ORNL/TM-2021/13

Monitoring Radiochemical Processing Streams for the ^{238}Pu Supply Program with Process Pulse II

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February 2021

OAK RIDGE NATIONAL LABORATORY
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Radioisotope Science and Technology Division

MONITORING RADIOCHEMICAL PROCESSING STREAMS FOR THE ^{238}PU SUPPLY PROGRAM WITH PROCESS PULSE II

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February 2021

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

MCR	multivariate curve resolution
MDD	modified direct denitration
NASA	National Aeronautics and Space Administration
NpO_2	neptunium oxide
ORNL	Oak Ridge National Laboratory
P5AXPu	plutonium anion exchange
P5MX	monoamide solvent extraction
PLS	partial least squares
PLSR	partial least squares regression
PP	Camo Analytics Process Pulse II
PuO_2	plutonium oxide
REDC	Radiochemical Engineering Development Center
SGolay	Savitzky-Golay
SNV	standard normal variate
TBP	tri-butyl phosphate
UID	user identification
UV-Vis-NIR	Ultraviolet near-infrared

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EXECUTIVE SUMMARY

Oak Ridge National Laboratory (ORNL) is developing advanced spectroscopic and real-time monitoring capabilities to improve the timeliness of analytical measurements and process decisions for the ^{238}Pu Supply Program. Reducing the time, resources, and costs associated with each production campaign is critical because overlapping campaigns will be required to meet the production goals of the National Aeronautics and Space Administration. Real-time, in situ analytical measurements in the heavily shielded hot cells at the Radiochemical Engineering Development Center (REDC) will allow for rapid process information feedback and operational benefits that help the ^{238}Pu supply program scale-up production efforts.

Noteworthy steps were taken during Campaign 5 to establish the ability to monitor processing streams in real time with spectrophotometry and a commercially available online monitoring software called The Unscrambler X Process Pulse II (PP) multivariate statistical process monitoring system by Camo Analytics (version 5.60). PP automates univariate-type calculations within the software itself and executes multivariate models built using The Unscrambler X (version 10.4 or newer). The Unscrambler is a commercially available data analysis software made by the same company. PP is composed of easy-to-use-tools for all personnel, including data scientists and technicians. The software can be used to plot analyte concentration profiles, spectral data, and other process variables in real time. All process data are represented in a single view with interactive charts useful for viewing how a process evolves over time.

PP may be operated simultaneously from two or more locations. The quoted software package consists of up to three simultaneous users and five simultaneous configurations. These capabilities would enable, for example, a user to monitor modified direct denitration (MDD) feed solutions in Laboratory 109 with a configuration while another user is running four configurations during a mixer-settler run in the hot cell, and another user is monitoring/assisting from their office. The software is easily scalable to include additional simultaneous users and simultaneous configurations, if necessary, for future program needs. Configurations are combinations of data sources, models, action items, and output setup. A configuration will be generated for each of the routine processing events to guide technicians through the process. Technicians will blank the spectrometer, run the appropriate configuration(s), and make decisions based on the feedback provided by the software while making feed adjustments or monitoring radiochemical separations.

A four-month PP software trial was initiated on July 24, 2020. The software was thoroughly evaluated and tested during two full-scale processes, including two monoamide solvent extraction (P5MX) runs and three plutonium anion exchange (P5AXPu) column runs. Additional off-line tests were also completed. The following list summarizes the progress made during Campaign 5 in testing PP during each monoamide solvent extraction run, the Pu anion exchange column runs, and general testing.

1) P5MX monoamide extraction

    a. PP was tested during P5MX-1b and P5MX-2. Ultraviolet visible (UV-Vis) and near-infrared (NIR) spectra were collected in both the A- and B-banks with in-line Hellma dip-probes. Multiple PP configurations were implemented during each solvent extraction run without experiencing technical difficulties such as the software crashing or not responding. This was significant because each configuration was used to plot >10,000 spectral files over several days and the data set was as large or larger than the program's anticipated needs (~15,000 spectral files). PP configurations were used to plot qualitative Beer's law calculations, which accounted for baseline offsets, and displayed how the concentration profiles were trending with time. In P5MX-2, the strip flow rate was adjusted based on spectroscopic measurements that were highlighted by trends viewable with PP. UV-Vis-NIR spectra were collected on several stage samples which were also sent to analytical for alpha-particle spectrometry and inductively coupled plasma mass spectrometry. These results were used to assign an experimentally derived molar absorptivity to Np(VI) and calibrate multivariate regression models. The molar absorptivity of the predominant 1,221 nm peak in the Np(VI) spectrum was 41 $M^{-1}cm^{-1}$. Because of the high concentration of Np(VI) in B16, a molar absorptivity of 15 $M^{-1}cm^{-1}$ for the 1,178 nm shoulder provided the best sensitivity over the range of concentrations measured during each run. Multivariate models were built in The Unscrambler postrun to generate B-bank concentration profiles. These profiles were in good agreement with analytical results, and this multivariate model is ready for use in future monoamide solvent extraction runs.

b. Recommended areas for development

   - Develop configurations with multivariate models (e.g., partial least squares) built using The Unscrambler and compare measurements with Beer's law calculations.

   - Include action items in configurations that inform technicians whether the flow rate should be adjusted up or down based on predetermined criteria [e.g., Np(VI)/Np(V) ratio and/or concentration(s) in B16].

   - Implement a warning feature that alerts technicians to fix baseline offsets by shaking the probe. The A-bank probe was lost during the run; the exact cause is unknown. Including a notification that is based on predefined parameters to inform technicians would be useful if this kind of event occurs.

   - The integration time should be adjusted manually so that it can account for fluctuations in reference light intensity up or down. B-bank profiles were negatively impacted by an increase in the amount of light as stage positions B3-B7 were approached. The reference intensity could be manually set to ~40,000 cps, instead of the automated value near 55,000.

2) AXPu anion exchange column run and feed adjustment

   a. Key analysis points during the Pu anion exchange column runs include (1) the adjustment of Pu in the feed to Pu(IV), (2) identification of Pu(VI) in the effluent, and (3) determining the appropriate time to collect the ^{238}Pu product. UV-Vis and NIR spectra were collected with an Avantes 0.5 cm process flow cell connected to the effluent stream from the anion exchange column. Grab samples to characterize the feed and product bottles were analyzed in vacutainers placed in a cuvette holder. A partial least squares regression model was built in The Unscrambler from historical data for monitoring the column effluent. This model was used to calculate effluent concentration profiles of Np(IV), Np(V), Pu(III), Pu(IV), and Pu(VI), which were plotted in real time using PP. Action items were incorporated into the configuration, including switching to rework upon significant Pu(VI) and collecting the ^{238}Pu product in 1 L bottles. PP successfully pinpointed the appropriate time to switch to rework in each run. Upon significant Pu(VI) in the effluent stream, email/text notifications were sent to staff with a message stating to switch the effluent stream to rework. The same configuration conservatively determined when to make the Pu product cut in the first two runs. However, two additional PP configurations were included in the third column run to make the product cut decision at 1.2 wt% Np compared with Pu. This threshold can be readily adjusted and will allow technicians to make the product-cut decision. A model for Pu(III) and Pu(IV) was developed for the feed adjustment but was not tested during an actual processing event. It may already be sufficient for testing. However, additional spectra at high concentrations could be included in the model to improve its accuracy and sensitivity. This will be ready for testing during Campaign 6.

b. Recommended areas for development

- Continue building and testing multivariate models built using historical data to optimize the product cut. Compare multivariate curve resolution with partial least squares regression models.

- Analyze overall run performance from past Pu anion exchange runs. Compile Pu yield versed Np contamination in the product and use this information to inform model development. Develop an approach that combines real-time spectroscopy, data analysis, and operational simplicity, which will minimize the amount of material that needs to be reworked and maximize the product purity.

- Further develop feed adjustment model to quantify the ratio of Pu(III/IV/VI) in the feed. This may require some glove box testing to obtain well-characterized spectra and a change in the experimental setup that includes a smaller optical pathlength (e.g., 2 or 5 mm).

- Divide the overall range of solution conditions into subregions that are matched to local models or run multiple configurations which are specifically tailored for specific concentration ranges [e.g., Np(V) 980 nm vs. 616 nm peaks]. This will improve quantification of analytes in the effluent that are present at concentrations that vary over several orders of magnitude.

- Derive a model to quantify nitric acid concentration using NIR and/or UV-Vis spectral features. Test it on historical data before Campaign 6.

3) General off-line tests

a. The behavior of PP during loss of connection to the network was tested by pulling the ethernet cable while a configuration was running. This was tested on a configuration pulling data directly from a spectrometer and another that analyzes text files gathered from a watch folder.

b. Key findings

- The software can easily be rebooted, and configurations will continue running after connection is lost. The files acquired during an outage are stored in a memory buffer zone and are analyzed upon restart. Thus, the files displayed are on an inaccurate timescale and reflect the time when PP analyzed the spectrum rather than the time the file was collected.

4) Evaluation

Additional effort is required to acquire training data and build the software configurations. However, implementing this software will ultimately make spectroscopic measurements for the ^{238}Pu Supply Program more organized, informative, and user-friendly. With continued development, it will allow control room technicians to manage processing operations, thereby allowing research scientists to spend more time generating spectral training sets, multivariate models, and configurations to improve the feedback and measurements automated with PP to provide further operational benefits.

The PP software provides a platform and the building blocks needed to eventually run spectroscopic online monitoring tools to any extent the ^{238}Pu Supply Program needs. Even the minimum capabilities within this software will greatly benefit the program and, with more rigorous development, it may be used to track material inventory in real time. This software will expedite processing and improve process decisions. A detailed description of PP, key findings from testing, and recommended areas for future development are discussed in this report.

ABSTRACT

The commercially available process monitoring software Process Pulse (PP) by Camo Analytics was evaluated for real-time monitoring to improve radiochemical processing and control for the ^{238}Pu Supply Program. PP was tested during two monoamide solvent extraction (P5MX) runs and three plutonium anion exchange column runs (P5AXPu). Concentration profiles of Np in multiple valences were monitored continuously for several days with PP during P5MX solvent extraction runs. Univariate calculations (i.e., Beer's law) were used to show trends in Np concentration profiles. PP was also used to automate multivariate calculations during each AXPu column run in Campaign 5. A partial least squares regression (PLSR) analysis was used to predict concentrations of Pu(III), Pu(IV), Pu(VI), Np(IV), and Np(V) in the effluent streams from convoluted ultraviolet visible (UV-Vis) absorption spectra. Action items were included in PP configurations to advise technicians when to make important processing decisions (e.g., cut to collect the Pu product). Online monitoring will help prevent faulty batches, improve product consistency and quality, optimize resource use, reduce waste, and lower operations and resource costs. Once PP is fully integrated, it will help close the gap between research and development and production and allow technicians to operate optical spectroscopy for the routine analysis of radiochemical processing streams.

1. BACKGROUND AND MOTIVATION

1.1 PLUTONIUM-238 CHEMICAL PROCESSING

1.1.1 Characterization Needs

In 2011, the US Department of Energy and the National Aeronautics and Space Administration (NASA) initiated efforts to reestablish the domestic production of ^{238}Pu heat source material to power NASA spacecraft for deep space missions. Their efforts were successful and new ^{238}Pu was produced at Oak Ridge National Laboratory (ORNL) for the first time since US production ceased nearly 30 years prior. The ^{238}Pu Supply Program is scaling up production to meet NASA's projected needs (1.5 kg of plutonium oxide [PuO_2] per year on average) by 2025.

Targets containing ^{237}Np are irradiated in the High Flux Isotope Reactor and processed at the Radiochemical Engineering Development Center (REDC) before shipment of pure PuO_2 to Los Alamos National Laboratory. The chemical processing flow sheet for the recovery of the ^{238}Pu product comprises many steps (Figure 1.1). These steps include the preparation of neptunium oxide (NpO_2) feedstock for target fabrication, dissolution of irradiated Al–NpO_2 cermet pellets, selective Pu solvent extraction for the removal of fission products, separation of phosphorus and most of the Np from the Pu product by anion exchange, and conversion of each Pu and Np product stream back to oxide form. Efforts continue to seek improvements for the flow sheet while also minimizing cost, waste generation, and improving operations using the existing infrastructure within regulations at REDC.

One of these efforts focuses on optical spectroscopy and online monitoring, which are used to measure the oxidation state of Np and Pu and provide real-time process feedback. It is crucial to determine the valence composition of processing solutions (e.g., feed adjustments). Additionally, real-time process monitoring helps ensure that the solvent extraction mixer-settler and ion exchange column runs perform satisfactorily. Without real-time monitoring, the chance for process deviations would increase and could lead to rework. The program may not have the time nor infrastructure to rework materials when running multiple overlapping production campaigns in a year, a feat necessary to meet scale-up goals. Ultraviolet-visible-near-infrared (UV-Vis-NIR) spectrophotometry is the only functioning tool currently available for the program to acquire this essential information.

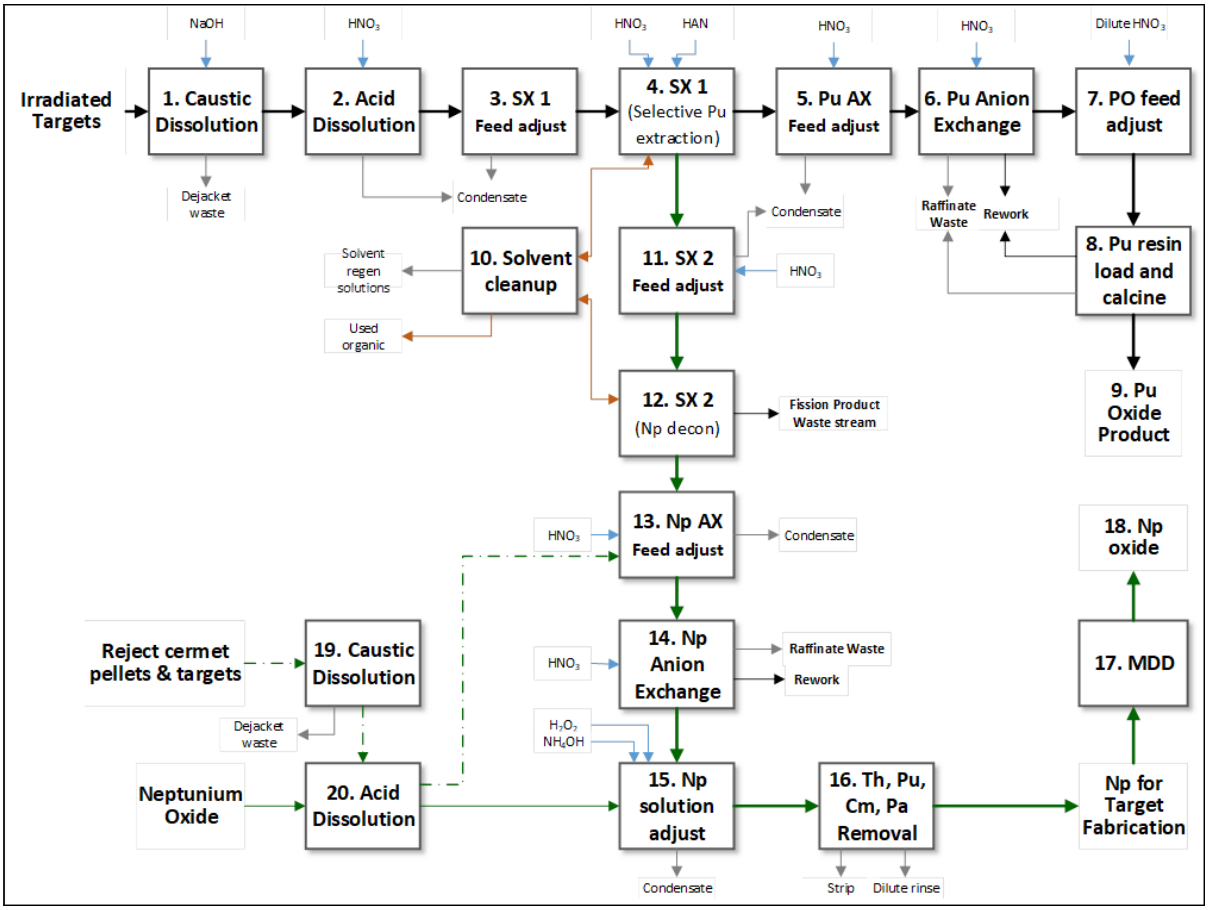


Figure 1.1. Example flow sheet for the Pu-238 Supply Program in Campaign 4.

1.1.2 Spectrophotometric Measurements and Manual Calculations

Chemical processing takes place in heavily shielded hot cells at REDC, which makes the timely quantification of samples by traditional analytical approaches (e.g., inductively coupled plasma mass spectrometry) challenging. Traditional methods require grab samples that need to be transferred across hot-cell cubicles or out of the hot cell entirely and require large dilutions of 1,000–10,000-fold. It generally takes anywhere from several hours to several days before results are attained. These techniques are not amenable to monitoring radiochemical separations in real time to inform process decisions and are not sensitive to the valence states of Np and Pu. On the contrary, optical spectroscopy can be used to simultaneously quantify the concentration and redox state of Np and Pu in situ and in near real time. Spectroscopic analyses can be performed remotely with fiber-optic cables that transport light between the control room and the hot-cell cubicles. UV-Vis-NIR absorbance spectroscopy has been used with great success since the program began. The desired level of precision and accuracy of spectrophotometric measurements required for each process in the flow sheet (Figure 1.1) varies significantly.

UV-Vis-NIR spectrometers acquire spectra that must be converted to process variables such as concentration. The concentration of analytes in solution is generally approximated by Beer's law calculations using molar extinction coefficients from the literature or values acquired by comparing spectra with samples analyzed by the analytical group. Univariate methods (e.g., Beer's law) can be applied to situations with good spectral resolution between peaks from different species and potentially in situations where accuracy isn't essential (even if some overlap exists). This single-variate approach has been used by staff and technicians and the arithmetic has been done "by hand," typically using a calculator or Microsoft Excel.

In systems with overlapping peaks (e.g., acid digest sample), deconvolution has been used with great success (Figure 1.2). Both accuracy and precision were desired in this example. The acid digest sample (containing Np, Pu, and fission products) was diluted seven-fold in water before analysis to reduce the absorbance of the sample to within the dynamic range of the spectrometer. Each spectrum was examined manually in Excel by deconvoluting the spectrum with historical reference spectra of each species present in the solution [i.e., Np(V), Pu(IV), and Pu(VI)]. The scaling factor applied to each reference spectrum was varied to minimize the residual difference between the sum of each contribution and the actual absorbance spectrum (Figure 1.2). This analysis was done after the data were collected either manually or by using the Solver program in Excel to determine the contribution of each species (Figure 1.3).

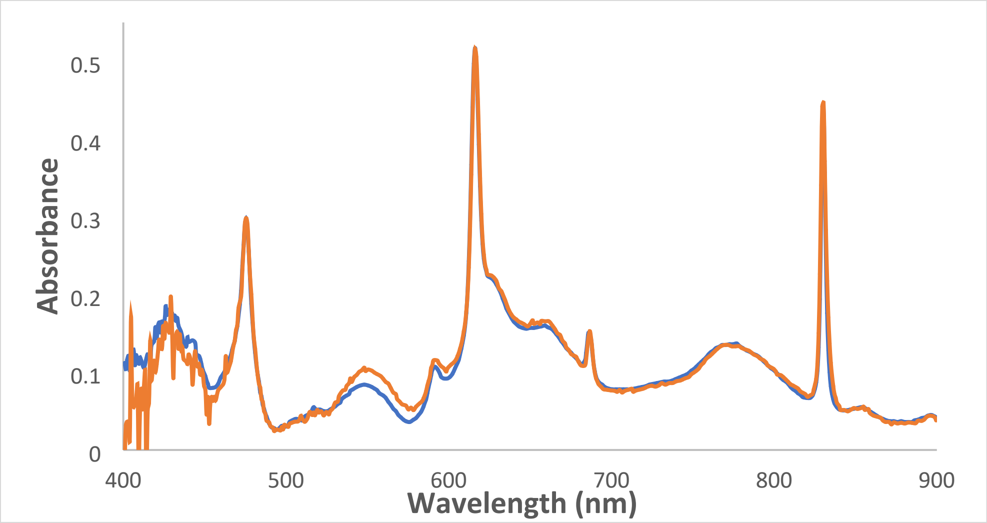


Figure 1.2. Actual absorption spectrum (blue) for a diluted sample of dissolved target solution compared with the modeled fit (orange).

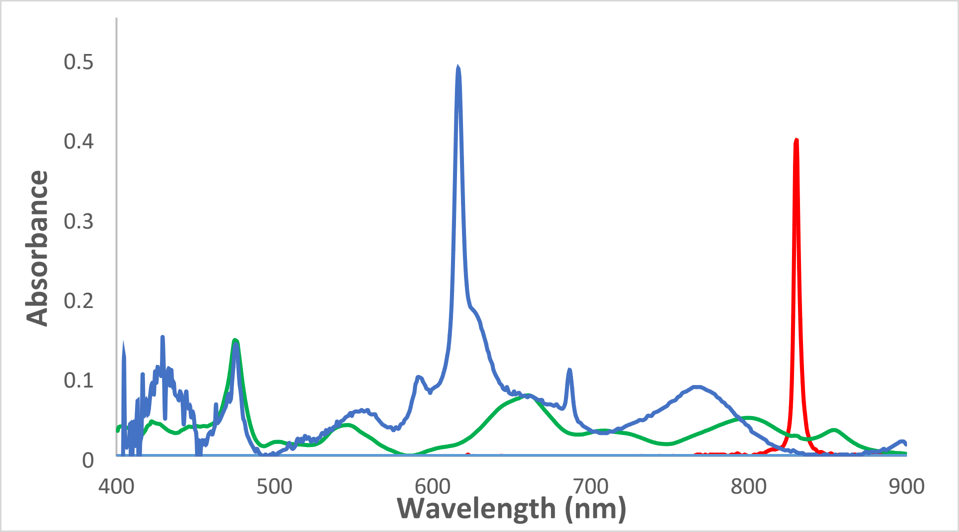


Figure 1.3. Individual components summed to fit spectral data for sample in Figure 1.2. Np(V) in blue, Pu(VI) in red, and Pu(IV) in green.

The results were promising. UV-Vis spectrophotometry measured 43.9 g Np/L and 4.7 g Pu/L, whereas the analytical group reported 46.8 g Np/L and 5.2 g Pu/L (±10%). The differences could be due to a lack of accurate reference data, particularly for the contribution of Pu(VI), which has spectral features that vary as a function of acidity, or any number of additional factors. Spectrophotometry reported results within 6% of analytical for Np and 10% for Pu concentration, provided the valence distribution of both Np, and Pu, required minimal dilution, and did not require transferring the samples out of the hot cell. These data show that UV-Vis spectroscopy can be used for informing process decisions while keeping the samples in cell. With the right equipment and glove box testing, these measurements may be accomplished without sample dilution and provide a sufficiently precise measurement for Np and Pu for process decisions independent of grab samples measured by the analytical group. This approach could be of even greater benefit to the program with multiple developments: (1) the calculations could be performed and viewed in real time, and (2) action items could be associated with the derived process variables. These developments would improve the timeliness of spectroscopic measurements and help the method be handed off to technicians for routine analysis. It is recognized that the real-time spectrophotometric measurements will not be used for inventory purposes; that data will be obtained through established sampling and analysis procedures.

1.1.3 Online Monitoring for Real-Time Analysis

Spectrophotometric measurements in the hot cells are acquired rapidly (~100–2000 ms). If the spectral data were evaluated with an online monitoring software system, it may provide the ^{238}Pu Supply Program with the ability to make processing decisions in real time during radiochemical separations. Online monitoring capabilities can be used to identify deviations from normal operating procedures so that technicians can readily adjust processing parameters for successful operations and inform timely process decisions. During production Campaign 4, Python scripts were written to provide Beer's-law-type calculations and partial least squares (PLS) predictions in an open-source integrated development environment, Spyder. This approach, which sought to develop a process monitoring software nearly from scratch, required a large amount of developmental work and continuous updates. Prepackaged software systems that can be used convert spectral signatures to analyte concentration and view the data in real time had not been tested until recently.

A commercially available process monitoring software was evaluated during a four-month trial period during production Campaign 5. PP is the industry-leading software that can be applied to a large variety of processing applications. This software was evaluated to determine whether it could make spectroscopic measurements more organized, timely, and informative for the ^{238}Pu Supply Program. is the software is advertised as a user-friendly system that will allow technicians to manage processing operations, thereby allowing scientists to generate training sets and build models that will improve the feedback and measurements automated by PP. Two main hubs are envisioned where this software could be operated on a routine basis. One computer (user) would operate from the control room and another in the Np pellet fabrication lab, Laboratory 109. Thus, at least two simultaneously operating iterations of the software will be needed. It may also be desirable to have another simultaneous user who could help from their office space. In addition to simultaneous users, the software must also manage multiple processing events simultaneously.

1.1.4 Software Requirements

The following list contains the software requirements identified by staff members. PP was evaluated against these criteria and the results can be found in Section 3.3.

1) **Stable.** The software does not crash if the internet/server crashes and can be easily restarted if necessary.

2) **Large data sets.** The software can collect multiple data sets composed of thousands of spectra across several days while quickly responding and not crashing.

3) **Technician friendly.** Technicians can navigate the software with relative ease and feel comfortable with the software.

4) **Real-time analysis.** Perform Beer’s law and multivariate calculations on spectral data collected in real time.

5) **Pretreatment options.** Pretreat spectral data before analysis with at least the following options: derivatives, baseline offset, smoothing, standard normal variate (SNV), and normalizing.

6) **Actionable items.** Provide warning/alarms with actionable items to help guide process decisions.

7) **Data historian.** Stores the data in a logical format that is easily retrievable.

8) **Multiple data sources.** Software can import files that are compatible with other software.

9) **Data import.** Imports numerous file types (e.g., ASCII and Excel) at once.

10) **Server.** Output processed spectral data directly to the server

11) **Compliant.** Software adheres to a compliance audit.

12) **Validated.** Software is properly validated.

13) **Security.** Software is compatible with internal security requirements.

14) **Compare historical data.** Visualize and compare multiple experimental runs (central data matrix).

15) **Multiple users and configurations.** Consists of at least four simultaneous configurations and two simultaneous users.

16) **Connects to spectrometers.** The software can directly connect to Ocean spectrometers such that PP is the only software required during a processing event.

17) **Web terminal.** View data online from on-site or off-site locations. Allows ten or more users to access at once.

2. PROCESS PULSE SOFTWARE

2.1 SOFTWARE DETAILS

2.1.1 General Software Information

PP is an intuitive, process monitoring software that reads data from numerous sources, executes a wide range of multivariate models available in The Unscrambler software package, and presents the data/results as they are gathered. The flexibility and capabilities of the software can be applied to numerous applications. A variety of data preprocessing transformations are available in The Unscrambler, including filling missing values, smoothing, normalization, multiplicative scatter corrections, derivatives, averaging, SNV, centering, weighting, transposition, adding noise, and user-defined transformation. Numerous multivariate techniques are also available and include principal component analysis, multivariate curve resolution (MCR), cluster analysis, multiple linear regression, principal component regression, and PLSR.

The italicized words throughout this section will be described in more detail in Section 2.1.3. The PP software is equipped to analyze all types of *data sources* (e.g., sensor and spectra) with direct import from analyzers (e.g., Ocean spectrometers) or direct import of files saved within a “watch” folder (e.g., ASCII and Excel). Process monitoring is visualized from the *dashboard* where early fault detection, process deviation warning(s), and optimization(s) are clearly visible through interactive charts. The dashboard contains intuitive tools for each role, including data scientists, engineers, technicians, and quality managers. Multiple users can view the dashboard from the *web terminal* using personal computers/phones. Thus, process engineers can visualize real-time hot-cell measurements from a remote location firsthand. From the web terminal, running *configurations* are selected, and users can specify which plots and data they wish to observe. Configuration(s) can be started from the web terminal, but they cannot be altered or stopped.

The type of method (e.g., no model), data source (e.g., Ocean spectrometer), transformations (e.g., baseline correction), calculated columns (e.g., Beer’s law calculation), external output information, notifications, and permissions are all specified in a configuration. *Notifications* (i.e., warnings and alarms) can be specified in configurations to inform the operator when to make decisions and offer predefined support (e.g., user defined, multiple criteria, and trend alarms). Warnings are shown in amber, and alarms are shown in red. These notifications appear in the *main view* and in the *warnings and alarms* tile in one of the *bottom tiles*. Warnings generally correspond to control limits. Warning notification(s) will provide a technician with the appropriate action to avoid any further issues if the variable is too high or too low. For example, if the Pu concentration goes above a user-defined concentration limit during a solvent extraction run, the software may be configured to warn operators with a message that tells them to increase the flow rate of a given stream at a predefined interval. Email messages containing notification details can also be configured so that process engineers may be aware of such processing events. *Trend analysis* allows users to interactively review trends in running configurations by looking at the *n* most recent windows over a given time frame. *In-process control* samples can be registered during process monitoring to store specific measurements. A record of in-process control sample results can be readily included in the reports and data reviews to allow the data to be efficiently viewed post-analysis.

The software can generate reports that provide a summary of the run and are defined in a *report template*. Data can also be viewed using the PP *data historian*. The historian keeps a record of the time each measurement is recorded, spectrum files, annotations, flags, comments, warnings, and so on. *Annotations* can also be added/edited as required post-run. Users can be specified and granted different levels of access to configurations including view, run, and/or modify. In off-line data, previous runs of a configuration can be overlaid with the current run in a combined plot. The data are aligned by user defined flags.

Spectral data transformations available in PP include the SNV, Savitzky-Golay (SGolay) derivative, baseline (linear and baseline offset), normalize, and SGolay smoothing for “no model” configurations. Real-time measurements are calculated by univariate methods (e.g., Beer’s law) specified within “no model” configuration. Raw, processed, and calculated data files (e.g., spectra and measurements) are saved within the PP historian and can be exported as Unscrambler, ASCII, and Excel files. This type of calculation may be useful for several processing events (e.g., Pu solvent extraction) in which relatively few species need to be quantified [i.e., Np(V) and Pu(III)] and they each have resolved absorption bands. Additionally, multivariate calculations are possible when running configurations with models (e.g., PLSR) built using The Unscrambler software package. These will be needed for processing events (e.g., Pu anion exchange) in which numerous species simultaneously exist with convoluted spectral features.

2.1.2 Installation Configuration

The PP *main service*, calculation engine, data collector, dashboard, and web terminal were installed on a local server. Additionally, the dashboard and data collector were installed on the local machine (i.e., T3630 workstation, Intel Core i9-9900K) located in the 7920-control room. The newest version of Oceanview software (2.07) was also installed on the PP computer. The PP computer was not granted access to connect to the REDC server because it can be logged into with a shared user identification (UID) account. Connecting to a server or another shared location is desirable because it would allow data to be easily transferred, avoid the need to manually retrieve the data with a USB, and provide another backup for the data files. The computer has a UID that was shared with each trustee, including shift workers and research staff. The computer has direct remote access from office desktop computers under the shared UID account. When logged in with the shared UID, elevation privileges do not work because it is not a Universal Computer Access Management System ID. The computer system is fully patched and managed by the information technology group to avoid network restrictions.

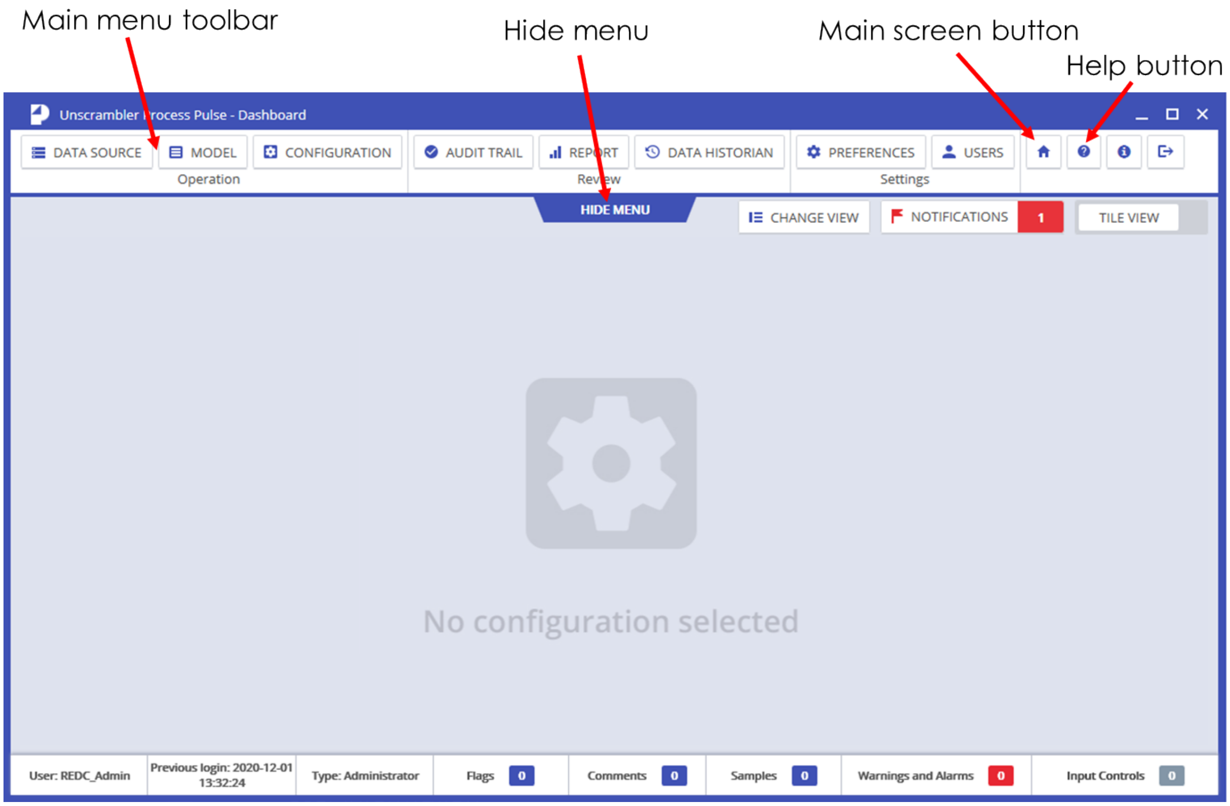
PP will be used for long experiments/data collection time frames (i.e., several days) and cannot be rebooted unexpectedly. Thus, an alternate patch schedule was proposed of the first Friday of every month. If the patch cannot occur on the prescribed day, the system will be patched within ±3 days of the first Friday of the month. Cybersecurity needs to be notified if this will happen or the system may be rebooted in the middle of a processing event. An information technology staff member will patch the system at the prescribed interval. The computer needs to be restarted after the patch takes place to avoid updates taking place in the middle of processing events. The system should be rebooted periodically with instructions included in the workflow.

Additional prerequisites, installation, and software update details can be found in the installation manual at the following link:

https://camo.com/downloads/products/ppii/5.60/Unscrambler%20Process%20Pulse%20-%20Installation%20Manual.pdf.

2.1.3 Getting Started with the Software

Opening and logging into PP opens the dashboard. Several key dashboard features are labeled (Figure 2.1). The dashboard refers to the comprehensive user interface where all functionalities are available and managed and is split into three sections: (1) the main menu toolbar, (2) the main view, and (3) the bottom tiles. Data sources, models, configurations, and the data historian can all be accessed from the main menu toolbar. Running configurations can be started, stopped, and viewed from the dashboard. The results plot(s) of running configurations are seen in the main view.



User: REDC_Admin

Previous login: 2020-12-01 13:32:24

Type: Administrator

Figure 2.1. Dashboard example with key features listed.

2.1.3.1 Main View

Once a configuration is started, it appears in the main view if the user logged into the system has been granted the appropriate permissions (Figure 2.2). For this example, three configurations have already been set up and started. This three-configuration setup was used to monitor the Pu anion exchange column runs. Configuration details are discussed in Section 2.3. Seven important features are labeled, and the descriptions for each are listed below. Transformed spectra data are viewable by clicking the sandwich icon in a running Configuration and selecting plots, transformed raw data, and spectral. Annotations add information to specific data points and can be added by right-clicking data points on a plot and selecting annotation management.

1) **Configuration card.** Clicking the configuration card will minimize the running configuration, and another click will open it again. The blue marker at the top indicates that the configuration is in view, and a red marker indicates that it is not in view (but still running in the background). In the example

shown in Figure 2.2, two of the three running configurations are in view. This card turns amber when warnings are triggered and red when alarms are triggered.

2) **Change view button.** This button allows users to organize multiple running configurations by changing the position of the configuration cards. Clicking this button toggles between viewing the configuration cards horizontally on top of the running configurations or vertically on the left side of the configurations.

3) **Notification button.** The button lists all active notifications from each running configuration. These will remain listed even after the configurations are stopped. They must be acknowledged to be removed from view (click button next to each notification).

4) **View toggle.** This tiles button allows users to toggle between multiple running configurations side by side (maximum of 10) or view only one configuration at a time.

5) **Data points.** In this example, the Np/Pu ratio configuration has two plots and the AXPu PLS_SGolay_downweighted configuration has four plots. Plot types can be customized in each configuration during setup. Once changed, the layout is stored for each user when logging in and out again unless a new revision is made.

6) **Spectra.** In this example, raw spectra were plotted as they were loaded in PP. Right-clicking the sandwich in this windowpane allows users to specify which kind of data are viewed. For example, preprocessed spectral data could also be plotted.

7) **Data points.** Data points like the absorbance value at specific wavelengths can also be plotted to view relative changes over time.

8) **Bottom warnings and alarms tile.** Clicking this tile opens a box that shows the warnings and alarms for the current each running configuration. When a notification appears, this tile must be selected to reveal the action item associated with each notification.

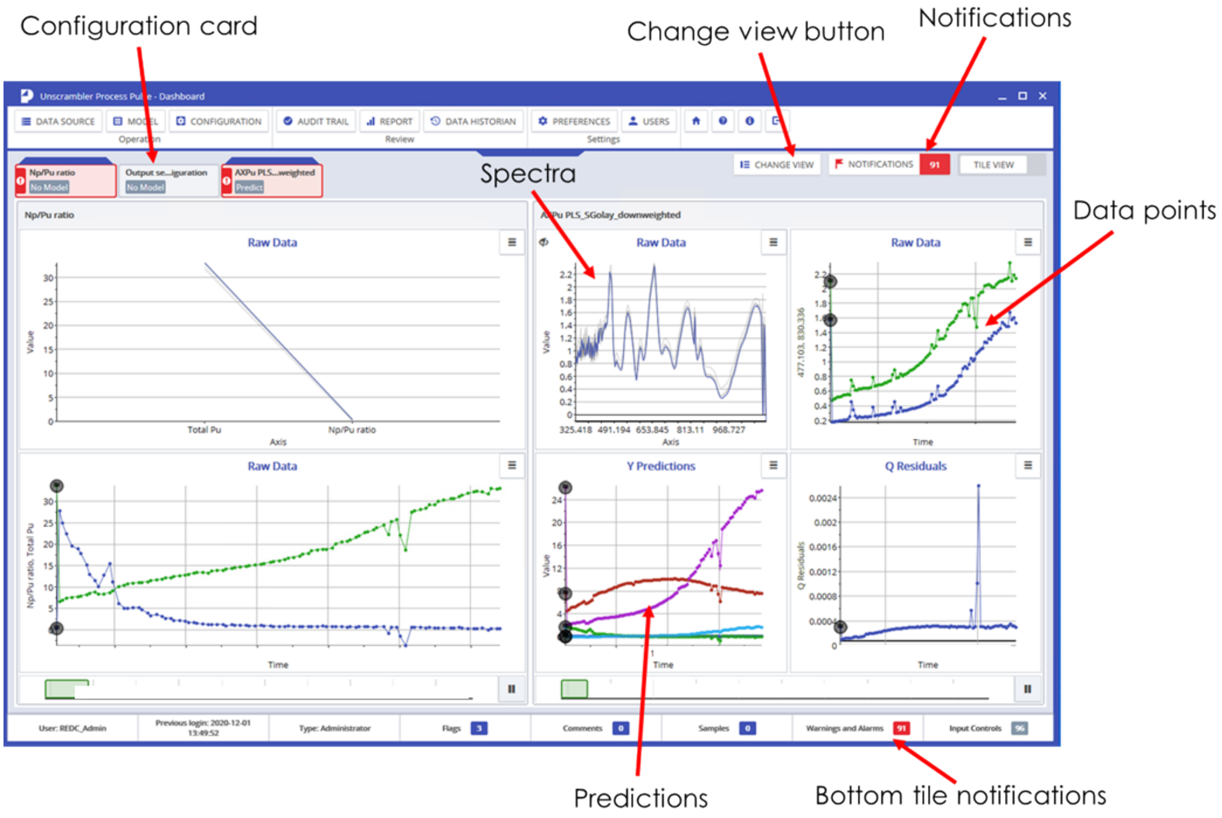


Figure 2.2. Main view with running configurations.

2.1.3.2 Data Sources

PP connects to data sources to retrieve data like ASCII UV-Vis spectra files. The data sources can be organized into four separate categories, including *Folder read-out*, *database*, *instrument*, and *others* (Table 2.1). Both folder read-out and instrument data sources were tested during the evaluation. The types of data sources available for PP continue to increase with each new version of the software. Additional data sources, like specific instrumentation not listed here, can be added for a fee.

Table 2.1. PP data source types

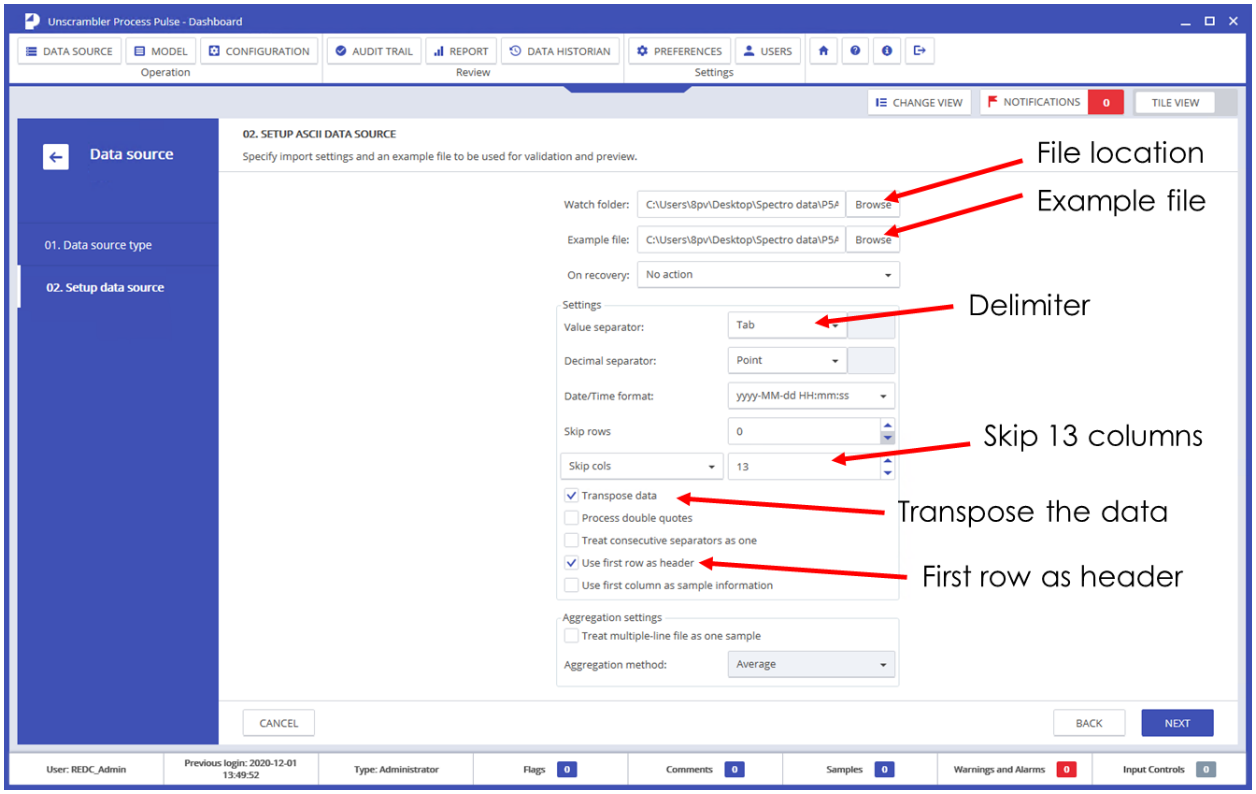
Folder read-out	Database	Instruments	Others
XML	LIMS	Bruker	Manual Sampling
OMNIC	ODBC	B&W Tek	Modbus
OPUS	PI	Kaiser	Pretreatment
VIAVI.SAM	PI AF	Keit	TCP/IP
GRAMS	–	Mettler Toledo	OPC DA
Brimrose	–	Viavi MicroNIR	OPC UA
Empower	–	Zeiss	OPC DA Spectral
JCAMP-DX	–	Ocean Optics	–
Image	–	Parsum	–
Excel	–	Sentronic	–
ASCII	–	tec5	–

The data source management page can be opened by clicking data source in the main toolbar. When using folder read-out mode, PP monitors a watch folder for new file activity—either new files being added or changes to existing files. To configure a data source, the data collector must be installed on the local machine and they are only accessible to the local machine. The following list describes the steps necessary to configure a new ASCII data source. Simply click next between each step in the setup to move to the next page.

1) **Add new source.** Selecting this button launches the process for connecting a new data source.

2) **Type.** Here the user will name the data source, specify which type (e.g., ASCII), and the location (local).

3) **Import settings.** The layout of the ASCII file must be specified. Specify the watch folder location on the desktop and select one example file. The sample file will normally be a "blank" spectrum. Several settings must be selected for the spectral files generated by the new Oceanview software. These settings include tab delimited, skip columns (13), transpose data, and use first row as header (Figure 2.3).



02. SETUP ASCII DATA SOURCE

Specify import settings and an example file to be used for validation and preview.

Watch folder: C:\Users\8pv\Desktop\Spectro data\P5A Browse

Example file: C:\Users\8pv\Desktop\Spectro data\P5A Browse

On recovery: No action

Settings

Value separator: Tab

Decimal separator: Point

Date/Time format: yyyy-MM-dd HH:mm:ss

Skip rows 0

Skip cols 13

☑ Transpose data

☐ Process double quotes

☐ Treat consecutive separators as one

☑ Use first row as header

☐ Use first column as sample information

Aggregation settings

☐ Treat multiple-line file as one sample

Aggregation method: Average

User: REDC_Admin
Previous login: 2020-12-01 13:49:52
Type: Administrator
Flags 0
Comments 0
Samples 0
Warnings and Alarms 0
Input Controls 0

Figure 2.3. Layout required to import and read Ocean UV-Vis spectra files.

1) **Assign variable alias.** The process values should be selected, and the wavelength values will fall under Current name and absorbance values under value. These values should match the structure of the file specified in the watch folder.

2) **Run mode settings.** Here the run mode is specified as either normal, external trigger, or self-trigger. Normal is the default run mode. This mode is used for configurations that are manually started by the user. Configurations can be triggered by predefined requirements and would require external trigger options to be defined in respective data sources.

3) **Preview.** The imported file can be previewed on the final page. It should look like the file specified in the watch folder, which in this case was a “blank” UV-Vis file (Figure 2.4). Select finish to create the new or updated data source.

325.418	326.214	327.011	327.807	328.603	329.399	330.195	330.991	331.787	332.583	33
-0.01080597	-0.00870021	-0.01295675	0.00568067	-0.00081762	0.0057962	0.00027777	0.01904742	-0.00081762	-0.0030594	0.0

Figure 2.4. Preview of imported spectral ASCII file.

Notably, the Oceanview software cannot be open while attempting to connect a spectrometer to PP. The spectrometers cannot connect to both software systems at the same time. Also, PP cannot connect to multiple spectrometers from the same computer simultaneously. The Oceanview driver will override PP. Spectrometer data sources can be refreshed (blanked) without altering the data source and creating a new revision. This is advantageous because the configuration’s setup to pull data from the Ocean spectrometer will not require a continuous update each time the spectrometer is blanked. The following list contains the steps necessary to configure an instrument (i.e., Ocean) data source. The spectrometer must be connected to the machine running the dashboard (no remote configuration). The Data Collector software and Ocean Optics Omnidriver must be installed.

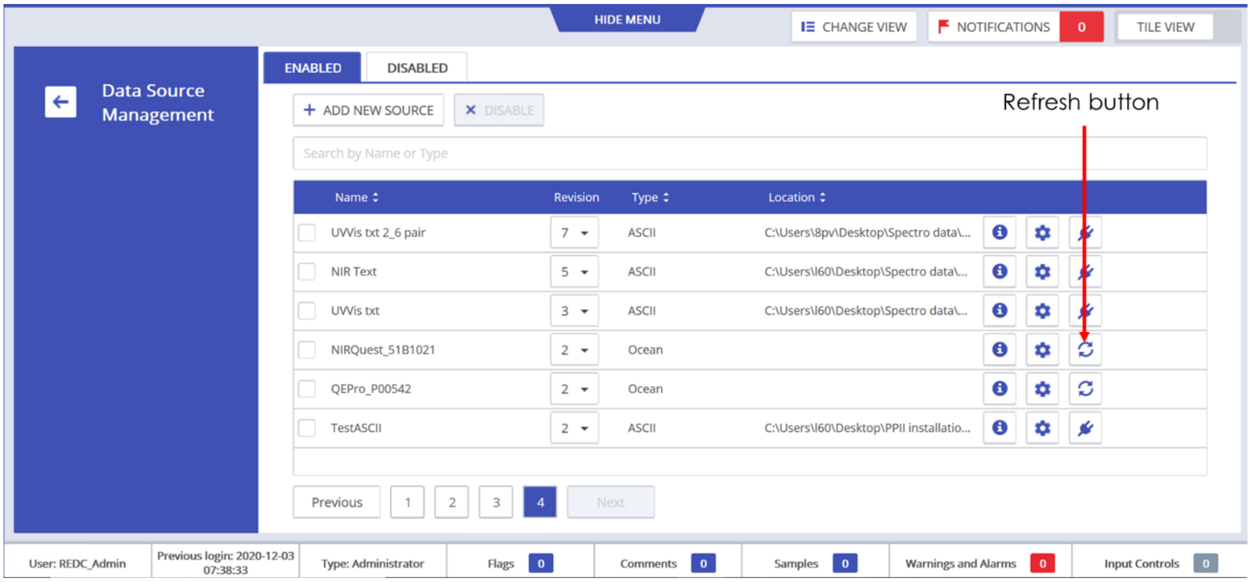
1) **Add new source.** Selecting this button launches the process for connecting a new data source.

2) **Type.** Here the user will name the data source and specify “Ocean” as the type.

3) **Set up Ocean data source.** Make sure the correct spectrometer is selected. Specify polling (e.g., save the spectrum file every 2 s), the integration time, and the number of scans to average.

4) **Reference scans.** Perform light and dark reference scans.

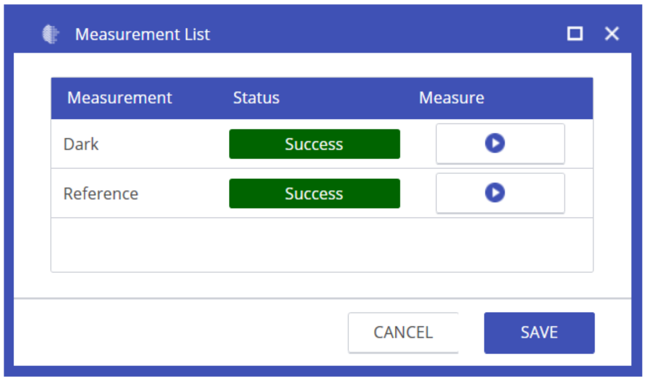
5) **Refresh.** This button is only available for instrument data sources. It allows the user to update the reference measurements (i.e., blank the spectrometer) without making additional changes to the data source information, as shown in Figure 2.5). The dark and reference spectra will be recorded by selecting the play button shown in Figure 2.6. The Status button color will change from gray to green when the measurements are collected.



Name	Revision	Type	Location
UVVis txt 2_6 pair	7	ASCII	C:\Users\8pv\Desktop\Spectro data\...
NIR Text	5	ASCII	C:\Users\I60\Desktop\Spectro data\...
UVVis txt	3	ASCII	C:\Users\I60\Desktop\Spectro data\...
NIRQuest_51B1021	2	Ocean	
QEPro_P00542	2	Ocean	
TestASCII	2	ASCII	C:\Users\I60\Desktop\PPII installatio...

User: REDC_Admin
Previous login: 2020-12-03 07:38:33
Type: Administrator
Flags 0
Comments 0
Samples 0
Warnings and Alarms 0
Input Controls 0

Figure 2.5. Data source management page with refresh button next to an Ocean data source labeled.



Measurement	Status	Measure
Dark	Success	
Reference	Success	

Figure 2.6. Measurement list.

2.1.3.3 Configurations

A configuration is typically set up by a developer and combines a data source, model(s), notifications, and output in the setup. After setup, the configurations can be used by technicians for routine process monitoring. Numerous configuration types exist in PP, including no-model, prediction, batch, dynamic MCR, and so on. The configuration type must have the same name as the model. No-model, dynamic MCR, and dynamic PCA configurations can collect and store data without predefined models.

A user can create a new configuration by selecting “new configuration” button in the configuration tab selected from the main menu toolbar (Figure 2.1). The following list describes the steps required when setting up a configuration.

1) **Configuration name.** The user must give the configuration a name. The user will be warned that they are going to modify an existing configuration when making changes to an existing configuration. It will create new revisions of the model, and the old revisions will still be accessible.

2) **Configuration type.** The user must also select a configuration type in the first setup page.

3) **Choose model.** The user must select a model. This does not apply to no-model configuration types. These models must be built using The Unscrambler and uploaded PP. They can be selected from a drop-down menu.

4) **Choose a data source.** The next step will be selecting a data source and the appropriate version number. In general, these will either be Ocean spectrometers or file folders (i.e., watch folder).

5) **Output.** In this section, the user will decide which results and graphs they wish to be available for plotting. These options will depend on the type of model and may include results such as scores, raw data, and outlier detection (e.g., Q residuals and influence plots). In general, these are not necessary to include.

6) **Layout.** The user can modify the layout on the Layout setup page and define what kind of information goes into each plot. Information displayed in these plots can be changed during process monitoring.

7) **External output.** The user can write data or results to third-party systems with PP. The output information is exported in parallel to the data being saved in the PP database. The process information (e.g., measured concentrations), file type, file name pattern, file structure, and destination must be specified.

8) **Notifications.** The user can specify notifications for each configuration. Notifications consist of warnings and alarms that are based on user-defined process limits. Exceeding the specific control limits triggers notifications and provides information to the operator about which steps to take to avoid further issues. Trend alarms are based on a series of measurements and triggered by a set of samples meeting a user defined limit equal to or less than the window size (e.g., 2 out of 3). Notifications can be provided to the operator in four distinct ways: (1) coloring of the configuration card, (2) the warnings and alarms bottom tile, (3) the notifications list, and (4) email notifications (optional). The first tab on the notifications page lists the defaults alarms from the Unscrambler X model type (if available). These can be disregarded if desired by clicking the *Ignore* button. User-defined, multiple-criteria, and trend alarms are all available options, and each can have a custom message associated with it. These alarms can be based on variables available in the data source used and output variables from the configuration (e.g., predicted Y values). Email and text (by phone number and carrier email address) recipients (users) for each notification can be set by checking the email checkbox and specifying the number of emails per minute. Users are created and defined by selecting "Users" on the main menu toolbar and defining the relevant information. All notifications for a configuration must have a unique name. When the same notification is repeated for successive samples, the total number of occurrences is displayed.

9) **Permissions.** Here the user can specify which users and groups will have permission to view and/or edit the configuration.

10) **Summary.** This page summarizes all the settings defined in the configuration setup. Selecting finish completes and creates the new configuration.

2.1.3.4 Data historian

The data historian is located on the main menu toolbar and includes data search, model search, flag search, central data matrix search, and data import. Users can review data from previous configuration runs using data search. The plots and interaction tools available during the run will also be available for the review. A list of annotations will be available for viewed and edited as required, and new annotations can be inserted if necessary. Annotations are split into flags, comments, or samples. Search options include the configuration name, revision, data source name, and the date/time. The refresh button can be used to upload new data that haven't populated yet. The data (e.g., spectra files) can be downloaded as an Excel file or pushed to The Unscrambler for further data analysis.

Additional details can be found in the PP user manual at the following link:

https://camo.com/downloads/products/ppii/5.60/Unscrambler%20Process%20Pulse%20-%20User%20Manual.pdf

3. PROCESS PULSE DEMONSTRATION AND EVALUATION

3.1 NEPTUNIUM MONOAMIDE EXTRACTION

3.1.1 Monitoring Goals and Scope

The ^{238}Pu Supply Program uses solvent extraction to purify the Pu product stream and the Np recycle stream. A large portion of the ^{237}Np irradiated in the High Flux Isotope Reactor does not convert to ^{238}Pu and requires purification before refabrication into mixed NpO_2–Al cermet targets. Liquid-liquid solvent extraction is used to accomplish a large portion of the purification. The process separates Np from most of the fission products accumulated from neutron irradiation. The extractant tri-butyl phosphate (TBP) has been used in every production campaign prior to Campaign 5 for both Pu and Np liquid-liquid extraction applications. During Campaign 5, a monoamide-based solvent extractant was implemented to purify the Np rework stream. Monoamide extraction has several operational benefits over the TBP system, and these will be discussed in another report.

Before the solvent extraction run, the feed must be monitored to quantify the oxidation state of Np during the feed adjustment and the concentration of nitric acid. Both parameters are critical for a successful solvent extraction run. Monitoring the extraction banks in real time during the mixer-settler runs is also useful to gauge the success of the run and whether modifications to operations (e.g., flow rates) are required to improve the run. The ability to monitor the valance of Np in real time is important to optimize run performance and ensure the run is proceeding as planned.

Solvent extraction runs will benefit from real-time spectroscopic measurements that determine whether Np is being extracted into and/or stripped from the organic phase before exiting the mixer-settler with the aqueous raffinate or unloaded organic solvent. The new PP monitoring tools are independent of the extractant used in the process because the analysis is focused primarily on the aqueous phase. This methodology will readily apply to systems using either TBP, monoamides, or another variation of an extractant. Additional advancements would be required to monitor the organic phase. The scope of the remainder of this section is to discuss how UV-Vis-NIR spectroscopy and the PP software were used to monitor Np concentration profiles during mixer-settler monoamide extraction runs in Campaign 5. It also discusses improvements that could be included in future runs.

3.1.2 Process Pulse Demonstration in Campaign 5

In Campaign 5, the Np valence and concentration profiles in both the A- and B-banks were monitored using UV-Vis-NIR spectroscopy and Hellma UV-Vis 5 mm in-line dip probes placed in various stages of a mixer-settler system. Spectra were collected in the A bank to monitor the valence and concentration of Np in the 4+, 5+, and/or 6+ oxidation states. Collecting both UV-Vis and NIR spectra is advantageous because the main Np(VI) absorption band is in the NIR region (peak at ~1,222 nm) and the Np(IV) species are best detected in the UV-Vis region (~700 nm). This requires two separate spectrometers and two running configurations. The B-bank was also monitored for Np(V) and Np(VI) concentration using a 5 mm dip probe to make sure that the Np was being extracted in the A-bank and then stripped in the B-bank before exiting with the unloaded organic solvent.

PP was tested during the P5MX-1b and P5MX-2 solvent extraction runs. In both runs, Np was converted to Np(VI) during the feed adjustment. During P5MX-1b, two configurations were executed simultaneously to plot the UV-Vis and NIR spectral data. The spectrometers were connected to the Oceanview software, which was used to save spectra ASCII files every 20 seconds over several days. Multiple PP configurations rapidly pulled txt files from individual watch folders as they were created. Spectra, data points, and calculated values were viewable in continually updated plots in the main view. Multiple researchers were able to view the dashboard and each running configuration from the web terminal during the run. These researchers logged in with the same UID credentials. Since then, separate UID credentials have been made for each researcher.

No catastrophic errors occurred during the run. PP effectively collected thousands of files in multiple configurations for the duration of the run. Results were viewable in real time and process variables from the entire run could be viewed simultaneously. Beer's law calculations to calculate Np(V) and Np(VI) concentrations were included in the configurations. The data sources were not set up properly. This resulted in inaccurate process variables (i.e., spectra), causing the magnitude of the calculated concentration to be off during the run. The absorbance bands were slightly shifted in PP, which resulted in skewed arithmetic. In addition to Np concentrations and raw spectra, multiple NIR absorption values, near ~1,220 nm for Np(VI) and ~979 nm for Np(V), were plotted against a baseline value (e.g., 940 nm) to observe changes in system performance. This will not be necessary in future runs if a baseline correction is used. B-bank stage profiles were taken by moving the dip-probe from B16–B4, and Annotations were assigned to each stage position while the measurements were taken. Annotations were also added during the run to account for a variety of processing events such as shaking the probe to fix the baseline and grab samples for analytical measurements. The annotations allowed researchers to keep track of and view events that took place during the run. *Manual sampling* data sources were created for A- and B-bank profile sampling points. These are referred to as in process control samples. They were added as *External samples* to specific data points during the run and time stamped appropriately. PP stored and retrieved this information automatically.

During P5MX-2, four total spectrometers were used, including a pair of UV-Vis and a pair of NIR spectrometers for each bank. The spectrometers were set up to collect spectra at predetermined 20 s time intervals using the Oceanview software. Four separate PP configurations pulled txt files from the watch folders and applied Beer's law calculations in real time. The predominant Np species in the monoamide-solvent extraction run were Np(V) and Np(VI). Each species has characteristic spectral signatures that can be correlated to concentration with univariate and/or multivariate regression approaches. The calculations were accurate and successfully used during P5MX-2 to monitor baseline-corrected Np(VI) and Np(V) concentration profiles during the run. The ASCII files were imported at slightly offset wavelength positions, which resulted in calculations that were somewhat off. This import issue has been addressed, and text files will be imported at the same wavelength positions reported in the Oceanview software.

Several key findings from both P5MX-1b and P5MX-2 are listed in the following items:

- Notably, flow rates (e.g., strip-phase in the B-bank) were adjusted during both runs to optimize performance. The decisions to adjust the flow rates were based on real time feedback provided by spectroscopy and PP monitoring and highlighted the importance of this development work.

- No catastrophic errors occurred during the run despite collecting and processing thousands of files over several days.

- The Beer's law calculations were slightly off because the import into PP shifted the wavelength positions slightly. However, the data will be imported properly in future iterations, and the calculations will reflect what researchers normally calculate "by hand" during the run, provided that the correct molar absorptivity is used.

- The run summary was not accessible on the data historian from the local machine (PP computer) after the run, but the data were viewable from the server where the main service was installed. A very large Excel file with all the data was downloaded.

- PP was unable to generate a report summarizing all the data (~14,000 files) collected during each run. The size of the data set was too large to be processed by PP on the local machine because it is a 32-bit application. The 32-bit application limits the amount of memory it can use. Generating a report is not essential since the data can be exported as an organized excel spreadsheet.

- The data historian is separate from the report generator. This affects report building, because if the data historian is unable to load the data, the report generator will not be able to access it and build a report.

- The data historian and the report generator appeared to work on smaller data sets (<600 files) in controlled tests.

- The annotations assigned to the data points corresponding to each stage position made it easier to go back and analyze B-bank profile data in more detail after the run. Ideally, the software would allow the user to save the spectral text files, in addition to the annotations, while taking grab samples. However, only PNG files of specific spectra at given time points can be saved.

- Notably, once a configuration is started, the calculations included in the running configuration cannot be changed. The configuration must be stopped, adjusted, and then restarted.

- If the Np will be converted to Np(VI) in future runs, as opposed to a mixture of Np(IV) and Np(VI), only two NIR spectrometers may be necessary to monitor each bank. In this situation, UV-Vis data may not be essential.

- Individuals logged into the web terminal must select which variables they would like to view.

3.1.3 Unscrambler and Process Pulse Analysis Post-run

PP can also be used post-run to test new configurations with different iterations of models, notifications, and other features. Historical data can be transferred into a watch folder to test the new parameters. Entire processing events can be recreated in a matter of seconds. This exercise will help staff acquire immediate feedback and examine how the software would have monitored the processing event with each new development.

To test this capability, NIR spectra from the first B-bank profile collected during P5MX-1b were analyzed post-run to develop a multivariate PLSR model in The Unscrambler. Spectra corresponding to data acquired in stages B3-16 were included in the training set. Data from the first profile were used in the calibration set because it corresponds to the time when the concentration of Np was highest during the run and covers the range of anticipated conditions. Np(V) and Np(VI) concentrations were assigned to these spectra using a molar absorptivity of 360 for Np(V) and either 38 for the 1,220 Np(VI) peak or 14 for the 1,178 nm Np(VI) shoulder. Models were tested using untreated, linear-baseline corrected, and SGolay first-derivative transformed data. Data transformation(s) were performed using Unscrambler and registered in the models that were uploaded to PP. A detailed description of how the multivariate models were developed and evaluated will be described in a separate report.

These PLSR models were tested after the run to determine which preprocessing approaches and molar absorptivity values provided the best calibration. ASCII files were dropped into watch folders to recalculate Np concentration profiles. The predictions were compared with grab samples analyzed by the analytical group. The example shown in Figure 3.1 highlights the different profiles generated by altering the training data. The Np(VI) B-bank profile with 38 assigned to the 1,220 peak (a) and 14 assigned to the 1,178 nm peak (b) are shown in Figure 3.1. The Np(VI) concentrations predicted using the model built from the training set, developed with an absorptivity of 14 assigned to the shoulder, matched analytical results more closely than the other set. Calibrating the system using the band near 1,220 nm did not work as well because the spectrometer was saturated near the maximum peak position. PP performed these calculations in a matter of seconds. This feature will allow data scientists to make fine adjustments to the models and test which adjustments make process improvements.

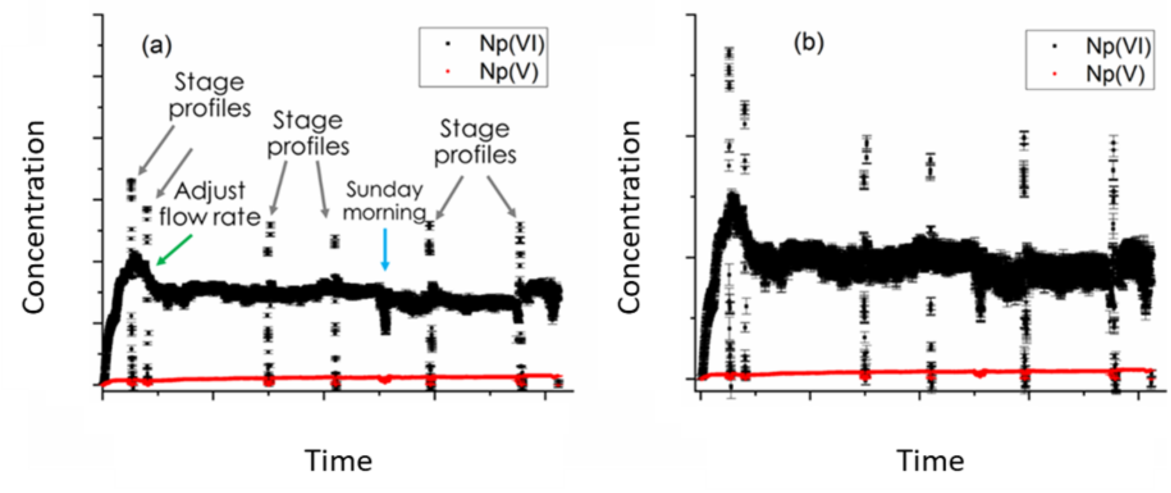


Figure 3.1. Np(V) and Np(VI) B-bank concentration profiles during run P5MX-1b.

3.1.4 Future Work

Several improvements could be made for future production campaigns, including developing enhanced multivariate models, incorporating notifications that provide technicians with clear action items (e.g., increase strip flow rate), and making changes to the equipment. Including the following items will improve the process information and help technicians make decisions without constant supervision.

The following list the most pertinent areas for development.

- Develop configurations with multivariate models and compare with Beer's law calculations. Run configuration on historical data and compare measurements with analytical results.

- Include action items in the configuration that inform technicians on appropriate actions for process adjustment (e.g., whether the strip solution flow rate should be adjusted up or down).

- Include action items in the configuration that will recognize when a probe is damaged, or the baseline is off and inform technicians how to remedy the situation. Shaking the probe every ~20 min could also be included in work instructions.

- Develop a configuration and model to recognize the valence of Np in the feed and inform whether it is ready to go.

- Install a new Hellma NIR dip-probe to improve Np(VI) quantification. This probe transmits light near 1,300 nm better than the UV-Vis probe that was used in Campaign 5.

- If continuous monitoring in B16 is desired, it may be advantageous to use a 2 mm probe instead of a 5 mm probe. With a smaller optical path, the response would likely fall within the dynamic range of the spectrometer.

- The A-bank probe was lost during the run; the exact cause is unknown. It would be useful to include a notification that is based on predefined parameters to inform technicians if this kind of event occurred. Back-up probes need to be available in future runs in case this happens again.

- Give technicians ample opportunity to test the configuration(s) prior to run operations with mentoring from researchers.

- The training set could be further optimized to match the analytical group more closely and calibrate the system.

- Include a linear-baseline correction, at a minimum, to correct for shifting baselines.

3.2 PLUTONIUM ANION EXCHANGE COLUMN RUNS

3.2.1 Monitoring Goals and Scope

The Pu anion exchange column runs in Campaign 5 (P5AXPu) were used to purify a campaign-sized batch of Pu and adjust the acid concentration to provide a proper feed for subsequent Pu cation exchange column runs. Several parameters are critical for the success of the Pu anion exchange column runs. Key analysis points include adjusting Pu in the feed to Pu(IV), identifying Pu(VI) in the effluent, identifying Np(V) and Np(IV) in the effluent, and determining the optimal time to collect the ^{238}Pu product. Much of the work in Campaign 5 was centered on developing a tool that informs technicians when to take the optimal cut of the ^{238}Pu product. This decision was based on two parameters: (1) minimize the amount of ^{238}Pu sent to rework, and (2) minimize the concentration of Np in the ^{238}Pu product (<0.5 wt%). Making the cut decision is challenging because several species coexist in the effluent stream with varying concentrations, including Pu(III), Pu(IV), Pu(VI), Np(V), Np(IV) and nitric acid. Convoluted absorption bands make "by hand" calculations during the run difficult. Thus, a multivariate regression (PLS) technique was developed to quantify the concentration of each Pu and Np species in the effluent stream.

PP was used to apply the multivariate calculations generated from The Unscrambler PLSR model to predict Np and Pu concentration profiles in real time. The software also included notifications to inform technicians when to switch to rework when Pu(VI) breakthrough occurred and collect the Pu product. These comparisons will be elaborated on in another report. The rest of Section 3.2 discusses several steps taken to build the multivariate model, a description of how PP was used to monitor each P5AXPu run, and development work that would improve this approach for future production campaigns.

3.2.2 Deconvolution and Multivariate Analysis

Absorption spectroscopy is sensitive to each of the relevant actinide species in anion exchange column runs. However, confounding spectral signatures from each analyte renders the quantification of individual species very difficult (Figure 3.2), which makes it particularly challenging to identify the optimal point to cut for the ^{238}Pu product. Predicting the concentration of each analyte using a univariate (Beer-Lambert) approach during Campaign 4 failed to distinguish between certain species with confounding peaks [e.g., Pu(IV) and Np(IV)]. This necessitated the development of a multivariate approach.

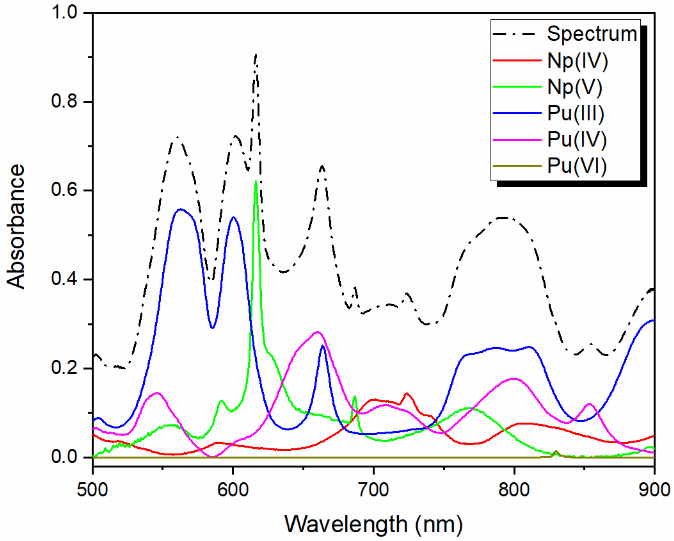


Figure 3.2. UV-Vis spectrum of a mixed Np-Pu solution and the contributions of Np(IV), Np(V), Pu(III), Pu(IV), and Pu(VI).

Spectra corresponding to "calibration standards" were selected from representative historical data sets collected during Campaign 4 AXPu anion exchange column runs. The individual contribution of each species in the spectra was identified manually by deconvolution to assign a concentration to each spectrum. The concentrations of Np(IV), Np(V), Pu(III), Pu(IV), and Pu(VI) were approximated by Beer's law and with extinction coefficients found in the literature or obtained experimentally. A total of 50 spectra collected during Campaign 4 were included in the training set used to build predictive models to monitor the effluent in Campaign 5.

MCR was tested because it can force predicted values to be nonnegative. However, that method did not appear to perform as well as a PLSR model built from the training set derived, in part, by manual deconvolution. PLSR is a commonly used mathematical approach to generate predictive models that correlate spectral signatures to analyte concentration. This technique is particularly useful when analyzing systems with covarying analytes because they can be modeled simultaneously. It relates the entire spectrum to a concentration matrix by reducing the dimensionality of the predictor matrix. The concentration or "response" matrix (Y matrix) was determined by deconvolution/Beer's law while the raw spectral data was used as the independent X matrix representing an $n \times m$ matrix of n samples across m wavelengths.

PLS analysis was performed using The Unscrambler X (version 10.4) software package by Camo Analytics. PLSR models were optimized independently by minimizing the root-mean-square error of the calibration and root-mean-square error of the cross-validation. Spectra (matrix X) were mean-normalized (divided each column by their mean values) before PLS analysis. This assigns a comparable absorption coefficient to each species to equalize the influence of each wavelength. Optical spectra are commonly preprocessed using a variety of transformations, including smoothing, mean centering, SNV analysis autoscaling, derivatives, and so on, to better interpret the spectra. The first derivative of each spectrum was also taken to minimize baseline offsets and smooth the data. The first derivative preprocessing step was registered with the model uploaded to PP, and the processed spectra could be viewed during the run if desired. Y-variance plots, regression coefficients, and regression metrics were evaluated to determine whether the model was describing reality. These details will be described in a separate report.

3.2.3 Campaign 5 Process Pulse Demonstration

A large glass column was filled with anion exchange resin and used for the separation. Np and Pu were converted to anionic nitrato complexes in a high-concentration nitric acid, loaded onto the column resin, and eluted with dilute nitric acid. Fission products and thorium were eluted with high- and mid-concentration nitric acid, respectively. The column effluent stream was monitored with UV-Vis-NIR spectroscopy using an in-line 0.5 cm flow cell hard piped to the effluent line (Figure 3.2). Stream samples were taken by redirecting the column effluent with a three-way valve to a collection vial. Stream samples were analyzed by the analytical group (i.e., alpha spectrometry, inductively coupled plasma mass spectrometry, H^+) to determine fission product, acid, thorium, Np, and Pu profiles and to allow comparisons with spectroscopic measurements.

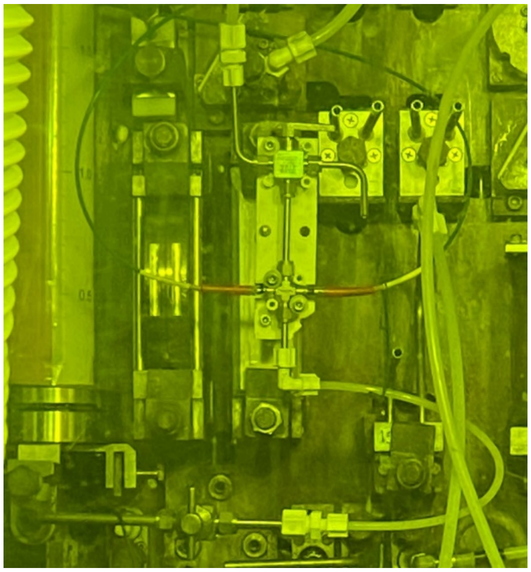


Figure 3.3. Flow cell and three-way valve for stream sample.

The valence of Pu [i.e., Pu(IV)] in the feed solution was confirmed by UV-Vis before loading the feed solution on the column for the first two runs. PLS and MCR models were developed to monitor the valence in the feed. However, these were not fully optimized, and they were not tested during the actual processing event with PP. They were tested on historical data and appeared to work satisfactorily, assuming that either an all Pu(IV) or a relatively even mix of Pu(III) and Pu(IV) exists.

A substantial amount of Pu(VI) was generated on the column during each run. Internal alpha dose may cause the oxidation of Pu(IV) to Pu(VI) because it generates redox active species (e.g., hydroxyl radicals) by alpha radiolysis and heat. In general, Pu(VI) first appeared at measurable concentrations during the high acid wash. Communicating to the technicians the exact point at which the main 830 nm absorption band appears in the spectrum is important. The effluent stream can then be switched to rework, and the effluent stream collected before the appearance of Pu(VI) can be treated as waste. The PLS model had the necessary detection limits for Pu(VI) and successfully pinpointed the initial time when Pu(VI) was measurable in the effluent stream during each column run. Additionally, PP notified staff that the effluent stream should be sent to rework via text/email notifications and warnings viewable in the main view.

A Pu product cut decision was also determined using PP. One prediction configuration was used during each run. In addition to this model, two "no model" configurations were also deployed during the third anion exchange column run. The "predict" model monitored a watch folder in which UV-Vis spectral ASCII files were saved at 10 s intervals using Oceanview. This configuration used the PLSR model developed in The Unscrambler to automate Y predictions (i.e., concentrations) of Np(IV), Np(V), Pu(III), Pu(IV), and Pu(VI) during the column run (Figure 3.4). These concentration profiles were viewable in real time to help inform when to make the product-cut decision. Notably, the overlap of the Np elution band tail and the Pu product front is shown in Figure 3.4. This highlights the need for real-time monitoring. The concentration profiles measured by PP (i.e., Np and Pu predictions) were compared with stream samples analyzed by the analytical group to determine how well the model performed. The model predictions for Pu concentration were in agreement. The data points sporadically deviating from the main profile are caused by bubbles in the solution that negatively affect the data being collected. This may be caused by an internal alpha dose. Trend alarms were used to minimize the possibility of triggering alarms/warnings based on these outliers.

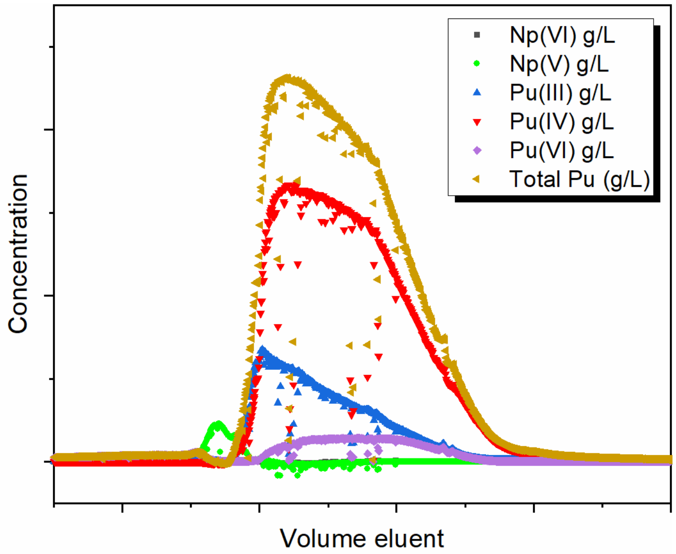


Figure 3.4. Np and Pu concentration profiles during a column run indicate the value of real-time monitoring to guide process decisions.

The predicted Y values were sent to a second data source located on the server. These ASCII files were comprised of the predicted values. A "no model" configuration was made to calculate the total Pu [i.e., the sum of Pu(III/IV/VI)] and calculate the ratio of Np to Pu as the sum of Np(IV) and Np(V) divided by the sum of Pu(III) and Pu(IV). Pu(VI) was not included in this calculation. If the alarm criteria had included Pu(VI), it would have triggered a product-cut notification based on a "good" Np/Pu ratio too early in the run. Notifications based on these calculations could not be included in this configuration because PP does not have this capability. Consequently, the calculated total Pu and Np/Pu ratio values were sent as output ASCII files to a third data source on the server. A third configuration was used to plot total Pu concentration and the Np/Pu ratio. A notification based on the Np/Pu ratio and total Pu concentration was included in this configuration. Email notifications were sent to several recipients upon the alarm activating.

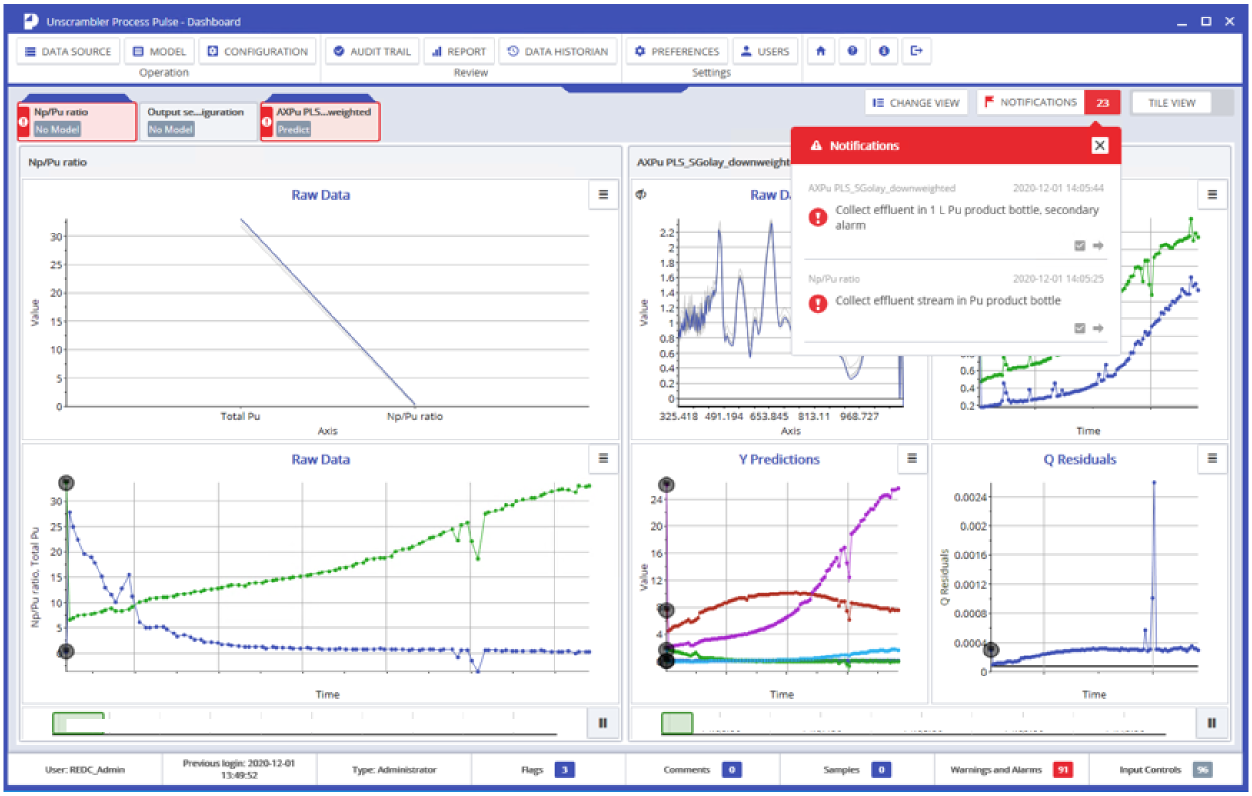
The main view of the third column run is shown in Figure 3.5. The Np/Pu ratio and total Pu concentration are shown on the left. On the right, the Y predictions, spectra, process variables (absorbance values), and Q-residuals (outliers) are all shown. The second configuration was not selected because it did not contain any data useful for informing process decisions. Different variables, like the first derivative spectra, can be viewed in each window by selecting the sandwich icon. The green scroll bar available for each configuration is shown at the bottom left of each configuration. It allows the users to zoom in on different time periods or zoom out to see all the data collected during the run. Right-clicking this portion of the view also allows the user to specify whether the entire data set or specific time frames could be viewed.

Figure 3.5. Main view observed during the processing event. Important process variables are labeled.

A warning for the first and third configuration was included to test which one would perform the best. These warnings were built on separate control limits. The first configuration had multiple-criteria alarms based on predicted (Y) Np and Pu concentration variables that were either too high or too low. This was referred to as the secondary alarm. The starting amount of Np and Pu and the overlap between the Np and elution peaks varied enough between runs that this approach would likely just be useful as a conservative estimate for the Pu product cut. A better understanding of the behavior of Np and Pu on the columns could enable this approach to be used but would likely require making criteria changes for each run. The

Np/Pu ratio appeared to provide the best cut decision that was relatively independent of the separation between elution peaks and the starting composition of the feed.

Each configuration card turned red when the alarm operation limits were met (Figure 3.6). The notifications also appear in the bottom tile and must be selected (clicked) to view the message. The warnings/alarms were tallied and viewable from the notifications list on the dashboard. This tab lists all notifications until they are acknowledged (i.e., the check box is clicked). The message "Collect effluent stream in Pu product bottle" can be easily tailored to convey the desired action steps. This requires that the user acknowledge or confirm that the message was received.



AXPu PLS_SGolay_downweighted 2020-12-01 14:05:44

Collect effluent in 1 L Pu product bottle, secondary alarm

Np/Pu ratio 2020-12-01 14:05:25

Collect effluent stream in Pu product bottle

User: REDC_Admin

Previous login: 2020-12-01 13:49:52

Type: Administrator

Flags 3

Comments 0

Samples 0

Warnings and Alarms 91

Input Controls 96

Figure 3.6. Main view notification observed during the processing event.

Annotations were added with time stamps to variables when events like stream samples took place. These annotations were recorded and included in the data file compiled after the run. This allowed staff to review the data without needing to reference hard copies of control room data sheets.

The following list shows several key findings.

- The concentration profiles for Np and Pu helped staff determine the best time to make the cut for the Pu product.
- PP consistently identified the appropriate time to switch to rework upon Pu(VI) in the effluent stream. In fact, PP notified staff before they realized Pu(VI) was in the effluent stream (~5 minutes). Staff did not notice the warning notifications in the main view.

- Email and text notifications were sent to staff members when the notification criteria were met. These notifications may be sent to the technicians' cell phones or to a shared computer in the control room to make the action items more obvious.

- PP allows output files from any configuration to be used as input into any other configuration. This provides a lot of flexibility and worked well.

- PP consistently identified a conservative time to collect the Pu product. In the first two runs, the cut decision PP made would have sent ~2 g of Pu to rework, but it helped ensure that the subsequent cation exchange column runs could be run without needing to achieve any Np/Pu separation.

- The final run included the actual Np/Pu ratio by using multiple configurations. It appropriately identified the time when the instantaneous Np/Pu ratio was near 1.2 wt%. However, it may be desirable to start collecting the product at a greater threshold during the final run. Specific details will be discussed in another report.

- PP configurations were started by a staff member at home before the run using the web terminal.

- Data were viewable by research staff from their office computers using the web terminal. A ~20 s time delay occurred between the control room data generation and the data being viewable from the web.

- PP was unable to generate a report summarizing all the data or view the data on the local machine. The number of files was too large but was viewable on the server where the main service is installed.

3.2.4 Future Work

Real-time, in situ quantification of Np and Pu concentrations with notifications was achieved using UV-Vis-NIR spectroscopy and PP, which demonstrated that PP could provide the necessary information to help make process decisions. Several items may be further developed and included in future production campaigns. These campaigns may include developing multivariate models, including notifications that provide technicians with clear action items (e.g., collect the Pu product) and making changes to the equipment. The most pertinent areas for development are listed in the following items: including these items will further enable technicians to operate AXPu columns without supervision.

- Develop "unsupervised" MCR models and rigorously compare measurements with "supervised" PLSR predictions.

- Continue comparing predictions to analytical results. Adjust the PLSR model calibration so that the predictions match the analytical results.

- Include Pu(VI) spectra as a function of acidity to improve Pu(VI) predictions during the high- and mid-concentration nitric acid washes.

- Include NIR spectral signatures to determine nitric acid concentration profiles and column gradients.

- Continue comparing cut points for minimizing Np in the product and maximizing the amount of the Pu product collected. Statistically define the product cut.

- Additional development work is required to quantify Pu(III/IV) in the feed solution with greater accuracy. Develop a configuration and model to recognize the valance of Pu in the feed and inform whether it is ready to go.

- Define equipment that may be used to measure the AXPu feed such that the signal is within the dynamic range of the spectrometer. A smaller pathlength would improve this measurement so that small concentrations of Pu(III) [e.g., ~0.5 g Pu(III)/L] in larger concentrations of Pu(IV) [e.g., ~15 g Pu(IV)/L] could be quantified.

- Write PP work instructions for technicians and other users with clear instructions and expectations. Give technicians ample opportunity to test the configurations prior to run operations, with mentoring.

- Include a flow cell "debubbler" to eliminate erroneous spectroscopic measurements.

3.3 PROCESS PULSE EVALUATION

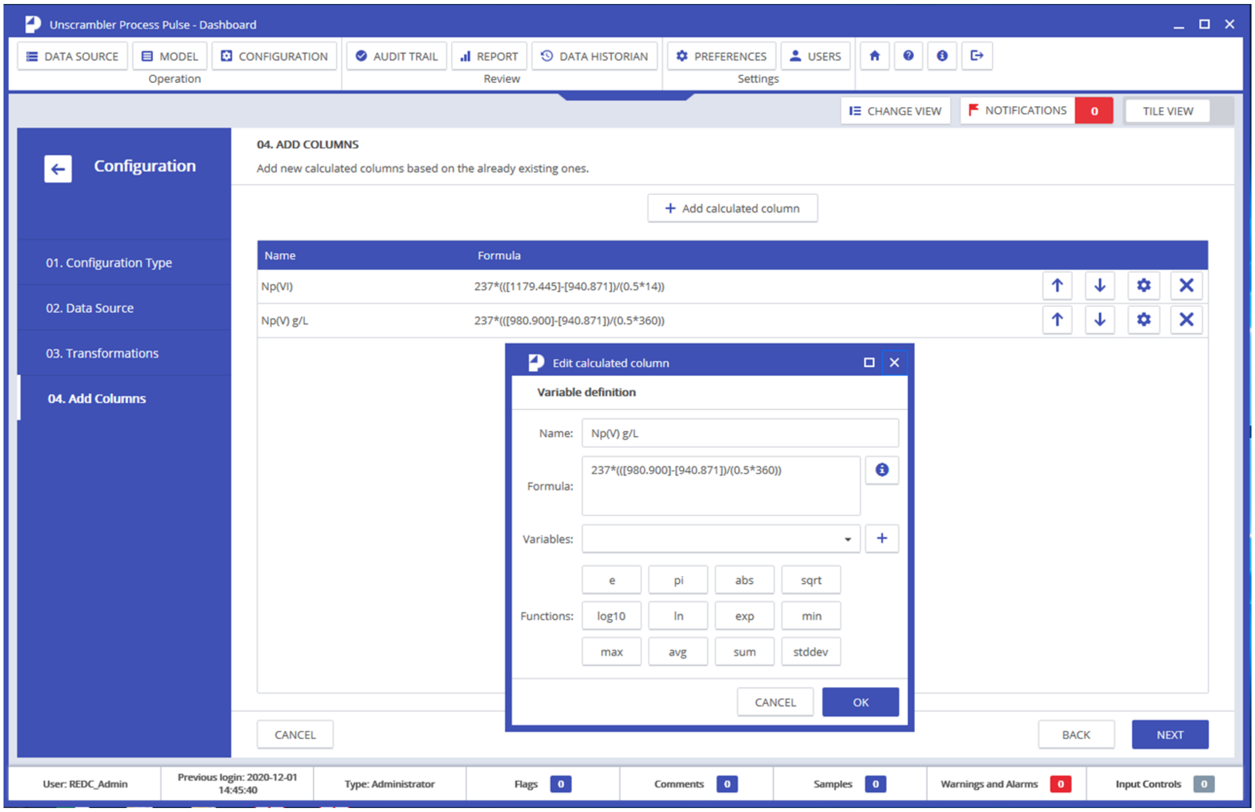
The following list contains the software requirements identified (in bold) and discussion of whether PP meets the requirements.

1) **Stable.** The software stops responding when the internet/server crashes because the main service is located on a server. However, it can easily be restarted and will continue collecting data where it left off. The time of each data point collected during the outage would be off, but all the data points would be plotted. If the main service were installed on the local machine (i.e., computer) it would continue operating during a server/internet outage. Data could not be collected in any configuration (with or without PP) in the event of a power outage.

2) **Large data sets.** The software is also able collect and process data sets with as many as ~14,000 files simultaneously over several days without crashing or bogging down. The software had difficulty retrieving this information post-run from the local machine. The information was accessible from the main service located on the server. PP did not have issues populating the data in real time from the dashboard, which is the primary need. Thus, these results are acceptable for the program's anticipated use cases.

3) **Technician friendly.** Intuitive software controls will allow technicians to operate the software without requiring in depth knowledge of spectroscopy or multivariate analysis. However, some level of training will be required to make sure the technicians are comfortable executing the PP and new Oceanview software. The software is intended to enable scientists to spend more time improving regression models and building configurations while technicians can confidently run the analyses during routine operations.

4) **Real-time analysis.** PP was used to perform both Beer's law and multivariate calculations on spectra data collected in real time. An example calculation used during the monoamide extraction run is shown in Figure 3.7. Subtracting baseline values to correct for baseline offset will not be necessary in future runs with the proper pretreatment selected. Calculations are applied to pretreated data when desired. The software was also used to evaluate historical data by dragging and dropping text files into watch folders. Beer's-law-type calculations are available in no model configurations. Multiplication, division, subtraction, and addition are available and numerous functions are also available including e, pi, abs, sqrt, log10, ln, exp, min, max, avg, sum, and stddev. Spectral absorbance values at specific wavelengths can be included in these calculations and are selected from a drop-down menu.



04. ADD COLUMNS

Add new calculated columns based on the already existing ones.

Name	Formula
Np(VI)	237*(([1179.445]-[940.871])/(0.5*14))
Np(V) g/L	237*(([980.900]-[940.871])/(0.5*360))

Variable definition

Name: Np(V) g/L

Formula: 237*(([980.900]-[940.871])/(0.5*360))

Variables:

Functions:

User: REDC_Admin

Previous login: 2020-12-01 14:45:40

Type: Administrator

Figure 3.7. Beer's law calculation and function example.

5) **Pretreatment options.** No model configurations have five pretreatment options built into the software, including derivatives (first, second, third, and fourth), baseline corrections (offset and linear offset), normalizing (area, unit vector, mean), SNV analysis, and smoothing (SGolay, 1–12 polynomial order). These pretreatment options and several more are included in prediction model configurations. The pretreatments are registered with the model when it is developed in the Unscrambler software. Then, PP automatically applies the transformation to new data being analyzed.

6) **Actionable items.** Testing demonstrated the usefulness of PP's built-in user-defined warnings/alarms that are based on process limits, including multiple-criteria alarms and trend alarms. Written action items can readily be associated with the notifications to help guide process decisions.

7) **Data historian.** The software stores the data in a logical format that is easily retrievable. The data can be viewed from PP if they do not exceed memory limits. Data can also be downloaded as an Excel file or as an Unscrambler file. The data can include spectra, calculated values, and annotations/flags accumulated during the run.

8) **Multiple data sources.** PP imports types of data, including direct imports from Analyzers (e.g., Ocean spectrometers), folder read-out (e.g., ASCII, Excel, and OPUS), and other systems such as OPC-DA, OPS-UA, and TCP/IP. However, this component is only partially satisfied because the current version of PP does not allow the collection of data directly from multiple spectrometers using the same local machine.

9) **Data import.** As many as five data sources can be imported at once. This will be sufficient to meet the program needs. Only one Ocean data source can be imported per computer at this time. Future versions of the software may allow more to be connected to a single machine at once.

10) **Server.** Processed spectral data is output directly to the server. The server where the PP main service is installed is not optimized to hold a large amount of data files. The current PP configuration does not allow files to be exported anywhere else. The server may need to be adjusted (e.g., more memory allocated) to account for the files being stored over time. A scheduled job could be created that periodically clears out files and moves them elsewhere.

11) **Compliant.** PP is compliant with 21 Code of Federal Regulations 11 and European Union Good Manufacturing Practice Annex 11 with model version control, searchable audit trails and audit trail reports.

12) **Validated.** The software is properly validated by users from multiple institutions. ORNL staff were able to test most of the necessary features multiple times during the trial period. Staff are aware of certain components that are not working to specifications. Several features do not work properly, but that will not affect the overall performance and PP's application to program needs.

13) **Security.** PP is compatible with internal security requirements. Information technology and security staff at ORNL approved of the installation and use of PP during the trial period.

14) **Compare historical data.** PP has a central data matrix where multiple experimental runs can be visualized and compared.

15) **Multiple users and configurations.** The PP package quoted consists of five simultaneously running configurations and up to three simultaneous users. For example, one user could be in the control room, another user in the Laboratory 109 operations, and a third stationed in their office with full access to the software. With five simultaneous configurations, it would be possible to run two UV-Vis and two NIR spectrometers in a mixer-settler run to monitor both the A- and B-banks while running a fifth configuration in Laboratory 109 for quantifying modified direct denitration (MDD) solutions.

16) **Connects to spectrometers.** The software can directly connect to Ocean spectrometers so that PP is the only software required during a processing event. However, the PP software can only connect to one spectrometer at a time. If the dashboard and data collectors are installed on multiple computers, each computer could simultaneously connect directly to a spectrometer. This limitation was discussed with Camo Analytics, and they intend to investigate upgrading the Ocean driver associated with PP in hopes that it will allow multiple configurations to run simultaneously while connected directly to the spectrometers.

17) **Web terminal.** Running configurations are viewable using the web terminal from anywhere that the internet can be accessed. Any number of users can view at the same time from the internet. Configurations can be started from the web terminal, but they cannot be altered or stopped. A ~20 s delay occurs between the processing event taking place in the hot cells and what the user sees in the web terminal.

The PP data historian and report generator did not work as advertised with large data sets. The data were not lost; that information was retrievable with direct access to the server where the PP main service was located. Because technicians are not likely to be expected to record and analyze the data post analysis, a simple work-around would be that another staff member could access the data log from the server. The research team suspects that the data historian and report generator did not work, at least in part, because PP is a 32-bit application, despite having a 64-bit operating system. A new PP software release is expected to be available in the first quarter of 2021. This PP software version will operate with a 64-bit application, which will allow access to more system memory. This upgrade may be sufficient to correct the data historian and report generator issues that were encountered. The new version will also be compatible with Python scripts. Python scripting is supported by the newest version of The Unscrambler (11.0) and will also be included in the new version of PP. This update will provide additional automated tasks and access to Python resources, including genetic algorithms and machine learning.

4. SUMMARY AND MAJOR CONCLUSIONS

4.1 CAMPAIGN 5

PP was evaluated during two full-scale monoamide extraction runs and three Pu anion exchange column runs. Np concentration profiles measured during the solvent extraction runs helped identify process adjustments. Real-time, in situ quantification of Np and Pu concentrations was achieved using UV-Vis-NIR spectroscopy, multivariate analysis, and PP during Pu anion exchange column runs. This quantification provided valuable information to help make process decisions and will help transition AXPu column runs to production, maximizing the amount of the Pu product collected while minimizing the amount of Np in the Pu product.

The four-month PP trial period allowed staff to gain experience with the software. Additional work will be required to develop the training data and build the configurations for each process that will eventually be run like clockwork by control-room technicians. This software provides the building blocks for a smooth-running spectroscopy and online monitoring tool that can be used to any extent the program needs. Even the minimum capabilities within PP will greatly benefit the program and, with more rigorous development, it could possibly be used to achieve feats like tracking material inventory in real time. More advanced iterations of this capability could benefit the program which often spends multiple days, on nearly a weekly basis, waiting for results from the analytical group.

PP software will be a useful real-time monitoring tool and improve the control of radiochemical processing streams. PP may be used on a routine basis whenever essential spectroscopic analyses are required in each step of the processing flow sheet. The overall impression of the software was very positive and a purchase order for the system was placed in December 2020.

4.2 LOOKING FORWARD TO CAMPAIGN 6

Significant progress was made toward establishing online monitoring to inform process decisions during hot-cell operations for the ^{238}Pu Supply Program during Campaign 5. Automated spectroscopic analyses will help transition spectroscopy and online monitoring capabilities to production and allow the program to gain more from the investments already in place. This capability will become more and more essential as the program processing efforts and quotas grow.

PP will help technicians rapidly identify and handle process deviations with fault detection and process deviation warnings and optimize the system performance. The software may be simultaneously operated on one computer user in the control room for hot-cell operations and another user in Laboratory 109 for MDD-related support. Additionally, another user can simultaneously log on to their office computer and help monitor and assist if necessary. The process of handing the work off to technicians will begin before the restart of Campaign 6 (~May 2021) and will be a major focus point. A procedure will be developed for nonexperts to execute configurations. Technicians will have the opportunity to run the software with research and development staff supervision. Training and support will be given during this time frame so that technicians will be able to run the software by Campaign 7.