact imaging system.

5.1 POWER

While the power of the laser output is held constant at the laser source, the available power at the sample is twice as great for the non-contact imaging system than it is for the fiber probe. Twice the Raman signal should be achievable by the non-contact system, allowing for greater sensitivity at the available system laser power.

5.2 DISTANCE

A change in distance of 0 to 1 cm between the fiber probe tip and the surface of a solid sample results in a 80% decrease in Raman signal intensity. Smaller changes in distance, 0.5 mm, result in a 10% decrease in signal. These data demonstrate the criticality of precise probe placement for reproducible results in making absolute Raman measurements for the determination of sample concentrations. This constraint is made more challenging in the hot cell environment, where the fiber probe is positioned with the use of a robotic arm operated by an external user. The current working solution to this requirement is the use of a probe that is placed directly into the solid sample.

The non-contact system is much less susceptible to distance. Once the camera optics are focused on the sample, translations along the optical axis of the camera lenses of several centimeters (1 to 2.5) result in minor changes in signal intensity of no more than 10%. The use of auto-focusing camera optics could reduce these variations in signal intensity. The absolute intensity of the Raman signal does decrease over large distances, on the order of feet. Within the hot cell environment, the changes in distance from the collection optics to the sample would be solely due to variations in the surface of the core sample. This situation was tested using a mixed $\text{Ca}(\text{NO}_3)_2$: NaNO_3 / K_2SO_4 : CuSO_4 mock core sample. The inorganic salts were mixed with water, layered in a glass tube, and pressed into a cylindrical "core". The core was positioned with its long (length) axis parallel to the table and perpendicular to the camera optical axis on a motorized

translational stage, which moved along the long axis of the sample, effectively scanning the sample through the field of view of the imaging system. The boundaries of the components (nitrate, sulfate) were parallel to the monochromator slits. The sample was allowed to sit for a week, during which time it absorbed moisture from the air and partially dissolved, deforming the surface of the core to give peak to trough distances of up to 0.5 inches. The fiber probe was positioned perpendicular to the optical axis of the scanning system, giving it the view of the same portion of the sample. The probe signal was maximized at the starting point, 0.0 mm from the surface. As the core was scanned, the signal due to the fiber probe rapidly diminished as the sample surface fell away. In addition, the fiber probe was "blind" to the weaker sulfate Raman scatter due to nitrate occluding to the surface of the probe. The non-contact system scanned the sample without more than 10% fluctuations in nitrate signal intensity, and was able to readily observe the sulfate regions of the core. In addition, the non-contact system detected nitrate in the sulfate regions of the sample. Over several days the nitrate signal grew stronger, and crystals of white nitrate were observed on the blue sulfate background.

5.3 SENSITIVITY

Comparison of the Raman spectrum of NaNO_3 taken at 1 second exposure with the fiber probe at 0.0 mm (Figure 9) and the non-contact imaging system in single point mode at 1.5 feet (Figure 22) illustrates the superior collection efficiency of the non-contact technique. The intensity of the 1066 cm^{-1} band of NaNO_3 by the non-contact method is 13 times greater than that obtained by the fiber probe.

The observed lower detection limit of the fiber optic probe at 10 second exposure time is 0.95 wt% $\text{K}_4\text{Fe}(\text{CN})_6$ in NaCl with a signal to noise ratio of 10. The non-contact probe can detect 0.14 wt% in NaCl with comparable signal to noise (12) at 1.5 feet. With 60 second exposure, the fiber probe can detect 0.14 wt% with a signal to noise of 2, while the non-contact system can distinguish 0.024 wt% from background with a signal to noise of 3. The spectrum of a 0.14 wt% ferrocyanide sample using both the fiber probe and non-contact systems with 60 second exposure are shown in Figures 23 and 24 respectively.

The moisture study described in section 4.5 demonstrated that a sample with 20% moisture content gave a Raman signal 73% less intense than the same sample with little or no moisture content. Thus, the lower limits of detection of ferrocyanide in a real, moist sample will be at a higher level than the dry samples probed in this study. More realistic limits are probably 1 wt% by fiber probe, and 0.1 wt% by non-contact without post-collection data processing for signal extraction.

5.4 BACKGROUND LIGHTING

Comparison of Figures 8 and 16 show that the non-contact imaging Raman technique is more prone to interference from room lights than the fiber probe. The ratio of the 1066 cm^{-1} Raman peak of NaNO_3 to the 579 nm Hg line from fluorescent lighting is three times greater for the fiber probe data than for the non-contact data. Exclusion of room

Figure 22: Raman spectrum of NaNO₃. Non-contact Raman imaging system. 1 second exposure. Single point mode.

Figure 23: Raman spectrum of 0.14 wt% K₄Fe(CN)₆ in NaCl. Fiber optic probe. 60 second exposure.

Figure 24: Raman spectrum of 0.14 wt% $\text{K}_4\text{Fe}(\text{CN})_6$ in NaCl. Non-contact Raman imaging system. Single point mode. 60 second exposure.

lights, particularly Hg based lamps, is important for the non-contact system, particularly since the 577 and 579 nm bands of Hg fall at 2105 and 2165 cm^{-1} relative to 514.5 nm, in the region where weak ferri- and ferro-cyanide bands may be found. The line from sodium based lights resides at 2487 cm^{-1} .

5.5 GLASS FIBER RAMAN

There were no glass Raman peaks due to glass fibers in the non-contact system in the configuration described in this study. The conceptual design detailed in section 6.1 includes a fiber optic to bring laser excitation from an external source into the hot cell environment. The potential for glass Raman signals exists in that configuration. However, unlike the fiber probe, a band pass filter can be introduced into the system to remove unwanted fiber background prior to excitation of the sample. The filter would never be closer than a foot or so to potentially radioactive core samples, and may be lead shielded to further reduce or possibly eliminate radiation damage to the filter. In the fiber probe, such a filter would be within millimeters of the radioactive core samples.

5.6 INTERFERENCES

As there is no contact between the collection optics of the imaging system and the core or solid samples, there is little or no interference due to occlusion of sample on the collection optics. In addition, the much larger surface area of the collection optics would be far less susceptible to interferences than the comparatively small area of the fiber probe.

6.0 CONCLUSIONS

Both the remote fiber optic probe and the non-contact, line-of-sight, imaging Raman systems are capable of the characterization of molecular species in a hot cell environment. The non-contact system offers the advantages of little or no contamination by samples, higher signal levels and sensitivity, and less stringent positional constraints in the placement of the collection optics relative to the sample. The great strength of the non-contact imaging system is its ability to rapidly scan the entire surface of a core sample. The time allocated to the sampling of individual cores can be greatly reduced with a rapid surface scan method.

The fiber optic probe offers the advantages of compact size and easy construction, as well as the ability to interrogate the interior of core samples with a "mash" probe that can be driven within the sample. The fiber probe is also less susceptible to interferences from external light sources.

In conclusion, a core characterization scheme that provides both fiber optic and non-contact capabilities would be the recommendation of this report. The techniques can be used in a complementary fashion. The non-contact imaging system provides rapid scanning of core surfaces. If a hot spot is located, it can be further, more intimately

investigated using the non-contact system in single-point mode, or the fiber optic probe. The fiber optic probe would then be used to probe the interior of the core sample to pinpoint the exact source of contamination, and determine if interior concentrations are realistically reflected in the surface measurements.

6.1 CORE SCANNING SYSTEM RECOMMENDED SPECIFICATION

A non-contact core imaging system must be capable of standing alone in a hot cell environment, with light and electricity supplied by enclosed cables and fiber optics. The test system described in this report, while suitable for lab bench-top studies, is inappropriate for hot cell use as it uses open laser beams that are steered by mirrors. In a conceptual design for a hot cell non-contact Raman imaging system, a radiation hardened optical fiber transmits laser light from the laser head into the hot cell through available cable conduits. The natural divergence of the fiber optic is used to rapidly expand the beam to 1 or 2 inches, where it is then collimated with the appropriate spherical lens. The collimated beam is passed through a band pass filter to remove fiber optic Raman signal from the launch fiber, then focused down to a vertical slit image, or stripe, on the core sample using a cylindrical lens. The lens should be chosen with a long confocal length to evenly illuminate the uneven surface of the core sample. Camera optics, either fixed or auto-focusing, are used to image the laser stripe onto an array of fiber optics vertically arranged as an image quality fiber optic "tape" or stripe bundle. Such a bundle can be purchased from a commercial vendor. The fibers then pass back through the conduit, and are arranged as a vertical slit image using the existing optical rail on the CHROMEX IS-50 system already in use at WHC. The surface image of the sample is maintained through the imaging vertical fiber optic bundle, and can be interrogated by binning the CCD chip using multiple stripes.

The focus of this report has been on Raman Spectroscopy. However, the non-contact imaging system is not limited to Raman alone, and may offer the opportunity to integrate other optical techniques developed elsewhere, such as near IR surface moisture scanning, and continuous wave or pulsed fluorescence spectroscopy for organic complexes, into the system for a complete core scanning system.

7.0 ACKNOWLEDGMENT

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