

Controlling Plutonium Oxidation State for the Development of a Reliable Solution-Phase Assay

Sara Adelman^{1*}, Nell Carver¹, Tony Cava¹, Robert Jump¹, John Matonic¹, Kimberly Muscarella¹, Bianca Ramirez¹

¹Los Alamos National Laboratory, Los Alamos NM; *sadelman@lanl.gov

The redox mobility of plutonium is both a blessing and a curse; thus, controlling the oxidation state of plutonium lies at the heart of its solution-state chemistry. One important target oxidation state is Pu(VI) (PuO_2^{2+}) due to its structural similarities to UO_2^{2+} and NpO_2^{2+} , its interaction with common extractants used in separation schemes, and its strong optical absorption peak that can be used for solution-phase quantification. The formation of PuO_2^{2+} typically requires strong chemical oxidants such as ozone, silver(II), cerium(IV), or dichromate. Once formed, PuO_2^{2+} typically survives in isolation for a few hours to a few days depending on environmental and solution conditions. When PuO_2^{2+} is the target for a quantitative analytical assay, it is crucial to understand its stability to ensure reliable and robust measurements. This work investigates the formation and subsequent stability of PuO_2^{2+} in cerium(IV)-containing nitric acid media using near-infrared optical absorption spectroscopy (NIRS). Our work identifies conditions that stabilize PuO_2^{2+} in solution without the exclusion of air for several months. Additionally, we confirmed that sulfate is an excellent ligand for PuO_2^{2+} and readily complexes the ion even in extreme excess of nitrate. These results demonstrate that controlling plutonium oxidation state and speciation in solution enables the development of a robust and reliable quantification technique.