Improvements to the Analysis of Lanthanides in Nuclear Forensics Samples

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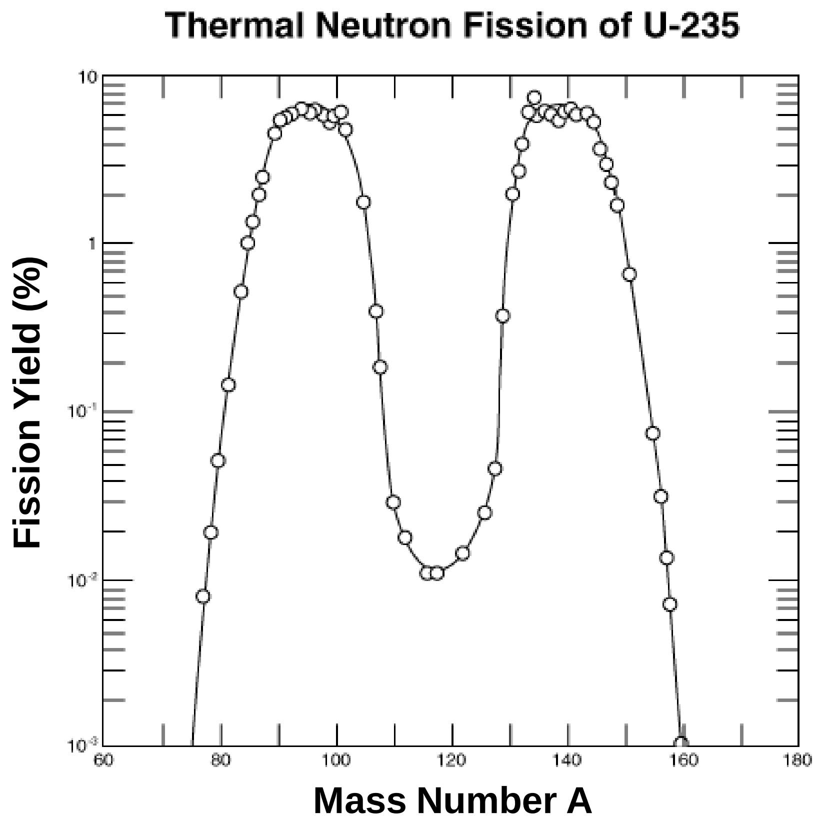
Aim

- 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.

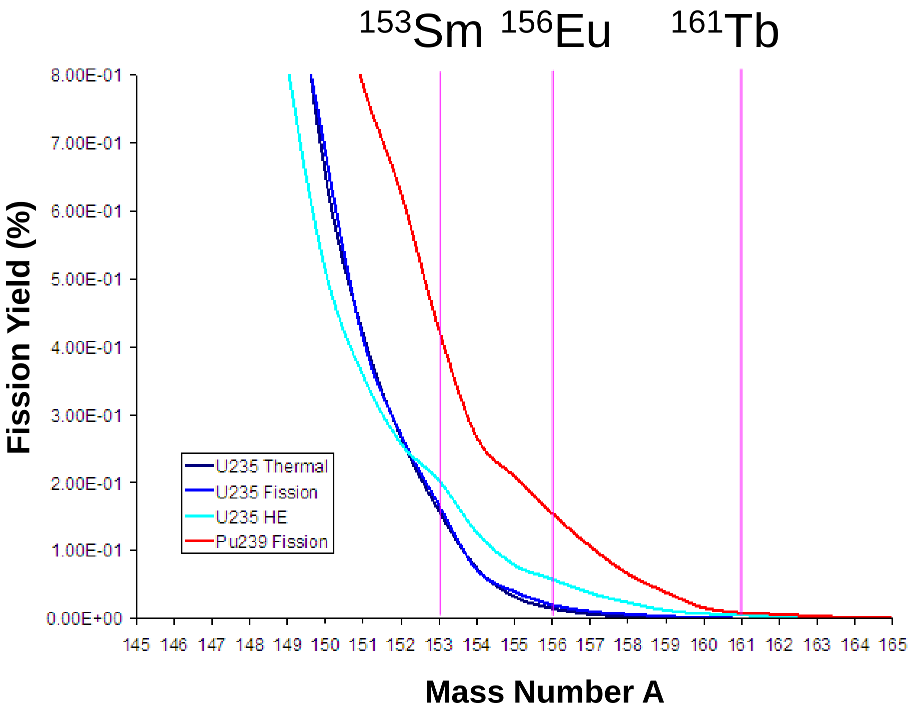
Nuclear Fission



- The lanthanides and Y are fission products of interest in nuclear forensic samples.

Lanthanides Present in Fission Samples

Nuclide	Half-life (days)	^{235}U Thermal Fission Yield % (atoms/fission)
^{141}Ce	32.50	5.85
^{143}Ce	1.377	5.96
^{144}Ce	284.6	5.50
^{147}Nd	10.98	2.25
^{153}Sm	1.928	0.158
^{156}Eu	15.2	0.0149
^{161}Tb	6.91	$8.53x10^{-5}$



Lanthanide Intra-group Separation

Current AWE method:

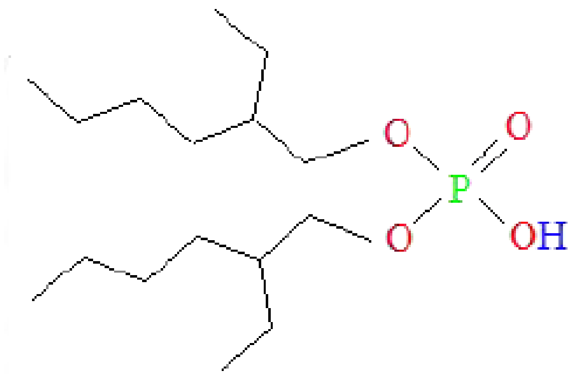
- Lanthanides are separated from each other by cation exchange column using 0.5 M α-hydroxyisobutyric acid (HIBA) pH 3.30 → 3.75 as eluent.
- 500 µg of each Lanthanide and Y are added as carriers.
- 2 samples are processed at a time due to lab space and equipment availability.
- Purified Sm, Eu, Tb,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

Issues:

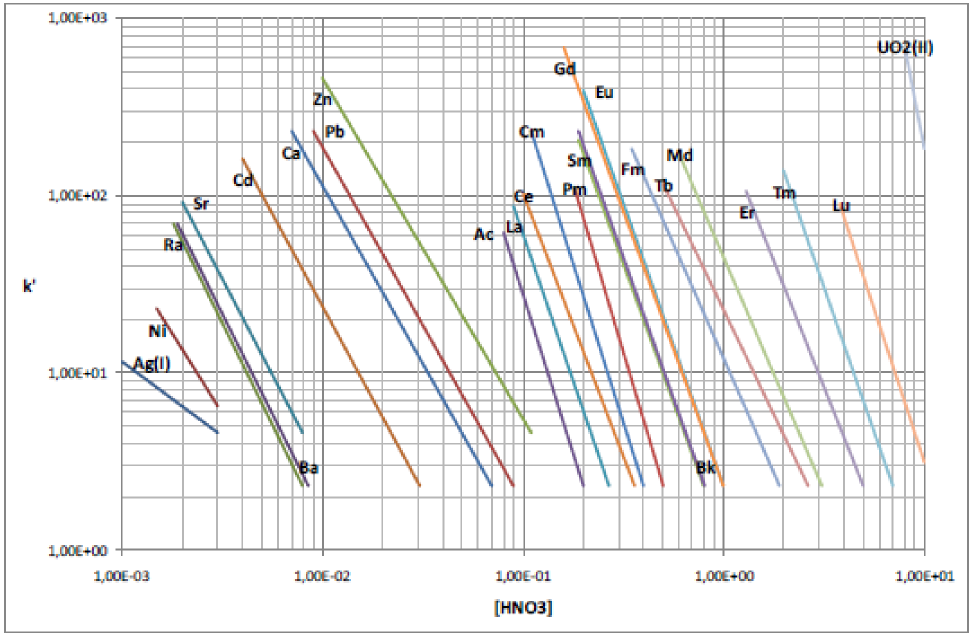
- Low chemical recoveries (10%-40%).
- Significant lab time and space.
- Not possible to measure the terbium fraction by the current method due to its very low fission yield, short half-life, and low chemical recovery.

Lanthanide Separation Using LN Resin

LN Resin



di(2-ethylhexyl)orthophosphoric acid (HDEHP)



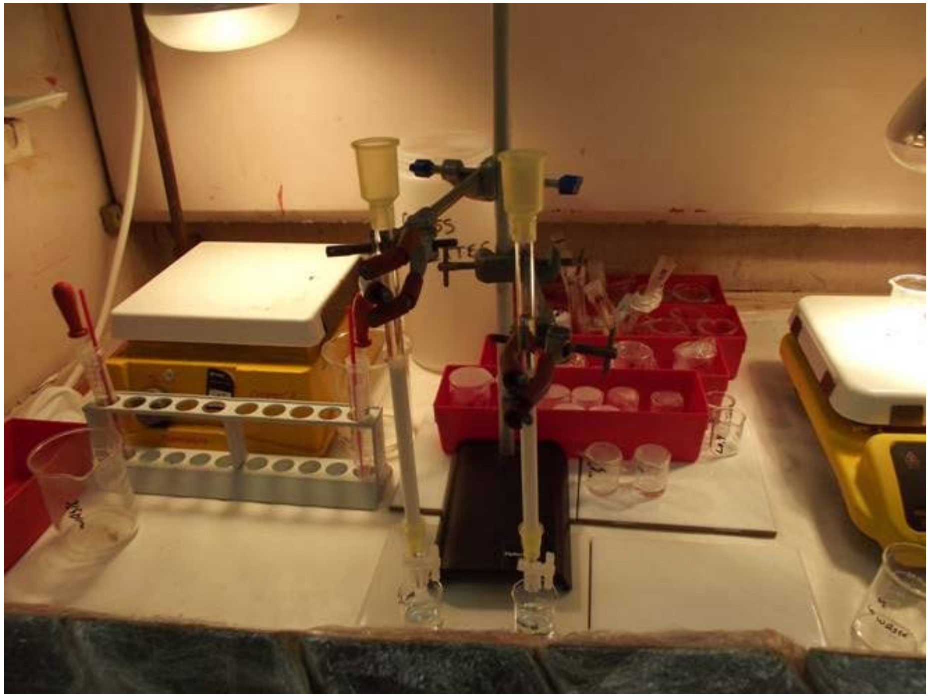
Retention of Various Elements on LN Resin

$$Ln^{3+}_{(aq)} + 3NO^{-}_{3(aq)} + nLN_{(org)} \leftrightarrow \left[Ln(LN)_n(NO_3)_3\right]_{(org)}$$

Parameters Investigated

- **Resin particle size**
  - 50-100 µm
- **Nitric acid gradient:** 0.01-8 M HNO_3
  - 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

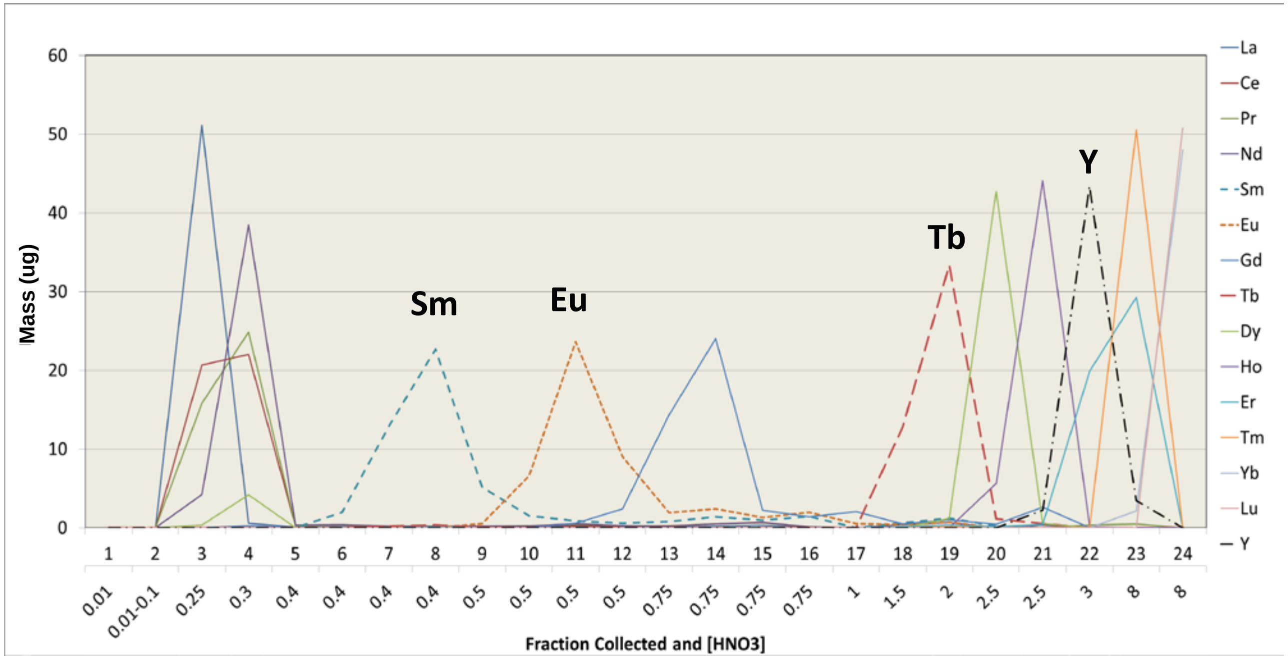
Experiment Setup



Original setup

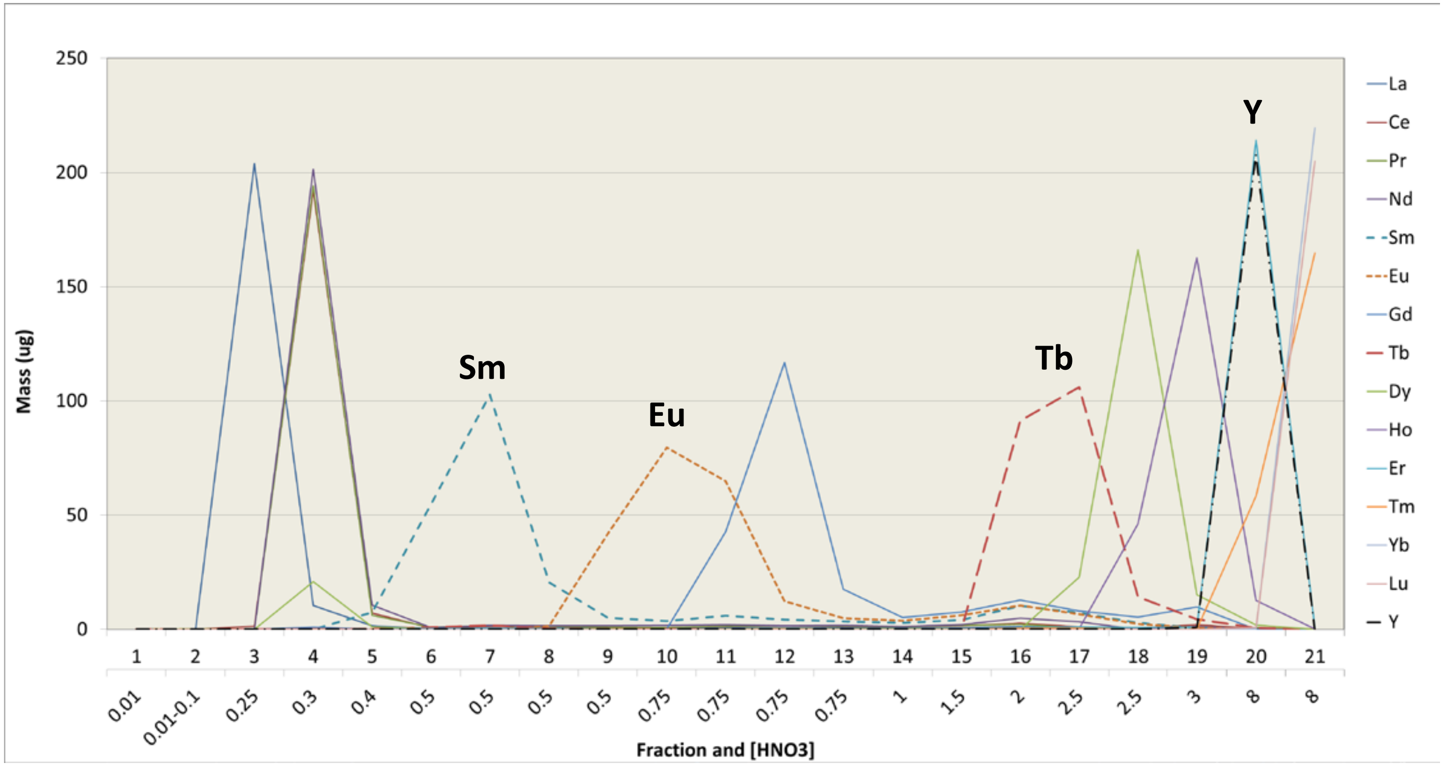
New setup

Elution Profile for Lanthanides and Y (1)



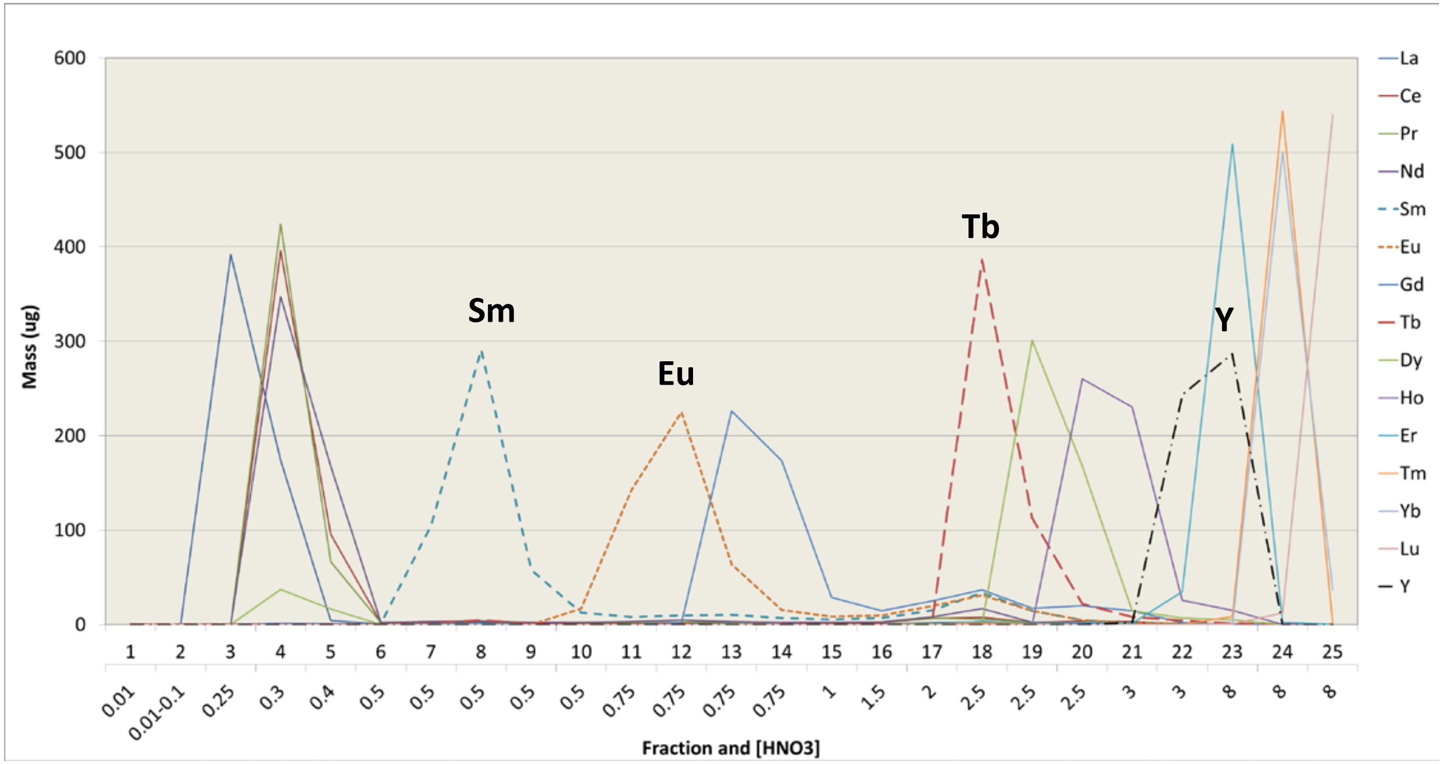
- A75-16
- Sample: 50 µg of 14 lanthanides & Y
- Resin mass: 0.78 grams
- LN resin 50-100 µm
- Eichrom 2 mL plastic columns, ID 0.8 cm

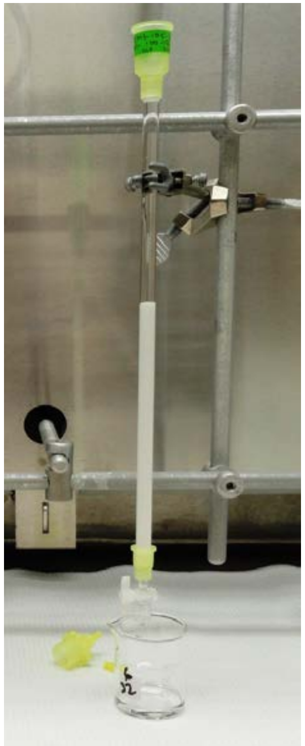
Elution Profile for Lanthanides and Y (2)



- 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

Elution Profile for Lanthanides and Y (3)





- 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"

Carrier Mass (µg)	Resin Mass (g)	Matrix	First Separation		Second Separation	
			Sample ID	% Yield	Sample ID	% Yield
50	0.78		A75-17	3.7	A75-20	2.1
50	0.78	SRM-90A	A75-19	1.9	A75-21	1.9
200	1.2	SRM-90E	A75-29	2.5	A75-36	2.4
200	1.2		A75-31	12.0	A75-37	3.0
200	1.56		A75-33	10.5	A75-38	2.8
500	1.56		A75-35	13.4	A75-39	2.7

AWE

Tb Purification Using Second Column

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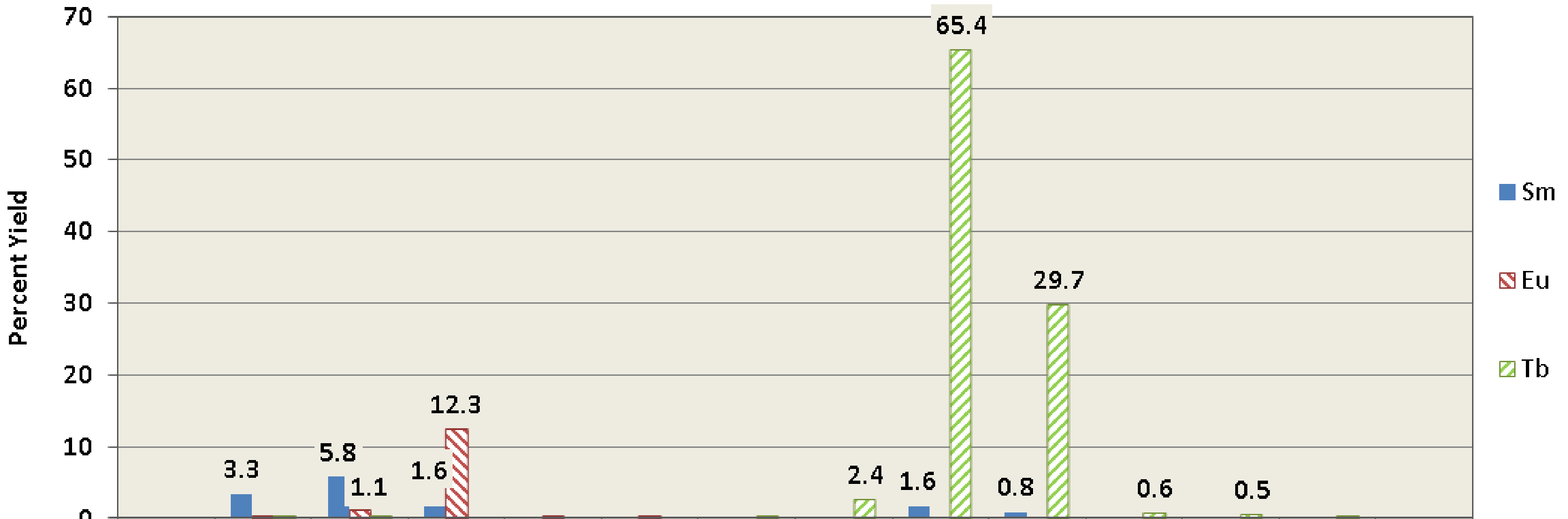


	0.5	0.5	0.75	0.75	0.75	0.75	0.75	1	1.5	2	2.5	2.5	3	8
Sm	0.0	3.3	5.8	1.6	0.0	0.0	0.0	0.0	1.6	0.8	0.3	0.0	0.0	0.0
Eu	0.0	0.0	1.1	12.3	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tb	0.0	0.1	0.1	0.0	0.0	0.0	0.0	2.4	65.4	29.7	0.6	0.5	0.0	0.0

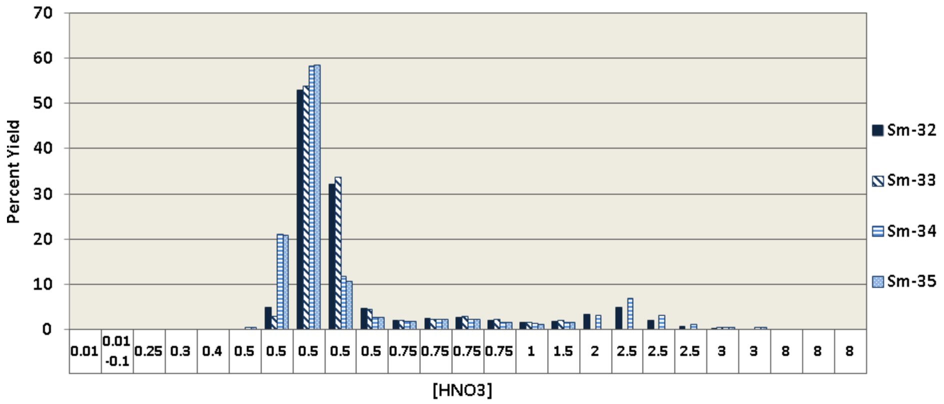
[HNO3]

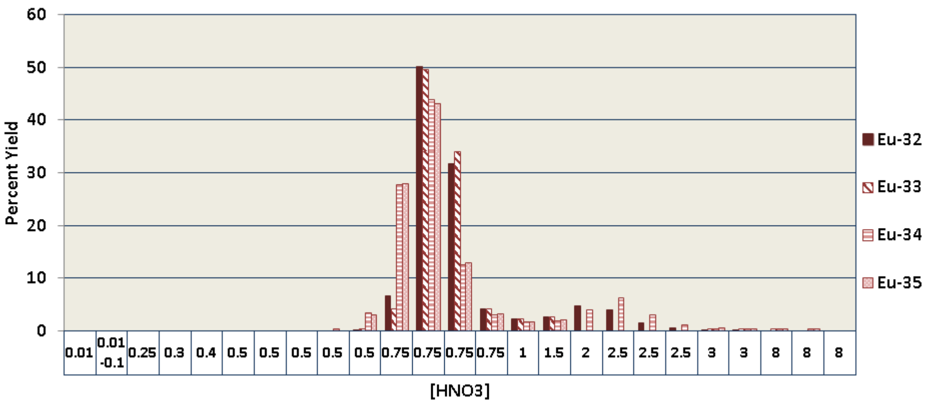
- A75-39
- Sample: 500 µg of 14 lanthanides & Y
- Resin mass: 0.78 grams
- LN resin 50-100 µm
- Eichrom 2 mL plastic columns, ID 0.8 cm

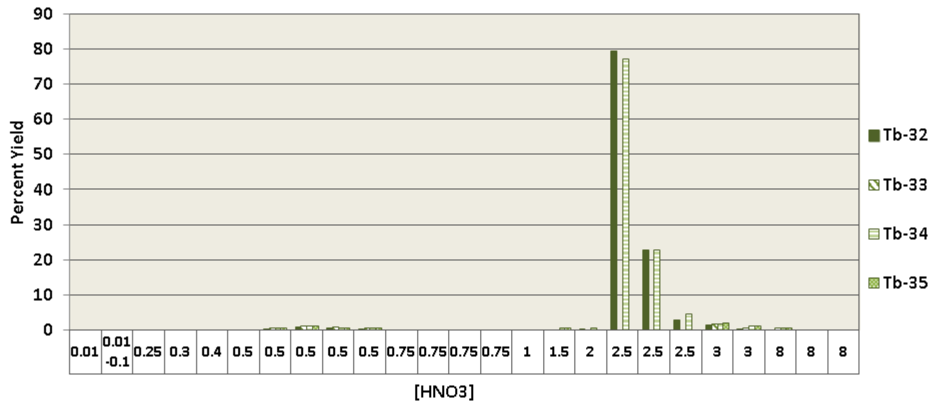
Reproducibility – Carrier Loading

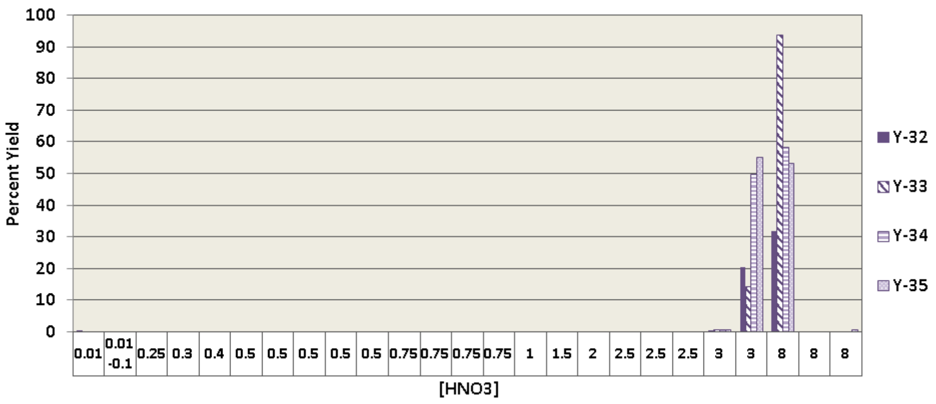
- Resin mass: 1.56 grams
- LN resin 50-100 µm
- Biorad 30 cm glass column, ID 0.7 µm
- A75-32: 200 µg of 14 lanthanides & Y
- A75-33: 200 µg of 14 lanthanides & Y with second column
- A75-34: 500 µg of 14 lanthanides & Y
- A75-35: 500 µg of 14 lanthanides & Y with second column

Reproducibility – Carrier Loading





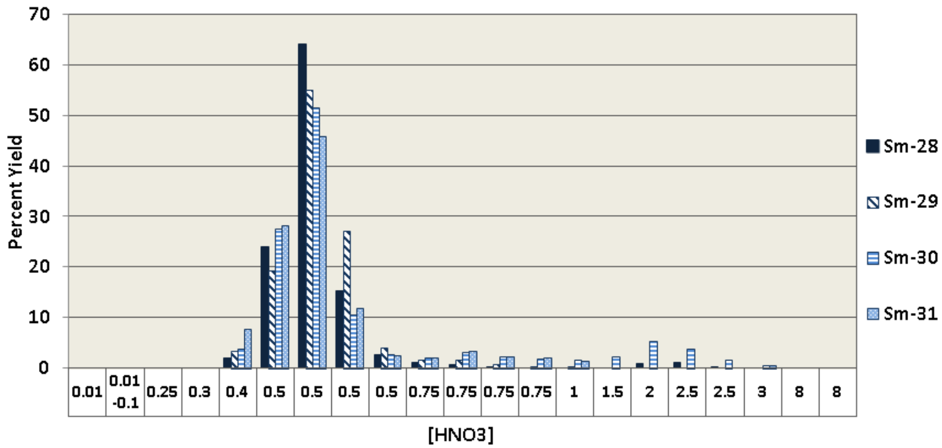


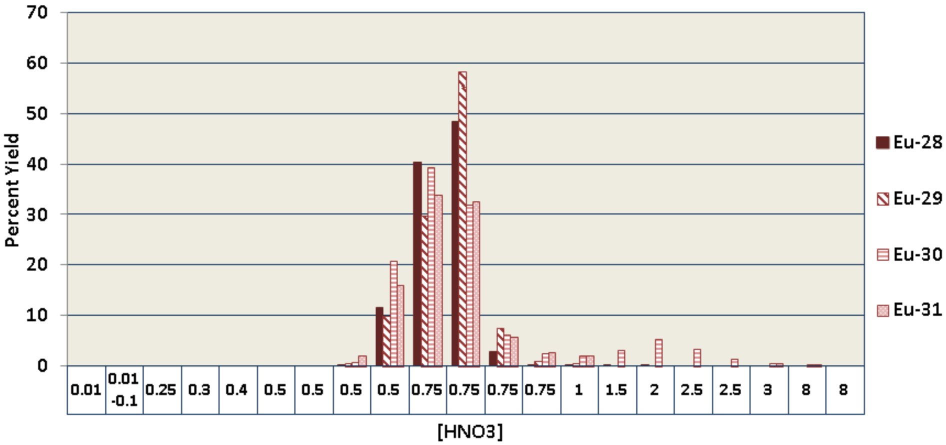


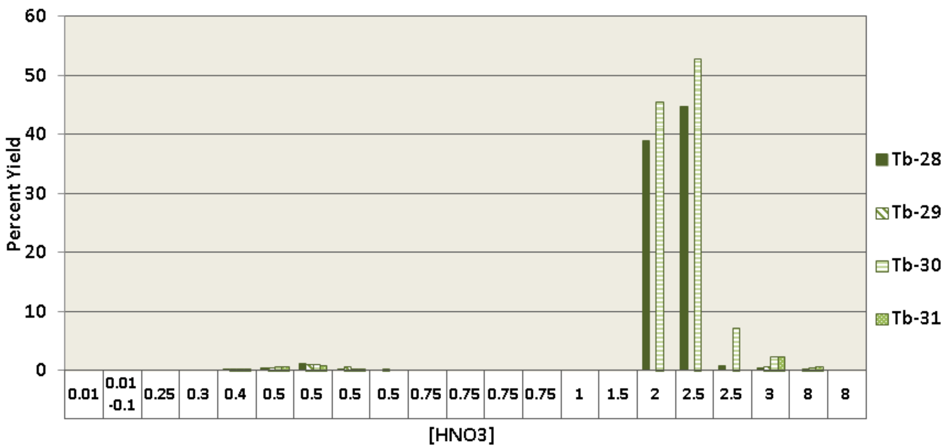
Reproducibility – Matrix (SRM-90E)

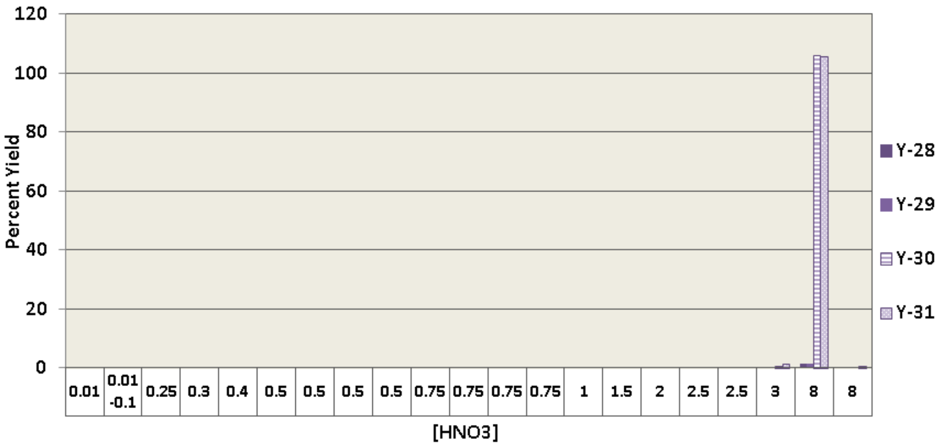
- Resin mass: 1.20 grams
- LN resin 50-100 µm
- Biorad 20 cm glass column, ID 0.7 µm
- A75-28: 200 µg of 14 lanthanides & Y with matrix
- A75-29: 200 µg of 14 lanthanides & Y with matrix and second column
- A75-30: 200 µg of 14 lanthanides & Y
- A75-31: 200 µg of 14 lanthanides & Y with second column

Reproducibility – Matrix (SRM-90E)





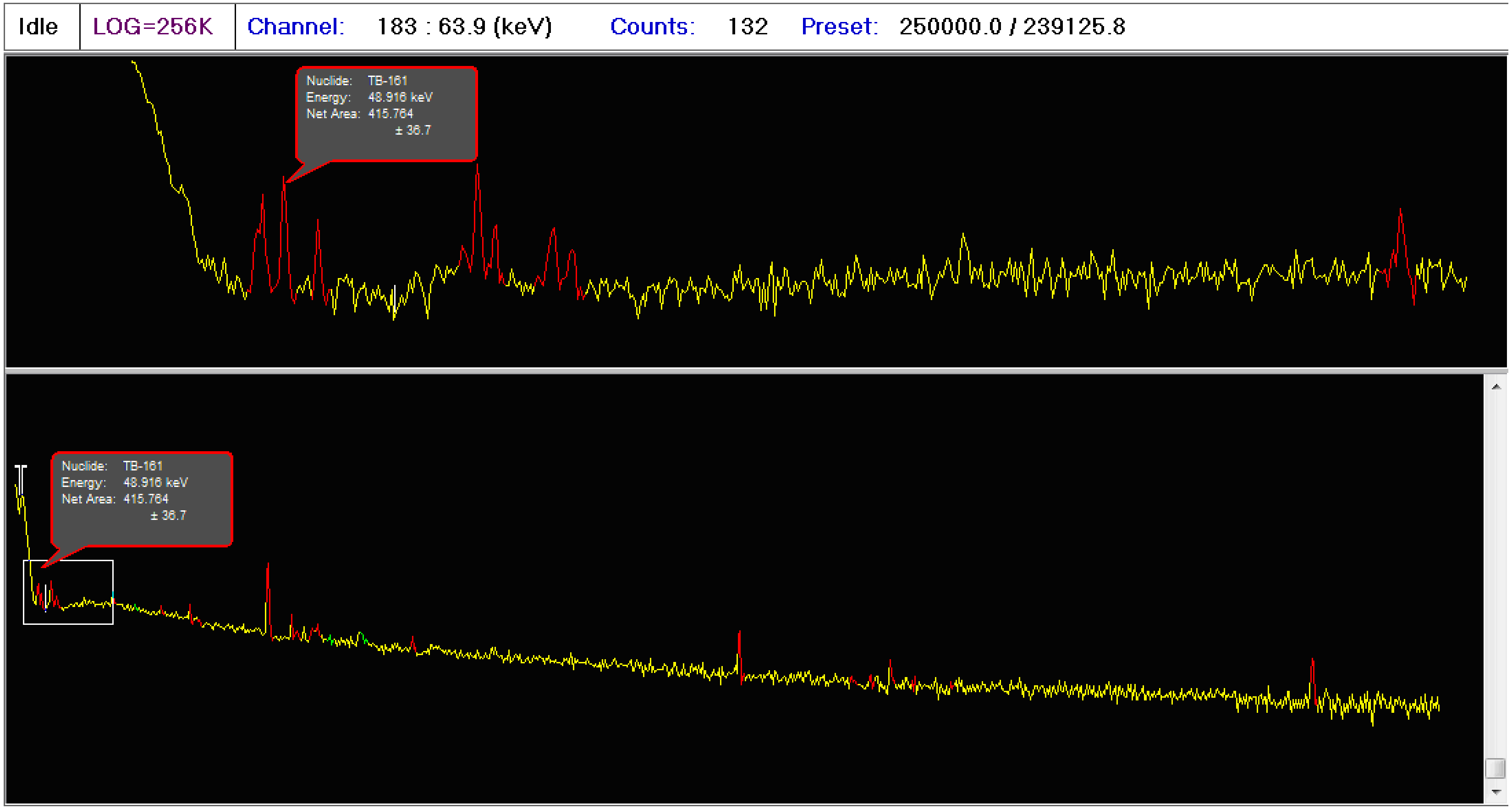




Results for Inter-comparison Sample

Nuclide	AWE (atoms/gram)		PNNL (atoms/gram)	
^{153}Sm	2.50×10^9	7.5%	2.59×10^9	2.4%
^{156}Eu	4.04×10^8	6.4%	4.06×10^8	4.4%
^{161}Tb	5.21×10^6	4.7%	5.64×10^6	4.4%

Gamma Spectrum for Purified ^{161}Tb



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

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