EIC
Laboratories

APPLICATION SUMMARY

In-situ Monitoring of Nuclear Waste

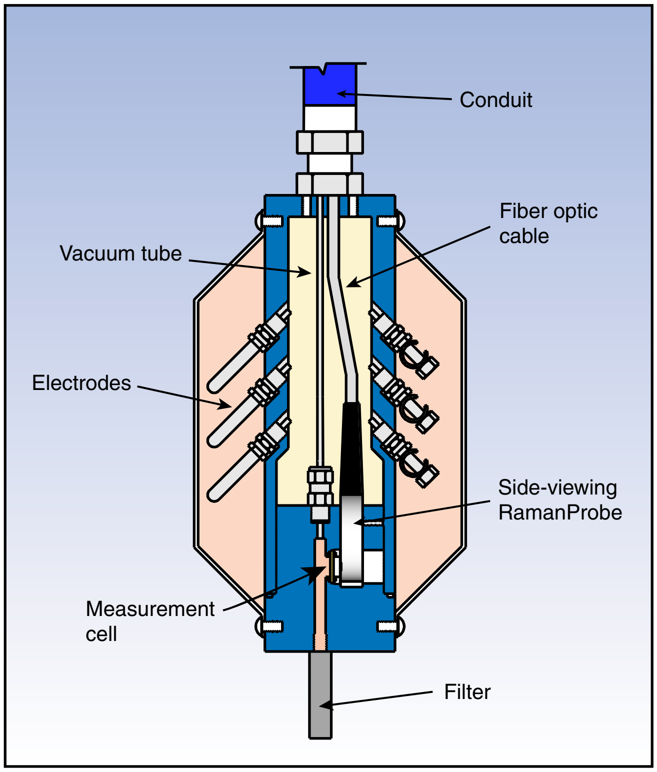
Introduction[1]

The Department of Energy (DOE) has 332 underground tanks used to process and store over 100 million gallons of high level radioactive waste (HLW). Some of these tanks are made of only a single shell of steel, and would pose a serious threat to the public should the tank walls be compromised by corrosion. These HLW tanks often contain high levels of nitrate due to the use of nitric acid in fuel nuclear weapons materials processing. To minimize the corrosive effects of nitrate on steel, the tank contents are maintained at an elevated pH and at an optimum nitrite level.

Monitoring the concentration of nitrate, nitrite, and hydroxide in the tanks is necessary so that the complicated, costly, and potentially hazardous procedure of opening the tanks to add hydroxide is only performed when necessary. Presently, the tank composition is monitored off-line by a slow and risky procedure of liquid sampling, preservation, transport, storage, preparation, and analysis with a pH meter and an ion chromatograph in a hot cell. An *in-situ* montoring technique that can endure the harsh conditions of the radioactive chemical waste (1,000 rad/hr, 90 ^{0}C, and 10 molar OH^{-}) is highly desirable. An additional obstacle for optical monitoring techniques is that analysis must be performed in turbid solutions without interference from other sample components. In an ongoing project with the DOE, EIC Laboratories has designed and tested an in-situ probe and Raman spectrograph for the monitoring of HLW.

Probe Development

The project requires a single *in-situ* probe that incorporates both the Raman sensor as well as an electrochemical noise (EN) sensor, developed at Hanford, WA, and at the Savannah River Site, SC. EN measures the potential and current fluctuations of metal in solution, and has the capability of monitoring both localized and general corrosion.



The combined Raman/EN probe for *in-situ* HLW monitoring.

Constructed of stainless-steel, the probe incorporates a side-viewing Raman fiber optic sensor.[2] The HLW solution is drawn up through a stainless-steel filter and into a small sample chamber. Raman measurement is performed through a quartz window on the sample chamber. The solution can then be discharged back into the tank. If necessary, calibration solutions can be introduced into the probe from external sources.

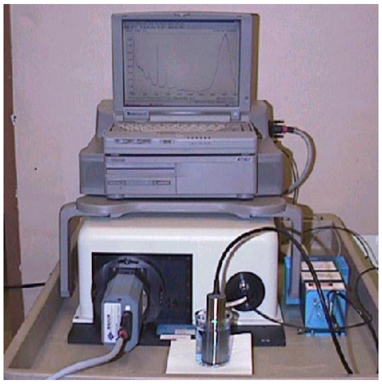
A rugged cable, housing the electrical wires and fiber optic cables, is used to raise and lower the probe into the tank. A deployment platform is currently under construction to support and control the probe height.

---

[1] Introductory material courtesy of the Department of Energy.

[2] Note: Raman instrumentation used and developed in this application are available from EIC's commercial affiliate, InPhotonics, Inc. Visit us on the web at www.inphotonics.com.

Raman Instrumentation



Charged-coupled devices (CCDs) used as detectors for Raman spectroscopy have little quantum efficiency at wavelengths above 1000 nm. It was important for this project that an appropriate excitation laser wavelength was selected to provide ample spectral range while avoiding fluorescence backgrounds from the HLW. Many commercial Raman spectrometers employ 785 nm excitation, however this results in a spectral range limit of about 3100 cm^{-1}. A custom spectrograph was designed for operation with 670 nm excitation. This spectrograph enabled measurement of 200 - 4000 cm^{-1} (Stokes) at 4 cm^{-1} resolution with excellent sensitivity and no moving optical components.

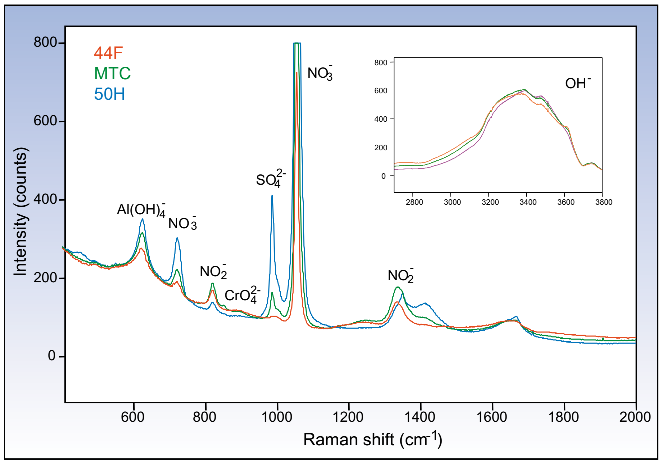
Because all optical filtering is performed within the fiber optic probe, the sensor itself was custom-modified for operation at 670 nm excitation.

Laboratory Tests

Five solutions containing known quantities of nitrate, nitrite, hydroxide and other relevant anions were prepared as a training set. Raman spectra were measured and calibration curves were constructed as peak height versus concentration. A test set of solutions simulating HLW was prepared by mixing known quantities of salt solutions. The three anions were determined by standard analytical methods: nitrate and nitrite were determined by using ion chromotography (IC), while hydroxide ion concentration was determined via titration.

The goal of the monitoring system was for agreement within 10% of the current analytical methods. This was achieved immediately for hydroxide, nearly achieved for nitrite, but not for nitrate. It was observed that the carbonate band is close to the strongest nitrate band at 1054 cm^{-1}. By selecting a less intense nitrate peak at 722 cm^{-1} for the analysis, the nitrate determination became successful as well.

Additional testing was performed using radioactive waste samples. The data were shown to be reproducible over a 70-day period, even though the system was shut down between each set of measurements. Calibration was not required at the start of each measurement period, and there was no apparent damage to the probe optics from the radiation levels.



Waste Sample	Ion	Raman Result (M)	IC Result (M)	Δ(IC-Raman)	% Error
44F	NO_3	0.4427	0.475	0.0323	6.8
44F	NO_2	0.4674	0.462	-0.0054	-1.17
44F	OH	3.87	4.02	0.15	3.73
50H	NO_3	2.4191	2.36	-0.0591	-2.5
50H	NO_2	0.2423	0.257	0.0147	5.72
50H	OH	1.3	1.3	0	0
Mix	NO_3	0.9878	0.89	-0.0978	-10.99
Mix	NO_2	0.6502	0.676	0.0258	3.82
Mix	OH	2.62	2.54	-0.08	-3.15

Representative Raman spectra and quantitative data of HLW solutions.

Future Tasks

As of December 2001, the deployment platform was being tested. This monitoring system is scheduled to be installed at the Savannah River Site during the 2002 calender year.

For more information, please contact:

Dr. Job Bello
Senior Scientist, Spectroscopy Division
bello@eiclabs.com

---

111 Downey Street
Norwood, MA 02062
Phone (781)769-9450
Fax (781)551-0283
www.eiclabs.com