Quantitation and Ratio Determination of Uranium Isotopes in Water and Soil Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

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Introduction

- Uranium – overview
- Sample prep:
  - water – EPA 3020
  - Soils – EPA 3052 (modified)
- Analysis – ICP-MS
  - water – EPA 200.8
  - soils – EPA 6020
  - Quality Controls
- ICP-MS and α-Spec
- Summary
- Questions
Introduction

- Ubiquitous element
- Naturally Occurring U Isotopes:
  234 (0.0055%, 0.245 E6 yr.), 235 (0.72%, 703 E6 yr.), 238 (99.275%, 4,468 E6 yr.)
- Natural U235/238 atomic Ratio: 7.2 x 10^-3
- Natural U234/238 α activity Ratio: 1 (secular equilibrium)
- Used for fuel in atomic energy and warfare
- Depleted Uranium DU: 235 Isotope Quantity Reduced
  U235/238 atomic Ratio: 2 x 10^-3
Sample Preparation

- Water - EPA 3020
  Acid digestion

- Soils – EPA 3052 (modified)
  Acidic microwave digestion
  Complete digestion

- Ratio – Depends on Matrix (see methods above)
Sample Analysis  ICP-MS

- Water - EPA 6020
- Soils – EPA 200.8
- Ratios – In house Method
Sample Analysis  QC

- Sample Duplicates – precision check
- Blanks – contamination check
- Laboratory Control Samples – accuracy check
- Matrix Spikes – matrix effect
- *Mass bias correction standard
# Analysis Recovery QC

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Soil</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duplicates</td>
<td>---</td>
<td>≤ 20 % RPD</td>
<td>---</td>
</tr>
<tr>
<td>Blanks</td>
<td>&lt; RL</td>
<td>&lt; RL</td>
<td>---</td>
</tr>
<tr>
<td>LCS</td>
<td>± 15 %</td>
<td>± 20 %</td>
<td>---</td>
</tr>
<tr>
<td>MS</td>
<td>± 30 %</td>
<td>± 30 %</td>
<td>---</td>
</tr>
<tr>
<td>Inst Spike</td>
<td>± 20 %</td>
<td>± 20 %</td>
<td>---</td>
</tr>
<tr>
<td>ISA / ISB</td>
<td>---</td>
<td>± 20 %</td>
<td>---</td>
</tr>
</tbody>
</table>
Common Analysis Techniques

- α Spectroscopy
- ICP-MS
α Spectroscopy

- Measures 234 and 238 isotopes
  U-234 from the Uranium Decay Series
  $^{238}\text{U} \rightarrow ^{234}\text{Th} \rightarrow ^{234}\text{Pa} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow \ldots$

- Sample preparation required (matrix removed)

- Tracer added for quantification

- Measure α particles from radioactive decay

- Ratio and Concentration in same analysis

- Detection limits – depends on count time
ICP- MS

- Measures 235 and 238 isotope ions
  - 235 from the Actinium Decay Series
    \[ \text{U}^{235} \rightarrow \text{Th}^{231} \rightarrow \text{Pa}^{231} \rightarrow \text{Ac}^{227} \rightarrow \ldots \]  
- Sample preparation
- Count ions
- Conc. and Ratio: two different analyses
- Detection limit: matrix and instrument
## ICP-MS 235/238 Ratio Comparison

<table>
<thead>
<tr>
<th>Uncorrected Bias</th>
<th>Corrected Bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.51 x10^{-3}</td>
<td>7.24 x10^{-3}</td>
</tr>
<tr>
<td>6.82 x10^{-3}</td>
<td>7.18 x10^{-3}</td>
</tr>
<tr>
<td>6.58 x10^{-3}</td>
<td>7.25 x10^{-3}</td>
</tr>
<tr>
<td>6.24 x10^{-3}</td>
<td>7.14 x10^{-3}</td>
</tr>
<tr>
<td>6.74 x10^{-3}</td>
<td>7.22 x10^{-3}</td>
</tr>
</tbody>
</table>

Accepted Ratio value 7.26 x10^{-3}
ICP- MS

- Measures 235 and 238 isotope ions
  - 235 from the Actinium Decay Series
    \[ {\text{U}}_{235} \rightarrow {\text{Th}}_{231} \rightarrow {\text{Pa}}_{231} \rightarrow {\text{Ac}}_{227} \rightarrow \ldots \]

- Sample preparation
- Count ions
- Conc. and Ratio: two different analyses
- Detection limit: matrix and instrument
Choices

- α Spectroscopy
- ICP-MS

Questions you need answered:
  Concentration?
  Ratio?
### ICP-MS and α Spec

<table>
<thead>
<tr>
<th>ICP-MS</th>
<th>α Spec</th>
</tr>
</thead>
<tbody>
<tr>
<td>235 Conc. Sufficient for ratio</td>
<td>Long count time</td>
</tr>
<tr>
<td>Ratio &amp; Conc. Separate Analysis</td>
<td>Ratio &amp; Conc. Same Analysis</td>
</tr>
<tr>
<td>Correct ratio? – bias, conc.</td>
<td>Correct ratio – recoil effect</td>
</tr>
<tr>
<td>100 mL sample</td>
<td>1 L sample</td>
</tr>
</tbody>
</table>
Acknowledgments

Army Institute of Public Health (AIPH)
EMDQ
Questions

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