

Spectroscopic Online Monitoring for Process Control and Safeguarding of Radiochemical Fuel Reprocessing Streams – 13553

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ABSTRACT

There is a renewed interest worldwide to promote the use of nuclear power and close the nuclear fuel cycle. The long term successful use of nuclear power is critically dependent upon adequate and safe processing and disposition of the used nuclear fuel. Liquid-liquid extraction is a separation technique commonly employed for the processing of the dissolved spent nuclear fuel. The instrumentation used to monitor these processes must be robust, require little or no maintenance, and be able to withstand harsh environments such as high radiation fields and aggressive chemical matrices.

This paper discusses application of absorption and vibrational spectroscopic techniques supplemented by physicochemical measurements for radiochemical process monitoring. In this context, our team experimentally assessed the potential of Raman and spectrophotometric techniques for on-line real-time monitoring of the U(VI)/nitrate ion/nitric acid and Pu(IV)/Np(V)/Nd(III), respectively, in solutions relevant to spent fuel reprocessing. Both techniques demonstrated robust performance in the repetitive batch measurements of each analyte in a wide concentration range using simulant and commercial dissolved spent fuel solutions. Static spectroscopic measurements served as training sets for the multivariate data analysis to obtain partial least squares predictive models, which were validated using on-line centrifugal contactor extraction tests. Satisfactory prediction of the analytes concentrations in these preliminary experiments warrants further development of the spectroscopy-based methods for radiochemical safeguards and process control.

INTRODUCTION

Raman [1-5] and ultraviolet-visible-near infrared (UV-vis-NIR) [4, 6-11] spectroscopies are analytical techniques that have been extensively used for measuring the concentrations of various organic and inorganic compounds, including actinides. Additionally, the measurement of physical properties has also been proposed for on-line monitoring of fuel reprocessing systems [12]. The feasibility of on-line control of nuclear fuel reprocessing streams by using analytical techniques was investigated as early as the 1970s [13]. The corresponding spectrometers used under laboratory conditions are easily convertible to process-friendly configurations allowing remote measurements under flow conditions. In the discussed monitoring system, fiber-optic Raman and UV-vis-NIR probes allow monitoring of the chemical components encountered in various aqueous and organic streams within the plutonium uranium extraction (PUREX)

flowsheet. A Raman probe is applied to monitor high concentration Raman-active species, including oxo-metal ions, such as uranyl, components of the organic solvent, inorganic oxo-anions, and water. Other actinides and lanthanides are monitored remotely by vis-NIR spectroscopy. Even though Pu(VI) and Np(V,VI) species are Raman active, they are expected to be present in the dissolved fuel at low concentrations, prohibiting their quantification by the Raman method. However, the Pu species can be measured by visible absorption spectroscopy using multiple wavelengths for its quantification, and Np species can be monitored by vis-NIR spectroscopy [14]. Principal spectroscopic signatures of U, Pu, and Np analytes in different oxidation states are shown in Table 1.

In recent studies, our research group has demonstrated the applicability of optical spectroscopy for quantitative determination of Pu, U, Np, and Nd species in different oxidation states present in the dissolved spent fuel streams [14-16]. In addition, we have performed near real-time analysis on feed and raffinate solution samples produced from a centrifugal contactor system instrumented with Raman [17] and vis-NIR spectroscopic equipment [5, 17]. In this work, toward the goal of quantifying chemical material in real-time within a flow extraction system, we performed quantitative spectroscopic measurements of simulated PUREX process solutions using a counter-current centrifugal contactor extraction system and demonstrated that mass balance was obtained at the conclusion of the experiment.

Table 1. Spectroscopic Signatures of U, Np, and Pu Species.

Oxidation State	Complex Ion	Raman	vis-NIR, nm
U(VI)	UO ₂ ²⁺	870 cm ⁻¹	415
Pu(VI)	PuO ₂ ²⁺	833 cm ⁻¹	833
(IV)	Pu ⁴⁺		476, 815
(III)	Pu ³⁺		560, 602
Np(VI)	NpO ₂ ²⁺	854 cm ⁻¹	1223
(V)	NpO ₂ ⁺	767 cm ⁻¹	980
(IV)	Np ⁴⁺		953-973, 700-730
(III)	Np ³⁺		980, 790, 550-650

On-line monitoring of nuclear waste stream was successfully demonstrated by combining spectroscopic measurements with physiochemical measurements (conductivity, density, temperature) in real-time quantitative determination of chemical components in the waste [18, 19]. This new online monitoring system, which features Raman spectroscopy combined with a Coriolis meter and a conductivity probe, has been recently developed by our research team to provide immediate chemical data and flow parameters of high level radioactive waste streams. This process monitoring system is used to measure the concentration of components of solutions of high brine/high alkalinity wastes during retrieval from Hanford waste storage tanks, such as nitrate, nitrite, chromate, aluminate, phosphate, sulfate, carbonate, and hydroxide. The Raman

bands of interest for these species are well resolved and have been easily incorporated into a chemometric model for quantitative analysis of the solution components.

EXPERIMENTAL

Raman measurements were performed with an InPhotonics RS2000 high-resolution Raman spectrometer containing a thermoelectrically cooled charged coupled device (CCD) detector operating at -55°C ; a 670-nm, 150-W, visible diode laser as the excitation source, and an InPhotonics RamanProbe™ focused fiberoptic probe operated in a 180° back reflection mode. The laser beam focal point was 5 mm beyond the end of the laser probe tip, and the measured laser intensity at the sample was typically 50 mW. An integration time of 10 seconds was used for each acquisition, and 20 acquisitions were taken and averaged for each sample.

Vis-NIR measurements were performed using a Mikropack HL-2000-FHSA Halogen Light Source with attenuator, Ocean Optics fiber optic cables, and an Ocean Optics USB2000 Miniature Fiber Optic Spectrometer (500- to 1200-nm wavelength detection range). Each acquisition had 100 scans, each with an integration time of 12 ms. NIR measurements in the 900- to 1700-nm wavelength range were performed with a Mikropack HL-2000-FHSA halogen light source with attenuator and a 0.3 neutral density filter, Ocean Optics fiber optic cables, and an Ocean Optics NIR-512 temperature-regulated NIR spectrometer. Each acquisition averaged 100 scans, each with 15-ms integration time. Deionized water or water-washed tri-butyl phosphate (TBP)/*n*-dodecane solution was used to collect reference spectra for vis-NIR measurements of the aqueous or organic solutions, respectively.

Spectroscopic Measurements of Fuel Simulants

The PUREX solvent system was the guide for selecting the various feed concentrations and solvent system bounding the choice of spectroscopic measurements. The initial effort was directed toward evaluating flowsheet specifications for preparing solutions meeting the current process flowsheet conditions and concentrations [20]. To demonstrate the feasibility of using spectroscopic techniques for the process monitoring and control of the PUREX flowsheet, a 0.8-M HNO_3 solution matrix was selected as the baseline feed solution. The simple feed simulant (1.33 M $\text{UO}_2(\text{NO}_3)_2$ in 0.8 M HNO_3) served as the matrix for the Pu(IV) and Np(V, VI) measurements at variable concentrations in the 0- to 10-mM range. The organic solvent extraction solution containing 30 vol% TBP in dodecane was prepared and loaded with actinide nitrates by batch contact equilibration with the PUREX feed simulant solutions.

A Raman spectrum of a feed simulant containing 1.33 M uranyl nitrate in 0.8-M nitric acid solution is shown in Figure 1 (blue spectrum). This spectrum shows two strong bands, indicative of UO_2^{2+} (870 cm^{-1}) and NO_3^- (1047 cm^{-1}). The PUREX organic solvent was used as an extractant of the feed solution resulting in an organic phase containing $\text{UO}_2(\text{NO}_3)_2$. The Raman spectrum of the loaded solvent is also shown in Figure 1 (red spectrum). The Raman bands due

to the solvent dodecane and TBP as well as $\text{UO}_2(\text{NO}_3)_2$ were observed. The UO_2^{2+} (859 cm^{-1}) and NO_3^- (1029 cm^{-1}) bands were both shifted to lower energy in the organic phase spectrum compared to the aqueous phase spectrum. The spectrum of the loaded solvent was compared to the spectrum of water-washed TBP/dodecane, and it was observed that the bands due to solvent do not interfere with the uranyl or nitrate Raman bands. The intensity of the uranyl band (870 cm^{-1}) decreased from the initial spectrum to the final spectrum, indicating a reduced concentration of UO_2^{2+} in the aqueous phase after extraction. It thus was demonstrated that the depletion of uranyl ion from the aqueous phase upon extraction can be easily followed using Raman spectroscopy.

A series of feed simulant solutions containing 0.0003 to 1.31 M $\text{UO}_2(\text{NO}_3)_2$ in 0.8 M HNO_3 were prepared and subjected to Raman measurements. The obtained spectral overlay is shown in Figure 2 (left). A linear relationship was observed between the Raman response of the respective UO_2^{2+} (870 cm^{-1}) and NO_3^- (1047 cm^{-1}) bands and the concentration of $\text{UO}_2(\text{NO}_3)_2$ and nitrate in 0.8-M HNO_3 solution. A series of extractant phase solutions containing 0 to 0.41 M $\text{UO}_2(\text{NO}_3)_2$ in TBP/dodecane were prepared and measured by Raman spectroscopy and are shown in Figure 2 (right). The inset for both $\text{UO}_2(\text{NO}_3)_2$ in HNO_3 and in TBP/dodecane (Figure 2, left and right, respectively) shows that the Raman response vs UO_2^{2+} concentration in solution is linear, allowing for quantitative measurement of U in aqueous and organic solutions.

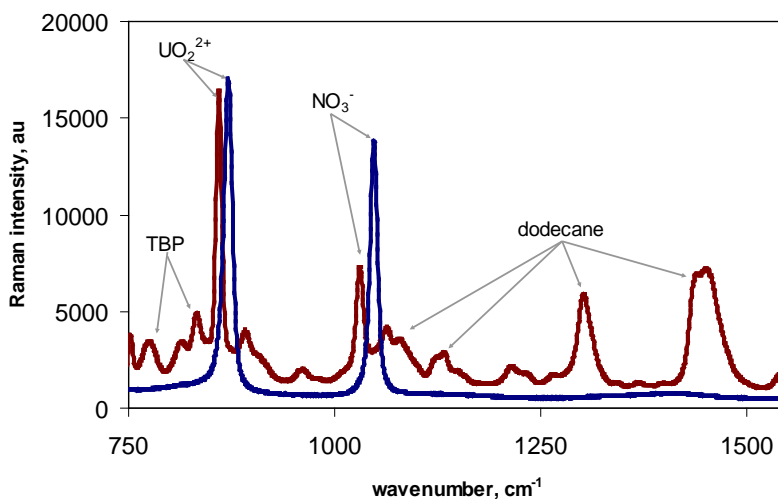


Figure 1. Raman Spectra of $\text{UO}_2(\text{NO}_3)_2$ in Aqueous Solution (blue spectrum) and Extracted into 30 vol% TBP in Dodecane (red spectrum)

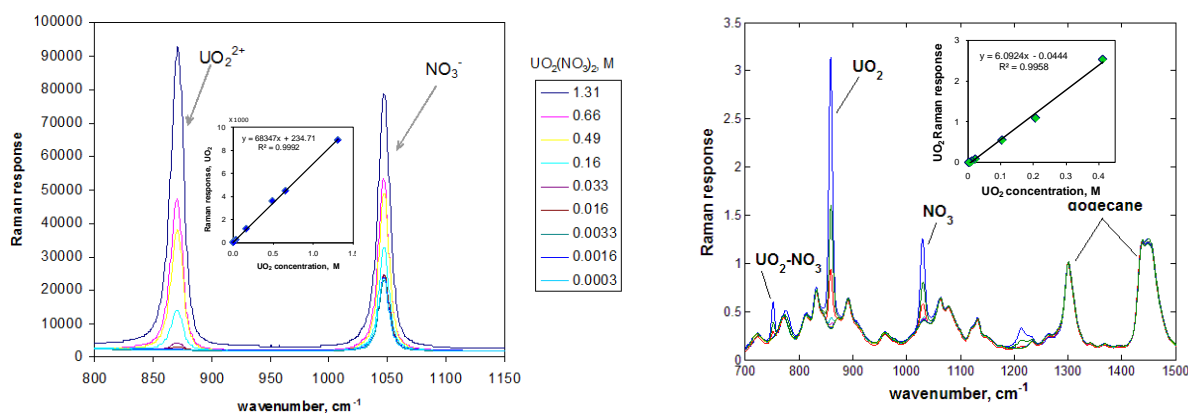
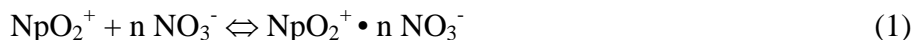
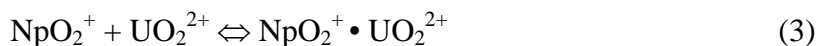


Figure 2. (Left) Raman Spectra of Variable $\text{UO}_2(\text{NO}_3)_2$ in 0.8 M HNO_3 ; (Right) Spectra of Variable $\text{UO}_2(\text{NO}_3)_2$ extracted into TBP/dodecane solvent. The inset for both figures shows the linear Raman response vs UO_2^{2+} concentration in solution.

Np is present in the dissolved spent fuel predominantly as Np(V) and Np(VI) in the NpO_2^+ and NpO_2^{2+} chemical form, respectively. Its redox equilibrium $\text{Np(IV)} \Leftrightarrow \text{Np(V)} \Leftrightarrow \text{Np(VI)}$ highly depends on multiple factors, including solution composition, temperature, etc. [10]. This redox chemistry determines Np distribution into TBP/dodecane phase, and its monitoring is desirable. The aqueous speciation of Np(V) is complex because of its coordination with nitrate anion and the formation of cation-cation complexes in accord with reactions 1 and 2 [11]:



where M^{n+} is transition or f-metal cation. In the dissolved spent fuel, the complex species $\text{NpO}_2^+ \cdot \text{UO}_2^{2+}$ formed as described by reaction 3 are the most prominent.



The splitting of the NpO_2^+ band at 981 nm observed in the 1-M HNO_3 solution into two bands occurs in the presence of U(VI) at the concentration ranges typical to the dissolved spent fuel streams. As a result, Np(V) spectroscopic properties are highly mobile and dependent on solution composition. To this end, understanding and quantifying Np(V) chemistry is needed to correctly interpret its vis-NIR spectra.

To investigate the spectral nature of Np in the PUREX process, a series of solutions of variable Np(V) concentration in 1.33 M $\text{UO}_2(\text{NO}_3)_2$ and 0.8 M HNO_3 were prepared; the vis-NIR spectra are shown in Figure 3 (left). Two bands are observed for the Np(V) in the PUREX feed solution, a result of the equilibrium between two neptunium solution species, the free Np(V) and a cation-cation interaction complex between Np(V) and UO_2^{2+} (981 nm and 998 nm respectively) [21].

Figure 3 (right) shows the standard plots for the Np(V) vis-NIR data in the simulant feed solution shown in Figure 3 (left). The molar extinction coefficient of the Np(V) and Np(VI) bands are dependent on the nature and concentration of the interacting ligands in solution, with the molar absorptivity of Np(VI) 1220 nm, Np(V) 978 nm, and Np(V)•U(VI) 990-nm bands depending upon the presence of uranyl, acid, inorganic salt, and total ionic strength (at constant temperature). To quantify this effect, we have measured the molar absorptivity of 978- and 990-nm bands of Np(V) and the 1222-nm band for Np(VI) as a function of ionic strength, with the ionic strength adjusted using HNO₃, NaNO₃, and uranyl nitrate.

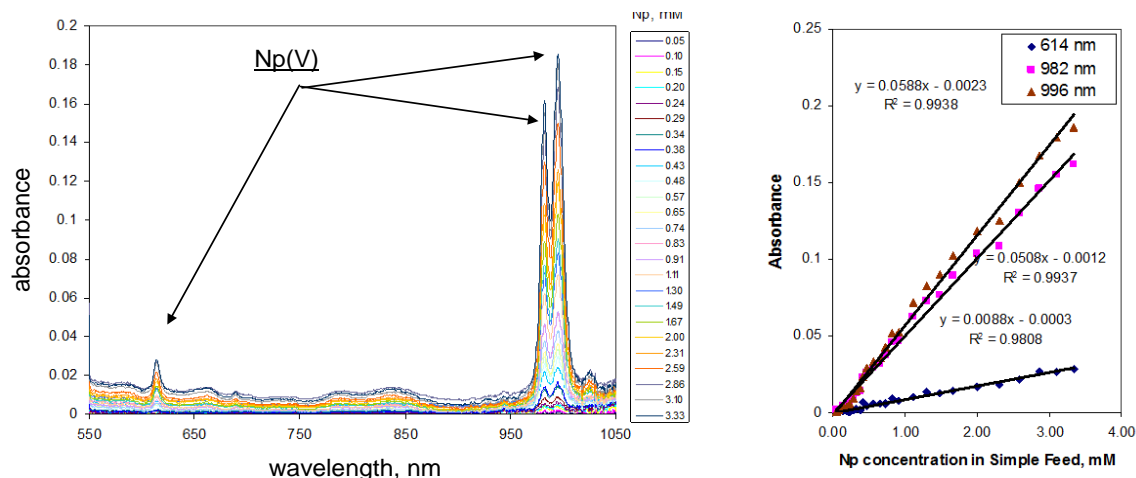


Figure 3. (left) Spectra of Np(V) Added to Simple Feed. Feed composition: 1.3 M UO₂(NO₃)₂ in 0.8 M HNO₃. (Right) Standard Curve of Np(V) vis-NIR data in simulant feed solution.

A series of feed simulant solutions containing 0.1 – 10 mM Pu(IV) in 1.33 M UO₂(NO₃)₂ and 0.8 M HNO₃ matrix was prepared and subjected to vis-NIR measurements. The obtained spectral overlay is shown in Figure 4 (left). It was observed that Pu(IV) spectral features at 500 – 1000 nm were not obstructed by spectroscopic features of UO₂(NO₃)₂ or HNO₃ and linear calibration plots were obtained using four characteristic Pu(IV) bands in this region (Figure 4 right). The detection limit for Pu(IV) was determined to be 0.08 mM using the 659 nm band.

To evaluate the feasibility of Np(V) quantification in solutions containing significant concentrations of Pu(IV), a series of feed simulant solutions containing 0.1 mM Np(V) and a variable concentration of 0.1 – 10 mM Pu(IV) in 1.33 M UO₂(NO₃)₂ and 0.8 M HNO₃ matrix was prepared and immediately measured using UV-vis-NIR, and is displayed in Figure 5. The spectral overlay shown in this figure illustrates that the Np(V) is detected in the presence of large excesses of Pu(IV) and U(VI); Np was 100 times less concentrated than Pu, and 13,000 times less concentrated than U is solution. A conservative measure of the detection limit of Np(V) can be established at < 0.1 mM under PUREX flowsheet conditions.

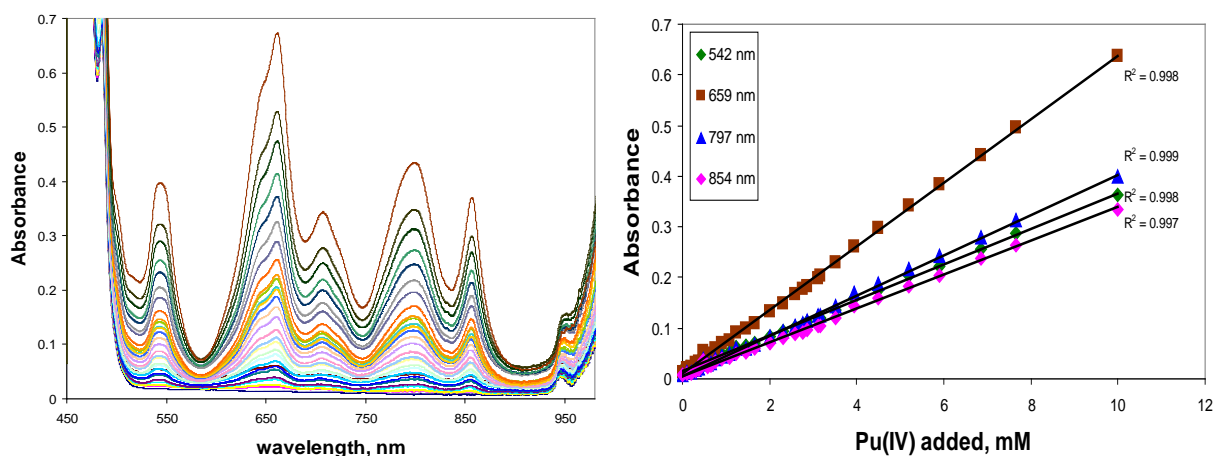


Figure 4. (Left) Absorption Spectra of 0.1 – 10 mM Pu(IV) in Simple Feed (1.33 M $\text{UO}_2(\text{NO}_3)_2$ and 0.8 M HNO_3). (Right) Calibration plots of Pu(IV) in Simple Feed.

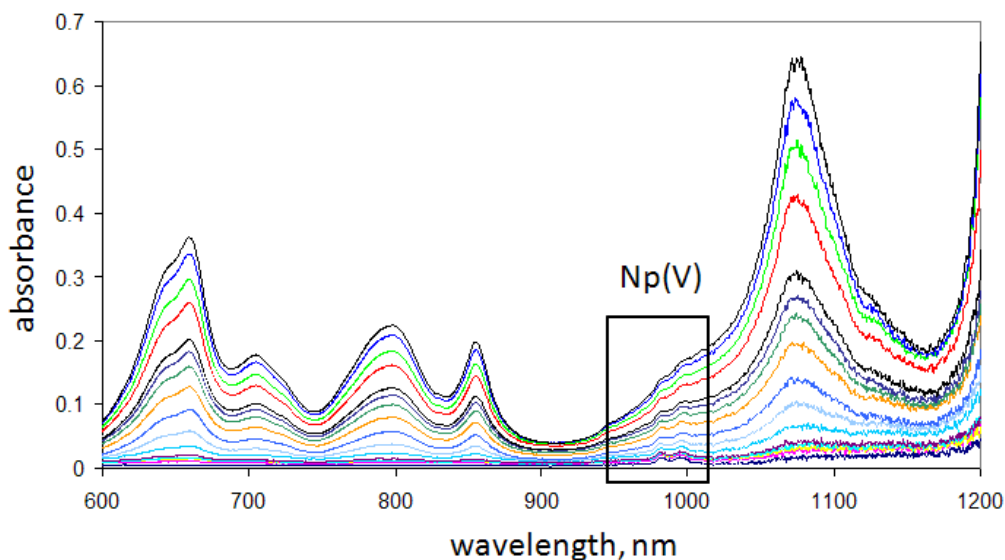


Figure 5. Vis-NIR Spectra of Constant Np(V) and Variable Pu(IV), in Simple Feed

Spectroscopic Measurements of Commercial Fuel

High burn-up commercial fuel (ATM-109) samples were available at PNNL[14]. The rods were irradiated in the Quad Cities I reactor with a total of 3508 on-power days in the reactor. Post-irradiation examinations were performed at GE's Vallecitos Nuclear Center, and pieces of the ATM-109 fuel were subsequently sent to PNNL. The fuel dissolved for the demonstration has a burn up of 75 MWd/kgU and an initial enrichment of approximately 3%.

A portion of the ATM-109 fuel was removed from its cladding and dissolved in concentrated nitric acid. Once the fuel was dissolved, the acid strength was adjusted to prepare samples of each fuel at five different acid strengths: 0.3, 1.3, 2.5, 3.8, and 5.1 M. The solutions mimic the feed stream for a PUREX process in uranium concentration and provide a range of acid variations that might occur in the feed stream. The dilution was performed to keep the uranium concentration constant (near 0.7M), regardless of the acid strength.

A batch separation was performed using a portion of the samples. Using a batch technique for the first stage of the PUREX process, the acid adjusted aqueous solution was mixed with a 30 vol% TBP-dodecane mixture. The mixture was allowed to reach an equilibrium distribution and then the phases were separated.

Direct Raman measurements of the aqueous/nitric acid feed and raffinate solutions performed on the ATM-109 commercial fuel are shown in Figure 6 (left). This figure also contains a measurement of a feed fuel simulant (containing 1.3 M $\text{UO}_2(\text{NO}_3)_2/0.8\text{M HNO}_3$) for comparison of the Raman response between simulants and actual fuel samples. The spectral features responsible for the UO_2^{2+} and NO_3^- bands (870 and 1047 cm^{-1} respectively) in the fuel feed and raffinate samples are in excellent agreement with those contained within the Simple Feed simulant. The TBP-dodecane extract phase of the fuel was also measured by Raman spectroscopy. Figure 6 (right) contains the Raman spectrum of the TBP-dodecane phase of ATM-109 and the extract phase of the feed simulant for comparison. The Raman band locations for the UO_2^{2+} and NO_3^- bands (858 and 1029 cm^{-1} respectively) between the actual commercial fuel and simulant are in excellent agreement. Other bands observed in the extractant phase Raman spectra are assigned to the solvent (TBP and dodecane).

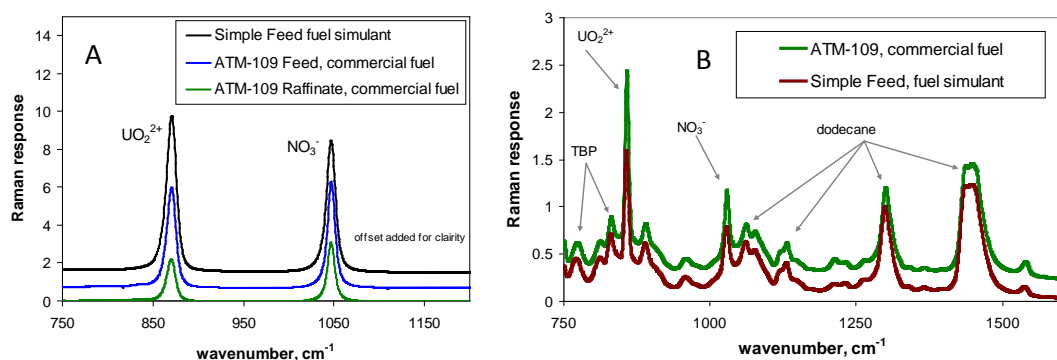


Figure 6. (A) Raman spectra of ATM-109, high burn up BWR commercial fuel feed and raffinate solutions, and simple feed simulant solution. ATM-109 Feed solution contains 0.3 M HNO_3 , simple feed contains 1.33 M uranyl nitrate in 0.8 M HNO_3 . (B) Raman spectra of TBP-dodecane extraction solutions of ATM-109 commercial fuel and simple feed simulant solution.

Spectrophotometric measurements of the aqueous feed solutions of the ATM-109 commercial fuel samples were performed using vis-NIR spectral region. Plutonium in both Pu(IV) and Pu(VI) oxidation states was observed in the commercial fuel feed, with varying concentrations depending on final HNO₃ concentration, as is apparent in Figure 7. Neptunium as Np(V) and Np(VI) were observed in all solutions, with Np(V) being more prominent at lower acid concentrations, and Np(VI) being more prominent at higher concentrations[14].

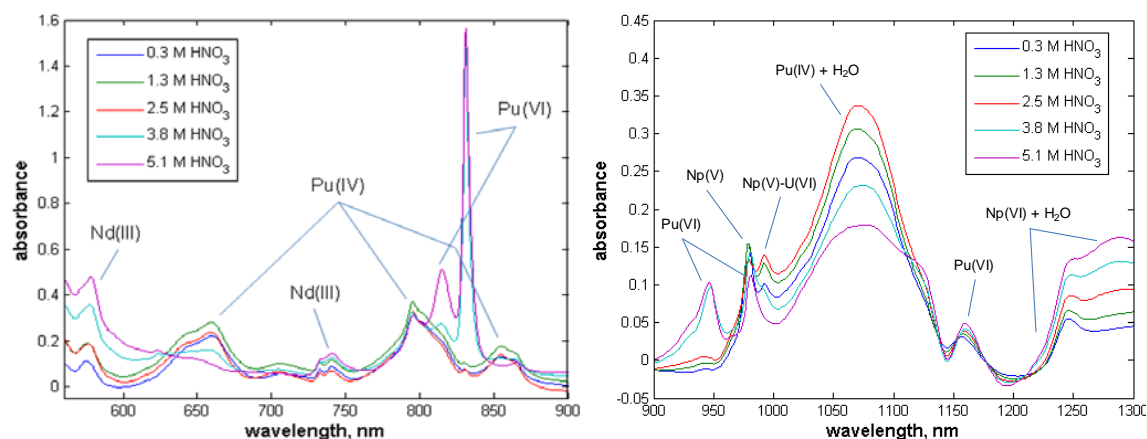


Figure 7. Vis-NIR spectra of ATM-109 commercial fuel. Aqueous feed acid concentrations range 0.3M – 5.1 M HNO₃.

The Raman and vis-NIR spectra of the ATM-109 feeds were subjected to chemometric analysis and standard Beers Law spectral analysis to determine the concentrations of U, Pu and Np present in solution. The resulting concentrations are contained in Table 2. For comparison, the ICP-MS results are also displayed as well as the ORIGEN code calculations for these fuel samples. From this table, it is evident that the spectroscopic method is in excellent agreement with the standard ICP-MS analysis.

Table 2. Analytical Results for ATM-109 Commercial Fuel Sample. Concentrations listed in molar units.

ATM-109	U	Pu	Np	Nd
ORIGEN	7.20E-01	7.50E-03	4.60E-04	1.10E-02
ICP-MS	7.20E-01	9.00E-03	4.70E-04	8.40E-03
Spectroscopic	7.20E-01	8.90E-03	4.70E-04	1.10E-02
Spectroscopic/ICP ratio	1.0	0.99	1.0	1.3

Process Monitoring Demonstration Using Centrifugal Contactors

To test the on-line and real-time aspects of process monitoring, we set up a counter-current solvent extraction testing apparatus for use with spent fuel separations processing. The counter-current design is based on multiple banks of 2-cm centrifugal contactors. The bank consisting of 16 centrifugal contactors was installed in a shielded glove box for use in testing radioactive materials.

The spectroscopic instrumentation is connected to the bank of centrifugal contactors located within the shielded glovebox containment. A photograph of the inside of the shielded glove box showing the bank of 16 centrifugal contactors is depicted in Figure 8 (left). Fiber-optic cables are used to connect the spectroscopic instrumentation to the solutions probes attached to the centrifugal contactors. Spectroscopic instrumentation is located outside of the shielded containment with the optical probes located inside the containment. The optical cables are passed through the glove port cover into the glove box containment.

Flow testing of the centrifugal contactor system located within the shielded glovebox facility used feed solutions containing $\text{UO}_2(\text{NO}_3)_2$, and nitric acid. The organic solvent system used for this demonstration was TBP/dodecane with an aqueous feed containing variable concentrations of U and nitric acid. The concentrations for the aqueous and organic phases simulated conditions used in the PUREX process.

Figure 8 (right) contains a schematic representation of the bank of contactors used in our initial study. A bank of four centrifugal contactors is used for extraction. The locations of Feed, Raffinate, Organic inlet, and loaded Organic product streams are shown. The vis-NIR and Raman monitoring probes are positioned on the Raffinate stream. The flow tests used a series of solutions with variable concentrations of U and nitric acid.

A series of solutions, sequentially increasing in nitric acid and then increasing in $\text{UO}_2(\text{NO}_3)_2$, were introduced into the centrifugal contactor flow loop system. Raman spectra were collected concurrent with the additions of HNO_3 and $\text{UO}_2(\text{NO}_3)_2$ into the feed. The concentrations were built up incrementally starting with the addition of nitric acid with the following concentrations: 0, 0.5, 1, 2, 4, 5, and 6 M HNO_3 . Starting with the concentration of 6 M HNO_3 , uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$ was added to the previous solution to yield final solutions ranging in U(VI) from 0.1 to 0.6 M, in 0.1 M increments.

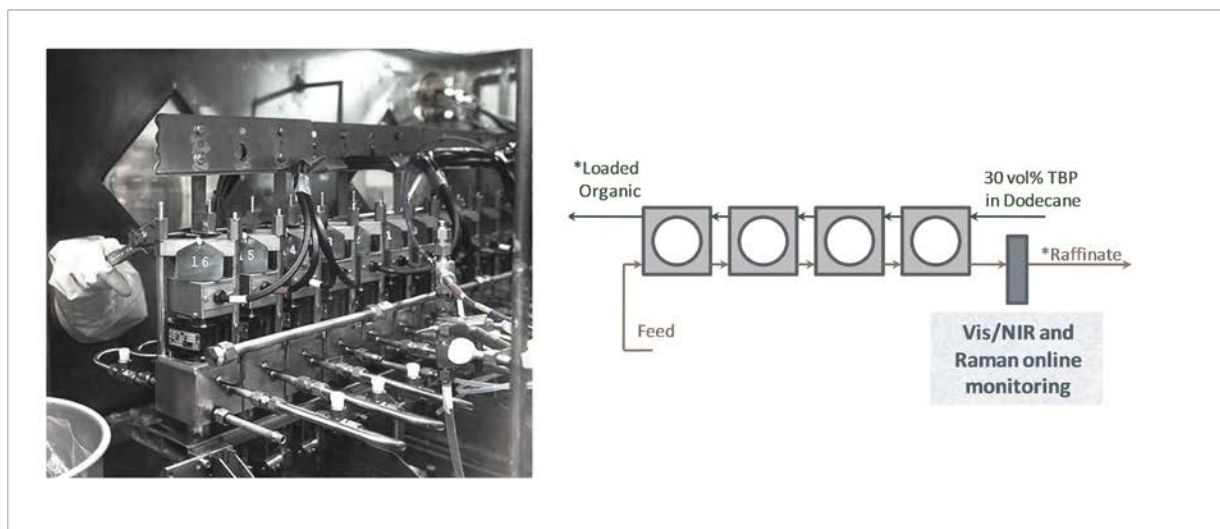


Figure 8. (left) Photograph Showing Inside of Shielded Glovebox. The bank of 16 centrifugal contactors is visible in the photo. (right) Schematic of Centrifugal Contactor System.

During the additions, Raman measurements were being taken at the on-line monitoring point designated within the schematic in Figure 8. Figure 9 (left) shows the Raman spectra taken over the time frame of the nitric acid and uranium additions. Several spectral features are apparent within this figure: the water region at 3000 to 4000 cm^{-1} ; the nitrate band at 1050 cm^{-1} ; and the UO_2^{2+} at 871 cm^{-1} . By using a chemometric model formed from spectra containing known quantities of $\text{UO}_2(\text{NO}_3)_2$ and HNO_3 , a successful translation of the model based on static measurements to on-line measurements for on-line monitoring was achieved. Figure 9 (right) contains the expected and predicted concentrations of the Raman on-line measurements and shows excellent agreement between values. The light blue lines are the expected concentration of analyte in solution; the red, green, and dark blue lines are the predicted concentration of HNO_3 , total nitrate, and $\text{UO}_2(\text{NO}_3)_2$ respectively. It is worth noting that the model is capable of not only predicting the UO_2^{2+} and nitrate concentrations but is also capable of differentiating between total nitrate and nitric acid. The distinction between nitrate and nitric acid is due to the inclusion of all the spectral data within the Raman spectrum, including the water region (3000 to 4000 cm^{-1}) and multiple nitrate bands (of which 1050 cm^{-1} is the largest), which show subtle but reproducible changes based on acid content and the ionic strength of the solution.

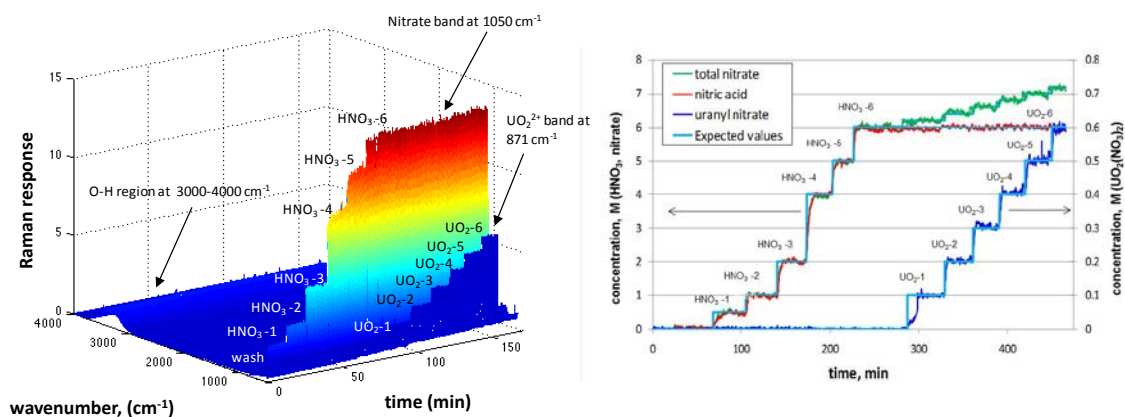


Figure 9. (left) Real-Time Raman Monitoring of the Fuel Simulant Extraction Solution. (right) Measured and Predicted Raman On-Line Measurements Showing Excellent Agreement Between Values.

CONCLUSIONS

The quantitative determination of uranyl and nitrate species in a simulant fuel reprocessing solution was performed using Raman spectroscopy; and the quantitative analysis of the solution species Pu(IV) and Np(V) were demonstrated by vis-NIR spectroscopy. Uranyl nitrate was also quantitatively measured by Raman spectroscopy in the loaded extraction phase containing 30 vol% TBP in dodecane. These preliminary experiments demonstrate the feasibility of the application of Raman and UV-vis-NIR techniques for process monitor development for fuel recycling solutions.

Real-time chemometric analysis was performed on feed and raffinate solution samples produced from a centrifugal contactor system instrumented with Raman spectroscopic equipment. Simulant testing of the centrifugal contactor system deployed within a shielded glovebox with the system $\text{UO}_2(\text{NO}_3)_2/\text{HNO}_3$ demonstrated real-time chemometric analysis of Raman spectral data collected on variable feed and raffinate streams. The analysis successfully followed the $\text{UO}_2(\text{NO}_3)_2$, HNO_3 , and total NO_3^- for 0 to 0.6 M, 0 to 6 M, and 0 to 7.2 M, respectively.

PNNL is continuing to investigate in spectroscopic-based approaches for real-time, on-line monitoring of fuel cycle processes. Process monitor spectroscopic equipment has been tested for spectroscopic measurements of principal components of PUREX simulant solutions. Baseline data are now available for U, Pu, Np, nitric acid, and TBP-dodecane.

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