Application of Absorption Spectroscopy to Actinide Process Analysis and Monitoring

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INTRODUCTION

The characteristic strong colors of aqueous actinide solutions form the basis of analytical techniques for actinides based on absorption spectroscopy. Colorimetric measurements of samples from processing activities have been used for at least half a century [1]. This seemingly mature technology has been recently revitalized by developments in chemometric data analysis. Where reliable measurements could formerly only be obtained under well-defined conditions, modern methods are robust with respect to variations in acidity, concentration of complexants and spectral interferents, and temperature.

This paper describes two examples of the use of process absorption spectroscopy for Pu analysis at the Savannah River Site, in Aiken, SC. In one example, custom optical filters allow accurate colorimetric measurements of Pu in a stream with rapid nitric acid variation. The second example demonstrates simultaneous measurement of Pu and U by chemometric treatment of absorption spectra [2]. The paper concludes with a description of the use of these analyzers to supplement existing technologies in nuclear materials monitoring in processing, reprocessing, and storage facilities.

DESCRIPTION OF THE WORK

Optical absorbance measurements are converted to analyte concentration through the application of the Beer-Lambert Law:

$$A(\lambda) = \Sigma_i \, \varepsilon_i(\lambda) \, b \, c_i \qquad (1)$$

where A is the solution absorbance at wavelength λ, ε_i and c_i are the molar absorptivity and concentration, respectively, of the ith species in solution, and b is the optical pathlength of the measurement. Changes in absorbance are assumed only to be due to changes in the analyte. When this assumption is invalid, accurate concentration measurements may still be possible if one can integrate absorbance over a range of λ that provides a constant effective ε. Thus simple colorimetric equipment can be used to make a measurement in a complex matrix.

An example is the installation of a colorimeter to measure plutonium concentration in the range of 0.1 - 1.5 grams/liter (g/L) in the heart cut from an anion exchange column, during which nitric acid concentration decreases rapidly from 8 moles/liter (M) to 2 M. While Pu remains in the +4 oxidation state, the absorption spectrum changes due to the varying distribution of Pu-nitrate complexes, as shown in Figure 1. Commercially available filters near the strong 475 nm band do not accommodate the spectral variation, requiring the development of a customized filter.

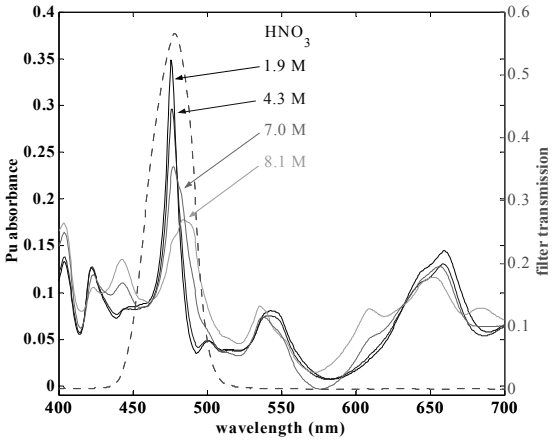

Fig. 1. Pu^{4+} absorbance spectrum as a function of nitric acid concentration, 1 cm pathlength. Dotted line shows filter transmission used for this colorimetric application.

When it is feasible to obtain and analyze the full absorption spectrum, chemometric analysis allows the user to extract that portion of spectral variation which correlates to analyte concentration [3]. Method accuracy can be comparable to colorimetry of pure analyte solutions [4]. An example is the simultaneous measurement of U (as UO_2^{2+}) and Pu (as Pu^{3+}) in solutions from spent fuel processing. Pu directly interferes with U absorption in the 390-440 nm range and can be present in 10-fold excess. Also, small amounts of metallic cations present from the dissolved starting material could

overlap spectrally with both U and Pu. Statistical toleration of these interferences reduces the need for sample cleanup and dilution, improving the uncertainty and making *in situ* measurements more feasible.

RESULTS

The customized filter used in the colorimetry application is a stack of a colored glass long-pass filter and an interference short-pass filter in a holder that permits continuous adjustment of the angle of incidence of the light. Instrument performance is simulated based on the convolution of the acid-dependent absorbance spectra, filter transmittance as a function of angle, and spectral output of the colorimeter lamp. The prediction for a filter angle of 20^0 (with a transmittance shown in Figure 1) is that the instrument response will remain constant within ±5% for nitric acid variation between 2-9 M. Actual measurements are accurate to ~11%, with additional contributions to the uncertainty arising from absorbance variations at the reference wavelengths and uncertainty in the Pu concentration of the standards. The instrument performance is still sufficiently accurate for process control.

Simultaneous measurement of U and Pu is achieved through partial least-squares analysis of absorption spectra. Prediction results for U ~ 0.25 g/L as a function of [Pu]/[U] ratio are shown in Figure 2. The accuracy of the measurement is constant until [Pu] ~ 2 g/L, for which the absorbance due to Pu (0.45) is 11x the absorbance due to U (0.04). Given this difference and the intrinsically weak U absorbance, the observed prediction errors are reasonable.

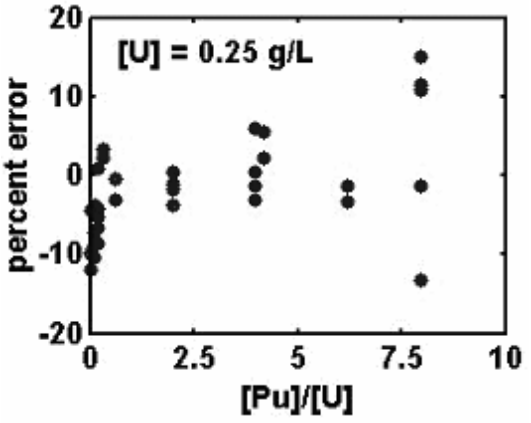

Fig. 2. [U] prediction results by absorption spectroscopy, as a function of [Pu] concentration.

Both examples presented here indicate the potential of absorption spectroscopy as a complementary technique to counting methods for actinide accountability measurements in the nuclear processing/reprocessing environment. The technique is best suited for liquid streams where knowledge of the isotopic distribution is not critical. As with any online analysis method, implementation cost is a significant concern. Optical fibers and multiplexers offer savings by allowing use of the same spectrometer and computer at multiple points. However, routine use will probably not occur until costs, footprint, and ease of use approach completely mature devices such as pressure transducers or thermocouples. White-light LEDs, miniature spectrometers, and dedicated processing chips will be the elements of the next generation of devices. These parts exist individually, but have not been packaged on a low-cost, high-volume basis. When these devices become available, their use at many locations in the process, combined with statistical analysis, could be a meaningful way to detect material diversion and promote nuclear safeguards.

REFERENCES

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