

## ONLINE MONITORING OF RADIOCHEMICAL PROCESSING STREAMS FOR THE PLUTONIUM-238 SUPPLY PROGRAM

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*Online monitoring with spectrophotometry is being developed to improve the timeliness of analytical measurements for the Plutonium-238 Supply Program at Oak Ridge National Laboratory. A commercially available online monitoring software was used to calculate and view process data in real time to help identify process deviations and optimize system performance. Monitoring detailed process data will improve processing efficiency and help technicians make decisions during hot-cell operations.*

### I. INTRODUCTION

Plutonium-238 is being produced at Oak Ridge National Laboratory (ORNL) for National Aeronautics and Space Administration (NASA) space applications. Neptunium- (Np-) containing targets are irradiated at the High Flux Isotope Reactor (HFIR) to produce <sup>238</sup>Pu. Radiochemical separations such as liquid-liquid extraction and ion exchange chromatography are used to purify the <sup>238</sup>Pu product.<sup>1</sup> The program is scaling up production efforts to meet the NASA's need, which is 1.5 kg of plutonium(IV) dioxide (PuO<sub>2</sub>) per year on average by 2025. The effort focuses on developing spectroscopic and real-time monitoring tools for rapid analysis and process feedback during radiochemical separations used for Np processing and purification of the Pu product.<sup>2,3</sup>

Spectrophotometry, or absorption spectroscopy, is a technique that quantitatively measures the amount of light absorbed by a molecule as a function of wavelength. Absorbance is proportional to the concentration of a light-absorbing species and can be quantified using Beer's law when the optical pathlength and molar absorptivity of the substance is known.<sup>4</sup> This univariate approach breaks down in complex systems with overlapping absorption bands, shifting baselines, and dependencies on solution conditions.<sup>5,6</sup> Multivariate data analysis (e.g., partial least squares regression [PLSR]) can be used to describe complex systems by correlating the entire spectrum (instead of a single wavelength) to the concentration of species in solution.<sup>3,7</sup>

Spectrophotometry and the appropriate regression analysis can be used for timely analytical measurements in harsh environments, such as heavily shielded hot

cells.<sup>3,8</sup> Fiber-optic cables can transmit light for hundreds of meters and allow ultraviolet/visible/near infrared (UV-Vis-NIR) absorption measurements to be made in cells while personnel operate equipment in a control room. This enables spectroscopic measurements of materials located in the hot cells at the Radiochemical Engineering Development Center at ORNL without transferring samples out of the cells.<sup>3</sup>

The Unscrambler by Camo Analytics is a powerful software tool useful for multivariate data analysis. It can also be used to apply a variety of preprocessing methods (e.g., derivatives, smoothing, scaling) to spectral data to improve the analysis.<sup>9</sup> Multivariate models and spectral data transformations developed using the Unscrambler are automated with Process Pulse II (PP) by Camo Analytics, a commercially available online monitoring software. PP is compatible with numerous data sources and accessible to all users, including process engineers and technicians. In production Campaign 5, PP was evaluated during two full-scale Np monoamide solvent extraction (P5MX) and three plutonium anion exchange (P5AXPu) runs. A brief description of the software, key findings, and future work is discussed herein.

### II. EXPERIMENTAL

The Unscrambler X (version 10.4) software package was used to develop a PLSR model. Spectra were mean normalized before PLSR analysis to equalize the influence of each variable. The model was optimized by minimizing the root mean square error of the cross validation. A Savitsky-Golay first derivative algorithm was applied to the spectra to remove baseline offsets and smooth the data.<sup>9</sup> The PP Multivariate Statistical Process Monitoring system by Camo Analytics (version 5.60) was used to automate univariate and multivariate calculations, view process variables, and notify staff when certain process conditions were reached. Ocean Insight spectrophotometers QE Pro and NIRQuest were used for UV-Vis and NIR absorption measurements, respectively. Spectral data were acquired as ASCII files using OceanView software (version 2.0.7). Hellma UV-Vis diprobes with varying pathlengths (220 mm) and an Avantes 5 mm in-line flow cell were used. The halogen light (HL-2000 by Ocean Optics) and transmitted signals

were directed into and out of the hot cell using nearly 20 m of ThorLabs multimode SMA fiber patch cables (FG550LEC-Custom). Chemical reagents were commercially obtained (ACS grade).

### III. PP DEMONSTRATION

Spectrophotometry is an important component of the  $^{238}\text{Pu}$  Supply Program and is well-suited for determining Np and Pu concentrations in various oxidation state(s) in feed solutions and for monitoring separations. UV-Vis-NIR spectrometers collect spectra at relatively rapid intervals (e.g., 10 - 1,000 ms) and contain a wealth of information. The data are more intuitive for users to understand when converted to process variables, such as concentration. Converting spectra to process variables in real time assists users monitoring complex systems.

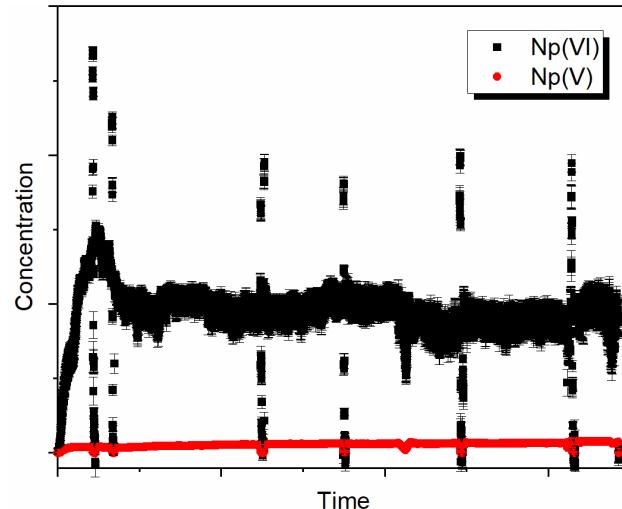
Most software/programing online monitoring options require a large investment upfront (i.e., mostly for customizing to a specific application) and extensive updates. PP is an “off-the-shelf” software package designed specifically for online process monitoring. The software has configurable dashboards where results are displayed in a choice of plots and alarms that are used to alert users of potential issues or action items. Software configurations were set up by research and development staff to monitor both P5MX solvent extraction and P5AXPu anion exchange column runs. Configurations included combinations of data sources, models, notifications, and output settings that can be used later by technicians to monitor these processes.

#### III.A. Neptunium Monoamide Extraction

During Campaign 5, the  $^{238}\text{Pu}$  Supply Program used a monoamide-based extractant for the first time to separate recycled Np from most of the fission products. The recycled  $^{237}\text{Np}$  will be refabricated into targets to make more  $^{238}\text{Pu}$ . Spectroscopic measurements of the aqueous phase were used to ensure that Np was extracted into and stripped from the organic phase before exiting with the raffinate and unloaded organic solvent. Both UV-Vis and NIR spectral data were recorded using multiple dip-probes placed in the settlers of a mixer-settler liquid-liquid extraction system. Data from the entire run, which spanned multiple days, were viewable in interactive charts using the PP main view.

In this example, Np(V) and Np(VI) concentrations were measured in the stripped aqueous product stream (see Figure 1). A dip-probe was left primarily in one location to monitor the aqueous phase composition of the product stream to inform how Np was being stripped from the loaded solvent and to evaluate the system dynamics over time. The product concentration profile changed near the beginning of the run when process conditions were adjusted (see Figure 1). Periodically, the probe was

moved to other stages to obtain bank profiles. These data are shown at discrete times in Figure 1 at concentrations above and below the relatively stable product profile. Concentration profiles were significantly different than expected based on calculations from a solvent extraction model. This further justified the need for a monitoring tool and revealed opportunities for studies to improve elements of the process model.



**Fig. 1.** Np(VI) and Np(V) strip bank concentration profiles. High- and low-concentration points correspond to stage profiles taken at discrete times during the operation.

The spectral data were corrected for baseline offsets using a linear baseline transformation and converted to concentration using Beer's law. The concentration of Np(V) and Np(VI) were determined using the 980 nm peak and the shoulder of the 1,220 nm peak, respectively. Molar absorptivity values were determined by comparing spectroscopic measurements at a given time with grab samples analyzed by inductively coupled plasma mass spectrometry (ICP-MS), which provided a pseudo-calibrated system. The absorptivity values agreed with published data.<sup>6</sup> Comparing the Np concentration measured by spectroscopy with the ICP-MS data revealed that this approach may have the potential to provide more than just trends and qualitative profiles, if desired.

Based on the feedback provided by online monitoring, flow rates were adjusted during the run to minimize Np loss to the raffinate and ensure complete stripping of Np from the organic solvent. This demonstrated the ability to evaluate and optimize the performance of solvent extraction runs. Future iterations of the software configuration will include notifications and action items to inform users when/if changes are needed.

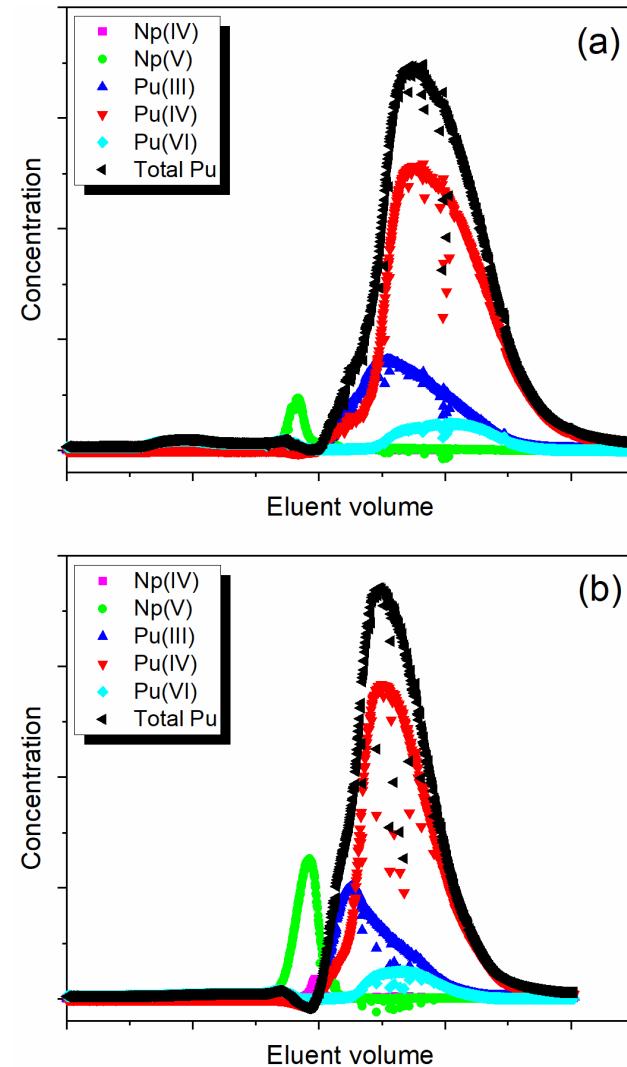
### III.B. Plutonium Anion Exchange

Plutonium anion exchange (AXPu) column runs are used to purify the Pu recovered by solvent extraction from the dissolved targets. AXPu runs remove phosphorus-containing contaminants (e.g., solvent degradation products), thorium, fission products, and most of the Np from the  $^{238}\text{Pu}$  product. Np(IV) and Pu(IV) are converted to anionic complexes in high-concentration nitric acid, loaded onto a large column filled with anion exchange resin, and eluted with dilute nitric acid. Key analyses include identifying the Pu(VI), Np(V), and Np(IV) in the effluent and determining the appropriate time to collect the eluate as a Pu product cut. Determining the best time to begin collecting the Pu product is challenging and arguably the most important task. The decision is based on opposing factors: (1) maximizing the yield of Pu product per run, while (2) simultaneously minimizing the carryover of Np in the product. This allows the subsequent cation exchange runs to proceed efficiently and helps meet the heat source  $\text{PuO}_2$  product specifications (i.e., Np in the total Pu product <0.5 wt%).

An in-line, flow cell was used to monitor the AXPu column with UV-Vis and NIR absorption spectroscopy. The concentrations of Np and Pu were predicted using a PLSR model. A multivariate approach was necessary to distinguish each analyte in the convoluted spectra. The PLSR model was developed using a representative set of training samples acquired from historical data from production Campaign 4. Spectra were manually deconvoluted by applying scaling factors to historical reference spectra and minimizing the residual difference between the sum of each contribution and the actual spectrum. This method assigned concentration values for each species and comprised the “concentration” response matrix (Y) while the unaltered spectral data represented the independent matrix (X). PLSR analysis was used to correlate the convoluted spectra to concentration by iteratively maximizing the covariance between these two data matrices. The explained variance, regression coefficients, and overall metrics suggested that it was performing well and could be used to describe the system. The prediction performance improved when a first derivative was applied to the spectra.

The Np(IV), Np(V), Pu(III), Pu(IV), and Pu(VI) concentration profiles were calculated and viewed in real time during each AXPu column run in Campaign 5. Examples from two of the runs are shown in Figure 2. The elution profiles for Np and Pu vary from run to run, with most of the Np eluting before the Pu. However, a significant portion of the Np tail is present while the Pu front elutes, which makes it challenging to optimize the product cut.

The software helped identify the appropriate time to start collecting the Pu product. The criteria for this decision limit were based on two parameters: (1) a predefined calculated Np/Pu ratio and (2) the total amount of Pu, such as Pu(III) and Pu(IV). Notifications appeared on the monitoring screen when process limits were exceeded and included relevant action items. These were also sent by text/email to staff members. The predicted Pu concentration results matched alpha spectroscopy results from the analytical group within ~10%. Models will be refined with data obtained at different acidities to match radiochemical analyses more closely.



**Fig. 2.** Predicted Np(IV), Np(V), Pu(III), Pu(IV), and Pu(VI) and total Pu concentration profiles for the first (a) and third (b) column run.

#### IV. CONCLUSIONS

This work highlights a major improvement toward establishing an online monitoring capability for the  $^{238}\text{Pu}$  Supply Program at ORNL. Spectroscopic measurements prompted operational adjustments to optimize run performance during solvent extraction runs and helped identify an optimal product cut decision in anion exchange column runs during hot-cell operations. The results indicate that real-time monitoring adds value to an essential part of the overall process and enhances the control of the radiochemical processing streams. Fully integrating PP will help close the gap between research and development and production by automating spectroscopic analyses. Future work will focus on optimizing configurations and training staff members who support processing to use this capability for routine analysis.

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