Raman Based Process Monitor For Continuous Real-Time Analysis Of High Level Radioactive Waste Components

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ABSTRACT

A new monitoring system was developed at Pacific Northwest National Laboratory (PNNL) to quickly generate real-time data/analysis to facilitate a timely response to the dynamic characteristics of a radioactive high level waste stream. The developed process monitor features Raman and Coriolis/conductivity instrumentation configured for the remote monitoring, MatLab-based chemometric data processing, and comprehensive software for data acquisition/storage/archiving/display. The monitoring system is capable of simultaneously and continuously quantifying the levels of all the chemically significant anions within the waste stream including nitrate, nitrite, phosphate, carbonate, chromate, hydroxide, sulfate, and aluminate. The total sodium ion concentration was also determined independently by modeling inputs from on-line conductivity and density meters. In addition to the chemical information, this monitoring system provides immediate real-time data on the flow parameters, such as flow rate and temperature, and cumulative mass/volume of the retrieved waste stream. The components and analytical tools of the new process monitor can be tailored for a variety of complex mixtures in chemically harsh environments, such as pulp and paper processing liquids, electroplating solutions, and radioactive tank wastes.

The developed monitoring system was tested for acceptability before it was deployed for use in Hanford Tank S-109 retrieval activities. The acceptance tests included performance inspection of hardware, software, and chemometric data analysis to determine the expected measurement accuracy for the different chemical species that are encountered during S-109 retrieval.

INTRODUCTION

Intensive programs in the U.S. Department of Energy complex to find solutions to the difficult problems related to treatment and disposal of high-in-sodium high-level nuclear wastes stored in underground tanks at several sites have recently highlighted needs for the monitoring of complex aqueous salt solutions and determination of their sodium content.[1,2] These nuclear waste solutions are highly caustic, contain elevated concentrations of nitrate, and characterized by high radiation levels due to the presence of the radioactive cesium and strontium isotopes as fission products.[3,4] Traditional grab sampling technique and laboratory analysis of the tank waste samples is associated with enhanced health risks due to the high radiation fields.[5] It is costly, time consuming, and in case of the continuous operations can cause their interruptions for prolong times. Furthermore, conventional methods tend to provide only a sporadic picture of the materials being monitored. The current retrieval capability for Hanford waste streams

monitoring is limited to total flow measurements, an on-line gamma monitor (for gross gamma), and periodic grab samples, which are analyzed in a standard laboratory.

To address the need for current retrieval status, we proposed using an on-line real-time process monitor system. The methods used to monitor these processes must be robust (require little or no maintenance) and must be able to withstand harsh environments (e.g., high radiation fields and aggressive chemical matrices). The ability for continuous online monitoring allows the following benefits:

- Improvement of operational safety;
- Doesn't require personnel involvement to perform grab samples;
- Real-time information on flow parameters and solution composition;
- Doesn't interrupt continuous retrieval
- Elimination of human error.

Raman spectroscopy is an analytical technique that has extensively used for measuring the concentrations of the various organic and inorganic compounds.[6,7] The project R&D goals were to develop chemometric models to measure real-time concentrations of key analytes in the waste stream, including NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, AlO_2^-, CO_3^{2-}, CrO_4^{2-}, OH^- by Raman spectroscopy and total sodium concentration by a combination of conductivity and density measurements. The overall objective of this work was to provide CH2M HILL Hanford Group, Inc. (CH2M HILL) with process monitoring instruments capable of measuring the concentration of components of solutions obtained from saltcake retrieval activities in Hanford Tank S-109. In this work, we developed proper testing protocols for ensuring that the Raman-based monitoring system could be operated to provide useful waste-stream chemical information. The tests described in this paper were executed to assess the performance of the process monitoring instruments and of the chemometric model to ensure that the instruments yield acceptable results when used as intended.

RESULTS AND DISCUSSION

Proper choice of instrumentation is critical for the successful development of a process monitoring system. In this work, we utilized commercial Raman RS2000 echelle spectrograph (Inphotonics Inc.). The system was equipped with a stabilized 670 nm, 150-mW visible diode laser as the excitation source. Data were collected at 1 cm^{-1} spectral resolution over a range of 200 - 4000 cm^{-1} stokes shift (Raman shift from 670 nm). Samples were measured with InPhotonics' focused fiber optic probe (RamanProbe™) with a thermoelectrically-cooled CCD detector, normal operating temperature –55°C. The laser beam was coupled to the sample through a 100 m fiber-optic cable and probe assembly, which focused the excitation beam directly into the waste stream; this also precluded any air gap between the laser source and the sample. The focal point of the laser beam was 5 mm beyond the end of the laser probe tip, the measured laser intensity at the sample was typically 50 mW, the excitation laser beam diameter at the sample was measured as 3 mm. Molecue® acquisition software with GRAMS 32® data manipulation software was used to process the Raman data. The

Raman probe was demonstrated to tolerate 17.6 MR radiation field without a change in performance characteristics[8]. It was estimated that the maximum dose rate the probe would receive would be 50 mR h^{-1} over an approximate 20,000 hour life time, or 1,000 R.[9]

Flow-through conductivity and Coriolis sensors, the latter is capable of simultaneously measuring temperature, flow rate, and density of the waste stream, were selected based on the deployment technical specifications and chemical and radiological stability requirements. The toroidal conductivity sensor (Rosemount Analytical, model 242) was equipped with Model 5081-T transmitter and 100 m interconnecting cable. The coriolis sensor (Micro Motion, Inc., model T100) was equipped with Model 2700 transmitter and 100 m interconnecting cable. Both instruments were calibrated at the certified analytical laboratories using standard procedures.

All three instruments were obtained in duplicate and assembled in laboratory and field-deployable configurations. The laboratory measuring system was used to acquire data needed for the chemometric models development and testing. The field-deployable manifold system was verified for adequate performance and delivered to the client.

The Raman signal, conductivity, and density measurements are sensitive to, and depend upon the solution chemical composition and ionic strength, temperature, presence of the solid particulates and bubbles. A corresponding database was needed for the development of chemometric models. To build this database, we measured solutions of individual sodium salts and their mixtures in wide concentration range, and under variable temperatures, and with the added complexity of the presence of bubbles and solid particulates within the system. The instrument performance under variable flow conditions was established by measuring solutions in static mode and under variable 2 – 20 gallon min^{-1} (GPM) flow rate.

Static measurements of the 86 concentrated solutions of the single sodium salts $NaNO_3$, NaOH, $NaNO_2$, $NaAlO_4$, Na_2CO_3, Na_2SO_4, Na_2CrO_4, and Na_3PO_4, which constitute the principle components of the dissolved salt cake, and their mixtures were performed by all three instruments at room and several elevated temperatures. Preliminary Raman chemometric model was developed using these static measurements. Figure 1 shows a typical Raman spectrum containing multiple ionic species.

Flow measurements containing a total 6 flow tests were performed: 5 tests used a laboratory scale bench-top flow loop; 1 test combined the field-scale manifold and laboratory flow loop. The flow rate studied was variable, 2 - 20 GPM range. Two typical experimental protocols were used. In the first one, the flow loop was initially filled with laboratory tap water and checked for leaks and proper pump function. A calculated amount of solid $NaNO_3$ was incrementally added to the feeding/receiving reservoir to achieve final concentration of about 14 wt%. Calculated amounts of other neutral sodium salts were added to the solution in the same manner. Finally, 50 wt% NaOH solution was added to the system. Measurements were taken after each salt addition. In the second protocol, the 10 wt% NaOH solution was incrementally obtained,

and other sodium salts were added to it. The temperature was varied from 15 to 50°C. Figure 2 shows the series of Raman spectra taken under variable temperatures for a solution containing sodium nitrate. Gas N_2 bubbles were introduced into flow system at controlled variable rates up to 6% of the solution flow rate. The effect of $Fe(OH)_3$ solids was studied, up to 1% solids loading; Figure 3 contains a series of spectra taken as a function of added $Fe(OH)_3$. A revised Raman chemometric model incorporated flow measurements. The sodium model for prediction of total Na concentration was developed based on conductivity / density / temperature from the static and flow measurements.

To verify performance of the field-deployable manifold system, it was connected with the laboratory flow loop system and filled with water. Solid $NaNO_3$ was added to obtain 2.7 wt% solution. The performance of the two Coriolis sensors (temperature, flow rate, density, and total mass and volume) and two conductivity sensors was compared at variable flow rates and adjusted as needed. The performance of the two Raman instruments was be compared by monitoring the outputs from the predictive model and software. To gather more information on the performance of the Raman instruments, other sodium salts were added to the flow system. The final composition of the test solution was 4.94 wt% $NaNO_3$, 5.1 wt% $NaNO_2$, 1.0 wt% Na_2SO_4, and 1.2 wt% Na_2CO_3. Both instruments adequately monitored a continuous change in the solution composition. The outputs from the Raman instruments were in agreement, and no adjustment was necessary.

The data acquisition, data storage, and data archival were tested. The successful signal transfer from the Coriolis and conductivity transmitters to the data acquisition system, data processing and storage were verified.

The final test of the predictive software was achieved during an acceptance test, which verified the chemometric models using two simulant solutions. The compositions of these solutions targeted the early and late chemical concentrations of the actual single-shell tank feed solutions and are listed in Table 1.[10] "Early" feed refers to the composition of dissolved saltcake early in the S-109 retrieval process. "Late" feed is the composition of dissolved saltcake late in the retrieval process. The tests uses each solution (early and late feeds) to mimic process conditions and demonstrate the process monitor system's ability to measure the concentrations of the major components, which are sodium salts of NO_3^-, NO_2^-, SO_4^{-2}, CO_3^{-2}, CrO_4^{-2}, PO_4^{-3}, $Al(OH)_4^-$ and OH^-. The early and late feeds were prepared and analyzed at independent analytical laboratory.

Detection Limits:
The detection limit for each analyte is used in part to estimate the accuracy and precision of that analyte. The detection limit is fundamentally limited by measurement noise. The single wavenumber that locates the position of the Raman band maximum (*M)* was used to determine the absolute intensity of the signal for each analyte. All Raman spectra were recorded using a 15-second integration time. For each analyte, the calibration plot (Raman signal intensity versus analyte concentration) was obtained using 3–4 standard solutions in a wide concentration range and then subjected to linear regression analysis.

Satisfactory fits to the data were obtained for all analytes, which is reflected by the R^2 values being greater that 0.99 for all analytes except hydroxide ($R^2 = 0.9869$). The magnitude of the yielded slope *m* is the measure of the Raman technique's sensitivity for the particular analyte. Very different slopes were observed for the studied analytes, from 26 for the least-sensitive, hydroxide, to 2805 for the most-sensitive, chromate.
The Raman detection limit information for each analyte was estimated using Raman spectra collected for the individual sodium salt solutions over a wide concentration range and is listed in Table 2. Based on an IUPAC treatment[11], equation 1 was adopted for the evaluation of the detection limit of the Raman measurements,

$$DL = \frac{kS_b}{m + tS_m} \qquad (1)$$

where *DL* is detection limit, *k* is a numerical coefficient, *m* is the slope, S_b and S_m are standard errors for the intercept and slope of a calibration plot, respectively, and *t* is Student's value for (n – 2) degrees of freedom at the chosen confidence level. In accord with IUPAC recommendations[4], *k* value of 3 was applied which in turn calls for a 99.87% confidence level.

Because Raman signal for the free hydroxide overlaps with the water band for NaOH, noise standard deviation was taken as the standard deviation of the difference between actual and fitted intensity of the water band at 3604.4 cm^{-1} calculated for the 3595 to 3614 cm^{-1} region using the hydroxide-free analyte static samples. Single analyte static samples used to develop the chemometric model were used in this evaluation.

Examination of the detection limits reported in Table 2 suggests that they are lower than the concentration of the analytes of interest in the early and late feed solutions (Table 3) except for the NaOH concentration of 0.073 %wt in the late feed solution. Concentrations of sodium phosphate (early feed), aluminate and nitrite (late feed) approach the Raman detection limit, which is expected to affect the accuracy and precision of the measurements of these analytes.

Accuracy and Precision:
The associated flow loop was filled with either early or late feed solution. A reproducibility test was performed that consisted of long-term data acquisition; a total of 2028 and 779 replicate measurements were collected for early and late feed, respectively. The accuracy and precision of measurement will change depending on the concentration of each analyte and on the concentrations of other species in the solution. For this reason, the values for accuracy and precision for the early and late feeds differ from one another. Because of the replicative nature of the testing, the accuracy and precision can be estimated for each analyte in these feeds. The relative error and absolute deviation are measures of accuracy; the standard deviation, variance, and coefficient of variation are measures of precision. The acceptance test criteria for each analyte were stated as a ±20% relative error or as a ±0.5 wt% absolute error. Table 3 compares the wt% concentrations of the major components of the early and late feeds calculated by chemometric predictive software and reported as averaged data with the corresponding

values obtained in alternative analyses performed at the independent laboratory. The predicted values were highly reproducible, which is reflected by the small standard deviation values given in parentheses. The highest standard deviation was observed for NaOH and is due to the overlapping of the free hydroxide vibrational Raman band with that of water, which is a fundamental difficulty in detecting this analyte. Close agreement between actual and average predicted values was observed for all analytes resulting in small absolute deviation (Table 3). Relative errors became larger as the analyte concentration decreased and approached the detection limit, and values of 27, 25, and 21% were observed for the sodium chromate (late feed), sodium nitrite (late feed), and sodium phosphate (early feed), respectively; nevertheless, the absolute errors for these analytes were still less than the 0.5 wt% acceptance criteria. NaOH in the late feed could not be measured accurately because it is present in the solution at concentrations below the Raman detection limit. The chemical monitoring system provides adequate measurements for the early feed solution, which is characterized by low water activity and high ionic strength and density, and contains sodium salts at their saturation limit. As a result, it represents a special challenge for traditional wet analysis methods.

Presented in Table 3 are the absolute range (high and low values recorded over the repeated analysis), variances, and coefficients of variation for the predicted concentrations. Even though replicate values vary over a wide range, their variances and coefficients of variation are low, indicating that only a few deviated significantly from the average; the vast majority of the replicates clustered around the average values.

SUMMARY

PNNL has developed a process monitoring system capable of measuring concentrations of the components of solutions obtained from saltcake retrieval activities in Hanford Tank S-109. The process monitor system, which is composed of a Raman spectrometer, conductivity probe, and Coriolis flow meter, was assembled in a field-deployable configuration.

The acceptance tests verifying the acceptability of chemometric model analysis and software functionality were completed before they were deployed for use in S-109 retrieval activities. The compositions of two solutions that target the “early” and “late” feed chemical concentrations of the SST feed solutions were used for acceptance testing. The tests using each solution mimic process conditions and demonstrate the process monitor system’s ability to measure the concentrations of the major components, which consist of sodium salts of NO_3^-, NO_2^-, SO_4^{-2}, CO_3^{-2}, CrO_4^{-2}, PO_4^{-3}, $Al(OH)_4^-$, and OH^-. The detection limit was determined for each analyte and found to be lower than the concentrations of the analytes of interest in the early and late feed solutions, except for the NaOH concentration in the late feed solution (0.073 wt%). Concentrations of the sodium phosphate (early feed), aluminate and nitrite (late feed) approach the method’s detection limit, which resulted in large uncertainties in the accuracy and precision for the specific analytes described in this report.

Based on measurements with the early and late feeds, the accuracy and precision of each analyte was determined. The concentrations predicted by the chemometric model were highly reproducible. The highest standard deviation was observed for NaOH. Close agreement between the actual and average predicted values was found for all analytes with relative errors for most analytes being within the acceptance criterion of ±20% relative error. The absolute error for all analytes was less than the ±0.5 wt% acceptance criterion. NaOH in the late feed could not be measured accurately because it is present in the solution at concentration levels below the Raman detection limit.

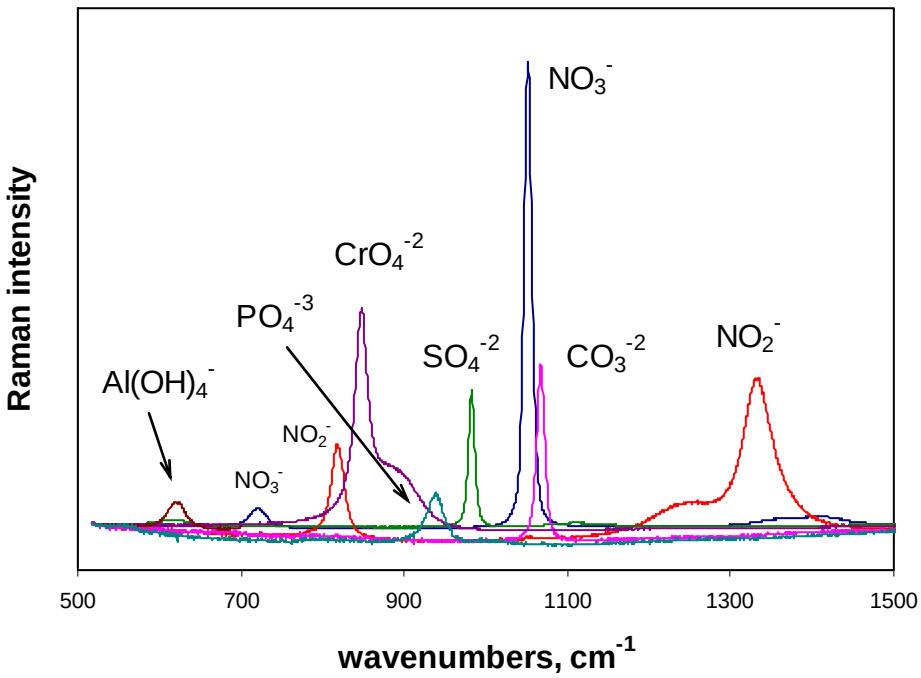


Figure 1. Raman Spectrum Showing Multiple Ionic Species in Solution. The region from 500 to 1500 cm^{-1} is sensitive to all oxy ions of interest.

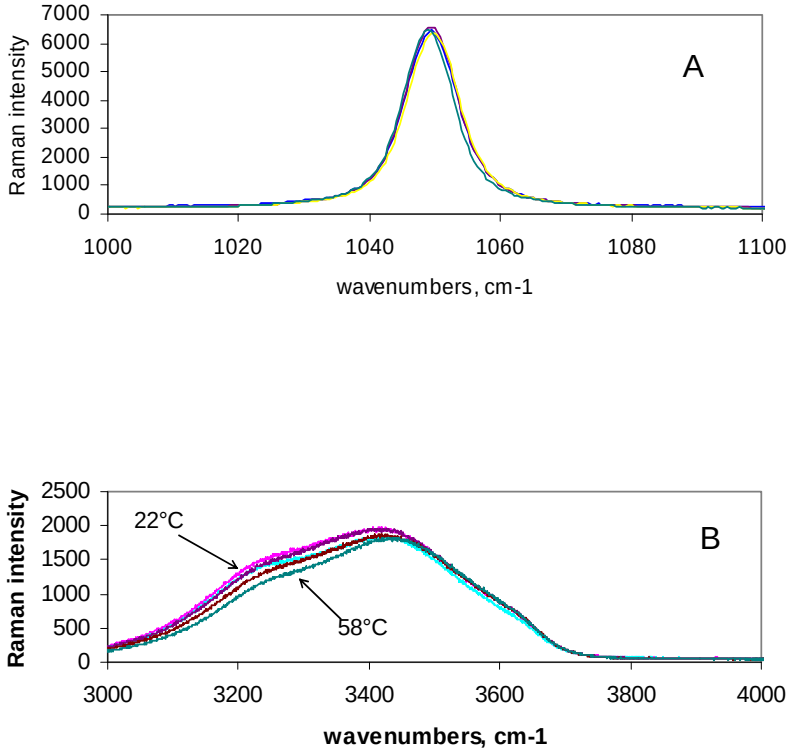
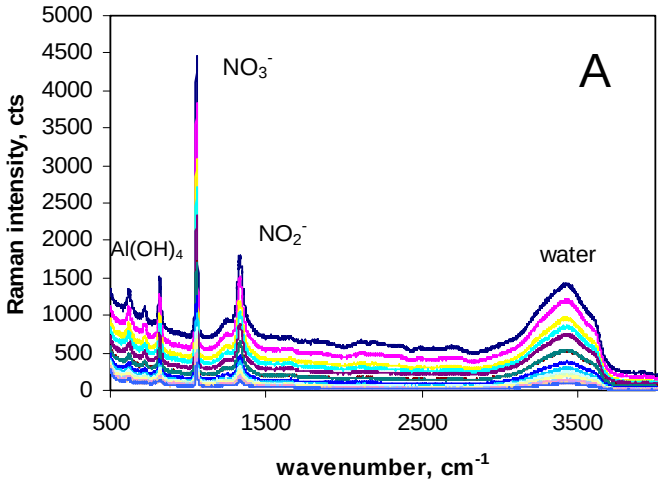


Figure 2. Variable Temperature Raman Spectra of Sodium Nitrate Solution. Figure 2A, shows the nitrate band at 1050 cm^{-1} is insensate to variations in temperature; Figure 2B, the water region at 3000-3800cm^{-1} is sensitive to variations in temperature.



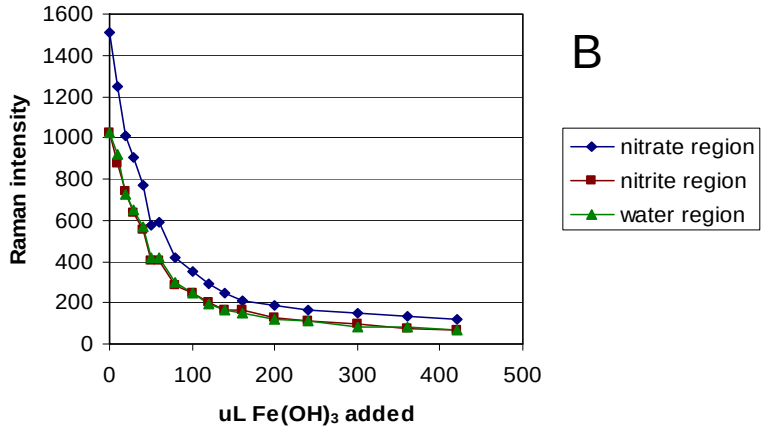


Figure 3. Raman Spectra of a Mixture Containing Nitrate and Nitrite in Aqueous Solution Taken as a Function of Added $Fe(OH)_3$ Solids. Figure 3A shows the change in the Raman signal over the entire spectrum. Figure 3B shows the change in Raman signal is consistent over the entire Raman spectrum as represented by the intensity of the nitrate, nitrite, and water signal being affected the same as a function of solids loading.

Table 1. Chemical Compositions of the SST Feed Simulant Solutions

Analyte	Early Feed			Late Feed		
	Calculated M (a)	**Found M** (b)	**%wt, based on found M** (c)	**Calculated M** (a)	**Found M** (b)	**%wt based on found M** (c)
%wt H_2O	NA	56.2		NA	81.4	
Density	NA	1.42		NA	1.15	
OH	1.66	1.67	4.70 as NaOH	0.023	0.021	0.073 as NaOH
TOC	0.02	<0.03		0.02	<0.03	
TIC	0.58	0.61	4.55 as Na_2CO_3	0.24	0.24	2.21 as Na_2CO_3
Al	0.48	0.52	4.32 as $NaAl(OH)_4$	0.040	0.044	0.45 as $NaAl(OH)_4$
Cr	0.080	0.079	0.92 as Na_2CrO_4	0.018	0.018	0.26 as Na_2CrO_4
Fe	0.0000	0.0001		0.0000	<0.00002	
K	0.030	0.026		0.010	0.009	
Na	8.53	7.87	12.75	2.84	2.62	5.24
P	0.025[a]	0.025		0.050	0.052	
S	0.14	0.13		0.17	0.17	
Si	0.0000	0.0005		0.0000	<0.0002	
F	0.007[a]	<0.016		0.100	0.098	
Acetate	NA	NA		NA	NA	
Cl	0.08	0.08	0.33 as NaCl	0.010	0.009	0.051 as NaCl
NO2	0.82	0.86	4.18 as $NaNO_2$	0.070	0.073	0.44 as $NaNO_2$
NO3	3.90	3.98	23.82 as $NaNO_3$	1.60	1.59	11.75 as $NaNO_3$
PO4	0.025	0.025	0.29 as Na_3PO_4	0.050	0.055	0.78 as Na_3PO_4
SO4	0.14	0.14	1.40 as Na_2SO_4	0.17	0.17	2.10 as Na_2SO_4
Oxalate	0.010	<0.031		0.010	0.011	
Cs (µg/mL)	2.4	2.3		0.24	0.23	
Mass balance	100.0	97.8		100.0	99.3	
Charge balance	1.00	0.90		1.00	0.92	

(a) Intended molar (M) analyte concentrations calculated based on simulant preparation protocol.

(b) Molar analyte concentrations determined by analysis at CH2M HILL's 222-S Laboratory (Herting 2004).

(c) Analyte concentrations in %wt calculated based on M analyte concentrations determined by analysis at CH2M HILL's 222-S Laboratory (Herting 2004).

Table 2. Detection Limits for Analytes

Analyte	Raman Band Maximum[a] cm^{-1}	Linear Regression[b]			Noise Standard Deviation S_b[c]	Detection Limit[d] %wt
		Slope *m*	Slope Standard Error	R^2		
$NaNO_3$	1050.3	728	15	0.9996	8.1	0.033
$NaNO_2$	1327.3	105.4	2.6	0.9988	6.6	0.19
Na_2SO_4	982.6	578	26	0.9980	9.0	0.047
Na_2CO_3	1067.9	263.3	2.3	0.9998	8.1	0.093
Na_2CrO_4	847.9	2805	31	0.9999	19	0.021
$NaAl(OH)_4$	620.9	208	33	0.9930	21	0.30
Na_3PO_4	939.7	93.3	7.8	0.9930	8.9	0.29
NaOH	3604.4	29.6	2.1	0.9898	3.7	0.38

(a) Position of the Raman band maximum (*M)* was used to determine absolute intensity of the analyte signal. All Raman spectra were recorded using a 15 sec integration time in the static mode. All analyte sample solutions analyzed here were applied for the development of the chemometric model.
(b) Linear regression analysis was performed for the calibration plot (Raman signal intensity versus analyte concentration) obtained using 3–4 analyte solutions over a wide concentration range.
(c) For all analytes but NaOH, noise standard deviation was determined using three blank samples for the wavenumber range $M \pm 5$ cm^{-1}. For NaOH, noise standard deviation was taken as standard deviation of the difference between actual and fitted intensity of the water band at 3604.4 cm^{-1} calculated for the 3595 – 3614 cm^{-1} region using the hydroxide-free analyte static samples.
(d) Detection limit = $3S_b / m$.

Table 3. Analysis of Predicted Component Concentrations by Chemometric Modeling for Early and Late Feed Simulant Solutions. Acceptance Test Criteria are ±20% relative error or ±0.5 %wt.

Analyte	%wt Analytical[a]	Saltpred[b] %wt Prediction						
		Average[c]		Absolute Range[d]	Variance[e]	Coefficient of Variation[f] %	Relative Error[g] %	Absolute Deviation[h] %wt
Early feed, data recorded 07/11/05 from 3:58 pm to 07/12/05 8:52 am; 2028 measurements								
NaOH	4.70	4.85	(0.25)	3.8 – 5.9	0.064	5.2	3.2	0.15
Na_2CO_3	4.55	5.02	(0.13)	4.4 – 5.4	0.016	2.6	10	0.47
$NaAl(OH)_4$	4.32	4.72	(0.11)	4.4 – 5.1	0.013	2.4	9.3	0.40
Na_2CrO_4	0.92	0.96	(0.02)	0.92 – 0.99	0.0002	1.6	4.3	0.04
$NaNO_2$	4.18	4.22	(0.04)	4.1 – 4.3	0.0018	1.0	1.0	0.04
$NaNO_3$	23.82	23.47	(0.17)	23.0 – 24.0	0.028	0.71	1.5	- 0.35
Na_3PO_4	0.29	0.35	(0.04)	0.21 – 0.64	0.0015	11.0	21	0.06
Na_2SO_4	1.40	1.43	(0.01)	1.4 – 1.5	0.0001	0.80	2.1	0.03
Na	12.75	12.87	(0.04)	12.8 – 13.0	0.0014	0.29	1.0	0.12
Late feed, data recorded 07/12/05 from 9:41 am to 3:41 pm; 779 measurements								
NaOH	0.073	0.0	(0.29)	0.0 – 1.1	0.087			- 0.073
Na_2CO_3	2.21	2.31	(0.04)	2.2 – 2.5	0.0015	1.7	4.5	0.10
$NaAl(OH)_4$	0.45	0.41	(0.03)	0.28 – 0.52	0.0011	8.2	8.9	- 0.04
Na_2CrO_4	0.26	0.19	(0.01)	0.17 – 0.29	0.00004	3.3	27	- 0.07
$NaNO_2$	0.44	0.33	(0.02)	0.23 – 0.41	0.0004	5.9	25	- 0.11
$NaNO_3$	11.75	11.89	(0.10)	11.4 – 12.3	0.0098	0.83	1.2	0.14
Na_3PO_4	0.78	0.75	(0.05)	0.20 – 1.2	0.0023	6.4	3.8	- 0.03
Na_2SO_4	2.10	2.0	(0.02)	2.0 – 2.3	0.0006	1.1	4.8	- 0.10
Na	5.24	5.38	(0.10)	3.9 – 5.9	0.0091	1.7	2.7	0.14

(a) Analyte concentrations in %wt calculated based on molar analyte concentrations determined by analysis at CH2M HILL's 222-S Laboratory (Herting 2004).
(b) MATLAB-based chemometric predictive software "Saltpred."
(c) Simple average $\bar{x} = \Sigma x / n$, where x is a single measurement and n is the number of measurements. Standard deviation is given in parentheses.
(d) Defined by the minimum and maximum predicted values in the given time interval.
(e) Variance $s^2 = \Sigma(x - \bar{x})^2 / n$.
(f) Coefficient of variation = ($s/\bar{x}$) × 100%.
(g) Relative error = 100% × (%wt analytical – $\bar{x}$) / %wt analytical.
(h) Absolute deviation = %wt analytical - $\bar{x}$.

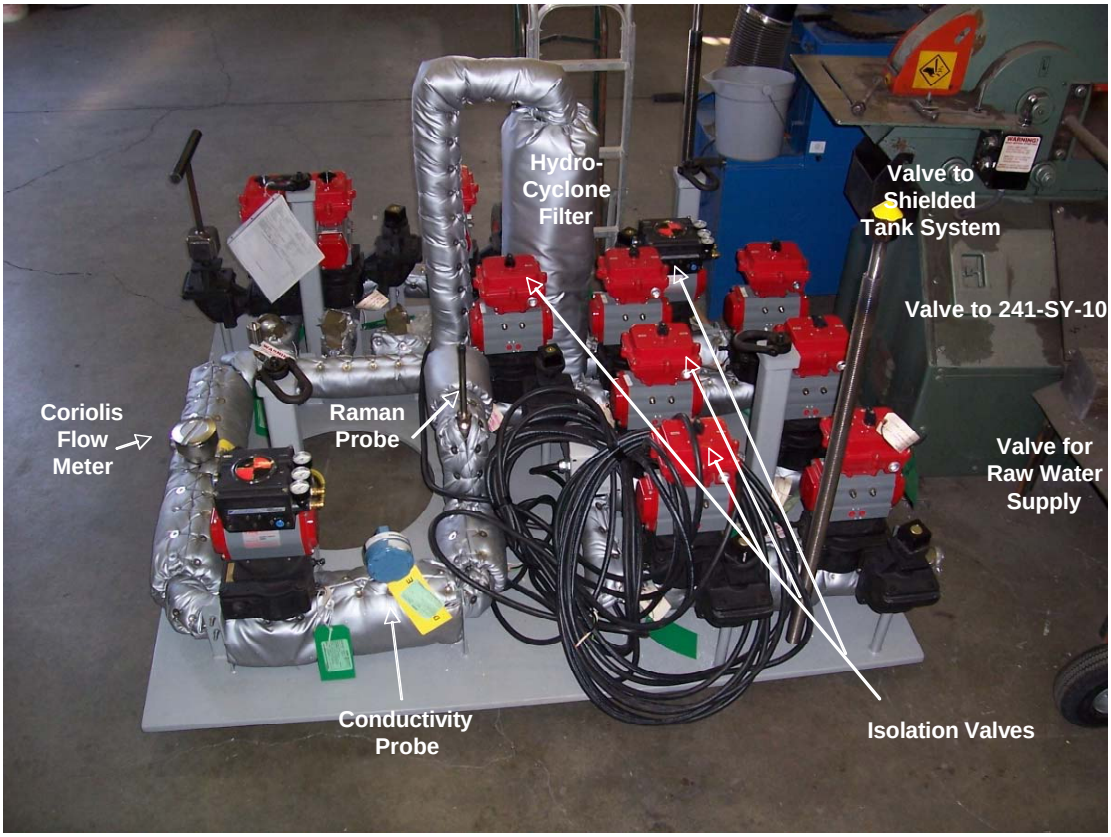


Figure 4. Assembled Process Monitoring System Accepted for Deployment.

REFERENCES:

[1] Bunker, B.; Virden, J.; Kuhn, B.; Quinn, R. in *Encyclopedia of Energy Technology and the Environment*, Wiley, 1995; pp. 2023–2032.
[2] *Nuclear Site Remediation: First Accomplishments of the Environmental Science Program*, ACS Symposium Series, Vol. 778, P. G. Eller and W. R. Heineman, Eds., American Chemical Society, Washington, DC, 2001.
[3] Gephart, R. E.; Lundgren, R. E. 1995. "*Hanford Tank Clean up: A Guide to Understanding the Technical Issues*," Report PNL-10773, Pacific Northwest National Laboratory, Richland, WA, U.S.A.
[4] *Nuclear Wastes: Technologies for Separations and Transmutation*, National Research Council, National Academy Press, Washington, D.C., 1996.
[5] *Science and Technology for Disposal of Radioactive Tank Wastes*, W. W. Schultz and N. J. Lombardo, Eds., Plenum Press, New York, 1998.
[6] Nakamoto, K.; 1997. "Infrared and Raman Spectra of Inorganic and Coordination Compounds" Parts A and B. John Wiley and Sons, New York, NY.
[7] Lin-Vien, D, NB Colthup, WG Fateley, and JG Grasselli. 1991. "Infrared and Raman Characteristic Frequencies of Organic Molecules". Academic Press, INC, San Diego, CA.
[8] Hobbs, DT. 2002. Laboratory Testing of a Raman-Based Measurement System for the Determination of Important Corrosion Species in Alkaline Salt Solutions, WSRC-TR-2001-00129, Savannah River Technology Center (SRTC).
[9] Bryan, SA, TG Levitskaia, and SI Sinkov. 2004. "Chemical and Radiochemical Stability of the Process Monitor System used in the Raman Probe System Project" Project # 47187; Pacific Northwest National Laboratory, Richland, Washington.
[10] Herting DL. December 10, 2004. *Preparation of Simulated Waste Samples for EM-21 Project*. Letter Report CH2M-0403873, CH2M HILL Hanford Group, Inc., Richland, Washington.
[11] Long G.L., Winefordner J.D., *Anal. Chem.* Volume: 55(7), (1983), pp. 712A – 724A.