Production of $^{236}\text{gNp}$ and $^{236}\text{Pu}$ at NPL

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Overview

- NPL and measurement
- How we got to here from there
- Neptunium-236g
- Plutonium-236
- Additional work
The NPL: 1900 – now

- Facilitates trade via measurement science – **metrology**
- 36,000 m² national laboratory facility on the Teddington site
  - Houses all NPL operations (except Neutron Metrology)
  - One of the most extensive and sophisticated measurement science building in the world
  - ~750 Staff, of whom ~550 directly involved in science
Ionising Radiation at NPL

- **Radiation Dosimetry**
  - Ranges from environmental levels to high-dose industrial levels
  - Mainly electrons and photons – from <10 keV to 25 MeV
  - Includes protons and light ions for radiotherapy
  - Modelling (Mainly Monte Carlo) underpins measurement

- **Neutron Metrology**
  - Neutron flux measurements from thermal to fast/cosmic energies
  - Thermal energies – reactor physics
  - Fast neutrons – nuclear data, fission and fusion
  - Cosmic rays – dose rates in aerospace, effects in electronics

- **Radioactivity**
  - Measurement standards for sealed and unsealed sources
  - Production of calibration sources for industry and hospitals
  - Calibration of measurement instruments and of sources
  - Researching new radionuclide production techniques
Why worry about $^{237}$Np?

- **Long lived actinide**
  - Apart from naturals, fourth longest lived
  - $t_{1/2}$: $2.144(7) \times 10^6$ years
  - $^{247}$Cm: $15.6(5) \times 10^6$ years
  - $^{236}$U: $23.43(1) \times 10^6$ years
  - $^{244}$Pu: $80.8(7) \times 10^6$ years

- **Decay product of $^{241}$Pu**
  - Activation of $^{235}$U: $^{235}$U$(n,\gamma)^{236}$U$(n,\gamma)^{237}$U($\beta$)$^{237}$Np
  - Member of ‘$4n+1$’ chain
  - $^{245}$Cm($\alpha$)$^{241}$Pu($\beta$)$^{241}$Am($\alpha$)$^{237}$Np($\alpha$)$^{233}$Pa($\beta$)$^{233}$U($\alpha$)$^{229}$Th…$^{209}$Bi

- **The forgotten actinide**
  - May have been >20 PBq (5.2 t) $^{241}$Pu discharged from Sellafield since 1950
Why are we interested in $^{236}\text{Np}$?

- **Nuclear physics**
  - A long-lived *odd-odd* nucleus ($^{236}\text{g}\text{Np}$)
  - Some outstanding needs to improve decay data

- **Chemical yield tracer**
  - Precursor to $^{236}\text{Pu}$ ($^{236}\text{m}\text{Np}$)
  - Suitable isotope dilution tracer for $^{237}\text{Np}$ measurements ($^{236}\text{g}\text{Np}$)

- **Some difficulties**
  - Singularly difficult to make – not a decay product
  - Production data is a bit sparse
  - Chemistry is interesting
Tracer Requirements

What do we expect from a tracer?


- Tracer exhibits same chemical behaviour as analyte:
  - Implies that the same element should be employed

- Tracer should not interfere with analyte measurement:
  - Preferable to measure by the same technique, or if the tracer does not register in the analyte measurement (and vice versa)

- Chemical equilibrium between tracer and analyte established at earliest possible point in the analysis:
  - Add the tracer as soon as possible and (for solids) employ total dissolution
Tracer Requirements

Furthermore:

- **Tracer should not be present in samples being analysed:**
  - Using nuclides present in the samples being analysed complicates analysis

- **Tracer should not introduce contamination:**
  - Purity requirement: may differ for mass spectrometry and radiometric measurements

- **Tracer should be traceable to national or international standards:**
  - Not strictly so: Measurements of γ emitting tracers may be relative
Which nuclide?

Need to be able to carry out mass spectrometry

- Neptunium-236g is only practical option
  - Can’t be produced by radioactive decay or neutron activation, so use charged particle irradiation
    Proton or deuteron activation of uranium at <50 MeV
  - LinAc irradiation uses $^{237}\text{Np} (\gamma,\text{n})$
    Can’t separate $^{236}\text{gNp}$ from $^{237}\text{Np}$

- Production routes
  - $^{236}\text{U}(p,n)^{236}\text{Np}$ also produces $^{234}\text{Np}$ and $^{235}\text{Np}$
  - $^{238}\text{U}(p,3n)^{236}\text{Np}$ also produces $^{237}\text{Np}$ and $^{238}\text{Np}$
  - $^{235}\text{U}(d,n)^{236}\text{Np}$ also produces $^{235}\text{Np}$ and $^{237}\text{Np}$
  - $^{236}\text{U}(d,2n)^{236}\text{Np}$ also produces $^{235}\text{Np}$ and $^{237}\text{Np}$
  - $^{238}\text{U}(d,4n)^{236}\text{Np}$ also produces $^{237}\text{Np}$ and $^{238}\text{Np}$
Nuclear parameters for $^{236}$Np

- **What we know**
  - $^{236}$Np is an odd-odd isobar
  - Q value of decay energy is (just) below $\beta^+$ energy of 1.022 MeV
  - Spin states not measured
  - Half lives 22.5 h ($^{236m}$Np) and $1.55 \times 10^5$ years ($^{236g}$Np)

- **What we assume (from data)**
  - The ground state has high spin – inferred from decay states which are high spin
  - *Vice versa* for the metastable state
Decay parameters for $^{236}$Np

- **Some nuclear physics**
  - Angular momentum coupling rules for $Z=93$ protons ($5/2^+$) and $N=143$ ($7/2^-$) neutrons give spins of $I^\pi=6^-$ and $I^\pi=1^-$ from $I^{\text{tot}} = 7/2^- \pm 5/2^+$
  - In other words...the $^{234}$U nucleus is a closed shell (92 protons and 142 neutrons)
  - Proton and neutron external to this shell with aligned spins are in the lower energy ground state
  - Proton and neutron external to this shell with opposed spins are in the higher energy metastable state

- **Decay parameters**
  - $^{236m}$Np: $\beta^-$: $47(\pm1)\%$  
    EC: $53(\pm1)\%$
  - $^{236g}$Np: $\beta^-$: $12.0(\pm0.6)\%$  
    EC: $87.8(\pm0.6)\%$
  - $^{236g}$Np: $\alpha$: $\sim0.16\%$ at 5.01 MeV predicted
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$^{235}\text{U}$</th>
<th>$^{236}\text{U}$</th>
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<td></td>
<td>Product</td>
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<td>Product</td>
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<td>p,n</td>
<td>$^{235}\text{Np}$</td>
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<td>$^{236}\text{Np}$</td>
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<tr>
<td>p,2n</td>
<td>n/a</td>
<td>$^{235}\text{Np}$</td>
<td>$\sigma$ presented</td>
</tr>
<tr>
<td>p,3n</td>
<td>n/a</td>
<td>n/a</td>
<td>$^{236}\text{Np}$</td>
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<tr>
<td>p,4n</td>
<td>n/a</td>
<td>n/a</td>
<td>$^{235}\text{Np}$</td>
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<tr>
<td>d,n</td>
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<td>$\sigma$ presented</td>
<td>$^{237}\text{Np}$</td>
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<td>d,2n</td>
<td>$^{235}\text{Np}$</td>
<td>$\sigma$ presented</td>
<td>$^{236}\text{Np}$</td>
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<td>d,3n</td>
<td>$^{235}\text{Np}$</td>
<td>$\sigma$ presented</td>
<td>$^{237}\text{Np}$</td>
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NPL Management Ltd - Internal
Cross sections for $^{236}\text{Np}$

Neptunium-236 production

Cross section (millibarns) vs. Particle energy (MeV)

- $^{238}\text{U}(p,3n)^{236}\text{Np}$ (Aaltonen et al, 1994)
- $^{238}\text{U}(p,3n)^{236}\text{Np}$ (Ageev et al, 1987)
- $^{238}\text{U}(d,4n)^{236}\text{Np}$ (Lessler et al, 1966)
- $^{236}\text{U}(d,2n)^{236}\text{Np}$ (Lessler et al, 1966)
- $^{235}\text{U}(d,n)^{236}\text{Np}$ (Wing et al, 1959)
- $^{236}\text{U}(d,n)^{236}\text{Np}$ (Ageev et al, 1994)
- $^{238}\text{U}(p,n)^{236}\text{Np}$ (Aaltonen et al, 1996)
- $^{238}\text{U}(d,4n)^{236}\text{Np}$ (Guzhovskii et al, 1994)
- $^{238}\text{U}(d,4n)^{236}\text{Np}$ (Wing et al, 1959)
- $^{235}\text{U}(d,n)^{236}\text{Np}$ (Lessler et al, 1966)
Production of $^{236g}$Np

Uranium-236 irradiation with protons

Cross section (millibarns)

Proton energy (MeV)

- U-236(p,2n)Np-235 (Aaltonen et al, 1996)
- U-236(p,2n)Np-235 (Aaltonen et al, 2005)
- U-236(p,n)Np-236 (Aaltonen et al, 1996)
- U-236(p,n)Np-236 (Aaltonen et al, 2005)
Summary of data

- **Do we form $^{236m}$Np or $^{236g}$Np?**
  - High spin state of $^{236g}$Np favours (or it should do!) high angular momentum reactions
  - Therefore, use higher incident energy for irradiation
  - But at higher energies, the cross section is lower

- **Impurities**
  - Higher energies risk the production of $^{235}$Np and $^{234}$Np
  - Lower energies risk the production of $^{237}$Np
  - Thick sources risk the production of $^{237}$Np due to beam energy degradation
  - Thick sources also yield more fission products
Formation ratio of $^{236\text{m}}\text{Np}:^{236\text{g}}\text{Np}$

Published data mainly theoretical

Ratio data as a function of energy

Ratio

Particle energy (MeV)

$R = \sigma_{\text{m}} / \sigma_{\text{g}}$
Summary of Irradiations

- Different options
  - The problem is the cross section data
  - Data generated 1959-1990
  - $^{\text{236}}\text{U}(p,n)^{\text{236}}\text{Np}$ 2011–date 10-20 mb (20-40 MeV) ✓
  - $^{\text{238}}\text{U}(p,3n)^{\text{236}}\text{Np}$ 2010–date 50-70 mb (15-30 MeV) ✓
  - $^{\text{235}}\text{U}(d,n)^{\text{236}}\text{Np}$ 2009–2011 ~5 mb (10-20 MeV) ✗

- Experiments from 2009
  - Aimed at $^{\text{236}}\text{Pu}$ and now $^{\text{236}}\text{gNp}$ production
  - Production of $^{\text{236}}\text{Pu}$ implies production of $^{\text{236}}\text{mNp}$ and $^{\text{236}}\text{gNp}$
  - Experiments in 2010 and 2011 with $^{\text{235}}\text{U}$ also produced large amounts of $^{\text{234}}\text{Np}$ and, presumably, $^{\text{235}}\text{Np}$
Target preparation

- Uranium metal: ☓ ☓ ☓
  - Catches fire, definitely not good
- Aqueous $\text{UO}_2(\text{NO}_3)_4$: ☓
  - Flaky, spalls easily, not good
- $\text{UO}_2(\text{NO}_3)_4$ in acetone: ☓ ☓
  - Goes all weird, not good
- $\text{UO}_2$ solid: ☑ ☑
  - Dissolution can take time
  - Does not burn, spall or expand
  - Therefore good
Separation chemistry

Either extraction chromatography
- TEVA resin
- Still use 10M HCl/0.1M NH₄I to remove plutonium
- Recover neptunium with dilute hydrochloric acid
- Need to recover $^{236}\text{U}$

or anion exchange chromatography
- AG1-X8 resin
- Still use 10M HCl/0.1M NH₄I to remove plutonium
- Recover neptunium with dilute nitric acid
- Need to recover $^{236}\text{U}$
Measurement of $^{236}$Np fraction
Summary to March 2014

- Neptunium-236g
  - Still need to finally tie down irradiation option
    - $^{236}\text{U}(p,n)$ purest
    - $^{238}\text{U}(p,3n)$ highest
  - Chemistry known, but requires final definition to maximise yield
  - Purity still to be measured (how much $^{237}\text{Np}$...appears to be low)
  - Will measure $\alpha$-emission branch (predicted, not observed), so decay scheme balances
  - Prediction that 1 µg available in 4Q14
  - Should be able to produce 1-10 µg annually
Additional benefits

- Fission products of interest (per irradiation)
  - Top interest
    - $^{93}\text{Zr}$, $^{113m}\text{Cd}$, $^{135}\text{Cs}$, $^{151}\text{Sm}$
  - Medium interest
    - $^{91}\text{Y}$, $^{103}\text{Ru}$, $^{155}\text{Eu}$
    - $^{95}\text{Zr}$, $^{106}\text{Ru}$, $^{144}\text{Ce}$
- Separation chemistry
  - Known for $\text{Y}^{3+}$, $\text{Zr}^{4+}$, $\text{Cs}^+$, $\text{Ce}^{3+}$, $\text{Sm}^{3+}$ and $\text{Eu}^{3+}$
  - Devised for $\text{Ru}^{n+}$ and $\text{Cd}^{2+}$

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Activity</th>
<th>ng</th>
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<tbody>
<tr>
<td>$^{91}\text{Y}$</td>
<td>31 MBq</td>
<td>34</td>
</tr>
<tr>
<td>$^{93}\text{Zr}$</td>
<td>1.2 Bq</td>
<td>120</td>
</tr>
<tr>
<td>$^{95}\text{Zr}$</td>
<td>35 MBq</td>
<td>44</td>
</tr>
<tr>
<td>$^{103}\text{Ru}$</td>
<td>13 MBq</td>
<td>11</td>
</tr>
<tr>
<td>$^{106}\text{Ru}$</td>
<td>920 kBq</td>
<td>7</td>
</tr>
<tr>
<td>$^{107}\text{Pd}$</td>
<td>&lt;1 Bq</td>
<td>3</td>
</tr>
<tr>
<td>$^{113m}\text{Cd}$</td>
<td>2.6 kBq</td>
<td>&lt;1</td>
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<td>$^{126}\text{Sn}$</td>
<td>1.6 Bq</td>
<td>2</td>
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<tr>
<td>$^{135}\text{Cs}$</td>
<td>9.1 Bq</td>
<td>180</td>
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<td>$^{144}\text{Ce}$</td>
<td>15 MBq</td>
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<td>13</td>
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<tr>
<td>$^{155}\text{Eu}$</td>
<td>17 kBq</td>
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</table>
How we got to here from there

- **Plutonium-236**
  
  - Plutonium yield tracers: $^{236}$Pu, $^{242}$Pu, $^{244}$Pu (and $^{237}$Pu)
  
  - Using $^{237}$Pu is not considered (short half-life, EC/\(\gamma\), but…)
  
  - Running out of suitably pure $^{242}$Pu
    
    $^{241}$Pu\( (n,\gamma) ^{242}\)Pu – needs an isotope separator
    
    $^{241}$Am\( (n,\gamma) ^{242}\)Am\( (EC) ^{242}\)Pu – needs patience
  
  - There’s hardly any suitably pure $^{244}$Pu
    
    $^{242}$Pu\( (n,\gamma) ^{243}\)Pu\( (n,\gamma) ^{244}\)Pu – needs patience and a mass separator
  
  - Plutonium-236 was available (expensive and sporadic)

  \[ \begin{align*}
  \sim 5 \text{ mb} & \quad ^{235}\text{U}(d,n) \\
  \sim 10-20 \text{ mb} & \quad ^{236}\text{U}(p,n) \text{ or } (d,2n) \\
  \sim 50-70 \text{ mb} & \quad ^{238}\text{U}(p,3n) \text{ or } (d,4n) \\
  \sim 5 \text{ mb} & \quad ^{237}\text{Np}(\gamma,n) \text{ or } (n,2n) \\
  \sim 5 \text{ mb} & \quad ^{235}\text{U}(\alpha,3n)^{236}\text{Pu} \\
  \end{align*} \]
Plutonium-236 (2009-)

- **Irradiation of $^{235}$U with deuterons**
  - Starting material $>$99.9% $^{235}$U
  - University of Birmingham cyclotron, 19 MeV deuterons

- **Irradiation of $^{236}$U with protons**
  - Starting material $>$99.7% $^{236}$U
  - University of Birmingham cyclotron, 25 MeV protons

- **Chemistry**
  - Dissolve target in hydrochloric acid
  - Pass through anion exchange column (AG1-X8, 100-200 mesh)
  - Uranium, neptunium, plutonium, zirconium and niobium retained by the resin
Plutonium-236 (2009-)

- Purification as before
  - Zirconium removed from column with 6M hydrochloric acid
  - Plutonium washed from column with 10M HCl/0.1M NH₄I
  - Neptunium washed from column with 3-6M hydrobromic acid
  - Repeat anion exchange steps to remove residual fission products
  - Niobium still difficult to remove

  **Proton irradiation:** purity obtained <0.001% \(^{238}\text{Pu}\)
  **Deuteron irradiation:** purity obtained ~0.02% \(^{238}\text{Pu}\)

  \(\text{(Proton irradiation of } U_{\text{nat}}: \text{purity obtained } 1.5(\pm0.2)\% \^{238}\text{Pu})}\)

- Preferred route, therefore, is \(^{236}\text{U}(p,n)^{236m}\text{Np}(\beta)^{236}\text{Pu}\)
- Yield \(^{238}\text{U}(p,3n)>^{236}\text{U}(d,2n)>^{236}\text{U}(p,n)>^{235}\text{U}(d,n)\)
Measurement of $^{236}\text{Pu}$ fraction

![Graph showing alpha energy (keV) vs. counts per channel with peaks at 4445 keV, 4494 keV, 5363 keV, 5320 keV, 5721 keV, and 5768 keV for $^{236}\text{U}$ and $^{236}\text{Pu}$.]
Summary to March 2014

- **Plutonium-236**
  - Straightforward operation
  - Chemistry require not further research…refinements possible
  - Purity is good (<0.001% $^{238}\text{Pu}$)
  - Can be made in quantities >100 kBq relatively easily
Continuing work

- **Project team**
  - Steven Judge, Group Leader (Project manager)
  - Prof Paddy Regan†, Nuclear Physics leader
  - Simon Jerome, Radiochemistry leader
  - Peter Ivanov, Lead chemist
  - Andy Pearce, Lead spectrometrist
  - Lynsey Keightley, γ-spectrometry
  - Cyrus Larijani, α-spectrometry

- **Aim for next 12-18 months**
  - Routine production of $^{236}$gNp
  - Maximise production; minimise impurities
  - Continue ‘production line’ for high purity $^{236}$Pu and selected fission products

† - Professor of radionuclide metrology at NPL/University of Surrey
Thank you for your attention.
Any questions?

National Measurement System

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NPL, LGC, NEL, National Measurement Office

The National Measurement System is the UK’s national infrastructure of measurement laboratories, which deliver world-class measurement science and technology through four National Measurement Institutes (NMIs): LGC, NPL, the National Physical laboratory, TUV NEL the former National Engineering Laboratory, and the National Measurement Office (NMO).