

# Photochemical Separation of Plutonium from Uranium.

## Supporting Information

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### Materials and Methods.

**General Consideration.** *Caution! The  $^{238}\text{Pu}$  [half-life ( $t_{1/2}$ ) = 87.7(1) y],  $^{239}\text{Pu}$  [ $t_{1/2}$  = 24,110(30) y],  $^{240}\text{Pu}$  [ $t_{1/2}$  = 6,561(7) y],  $^{241}\text{Pu}$  [ $t_{1/2}$  = 14.325(6) y], and  $^{242}\text{Pu}$  [ $t_{1/2}$  =  $3.75(2) \times 10^5$  y] isotopes – and their radioactive daughter products – present serious health threats because of their  $\alpha$ -,  $\beta$ -, and  $\gamma$ -emission and radioactive decay. Hence, all studies that involved manipulation of these isotopes were conducted in a radiation laboratory equipped with HEPA filtered hoods, continuous air monitors, negative pressure gloveboxes, and monitoring equipment for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -particle detection. Entrance to the laboratory space was controlled with a hand and foot monitoring*

instrument for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -emitting isotopes and a full body personal contamination monitoring station. Free-flowing solids were handled within negative pressure gloveboxes equipped with HEPA filters.

Plutonium used in this study was obtained as either residues from previous experiments, plutonium oxide, or in metallic form dissolved as previously described.<sup>1</sup> Depleted uranium used in these experiments was obtained as uranyl dichloride hydrate [ $\text{UO}_2\text{Cl}_2 \cdot (\text{H}_2\text{O})_x$ , Los Alamos National Laboratory legacy source] and uranyl nitrate hexahydrate [ $\text{UO}_2(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_6$ , Los Alamos National Laboratory legacy source]. All water used in these experiments was deionized and passed through a Barnstead water purification system until a resistivity of 18  $\text{M}\Omega$  was achieved. Optima grade aqueous solutions of hydrochloric acid [ $\text{HCl}_{(aq)}$ , Fisher], and nitric acid [ $\text{HNO}_{3(aq)}$ , Fisher] were obtained commercially and used as received. 2-propanol [ $(\text{CH}_3)_2\text{CHOH}$ , reagent grade, Sigma] and AG MP-1 anion resin 50-100 mesh (Bio-rad) were obtained commercially and used without further purification. Photochemical reactions were made using a Penn PhD Photoreactor M2 (Sigma) that was equipped with a 22,222.2  $\text{cm}^{-1}$  (450 nm) lamp. All irradiation experiments were performed in quartz fluorimeter cells (3 mL) that were equipped with screw top caps. Experiments were carried out in a fume hood or on the benchtop in sealed cuvettes, and no effort was made to exclude air and moisture.

**Preparation of a Uranyl(VI) Stock Solution.** In a fume hood and under ambient conditions, a solution (10 mL) of  $\text{UO}_2\text{Cl}_2 \cdot 2 \text{H}_2\text{O}$  (5.00 g, 14.7 mmol,  $\text{H}_2\text{O}$ ) was combined with a solution (10 mL) of CsCl (4.93 g, 29.3 mmol,  $\text{H}_2\text{O}$ ) in scintillation vial (25 mL). The solution (total volume = 20 mL) was filtered through a glass frit to remove an insoluble brown precipitate and the filtrate was transferred to a falcon tube (polyethylene, 50 mL). Concentrated  $\text{HCl}_{(aq)}$  (12 M, 3 mL) was

added dropwise to the tube and the yellow solution was gently swirled for 5 min. Leaving the vial uncapped and under a stream of filtered air for 16 h facilitated formation of long yellow crystalline needles of dicesium uranyl(VI) tetrachloride ( $\text{Cs}_2\text{UO}_2\text{Cl}_4$ ). The mother liquor was decanted from the crystals, the crystals were dried, and  $\text{Cs}_2\text{UO}_2\text{Cl}_4$  (900 mg, 1.311 mmol) was isolated in 9% crystalline yield. A  $\text{UO}_2^{2+}$  stock solution in HCl was prepared by dissolving  $\text{Cs}_2\text{UO}_2\text{Cl}_4$  (30.2 mg, 0.044 mmol) in  $\text{HCl}_{(aq)}$  (4.950 mL, 10 M) and adding  $(\text{CH}_3)_2\text{CHOH}$  (50  $\mu\text{L}$ ). The resulting solution was 8.9 mM in  $\text{UO}_2^{2+}$ , 17.8 mM in  $\text{Cs}^{1+}$ , nominally 10 M in  $\text{HCl}_{(aq)}$ , and 1% by volume  $(\text{CH}_3)_2\text{CHOH}$ .

**Photochemical Reduction of Uranyl(VI) to Uranium(IV).** In a fume hood and under ambient conditions, an aliquot of the  $\text{UO}_2^{2+}_{(aq)}$  stock solution (500  $\mu\text{L}$ ; 8.9 mM in  $\text{UO}_2^{2+}$ ; nominally 10 M  $\text{HCl}_{(aq)}$ , and 1%  $(\text{CH}_3)_2\text{CHOH}$  by volume) was added to a quartz cuvette that contained a stir bar. The solution was diluted with  $\text{HCl}_{(aq)}$  (500  $\mu\text{L}$ , 10 M) containing 2-propanol [ $(\text{CH}_3)_2\text{CHOH}$  1% by volume] to achieve a solution that was 4.45 mM in  $\text{U}^{6+}$  and nominally 10 M in  $\text{HCl}_{(aq)}$ . The cuvette was sealed and placed in a Penn PhD Photoreactor M2 that was equipped with a 22222.2  $\text{cm}^{-1}$  (450 nm) light emitting diode (LED) lamp. The LED intensity was reduced to 25%, which slowed rate of uranyl reduction to the point that it was monitored easily using absorption spectroscopy. The solution was stirred and irradiated for a total of 60 min. During the irradiation, we removed the cell from the photoreactor and monitored the uranyl photoreduction using UV-Vis spectroscopy at 1 min time points for the first 10 min, 5 min time points to 30 min, and 15 min time points to 60 min. The UV-Vis assays showed quantitative conversion of  $\text{UO}_2^{2+}_{(aq)}$  to  $\text{U}^{4+}_{(aq)}$  after 60 min of irradiation.

**Preparation of a Plutonium(IV) Stock Solution.** The following procedure was carried out in a fume hood and under ambient conditions. Be it dissolved plutonium oxide, dissolved plutonium metal, or a dissolved poorly defined plutonium residue, the plutonium source was purified as described previously.<sup>1</sup> This generated a chemically pure and oxidation-state pure  $\text{Pu}^{4+}_{(aq)}$  aqueous stock solution in  $\text{HCl}_{(aq)}$  (6 M). An aliquot (200  $\mu\text{L}$ , 3.6 mg Pu, 0.015 mmol Pu) of this  $\text{Pu}^{4+}_{(aq)}$  stock solution was transferred to a falcon tube (polyethylene, 50 mL). The aliquot was heated on a hotplate under a stream of filtered air until the liquid was removed and a soft dryness was achieved. The resulting residue was suspended in  $\text{HCl}_{(aq)}$  (1.980 mL, 10 M) and an aliquot of 2-propanol [ $(\text{CH}_3)_2\text{CHOH}$ ; 20  $\mu\text{L}$ ] was added. The resulting solution – which was 7.53 mM in plutonium, nominally 10 M in  $\text{HCl}_{(aq)}$ , and 1% by volume  $(\text{CH}_3)_2\text{CHOH}$  – was used for all subsequent plutonium experiments.

**Photochemical Reduction of Plutonium(IV) to Plutonium(III).** In a fume hood and under ambient conditions, an aliquot of the  $\text{Pu}^{4+}_{(aq)}$  stock solution [500  $\mu\text{L}$ ; 7.53 mM in Pu, 0.9 mg Pu; 0.0038 mmol; nominally 10 M in  $\text{HCl}_{(aq)}$ ] was added to a quartz cuvette that contained a magnetic stir bar. The solution was diluted with a solution that contained  $\text{HCl}_{(aq)}$  (500  $\mu\text{L}$ , nominally 10 M) and 2-propanol [ $(\text{CH}_3)_2\text{CHOH}$  1% by volume] to achieve a solution that was 3.765 mM in Pu and nominally 10 M in  $\text{HCl}_{(aq)}$ . The cuvette was sealed and placed in a Penn PhD Photoreactor M2 that was equipped with a 22222.2  $\text{cm}^{-1}$  (450 nm) LED lamp. The LED intensity was reduced to 25%, which slowed rate of plutonium reduction to the point that it was easily monitored using absorption spectroscopy. The solution was stirred and irradiated for a total of 60 min. During the irradiation, we removed the cell from the photoreactor and monitored plutonium photoreduction using UV-Vis spectroscopy at 1 min time points for the first 10 min, 5 min time points to 30 min, and 15 min

time points for the remaining 30 min. The UV-vis assays showed quantitative conversion of  $\text{Pu}^{4+}_{(aq)}$  to  $\text{Pu}^{3+}_{(aq)}$  after the full 60 min irradiation.

**Photochemical Separation of Plutonium from Uranium.** In a fume hood and under ambient conditions, an aliquot of the  $\text{UO}_2^{2+}_{(aq)}$  stock solution (500  $\mu\text{L}$ ; 4.5 mM uranium, 1.1 mg uranium, 0.0044 mmol; nominally 10 M in  $\text{HCl}_{(aq)}$ , 1% by volume 2-propanol) and an aliquot of the  $\text{Pu}^{4+}_{(aq)}$  stock solution (500  $\mu\text{L}$ ; 7.53 mM plutonium, 0.9 mg plutonium, 0.0037 mmol; nominally 10 M in  $\text{HCl}_{(aq)}$ , 1% by volume 2-propanol) were combined within a single quartz cuvette that contained a stir bar. To the same cuvette, AG MP-1 anion exchange resin (1 mL; mesh size = 50-100) was added, the cuvette was sealed, and the resulting brown mixture was briefly (1 min) agitated. The solution became colorless. The resin was allowed to settle (~5 min) and solution assayed using UV-vis spectroscopy. This measurement showed no absorbance from plutonium and uranium, confirming that  $\text{UO}_2^{2+}$  and  $\text{Pu}^{4+}$  had been bound by the resin and were no longer dissolved in solution. The cuvette was placed in a Penn PhD Photoreactor M2 that was equipped with a 22222.2  $\text{cm}^{-1}$  (450 nm) LED lamp. Then the mixture was stirred and irradiated for 30 min at 100% LED power during which time the solution became colored and electric blue. Analysis by UV-Vis spectroscopy showed (1)  $\text{Pu}^{3+}_{(aq)}$  in dissolved solution and (2) no detectable uranium. The solution was filtered through a Bio-Rad column (1 mL), washed with  $\text{HCl}_{(aq)}$  (1  $\times$  1 mL; 10 M), and labeled as “elution 1.” On a hot plate and under a stream of filtered air, the elution 1 solution volume was reduced to 1 mL. Subsequent analysis by ICP-MS showed elution 1 contained a 97.5% recovery of plutonium and the plutonium oxidation state was pure (90 % after 1 cycle) and +3. Meanwhile, dilute  $\text{HCl}_{(aq)}$  (0.5 M, 1 mL  $\times$  4) was loaded onto the column to strip all remaining actinides from the resin. This elution was labeled “elution 2.” On a hot plate and under a stream

of filtered air, the solution volume of elution 2 was reduced to 1 mL. Subsequent analysis using ICP-MS spectroscopy showed elution 2 contained uranium. The uranium recover was 90% and the uranium oxidation was pure (99% after 1 cycle) and +4.

### **Preparation of Plutonium(IV) and Uranyl(VI) Stock Solution in 1 M HNO<sub>3</sub>**

A UO<sub>2</sub><sup>2+</sup> stock solution in HNO<sub>3</sub> was prepared by dissolving UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O (155 mg) in 1 M HNO<sub>3</sub> (9.9 mL) and adding (CH<sub>3</sub>)<sub>2</sub>CHOH (100 μL). The resulting solution was 31 mM in UO<sub>2</sub><sup>2+</sup>, 1 M HNO<sub>3</sub> and 1% by volume (CH<sub>3</sub>)<sub>2</sub>CHOH. An aliquot (200 μL, 3.6 mg Pu, 0.015 mmol Pu) of the Pu<sup>4+</sup><sub>(aq)</sub> stock solution described above was transferred to a falcon tube (polyethylene, 50 mL). The aliquot was heated on a hotplate under a stream of filtered air until the liquid was removed and a soft dryness was achieved. The resulting residue was suspended in 6 M HNO<sub>3(aq)</sub>, (2 mL) returned to the hotplate and reduced to dryness again. The resulting residue was then suspended in 1 M HNO<sub>3</sub> (1.980 mL) and an aliquot of 2-propanol [(CH<sub>3</sub>)<sub>2</sub>CHOH; 20 μL] was added.

**ICP-MS Analysis.** The absolute concentrations of uranium and plutonium in separated process solutions were determined using isotope dilution inductively-coupled mass spectrometry (ID ICP-MS). Aliquots of the separated U and Pu fractions were prepared for analysis by first completing a series of analytical dilutions using optima-grade 2% nitric acid. A weighed portion of the final dilution sample was then combined with weighed aliquots of <sup>233</sup>U (LANL stock) and <sup>242</sup>Pu (analytical dilution of NIST SRM 4334g) isotope dilution spikes and then diluted to volume with optima-grade 2% nitric acid. The samples were analyzed using a Thermo X-series II quadrupole ICPMS equipped with a standard spray chamber. Samples were introduced with an Elemental Scientific, Inc. SC-2 DX autosampler using a parastaltic pump providing a flow rate of 0.3mL/min.

Under these conditions the  $^{238}\text{U}$  detection sensitivity is typically  $1.5\text{E}+05$  cps/ppb. The analytical samples were bracketed with solutions of NBS natural uranium SRM 960 to determine instrumental mass bias corrections as well as corrections at mass 239 from  $^{238}\text{UH}^+$ . Data was collected for isotopes: 233, 234, 235, 236, 238, 239, 240, 241, and 242. Instrumental mass bias across this range was also verified using IRRM 74/1 and NBL CRM 128.

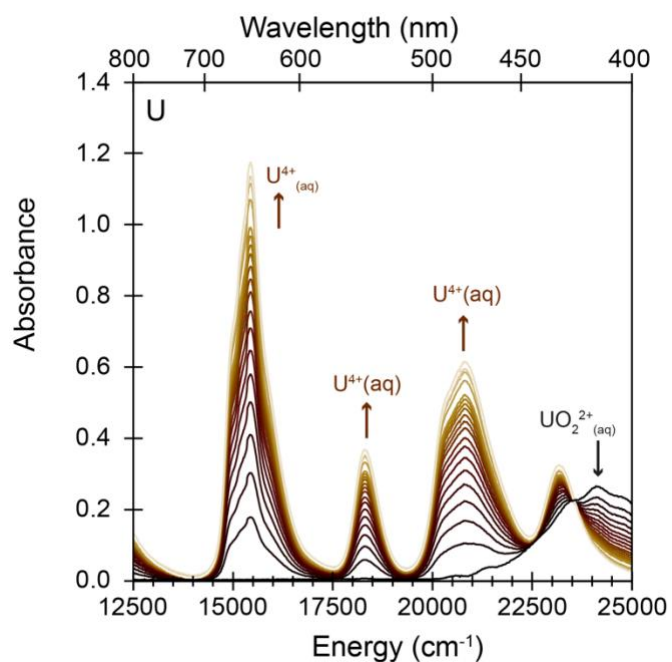
## Supporting Data.

**NMR Results.** All NMR spectra were collected on a Bruker Avance 400 MHz spectrum operating with a 5 mm broadband probe.  $^1\text{H}$  NMR data was collected at 400.13 MHz in  $\text{H}_2\text{O}$  (spiked with  $\text{D}_2\text{O}$  to allow for locking) and referenced to the residual 2-propanol solvent peak at 1.18 ppm.

**Acetone in Uranyl System:**  $^1\text{H}$  NMR ( $\text{H}_2\text{O}$  400 MHz):  $\delta_{\text{H}}$  1.18 (d, 6H,  $(\text{CH}_3)_2\text{CHOH}$ ), 2.23 (s, 6H,  $(\text{CH}_3)_2\text{CO}$ ), 4.13 (m, 1H,  $(\text{CH}_3)_2\text{CHOH}$ )

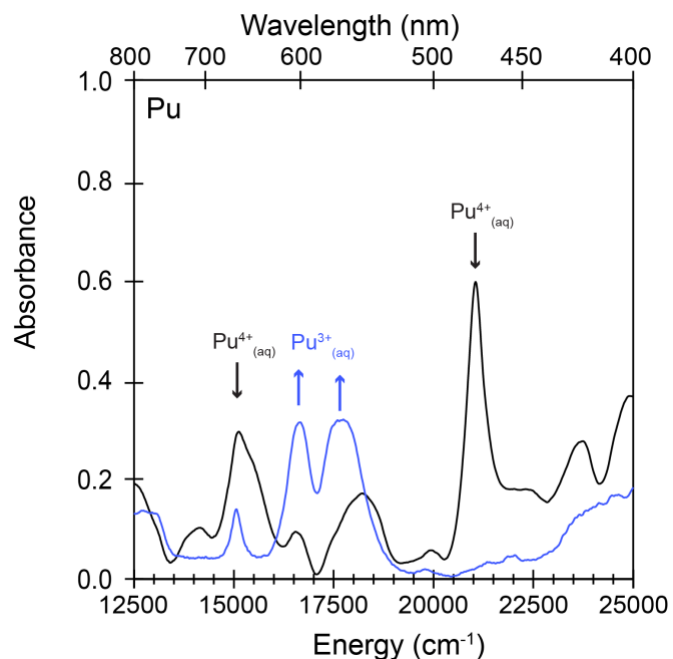
**NOTE:** To overcome issues with the locking the NMR from paramagnetic plutonium, the plutonium was predicated using ammonium hydroxide ( $\text{NH}_4\text{OH}$ , 15 M, dropwise addition) prior to NMR spectroscopic analysis. The solid  $\text{Pu}(\text{OH})_x$  was then removed by filtration and the sample was subsequently analyzed.

**Acetone in Plutonium System:**  $^1\text{H}$  NMR ( $\text{H}_2\text{O}$  400 MHz):  $\delta_{\text{H}}$  1.18 (d, 6H,  $(\text{CH}_3)_2\text{CHOH}$ ), 2.21 (s, 6H,  $(\text{CH}_3)_2\text{CO}$ ), 4.05 (m, 1H,  $(\text{CH}_3)_2\text{CHOH}$ )



**Figure S1. UV-Vis spectra obtained during photoreduction of a pristine solution of  $\text{UO}_2^{2+}_{(aq)}$ .**  $\text{UO}_2^{2+}$  (black trace) was reduced to  $\text{U}^{4+}_{(aq)}$  (gold trace). All spectra were obtained in  $\text{HNO}_3_{(aq)}$  (1 M) that was spiked with  $(\text{CH}_3)_2\text{CHOH}$  (1% by volume) and irradiations utilized a Penn Photoreactor with an excitation energy of  $22,222.2 \text{ cm}^{-1}$  (450 nm).





**Figure S2. UV-vis spectra obtained before and after photoreduction of a pristine solution of Pu<sup>4+</sup>.** Pu<sup>4+</sup> (black trace) was reduced to Pu<sup>3+</sup><sub>(aq)</sub> (blue trace). Spectra were obtained in HNO<sub>3(aq)</sub> (1 M) that was spiked with (CH<sub>3</sub>)<sub>2</sub>CHOH (1% by volume) and irradiations utilized a Penn Photoreactor with an excitation energy of 22,222.2 cm<sup>-1</sup> (450 nm).

## References

- (1) S. K. Cary, K. S. Boland, J. N. Cross, S. A. Kozimor, B. L. Scott. *Polyhedron*, 2017, **126**, 220–226.