

# Integrated Raman Sensor for In-Tank Corrosion Chemistry Monitoring

Characterization, Monitoring, and Sensor  
Technology Crosscutting Program and  
Tanks Focus Area



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# **Integrated Raman Sensor for In-Tank Corrosion Chemistry Monitoring**

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Characterization, Monitoring, and Sensor Technology  
Crosscutting Program and  
Tanks Focus Area

*Demonstrated at*  
Savannah River Site  
Aiken, South Carolina

# **INNOVATIVE TECHNOLOGY**

Summary Report

## ***Purpose of this document***

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://www.em.doe.gov/ost> under "Publications."



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# SECTION 1 SUMMARY

## Technology Summary

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The DOE has 280 underground tanks used to process and store more than 90 million gallons of high-level radioactive chemical waste. Corrosion of the tank walls occurs because many of the tanks contain high concentrations of nitrate, which promotes the pitting and stress corrosion cracking of steel. To minimize corrosion, the tank contents are maintained at an elevated pH through the addition of sodium hydroxide and are maintained at an enhanced nitrite level. To ensure that the proper chemistry in a waste tank is maintained, it is important to monitor the concentrations of nitrate, nitrite, and hydroxide periodically, and to take appropriate measures as needed to restore optimum anti-corrosive conditions.

The Raman probe utilizes Raman spectroscopy, an optical method that detects many organic and inorganic chemicals in the media surrounding the probe. When laser light is beamed through a sapphire window, the light hits the sample, causing molecules to vibrate in a distinctive way, creating a vibrational “fingerprint.” The optical vibrational signal is captured and transmitted via fiber-optic cables to an analyzer, where it is compared to known fingerprints. The result is an analysis of the material surrounding the probe. With this tool, corrosion of the tank walls can be minimized through efficient maintenance of tank chemistry. Figure 1 is a photograph of the Raman probe housing that is designed for deployment inside a high-level waste (HLW) tank. Also attached to the outside of the housing are electrodes that are part of an Electrochemical Noise (EN) probe system that is designed to measure actual rates of corrosion *in situ*. This second technology is being co-deployed with the Raman probe but is not the subject of this report.



Figure 1. Raman Probe Housing with EN Electrodes Attached; see Figure 4 for Details.

The monitor system uses an echelle-based Raman spectrograph with a fiber-optic Raman sensor probe deployed *in situ* in waste tanks. The instrument can measure nitrate, nitrite, and hydroxide over the full range of concentrations of significance to DOE. The instrument is operated remotely, with only a small, lightweight probe and composite cable deployed in the tank by an enclosed water tight reel mechanism that mounts on the top of a tank riser.

Users of this technology are anticipated to be the operations divisions of DOE contractors at the Savannah River Site (SRS) and the Hanford Reservation (Hanford). These two sites maintain carbon steel tanks that must be protected from corrosion. Deployment of the monitor is most advantageous for tanks where frequent waste transfers occur. As waste remediation operations increase at these sites, the need for corrosion monitoring and control is expected to grow. The Raman system described here has been designed specifically for SRS; adaptation to Hanford needs is projected to be straightforward.

Current analytical protocols for the analysis of nitrate, nitrite, and hydroxide in HLW tanks involve liquid sampling, preservation, transport, storage, preparation, and analysis with a pH meter and

an ion chromatograph in a hot cell. These steps are slow, expensive, and present a major risk of exposure for site personnel and analysts.

Implementing *in situ* Raman sensors significantly reduces analysis time, which for liquid sampling often can be weeks or more. Eliminating all the steps prior to analysis as well as the need for specialized facilities and equipment for the analysis reduces cost. Risk to site workers is reduced because “hot” samples do not have to be handled or transported. More significant cost savings are achieved by reducing the amount of caustic added to the tanks by allowing the addition of just the minimum needed to inhibit corrosion. Consequently, the amount of additional solid waste that must be ultimately processed is reduced.

## **Demonstration Summary**

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The component technologies of the integrated Raman probe have been demonstrated and tested in several ways. Those demonstrations include the following:

### **Raman Probe** (See ITSR OST TechID1544, July 1999).

A Raman probe was developed for soil subsurface deployment using a cone penetrometer by engineering and optimizing the technologies to work together. The cone penetrometer is a hydraulically pushed pipe train, originally developed for geological and groundwater applications, equipped with sensors that measure physical parameters such as soil moisture, temperature, and pH. Changes made specifically to support the Raman probe involved adapting the Raman probe for in-tank and subsurface field use and developing real-time data analysis.

In 1998, two demonstrations of the Raman probe cone penetrometer system were performed for *in situ* characterization of organic bearing tank waste and for *in situ* detection of soil contamination. For the first demonstration, all of the hardware was radiation hardened, designed for and tested in the high-radiation, highly caustic chemical environment of waste storage tanks. A sealed sapphire window was added to the system to allow laser light to pass through the window and interrogate the sample or the environment. The resulting data signal is transmitted back to the optical collection system for subsequent data analysis. Actual probe testing was done in a hot cell. A similar system was demonstrated at the Savannah River Site A/M area to directly measure dense nonaqueous phase liquids in subsurface soils.

### **Electrochemical Noise Corrosion Monitor System** (See ITSR OST TechID1985, May 1999).

On-line monitoring of the actual corrosion process using an EN technique was demonstrated. EN-based corrosion monitoring probes are currently deployed in storage tanks at the Hanford Reservation. Initial deployment occurred September 1997 followed by installation of a second-generation unit in September 1998.

In addition to these demonstrations, a feasibility study, design review, and radiation test were undertaken by EIC Laboratories to demonstrate the suitability of an *in situ* Raman sensor. Savannah River Technology Center (SRTC) performed hot sample testing to provide detailed evidence of the sensor’s efficacy.

The feasibility study established the ability of Raman spectroscopy to detect and measure levels of nitrate, nitrite, and hydroxide in aqueous solutions. It also tested the effect of optical fiber length. A design review was performed to verify that the probe and deployment mechanism met SRS safety and design criteria.

After initial testing was satisfactorily completed, the conceptual design for a field-deployable system integrating the Raman sensor and EN sensor into a single probe was prepared. This ITSR focuses on Raman technology. The electrochemical noise technique, discussed in ITSR OST/TMS TechID1985, is specifically designed to measure corrosion rates and to detect the onset of pitting and cracking. The integrated probe can determine whether additional corrosion inhibitor is required and, if so, provide information on the quantity of inhibitor needed.

A radiation experiment was conducted at the University of Massachusetts Lowell Radiation Laboratory. Various materials used in the Raman probe were placed in a gamma cave and exposed to a Cobalt-60 source to validate radiation hardness.

### **Hot sample test**

Tests of waste samples decontaminated of Cesium, as well as actual waste samples within a shielded cell, were performed at SRS (Hobbs 2001). The tests were used to establish accuracy of the Raman method using samples that closely resembled those found in HLW tanks at SRS and Hanford.

### **Cold acceptance test**

A cold acceptance test of the entire probe, control and deployment system was performed by SRS at the facility of Hiline Engineering and Fabrication, fabricator of the deployment reel mechanism. A 40-foot platform was erected, and the reel mechanism, cabling probe, and all control instrumentation were mounted on the top of the platform. The satisfactory operation of all aspects of the system was validated. Operations tested include Raman probe assay of hydroxide, nitrate, and nitrite ions in waste simulant, EN probe functionality, movement of the reel to raise and lower the probe, controls for reel movement and height adjustment, and spray washing capability. The cable and reel enclosure were leak tested for compliance with safety and acceptance requirements. Figure 2 is a photograph of the test platform with the integrated probe system mounted on the top.



Figure 2 Deployment Mechanism Mounted on Test Platform.

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## Other

All published Innovative Technology Summary Reports are available at <http://www.em.doe.gov/ost> under "Publications." The Technology Management System, also available through the EM-50 Web site, provides information about Office of Science and Technology (OST) programs, technologies, and problems. The OST Reference Number for the *Integrated Raman Sensor for In-Tank Corrosion Chemistry* is 2015 and for the (Electrochemical Noise) *Corrosion Probe Monitor System* is 1985.



## SECTION 2 TECHNOLOGY DESCRIPTION

### Overall Process Definition

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Raman spectroscopy is a powerful tool for identifying unknown chemicals by their vibrational spectra. Laser light selected from the visible or near infrared parts of the spectrum is efficiently transmitted via fiber-optic cables to interrogate the sample. This arrangement makes the sensor ideal for remote applications, such as in hazardous waste tanks. Raman spectroscopy can be used to detect a wide variety of organic and inorganic chemicals. Frequency-shifted, scattered laser light is collected, transmitted back via fiber-optic cable, and dispersed through a spectrometer to display the Raman spectrum that can uniquely “fingerprint” and quantitate the interrogated molecular species.

The in-tank Raman probe instrumentation consists of an echelle spectrometer, laser, sample chamber, optical probe, and sample pumps; see the instrumentation diagram in Figure 3. An EIC echelle spectrometer with a thermoelectrically cooled, charge-coupled device (CCD) detector is used for Raman spectral acquisition. EIC’s proprietary RS2000 data acquisition software is used for data acquisition and Galactic Industries Grams/32 Version 5 software is used for spectral processing. A Process Instruments, Inc., 670-nm laser is used for Raman excitation. Both laser and spectrometer are coupled to the Raman probe via a 90-foot length of optical fiber cable. The cable contains two optical fibers: one for transmitting the monochromatic laser light (90- $\mu\text{m}$  core silica fiber), and the other for transmitting the Raman signal (200- $\mu\text{m}$  core silica fiber).

A vacuum/pressure pump is used for filling and purging the in-tank probe sample chamber. The vacuum port is used to pull liquid into the sample chamber. The vacuum is limited to a maximum of 2” of Hg in order to prevent waste liquid from being pulled out of the tank. A check valve is also attached to the vacuum line to ensure one-way flow through the line; (i.e., the vent to atmosphere only serves to provide air flow into the vacuum line). On the pressure port of the pump, an adjustable pressure relief valve and pressure gauge are attached for precise control of the pressure applied to the sample chamber. A two-way solenoid valve is attached to the pressure port to control flow during vacuum/pressure operation. One port of the pressure port solenoid valve is connected to the sampling chamber line while the other port is connected to a line vented to the waste tank vapor space.

During vacuum operation of the pump, liquid waste is pulled into the sample chamber. Purging of the sample chamber is done by connecting the pressure port to the probe sampling chamber line. Electronic solenoid valves are utilized with the pumps to allow computer system control of the operational sequence of the Raman sampling operation.

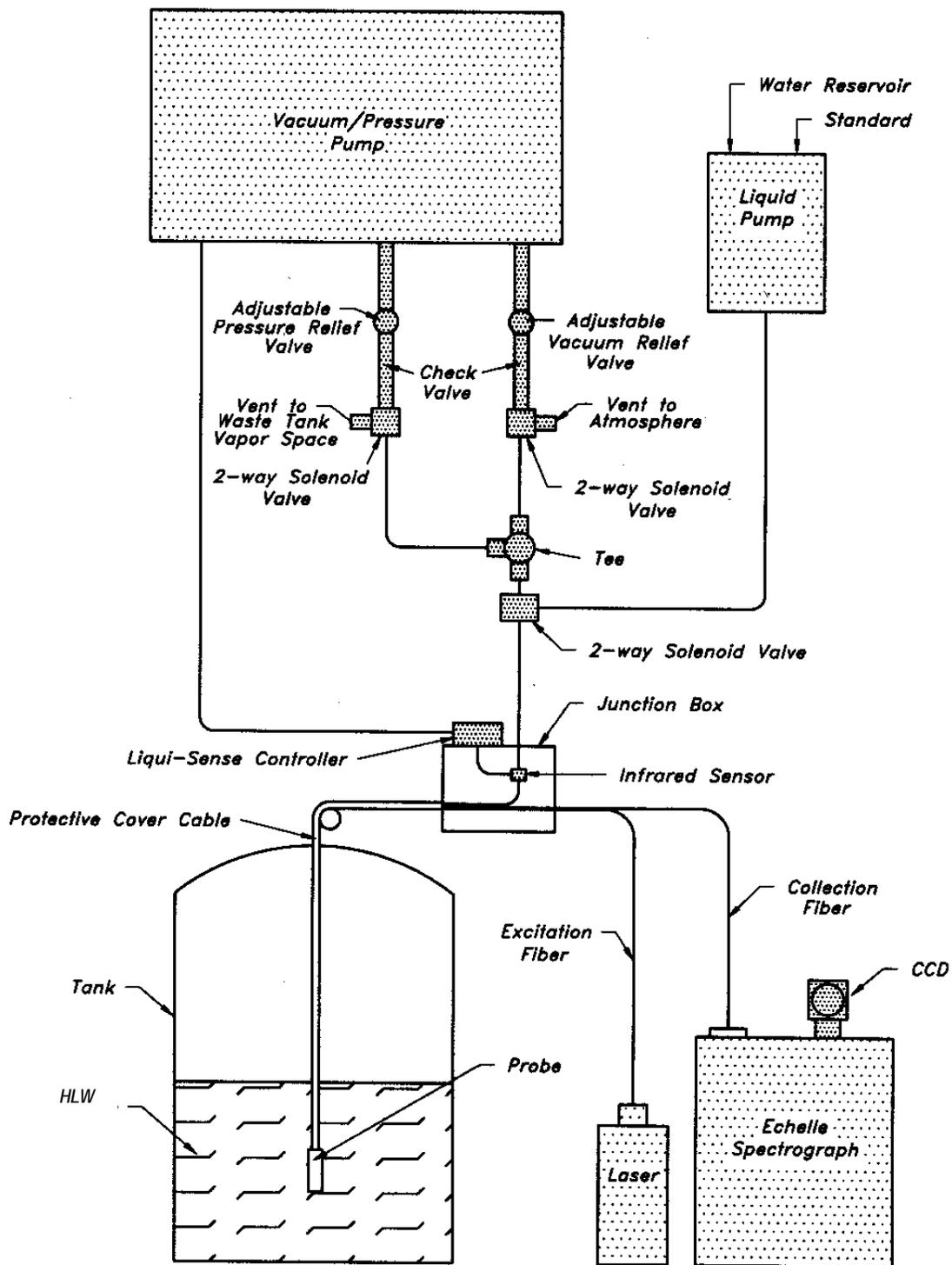


Figure 3. Diagram of In-Tank Raman Probe Instrumentation

## System Operation

### Raman sampling sequence

The sample chamber of the Raman probe is nominally 2 mL in volume. Prior to drawing a liquid sample from the waste supernate, a sufficient quantity of clean water is used to flush the sampling chamber and the 1- $\mu\text{m}$  filter and to provide verification of probe operability. (Clean water has a specific Raman signature.) Water is then purged from the sample chamber and liquid waste is pulled into the sample chamber by the vacuum pump through a filter designed to restrict particles exceeding 1- $\mu\text{m}$  diameter. After analysis of the sample, the system is re-flushed with clean water so the chamber is filled with water during downtime of the Raman system.

The main body of the integrated Raman-EN probe consists of two sections. A drawing of the assembled probe is shown in Figure 4.

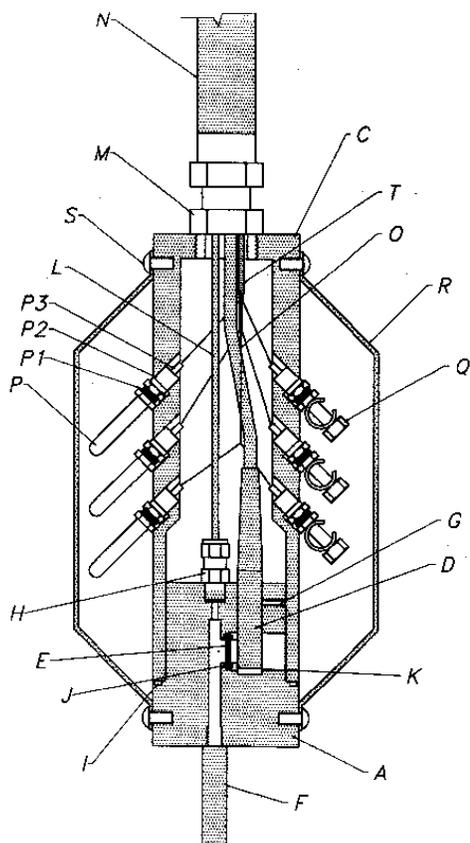


Figure 4. Assembled Raman-EN Probe

(Not all letters on the diagram are referenced in the text; see the following note.) The bottom section (A) contains the sampling area, the metal filter tube (F), and the Raman probe (D). The metal filter tube (F) screws onto the bottom of probe body at the inlet of the sampling area and is used to prevent suspended particles in the tank waste from entering the sampling area of the probe. A 2.1-mL cavity is drilled in the center of the probe body to serve as the sampling cell.

The top opening of the sampling cell connects to a vacuum/pressure/liquid line (L) via a stainless steel Swagelok tube fitting (H). This tubing line is connected to the pumps outside the HLW tank. The functions of the vacuum/pressure/liquid line tubing are for drawing waste samples into the sampling area of the probe, flushing the sampling area with water, and introducing standards into the sampling area from outside the HLW tank. A

sapphire window (E) sits perpendicular to the sampling cell. Its purpose is to isolate the Raman probe from the waste tank sample. Next to the sapphire window, a compartment

accommodates a side viewing 670-nm fiber-optic Raman probe (D). The 10-mm focal length lens of the probe focuses into the solution inside the sampling area. Electrodes associated with the EN section of the probe extend from the side (P and Q). They are protected by a guard ring (R). Probe body section C (top section) is used as a protective cover for the probe optical fiber (O) and the vacuum/pressure/liquid line (L). On top of the probe body section C, a male National Pipe Taper (NPT) thread adapter is attached that mates to an NPT swivel connector (M) attached to the conduit protective cover hose (N). The protective cover hose is made of stainless steel interlock metal hose with an outside coating of polyethylene for liquid sealing and easy cleaning of the outer hose surface. The protective hose (N) is a protective cover for the 90 feet of fiber-optic cable (O) and vacuum/pressure/liquid tubing.

Deployment of a probe into the liquid waste of a tank is implemented via a single-track reel mechanism while tank contents are not in motion. Prior to the operation of mixing pumps, it is necessary to raise the probe clear of the waste. The probe is adjusted to various heights within the waste to determine differences in waste composition and corrosion degradation.

A picture of the reel mechanism within its leak-proof enclosure is shown in Figure 5. The stand supporting the reel is to be mounted directly on a tank riser. A spray ring is included to wash contamination from the cable and probe housing. Several leaded glass inspection ports are included to provide visual and mechanical access to the reel and probe. Figure 6 is a photograph of the mechanism with the top half of the enclosure removed, revealing cable partially wound on the reel.

With this deployment mechanism, the corrosion probe can be deployed in unagitated liquid at various elevations, following tank events such as material addition or removal. Raman spectroscopy requires a sampling sequence (flushing, sample introduction, and measurement) for each analysis. During the raising operation, the spray ring is used to remove contamination and salt from the outside of the cable. The probe is designed with minimal crevices and hidden areas to maximize the efficiency of the decontamination process.



Figure 5. Reel Deployment Mechanism



Figure 6. Cable Wound on Reel

## SECTION 3 PERFORMANCE

### Testing and Demonstrations

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Throughout its development, the Raman probe was subjected to a series of tests of increasing rigor, culminating in a cold acceptance test and demonstration of the entire system. These tests and demonstrations included a feasibility test, radiation testing, hot cell testing, and the final acceptance test and demonstration.

#### Raman feasibility study

The goal of the feasibility study was to evaluate Raman technology as the basis for an *in situ* probe for the determination of nitrate, nitrite, and free hydroxide concentrations in HLW tanks. EIC Laboratories, which had developed a Raman probe for use in a cone penetrometer, conducted the study. Specific tasks were to:

- Establish minimum detectable concentrations and linear dynamic range in aqueous solutions for nitrate, nitrite, and hydroxide, as well as other potentially interfering anions.
- Determine the effect of optical fiber length (up to 100 ft.) on Raman sensitivity.
- Evaluate potential interferences to the detection of nitrate, nitrite, and hydroxide through the analysis of mixtures, including formulations similar in composition to real waste tank contents at SRS.

Results of the feasibility study show that fiber-optic Raman spectroscopy can be used to monitor nitrate, nitrite, and hydroxide ions at concentrations relevant to those found in corrosion-controlled HLW tanks such as those at the SRS. These findings agree with the results of Raman analyses of waste tank anions in actual SRS tank waste that were conducted previously by Marston (1975). Marston utilized a 488-nm argon ion laser as the excitation source for the Raman analysis of waste tank anions. His results indicated that seven polyatomic anions including nitrate, nitrite, and hydroxide are readily analyzed with the Raman technique.

A second objective was to determine the compatibility of materials that are used in the construction of the Raman probe and sampling chamber. These components must exhibit stability under highly caustic conditions, temperatures, and radiation fields. Test results indicate that the components used in the in-tank Raman probe will withstand heat, caustic conditions, and radiation.

#### Radiation test

Candidate materials for the in-tank integrated Raman-EN sensor were exposed to gamma radiation to determine if high radiation has any effect on these materials. It is anticipated that the in-tank sensor will be exposed to a 1000 Rad/hour over its two-year design life. At this rate, sensor components will be exposed to a total radiation dose of 17.5 MRad. Thus, in order for the Raman sensor to be useful for waste tank monitoring, it is necessary that the probe components not degrade under a high radiation environment during the two-year deployment of the probe in the waste tank.

Materials tested consisted of the Raman probe, probe conduit, electrical cable, O-rings, vacuum tubing, sapphire window, and Raman probe optical filters. Prior to radiation testing, the Raman probe, sapphire window, and optical filters were characterized for throughput and spectral properties. After radiation testing, each component was evaluated for changes in mechanical properties and color. The Raman probe, optical filters, and sapphire window were also characterized for their throughput and spectral properties.

Materials used in the sampling chamber, such as the polyethylene tubing for vacuum and pressure, ethylene propylene O-ring, sapphire window, and stainless steel probe conduit with silicone sleeve, will survive the radiation dose that the probe would receive during a two-year in-tank deployment. Radiation test results also indicate that the radiation level in the waste tank will not affect the performance of the Raman probe during two-years in the HLW tank.

### **Hot cell test**

Testing of simulants and actual waste samples took place over an 18-month period at SRTC. This testing included work in a lab with simulant samples, waste samples decontaminated of cesium, and actual HLW sample testing within the confines of a shielded cell. The probe used in the shielded cell tests was not itself the prototype integrated Raman-EN sensor, but it did incorporate its prototype optics. Test objectives included:

- Compare measurements of nitrate, nitrite, and free hydroxide concentrations in SRS waste samples using the EIC Raman system to those determined by current standard analytical methods.
- Determine if SRS waste samples exhibit significant fluorescence upon excitation with laser light at 670-nm wavelength.
- Determine the effect, if any, of solids present in the waste samples.
- Determine if background radiation in the SRTC Shielded Cells requires additional shielding for the Charge Coupled Device (CCD) camera and echelle spectrograph.

EIC provided SRTC with the Raman measurement system, which consisted of a laptop computer for control and data acquisition, a Process Instruments Inc. diode laser (180-mW at 670-nm wavelength), CCD camera and echelle spectrograph, fiber-optic cabling, and the probe itself.

Radioactive testing featured two types of samples: as-received supernate samples, and supernate samples treated to remove most of the gamma-producing Cesium. The dose rates from high gamma activity of the as-received samples are very high. For these samples, researchers obtained Raman measurements in shielded cell facilities (remote-handled). The treated samples have low radiation dose rates and, therefore, researchers obtained Raman spectra of the low gamma activity samples in a radio-hood (contact-handled).

Testing utilized two probe designs: end-mounted and side-mounted. Initial testing featured the end-mounted probe situated with the window facing down into the salt solution. Spectra obtained in this configuration exhibit large variances in the signal intensity. EIC subsequently provided a side-mounted probe. Testing with this probe design exhibited good reproducibility.

## Simulated Waste Solution Testing

Nitrate, nitrite, and hydroxide concentrations were determined in five simulated waste solutions prepared by researchers at SRTC. Upon initial testing, nitrate concentrations determined by the Raman method were consistently greater than both the known value and the value determined by ion chromatography. A goal of the development of the Raman measurement system is agreement with current analytical methods to within  $\pm 10\%$ . This goal initially was achieved for hydroxide determination, nearly achieved for nitrite, but not for nitrate. Improved accuracy was achieved by using more sophisticated calibration standards that contained more of the actual waste components. The improved calibration standards allow compensation for signals produced by other molecular species in the waste solution.

## Testing with Decontaminated Radioactive Solutions

Initial radioactive testing featured three radioactive solutions archived at SRTC: Tank 44F, Tank 50 H, and a multi-tank composite of more than 20 different tank samples. All three samples had been treated to remove the bulk of the radioactivity. This treatment enabled researchers to contact-handle the solutions in a radiohood. All measurements with these solutions used the side-mounted Raman probe.

Nitrite and hydroxide concentrations determined by Raman spectroscopy exhibited excellent agreement with the standard methods based on the calculated percent differences. Nitrate concentrations determined by Raman spectroscopy exhibited better agreement in this data set than with simulated waste solutions, although with greater range for the percent differences.

Based on these results with decontaminated radioactive waste solutions, it was concluded that the Raman measurement system is capable of determining nitrate, nitrite, and hydroxide concentrations with the accuracy and precision required for the monitoring of corrosion chemistry.

## Testing with Radioactive Waste Samples in the Shielded Cells Facility

The Raman measurement system was installed in the SRTC shielded cells facility. Testing featured four archived HLW supernate samples. All of the samples contained entrained solids to some degree, as evidenced by a cloudy appearance. The entrained solids significantly affected the Raman signal intensity. In effect, the solids raised the lower detection limits and required the addition of an internal standard. Because of these results, the in-tank Raman measurement system was equipped with a sintered metal filter to prevent light scattering interference from suspended particles in the sample.

In general, results indicated good agreement (a range of  $\pm 15\%$ ) between the Raman and standard analytical methods, using a calibration of the system obtained immediately before installation in the shielded cells in conjunction with a single point correction method.

## Conclusions

Testing demonstrated that a Raman-based measurement system can accurately and precisely determine nitrate, nitrite, and hydroxide concentrations in simulated and radioactive waste solutions. The system exhibited linear responses over the range of analyte concentrations from 0.1 M to 8.0 M. Results with waste tank samples indicated that entrained solids must be

removed to provide quantitative measurements when using an external calibration methodology. The tested system exhibited very reproducible performance and maintained calibration when the system was shut down between sets of measurement.

Average values for the analytes agreed within  $\pm 12\%$  with those determined by standard analytical methods for filtered tank samples in a radiohood installation. Poorer agreement was observed with measurements taken in the SRTC Shielded Cells and is attributed to damage to the excitation channel of the system that probably occurred during cell installation.

In addition, it was found that fluorescence of other chemical components in the waste samples does not interfere with the Raman analysis. These results agree with earlier findings of Marston (1975) who indicated that fluorescence does not interfere in the quantitation of the waste tank anions.

### **Cold acceptance test**

EIC Laboratories, Inc. was the primary contractor for the fabrication of the probe and deployment assembly while Westinghouse Savannah River Company (WSRC) conducted the cold acceptance testing. The Instrumentation and Evaluation Section (IES) of SRTC and Concentration Storage and Transfer Control group (CS&TC) of WSRC designed and fabricated the instrumentation required to control various aspects of probe operation such as data collection, probe elevation change, sample collection, and pneumatic sample line flushing. The testing was conducted at the facility of Hiline Engineering and Fabrication in Richland, WA. Successful completion of the corrosion and chemical species probe acceptance test procedure was required before the probe deployment assembly and peripheral equipment could be shipped to WSRC for installation on HLW Tank 43.

At the working group acceptance test, the contractor set out to confirm that the probe head assembly could perform in accordance with the pre-established procedure. Elements of the cold test itself included the following:

- Install system at 40 feet.
- Connect probe to cable and vacuum/pressure tubing, inside protective conduit.
- Install conduit onto reel.
- Perform pressure and vacuum tests on tubing.
- Use Raman process to verify analysis of simulated waste in a container placed at tank bottom level.
- Perform cooling and functional tests of control cabinet.
- Run liquid supply pump.
- Run air pressure supply pump.
- Run vacuum pump.
- Check desktop computer programming.
- Operate pulley assembly.
- Demonstrate Raman sample sequence (which required operation of all three pump systems and electronic laser generating and analysis equipment).

The test demonstrated that the Raman probe can be safely deployed in a HLW level waste tank, then used to analyze the contents of the tank.

## SECTION 4 TECHNOLOGY APPLICABILITY AND ALTERNATIVES

### **Competing Technologies**

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With the exception of process knowledge and tank waste chemistry sampling, no baseline corrosion chemistry monitoring system currently exists.

#### **In-tank waste analysis**

Traditional analysis of tank wastes has required that a sample be removed from a tank and transported to a hot cell. There it is analyzed by various wet chemical techniques; for instance, thermogravimetric analysis for water content and ion chromatography for certain ionic species. Sample removal, transport, and inventory maintenance are complicated because the radioactivity and variety of chemical constituents necessitate remote handling and minimized exposure. The sampling and manipulation required for sample analysis result in long time lags before data are available for decision-making.

Available technologies for corrosion monitoring have progressed to a point where it is feasible to monitor and inhibit corrosion by on-line monitoring of the corrosion process and direct addition of corrosion inhibitors.

#### **EN technique**

The EN technique has the capability of monitoring both localized and general corrosion; see the ITSR for OST/TMS TechID1985. Localized corrosion of waste tanks including pitting and stress corrosion cracking are of concern. EN measures the potential and current fluctuations of a metal in solution. These fluctuations are perturbations resulting from electrochemical reactions occurring at the metal surface and are low frequency (1Hz), small amplitude signals. EN has been used in numerous industries, including chemical processing, oil and gas, and fossil fuel power.

### **Technology Applicability**

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SRS has 25 tanks that can benefit from this technology. The primary additional application for corrosion probe monitoring is 28 storage tanks located at Hanford. Other potential users may exist across the DOE complex.

The Raman sensor can monitor other oxyanions (e.g., silicate), ferrocyanide/ferricyanide, and organic chemicals such as chelating agents in tanks. The Raman sensor can also be used to analyze the contents of 55-gallon drums, bottles, and other waste containers slated for disposal by incineration or other means.



## SECTION 5 COST

### Methodology

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Direct cost comparison of this technology with current methods is not yet completely feasible because an entire Raman on-tank sampling sequence, including probe deployment and on-site analysis, has yet to be demonstrated as a single test. However, each of the elements of the sequence has been performed as part of cold acceptance testing, and test results indicate that this approach is less labor-intensive while providing accurate results. By taking less time, requiring fewer resources, and reducing chemical additions to the tanks in comparison to current methods, Raman sampling clearly will result in cost savings.

### Cost Analysis

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#### Introduction

The present method to verify that the chemical composition of liquid tank waste is within corrosion control limits at SRS and Hanford is sampling and laboratory analysis, a time-consuming, labor-intensive process that involves issues of safety, decontamination, and transport, among others.

The Raman probe and deployment device will allow on-site, *in situ* chemical analysis on a more frequent basis. Thus, cost savings will be achieved not only in terms of labor and time, but also in terms of the increased accuracy of available data, allowing more precise control of the addition of NaOH. Reducing the amount of NaOH added will, in turn, reduce the volume of solid vitrified waste ultimately generated; this reduction will represent a substantial additional cost savings. In this section, cost savings are projected for SRS, the first probe deployment site. Potential additional savings at Hanford are also discussed below.

#### Baseline technology: Dip bottle sampling

##### Technology assumptions

Process: Samples are collected using a bottle on a string process that involves manually collecting HLW at various levels in a tank using a dip bottle. The sample must be secured and transported in a shielded cell, partially decontaminated, and, finally, analyzed under carefully controlled, remote-handled laboratory conditions.

Schedule: Tanks at SRS that have been characterized as “active” based on the condition of the HLW they contain are sampled four times per year on average.

##### Cost assumptions

A technical report generated at SRS (Wiersma 1998) has put the cost of this process at \$50,000 per sample.

## Raman probe

### Technology assumptions

Process: A deployment device stationed at a HLW tank is remotely manipulated to lower the Raman sensor into the tank. Data from the sensor is transmitted to on-site instrumentation.

Schedule: The present schedule of four samples per year will be maintained, although the Raman device would facilitate more frequent testing and would provide rapid results on demand.

### Cost assumptions

Capital costs:

- Deployment mechanism: \$75,000
  - Spectrometer (including echelle and laser): \$85,000
  - 5 Probes @\$5000/each: \$25,000
  - Umbilical cord: \$1,000
- Total: \$186,000

A life span of 10 years is assumed for this configuration under the condition that the probe is replaced every two years. The equipment, once in place, is relatively inexpensive to operate. The maintenance and operating cost per sample is estimated at \$5,000. A 0.25 full-time employee (FTE) technician is sufficient to monitor data from the instrumentation. Assuming an FTE of \$100,000, that places annual labor costs at \$25,000.

## Cost Comparisons

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### Sampling and analysis

Baseline (one HLW tank)			
Samples/year	Cost/sample (incl. labor)	Total cost/year	Cost/10 years
4	\$50,000	\$200,000	\$2 million

Raman device (one HLW tank)					
Samples/year	Cost/sample	Labor/year	Total cost/year	Capital costs	Cost/10 years
4	\$5,000	\$25,000	\$45,000	\$186,000	\$636,000

As can be seen from the comparison of sampling and analysis costs for a single tank at the SRS over 10 years in the above table, the cost savings of the Raman device deployed at a single SRS tank is \$1.36 million, or \$136K per year on the basis of reduced sampling costs alone.

If a second portable Raman deployment mechanism were to be fabricated, a second deployment at the SRS could take place in which one deployment mechanism, probe, and

associated instrumentation would serve four tanks (in a “four-pack” configuration). Assuming similar capital costs for this second deployment, the total 10-year cost of Raman sampling at the rate of four times per year per tank equals \$2 million versus the baseline cost total of \$8 million, for a savings of \$6 million or \$600K per year. Similar sampling cost savings can be realized at the Hanford tank farms as well.

### **Material and solid waste processing**

Even more significant cost savings are evident when the cost of adding and later processing excessive amounts of corrosion inhibiting chemicals such as caustic (NaOH) and sodium nitrite is considered. It has been believed that inaccurate and infrequent sampling data frequently lead to the addition of more NaOH than needed. Estimates of such costs have been made at Hanford but can be applied to SRS as well.

Presently at Hanford, in addition to sampling costs, \$7.5 million is budgeted annually for the addition of NaOH to four tanks that require such treatment as a way to keep corrosivity within acceptable parameters. It is estimated that as much as 50% of the NaOH added could be eliminated with the use of the integrated Raman-EN sensor. Thus, a savings in chemical cost of \$3.75 million per year for four tanks or \$937K per tank per year could be realized.

Moreover, NaOH is the waste limiting constituent in glass production. Avoiding the extra NaOH would reduce the addition of Na to the tank by 51 metric tons. Based on a 25% waste oxide loading figure, this avoidance would reduce low-level glass production by 204 metric tons. Estimates for glass production range from \$750,000 to \$1,250,000 per metric ton. Thus, in this example, the cost savings of using a corrosion probe to monitor corrosion on the basis of waste reduction would amount to \$153 million to \$255 million when bringing a tank back into specification. If it is assumed, conservatively, that any given tank will require NaOH additions of this magnitude only over an average period of 10 years, the savings attributable to cost savings is in the range of \$15 million to \$25 million per year per tank.

The overall cost savings can be seen to be the sum of the savings from the replacement of baseline sampling and analysis work with *in situ* sampling, the reduction of the amount of corrosion inhibitors added to the tanks, and the reduction in the amount of solid waste to be processed due to inhibitor addition. On a single tank per year basis the total cost savings may be estimated to be \$136K + \$937K + \$15 million for a total of \$16 million. This cost savings estimate is dominated by the \$15M per year per tank savings resulting from avoidance of solid waste processing which must be considered very approximate but is likely to be significant in nearly all cases.

### **Cost Conclusions**

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Implementing the proposed *in situ* Raman sensor will provide significant cost savings by reducing costs associated with sampling, analysis, the addition of corrosion inhibitors, and the processing of additional solid waste. While these cost savings will vary with tank history and tank usage, the magnitude of the cost savings possible exceeds the uncertainty in their estimates more than enough to justify the use of the Raman probe in spite of uncertainties in the estimates. If portable Raman systems are implemented to monitor multiple physically adjacent tanks, this more extensive usage will lead to more extensive savings.



## SECTION 6 REGULATORY AND POLICY ISSUES

### Regulatory Considerations

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The use of any technology for environmental remediation and waste management is constrained by state, federal, and local regulations that differ among DOE sites. State and local regulations can vary widely, despite efforts by U.S. Environmental Protection Agency and states to encourage acceptance of regulatory reciprocity of testing from one state or region to another. No regulatory or permitting issues have been identified with the Raman probe. The Comprehensive Environmental Response, Compensation, and Liability Act evaluation criteria do not apply to the intended application of this technology. The following are site-specific regulatory/permitting requirements:

- DOE Order 5820.2A, Radioactive Waste Management, requires monitoring of cathodic protection systems, methods for periodically assessing waste storage system integrity, and adjustment of waste chemistry to control corrosion. Raman probe monitoring would assist the adjustment of waste chemistry; the real-time corrosion monitoring by the EN probe would assist in-tank integrity assessment.
- DOE-STD-1073-93, Configuration Management, requires implementation of a Material Condition and Aging Management Program to control aging processes in major equipment and components. The primary aging processes in waste tank systems are corrosion-related.

At SRS, special permits are not required for operation of the Raman/EN probe. Internal reviews of design and of safety procedures are required before delivery, installation, and operation. Operation of the probe is not expected to have an impact on current regulatory considerations because no new chemicals are added to the tanks. There is no significant alteration in radiation source terms or increase in worker exposure, and there is no change in tank control procedures.

### Safety, Risks, Benefits, and Community Reaction

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This method of testing will provide a safe approach to maintaining chemical balances that will help minimize corrosion of tank walls. This benefit in itself is a step forward in safety because of the risk posed to the public and the environment if corrosion compromised the tank walls. In addition, performing measurements *in situ* will minimize the need to transport and store highly radioactive material, reducing cost and potential worker exposure. Finally, more accurate measurements of tank chemistry will reduce the chances of adding unnecessary sodium hydroxide, and thereby help ameliorate the overall problem of liquid waste storage and substantially reduce the volume of vitrified solid wastes ultimately produced.



## SECTION 7 LESSONS LEARNED

### **Implementation Considerations**

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The Raman spectroscopy technology is well understood and has been shown to work in an environment relevant to DOE. Probes that can house an *in situ* Raman sensor have been demonstrated.

The process requires a trained technician, a deployment device and platform, and instrumentation, all of which can be made available without extensive additional research and development.

### **Technology Limitations and Needs for Future Development**

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The accuracy and reliability of the technology must be developed through continued testing. Although various aspects of the Raman sampling sequence have been demonstrated in the laboratory and on-site, the results of these demonstrations have suggested that the equipment and the process may require further refinement to ensure long-term operability.

The tests performed at SRTC revealed the importance of periodic calibration of the Raman probe. Variances in results may be reduced as the calibration process is refined. During initial operation, validation of analytical results through confirmatory analyses of samples may be expected.

### **Technology Selection Considerations**

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Elements of this technology have been shown to work accurately and efficiently, establishing the probe's efficacy as a tool to assess tank chemistry and the ability of the delivery device to function in field conditions. Now the new technology must establish a track record through deployment and testing in an on-site setting.

The manner of deployment will vary from site to site. Tank configurations at SRS and Hanford are not identical, and the contents of the tanks require different levels of monitoring.



## APPENDIX A

### REFERENCES

Hobbs, D.T. (2001) "Laboratory Testing of a Raman-Based Measurement System for the Determination of Important Corrosion Species in Alkaline Solutions", WSRC-TR-2001-00129.

Marston, A.L. (1975) *Analysis of Radioactive Waste Supernate by Laser-Raman Spectrometry*, Nucl. Technol. , 25, 576-579.

Wiersma, B.J. (1998) "Sample Frequency for Tanks that Contain Waste with a High Hydroxide Concentration (U)", WSTC-TR-98-00130(U).