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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: 7.2×10^{-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: 2×10^{-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

	Water	Soil	Ratio
Duplicates	---	$\leq 20\%$ RPD	---
Blanks	< RL	< RL	---
LCS	$\pm 15\%$	$\pm 20\%$	---
MS	$\pm 30\%$	$\pm 30\%$	---
Inst Spike	$\pm 20\%$	$\pm 20\%$	---
ISA / ISB	---	$\pm 20\%$	---

Common Analysis Techniques

✦ **α Spectroscopy**

✦ **ICP-MS**

α Spectroscopy

- ✦ **Measures 234 and 238 isotopes**
U-234 from the Uranium Decay Series
U238 $\rightarrow$ Th234 $\rightarrow$ Pa234 $\rightarrow$ U234 $\rightarrow$ Th230 $\rightarrow$
- ✦ **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
U235 → Th231 → Pa231 → Ac227 →
- ✦ **Sample preparation**
- ✦ **Count ions**
- ✦ **Conc. and Ratio: two different analyses**
- ✦ **Detection limit: matrix and instrument**

ICP- MS 235/238 Ratio Comparison

Uncorrected Bias	Corrected Bias
6.51 x10 ⁻³	7.24 x10 ⁻³
6.82 x10 ⁻³	7.18 x10 ⁻³
6.58 x10 ⁻³	7.25 x10 ⁻³
6.24 x10 ⁻³	7.14 x10 ⁻³
6.74 x10 ⁻³	7.22 x10 ⁻³

Accepted Ratio value 7.26 x10⁻³

ICP- MS

- ✦ **Measures 235 and 238 isotope ions**
235 from the Actinium Decay Series
U235 → Th231 → Pa231 → Ac227 →
- ✦ **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

ICP-MS	α Spec
235 Conc. Sufficient for ratio	Long count time
Ratio & Conc. Separate Analysis	Ratio & Conc. Same Analysis
Correct ratio? – bias, conc.	Correct ratio – recoil effect
100 mL sample	1 L sample

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Questions

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