

Electrochemically-Modulated Separation and Concentration of Actinides Including Uranium and Plutonium

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ABSTRACT

A method has been developed and used on-line with inductively couple plasma mass spectrometry for the rapid separation and concentration of uranium prior to elemental and isotopic analysis. This methodology is termed electrochemically-modulated separation (EMS) and relies on the ability to change the analyte retention of a surface by changing (i.e., modulating) the voltage applied to an electrode exposed to the sample. In this work, EMS is coupled to an inductively coupled plasma time of flight mass spectrometer (ICP-TOF-MS); the hybrid approach is found to improve the sensitivity by nearly two orders of magnitude and vastly reduces bench top chemistry. Separation of uranium, as well as other elements, can be effected in minutes with minimal chemistry. The utility of ICP-TOF-MS for isotopic analysis of transient signals is demonstrated. Useful isotope ratios are determined directly from the analysis of a non-diluted seawater sample, arguably one of the most challenging matrices. Proof-of-principle experiments are shown that a similar approach is suitable for plutonium separations

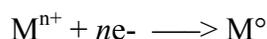
INTRODUCTION

Presently, trace levels uranium and plutonium are separated from a variety of environmental samples including: water, soils, sediments, vegetation and various filter and concentrating materials for thermal ionization mass spectrometry (TIMS) analyses by a variety of ion exchange techniques. The chemical separation is time consuming and costly, and generates significant amounts of waste requiring disposal. Often, methods have to be customized for each sample media and must provide exceedingly high decontamination factors to be compatible with mass spectrometric analysis. The EMS technique presented here promises to decrease required time, reduce the cost and improve the performance of the chemical separation for mass spectrometric analysis.

Electrochemically-modulated separation (EMS) is in most cases, similar to electrochemical stripping analysis [1], though usually more sensitive, selective and robust when combined with mass spectrometry. Problems common to electrochemical stripping analysis such as high hydrolysis currents and gas generation are avoided with mass spectrometric detection. The method relies on the ability to change the analyte retention of a surface by changing (i.e., modulating) the voltage applied to an electrode exposed to the sample. Electrochemical accumulation has been exploited as a means of matrix removal in several areas of atomic spectrometry, including ICP-AES [2] and ICP-MS [3-5]. These hybrid approaches have been thoroughly reviewed [6] and are known to have greater sensitivity, specificity, and utility than either of the techniques alone.

ORNL has been investigating the use of flow-by microliter volume electrochemical cells for specific analyte concentration and cleanup prior to detection by ICP-MS [7-10]. We demonstrated that a thin-layer, flow-by cell design yielded high analyte deposition efficiency and matrix elimination capabilities. The EMS-ICP-MS provided > 100-fold signal enhancements with less than 250 μL of sample [11] and required a total analysis time of only 5 minutes. Efficient matrix elimination was also demonstrated. We recently reported on a novel separation scheme for uranium that is used in this study and involves an anodized glassy carbon working electrode [10].

EMS is basically a two-step process involving a preconcentration step (at the working electrode) and a stripping step. The first step of the procedure is an electrolytic accumulation (deposition) of the analyte from the sample solution onto the working electrode; the corresponding electrochemical reaction is



which results in a metallic film on the surface. This first electrolytic step is in effect an electrochemical extraction in which the analyte is preconcentrated in or on the electrode at a much higher level than it exists in solution (generally 100-1000 times greater depending on the deposition time). Furthermore, the extraction can be element-specific based on the redox potentials or a bulk deposition (all metals accumulated) when mass spectrometer specificity is adequate for the resolution of chemical interferences and matrix effects are not limiting. For example, TIMS is sensitive to concomitant elements which must be removed in separation, while ICP-TOF-MS is largely matrix insensitive and bulk accumulation will suffice.

The second step of the method, referred to as stripping, involves oxidation of the metal from the electrode surface back into the solution according to the reaction



with a concurrent measurement of the current flow at the electrode. In a flow system, rapidly stripping the metal back into solution results in a highly concentrated solution of the metal ions of interest which is presented to the mass spectrometer and is detected as a transient peak.

Inductively coupled plasma mass spectrometry, introduced in the 1980's, is a mainstay technique for elemental analysis due to its broad element coverage and sensitivity. Recent coupling of this source with TOF-MS provides "psuedo-simultaneous" detections for full elemental and isotopic coverage. Additionally, up to 30,000 spectra are recorded per second. These advantages make ICP-TOF-MS ideal for isotopic analysis of transient analyte such as those generated via EMS.

EXPERIMENTAL

Mass spectral data for uranium were acquired with a Optimass 8000 (GBC Scientific, Inc., Melbourne Australia), fitted with a Micromist nebulizer and a cyclonic spray chamber operating with a solution uptake of 80-100 μL per minute and a 2 second accumulation period. Plutonium data was generated in a single ion monitoring mode on a VG Plasmaquad II (VG Elemental,

Winsford, Cheshire, UK) fitted with a model M2 microconcentric nebulizer (CETAC Technologies, Inc, Omaha, NE).

A gas displacement pump was used for sample delivery through the thin-layer electrochemical cell shown in Figure 1. The working electrode is a 6 mm diameter glassy carbon disk, embedded in a PEEK block (Bioanalytical Systems, Inc., West Lafayette, IN). The counter electrode is a rectangular platinum foil, press-fit and epoxied into a PEEK block. The Teflon spacing gasket (Bioanalytical Systems, Inc.) is 16 μm thick, defining a cell volume of $\sim 1.1 \mu\text{L}$. A Ag/AgCl reference electrode (model RE-3, Bioanalytical Systems, Inc.) makes contact with the solution at the center of the cell via a 500- μm i.d. channel.

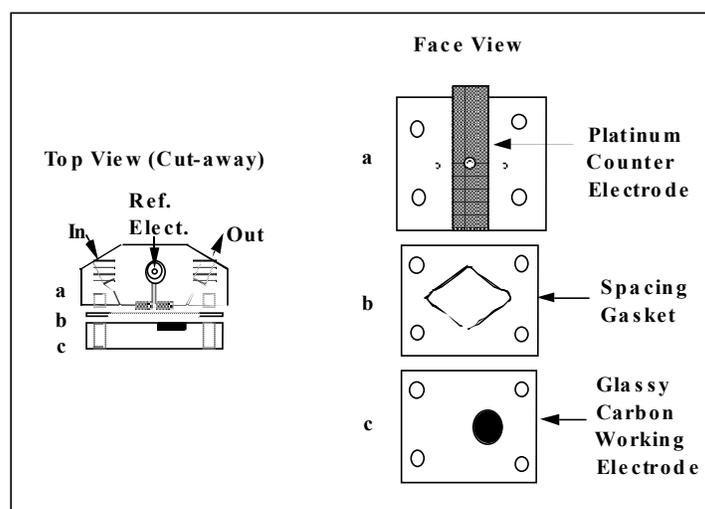


Figure 1. Schematic of thin-layer flow-by electrochemical cell.

RESULTS

No electrochemical affinity for uranium is observed prior to anodization of the GC electrode. The anodization procedure involves holding the GC working electrode at +1.85 volts for several minutes in the presence of 1% (v/v) HNO_3 . The anodized electrode is quite robust and can be used for more than eight hours without regeneration of the oxidized surface. The surface remains active, though performance can be degraded when fouled with organic species. Shown in Figure 2 is a temporal signal profile generated using a 10 ng/mL stock solution of U. A 1 mL sample loop was used to initiate the experiment. The sample was injected while holding the electrode at +0.2 V, allowing a continuous nebulization signal level to be obtained. Stepping the voltage to -0.2 resulted in deposition of U on the GC electrode with a 67% deposition efficiency. Uranium was accumulated at this potential for 3.5 minutes, followed with a 1 minute rinse out using 1% (v/v) HNO_3 . Following the rinse, the GC working electrode potential was stepped to +1.20 V. In this oxidation step, the U accumulated from < 0.35 mL of sample is stripped back into the $\sim 1 \mu\text{L}$ volume, resulting in a volumetric concentration and a signal enhancement of 28.8 over the continuous nebulization signal.

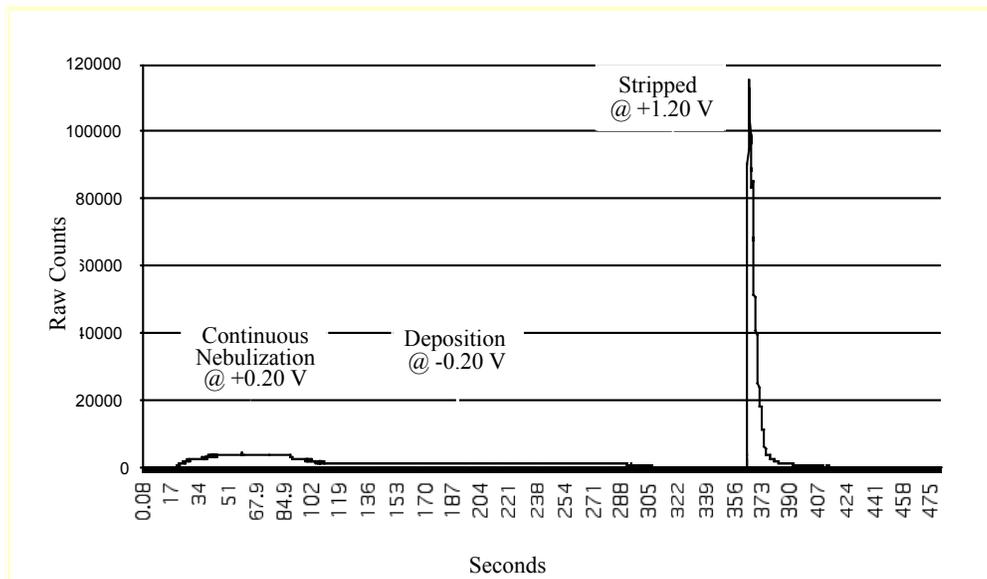


Figure 2. Temporal signal profile of EMS-ICP-TOF-MS ^{238}U (10 ng/mL U).

It should be noted that the experiment above required only the use of potential to effect the accumulation of U. No chemical elution is required in distinct contrast to column chemistries, where changes in mobile phase or pH are required that can result in sample contamination

EMS-ICP-TOF-MS of uranium in seawater is demonstrated in Figure 3. Given the high level of dissolved solids, seawater is arguably one of the most challenging matrices for ICP-MS. In this application, uranium was selectively accumulated on an anodized glassy carbon electrode directly from seawater with no dilution — the required electrolyte is naturally present in this matrix. The separation is highly specific for uranium. To date, the only element known to codeposit with U is Th.

During deposition, all salts that were not deposited were directed away from the ICP to waste. All of the isotopes were monitored simultaneously for the Certified Reference Material NASS-4 Open Ocean Seawater. Uranium concentration is 2.68 ng/mL. The uranium was accumulated for 3 min prior to stripping (~0.3 mL sample consumed) and the results for ^{234}U , ^{235}U , and ^{238}U are shown in Table 1. It is noteworthy that only 44 femtograms of ^{234}U is required to determine an isotopic value that, in the absence of bias and detector deadtime correction, is in within a factor of two from natural abundance.

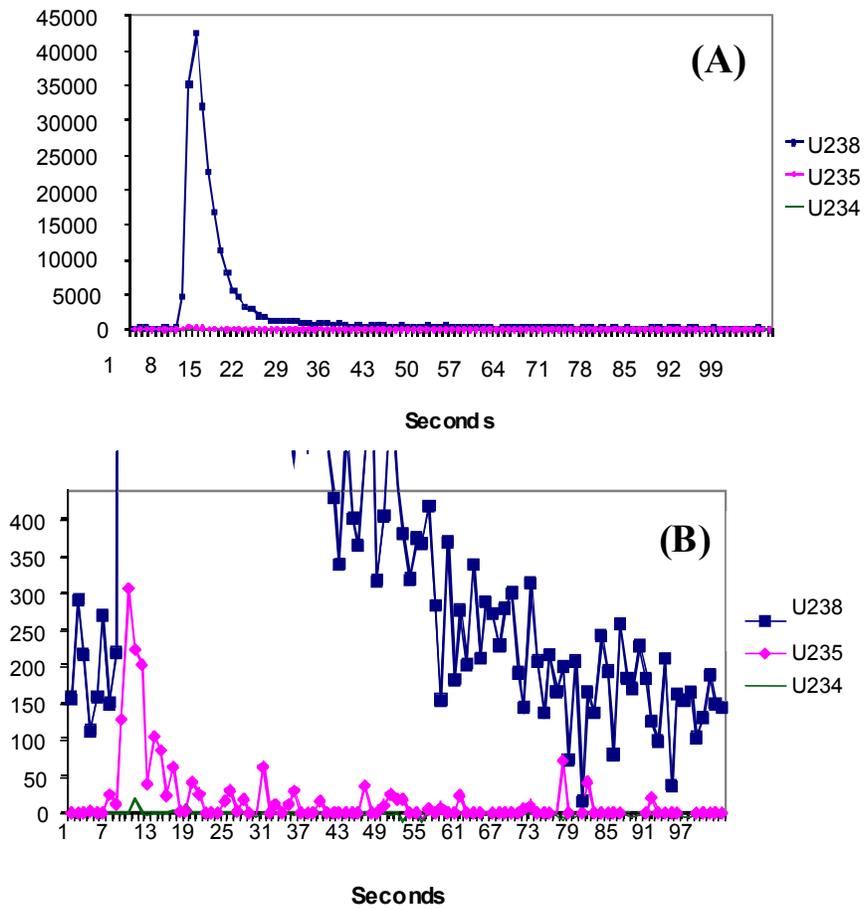


Figure 3. Isotope signal profiles for uranium following EMS from undiluted NASS-4 Open Ocean Seawater (A) x 1 and (B) x 100.

Table 1. Isotopic analysis of uranium (2.68 ng/ml) in NASS-4 Open Ocean Seawater by EMS-ICP-TOF-MS.

<i>Isotope</i>	<i>234U</i>	<i>235U</i>	<i>238U</i>
Isotopic Concentration, ng/ml	0.000147	0.0193	2.66
Sample Size, g	4.4E-14	5.78E-12	7.98E-10
Atom % Measured	0.0031	0.72	99.28
Atom % Nat. Abundance	0.0055	0.72	99.27

Proof-of-principle experiments shown in Figure 4 show that this approach is promising for plutonium separations. Here, two ^{242}Pu peaks are shown (two successive experiments), each stripped following extraction from a 400 fg/ml solution (800 μL total sample size). The volumetric concentration effect is seen in comparing the stripped Pu peaks to the area representing the continuous nebulization signal. The detection capability is increased 50-100 times. Unlike U however, Pu is apparently deposited onto and stripped from the platinum counterelectrode as +1.15 V and -0.15 V, respectively, was applied to an anodized glassy carbon working electrode. This conclusion is consistent with the experiments of Almon, who first demonstrated the ability to perform differential pulse stripping voltammetry of Pu on a Pt working electrode [12]. In our studies, Pu was extracted from a 320fg Pu sample in 800 μL and detected well above typical signals for this concentration. Performed off-line, this separation should be suitable for the preparation of small quantities of Pu for TIMS.

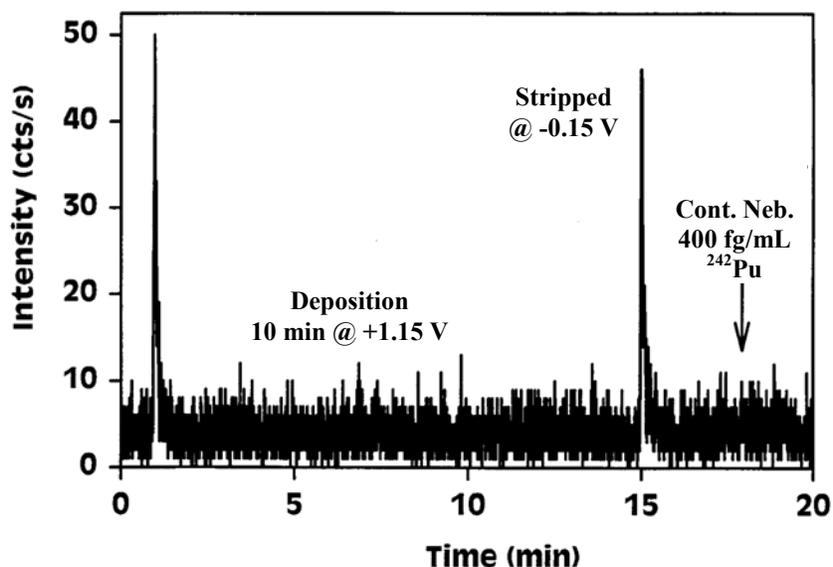


Figure 4. Temporal signal profile of successive EMS-ICP-MS measurements of ^{242}Pu (400 fg/mL, 10 min deposition).

CONCLUSIONS

It is thought that laboratories practicing conventional column separations will benefit from the rapid EMS separations of U and Pu. EMS, particularly when coupled on-line with mass spectrometry, will result in significant time savings by eliminating the sample-to-sample variability encountered with conventional redox and column chemistry. It is anticipated that the electrolytic nature of this technique will provide more reproducible redox chemistry, which is free from interferences of elements outside the Pu redox chemical window. The preconcentration and selectivity afforded by electrochemical stripping techniques will provide increased sensitivity and the elimination of matrix- and sample preparation-related problems (chemical and physical). The simplicity of the system will result in ease of use as well as high sample throughput. EMS system will provide a means of rapid (and potentially automated) sample separation/concentration. The ability to use multiple electrodes in the EMS procedure or the use of tandem electrodes should allow simultaneous collection/separation of U and Pu. This work also has the potential to be extended to other elements of interest.

ACKNOWLEDGEMENT

Research sponsored by the Office of Research and Development, U.S. Department of Energy, under Contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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