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?

$^{237}$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 $^{238}\text{U}$, $^{235}\text{UH}_2$
  - AMS: Lack of isotopic spike hinders quantification

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- MS: background from $^{238}\text{U}$, $^{235}\text{UH}_2$
- 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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**237Np spike project**

- **Plan:** Develop isotopic spike for $^{237}\text{Np}$
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  - Current focus: $^{232}\text{Th}(^7\text{Li},3n)^{236}\text{Np}$ reaction

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

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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
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• Fluoride molecular anions for actinides?
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• 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>
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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. An stands for U, Np, Pu or Am.

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Isobaric contaminations can be monitored with this data.
- First application: $^{236}$U in prospective $^{236}$Np spike material.
- UF$_4^-$, NpF$_4^-$ candidates for U – Np separation with ILIAMS.
Materials and Methods
• Reference material
  ◦ $^{236}\text{U}$, $^{237}\text{Np}$, $^{242}\text{Pu}$, $^{243}\text{Am}$ (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
Sample preparation

• Reference material
  ◦ $^{236}\text{U}$, $^{237}\text{Np}$, $^{242}\text{Pu}$, $^{243}\text{Am}$ (3x10^8 at) in nitric sol.
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• Material from $^{232}\text{Th}(^7\text{Li},3n)^{236}\text{Np}$ 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
• AnF$_m$O$_n$$^{-1}$ selected by low energy mass spectrometer
- $\text{AnF}_m\text{O}_n^{-1}$ selected by low energy mass spectrometer
- He-stripping destroys molecules

Measurements at VERA

$+1.7\text{ MV}$
Measurements at VERA

- $\text{AnF}_m \text{O}_n{}^1$ selected by low energy mass spectrometer
- He-stripping destroys molecules
- High energy mass spectrometer selects $\text{An}^{3+}$
• AnF$_m$O$_n^{1-}$ selected by low energy mass spectrometer

• He-stripping destroys molecules

• High energy mass spectrometer selects An$^{3+}$

• An$^{3+}$ detected in Bragg type ionization chamber
Measurements at VERA

- \( \text{AnF}_m \text{O}_n^{-1} \) 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

- 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 $\text{AnF}_m \text{O}_n/\text{AnF}_5$ ratios
Formation distribution: reference materials

- Characteristic $\text{UF}_m \text{O}_n^-/\text{UF}_5^-$ ratios

![Graph showing weighted means for $\text{UF}_m \text{O}_n^-/\text{UF}_5^-$ ratios]

Reference material

- $\text{UF}_4$ to $\text{UF}_5$

- $\text{UF}_3 \text{O}_2$ to $\text{UF}_5$

- $\text{UF}_3$ to $\text{UF}_5$

- $\text{UF}_2 \text{O}_2$ to $\text{UF}_5$

- $\text{UF}_4$ to $\text{UF}_5$
Characteristic $\text{AnF}_m\text{O}_n^-/\text{AnF}_5^-$ ratios for U, Np

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
- $\text{U}$
- $\text{Np}$
Formation distribution: reference materials

- Characteristic $\text{AnF}_m\text{O}_n^-/\text{AnF}_5^-$ ratios for U, Np, Pu
Formation distribution: reference materials

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

$\text{UF}_4^-$, $\text{NpF}_4^-$ for ILIAMS?
- Hypothesis: correlation anion formation ratio to $e^-$ detachment energy?
- Suppression of U vs Np by one order of magnitude in ion source
• Ratios shift between beamtimes, separation for AnF$_4^-$ remains stable
  ◦ reference materials for every beamtime
• Ratios shift between beamtimes, separation for AnF$_4^-$/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:
  - m237 on irradiated targets (~ 10% of m236)
    - Co-produced $^{237}$Np!

  - m237 AnF$_4^-$/AnF$_5^-$ ratio compatible with reference Np ($1\sigma$)
• m236 AnF$_4^-$/AnF$_5^-$ ratio is compatible with ref. Np (1σ)
  – Isobaric $^{236}$U interference is negligible
- m236 \( \text{AnF}_4^-/\text{AnF}_5^- \) ratio is compatible with ref. Np (1σ)
  - Isobaric \( ^{236}\text{U} \) interference is negligible

- The production and separation of \( ^{236}\text{Np} \) was successful
Conclusions and outlook

• 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 NpF$_4^-$ formation
Appendix
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/oxyfluorides
  - Similar to long measurement duration
  - Fluorine supply affects formation probabilities

- Increasing PbF$_2$ further (1:18) has no significant effect
How stable are the ratios between Beamtimes

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