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Distribution of Actinides between the Aqueous and Organic Phases in the TALSPEAK Process

Fuel Cycle Research & Development

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SUMMARY

One objective of the US Department of Energy's Office of Nuclear Energy (DOE-NE) is the development of sustainable nuclear fuel cycles which improve uranium resource utilization, maximize energy generation, minimize waste generation, improve safety, and complement institutional measures limiting proliferation risks.[1] Activities in progress which support this objective include the development of advanced separation technologies to recover the actinides from used nuclear fuels. With the increased interest in the development of technology to allow closure of the nuclear fuel cycle, the TALSPEAK process is being considered for the separation of Am and Cm from the lanthanide fission products in a next generation reprocessing plant. However, at this time, the level of understanding associated with the chemistry and the control of the process variables is not acceptable for deployment of the process on an industrial scale. To address this issue, DOE-NE is supporting basic scientific studies focused on the TALSPEAK process through its Fuel Cycle Research and Development (R&D) program. One aspect of these studies is an experimental program at the Savannah River National Laboratory (SRNL) in which temperature-dependent distribution coefficients for the extraction of actinide elements in the TALSPEAK process were measured. The data were subsequently used to calculate conditional enthalpies and entropies of extraction by van't Hoff analysis to better understand the thermodynamic driving forces for the TALSPEAK process.

In the SRNL studies, the distribution of Pu(III) in the TALSPEAK process was of particular interest. A small amount of Pu(III) would be present in the feed due to process losses and valence adjustment in prior recovery operations. Actinide elements such as Np and Pu have multiple stable oxidation states in aqueous solutions; therefore the oxidation state for these elements must be controlled in the TALSPEAK process, as the extraction chemistry is dependent upon the actinide's valence. Since our plans included the measurement of Pu(III) distribution coefficients using a Np(V) solution containing small amounts of ^{238}Pu, it was necessary to demonstrate that the desired oxidation states of Np and Pu are produced and could be stabilized in a buffered lactate solution containing diethylenetriaminepentaacetic (DTPA). The stability of Np(V) and Pu(III) in lactic acid/DTPA solutions was evaluated by ultraviolet-visible (UV-vis) spectroscopy. To perform the evaluation, Np and Pu were added to solutions containing either hydroxylamine nitrate (HAN) or ferrous sulfamate (FS) as the reductant and nominally 1.5 M lactic acid/0.05 M DTPA. The pH of the solution was subsequently adjusted to nominally 2.8 as would be performed in the TALSPEAK process.

In the valence adjustment study, we found that it was necessary to reduce Pu to Pu(III) prior to combining with the lactic acid and DTPA. The Pu reduction was performed using either HAN or FS. When FS was used, Np was reduced to Np(IV). The spectroscopic studies showed that Np(V) and Pu(III) are not stable in lactic acid/DTPA solutions. The stability of Np(IV)- and Pu(IV)-DTPA complexes are much greater than the stability of the Np(V)- and Pu(III)-DTPA complexes, and as a result, Np is slowly reduced to Np(IV) and Pu is slowly oxidized to Pu(IV) due to the reduced activity of the more stable complexes. When Np(V) was added to a solution containing a 1.5 M lactic acid/ammonium lactate buffer and 0.05 M DTPA, approximately 50% of the Np was reduced to Np(IV) in the first day. The fraction of Np(V) in the solution continued to diminish with time and was essentially reduced to Np(IV) after one week. When Pu(III) was added to a lactic acid/DTPA solution of the same composition, the spectrum recorded following at least two days after preparation of the solution continued to show some sign of Pu(III). The Pu(III) was completely oxidized to Pu(IV) after 3-4 days.

The UV-vis spectroscopy demonstrated that Np(V) and Pu(III) were the predominate valences in the lactic acid/DTPA solution for the better part of a day following solution preparation. Based on these results, we chose to initially add HAN to the actinide tracer solution prepared for the distribution coefficient measurements (to produce Pu(III)) prior to combining with lactic acid and DTPA. The distribution coefficient measurements were expected to be complete in 2-3 h; therefore, Np(V) and Pu(III)

valences would predominate in the solution during this time. Prior to adding the HAN to the actinide tracers, we added sufficient Am(III) activity to allow the measurement of distribution coefficients during the extraction experiments. Protactinium (V) distribution coefficients were also measured using the activity which was in secular equilibrium with the ^{237}Np. The actinide distribution coefficients were measured at pH 2.8 and 3.5 and covered a range of temperatures from nominally 20 to 60 °C.

The actinide distribution coefficient measurements showed that Np(V) and Pa(V) were more strongly extracted into the bis-(2-ethylhexyl)phosphoric acid (HDEHP) solvent than Pu(III) and Am(III). The increased extraction of the Np and Pa was due to the increased stability of the Pu(III)- and Am(III)-DTPA complexes compared to the stability of the Np(V)- and Pa(V)-DTPA complexes. The stability of the 3+ complexes prevents the extraction of the Pu and Am into the solvent to a greater extent. The actinide distribution coefficients decreased with decreasing pH and increasing temperature. The decrease in the distribution coefficients with pH is due to the protonation of the HDEHP solvent which reduces the number of available complexation (i.e., ion exchange) sites. The decrease in the distribution coefficients with temperature is due to the exothermic nature of the extraction process. At pH 3.5, the conditional enthalpies of extraction were approximately -10 kJ/mole for Pu(III) and Am(III), -40 kJ/mol for Np(V), and -48 kJ/mol for Pa(V). The entropies of extraction were negative which results in more positive free energies of extraction as the temperature increases. The uncertainties associated with the majority of the conditional thermodynamic properties varied between approximately 10 and 50%. The nonlinearity in the data was attributed to changes in the enthalpy of extraction over the temperature range; although, the instability of Np(V) and Pu(III) likely contributed to the variance.

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ACRONYMS

$A_{An,a}$ – activity of an actinide element in the aqueous phase
$A_{An,o}$ – activity of an actinide element in the organic phase
(aq) – aqueous phase
C_{Am} – concentration of Am
C_{DTPA} – concentration of DTPA
C_{LA} – concentration of lactic acid
C_{Np} – concentration of Np
C_{Pa} – concentration of Pa
C_{Pu} – concentration of Pu
$D_{Am,o/a}$ – Am distribution coefficient
$D_{An,o/a}$ – actinide distribution coefficient
$D_{Np,o/a}$ – Np distribution coefficient
$D_{Pa,o/a}$ – Pa distribution coefficient
$D_{Pu,o/a}$ – Pu distribution coefficient
dpm – disintegrations per minute
DTPA – diethylenetriaminepentaacetic
DIAMEX – diamide extraction
EDTA – ethylenediaminetetraacetic acid
FS – ferrous sulfamate
GPHA – gamma pulse height analysis
HDEHP (or HA) – bis-(2-ethylhexyl)phosphoric acid
HAN – hydroxylamine nitrate
log(K) – common logarithm of equilibrium constant
N/A – not available
(or) – organic phase
R – ideal gas constant
R&D – research and development
RPM – revolutions per minute
SRNL – Savannah River National Laboratory
SRS – Savannah River Site
TALSPEAK – Trivalent Actinide Lanthanide Separation with Phosphorous-reagent Extraction from Aqueous Komplexes
TRPO – trialkylphosphine oxide
TRUEX – transuranic extraction
UV-vis – ultraviolet-visible
Δc_p – change in heat capacity
ΔG^0 – standard free energy of extraction
ΔH^0 – standard enthalpy of extraction
ΔS^0 – standard entropy of extraction

SEPARATIONS CAMPAIGN

DISTRIBUTION OF ACTINIDES BETWEEN THE AQUEOUS AND ORGANIC PHASES IN THE TALSPEAK PROCESS

INTRODUCTION

Background

Used reactor fuels are currently reprocessed in multiple countries using the PUREX process [2] to recover the U and Pu for future use. However, the small amounts of Np, Am, and Cm (minor actinides) produced during fuel irradiation are not recovered and are currently discarded with the fission products as high level waste. If desired, Np produced in irradiated fuels can be recovered by making slight modifications to the PUREX process to control the Np valence and extraction into the tributyl phosphate solvent.[3,4] For complete closure of the nuclear fuel cycle, the Am and Cm isotopes produced during fuel irradiation must also be recovered. The isolation and purification of the minor actinides would allow additional energy production following fabrication of fuels or targets for advanced reactors using these materials. The elimination of essentially all of the actinide materials from the high level waste generated during fuel reprocessing would also improve the performance of a geologic repository by removing radiotoxic, long-lived transuranic isotopes from the waste and reducing the heat generated by radioactive decay.

An efficient separation process which recovers Am and Cm during the reprocessing of nuclear reactor fuels has not been demonstrated on an industrial scale. One of the issues with the recovery of Am and Cm in a single process is the similarity of the chemistry of the lanthanide fission products. Solvent extraction processes have been developed which allow the separation of Am, Cm, and the lanthanide elements from other waste components using extractants such as malonamids (the DIAMEX process) or phosphine oxides (the TRUEX or TRPO processes).[5] The subsequent separation of the Am and Cm from the lanthanide fission products requires a separate process. In 1964, Weaver and Kappelmann [6] reported the development of a process to separate transplutonium elements from the lanthanides by preferentially extracting the lanthanides from an aqueous solution containing lactic acid and the sodium salt of DTPA into HDEHP. The process was titled TALSPEAK for Trivalent Actinide Lanthanide Separation with Phosphorous-reagent Extraction from Aqueous Komplexes. Under optimal conditions for the TALSPEAK process, Nd was the least extractable of the lanthanides and Cf was the most extractable of the transplutonium elements. The process can also be performed in a reverse mode in which the transplutonium elements and the lanthanide fission products are extracted into the HDEHP solvent and the transplutonium elements are stripped using a solution containing lactic acid and DTPA.

With the increased interest in the development of technology to allow closure of the nuclear fuel cycle, the TALSPEAK process is being considered for the separation of Am and Cm from the lanthanide fission products in a next generation reprocessing plant. However, at this time, the level of understanding associated with the chemistry and the control of the process variables is not acceptable for deployment of the process on an industrial scale. One issue of concern is the lack of understanding associated with the thermodynamic and kinetic driving forces of the separation. To address this issue, DOE-NE is supporting basic scientific studies focused on the TALSPEAK process through its Fuel Cycle R&D program. One element of these studies is the measurement of actinide distribution coefficients in the TALSPEAK process as a function of temperature so thermodynamic properties can be calculated using the van't Hoff equation.[7] Of particular concern, is the distribution of Pu(III) between the aqueous and organic phases. A small amount of Pu and Np would be present in the feed to the TALSPEAK process due to process losses from prior recovery operations. If the TRUEX process is used to separate the lanthanide fission products and the transuranic elements from other fission products, the Pu and Np oxidation states must be adjusted to Pu(III) and Np(IV) for efficient extraction.[8] The actinide elements are stripped from the TRUEX solvent using a buffered lactate solution containing DTPA at approximately pH 5. Following the adjustment of the solution pH (to 2.8), the product from the TRUEX process becomes the feed to the TALSPEAK process.[9]

Objectives

To better understand the thermodynamic driving force for the extraction of transuranic elements in the TALSPEAK process, a series of experiments was performed to measure the distribution of Np(V), Pu(III), Am(III), and Pa(V) between the aqueous and organic phases as a function of temperature. The van’t Hoff equation was then used to calculate the conditional enthalpies and entropies of extraction. The thermodynamic properties were considered conditional, since they were based on the variation of distribution coefficients as a function of temperature, rather than the extraction equilibrium constant.[5] Prior to measuring the actinide distribution coefficients it was necessary to demonstrate the stability of Pu(III) in a buffered lactate solution containing DTPA. Plutonium (III) was prepared using both HAN and FS as reductants. Ultraviolet-visible spectroscopy was used to determine the valence of both Np and Pu over time during the stability experiments. The experimental methods used to perform the distribution coefficient measurements and stability experiments and a discussion of the results are presented in the following sections.

EXPERIMENTAL

Valence Adjustment Study

Actinide elements such as Np and Pu have multiple stable oxidation states in aqueous solutions; therefore, the oxidation state for these elements must be controlled in the TALSPEAK process, as the extraction chemistry is dependent upon the actinide's valence. Since our plans included the measurement of Pu(III) distribution coefficients using a Np(V) solution containing small amounts of ^{238}Pu, it was necessary to demonstrate that the desired oxidation states of Np and Pu are produced and could be stabilized in a buffered lactate solution containing DTPA. To accomplish this task, Np and Pu were added to solutions containing either HAN or FS as the reductant and nominally 1.5 M lactic acid/0.05 M DTPA. The pH of the solution was subsequently adjusted to nominally 2.8, consistent with the TALSPEAK process operating conditions. The predominant valences of the actinides were then determined by UV-vis spectroscopy. The details of the experimental procedures are discussed in the following sections.

Nuclear Materials

The Np and Pu solutions used for the valence adjustment studies were initially purified by anion exchange. A characterization of each solution is provided in Table 1.

Table 1 Actinide stock solution concentrations

Element	Concentration		HNO_3
	g/L	dpm/mL	(M)
Np	32.0	5.00E+07	1.5
Pu	45.3	6.65E+09	1.0

The Np and Pu solutions used in the study were more concentrated than the solution used to measure distribution coefficients to ensure that the spectrometer sensitivity was sufficient to obtain representative spectra. The Pu used in the study was weapons grade (i.e., nominally 94% ^{239}Pu and 6% ^{240}Pu).

Solution Preparation

Since UV-vis spectra of Np and Pu in buffered lactate solutions containing DTPA were not available as references, the spectrum of four actinide-containing solutions were initially recorded with increasing complexity to understand the changes in the spectra due to each component. The four solutions included: (1) 0.1 M HNO_3, (2) 1.5 M lactic acid, (3) 1.5 lactic acid/0.05 M DTPA, and (4) 1.5 M lactic acid/0.05 M DTPA/0.1 M HAN. Four solution containing nominally 3 g/L Np and four solutions containing nominally 4 g/L Pu were prepared. The Np and Pu concentrations were held constant by adding 1 mL of the actinide-containing solution to 10 mL of the four solutions.

Since we planned to adjust the pH of the actinide solutions to 2.8 prior to measuring the distribution coefficients, the pH of the buffered solutions was also adjusted to the same value using 3.9 M NH_4OH prior to recording the spectrum. To estimate the volume of NH_4OH required to adjust the pH to the desired value following the addition of 1 mL of the Np solution (containing 1.5 M HNO_3) or 1 mL of the Pu solution (containing 1.0 M HNO_3), a 1.5 M lactic acid solution containing 0.05 M DTPA was prepared to simulate the adjustments. When 1 mL additions of 1.5 and 1.0 M HNO_3 were added to 10 mL aliquots of a 1.5 M lactic acid/0.05 M DTPA solution, the volumes of 3.9 M NH_4OH required to adjust the pH back to 2.8 were 0.2 and 0.3 mL, respectively. Dilution of the lactic acid and DTPA due to the addition of the actinide solution and the subsequent adjustment of the pH were taken into account during the preparation of the solutions. The preparation of the four solutions including the pH adjustments is described in Appendix A.

The UV-vis spectra were recorded using a Zeiss diode array spectrometer controlled by a Windows NT-based computer. We used a 1 cm path length cuvette holder with 1 cm disposable cuvettes inside a radiological glovebox. The cuvette holder was connected to the spectrometer using fiber optic cables. A detailed list of the spectrometer components is provided below.

- Spectrometer: Diode array spectrometer based on the Zeiss MCS module (190-1024 nm range, approximately 0.8 nm/pixel); interfaced to computer through Hamamatsu C4070 driver/amplifier board; power supply – Condor D.C. Power Supplies model MTLL-5W-A.
- Fiber optic cable: Ceramoptec or Polymicro, IR grade, 400 micron low-OH core with SMA fittings on each end.
- Computer: Texas Micro industrial PC, IPC-6806P.233MHz , Windows NT.
- Data acquisition card: National Instruments AT-AI-16XE-10 Multiple I/O Board (16-bit resolution, 16 analog and 8 digital inputs).
- Light source: Ocean Optics Tungsten Halogen Lamp Housing, LS-1.
- Variable attenuator: Oz Optics Part # BB-200-55-300 600-SP to adjust light levels.
- Cuvette block: SRNL fabricated plexiglass cuvette holders with two lenses.

During the preparation of solution (4), the required volume of HAN was combined with the lactic acid/DTPA solution prior to the addition of the Np or Pu. When the Pu was added to the solution, we did not observe a color change. Solutions containing Pu(III) are blue when viewed by reflected light.[10] When the spectra of the solutions which contained Pu in 1.5 M lactic acid/0.05 M DTPA and 1.5 M lactic acid/0.05 M DTPA/0.1 M HAN were compared, they were essentially the same which indicated that the HAN had not reduced the Pu (see the Results and Discussion section for more detail). Since the Pu was not reduced by HAN in the buffered lactate solution containing DTPA, we chose to prepare solutions in which either HAN or FS was added to the Np and Pu solutions prior to combining with the lactic acid and DTPA. Both HAN and FS will reduce Pu(IV) to Pu(III) and FS will reduce Np(V) to Np(IV).[11-12] The four solutions prepared for study included: (1a) Np + HAN added to 1.5 M lactic acid/0.05 M DTPA, (2a) Pu + HAN added to 1.5 M lactic acid/0.05M DTPA, (3a) Np + FS added to 1.5 M lactic acid/0.05 M DTPA, and (4a) Pu + FS added to 1.5 M lactic acid/0.05 M DTPA. Prior to recording the UV-vis spectrum of each solution, the pH was adjusted to nominally 2.8. The preparation of the four solutions including the pH adjustments is described in Appendix A. The spectrum of the four solutions was recorded within 90 min of preparation and after nominally 1, 2, 3, 7, and 8 days.

Distribution Coefficient Measurements

The distribution of Np(V), Pu(III), Am(III), and Pa(V) between 1 M HDEHP (in dodecane) and an aqueous phase containing a 1.5 M lactic acid/ammonium lactate buffer and 0.05 M DTPA was measured as a function of temperature. The experimental methods used to perform this work are described below.

Nuclear Materials

The actinide distribution coefficient measurements were made using dilute solutions of the nuclear materials. To achieve good counting statistics, the desired range of activities for the Np, Pu, and Am were 10^5-10^6, 10^8-10^9, and 10^4-10^5 dpm/mL, respectively. The Pa distribution coefficients were measured using the activity (10^5-10^6 dpm/mL) which was in secular equilibrium with the ^{237}Np. The Np used for the measurements was initially purified by anion exchange. Since the Np was previously used to produce ^{238}Pu oxide, the alpha activity of the solution was primarily from this isotope. The characterization of the Np/Pu stock solution used to provide the actinide tracers is shown in Table 2.

Table 2 Np/Pu stock solution concentrations

Np		Pu		Nitric Acid
(M)	(dpm/mL)	(M)	(dpm/mL)	(M)
1.35×10^{-1}	4.98×10^{7}	4.88×10^{-4}	4.42×10^{9}	1.5

The ^{241}Am used for the distribution coefficient measurements was initially purified using a chromatographic resin. A stock solution was prepared by diluting a 0.1 mL aliquot of a 1.30×10^9 dpm/mL solution with 10 mL of 0.1 M HNO_3. The final Am and HNO_3 concentrations were 1.28×10^7 dmp/mL (6.98×10^{-6} M) and 0.11 M, respectively.

Solvent Preparation

The organic phase used for all distribution coefficient measurements was 1 M HDEHP. The desired concentration of HDEHP was prepared by diluting with dodecane. To prepare the solution, the target mass of HDEHP was transferred to a volumetric flask which was diluted to volume with dodecane.

Extraction Experiments

The aqueous phase used for the actinide distribution coefficient measurements was prepared by initially adding a 250 µL aliquot of the Am stock solution to 1 mL of the Np/Pu stock solution. A 100 µL aliquot of 1.77 M HAN was subsequently added to reduce the Pu to Pu(III). The combined solutions were swirled to ensure that the HAN and the actinides were well mixed. No color change was observed due to the dilute concentration of the Pu. The actinide solution was then combined with an 11.4 mL aliquot of a 1.9 M lactic acid/0.06 M DTPA solution. All transfers of solution were performed using calibrated pipettes with precisions and accuracies typically < 1%. Following the combination of the solutions, the pH was adjusted to either 2.8 or 3.5 by the addition of 3.9 M NH_4OH. The pH of the solution was measured using an Accumet® Basic AB15 pH meter which was calibrated using pH 1, 3, and 6 buffer solutions. The preparation of the lactic acid/DTPA solution and calculations summarizing the final composition of the aqueous phase used in the TALSPEAK extractions are presented in Appendix A.

The actinide distribution coefficients were measured as a function of pH and temperature. The temperatures were selected to bracket the potential operating range. The conditions for each series of measurements are summarized in Table 3.

Table 3 Conditions for distribution coefficient measurements

Experiment	pH	Temperature (°C)
TAL-1	2.8	20.0
TAL-2	2.8	59.0
TAL-3	3.5	20.0
TAL-4	3.5	59.5
TAL-5	3.5	40.0

To perform a series of extractions, 2 mL of the aqueous phase (containing the actinide elements in the 1.5 M lactic acid/ammonium lactate buffer and 0.05 M DTPA) were combined with 2 mL of the HDEHP solvent. This organic to aqueous ratio was used for all extractions. Two milliliters of the aqueous and organic phases were added to six, 15 mL centrifuge tubes. The centrifuge tubes were capped and placed in a Eppendorf Thermomixer R, heating/cooling block to maintain the extraction temperature at the desired value. The heating/cooling block also provided agitation at a maximum of 750 RPM. Once the extraction temperature was reached, the aqueous and organic phases were mixed for 1 h. Since the intensity of the mixing was not sufficient to form an emulsion at the conical end of the centrifuge tubes, each tube was removed from heating/cooling block and manual mixed by shaking the tube. Manual mixing was performed at 15, 30, and 45 min into the extraction period. Once the extraction period was complete, the phases were allowed to equilibrate at temperature for 1 h. At the beginning of the equilibration period, a cap was removed from one of the centrifuge tubes to allow insertion of a calibrated thermometer. The extraction temperatures given in Table 3 were recorded using this thermometer.

To ensure that the extraction temperature remained constant during sampling, a procedure was developed to remove a sample of the organic and aqueous phases using a disposable transfer pipette without removing the centrifuge tube from the heating/cooling block. The procedure involved premarking pipettes at a height which placed the tip at the middle of the organic phase when the mark was even with the top of the centrifuge tube. This procedure allowed the removal of an approximate 1 mL sample of the organic phase. To remove a sample of the aqueous phase, the pipette bulb was compressed and inserted into the centrifuge tube until the tip touched the bottom. An approximate 1 mL sample of the aqueous phase was then removed from the bottom of the tube by releasing the bulb. The Np, Pu, Am, and Pa activities in the aqueous and organic phases were measured by Gamma Pulse Height Analysis (GPHA).

RESULTS AND DISCUSSION

Valence Adjustment Study

The UV-vis spectra of Np and Pu in buffered lactate solutions containing DTPA were not available as references; therefore, spectra were initially recorded with increasing solution complexity to understand the changes in the spectra due to the addition of the lactate buffer, DTPA, and HAN. Reference spectra for Np and Pu are provided in Figures 1 and 2, respectively. The solutions for which spectra were recorded included each actinide in solutions containing (1) 0.1 M HNO_3, (2) 1.5 M lactic acid, (3) 1.5 M lactic acid/0.05 M DTPA, and (4) 1.5 M lactic acid/0.05 M DTPA/0.1 M HAN.

Np Reference Spectra

The UV-vis spectrum of Np in 0.1 M HNO_3 (Figure 1) showed that essentially all of the Np was initially present as Np(V). Characteristic Np(V) peaks at 615 and 980 nm were observed. The UV-vis spectra of Np(IV) solutions also have a characteristic peak between 960 and 980 nm (depending upon the HNO_3 concentration); however, we attribute the peak in this spectrum to Np(V) due to the absence of the characteristic Np(IV) peak at 700 nm. When the 0.1 M HNO_3 was replaced with 1.5 M lactic acid/ammonium lactate, the spectrum changed very little. Neptunium (V) was still the predominate valence state. However, when 0.05 M DTPA was added to the solution, the spectrum became much more complicated. A new peak appeared at 741 nm which was attributed to Np(IV). The reduction of Np(V) to Np(IV) was due to the stability of Np(IV)-DTPA complex compared to the Np(V)-DTPA complex. It should be noted that the spectrum of this solution was recorded approximately 18 h following preparation. The equilibrium constants (log K) for the Np(IV)-DTPA complex in 0.5 and 1.0 M $NaClO_4$ are 29.29 ± 0.02 and 30.33 ± 0.12, respectively.[13] The equilibrium constant for the Np(V)-DTPA complex is not reported; however, equilibrium constants for both the Np(IV) and Np(V)-ethylenediaminetetraacetic acid (EDTA) complexes are available. The (log K) value for the Np(IV) complex in 1.0 M $NaClO_4$ is 24.55 ± 0.03 while the (log K) value for the Np(V) complex in 0.1 M $NaClO_4$ is only 7.33 ± 0.06.[13] By analogy, the equilibrium constant for the Np(IV)-DTPA complex should also be orders of magnitude larger than the equilibrium constant for the Np(V)-DTPA complex. The stability of the Np(IV) complex lowers the Np(IV) activity which results in the slow reduction of Np(V) to the more stable valence state. When HAN was added to the lactic acid/ammonium lactate solution containing DTPA, the Np spectrum did not change. Hydroxylamine nitrate does not reduce Np(V) to Np(IV); [11] therefore, this result is expected.

Pu Reference Spectra

The UV-vis spectrum of Pu in 0.1 M HNO_3 (Figure 2) showed the presence of Pu(III) (peaks at 560, 600, and 663 nm), Pu(IV) (peak at 470 nm), and Pu(VI) (peak at 831 nm); although, the predominate valence was Pu(IV). When the 0.1 M HNO_3 was replaced with 1.5 M lactic acid/ammonium lactate, the Pu(IV) peak became larger and shifted to 485 nm. The peaks which were attributed to Pu(III) and Pu(VI) disappeared and a number of other peaks appeared. When 0.05 M DTPA was added to the buffered lactate solution, the spectrum became even more complicated. The Pu(IV) peak shifted to 498 nm and additional peaks appeared in the spectrum. The addition of HAN to the Pu-containing solution had essentially no effect on the spectrum. This supports our visual observation (based on the solution color not changing to blue) that HAN will not reduce Pu(IV) to Pu(III) in a solution containing a lactic acid buffer and DTPA.

Reduction of Actinide Valences Using HAN and FS

Since Pu was not reduced by HAN in the buffered lactate solution containing DTPA, solutions were prepared in which HAN and FS were added to aliquots of the Np and Pu stock solutions prior to combining with the lactic acid and DTPA. When either the HAN or FS was added to the Pu solution, the solution turned blue which is indicative of Pu(III).[10] After combination with the lactic acid and DTPA, the UV-vis spectrum for each solution was recorded. The Np (see Figures 3 and 4) and Pu (see Figures 5 and 6) spectra are compared with the spectra of the Np and Pu solutions (from Figures 1 and 2, respectively) in which HAN was added to the buffered DTPA solution prior to adding the actinides.

Figure 3 compares the UV-vis spectra of Np solutions in which HAN was added to an aliquot of the Np stock solution prior to combining with the lactic acid and DTPA and in which Np was added to a solution containing lactic acid, DTPA, and HAN. The spectrum of the solution in which HAN was added to an aliquot of the Np stock solution showed that the predominate Np valence was still Np(V). The spectrum of this solution was recorded within approximately 90 min of the solution preparation. Therefore, only a small portion of the Np(V) had been reduced to Np(IV) due to the stability of the Np(IV)-DTPA complex. The spectrum of the solution in which Np was added to a solution containing lactic acid, DTPA, and HAN was recorded approximately 18 h following preparation and showed the presence of significantly more Np(IV). The HAN had no effect on the distribution of Np valences. Figure 4 compares the UV-vis spectra of Np solutions in which FS was added to an aliquot of the Np stock solution prior to combining with the lactic acid and DTPA and in which Np was added to a solution containing lactic acid, DTPA, and HAN. The spectrum of the solution containing FS shows that the predominate Np valence was Np(IV). Ferrous sulfamate has historically been used to reduce Np(V) to Np(IV) in both ion exchange and solvent extraction applications.[12] The two Np spectra presented on Figure 4 are very similar, except for the very broad peak centered at approximately 425 nm which can be attributed to Fe(II) in the solution.

Figure 5 compares the UV-vis spectra of Pu solutions in which HAN was added to an aliquot of the Pu stock solution prior to combining with the lactic acid and DTPA and in which Pu was added to a solution containing lactic acid, DTPA, and HAN. When the Pu and HAN were combined, the solution turned blue which indicated the presence of Pu(III). The spectrum of the solution which resulted from combining the Pu(III) with lactic acid and DTPA is significantly different from the spectrum of the solution in which the Pu was added to a solution containing lactic acid, DTPA, and HAN. The three peaks between 550 and 630 nm were attributed to the presence of Pu(III) in the lactic acid/DTPA solution. It should be noted that the spectrum of this solution was recorded within approximately 90 min of preparation. Although, the spectrum was recorded shortly after the solution was prepared, a small peak at 498 nm was observed which can be attributed to Pu(IV). Figure 6 compares the UV-vis spectra of Pu solutions in which FS and HAN were added to aliquots of the Pu stock solution prior to combining with lactic acid and DTPA with the spectrum of the solution in which Pu was simultaneously combined with lactic acid, DTPA, and HAN. As with HAN, it is well documented that FS will reduce Pu to Pu(III).[12] The spectra of the solutions which resulted from the addition of Pu(III) to the lactic acid and DTPA are very similar. Both spectra contain the three peaks between 550 and 630 nm which were attributed to Pu(III). Even though the spectrum of the solution in which the Pu was reduced using FS was recorded within approximately 90 min of preparation, a small peak attributed to Pu(IV) at 498 nm was observed.

Stability of Np(V) and Pu(III) in Lactic Acid/DTPA Solutions

The reference spectra of Np in lactic acid/DTPA solutions demonstrated that Np(V) is not stable in this matrix. The Np(V) was slowly reduced to Np(IV) due to the stability of the Np(IV)-DTPA complex. In addition, the spectra of the Pu(III) solutions generated by the addition of either HAN or FS showed the presence of Pu(IV). Therefore, the spectra of the Np and Pu solutions in which HAN and FS were added prior to combining with lactic acid and DTPA were recorded as a function of time to assess the stability of the Pu(III) and Np(V). The UV-vis spectra of the four solutions were recorded following nominally 1, 2, 3, 7, and 8 days after preparation. The Np spectra of the solutions containing HAN and FS are shown on Figures 7 and 8, respectively, and the Pu spectra of solutions containing HAN and FS are shown on Figures 9 and 10, respectively.

The stability of Np(V) in the lactic acid/DTPA/HAN solution is illustrated in Figure 7. The baseline UV-vis spectrum was recorded within about 90 min of the solution preparation. At this time, Np(V) was the predominate valence in the solution. Within approximately 24 h, a significant amount (perhaps as high as 50%) of the Np(V) was reduced to Np(IV). The fraction of Np(V) in the solution continued to diminish with time and was essentially reduced to Np(IV) after one week. Figure 8 illustrates the stability of Np(IV) in the buffered lactate/DTPA solution following reduction of the Np with FS. The baseline spectrum was recorded within approximately 90 min of the solution preparation and showed complete reduction of the Np. Over the next 8 days, the spectrum was essentially unchanged. Neptunium (IV) is the preferred valence in this system due to the stability of the Np(IV)-DTPA complex.

The stability of Pu(III) in the lactic acid/DTPA/HAN solution is illustrated in Figure 9. The baseline UV-vis spectrum was recorded within approximately 90 min of the solution preparation. Plutonium (III) is clearly the predominate valence at this time; although, the small peak at 498 nm indicates the presence of Pu(IV). After one day, the three peaks between 550 and 630 nm (which are attributed to Pu(III)) are still visible, but significantly reduced. After 2 days, the peaks have nearly disappeared and after 3 days, the peaks are gone. Therefore, it appears that the Pu(III) completely oxidized to Pu(IV) after approximately 3 days. The oxidation of Pu(III) to Pu(IV) can be explained in an analogous manner to the reduction of Np(V) to Np(IV). The Pu(IV)-DTPA complex is much more stable than the Pu(III)-DTPA complex. The equilibrium constants (log K) for the Pu(IV)- and Pu(III)-DTPA complexes are 35.39 and 29.5, respectively.[14] The stability of the Pu(IV) complex lowers the Pu(IV) activity which results in the slow oxidation of the Pu(III) to the more stable valence state. The stability of Pu(III) in the lactic acid DTPA solution which was produced by reduction with FS is shown on Figure 10. The baseline UV-vis spectrum was recorded within approximately 90 min of the solution preparation. The peaks between 550 and 630 nm show that Pu(III) was initially the predominate valence in the solution; although a small Pu(IV) peak was also observed at 498 nm. The Pu(III) peaks are not as well defined as in the spectrum of the solution in which the Pu was reduced with HAN. However, the spectra recorded following one, two, and three days after preparation of the solution continued to show some sign of Pu(III) in solution. The Pu(III) was completely oxidized to Pu(IV) after approximately 4 days.

The two series of UV-vis spectra demonstrated that Np(V) and Pu(III) are the predominate valences in the lactic acid/DTPA solution for the better part of a day following solution preparation. It is necessary to reduce the Pu to Pu(III) using either HAN or FS prior to combining with the lactic acid and DTPA. Stable Np(IV) is produced in the lactic acid/DTPA solution if FS is initially combined with the Np prior to solution preparation. Based on these results, we chose to initially add HAN to the actinide tracer solution prepared for the distribution coefficient measurements (to produce Pu(III)) prior to combining with lactic acid and DTPA. The distribution coefficient measurements were expected to be complete in 2-3 h; therefore, Np(V) and Pu(III) valences would predominate during this time.

Distribution Coefficient Measurements

Actinide Distribution Coefficients

The activity of Np, Pu, Am, and Pa measured in the aqueous and organic phases during the TALSPEAK extraction experiments are shown in Appendix C. The activity of the actinides in each phase were subsequently used to calculate distribution coefficients ($D_{An,o/a}$) which are defined as the ratio of the activity of the actinide element in the organic phase ($A_{An,o}$) to the activity of the actinide element in the aqueous phase ($A_{An,a}$) (equation 1).

$$D_{An,o/a} = \frac{A_{An,o}}{A_{An,a}} \qquad (1)$$

The actinide distribution coefficients for the triplicate extraction experiments at each pH for the range of temperatures are given in Appendix C. The average values are shown in Tables 4 and 5 for the experiments performed at pH 2.8 and 3.5, respectively.

Table 4 Actinide Distribution Coefficients in the TALSPEAK Process at pH 2.8

Element	20.0 °C		59.0 °C	
	$D_{An,\ o/a}$	Relative Std. Dev. (%)	$D_{An,\ o/a}$	Relative Std. Dev. (%)
Np	9.17E+00	3.6	1.15E+00	20.7
Pu	7.56E-02	10.8	4.06E-02	20.7
Am	3.89E+00	5.4	1.48E+00	4.7
Pa	1.14E+02	15.3	2.95E+01	25.3

Table 5 Actinide Distribution Coefficients in the TALSPEAK Process at pH 3.5

Element	20.0 °C		40.0 °C		59.5 °C	
	$D_{An,\ o/a}$	Relative Std. Dev. (%)	$D_{An,\ o/a}$	Relative Std. Dev. (%)	$D_{An,\ o/a}$	Relative Std. Dev. (%)
Np	4.45E+00	7.9	2.36E+00	10.2	5.88E-01	7.8
Pu	4.58E-02	8.7	5.06E-02	5.0	2.56E-02	29.4
Am	5.19E-01	3.6	4.49E-01	9.0	2.98E-01	3.8
Pa	9.45E+01	5.4	5.68E+01	33.9	7.62E+00	13.5

The initial TALSPEAK extraction experiments were performed at pH 2.8 based on the acidity of the feed solution used by Argonne National Laboratory in a series of process demonstrations.[9] However, the measured distribution coefficients for Am were greater than unity indicating that a majority of the Am was extracted into the solvent. Since the objective of the TALSPEAK process is to retain the Am in the aqueous phase, we chose to increase the pH (to 3.5) in subsequent extractions to lower the distribution coefficients. Inspection of the Am data in Tables 4 and 5 shows an approximate order of magnitude decrease in the distribution coefficients when the pH was increased from 2.8 to 3.5. However, the distribution coefficient measured for Am at 20 °C (and pH 3.5) is still larger than the value (6.5E-02) reported by Nilsson et al. [5] for similar conditions. In future work, it would be beneficial to perform additional measurements without the presence of HAN in the aqueous phase to ensure that its presence had no effect on the extraction of Am into the HDEHP solvent.

The actinide distribution coefficients in Tables 4 and 5 show that Np(V) and Pa(V) were more strongly extracted into the HDEHP solvent than Pu(III) and Am(III). The increased extraction of Np and Pa can be attributed to the stability of the Pu(III)- and Am(III)-DTPA complexes compared to the Np(V)- and Pa(V)-DTPA complexes. The stability of the 3+ complexes prevents their extraction into the solvent to a much greater extent. The distribution coefficients for each actinide decreased with decreasing pH and increasing temperature. The decrease in the distribution coefficients with pH is due to the protonation of the HDEHP solvent which reduces the number of available complexation (i.e., ion exchange) sites. The decrease in the distribution coefficients with temperature is due to the exothermic nature of the extraction process. The enthalpies of extraction calculated using the van't Hoff analysis (see following section) are exothermic.

The uncertainty in the distribution coefficients generally increase at the highest temperature used for the extractions. This is likely due to the increased temperature gradient in the Thermomixer R heating/cooling block. Above 45 °C, the uncertainty in the temperature control increases from ± 0.5 to ± 2 °C. The instability of the Np(V) and Pu(III) at approximately 60 °C may also contribute to the uncertainty for these elements. At this temperature, the reduction of Np and the oxidation of Pu would proceed at faster rates; therefore, the difference in the distribution of Np and Pu valences between the first and last sample removed from the heating/cooling block would be greater, which would change the distribution between phases.

Thermodynamic Properties

The actinide distribution coefficients measured at different temperatures can be used to calculate conditional enthalpies (ΔH^0) and entropies (ΔS^0) of extraction. The thermodynamic properties are considered conditional, since they are based on the variation of distribution coefficients as a function of temperature, rather than the extraction equilibrium constant (K).[5]

The free energy of extraction is defined by equations 2 and 3.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{2}$$

$$\Delta G^0 = - RT \ln K \tag{3}$$

Combining the equations and rearrangement results in equation 4,

$$\ln K = - \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{4}$$

which shows that a plot of the natural log of the extraction equilibrium constant as a function of the reciprocal thermodynamic temperature should be linear with a slope of $-\Delta H^0/R$ and a y-intercept of $\Delta S^0/R$. To calculate the conditional enthalpies and entropies of extraction for the TALSPEAK process, the natural log of the actinide distribution coefficients were plotted as a function of the reciprocal thermodynamic extraction temperature on Figures 11 and 12 for the series of experiments performed at pH 3.5 and 2.8, respectively. The thermodynamic properties calculated from the van't Hoff analysis are provided in Table 6 (see Appendix C for calculations).

The uncertainties associated with the majority of the conditional thermodynamic properties given in Table 6 vary between approximately 10 and 50%. Inspection of the data at pH 3.5 on Figure 11 and the correlation coefficients for the regression analysis (Appendix C) show varying degrees of nonlinearity including curvature. The plots at pH 2.8 include six extractions for each actinide; however, the experiments were only performed at two temperatures and would likely show curvature over the temperature range as observed for pH 3.5. The UV-vis spectra recorded to investigate the stability of Np(V) and Pu(III) in lactic acid/DTPA solutions showed that Np(IV) and Pu(IV) are the most stable valences. The reduction of Np(V) and the oxidation of Pu(III), especially at the highest extraction temperature, would result in changes to the distribution of Np and Pu valences which contribute to the uncertainty in the van't Hoff analysis. However, the extractions were performed and samples removed within 2-3 h, and as a result, the majority of the Np and Pu should have still been present as Np(V) and

Pu(III). To understand the rates at which Np(V) is reduced and Pu(III) is oxidized in lactic acid/DTPA solutions, an investigation of the oxidation/reduction kinetics should be performed as future work.

Table 6 Thermodynamic properties calculated from van't Hoff analysis

pH	Element	ΔH^0 (kJ/mol)	Std. Dev. ΔH^0 (kJ/mol)	Rel. Std. Dev. ΔH^0 (%)	ΔS^0 (J/mol K)	Std. Dev. ΔS^0 (J/mol K)	Rel. Std. Dev. ΔS^0 (%)
3.5	Np	-39.6	4.9	12.3	-122	16	12.9
	Pu	-10.5	5.0	47.4	-60.4	16.0	26.6
	Am	-10.7	1.9	17.5	-41.6	6.1	14.6
	Pa	-48.3	9.0	18.7	-125	29	23.3
2.8	Np	-43.0	2.6	6.1	-128	8	6.6
	Pu	-13.0	2.8	21.3	-65.7	8.9	13.5
	Am	-19.8	0.8	4.3	-56.3	2.7	4.8
	Pa	-28.0	3.5	12.4	-56.2	11.1	19.8

Since the van't Hoff plots for Am and Pa (see Figure 11) also show the same curvature and the Am(III) and Pa(V) valences are stable, it is likely that the enthalpy of extraction for the actinides is not constant over the temperature range. Integration of the van't Hoff equation assumes that the enthalpy of reaction is temperature-independent. Changes in enthalpy with temperature can be addressed using either a change in heat capacity (Δc_p) term or the use of an empirical power series in temperature for the heat capacity.[7] Naghibi et al. [15] emphasized that when calorimetric data are subjected to nonlinear least-squares analysis using the integrated form of the van't Hoff equation with a nonvanishing but temperature-independent heat capacity change, the curvature of the van't Hoff plot becomes evident.

Another possibility which could affect the linearity of the van't Hoff plots are changes in the chemistry which occur due to changes in the lactic acid protonation with temperature. Rao [16] has measured the protonation constants of lactic acid as a functions of temperature. Results from this study are shown in Table 7.

Table 7 Protonation constants of lactic acid

Reaction	logβ				
	10 °C	25 °C	40 °C	55 °C	70 °C
$L^- + H^+ = HL$	3.46	3.67	3.68	3.70	3.72

L ≡ lactate
ionic strength = 1.0 M $NaClO_4$

Small changes in the protonation constants of lactic acid occurred as the temperature was increased from 25 to 55 °C; however, these small changes would not be expected to have a significant effect on the extraction of the actinides into HDEHP.

To address the nonlinearity of the data associated with the van't Hoff plots, future distribution coefficient measurements for the extraction of the actinide elements in the TALSPEAK process should permit the regression analysis to be performed over a more narrow temperature range. Changes in the enthalpy of extraction with temperature are likely responsible for the curvature observed in the distribution data; therefore, the evaluation of data measured over a narrow temperature range should result in a more accurate analysis. The instability of Pu(III) and Np(V) in lactic acid/DTPA solutions is not an issue in the TALSPEAK process; however, any hold-up in processing the feed solution would ensure that significant amounts (if not all) of the Pu and Np are present as the more stable Pu(IV) and Np(IV) valences. Therefore, measuring the distribution of Np(IV) and Pu(IV) between the TALSPEAK aqueous and organic phases and performing the van't Hoff analysis would be an appropriate focus of future studies.

CONCLUSIONS

To better understand the thermodynamic driving force for the extraction of actinide elements in the TALSPEAK process, an experimental study was performed to measure the distribution of Np(V), Pu(III), Am(III), and Pa(V) between the aqueous and organic phases as a function of temperature. The conditional enthalpies and entropies of extraction were subsequently calculated by van't Hoff analysis. Prior to performing the extraction studies, the stability of Np(V) and Pu(III) in lactic acid/DTPA solutions was evaluated by UV-vis spectroscopy. We found that it was necessary to reduce Pu to Pu(III) prior to combining with the lactic acid and DTPA. The reduction was performed using either HAN or FS. When FS was used, Np was reduced to Np(IV). The spectroscopic studies showed that Np(V) and Pu(III) are not stable in the lactic acid/DTPA solutions used as the aqueous phase in the TALSPEAK process. The stability of Np(IV)-DTPA and Pu(IV)-DTPA complexes are much greater than the stability of the Np(V)-DTPA and Pu(III)-DTPA complexes, and as a result, Np is slowly reduced to Np(IV) and Pu is slowly oxidized to Pu(IV) due to the reduced activity of the stable complexes. When Np(V) was added to a solution containing a 1.5 M lactic acid/ammonium lactate buffer and 0.05 M DTPA, approximately 50% of the Np was reduced to Np(IV) in the first day. The fraction of Np(V) in the solution continued to diminish with time and was essentially reduced to Np(IV) after one week. When Pu(III) was added to a lactic acid/DTPA solution of the same composition, the spectrum recorded following at least two days after preparation of the solution continued to show some sign of Pu(III). The Pu(III) was completely oxidized to Pu(IV) after 3-4 days.

The actinide distribution coefficient measurements showed that the 5+ actinides (Np and Pa) were more strongly extracted into the HDEHP solvent than the 3+ actinides (Pu and Am). The increased extraction of Np and Pa was attributed to the increased affinity of the DTPA for the 3+ actinides compared to the 5+ actinides. The stability of the 3+ DTPA complexes prevents the extraction of Pu and Am into the solvent to a greater extent. The actinide distribution coefficients decreased with decreasing pH and increasing temperature. These trends in the data are due to the protonation of the HDEHP solvent (which reduces the number of complexation sites) and the exothermic nature of the extraction process. At pH 3.5, the conditional enthalpies of extraction were approximately -10 kJ/mole for Pu(III) and Am(III), -40 kJ/mol for Np(V), and -48 kJ/mol for Pa(V). The entropies of extraction were negative which results in more positive free energies of extraction as the temperature increases. The uncertainties associated with the majority of the conditional thermodynamic properties varied between approximately 10 and 50%. The nonlinearity in the data is primarily attributed to changes in the enthalpy of extraction over the temperature range; although, the instability of Np(V) and Pu(III) likely contributed to the variance.

FUTURE WORK

Recommendations for areas of additional study to follow the actinide distribution coefficient measurements and thermodynamic analysis discussed in this report fall into two distinct areas. The spectroscopic studies showed that Np(V) and Pu(III) are not stable in lactic acid/DTPA solutions. To understand the rates at which Np(V) is reduced and Pu(III) is oxidized in these solution, an investigation of the oxidation/reduction kinetics should be performed as future work. The measurement of additional distribution coefficients for Np, Pu, Am, and Pa is also recommended. Since we demonstrated that the most stable Np and Pu valences in lactic acid/DTPA solutions are Np(IV) and Pu(IV), measuring distribution coefficients for the 4+ oxidation states in the TALSPEAK process and performing the van't Hoff analysis would be an appropriate focus of future work. It would also be beneficial to perform additional measurements for Am without the presence of HAN in the aqueous phase to ensure that its presence had no effect on the extraction of Am into the HDEHP solvent.

REFERENCES

1. Nuclear Energy Research and Development Roadmap – Report to Congress, United States Department of Energy Office of Nuclear Energy, Washington, DC (2010).

2. L. R. Morss, N. M. Edelstein, and J. Fuger, Eds., *The Chemistry of the Actinide and Transactinide Elements,* 3rd ed., Springer, Dordrecht, The Netherlands, Vol. 2, pp 841-844 (2006).

3. L. R. Morss et al., pp 704-705.

4. M. L. Hyder, W. C. Perkins, M. C. Thompson, G. A. Burney, E. R. Russell, H. P. Holcomb, and L. F. Landon, *Processing of Irradiated Enriched Uranium Fuels at the Savannah River Plant*, DP-1500, E. I. du Pont de Nemours & Co., Aiken, SC (1979).

5. M. Nilsson and K. L. Nash, *Review Article: A Review of the Development and Operational Characteristics of the TALSPEAK Process*, Solvent Extr Ion Exc, 25, pp 665–701 (2007).

6. B. Weaver and F. A. Kappelmann, Talspeak, *A new method of separating americium and curium from the lanthanides by extraction from an aqueous solution of an aminopolyacetic acid complex with a monoacetic organophosphate or phosphonate*, ORNL-3559, Union Carbide Corporation, Oak Ridge, TN (1964).

7. K. Denbigh, *The Principles of Chemical Equilibrium*, 3rd ed., Cambridge University Press, Cambridge, United Kingdom, pp. 143-144 (1971).

8. L. R. Morss et al., pp 707-708.

9. C. Pereira, L. E. Maggos, G. F. Vandegrift, M. C. Regalbuto, K. Alford, A. Bakel, D. Bowers, J. P. Byrnes, M. A. Clark, J. R. Falkenberg, A. V. Gelis. L. Hafenrichter, A. S. Hebden, M. Kalensky, J. F. Krebs, R. A. Leonard, A. Leyva, K. J. Quigley, D. Stepinski, Y. Tsai, and V. S. Sullivan, *Results of the 2007 TALSPEAK Spent Fuel Demonstration*, Letter Report, Argonne National Laboratory, Argonne, IL (2007).

10. J. M. Cleveland, *The Chemistry of Plutonium*, American Nuclear Society, La Grange Park, IL, p 12 (1979).

11. M. C. Thompson and T. S. Rudisill, *Literature Review of Complexants and Reductants for Plutonium and Neptunium for the UREX Process*, Letter Report, Savannah River Technology Center, Aiken, SC (2002).

12. G. F. Kessinger, E. A. Kyser and P. M. Almond, *Literature Review: Reduction of Np(V) to Np(IV) – Alternatives to Ferrous Sulfamiate*, SRNL-STI-2009-00610, Savannah River Nuclear Solutions, Aiken, SC (2009).

13. L. R. Morss et al., p 780.

14. L. R. Morss et al., p 1178.

15. H. Naghibi, A. Tamura, and J. M. Sturtevant, *Significant discrepancies between van't Hoff and calorimetric enthalpies*, Proc Natl Acad Sci USA, 92, pp 5597-5599 (1995).

16. L. Rao, *Understanding Actinide/Lanthanide Speciation under TALSPEAK Conditions*, AFCI-SEPA-PMO-MI-DV-2009-000xxx, Lawrence Berkeley National Laboratory, Berkeley, CA (2009).

Figure 1 Reference Spectra for Np in buffered lactic acid/DTPA systems

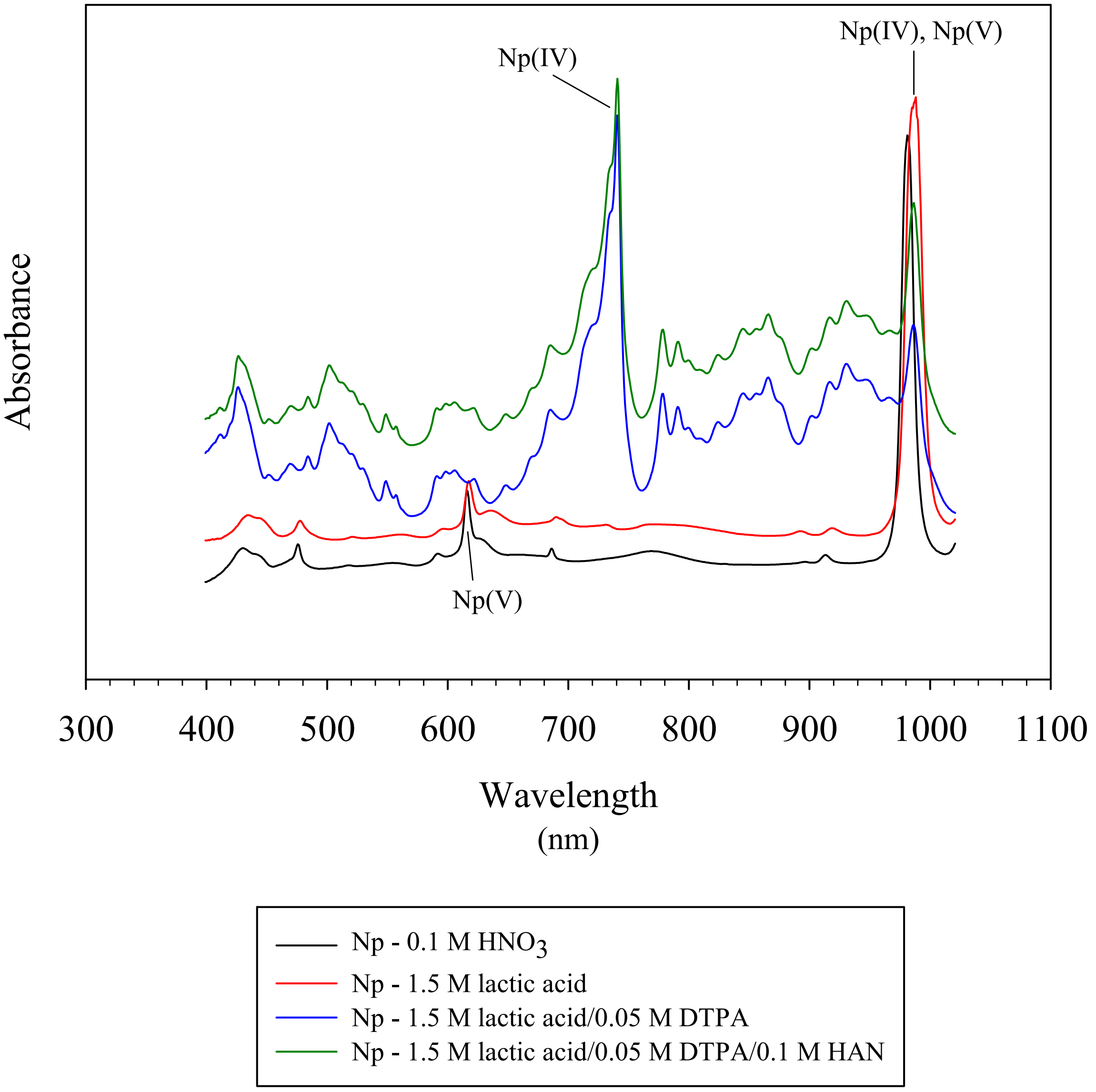


Figure 2 Reference Spectra for Pu in buffered lactic acid/DTPA systems

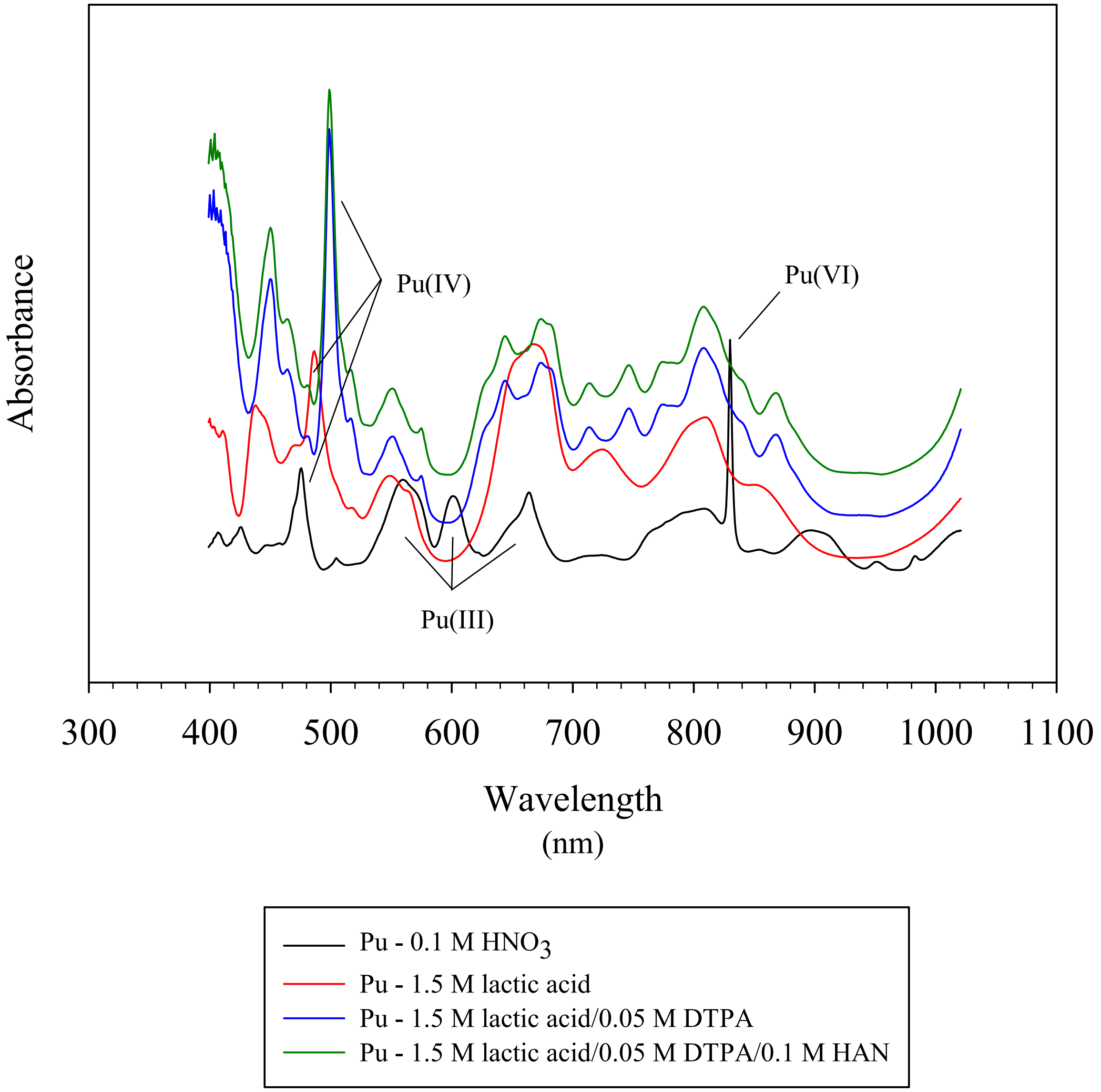


Figure 3 UV-vis spectrum of Np + 0.1 M HAN added to 1.5 M lactic acid/0.05 M DTPA

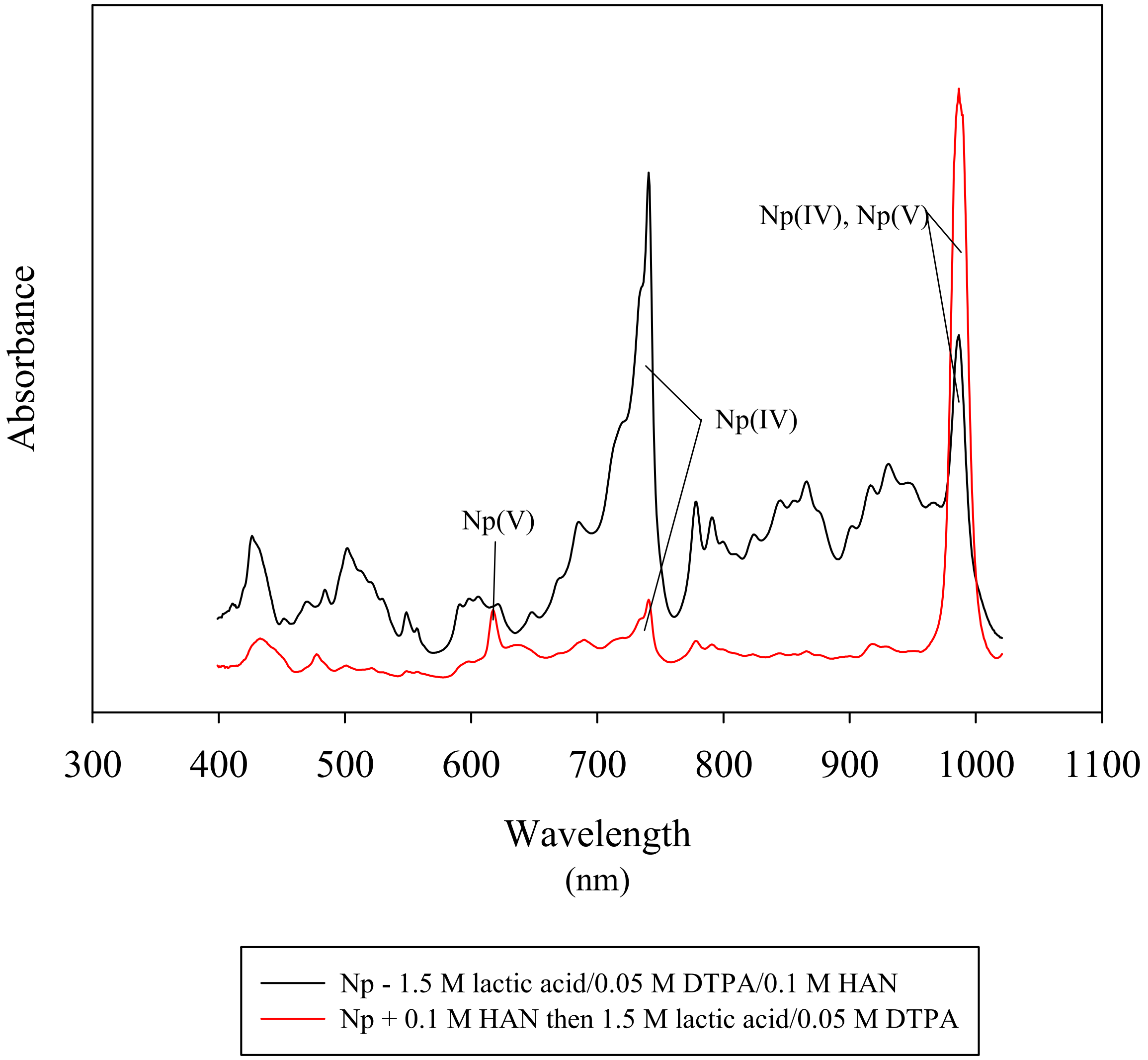


Figure 4 UV-vis spectrum of Np + 0.1 M FS added to 1.5 M lactic acid/0.05 M DTPA

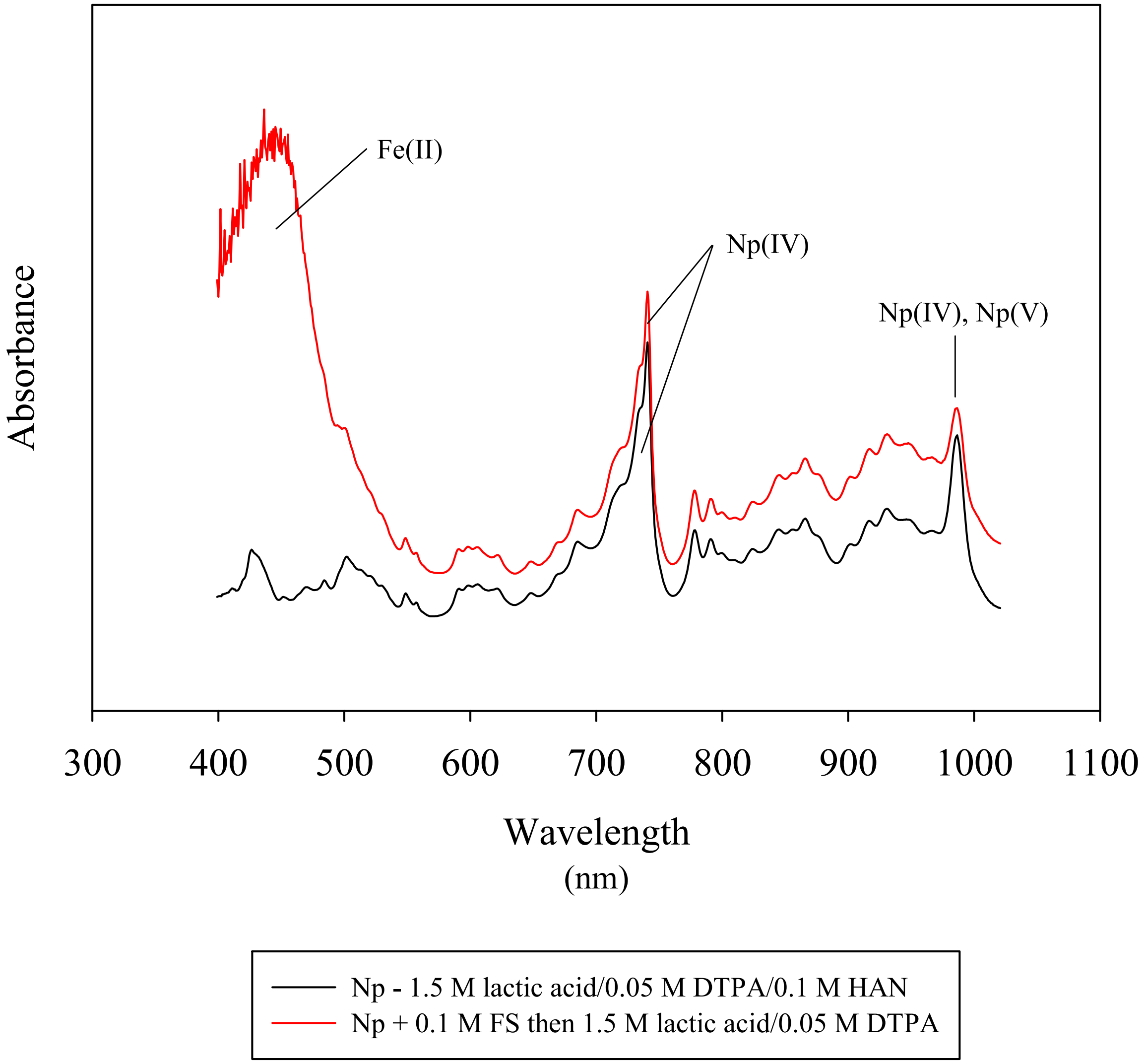


Figure 5 UV-vis spectrum of Pu + 0.1 M HAN added to 1.5 M lactic acid/0.05 M DTPA

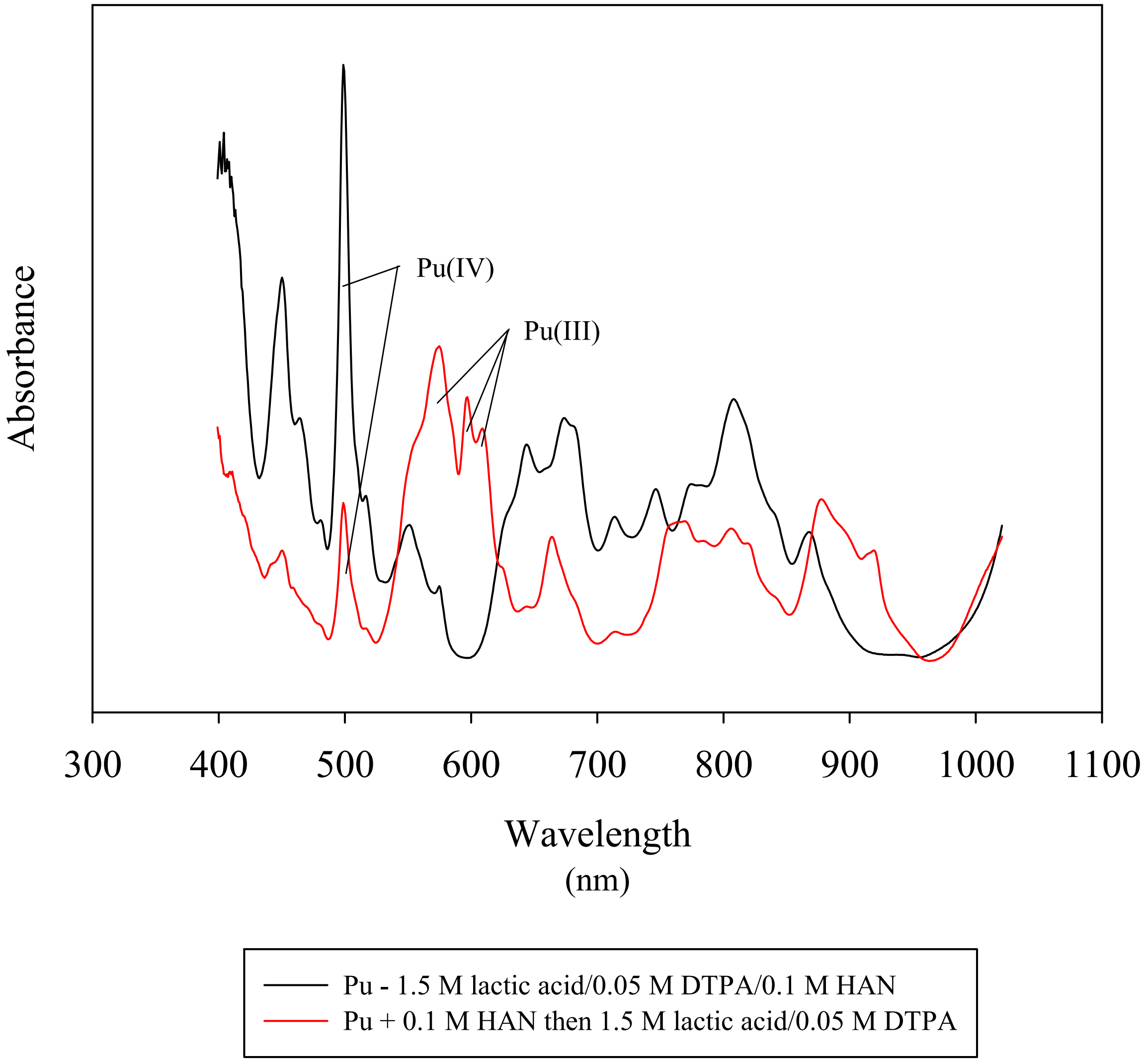


Figure 6 UV-vis spectrum of Pu + 0.1 M FS added to 1.5 M lactic acid/0.05 M DTPA

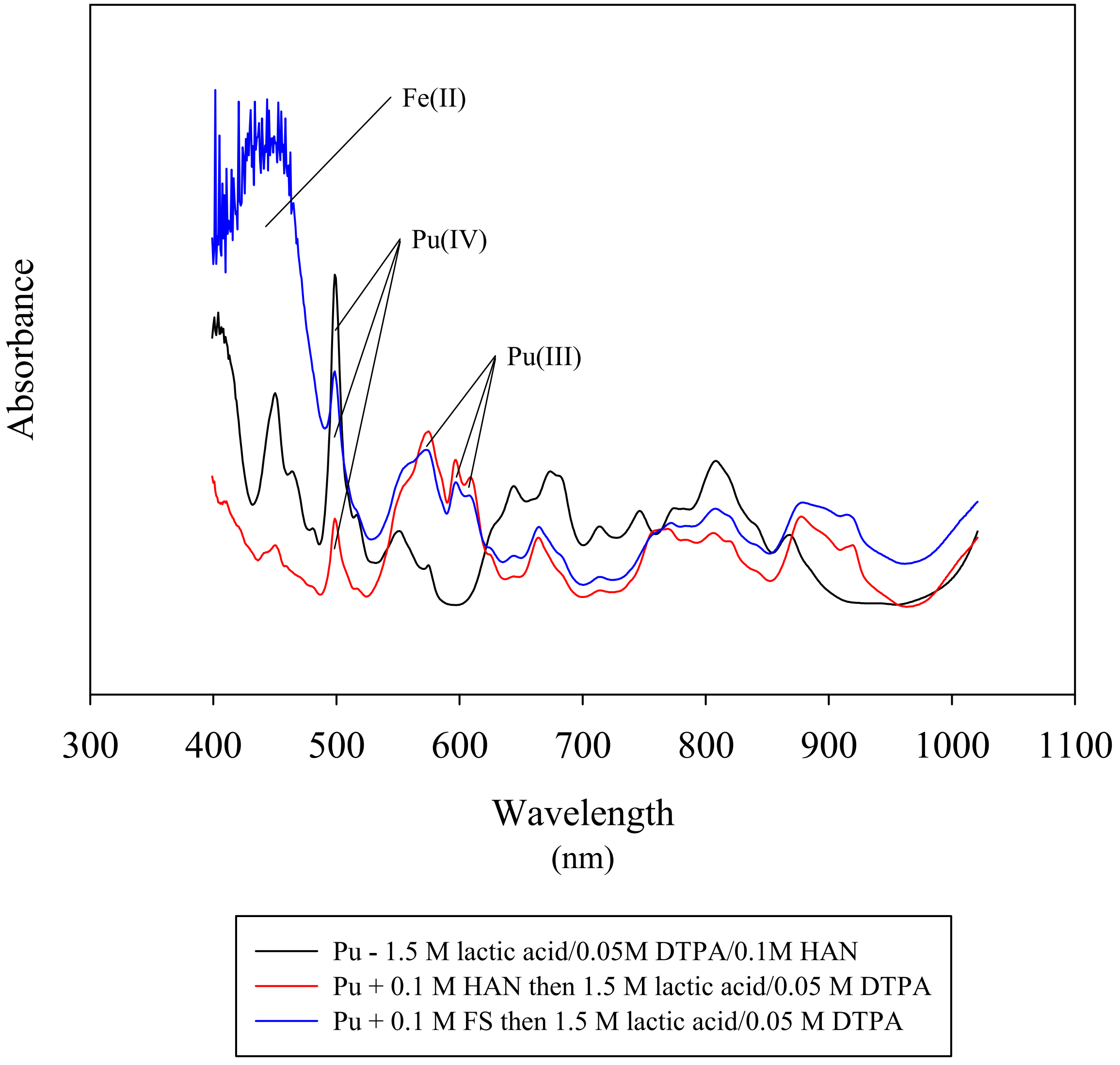


Figure 7 UV-vis spectra of Np(V)/HAN/lactic acid/DTPA solution

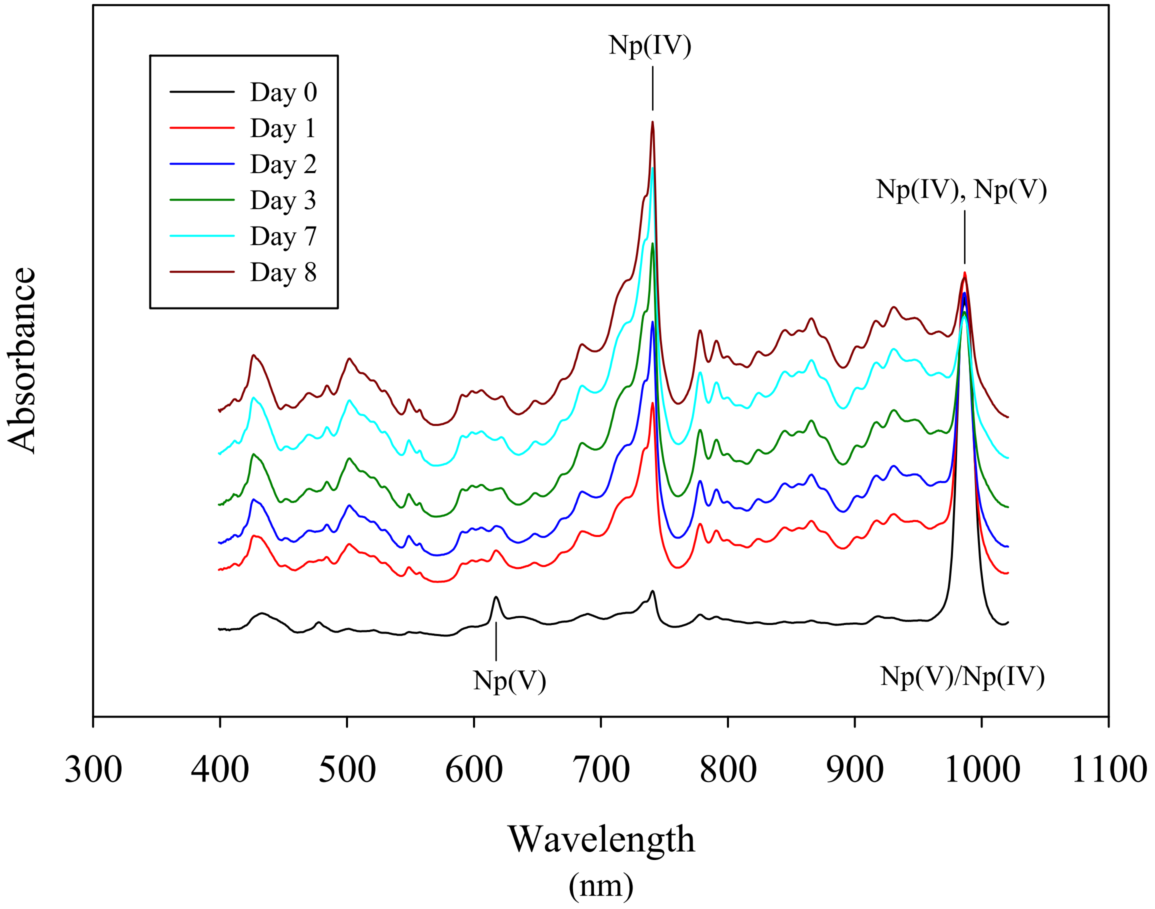


Figure 8 UV-vis spectra of Np(V)/FS/lactic acid/DTPA solution

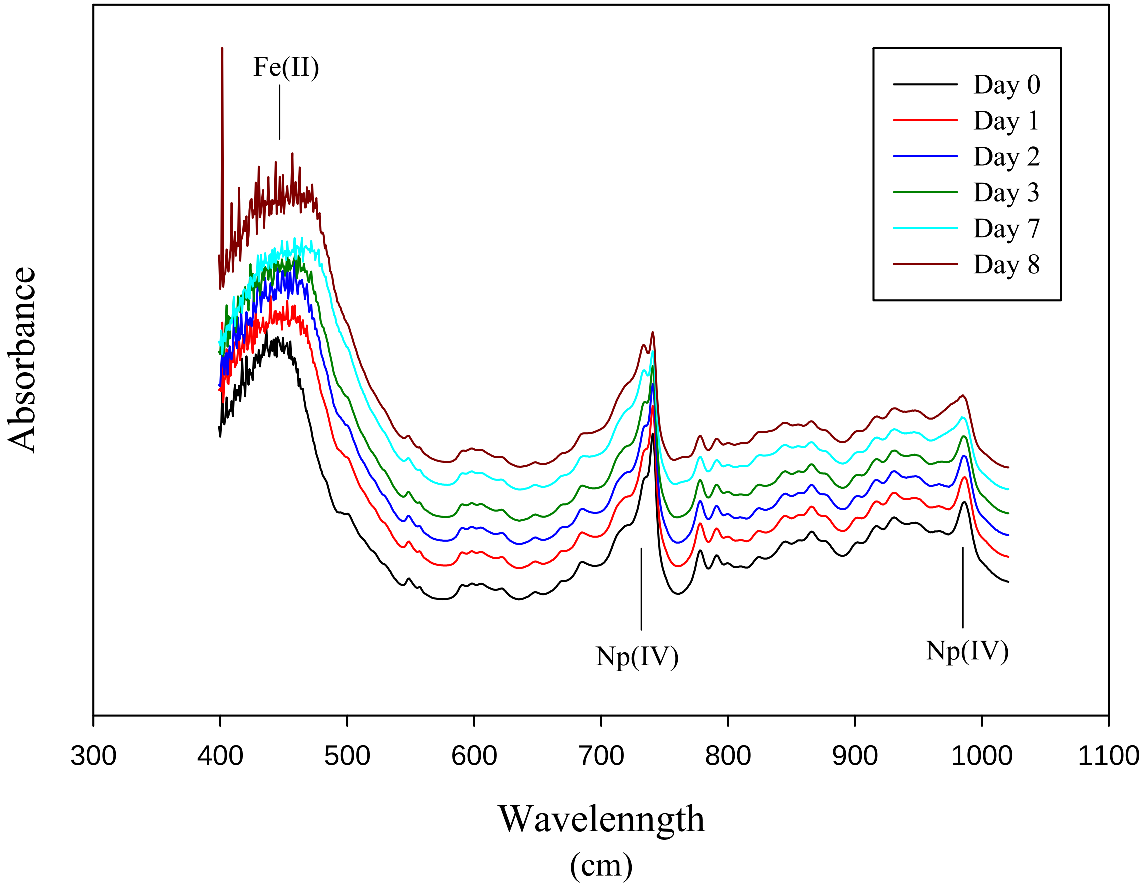


Figure 9 UV-vis spectra of Pu(III)/HAN/lactic acid/DTPA solution

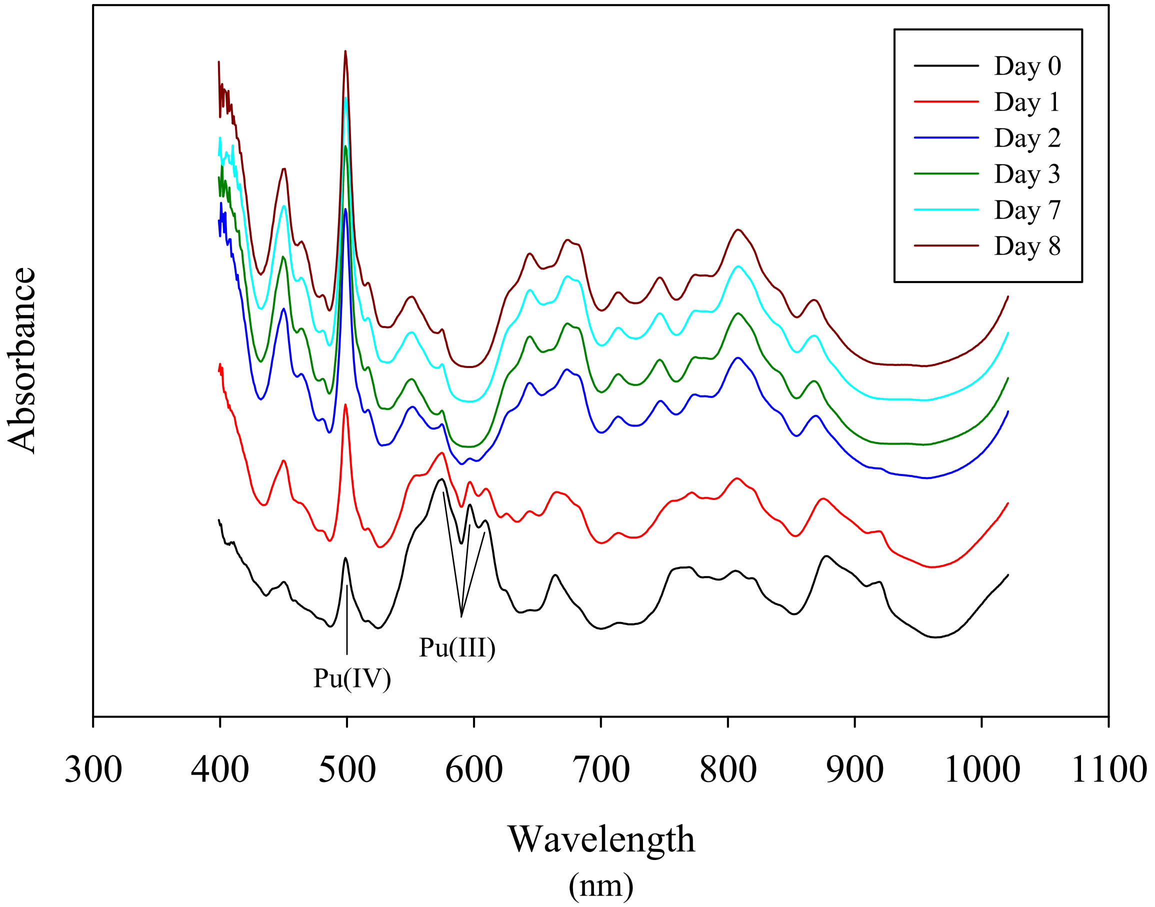


Figure 10 UV-vis spectra of Pu(III)/FS/lactic acid/DTPA solution

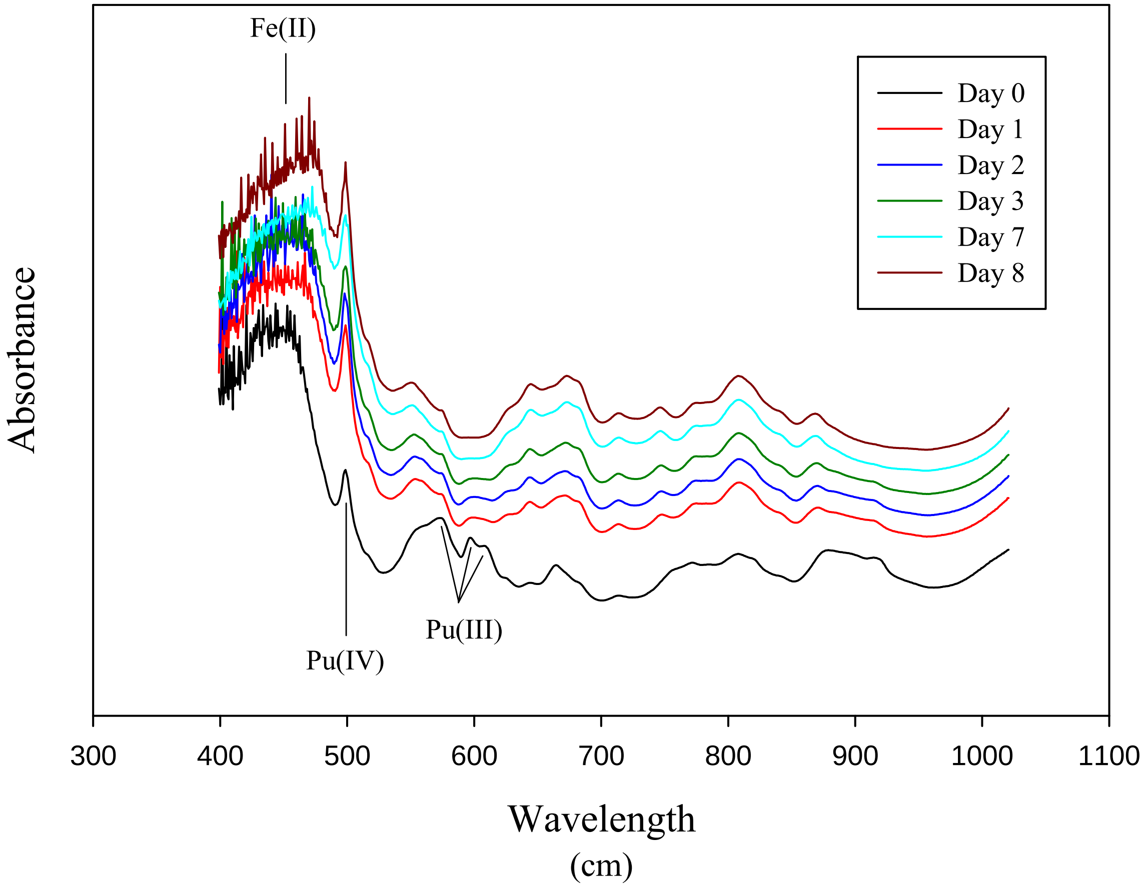


Figure 11 van't Hoff analysis for TALSPEAK extractions at pH 3.5

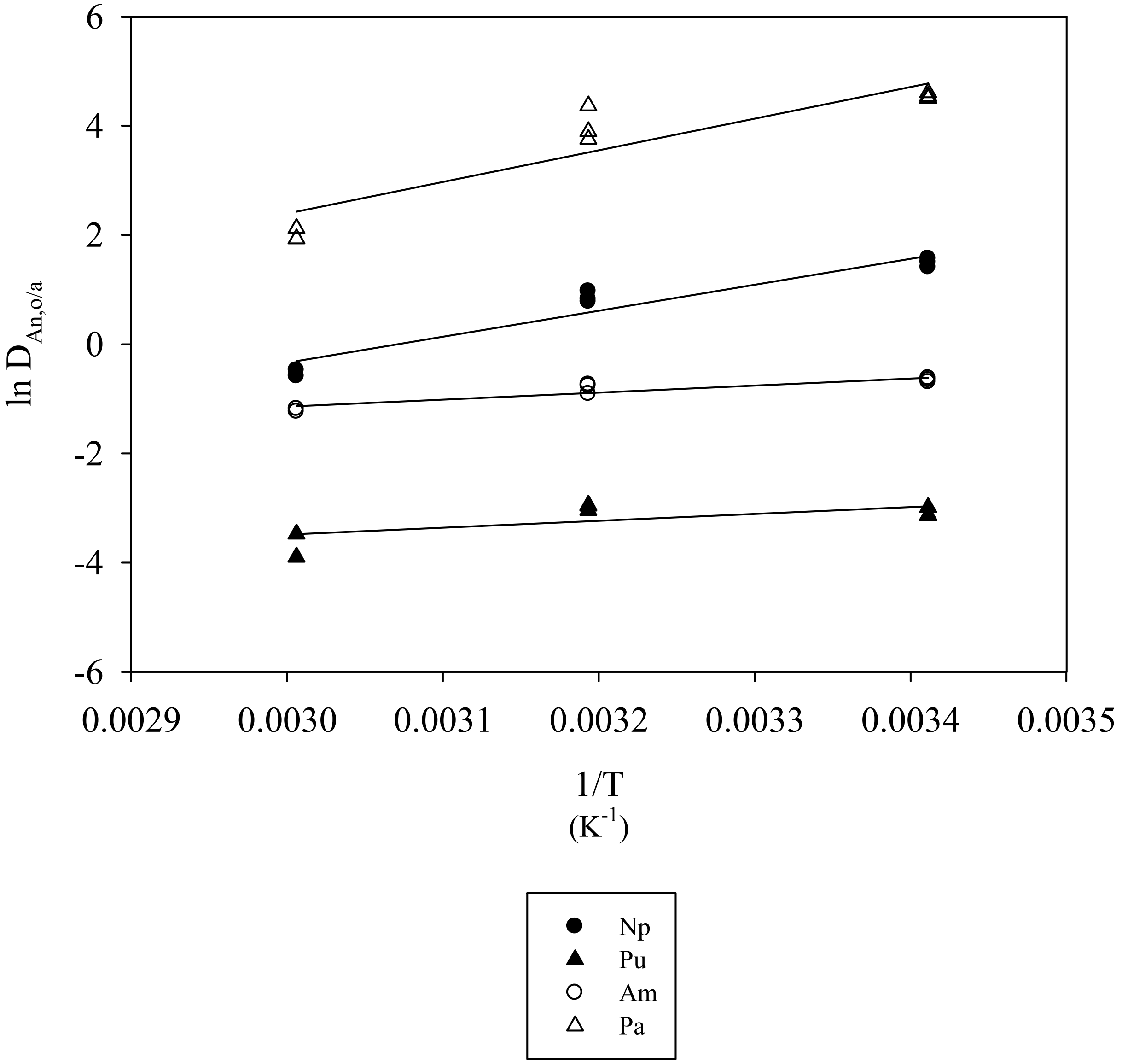
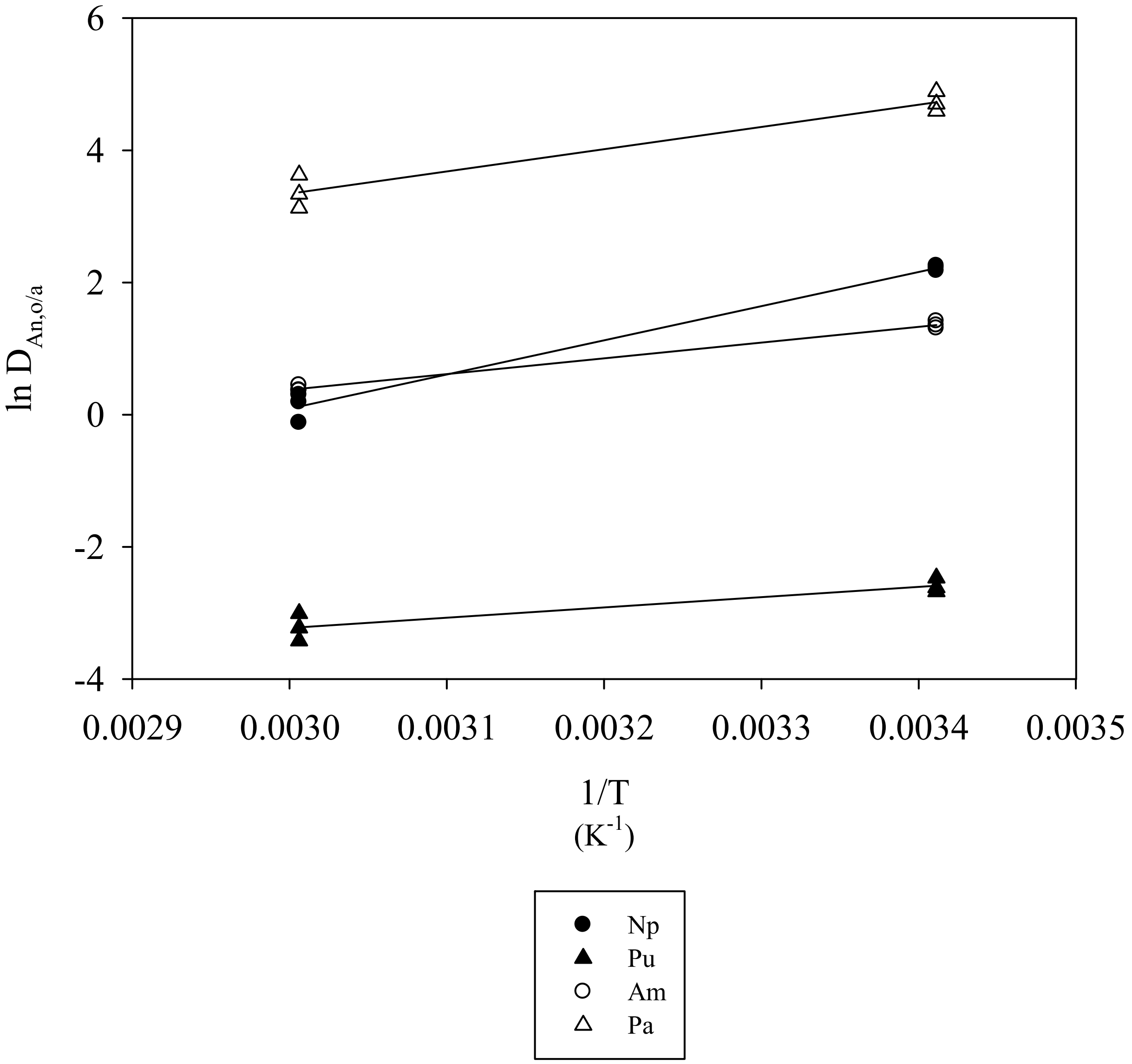


Figure 12 van't Hoff analysis for TALSPEAK extractions at pH 2.8



Appendix A

Solution Preparation for Valence Adjustment Study

Chemical Reagents

The manufacturer and purity information for the chemicals used in the valence adjustment study and distribution coefficient measurements are provided in Table A.1.

Table A.1 Chemical manufacturer and purity information

Chemical	Manufacturer	Concentration	Purity
lactic acid	Sigma Aldrich	85 wt %	(1)
DTPA	Aldrich		97 wt %
NH_4OH	Fisher Scientific	29.05 wt % (7.8 M)	(2)
HNO_3	Fisher Scientific	15.0 M(3)	(2)
HAN	(4)	1.77 M	N/A
FS	(4)	~ 2.4 M	N/A
HDEHP	Sigma Aldrich		97 wt %
Dodecane	Sigma Aldrich		> 99 wt %

(1) ACS Reagent
(2) Certified ACS PLUS
(3) Analyzed by titration.
(4) Manufacturer is unknown; reductant was obtained from the SRS H-Canyon facility.

Solution Preparation for UV-vis Spectroscopy

0.1 M HNO_3 Solution

A 1.0 M HNO_3 stock solution was initially prepared by diluting concentrated (15 M) HNO_3 with deionized water. To obtain a 0.1 M HNO_3 solution once the Np or Pu was added and the pH was adjusted to 2.8, it was necessary to initially prepare a solution containing 0.11 M HNO_3. The solution was prepared by diluting a portion of the 1.0 M HNO_3 stock solution to the desired concentration with deionized water.

1.5 M Lactic Acid Solution

To obtain a 1.5 M lactic acid solution once the Np or Pu was added and the pH was adjusted to 2.8, it was necessary to initially prepare a solution containing 1.7 M lactic acid. One hundred milliliters of 1.7 M lactic acid were prepared by transferring 17.8006 g of 85 wt % lactic acid to a volumetric flask and diluting the flask to volume with deionized water. The pH of the lactic acid solution was preadjusted to nominally 2.8 by adding approximately 2.5 mL of 7.8 M NH_4OH. The pH of the solution was measured using an Accumet® Basic AB15 pH meter which was calibrated using pH 1, 3, and 6 buffer solutions.

1.5 M lactic acid/0.05 M DTPA Solution

To obtain a 1.5 M lactic acid/0.05 M DTPA solution once the Np or Pu was added and the pH was adjusted to 2.8, 1.7 M lactic acid was used to prepare a solution containing 0.06 M DTPA. To prepare 50 mL of the solution, 1.1004 g of DTPA were transferred to a 100 mL beaker. Approximately 40 mL of 1.7 M lactic acid were added. The solution was stirred using a magnetic stir bar and heated at 70-80 °C. A watch glass containing water was placed on the beaker to reduce evaporation losses. To dissolve the solids, it was necessary to increase the pH by adding 4.40 mL of 3.9 M NH_4OH. The solution was transferred to a 50 mL volumetric flask which was diluted to volume with 1.7 M lactic acid. The pH of the lactic acid/DTPA solution was preadjusted to nominally 2.8 by adding approximately 0.25 mL of 7.8 M NH_4OH.

1.5 M lactic acid/0.05 M DTPA/0.1 M HAN Solution

To obtain a 1.5 M lactic acid/0.05 M DTPA solution once the Np or Pu and HAN were added and the pH was adjusted to 2.8, it was necessary to initially prepare a solution containing 1.8 M lactic acid and 0.06 M DTPA. One hundred milliliters of 1.8 M lactic acid were prepared by transferring 19.0578 g of 85 wt % lactic acid to a volumetric flask and diluting the flask to volume with deionized water. To prepare 50 mL of solution containing 1.8 M lactic acid/0.06 M DTPA, 1.1778 g of DTPA were initially transferred to a 100 mL beaker. Approximately 40 mL of 1.8 M lactic acid were added. The solution was stirred using a magnetic stir bar and heated. A watch glass containing water was placed on the beaker to reduce evaporation losses. To dissolve the solids, it was necessary to increase the pH by adding 2.5 mL of 3.9 M NH_4OH. The solution was transferred to a 50 mL volumetric flask which was diluted to volume with 1.8 M lactic acid. The pH of the lactic acid/DTPA solution was nominally 2.8 and was not adjusted. To achieve 0.1 M HAN in the final solution, a 0.65 mL aliquot of a 1.77 M solution was added to 9.35 mL of the 1.8 M lactic acid/0.06 M DTPA solution.

Test Solution Preparation

The assembly of the four Np and Pu test solutions prepared for the valence adjustment study are summarized below.

Solution 1 (Np) – 0.10 M HNO_3/3 g/L Np
Preparation: 10 mL 0.11 M HNO_3 + 1 mL 32.0 g/L Np

Solution 1 (Pu) – 0.10 M HNO_3/4 g/L Pu
Preparation: 10 mL 0.11 M HNO_3 + 1 mL 45.3 g/L Pu

Solution 2 (Np) – 1.5 M lactic acid/3 g/L Np
Preparation: 10 mL 1.7 M lactic acid + 1 mL 32.0 g/L Np

Solution 2 (Pu) – 1.5 M lactic acid/4 g/L Pu
Preparation: 10 mL 1.7 M lactic acid + 1 mL 45.3 g/L Pu

Solution 3 (Np) – 1.5 M lactic acid/0.05 M DTPA/3 g/L Np
Preparation: 10 mL 1.7 M lactic acid/0.06 M DTPA + 1 mL 32.0 g/L Np

Solution 3 (Pu) – 1.5 M lactic acid/0.05 M DTPA/4 g/L Pu
Preparation: 10 mL 1.7 M lactic acid/0.06 M DTPA + 1 mL 45.3 g/L Pu

Solution 4 (Np) – 1.5 M lactic acid/0.05 M DTPA/0.1 M HAN/3 g/L Np
Preparation: 9.35 mL 1.8 M lactic acid/0.06 M DPTA + 0.65 mL HAN + 1 mL 32.0 g/L Np

Solution 4 (Pu) – 1.5 M lactic acid/0.05 M DTPA / 0.1 M HAN/4 g/L Pu
Preparation: 9.35 mL 1.8 M lactic acid/0.06 M DTPA + 0.65 mL HAN + 1 mL 45.3 g/L Pu

pH Adjustment

The pH of the buffered solutions (numbers 2-4) was adjusted to nominally 2.8 using 3.8 M NH_4OH. The NH_4OH was added drop-wise using a disposable transfer pipette. A Thermo Scientific Orion 3 Star pH meter was used for the measurements. The instrument was calibrated using pH 2, 4, and 7 buffer solutions. The pH adjustments are summarized in Table A.2.

Table A.2 pH adjustment of buffered lactate solutions

Solution No.	Composition	Initial pH	Drops NH_4OH Added	Final pH
2	Pu – 1.5 M lactic acid	2.35	9	2.76
2	Np – 1.5 M lactic acid	1.31	20	2.77
3	Pu – 1.5 M lactic acid/0.05 M DTPA	2.46	8	2.77
3	Np – 1.5 M lactic acid/0.05 M DTPA	1.92	15	2.79
4	Pu – 1.5 M lactic acid/0.05 M DTPA/0.1 M HAN	2.21	13	2.77
4	Np – 1.5 M lactic acid/0.05 M DTPA/0.1 M HAN	1.55	28	2.78

Preparation of Additional Solutions for UV-vis Spectroscopy

Four additional solutions were prepared for analysis by UV-vis spectroscopy in which the reductant was added to the actinide solution prior to combining with the buffered lactate solution containing DTPA. Both HAN and FS were used as reductants. The four solutions prepared for study included: (1a) Np + HAN added to 1.5 M lactic acid/0.05 M DTPA, (2a) Pu + HAN added to 1.5 M lactic acid/0.05M DTPA, (3a) Np + FS added to 1.5 M lactic acid/0.05 M DTPA, and (4a) Pu + FS added to 1.5 M lactic acid/0.05 M DTPA. The volume of the HAN and FS stock solutions added to the actinide solutions was sufficient to achieve a concentration of 0.1 M when combined with the lactic acid and the DTPA. The lactic acid/DTPA solutions prepared for the initial spectroscopic studies were used to prepare the four solutions. The assembly of the test solutions are summarized below.

Solution 1a (Np/HAN) – 1.5 M lactic acid/0.05 M DTPA/0.1 M HAN/3 g/L Np
Preparation: 1 mL 32.0 g/L Np + 0.65 mL HAN added to 9.35 mL 1.8 M lactic acid/0.06 M DPTA

Solution 2a (Pu/HAN) – 1.5 M lactic acid/0.05 M DTPA/0.1 M HAN/3 g/L Pu
Preparation: 1 mL 45.3 g/L Pu + 0.65 mL HAN added to 9.35 mL 1.8 M lactic acid/0.06 M DPTA

Solution 3a (Np/FS) – 1.5 M lactic acid/0.05 M DTPA/0.1 M FS/3 g/L Np(1)
Preparation: 1 mL 32.0 g/L Np + 0.65 mL FS added to 9.35 mL 1.7 M lactic acid/0.06 M DPTA

Solution 4a (Pu/FS) – 1.5 M lactic acid/0.05 M DTPA/0.1 M FS/3 g/L Pu
Preparation: 1 mL 45.3 g/L Pu + 0.65 mL FS added to 9.35 mL 1.8 M lactic acid/0.06 M DPTA

(1) The amount of 1.8 M lactic acid/0.06 M DTPA available was not sufficient to prepare the FS-containing solution; therefore, the solution was prepared using the 1.7 M lactic acid/0.06 M DTPA stock solution instead. The final concentration of lactic acid was approximately the same.

The pH of the buffered solutions was adjusted to nominally 2.8 using 3.8 M NH_4OH. The NH_4OH was added drop-wise using a disposable transfer pipette. The pH adjustments are summarized in Table A.3.

Table A.3 pH adjustment of actinide solutions containing HAN and FS

Solution No.	Composition	Initial pH	Drops NH_4OH Added	Final pH
1a	(Np + 0.1 M HAN) + 1.5 M lactic acid/0.05 M DTPA	2.07	16	2.79
2a	(Pu + 0.1 M HAN) + 1.5 M lactic acid/0.05M DTP	1.77	22	2.76
3a	(Np + 0.1 M FS) + 1.5 M lactic acid/0.05 M DTPA	2.71	31	2.77
4a	(Pu + 0.1 M FS) + 1.5 M lactic acid/0.05 M DTPA	1.24	45	2.78

Appendix B

Solution Preparation for Distribution Coefficient Measurements

Chemical Reagents

The manufacturer and purity information for the chemicals used in the distribution coefficient measurements is provided in Table A.1.

Preparation of 1.9 M lactic acid/0.05 M DTPA

To obtain a 1.5 M lactic acid/0.05 M DTPA solution once the Np or Pu and HAN were added and the pH was adjusted to 2.8 (or 3.5), it was necessary to initially prepare a solution containing 1.9 M lactic acid and 0.06 M DTPA. Two hundred milliliters of 1.9 M lactic acid were prepared by transferring 40.6831 g of 85 wt % lactic acid to a volumetric flask and diluting the flask to volume with deionized water. To prepare 200 mL of solution containing 1.9 M lactic acid/0.06 M DTPA, 4.9567 g of DTPA were initially transferred to a 250 mL beaker. Approximately 150 mL of 1.9 M lactic acid were added. The solution was stirred using a magnetic stir bar and heated. A watch glass containing water was placed on the beaker to reduce evaporation losses. To dissolve the solids, it was necessary to increase the pH by adding 4.4 mL of 7.8 M NH_4OH. The solution was transferred to a 200 mL volumetric flask which was diluted to volume with 1.9 M lactic acid. The pH of the solution was subsequently adjusted from 2.58 to 2.80 by the addition of 55 drops of 7.8 M NH_4OH.

TALSPEAK Extractions

The activities of the Np, Pu, and Am in the stock solutions are summarized in Table A.4.

Table A.4 Actinide concentrations in stock solutions

Np/Pu Solution		Am Solution	
Element	Activity (dpm/mL)	Element	Activity (dpm/mL)
Np	4.98×10^7	Am	1.28×10^7
Pu	4.42×10^9		

To prepare the actinide solution for subsequent addition to the lactic acid/DTPA solution, a 250 µL aliquot of the Am stock solution was combined with 1 mL of the Np/Pu stock solution. A 100 µL aliquot of 1.77 M HAN was then added to reduce the Pu to Pu(III). The concentrations of Np (C_{Np}), Pu (C_{Pu}), Am (C_{Am}), and HAN (C_{HAN}) in this solution are calculated by equations A.1-A.4, respectively.

$$C_{Np} = \frac{\left(4.98 \times 10^7 \ \frac{\text{dpm}}{\text{mL}}\right)(1.0 \text{ mL})}{(1.0 \text{ mL} + 0.25 \text{ mL} + 0.10 \text{ mL})} = 3.69 \times 10^7 \ \frac{\text{dpm}}{\text{mL}} \quad \text{A.1}$$

$$C_{Pu} = \frac{\left(4.42 \times 10^9 \ \frac{\text{dpm}}{\text{mL}}\right)(1.0 \text{ mL})}{(1.0 \text{ mL} + 0.25 \text{ mL} + 0.10 \text{ mL})} = 3.28 \times 10^9 \ \frac{\text{dpm}}{\text{mL}} \quad \text{A.2}$$

$$C_{Am} = \frac{\left(1.28 \times 10^7 \ \frac{\text{dpm}}{\text{mL}}\right)(0.25 \text{ mL})}{(1.0 \text{ mL} + 0.25 \text{ mL} + 0.10 \text{ mL})} = 2.38 \times 10^6 \ \frac{\text{dpm}}{\text{mL}} \quad \text{A.3}$$

$$C_{HAN} = \frac{\left(1.77\ \frac{mol}{L}\right)\left(\frac{1\ L}{1000\ mL}\right)(0.10\ mL)}{(1.0\ mL + 0.25\ mL + 0.10\ mL)\left(\frac{1\ L}{1000\ mL}\right)} = 0.13\ \frac{mol}{L}$$

The actinide solution was then combined with an 11.4 mL aliquot of 1.9 M lactic acid/0.06 M DTPA to prepare the aqueous phase for the extractions. Once the solutions were combined, the pH was adjusted to nominally 2.8 or 3.5 using 3.9 M NH_4OH. The pH of the solution was measured using an Accumet® Basic AB15 pH meter which was calibrated using pH 1, 3, and 6 buffer solutions. During the preparation of the lactic acid/DTPA solution, we assumed that approximately 1.5 mL of NH_4OH would be required to adjust the pH to the desired value. The number of drops of NH_4OH required to perform the adjustment and the initial and final pH of the aqueous phase are provided in Table A.5 for each series of measurements.

Table A.5 Aqueous phase pH adjustment for TALSPEAK extractions

Experiment	Drops NH_4OH Added	Initial pH	Final pH
TAL-1	20	< 2.41⁽¹⁾	2.93
TAL-2	14	2.12	2.81
TAL-3	37	2.10	3.49
TAL-4	40	2.18	3.50
TAL-5	42	2.08	3.49

(1) Initial reading was incorrect due to electrode position.

The final concentrations of each component (Np, Pu, Am, HAN, lactic acid (C_{LA}), and DTPA (C_{DTPA})) in the aqueous phase are calculated by equations A.5-A-10. The calculations assume that nominally 1.5 mL of 3.9 M NH_4OH were added during the pH adjustments.

$$C_{Np} = \frac{\left(3.69 \times 10^{7}\ \frac{dpm}{mL}\right)(1.35\ mL)}{(1.35\ mL + 11.40\ mL + 1.50\ mL)} = 3.50 \times 10^{6}\ \frac{dpm}{mL} \qquad A.5$$

$$C_{Pu} = \frac{\left(3.28 \times 10^{9}\ \frac{dpm}{mL}\right)(1.35\ mL)}{(1.35\ mL + 11.40\ mL + 1.50\ mL)} = 3.10 \times 10^{8}\ \frac{dpm}{mL} \qquad A.6$$

$$C_{Am} = \frac{\left(2.38 \times 10^{6}\ \frac{dpm}{mL}\right)(1.35\ mL)}{(1.35\ mL + 11.40\ mL + 1.50\ mL)} = 2.25 \times 10^{5}\ \frac{dpm}{mL} \qquad A.7$$

$$C_{HAN} = \frac{\left(0.13\ \frac{mol}{L}\right)\left(\frac{1\ L}{1000\ mL}\right)(1.35\ mL)}{(1.35\ mL + 11.40\ mL + 1.50\ mL)\left(\frac{1\ L}{1000\ mL}\right)} = 0.0124\ \frac{mol}{L} \qquad A.8$$

$$C_{LA} = \frac{\left(1.9\ \frac{\text{mol}}{\text{L}}\right)\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)(11.4\ \text{mL})}{(1.35\ \text{mL} + 11.40\ \text{mL} + 1.50\ \text{mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)} = 1.5\ \frac{\text{mol}}{\text{L}} \qquad \text{A.9}$$

$$C_{DTPA} = \frac{\left(0.06\ \frac{\text{mol}}{\text{L}}\right)\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)(11.4\ \text{mL})}{(1.35\ \text{mL} + 11.40\ \text{mL} + 1.50\ \text{mL})\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)} = 0.05\ \frac{\text{mol}}{\text{L}} \qquad \text{A.10}$$

Appendix C

Np and Pu Distribution Coefficients

Measured Actinide Activities in the TALSPEAK Organic and Aqueous Phases

TALSPEAK extraction experiments were performed using an aqueous phase containing a 1.5 M lactic acid/ammonium lactate buffer and 0.05 M DTPA. The aqueous phase was adjusted to either pH 2.8 or 3.5. At pH 2.8, extraction experiments were performed at 20.0 and 59.0 °C. The experiments at pH 3.5 were performed at 20.0, 40.0, and 59.5 °C. The organic phase used for each extraction experiments was 1.0 M HDEHP in dodecane. Each experiment was performed in triplicate. The Np, Pu, Am, and Pa activities measured in each series of experiments are given in Tables C.1-C.5.

Table C.1 Activity measurements for Experiment TAL-1
(pH 2.8, temperature 20.0 °C)

Element	Organic Counts (dpm/mL)	1 sigma uncertainty (%)	Aqueous Counts (dpm/mL)	1 sigma uncertainty (%)
Np	1.12E+06	0.10	1.27E+05	0.37
Np	1.28E+06	0.10	1.35E+05	0.37
Np	1.16E+06	0.10	1.26E+05	0.37
Pu	1.82E+04	2.70	2.64E+05	0.26
Pu	2.27E+04	2.30	2.68E+05	0.20
Pu	1.90E+04	2.70	2.60E+05	0.25
Am	2.35E+05	0.30	6.37E+04	0.41
Am	2.71E+05	0.30	6.59E+04	0.40
Am	2.44E+05	0.30	6.32E+04	0.41
Pa	5.14E+05	0.10	4.66E+03	1.62
Pa	5.90E+05	0.10	5.97E+03	1.53
Pa	5.32E+05	0.14	3.99E+03	1.78

Table C.2 Activity measurements for Experiment TAL-2
(pH 2.8, temperature 59.0 °C)

Element	Organic Counts (dpm/mL)	1 sigma uncertainty (%)	Aqueous Counts (dmp/mL)	1 sigma uncertainty (%)
Np	2.57E+05	0.20	2.13E+05	0.20
Np	2.72E+05	0.20	2.02E+05	0.20
Np	2.14E+05	0.20	2.42E+05	0.20
Pu	5.01E+03	4.91	1.26E+05	0.40
Pu	5.88E+03	5.30	1.19E+05	0.40
Pu	4.05E+03	5.30	1.24E+05	0.40
Am	5.24E+04	0.60	3.63E+04	0.60
Am	5.26E+04	0.70	3.37E+04	0.70
Am	5.11E+04	0.70	3.56E+04	0.70
Pa	2.62E+05	0.20	6.97E+03	1.20
Pa	2.58E+05	0.20	1.13E+04	1.00
Pa	2.48E+05	0.20	8.80E+03	1.10

Table C.3 Activity measurements for Experiment TAL-3
(pH 3.5, temperature 20.0 °C)

Element	Organic Counts (dpm/mL)	1 sigma uncertainty (%)	Aqueous Counts (dmp/mL)	1 sigma uncertainty (%)
Np	3.76E+05	0.174	7.86E+04	0.411
Np	3.41E+05	0.176	8.36E+04	0.397
Np	3.51E+05	0.221	7.83E+04	0.410
Pu	5.14E+03	2.25	1.19E+05	0.352
Pu	5.34E+03	4.25	1.22E+05	0.341
Pu	5.84E+03	4.09	1.16E+05	0.359
Am	2.89E+04	1.11	5.57E+04	0.430
Am	2.82E+04	1.05	5.64E+04	0.507
Am	2.86E+04	1.18	5.32E+04	0.489
Pa	2.70E+05	0.198	2.70E+03	2.02
Pa	2.61E+05	0.202	2.79E+03	2.01
Pa	2.68E+05	0.200	2.98E+03	2.04

Table C.4 Activity measurements for Experiment TAL-4
(pH 3.5, temperature 59.5 °C)

Element	Organic Counts (dpm/mL)	1 sigma uncertainty (%)	Aqueous Counts (dmp/mL)	1 sigma uncertainty (%)
Np	1.29E+05	0.289	2.08E+05	0.246
Np	1.06E+05	0.320	1.04E+05	0.324
Np	1.11E+05	0.313	2.00E+05	0.249
Pu	2.62E+03	8.13	8.46E+04	0.497
Pu	1.98E+03	10.8	2.25E+03	9.01
Pu	1.64E+03	13.1	8.07E+04	0.510
Am	1.44E+04	1.70	4.70E+04	0.638
Am	1.43E+04	1.72	1.41E+04	2.00
Am	1.31E+04	1.71	4.51E+04	0.597
Pa	1.92E+05	0.240	2.30E+04	0.738
Pa	1.83E+05	0.248	1.79E+05	0.246
Pa	1.71E+05	0.256	2.48E+04	0.694

Table C.5 Activity measurements for Experiment TAL-5
(pH 3.5, temperature 40.0 °C)

Element	Organic Counts (dpm/mL)	1 sigma uncertainty (%)	Aqueous Counts (dmp/mL)	1 sigma uncertainty (%)
Np	2.95E+05	0.157	1.12E+05	0.373
Np	2.62E+05	0.208	1.15E+05	0.362
Np	2.76E+05	0.195	1.27E+05	0.354
Pu	4.94E+03	5.36	9.54E+04	0.443
Pu	4.85E+03	5.68	9.25E+04	0.450
Pu	5.01E+03	5.34	1.05E+05	0.436
Am	2.27E+04	1.30	4.76E+04	0.577
Am	2.19E+04	1.27	4.69E+04	0.584
Am	2.11E+04	1.29	5.24E+04	0.566
Pa	1.74E+05	0.254	2.21E+03	2.94
Pa	1.69E+05	0.257	3.45E+03	1.88
Pa	1.68E+05	0.258	3.94E+03	1.77

Calculated Distribution Coefficients

The actinide distribution coefficients were calculated for each of the extraction experiments using equation 1. The values are given in Tables C.6-C.10.

Table C.6 Calculated distribution coefficients for Experiment TAL-1
(pH 2.8, temperature 20.0 °C)

Element	$D_{An, o/a}$	1 sigma uncertainty (%)
Np	8.82E+00	0.39
Np	9.48E+00	0.39
Np	9.21E+00	0.39
Pu	6.89E-02	2.71
Pu	8.47E-02	2.30
Pu	7.31E-02	2.71
Am	3.69E+00	0.52
Am	4.11E+00	0.48
Am	3.86E+00	0.50
Pa	1.10E+02	1.62
Pa	9.88E+01	1.54
Pa	1.33E+02	1.78

Table C.7 Calculated distribution coefficients for Experiment TAL-2
(pH 2.8, temperature 59.0 °C)

Element	$D_{An, o/a}$	1 sigma uncertainty (%)
Np	1.21E+00	0.31
Np	1.35E+00	0.32
Np	8.84E-01	0.31
Pu	3.98E-02	4.92
Pu	4.94E-02	5.36
Pu	3.27E-02	5.35
Am	1.44E+00	0.89
Am	1.56E+00	1.00
Am	1.44E+00	1.00
Pa	3.76E+01	1.26
Pa	2.28E+01	1.02
Pa	2.82E+01	1.14

Table C.8 Calculated distribution coefficients for Experiment TAL-3
(pH 3.5, temperature 20.0 °C)

Element	$D_{An, o/a}$	1 sigma uncertainty (%)
Np	4.78E+00	0.45
Np	4.08E+00	0.43
Np	4.48E+00	0.47
Pu	4.32E-02	2.28
Pu	4.38E-02	4.26
Pu	5.03E-02	4.11
Am	5.19E-01	1.19
Am	5.00E-01	1.17
Am	5.38E-01	1.28
Pa	1.00E+02	2.03
Pa	9.35E+01	2.02
Pa	8.99E+01	2.05

Table C.9 Calculated distribution coefficients for Experiment TAL-4
(pH 3.5, temperature 59.5 °C)

Element	$D_{An, o/a}$	1 sigma uncertainty (%)
Np	6.20E-01	0.38
Np(1)	1.02E+00	0.46
Np	5.55E-01	0.40
Pu	3.10E-02	8.14
Pu(1)	8.80E-01	14.1
Pu	2.03E-02	13.2
Am	3.06E-01	1.82
Am(1)	1.01E+00	2.64
Am	2.90E-01	1.81
Pa	8.35E+00	0.78
Pa(1)	1.02E+00	0.35
Pa	6.90E+00	0.74

(1) Second replication is an outlying data point.

Table C.10 Calculated distribution coefficients for Experiment TAL-5
(pH 3.5, temperature 40.0 °C)

Element	$D_{An, o/a}$	1 sigma uncertainty (%)
Np	2.63E+00	0.40
Np	2.28E+00	0.42
Np	2.17E+00	0.40
Pu	5.18E-02	5.37
Pu	5.24E-02	5.69
Pu	4.77E-02	5.36
Am	4.77E-01	1.42
Am	4.67E-01	1.40
Am	4.03E-01	1.41
Pa	7.87E+01	2.95
Pa	4.90E+01	1.90
Pa	4.26E+01	1.79

van’t Hoff Analysis

The slope and y-intercept from the linear regressions performed to calculate the conditional enthalpies and entropies of extraction from the TALSPEAK distribution data are summarized in Table C.11.

Table C.11 Linear regressions results from van't Hoff analysis

pH	Element	Slope	Standard Deviation Slope	y-intercept	Standard Deviation y-intercept	Correlation Coefficient
3.5	Np	4762	584	-14.63	1.89	0.9578
	Pu	1261	597	-7.268	1.930	0.6529
	Am	1287	225	-5.004	0.729	0.9189
	Pa	5806	1085	-15.03	3.506	0.9093
2.8	Np	5173	315	-15.43	1.01	0.9927
	Pu	1559	332	-7.905	1.067	0.9201
	Am	2384	102	-6.774	0.328	0.9964
	Pa	3367	416	-6.756	1.338	0.9708

The conditional enthalpies and entropies of extraction for the actinide elements were calculated using equations C.1 and C.2, respectively,

$$\Delta H^0 = -\text{(slope)}\, R \tag{C.1}$$

$$\Delta S^0 = \text{(y-intercept)}\, R \tag{C.2}$$

where R is the ideal gas constant. The values are shown in Table 7 for each of the actinide element.