Relative Formation Probabilities for Fluoride and Oxyfluoride Anions of U, Np, Pu and Am in Accelerator Mass Spectrometry Measurements at VERA

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Why is this interesting?

$^{237}\text{Np}$ spike project

- Second most abundant anthropogenic actinide in the environment?
- Released by nuclear weapons tests and industry
- Potential environmental tracer
  - Long lived and highly mobile in water

Magill et al., Nucleonica GmbH, 2006
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- Challenging to measure in general environment:
  - Decay counting: very large samples ($T_{1/2}$!)
  - MS: background from $^{238}$U, $^{235}$UH$_2$
  - AMS: Lack of isotopic spike hinders quantification

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- Challenging to measure in general environment:
  - Decay counting: very large samples (T_{1/2}!)
  - MS: background from 238U, 235UH₂
  - AMS: Lack of isotopic spike hinders quantification
    - Different isotope of Np to add to sample for relative measurements

- Severely understudied!

Magill et al., Nucleonica GmbH, 2006
• Plan: Develop isotopic spike for $^{237}$Np
  ◦ Joint Project: Universities of Vienna, Tsukuba and Kanazawa
  ◦ Current focus: $^{232}$Th($^7$Li,3n)$^{236}$Np reaction

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Why is this interesting?

237Np spike project

- Plan: Develop isotopic spike for 237Np
  - Joint Project: Universities of Vienna, Tsukuba and Kanazawa
  - Current focus: 232Th(7Li,3n)236Np reaction

- Problem: Isobaric interference from 236U
  - Co-production in irradiation for spike production?
    - Need a method to distinguish 236U and 236Np!
  - 236U in environmental samples
    - U – Np Isobar separation necessary for 236Np spike
      - ILIAMS?

Magill et al., Nucleonica GmbH, 2006
AMS: negative ions
  - Actinides do not form sufficient atomic anions
  - Molecular anions
• AMS: negative ions
  ◦ Actinides do not form sufficient atomic anions
    → Molecular anions

• Fluoride molecular anions for actinides?

AMS: negative ions
  ○ Actinides do not form sufficient atomic anions
    ➔ Molecular anions

Fluoride molecular anions for actinides?

○ Research at VERA is focused on mixing oxide materials in Fe$_2$O$_3$ with PbF$_2$
  ➔ In situ fluoridization inside the Cs-sputter ion source
  [M. Kern, this meeting]
The relative formation probabilities for a range of (oxy-)fluoride molecular anions of U, Np, Pu and Am have been systematically investigated.

<table>
<thead>
<tr>
<th>AnF$_5^-$</th>
<th>AnF$_4$O$^-$</th>
<th>AnF$_3$O$_2^-$</th>
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<td>AnF$_4^-$</td>
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An stands for U, Np, Pu or Am.
The relative formation probabilities for a range of (oxy-)fluoride molecular anions of U, Np, Pu and Am have been systematically investigated.

Isobaric contaminations can be monitored with this data:
- First application: $^{236}\text{U}$ in prospective $^{236}\text{Np}$ spike material

$\text{UF}_4^-$, $\text{NpF}_4^-$ candidates for U – Np separation with ILIAMS
Materials and Methods
• Reference material
  ◦ $^{236}$U, $^{237}$Np, $^{242}$Pu, $^{243}$Am (3x10$^8$ at) in nitric sol.
  ◦ Dried with 300µg Fe
  ◦ Ignition (800°C)
  ◦ Mixed with PbF$_2$ (1:9 mass ratio)
  ◦ Required in every beamtime
• Reference material
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• Material from $^{232}$Th($^7$Li,3n)$^{236}$Np irradiation
  ◦ RIKEN Nishina Center for Accelerator Based Science
    – Chemical purification at University of Tsukuba
  ◦ Previously measured at VERA in oxide form
    – Residue mixed with PbF$_2$ for isobar analysis
• $\text{AnF}_m \text{O}_n^{1-}$ selected by low energy mass spectrometer
Measurements at VERA

- $\text{AnF}_m \text{O}_n^{-1}$ selected by low energy mass spectrometer
- He-stripping destroys molecules
• $\text{AnF}_m\text{O}_n^{-1}$ selected by low energy mass spectrometer
• He-stripping destroys molecules
• High energy mass spectrometer selects $\text{An}^{3+}$
- $\text{AnF}_m\text{O}_n^{-1}$ selected by low energy mass spectrometer
- He-stripping destroys molecules
- High energy mass spectrometer selects $\text{An}^{3+}$
- $\text{An}^{3+}$ detected in Bragg type ionization chamber
• AnFmO₁⁻ selected by low energy mass spectrometer

• He-stripping destroys molecules

• High energy mass spectrometer selects An³⁺

• An³⁺ detected in Bragg type ionization chamber

• 24 machine setups with masses 306u to 338u measured on each target
  - Only electrostatic components were adjusted
    - magnetic rigidity constant for all setups
Results

All results are stated in the form of $\frac{\text{AnF}_m\text{O}_n}{\text{AnF}_5}$ ratios
- Characteristic $\text{UF}_m\text{O}_n^-/\text{UF}_5^-$ ratios
Characteristic $\text{AnF}_m \text{O}_n^-/\text{AnF}_5^-$ ratios for U, Np
Formation distribution: reference materials

- Characteristic $\text{AnF}_m\text{O}_n^-/\text{AnF}_5^-$ ratios for U, Np, Pu
Characteristics $\text{AnF}_m\text{O}_n^- / \text{AnF}_5^-$ ratios for U, Np, Pu, Am

Formation distribution: reference materials

Weighted means for $\text{AnF}_m\text{O}_n^- / \text{AnF}_5^-$

An stands for U, Np, Pu or Am

Reference material:
- U
- Np
- Pu
- Am
Characteristic $\text{AnF}_m\text{O}_n^-/\text{AnF}_5^-$ ratios for U, Np, Pu, Am

- Isobaric contaminations shift formation ratios
- $\text{AnF}_4^-/\text{AnF}_5^-$!
- Characteristic AnF$_m$O$_n^-$/AnF$_5^-$ ratios for U, Np, Pu, Am
  - Isobaric contaminations shift formation ratios
  - AnF$_4^-$/AnF$_5^-$!

- UF$_4^-$, NpF$_4^-$ for ILIAMS?
  - Hypothesis: correlation anion formation ratio to e$^-$ detachment energy?
  - Suppression of U vs Np by one order of magnitude in ion source
Analysis of irradiated samples

- Ratios shift between beamtimes, separation for AnF$_4^-$ remains stable
  - reference materials for every beamtime
Analysis of irradiated samples

- Ratios shift between beamtimes, separation for $\text{AnF}_4^−/\text{AnF}_5^−$ is stable
 - Reference materials for every beamtime
Analysis of irradiated samples

- Ratios shift between beamtimes, separation for AnF$_4^-$/AnF$_5^-$ is stable
  - Reference materials for every beamtime

- QC for measurement: m$^{237}$ on irradiated targets (~10% of m$^{236}$)
  - Co-produced $^{237}$Np!

- m$^{237}$ AnF$_4^-$/AnF$_5^-$ ratio compatible with reference Np (1σ)
Analysis of irradiated samples

- $m_{236} \text{AnF}_4^-/\text{AnF}_5^-$ ratio is compatible with ref. Np (1σ)
  - Isobaric $^{236}\text{U}$ interference is negligible
Analysis of irradiated samples

- m236 AnF$_4^-$/AnF$_5^-$ ratio is compatible with ref. Np (1σ)
  - Isobaric $^{236}$U interference is negligible

- The production and separation of $^{236}$Np was successful
• The relative formation probabilities for

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are characteristic for U, Np, Pu and Am

◦ This distribution can be used to identify isobaric contaminations

• This method could show that $^{236}$Np was successfully produced and chemically separated from $^{236}$U

◦ Isotopic spike for environmental $^{237}$Np?

• The next steps:

  ◦ ILIAMS separation of U and Np
  ◦ Maximize NpF₄⁻ formation
How stable are the ratios with increasing duration of the measurement?

AnF₅Oₙ/AnF₅ per sequence

Sequence 1
- q1_1
- q2_1

Sequence 2
- q1_2
- q2_2

~1.2h/seq
How stable are the ratios with increasing duration of the measurement?

- Ratios change significantly after the first two sequences
- All targets should be measured for 2 sequences (~2.5h) for consistent results
How stable are the ratios for different mixing rates with PbF\(_2\)?

- Reducing mixing ratios to 1:4.5 increases lower fluorides/oxfluorides
  - Similar to long measurement duration
  - Fluorine supply affects formation probabilities
- Increasing PbF\(_2\) further (1:18) has no significant effect
• $\text{AnF}_m \text{O}_n^-/\text{AnF}_5^-$ ratios change between beamtimes
  ◦ Ion source conditions?
  ◦ Tuning?
• Separation for $\text{AnF}_4/\text{AnF}_5$ remains stable
  ◦ Method is robust against tuning variations!
• Reference samples have to be included in every measurement