

Electrochemically-Modulated Separation and Mass Spectrometric Analysis of Actinides in Difficult Matrices

Douglas C. Duckworth, Scott A. Lehn and Martin Liezers

Pacific Northwest National Laboratory, Richland, WA

The goal of this research is to develop electrochemically “switchable” separations that can be performed on-line with mass spectrometry for rapid elemental and isotopic analysis of actinides. The separation of uranium and plutonium, as well as other actinide elements, from complex solutions such as seawater, radioactive wastes and nuclear reprocessing solutions will benefit from a separation process that does not employ redox chemicals but instead relies solely on potentials applied to chemically modified target electrodes. Such an approach requires very little power and is easily automated. It is therefore readily employed in harsh environments for remote sampling and analysis.

Electrochemically-modulated separations (EMS) are a straightforward means of isolating and preconcentrating elements for analysis and may include a variety of traditional electrochemical stripping techniques in which elements (e.g. Ag, Tl, Cd, Pb) are accumulated at electrochemical working electrodes and subsequently stripped off into a clean carrier solution for spectroscopic analysis [1]. EMS can employ solely aqueous chemistry and uses electrochemical redox adjustment of oxidation state to “trigger” reversible chelation / complexation. Less tractable elements (e.g., uranium and plutonium), based on redox potentials, can therefore be extracted from difficult matrices following redox adjustment and chelation with electrode chelation sites [2, 3]. Simply put, separation is achieved by a small voltage step that is applied to the target electrode to turn “on” or “off” the specific actinide affinity of an electrode. This separation technology employs both redox and chelation chemistry to effect highly selective accumulation of target actinides, and results in element separation, matrix elimination and analyte preconcentration.

Prior studies have developed protocols and preliminary insight into EMS processes for U and Pu [2,3]. A simple approach to chemical modification of the electrode surface has been used that requires only the electrochemical activation (oxidation) of glassy carbon (GC) electrodes via anodization in nitric acid. Separation occurs following redox adjustment of solvated cations in solution. Uranium is bound to oxygen moieties at the anodized glassy carbon (AGC) surface, presumably upon adjustment to U(IV). In contrast, Pu(IV) complexes form with interstitial anions (nitrate, sulfate) deposited during anodization of the GC [2]. U and Pu analytes are released upon oxidation and reduction, respectively, allowing complete separation due to widely divergent redox potentials. This presentation will highlight the coupling of EMS on-line with ICP-MS for elemental and isotopic analysis of uranium and plutonium, with a focus on empirical optimization studies and analytical performance metrics.

1. Zhou, F.M., *Stripping analysis combined on-line with inductively coupled plasma-atomic emission spectrometry and with inductively coupled plasma-mass spectrometry*. *Electroanalysis*, 1996. **8**(10), 855.
2. Clark, W.J., William J. Clark, Jr., Sea H. Park, Debra A. Bostick, Douglas C. Duckworth, and Gary J. Van Berkel, *Electrochemically modulated separation, concentration, and detection of plutonium using an anodized glassy carbon electrode and inductively coupled plasma mass spectrometry*. *Analytical Chemistry*, 2006. **78**(24), 8535.
3. Pretty, J.R., D.C. Duckworth, and G.J. Van Berkel, *Electrochemical sample pretreatment coupled on-line with ICP-MS: Analysis of uranium using an anodically conditioned glassy carbon working electrode*. *Analytical Chemistry*, 1998. **70**(6), 1141.