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INNOVATIVE TECHNOLOGY
Summary Report

Raman Probe

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

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INNOVATIVE TECHNOLOGY
Summary Report

Raman Probe

OST Reference #1544

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

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Demonstrated at
Hanford Site
Richland, Washington
and
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 if 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://OST.em.doe.gov under "Publications."

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SECTION 1

SUMMARY

Technology Summary

The Raman probe (Figure 1) is deployed in high-level waste tanks with the cone penetrometer (CPT). These technologies are engineered and optimized to work together. All of the hardware is radiation hardened, designed for and tested in the high-radiation, highly caustic chemical environment of U.S. Department of Energy's (DOE's) waste storage tanks. When deployed in tanks, the system is useful for rapidly assessing the species and concentrations of organic-bearing tank wastes.

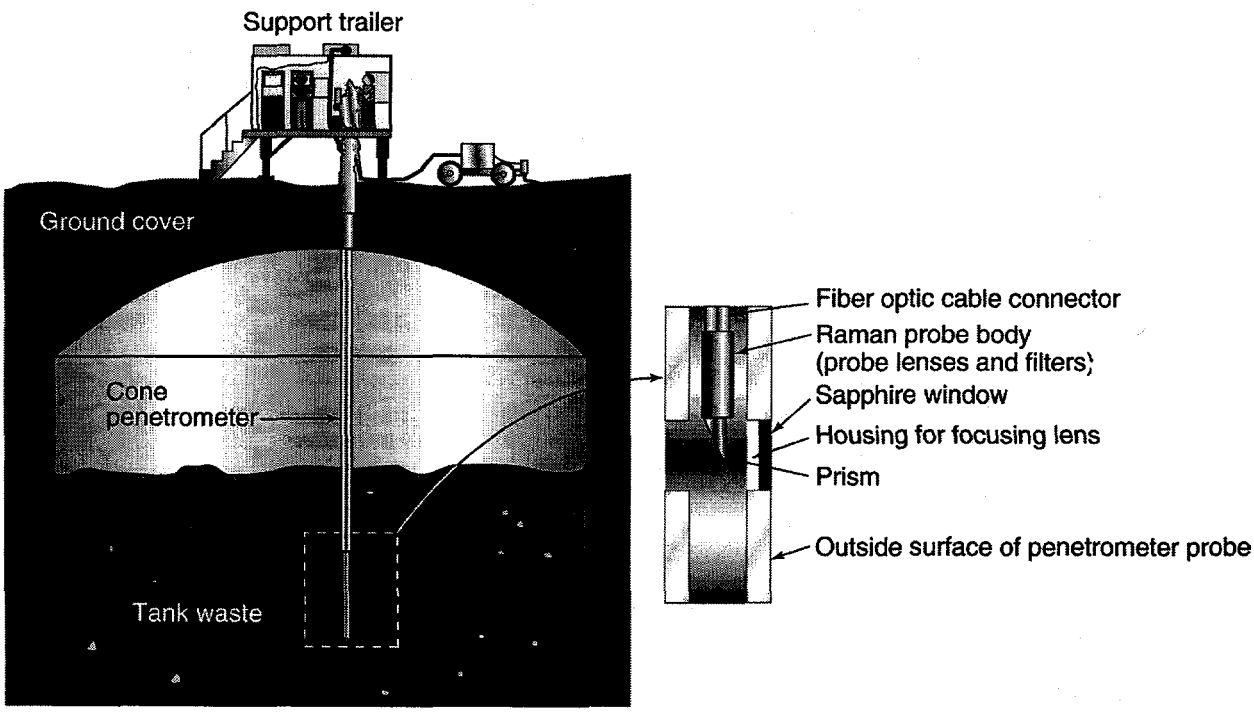

Figure 1. Raman probe deployed by a cone penetrometer inside an underground storage tank.

The CPT was originally developed for geological and groundwater applications, with sensors that measure physical parameters such as soil moisture, temperature, and pH. When deployed, it is hydraulically forced directly into the ground rather than using boring techniques utilized by rotary drilling systems. There is a separate Innovative Technology Summary Report for the CPT, so this report will focus on the changes made specifically to support the Raman probe. The most significant changes involve adapting the Raman probe for in-tank and subsurface field use and developing meaningful real-time data analysis. A sealed sapphire window was added to the system. Laser light passes through the window and interrogates the sample or the environment, and the resulting data signal is transmitted back to the optical collection system for subsequent data analysis. The window is brazed into the stainless steel CPT, and the braze forms a chemical- and pressure-resistant physical seal around the sapphire window, providing a mechanical buffer between the sapphire and stainless steel mount.

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 vibrational signal is captured and transmitted via fiber optic cables to an analyzer, where it is compared to known vibrational signals. The final result is an analysis of the material surrounding the probe.

This system has been designed for two main applications:

- The Tanks Focus Area (TFA) and Lawrence Livermore National Laboratory (LLNL) developed an instrument to collect characterization data directly inside the harsh radioactive and chemical environment of DOE waste storage tanks. The Raman signal is sent to a neural network system (development was cofunded by the Characterization, Monitoring, and Sensor Technology [CMST] Crosscutting Program), which analyzes the data and determines which compounds are present (and their concentrations). Analytical data for tank waste are currently collected by core samples and grab samples, requiring significant time for sample handling and analysis and increasing the possibility for worker exposure. This instrument has been tested with tank waste in hot cells at Hanford to provide data to resolve tank safety concerns. The Raman probe can also be used to characterize the vadose zone surrounding tanks to estimate leaks and determine remedial action and site closure plans.

- The CMST Crosscutting Program and EIC, Inc. developed an instrument optimized to collect data on the extent of soil contamination. These data are currently collected by drilled core samples and monitoring wells. Conventional techniques may require the addition of drilling fluid and foreign material such as gravel and concrete to stabilize wells. They are time-consuming, expensive, and labor-intensive and can result in cross-contamination. In February and June 1998 this instrument was tested along with the LLNL-developed instrument on in situ trichloroethene (TCE) and tetrachloroethene (PCE) soil contamination at the Savannah River Site. Use of the Raman probe for measuring soil contamination provided proof of concept for the in-tank deployment system.

Demonstration Summary

This report describes work funded by DOE EM-50/TFA, EM-50/CMST, Federal Energy Technology Center (FETC), and EM-30/Tank Waste Remediation System from FY 1994 to FY 1998. Collaborators during the research, development, and testing of the equipment included staff from Westinghouse Hanford Co.; Lawrence Livermore National Laboratory; Special Technology Laboratory; Numatec Hanford Corporation; EIC, Inc.; and Applied Research Associates, Inc.

Testing of the complete LLNL system was conducted in a hot cell in the 222-S Laboratory at the Hanford site in summer 1997. Both instruments were tested in situ on solvent-contaminated soils (TCE and PCE) at the Savannah River Site in February and June 1998.

Tank Waste Analysis

Acceptance testing demonstrated in-tank measurement capabilities and real-time data analysis. Raman spectra scans were generated for 135 archived waste samples from 14 Hanford tanks and compared to the wet chemical analyses completed previously. The Raman probe demonstration resulted in more than 99 percent accuracy for compound identification and greater than 93 percent accuracy in identifying both the compounds and the concentration. Where the Raman results did not agree with the earlier analyses, it is not clear whether the discrepancy is related to sample aging and drying, errors in recorded data resulting from representative sampling or method precision and accuracy, or problems with the new instrument. The results showed that extensive calibration and training of the neural network improves performance.

In Situ Soil Contamination Detection

Field testing and evaluations demonstrated the first direct measurements of dense, nonaqueous-phase liquid (DNAPL) in subsurface soils. The probes were tested in two locations at the Savannah River Site A/M Area Seepage Basin, one in the vadose zone and one in the saturated zone. Raman spectra were taken every 3 ft as the CPT was pushed down and every 0.5 ft where the spectral data or soil sampling indicated the presence of PCE or TCE. In the saturated zone, the Raman data detected the presence of PCE at 101.5 and 102 ft below ground surface, exactly where geological analysis would predict the highest levels on contamination. In the vadose zone, the probe results agreed with the sampling results except between 15 and 21 ft below ground surface, where sampling showed contamination but the probe did not. It is possible that the contamination is not evenly distributed due to geological heterogeneity and also possible that a longer spectra acquisition time is necessary.

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Other

All published Innovative Technology Summary Reports are available at http://ost.em.doe.gov 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 Raman probe is 1544.

SECTION 2

TECHNOLOGY DESCRIPTION

Overall Process Definition

Raman Probe

Raman spectroscopy is a powerful tool for classifying unknown chemicals by their vibrational spectra. Laser light in the visible and near infrared parts of the spectrum is efficiently transmitted via fiber optic cables to interrogate the sample. This makes the sensor ideal for remote applications (such as deep underground or in waste tanks unsafe for people). Since it is a vibrational technique, Raman spectroscopy is nonspecific and can be used to detect a wide variety of organic and inorganic chemicals. The frequency-shifted, scattered laser light is collected, transmitted via fiber optic cable, and dispersed in a spectrometer to display the Raman spectra, which can uniquely "fingerprint" the interrogated molecular species.

Raman probes were designed for collimated, colinear laser excitation and signal collection. The collinear probe was chosen for maximal overlap of the interrogated area and its inherently compact design (which eases placement in the limited space of the CPT). The probe sits in the CPT/Raman probe interface along the penetrometer vertical axis, screwed directly into the penetrometer pipe, making it an integral part of the penetrometer. Laser light from the probe bounces off the gimbal-mounted silvered mirror (see Figure 2) and exits the sapphire window, where it interrogates the tank waste and sends the Raman signal back for collection and analysis.

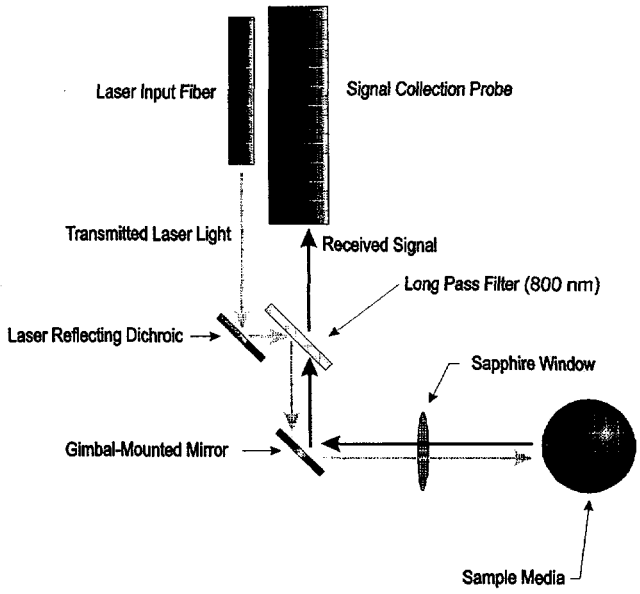

Figure 2. Raman probe operation.

Sapphire Window

Previous sensors deployed on the CPT measured physical properties of the soil or waste in which the probe was inserted. Using a spectroscopic technique to determine chemical properties of the waste required a major change to the CPT: a "window" through which the laser light exits and the resulting signal is collected. The window must withstand abrasive scraping and pressure that the sidewall of the cone penetrometer pipe is subjected to during a push and also be sealed into the CPT wall to withstand the waste tank environment without leaking or being damaged.

The window assembly provides optical communication between the vertically seated Raman probe and the tank waste environment along the radial axis of the housing (see Figure 3). It consists of a hardened 420-SS insert that mates with the circular opening in the housing. The insert is locked down in the housing with an opposing screw and sealed with durometer-50 neoprene O-rings. The window assembly houses a sapphire window, which provides access to the tank waste material without compromising mechanical strength or chemical resistance. The window is situated in the outer wall of the window assembly. Sapphire (also known as "corundum"), a form of alpha-aluminum oxide, has been used in previous geological applications of the cone penetrometer. The physical properties of sapphire are shown in Table 1.

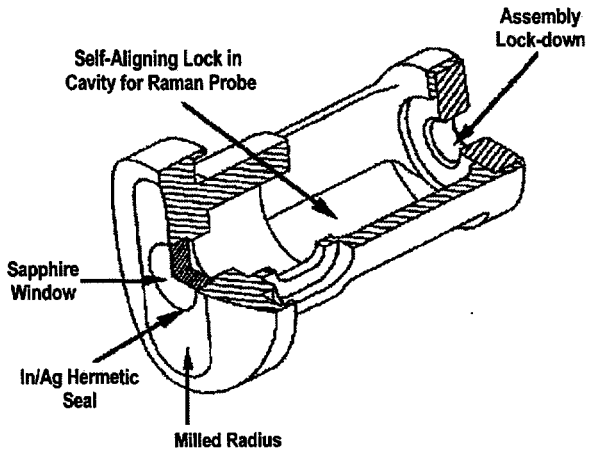

Figure 3. Sapphire window assembly.

Table 1. Physical properties of sapphire

Moh hardness	9
Tensile strength	10^5 psi
Compression strength	3×10^6 psi
Young's Modulus	5×10^7 psi

The window is 6.5 mm in diameter and 2 mm thick. The sapphire window resides within a milled flat on the outer surface of the window assembly, which provides a surface flush with the window. The surface tolerance of the window relative to the outer wall of the window assembly is +0.002/-0.000 inches. This tolerance does not allow for a small dead space that a recessed window would have, eliminating the possibility of contaminating the external surface of the window with tank waste during a push. The sapphire window is edge-metallized with a 0.005-inch layer of silver and is hermetically sealed directly to the stainless steel body of the window assembly with an indium-silver eutectic alloy selected for its corrosion resistance in the highly alkaline tank waste.

Neural Network

The LLNL and EIC, Inc. instruments were developed for two different applications: in-tank waste constituent analysis and in situ soil contamination detection. The data requirements for these two applications differ. Hanford tank waste can have hundreds of constituents, and waste treatment systems can require accurate knowledge of the concentrations of certain constituents. These factors led the LLNL team to develop a neural network for identifying compounds and quantifying concentration data from its instrument. Soil contaminant mixtures typically contain only two or three compounds, and the EIC, Inc. instrument does not have an associated neural network for data processing. Rather it uses the spectra to indicate the presence or absence of a contaminant. It is designed for screening an area to optimize the placement of sampling boreholes and monitoring wells.

The ability to analyze the Raman spectra of wastes is complicated by several factors:

- The concentrations of some compounds of interest are very low.
- The waste is a complex mixture of many types of chemicals.
- Many of the Raman spectra show a pronounced peak from silica, which can obscure other peaks.

The neural network developed with the LLNL CPT-deployed Raman probe removes the silica Raman spectra and identifies and quantifies the signal.

A review of PUREX, B Plant, T Plant, and phosphate fuel reprocessing methods and tank waste hot cell characterization reports from the past 20 years of analyzing supernatant grab samples and drill auger cores was used to develop the list of chemicals included in the neural network. The list includes carbon- and hydrogen-rich complexing agents such as nitrilotriacetic acid, ethylene diamine tetra-acetic acid, tributyl phosphate, triphenyl phosphine oxide, dimethylamine hydrochloride, acetate, citrate, sodium succinate, sodium formate, butanedionate, and acetone and inorganic oxidants and reducing agents such as sodium nitrate, sodium nitrite, sodium chromate, sodium dichromate, sodium ferrocyanide, sodium nickel ferrocyanide, sodium sulfate, sodium aluminate, sodium cyanate, bismuth phosphate, ammonium nitrate, and uranyl. The Raman probe can identify all of these compounds. The chemical compositions of waste need to be known because of concerns over chemical compatibility hazards. Organic chemicals and oxidizers are of concern because of flammability. Nitrate and nitrite levels affect corrosion. Phosphate levels need to be known before wastes can be allowed to mix in transfer lines because formation of sodium phosphate crystals forms a viscous gel that reduces the ability to pump and move wastes.

System Operation

System operation requirements for deployment of the Raman probe are as follows:

Special operational parameters
Due to the highly radioactive nature of high-level waste sludge, in-tank deployment requires shielding for workers and radiation-hardened and chemically resistant system components. These requirements also apply to deployment of the probe near the tank to determine tank leakage although radiation and chemical resistance requirements are less stringent.

Materials, energy, other expendable items
The Raman probe can be used inside a waste tank to reduce materials and energy requirements for characterizing the tank contents. Currently, the chemicals in the tank are determined by taking a core sample of the tank waste, transporting the sample to a laboratory, and performing chemical analyses. Average laboratory analyses cost up to $300,000 and take up to three months to prepare and plan for the extraction.

Personnel required
Operators are required for operating the computer data acquistion system. The CPT push and the lowering of the probe into the CPT are automated. On-site technicians must oversee automated operations.

Secondary waste stream
The CPT-deployed probe generates less secondary waste than sampling and analysis (e.g., disposal of sample).

Potential operational concerns and risks
The probe must undergo operational readiness testing to allay concerns about in-tank hazards during probe deployment.

SECTION 3

PERFORMANCE

This section describes the testing of the LLNL instrument at Hanford on actual tank waste during summer 1997 and the testing of both instruments on in situ soil contamination at Savannah River in February and June 1998.

Demonstration Plan

LLNL Instrument in Hanford Tank Waste

Testing new equipment for the harsh conditions of DOE tanks follows a regular progression:

- Phase 1: Test equipment with simulated, nonradioactive waste in an environment such as a fume hood.
- Phase 2: Test equipment with actual waste under the controlled conditions of a laboratory glovebox.
- Phase 3: Test equipment with actual waste in the actual conditions of a tank or contaminated soil.

The CPT-deployed Raman probe test was streamlined by the well-known capabilities of both systems before they were combined. Nonetheless, several of the critical component tests are described briefly below.

Testing the Sapphire Window

Any time a break is made in a continuous piece of material, there is a possibility that the area of the discontinuity will be weaker than the rest of the material. Penetrometer push tests were performed to evaluate the integrity of the sapphire window assembly and the stainless steel housing under harsh deployment conditions. A 20-ton push test through sand, hard gravel, and clay produced no visible detrimental physical effects. The sapphire window was unmarred, though the stainless steel cone penetrometer pipe itself was deeply scratched. During a 45-ton push, the hardened stainless steel around the window compressed less than 0.0015 inch, and the compression was completely elastic. This test represented significantly more force than the maximum 35 tons under which the equipment is designed to operate.

Effects of Radiation on Electronics and Optics

Electronic and optical components are known for being sensitive to radiation environments. Before testing on actual tank samples, the sapphire window, the indium-silver window braze, electronics, and other optical components were subjected to controlled doses of radiation and chemical testing in a 600-rad/h gamma ray pit at Hanford. The probe assembly was immersed in caustic tank waste simulant containing 4 *M* NaOH, 2 *M* $NaNO_3$, and 4 *M* $NaNO_2$, some of the most reactive and highest-concentration materials in tank waste. The optics were visually inspected and showed no sign of darkening. The sapphire window and the indium-silver seal were analyzed by scanning electron microscopy and atomic force microscopy before and after a 17-day exposure and found to be unaffected by the exposure. Further analysis by radiograph was performed for characterization of pinholes or cracks in the seal, but no leaks were found. The sapphire window was completely unaffected by either the chemicals or the radiation. The total radiation dose at the end of the 17-day test was approximately 350,000 rad.

Complete System Qualification Test—LLNL Instrument

A complete LLNL CPT-deployed Raman probe was installed in a hot cell in the 222-S Analytical Laboratory on the Hanford Site in spring 1997. To mimic the installation of the probe inside a tank, the Raman probe was installed in the hot cell, and the system was operated from the CPT trailer located outside the laboratory hot cell facility. Light scattered from the sample was transmitted by fiber optic cable to the spectrometer in the trailer.

Raman spectra were collected by placing the sample containers against the probe window. Samples were analyzed over 30 seconds using cosmic spike rejection and dark current subtraction to eliminate radiation spikes and background fluctuations from the hot cell or instrument variability. Three duplicate sets of spectra were obtained for each sample at different sampling locations or after mixing slurry samples to account for variability inherent in heterogenous samples.

The qualification test used four types of materials:

- varying tank matrices for calibrating and training the neural network;
- standards varying in water, nitrate, oxalate, and citrate concentration;
- archived tank waste samples; and
- test soil samples to determine the efficacy of the instrument for measuring in situ soil contamination.

Five tank matrices of varying colors, shades, and consistencies were used for calibrating and training the neural network. These were spiked with a range of nitrate, citrate, and oxalate concentrations, as shown in Table 2.

Table 2. Calibration and neural network training matrices

Tank matrix	Avg. NO_3 wt % in matrix	Color	H_2O	Spiking Range (wt %)		
				NO_3	Citrate	Oxalate
AW-103	1.5	white	40–80	0.4–28.4	0–25.5	0–23.7
U-103	38	gray	43–66	3.6–33.5	0–27.6	0–26.7
T-203	6	black	47–88	1.3–28.7	0–25.6	0–33.3
BY-110	33.8	red	42–59	3.7–33.2	0–29.4	0–32.6
S-107	8	brown/grey	42–70	1.4–28.2	0–26.9	0–33.0

Concentration standards were formed by adding nitrate and carbonate to a blank Hanford soil matrix containing no constituents of interest. Nitrate concentrations ranged 0.1–20 wt %. Carbonate has been shown to interfere with spectral analysis of nitrate in supernatant solutions. To test the extent of interference, carbonate was added to some standards in concentrations of 5 and 10 wt %.

Raman spectra scans were generated for 135 archived waste samples from 14 tanks and compared to wet chemical analysis completed previously on the same samples. The correlation between Raman results and wet chemical results were evaluated by LLNL. The data produced by the CPT-deployed Raman probe did not always agree with the data collected earlier using thermogravimetric analysis to measure water content and ion chromatography to measure nitrate and oxalate concentrations. More analysis will be necessary to determine the reason for the discrepancy. As extensive time may have elapsed between the sample analysis by the old methods and the new technique, the discrepancies may be due to samples drying and aging during storage or errors in recorded data.

The Raman probe is continuing to be used in the 222-S Laboratory to determine the chemical composition of over 1,600 archived tank waste samples. While the LLNL CPT-deployed Raman probe was originally developed for in situ tank characterization, its potential application has expanded to include possibly contaminated soils under and around tanks. Soils were tested in two conformations: using a 4-mm standoff and wrapping the soil directly onto the probe window.

Demonstration Plan—EIC, Inc. and LLNL Instruments on In Situ Soil Contamination at Savannah River Site

In the A/M area at the Savannah River Site, a large solvent plume consisting primarily of the solvents TCE and PCE encompasses an area of several square miles in unconsolidated Coastal Plain sediments. Historical records indicate that over 1 million kg of solvent was released to the subsurface from an unlined seepage basin in this area. Multiple source zones are associated with the plume and have been identified below solvent storage tanks (321-M), the subsurface sewer lines, and an unlined seepage basin (M-Basin). Two of the well-characterized source areas in A/M area, one in the unsaturated zone and one in the saturated zone, were used for the evaluation of the Raman sensors for in situ detection of PCE and TCE using the CPT.

Major Objectives of the Demonstration
Initial testing of the Raman sensor for contaminant detection was done in 1992 using an argon laser (wavelength 415 nm). The results from this field trial were not useful due to the large fluorescent background present in all the spectra. However, the results did show a large increase in the fluorescent intensity at the depths where DNAPLs were likely. TCE and PCE do not fluoresce at this wavelength; however, some compounds that are soluble in TCE and present in the subsurface at Savannah River Site, such as synthetic oils or natural organic material, may fluoresce at this wavelength.

In February and June of 1998, an evaluation of the LLNL and EIC, Inc. Raman probes was done as part of the OST's Site Characterization and Analysis Penetrometer Sensor Program. This program is funded by the CMST Program to provide robust cost and performance evaluation of innovative technologies for use with the CPT. The purpose was to evaluate the use of CPT-deployed Raman spectroscopy to detect DNAPLs in the subsurface.

Boundaries of the Demonstration
This evaluation used probes with a 785-nm laser that was selected to reduce the background fluorescence. The probes were evaluated at two locations in the A/M Area Seepage Basin: one in the vadose zone (321-M Area Solvent Storage Tanks) and one in the saturated zone (M Basin).

During the evaluation at each waste site, Raman spectral samples were taken every 3 ft as the CPT was advanced. In sediments where results from soil sampling and analysis indicated the presence of DNAPL, Raman spectral samples were taken every 0.5 ft to give detailed information about the depth and location of DNAPLs. The scans were taken for 10 seconds at a minimum and longer (60 seconds) if there was a suggestion of DNAPLs due to spectral or geologic evidence.

To assess the capability of the Raman technology to successfully identify compounds, sediment samples were collected using a drill rig in locations adjacent to CPT pushes. The PCE and TCE soil concentrations were measured by laboratory analyses. In clay layers known to contain DNAPLs, samples were taken every 0.5 ft to give the same detailed information about the depth and concentration of DNAPLs as acquired by the Raman probe.

System Performance

Performance Results—Hanford Tank Waste Demonstration
The LLNL probe and neural network have been demonstrated to give greater than 99 percent accuracy for compounds identification and greater than 93 percent accuracy in identifying both the compound and its concentration.

Test results showed that organic constituents can be detected above 20 wt % due to a high noise level in the 3,000 cm^{-1} region of the spectrum. Spectral acquisition is poorer in dark-colored samples, as the samples absorb more photons and scattering efficiency decreases. This effect both reduces the signal and increases the noise. Lighter-colored, gray, and white samples reveal increased signal and decreased noise. Nitrate peaks were detectable at concentrations above 5 wt %.

The results of the probe test of contaminated soils are shown in Figure 4. The graph shows that for the limited number of samples tested, the probe appears to be significantly more sensitive (able to detect a lower nitrate concentration) when the soil is wrapped around the window and there is no air gap between the window and the soil. This fact is fortunate, since in a real CPT push near a tank, the soil will most probably be in contact with the window, without an air gap.

One advantage of the CPT-deployed Raman probe for monitoring environmental contamination outside tanks is that a conventional drilling system or monitoring well may require the use of drilling fluids or addition of materials such as grout to stabilize the well. The absence of foreign materials means that the resulting signal is more likely to be truly resulting from in situ contamination.

Performance Results—Savannah River Site Demonstration
The first location used to evaluate the capability of Raman technology was adjacent to the A/M Area Seepage Basin, where the DNAPL contamination is located below the water table. The probe provided

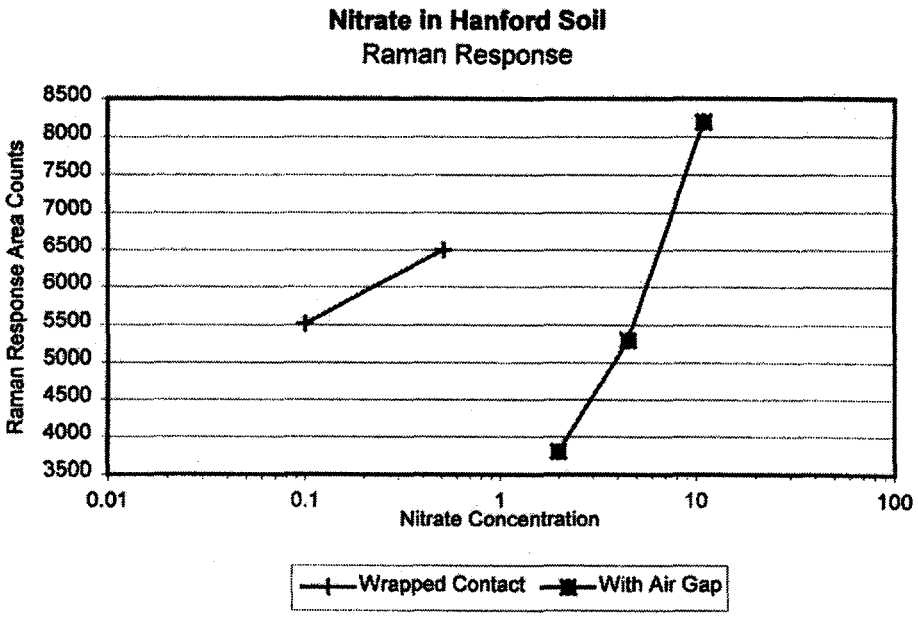

Figure 4. Nitrate concentrations (wt %) in Hanford soil.

geophysical data based on tip pressure and sleeve resistance. This data were used to infer lithology. The Raman probe measured PCE located at depths of 101.5 and 102.0 ft below ground surface, which correspond exactly to the depth of clay layers determined by the geophysical data for that push. Fluorescent background levels were found to be 2.5 to 3 times as great when DNAPL was present as compared to average background fluorescence levels for uncontaminated soils. Figure 5 depicts the soil concentrations of TCE and PCE measured in the laboratory relative to Raman spectra for PCE and high fluorescence signals.

Figure 6 shows shows the reults of additional CPT/Raman pushes completed at the 321-M Solvent Storage area, where contamination is located above the water table. Spectra were taken at 3-ft intervals in coarse-grained sediments and at 0.5-ft intervals in finer-grained sediments to a depth of 40 ft. The spectra with DNAPL peaks did not have high background fluorescence; this observation may be explained by the pure nature of these solvents. The Raman probe identified PCE in both fine- and coarse-grained layers and TCE in a fine-grained layer that corresponds with highest soil concentration found in sampling. However, at several locations at 321-M, there is disagreement between the soil and Raman data from 15 to 21 ft. Concentrations measured in sediment samples were high from 15 to 21 ft, but the spectral analyses did not show evidence of DNAPL peaks.

Several explanations of the discrepancy are plausible. First, the results could be due to fine-scale heterogeneities in the distribution of DNAPL residing in clay lenses of varying depths and thickness. A second possible explanation for the Raman probe's failure to detect DNAPL could be that the time interval was too short. Generally, spectra were taken for 10 seconds. If peaks were seen or there was suspicion of DNAPL, a longer spectrum was taken. This condition occurred at the M Area Seepage Basin, where the probe did not initially detect DNAPL during the push, but on retrieval a longer spectrum was taken at 99 ft. When a 60-second spectrum was taken, there was spectral confirmation of the presence of PCE. The fluorescent background of the 10-second spectrum at this depth would not have suggested the presence of DNAPL. This observation suggests that the acquisition parameter for characterization must be carefully selected.

Both figures 5 and 6 show results of the EIC, Inc. probe, comparing depths where DNAPL was detected using the Raman probe and sediment analysis results at the M Area. PCE and TCE soil concentrations are plotted against depth using solid shapes. The Raman data are plotted with open shapes, simply indicating presence or absence of PCE or TCE as indicated by spectral peaks. The "x" symbols indicate depths that were characterized by high fluorescence in the background of the Raman spectrum. (The EIC, Inc. probe does not use a neural network to process the data, so the spectra simply indicate presence or absence of contaminant but not concentration. Results of the LLNL probe test were not available when this report was produced.)

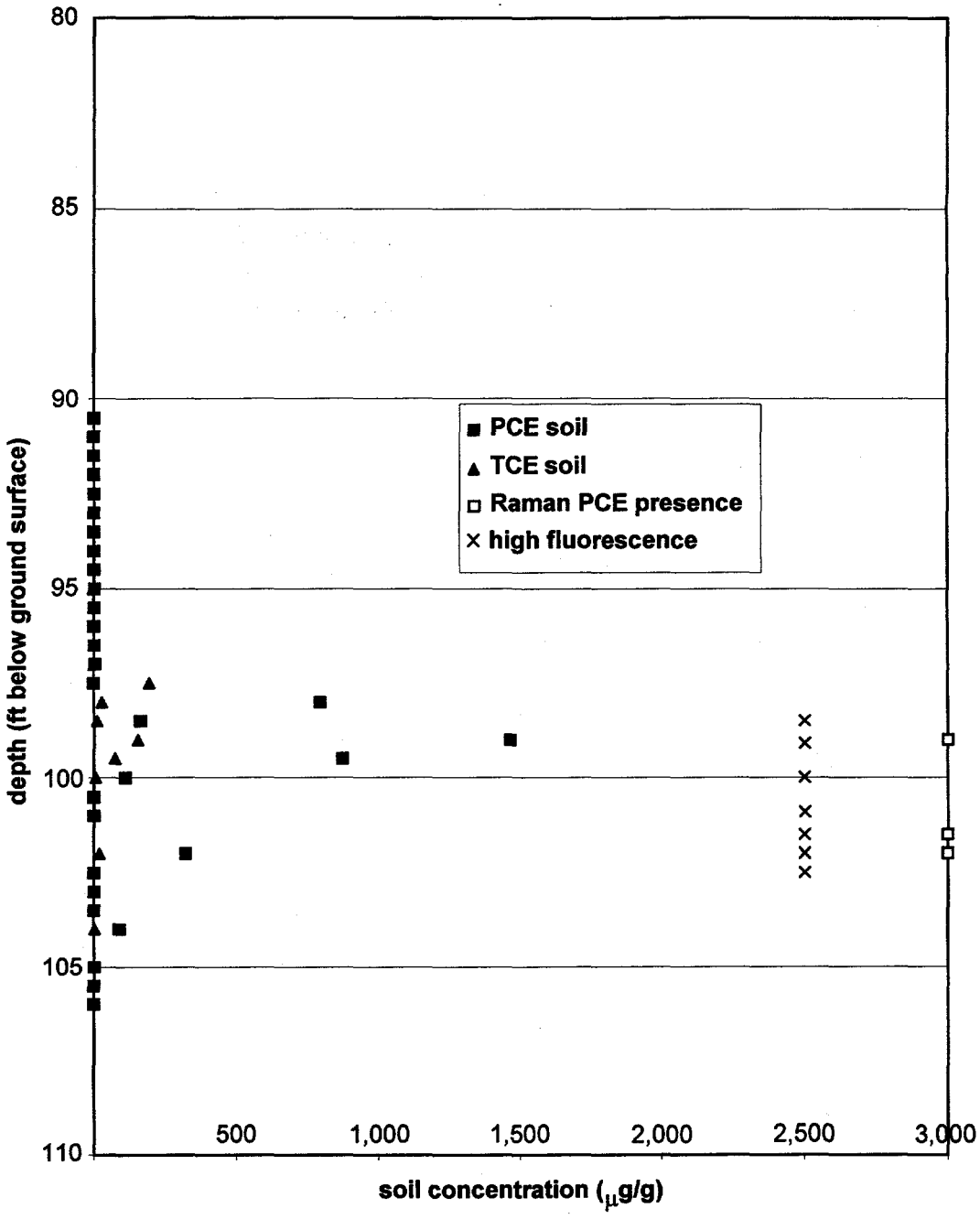

Figure 5. Raman and fluorescence vs soil concentrations (M Area Basin).

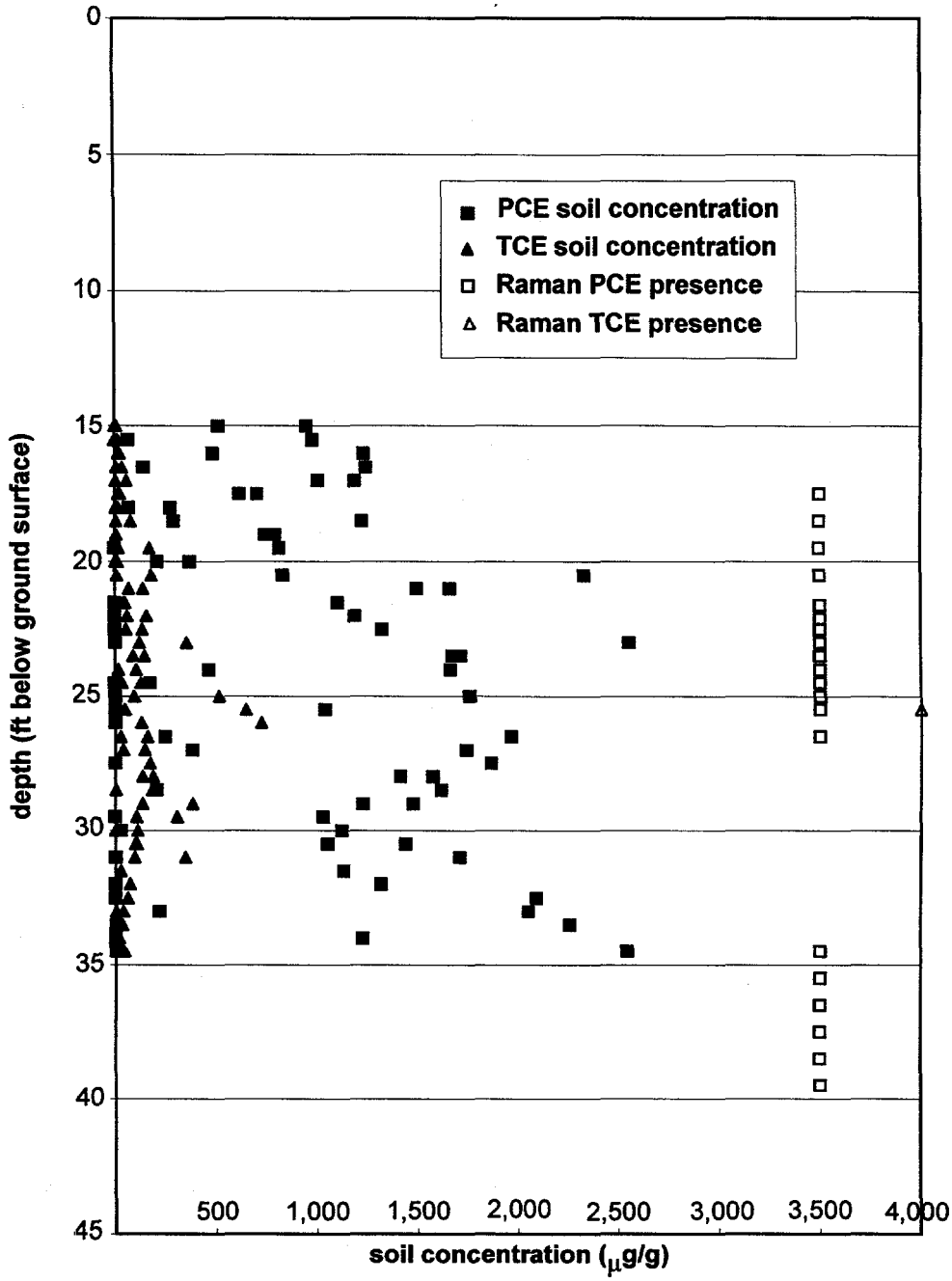

Figure 6. Raman vs soil concentrations (321-M Solvent Storage Tank).

SECTION 4

TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Technology Applicability

As the list of chemicals in Section 2 shows, CPT-deployed Raman probe can be used to detect and quantify a wide range of chemicals. It is also a fairly straightforward matter to add chemicals to this list. The CPT can also be used to deploy other sensor packages.

Competing Technologies

In-Tank Waste Analysis
Traditional analysis of wastes or soils has required that a sample be removed from a tank or soil location of interest 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.

In Situ Soil Analysis
The baseline selected for this technology in unconsolidated sediments is sampling by a drilling rig with sampling equipment. The type of information gained from use of the Raman does not completely overlap that from the baseline. The baseline method is significantly more expensive yet yields a more robust result, i.e., quantitative analysis of contaminant distribution. The EIC, Inc. Raman technique is qualitative; a positive result unequivocally identifies the compound that is present in a separate phase but does not give any quantitative information on concentration of the dissolved phase. The negative result indicates only that the sensor did not detect DNAPL. It is best used in a screening mode in the early stages of characterization to optimize the subsequent characterization efforts. The LLNL instrument should indicate concentration after calibration and neural network training, but results of this test were not available when this report was written. No other compound-specific technology currently exists to identify contaminants in situ.

Patents/Commercialization/Sponsors

The system tested consists of three main components: the CPT, the neural network, and the Raman probe. The CPT is commercially available from Applied Research Associates in Albuquerque, N.M. The neural network was developed for DOE by Physical Optics Corporation. The Raman probe developed by LLNL does not have a commercial partner but is seeking one. The Raman probe developed by EIC, Inc. is commercially available.

SECTION 5

COST

Introduction

For over 45 years, characterization of the vadose zone and soils around tanks has been performed at Hanford using cable-tool drilling to install sampling and logging wells. A 3- to 5-ft-long core barrel is driven into the ground, the soil from that location is removed, and a steel casing is installed, permitting future monitoring. Samples can be taken using a split-spoon as the soil is removed, and these are analyzed in a laboratory. An inherent problem with this method is that it cannot target "hot spots" or areas with particular constituents of concern.

The CPT-deployed Raman probe allows data to be collected and analyzed while the push is ongoing. Samples can be targeted to areas of particular interest, decreasing analytical costs. The CPT does not require drilling muds or fluids, decreasing waste disposal costs. The CPT is also a smaller diameter than conventional cores, which allows for more rapid drilling.

In the interest of brevity, this analysis focuses on the costs that will be different for the two technologies and does not include fixed costs such as permitting, training, oversight by health and safety personnel.

Cost Analysis

Assumptions—Sampling and Logging Wells (Cable-Tool Drilling)

Technology Assumptions

- Six sampling and logging wells are drilled each year for 10 years, for a total of 60 wells. Although it is technically feasible to drill more than six wells per year, it is assumed that administrative considerations such as permitting, etc. limit the number of wells that can be drilled in one year.
- The wells are each drilled to a depth of 120 ft.
- The drilling rate is 8 ft per day, requiring 15 days to drill a well, for a total of 90 days of drilling per year.
- The completed wells will have a steel casing for their entire length.
- Upon completion, each well will be filled with a suitable filling material, which for purposes of this study is assumed to be grout.
- All activities will be completed in a manner that complies with federal and state permitting and environmental regulations.

Costing Assumptions

- The accuracy range of the cost estimates should be considered within the range +50/-30 percent.
- The capital cost of the well drilling rig is $200,000. The salvage value of the rig is $100,000, based on an equipment life of 20 years.
- Mobilization and demobilization require three days for this technology.
- The burdened labor rates for operating labor are $65/h for oversight engineer, $40/h for operator, $30/h for helper/technician, and $25/h for laborer.
- Radioactive waste disposal costs are $25/ft of drilling.
- Analytical costs are not included.
- The operating and maintenance costs are those given in the Table 3.

Table 3. Costs associated with the baseline method

Item	Unit cost
Carbon steel casing	$8/ft
Fuel, expendables, and maintenance supplies	$150/operating day
Bentonite annular seal	$4/ft
Grout	$8/ft
Pipes and wire	$7/ft

Assumptions—Raman Probe Technology

Technology Assumptions

- The CPT screening pushes will be made in each location where a sampling and logging well would have been placed, for a total of 60 locations.
- The pushes in each location will be made to a depth of 120 ft.
- At all 60 locations, the first push will be equipped with sensors to determine the depth at which contamination may occur. The second push will use grout to fill the cavity produced by the first push. Grouting is assumed for this study, but may not always be necessary.
- There is a 50% probability that the screening push will detect the presence of constituents of concern. As a consequence, additional sampling pushes will be required at 30 locations, but will not be required at the remaining locations.
- The 30 sampling pushes will be located adjacent to the screening pushes to take soil samples from the contaminated zone. The sampling pushes will be followed by a total of 30 pushes which will use grout to fill the cavity produced by the sampling push.
- Sampling will require 10 working days at each location where contamination is discovered by the sampling push. This would be time to relocate and set up the rig, make the four pushes as described above, and perform other required activities (decontaminate push rods, calibrate instruments, etc.).
- Sampling will require five working days at each location where contamination is absent.
- All activities will be completed in a manner that complies with federal and state permitting and environmental regulations.
- It will require six years to complete the pushes at 60 locations. Although the technology is capable of greater completion rates, administrative considerations will limit the number of completed locations to one per month. The number of completed locations will be six the first year and will increase in the manner shown in Table 4.

Table 4. Production schedule

Year	Completed locations/year	Total completed locations
1	6	6
2	8	14
3	10	24
4	12	36
5	12	48
6	12	60

Costing Assumptions

- The accuracy range of the cost estimates should be considered within the range +50/-30 percent.
- The capital cost of the CPT rig is $500,000. The salvage value of the rig is $300,000, based on an equipment life of 15 years.
- The burdened labor rates for operating labor are $75/h for oversight scientist, $40/h for operator, $30/h for helper/technician, and $25/h for laborer.
- Radioactive waste from decontaminating the push rods is generated at the rate of 1 gpm of push rod, and waste disposal costs are $1,000/55-gal drum.
- Analytical costs have not been included. CPT should make more efficient use of data.
- Push rod must be replaced after every 12 pushes or 1,440 ft.
- The operating and maintenance costs are those given in Table 5.

Table 5. Costs associated with the CPT-deployed Raman Probe

Item	Unit cost
Fuel, expendables, and maintenance supplies	$165/day
Grout	$1.33/ft
Push rods	$65/3-ft section

Cost Savings versus Alternative Technologies

The highest total annual cost for both technologies, as for most projects, is incurred in the first year due to capital and mobilization costs. From the second year to the second-to-last year, costs reflect operations and maintenance. They are uniform for the cable-tool drilling, and for the CPT they increase in proportion to the number of sites completed each year. The costs in the last year (year 10 for the cable tool drilling, year 6 for CPT) reflect final demobilization sampling and salvage value of the equipment. The estimated difference in total life cycle present values comparing the application of the CPT in place of sampling and logging wells in a comprehensive vadose zone characterization program at the Hanford Site is $930,000.

In 1993, the Environmental Technology Cost Analysis Program at Los Alamos National Laboratory evaluated the costs of using CPT for the characterization of contaminated soil regions around tanks and other contaminated areas of DOE sites (Booth, Durepo, and Temer 1993). The report did not specifically examine CPT-deployed Raman probe for sampling inside tanks, as that application had not yet been developed. Some of the conclusions of the report with regard to soil sampling, however, can be applied to tank waste samples.

The report concluded that CPT can save 60 percent over the use of conventional monitoring wells because half of the monitoring wells would not need to be emplaced. But the largest cost savings are due to being able to optimize the locations of wells, saving costs of drilling wells that may not be useful. Similarly, the CPT-deployed Raman probe may not completely replace core samples but will be able to indicate the locations in tanks that will yield the most useful core samples: the most representative or most extreme conditions, as needed. This report concluded that for the same cost, the CPT can completely characterize 13 times more locations than can standard cable-tool core holes.

As more demonstration projects are completed using the CPT-deployed Raman probe, more comprehensive cost analyses will be possible. Clearly one factor that will influence the decision of which technology to use is the type of information required.

SECTION 6

REGULATORY AND POLICY ISSUES

Regulatory Considerations

The use of any technology for environmental remediation and waste management is constrained by state, federal, and local regulations, which will differ at each DOE site. State and local regulations can vary widely, despite some efforts by U.S. Environmental Protection Agency and states to encourage regulatory reciprocity: acceptance of testing from one state or region to another. No regulatory or permitting issues have been identified with CPT-deployed Raman probe. It does not appear to be controversial in terms of public acceptance.

The regulatory, permitting, and safety issues are different and would need to be handled separately for in-tank applications and vadose zone monitoring. At Hanford, some of the regulations covering vadose zone testing include the following:

- well construction and abandonment procedures specified in Washington Administration Code (WAC) 173-160,
- Clean Air Act permitting specified in WAC 173-400-102 (5) and WAC 173-460-020 (15), and
- review of activities against the analysis and requirements of the Basis for Interim Operations.

At Savannah River, special regulatory permits are not required for operation of the CPT-deployed Raman probe. Regulatory approval is typically handled by submitting a drilling plan to the appropriate regulatory agency for their approval prior to the initiation of field activities. Typically these drilling plans require that investigation-derived wastes (drilling fluids, cuttings, and equipment decontamination fluids) be handled according to Resource Conservation and Recovery Act requirements. The operation of the CPT generates significantly reduced amounts of investigation-derived wastes.

In most subsurface characterization investigations for DNAPL, the Raman probes will be used to optimize selection of locations for more expensive and robust analytical activities, such as collection of samples for laboratory analysis. The "real-time" nature of the results, combined with a flexible site investigation program, can be used for on-site decision making that can significantly improve the quality and decrease the duration and cost of the investigation.

Safety, Risks, Benefits, and Community Reaction

Because of the decreased risk from sample collection, analysis, and waste handling, the CPT-deployed Raman probe complies with as low as reasonably achievable principles. The normal procedures associated with work with lasers are applicable, and the spectroscopy staff must be trained in the operation of the Raman probe and spectrometer.

SECTION 7

LESSONS LEARNED

Implementation Considerations

In the implementation of a new method, it is always important to know how the old methods and the new methods correlate. The data produced by the LLNL CPT-deployed Raman probe analyzing tank waste did not always agree with the data collected earlier using thermogravimetric analysis to measure water content and ion chromatography to measure nitrate and oxalate concentrations. More analysis will be necessary to determine the reason for the discrepancy. As extensive time may have elapsed between the sample analysis by the old methods and the new technique, the discrepancies may simply be due to sample drying and aging during storage or errors in recorded data. The data produced by the EIC, Inc. instrument did not always agree with sampling results, possibly due to variations between the two deployment locations or length of time allowed for spectra collection.

Technology Limitations and Need for Future Development

Additional neural network training will be necessary for different constituents and to clearly define the detection limits for the four compounds measured during the first system qualification test at Hanford. This fact is especially true for dark-colored samples, which scatter less light than lighter-colored samples and thus show weaker signal and more noise.

Future development will also need to include continued investigation of why the Raman spectral analysis of some samples did not agree with earlier results from thermogravimetric analysis and ion chromatography and optimization of the length of data acquisition.

With proper neural network training, this technique will permit waste and soil samples to be analyzed more quickly and consequently allow for more samples to be analyzed than is currently possible. The instruments also provide a screening process to indicate areas of high soil contamination for locating boreholes and monitoring wells.

Technology Selection Considerations

The Raman sensor delivered to Hanford suffered an 80 percent light loss when the fibers were installed in the probe. A next-generation probe should be built with improved and "hard-wired" Raman fiber optics. Additionally, the fiber optic cable was noted to be fragile and may require additional jacketing with flexible, ribbed conduit to minimize the possibility of kinking, bending, or breaking the fiber over its 250-ft length.

No major operational problems were noted in the test; however, several elements of the design were noted as being particularly successful. As shown in Figure 4, Raman spectral analysis of soil samples was more sensitive when the probe was in direct contact with the soil. This effect is advantageous since it is representative of the conditions that will exist when the probe is deployed to measure soil contamination. The laser was shown to be stable, and the spectrometer did not exhibit frequency shifts. This stability is most likely due to its permanently fixed optics.

For the in-tank application, it was necessary to isolate the Raman probe chamber by potting (to meet flammable gas concerns) and to use quick-disconnect connectors. These adaptations were driven by safety constraints and the requirement that the fiber optic cable be detachable at the probe head for retraction from the CPT when deployed. This difficult set of conditions resulted in loss of probe sensitivity and reliability. Misaligned and poor connections caused the probe's signal strength to drop considerably. Quick-disconnect connections in fiber optics should be avoided if at all possible because of the potential for misalignment and foreign material in the connections.

APPENDIX A

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APPENDIX B

ACRONYMS

CMST	Characterization, Monitoring and Sensor Technology
CPT	cone penetrometer
DNAPL	dense, nonaqueous-phase liquid
DOE	Department of Energy
EPA	Environmental Protection Agency
FETC	Federal Energy Technology Center
LLNL	Lawrence Livermore National Laboratory
OST	Office of Science and Technology
PCE	tetrachloroethene
TCE	trichloroethene
TFA	Tanks Focus Area
WAC	Washington Administrative Code