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

Andreas Wiederin[1]

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Joint Annual Meeting of ÖPG and SPS 2021

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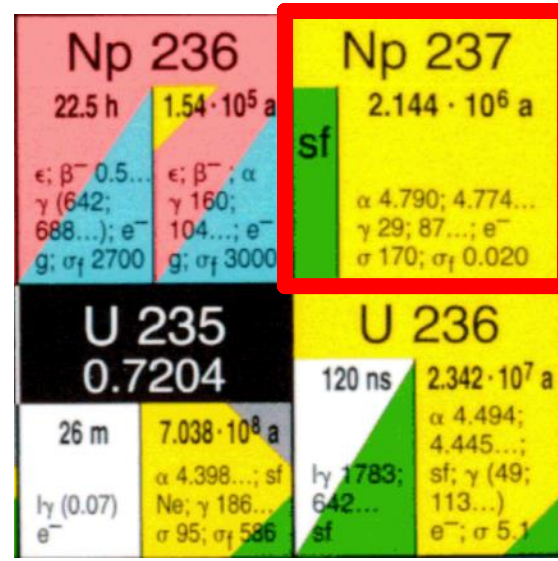
Why is this interesting?
^{237}Np spike project

- **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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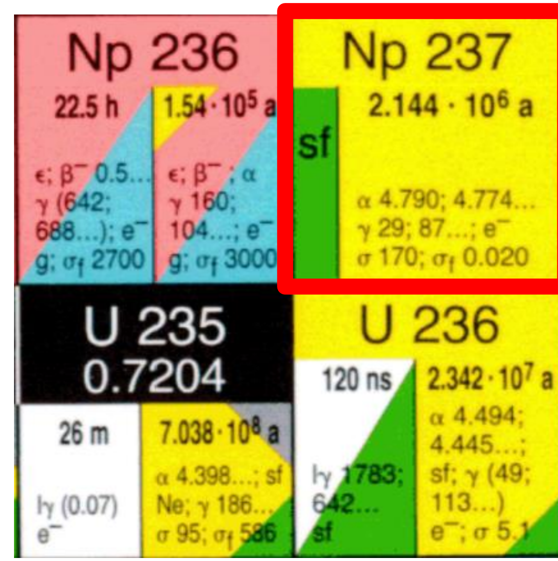
  - **Decay counting: very large samples ($T_{1/2}$!)**
  - **MS: background from ^{238}U, ^{235}UH$_2$**
  - **AMS: Lack of isotopic spike hinders quantification**



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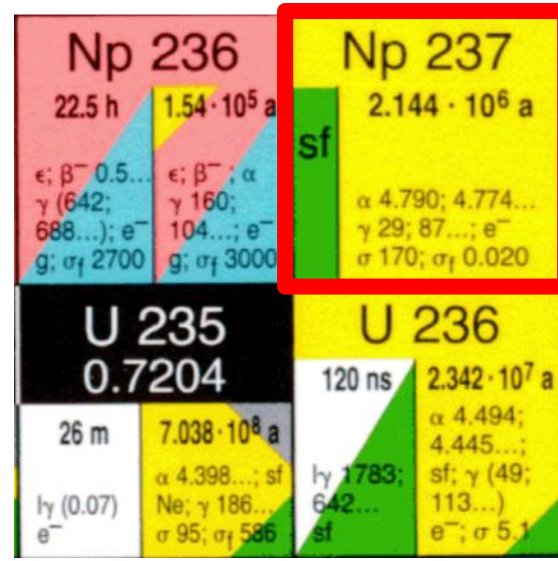
    - **Different isotope of Np to add to sample for relative measurements**

- **Severely understudied!**



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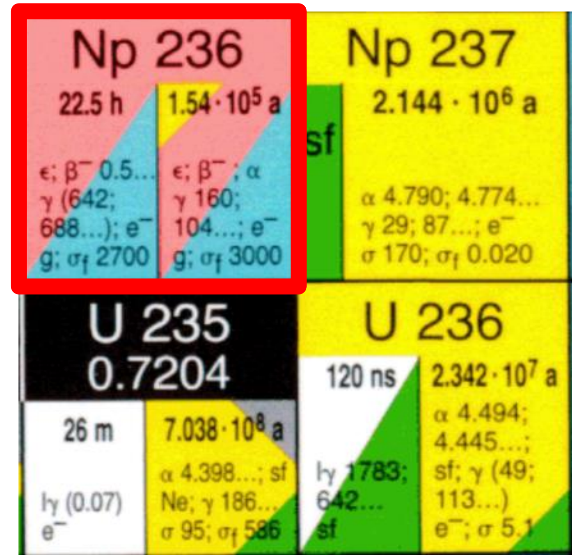
- **Plan: Develop isotopic spike for ^{237}Np**
  - **Joint Project: Universities of Vienna, Tsukuba and Kanazawa**
  - **Current focus: ^{232}Th(^{7}Li,3n)^{236}Np reaction**



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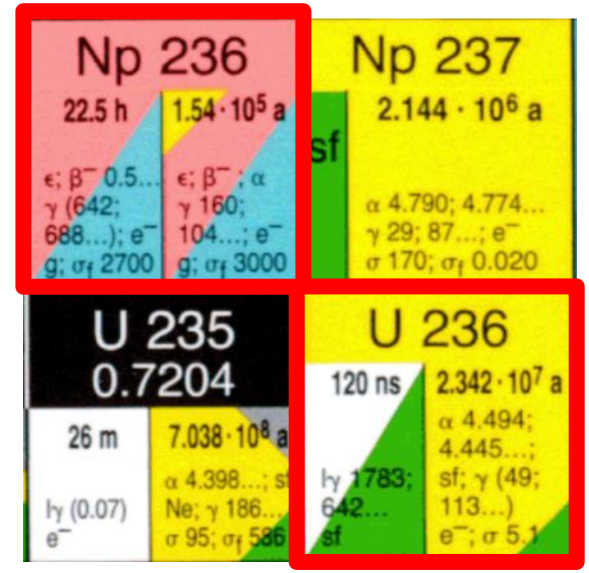

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- Problem: Isobaric interference from ^{236}U
  - Co-production in irradiation for spike production?
    - Need a method to distinguish ^{236}U and ^{236}Np!
  - ^{236}U in environmental samples
    - U – Np Isobar separation necessary for ^{236}Np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

Fluoride molecular anions of actinides

- **AMS: negative ions**
  - **Actinides do not form sufficient atomic anions**

  ⟶ **Molecular anions**

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- **Fluoride molecular anions for actinides?**

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  - **Research at VERA is focused on mixing oxide materials in Fe_2O_3 with PbF_2**

  → **In situ fluoridization inside the Cs-sputter ion source**

  [M. Kern, this meeting]

Fluoride molecular anions of actinides

- **The relative formation probabilities for a range of (oxy-)fluoride molecular anions of U, Np, Pu and Am have been systematically investigated**

AnF_5^-	AnF_4O^-	$AnF_3O_2^-$
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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

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Materials and Methods

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Sample preparation

- 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

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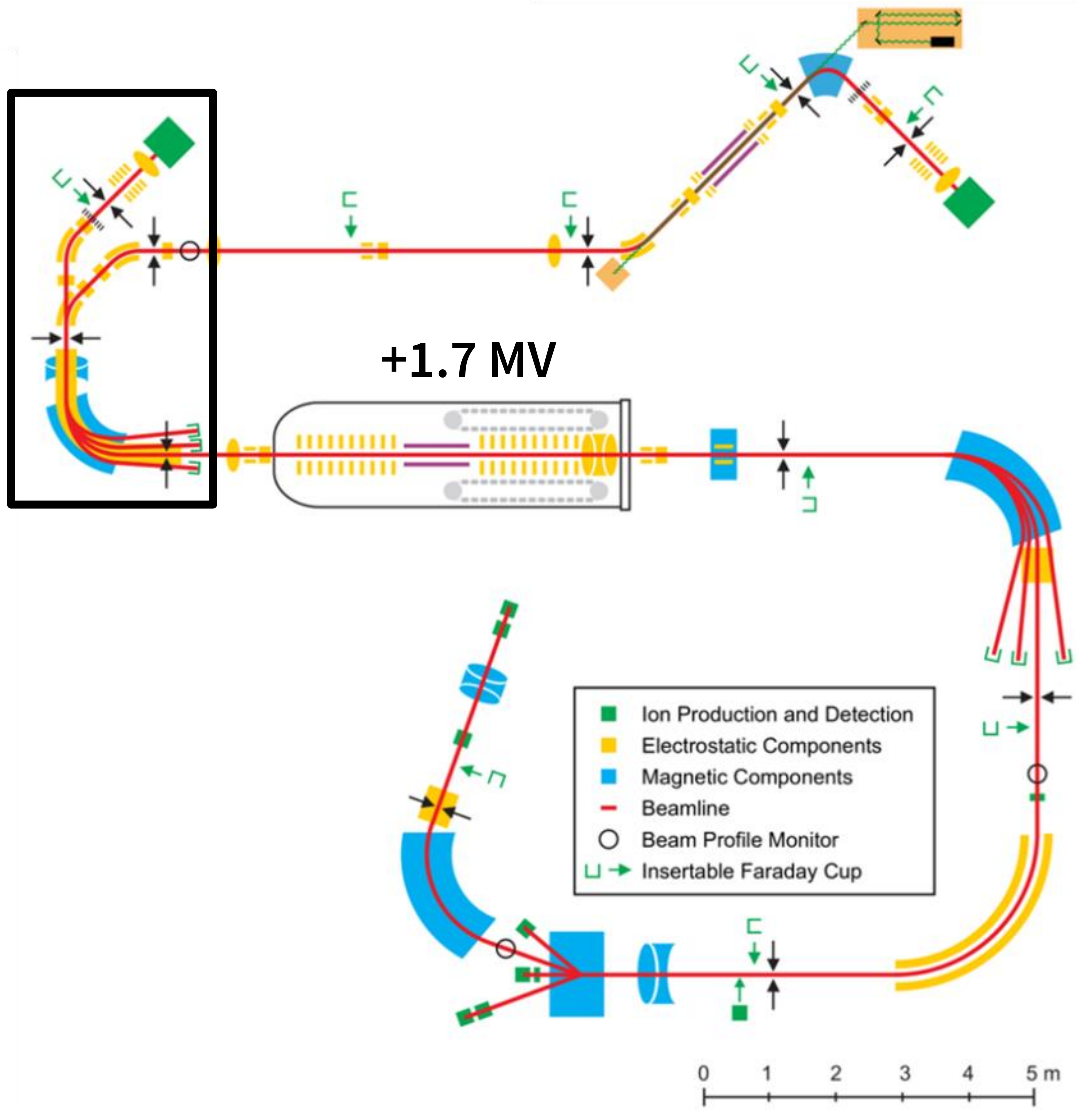
- Material from $^{232}Th(^7Li,3n)^{236}Np$ irradiation
  - RIKEN Nishina Center for Accelerator Based Science
    - Chemical purification at University of Tsukuba

  - Previously measured at VERA in oxide form
    - Residue mixed with PbF_2 for isobar analysis

Measurements at VERA

- $AnF_mO_n^{1-}$ selected by low energy mass spectrometer



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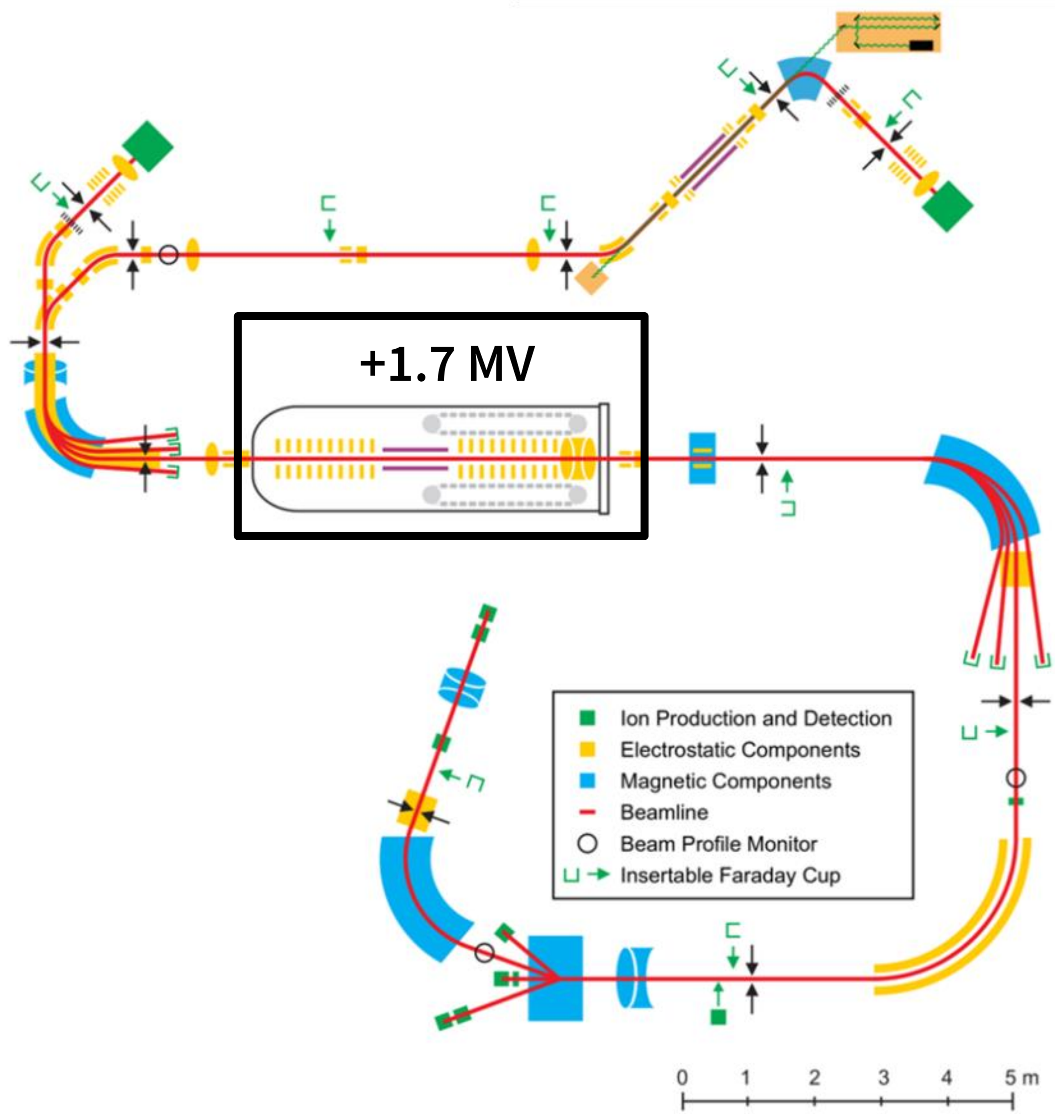

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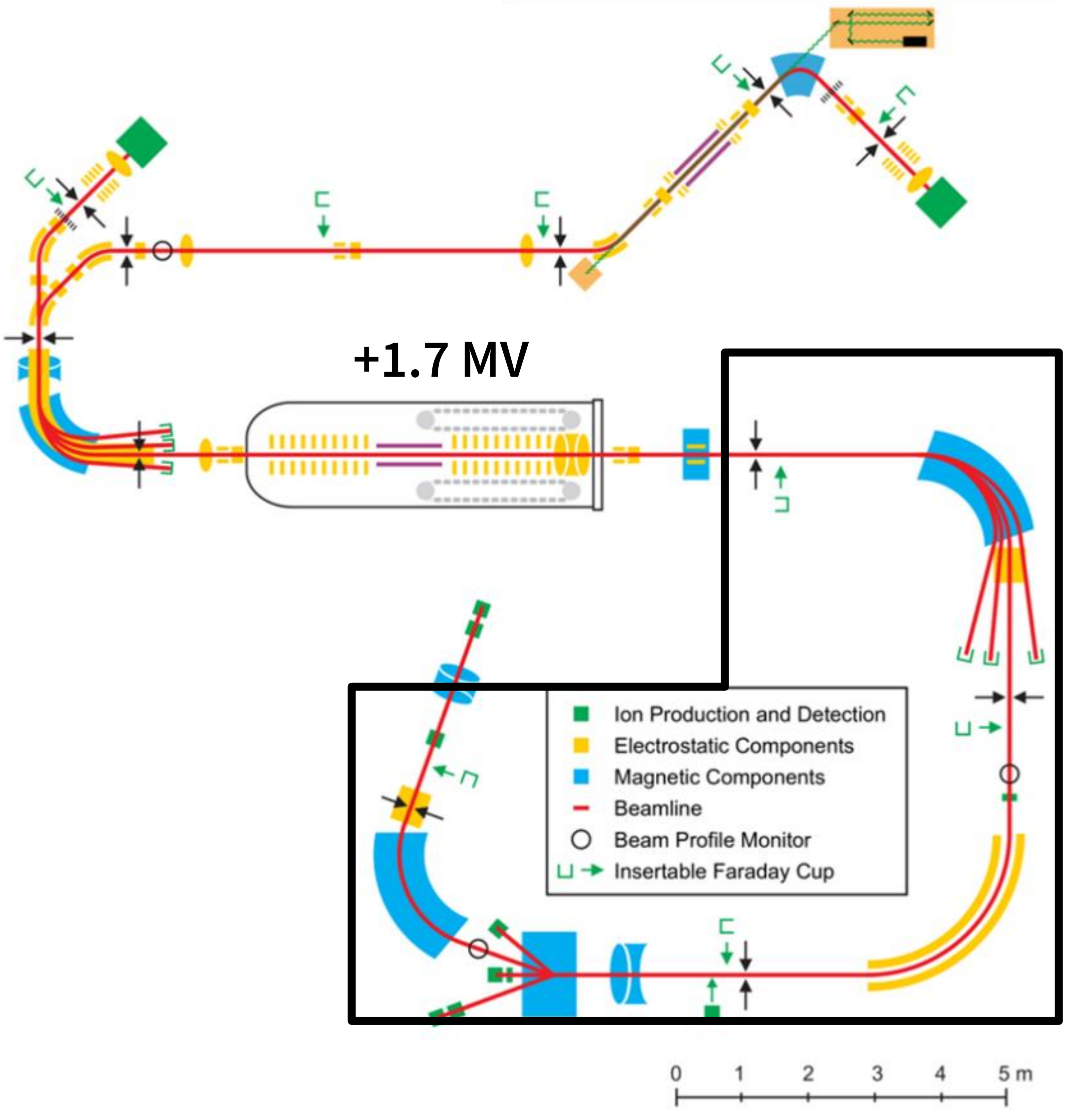

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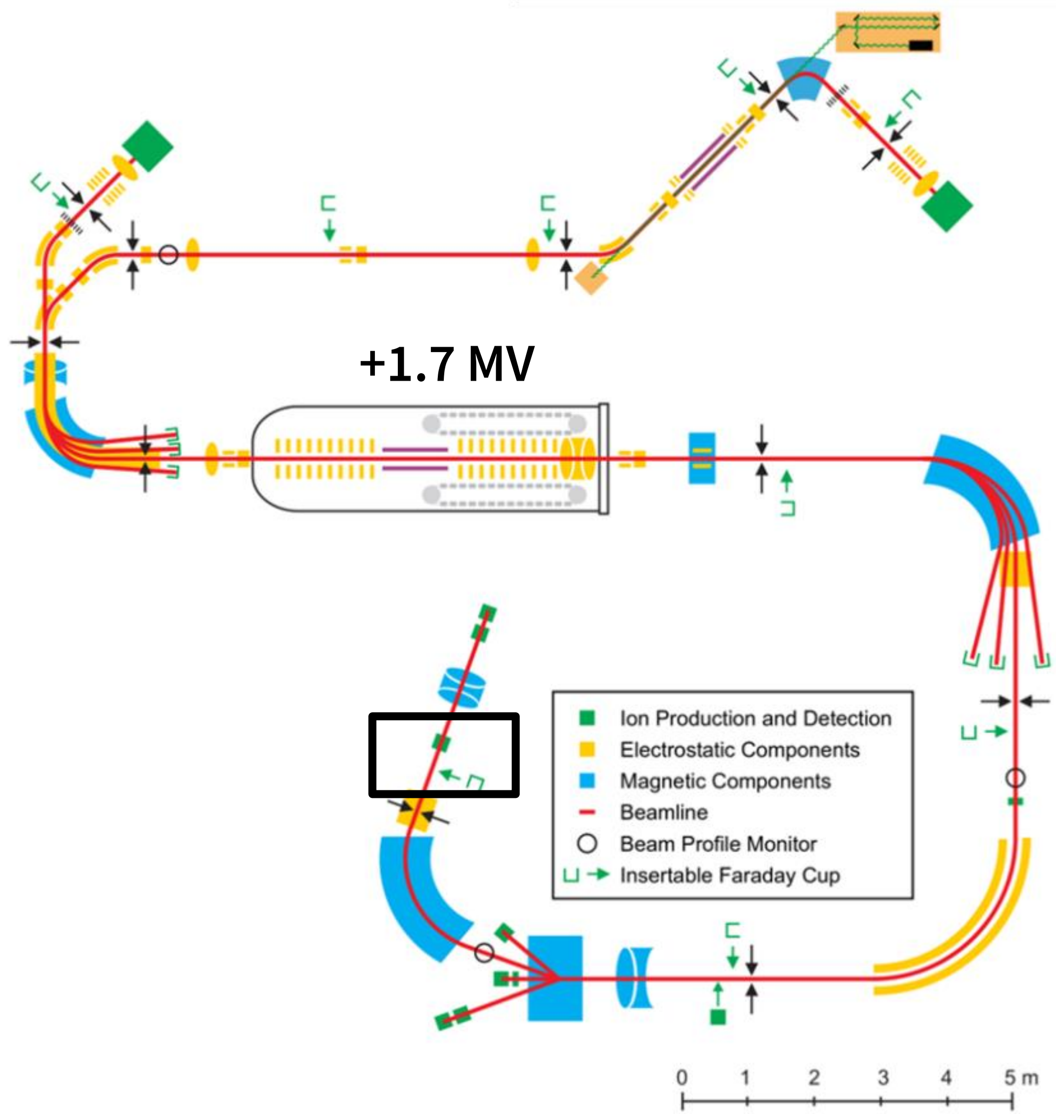

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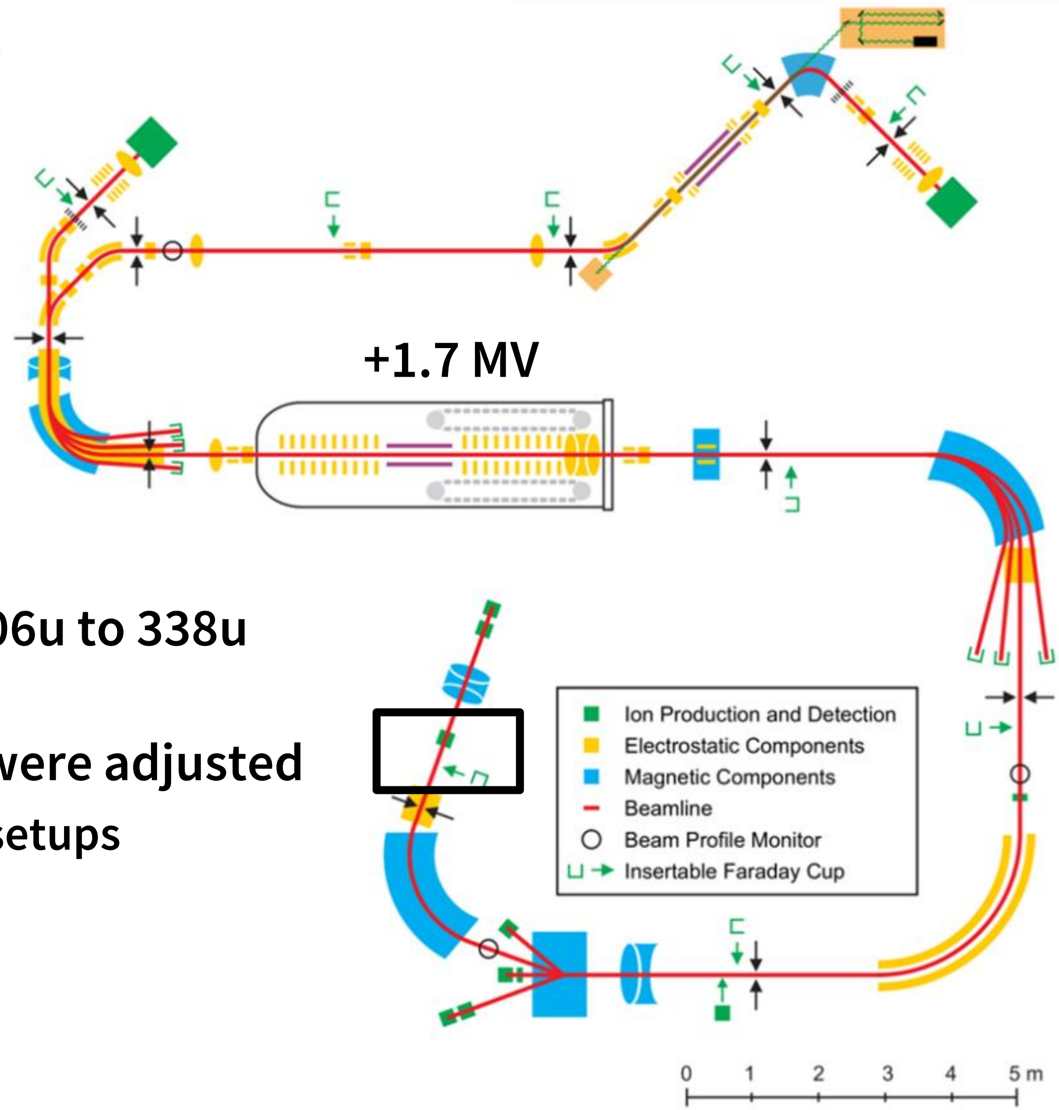


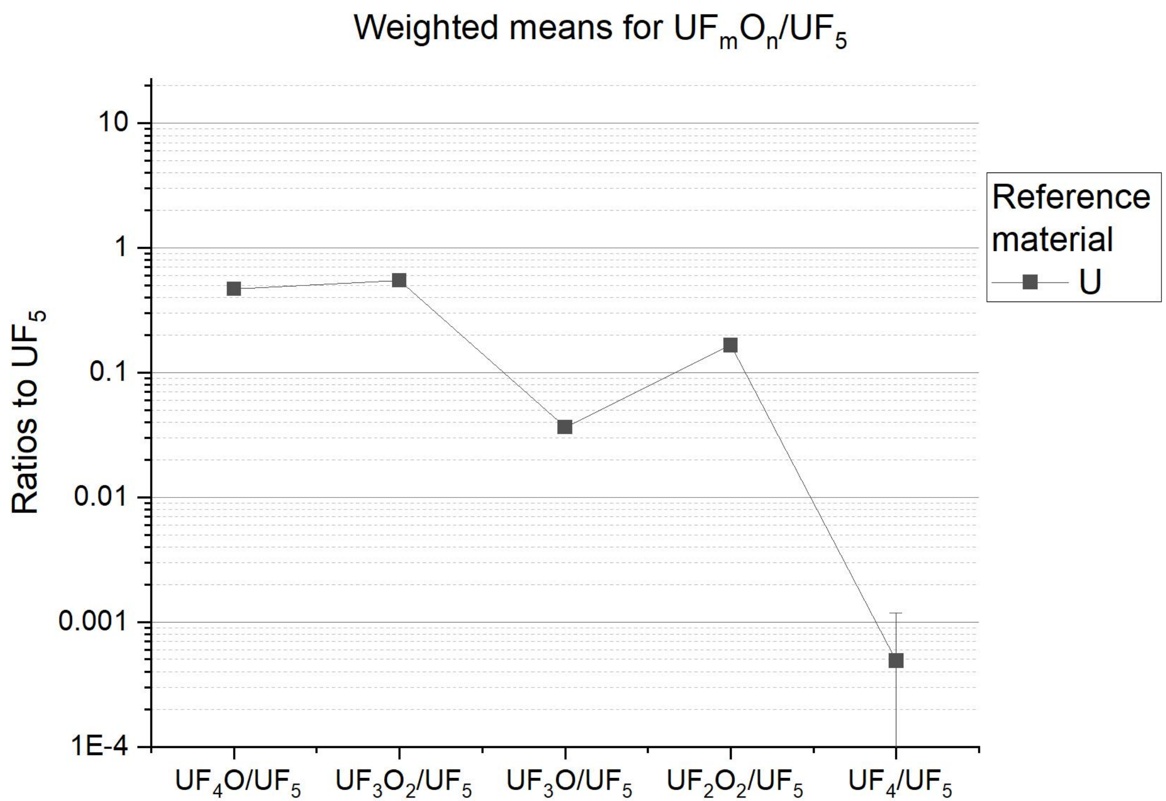
- 24 machine setups with masses 306u to 338u measured on each target
  - Only electrostatic components were adjusted
    - magnetic rigidity constant for all setups

Results

All results are stated in the form of AnF_mO_n/AnF_5 ratios

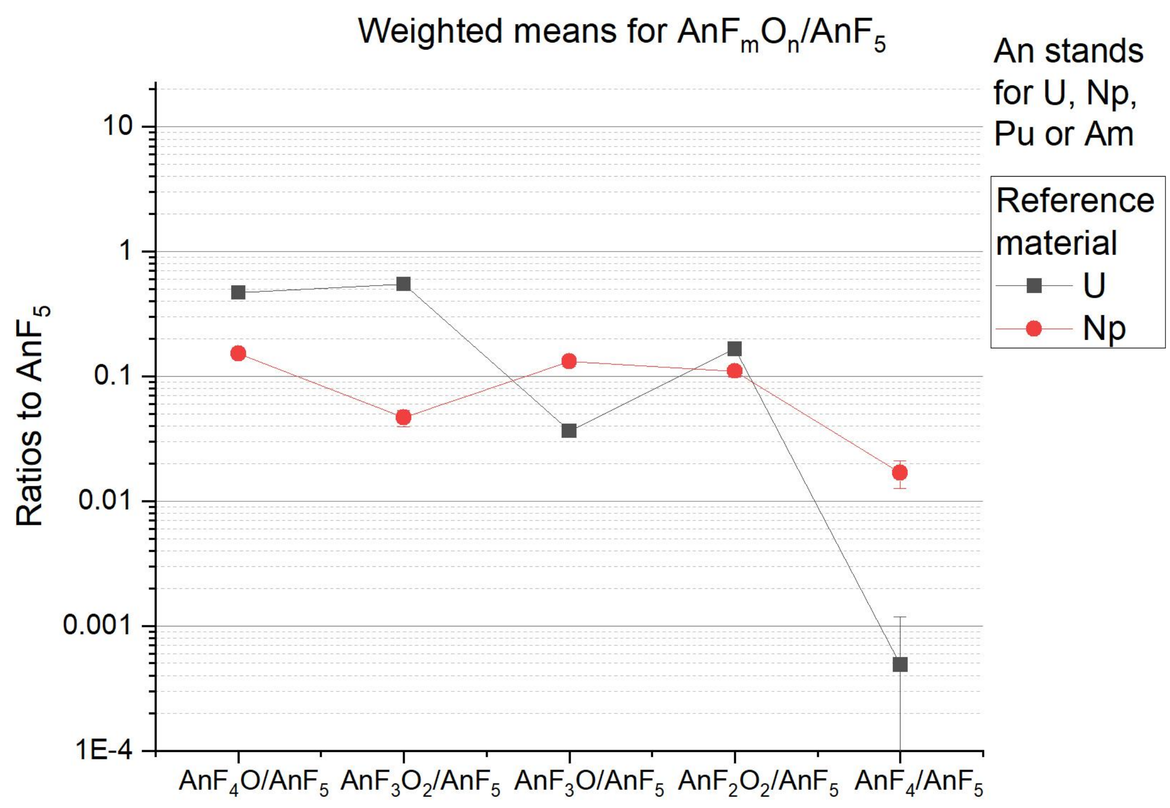
Formation distribution: reference materials

- Characteristic $UF_mO_n^-$ / UF_5^- ratios



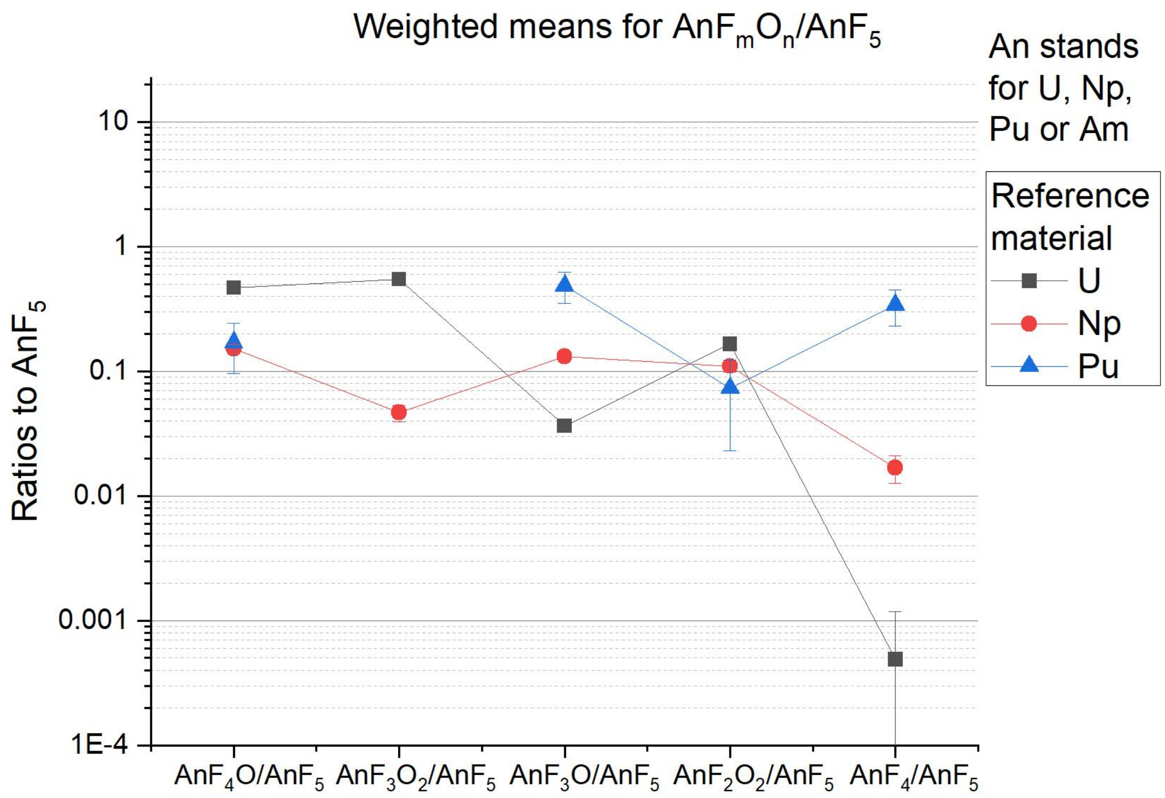
Formation distribution: reference materials

- **Characteristic $AnF_mO_n^-$ / AnF_5^- ratios for U, Np**



Formation distribution: reference materials

- **Characteristic $AnF_mO_n^-$ / AnF_5^- ratios for U, Np, Pu**



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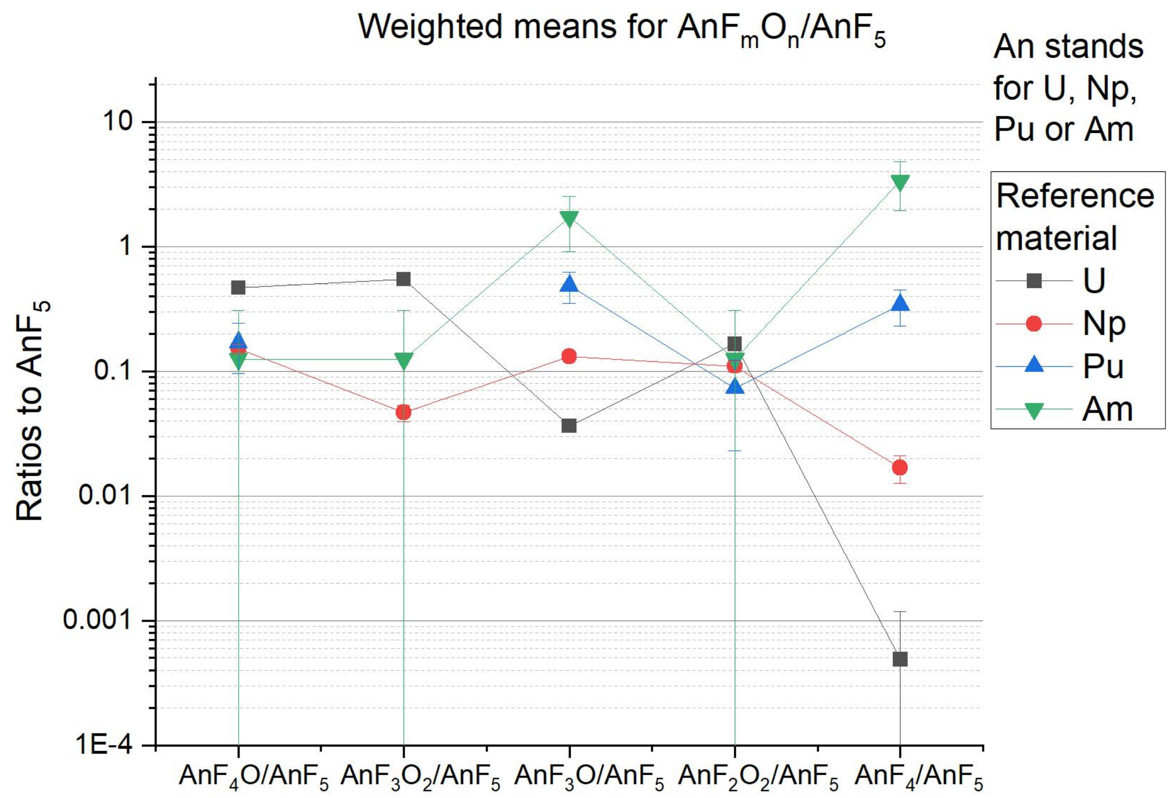

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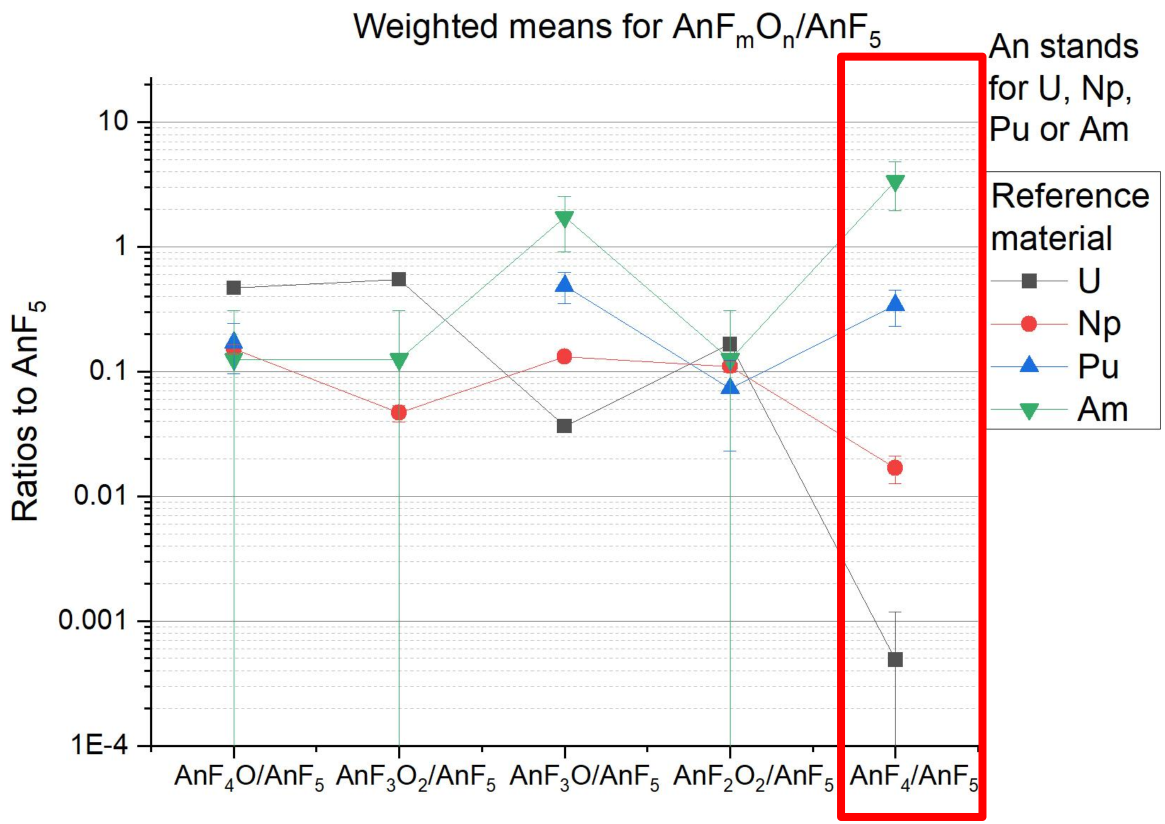
  - Isobaric contaminations shift formation ratios
  - AnF_4^-/AnF_5^-!



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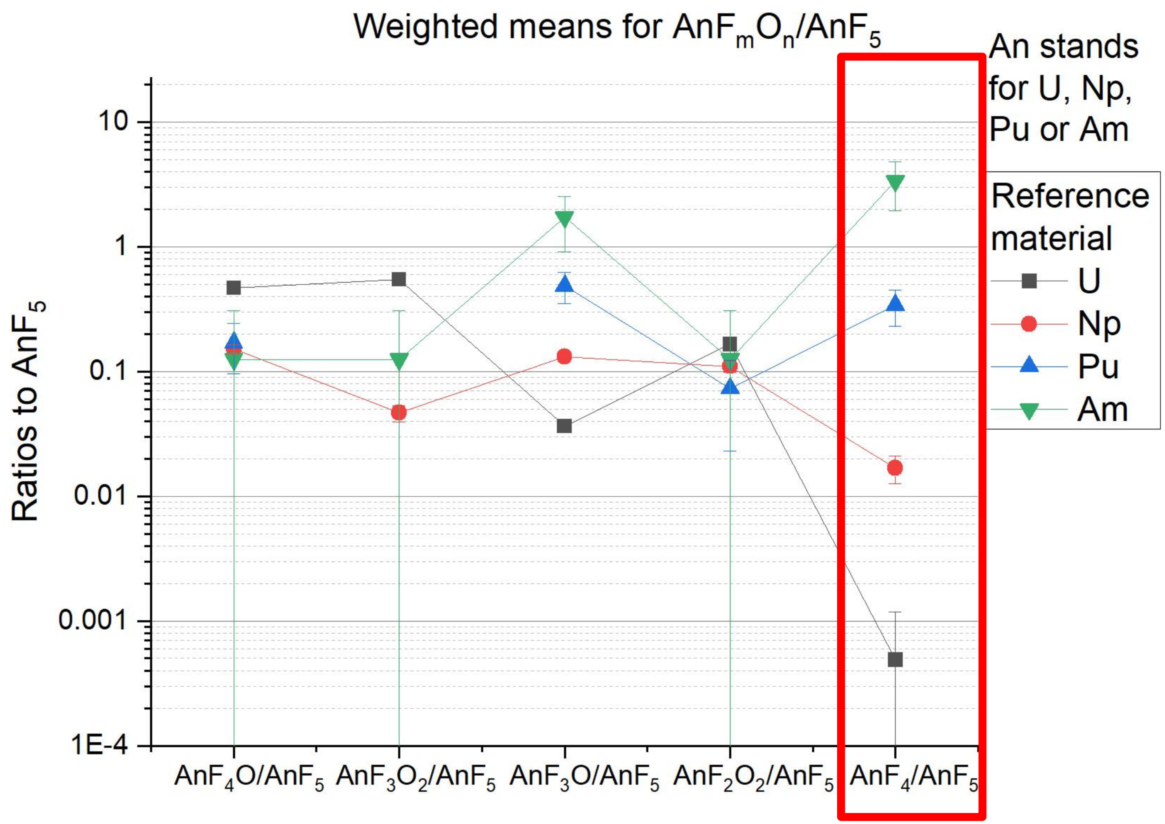
  - **Isobaric contaminations shift formation ratios**
  - **AnF_4^-/AnF_5^-!**
- **UF_4^-, NpF_4^- for ILIAMS?**
  - **Hypothesis: correlation anion formation ratio to e^- detachment energy?**
  - **Suppression of U vs Np by one order of magnitude in ion source**



Analysis of irradiated samples

- **Ratios shift between beamtimes, separation for $AnF4_4^-$ remains stable**
  - **reference materials for every beamtime**

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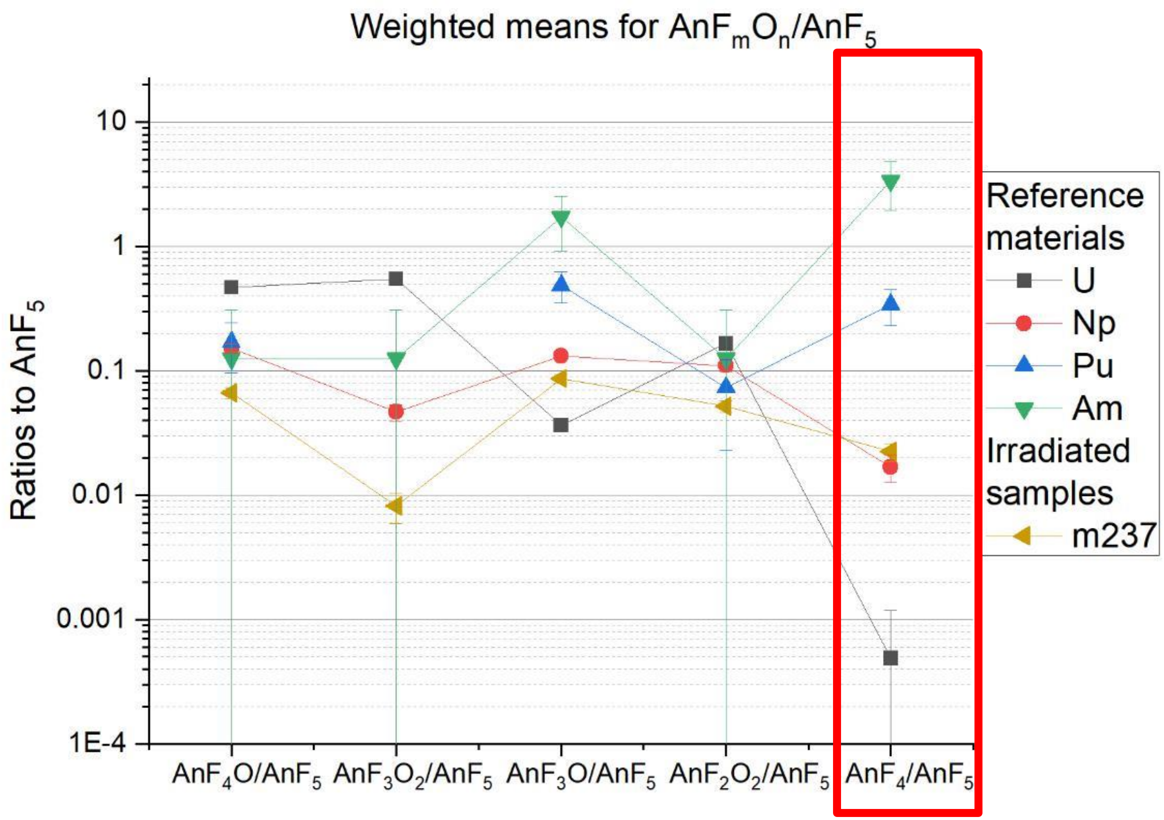

Analysis of irradiated samples

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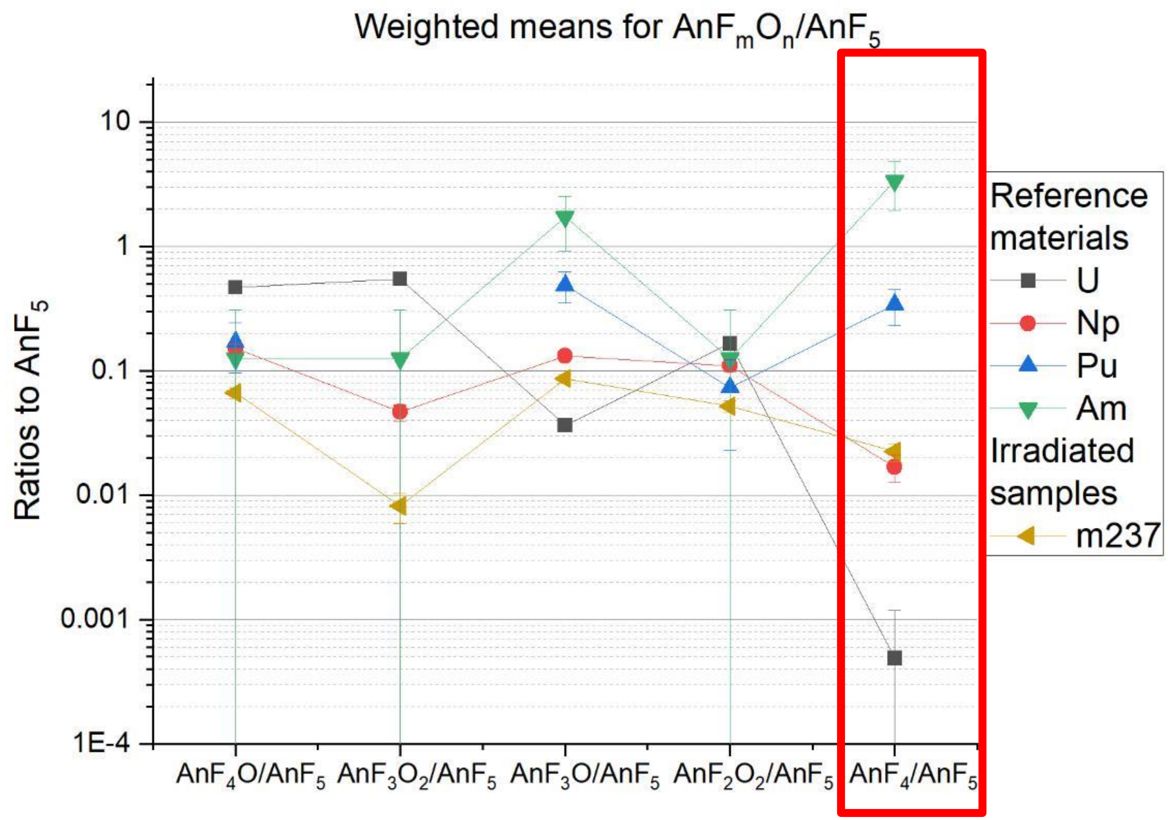
  - **Reference materials for every beamtime**

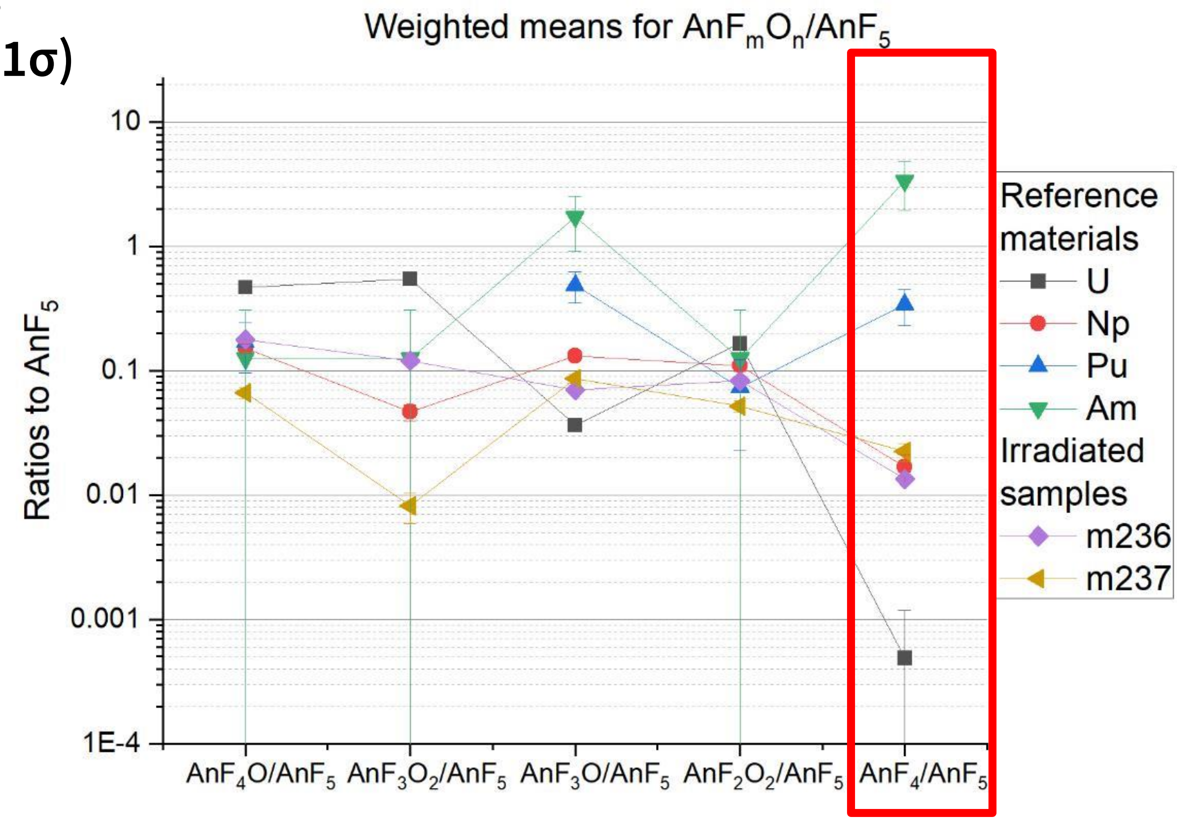
- **QC for measurement: m237 on irradiated targets (~ 10% of m236)**
  - **Co-produced ^{237}Np!**

  - **m237 AnF_4^-/AnF_5^- ratio compatible with reference Np (1σ)**



Analysis of irradiated samples

- m236 AnF_4^-/AnF_5^- ratio is compatible with ref. Np (1σ)
  - Isobaric ^{236}U interference is negligible



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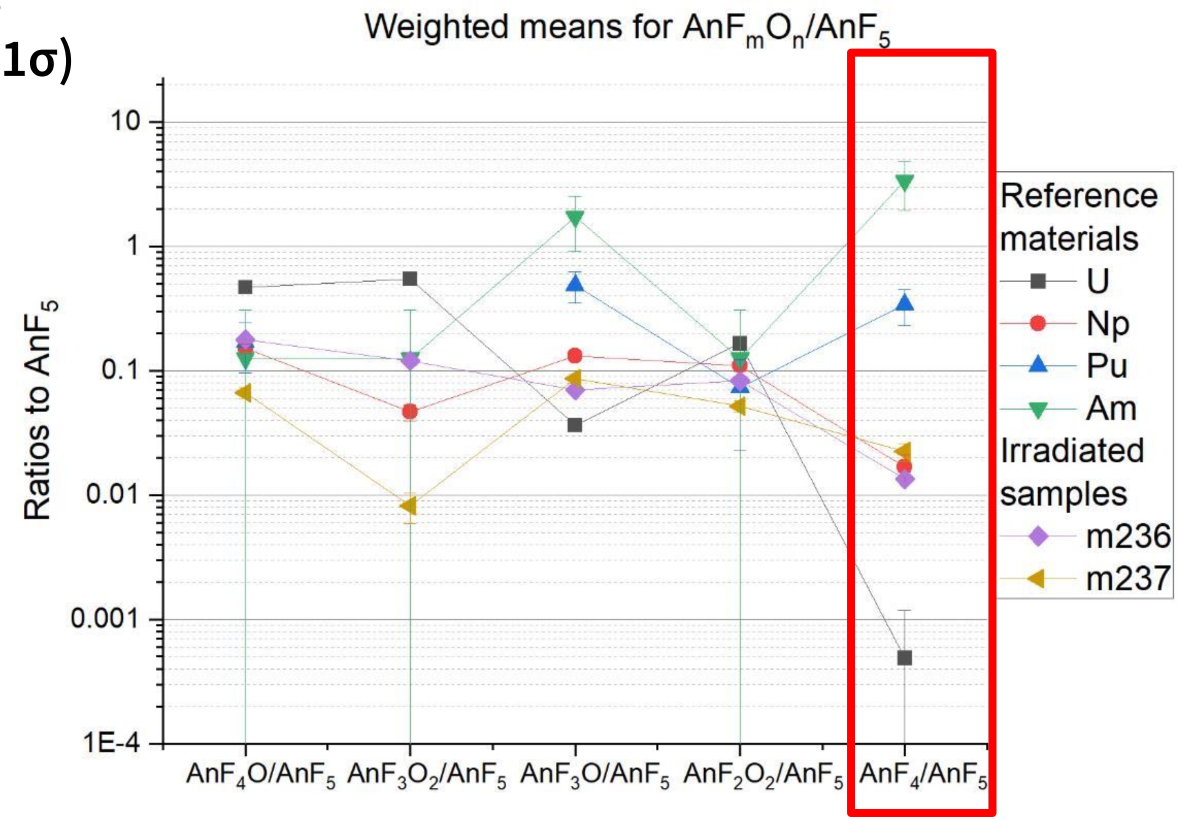
- **m236 AnF_4^-/AnF_5^- ratio is compatible with ref. Np (1σ)**
  - **Isobaric ^{236}U interference is negligible**
- **The production and separation of ^{236}Np was successful**



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Conclusion and outlook

- The relative formation probabilities for

AnF_5^-	AnF_4O^-	$AnF_3O_2^-$
AnF_3O^-	$AnF_2O_2^-$	AnF_4^-

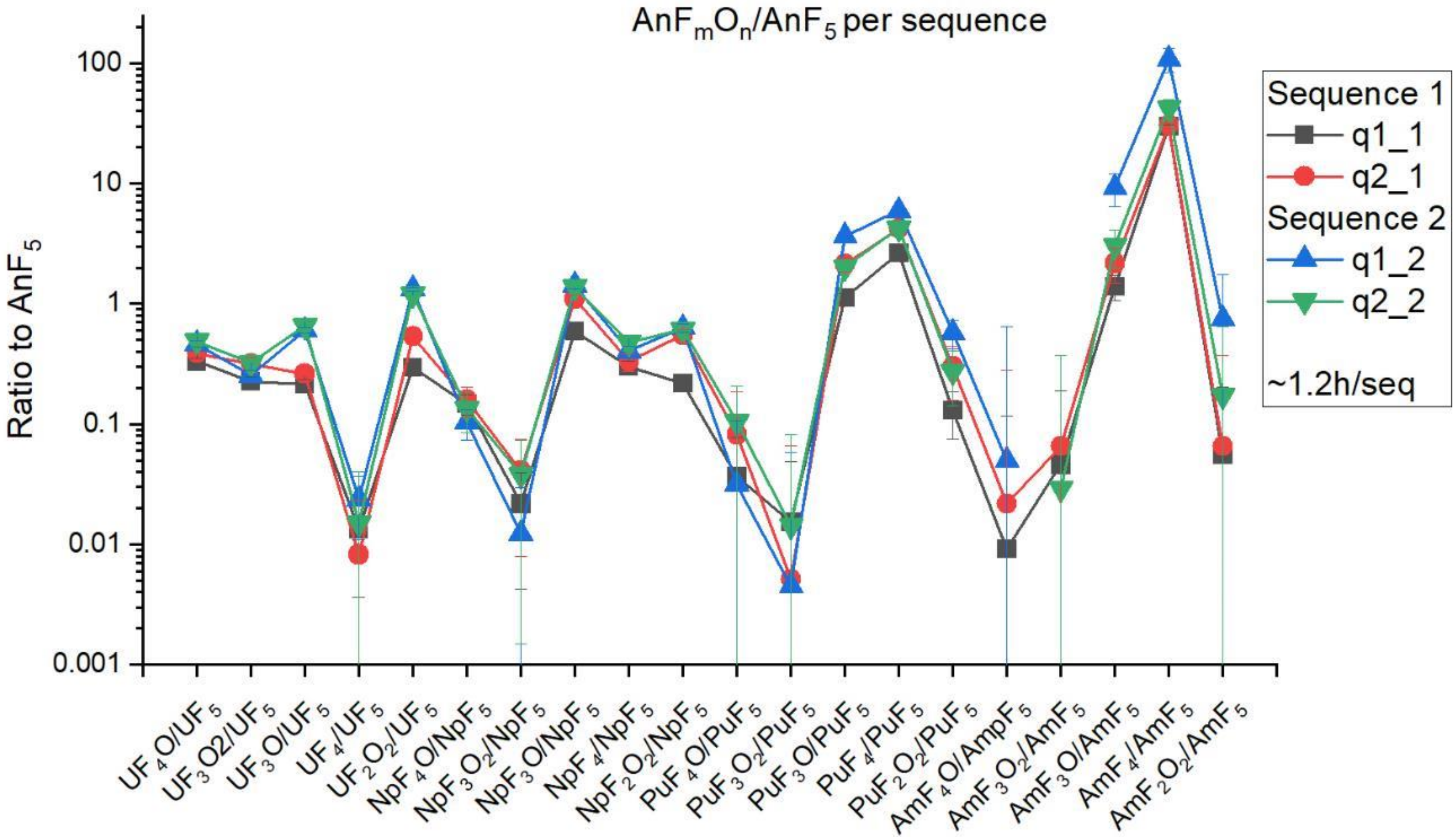
are characteristic for U, Np, Pu and Am

  - 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?



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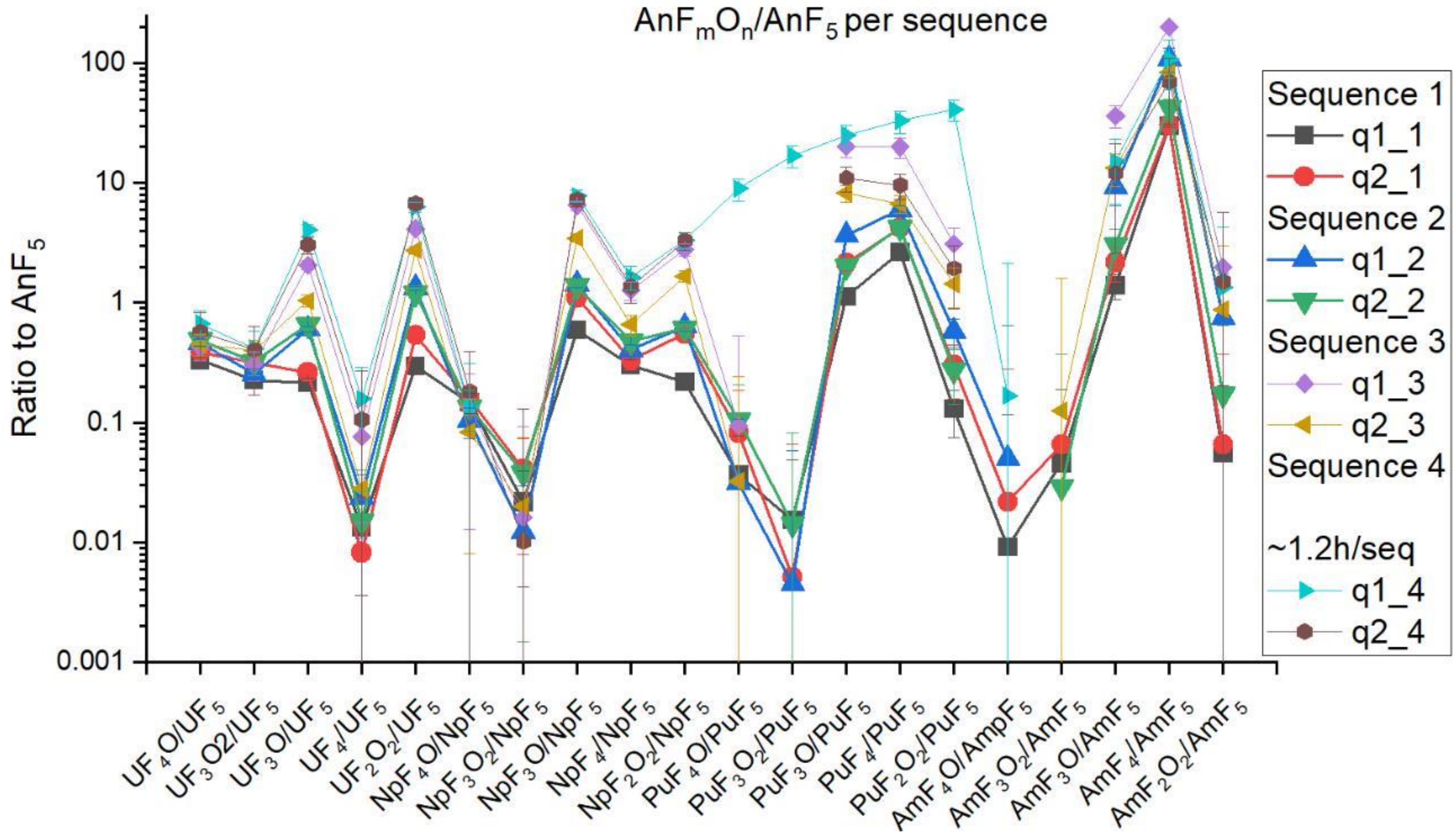
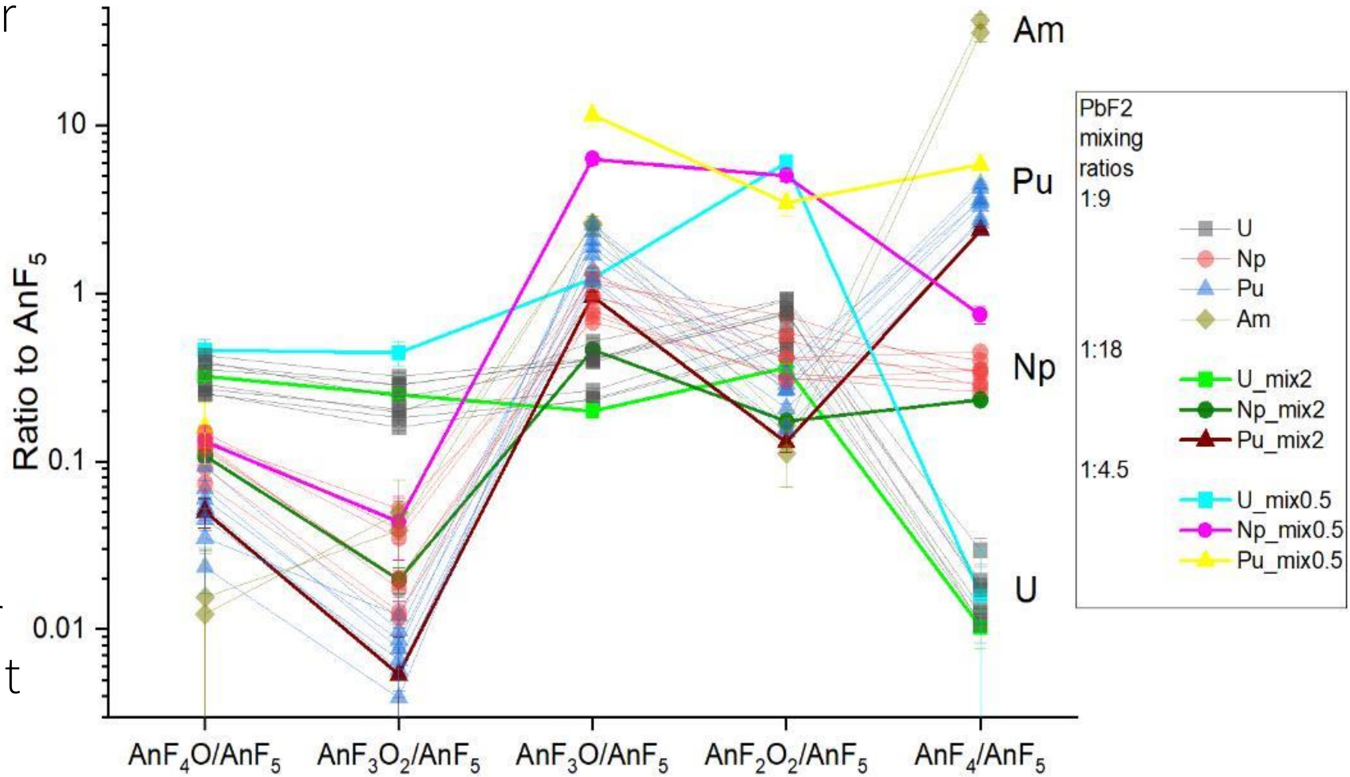


- Ratios change significantly after the first two sequences
- All targets should be measured for 2 sequences (~2.5h) for consistent results

How stable are the ratios for different mixing rates with PbF_2?

- Reducing mixing ratios to 1:4.5 increases lower fluorides/oyxfluorides
  - Similar to long measurement duration
  - Fluorine supply affects formation probablilities
- Increasing PbF_2 further (1:18) has no significant effect



How stable are the ratios between Beamtimes

- $AnF_mO_n^-/AnF_5^-$ ratios change between beamtimes
  - Ion source conditions?
  - Tuning?
- Separation for AnF_4/AnF_5 remains stable
  - Method is robust against tuning variations!
- Reference samples have to be included in every measurement