

## Task 29

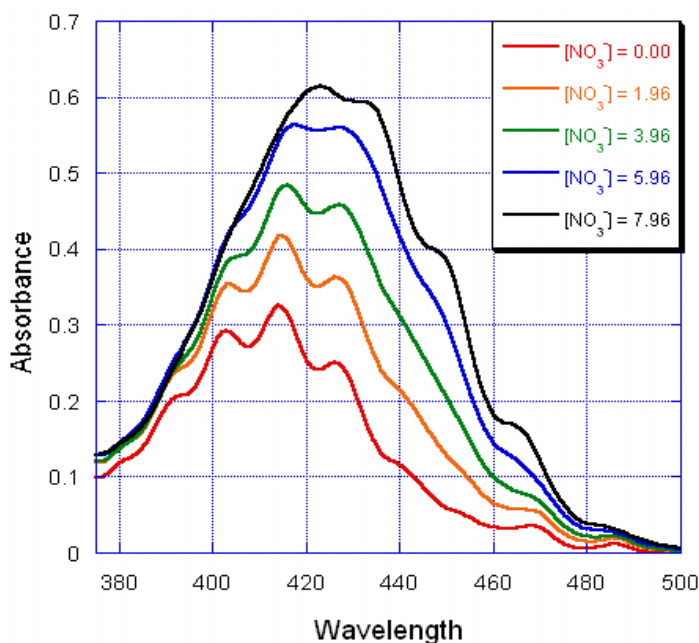
# Investigation of Optical Spectroscopy Techniques for On-Line Materials Accountability in the Solvent Extraction Process

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## BACKGROUND

One of the primary challenges facing any advanced fuel cycle is the proliferation resistance of that fuel cycle, especially the potential for illicitly diverting nuclear material from the fuel cycle for other purposes. The key step in almost all of the fuel cycles currently under evaluation in the Advanced Fuel Cycle Initiative is the chemical separation and partitioning of used nuclear fuel, either as the starting point for treating existing used fuel, or as a key step in the recycling and destruction of the higher actinides. Any partitioning of the actinides has the potential for decreasing the proliferation resistance of the fuel cycle unless the process or plant can be designed to prevent, or at least detect, the diversion of nuclear material from the process. To address this concern, the AFCI has proposed that any new separations plant include in its design an integral system capable of providing materials accountability for the actinide elements to minimize the potential for undetected diversion of material.

Optical spectroscopic techniques, such as Ultraviolet-Visible Spectroscopy (UV/Vis) and Laser Fluorescence Spectroscopy (LFS), allow for the on-line, real-time analysis of the actinide elements for a solvent extraction process. UV/Vis and LFS are quantitative analytical techniques that have been used for measuring the concentration of the actinides under laboratory conditions, and are easily adaptable to multiple sampling geometries, such as dip probes, fiber-optic sample cells, and flow-through cell geometries. In UV/Vis spectroscopy, the sample is illuminated by a continuous spectrum (from the UV through the Visible wave-



Effect of increasing nitrate concentration on uranyl spectra.  
 $[UO_2^{2+}] = 0.047 M$ ,  $[H^+] = 2.0 M$

lengths). The transmitted light is measured, allowing the determination of the absorbance of the light as a function of wavelength. The wavelength of the absorbance is dependant on the electronic structure of the absorbing atom, and is proportional to the concentration of the absorbing element in the sample. For LFS, the sample is illuminated at a single wavelength, which is absorbed by the target atoms in the sample. The energy absorbed is re-emitted through fluorescence. The wavelength of the absorbance, and the fluorescence-response, is again dependant on the electronic structure of the absorbing atom, and is proportional to the concentration of the absorbing element in the sample. In addition to the potential materials accountability applications, UV-Vis Spectroscopy and LFS can provide information regarding the speciation of the actinides in the process stream (oxidation state, complex formation, etc.). This information will help elucidate the behavior of the actinides under process conditions, improving the understanding of the chemical interactions underlying these separations processes.

## RESEARCH OBJECTIVES AND METHODS

The long-term goal of this project is the evaluation of optical spectroscopy-based techniques for the on-line, real-time determination of actinide element concentrations in fuel recycling plant process streams. To generate the information necessary to evaluate the potential of these systems, initial experiments will focus on determining the detection limits for UV/Vis and LFS will be measured for the actinide elements under chemical conditions representative of the process streams for the UREX+ process. The system will then be systematically explored to examine the impact of acid concentration, nitrate concentration, redox potential, diluent concentration, ligand concentration, and contaminant/fission product concentration on the sensitivity of these techniques. The potential for interferences will also be examined.

The research objectives are:

- To evaluate the potential for utilizing UV-Visible and laser fluorescence spectroscopy to determine actinide concentrations under process conditions.
- To examine the impact of process environment on the sensitivity of UV-Visible and laser fluorescence spectroscopy to the actinides, including the impact of acid concentration, solvent concentration, ligand concentration (TBP, AHA), coloring agents (iron, fission products, etc.), competing actinide elements.

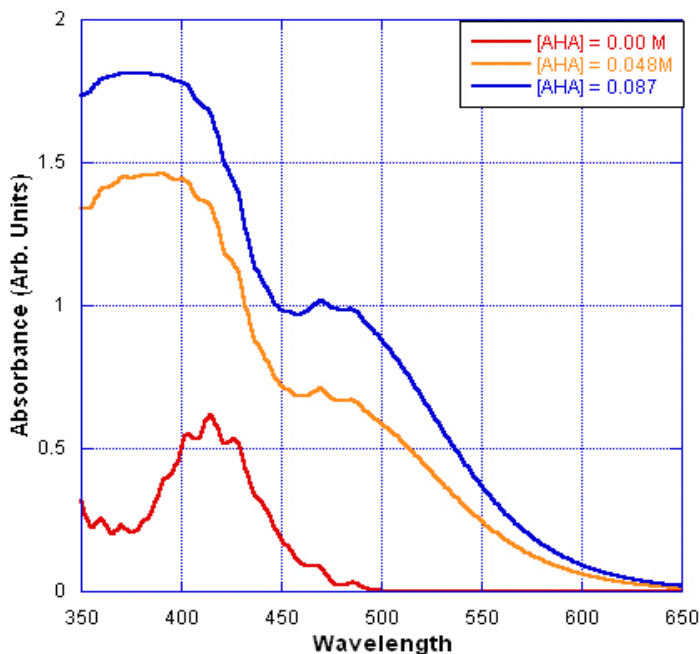
## RESEARCH ACCOMPLISHMENTS

To evaluate the potential application of UV/Visible spectroscopy for the determination of uranium in the aqueous process streams of the UREX process the impact of process chemical conditions on the absorbance behavior of the uranyl ion was examined. The process streams of interest are distinguished by three main vari-

ables in the aqueous system: the metal ion concentration, the acid concentration, and ligand concentration ( $\text{NO}_3^-$ , AHA). General trends were observed in the molar absorptivity constants as conditions were varied. The most noticeable changes occurred as the nitrate concentration was increased. The figure on the opposite page shows the effect of increasing nitrate concentration at constant metal and acid concentrations. There is a large change in the molar absorptivity constant as the concentration of the free uranyl ion is decreased and two or more uranyl nitrate solution complexes become dominant. An accompanying shift in the uranium spectrum, as well as a wavelength shift at the peak intensity was observed as the nitrate concentration was increased from 2 M to 8 M.

The UREX feed stream and uranium product will both have molar quantities of uranium present. The concentration of uranium in these streams is expected to exceed the linear range of detection for a 1 cm path length cell, which will require either the reduction of the path length or the dilution of the feed prior to analysis. In designing the equipment train for the recycling plant, a slip stream could be extracted from the feed or uranium product streams for analysis. This slip stream could easily be mixed in a controlled mass ratio with a diluent stream of nitric acid or passed through a reduced diameter section to provide a significant reduction in path length.

The raffinate and technetium streams are expected to have signifi-



Effect of increasing AHA concentration on uranyl spectra at  $\text{pH}=2$ .  $[\text{UO}_2^{2+}] = 0.094 \text{ M}$ ,  $[\text{NO}_3^-] = 1.2 \text{ M}$

## ACADEMIC YEAR HIGHLIGHTS

- ◆ N.A. Smith, G.S. Cerefice, and K.R. Czerwinski, "Application of Optical Techniques for On-Line Materials Accountability in the UREX Solvent Extraction Process," *Proceedings from the 47<sup>th</sup> Annual Institute For Nuclear Materials Management Annual Meeting*. July 16 – 20, 2006. (IN PRESS)
- ◆ N.A. Smith, G.S. Cerefice, and K.R. Czerwinski, "Optical techniques for improved materials accountability in the UREX+ process," Oral Presentation, American Chemical Society National Meeting, Atlanta, GA, March 30, 2006.

cantly lower concentrations of uranium. The primary differences in these streams are the nitric acid concentrations and the presence of AHA in the raffinate stream. In these streams, the expected concentrations will likely fall below the detection limits observed for a 1 cm optical path.

In addition to the potential applications for direct, on-line concentration measurements, UV/Visible spectroscopy may also provide analysts with the ability to directly observe process chemistry. From a proliferation resistance point-of-view, two observations show immediate promise. By examining the absorbance spectrum, it should be possible to detect the conversion of a recycling plant from the UREX process, which does not separate plutonium, to the PUREX process, which does result in a purified plutonium product due to the associated increase in molar absorptivity along with a change in peak shape. The spectrum loses individual peaks and is replaced by one broad, flat peak. This change in process chemistry could also be detected in the raffinate stream. The presence, or absence, of AHA in the raffinate stream becomes significantly more pronounced as the pH of the analyzed stream is increased. By titrating a slip stream from the raffinate product stream to higher pH, and comparing the observed spectrum to one from a second, unaltered slip stream, the presence of AHA in the raffinate can be confirmed.

## FUTURE WORK

For the remainder of the first project year, work will focus on the evaluation of laser fluorescence for the determination of uranium concentration in the aqueous streams of the UREX+ process. In the second year of the project, work will expand along two fronts. The current work examining the determination of uranium concentrations in the aqueous system will be expanded to examine the determination of the higher actinide concentrations in these process streams. In a parallel effort, the evaluation of uranium concentration measurement by optical spectroscopy techniques in the organic process streams of the UREX+ separations process will begin.

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