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Optical Spectroscopy: Quarterly Report: 01/01/06 – 03/31/06

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Highlights

- Laser system alignment finished, site visit scheduled for final spectrometer configuration
- Initial studies on $\text{UO}_2^{2+}/\text{NO}_3^-/\text{H}^+$ completed; preliminary data regression in progress
- Preliminary work on uranyl/AHA and organic/aqueous interface systems started

Papers/Publications/Presentations

- “Optical techniques for improved materials accountability in the UREX+ process”
N.A. Smith, G.S. Cerefice, K.R. Czerwinski, Oral Presentation, 231st National Meeting of the American Chemical Society, Atlanta, GA, March 29, 2006

Technical Summary

Aqueous Uranyl System

Initial studies on the uranyl/nitrate/acid system have been completed. Full spectra were taken of each sample in order to determine ligand effects on the entire uranyl spectra. Effects relating not to the nitric acid concentration, but the total nitrate ion present were observed (Fig. 1). The effect was generally a linear increase with total nitrate added. However there was a slight variation associated with the total acid concentration which can be seen in (fig 2). A peak shift, indicative of a speciation change was also observed.

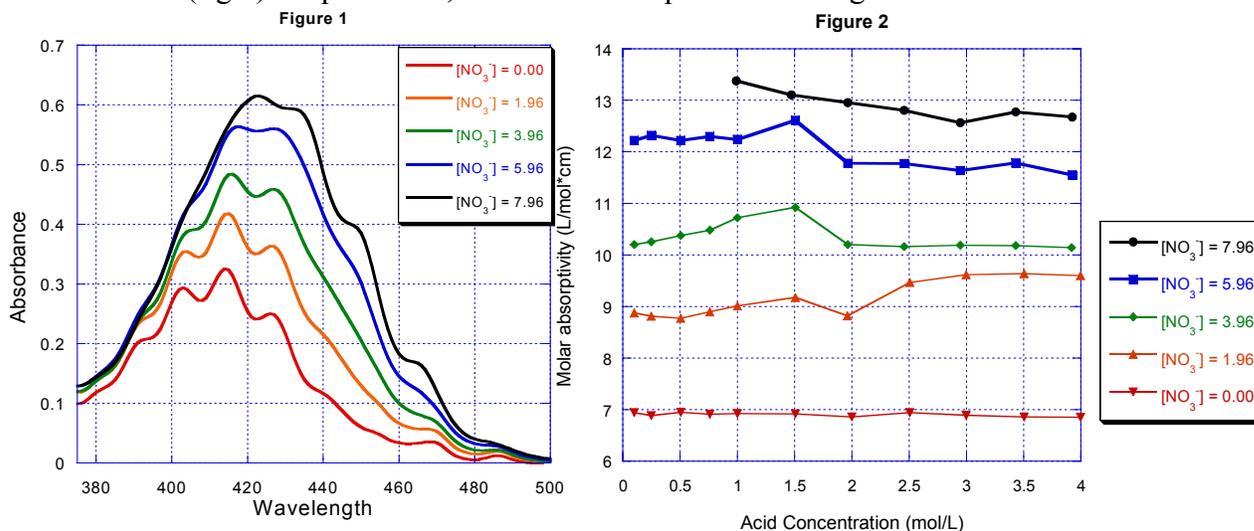


Fig 1) Uranyl spectra in the presence of increasing nitrate concentrations $[\text{UO}_2^{2+}] = 0.047 \text{ M}$, $[\text{H}^+] = 2.00 \text{ M}$
Fig 2) Molar absorptivities at peak absorbance $[\text{UO}_2^{2+}] = 0.047 \text{ M}$, $[\text{H}^+] = \{0.100 \text{ M} - 4.00 \text{ M}\}$

Preliminary analysis has shown that the general peak shape and height can be qualitatively predicted from the total nitrate in the system. Conversely, a change in nitric acid concentration could be qualitatively detected by spectral analysis.

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The presence of the peak shifting and the peak broadening in figure 1 suggests that there is a change in speciation occurring. Based solely on the peak shift, it appears that the nitrate (mono- or di-) species becomes the dominant spectroscopic contributor around $[\text{NO}_3^-]_{\text{total}} \approx 6.00 \text{ M}$. There has also been some speculation that the uranyl ion is dimerizing under these conditions. However, these, at this time, are still only hypotheses. In order to resolve the speciation, and the spectra, of this system, potentiometric titrations and/or EXAFS experiments are being considered.

In order to more accurately determine the presence of a speciation driven peak shift in process, derivative spectra analysis is being looked into (fig. 3). With a first derivative spectrometer setup, the peak shift associated with an increase in nitrate concentration could be carefully monitored. This method has the potential to allow near real time analysis of process parameters without the need for a full spectrum. A region of interest on the order of 20-30 nm could be monitored.

Further work on the aqueous system will involve the addition of other ligands that are present in the UREX+ system, specifically, AHA. Also, the direct addition of chromophores to the process streams is being considered.

Due to the large fluorescence and absorption properties of the uranyl ion, efforts are being directed to adapting UV-Vis and TRLFS procedures into denial methods that could certify a stream as being uranium free, thus eliminating the need to monitor downstream for uranium. This methodology has the potential to be expanded to the other actinides of interest as well.

Laser Fluorescence Laboratory

The TRLFS system is in final stages of setup. Time resolution problems are in the process of being resolved. Problems due to a mismatch between the laser output aperture and the spectrometer entrance have been corrected with the addition of an optical periscope. Spectrometer has been effectively calibrated with Hg:Ar calibration source and is ready. Final installation of barrier curtains is ready pending final configuration by Princeton Instruments.

