WPO311106

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to: Sandia WIPP Records Center

from: Ruth F. Weiner RW

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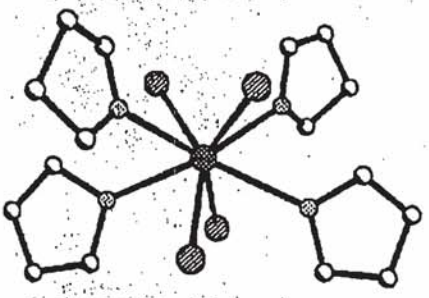

TELEFAX TRANSMITTAL

Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico, 87545

TO: Ruth Weiner
SNL

FROM: Dave Clark
Los Alamos National Lab
MS-G739
Los Alamos, N.M. 87545
FAX: 505 665-4624
Phone:

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3 **Pages total**

Ruth,

enclosed is a two page monthly report for our first month in the WIPP. I included some spectra of Nd(III) with the OPO laser. We'll try to get you some more figures of Pu oxidation states in brine, but we still have electricians in our labs (& in the way!)

Best, Dave

WPO 31106

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WIPP Oxidation State Distribution Monthly Report - July 1995

David L. Clark, C. Drew Tait, Los Alamos

This month we put together rev0 of a test plan for the Oxidation State Distribution and Actinide Redox States projects. This was done in collaboration with Andy Felmy and Dhanpat Rai at the Pacific Northwest Laboratory and in collaboration with SNL. We also completed a draft version of a new QAPJP, and adopted and trained to procedures under the ESM program. Meetings were held with Van Bynum and Ruth Wiener to work out the details of the project, and both Van and Ruth were given tours of the facilities and the new instrumentation.

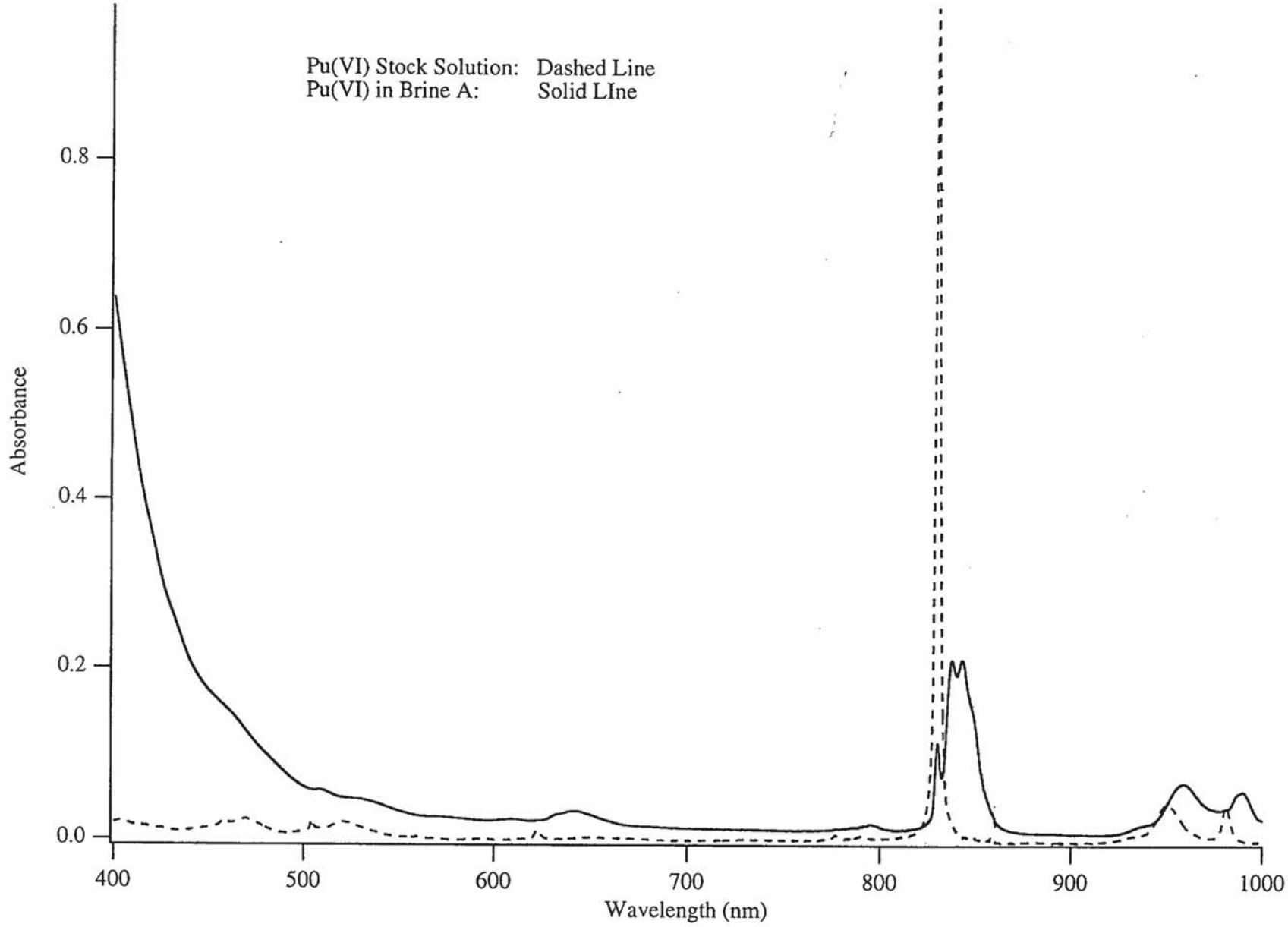
This month we received shipment of the new MOPO laser system for the Photoacoustic Spectrometer. The MOPO laser was installed, and testing for the conversion from a dye laser to the MOPO was initiated. After one week, data acquisition software was modified for the new system, and test spectra were recorded for a standard Nd(III) solution in 0.1M HCl. It was noted that the near infrared frequencies (idler output) of the laser output were not properly excluded, and this gave rise to NIR interference from water absorbances with the test sample. Similar problems with the transition to the MOPO laser have been reported by others. Within one week, careful re-alignment of the system successfully removed all traces of this interference. The absorption spectrum of 0.001M Nd(III) in 0.1M perchloric acid recorded on a conventional UV-VIS-NIR spectrometer is shown in Figure 1. The three characteristic peaks occur at 512, 521, and 573 nm as expected. Figure 2 shows the PAS of 0.0001M Nd(III) in 0.1M HCl in which the interference from the NIR clearly masks the Nd(III) absorption spectrum. After realignment of the system, the interference peaks are removed from the spectrum. This is shown in the PAS in Figure 3 where the characteristic absorption bands and relative intesities of Nd(III) are clearly reproduced at 512, 521, and 573 nm and can be compared to the conventional absorption spectrum shown in Figure 1.

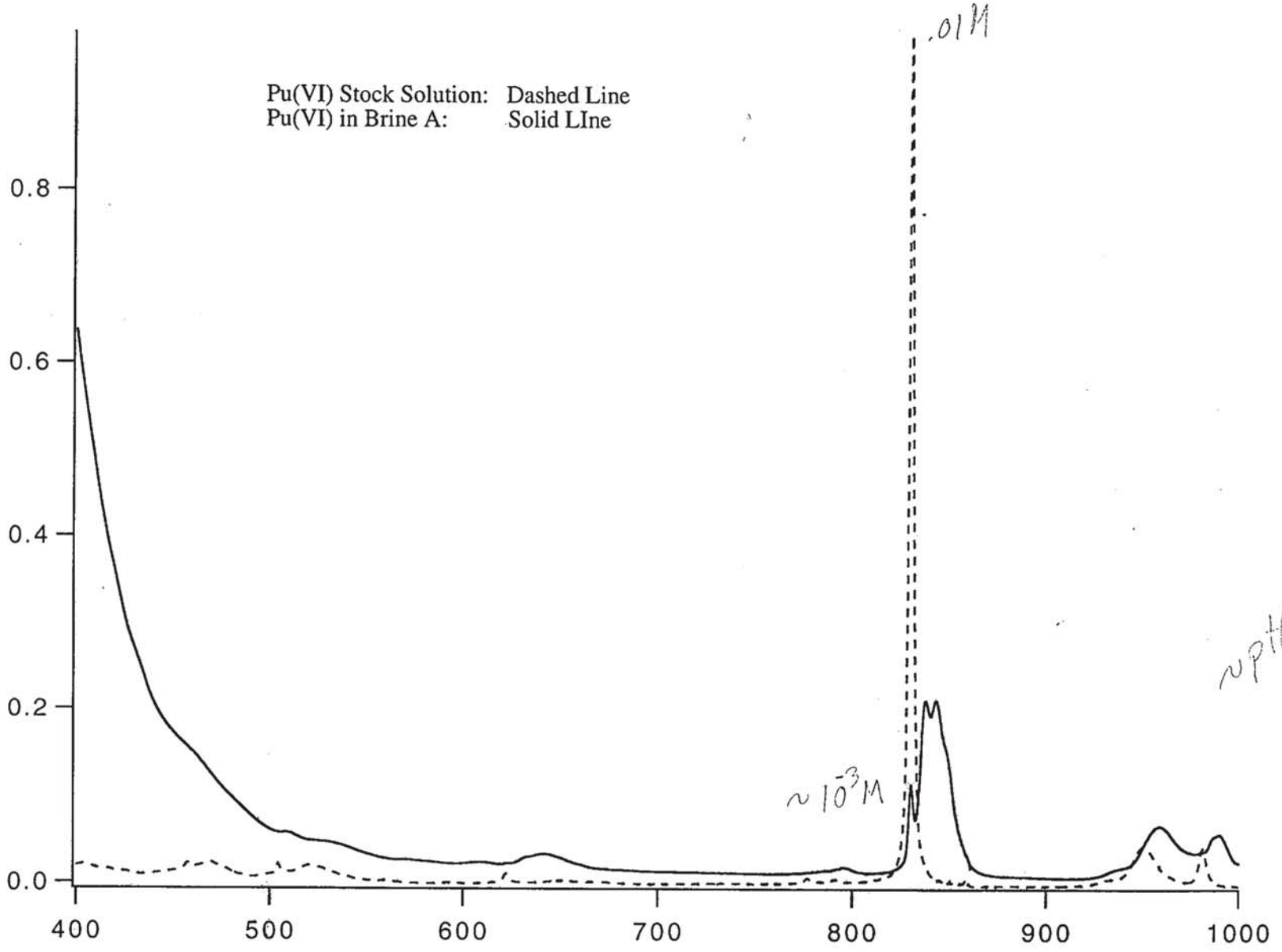
Purification of over 1 gram each of Pu-239 and Pu-242 solutions by anion exchange chromatography were also completed. The electrochemical system for preparation of pure oxidation states was set up, and electrochemical synthesis is expected to commence during the next week. The absorption spectrum of oxidation state pure Pu(IV) was obtained.

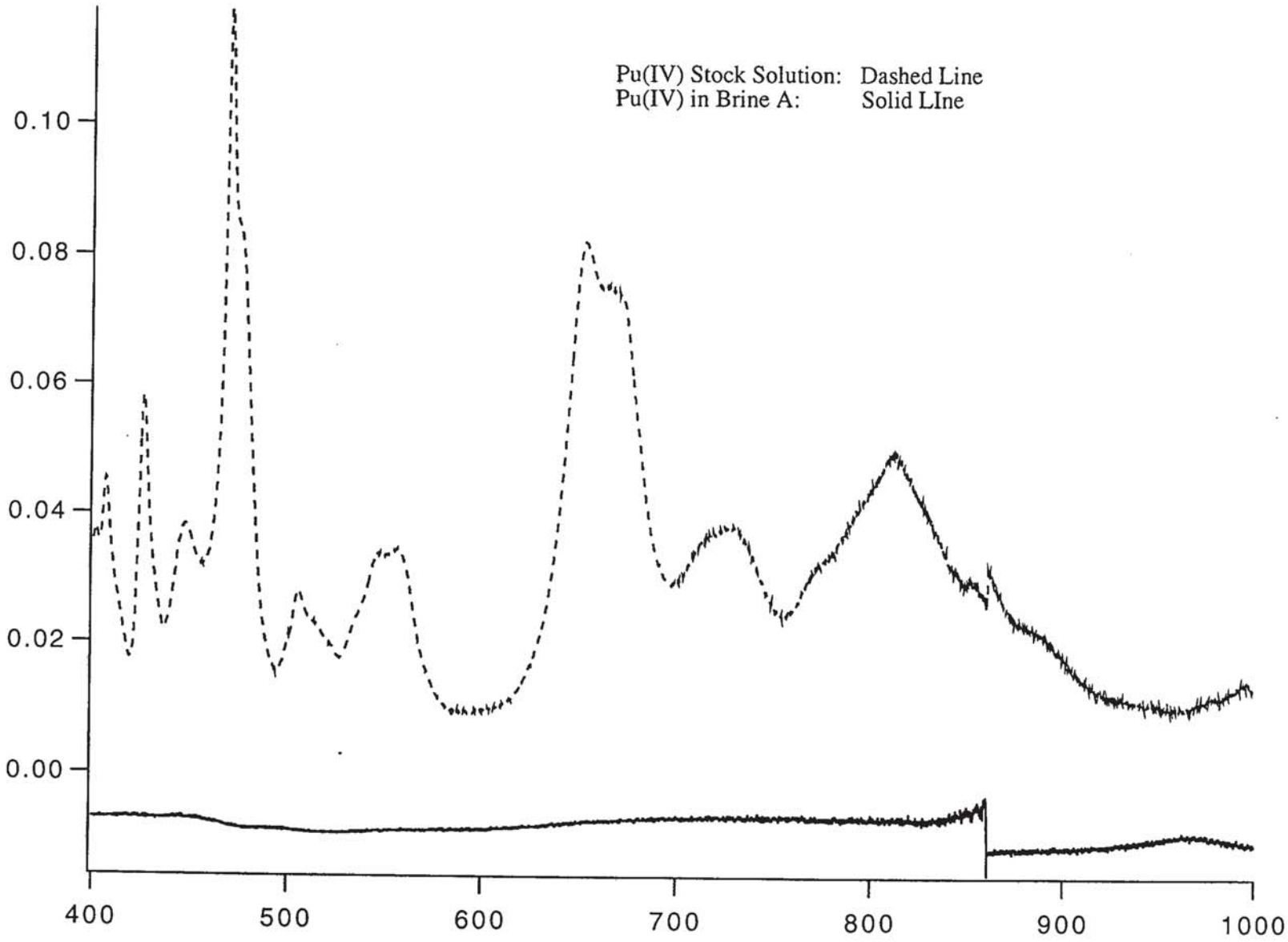
WIPP Oxidation State Distribution Monthly Report - August 1995 - Contract AP-2274

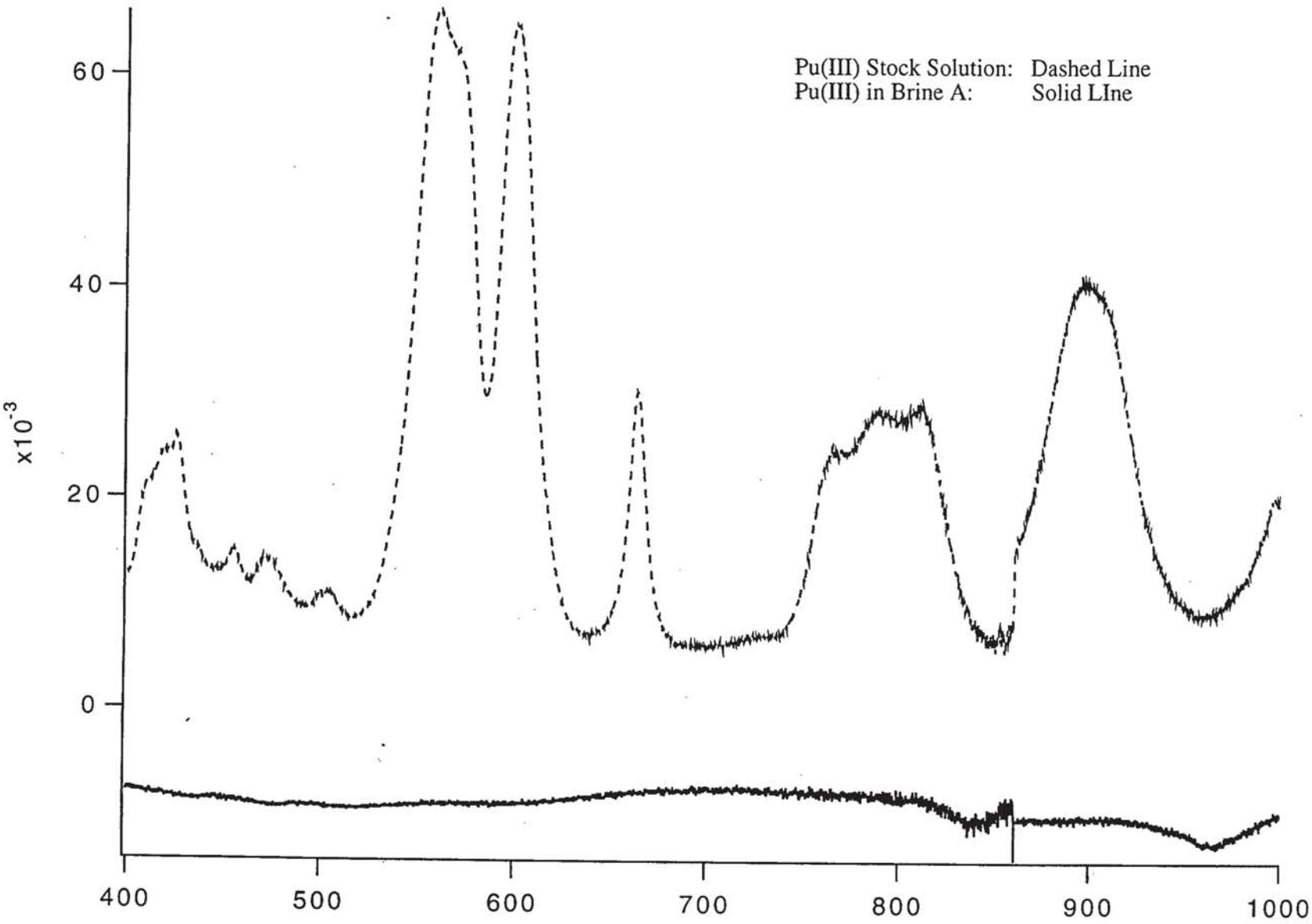
Preparation of oxidation state pure solutions of Pu(III), Pu(IV), Pu(V), and Pu(VI) was completed using electrochemical synthesis, and the oxidation state purity assayed using conventional VIS-NIR spectroscopy. Samples of synthetic Brine A were filtered, and oxidation state pure plutonium solutions were added, and absorption spectra for the different Pu oxidation states in Brine A was recorded. Not surprisingly, solutions of the lower oxidation states Pu(III), Pu(IV), and Pu(V) were relatively insoluble in Brine A, resulting in precipitation. The solids were separated via centrifugation, and the absorption spectra recorded. The plutonium concentration in solution is at the limit of detection using conventional absorption spectroscopy in a 1 cm cell. The pathlength will be changed to 10cm, and the spectra examined again. Finally, the spectra will be recorded using PAS. The Pu(VI) oxidation state was found to be quite soluble in Brine A, and no precipitation was observed. The NIR spectra indicate that very little of the Pu(VI) aquo ion remains, and that complexation, presumably by chloride, is observed as indicated in a shift of the main absorption band.

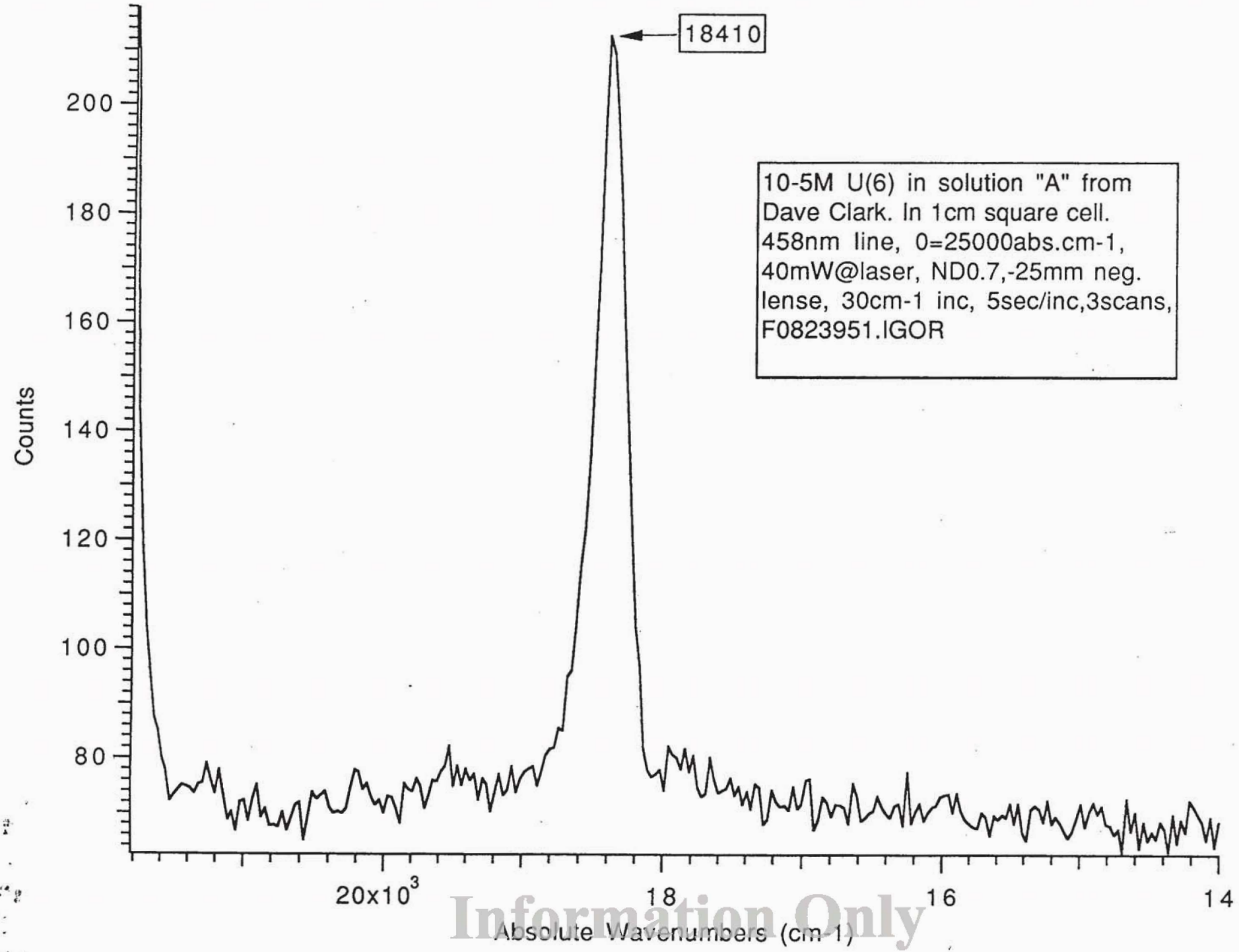
The new OPO laser is working, but we experienced a problem with the Nd:YAG laser. A service representative has been called, and we hope to begin acquisition of PAS spectra soon. The Fluorescence system was set up and tested, and we obtained fluorescence of a 10 micromolar U(VI) sample in Brine A with only 3 scans. We will examine a 10 nanomolar sample, and then proceed to STTP samples which show high uranium concentrations.

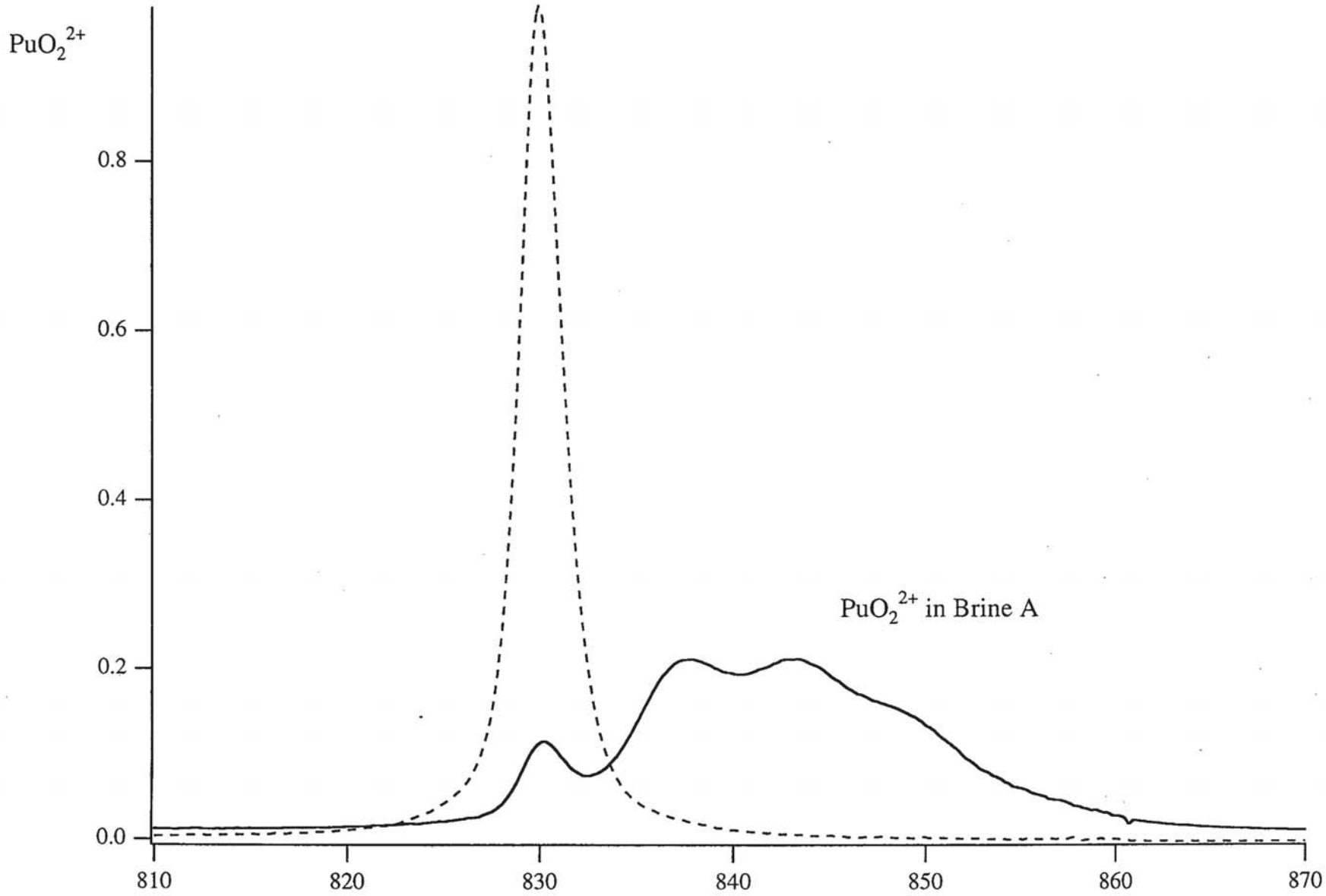












WIPP Oxidation State Distribution Monthly Report - September 1995

This month we initiated and completed the electrochemical synthesis of oxidation state pure stock solutions of Pu(III), Pu(IV), Pu(V), and Pu(VI). These samples were assayed using UV-VIS-NIR spectroscopy to assure that each solution contained a single oxidation state of plutonium. Aliquots of each oxidation state solution were added to a sample of either Brine A or Castile Brine, and the electronic spectrum obtained using conventional UV-VIS-NIR absorption spectroscopy. In general, it was found that Pu(VI) was very soluble in both brine solutions, while lower oxidation states were relatively insoluble. The Pu(VI) spectra in both brine solutions reveal a substantial decrease in the amount of Pu(VI) aquo ion, and absorption maxima due to many new Pu(VI) solution species are observed. An expanded region of the spectrum in the range 810-870 nm is shown in Figure 1.

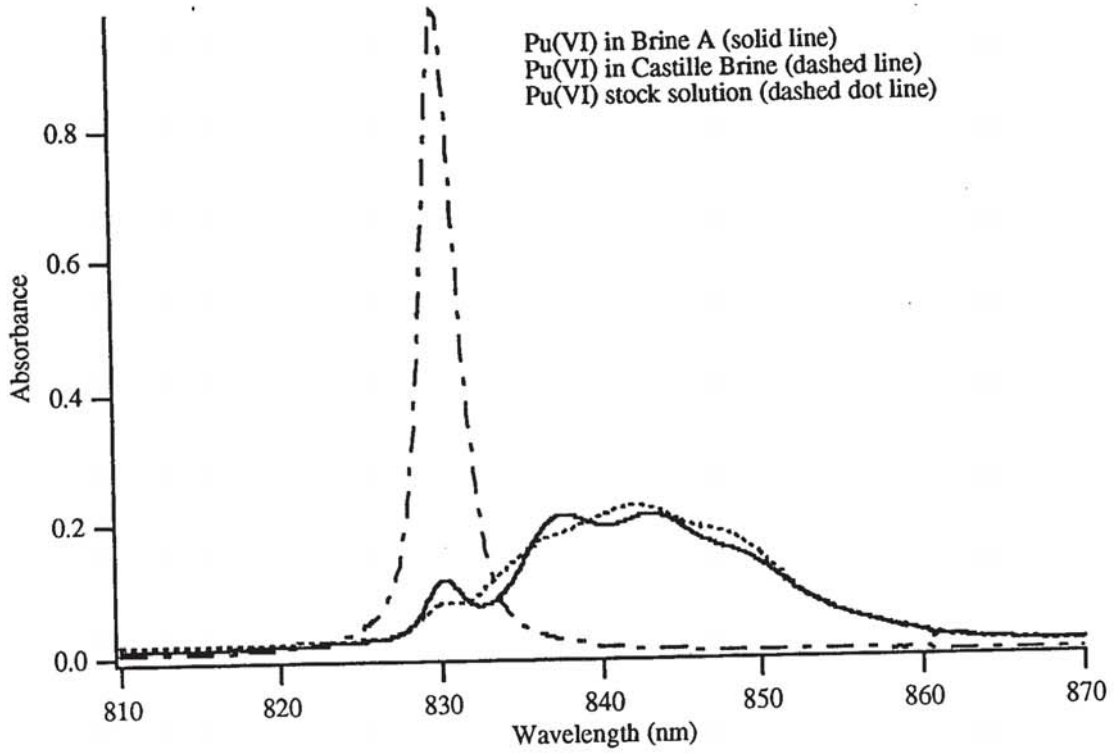


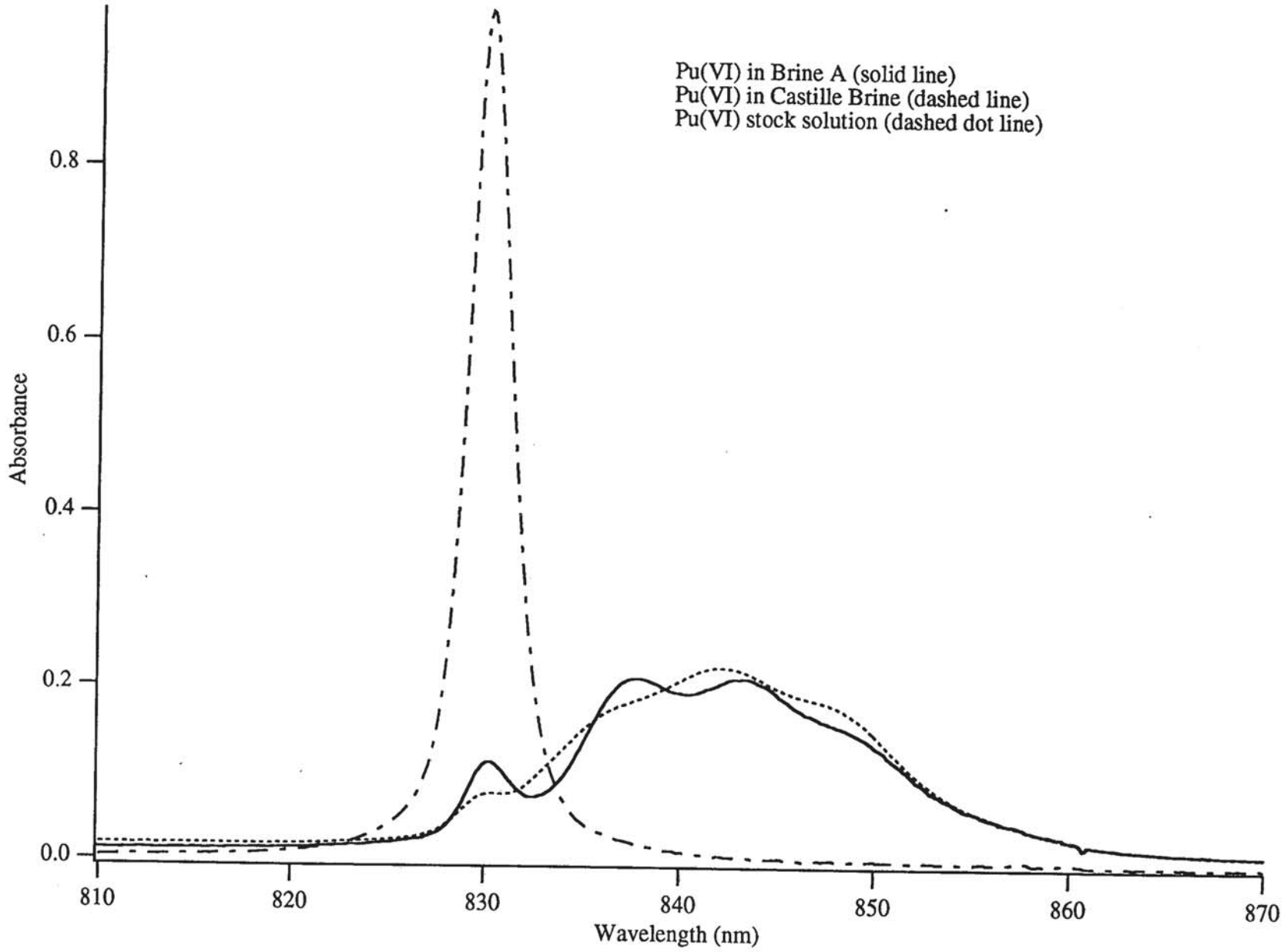
Figure 1.

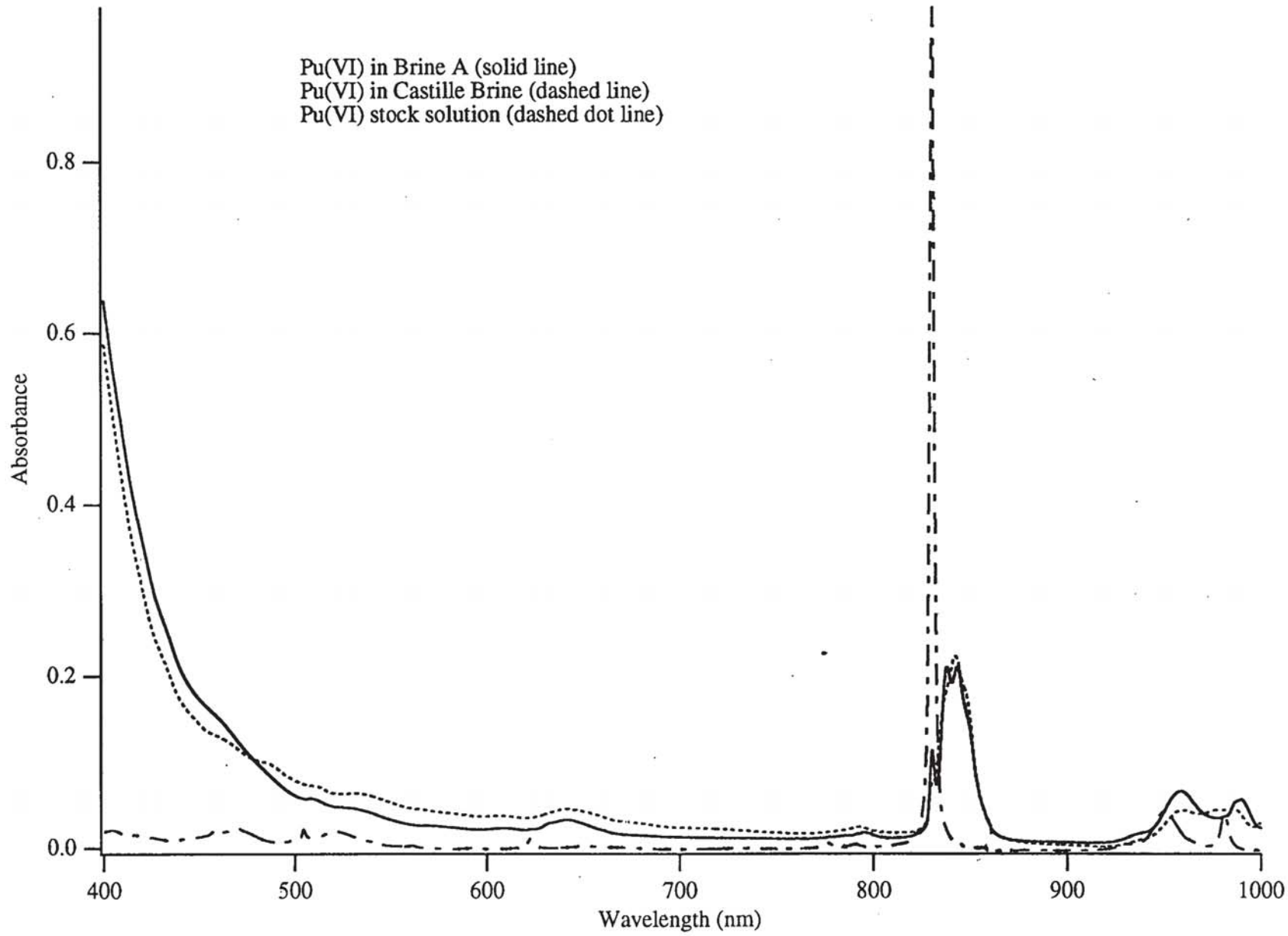
In contrast, when stock solutions of the other Pu oxidation states were added to either Castile or Brine A solutions, precipitation was observed. The precipitate was removed by centrifugation and the absorption spectrum recorded. Spectra were barely observable using conventional UV-VIS-NIR spectroscopy in 1 cm pathlength cells, but characteristic absorption features were observed in 10 cm pathlength cells. Spectra of the lower oxidation states of Pu in both brine solutions will be determined by photoacoustic spectroscopy.

Sample cells for the determination of photoacoustic spectra of STTP samples were discussed and a cell design was agreed upon by the LANL investigators. The sample cell must remain anaerobic conditions during the timeframe of an absorption measurement in order to determine oxidation states in STTP samples. The cell design is based on 14 years of experience using Schlenk techniques for the manipulation of highly air sensitive

materials, including U(III) in nonaqueous solutions. It was decided that a cell design that was effective in the study of U(III) by conventional UV-VIS-NIR spectroscopy would be acceptable for the present work, and cells were ordered. Upon arrival, the LANL glass shop will make the necessary modifications to add stopcocks to turn them into Schlenk cells.

The YAG laser that came with the new MOPO laser system for photoacoustic spectroscopy experienced a factory defect, and the new photoacoustic spectroscopy system could not be operated for several weeks. This laser problem was not associated with the new MOPO laser itself, but with a defective mirror in the YAG laser. The instrument company responded, and following a service call, the instrument is now back up and running in excellent condition.





WIPP Oxidation State Distribution Monthly Report - October 1995

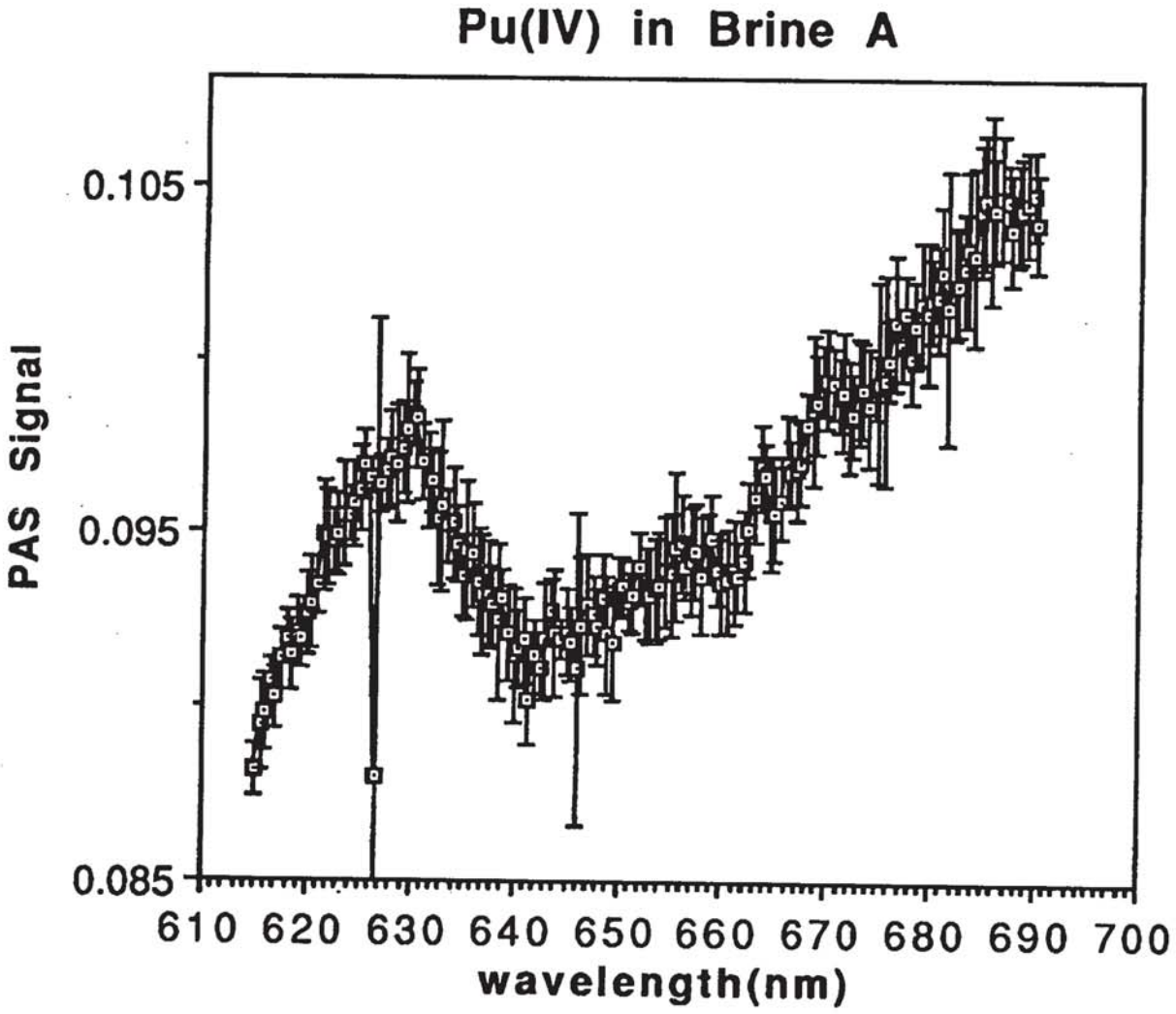
This month we initiated experiments aimed at the reducing properties of various redox agents towards Pu(VI). Iron metal wire was observed to cause reduction as evidenced by the decrease in the Pu(VI) absorbance band in the NIR spectrum. This feature continued to decrease in intensity and ultimately reached what appeared to be a steady concentration as the iron wire became totally encrusted in corrosion. Other reducing agents were ordered.

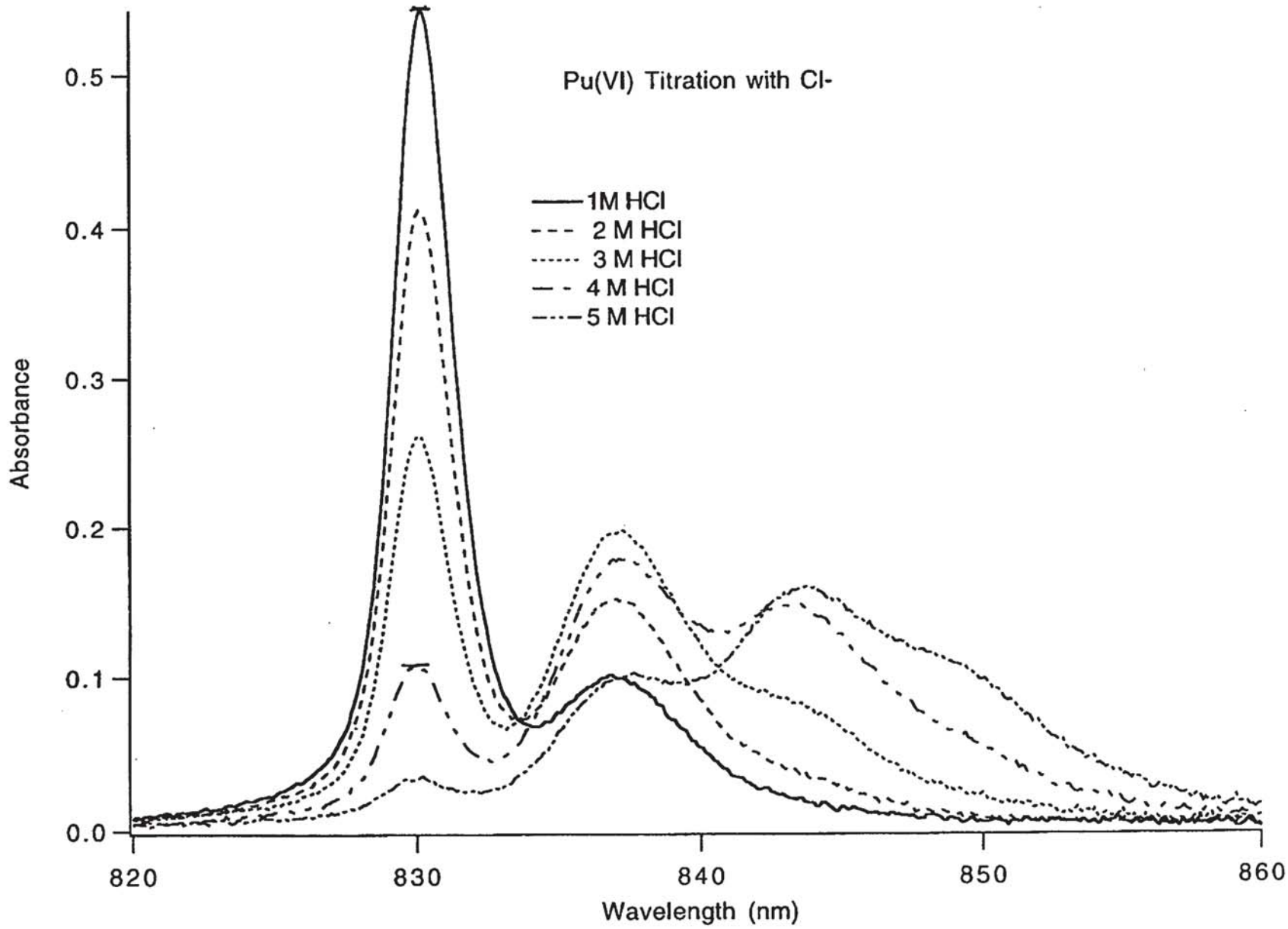
Last month we noted that when stock solutions of Pu in oxidation states lower than hexavalent were added to either Castile or Brine A solutions, precipitation was observed. The precipitate was removed by centrifugation and the absorption spectrum recorded. Spectra were barely observable using conventional UV-VIS-NIR spectroscopy in 1 cm pathlength cells, but characteristic absorption features were observed in 10 cm pathlength cells. This month we examined the spectrum of a solution that was originally Pu(IV) in Brine using photoacoustic spectroscopy. This spectrum is attached. We are now examining this spectrum in the more characteristic region between 460-500 nm.

Sample cells for the determination of photoacoustic spectra of STTP samples were ordered. Cells with a 1cm pathlength arrived near the end of the month, while the 2 cm pathlength cells are still being manufactured. Upon arrival, the LANL glass shop will make the necessary modifications to add stopcocks to turn them into Schlenk cells. We anticipate beginning of spiking experiments as soon as these cells are readied.

The Pu(VI) spectra recorded in brine showed interesting absorpiton features that were interpreted as new Pu(VI) chloride species. To be sure that this interpretation was correct, a titration of Pu(VI) with chloride ion was performed, and the resulting spectra are shown as an attachment.

Post-It™ brand fax transmittal memo 7671	# of pages ▸ 3
To Roth Weiner	From D. L. Clark
Co.	Co.
Dept.	Phone #
Fax # 505 848 0811	Fax #





From: David L. Clark <101159@incdp3.lanl.gov>
To: Ruth F. Weiner <rfweine@nwer.sandia.gov>
Date: 12/12/95 1:45pm
Subject: Re: Milestone

Ruth,

Sorry for the tardiness in this monthly report. Drew and I really appreciate all the work you've done at SNL to help cover for us during times of extreme stress!!! We put the following monthly together from memory, so I apologize that I can't give you some really nice spectra to show your colleagues this time. I will get copies of these to you as soon as I get back on Friday.

Here is the monthly report.

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WIPP Monthly Report for November 1995.

This month, efforts focused on PAS measurements of actual STTP samples. Two STTP samples were examined using our new cells. The first PAS measurement on actual waste was determined on an archived sample that showed high Pu solubility in the presence of cement. The conventional absorption spectrum was obtained, which provided very little information. However, the PAS established that a small absorption feature did occur in the Pu(IV) region, but the intensity could not account for the quantity of Pu in solution. Comparison to spiking experiments in which Pu(IV) was added to brine solutions showed small spectral features identified as Pu(IV) radiocolloid. Scanning through the Pu(V) region revealed a very strong absorption feature in the Pu(V) region near 560 nm. This spectrum revealed excellent signal-to-noise and established that high quality PAS measurements can in fact be obtained with our OPO laser system on actual waste. Another STTP sample was chosen for PAS analysis. This sample also showed high Pu solubility, and was taken from an STTP container that contained organic chelators. This sample showed a very strong PAS signal and a strong absorbance band near 485 nm characteristic of Pu(IV). While this is still preliminary data, the present observations appear consistent with expectations. In the presence of organic chelators, we observe Pu(V) and chelated Pu(IV) , while in the absence of chelators, we observe Pu(V) and some Pu(IV) radiocolloid. These samples will continue to be monitored with time to examine how the oxidation state distribution changes, as well as be the basis for further Pu spiking experiments with known oxidation states to quantify the amounts of the various oxidation states of Pu present in STTP.

During spiking experiments, we observed that Pu(VI) showed high solubility in brine. Additional experimentation showed that chloride complexes were formed under the conditions of the brine. Reducing agents, Fe(0) and Fe(II) were added to the Pu(VI) solutions, and some reduction to Pu(V) was observed, but experiments are ongoing.

We spent a good deal of effort on QA activities this month. Many hours were spent in meetings, revising QA plans, and responding to QA questions. The time spent on these activities has pushedback some spiking experiments.
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