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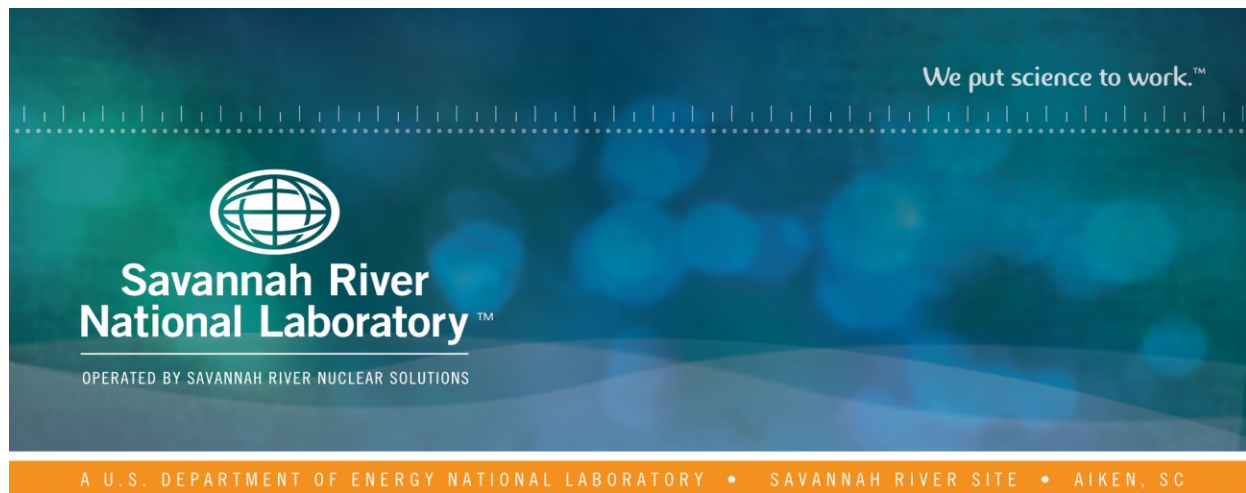
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Spectrophotometers for Uranium Monitoring in H Canyon

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SRNL-STI-2018-00325, Revision 0

November 28, 2018



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EXECUTIVE SUMMARY

SRNL Analytical Development and R&D Engineering have developed an On-Line Monitoring Spectrophotometer to provide measurements of uranium and nitric acid at several locations in H Canyon Second Uranium Cycle. Instruments are installed at Tanks 15.4, 16.8, 17.4, 17.5, and 18.7. Two-sigma uncertainties for the instruments are 5.3% uranium (all tanks) and 11% nitric acid (Tanks 16.8 and 17.5). The spectrophotometers are of similar design to those recently installed in HB-Line for Pu monitoring, although some changes have been made to make them more suitable for uranium measurements. A full description of design, components, and operating procedures is given.

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LIST OF ABBREVIATIONS

DAS	Diode Array Spectrophotometer
LED	Light Emitting Diode
M&TE	Measurement and Test Equipment
MC	Mean Center
MSC	Multiplicative Scatter Correction
NGS	Next Generation Spectrophotometer
OLMS	On-Line Monitoring Spectrophotometer
PL	Piecewise Local
PLS	Partial Least Squares
SG	Savitzky-Golay
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SRTC	Savannah River Technology Center

1.0 Introduction

This report describes the development and calibration of On-Line Monitoring Spectrophotometer (OLMS) systems for uranium and nitric acid measurement at five tanks at the Savannah River Site (SRS) H Canyon facility. The interest for this work arises from a larger effort to realize a processing throughput increase of 50% in H Canyon.^{1,2} Implementation of online monitoring has the potential for substantial improvements by decreasing the number of sampling points which require time-consuming and comparatively expensive off-line analysis. Of several instrument and sensor technologies being considered, online spectrophotometry is the first to be pursued, for several reasons. First, there is a long history of absorption spectroscopy being used successfully in H Canyon for measurements at these tanks.^{3,4,5} Second, the supporting infrastructure installed or refurbished in 2002 for the previous iteration of these instruments – optical fibers, air-lift samplers, and flow cells – remain in the facility and are in good enough condition to support reuse. Third, Savannah River National Laboratory (SRNL) has recently developed and successfully installed a new, state of the art spectrophotometer system for Pu monitoring in HB-Line (Next Generation Spectrophotometer, or NGS) which is readily adapted for this application.^{6,7,8} The instrumentation thus developed includes technical improvements and changes for use in H Canyon. New chemometric calibration models for uranium and nitric acid have also been developed for the first time using a piecewise local modeling approach.⁷ This report is intended primarily to serve as a reference for these development efforts. Details that have not changed since the previous development work for HB-Line and are not included here can be found in Reference 6.

1.1 Chemistry and spectroscopy of U nitrate

The spectroscopic behavior of the uranyl ion, UO_2^{2+} , in nitric acid solutions has long^{9,10} been of interest due to the advantages that would arise from real-time monitoring of nuclear materials processing. In aqueous solutions, uranyl ion is strongly colored and readily observed at process-relevant concentrations. The analytical challenges are due to the influence of complexing ligands (particularly nitrate, NO_3^-) on the uranyl spectrum^{11,12,13,14}, the influence of temperature on the complexation¹⁵, and the potential interference of other colored species in the solution (whether other actinides or transition metals).⁵ Examples of these effects on uranyl spectra within the range of potential processing conditions in H Canyon are shown in Figures 1-3. Acidity variations alter the spectrum by changing the relative proportion of the uranyl nitrate species $\text{UO}_2(\text{NO}_3)_x^{2-x}$, with $x = 0, 1, 2$ within the conditions explored here. Increasing temperature decreases the nitrate complex formation constant without associated changes in the ionic strength of the solution. The spectral effects are not identical to those arising from changes in acidity. Absorption by transition metals such as Cr, Fe, and Ni overlap with uranyl absorbance but are uncorrelated with changes to uranium, acid, or temperature. It is apparent that the straightforward application of Beer's Law* to convert solution absorbance to uranium or nitric acid concentration is not possible. These factors have led to the recognition at SRNL^{3,5,16} and elsewhere^{17,18,19} of the necessity of coupling spectrophotometry with chemometric multivariate analysis techniques, such as partial least-squares (PLS) analysis, to decouple these confounding effects. The techniques correlate spectral changes with changes in the concentration of the species being measured, excluding spectral variations due to other factors. A more complete explanation of PLS can be found in the above references.

1.2 Sampling points in H Canyon

For this project, spectrophotometers were installed to monitor uranium and nitric acid at five tanks in the H Canyon Second Uranium Cycle: 15.4, 16.8, 17.4, 17.5, and 18.7. The nominal ranges and recent historical measurements for uranium and nitric acid are shown in Table 1. By virtue of being in Second Uranium

* $A(\lambda) = \epsilon(\lambda) \cdot b \cdot c$, where the absorbance A at wavelength (λ) is equal to the product of the analyte-specific molar absorptivity ϵ , the pathlength b , and the analyte concentration c . For solutions with multiple absorbing species, the total absorbance is equal to the sum of the absorbances of the individual species.

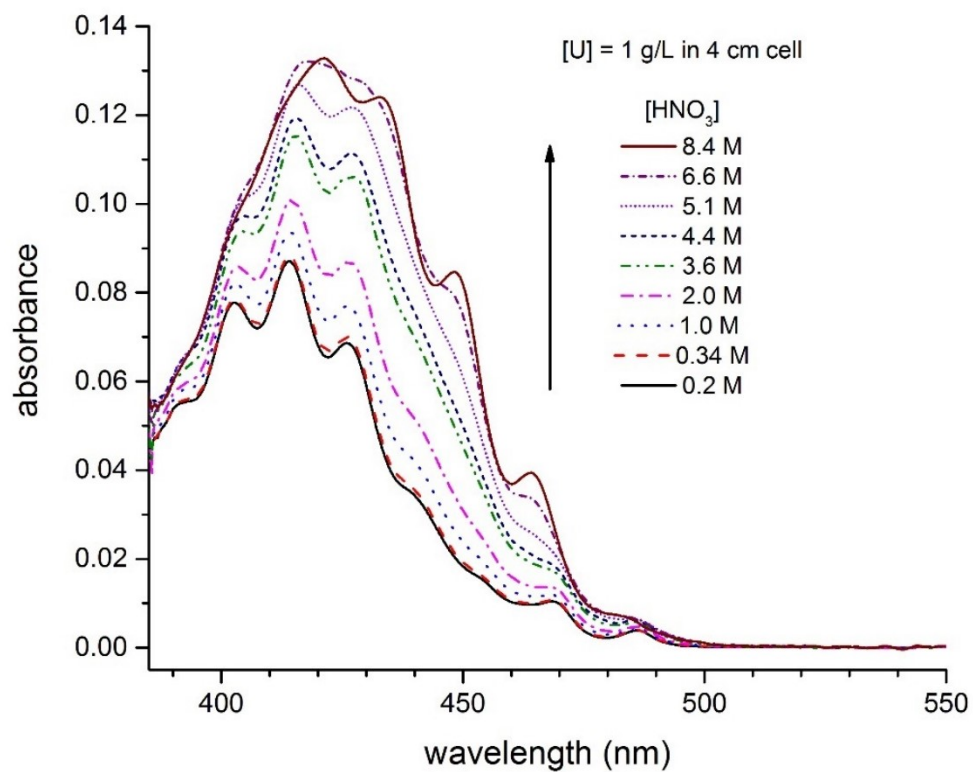


Figure 1. Acidity dependence of uranyl nitrate spectra.

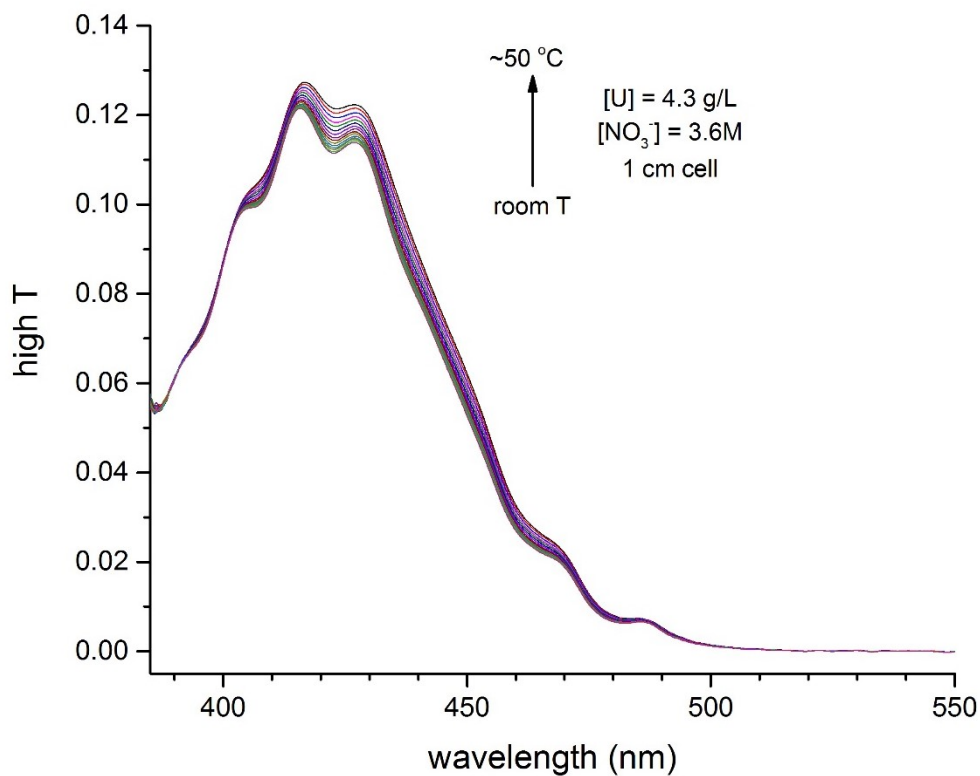


Figure 2. Temperature dependence of uranyl nitrate spectra.

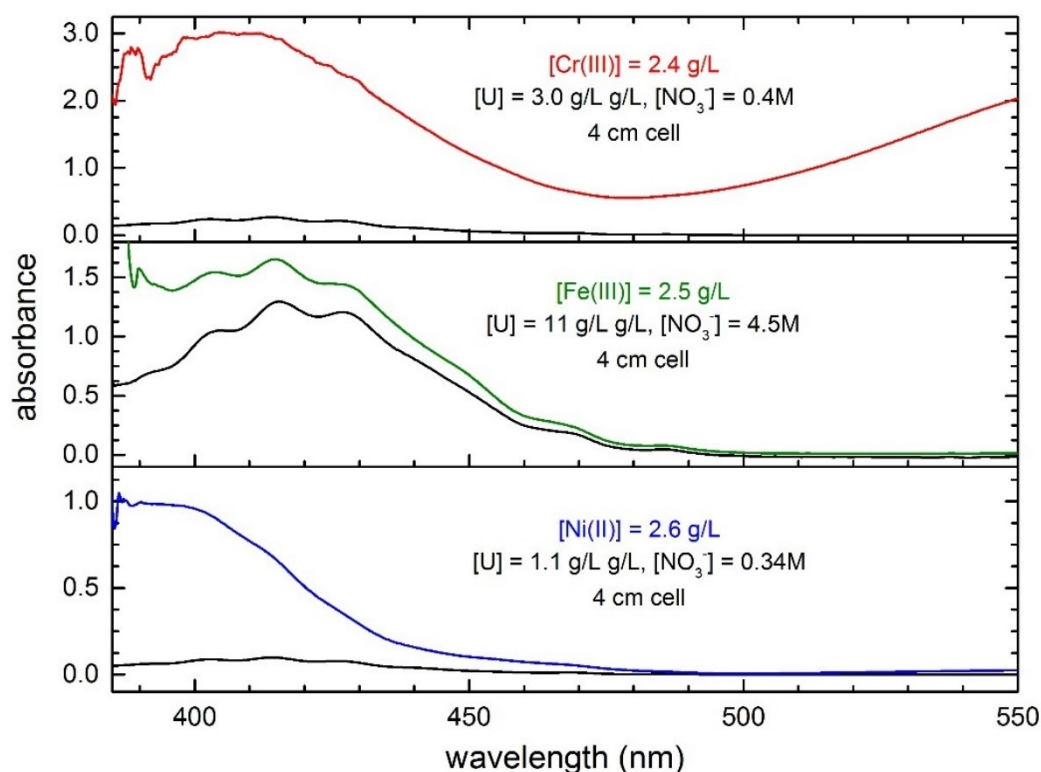


Figure 3. Effects of interferents on uranyl nitrate spectra.

Table 1. Concentration ranges for Second Cycle Tanks.

Tank	Uranium (g/L)		Nitric acid (M)	
	Expected Range	Observed	Expected Range	Observed
15.4	1.5 – 8.5	3.1 – 7.1	0.1 – 0.35	0.16 – 0.30
16.8	3.5 - 12	3.7 – 5.7	4 - 8	5.2 – 6.6
17.4	1.5 – 8.5	2.0 – 4.5	0.1 – 0.35	0.15 – 0.21
17.5	0.25 – 5.0	0.85 – 2.8	0.15 – 0.55	not meas.
18.7	3.5 - 12	0.25 – 8.5	4 - 8	5.1 – 7.4

Cycle, all solutions will have passed through the First Uranium Cycle and are expected to be free of other actinides (especially plutonium) and transition metals that would be present immediately after fuel dissolution. Occasionally, low concentrations of transition metals are found in Second Cycle due to tank degradation. Solution temperature will be largely determined by equilibration with facility infrastructure and is unlikely to exceed 35 °C.

The primary need for this instrumentation is measurement of uranium concentration at all five tanks. Measurement of acidity is only of interest at Tanks 16.8 and 18.7.

1.3 Instrumentation

As with the NGS, the OLMS is a dual beam diode array spectrophotometer. The dual beam configuration is generally preferred for absorbance measurements, since lamp noise and drift affect reference and sample

measurements simultaneously and can be divided out. However, arranging diode array spectrometers (DAS) in the double beam configuration is problematic due to the different wavelength and intensity responses of traditional DASes, which complicate the calculation of the absorbance value. The NGS and OLMS address this problem with near-real time wavelength calibration and rigorous corrections for intensity nonlinearities* for each spectrometer independently. Once corrected, the intensity spectra from each DAS are interpolated to a common wavelength basis, and these virtual spectra are used for the absorbance calculation. This approach is validated through the measurement of NIST-traceable absorbance standards. For all NGS and OLMS instruments produced to date, standards with absorbances up to 2.2 (~0.6% transmittance) are reproduced within tolerances and have maintained that accuracy *without further adjustment* in the field or laboratory. The functional equivalence of the instruments, validation to primary standards (wavelength and absorbance), and stability allow chemometric prediction models developed with one spectrophotometer to be considered secondary standards. These models can be used directly on other instruments without adjustment and without loss of measurement accuracy. This property was proven for Pu measurements in Ref. 6 and will be demonstrated here for U and nitric acid measurements.

1.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This work was undertaken pursuant to the Technical Task Request NMMD-HTS-2017-3403, which is provided in Appendix A.

2.0 Spectrophotometer Hardware

The OLMS hardware is, in design and hardware, similar but not identical to the NGS. The discussion of the hardware will emphasize the differences between the systems. Similarities not discussed here are included by reference to the NGS report [6].

2.1 Overall design and operation principle.

A picture of the cabinet, installed in the H Canyon Control Room, is shown in Figure 4. There are five individual units, one for each tank. The front panel contains a touch-screen monitor with a continual display of instrument readings and status. Above the screen is a square cuvette holder to receive absorbance standards during calibration. There are two banana plug ports which allow manual testing of the 4-20 mA output for the uranium and nitric acid reporting channels. Ethernet and USB ports allow communication with the computer. The racks can be slid in or out of the cabinet for maintenance. A retractable keyboard and monitor is mounted between the second and third instruments (counting from the top). The keyboard and monitor are switchable between each instrument.

Light from two sources, a blue-enhanced light-emitting diode (LED) lamp and a mercury (Hg) lamp, is coincident on the surface of a 50/50 beamsplitter, allowing each lamp's output to be split into a sample and a reference arm.[†] The intensity of each lamp can be adjusted with an iris. The light in each arm is directed towards and focused into an optical fiber. The reference fiber arm is looped under the plate, emerges to the top side to pass light through an iris to allow intensity adjustment, and is eventually directed to the reference spectrometer. The sample fiber arm passes through the absorbance standard cuvette holder before the light is coupled to the fiber connected to optical flow cell attached to the tank sampler. Light returning from the sampler is directed to the sample spectrometer. The controlling

* Sources for the nonlinearities include stray light, second-order grating effects, and array readout anomalies.

[†] Component specifications can be found in the parts list (Appendix E).

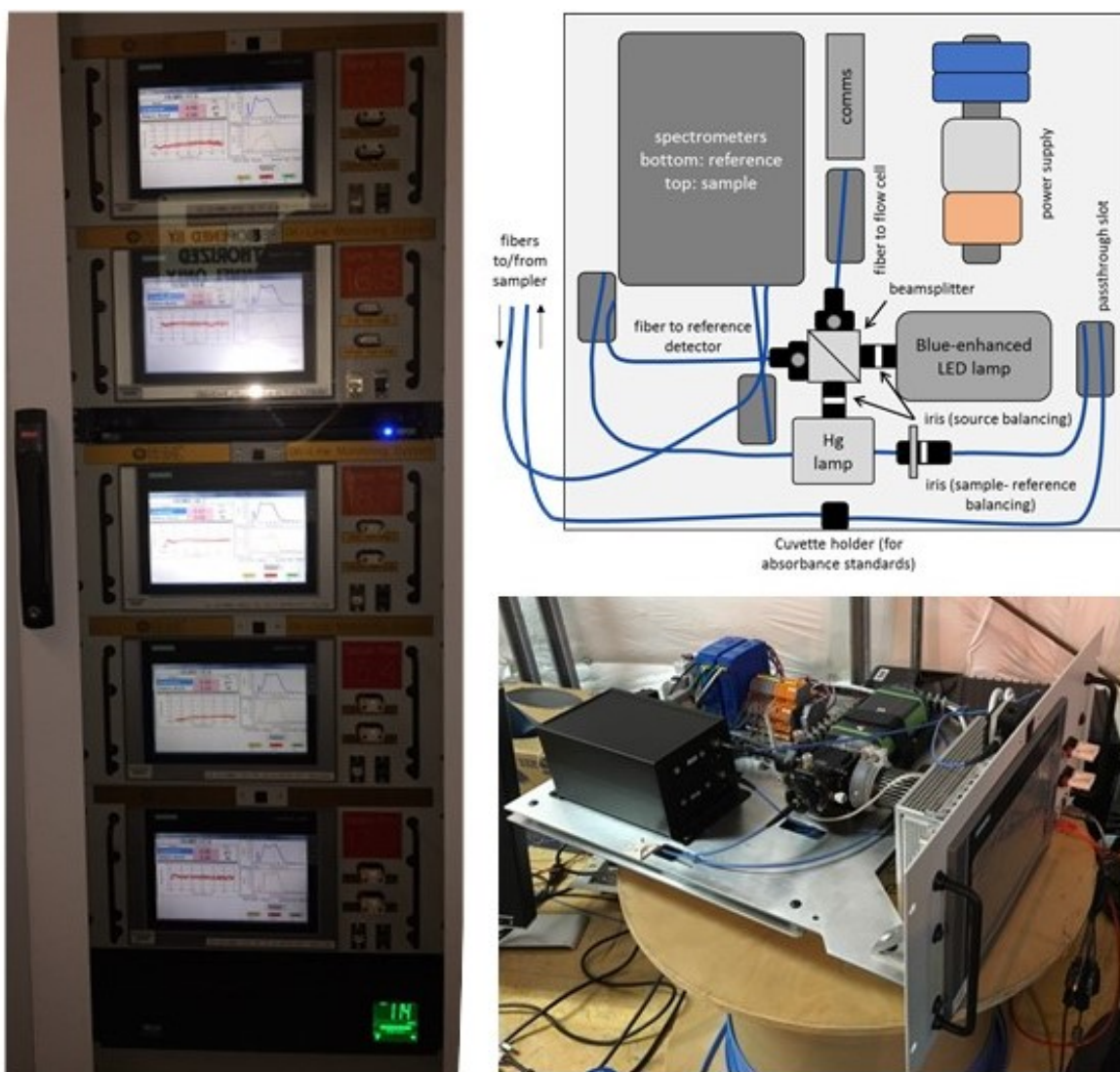


Figure 4. (Left) Front view of OLMS installed in H Canyon. (Right, top) Schematic diagram of spectrophotometer plate. (Right, bottom) Picture of spectrophotometer plate.

computer and touch-screen monitor are mounted on the front panel, and associated power supplies, communication ports, and other electronics are mounted on the plate and connected accordingly.

2.2 Comparison of OLMS with NGS

Light sources. The general principle for choosing the light sources is the same for the two instruments. One lamp is used as the primary source for sample measurements, and the other is used primarily for wavelength calibration of the spectrometers. For the OLMS, the blue-enhanced LED replaces a tungsten-halogen lamp. The lifetime of the LED is rated to >60,000 hours, greatly reducing anticipated maintenance for this component.* And with appropriate modification (see below), a higher proportion of the spectral

* This rating is defined for lamp operation at full voltage (10 V). Here, the lamp is operated at 5 V, which should lead to a still longer life.

output occurs between 400-500 nm, coincident with uranyl absorption. The Hg lamp replaces a xenon (Xe) flash lamp. It has several emission lines which are in the vicinity of the uranyl absorption, are spectrally narrower than the Xe lines with less line overlap, and have no ambiguity in the line positions (several Xe lines were found to be unsuitable due to these concerns). These factors improve the wavelength calibration process.

It should be noted that the lifetime of the Hg lamp is only ~2,000 hours, much shorter than the Xe flash lamp. In order to preserve the lifetime of the lamp and reduce any complications that arise from the sharp features of the lamp emission in the final absorbance spectrum, the operation of the lamps has been changed. Rather than be done continuously, wavelength calibrations are only performed at the beginning of a measurement cycle, and the Hg lamp is off at all other times. This change takes advantage of the discrete nature of the sample measurements in this application, where operating conditions (temperature in the cabinet and facility, for example) are not expected to vary widely. Similar conditions were observed during HB-Line operation for a longer measurement period during a column elution.

Filtering of the LED output. The blue-enhanced LED integrates white-emitting and blue-emitting LEDs. The nominal range of the “white” output is ~450-710 nm, representing the points where the output is 10% of the maximum intensity. The blue LED has a peak at 415 nm, with a nominal range of 395-430 nm. The combined output of the two LEDs results in an intensity trough at ~435 nm, as shown in Figure 5. It is also apparent that the balance between the LEDs is heavily in favor of the white LED. This results in comparatively low intensities across the blue region, coincident with the range of uranyl absorption. Uncorrected, this leads to increased noise and poorer accuracy at higher absorbances. Without the filter, the highest useful solution absorbance that could be measured was about 1.7.

The output is color-balanced by introduction of a blue-pass (or, “temperature balance”) filter (Hoya LB-200) between the lamp and the fiber connection. This filter preferentially passes light between 350-450 nm. The effect on the lamp output is shown in Figure 5. Using the filter allows an increase of the lamp operating voltage and/or integration time to boost the blue light intensity without saturating the detector in other parts of the spectrum. The result is an upper limit of solution absorbance that is greater than 2.0.

Lamp warmup period. For many instruments, a warm-up period of 15-60 minutes is required. During the instrument development phase, the LED lamp required a longer warm-up. This observation was attributed as a consequence of the imaging of the lamp output into the fibers in the reference and sample arms. The emitting element of the lamp is an array of white and blue micro-LEDs. The fiber imaging is 1:1; that is, the 400 (reference) or 600 (sample) μm diameter fibers sample an equivalently sized area on the lamp. Part of the alignment of the system maximizes the relative intensity of the blue-emitting LEDs. As the instrument warms up, the positions of the reference and sample arm image planes can shift across the face of the lamp and drift from each other, changing the relative proportions of blue and white light collected in each arm. If an intensity balance is defined as “zero” before the lamp is fully warmed and the positions stabilize, the drift will lead to an offset. Where the blue/white balance changes, the offset can be more than a simple linear change. Given the coincidence of the blue lamp peak and the uranium absorbance peak, the offset can mimic a uranium signal and lead to a bias in the reading. An example of this is shown in Figure 6, left. The spectrophotometer was blanked as soon as possible after starting (less than one minute). Within 15 minutes, a strong negative peak appeared, with an apparent bias in U reading of -0.25 g/L. The bulk of the change occurred within an hour, with a larger bias of -0.35 g/L, although the readings and intensities required 3 and 8 hours, respectively, to stabilize (Figure 6, right).

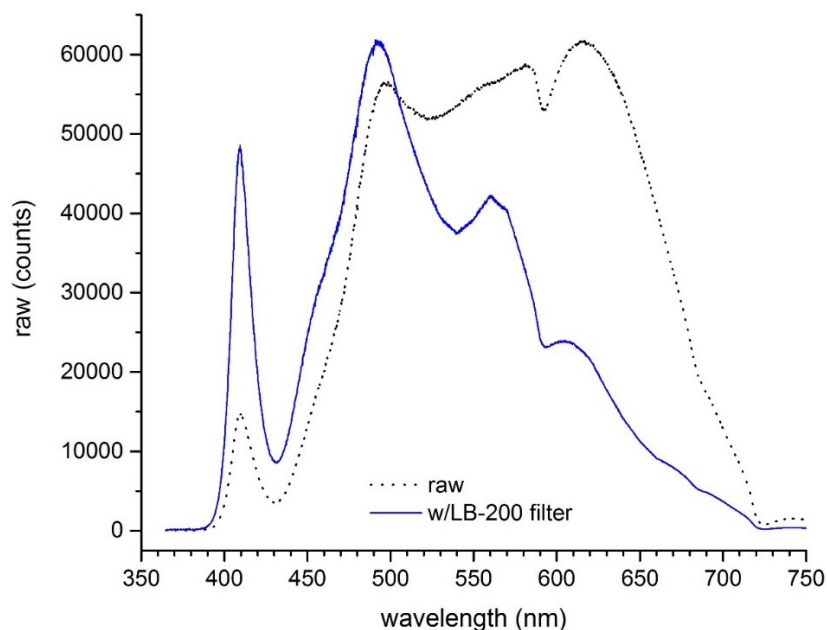


Figure 5. LED lamp emission with and without temperature balance filter.

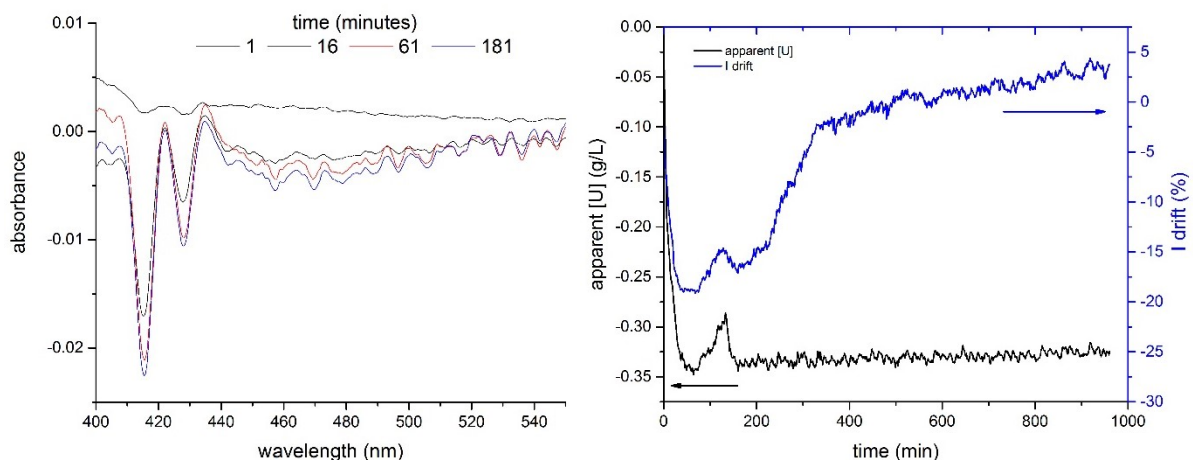


Figure 6. (Left) Absorbance spectrum artifacts during lamp warmup. (Right) U measurement drift during warmup (black) and intensity drift (blue).

In practice, the warm-up period is enforced by keeping the LED lamp on at all times the instrument is on, except when the wavelength alignment is being performed. The alignment process takes only a few minutes, during which time the lamps do not cool off significantly. As the automated control routine has the measurement of a fresh blank spectrum following the wavelength alignment, these considerations are transparent to the user. Other operating instructions will specify a 3-hour warmup period.

Communications with DCS. The most important change is the introduction of a digital input from the DCS, which represents a “switch on.” This input allows the control room operator to awaken the instrument from an idle mode, initialize a calibration and re-zeroing procedure, and start measurements. Instrument outputs

to the DCS are two 4-20 mA analog signals (uranium concentration and acid concentration) and two 24 V digital signals (“instrument valid” and “data valid”). The “instrument valid” signal (“trouble” alarm) is activated if there is a problem with the instrument that prevents a good reading (for example, lamp failure or an unresponsive component). The “data valid” signal (“woe” alarm) is activated if there is an indication of increased uncertainty in the reported results, which may occur if the absorbance is too high, if there is too much noise in the spectrum, or if there is a bad data fit. As the switch on, instrument diagnostics, and data analysis features are all implemented through the control software, their details are discussed more thoroughly in Section 3 (Software).

User interface features. The NGS contains indicator lights dedicated to specific operating conditions and errors, such as being offline for calibration or maintenance, trouble/warning lights, and specific lights for health of the two lamps. These lights have been replaced completely by indicators on the computer screen. Likewise the toggle switch control for taking the instrument offline has been replaced by a touch screen command and/or command from the DCS.

For the OLMS, as with the NGS, verification of the accuracy of the absorbance measurements is done with NIST-traceable metal oxide film absorbance standards. However, the cuvette holder has been moved from its mount on the beamsplitter apparatus in the NGS to the front panel on the OLMS. The advantage of this relocation is that it is no longer necessary to slide the instrument out of the cabinet in order to conduct a calibration. In addition to being more convenient, it eliminates unnecessary motion of the fibers within the cabinet, which could lead to small baseline shifts. The disadvantage of this shift is that the throughput of the sample arm has decreased (by ~30%) due to the extra fiber couplings and the mismatch between the 600 μm diameter fiber in that arm of the spectrometer and the 400 μm fiber used to bring the light to the sampler flow cell. This light loss is compensated by increasing the capture efficiency of the lamps into the fibers, increasing the integration times and operating the lamp at higher intensity, and maintaining the fiber ends and flow cell in the sample aisle.

Other features. The OLMS does not have an integrated check filter, as was the case for the NGS. Any function that the check filter would provide can be obtained through the panel-mounted cuvette holder without opening the system. It is also noteworthy that unlike in HB-Line, it is possible to measure standards directly by pouring them into the flow cell.

Drawings and spare parts. Lists of these items are provided in Appendix E and can be accessed through Site repositories.

3.0 Control Software

3.1 Overview.

The general nature of the instrument control software for the OLMS is unchanged from the software developed for NGS. Specific features of the software include:

- Program organization using individual modules for data acquisition, spectral interpretation, and communication of results, all called from a main program module.
- Wavelength calibration which includes automatic peak finding, fitting peaks to a table of known values, adjustment of the wavelength values of individual pixels, and interpolation of the measured intensities to a fixed array of wavelengths.
- Intensity corrections for stray light and chip response nonlinearities.
- Conversion of the data to a “virtual instrument,” which places the intensity spectra of the two diode arrays on a common wavelength basis to allow calculation of accurate absorbance spectra.

- A piecewise local (PL) partial least-squares (PLS) scheme to interpret absorbance spectra to generate uranium and acidity results.
- Communication of results and instrument status to the “outside,” both on-instrument display and the DCS.
- Archiving of the raw and processed data, analysis results, and instrument diagnostics.

New features of the OLMS control software are described below.

3.2 Programs and tools.

The data acquisition program, *OLMS-Main*, was written in Visual Basic (*VB.net*, version 4.0). Spectrophotometers are controlled through drivers provided by the vendor (Avantes: *AS5216.dll*, version 2.2.0.0, and *AvaSpec-USB2.dll*, version 1.6.0.1). PLS models are converted to callable functions by an interpreter from Eigenvector Research, Inc. (*ModelExporterInterpreter.dll*, version 1.0.0.0). Programs are run in Windows 10.

Work instructions for operation and calibration are given in Appendices B-D.

3.3 Quality assurance.

A description of the overall nature and purpose of the OLMS software is provided in Technical Task Request (TTR) NMMD-HTS-2017-3403, “H-Canyon Spectrophotometer Development and Installation” (Appendix A) and the Software Classification Document (SWCD), B-SWCD-H-00640, “HCA SNF-TI ALSR H-Canyon Spectrophotometer Software”. Per the OLMS SWCD, the software has been classified as GS by applying the requirements of Manual E7, Procedure 5.01. Software Quality Assurance (SQA) requirements applicable to GS software will be implemented in the development and maintenance of the OLMS software. Additionally, per the SWCD, an enhanced graded approach will be implemented based on the spectrophotometer unit’s functional classification of “GS-C” in accordance with the H-Canyon Double Contingency Analysis (DCA) and Manual 1E7, Procedure E-102, “Functional Classifications”. The system’s “GS-C” designation indicates that a higher level of maintenance and functional checks beyond the standard GS functional classification should be implemented. Specifically, the OLMS enhanced graded approach included the development of a Requirements Specification (RS), a Requirements Traceability Matrix (RTM), and completion of Software Testing as defined in a Software Test Plan (STP). The Software Quality Assurance Plan implementing this approach is defined in document B-SQP-H-00075, “H-Canyon On-Line Monitoring System (OLMS) Software Quality Assurance Plan (SQAP)”.

Testing included validating all critical requirements defined in the “H-Canyon On-Line Monitoring System (OLMS) Software Requirements Specification (RS)”, B-RS-H-00295. Software requirements were linked to the test case where they were validated in the “H-Canyon On-Line Monitoring System (OLMS) Requirements Traceability Matrix (RTM)”, B-RTM-H-00061. H-Canyon On-Line Monitoring System (OLMS) software version 1.00 functional testing was successfully completed on July 10th, 2018. All test cases as detailed in the “H-Canyon On-Line Monitoring System (OLMS) Software Test Plan (TP)”, B-STP-H-00778 Rev 0, were completed without any failures. Testing resulted in minor redlines to several test cases which did not affect the intent or scope of the test. Field installation checkouts identified several required minor revisions to the software which were incorporated in software version 1.01 and successfully regression tested on August 2nd, 2018 as detailed in “H-Canyon On-Line Monitoring System (OLMS) Software Test Plan (TP)”, B-STP-H-00778 Rev 1. Test Results are provided in the “H-Canyon On-Line Monitoring System (OLMS) Software Functional Test Report (TR)”, B-TR-H-00057, Rev. 1.

The spectrophotometer instrument, which is the measurement component of the OLMS, includes embedded firmware that cannot be changed by SRS personnel and is therefore exempt from the SQA process per SRS 1Q Quality Assurance Manual, Procedure 20-1, “Software Quality Assurance”. The OLMS system will be controlled as installed process instrumentation (IPI) subject to 1Q, Procedure 12-2, “Control of Installed Process Instrumentation”.

3.4 Program flow.

The top-level schematic of the program is shown in Figure 7. The general functions of each subsystem are the same as for the NGS and are described in the figure and in Ref. 6. Changes from the NGS software are:

- The check filter control signal between the main module and the spectrometer subsystem is eliminated.
- There is no watchdog timer between the main module and the I/O subsystem.
- The I/O subsystem accepts input from the DCS and passes a related signal to the main module.

These changes validate the architecture chosen during development of the NGS system. Specifically, there are significant changes in the spectrometer subsystem module, but these are implemented without substantial changes to the model or I/O subsystems.

General operation of the instrument is started by double-clicking the *OLMS* icon on the Windows desktop after bootup.

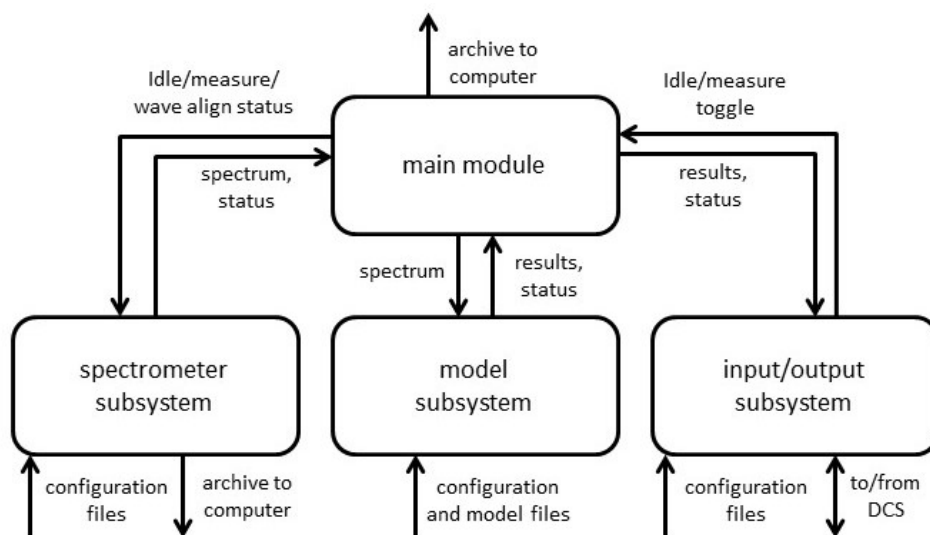


Figure 7. Top-level schematic of OLMS control program.

3.4.1 Spectrophotometer subsystem.

Under normal operating conditions, the OLMS may be in one of three modes: idle, measure, or wavelength alignment.* The default mode is “idle”. Upon command from the DCS, the system will be turned to “measure”. As part of the process to start taking measurements, the instrument will automatically pass through the “wavelength alignment” mode.

* The OLMS can also be put into a standard validation mode to confirm proper readings of the NIST-traceable absorbance filters, but this is only done intermittently.

The idle mode is algorithmically simple. After having read in a configuration file during startup, the system will continually read intensity spectra from the two spectrometers. It will not process the data in any way or pass the data back to the main module. The purpose of idle mode is to maintain the LED lamp and spectrometers in a stable state so the instrument can immediately perform reliably when put into measure mode. In idle mode, the “instrument valid” output is set to “true” and the “data valid” output is “false”. The LED lamp is on and the Hg lamp is off. The integration time is short and the number of samples averaged is low, to allow for more rapid response when the instrument is switched to measure mode.

Receipt of the “measure” signal from the DCS triggers the flow diagram shown in Figure 8 and Figure 9. This sequence differs from the NGS system in that the wavelength alignment and sample measurement steps are decoupled. The first few steps prepare the instrument for measurement by automatically obtaining a new zero/reference spectrum and refreshing the wavelength calibration. These need to be done with a cell that does not contain a uranium-bearing solution. The confirmation is done by acquiring a spectrum, analyzing for uranium content in the model subsystem, and observing that the uranium reading is below a certain threshold. The spectrum is acquired by using the most recently acquired blank* and the most recent wavelength calibrations. Any drifts since the last use are not likely to lead to a significant bias in uranium concentration, at least for the purposes of determining whether or not the flow cell needs to be flushed. If the cell is deemed to have uranium in it (the reading is above the threshold), the program will stay on this step until the condition is resolved by flushing the cell.

Once the cell is confirmed to be clean, the program acquires a new wavelength calibration for the two spectrometers. Here, the LED lamp is turned off and the Hg lamp is turned on. After a small wait for the Hg lamp to stabilize, a spectrum is taken, peaks are found, and corrections are made to fit the peaks to known lines in the same manner as for the NGS system. The new wavelength calibration parameters are loaded into the program and written to a configuration file.

The program then moves to taking a fresh blank. The LED lamp is turned on and the Hg lamp is turned off. Usually, the wavelength calibration step only takes a few minutes, and so the LED lamp and the alignment do not change substantially from their previous stable condition in idle mode. Nonetheless, the program will pause and collect intensity spectra until internal diagnostics confirm that the system is stable. Once that is achieved, the program will collect and record the new blank and write it to disk.

Only at this point will the instrument indicate it is in “measure” mode, which is an indication that the sampler should be circulated to bring tank contents to the flow cell. While the sampler is circulating, it is likely that the turbulence associated with the air/liquid mix will preclude obtaining good data. During this time, the “instrument valid” indicator will be “true” but the “data valid” indicator will be “false”, due to the data not passing consistency checks. When the sampler is stopped and the solution remains still, the “data valid” indicator will turn “true” and results can be read.

* If there is no trustworthy blank spectrum (the instrument is being turned on for the first time, has been unused for a long time, or the LED has been replaced), then a new blank must be recorded manually. Instructions for this task are in Appendix D.

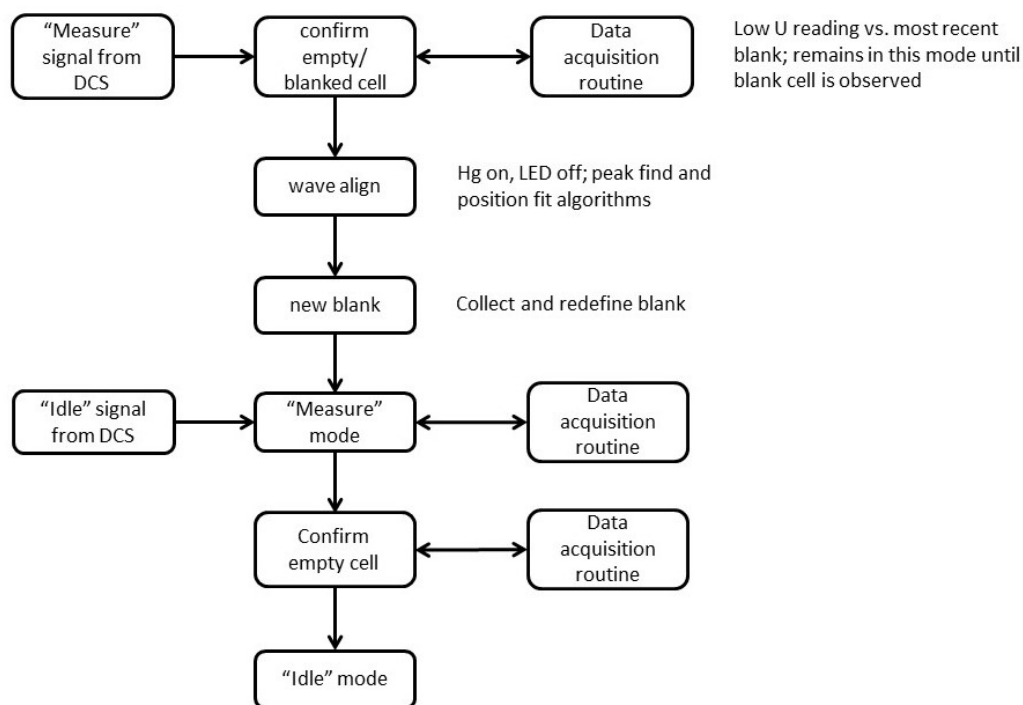


Figure 8. Flowsheet for spectrophotometer subsystem.

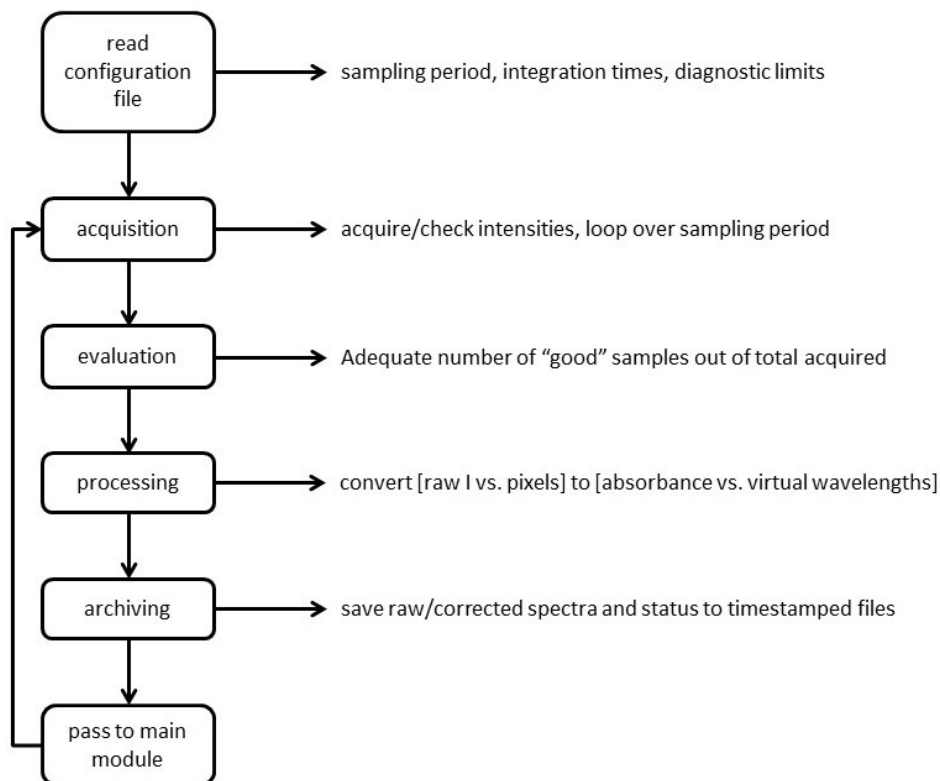


Figure 9. Data acquisition routine called in spectrophotometer subsystem flowsheet.

The data acquisition routine of Figure 9, which is called during measure mode as well as in the preparatory steps, is identical to the spectrophotometer subsystem developed for the NGS.

The instrument will remain in this mode, continually updating results, until an “idle” signal is received from the DCS. When this occurs, the instrument will switch to looking for the condition of a rinsed cell, using the same criteria as at the beginning of the measure cycle. Once this situation is achieved, the instrument will stay in idle mode until the next “measure” signal is received.

The calibration procedure is entered while the instrument is in idle mode. This operation is performed from the computer screen; input from the DCS is not expected. The general procedure is functionally identical to that for the NGS system. The only change is the absorbance for each checked wavelength is averaged over a 1 nm window about the check wavelength, rather than using a single-point measurement. Averaging reduces the effect of measurement noise, especially for the higher absorbance standards, without otherwise impacting the accuracy of the measurement. The program also now writes the results into text files, in addition to saving screen shots (see Figure 10) of the absorbance.

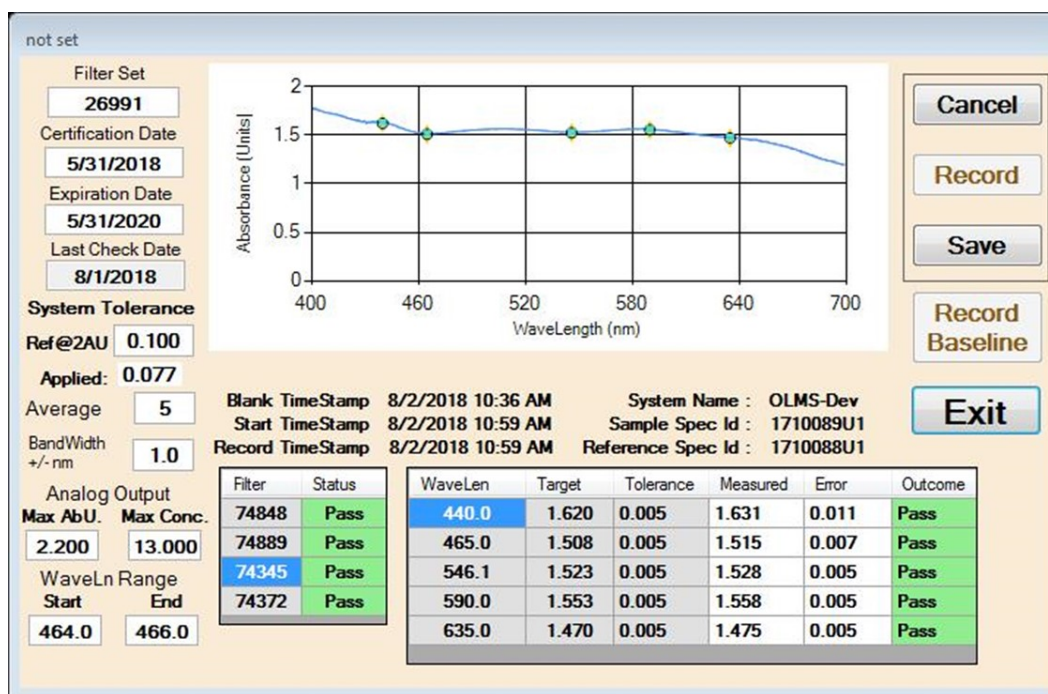


Figure 10. Screenshot of absorbance standard test results.

3.4.2 Modeling subsystem

Analysis of the absorbance spectrum to determine uranium and nitric acid concentrations is performed according to a piecewise local analysis scheme. The scheme automatically evaluates the spectra according to several criteria to determine which local models are applicable. Eight analysis scenarios are possible based on maximum solution absorbance, detected spectral interferences, and apparent solution acidity. This flowsheet, with the pathways labeled, is shown in Figure 11. Pathway 1 is expected for clean (no spectral interferences), low (< 1.2 M) acid solutions in Tanks 15.4, 17.4, and 17.5. Pathway 3 is expected for clean, high (> 4.0 M) acid solutions in Tanks 16.8 and 18.7.

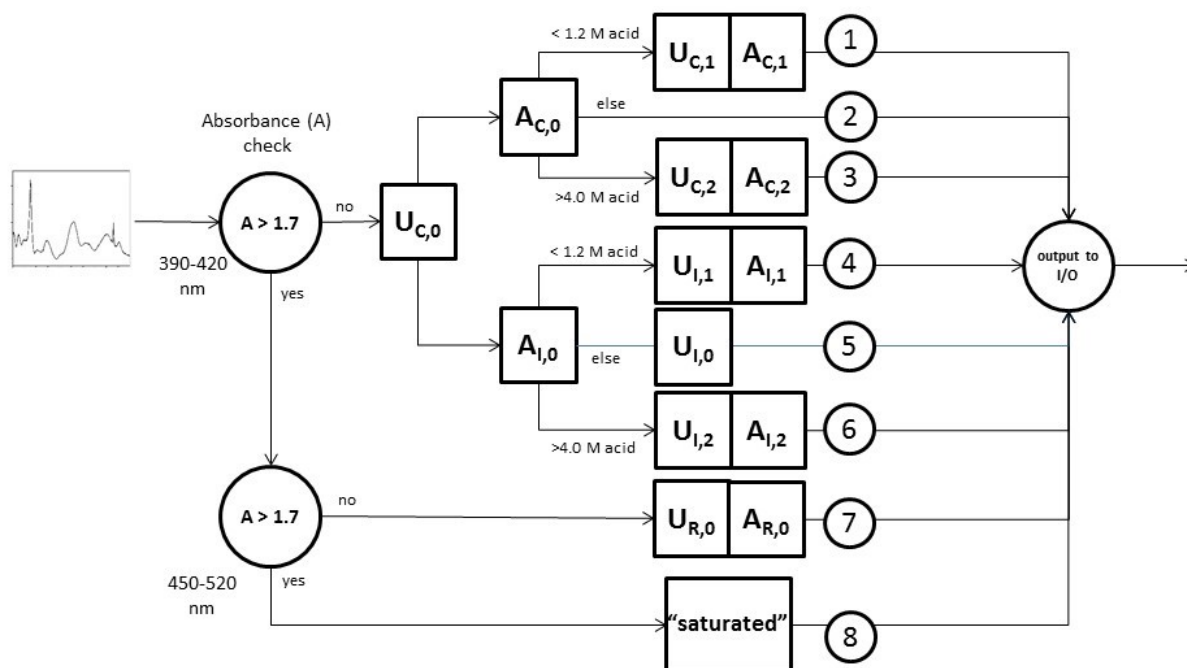


Figure 11. Piecewise local PLS flowsheet for uranium and nitric acid analysis.

The first check is to confirm that the maximum absorbance for the wavelengths 390 – 420 nm, where the strongest absorbance by uranyl nitrate complexes occurs, is within the range of absorbances for which the instrument has been verified by absorbance filter checks. If the check is passed, the second check is based on the results of spectral analysis with the uranium predictive model ($U_{C,0}$). $U_{C,0}$ is “clean” (no interferences) and global (full range of nitric acid concentrations). The important result of this analysis is not the uranium concentration *per se*, but the residuals of the fit. High residuals are indicative of the presence of interferences. Selection of the residual threshold is discussed in more detail in Section 4. Spectra with low residuals are analyzed with a global acidity model ($A_{C,0}$) to classify the solution as low, high, or medium acidity. Once the evaluation is complete and the analysis pathway is fully determined, the spectrum is reanalyzed with appropriate local uranium and acidity models. These models are developed from standards appropriate for the pathway. Spectra in Pathway 2 are not reanalyzed, but rather the results of the global uranium and acidity models are reported.

High residuals for $U_{C,0}$ leads to Pathways 4 through 6, the low, medium, and high acidity pathways for interferent-containing solutions. Pathway 7 is invoked if the initial absorbance check exceeds the selected limit of the spectrometer, which should only happen for uranium concentrations above the expected process conditions, very high interferent concentrations, or large baseline offsets. The response of the flowsheet is to evaluate the spectrum over a different wavelength range where uranyl nitrate absorbances may still be “on scale”. In this pathway, there is no effort made to determine the source of the larger absorbance, and so only global interferent models for uranium and acid are applied. Pathway 8 covers the case where the second absorbance check fails. Here, no analysis is possible and the instrument will generate a default response (and indicate that the data is “invalid”). Pathways 4 through 8 are not expected to be used under normal processing conditions for the five tanks of the initial installation.

3.4.3 Input/output subsystem

Generally, the conditions that influence the value of the “data valid” signal will simultaneously affect the uranium and acid analyses. However, there is a scenario where the uranium analysis would be good but the acid analysis would be questionable. This occurs when the uranium value is less than 0.5 g/L (below the limit of quantitation). Because the acidity is inferred from its effect on the uranyl nitrate absorption, enough uranium must be present in the solution to obtain a useable spectrum. Alternately stated, this method cannot determine the concentration of a pure nitric acid solution. This scenario is addressed by using a different convention for the 4-20 mA output. The bottom of the full range (0 M acid) is represented by 5 mA rather than 4. (The top of the range, 20 mA, is 10 M.) When the uranium reading is below 0.5 g/L, the output is driven to 4 mA (yielding a negative output) if the acid analysis is uncertain.

3.4.4 Instrument operation, calibration and troubleshooting

Detailed instructions for instrument operation, setting a new blank, and performing a calibration check with absorbance standards may be found in Appendices B-D.

The instrument display during standard operation (“measure” mode) is found in Figure 12. Concentrations are displayed in the upper left corner, above the absorbance spectrum. Individual intensity spectra for the reference (blue curve) and sample (orange curve) spectrometer are also displayed. In the “DCS IO box”, status indicators are provided for the digital signals. “Switch On” is the input from the DCS controlling entry into “measure” mode, “Instrument Valid” is an overall instrument health indicator, and “Data Valid” indicates a strength of confidence in the reported results. Diagnostic indicators for the Spectro, I/O, and Model subroutines are provided below the intensity curves.

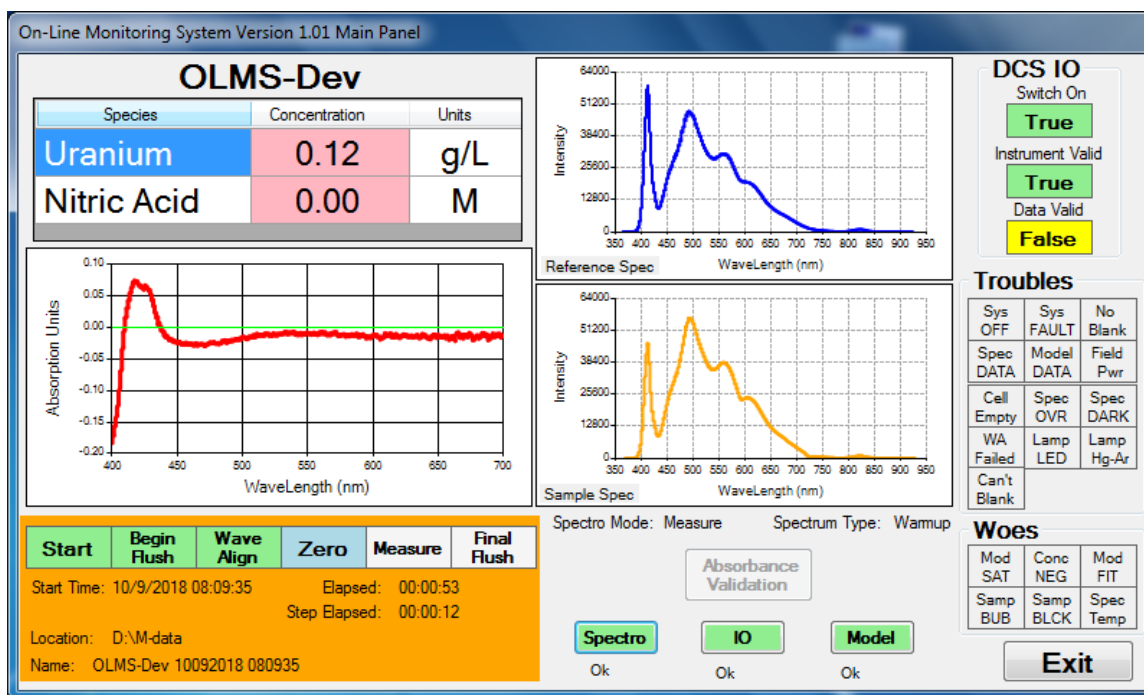


Figure 12. OLMS instrument display when in Measure mode.

The Troubles and Woes sections on the panel provide specific diagnostics for instrument or sampler operation. In general, Trouble signals will cause the “Instrument Valid” indicator to become False, and Woe signals will lead to a “Data Valid” signal of False. Explanations of the individual errors are provided in Table 2 (Troubles) and Table 3 (Woes).

Table 2. Troubleshooting Guide for Trouble Alarms.

Error	Cause	Response
Sys OFF	The System Offline trouble alarm is asserted if any subsystem is offline or if an Absorption Check is in progress. A subsystem is offline if it is unlocked or in Maintenance mode.	Reveal the causal subsystem panel (the access button background color will be gold) and click either the Lock or Close button.
Sys Fault	The system fault trouble alarm is asserted if any subsystem is in an inoperable state, due to either a hardware fault or an invalid parameter.	Reveal the causal subsystem panel (the access button background color will be red). Examine panels for an invalid entry or hardware fault notification. Consult with SRNL for troubleshooting and rectification.
No Blank	The No Blank trouble alarm is asserted if there is no available blank spectrum to be read from the disk for the spectrometers installed in the system. This alarm will occur if a spectrometer is replaced or this is a new system.	Perform a manual blank from the spectrometer subsystem panel.
Spec DATA	The Spectrometer Data trouble alarm is asserted if the spectrometer subsystem does not acquire a new spectrum within the allowed time as specified by the parameter “NoData Trouble Time” in the setup file “Setup-OLMS.ini”.	This alarm would typically occur if the spectrometer subsystem faults. Consult with SRNL for troubleshooting and rectification.
Model DATA	The Model Data trouble alarm is asserted if the model subsystem does not return results from spectrum within the allowed time as specified by the parameter “NoData Trouble Time” in the setup file “Setup-OLMS.ini”.	This alarm would typically occur only if a software glitch in the model subsystem processing prevents completion. Consult with SRNL for troubleshooting and rectification.
Field Pwr	The Field Power trouble alarm is asserted if no power condition is detected on the field side of the IO signals. This power is supplied by the DCS and detected by the second digital input in the IO system.	Check the fuse located in the DCS power supply. Check the fuse in the 750-601 supply module in the IO block assembly.
Cell Empty	The sample cell empty trouble alarm is asserted if the program determines the sample cell is not flushed during either the “Begin Flush” or “Zero: steps during a measurement cycle. A cell is determined to be flushed by the program if: <ul style="list-style-type: none"> • The measured Uranium concentration is less than the “Empty Cell Concentration” parameter in the “Setup-OLMS.ini” file. • The “Mod Fit” woe alarm is not asserted. (Low uncertainty) • The “Samp BUB” woe alarm is not asserted. (Low noise spectrum) • The sample spectrum minimum intensity requirement is met. 	Flush the sample cell. If the sample cell is known to be flushed, perform a manual blank. Consult with SRNL for further troubleshooting and rectification solutions.
Spec OVR	The spectrometer over range trouble alarm is asserted if, during a measurement cycle and the LED lamp is on, the input spectrum to either spectrometer is over range as determined by the “Saturation Threshold” parameter located on the Spectrometer Subsystem “Process Settings” tab.	Reset the LED lamp level to below the saturation threshold.

Spec DARK	The spectrometer dark trouble alarm is asserted if the last acquired dark spectrum of either spectrum contains more than 10 elements of greater than 500 counts intensity. This trouble condition is tested in a Measurement cycle when the spectrometer acquisition mode is switched to either “Measure” or “Wave Align”.	An increase in the number of “hot” pixels in the dark spectrum is indicative of a failing spectrometer. Consult with SRNL for further troubleshooting and rectification solutions.
WA Failed	The wavelength alignment trouble alarm is asserted if either spectrometer could not complete the wave alignment process in the “Wave Align” step of the measurement cycle.	Verify and adjust wave alignment acquisition parameters to adjust light to appropriate levels. Check for Lamp Hg-Ar trouble. Consult with SRNL for further troubleshooting and rectification solutions.
Lamp LED	The LED lamp trouble alarm is asserted if the LED lamp intensity, as detected by the reference spectrometer, is out of allowed tolerances during a measurement cycle. The average lamp intensity must not have drifted by more than the “Light Level Allowance” parameter from the last blank spectrum or be less than the “Minimum Intensity” level at the “Monitor Wavelength” parameters located on the Spectrometer Subsystem “Process Settings” tab.	Reset the level of the LED lamp if necessary. Perform a manual blank.
Lamp Hg-Ar	The Hg-Ar lamp trouble alarm is asserted if no Hg-Ar emission lines are detected by either spectrometer in the “Wave Align” step during a measurement cycle.	Check Hg-Ar lamp function. Replace lamp if necessary. Consult with SRNL for further troubleshooting and rectification solutions.
Can’t Blank	The can’t blank trouble alarm is asserted if conditions for acquiring a blank spectrum are not satisfied during the “Zero” step in a measurement cycle. Required conditions are: <ul style="list-style-type: none"> • The previous wave alignment was successful. • Neither spectrometer has “Spec OVR” fault. • Both spectrometers exceed the minimum intensity requirement. • Neither spectrometer is warming up. • Neither spectrometer acquired spectrum is overly noisy. 	Perform action to rectify non-compliant condition. Perform a manual blank. Consult with SRNL for further troubleshooting and rectification solutions.

Table 3. Troubleshooting Guide for Woe Alarms

Error	Cause	Response
Mod SAT	The model saturated woe alarm is asserted from the model subsystem if the sampled solution absorption level exceeds the maximum measurable capacity of the model.	Consult with SRNL for troubleshooting and rectification solutions.
Conc NEG	The negative concentration woe alarm is asserted from the model subsystem if the calculated concentration is less than the “Neg Limit” parameter (located on the Model subsystem panel).	Flush the sample cell. Restart the measurement cycle.
Mod FIT	The model fit woe alarm is asserted from the model subsystem if either the residual is above the “Max Residual” parameter (located on the Model subsystem panel) or there is interfering material in the sampled solution.	Consult with SRNL for troubleshooting and rectification solutions.
Samp BUB	The sample bubble detected woe alarm is asserted from the spectrometer subsystem if a high noise level is detected in the	None. Condition resets when solution stabilizes.

	acquired spectra typically encountered when the sampler is on.	
Samp BLCK	The sample blocked detected woe alarm is asserted from the spectrometer subsystem if the intensity of the spectra from the sample spectrometer is less than the “Check Intensity Threshold” at the “Check Intensity Wavelength” parameters located on the Spectrometer Subsystem “Process Settings” tab. Typically, this condition will occur if either the sample solution extra saturated or if the sample cell is dry.	Flush, then resample tank. Consult with SRNL for troubleshooting and rectification solutions.
Spec Temp	The spectrometer woe alarm is asserted if the spectrometer internal temperature drifts more than the “Temperature Band” parameter (located on the Spectrometer Subsystem “Process Settings” tab) from the temperature during the last wave alignment.	Reset the measurement cycle to perform a wavelength alignment.

4.0 Calibrations

This section provides an overview of the chemometric models used to interpret absorbance spectra to derive uranium and nitric acid concentrations, a description of the standard solutions, and the results of the statistical analysis. As for the NGS system, the prediction models are treated as secondary standards that are expected to be valid when spectrometers are shown to be accurate against primary standards for wavelength and absorbance.

4.1 Overview.

The interpretation of spectra to determine uranium and nitric acid concentrations is done with Partial Least Squares (PLS) analysis.^{20,21} PLS is sensitive to correlations between spectral variations and changes in the concentrations of the desired analyte. This approach is well suited for the analysis of process solutions because it does not require any *a priori* knowledge of the solution conditions, nor does it require those other conditions to be measured in order to deduce the desired result. The most important criterion to be met is that all potential sources of spectral variance are included in the calibration set. Further discussion of the PLS method, at varying levels of intuitive understanding and/or mathematical rigor, can be found in the above references, as well as in Ref. 6.

The piecewise local PLS modeling approach taken here is a refinement of previous chemometric analyses,^{4,5,11} inspired by the approach used by our group for Pu monitoring in HB-Line.^{6,7} The motivation for applying piecewise local PLS arises from the general property of principal component analysis methods that one fitting factor is required for each independent condition that causes spectral changes. For both Pu and U nitrate analyses, there are a large number of conditions that can influence the spectra. However, not all of these are relevant for any given solution. For example, in the Pu analysis, certain Pu oxidation states are only present at low acidity. A single global model that responds to all of the sources of spectral variation would have too many fitting factors for (that is, overfit) any one individual spectrum. Local models, restricted to a subset of the overall condition range, are equally or more accurate than global models. They are also more robust if unexpected conditions arise. Examples of unexpected conditions observed during HB-Line operation included non-anticipated interferents and poor spectrum quality due to flow turbulence, as described in Ref. 7.

4.2 Methods.

The scheme of uranium and nitric acid concentrations in the standard solutions is shown in Figure 13. Also indicated are the expected concentrations for Tanks 15.4, 17.4, and 17.5, the “low acid” tanks, and for Tanks 16.8 and 18.7, the “high acid” tanks. Solutions which were analyzed at elevated temperatures are indicated with a “T”.

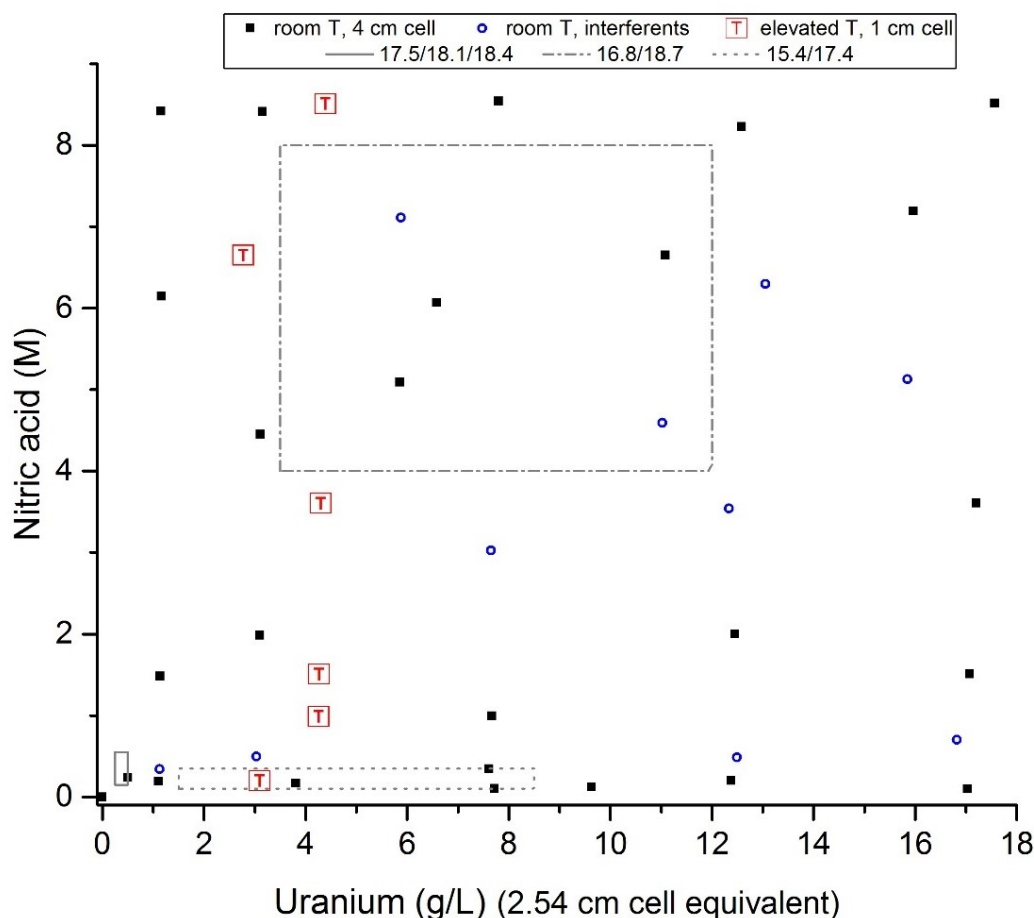


Figure 13. Calibration standards scheme and relation to expected tank conditions.

Calibration solutions were prepared gravimetrically from uranium and nitric acid stock solutions, distilled water, and aliquots of Fe^{3+} , Ni^{2+} , or Cr^{3+} stock solutions in weak nitric acid. The depleted uranium stock solution was prepared by dissolving U_3O_8 in heated dilute nitric acid. The final concentration was measured by potentiometric titration (Davies-Gray Analysis) to be 0.036729 g U /g solution, or 38.611 g U/L.* The acidity was determined to be 0.0976 M. The nitric acid stock solution was prepared by gravimetrically diluting 16 M concentrated nitric acid with distilled water to a final concentration of 12.65 M. Interferent solutions were originally prepared as 10 g/L solutions in ~0.8 M nitric acid.

Delivered masses were measured with an analytical balance enrolled in the Site M&TE program. Densities were measured with a Parr DMA 35N densitometer, verified before and after each use to an accuracy of ± 0.0003 g/mL. Approximately 100 mL of each solution was made and stored in plastic vials. The uncertainties in the final U and acid concentrations for the standards are calculated by propagation of uncertainties of the individual M&TE measurements and of the stock solution concentrations. For U, the uncertainty (1σ) ranges from 0.56 – 0.60%; for nitric acid, the range is 5.04 – 5.07%. For conservatism, the larger value of each range is assumed.

* M.E. Morales-Arteaga and N.A. Johns to R. Young, “Characterization of DU U_Stock A and U_Stock B for Uranium Content”, SRNL-L4600-2018-00034, 7/6/2018.

Absorbance spectra of the calibration solutions were measured with all five field spectrophotometers. Each instrument was confirmed to have passed the measurement check of the NIST-traceable absorbance standards before and after the solution measurements and was automatically calibrated for wavelength response to the Hg lamp emission. Calibration solutions were measured using two different cells. All solutions were measured at laboratory temperature (~20-25 °C) using a 4 cm low volume flow cell. For these measurements, several solution exchanges were repeated until the spectra stopped changing – that is, the previous standard in the flow cell had been fully exchanged. A subset of the calibration set was also measured in 1 cm sealed cuvettes at a range of temperatures from 20 °C to approximately 50 °C. For these solutions, the cuvettes were kept at 60 °C in a heated block until measurement. Each cuvette was taken from the block, immediately placed in the cuvette holder, and monitored spectroscopically as the solution cooled until no further changes were observed. Temperature was not explicitly monitored during these measurements. Based on similar work done during NGS development, the highest temperature is likely to be 50 °C.

Calibration spectra with contributions from transition metals were obtained in two ways. As shown in Figure 13, a number of standards were prepared with these species already added at concentrations of ~2.5 g/L. Example spectra are shown in Figure 3. It is apparent that the Cr(III) levels were too high, as absorbances were saturated for a 4 cm cell. Fe(III) and Ni(II) also added substantially to the absorbance, limiting the number of standards that could be used for building models in Pathways 4-6. Therefore, additional calibration spectra were constructed by recording spectra of pure interferent solutions and adding them in random proportions to spectra of clean uranyl nitrate. Previous work⁵ has shown that at process-relevant concentrations, there is no interaction of the interferents and uranyl nitrate, and the total spectrum is equal to the sum of the individual components. Both types of interferent spectra were used with equal consideration when constructing models.

4.3 Calibrations

All calibration models were made using the PLS_Toolbox software set, which operates in the Matlab environment. Once the calibrations were optimized, they were converted into standalone XML files which could be called by the data acquisition software using ModelExporter.*

All data sets were pre-processed to make them more amenable to analysis. The spectral set (X-block) was smoothed and derivatized using the Savitzky-Golay method.²² In the tables below, this process is denoted as SG(*pts*, *poly*, *order*), where *pts* indicates the size of the smoothing window (a larger value indicating more smoothing), *poly* the order of the polynomial used to fit the data within the window, and *order* the order of the derivative of the data (e.g. 1 = first derivative, 2 = second derivative). Both the X- and Y-blocks (the latter referring to the concentrations of the solutions) were typically mean-centered (MC), that is, the values were adjusted by subtracting the average of the data block.

For the uranium analyses, the Y-block (uranium concentrations) were adjusted to mimic the response from a 1 inch (2.54 cm) cell. Specifically, Beer's Law shows that the absorbance is proportional to the product of concentration and path length. Thus, an absorbance measured for a concentration c in a 4 cm flow cell would be the same as for a concentration $[c \times (4/2.54)]$ in a 1 inch cell. Likewise, the concentrations for the solutions measured in the 1 cm cuvette are changed to $c/2.54$ in the models that will be applied for measurements in the field.

A different processing step is required for nitric acid calibrations. It is well-established that at the concentrations in the Second Uranium Cycle, the distribution of uranyl nitrate species is essentially independent of the uranium concentration.^{5,11} This occurs because the nitrate concentration is several orders

* PLS_Toolbox: Version 8.2.1, Eigenvector Research, Inc. Matlab: Version R2016a, Mathworks, Inc. Model Exporter: Version 3.3.0, Eigenvector Research, Inc.

of magnitude larger than the uranium concentration and the nitrate formation constant is weak.¹⁴ Thus, the shape of the absorbance spectrum remains the same for a given acidity, only changing magnitude in proportion to the total uranium concentration. Because PLS is sensitive to magnitude, acidity models require spectra to be normalized to remove the effect of uranium on the analysis. This change also removes the dependence of the spectrum on path length. Thus, the adjustments described above for uranium models are not required for nitric acid. In past work, the normalization was done by dividing the spectrum by a peak maximum or the total area of the spectrum. Neither technique is particularly useful for this data set, due to the influence of interfering species. Another normalizing technique which proves more generally applicable is Multiplicative Scatter Correction (MSC).^{23,24}

In MSC, the test spectrum to be corrected is regressed against a reference spectrum - in this case, the average spectrum of the calibration set. The regression generates a multiplication factor that is applied to the test spectrum. MSC is designed to correct for baseline offsets and pathlength differences due to light scattering. Since, for the purposes of acid measurements, changes in uranium concentration are equivalent to changes in path length, this correction technique normalizes spectra without prior knowledge of uranium concentration. An example of the efficacy of the treatment is shown in Figure 14. Here, a subset of the calibration data for the high-acid acidity prediction model $A_{C,2}$ is shown before (left) and after (right) MSC treatment. This data contains spectra of solutions with acidities ranging from 8.2-8.5 M and U concentrations between 1.1-12.6 g/L. The large signal variation associated with uranium is eliminated, with subtler distinctions due to the small acidity variance now emphasized.

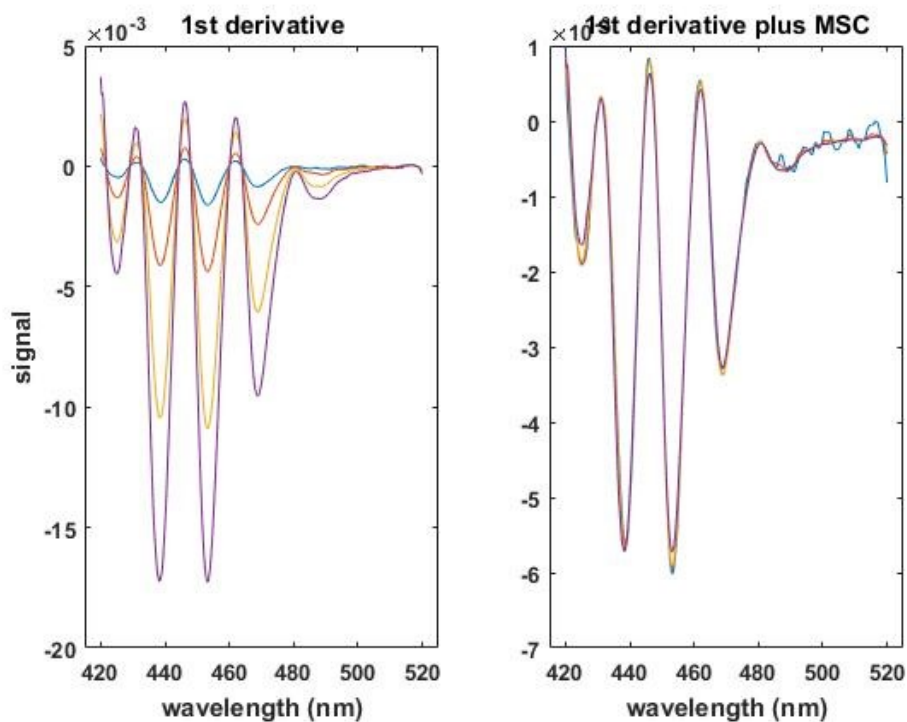


Figure 14. Efficacy of MSC for normalizing spectra with varying U concentrations.

Table 4 summarizes the parameters and fit statistics for the local, clean models for Pathways 1-3. These models were made with data from one spectrophotometer. Cross-validation from within the calibration set was performed by randomly splitting the data into 8-10 sets, with each set being sequentially used as a validation for a model made with the remaining data. This process was repeated 5 times, with the final model being an average result for all the iterations. The signal-to-noise ratio for the last PC is estimated

using a principal components analysis method developed by Spiegelman *et al.*^{25,26} This information is used to confirm the number of PCs which will be included in the prediction models without overfitting the data. A signal-to-noise ratio over 3 is considered acceptable for a PC to have significance. Additional validation was done using spectra of the same standards obtained with the other spectrophotometers.

Table 4. Fit parameters and results for the non-interferent models (Pathways 1-3).

Pathway	1	2	3
Concentration Ranges	U: 0 – 17.1 M Acid: 0.1 – 2.0 M	U: 0 – 17.1 M Acid: 0.1-8.5 M	U: 0 – 12.6 M Acid: 4.5 – 8 M
Uranium model	U_{C,1} (Uc1v1)	U_{C,0} (Uc0v2)	U_{C,2} (Uc2v1)
Pre-processing	X: SG(3,11,1), MC Y: MC	X: SG(3,31,1), MC Y: MC	X: SG(3,11,1), MC Y: MC
Wavelengths	410 – 500 nm	405 – 500 nm	410 – 500 nm
PCs	3	5	4
RMSE (C/CV)	0.032 / 0.066 g/L	0.051 / 0.074 g/L	0.057 / 0.111 g/l
Bias (C/CV)	0 / 0.004 g/L	0 / 0.004 g/L	0 / -0.016 g/L
R ² (C/CV)	0.99993 / 0.99967	0.99985 / 0.99971	0.99975 / 0.99923
s/n last PC	6	3.3	5
Nitric acid model	A_{C,1} (Ac1v4)	A_{C,0} (Ac0v5)	A_{C,2} (Ac2v3)
Pre-processing	X: SG(51,3,1), MSC, MC Y: MC	X: SG(51,3,2), MSC Y: MC	X: SG(51,3,1), MSC, MC Y: MC
Wavelengths	420 – 530 nm	420 – 530 nm (2)	420 – 530 nm
PCs	6	5	5
RMSE (C/CV)	0.010 / 0.027 M	0.28 / 0.31 M	0.071 / 0.120 M
Bias (C/CV)	0 / -0.002 M	-1e-5 / -0.002 M	0 / -0.010 M
R ² (C/CV)	0.9993 / 0.9965	0.990 / 0.988	0.9986 / 0.9962
s/n last PC	5	4	8

(1) Abbreviations: SG = Savitzky-Golay function (see text); MC: mean center; MSC: Multiplicative Scatter Correction (see text); RMSE: root mean-square error; C: calibration; CV: cross-validation; PC: principal component; s/n: signal-to-noise ratio. (2) Subset of wavelengths within this range, as explained in the text.

Residual plots for each of these models are shown below. For each model, three plots are shown. The calibration plot (a) shows the self-prediction results for the model that was built using the data from a single spectrophotometer. The validation plot (b) shows the results from using the model to predict the concentrations from spectra generated with the other instruments. Mean values are plotted, with error bars showing the variance across instruments. The absolute error plot (c) summarizes the errors for all the standards in the quantity

$$error_i = |(\bar{x}_i - \langle x \rangle_i)| + \sigma_i,$$

where the first term captures the bias error (absolute value of the difference between the average calibration/validation result for all spectrophotometers and the expected value) for each standard i and the second term contains the variation between measurements of the same standard on different spectrophotometers.

For both uranium and acid predictions, the local models (C,1 and C,2) outperform the global model (C,0) in accuracy. Figure 21 compares the local and global model results directly for standards common to each model. Specifically, the difference of the error metric in the above equation, expressed as a percentage of the known value, is shown. A positive value means that error of the global model is larger than the error

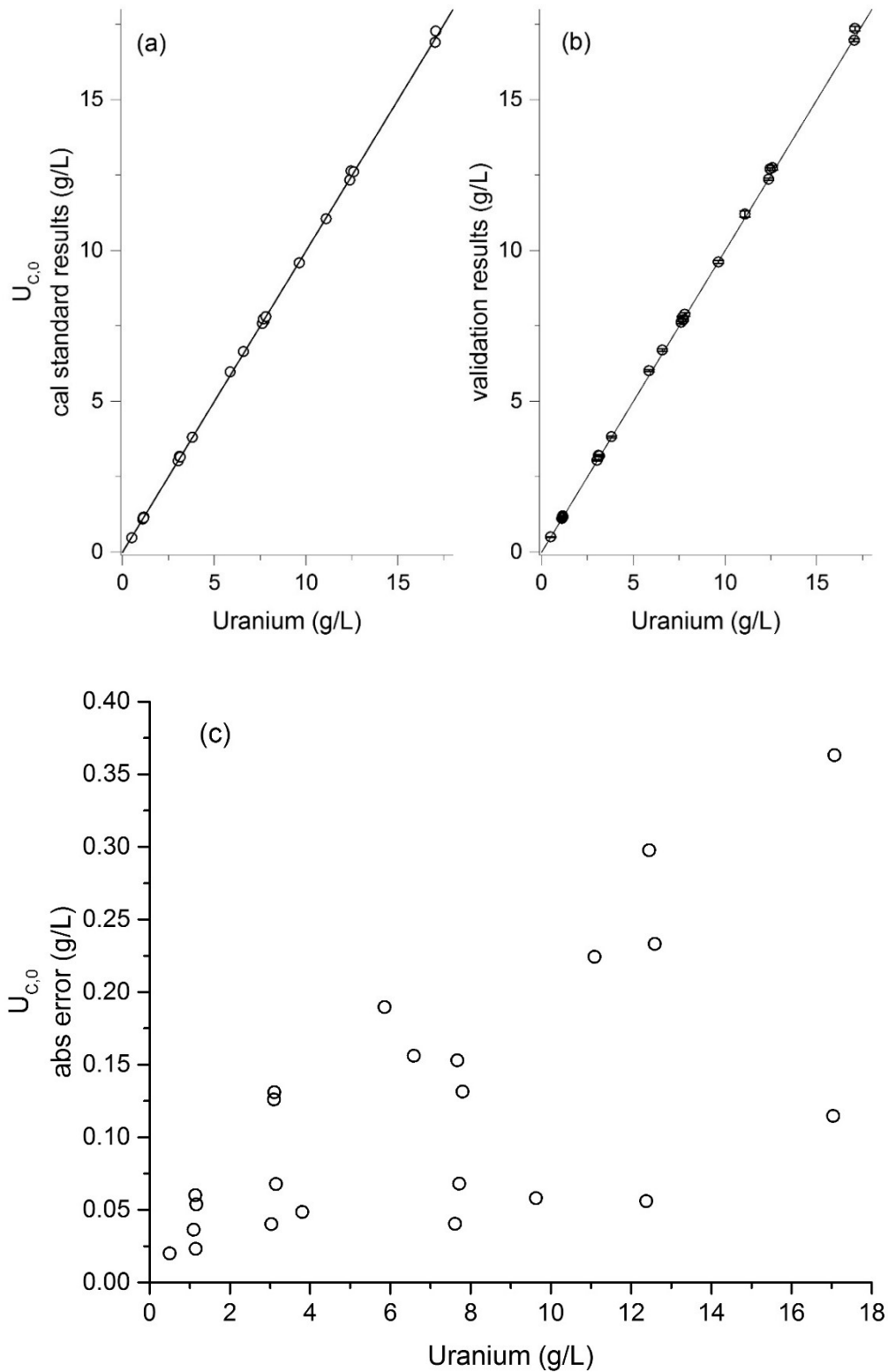


Figure 15. Results for model $U(c,0)$ (non-interferent, global uranium prediction model, Pathway 2).
(a) Calibration standards. (b) Validation standards. (c) Absolute errors, calibration standards.

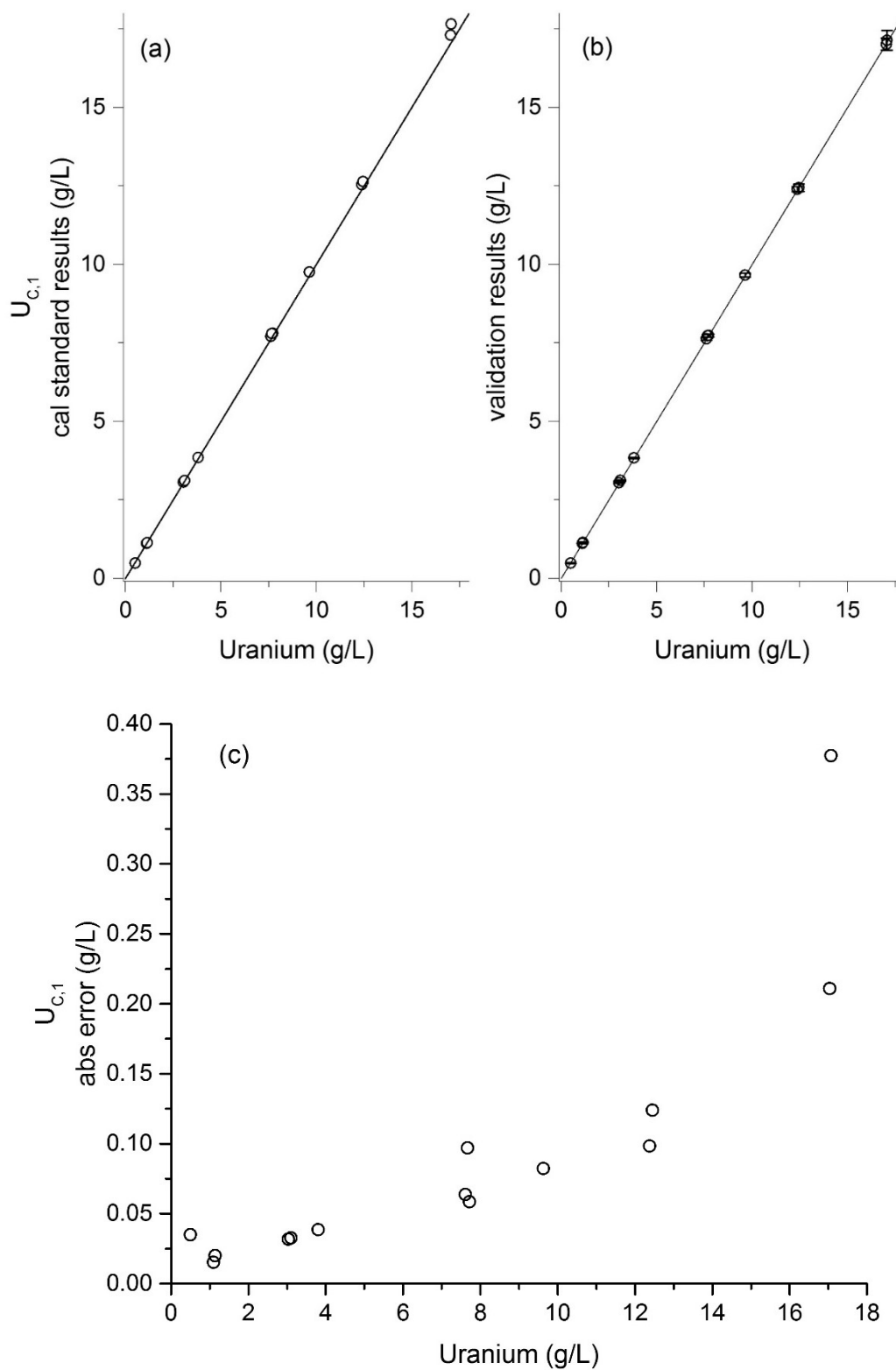


Figure 16. Results for model U(c,1) (non-interferent, low-acid uranium prediction model, Pathway 1). (a) Calibration standards. (b) Validation standards. (c) Absolute errors, calibration standards.

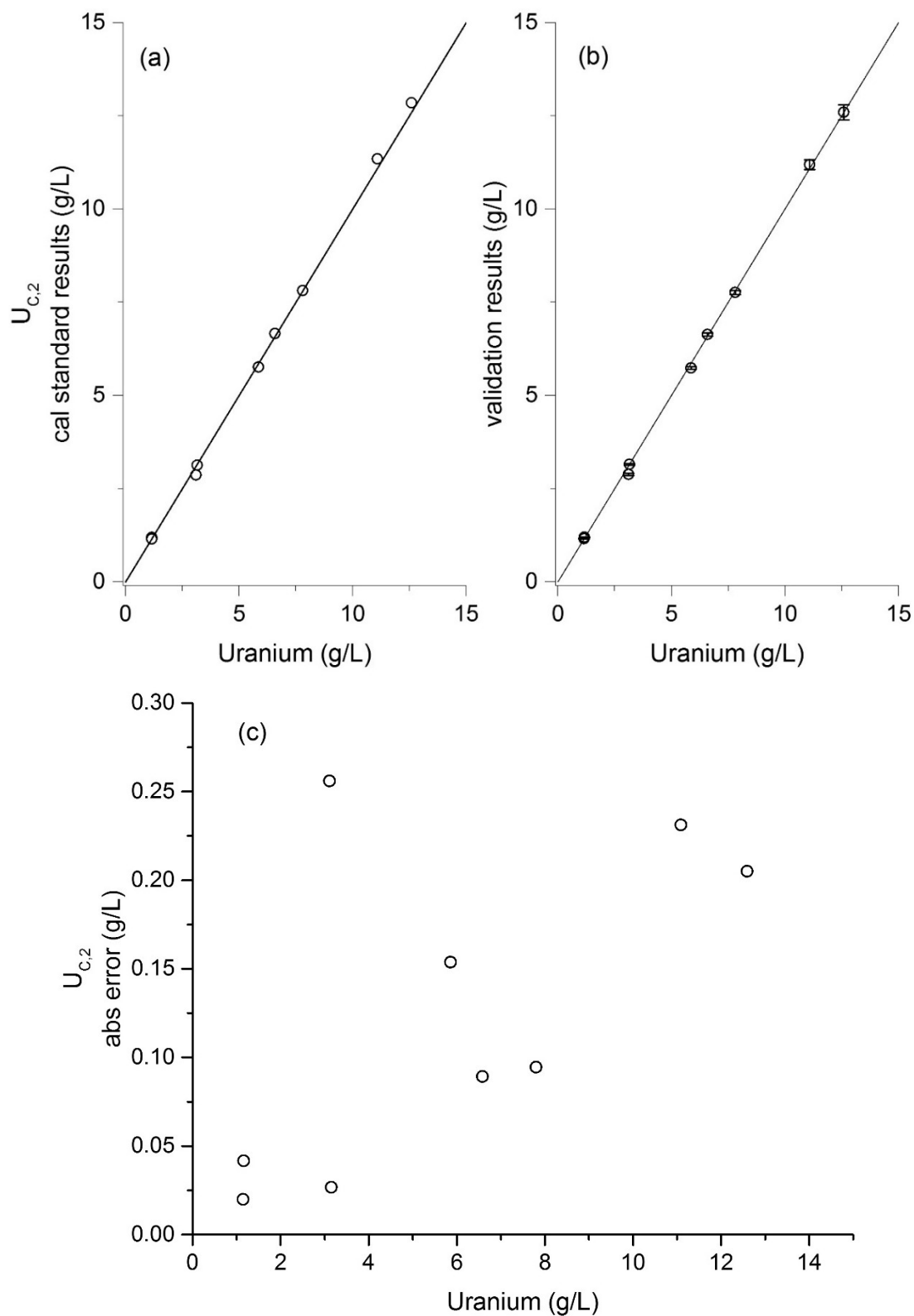


Figure 17. Results for model U(c,2) (non-interferent, high-acid uranium prediction model, Pathway 3). (a) Calibration standards. (b) Validation standards. (c) Absolute errors, calibration standards.

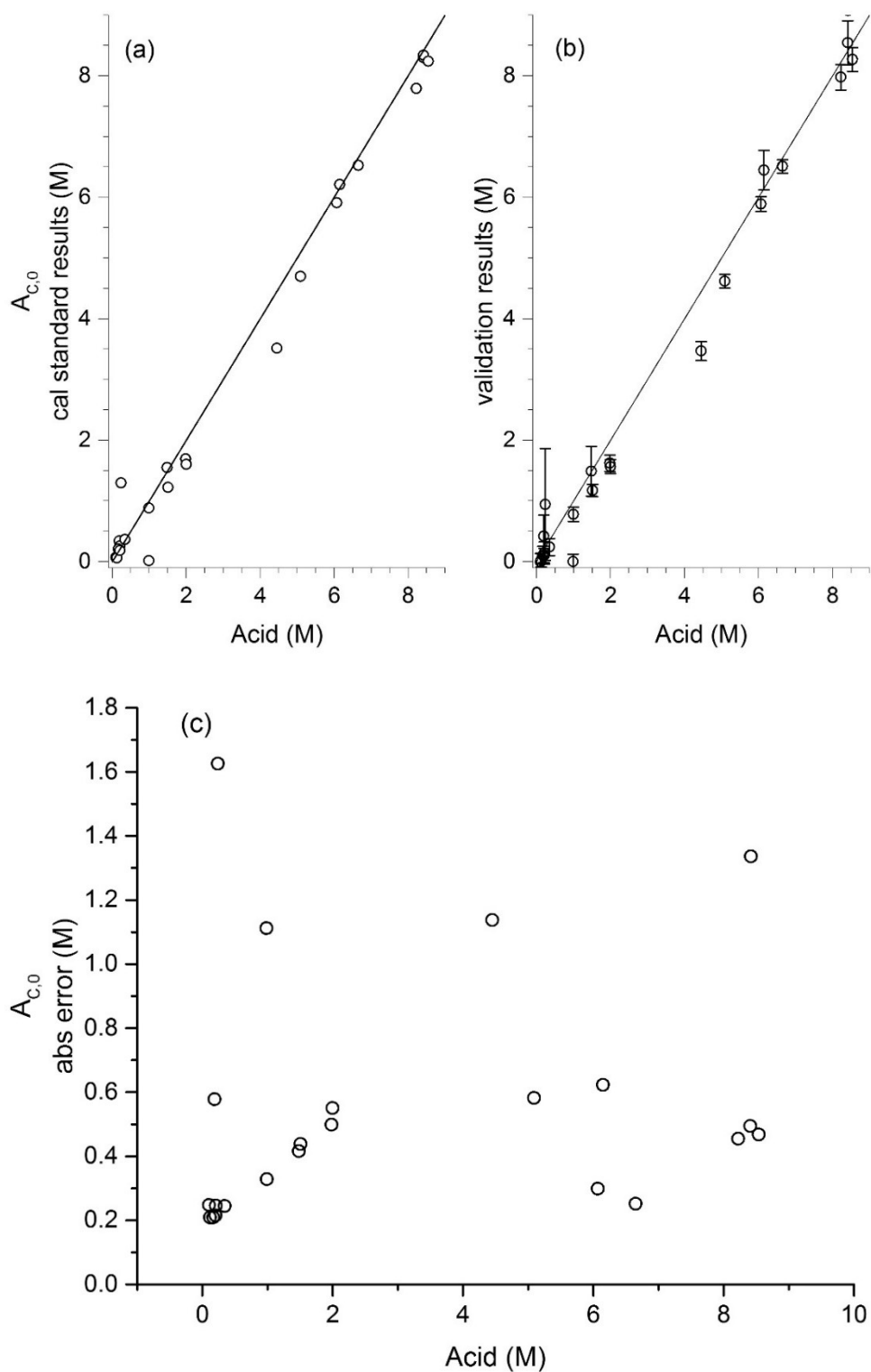


Figure 18. Results for model A(c,0) (non-interferent, global nitric acid prediction model, Pathway 2). (a) Calibration standards. (b) Validation standards. (c) Absolute errors, calibration standards.

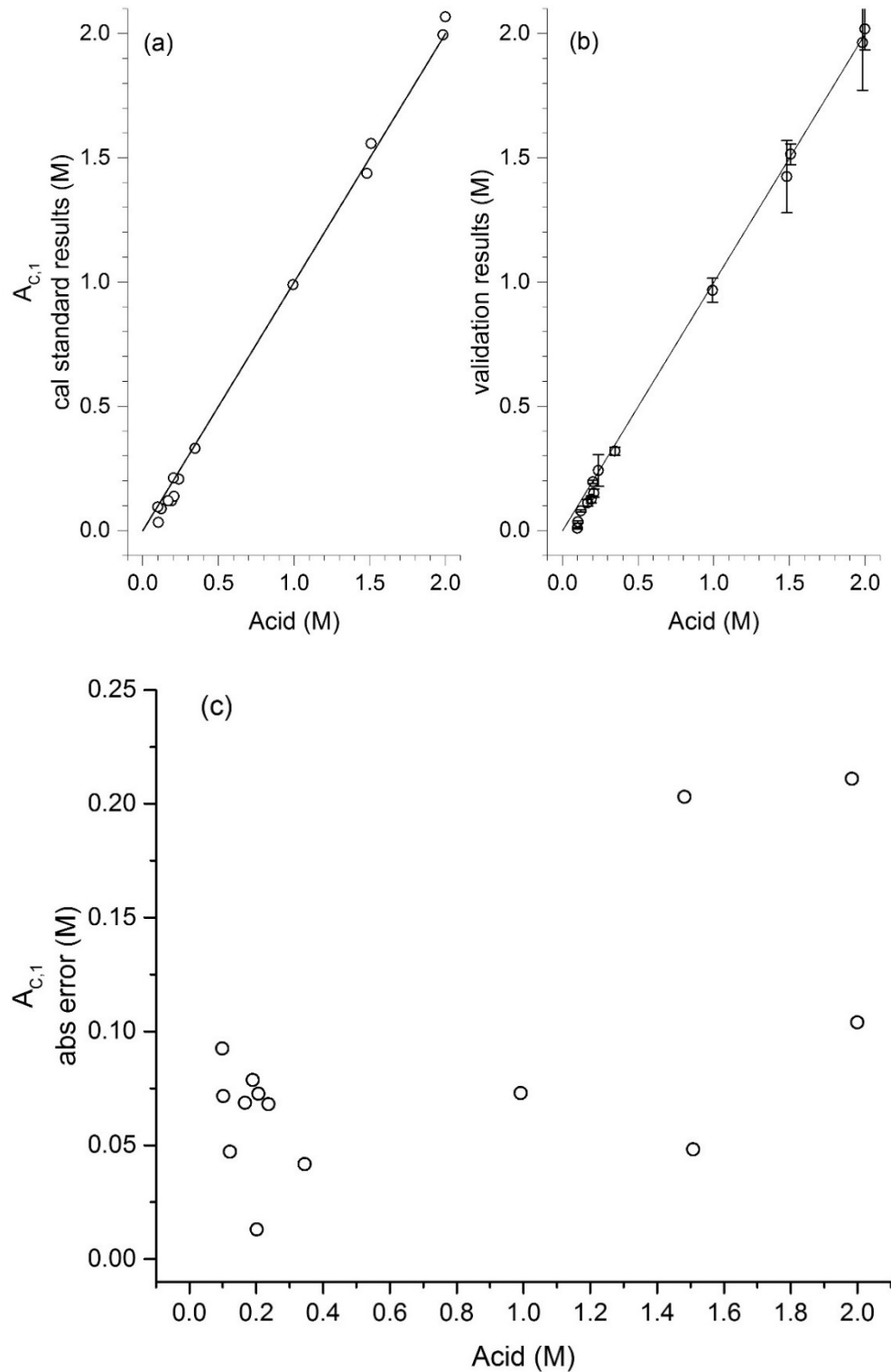


Figure 19. Results for model A(c,1) (non-interferent, low-acid nitric acid prediction model, Pathway 1). (a) Calibration standards. (b) Validation standards. (c) Absolute errors, calibration standards.

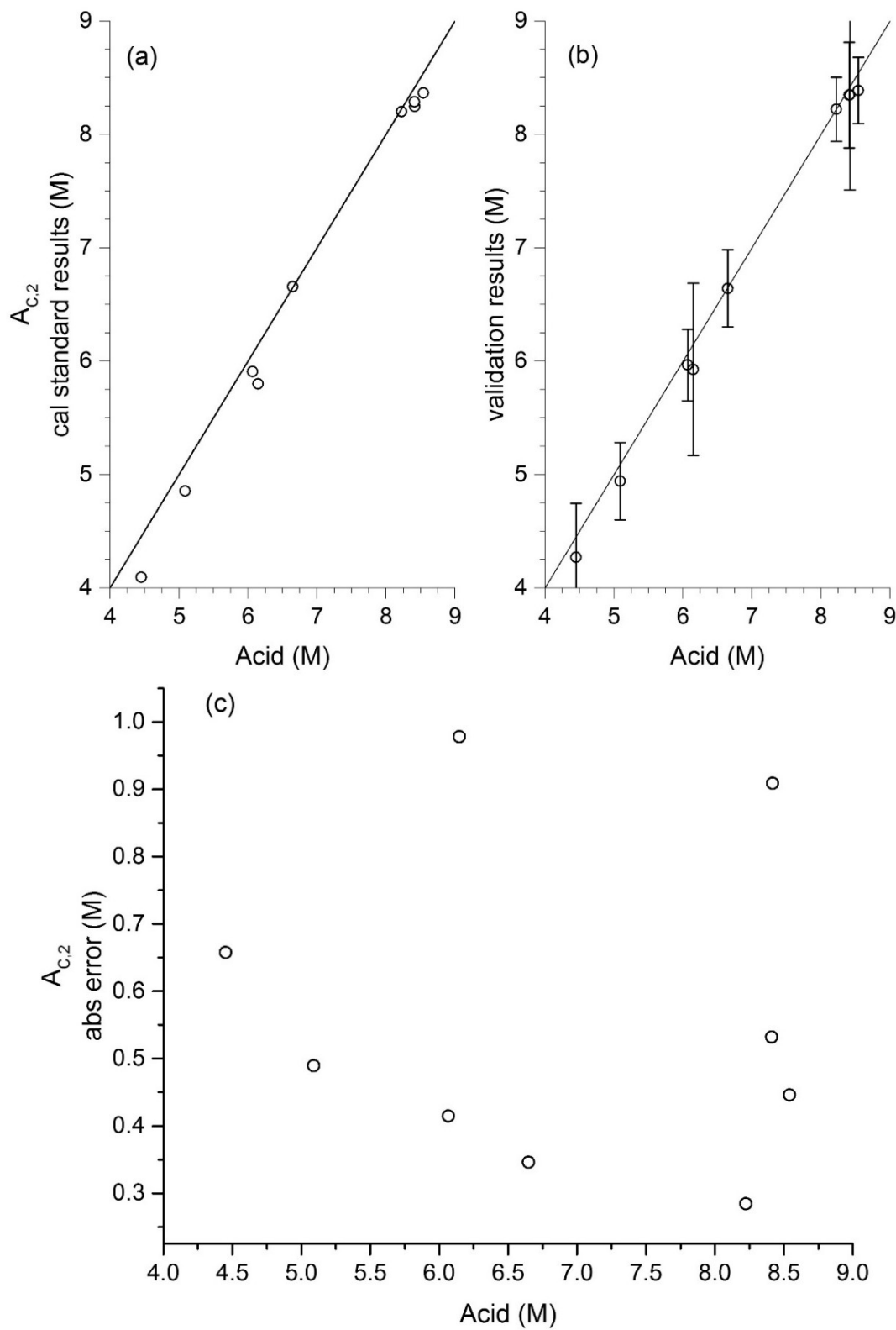


Figure 20. Results for model A(c,2) (non-interferent, high-acid nitric acid prediction model, Pathway 3). (a) Calibration standards. (b) Validation standards. (c) Absolute errors, calibration standards.

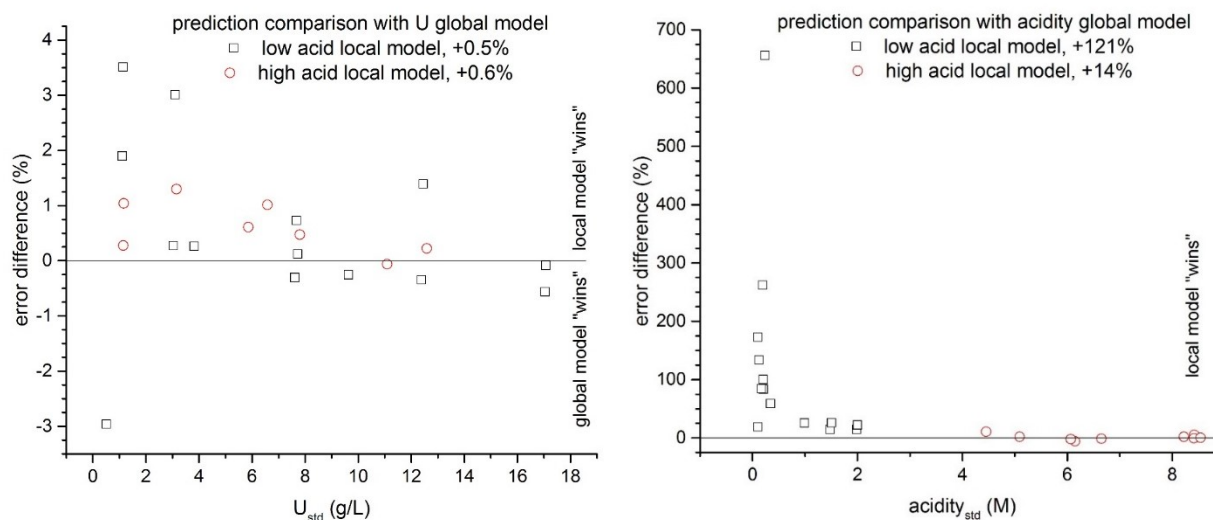


Figure 21. Comparison of local (low- and high-acid) models with global models, for non-interferent standards. (Left) Uranium. (Right) Nitric acid.

for the local model. For the U models at low and high acids, the improvements are 2.1% to 1.6% (+0.5%) and 2.5% to 1.9% (+0.6%), respectively. For the acidity models, the improvements are 150% to 29% (+121%) and 24% to 10% (+14%), respectively. For all four comparisons, the local prediction models provide higher accuracy than the global models.

The efficacy of including temperature variation in the model calibration set is shown in Figure 22. Here, uranium concentration predictions from the global model U(C,0) are compared to the results from a model based on room temperature data only. While the models give similar results at room temperature, the room

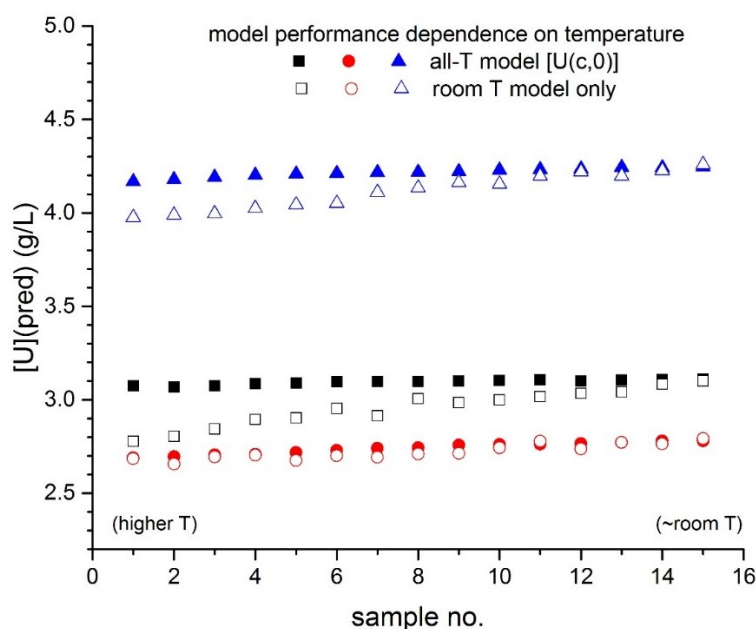


Figure 22. Necessity of including temperature variance in uranium prediction models.

temperature model has a larger negative bias at higher temperatures. For the 6 solutions tested, the bias ranges from -1.4% to -9.7% for the room temperature model, and -2.0% to -4.1% for the all-inclusive model. This effect is comparable to what was observed in previous work. Due to this experience, temperature variance was assumed to be important for all models prepared for this monitor, and no other comparisons were made for the effects with and without inclusion of temperature effects.

One significant effect of the primary (wavelength, absorbance) calibrations for each spectrophotometer is the equivalence of the spectra with respect to application of the models, shown in Figure 23. Each panel represents one of the “clean” uranium and acidity models described above. Residuals for each spectrophotometer against each standard are tracked by standard. The standards are arranged in order of lowest to highest concentration. The prediction residuals are highly correlated, with the spread of errors across instruments for a given standard being comparable to the prediction mean error. There is also a consistent pattern to the relative residuals between instruments. For example, in the U(C,0) model, “Spec 2” and “Spec 3” have a consistently more positive bias, whereas “Spec 4” and “Spec 5” are consistently more negative. This suggests that the variation in meeting the tolerances of the primary standards translates consistently into variation in reproducing the secondary standards.

The performance of the clean local models is the basis for the instrument uncertainty analysis which has been provided to the facility* and is included in Appendix F for reference.

A critical element of the piecewise local scheme is proper automated identification of solutions containing spectral interferences. Identification is based on fit residuals for the global U prediction model U(C,0), assuming the absorbance check is passed. The relationship between residual and prediction error is shown in Figure 24 for all calibration spectra, including those with simulated interferences added. There is a distinct segregation of clean and interferent spectra, although in some cases high residuals occur for clean spectra despite low prediction errors. The horizontal line represents the threshold chosen to conservatively exclude interferent-containing spectra from being analyzed with a clean model.

The residual threshold was chosen to allow for the possibility of a false-positive indication of interferences. Figure 25 compares the results for all calibration standards above the residual threshold when analyzed by U(C,0) and by U(I,0), the interferent-containing global model. Clean solutions (blue dots) are equally distributed around the dashed line, indicating that on the whole, predictions on these solutions are equally good with both models. (The median error ratio between the two models is 1x, that is, there is no improvement for one versus the other.) Thus, there is little risk in setting a conservative residual threshold when trying to maximize performance under normal operations.

As intended with interferent models, the prediction accuracy for the interferent-containing standards is greatly improved, although still quite large in some cases. It should be noted that the results in Figure 25 do not represent any further classification for acidity (Pathways 4 and 6) or high absorbance (Pathway 7). The full performance of the piecewise local scheme for all solutions can be assessed when each standard is analyzed by the appropriate local models. These results are shown for uranium in Figure 26 and for nitric acid in Figure 27. For Pathways 4-6, the predictions using the appropriate local models are shown with solid dots, while the open dots show the results from using the corresponding clean models. For uranium, all local interferent models provide a highly linear response with reasonable accuracies. Note that the clean models show a uniformly high bias that is attributable to the inability of those models to differentiate between the interferent and uranyl nitrate absorbances. The local nitric acid prediction models are less successful. The cause for this behavior has not been fully explored, and it is possible that improved models could be generated should the need arise.

* R.J. Lascola to J.D. Bickley, “Uncertainty Analysis for OLMS Spectrophotometers”, SRNL-L4000-2018-0008, Rev. 0, August 28, 2018.

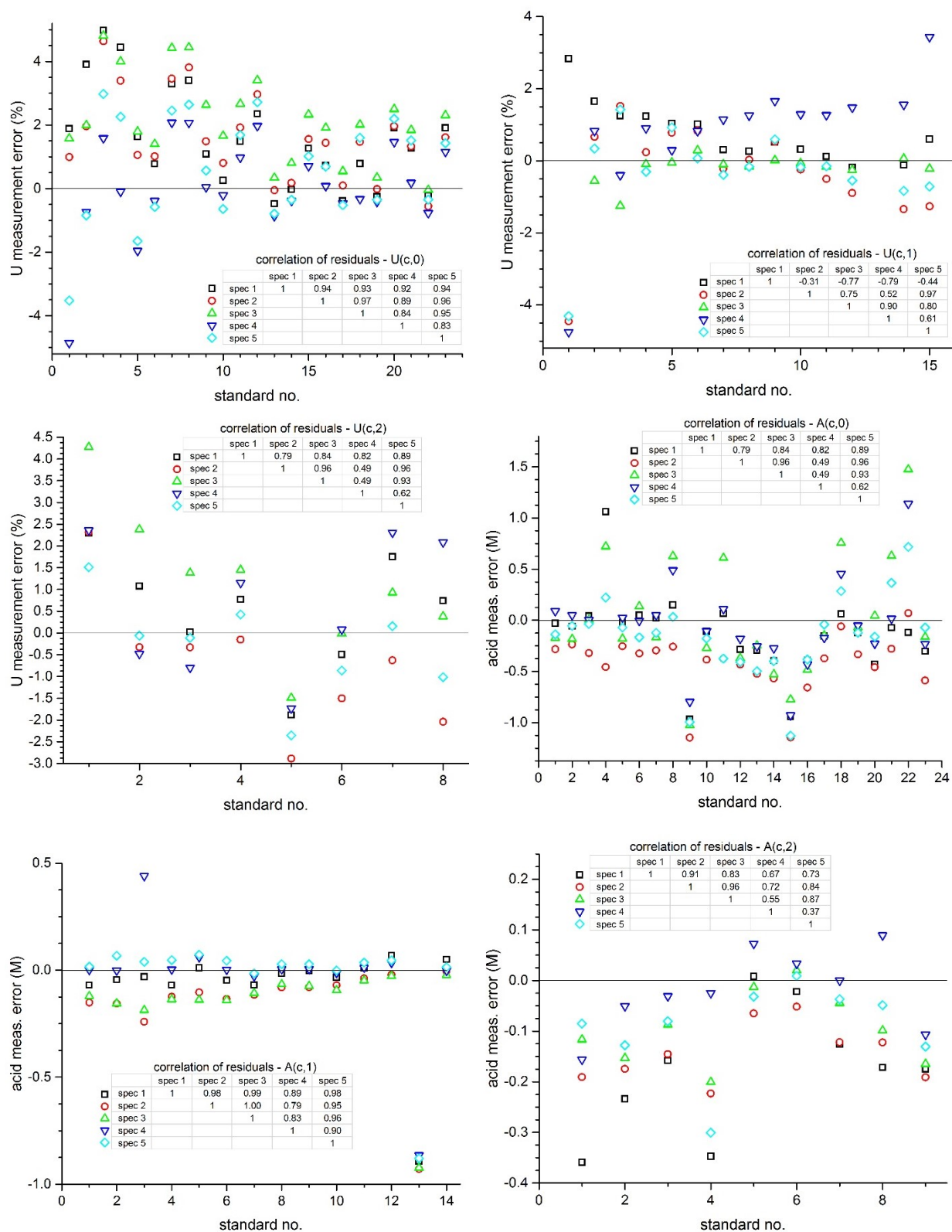


Figure 23. Variation of predictions across spectrophotometer for all non-interferent uranium and nitric acid models.

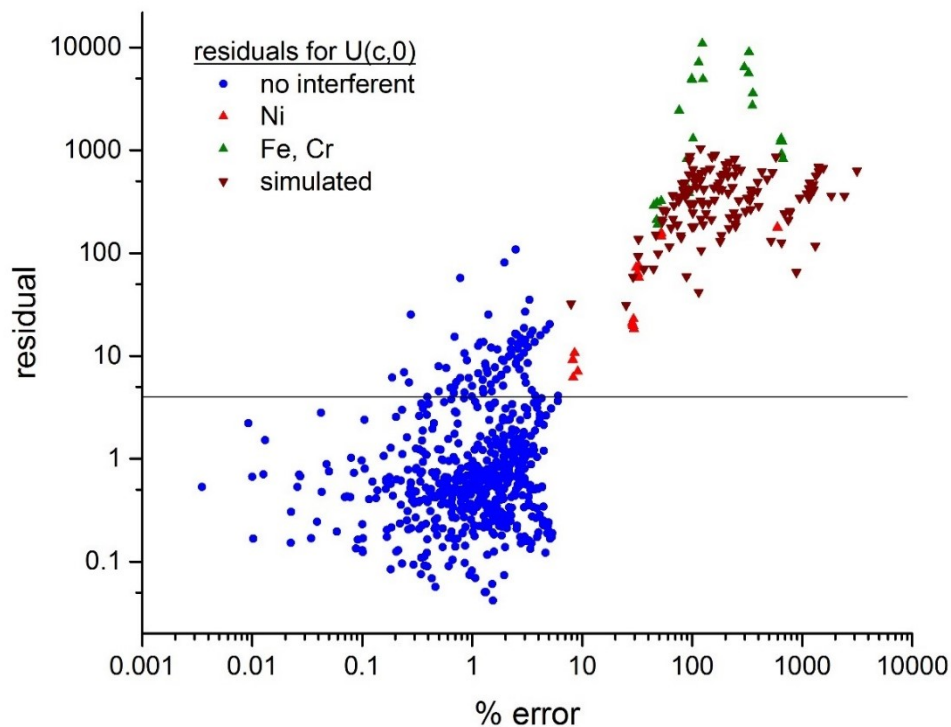


Figure 24. Relation of fit residuals to prediction error for interferent screening model (global uranium model). Straight line represents screening threshold.

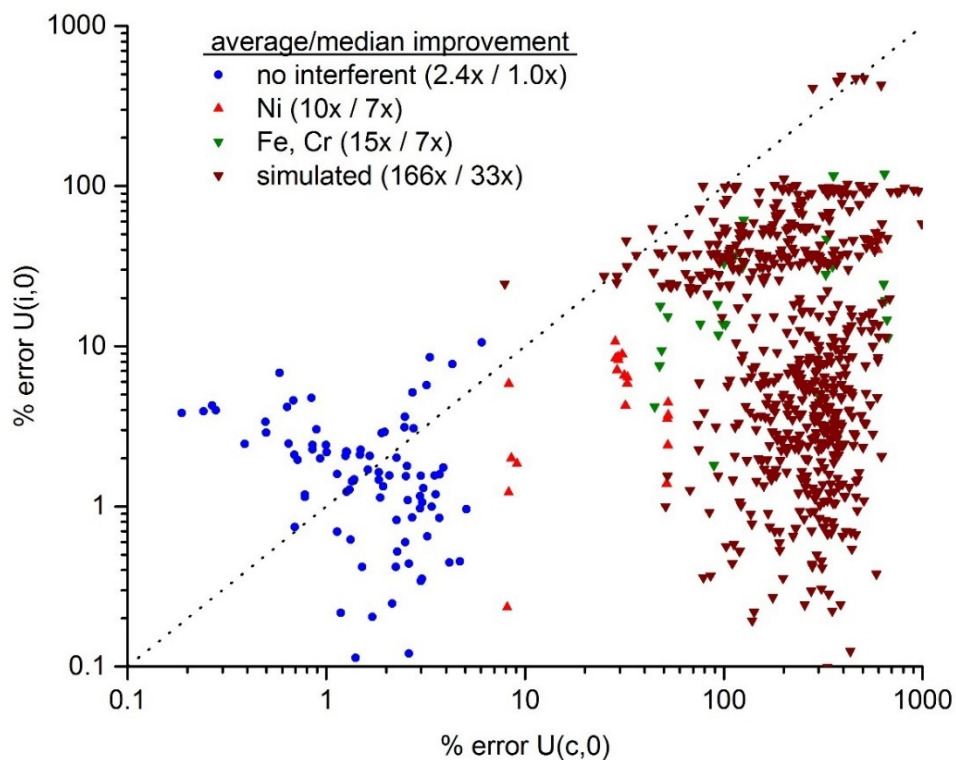


Figure 25. Comparison of results from non-interferent and interferent global uranium models for spectra with residuals above the screening threshold.

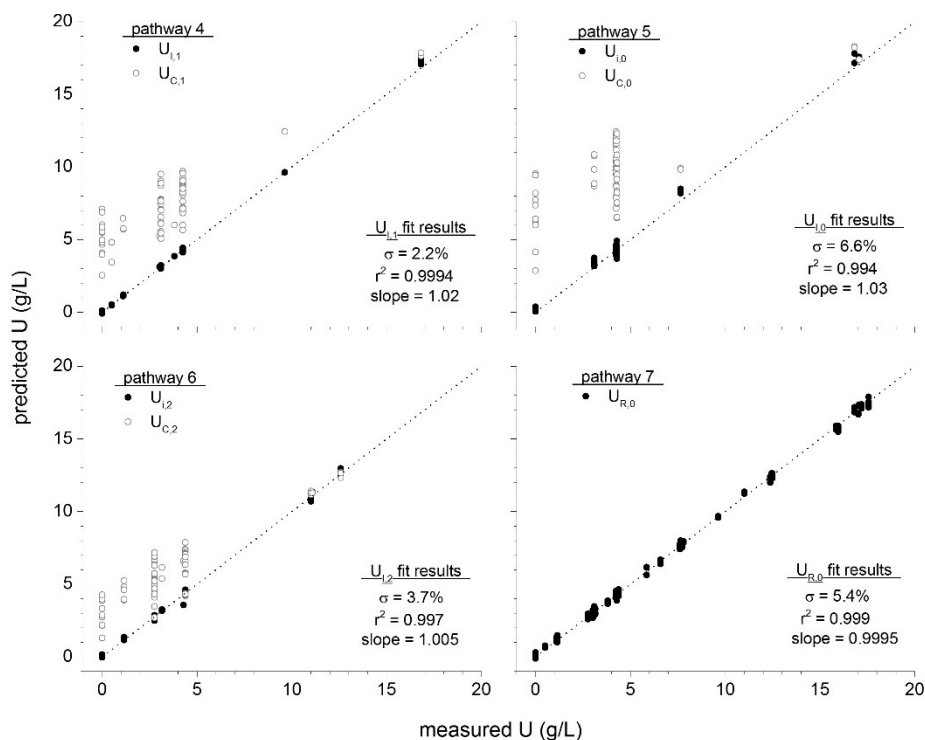


Figure 26. Prediction results for uranium models, Pathways 4-7. Results from non-interferent models shown for Pathways 4-6.

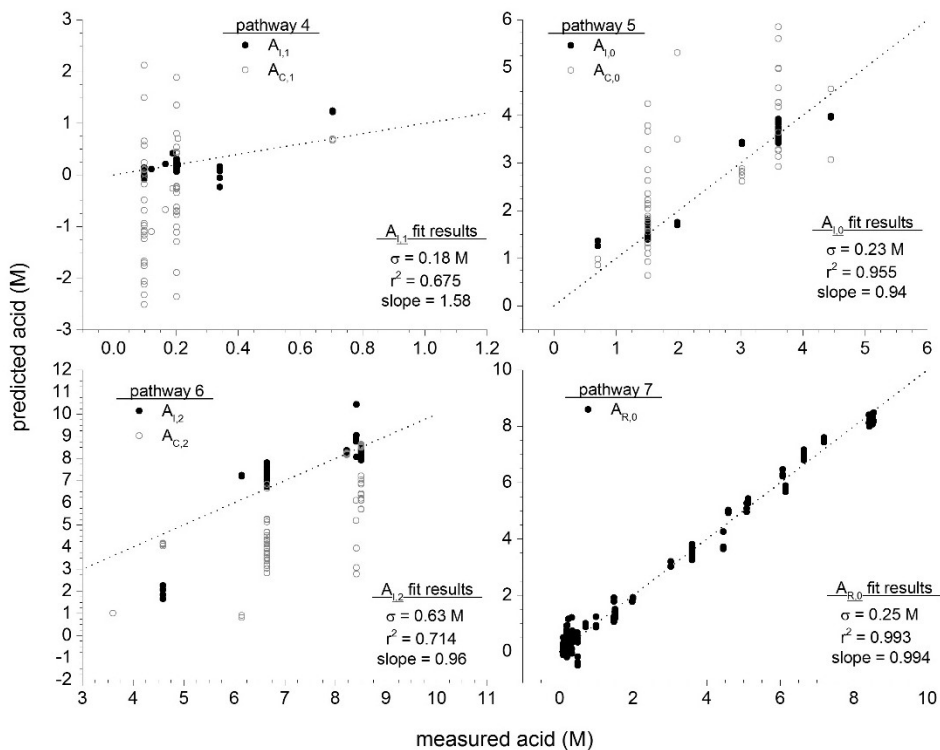


Figure 27. Prediction results for nitric acid models, Pathways 4-7. Results from non-interferent models shown for Pathways 4-6.

A summary of the fitting results for all models in the pathway is shown in Table 5. These results include uncertainties from the predictions only, and do not include uncertainties from the concentrations of the standards. Therefore, the values here are slightly smaller than those reported in the final uncertainty analysis in Appendix F. The “Standard Error U Blank” column shows the uncertainty for solutions with no uranium. For Pathways 4-6, this includes spectra with the interferents. The last two columns indicate the poor results from applying the clean models to spectra with interferents.

Table 5. Summary of Fit Results for All Pathways

Pathway	Description	Standard ^a Error U (%)	Standard ^a Error Acid (M)	Standard ^a Error U Blank (g/L)	Standard ^a Error From Clean U Model (%)	Standard ^a Error From Clean Acid Model (M)
1	C,1	2.1	0.054	0.047	---	---
2	C,0	2.0	0.268	0.016	---	---
3	C,2	2.5	0.125	0.022	---	---
4	I,1	2.2	0.175	0.055	109	2.37
5	I,0	6.6	0.230	0.109	62	1.32
6	I,2	3.7	0.628	0.068	69	2.16
7	R,0	5.4	0.248	0.105		
1-3	all clean	2.4	0.18			
1-7	all spectra	4.1	0.29			

a – Errors expressed as 1σ .

5.0 Qualifications

At the time of this writing, a formal qualification scheme has not yet started. Solutions from all five tanks will be analyzed both by the OLMS and by off-line methods.

6.0 Conclusions

SRNL has developed an On-Line Monitoring Spectrophotometer to measure uranium and nitric acid concentrations in H Canyon Second Uranium Cycle. Five instruments have been installed, at Tanks 15.4, 16.8, 17.4, 17.5, and 18.7. These instruments provide measurements on demand from the H Canyon DCS. The prediction scheme is based on a piecewise local partial least squares analysis scheme, which classifies spectra based on the automated detection of absorbance level, acidity, and presence of interfering species and applies prediction models tailored to the localized set of conditions. This scheme provides more accurate results than the use of a global model which assumes the presence of these complicating conditions. Including uncertainties inherent to the calibration standards and the flow cell path length, the overall uncertainties for measurements, expressed as 2σ , are 5.3% (uranium) and 11% (nitric acid, Tanks 16.8 and 18.7 only). The instruments are configured with long lifetime light sources, which should greatly reduce maintenance requirements compared to colorimeters and previous versions of the spectrophotometers. They also have significant internal diagnostics that are readily available for troubleshooting purposes.

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Appendix A. Technical Task Request NMMD-HTS-2017-3403

USM 11A-220 (REV 2-11-2008)

PTOC, HBT, E7, 2.0.4

Technical Task Request

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Funding Source EMO Budget		Modification Traveler No MT-HCA-2017-00007		Technical Task Request No. NMMD-HTS-2017-3403		Revision 0	
Design Authority Engineer (Signature)		Name (Print) Jeff Bickley		Phone 208-8584		Site Address 704-2H / 185	
Performing Organization Analytical Laboratories		Design Authority Manager* (Signature) N/A				Date 11/14/2017	
Task Description H-Canyon spectrophotometer development and installation						Due Date 07/31/18	
Task Activity <input checked="" type="checkbox"/> All activities are to be performed and documented in accordance with Manual E7. Specific procedures are referenced with the associated tasks. <input type="checkbox"/> Task Specific QA Plan, Reference: _____							
Definition of Scope of Modification <input type="checkbox"/> Not applicable to this request. <input checked="" type="checkbox"/> Provided, Reference: <u>See Attached</u> <input type="checkbox"/> To be developed as part of this request. Specific activities are: <input type="checkbox"/> Scoping Studies <input type="checkbox"/> Feasibility Studies <input type="checkbox"/> Technology Assessment <input type="checkbox"/> Technology Development <input type="checkbox"/> Inputs and Assumptions <input type="checkbox"/> Other, Specify: _____							
Functional Requirements and Basis <input type="checkbox"/> Not applicable to this request. <input checked="" type="checkbox"/> Provided, Reference: <u>See Attached</u> <input type="checkbox"/> To be developed as part of this request. Specific activities are: <input type="checkbox"/> Develop functional performance requirements to be included as part of the MT or Task Requirements and Criteria.							
Facility Hazard Category <input checked="" type="checkbox"/> Nuclear 2 <input type="checkbox"/> Radiological <input type="checkbox"/> Chemical (Low) <input type="checkbox"/> To be developed as part of this request (Manual 11Q) <input type="checkbox"/> Nuclear 3 <input type="checkbox"/> Chemical (High) <input type="checkbox"/> Other Industrial							
Functional Design Criteria <input type="checkbox"/> Not applicable to this request <input checked="" type="checkbox"/> Provided, Reference: <u>See Attached</u> <input type="checkbox"/> To be developed as part of this request. Specific activities are: <input type="checkbox"/> Alternative Studies <input type="checkbox"/> Develop functional design criteria to be included as part of the MT or Task Requirements and Criteria.							
Functional Classification <input type="checkbox"/> Safety Class <input type="checkbox"/> Production Support <input type="checkbox"/> To be developed as part of this request. <input type="checkbox"/> Safety Significant <input checked="" type="checkbox"/> General Service							
Criteria Technical Review <input checked="" type="checkbox"/> Not applicable to this request. <input type="checkbox"/> To be performed as part of this request.							
Design and Analysis/Technical Baseline Development <input type="checkbox"/> Not applicable to this request. <input checked="" type="checkbox"/> Provided, Reference: <u>See Attached</u> <input type="checkbox"/> To be developed as part of this request. Specific activities are: <input type="checkbox"/> Calculations <input type="checkbox"/> FDD <input type="checkbox"/> Functional Acceptance Criteria <input type="checkbox"/> Drawings <input type="checkbox"/> SDO <input type="checkbox"/> Technical Specifications <input type="checkbox"/> Specifications <input type="checkbox"/> CHAP <input type="checkbox"/> Other, Specify: <input type="checkbox"/> DSA <input type="checkbox"/> Quality Inspection Plans							

OSR 19-255 (Rev 2-19-2009)

Technical Task Request (Continued)

Page 2 of 5

Design and Analysis/Technical Baseline Document Technical Review	
<input checked="" type="checkbox"/> Not applicable to this request <input type="checkbox"/> To be performed as part of this request.	
Acceptance Testing	
<input type="checkbox"/> Acceptance Testing is Not Part of this Request <input type="checkbox"/> Test Procedure Provided, Reference: <input type="checkbox"/> Test Procedures to be Developed as Part of this Request <input checked="" type="checkbox"/> Test Results Provided, Reference: See Attached <input type="checkbox"/> Test Results Evaluation Not Part of this Request <input type="checkbox"/> Test Acceptance Report to be Provided as Part of this Request	
Other Reviews/Reports Required?	
<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No See Attached	
Technical Agency Analytical Laboratories	Name (Print) Clint Gregory
Acceptance of Task (Signature of Technical Agency Manager)	Date
Closure/Deliverables Provided See Attached	
Design Authority Engineer	Date
Design Authority Manager*	Date

* Design Authority Manager's signature required if request is not associated with an MT.

Basic scope: Develop a plant-grade optical absorption instrument to determine uranium and nitric acid concentrations in H Canyon tank samples based on spectrophotometers. The instrumentation will replace the existing instrumentation located in the H Canyon Control Room, but use the same optical fibers and tank samplers. The fibers and samplers have been determined to be functional (SRNL-L4100, 2017-00010, August 24, 2017). SRNL will develop and deliver 5 spectrophotometers and a cabinet to house the instruments. SRNL will also develop a sixth spectrophotometer and keep it as a development and troubleshooting instrument.

Functional requirements: (what it must do)

- R.1 Each unit shall measure uranium and nitric acid concentrations in sampled solutions with a uranium concentration range no less than between 0.5-10 g/L.
- R.2 Each unit shall measure uranium and nitric acid concentrations in sampled solutions with a concentration range no less than between 1-7 M.
- R.3 Each unit shall measure uranium and nitric acid concentrations in sampled solutions between temperatures of 20-45 °C.

Performance requirements: (how well must it measure, how reliable, available, maintainable, inspectable, and expandable is the unit)

- PR.1 Each spectrophotometer unit shall measure and report the total uranium concentration with a maximum uncertainty at a 95% confidence limit of 5%.
- PR.2 Each spectrophotometer unit shall measure and report the total nitric acid concentration with a maximum uncertainty at a 95% confidence limit of 10%.
- PR.3 Each spectrophotometer unit shall measure tank solutions that have been circulated through a flow cell attached to the air-lift sampler to which the spectrophotometer is dedicated.
- PR.4 Each spectrophotometer unit will recognize the presence of excess turbulence in the sampled solution, will suppress reporting readings under such conditions, and will indicate the presence of these conditions. Each unit will also generate a trouble alarm for lamp failure, computer component failure, and loss of communication with the DCS.
- PR.5 Each spectrophotometer unit shall be automatically calibrated for wavelength accuracy against atomic emission lines present in the light source. Each unit shall be periodically checked for absorbance measurement accuracy against NIST-traceable absorbance standards.
- PR.6 Each spectrophotometer unit shall be configured so that a new uranium or nitric acid calibration model developed in the laboratory on a development unit can be installed in the field without requiring removal of the field unit.

Interface requirements: (physical, electrical, mechanical, control room, display conditions)

- IR.1 The spectrophotometer equipment shall be designed to be installed in the H Canyon control room.
- IR.2 The spectrophotometer equipment shall be compatible with existing H Canyon control room fiber optic connections, normal power supplies, and sampler flow cells.

IR.3 The spectrophotometer equipment shall include an independent Uninterruptible Power Supply (UPS) with voltage regulator.

IR.4 The spectrophotometer unit shall be designed with a computer with direct programming capability, with software that applies a calibration algorithm for determining the uranium and nitric acid concentrations without requiring a user prompt, that generates results in real time, that can report results on demand, and that interfaces with a local instrument display and the Distributed Control System (DCS).

IR.5 The spectrophotometer unit shall report uranium and nitric acid concentrations to the local instrument display and to the DCS. The latter shall be reported through separate 4-20 mA analog output signals.

IR.6 The 4-20 mA analog output signal to the DCS shall be grounded at the spectrophotometer unit or shall incorporate signal isolators.

IR.7 The spectrophotometer unit shall report an alarm condition to the local instrument display and to the DCS. The latter shall be reported through a digital output signal.

IR.8 The spectrophotometer equipment cabinet shall include a capability for physical anchoring to the facility structure.

IR.9 Each spectrophotometer unit shall have an expandable input/output (I/O) capability to report additional unit information to the local instrument display or DCS (as appropriate) upon request by H Canyon Engineering.

Additional design input information:

DI.1 The functional classification of the spectrophotometer units will be defined by H Canyon Engineering. Equipment and component procurement and R&D activities will be conducted to ensure reliability and quality consistent with the functional classification.

Deliverables:

In addition to the spectrophotometer units and associated cabinet and display monitors, SRNL shall provide:

D.1 Documentation providing inputs to be used in support of the H Canyon uncertainty calculation for the instrumentation. Specific inputs will be developed with H Canyon Engineering and will include measurement uncertainty across all expected operating conditions and consider instrument noise, drift, and upset conditions.

D.2 Documentation supporting: quality control of the project hardware and software development (TTQAP, SQAP, etc.); procurement of components and standards and associated calibration services in accordance with Manual 1Q, Procedure 7-2; handling and storage of the MS&E components and any industry standard used for the verification of performance in accordance with Manual 1Q, Procedure 13-1 so as not to affect accuracy once performance has been verified; and hardware and software as-built configuration (for example, including component part numbers, arrangement, software operating system versions, software logic flowcharts) and software configuration control once the MS&E performance has been verified.

NMMD-HTS-2017-3403, Rev. 0
H-Canyon Spectrophotometer Development & Installation

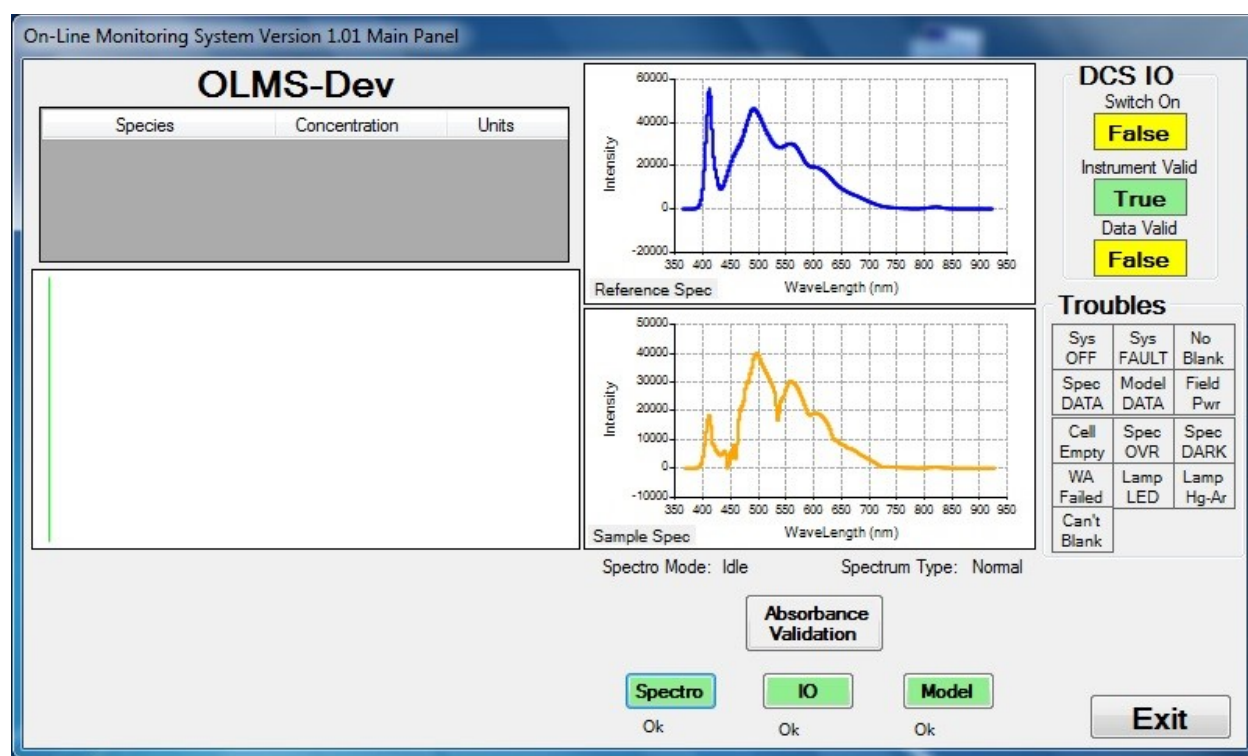
Page 5 of 5

- D.3 Documentation/report of the spectrophotometer system measurement method, including documentation of controls that ensure the required accuracy and precision are met, and verification using U/nitric acid solutions.
- D.4 Documentation providing spectrophotometer unit operating and maintenance instructions.
- D.5 Field support for the spectrophotometer field installation, performance verification prior to turnover for operation, and determination of performance verification frequency.

Appendix B. Operation Work Instructions

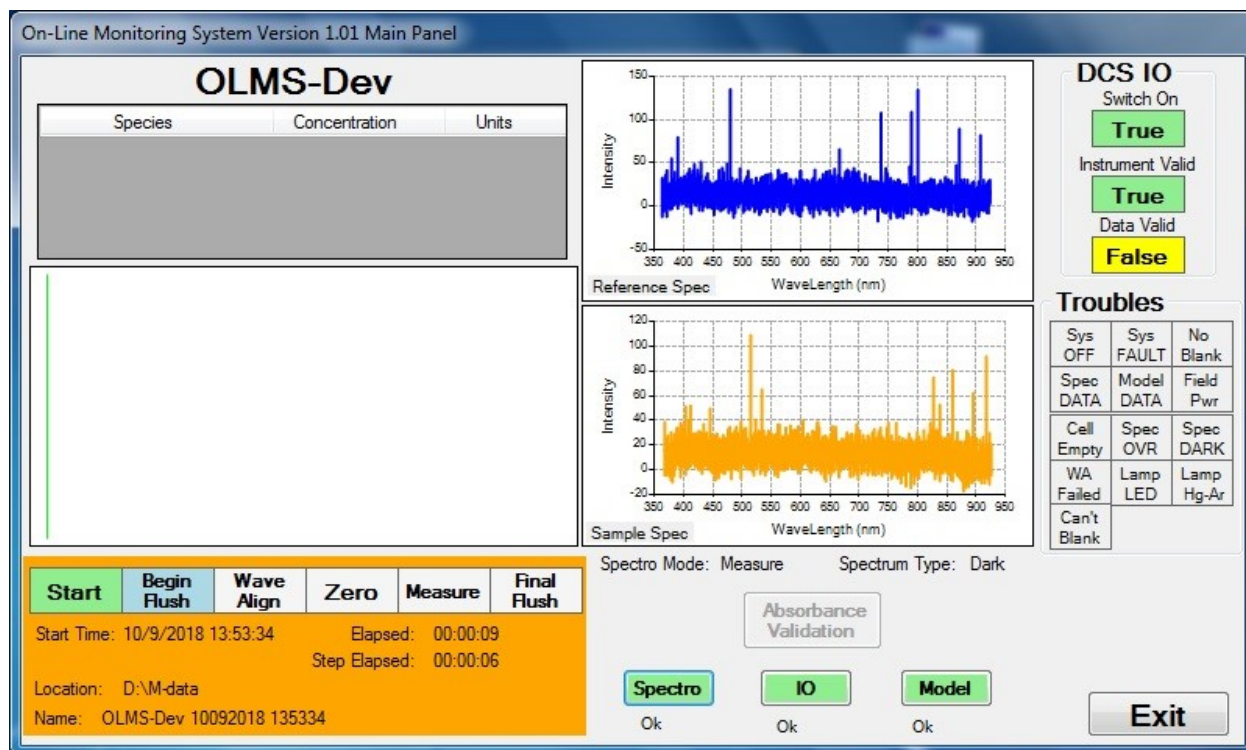
A Spectrophotometer measurement cycle is triggered by a digital signal received from the H-Canyon DCS system. Before starting a measurement:

- The spectrometer system should have been allowed to stabilize for at least three hours.
 - There is a flush solution in the sampler flow cell and the cuvette holder is empty.
1. If the OLMS_Main program is not running, from C:\OLMS directory, start the **OLMS_Main.exe** control program. The program takes about 30 seconds to load, then the main control panel opens. Wait for at least three hours after starting the program for the instrument to stabilize.
 - a. Verify there are no other **RED** Trouble Alarms.
 - b. Resolve any alarms before continuing.

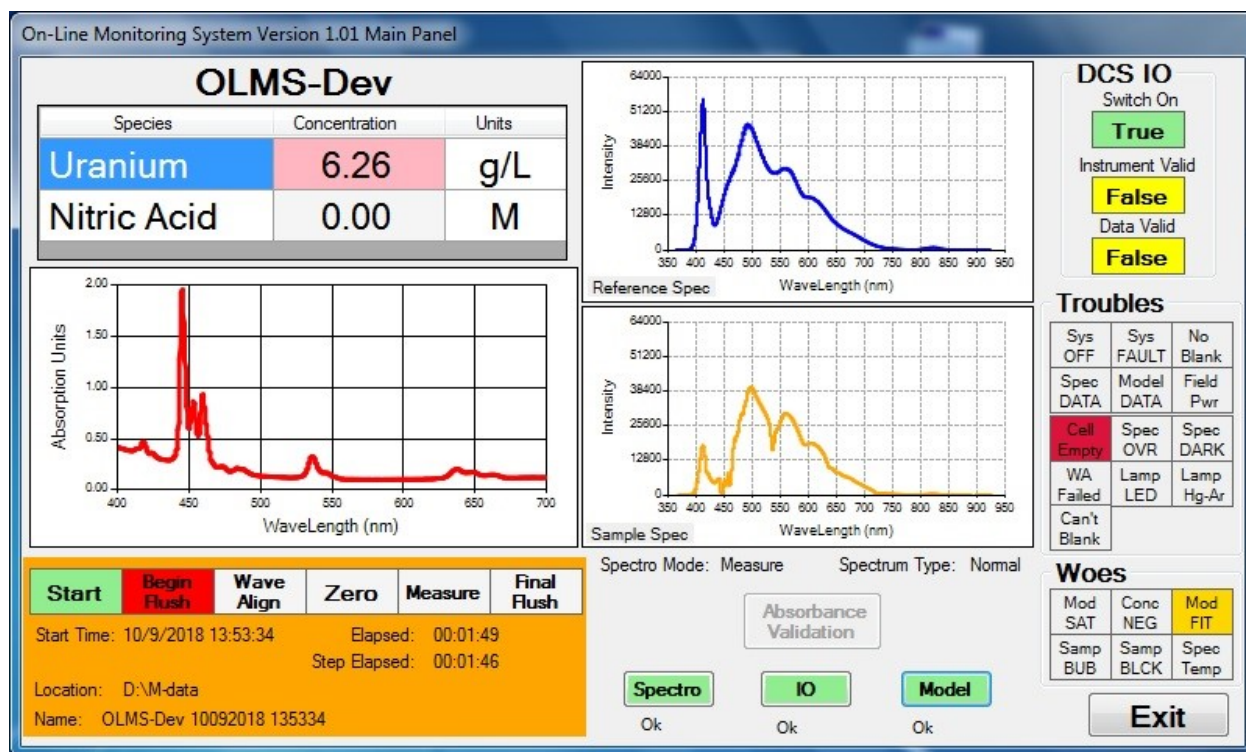


2. A DCS digital signal triggers the **Start** of a new measurement cycle:
 - a. Measurement Cycle window opens and displays cycle progress
 - b. Spectro Mode: switches from **Idle** to **Measure**
 - c. Spectrum Type: switches to **Warm Up** for 30 seconds
 - d. Spectrum Type: switches to **Normal** when the lamp stabilizes
 - e. DCS I/O indicates **Switch On** = **True**
Instrument Valid = **True**

3. The **BeginFlush** cycle begins immediately after lamp stabilization. It tests sample optical path:
 - a. Spectrum Type: indicates **Dark** while the spectrometers measure the DarkLevel
 - b. Spectro Mode: switches to **Measure** to verify the sample cell is flushed.

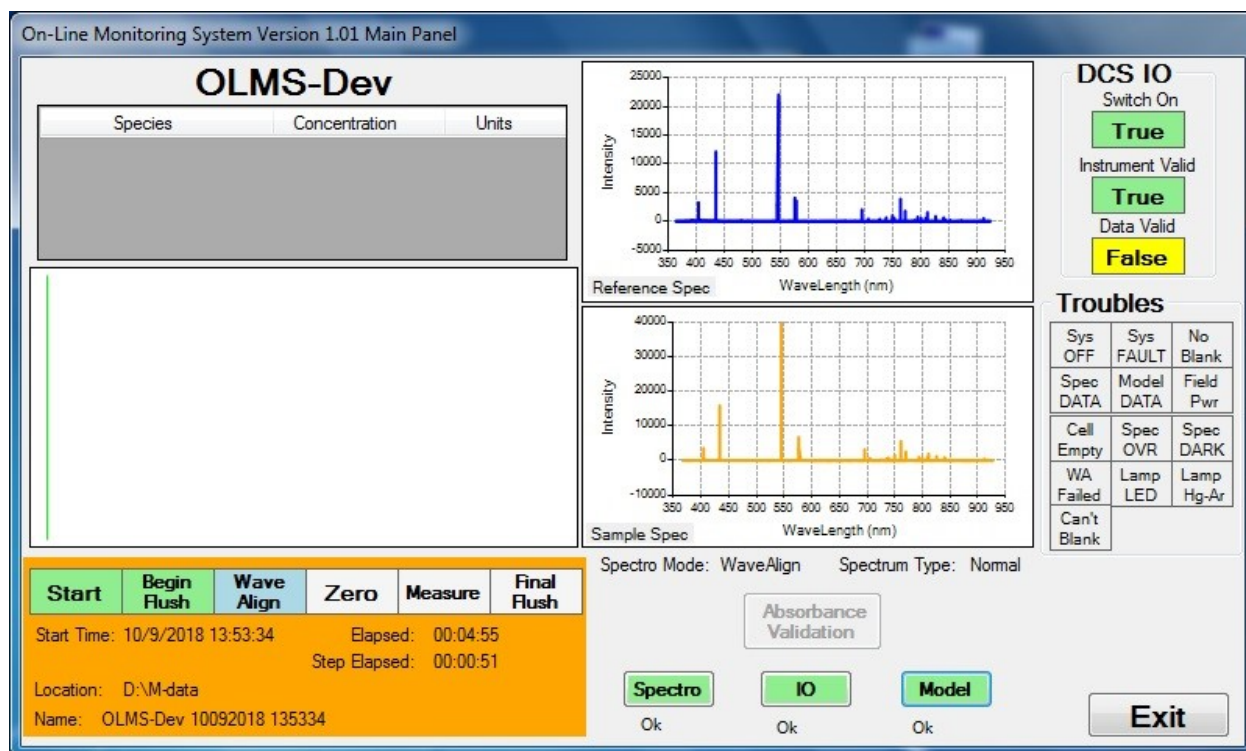


4. If any of the following conditions^a exist, the **BeginFlush** cycle will Fail.
- Uranium detected above the LowLevel set point
 - Lamp intensity @ Monitor_Wavelength is below the Minimum_Intensity
 - Lamp intensity is greater than the Saturation_Threshold
 - Lamp Stability is greater than the Stability_Threshold
 - DCS I/O indicates **Switch On** = **True**
Instrument Valid = **False**
 - Resolve any “out of limits” conditions before continuing with the measurement.

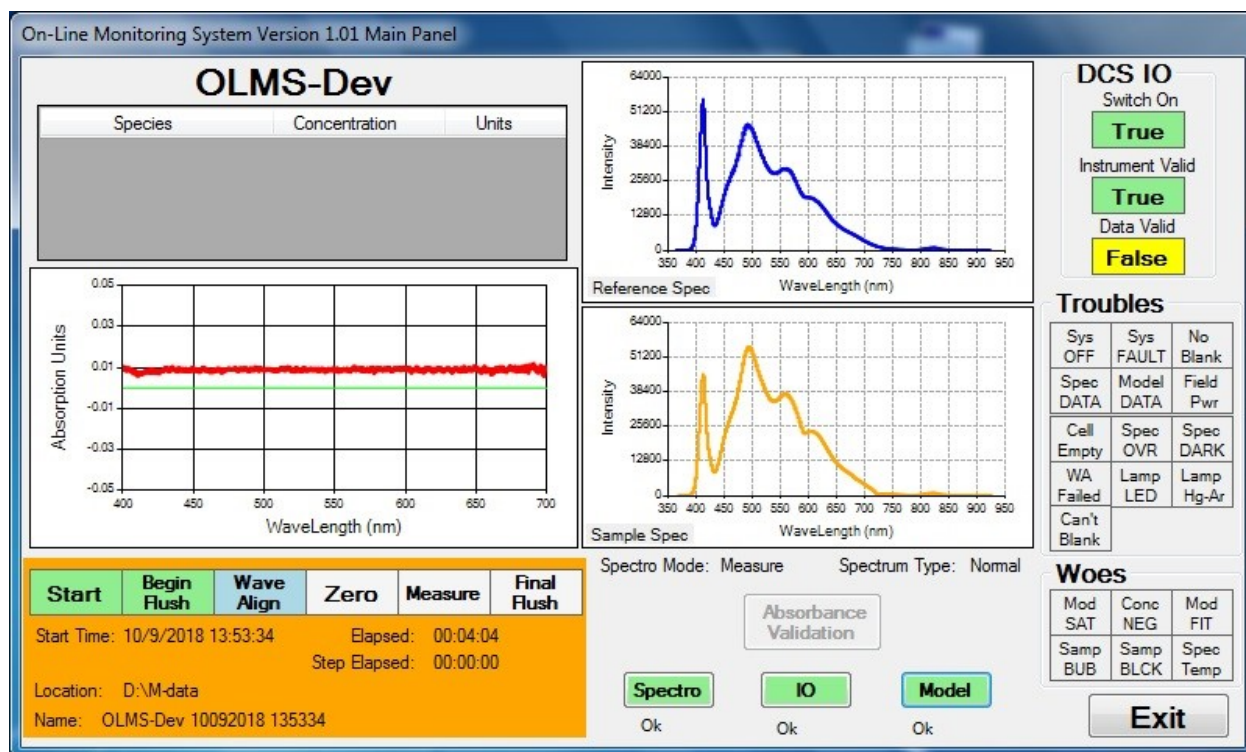


^a Conditions are specified in the Setup_OLMS.ini file.

5. After the **BeginFlush** cycle, the **WaveAlign** cycle calibrates spectrometer wavelength:
 - a. Spectro Mode: switches to **WaveAlign**
 - b. Spectrum Type: indicates **Dark** while the spectrometers measure the DarkLevel
 - c. Spectrum Type: switches to **Warm Up** to allow the Hg_lamp to stabilize.
 - d. Spectrum Type: switches to **Normal** to collect Hg lamp emission.
 - e. If any of the following conditions are detected the **WaveAlign** cycle will Fail
 - i. Hg line intensity too low or not found
 - ii. Hg line position not stable
 - iii. Required number of Hg lines not detected
 - iv. DCS I/O indicates **Switch On** = **True**
Instrument Valid = **False**
 - f. Resolve any “out of limits” conditions before continuing with the measurement.

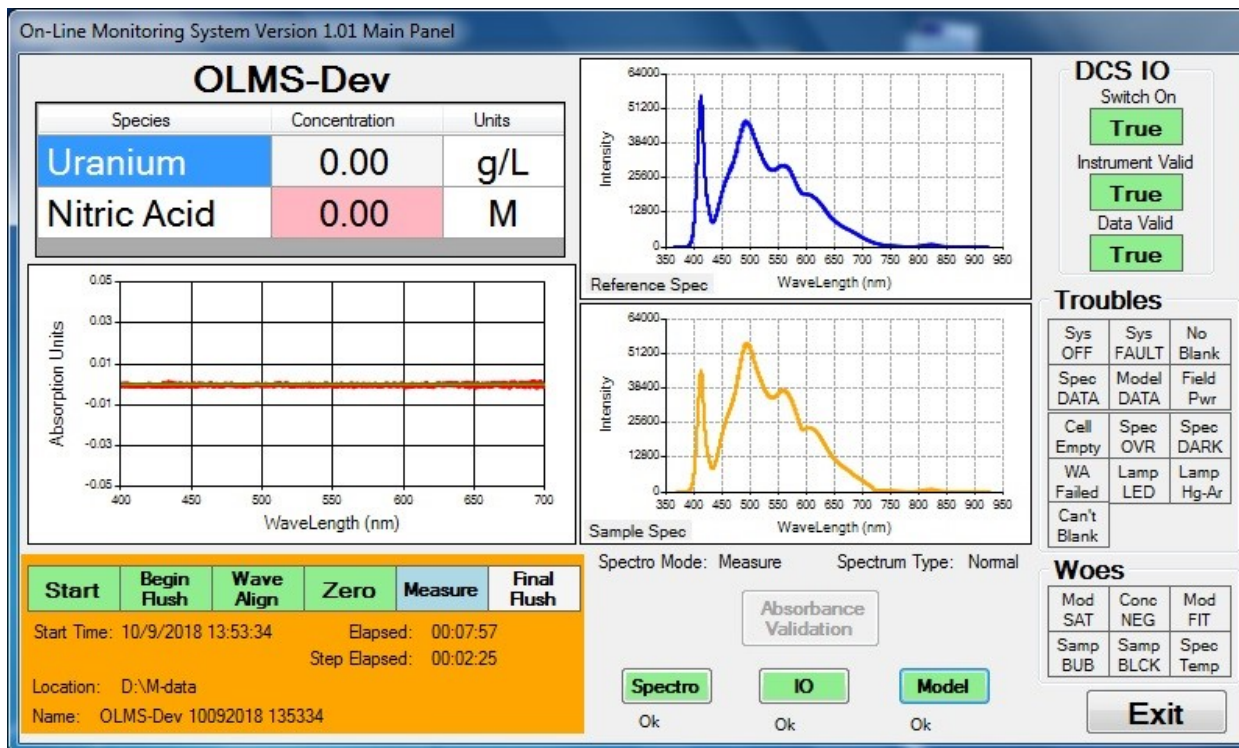


6. After the **WaveAlign** cycle, the **Zero** cycle collects a Blank Spectrum:
 - a. Spectro Mode: switches to **Measure**
 - b. Spectrum Type: indicates **Dark** while the spectrometers measure the DarkLevel
 - c. Spectrum Type: switches to **Warm Up** to allow the LED_lamp to stabilize.
 - d. Spectrum Type: switches to **Normal** to collect LED lamp emission.
 - e. If any of the following conditions are detected the **Zero** cycle will Fail
 - i. Uranium detected above the LowLevel set point (Specified in Setup_OLMS.ini)
 - ii. Lamp intensity @ Monitor_Wavelength is below the Minimum_Intensity
 - iii. Lamp intensity is greater than the Saturation_Threshold
 - iv. Lamp Stability is greater than the Stability_Threshold
 - v. Drift from previous Blank measurement greater than Light_Level_Allowance
 - vi. DCS I/O indicates **Switch On** = **True**
Instrument Valid = **False**
 - f. Resolve any “out of limits” conditions before continuing with the measurement.

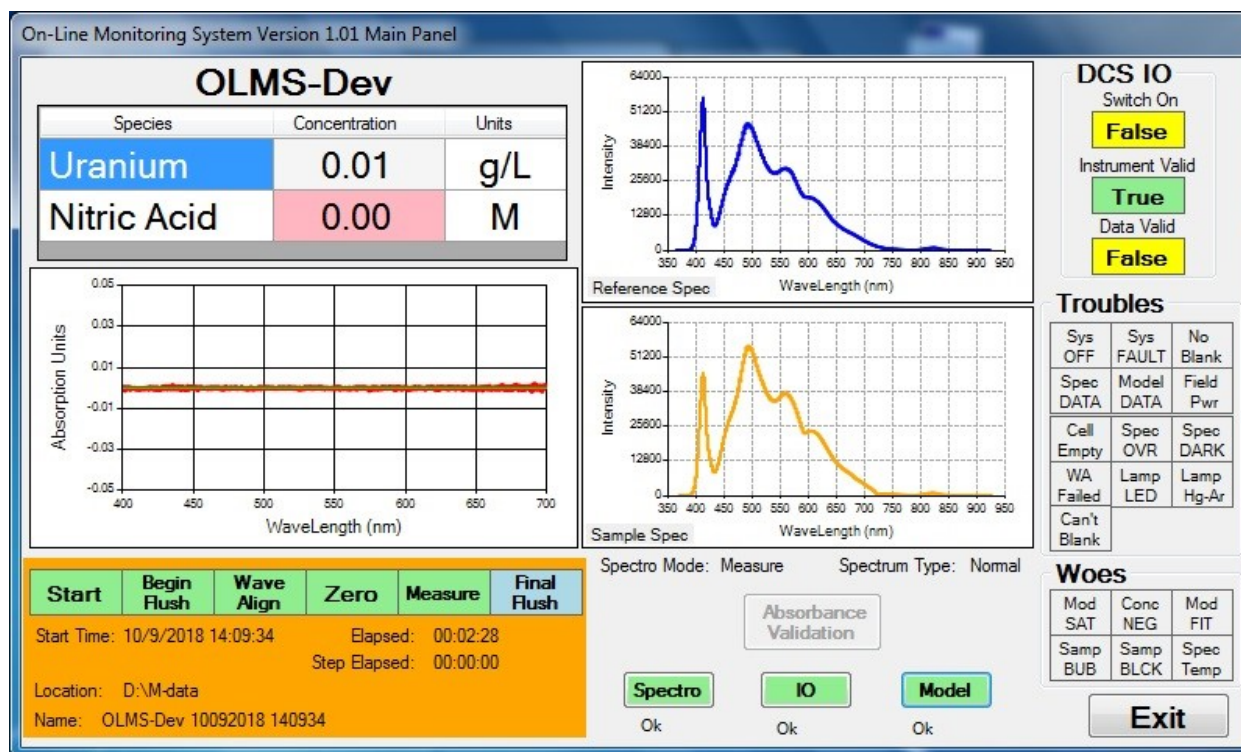


7. After the **Zero** cycle, the **Measurement** cycle measures Uranium and Nitric acid concentrations:
 - a. Spectro Mode: switches to **Measure**
 - b. Spectrum Type: switches to **Normal** to collect LED lamp emission.
 - c. DCS I/O indicates

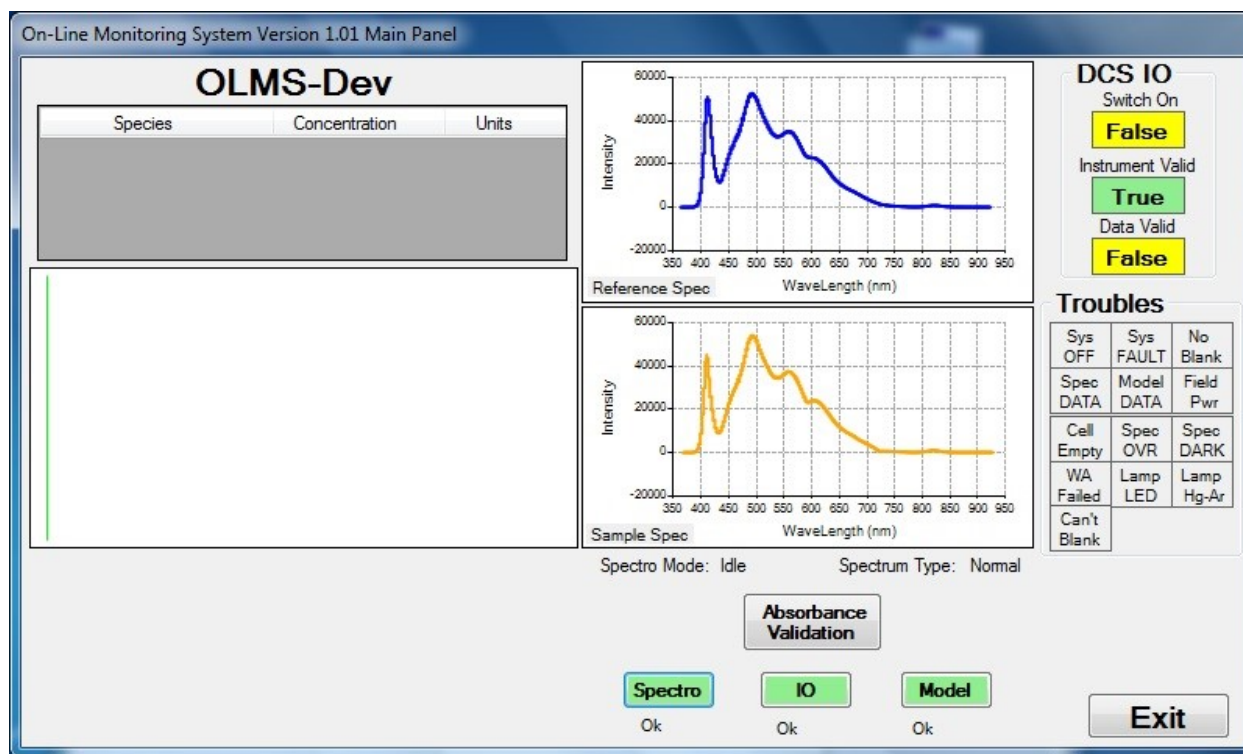
Switch On	=	True
Instrument Valid	=	True
Data Valid	=	True
 - d. If any of the following conditions are detected the **Measure** cycle will Fail
 - i. Lamp intensity @ Monitor_Wavelength is below the Minimum_Intensity
 - ii. Lamp intensity is greater than the Saturation_Threshold
 - iii. Lamp Stability is greater than the Stability_Threshold
 - iv. Drift from previous Blank measurement greater than Light_Level_Allowance
 - e. Resolve any “out of limits” conditions before continuing with the measurement.
 - f. Initiate Canyon sampler operation and continue until Uranium concentration stabilizes.
 - g. After Uranium concentration has stabilized, turn off the Canyon sampler to obtain low noise Uranium and Nitric acid concentrations.
 - h. It may be necessary to cycle the Canyon sampler On and Off several times to assure that the measured sample is representative of the Canyon Tank contents.



8. When the DCS signals the end of the **Measure** cycle, the **FinalFlush** Cycle begins.
 - a. DCS I/O indicates **Switch On** = **False**
Instrument Valid = **True**
 - b. Initiate Canyon sampler Flush operation
 - c. The instrument will remain in **FinalFlush** cycle until the uranium concentration has dropped below the LowLevel set point (Specified in Setup_OLMS.ini)
 - d. It may be necessary to flush the Canyon sampler several times.
 - e. If any of the following conditions are detected the **FinalFlush** cycle will Fail
 - i. Uranium detected above the LowLevel set point (Specified in Setup_OLMS.ini)
 - ii. Lamp intensity @ Monitor_Wavelength is below the Minimum_Intensity
 - iii. Lamp intensity is greater than the Saturation_Threshold
 - iv. Lamp Stability is greater than the Stability_Threshold
 - v. Drift from previous Blank measurement greater than Light_Level_Allowance
 - f. Resolve any "out of limits" conditions before continuing.



9. After the instrument has exited the **FinalFlush** cycle, it reverts to **Idle Mode**.
 - a. Spectro Mode: **Idle**
 - b. DCS I/O indicates **Switch On** = **False**
 Instrument Valid = **True**



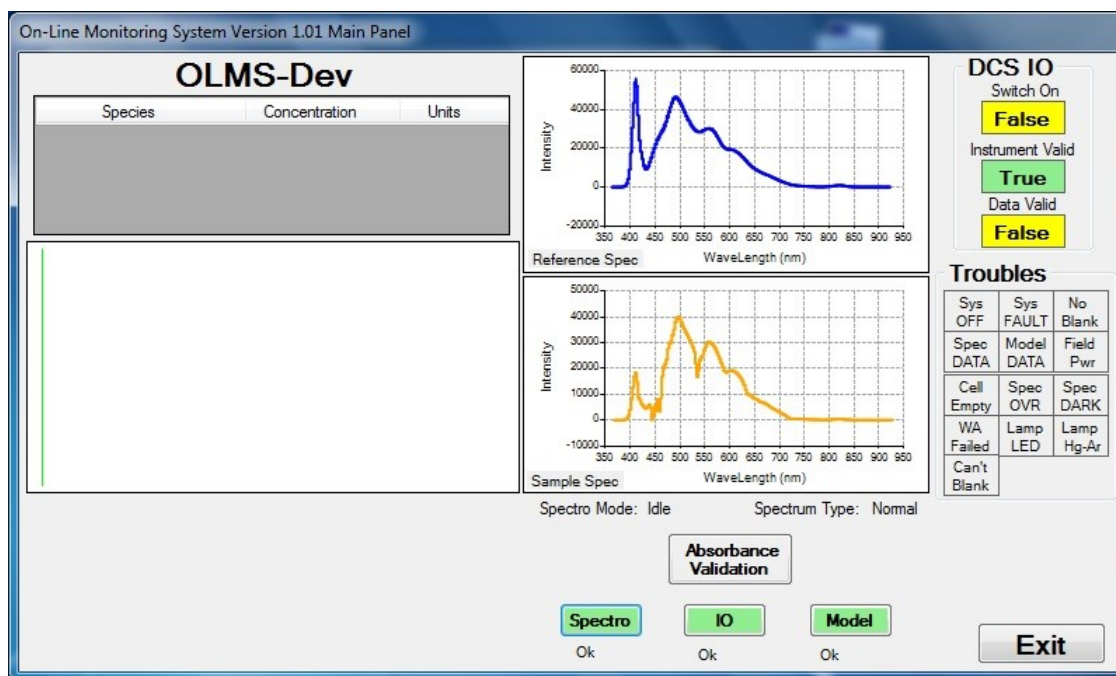
Appendix C. Calibration Work Instructions

Spectrophotometer calibration is based on the confirmation of the instrument's ability to accurately measure absorbances for NIST-traceable standards. Personnel performing the calibration will be guided through the process by these work instructions and prompts given by the instrument control program.

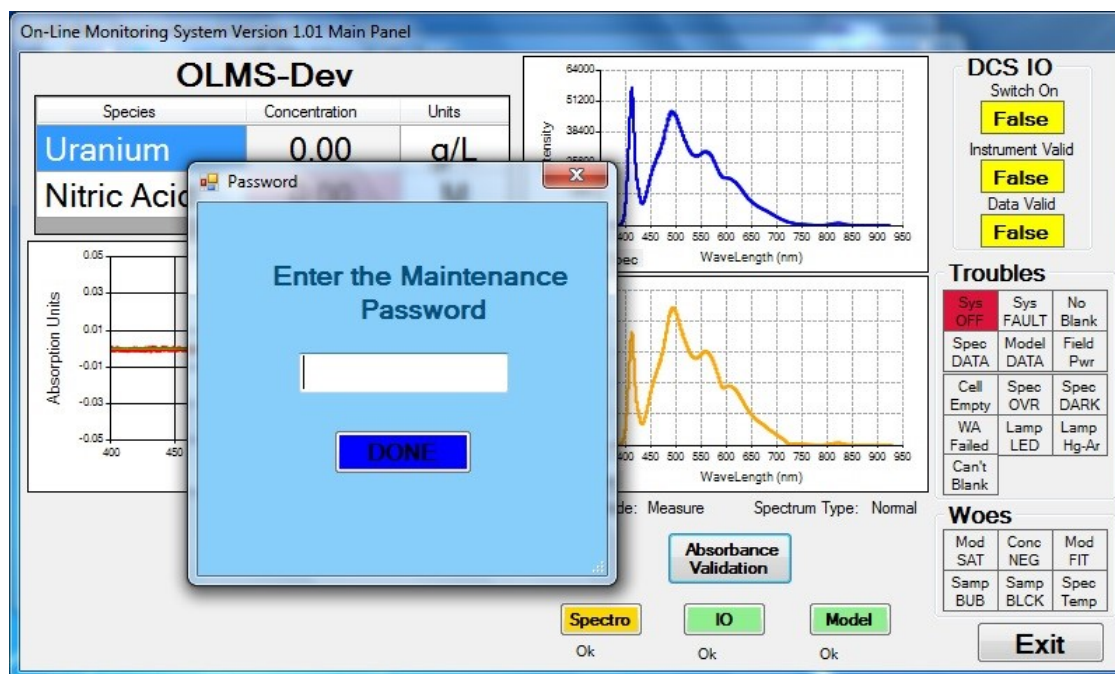
Note that recording a blank spectrum is equivalent to the "Zeroing" function of the colorimeter. Accordingly, if it is deemed necessary, the "Zeroing" steps may be carried out without otherwise completing the calibration as described in subsequent steps.

When handling the absorbance standards, avoid touching the glass surfaces of the standards. There is ample room to grip the top portion of the standards when inserting or removing them from the storage box or the cuvette holder on the instrument face plate. Cotton gloves may be worn to help protect against fingerprints.

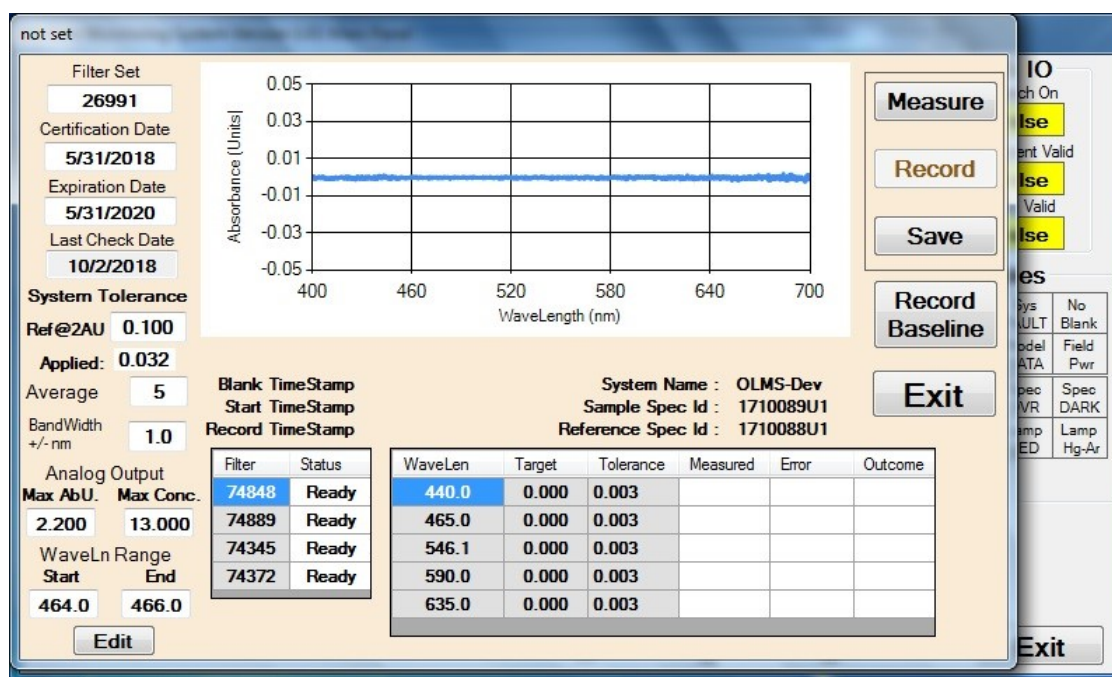
1. If the OLMS_Main program is not running, from **C:\OLMS** directory, start the **OLMS_Main.exe** control program. The program takes about 30 seconds to load, then the main control panel opens. Wait for at least three hours after starting the program for the instrument to stabilize. Verify there is a flush solution in the sampler cell and the cuvette holder is empty.
 - a. Verify there are no other **RED** Trouble Alarms.
 - b. Resolve any alarms before continuing.



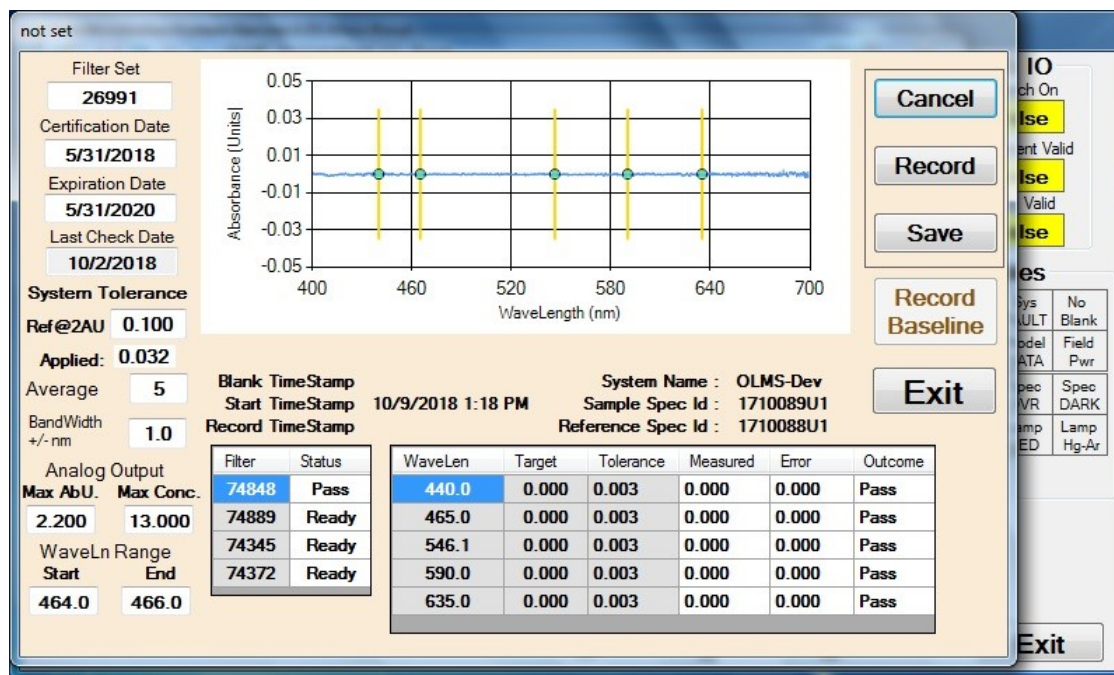
2. Execute Spectrometer Blank Measurement (see Appendix D).
3. Click <**Absorbance Validation**> button
 - a. Enter the Maintenance Password (Maint) to start Absorbance Validation



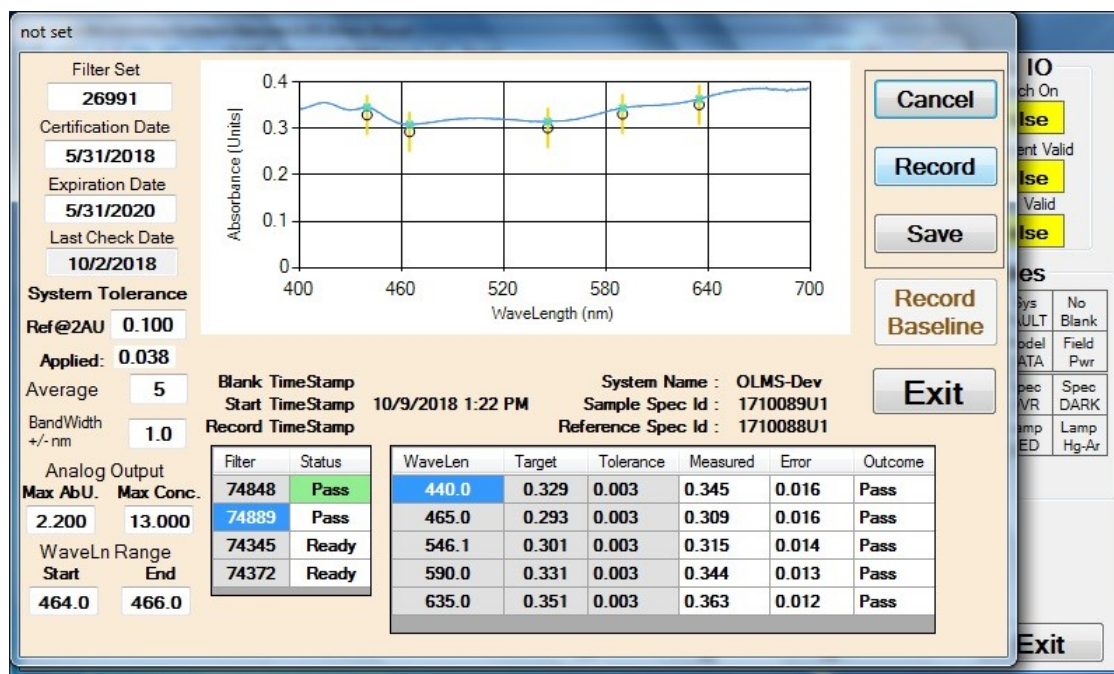
- b. The Absorbance Validation panel opens. Verify:
 - ii. Filter_Set and Certification_Date match the absorbance standards
 - iii. Expiration Date is not past



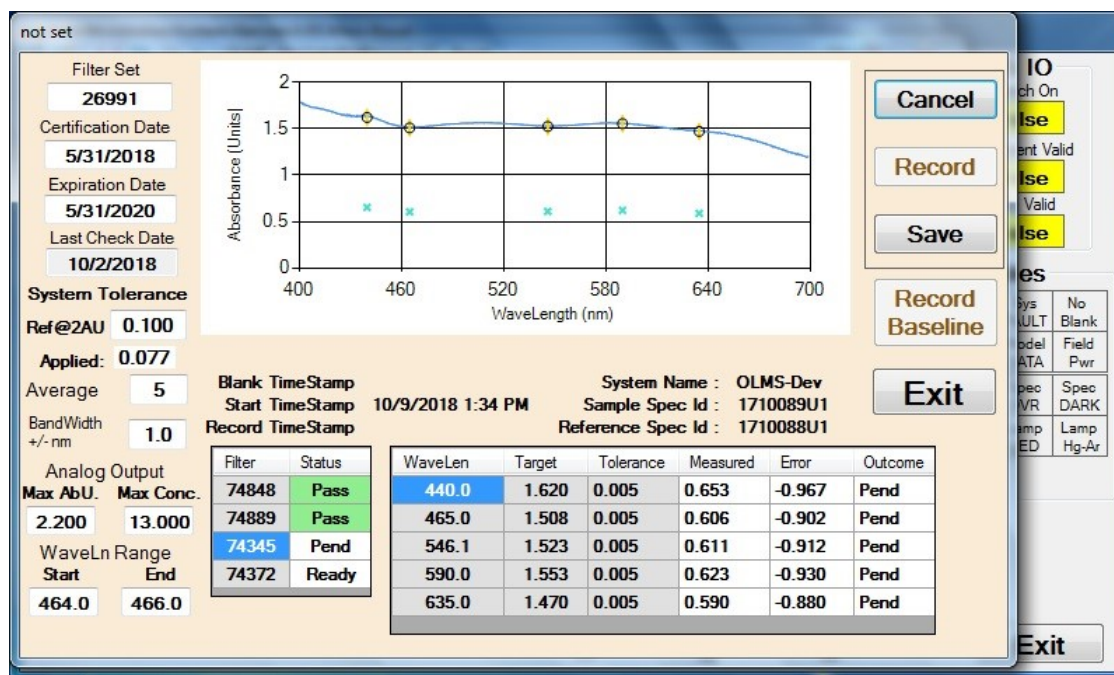
- c. For each standard in the [Filter list]:
 - i. Verify the Cuvette holder is empty
 - ii. Click <RecordBaseline> and wait for measurement to zero
 - iii. Select the standard name in the [Filter list]
 - iv. Insert the **Selected Filter** in the cuvette holder
 - v. Click <Measure> and wait for measurement to stabilize.

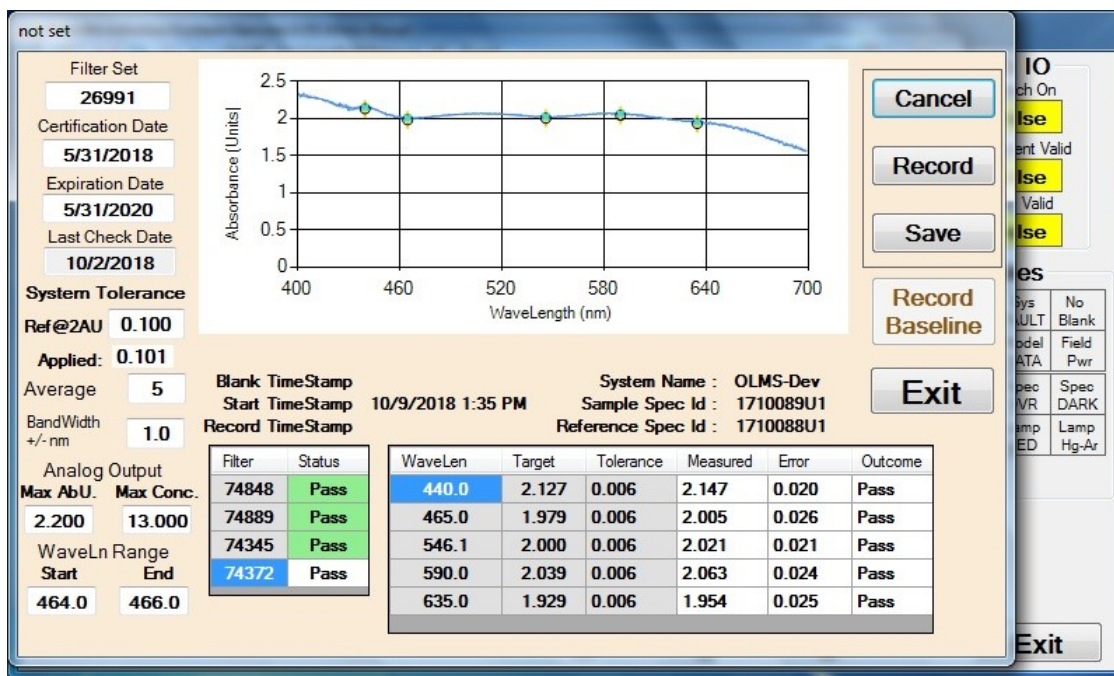


- vi. When Outcome changes from Pend to Pass click <Record>
- vii. If Outcome is **Fail**, repeat from **step 2**.

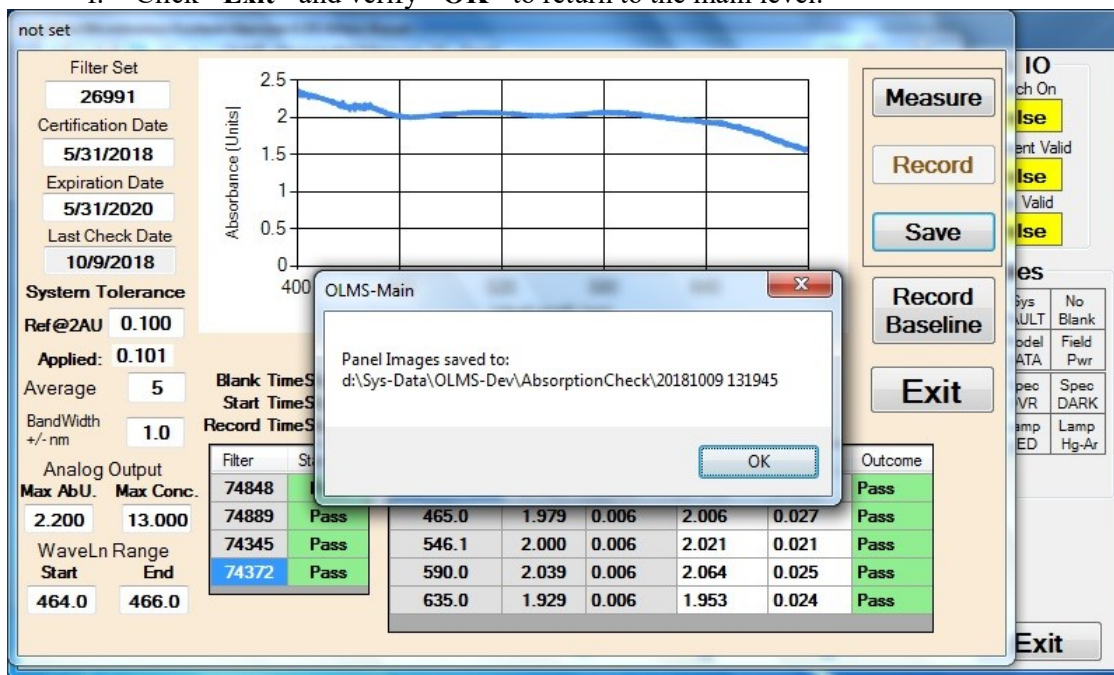


d. Repeat step 2.b. for all standards in the [Filter_list]





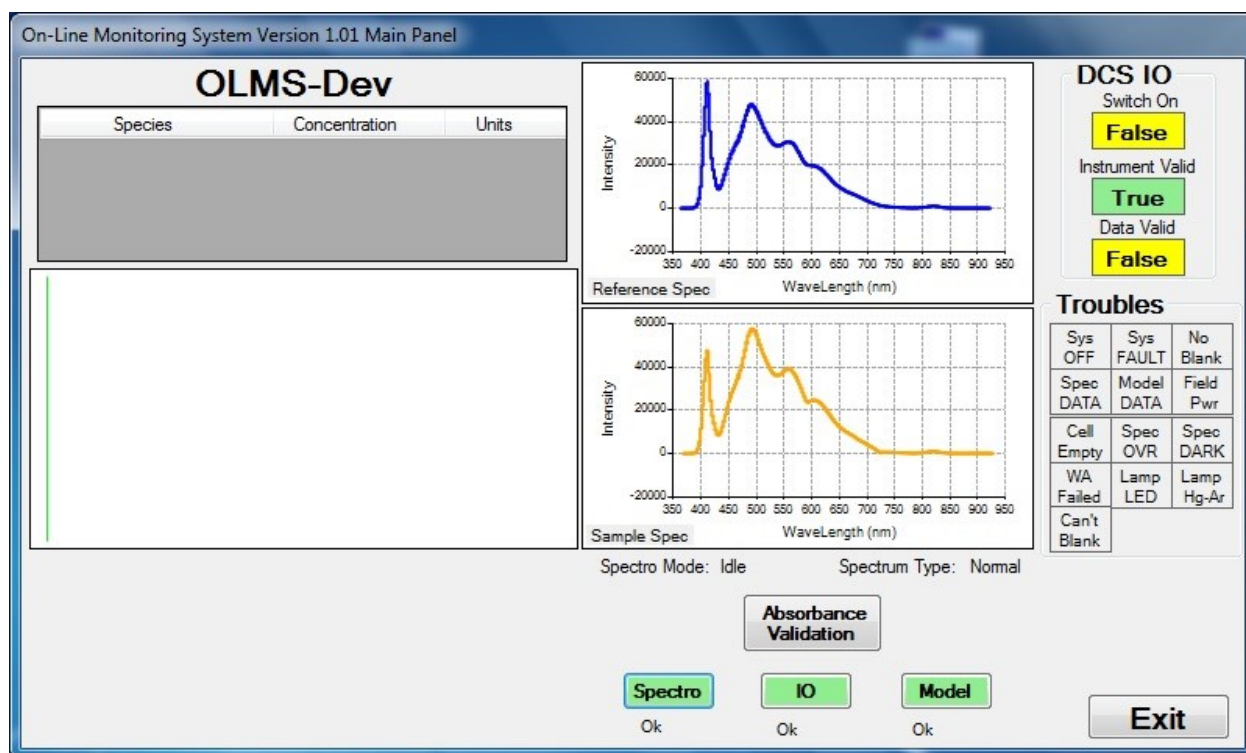
- e. After all standards have been measured, click <Save>.
- f. Click <Exit> and verify <OK> to return to the main level.



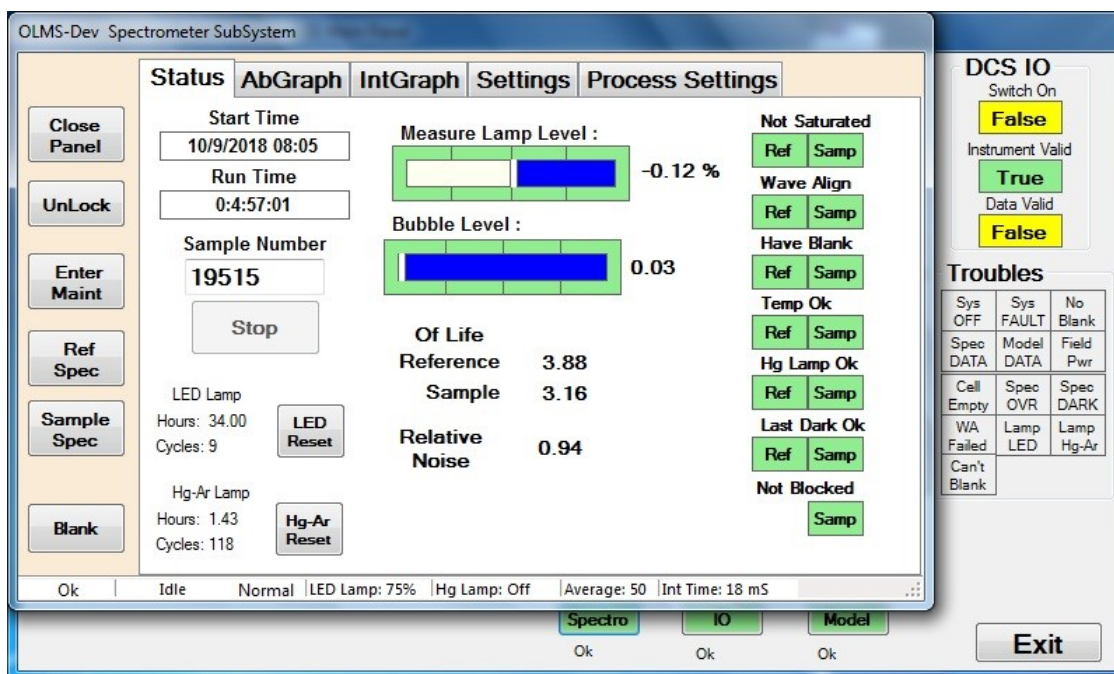
Appendix D. Work Instructions for Spectrophotometer Blank

Collecting a spectrometer blank measurement is equivalent to the “Zeroing” function of the colorimeter. Accordingly, if it is deemed necessary, these steps may be carried out without compromising other procedures unless specifically noted.

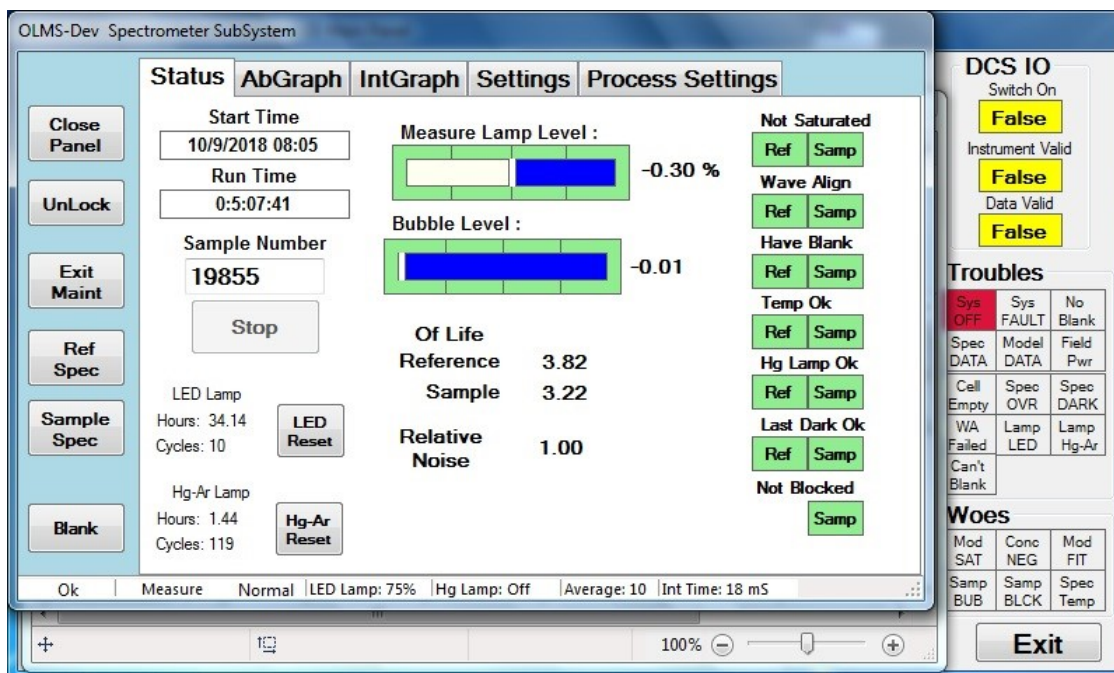
1. If the OLMS_Main program is not running, from **C:\OLMS** directory, start the **OLMS_Main.exe** control program. The program takes about 30 seconds to load, then the main control panel opens. Wait for at least three hours after starting the program for the instrument to stabilize. Verify there is a flush solution in the sampler cell and the cuvette holder is empty.
 - a. Verify there are no other **RED** Trouble Alarms.
 - b. Resolve any alarms before continuing.



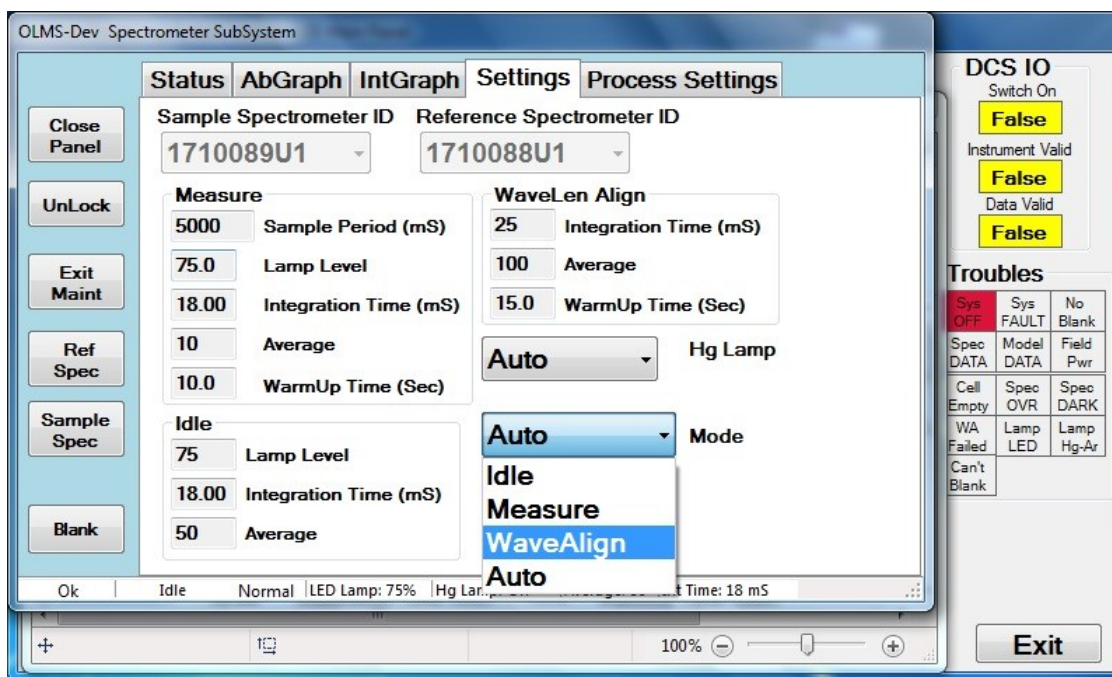
2. Click the **<Spectro>** button to open the Spectrometer control panel.



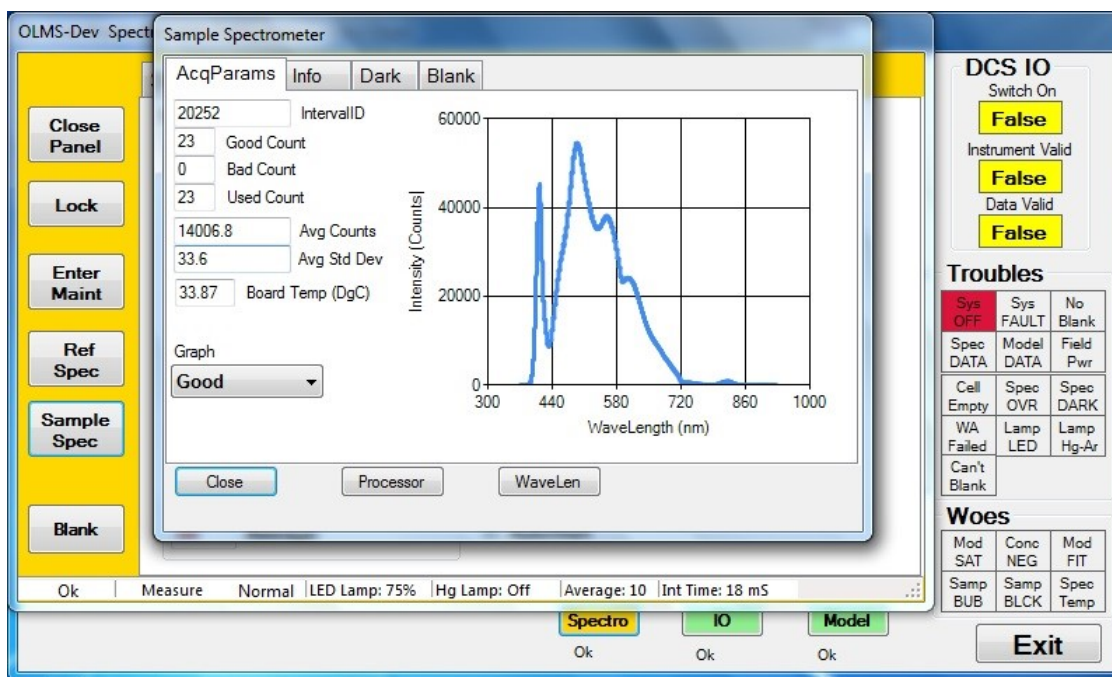
- Click <Enter_Maint> button and sign in Maintenance Mode. (Maint)
- Note Blue Frame color indicating Maintenance mode is active
- Verify cuvette holder is empty.
- Verify Lamp Life (Of Life > 2) for both Reference and Sample spectrometers



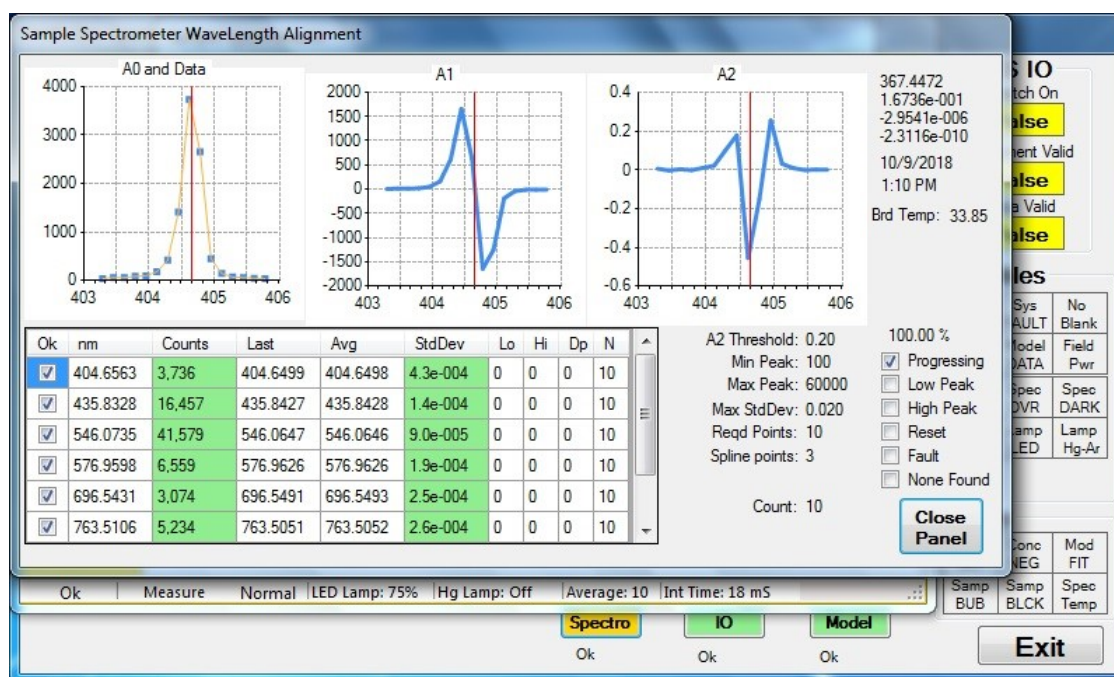
3. Click <Settings> Tab
 - a. Click Mode selection box and choose <WaveAlign>



- b. Click <SampleSpec> button
 - i. Click <WaveLen> button



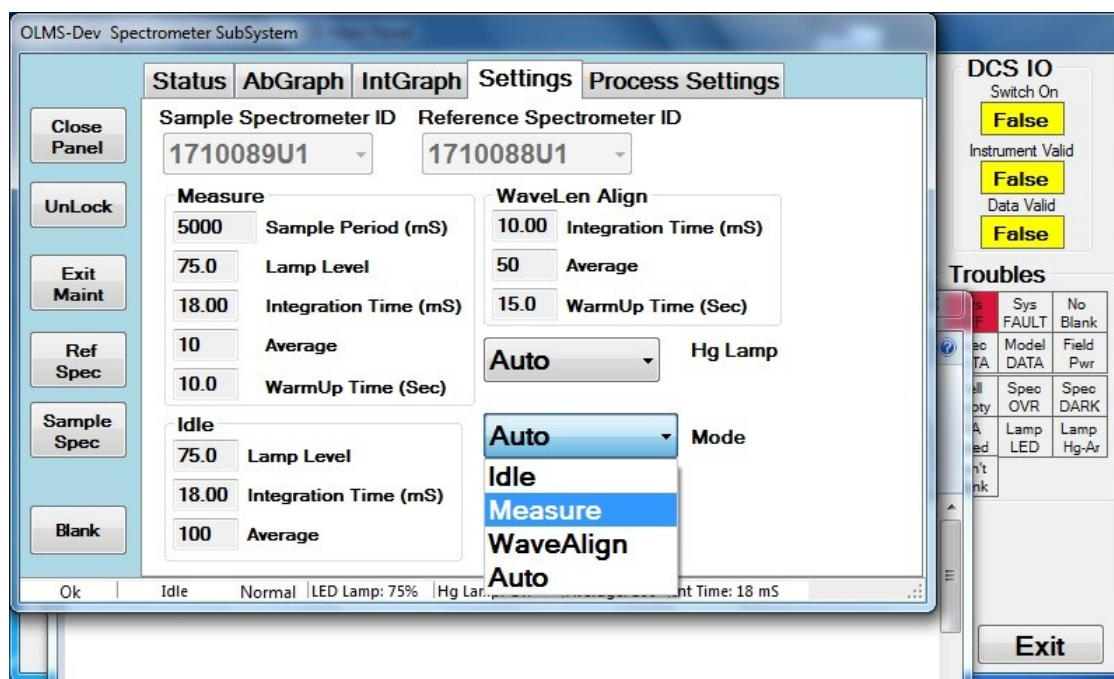
ii. Note completion of 10 measurements for all Hg lines.



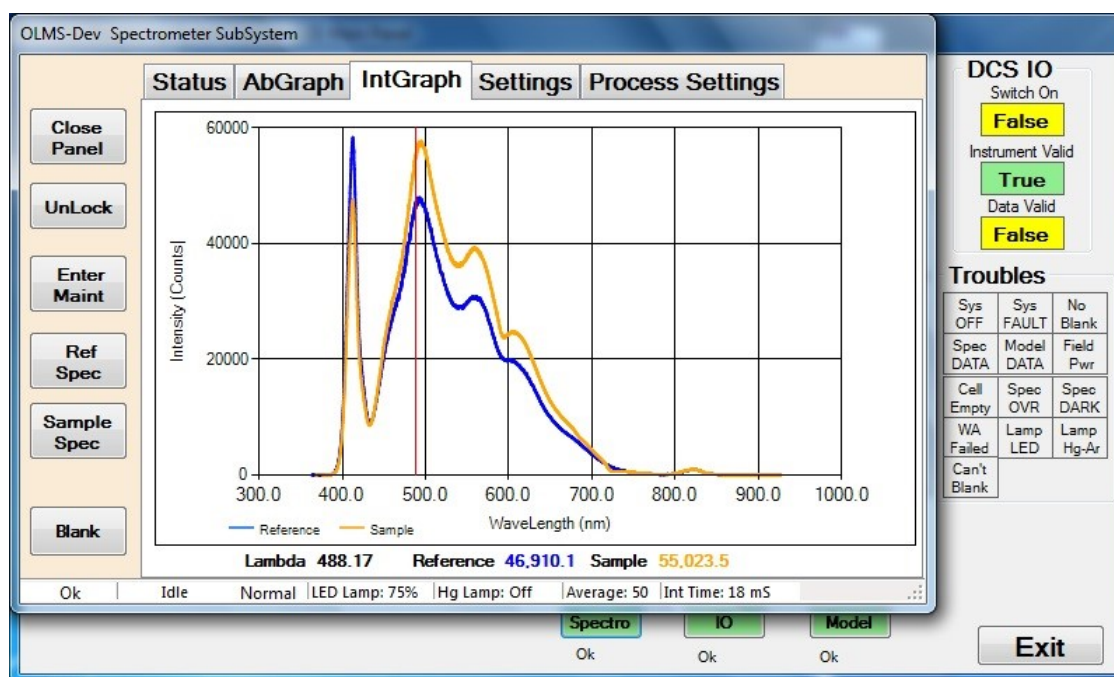
iii. Click <ClosePanel> on Wavelength Alignment Panel

iv. Click Close on Sample_Spectrometer Panel

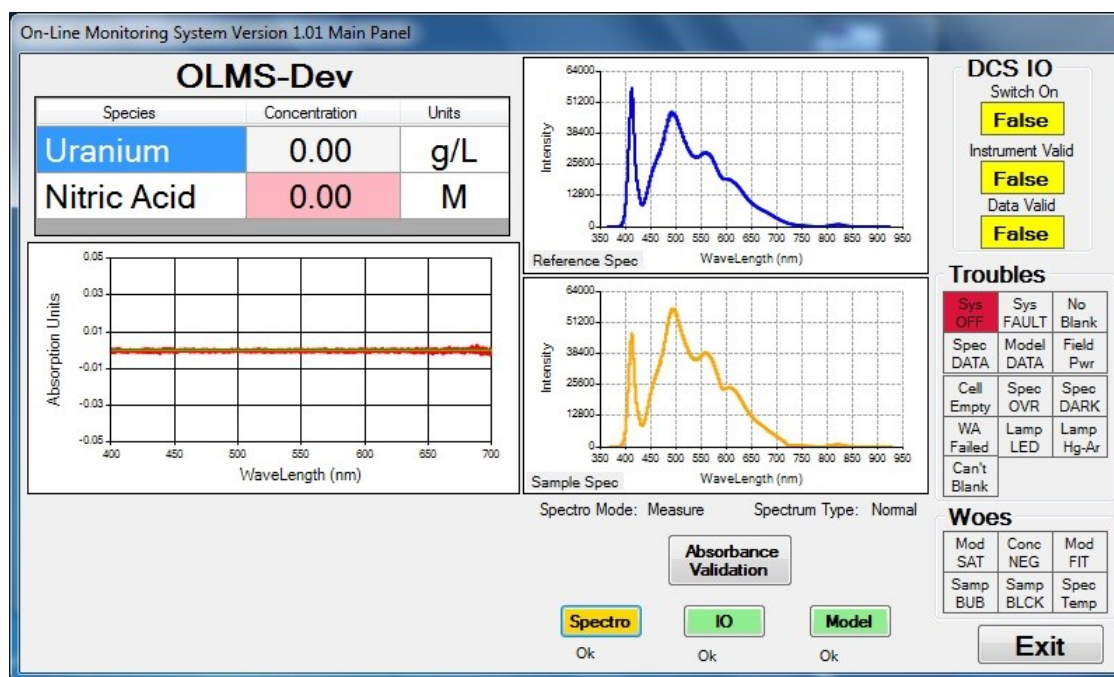
4. Click <Settings> Tab and Click Mode selection box to choose <Measure>



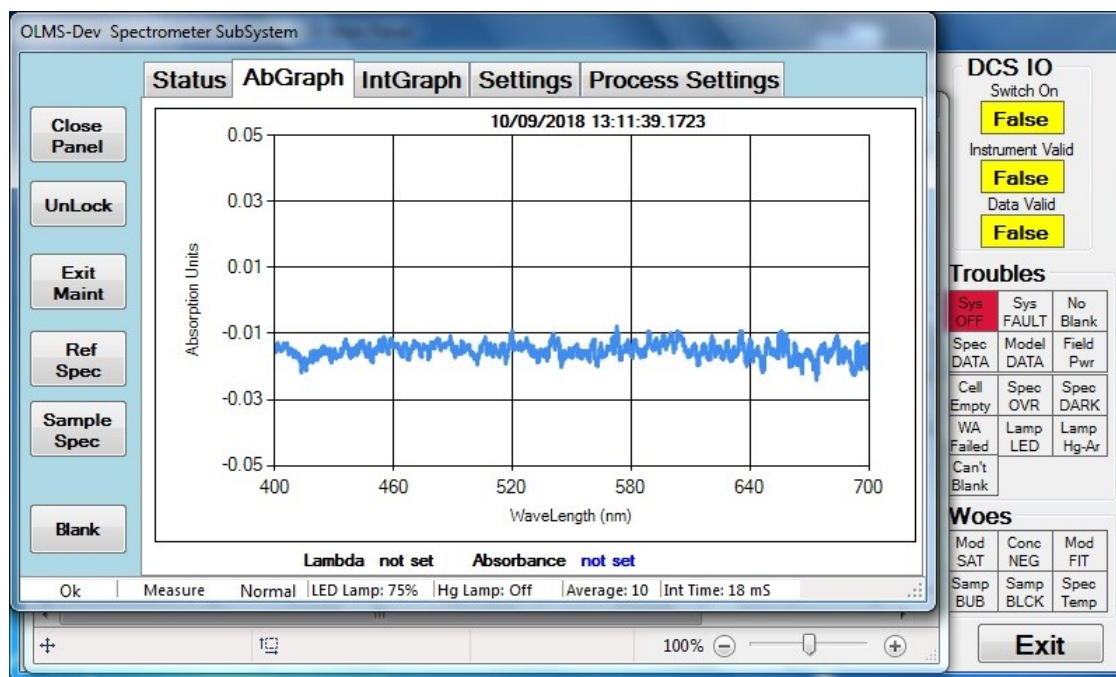
- Click the <IntGraph> tab and verify that the Sample and Reference intensities are within scale (less than 60,000 counts maximum) and balanced (maximum counts for each are roughly equal, even if the maxima occur at different wavelengths).



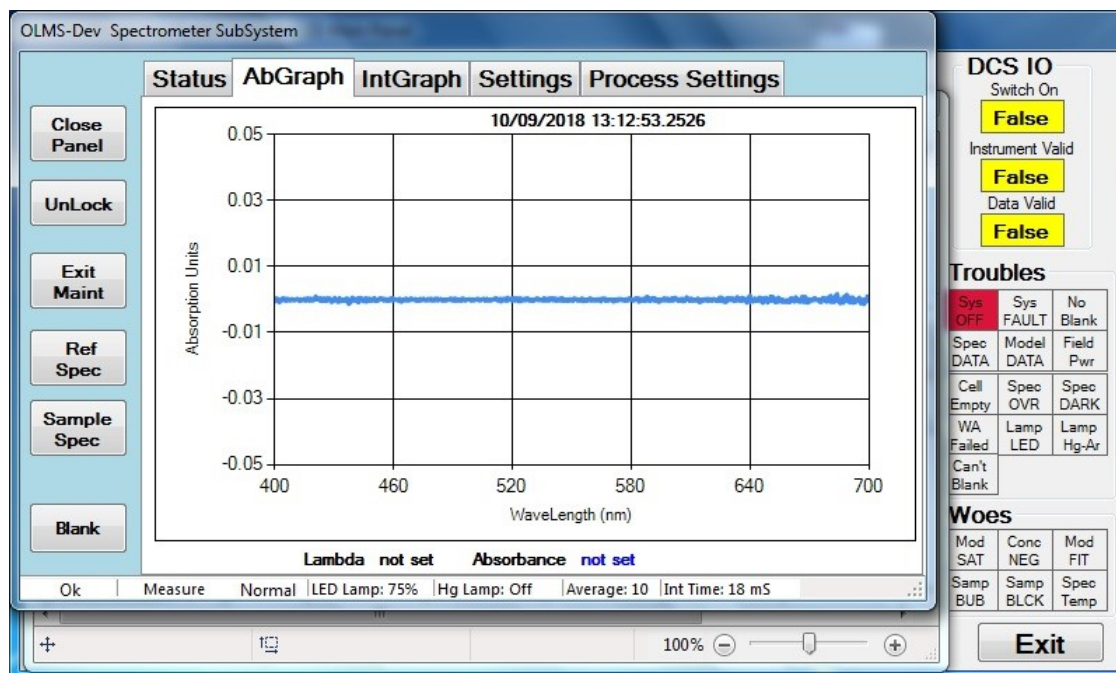
- Select the OLMS Main_Panel to verify that Uranium Concentration is less than 0.05 g/L



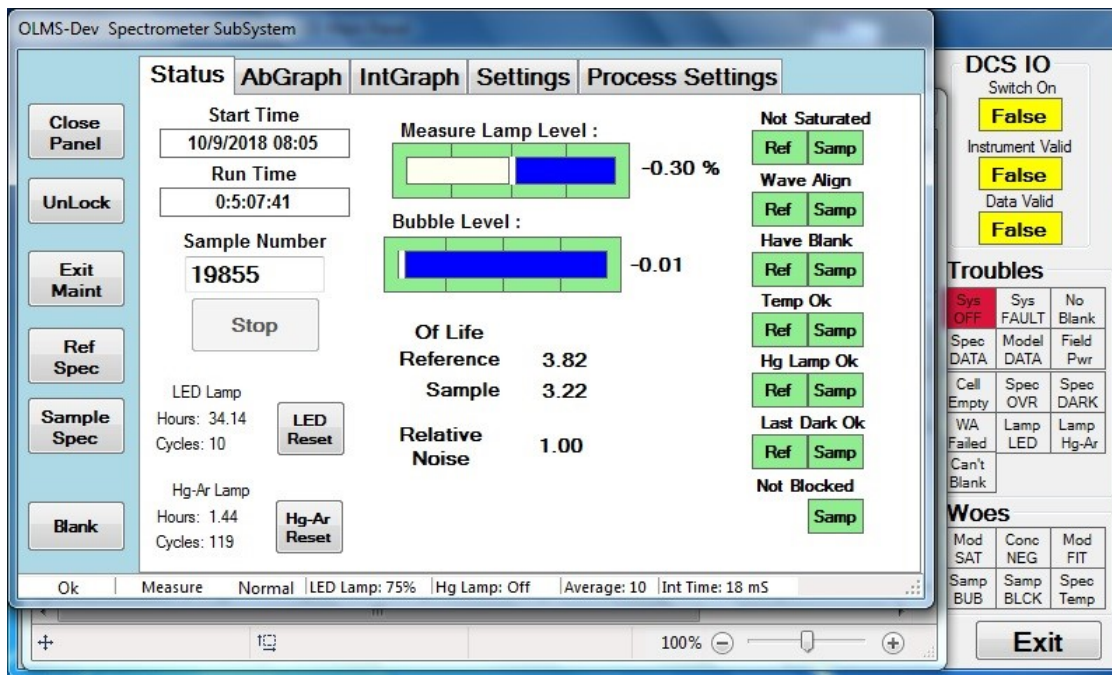
7. Select the Spectro_Panel, <AbGraph> tab and verify that the absorbance is free from interferent signals (largely flat across the spectral width).



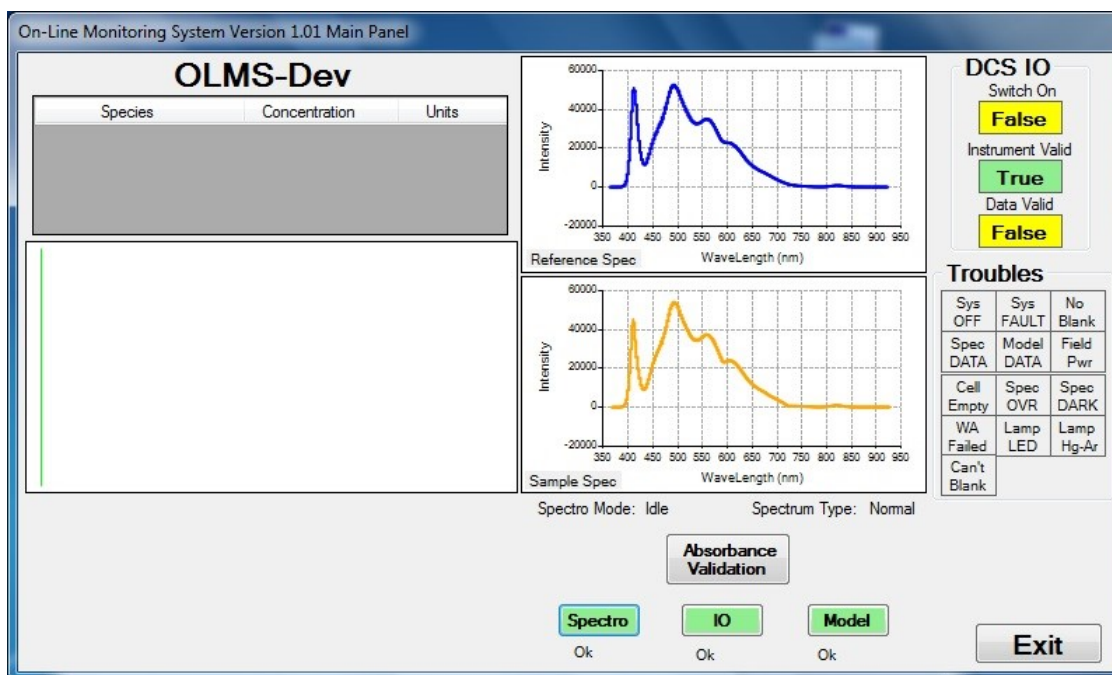
8. Click the <Blank> button to collect and store a Blank Spectrum.



9. Select the <Status> tab
 - a. Lamp Level indicator should be mid-scale and green
 - b. All Status indicators should be green
 - c. Of Life Reference and Sample readings should be greater than 2.



10. Click <Close_Panel>



Appendix E. Schematics and Spare Parts List

Instrument schematics can be obtained through Site Document Control. Drawing numbers are listed below. Note that component part lists are included in the drawing.

<u>DRAWING #</u>	<u>Rev</u>	<u>TITLE</u>
L-L0-H-00064	1	Rack Enclosure Arrangement
R-R4-H-00983	0	Rack Enclosure Details & Subassembly
L-L2-H-00056	1	I/O Panel Subassembly & Details
L-L1-H-00113	0	Spectrophotometer Assembly
L-L2-H-00057	0	DIN Rail Components Subassembly
L-L2-H-00055	0	Optical Bench Subassembly
R-R4-H-00991	0	Additive Manufacturing Parts Details
R-R4-H-00984	0	Spectrophotometer Details Sheet 1
R-R4-H-00990	0	Spectrophotometer Details Sheet 2
R-R4-H-00994	0	Spectrophotometer Details Sheet 3
L-L2-H-00065	0	Spectrometer Connections Subassembly
L-L9-H-00110	0	Wiring Connection Diagram Sheet 1
L-L9-H-00111	0	Wiring Connection Diagram Sheet 2

Appendix F. Uncertainty Analysis: SRNL-L4000-2018-00008.



SRNL-L4000-2018-00008, Rev. 0

August 28, 2018

From: R.J. Lascola, 999-2W

To: J.D. Bickley, 704-2H

Technical Review: P.E. O'Rourke, 8/27/18

Uncertainty Analysis for OLMS Spectrophotometers

Introduction

SRNL has developed absorption spectrophotometers to monitor uranium and nitric acid concentrations at various sampling points of the H Canyon Second Uranium Cycle process. Initial installation locations are Tanks 15.4, 16.8, 17.4, 17.5, and 18.7. This document describes and quantifies inputs to the final loop uncertainty calculation, assuming that the calculation will be analogous to the calculations for the 1CU¹ and 1EU² colorimeters. There will be changes to the source terms (Section 4.1 of the colorimeter calculations), assumptions (Section 4.2), and analytical methods and computations (Section 5.1) due to the different operating principles of the spectrophotometer and colorimeter. A similar comparison was used to describe the uncertainties for the spectrophotometers recently installed in HB-Line.³

Operating Principles

A brief discussion of the measurement principles for the colorimeters and spectrophotometers will provide the necessary background for a discussion of the uncertainty source terms. In both instruments, the uranium concentration is determined by measuring the wavelength-dependent light absorption spectrum of the solution. Concentration and absorption are related through the Beer-Lambert Law,

$$A_{\text{total}}(\lambda) = \sum_i \varepsilon_i(\lambda) b c_i,$$

where A is the solution absorbance at wavelength λ , c_i is the concentration of the absorbing species i , b is the length of solution through which the incident light is transmitted, and ε_i is a species-specific, wavelength-dependent absorptivity coefficient.

The colorimeters measure A_{total} at a single wavelength⁴, with the assumption that there is a single uranium-containing species present in the solution and that there are no other species that absorb light at that wavelength (that is, $i = 1$). As b and ε are constant under these conditions, uncertainties in the measurement of A_{total} directly translate to c . This sensitivity is reflected in the colorimeter uncertainty

¹ D. Raiford, "Instrument Loop Uncertainty for First Uranium Cycle 1CU Colorimeter", J-CLC-H-00953, Rev. 1, May 2015.

² D. Raiford, "Instrument Loop Uncertainty for First Uranium Cycle 1EU Colorimeter", J-CLC-H-00684, Rev. 4, June 2015.

³ R.J. Lascola, "Uncertainty Analysis for AFS-2 Spectrophotometers", SRNL-L4000-2015-00029, July 29, 2015.

⁴ Technically, the colorimeter measures an averaged absorbance over a narrow band of wavelengths defined by an optical filter.

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calculations, where the vendor values for repeatability/accuracy and absorbance range, reported in absorbance units, are translated to U concentrations.

The relationship of absorbance to concentration for the spectrophotometers is more complicated, because $i > 1$ in the tanks being monitored. There are multiple uranium-containing species present, of the form $\text{UO}_2(\text{NO}_3)_x^{(2-x)+}$, with the relative proportion of these species dependent on the nitric acid concentration.⁵ Other factors, such as the solution temperature and the possible presence of interferents (Fe, Ni, Cr), can also cause absorbance that has no correlation to uranium. Examples of the effects of these factors on the spectra are shown in Figure 1. Beer's Law, as described above, is not sufficient to determine uranium concentration. Likewise, determination of the nitric acid concentration cannot be done directly from Beer's Law. Instead, statistical models developed from the spectra of multiple standards, spanning the ranges of uranium, nitric acid, and the confounding factors expected during the process, are used to infer the desired concentrations. A detailed discussion of the models is beyond the scope of this memo, but will be included in the final report for the instruments.⁶

The absorbance spectra have underlying uncertainties in wavelength and absorbance based on the accuracy of reproducing known values of primary standards (the fundamental physical constants of atomic emission wavelengths, and NIST-traceable absorbances of reference filters). However, it is prohibitive to propagate those uncertainties through the models to determine uncertainties in uranium and nitric acid concentrations. Instead, we will report uncertainty concentrations directly, based on the ability to reproduce known concentrations in uranyl nitrate solutions (secondary standards) measured in the laboratory. These standards include contributions from the interfering factors described above.

The relationship between the primary and secondary standards is established by pooling the results for uranium and nitric acid measurements for all five instruments. Together, the five instruments sample the instrument variation that can occur while still meeting the measurement criteria for the primary standards.

A further refinement comes from the use of an automated analysis flowsheet, which is shown in Figure 2. A series of preliminary data analyses are done which yields a rough estimate of acidity, presence of interferents, or high absorbance which might invalidate the use of certain parts of the spectrum. These analyses select a particular pathway through the flowsheet, resulting in the use of specific uranium and nitric acid prediction models. The flowsheet is very general and is intended to cover scenarios outside those expected for Second Cycle solutions. Second Cycle solutions are expected to follow pathways 1-3 in Figure 2. Uncertainties in uranium and nitric acid concentrations will be reported based on these pathways.

⁵ R.J. Lascola *et al.*, "On Line Spectrophotometric Measurement of Uranium and Nitrate in H Canyon", WSRC-TR-2002-00334, July 31, 2002.

⁶ R.J. Lascola *et al.*, "Spectrophotometers for Uranium Monitoring in H Canyon", SRNL-STI-2018-00325, September 2018 (in preparation).

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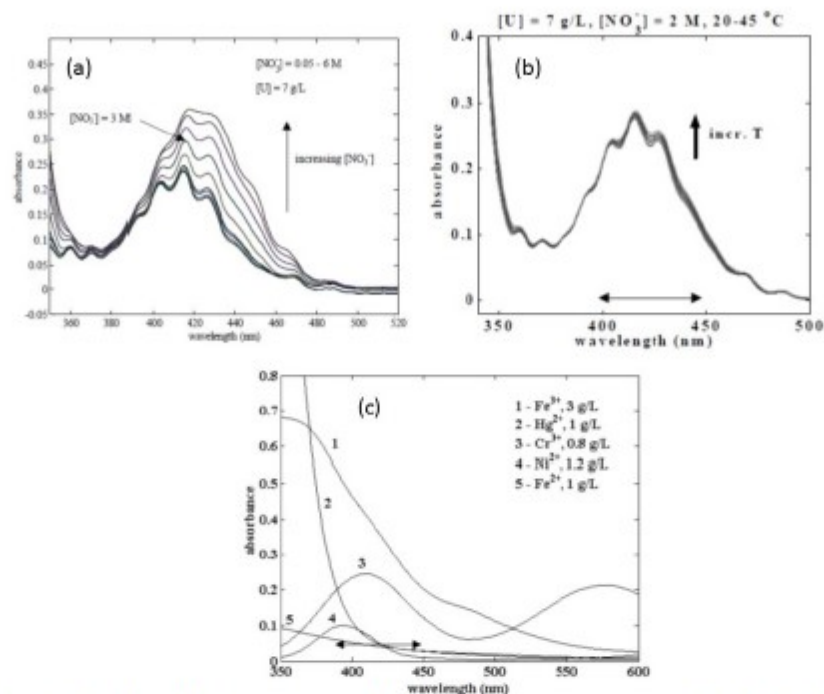


Figure 1. Effects of (a) acidity, (b) temperature, and (c) interfering species on uranyl nitrate absorbance spectra. From Ref. 5.

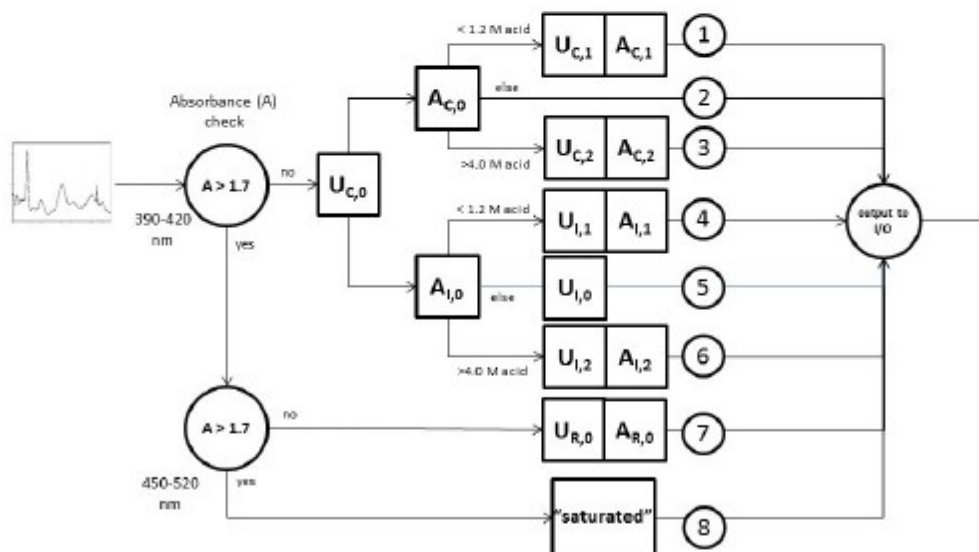


Figure 2. Flow sheet for spectral analysis. Pathways 1-3 apply to Second U Cycle tanks.

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Source Terms

Table 1 summarizes the “photometric analyzer” source terms for the colorimeter uncertainty calculations^{1,2} and indicates the appropriate value or redefinition for the spectrophotometers. All uncertainties are expressed on a 1 σ basis. Additional comments on each line item are provided below.

Table 1. Source Terms for Colorimeters and Spectrophotometers.

Input Data	Colorimeter	Spectrophotometer
Ambient Temperature	-10 °C to 40 °C	20 °C to 50 °C
Repeatability/Accuracy	0.04 AU	U: 2.64% Nitric acid: 5.5% (Tanks 16.8, 18.7 only)
Absorbance Range	± 2.000 AU	n/a
Analog Output	4 – 20 mA	4 - 20 mA
Input Calibration Range	0 – 15 g U/L 0.2 – 0.5 M nitric acid	See Table 2 and related discussion.
Spec % (Recal)	5.000%	See discussion of 5.1.3 below.
Calibration Interval	12 month + 25%	12 month + 25%

1. Ambient Temperature. The cited temperature indicates the variation in solution temperature for which absorbance data was collected and included in the prediction models. This variation is included in the repeatability/accuracy term, as discussed below. A spectrophotometer system was also tested in an environmental chamber in 781-A. The chamber temperature was cycled overnight, with temperatures ranging from 24 – 37 °C, and wavelength calibration was tracked by observing shifts in the positions of the emission lines from the mercury (Hg) lamp built into the system. Lines were seen to shift by approximately 0.05 nm/pixel at 420 nm to 0.15 nm/pixel at 700 nm. However, the wavelength calibrations (based on a fit to 8 Hg lines across the spectrum) were accurate to within 0.002 – 0.01 nm regardless of temperature. This range of variation is far smaller than the widths of the uranyl nitrate peaks being analyzed and is inconsequential for the analysis. The effect of instrument temperature drift on absorbance is minimized by the measurement procedure. The instrument automatically makes a new blank before the sample is circulated. The temperature in the facility should not vary substantially in the <30 minutes required to take circulate the sampler and acquire a measurement. Therefore, any drift should be minimal and there should be no uncertainty source term associated with facility temperature.

2. Repeatability/accuracy. The accuracy of the system for U or nitric acid measurements can be roughly divided into three components:

- the uncertainty of the target concentrations in the calibration standards
- the accuracy of the models in reproducing the target concentrations
- added uncertainty associated with making measurements in the facility (rather than the laboratory)

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The first two components are not entirely separable since the models will try to reproduce any errors in the standard concentrations. However, ~90% of the uncertainty in the uranium concentrations, and practically all of the uncertainty in the nitric acid concentrations, is due to uncertainties in the stock solutions used to make the standards. This error is systematic rather than random, since it will be in the same direction for all of the standards, and thus to a very good approximation these two terms can be treated as independent. The third component is also independent, and thus the overall source term can be calculated as the addition in quadrature of the individual components.

Uncertainty of target concentrations. (σ_C) Due to the predominance of the uncertainty coming from the stock solution concentrations, these uncertainties are consistent across all calibration solutions. For U, the values range from 0.56 – 0.60%. For nitric acid, the values range from 5.04 – 5.07%. For simplicity, and with a slight amount of conservatism, the uncertainties are assumed constant at the largest values: 0.60% for U and 5.07% for nitric acid.

Accuracy of calibration models. (σ_M) A full description of the measurement of the standards and the resulting absorbance models will be included in the final report. A summary of the results is presented here. Absorbance spectra for all calibration standards were obtained with the 5 field spectrophotometers and the SRNL development unit, using a 4 cm pathlength flow cell. A subset of standards was sealed in 1 cm cuvettes and heated to approximately 55-60 °C; absorbance spectra were measured as these solutions cooled. Values of the U concentrations were adjusted for pathlength so that all measurements were equivalent to being done with a 2.54 cm flow cell (nominal sample path length). Acidity values did not require adjustment, as spectra are normalized before that analysis.

Calibration models were made from spectra obtained with one of the instruments. Spectra from the other instruments were used to validate the models. The uncertainties reported here are based on the combined prediction errors for all spectra, based on the results generated by passing each spectrum through the flowsheet in Figure 2. These values therefore include all uncertainty contributions from the different spectrophotometers, from different solution temperatures, and from measurements on multiple days.

The analysis flowsheet differentiates between “low” (< 1.2 M) and “high” (> 4.0 M) acidity solutions (pathways 1 and 3, respectively). Pathway 1 covers solutions in Tanks 15.4, 17.4, and 17.5. Pathway 3 covers solutions in Tanks 16.8 and 18.7. Table 2 summarizes the analysis results for these pathways.

Table 2. Uncertainties for Uranium and Nitric Acid Measurements.

Pathway	Uranium		Total nitric acid		
	Standards Range (g/L)	Uncertainty (1 σ) (%)	Standards Range (M)	Uncertainty (1 σ) (%)	Uncertainty (1 σ) (M)
1	0.5 – 17	2.0%	0.1 – 1.2	34%	0.054 M
2	0.5 – 12.5	2.1%	1.2 – 4.0	11.5%	0.27 M
3	0.5 – 12.5	2.50%	4.0 – 8.5	2.1%	0.13 M

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The ranges specified for the uranium calibration represent the concentration ranges of the standards included in the calibration model. Spectra were screened based on their maximum absorbances satisfying the first absorbance criterion noted in Figure 2. Because a finite number of standards were made, these ranges do not represent the maximum U concentration that might be expected to pass the criterion and be included in pathways 1, 2, or 3. Based on linear extrapolation of the calibration spectra, we expect that the maximum U for the three pathways will be 17.4, 14.6, and 12.8 g/L, respectively. The maximum U concentration decreases with increasing acidity as suggested by Figure 1(a).⁷

Uncertainty associated with field measurements. (σ_F) Past work has shown that the accuracy of measurements with the on line spectrophotometers is tolerant of some baseline offsets associated with sampler operation.⁵ This version of the spectrophotometers will be operated with samples being held in the flow cell. Also, there are automated checks of baseline offset in the data acquisition program that will help ensure a proper filling of the flow cell.

Therefore, the only contribution to the uncertainty which is expected to arise from field operation is the systematic bias associated with uncertainty in the path lengths of the laboratory cuvettes and the sampler flow cell. For the spectrophotometers installed in HB-Line, this combined term was estimated as 0.60%.³ For this work, the same value may be used. Both the 1 and 4 cm flow cells used to generate standard spectra have the same tolerance (0.1%, having been obtained from the same manufacturer). The sampler flow cell is constructed similarly to the cell used in HB-Line, which has a tolerance of 0.59%.⁸ In quadrature, these values combine to yield 0.60%.

Combined uncertainties. (1) Uranium (σ_U). All three contributions (σ_C , σ_M , σ_F) apply in this case. As pathways 1 and 3 have similar model uncertainties, we will apply the largest value for all cases.

$$\begin{aligned}\sigma_U &= [\sigma_C^2 + \sigma_M^2 + \sigma_F^2]^{1/2} \\ \sigma_U &= [(0.60\%)^2 + (2.5\%)^2 + (0.60\%)^2]^{1/2} \\ \sigma_U &= 2.64\%.\end{aligned}$$

(2) Total nitric acid (σ_A) – Tanks 16.8 and 18.7. Because the absorbance spectra are normalized to total signal as part of the nitric acid analysis, the uncertainty associated with flow cell path length does not apply to this calculation. This calculation is presented only for the higher acidity tanks covered by pathway 3, as requested by H Canyon Engineering.

$$\begin{aligned}\sigma_A &= [\sigma_C^2 + \sigma_M^2]^{1/2} \\ \sigma_A &= [(5.07\%)^2 + (2.1\%)^2]^{1/2}\end{aligned}$$

⁷ Note that pathway 7 allows for the analysis of higher U concentrations by analyzing spectra only at the wavelengths where uranyl nitrate has smaller absorptivities. However, as these concentrations are beyond the bounds of Second Cycle processing, spectrophotometer performance under these conditions is not included in this memo. It will be included in the final report (Ref. 6).

⁸ R.J. Lascola, "Colorimeter Development for Np Measurements in HB-Line", WSRC-TR-2003-00525, November 2003.

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$$\sigma_A = 5.5\%.$$

Both U and total acid uncertainties are in terms of “percent of reading”.

3. Absorbance range. In the 1CU and 1EU uncertainty reports, the absorbance range is converted to an equivalent U concentration to provide an upper limit of the instrument range. For the spectrophotometers, the upper limit of U readings is provided directly. Therefore, the absorbance range is not required for this calculation.

4. Analog output. The spectrophotometers communicate with the Control Room DCS by means of 4-20 mA current output.

5. Input calibration range. These values are discussed in conjunction with Table 2.

Assumptions

4.2.3. For the initial uncertainty calculation, the assumption of 0.5 of the assessed calibration accuracy per year should be assumed. SRNL has not collected long-term drift data to fully support a smaller value. The arguments presented below suggest that the drift ought to be smaller than the above assumption. We suggest that periodic validation with the NIST-traceable absorbance standards over the course of the next 6 months will be sufficient to establish the smaller value. The validation will not involve an adjustment of the spectrophotometers and thus can be used in service of a long-term drift measurement.

The drift value for the spectrophotometers is expected to be small. For Second Cycle tanks, the instruments are programmed to automatically re-acquire a blank spectrum (effectively, re-zeroing) before every sample analysis. This practice essentially eliminates baseline drift from the measurement, in so far as facility/equipment temperature, lamp aging, and other equipment changes will be negligible over the course of the measurement. The practice also automatically compensates for differences in light throughput between the reference and sample arms of the spectrophotometer, which is the largest cause of error for subsequent absorbance measurements. The spectrophotometer also automatically performs a wavelength calibration before each measurement. Furthermore, the uranium and acid calibration models include taking second derivatives of the absorption spectra, which will remove the effects of drifts associated with constant or linear offsets.

4.2.5. For the colorimeters, the M&TE is the U calibration solutions. In the facility, the instruments are validated to be within the tolerances of the primary standards (NIST-traceable absorbance filters and mercury lamp emission lines). The verification of the primary standards in the facility assures that the instrument is operating with the same accuracy and precision as in the laboratory where the data on which the secondary standards (uranium and acid prediction models) are based were collected. The uncertainty of the prediction models is based on results obtained with multiple spectrophotometers which span the tolerance range of the primary standards. Thus, the M&TE accuracy should be the same as the secondary standard uncertainty (2.64% for uranium and 5.5% for nitric acid).

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Analytical Methods and Computations

5.1.3 Sensor Calibration Accuracy. Prediction accuracies are 2.64% for uranium (all tanks) and 5.5% (nitric acid, tanks 16.8 and 18.7 only). Application of the IPI calibration tolerance is at the discretion of the facility.

5.1.4 Sensor Measurement and Test Equipment Accuracy. Per the discussion of assumption 4.2.5 above, the prediction accuracies of 2.64% for uranium (all tanks) and 5.5% (nitric acid, tanks 16.8 and 18.7 only) should be used.

5.1.5 Sensor Drift. Per the discussion of assumption 4.2.3 above, in the absence of drift data, the drift should be assumed to be equal to one half of the assessed calibration accuracy per year. This value may be subject to revision based on collected data.

Other aspects of the analyzer calculation in Section 5.1 should not change.

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