

Dual-Remote Raman Technology for In-Situ Identification of Tank Waste – 13549

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ABSTRACT

A new Raman spectroscopic system for *in-situ* identification of the composition of solid nuclear tank waste is being developed by collaborative effort between Pacific Northwest National Laboratory (PNNL) and EIC Laboratories, Inc. The recent advancements in Raman technology allow probing the chemical composition of the tank waste without sample collection. In the newly tested configuration, the Raman probe is installed on the top of the tank riser and sends the incident laser beam to the bottom of the tank, 10 – 70 feet away. The returning light containing chemical information is collected by the Raman probe and is transmitted via fiber optic cable to the spectrometer located outside the tank farm area. This dual remote technology significantly expands currently limited options for the safe rapid *in-situ* identification of the solid tank waste needed for the retrieval decisions.

The developed Raman system was extensively tested for acceptability prior to tank farm deployment. This testing included calibration of the system with respect of the distance between the Raman probe and the sample, incident laser beam angle, and presence of the optical interferences. The Raman system was successfully deployed on Tank C-111 at the US DOE Hanford site. As the result of this deployment, the composition of the hardpan at the bottom of C-111 tank was identified.

Further development of the dual-remote Raman technology will provide a significant safety enhancement eliminating the potential of personnel radiation exposure associated with the grab sample collection and expands options of the rapid and cost-effective *in-situ* chemical analysis of the tank waste.

INTRODUCTION

Tank waste retrieval operations at U.S. Department of Energy (DOE) sites are tremendously challenging. The chemistry is highly complex and involves multi-phase materials that may require multiple approaches to retrieve. Controlling these processes requires a wealth of information regarding the chemistry, chemical engineering, and material science involved. Tank waste samples are intensely radioactive and both difficult and expensive to obtain. In many cases, the sampling involves specialized robotic applications or other stand-off approaches for

obtaining a single sample. The development of *in situ* characterization technologies is needed to assist in:

- Process operations, such as retrieval (in-line)
- Screening situations for process understanding (*in situ*)
- Assisting closure operations to determine the extent of cleaning.

Raman spectroscopy can be used as a means to determine mineral and chemical species present in waste tank heels *in situ*. Raman spectroscopy is a vibrational spectroscopic method that provides information on molecular structure, which in turn can be applied to identifying specific species present in a sample material. In this respect, each mineral or chemical compound that has Raman-active vibrations will display a characteristic “fingerprint” in the Raman spectrum. Modern fiber-optic technology makes it possible to measure Raman spectra from remote locations. A schematic illustrating the intended use of the telescopic Raman system is shown in Figure 1.

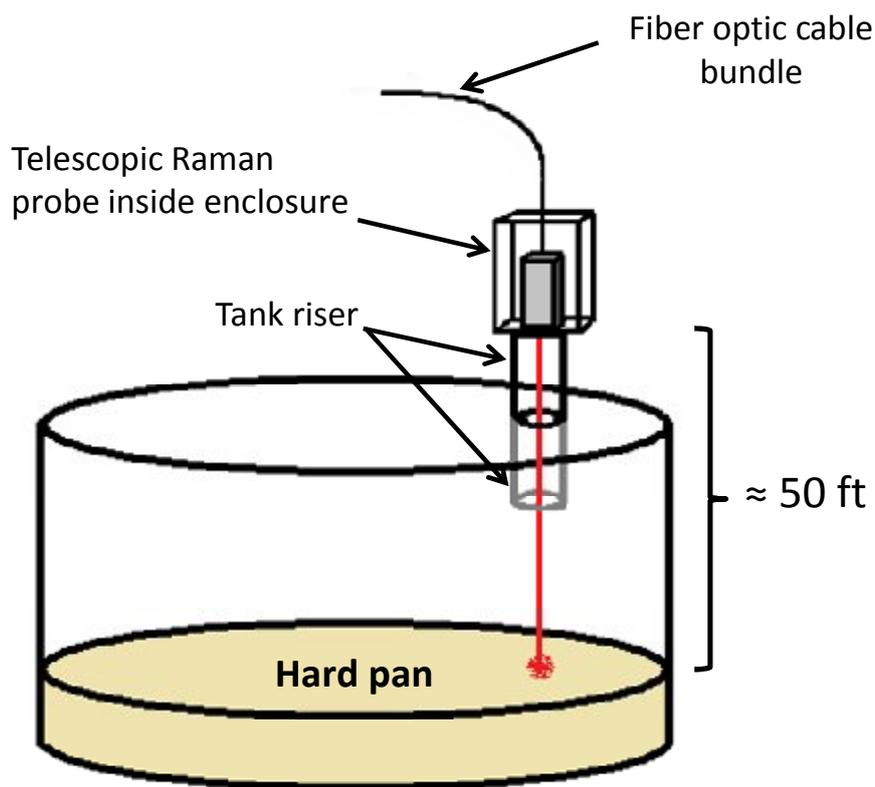


Figure 1. Schematic Illustrating the Intended use of the Telescopic Raman System Developed in this Work for *In Situ* Analysis of the C-111 Hard-pan Heel

During the last decade, Pacific Northwest National Laboratory (PNNL) has investigated the use of spectroscopic monitoring approaches for real-time, on-line monitoring of high-level waste from Hanford and Savannah River Site tank waste materials. Work at PNNL has supported the maturation of a Raman spectroscopy system suitable for use in chemical species measurements and/or monitoring. This system is applicable to on-line/in-line monitoring of waste retrieval and processing and already has been applied to a number of activities at Hanford. For example, a Raman process monitor was developed and constructed for implementation during the Tank S-109 saltcake retrieval project [1, 2]. Additionally, a full quality assurance/quality control (QA/QC) HASQARD-compliant protocol for a laboratory-based Raman method for sludge leaching solution measurements was developed, “Raman Analysis of Aqueous Solutions,” PNNL Technical Procedure, RPG-CMC-240 [3]. This commercial procedure was deployed for service as an analytical tool for the Waste Treatment Plant, Pretreatment Engineering Platform (PEP) and successfully analyzed 470 samples over a six-month period of continuous use (November 2008 to April 2009).

In FY2011 PNNL tested the concept of positioning a telescopic Raman probe on top of a waste tank riser so it can be used to directly probe the composition of the tank heel. This technology can be applied to meet the Washington River Protection Solutions (WRPS) need for identifying the composition of tank hard-pan heels and in-tank liquids. The objective of this project is to provide WRPS with the capability of *in situ* rapid measurement of hard-pan components within Hanford underground tanks. The specific goal of the work was to develop methodology for the remote qualitative identification of the major components of the C-111 tank hard-pan heel.

EXPERIMENTAL

The Raman telescope system consists of a fiber-optic Raman telescope with computer-controlled focusing that can be used to acquire Raman spectra from samples at a standoff distance of ≥ 50 ft. The key components of the Raman telescopic probe are a modified InPhotonics RamanProbe™, a linear actuator with a mounted miniature eyepiece plano concave lens (6 mm diameter, -6 mm focal length), and a 50-mm-diameter achromatic doublet objective lens (100-mm focal length). The Raman probe is fiber optically coupled to a Raman spectrograph and a laser. The system was equipped with a stabilized 670 nm, 1 W (variable power) visible diode laser as the excitation source. To minimize the laser spot at the sample, a small-core, low-divergent (10- μm core, 0.1-numerical aperture) step-index multimode optical fiber was used for coupling the laser to the Raman probe. This resulted in a diffuse laser spot (~ 5 -mm-diameter beam) at the sample at >50 ft standoff distances. The focus of the telescope can be adjusted electronically with a computer, which precisely controls the movement of the linear actuator with the mounted eyepiece. The linear actuator is connected to a small, low-power, stepper motor driver card inside the telescope that is connected to the computer via a serial line. The probe focus can be adjusted from 10 ft to 70 ft.

Two main types of laboratory samples were prepared for this study: pressed powder pellets and tamped powders in straight-shell glass vials. The purpose of making pressed pellets was to have a large, free surface of powdered sample that could be mounted perpendicular to the beam path and used for the variable distance and angle measurements. The purpose of creating the tamped surfaces was to have a series of pure phase and multi-component mixtures, where a free surface of powdered materials could be analyzed either in contact mode or at various distances.

RESULTS AND DISCUSSION

This section describes the use of the telescopic Raman system for the measurement of tank waste material from within Tank C-111. Prior to the deployment of the telescopic Raman system for *in-situ* measurements, the system was extensively tested within the laboratory using simulated waste materials and pure chemical standard materials of phases expected to be within Tank C-111. The initial sections below describe the laboratory testing and the creation of a “training” database used to build datasets of variable salt composition and distances. The “training” set was used to form chemometric models for the predicting of additional telescopic Raman probe measurements at variable distances and composition. Subsequent sections are devoted to deployment activities within the Hanford C-Tank farm. The last section compares the *in-situ* measurements of Tank C-111 hard-pan material with Raman measurements of archived C-111 grab sample material.

Development of Training Set for Telescopic Raman Probe

Figure 2 shows a photograph of the telescopic Raman probe deployed within the laboratory for measurements at variable distances. A close-up view of a test sample illuminated under Raman laser light (670 nm) is also shown in this figure. Multiple samples were measured by the telescopic Raman system at variable distances using multiple salt compositions likely present in Hanford tank waste. A data set of individual samples, which were combinations of components, including NaNO_3 , NaNO_2 , Na_2CO_3 , Na_2SO_4 , Na_2CrO_4 , Na_3PO_4 , $\text{Na}_2\text{C}_2\text{O}_4$, $\text{NaAl}(\text{OH})_4$, boehmite, and gibbsite, was prepared. These samples were measured at distances ranging from 10 to 50 ft. Figure 3 shows an example of Raman spectra of multiple samples containing variable component mixtures.

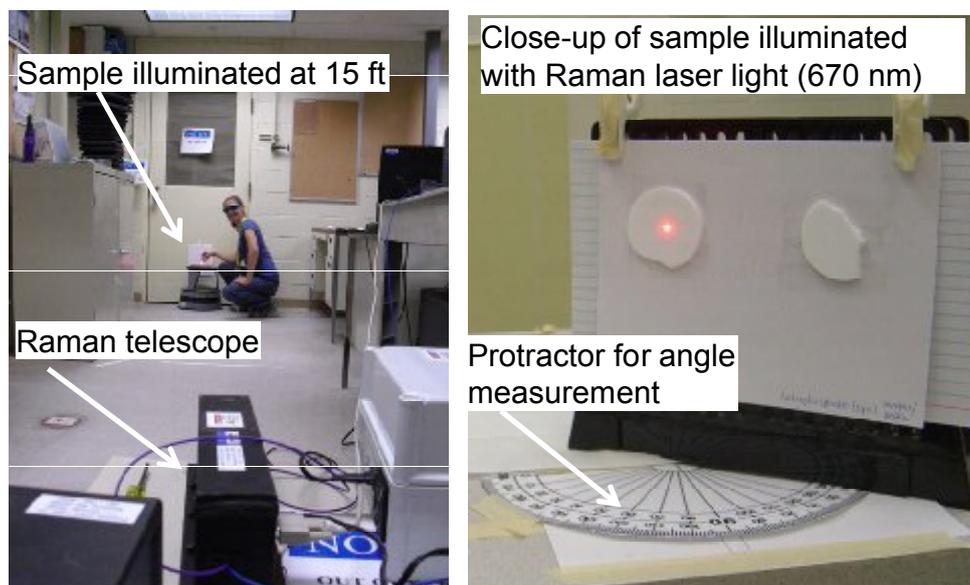


Figure 2. Photograph Showing (left) the Telescopic Raman Probe Deployed Within the Laboratory for Measurements at 15 ft; and (right), a Close-Up of a Test Sample Illuminated Under Raman Laser Light (670 nm)

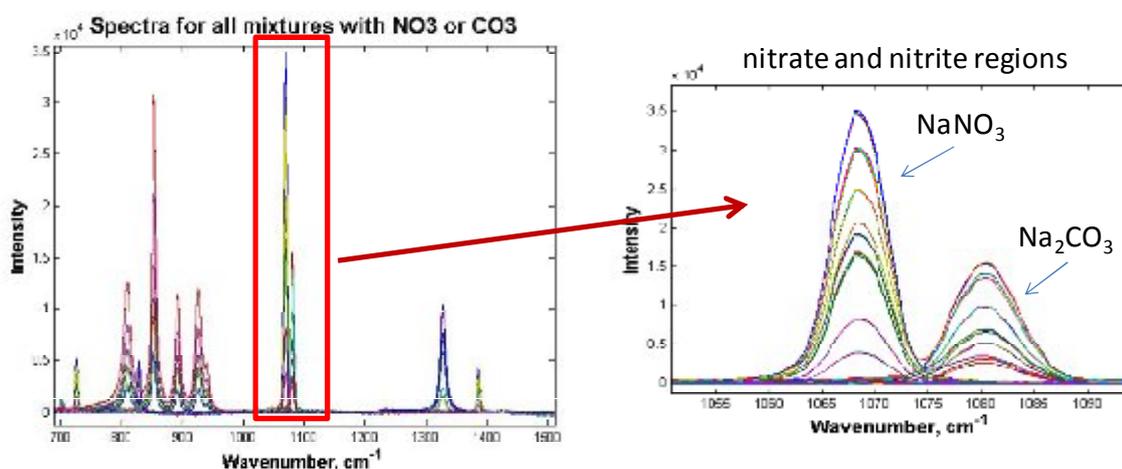


Figure 3. Example of Raman Spectra Containing Variable Component Mixtures. The changes in Raman band location and intensity are used in the chemometric model to predict the composition of a new sample spectrum.

Telescopic Raman System for Tank Deployment

A schematic drawing of the flange assembly containing the shielded housing and Raman telescopic probe is shown in Figure 4 (left). This figure depicts the Raman probe as it would be

positioned within the housing, ready for attachment of the flange to the tank C-111 riser. Figure 4 (right) is a photograph of the flange assembly with the telescopic probe attached. Prior to field deployment, the complete telescopic Raman system was inspected by the appropriate WRPS electrical and laser safety representatives who certified the system met all electric/electronic and laser standards, respectively.

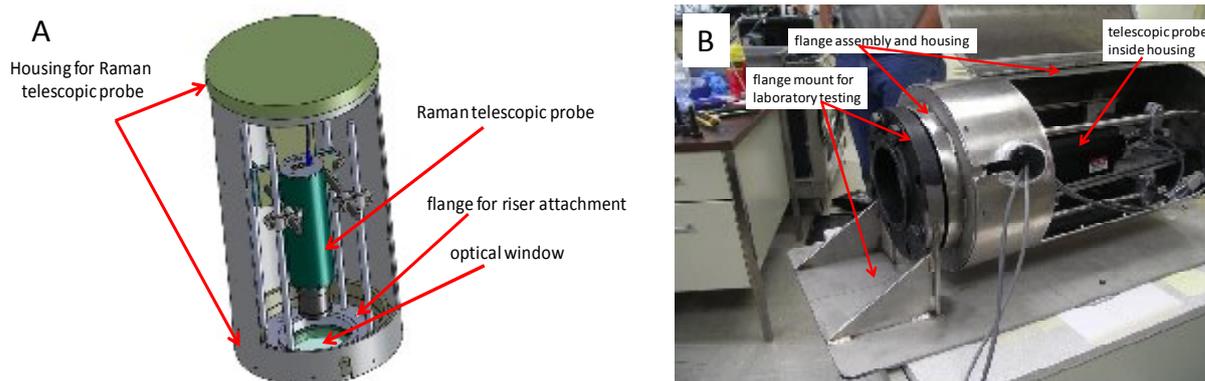


Figure 4. A) schematic drawing of the flange assembly containing the shielded housing and Raman telescopic probe. B) Photograph of Flange Assembly and Housing Containment with Raman Telescopic Probe Installed

Deployment of Raman System to Hanford Tank C-111

The Raman system was deployed to Hanford Tank C-111 during December 2011 through May 2012. The Raman instrumentation was housed within a trailer outside the tank-farm boundary, while the Raman probe was attached to the riser on Tank C-111. The fiber-optic cable connecting the Raman instrumentation (in trailer) to the probe (on-tank) stretched a distance of approximately 300 ft. The placement of the fiber-optic cabling within the protective track is shown in the photograph in Figure 5. Figure 6 is a photograph of the Raman assembly installed on Riser-7 on Tank C-111. Figure 6 (right) is a photograph of the in-tank video screen, showing the laser beam on the floor of Tank C-111, where the laser point of focus (bright spot in center), the “halo”, and laser beam are observed. The ability to see the laser beam path in the tank, in this figure, is a result of the amount of fog within the tank causing light scattering from the fog particulates.

The “halo” observed within the tank, as documented in the photographs in Figure 6 is explained by the arrangement of the Raman probe within the protective housing at the top of the 12 inch riser. The laser is focused through the quartz window separating the probe compartment from the tank environment within the riser giving rise to laser light scattering at the air-quartz

interface. The laser light interaction with the quartz window as well as other optical components within the Raman system causes some laser light to be scattered in all directions. Some of the scattered light will happen to pass from the end of the riser, and illuminate the bottom of the tank (C-111 tank floor). The result is a circle of light (“halo”) cast on the tank floor, with the rest of the tank being in shadow, by the riser. When the laser is aligned to emerge from the riser, it will appear as a bright spot within the “halo” at the tank floor. Since the tank riser is the cause of the shadow for the “halo”, the laser point of focus is limited to be within the area of the “halo”.

The video-photograph of the tank floor in Figure 7 shows the general area where Raman measurement were taken under Riser-7; the laser is focused at the upper portion of the figure. This figure shows the same video-photograph annotated with locations of Raman spectra taken superimposed on the figure. The video-photograph shows the entire region of data collection, the “halo” is difficult to see in this view, however, the light and dark patches on the tank floor are easily observed. The data collected centered on white clumps at the 6, 9, and 12 o’clock positions (211-213, 201-206, and 210 respectively). There were several dark spots at just above center of the viewing area (208 and 209), and a measurement was taken at a region of no apparent feature (grey area at position 207).

Figure 8 contains the comparison of in-tank C-111 spectra 201 through 206 (“light” areas) compared with a literature sample of nitrate–cancrinite $[\text{Na}_8(\text{Al}_2\text{Si}_2\text{O}_8)_3(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}]$ [4]. This literature spectrum is a good match for the multiple regions of interest; both the 1050 cm^{-1} region (active for nitrate/carbonate) and the 800 cm^{-1} and 600 cm^{-1} bands assigned to the aluminosilicate stretching modes match the C-111 spectra well. The observed bands in the in-tank spectra are broadened, as is expected since the in-tank material is expected to be a mixture of substances, which will give rise to peak broadening. Other aluminosilicate mineral phases of similar compositions, namely Scapolite $[\text{Ca}_4(\text{Al}_2\text{Si}_2\text{O}_8)_3(\text{CO}_3)]$, and carbonate-cancrinite $[(\text{Na})_8(\text{Al}_2\text{Si}_2\text{O}_8)_2(\text{CO}_3)_2 \cdot (2\text{H}_2\text{O})]$ (taken from the literature database University of Arizona (RRUFF) database) were also a reasonable match for the in-tank measurements.

In addition, archive samples of tank C-111 tank waste were available for analysis using the Raman technique within our laboratory. The Raman spectral analysis of two Tank C-111 grab samples are consistent with the Raman spectra of C-111 hardpan material collected *in-situ* using telescopic system deployed on the tank riser; confirming the presence of cancrinite carbonate $[\text{Na}_8(\text{Al}_2\text{Si}_2\text{O}_8)_3(\text{CO}_3) \cdot 2\text{H}_2\text{O}]$ and potentially gibbsite within the hard-pan material of Tank C-111.

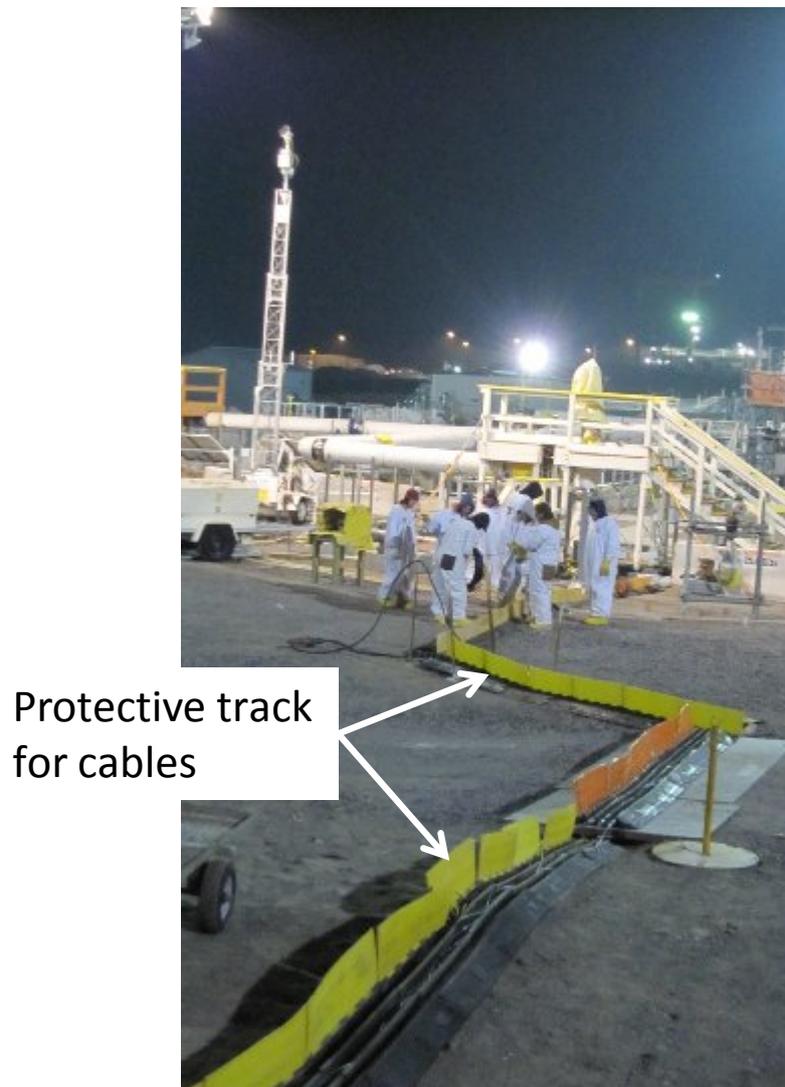


Figure 5. Photograph Showing Field Crew Positioning Telescopic Probe at Tank and Placing Fiber-optic and Electrical Cables within Protective Track.

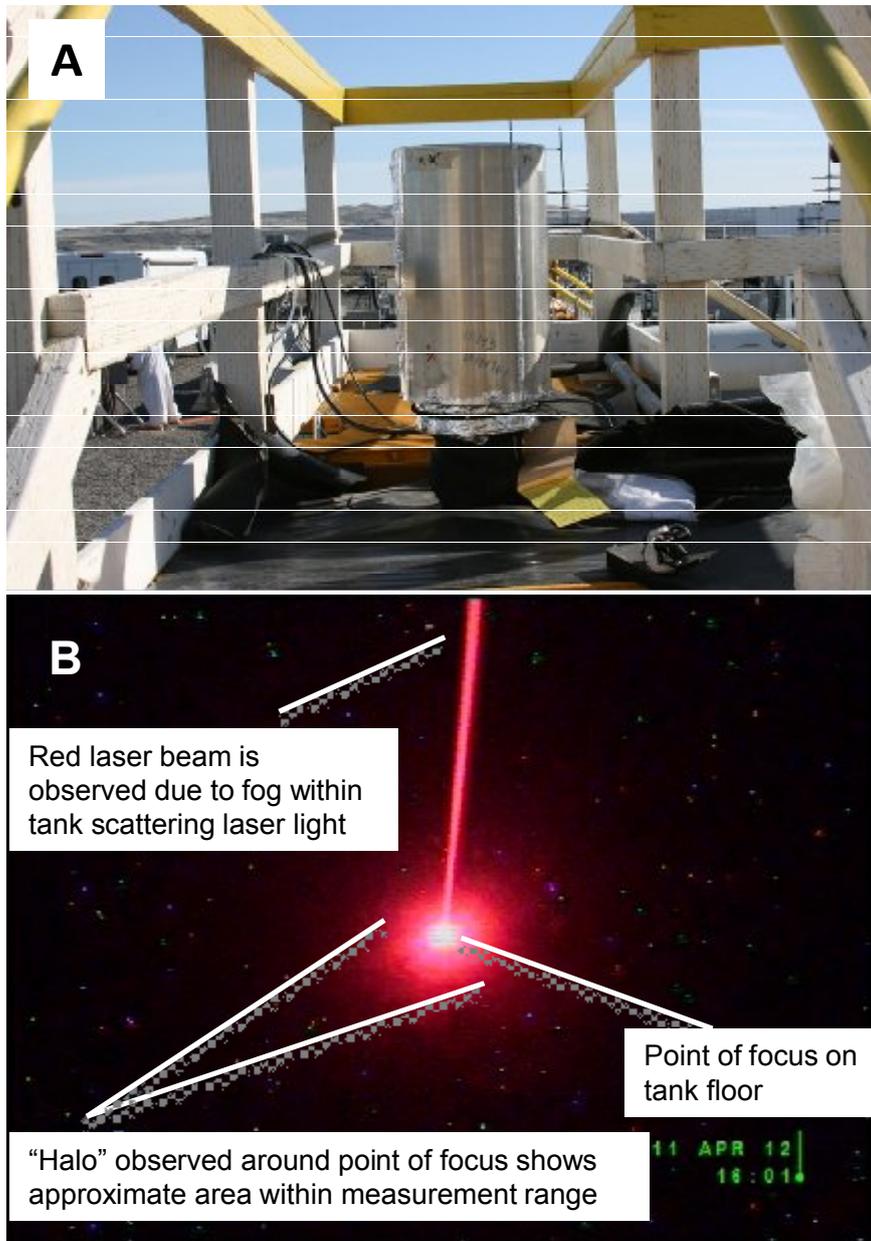


Figure 6. (A) Photograph of Raman Assembly Installed on Tank C-111, Riser-7. (B) . Photograph show area “halo” of illumination on tank floor below riser, and laser beam through fog, and point of focus on tank floor.

Circle is approximate area within Raman range

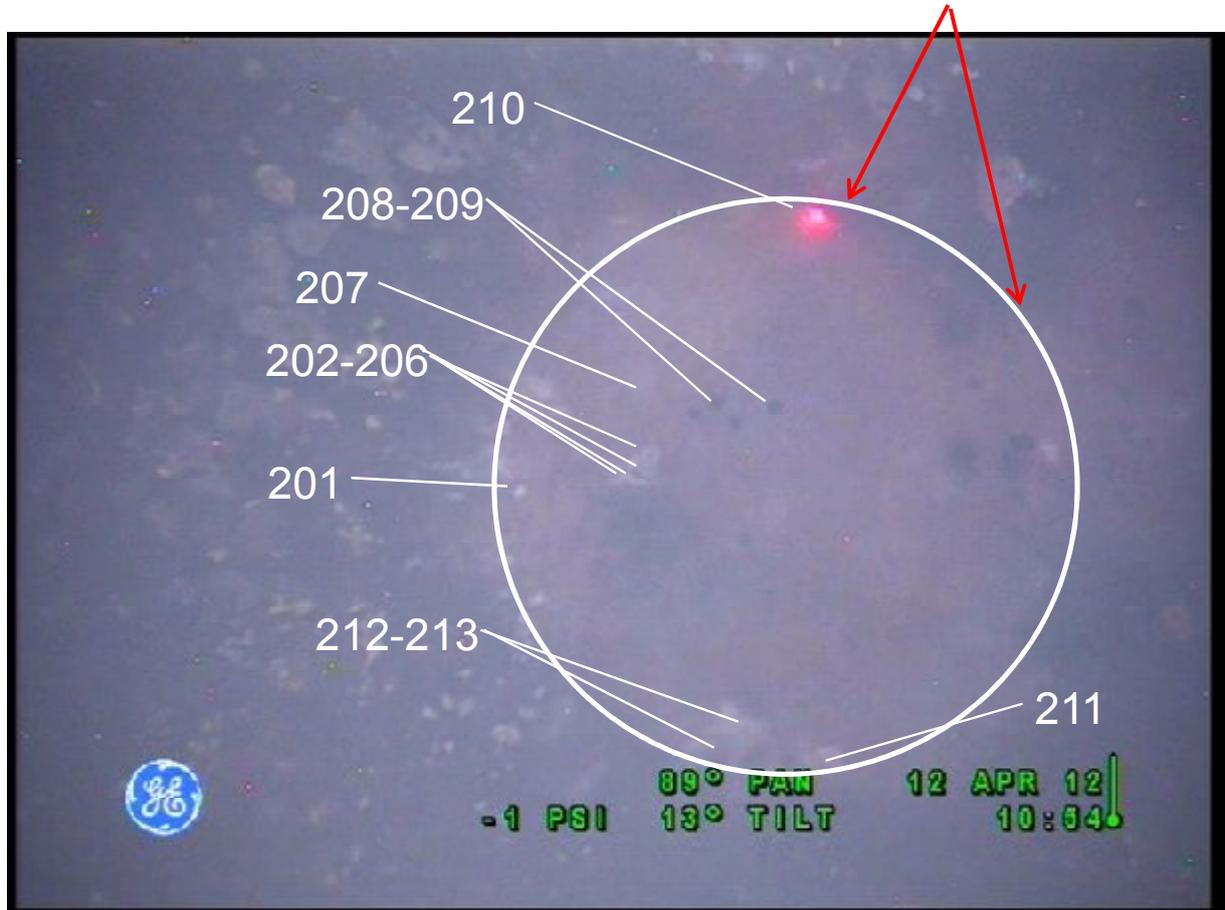


Figure 7. Annotated Photograph showing locations of Raman Measurements, April 12, 2012. (Photograph 208 taken from videography). Location of spectra: 201 white “clump”; 202-206 large white “clump”; 207 blank grey area; 208-209 black spots/holes; 210 white area; 211-213 white “clumps”.

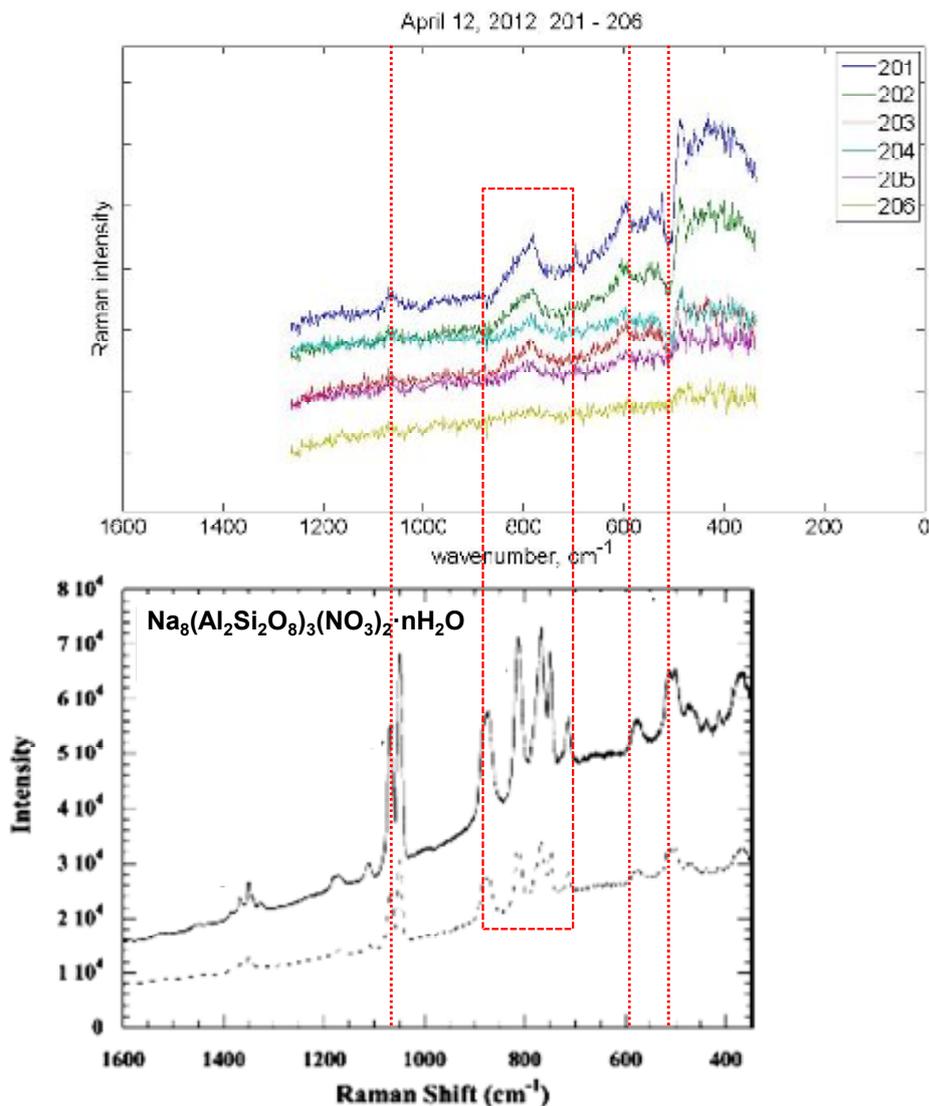


Figure 8. Comparison of In-tank Measurement with Literature Spectrum of Nitrate-cancrinite [$\text{Na}_8(\text{Al}_2\text{Si}_2\text{O}_8)_3(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$]. Good match from literature (Environ Sci Technol. 2004, 38, 4432-4438). The x-axis scale is reversed in the C-111 in-tank spectra, in order to match the x-axis scale of the literature spectrum.

CONCLUSIONS

Collaboration between the Pacific Northwest national Laboratory and EIC Laboratories, Inc. led to the development of a prototype telescopic Raman probe that can be mounted on risers on top of the waste tanks at the Hanford Site to remotely analyze precipitates left behind as the tanks are

emptied. A laser source coupled with the appropriate telescopic lenses and spectrometer enables the user to remotely identify compounds (e.g., aluminum hydroxide or calcium phosphate solids) in test samples up to 50 feet away. A 300-foot fiber optic cable transfers laser light to and from sources and detectors outside the tank farm boundary during data collection. Unknown spectra are then compared with a library of pure and mixed-phase samples of possible tank precipitates for identification. This work builds upon extensive experience and breadth of expertise in using physical and spectroscopic parameters to monitor and characterize various waste streams.

This work demonstrated the utility of the telescopic Raman system for *in-situ* measurement of tank waste components. In-tank measurement confirmed the presence of several aluminum-containing phases within the tank waste. This work also documents the results of the Raman measurements of the archive C-111 sludge samples and their comparison with *in-situ* Raman measurements of the C-111 hardpan material. The major findings include the spectroscopic confirmation of Gibbsite and cancrinite carbonate $[\text{Na}_8(\text{Al}_2\text{Si}_2\text{O}_8)_3(\text{CO}_3)\cdot 2\text{H}_2\text{O}]$ within the tank waste grab samples. Raman spectra of two Tank C-111 grab samples are consistent with the Raman spectra of C-111 hardpan material collected *in-situ* using telescopic system deployed on the tank riser; confirming the presence of cancrinite carbonate $[\text{Na}_8(\text{Al}_2\text{Si}_2\text{O}_8)_3(\text{CO}_3)\cdot 2\text{H}_2\text{O}]$ and potentially gibbsite within the hard-pan material of Tank C-111.

The quality of the spectra collected using telescopic and contact Raman systems is comparable confirming adequate performance of the telescopic Raman system and its usability for the determination of the Raman-active components in the composition of the tank sludge *in-situ*.

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