

## **Electrochemically-modulated Separation and Analysis of Uranium and Plutonium**

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Typical separation methods for uranium, plutonium, and other actinides rely on time-intensive conventional redox and column chemistry, and are prone to sample specific variability. An alternative method for actinide separation, electrochemically-modulated separation (EMS), promises to significantly reduce bench top chemistry, required time, matrix dependence, and waste generation. EMS, which utilizes the ability to change a surface's analyte retention by changing the voltage of an electrode exposed to the sample, is in some cases similar to electrochemical stripping analysis, although usually more sensitive, selective, and robust when coupled with mass spectrometric detection. Problems common to electrochemical stripping analysis such as high hydrolysis currents and gas generation are avoided by mass spectrometric detection, and EMS allows greater flexibility in electrode and analyte chemistry. EMS is essentially a two step process; (1) an electrochemical extraction in which the analyte is concentrated in or on the electrode and (2) stripping the target element into a clean solution, resulting in a concentrated solution that can be loaded for thermal ionization mass spectrometry or analyzed on-line by inductively-coupled plasma mass spectrometry (ICP-MS).

Development work at ORNL has demonstrated separation of uranium from seawater, arguably one of the most difficult matrices, with on-line analysis by a simple ICP-quadrupole MS. Preliminary results for plutonium are encouraging. In addition to providing rapid separations, EMS provides a dramatic enhancement in sensitivity for on-line analytical methods, improving detection capability in the plutonium experiments by 50-100x compared to direct analysis of the original analyte solution. Results from a new experimental set-up, operational this spring, using an electrochemical cell interfaced with an ICP-TOF-MS (time-of-flight mass spectrometer), will also be presented.

In addition to offering greater speed and reduced costs, the EMS method is very flexible. It is amenable to large volume sampling or analysis of very small samples, and can be targeted to a wide variety of additional elements. Both isotopic and concentration determinations can be performed, and the technique is potentially adaptable to automated sample preparation.

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