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

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Overview

Electrochemically-modulated separations (EMS) are shown to be simple and effective sampling approaches for U and Pu that can be performed on-line with ICP-MS

Introduction

Electrochemically-modulated separation (EMS) involves a redox "switchable" process in which, under controlled potential, an analyte is:

- selectively accumulated from solution
- released into a clean solvent for analysis

EMS is a promising method for sampling difficult matrices such as those with high dissolved solids or highly radioactive solutions and is readily amenable for use on-line with inductively coupled plasma mass spectrometry (ICP-MS).

Benefits of using EMS on-line with ICP-MS in harsh environments and for difficult matrices

- Minimal sample handling
- Redox and m/z specificity
- Efficient matrix elimination
- Dilutions not required prior to ICP-MS
- No redox chemicals
- Solely aqueous chemistry
- Chemistry within a closed system
- Volumetric concentration of analyte
- Improved S/N and S/B
- Rapid (high throughput) elemental and isotopic analysis

EMS 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 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]. This separation technology employs both redox and chelation chemistry to effect highly selective accumulation and is shown here for U and Pu.

Experimental

- EMS experiments are performed using a customized (Bioanalytical Systems, Inc.) amperometric (flow-by) electrochemical cell (Figure 1a-1c) interfaced to the ICP-MS. This three electrode system includes a Ag/AgCl reference electrode, Pt auxiliary electrode, and an offset anodized 6 mm diameter glassy carbon working electrode (Shown with a 4 electrode configuration in Figure 1b).
- A CH Instruments Model 832B potentiostat (CHI 1220A shown in Figure 2) controls the EMS experiments
- A gas displacement pump provides solution flow and is controlled using an automated FAST flow injection valve (Elemental Scientific).

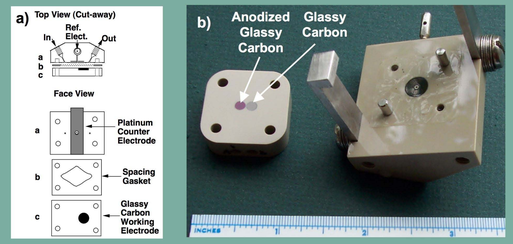

Figure 1a) Schematic of the three electrode flow cell. Figure 1b) Flow-By Electrochemical Cell, shown with dual working electrodes, anodized glassy carbon (left) and glassy carbon (right). This anodized glassy carbon electrode was conditioned in 0.46 M nitric acid using multiple double-potential steps (+1.85 & +0.85 V vs. Ag/AgCl, 20 sec/cycle)

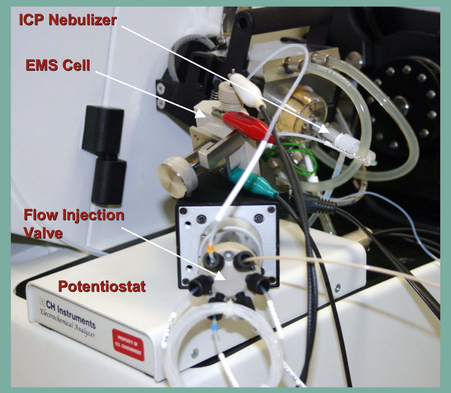

Figure 1c. Flow-by Electrochemical Cell Interfaced with ICP-MS

- Procedure: A glassy carbon (GC) electrode is anodized at highly positive potentials (1.85 V vs Ag/AgCl) in HNO_3
- Mass spectral signal is stabilized at a non-accumulating potential
- Potential of the GC electrode is stepped to an accumulating value (more positive for Pu, more negative for U)
- Analyte is retained on the GC electrode at accumulating potential while rinse solution eliminates matrix species
- Potential of the GC electrode is stepped to a releasing potential (negative for Pu, positive for U) allowing analyte to flow into MS

Results and Discussion

- The selective nature of the EMS process for U is shown in Figure 2
  - U is retained at ~ -0.2 V
  - U is released at ~ +1.0 V
  - Replicates are highly reproducible

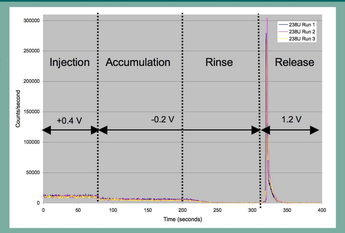

Figure 3. Three step process for accumulation and release of uranium

- The selective nature of the EMS process for Pu is shown in Figure 3a-b
  - ^{244}Pu (4.2 ppt) is retained at potentials ~ +1.0 V, but U is retained only at potentials < -0.15 V and is not accumulated
  - Pu signal intensity is enhanced by a factor of 70x over continuous nebulization conditions following a 15 minute accumulation
  - Pu deposition efficiency varies from 50% at the outset to ~20% prior to rinsing
  - Following preconcentration, ^{239}Pu signal is detectable at a concentration of 220 attograms; no evidence of $^{238}U+^{1}H^{+}$ is noted
- Figure 4 shows that EMS can be used to isolate and preconcentrate uranium from very complex solutions, including seawater[4]

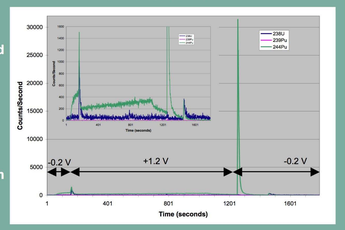

Figure 3a. EMS showing selective plutonium preconcentration from a solution containing both plutonium and adventitious uranium

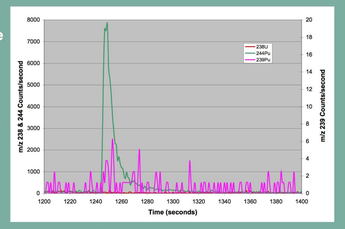

Figure 3b. ^{239}Pu (220 attogram) signal detected above background due to EMS preconcentration from a solution containing both plutonium and adventitious uranium

Uranium in NASS-4 Open Ocean Seawater

Isotope	234U	235U	238U
Isotopic Concentration (ng/ml)	0.00016	0.0193	2.66
Sample Size (gram)	4.9E-14	5.78E-12	7.98E-10
Atom % Measured	0.003	0.72	99.28
Atom % Certified Abundance	0.006	0.72	99.27

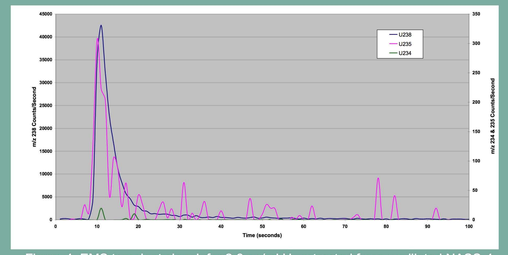

Figure 4. EMS transient signal for 2.6 ng/ml U, extracted from undiluted NASS-4 Open Ocean Seawater

- EMS-ICP-MS provides a rapid means of isotope ratio measurement
  - ^{239}Pu isotopic analysis is facilitated by the reduction in $^{238}U+^{1}H^{+}$ via uranium matrix elimination
  - (Figure 5) Pu mass responses and isotope ratios are measured in the presence of a 15,000-fold excess of U
  - Accurate $^{239}Pu/^{244}Pu$ ratios are quite discernable at [^{239}Pu]=2.17 ppq on a quadrupole mass spectrometer ($^{239}U/^{244}Pu$ = 5 x 10^{7})

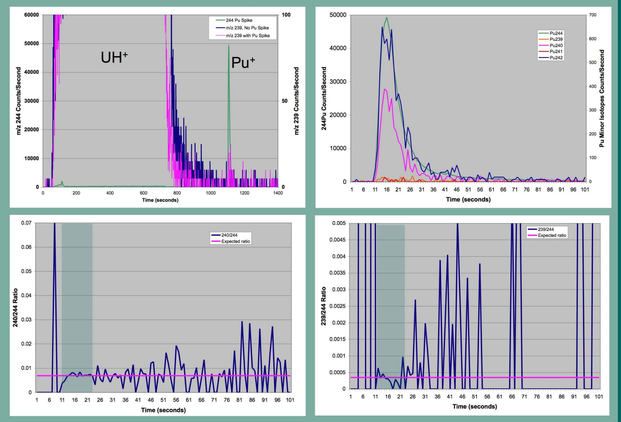

Figure 5. Use of EMS coupled on-line with quadrupole ICP-MS. ^{239}Pu is selectively accumulated and analyzed in the presence of $^{238}U+^{1}H$. Isotopic ratio comparison of masses 238, 239, and 244 confirms the observation. U was 15,000 times more concentrated (94 ppb U) than ^{244}Pu in the sample solution and 5 x 10^{7} more concentrated than ^{239}Pu.

- Analysis of isotopic ratios of ^{239}Pu to ^{244}Pu using EMS coupled to multicollector (MC) ICP-MS instrument (ThermoElectron Neptune)[4]
  - Accomplished in the presence of U despite [U] > 1000x [Pu] resulting in significant levels of $^{238}U+^{1}H$ as interfering species

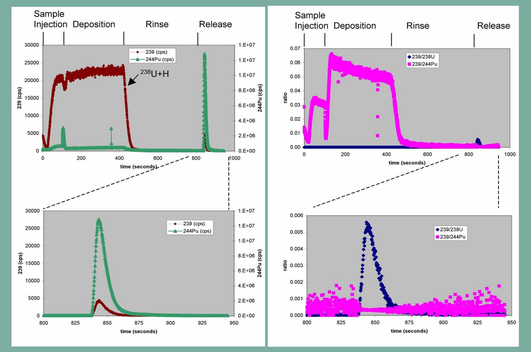

Figure 6. Use of EMS coupled with a multicollector (MC) ICP-MS.[3] U was three orders of magnitude more concentrated than Pu in the sample solution.

Conclusions

- A novel approach to Pu and U separation, preconcentration and analysis has been developed that is highly selective for U and Pu
  - Retention at very different potentials allows mixed U/Pu samples to be rapidly analyzed
  - Very applicable to difficult matrices and harsh environments
- The EMS process is very promising for analytical applications
  - Reduced chemical noise
  - Rapid, on-line separations
- The combination of redox chemistry, surface complexation chemistry, and m/z specificity provide a very selective approach to elemental and isotopic analysis

Future Studies

- Optimize EMS parameters for U
- Integrate ESI SC-2 auto-sampler
- Develop and characterize EMS-MC-ICP-MS and compare to conventional separations and analysis via thermal ionization MS
- Extend EMS to other actinides (Np, Am, Cm) and applications

References

1. Feimeng Zhou, (2005) "Electrochemistry Combined On-Line with Atomic Mass Spectrometry and Related Techniques for Trace-Metal Analysis and Electrode-Reaction Studies", *Trends Anal. Chem.*, 24(3), 218.
2. J.R. Pretty, D.C. Duckworth, G.J. Van Berkel, (1998) "Electrochemical Sample Pretreatment Coupled On-line with ICP-MS: Analysis of Uranium Using an Anodically Conditioned Glassy Carbon Working Electrode", *Anal. Chem.*, 70(6), 1141.
3. Data from Figure 4 and Figure 6 was acquired on Oak Ridge National Laboratory's Optimass 8000 ICP-TOF-MS and Neptune MC-ICP-MS, respectively, and is gratefully acknowledged.

Acknowledgements

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