

## ONLINE SPECTROPHOTOMETRIC MEASUREMENTS OF URANIUM AND NITRATE CONCENTRATIONS OF PROCESS SOLUTIONS FOR SAVANNAH RIVER SITE'S H-CANYON

Robert Lascola, Ronald R. Livingston, Mark A. Sanders,  
Jerry E. McCarty, and Judy L. Dunning  
Savannah River Technology Center  
Westinghouse Savannah River Company  
Aiken, SC

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### ABSTRACT

Safe and efficient operation of the Savannah River Site's solvent extraction process for uranium purification requires accurate measurement of uranium and nitric acid concentrations. Previous operations have relied only on laboratory analysis of process samples. To improve the efficiency of the process, we have installed an online fiber optic based analyzer that uses a multiplexer and diode array spectrometer to rapidly acquire absorption spectra at multiple process locations. This paper describes the hardware and software developments we have made to handle the requirements imposed by the unique sampling methods in H-Canyon. Performance characteristics of the spectrometer are also demonstrated.

### INTRODUCTION

A significant part of the Savannah River Site's (SRS) mission to protect national security and support nuclear nonproliferation is accomplished through the stabilization and management of nuclear materials. A large portion of this work is done at the site's H- and F-Canyons, which are used in the chemical separation of uranium and plutonium from reactor assemblies, process residues (scrap metals), and other sources. The preservation of nuclear safety and operating efficiency during this processing requires knowledge and control of many factors, including actinide concentrations and oxidation states, acid concentrations, and temperature at many points in the chemical process. Historically, the chemical content of the process solutions has been monitored through offline analysis via absorption spectroscopy, ion chromatography, mass spectrometry, and many other techniques. The usual disadvantages of offline analysis, resulting from sampling problems and laboratory limitations, are exacerbated by the solutions' nuclear material content, which imposes additional constraints.

Accordingly, we have developed and installed an online absorption spectrophotometer that allows remote analysis of the H-Canyon process through fiber optic couplings. This work builds upon pioneering efforts carried

out at SRS in the late 1980s<sup>1,2</sup>. These spectrophotometers were abandoned when the site's mission was redefined after the end of the Cold War. In this paper, we will describe the new spectrophotometer, which incorporates developments in both hardware and software that have not been previously reported. We will give particular emphasis to the sampling interface and computer software, which in some ways are uniquely suited for this application. We will also demonstrate the performance of the system for the monitoring of uranium and nitrate concentrations in the H-Canyon Second Uranium Cycle.

### INSTRUMENTATION

#### Overview

A diagram of the spectrophotometer is shown in Figure 1. The environmentally sensitive instrument components (lamp, computer, multiplexer, and spectrometer) are mounted in a standard 19-in. wide, 6-ft. tall rack located in the H-Canyon control room. The control room is climate-controlled and isolated from the process environment. The fiber optics used to connect sampler flow cells to the lamp and spectrometer (Ceramoptec, 400 micron high-OH silica core, hard silica cladding, Kevlar reinforcements) extend up to 100 meters to the flow cells (described below) which are located closer to the process environment. The lamp is a Xenon arc lamp (Hamamatsu, 75-watt) with fiber optic coupling equipment (Oriel Lamp housing and optics). The light passes through a multiplexer (Dicon, duplex 1 x 12, switching time ~ 0.5 second, with internal 400 micron fibers) and is directed to either a reference cuvette, a standard cuvette, or one of several sampler flow cells. Both cuvettes (Starna, 1 cm pathlength, quartz) are in the same location as the sampler flow cells, allowing the reference measurement to be made under similar conditions to the sample measurement. Collimating lenses used to pass light through the reference and sample solutions are described as part of the flow cell construction. The light returns to the multiplexer and is directed to a spectrometer (Zeiss MCS, 200-1100 nm, 1024 pixels, 0.8 nm pixel resolution, ~2.8 nm spectral

resolution, <0.0005 absorbance units peak-to-peak noise). The spectrometer is interfaced to an industrial grade computer (Texas Micro industrial PC, 586 processor, 233 MHz, with a data acquisition card from National Instruments, AT-AI6XE-10, 16-bit), which uses custom software developed for SRS applications (Onlinez, using Visual Basic 5.0 operating under Win NT). Following data processing, which incorporates chemometric analysis of the spectral data, the resulting data are provided to the H-Canyon digital control system by way of field point modules (National Instruments, FP-AO-200 (analog) and FP-DO-400 (digital)). The data acquisition and analysis program is also described in more detail below. Currently, four flow cells, a standard cuvette, and a reference cuvette are in use and three more process measurement points will be added.

### Sampling System and Flow Cell

The H-Canyon sampling system relies on aspiration of process solution aliquots from heavily shielded facilities to the flow cells, which are located about 35 feet above the process vessel being sampled. Vacuum alone is insufficient to raise the solution the necessary distance, so air is entrained in the pickup tube to allow transfer of sample aliquots. The solution first enters a collection vial through one of two tubes that penetrate a septum in the top of the vial. As solution continues to enter the vial, the

excess is pulled through the second tube, which connects to the flow cell with the inner of a series of two concentric tubes that enter the top of the flow cell. Solution with entrained air pulses through the flow cell, eventually leaving via the outer tube and returning by gravity to the tank. A schematic diagram of the sampling system is shown in Figure 2.

The body of the flow cell is constructed from a standard 1/2-in. stainless steel compression fitting union tee (Swagelock SS-810-3), with the optical path along the long axis of the tee. Light from the fiber optics is transmitted through the cell by means of two collimating lens assemblies (Equitech International). These assemblies have 1/2-in. stainless steel cylindrical bodies which form a seal using standard ferrules. The assemblies have sapphire windows, sealed to the stainless steel by pressure fittings and Kalrez o-rings. The fiber optics are attached to the lenses with SMA 905 connections. Design of the union tee limits insertion of the lens assemblies and provides an approximately one inch pathlength. The shoulders, which limit lens insertion, can be bored out when shorter pathlengths are required. At a one inch separation, a set of lenses installed as described will transmit approximately 65% of the incident light.

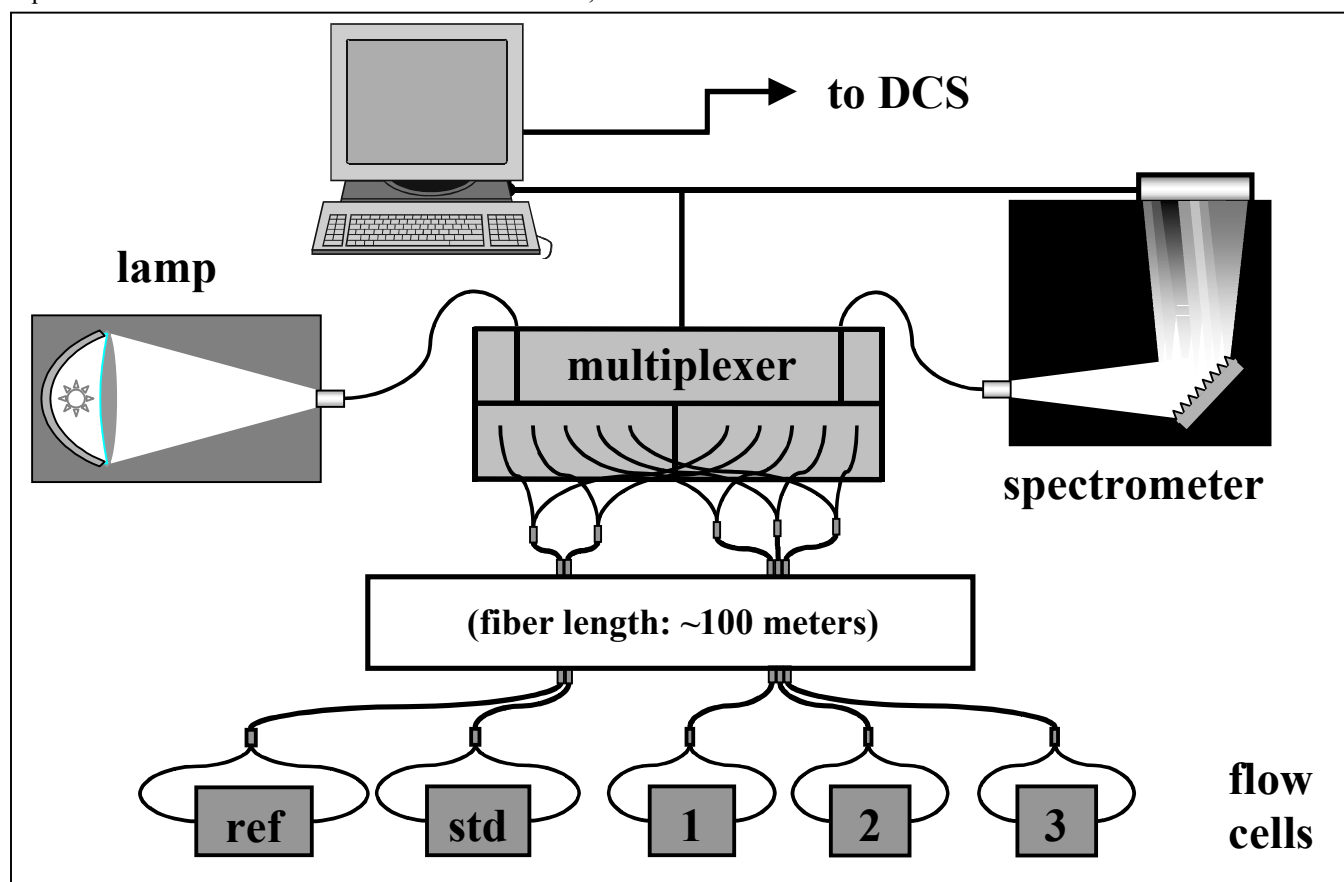


Figure 1. Schematic diagram of spectrophotometer. All lines represent fiber optics, except lines from the PC, which are communication lines. Up to seven flow cells will be included in the current application.

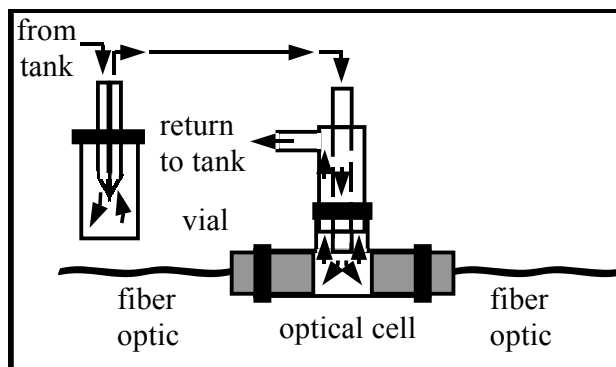


Figure 2. Schematic diagram of sampler interface and flow cell.

As stated previously, the solution enters and exits the flow cell through the top (middle) of the tee. Since the windows are recessed from the flow tube, the entering solution must force its way through or around the exiting solution to assure complete solution exchange. The rate of exchange can be controlled by varying the distance the flow tube extends into the tee. We have found that the tube should extend as far as possible into the tee without blocking the optical path. If the tube is recessed  $\frac{1}{4}$ -in. from the top of the optical path, the displacement of a highly concentrated uranium/nitric acid solution ( $d = 1.37 \text{ g/mL}$ ) by a more dilute solution ( $d = 1.16 \text{ g/mL}$ ) requires several hours. If the tube is in its optimum position, the exchange requires a couple of minutes.

Exchanges of solutions with similar densities occur in seconds.

Another factor governing sample exchange is the amount of air entrained in the sample. More air corresponds to a stronger pull by the vacuum; the solution enters the collection vial and flow cell with greater velocity, improving the mixing. Unfortunately, too much air adversely affects the spectra taken through the flow cell, since air bubbles scatter light, increasing the baseline, and exclude solution, decreasing the effective pathlength. The problems associated with entrained air are dealt with by rapid data acquisition and appropriate spectral processing. Figure 3 shows the time dependence of intensity fluctuations associated with a normally operating canyon sampler. With each pulse of solution that enters the flow cell, there is a period of turbulence that eventually dissipates, leaving a relatively clear window during which acceptable spectra can be obtained. However, the dissipation rate is not consistent between pulses, and there is no way to know *a priori* when the suitable data window will occur. Clearly, spectra must be obtained quickly to avoid the inadvertent inclusion of unacceptable data, and the spectra must be evaluated to assess their suitability. We have found that acceptable spectra (based on intensity) can be obtained with integration times on the order of 0.06-0.1 seconds. Faster spectra are limited by the clock speed of the data acquisition card.

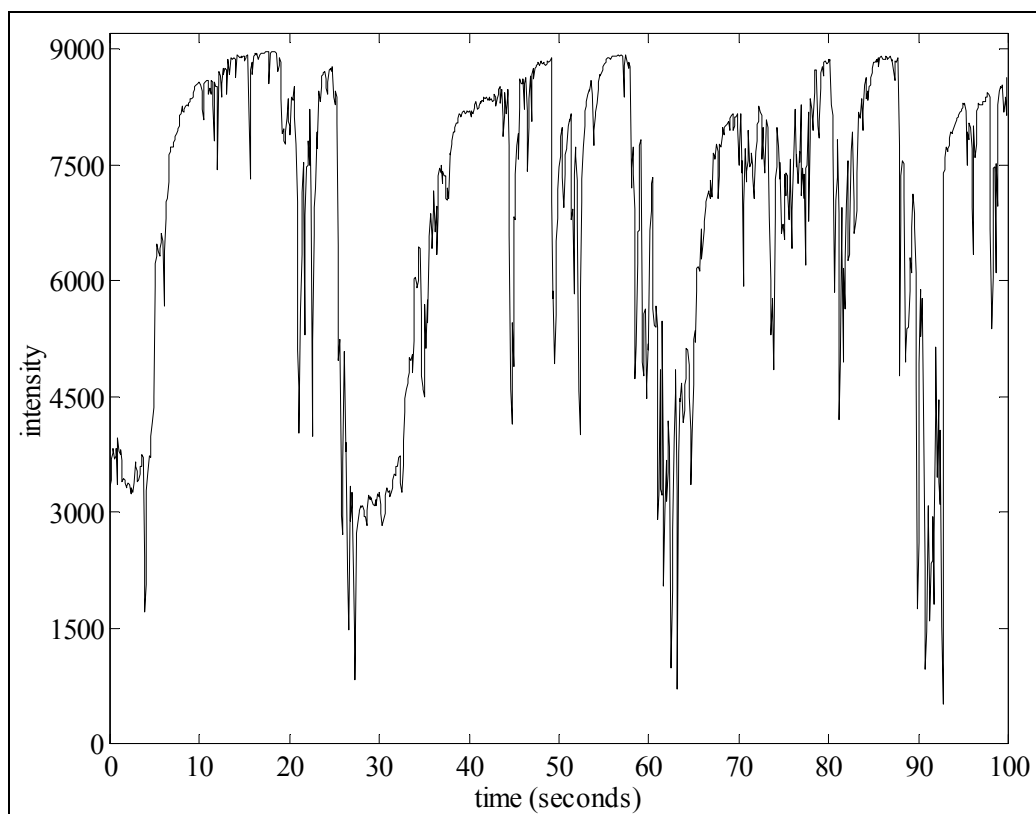


Figure 3. Influence of turbulence on flow cell throughput. Throughput measured at 480 nm, with 0.05 second integration time and 0.5 second sampling interval.

## Software

The data acquisition software (Onlinez), developed by the authors using the Visual Basic platform, is a flexible, modular program that controls all aspects of spectrophotometer operation. Measurement points are selected according to a scheduling routine with predetermined sampling priorities and measurement intervals. Each process location or measurement point has its own options file containing different data acquisition requirements (e.g. signal averaging, integration time, wavelength range) and unique mathematical treatment and modeling information for data reduction. These options are set on the basis of the chemometric requirements and the performance of the sampler during testing and then entered into the program prior to online analysis. Once these parameters have been read from file by the scheduling routine, the measurement routine is implemented. For an absorption measurement, the dark current, reference, and sample intensities are measured by moving the multiplexer to the appropriate position and recording the spectrum. Sample spectra are evaluated prior to use in calculating sample concentration by comparing the sample intensity at a wavelength with no absorption to the reference intensity at the same wavelength. If the sample intensity is less than an empirically established set point (a certain fraction of the reference intensity), the spectrum is rejected as having too much scatter due to turbulence. The number of accepted and rejected spectra are counted; limits have been set for the minimum and maximum number of spectra expected for normal operation of a given sampler and used for detecting abnormal sampler operation. When one limit is reached, data acquisition is stopped and the accepted data is averaged.

Analysis is carried out once the data are collected. Preprocessing consists of calculation of the absorbance spectrum, including corrections for optical path differences, and any mathematical manipulations. In particular, taking the second derivative of the absorption spectrum both eliminates the effects of a constant baseline offset and strongly reduces the effects of any interferent (such as  $\text{Fe}^{3+}$ ) that produces a sloping baseline. The resulting data are then analyzed with a predetermined model. The current version of the program allows the use of any of the standard linear regression techniques: PLS, PCR, CLS, and MLR<sup>3,4</sup>. Different predictive models and preprocessing can be applied to the same raw data, supporting multiple analyses. In the current application, the uranium and nitrate analyses are carried out with separate multivariate models rather than a single model which predicts both analytes. In fact, the results of the uranium prediction are used in the preprocessing for the nitrate prediction, demonstrating the flexibility of this approach. Once the analysis is complete, results are displayed on the computer screen, written to disk, and reported to the facility's digital control system as an analog signal.

In addition to recording data, the program also provides alarms for a wide variety of malfunctions. Lamp

failures are indicated by low intensity values in the reference and data channels. Poor spectral quality is indicated by large intensity differences between the reference (sealed cuvette) and sample channels; consistently low light at one channel may indicate a broken fiber optic or clouded flow cell. The possible presence of interferences is shown by large fit residuals or uncertainties. A handshaking signal is exchanged with the multiplexer to assure communication with that device. The presence of any of these conditions leads to a digital signal being sent to the control system as well as a message written to a log file on the computer which facilitates troubleshooting. In addition, there is a separate "watchdog" program running on the PC which monitors crashing of the main program. Divide by zero errors and spectrometer errors are detected in this manner. Finally, there is a watchdog associated with the field point modules that monitors a complete disabling of the computer and reports to the DCS.

## RESULTS

The performance of the spectrophotometer has been evaluated using PLS models developed for uranium and nitrate prediction in the uranium – nitric acid system. The calibration range is 0-11 g/L uranium and 0.05 -6 M nitrate (in the form of nitric acid). Spectral dependence on uranium and nitrate concentrations is shown in Figures 4a and 4b, respectively. The observed spectra are a sum of spectra of individual uranyl nitrate species ( $\text{UO}_2^{2+}$ ,  $\text{UO}_2\text{NO}_3^+$ , and  $\text{UO}_2(\text{NO}_3)_2$ ). At these concentrations, the equilibrium between these species is independent of uranium concentration, but changes significantly with nitrate<sup>5</sup>. Consequently, a linear PLS model applied to simple second derivative absorption spectra is well-suited to uranium analysis, but accurate nitrate predictions require additional spectral preprocessing.

Other workers<sup>1,6</sup> have found that normalizing the spectra to either maximum or integrated absorbance before analysis leads to a data set that is more linear with respect to nitrate. We have developed an accurate PLS prediction model for nitrate in these process solutions by normalizing the spectra to the result of the uranium analysis. This method more directly reflects the goal of the normalization, which is to account for the total number of uranyl nitrate species and reduce the fitting problem to one of analyzing the spectral shape changes<sup>1</sup>. It also is less sensitive to the baseline offsets caused by sampler turbulence, and is relatively easy to implement with the modular data acquisition software described above. We have developed models with root-mean-square validation errors of 0.08 g/L for uranium and 0.10 M for nitrate over a temperature range of 20-45°C. The details of both the uranium and nitrate models will be described in a separate publication<sup>7</sup>.

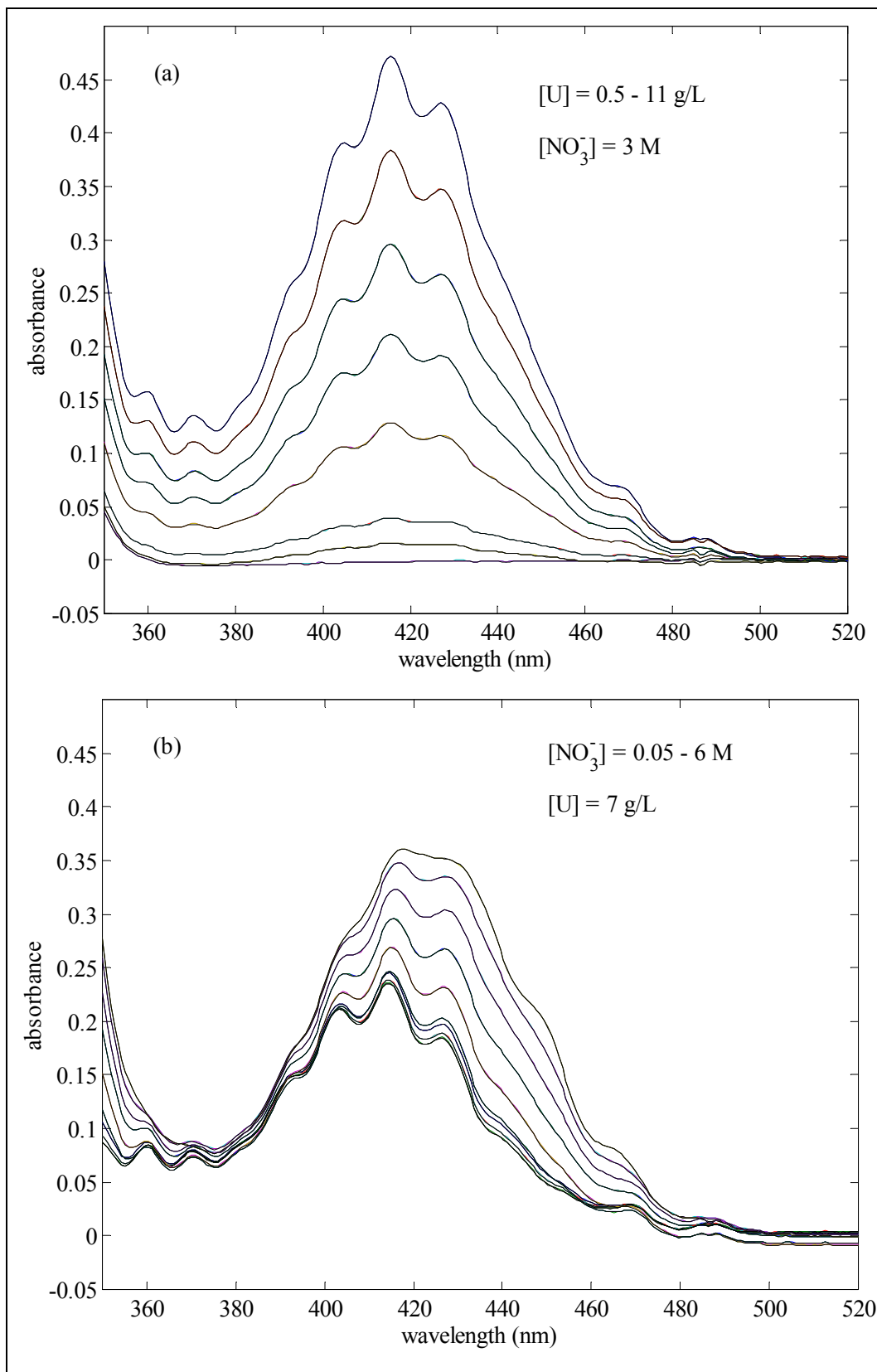


Figure 4. Dependence of uranyl nitrate spectra on (a) uranium and (b) nitrate concentrations.

Variations of the uranium and nitrate predictions arise from spectrophotometer variations as well as from operation of the sampler. The relative importance of these sources can be determined by comparing the signal variation from analysis of the standard cell (a sealed cuvette containing uranyl nitrate solution) to that from the process sampler(s). Typical results for uranium prediction are shown in Figures 5a and 5b. (Nitrate results are similar.) Note that the sampler is not usually run for periods longer than a couple of days; hence there is no extended data as for the cuvette studies. Nonetheless, one can see that the overall standard deviation and the peak-to-peak fluctuations in the sampler are approximately twice the values for the cuvette results. In both cases, the standard deviations are smaller than the standard deviation identified for use

of the model itself (*i.e.* based on laboratory evaluation). Therefore, operation of the spectrometer in the field is not the major source of uncertainty contributing to process measurement error.

As the online system is intended to largely replace offline analyses, it is useful to compare the performance of the two. Table I shows the comparison of online and offline analysis for uranium and nitrate measurements for flow cell and standard solutions. Predictions are generally within the 95% confidence limits for both uranium (0.16 g/L) and nitrate (0.20 M). Also, prediction capability is comparable to results reported by Bűrck<sup>6</sup> for spectra obtained in a laboratory environment. These results indicate that the online system is an effective replacement for offline analyses.

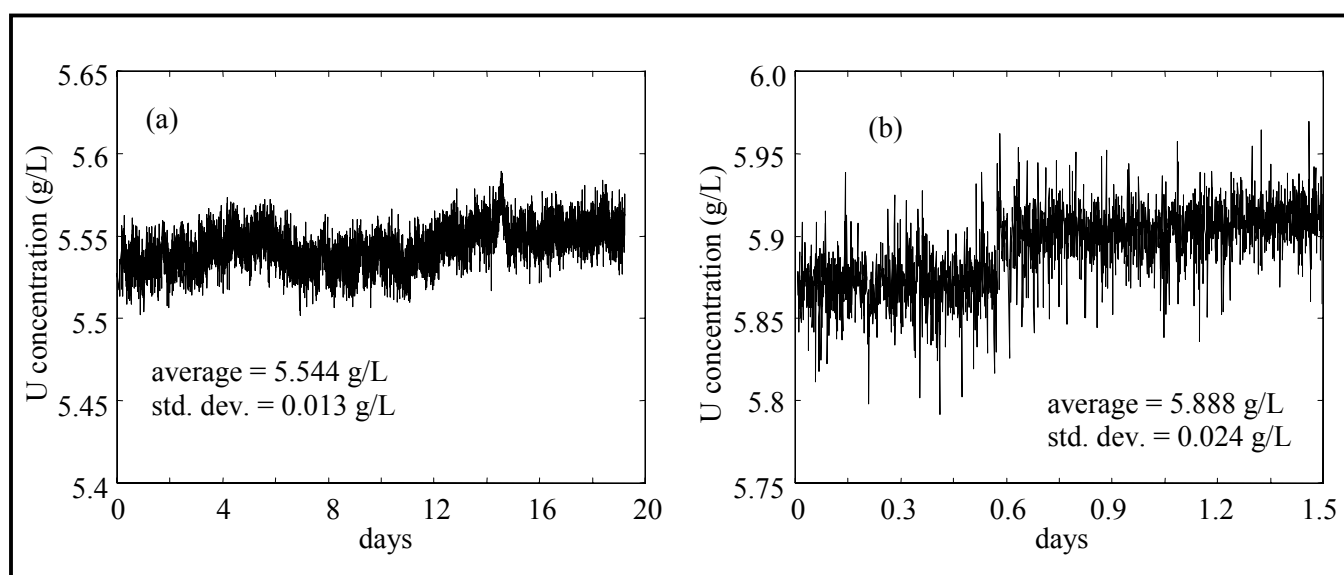


Figure 5. (a) Uranium measurements for a standard cuvette. (b) Uranium measurements taken for a circulating sampler.

Table I Comparison of Laboratory and Field Results for Uranium and Nitrate Analysis

Source	Uranium			Nitrate		
	Lab (g/L)	Field (g/L)	$\Delta$ (g/L)	Lab (M)	Field (M)	$\Delta$ (M)
FC	8.94	8.82	-0.12	5.93	5.88	-0.05
FC	1.93	1.90	-0.03	5.11	4.89	-0.22
FC	4.94	5.05	0.11	4.31	4.12	-0.19
FC	2.82	2.93	0.11	1.01	0.94	-0.07
FC	6.80	7.01	0.21	2.03	1.80	-0.23
FC	5.26	5.32	0.06	(lab measurement not obtained)		
S	2.97	3.09	0.12	3.75	3.66	-0.09
S	5.23	5.25	0.02	4.04	4.04	0.00
S	7.21	7.21	0.00	4.14	4.03	-0.09
S	3.14	3.11	-0.03	5.07	5.35	0.28
S	5.41	5.58	0.17	5.09	5.80	0.71
S	7.12	6.94	0.18	5.13	5.27	0.14
S	3.05	3.13	0.08	4.02	4.27	0.25
S	4.56	4.64	0.08	4.02	4.20	0.18
S	6.03	5.95	-0.08	4.02	4.01	-0.01
S	3.03	3.06	0.03	5.32	5.32	0.00
S	4.52	4.49	-0.03	5.32	5.43	0.11
S	6.04	6.02	-0.02	5.32	5.44	0.12

FC = Flow cell; S = standard cuvette. Lab result uncertainties for uranium are  $\pm 5\%$  ( $2\sigma$ ) and for nitrate (measured as acid) are  $\pm 10\%$  ( $2\sigma$ ).

## CONCLUSION

We have developed and installed a fiber optic based absorption spectrophotometer to analyze uranium and nitrate concentrations at multiple points in Savannah River Site's H-Canyon. The sampling mechanism requires analysis of turbulent process solutions with entrained air. We have developed a flow cell that allows sufficient degassing and rapid mixing of these solutions. We have also developed software that provides instrument control, real-time data screening, and alarm capabilities. The analysis capability and performance of the online system compares favorably with laboratory test results.

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