Improvements to the Analysis of Lanthanides in Nuclear Forensics Samples

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Aim

- To develop and establish a lanthanide method which separates lanthanides from each other using Eichrom LN Resin.
- The separation must be robust for different types of nuclear forensics samples, including sample sizes, sample matrices, and carrier loadings.
The lanthanides and Y are fission products of interest in nuclear forensic samples.
# Lanthanides Present in Fission Samples

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life (days)</th>
<th>$^{235}$U Thermal Fission Yield % (atoms/fission)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{141}$Ce</td>
<td>32.50</td>
<td>5.85</td>
</tr>
<tr>
<td>$^{143}$Ce</td>
<td>1.377</td>
<td>5.96</td>
</tr>
<tr>
<td>$^{144}$Ce</td>
<td>284.6</td>
<td>5.50</td>
</tr>
<tr>
<td>$^{147}$Nd</td>
<td>10.98</td>
<td>2.25</td>
</tr>
<tr>
<td>$^{153}$Sm</td>
<td>1.928</td>
<td>0.158</td>
</tr>
<tr>
<td>$^{156}$Eu</td>
<td>15.2</td>
<td>0.0149</td>
</tr>
<tr>
<td>$^{161}$Tb</td>
<td>6.91</td>
<td>8.53x10^{-5}</td>
</tr>
</tbody>
</table>
**Lanthanide Intra-group Separation**

**Current AWE method:**
- Lanthanides are separated from each other by cation exchange column using 0.5 M \( \alpha \)-hydroxyisobutyric acid (HIBA) pH 3.30 → 3.75 as eluent.
- 500 µg of each Lanthanide and Y are added as carriers.
- 2 samples are processed at a time due to lab space and equipment availability.
- Purified Sm, Eu, Tb, and Y are analysed by gamma counting.

**Issues:**
- Low chemical recoveries (10%-40%).
- Significant lab time and space.
- Not possible to measure the terbium fraction by the current method due to its very low fission yield, short half-life, and low chemical recovery.
Lanthanide Separation Using LN Resin

LN Resin

di(2-ethylhexyl)orthophosphoric acid (HDEHP)

Retention of Various Elements on LN Resin

\[ \text{Ln}^{3+} + 3\text{NO}_3^- + n\text{LN}_{(\text{org})} \leftrightarrow [\text{Ln}(\text{LN})_n(\text{NO}_3)_3]_{(\text{org})} \]
Parameters Investigated

- **Resin particle size**
  - 50-100 µm

- **Nitric acid gradient**: 0.01-8 M HNO₃
  - Effects elution rate of each lanthanide – optimization allows for separation of various elements such as Sm/Eu and Eu/Tb

- **Resin mass**
  - 50-100 µm: 0.78, 1.20 and 1.56 grams

- **Carrier mass loading**
  - 50, 100, 200 and 500 µg lanthanides and yttrium

- **Matrix mass loading**
  - 1 gram of NPL SRM-90A and 90E (lanthanides were separated from other elements by UTEVA/TRU columns).

- **Columns**
  - Eichrom, 2 mL plastic, 0.8 cm ID
  - Biorad, 20 & 30 cm glass, 0.7 cm ID
Experiment Setup

Original setup

New setup
Elution Profile for Lanthanides and Y (1)

- Sample: 50 µg of 14 lanthanides & Y
- Resin mass: 0.78 grams
- LN resin 50-100 µm
- Eichrom 2 mL plastic columns, ID 0.8 cm
- A75-30
- Sample: 200 µg of 14 lanthanides & Y
- Resin mass: 1.20 grams

- LN resin 50-100 µm
- Biorad 20 cm glass column, ID 0.7 cm
A75-34
Sample: 500 µg of 14 lanthanides & Y
Resin mass: 1.56 grams

LN resin 50-100 µm
Biorad 30 cm glass column, ID 0.7 cm
## Sm Co-elution in the “Tb Fraction”

<table>
<thead>
<tr>
<th>Carrier Mass (µg)</th>
<th>Resin Mass (g)</th>
<th>Matrix</th>
<th>First Separation</th>
<th>Second Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.78</td>
<td>A75-17</td>
<td>3.7</td>
<td>A75-20</td>
</tr>
<tr>
<td>50</td>
<td>0.78</td>
<td>SRM-90A</td>
<td>1.9</td>
<td>A75-21</td>
</tr>
<tr>
<td>200</td>
<td>1.2</td>
<td>SRM-90E</td>
<td>2.5</td>
<td>A75-36</td>
</tr>
<tr>
<td>200</td>
<td>1.2</td>
<td>A75-31</td>
<td>12.0</td>
<td>A75-37</td>
</tr>
<tr>
<td>200</td>
<td>1.56</td>
<td>A75-33</td>
<td>10.5</td>
<td>A75-38</td>
</tr>
<tr>
<td>500</td>
<td>1.56</td>
<td>A75-35</td>
<td>13.4</td>
<td>A75-39</td>
</tr>
</tbody>
</table>
Tb Purification Using Second Column

- A75-39
- Sample: 500 µg of 14 lanthanides & Y
- Resin mass: 0.78 grams
- LN resin 50-100 µm
- Eichrom 2 mL plastic columns, ID 0.8 cm
Reproducibility – Carrier Loading

- Resin mass: 1.56 grams
- LN resin 50-100 µm
- Biorad 30 cm glass column, ID 0.7 µm
- A75-32: 200 µg of 14 lanthanides & Y
- A75-33: 200 µg of 14 lanthanides & Y with second column
- A75-34: 500 µg of 14 lanthanides & Y
- A75-35: 500 µg of 14 lanthanides & Y with second column
Reproducibility – Matrix (SRM-90E)

- Resin mass: 1.20 grams
- LN resin 50-100 µm
- Biorad 20 cm glass column, ID 0.7 µm
- A75-28: 200 µg of 14 lanthanides & Y with matrix
- A75-29: 200 µg of 14 lanthanides & Y with matrix and second column
- A75-30: 200 µg of 14 lanthanides & Y
- A75-31: 200 µg of 14 lanthanides & Y with second column
Reproducibility – Matrix (SRM-90E)
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>AWE (atoms/gram)</th>
<th>AWE %</th>
<th>PNNL (atoms/gram)</th>
<th>PNNL %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{153}$Sm</td>
<td>2.50x10⁹</td>
<td>7.5%</td>
<td>2.59x10⁹</td>
<td>2.4%</td>
</tr>
<tr>
<td>$^{156}$Eu</td>
<td>4.04x10⁸</td>
<td>6.4%</td>
<td>4.06x10⁸</td>
<td>4.4%</td>
</tr>
<tr>
<td>$^{161}$Tb</td>
<td>5.21x10⁶</td>
<td>4.7%</td>
<td>5.64x10⁶</td>
<td>4.4%</td>
</tr>
</tbody>
</table>
Gamma Spectrum for Purified $^{161}$Tb

| Idle | LOG=256K | Channel: 183 : 63.9 (keV) | Counts: 132 | Preset: 250000.0 / 239125.8 |

Nuclide: Tb-161
Energy: 63.916 keV
Net Area: 415.764 ± 36.7
Conclusions

- Optimisation in LN resin particle size, resin mass, and nitric acid gradient is able to achieve:
  - resolution between Eu and Tb; Tb and Y;
  - clean Tb fractions suitable for LSC counting.

- The new method provides comparable separation to the conventional cation exchange method. The separation procedure is much quicker, easier, and safer for the operators.

- This method has been validated using an inter-comparison sample and successful results have been obtained.
Acknowledgements