ILM-RPT-002, Rev. 0
PNNL-28546 Rev. 0

AP-105 Melter Off-gas Condensate and EMF Evaporator Concentrate Raman and LIBS Qualitative Evaluation for the Use of In-Line Monitoring

March 2019

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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Executive Summary

Pacific Northwest National Laboratory (PNNL) was tasked with performing Raman spectroscopy and laser induced breakdown spectroscopy (LIBS) testing on the melter off-gas condensate generated during low-activity waste process testing of a sample from Hanford Site tank AP-105 and/or evaporate from evaporation of the condensate. This was a proof-of-principle demonstration that Raman spectroscopy and LIBS have the potential to be used as analytical tools for in-line process analysis of key aqueous phase analytes in radioactive process streams associated with the Hanford Tank Waste Treatment and Immobilization Plant.

The work completed under this project complements work completed for Washington River Protection Solutions, LLC (WRPS) with the development of in-line monitoring systems to characterize and quantify constituents of tank waste following Cs removal and filtration. The WRPS work is currently limited to Raman sensors and uses chemometric models for quantification of several anionic species in the sample system. Note that while this approach can be applied to off-gas condensate streams, new chemometric models are needed to accurately quantify analytes under off-gas condensate conditions.

The work completed under this project makes timely use of available samples and equipment at PNNL. The project used the opportunity to collect off-gas samples from planned AP-105 processing work and included the direct condensate and the evaporate from the Direct Feed Low-Activity Waste Radioactive Waste Test Platform. Samples were characterized by instruments already in place at PNNL, including a Raman spectrometer optimized for in-line monitoring of flowing and stationary samples as well as a LIBS instrument, which was optimized for static liquid droplet analysis. The ultimate objective was to determine if these techniques could be used to qualitatively characterize analytes present in the off-gas samples.

The off-gas condensate solutions from the submerged bed scrubber contain volatile species from melter operations. The analytical needs of the condensate have been established,[1] and include measurement of nitrate (NO_3^-), nitrite (NO_2^-), sulfur (as sulfate, SO_4^{2-}), chloride (Cl^-), fluoride (F^-), pH, and ^{137}Cs. In addition to these specified analytes, it is expected that chromate (CrO_4^{2-}), carbonate (CO_3^{2-}), and potentially phosphate (PO_4^{3-}) may be present in the condensate.

The testing confirmed that Raman as an in-line monitoring system was able to qualitatively observe NO_3^-, NO_2^-, aluminum (as aluminate, $Al(OH)_4^-$), SO_4^{2-}, CrO_4^{2-}, CO_3^{2-}, and PO_4^{3-} in the AP-105 melter feed evaporator condensate samples. The testing also confirmed LIBS as a potentially useful technique for in-line monitoring, able to qualitatively detect Na, N, Al, and tentatively Cr and Cl in a simulant stock evaporate solution. However, due to the low resolution capabilities of the presently available LIBS unit, testing of actual condensate samples was not attempted.

The next phase of testing should include the following:

1. Investigating alternative LIBS systems that are optimized specifically for the analytes of interest for higher resolution analytical capabilities.

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[1] Poirier MR, AM Howe, FR Miera, ME Stone, CC DiPrete, and ME Farrar. 2017. *WTP Real-Time In-Line Monitoring Program Tasks 4 and 6: Data Quality and Management and Preliminary Analysis Plan*. SRNL-RP-2017-00663, Rev. H, Savannah River National Laboratory, Aiken, SC.

2. Evaluation of quantitative range for Raman and LIBS in-line analytical systems for the observed compounds in Table S.1.
3. Development and quantitative models (Raman) and calibration curves (LIBS) for the accurate measurement of target analytes.
4. Demonstration of real-time quantification of species within off-gas condensate samples.

Table S.1. Summary of observable chemicals.

Compounds Observed	By Raman Spectroscopy	By LIBS Spectroscopy
Aluminate	X	X (as Al)
Nitrate (NO_3^-)	X	X (as N)
Nitrite (NO_2^-)	X	
Sodium (Na^+)		X
Sulfate (SO_4^{2-})	X	
Chloride (Cl^-)		X (as Cl, tentative)
Fluoride (F^-)		
Chromate (CrO_4^{2-})	X	X (as Cr, tentative)
Carbonate (CO_3^{2-})	X	
Phosphate (PO_4^{3-})	X	
pH		

Notes:

- X indicates species that were detected in standards and simulants.
- For details on species detected in off-gas condensate, see Sections 3.0 and 4.0.

Acronyms and Abbreviations

CCD	charge-coupled device
CRV	concentrate receipt vessel
DFLAW	Direct Feed Low-Activity Waste
DOE	U.S. Department of Energy
FEP	fluorinated ethylene propylene
IC	ion chromatography
ICP-OES	inductively coupled plasma-optical emission spectroscopy.
LA-LIBS	laser ablation - LIBS
LIBS	laser induced breakdown spectroscopy
M&TE	measurement and testing equipment
MP-AES	microwave plasma atomic emission spectroscopy
Nd:YAG	neodymium: yttrium aluminum garnet
NQAP	Nuclear Quality Assurance Program
NTU	nephelometric turbidity units
ORP	Office of River Protection
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
SBS	submerged bed scrubber
UHP	ultra high purity
VPH	volume phase holographic
WRPS	Washington River Protection Solutions, LLC
WTP	Hanford Tank Waste Treatment and Immobilization Plant

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1.0 Introduction

Pacific Northwest National Laboratory (PNNL) conducted proof-of-principle demonstrations to determine if Raman spectroscopy and laser induced breakdown spectroscopy (LIBS) have the potential to be used as analytical tools for in-line process analysis of key aqueous phase analytes in radioactive process streams associated with the Hanford Tank Waste Treatment and Immobilization Plant (WTP). The scope of these demonstrations was as follows:

- Raman: Modified existing Raman probe experimental protocol to perform Raman measurement of off-gas condensate solutions (the original off-gas condensate solution and a concentrated solution after boil-down).
- LIBS: The specific scope of the FY18 – FY19 task was for the fabrication of a liquid phase sample container that was used in the LIBS system to calibrate the instrument with aqueous phase standards and then measure key components in various representative liquid radioactive waste samples.

This work was conducted for the U.S. Department of Energy (DOE) Office of River Protection (ORP) as part of Task 3 for Interentity Work Order M0ORV00149.

This work was conducted under the *ORP WTP Process Optimization Strategic Initiative: formally Real-Time In-Line Monitoring Program Project Management Plan* (ILM-PMP-NQAP, Rev. 3), with testing being directed by the *Proof-of-Principal Demonstration of Raman and LIBS for In-Line Analysis of Key Aqueous Phase Analytes in Radioactive Process Streams* (Test Plan ILM-TP-001, Rev. 0, approved July 24, 2018).

1.1 Background

The *WTP Real-Time In-Line Monitoring Program Tasks 4 and 6: Data Quality and Management and Preliminary Analysis Plan,* SRNL-RP-2017-00663, Rev. H (Poirier et al. 2017), identified the potential benefits of using in-line monitoring instruments in the Direct Feed Low-Activity Waste (DFLAW) treatment process.

> *It is expected that the proposed in-line monitoring instruments will continuously sample and be monitored via control charts using standard deviations of the measured parameters. Continuous operation of sample loops would avoid issues with solids settling or drying of slurries in the line that could occur during idle periods. In addition, continuous operations would allow for any equipment issues or process upsets to be identified quickly*.

Poirier et al. (2017) discuss the potential to use Raman and LIBS in-line monitoring for sampling streams related to the concentrate receipt vessel (CRV), the submerged bed scrubber (SBS) condensate vessel, the evaporator feed vessel, and the evaporator concentrate vessel. A summary of DFLAW analytical needs is shown in Table 1. The highlights of the discussions are below:

> *Molecular analyses can be performed using either ion chromatography (IC) or Raman spectroscopy. In general, the IC is significantly more sensitive but requires substantially more development to accommodate sample preparation and measurement control issues as well as facilitate instrument maintenance and replacement of consumables. Raman, on the other hand, requires no sample preparation or consumables. Therefore,*

> *the development costs as well as the operation and maintenance will be much lower. Based on previous testing with simple simulants, it is reasonable to expect that Raman can make the nitrate, nitrate, sulfate, aluminate, and hydroxide measurements in the range specified for DFLAW feed.*
>
> *Elemental analysis can be performed with ICP-OES, MP-AES, or LIBS. ICP-OES is the most sensitive of the three instruments, the most expensive, and the most complex to operate and maintain. Of all the instruments proposed, development of ICP-OES for in-line remote-monitoring presents the most risk. MP-AES operates on the same principles as ICP-OES. It is an order of magnitude less sensitive than ICP-OES but still more than adequate for control of the DFLAW process. It is also much less complex to operate and maintain. It is advertised by the manufacturer as appropriate for unattended operation in a laboratory setting. LIBS is substantially less sensitive than the other two methods. In addition, most of the research indicates LIBS is most suitable for relative instead of absolute quantitative measurement. However, even if the measurements made are only relative to each other, it could still be a valuable tool in verifying material balances. As with Raman, the most valuable attribute of LIBS is that it does not require sample preparation or consumables. That, in concert with the fact that it requires a much smaller capital investment, makes it attractive over the instrument's lifecycle*.

This helped determine that Raman and LIBS in-line analytical methods needed to proceed to the proof-of-principle testing phase that was conducted and is detailed in this report.

Table 1. Poirier et al. (2017) summary of DFLAW analytical needs.

Analyte / Vessel	Feed Preparation			Melter Off-gas	Effluent Management Facility				
	CRV	Melter Feed Preparation Vessel	Melter Feed Vessel	SBS Condensate Collection	Low Point Drain Vessel	Evaporator Feed Vessel	Evaporator	Overheads Sampling Vessel	Evaporator Concentrate Vessel
Nitrate (NO_3)	X			X	X	X			X
Nitrite (NO_2)	X			X	X	X			X
Sulfate (SO_4)	X			X	X	X			X
Ammonia (NH_3)								X	
Aluminum (Al)	X	X							
Boron (B)		X							
Calcium (Ca)		X							
Chlorine (Cl)	X			X	X	X	X		X
Fluorine (F)	X			X	X	X			X
Iron (Fe)		X							
Lithium (Li)		X							
Manganese (Mg)		X							
Potassium (K)	X								
Silicon (Si)		X							
Sodium (Na)	X	X							
Titanium (Ti)		X							
Zinc (Zn)		X							
Zirconium (Zr)		X							
pH	X	X		X	X	X			X
^{137}Cs	X	X		X	X	X	X	X	X
Rheology		X	X						

Key to Color Code

Molecular Analysis
Elemental Analysis
pH
Radiochemical Analysis
Rheology

1.2 Test Objectives

The overall objectives of the Raman on-line monitoring demonstration task are to:

- Receive AP-105 SBS condensate samples; original dilute SBS condensate sample and the SBS sample after concentration via boil-down.
- Modify existing Raman probe experimental protocol to perform Raman measurement of off-gas condensate solutions.

The overall objectives of the LIBS on-line monitoring demonstration task are to:

- Fabricate a liquid phase sample container that can be manipulated within the LIBS system to act as primary and secondary containment for liquid radioactive samples.
- Demonstrate that the LIBS instrumentation can be calibrated for a set of analytes of interest over a range of useful aqueous phase concentrations.
- Demonstrate qualitative and, if possible, quantitative analysis of analytes of interest in a radioactive sample of melter off-gas condensate and a sample of off-gas condensate that has been concentrated by evaporation.

1.3 Success Criteria

The following proposed success criteria were included in the test plan originally outlining this work.

The Raman analysis and testing will be successful if:

- A sample of AP-105 SBS condensate samples—original dilute SBS condensate sample and the SBS sample after concentration via boil-down—is received for testing.
- The existing Raman probe and experimental protocol to perform Raman measurement of off-gas condensate solutions is modified for use with the SBS condensate samples.
- The original SBS off-gas condensate solution, and concentrated solution after boil-down, are successfully measured by the Raman technique.

The LIBS analysis and testing will be deemed successful if:

- A sampling apparatus is fabricated that can effectively contain radioactive liquid samples.
- The instrument is calibrated for the key constituents of interest and an off-gas condensate waste simulant is quantitatively characterized.
- Quantitative analyses are completed for a number of key constituents in the melter off-gas condensate waste and the evaporated off-gas condensate waste.

While qualitative and quantitative LIBS analysis of the samples was targeted, the lack of equipment optimization of the presently available J-100 LIBS unit for the analytes of interest in solution did not allow for successful application of this technique as originally planned.

1.4 Quality Assurance

This scope was conducted under DOE-ORP Interentity Work Order # M0ORV00140 and the PNNL Nuclear Quality Assurance Program (NQAP). Details of the quality assurance (QA) implementation are described in the *ORP WTP Process Optimization Strategic Initiative: formally Real-Time In-Line Monitoring Program Project Management Plan* (ILM-PMP-NQAP, Rev. 3), with testing being directed by the *Proof-of-Principal Demonstration of Raman and LIBS for In-Line Analysis of Key Aqueous Phase Analytes in Radioactive Process Streams* (Test Plan ILM-TP-001, Rev. 0, approved July 24, 2018).

The NQAP implements the requirements of DOE Order 414.1D, *Quality Assurance,* and 10 CFR 830 Subpart A, *Quality Assurance Requirements*. The NQAP uses ASME NQA-1-2012, *Quality*

Assurance Requirements for Nuclear Facility Applications, as its consensus standard and NQA-1-2012, Subpart 4.2.1 as the basis for its graded approach to quality.

The project adopted NQAP-2012, *Nuclear Quality Assurance Program (NQAP) Manual*, with its applicable implementing procedures as the project QA program. NQAP-2012 meets the requirements of ASME NQA-1-2012 and DOE Order 414.1D and is consistent with delivering the QA requirements defined by ASME NQA-1-2008 and ASME NQA-1a-2009. A graded approach to quality implementation is provided in NQAP-2012 Attachment B, *Documenting Project-specific QA Graded Approach*.

Two quality grading levels are defined by the NQAP. Although the future work to develop the inputs discussed in this plan will be graded as “Applied Research,” the scope of this testing and this report have been graded as and were implemented to the “Basic Research” Technology Level.

Testing deviations included the following:

- None

2.0 Test Systems and Methodologies

Both Raman and LIBS were used to characterize samples or simulants of the AP-105 evaporate condensate. This section describes the equipment used and the methods employed to measure and characterize the samples. These proof-of-principle measurements used commercial-off-the-shelf instruments that are currently maintained at PNNL.

2.1 Raman System

Spectral measurements were obtained using a Raman probe (beam diameter 125 μm) with a high-throughput volume phase holographic (VPH) grating Raman spectrograph (Spectra Solutions, Inc.) fiber optic spectrometer equipped with a diode-pumped solid state laser (671 nm) that delivers 250 mW of power at the full power setting, which was used during testing. A custom transmission VPH grating spectrograph with a thermoelectric-cooled charged coupled detector was used to record the Raman signal from the Raman probe over the spectral range of 200 to 4000 cm^{-1} at a resolution of ~ 6 cm^{-1}.

Custom-designed flow cells are used to interrogate flowing or stationary streams/samples. These can be designed to fit a variety of configurations and system requirements. For this demonstration, a static cell consisting of a quartz cuvette placed in-line to the flowing system was used. This was held in a cell holder that also held the Raman probe. The cell holder is also designed to hold a quartz flow cell that can be removed without disrupting system flow, so reference standards can be inserted at any time to confirm instrument performance.

Schematics of the cell holder and flow cell design used for analysis of waste solutions are depicted in Figure 1A and Figure 1B, respectively. Photographs of the Raman flow cell holder with flow cell and stationary cuvette in place are shown in Figure 1C and Figure 1D, respectively. Figure 2 is a photo of the entire Raman system, including the rack-mountable unit containing the light source and detector. While the flow configuration was not used for this work, the figures here depict how future in-line monitoring systems could be set up to monitor flow or even batch processes.

Table 2 provides a list of measurement and test equipment (M&TE) used during Raman testing.

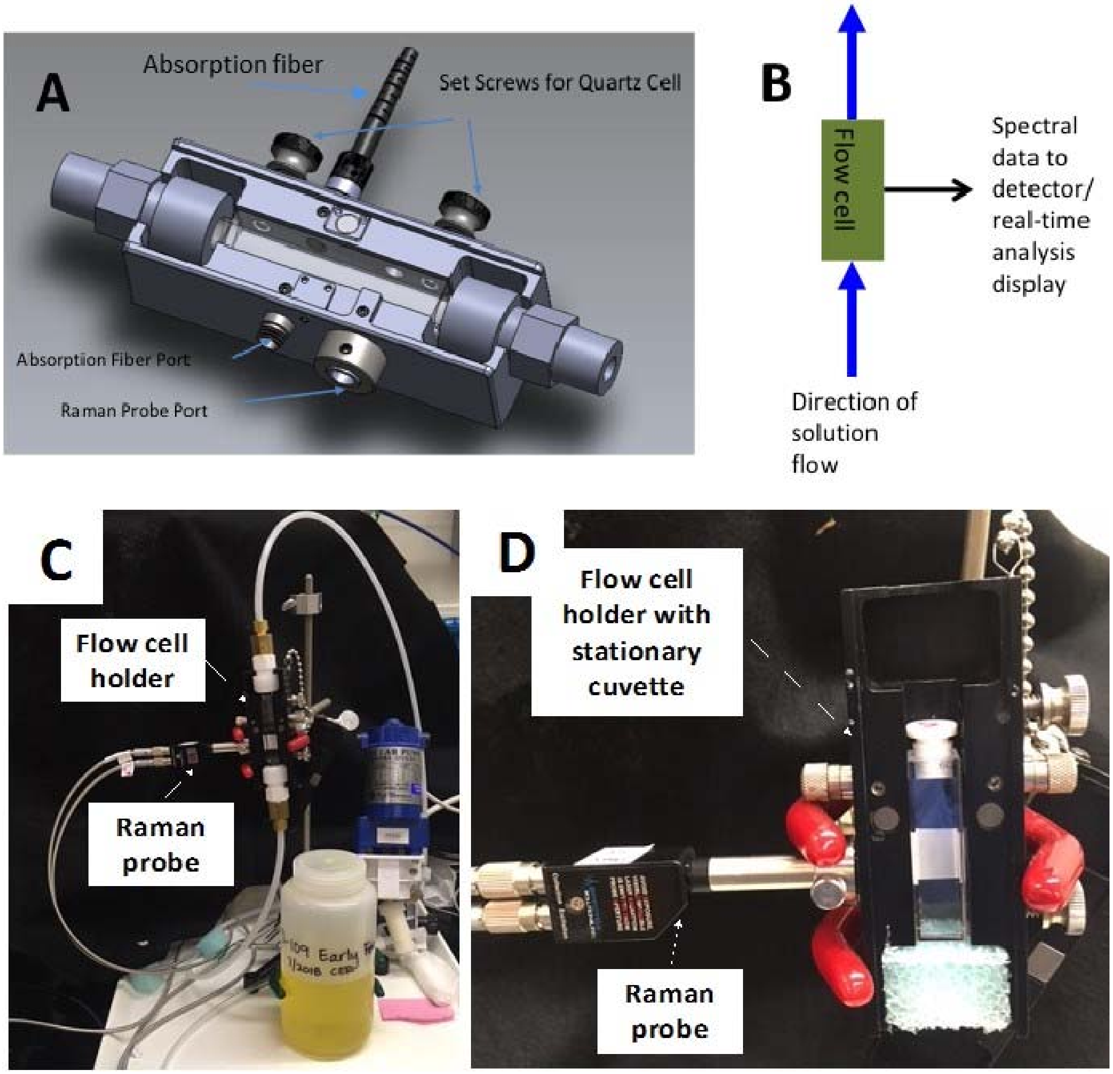

Figure 1. A) schematic of cell holder; B) schematic of how flow cell can be integrated to allow for measurement of flowing stream; C) photo of the Raman flow cell holder with flow cell; D) stationary cuvette in place.

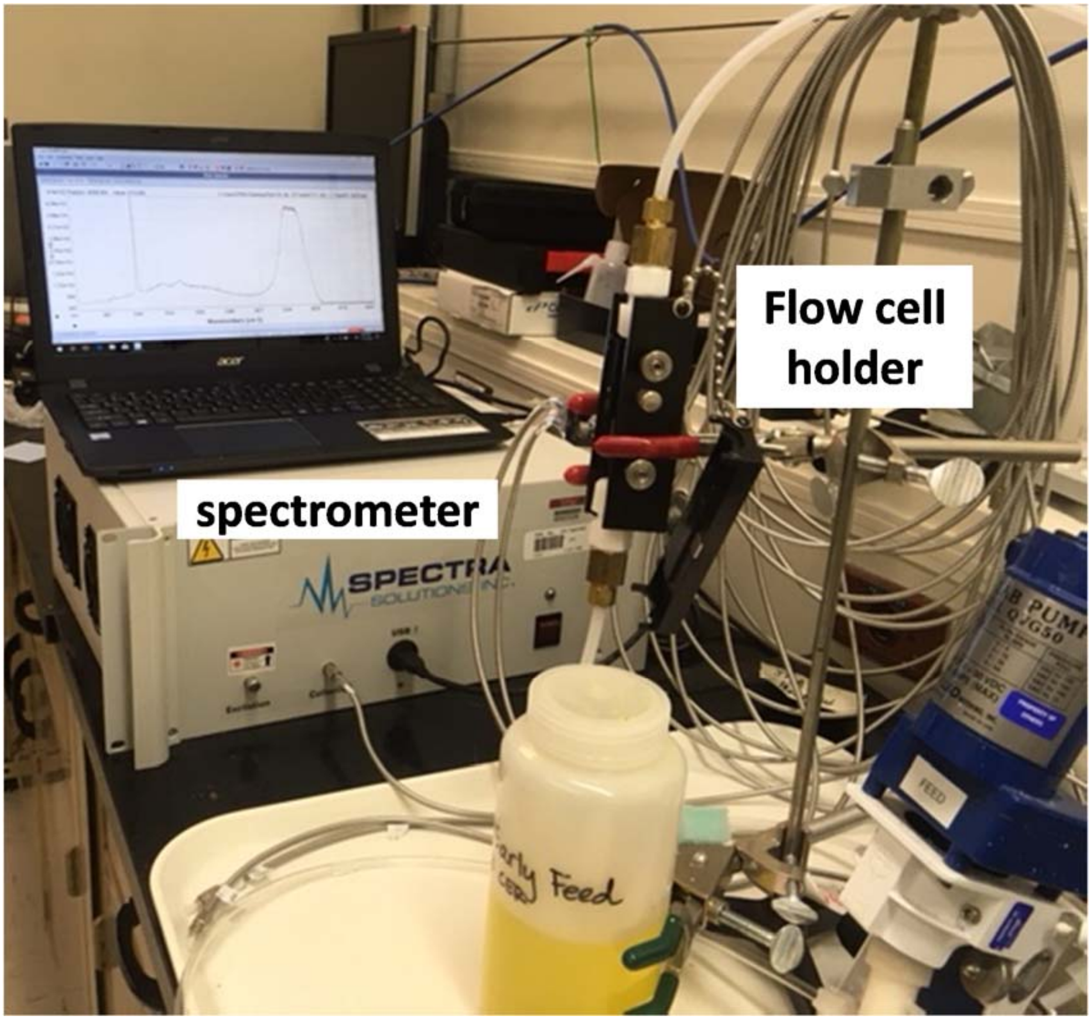

Figure 2. Photo of the Raman system, including the rack-mountable unit containing light source and detector.

Table 2. Raman M&TE used

M&TE Description	Serial #	Property ID
Raman Spectrometer System	00001	RAMS 671-1

2.2 Raman Methodology

The AP-105 samples were provided from the demonstration test of the DFLAW Radioactive Waste Test Platform using waste retrieved from Hanford storage tank AP-105 (Dixon et. al. 2018) and included the direct condensate as well as the condensate evaporate (condensate-to-evaporate ratio 10.7 g g^{-1}, pH adjusted to 12.0). Approximately 10 mL of each sample was obtained. Because this volume is too small to sustain a flow loop, samples were measured by stationary grab sample approach within the cell holder (Figure 1D). Samples were handled and loaded into the stationary cuvette within the radiological fumehood and then loaded into the cell holder for Raman measurement. Collection times of both 1 and 2 seconds were used. This allowed for direct comparisons to the spectra of standards (collected at 1 second) and examples of how signal to noise will change with increasing collection time. Fifty total spectra were collected of all samples and averaged by 5 (example of typical processing used for on-line, real-time monitoring) and by 50 (to generate spectra for qualitative comparisons). The concentrated condensate sample (after evaporation) contained solids that settled to the bottom of the vial/cuvette. These samples were measured after agitating the sample to suspend the particles in solution and after allowing the particles to settle. Pictures of the off-gas condensate samples before and after agitation are presented in Figure 3.

Raman spectra of condensate samples were compared to spectra of standards to allow for identification of Raman signatures. Standards included solutions of several species anticipated within Hanford tank waste that are Raman active or known potential interferents. Raman active species included sodium salts of NO_3^-, NO_2^-, CO_3^{2-}, CrO_4^{2-}, PO_4^{2-}, SO_4^{2-}, OH^-, $Al(OH)_4^-$, and oxalate. Non-Raman-active species included Na^+, K^+, and Cl^-. Raman active species have distinct and unique fingerprints that can be used to identify the analytes while non-active species might have indirect effects on response (e.g., altering the shape of the water band). Raman spectra of condensate samples were compared to standards to qualitatively determine composition of the samples.

While quantitative determinations were not made for this stage of the project, this capability could be developed by expanding the standards training set to fully capture sample/process complexity and building chemometric models. Furthermore, the addition of models would enable better resolution of Raman band interferences than simple visual comparisons as was completed for this stage of project work. This is discussed further under the conclusions section. This project builds on previous on-line monitoring experience and expands the application of Raman on-line monitoring and chemometric modeling to Hanford waste supernate (Bryan et al. 2008) as well as other fuel reprocessing solutions (Bryan et al. 2011; Lines et al. 2018; Nelson et al. 2018).

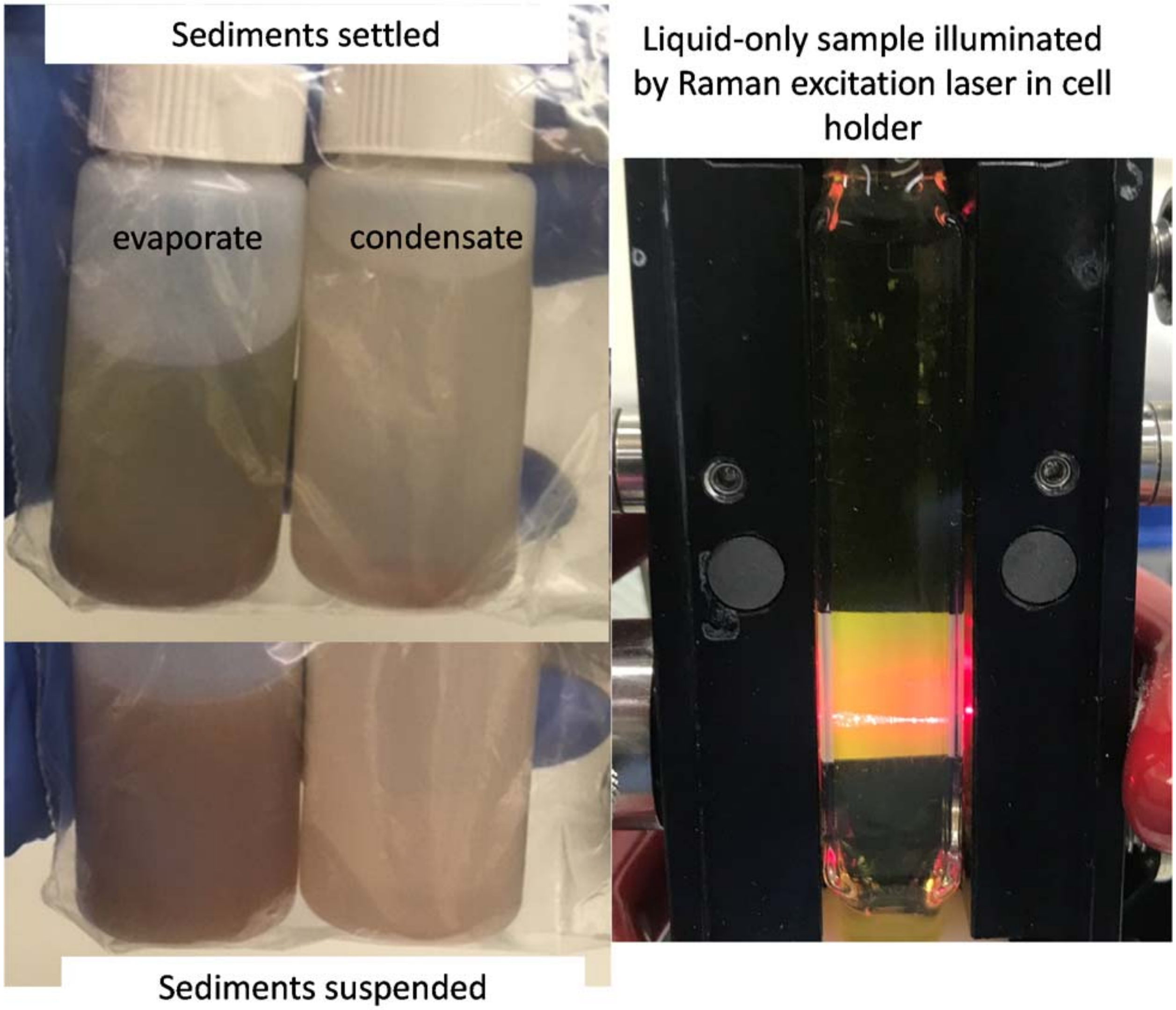

Figure 3. Photos of off-gas condensate and evaporate samples before and after agitation of suspended precipitates (left) and liquid-only sample illuminated by Raman excitation laser (right).

2.3 LIBS System

The LIBS is applied as an analytical technique by which a laser pulse is used to create a plasma cloud that can reach a temperature of 200,000 K. The resulting plasma causes complete ionization of atoms in the ablated material, resulting in emission of photons from elements present. The intensity of an element's photon emission lines is related to its concentration. Multiple standards that closely resemble the unknown material are used to calibrate photon emission lines so their intensities can be quantified. The LIBS system used in this study was an Applied Spectra J-100, tandem laser ablation - LIBS (LA-LIBS). This instrument uses a 266-nm laser [fourth harmonic of a 1064-nm neodymium:yttrium aluminum garnet (Nd:YAG) primary laser] and a charge-coupled device (CCD) system for spectroscopic analysis. Figure 4 shows the LA-LIBS system used in this study. A specially designed containment system and sample holder for analysis of aqueous radioactive samples was designed and fabricated (Figure 5).

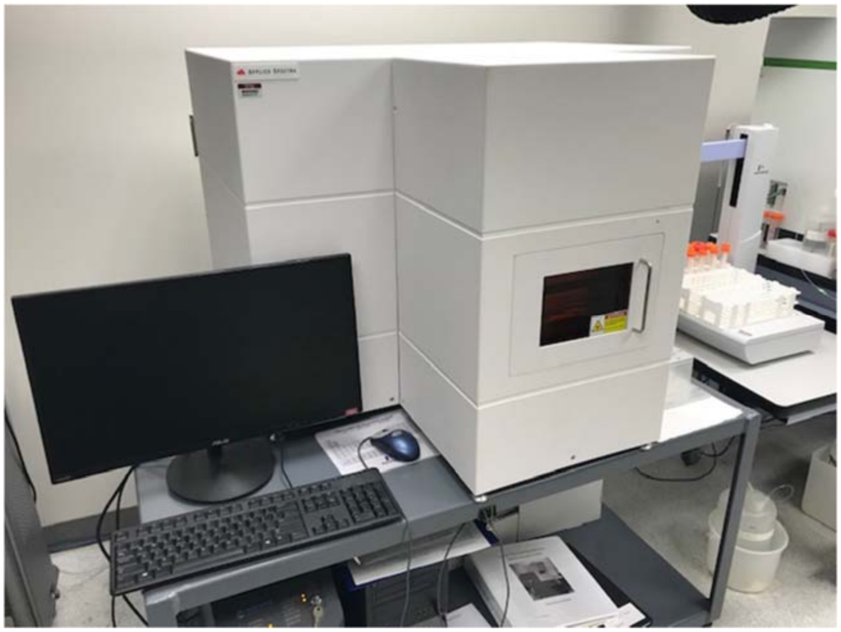

Figure 4. Photo of the Applied Spectra J-100, tandem LA-LIBS system.

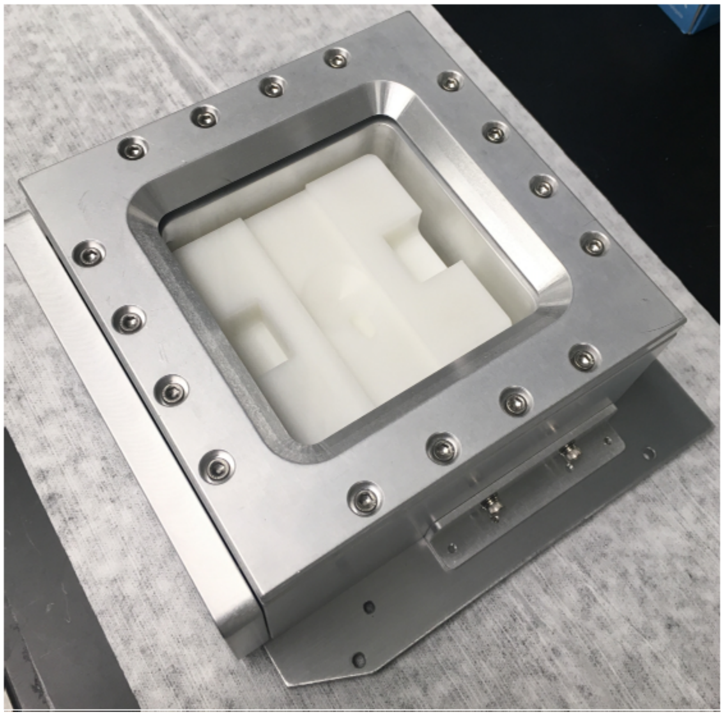

Figure 5. Photo of the specially designed sealed rad sample chamber and sample holder for the LIBS system.

Table 3 provides a list of M&TE equipment used during LIBS testing.

Table 3. LIBS M&TE used.

M&TE Description	Serial #	Property ID
Applied Spectra J-100, LA-LIBS System	S/N 100904	WD80473
Mettler Balance	1118410163	1118410163
Sartorius Balance	28550237	28550237
Sartorius Balance	28502513	28502513
Eppendorf Pipette (0.5-5 µL)	H66562B	
Eppendorf Pipette (1-10 µL)	H67034B	
Eppendorf Pipette (20-200 µL)	K44631F	
Eppendorf Pipette (100-1000 µL)	L22516B	
Eppendorf Pipette (100-1000 µL)	I27250D	

2.4 LIBS Methodology

2.4.1 Off-gas condensate simulant sample

A major goal of this work is to demonstrate the analysis of a radioactive waste stream sample that is representative of a waste stream from DFLAW. One such sample is the off-gas condensate from a demonstration test of the DFLAW Radioactive Waste Test Platform that was derived from Hanford storage tank AP-105 (Cantrell et al. 2018). In addition, another sample was produced by evaporating the off-gas condensate by a factor of 11.7 and then adjusting the pH to 12.0. Note that in the actual process, the pH of the condensate would be adjusted first and then evaporated. Based on the analysis of the off-gas condensate (Cantrell et al. 2018), a recipe was developed for a non-radioactive simulant stock solution that is 10 times the approximate composition of off-gas condensate as determined in Cantrell et al. (2018), containing the major components of interest: Na, Al, Cr, P, NO_3^-, SO_4^{2-}, Cl^-, and F^-. This stock solution standard is equivalent to the concentrations expected of the post-evaporation sample.

The measured concentrations of these components in the sample off-gas condensate are shown in Table 4 along with the concentration of a 10x solution, as modeled for the calibration standard stock solution.

Table 4. Concentrations of major chemical components in the off-gas condensate and evaporate solution.

Component	Concentration (mg L^{-1})	Concentration (mole L^{-1})	10x Concentration (mole L^{-1})
Al	36.5	1.35×10^{-3}	1.35×10^{-2}
Cr	11.5	2.21×10^{-4}	2.21×10^{-3}
P	2.5	8.07×10^{-5}	8.07×10^{-4}
SO_4^{2-}	85.7	8.92×10^{-4}	8.92×10^{-3}
Cl^-	937	2.64×10^{-2}	2.64×10^{-1}
F^-	22.7	1.19×10^{-3}	1.19×10^{-2}
Na	1,050	4.57×10^{-2}	4.57×10^{-1}
NO_3^-	17,100	2.76×10^{-1}	2.76

Based on these concentrations, the following recipe was designed to make up a liter of stock solution of simulant evaporate solution containing the elements most important to in-line monitoring (Table 5 and Table 6). No attempt was made to replicate the pH or solids composition of the original off-gas condensate or evaporate. The total stock solution was then diluted to a 1-L final volume with 18.2 MΩ·cm H_2O that had been purged with ultra high purity (UHP) argon for a minimum 10 minutes (to remove atmospheric N_2 from solution). Solubility of N_2 in pure water at 20°C and one bar is approximately 20 mg L^{-1}. For air, the solubility is approximately 16 mg L^{-1}, or 1.1×10^{-3} mol L^{-1}.

Table 5. Recipe for 10x concentrated off-gas condensate (evaporate) simulant stock solution.

Component	Formula Weight (g $mole^{-1}$)	Weight (g)
$NaAlO_2 \cdot xH_2O$	81.97	1.107
$Na_2Cr_2O_7 \cdot 2H_2O$	298.05	0.3293
$Na_3PO_4 \cdot 12H_2O$	380.12	0.3068
Na_2SO_4	142.04	1.267
NaCl	58.44	15.43
NaF	41.99	0.4997
$NaNO_3$	84.99T	12.33
HNO_3 (70% Optima)	15.8 mol L^{-1}	165.5 mL

Table 6. Recorded dry weights for components of off-gas condensate (evaporate) simulant solution.

Component	Weight (g)
$NaAlO_2 \cdot xH_2O$	1.1138
$Na_2Cr_2O_7 \cdot 2H_2O$	0.3340
$Na_3PO_4 \cdot 12H_2O$	0.3499
Na_2SO_4	1.2834
NaCl	15.4911
NaF	0.5017
$NaNO_3$	12.356

Concentrated (70%) Optima UHP grade HNO_3 was aliquoted to a volume of approximately 165.5 mL. Total mass of UHP HNO_3 used for dilutions was 230.85 g; density of UHP HNO_3 is 1.40 g cm^{-3} (mL). The HNO_3 was then added to 834.52 g of Ar-purged 18.2 MΩ·cm H_2O in a fluorinated ethylene propylene (FEP) 2-L bottle on a stir plate and containing a Teflon®-coated stir bar rotating at a speed of 400 rpm. Each salt chemical component was added to the solution slowly while maintaining a constant stir rate until the solids dissolved entirely; no particulates were noted in the simulant stock solution prior to testing. The pH of the simulant stock solution was not adjusted to match what is expected of the DFLAW waste stream sample; however, the pH of the solution is not expected to impact the recovery of LIBS signal during analysis.

2.4.2 Calibration standards for LIBS

To properly calibrate the LIBS system for quantitative analyses, a series of standard solution dilutions were created from the simulant stock sample (Section 2.4.1). A series of 100-, 50-, 25-, 10-, 5-, and 2-fold dilutions were created and brought up to a total solution volume of 20 mL each using Ar-purged 18.2 MΩ·cm H_2O in 20-mL borosilicate glass scintillation vials (Table 7). A sample of the original stock sample solution was also aliquoted into a glass vial to compare to the total stock stored under refrigeration in the FEP bottle to ascertain any impact of gaseous transfer through the plastic container. All micro pipetters were checked for performance prior to use to ensure accuracy of calibration by confirming the density of 18.2 MΩ·cm H_2O in triplicate.

Table 7. LIBS calibration standard dilutions and total solution masses.

Dilution	Volume Stock (mL)	Volume H_2O (mL)	Total Solution Mass[(a)] (g)
2x	10	10	21.05
5x	4	16	20.41
10x	2	18	20.27
25x	0.8	19.2	20.07
50x	0.4	19.6	20.04
100x	0.2	19.8	19.98

(a) Density of simulant stock solution: 1.101 g ml^{-1}.

In addition to the multi-elemental standard solutions, a series of single element standard dilutions were created from Inorganic Ventures 1000 µg mL^{-1} certified single element standard solutions for Al, Cr(III), P, S, Na, and Cl^-. Single element standards will be used to better constrain the wavelength lines identified during LIBS analysis of the off-gas condensate simulant samples.

3.0 Raman Results

Raman spectra were collected for both condensate samples, pre- and post-evaporation. Results were compared to measured standards to determine the composition of samples. Comparisons clearly indicate the presence of nitrate. There is potential that the spectra indicate the presence of other species (e.g., aluminate or alumina species), but advanced analysis methods are needed to confirm. Advanced analysis methods and tactics for improving resolution between interfering bands are discussed in the conclusions section.

3.1 Raman Test Results

3.1.1 Spectra of condensate samples

The off-gas condensate and evaporate samples were measured at multiple collection times (Figure 6). In the case of the liquid-only samples (precipitates in the condensate sample were allowed to settle and did not interfere with Raman measurement), the signal-to-noise ratios between the 1-second and 2-second integration times were comparable. Band shapes and locations were consistent between the condensate and evaporate samples, with band intensities for the evaporate generally being higher, indicating higher concentrations of species present. Note that the water band (3000 to 3750 cm^{-1}) does change shape between the condensate and evaporate samples. This is likely due to the change in pH and ionic strength of the sample. Furthermore, an increased background is observed in the evaporate sample as a broad hump across the spectral baseline. This is likely due to a couple of factors, including an increase in sample turbidity and the presence of a background analytes that appear to have a fluorescence signature. The turbidity will cause some light scatter, which can reduce overall signal, while the presence of a fluorescing species causes the general broad-hump shape of the baseline.

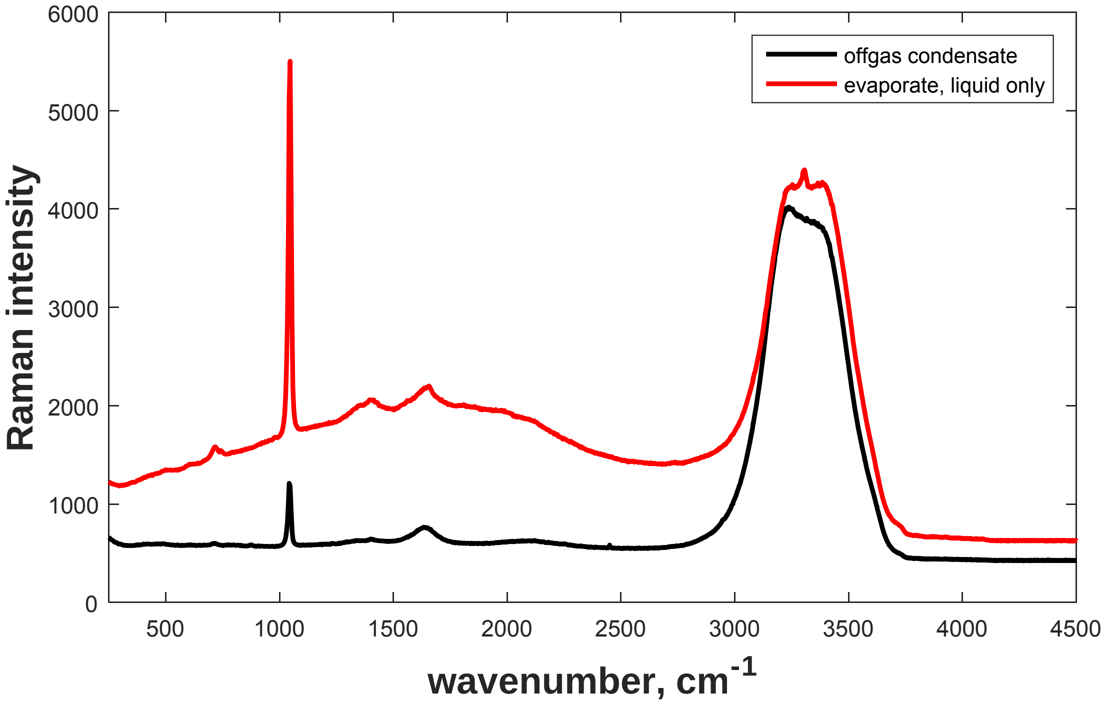

Figure 6. Spectrum of off-gas condensate sample before and after evaporating to reduce volume. Raman spectra collected as stationary grab samples at 1-second integration time. Note the evaporate line is offset by 200 intensity units to allow for easier comparison between samples.

Spectra were also collected of the off-gas condensate evaporate with the precipitates agitated to suspend the particles within the Raman interrogation window. The presence of solid particles in the Raman window causes scattering of the excitation and Raman response photons, and results in a decrease in overall signal intensity. This is consistent with previous studies that indicate increases in turbidity will decrease Raman response (Gasbarro et al. 2013). These studies also indicate that with proper data processing, turbidity effects will not inhibit accurate identification and quantification of target analytes.

Raman spectra of the agitated evaporate sample can be seen in Figure 7. As expected, Raman response is decreased. Interestingly, a change is observed in the background shape (large “hump” centered between ~1000 and 2500 cm^{-1}) that is consistent with the background observed for the liquid-only evaporate sample. The change in background shape does not interfere with qualitative analysis, and with proper processing will have minimal effects on quantitative processing.

Key response bands observed in the liquid-only sample are also observed with the solid present in the Raman window, though signal-to-noise is less than ideal for the solid-containing sample. While not specifically quantified for this project, previous work indicates significantly turbid solutions (up to 1000 NTU) can still be successfully monitored with Raman spectroscopy. Additionally, new advances in probe technology such as probes with built-in attenuated total reflectance capabilities may significantly increase the working range of Raman probes into higher turbidities.

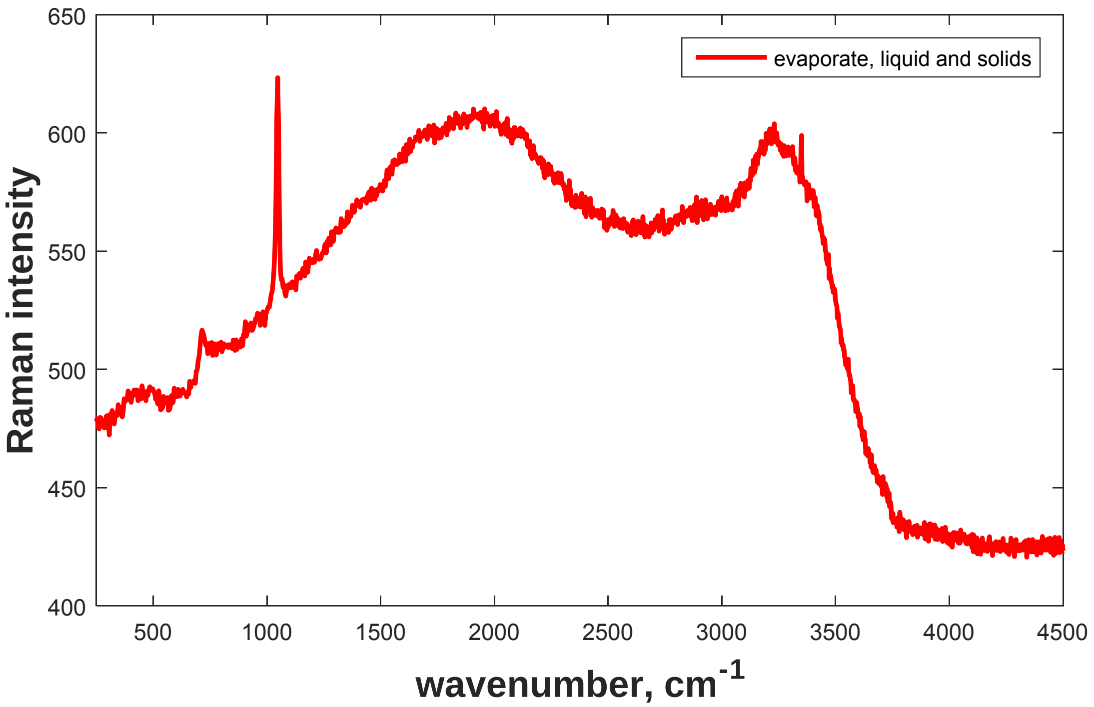

Figure 7. Spectrum of off-gas condensate sample after evaporating to reduce volume, and agitating to suspend precipitates within Raman interrogation window. Raman spectra collected as stationary grab samples at 1-second integration time.

3.1.2 Comparisons to standards

The off-gas condensate spectra from Figure 6 were compared to the standards to qualitatively determine composition of the condensate samples before and after evaporation to reduce condensate volume. Results can be seen in Figure 8. The nitrate bands are clear in both off-gas condensate samples (major band at 1047 cm^{-1}, minor bands at 719 cm^{-1} and 1403 cm^{-1}), with concentration noticeably increased in the sample after evaporation. The water bands (O-H stretching ~3000 to 3800 cm^{-1}, and O-H bending modes at ~1640 cm^{-1}) also indicate a clear change in ionic strength and pH after evaporation. Smaller bands appear to align with aluminate signals at 621 cm^{-1}, though band overlap makes it difficult to conclusively identify the presence of those species. The qualitative comparisons used here are simple overlap approaches to compare sample spectra to standards. Using advanced approaches may enable improved resolution and distinction between the species exhibiting band overlap. This is discussed further in the conclusions section.[1]

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[1] While not covered here, future work can include evaluation of Raman capability to identify and quantify the presence of ammonia within the sample stream.

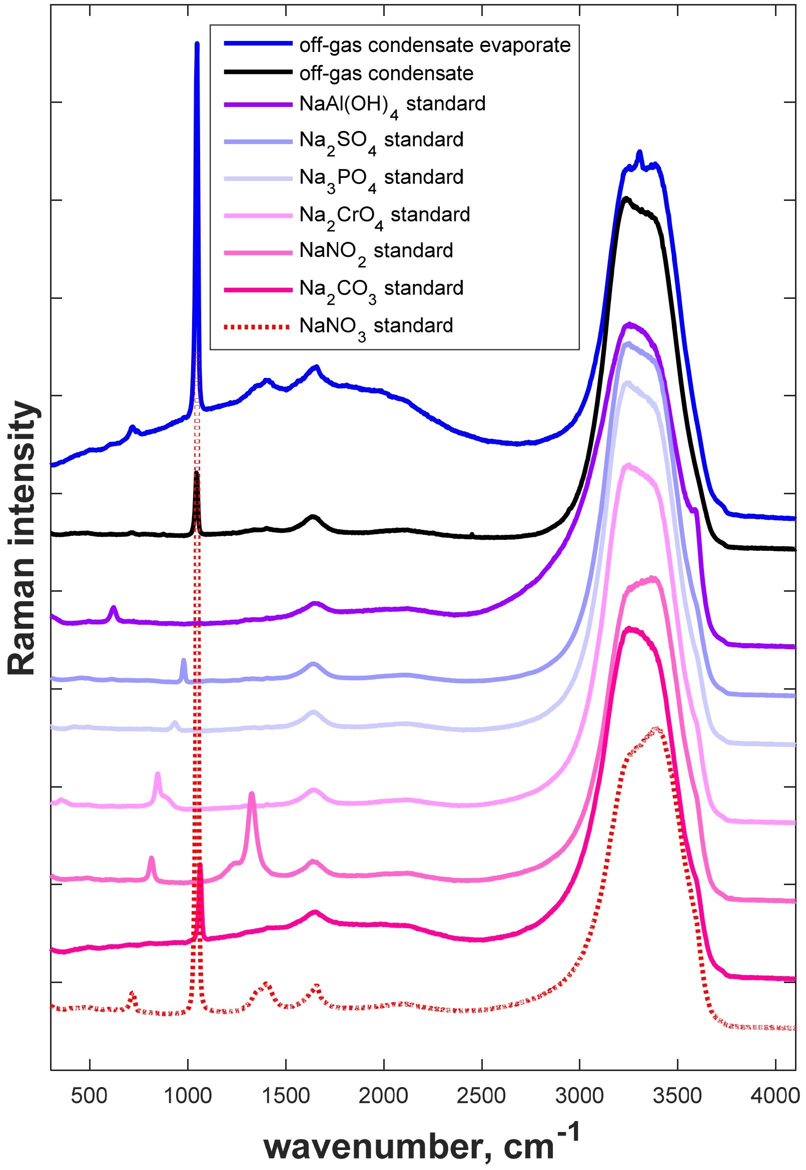

Figure 8. Overlap of standards to condensate samples before and after evaporation.

The spectra of the evaporate samples after agitation (to suspend precipitates within the Raman interrogation window) are not included in Figure 8. Bands displayed in this spectrum (Figure 7) are the same as those observed in the unagitated samples (Figure 6). Qualitative identification of analytes is consistent between the pre- and post-agitation spectra.

Overall, spectra conclusively demonstrate nitrate is present in the off-gas condensate, where the band can be clearly seen both before and after evaporation. Furthermore, the nitrate band clearly can be used to identify the presence of the species even when precipitates are present to interfere with optimum Raman response. Spectra suggest that other species, such as aluminate, may also be present, but due to band overlap this is currently difficult to confirm. Future work in automating and advancing spectral analysis will provide an avenue for accurate identification of species in the presence of interfering bands.

4.0 LIBS Results

LIBS spectra were collected for the simulant stock off-gas condensate (evaporate) solution as well as a 2-fold dilution of the simulant solution. Results were compared to catalogued line libraries to determine the composition of detectable analytes in solution. Results clearly indicate the presence of Na, N, O, and Al, with the remote possibility of Cr and Cl as well. However, resolvability of other analytes in the simulant evaporate solution requires advanced analytical methods and modifications of instrumentation to better resolve detection limits. Advanced analysis methods and equipment modifications for improving resolution are discussed in the conclusions section.

4.1 LIBS Test Results

4.1.1 LIBS analysis of simulant stock standard solution

The simulant stock standard evaporate solution, as well as a 2-fold dilution of the stock solution, was loaded into the standard sample chamber (equipped with a 2-mm quartz glass window) as a 0.2-μL droplet atop a parafilm-covered glass slide and ablated with a single 266-nm laser pulse at 100% power and a spectrometer delay of 100 ns. When compared to a catalogue line library, the spectra demonstrate the presence of numerous elemental analytes in solution, with a notable non-linear decrease in sensitivity between the stock solution and the 2-fold dilution of the simulant evaporate sample (Figure 9). Conclusively-identified elements in solution included Na, N, O, and Al, with the possibility of Cr and Cl also present. Sodium and nitrogen were the only potentially quantifiable peaks. A significant contribution of background noise from the parafilm-coated slide was also present in each spectra (Figure 9), prompting the consideration of modifying the sample holder for future testing (see Section 5.0).

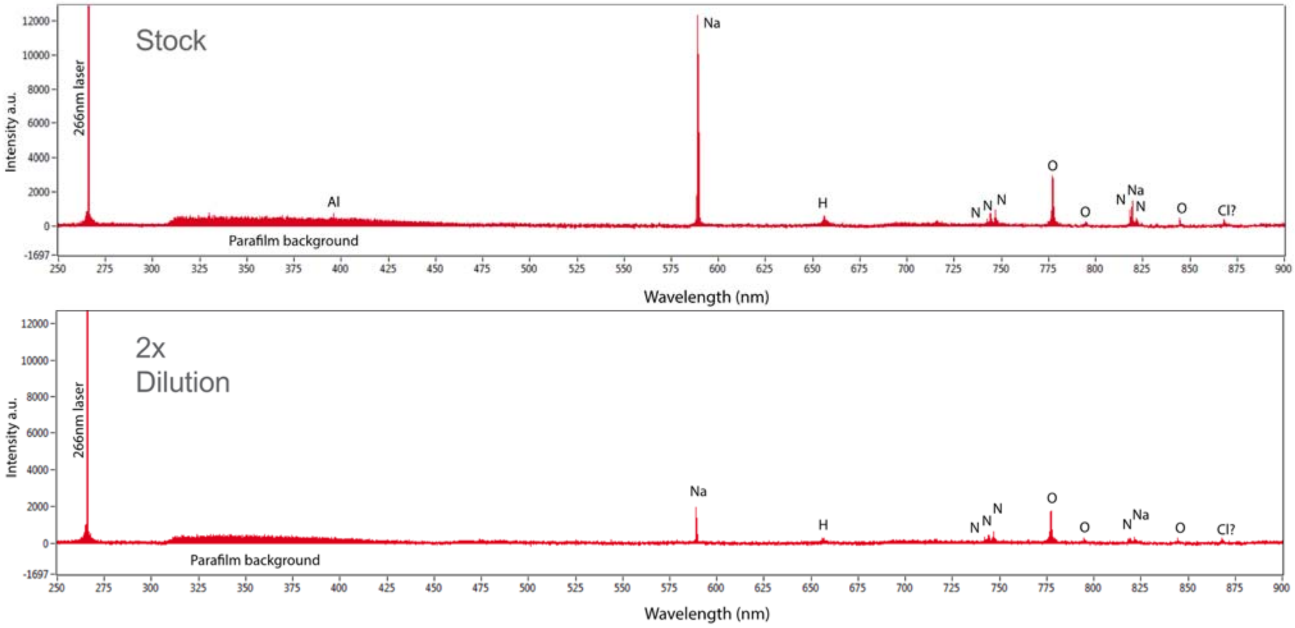

Figure 9. Spectra of identified elemental wavelengths detected during the LIBS analysis of the stock simulant standard solution (top) and the 2-fold dilution of the stock solution (bottom).

The simulant stock standard evaporate solution was also loaded into the custom-designed radioactive sample chamber (equipped with a 6.35-mm quartz glass window), again as a 0.2-µL droplet atop a parafilm-covered glass slide and ablated with a single 266-nm laser pulse at 100% power and a spectrometer delay of 100 ns. Spectral results of the sample ablation as compared to the standard sample chamber are provided in Figure 10. Note the decrease in sensitivity between the standard sample chamber and the radioactive sample chamber, likely attributable to the large difference between the thickness of the quartz glass window. Despite the lower sensitivity, however, the same analytes of interest are detected in both scenarios.

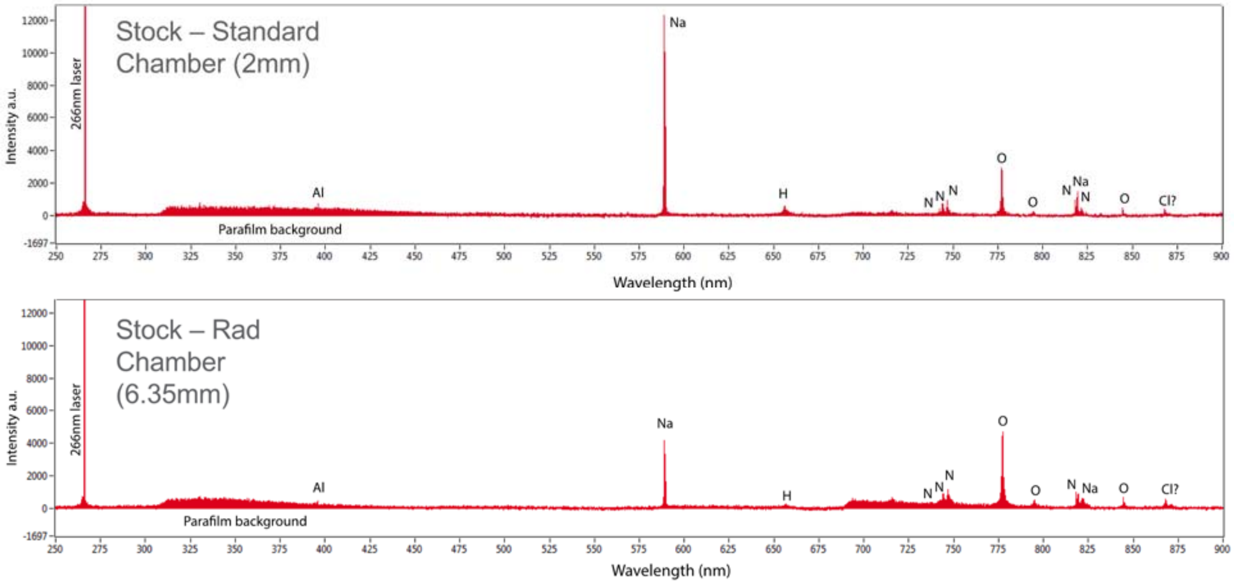

Figure 10. Spectra of identified elemental wavelengths detected during the LIBS analysis of the stock simulant standard solution for the standard sample chamber equipped with a 2-mm quartz glass window (top) and the custom rad sample chamber equipped with a 6.35-mm quartz glass window (bottom).

In addition to the readily identifiable spectra shown in Figure 9 and Figure 10, a re-scale of the x-axis shows the possible presence of Cr in the stock standard solution near the 266-nm laser wavelength (Figure 11), though laser noise in this wavelength range makes it difficult to ascertain the validity of the analyte detection. As a result, quantification of these peaks will not be possible with the current analytical setup of the J-100 LIBS system. Future directions that may better resolve the sensitivity of these and other analytes in solution are further discussed in Section 4.1.2 and Section 5.0.

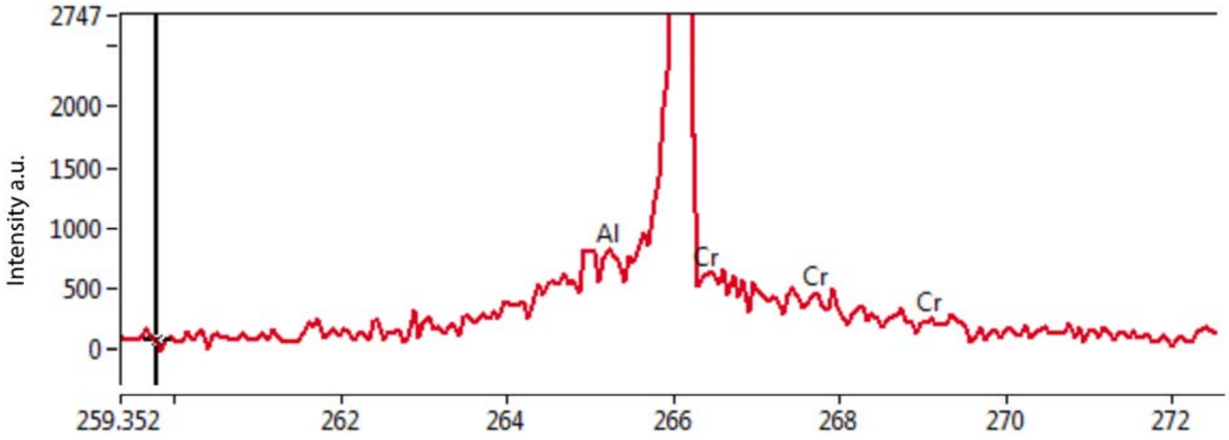

Figure 11. Zoomed-in spectra surrounding the 266-nm laser wavelength. While some Al and Cr identification lines should be located in this area, resolution is obscured by the current LIBS laser noise.

4.1.2 LIBS analysis of AP-105 off-gas condensate and evaporate solutions

The results obtained with the Applied Spectra J-100 LIBS system in its current configuration with the simulant solutions demonstrated that its sensitivity is inadequate to effectively quantify the elements of interest in the radioactive test samples (off-gas condensate and evaporate sample solutions derived from Hanford tank AP-105). As a result of these findings, further analysis of the actual radioactive samples was not attempted.

5.0 Conclusions

PNNL evaluated the potential for Raman and LIBS technologies to be used as in-line monitoring for the DFLAW treatment process. Raman spectroscopy conclusively identified the presence of NO_3^- in the condensate sample before and after evaporation to reduce volume. Spectra indicate other species might be present, specifically Al-bearing species; however, due to band overlap and the simple sample/standard comparison approach, it is difficult to positively identify the presence of these species. Improvement in data analysis approach may improve this resolution in addition to providing routes to quantify species present.

To increase the detection and sensitivity for analytes within condensate samples using the Raman method described in this report, several aspects should be considered. While the method deployed in this testing used a commercial-off-the-shelf system available at PNNL, modifications including laser wavelength, collection integration times, and advanced chemometric analysis of data are potential options with high likelihood to increase the sensitivity of detection for low concentration analytes within the condensate samples.

The LIBS technique conclusively identified the presence of Na, N, O, and Al in the stock standard simulant solution, as well as the presence of Na, N, and O in the 2-fold dilution of the stock solution. The presence of Cr in the stock solution, while tentatively identified, is overwhelmed by noise from the 266-nm laser, making it difficult to conclusively identify this analyte at this time. Additionally, the thickness of the custom rad sample chamber quartz glass window, as well as the current standard CCD detector onboard the J-100 LIBS system in-house, has proven to diminish the detection limits of all other analytes in solution, demonstrating that at this stage, the presently available base J-100 model lacks adequate sensitivity for the desired application. Modifications of the instrumentation and sample chamber/holder are required to increase sensitivity of analyses.

5.1 Recommendations for Additional Testing

Raman results indicate high-quality spectra of the samples can be obtained both before and after evaporation to reduce condensate volume. Current limitations in Raman response stem from the simplistic analysis approach used and the availability of the existing commercial-off-the-shelf system. Additional testing should include the following: 1) development of advanced identification and quantification algorithms; 2) exploration of increasing integration times to enhance signal to noise enabling detection of low concentration analytes; and 3) exploration of changing excitation wavelength (currently red, 671 nm) to a shorter wavelength (green, 532 nm) or lower to enhance the Raman intensity effect for analytes within the sample. These three areas are considered viable enhancements that have high likelihood for increased sensitivity and detection within condensate samples. Furthermore, design of the ports for probes should be considered to determine where in-line monitors could be installed.

The LIBS results indicate the high potential of applying this technique to the in-line monitoring process. However, the low limits of detection currently provided with the base model design of the J-100 LIBS unit suggest that other LIBS systems that are optimized specifically for the particular analytes of interest should be considered for more high resolution analytical results. Fabrication of a flow-through cell capable of being analyzed using a LIBS laboratory setup for both turbulent and laminar flow configurations will also be a focus in the next phase of testing.

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