ANALYTICAL MEASUREMENTS AND PROTOCOLS FOR THE QUALIFICATION OF NpO₂ TARGETS FOR IRRADIATION IN ORNL'S HIGH FLUX ISOTOPE REACTOR

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Presentation Overview

• Introduction – the use of Pu-238 in Radioisotope Thermoelectric Generators (RTGs)

• Background – modelling the activation of Np-237 for Pu-238 production

• Analytical efforts towards improving the modelling of fission products

• High precision fission product measurements using mass spectrometry
  – Inductively Coupled Plasma Mass Spectrometry
  – Isotope Dilution Methods
  – Comprehensive Rapid Semi-Quantitative Analysis Routine

• Future analytical efforts towards improving the modelling of fission products
"RTGs provided by DOE have enabled American scientists to explore the solar system for many years….

Apollo missions…, the Viking missions to Mars, the Pioneer, Voyager, Ulysses, Galileo and Cassini missions….

all used this safe, efficient and long-lasting power source."

Mars Science Laboratory Curiosity: 8 general-purpose heat source modules, 4.8 kg of PuO₂

Launched in 1977, Voyager 1 is currently 1.91×10¹⁰ km from Earth
Pu-238 Production Through the Irradiation of Al Doped NpO$_2$ Targets

- Np-237 + n → Np-238 (β decay 2.1d) → Pu-238

- Main Losses
  - Np-237 + n → Fission
  - Np-238 + n → Fission (large thermal neutron cross section)
  - Np-238 + n → Np-239 (β decay 2.4d) → Pu-239
  - Pu-238 + n → Pu-239 (large thermal neutron cross section)
  - Pu-239 + n → Fission
Fission Rates Drive the Target’s Heat Generation During Irradiation

• Capacity to produce Pu-238 is limited by heat production in the targets
  – The major source of heating is the fission of Np-238

• Np-237 loading density is currently based on nuclear transmutation codes that predict the fission rates which are not precisely known

• Measurements to improve the accuracy of nuclear data specific to Pu-238 production will allow for revised heating calculations which may be made such that the loading density of the Np-237 targets could be increased, thereby, increasing the production capacity for Pu-238
Analytical Goal

To provide empirical data of sufficient breadth, accuracy, and precision to allow for improvements for modelling target behavior during irradiations in ORNL’s High Flux Isotope Reactor.
Initial Demonstration Pellet Irradiations

• Pellets 1, 2, and 3:
  – Transferred from High Flux Isotope Reactor (HFIR) to the Radiochemical Engineering Development Center (REDC) or Irradiated Fuels Examination Laboratory (IFEL) – 14,000 R/hr (@30cm) each ~0.5g pellet

• Standard Radiochemical Analyses:
  – Gamma emitting fission products were measured lower than ORIGEN predicted values
  – ICPMS measured low and high mass fission products lower than ORIGEN predicted values
  – Both radiochemical and ICPMS measurements for Np-237 and Pu-238 were within 1%-5% of predicted
  – Standard measurement techniques indicated over-prediction of the number of fissions occurring in the targets and fission products in model by 20-40%
Chemical Development Stage – PELLET 5

- PELLET 2 dissolution also worked on developing the chemical processing

- Pu and Np determined via ICP-MS

- High precision (1-2% uncertainty) measurements of key lanthanide fission products were performed using enriched isotopes (isotope dilution mass spectrometry)

- Due to multistage dissolution the fission products were normalized to the determined neptunium mass for comparison
High Precision HPLC-IDMS

- **Sample** - Unknown Ln fission product mixture
- Spiked with *isotopically enriched standards* by mass
- Elements separated using a High Pressure Liquid Chromatography
- Purified element fractions analyzed using ICPMS
- Measured isotopics in *sample*, and in *sample + spike* used to determine isotopic masses of analyte to a 1-2% uncertainty using principles of GUM
Comprehensive Analyses – PELLET 6

• Single complete high precision pellet dissolution  
  – 2 duplicate dilutions by weight performed
• Full radiochemical analysis performed (10% uncertainty analysis)
• High precision isotope dilution mass spectrometry for high mass fission products on duplicate samples (1-2% uncertainty)
• Focused semi-quantitative rapid measurement routine to quantify low and high masses of the fission products (5% uncertainty)
### PELLET 6 Empirical Data vs. ORIGEN

#### ICPMS (actinides) Measured/ORIGEN

<table>
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<th>g/gNp</th>
<th>g/gNp</th>
<th>%</th>
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<tr>
<td>Neptunium 237</td>
<td>1.00E+00</td>
<td>1.00E+00</td>
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</tr>
<tr>
<td>Plutonium 238</td>
<td>1.13E-01</td>
<td>1.13E-01</td>
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<tr>
<td>Plutonium 239</td>
<td>1.45E-02</td>
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#### IDMS (fission products) Measured/ORIGEN

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<td>$^{154}$Sm</td>
<td>3.64E-05</td>
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- For heat calculations, individual isotope concentrations are not too important.
- Monitoring the total number of fissions is the goal of the model, therefore, we needed a measurement routine that would quantify as many fission events by mass as is possible.
• Abundant isotope chosen for each element

Machine parameter Relative Sensitivity Factor (RSF) element dependent (ionization efficiency)

– Each element has an associated error based on the predicted curve

– When an elemental RSF is modified the error for each element changes

– The elemental “best fit” semiquant curve is achieved when the modified RSF’s result in <2% error for each element
Semi-Quant Analyses – PELLET 6

- The semi-quantitative curve is validated using laboratory control standards.
- Enables direct analysis of a single dilution to yield quantitative results (>95% precision) without spiking, separation, or external calibration for individual elements.
Full fission product analysis using a semi-quantitative curve

- **Total** fission product gross mass agreed within ~2% precision
- IDMS of Ln and Cs validated the semi-quant curve to within ~2% accuracy
Next Step: High-Precision Irradiations at HFIR NAA Laboratory

- PT-1 facility has a well known neutron flux spectrum
- Accurate and reliable real-time measurement of flux
- PT-1 irradiation position is similar to target position – both magnitude and spectrum
238Np Fission Measurement Plan

• Model fission of 238Np, 238U, and 235U for the PT-1 spectrum
  – Already underway

• Measure U fission product production in PT-1 – verify model, calibrations, flux measurements

• Measure Np fission products using the production rate established for U – capture all of the fission products!
  – Initial irradiations and gamma counting in progress

• Use DNAA to evaluate 238Np DN yields

Delayed Neutron Counting System

18 He-3 detectors

Transport time ~3 sec

![Graph of Delayed Neutron Count Rate vs Count Time]
Initial Measurements on a Np$_2$O$_3$ Target

- Target inside welded vanadium can
- $^{140}$La is measurable with less decay than other fission products
  - $^{140}$La (1596 keV) is higher energy than the $^{238}$Np intense gamma-rays
  - Spectral effects, such as Compton scattering, are much reduced
- Other fission products such as $^{137}$Cs and $^{131}$I have been identified
- Longer decay times will be needed to measure other fission products because of the large amount of $^{238}$Np
Summary

**Irradiated Targets**

1. Hot Cell Dissolution
2. Primary Solution
   - Radiochemistry
   - Quant ICP-MS
   - HPLC-IDMS
   - Semi-quant ICP-MS
3. NAA protocols

**Empirical Data**

- Isotopic Data of Radionuclides
- Quantitative and isotopic data of Np/Al/Pu
- High Precision data of Lanthanide/Fission Product
- Semi-Quantitative data of all fission product masses
- High precision data for gaseous and short lived fission products

**Additional Content**

- Sensitivity (ICPS/PPB) vs Mass (AMU)
- Mass number (A) vs Atoms
- Measured and Calculated data comparison
Acknowledgments

All members of the Nuclear Analytical Chemistry and Isotopics Laboratories (NACIL) group at ORNL