Impact of Stable Target Mass on Metal Ion Separations by Extraction Chromatography Resins

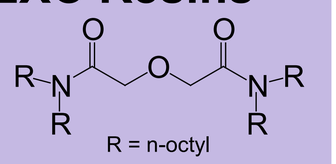
Madeleine Eddy and Daniel McAlister
Eichrom Technologies, Lisle, Illinois, USA

eichrom® TECHNOLOGIES
A GCI COMPANY
npo eichrom
1955 University Lane • Lisle, IL 60532 USA
www.eichrom.com

Abstract

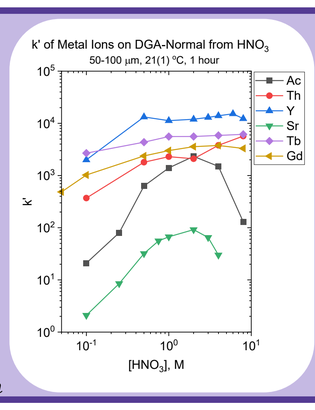
Extraction chromatography (EXC) is an essential tool in the separation and purification of high-specific-activity radionuclides from solid targets. The impact of target mass on the separations using EXC resins is primarily determined by the relative selectivity of the target metal and product radionuclide. Understanding how mass affects the resin performance, and how physical characteristics of the column can be modified to improve the process will lead to better separation system design in future applications. In this work we have focused on the impact of target mass for various systems on DGA-Normal and LN resins.

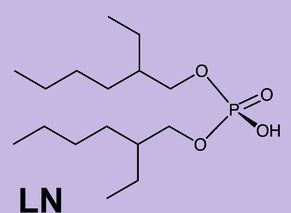
EXC Resins



DGA-Normal
Neutral, solvating extractant

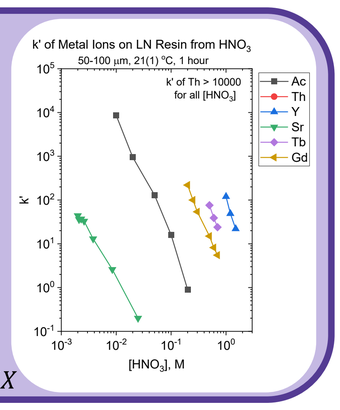
$M^{n+} + nX^- + yL \leftrightarrow ML_yX_n$



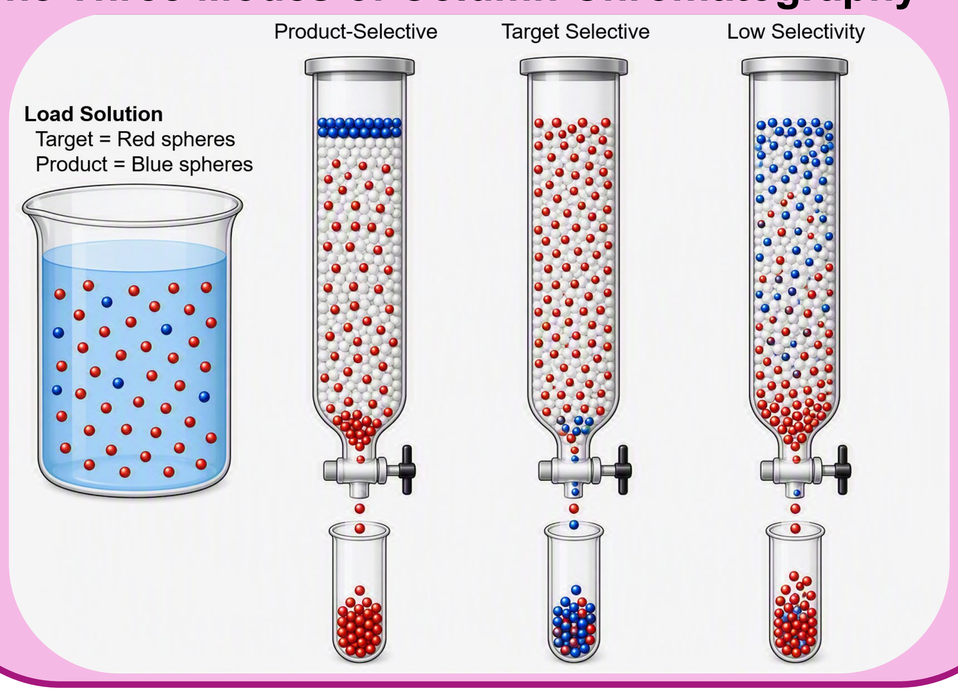


LN
Acidic, cation-exchange extractant

$M^{n+} + nX^- + nHL \leftrightarrow ML_n + nHX$



The Three Modes of Column Chromatography

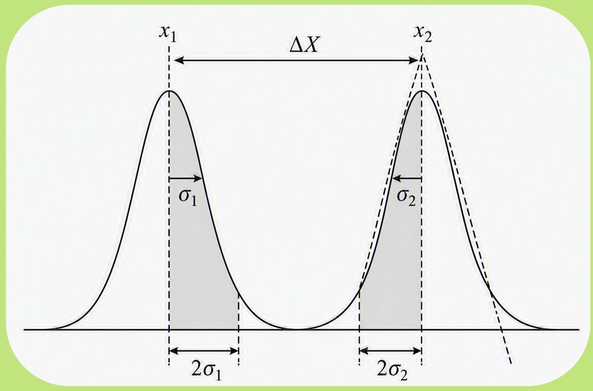


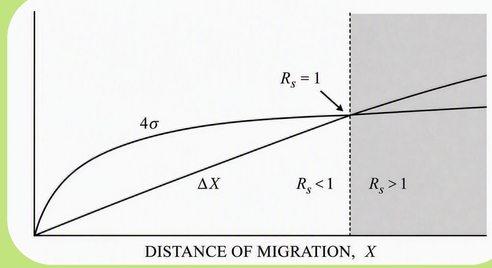
Separation Fundamentals

- Separation of two elements is dictated by chemical and physical properties
- Separation resolution (R_s) describes the extent of peak separation

$$R_s = \frac{\Delta X}{(2\sigma_1 + 2\sigma_2)}$$

Where $x_M \approx k'_M$ and $\Delta X \approx Separation\ Factor$

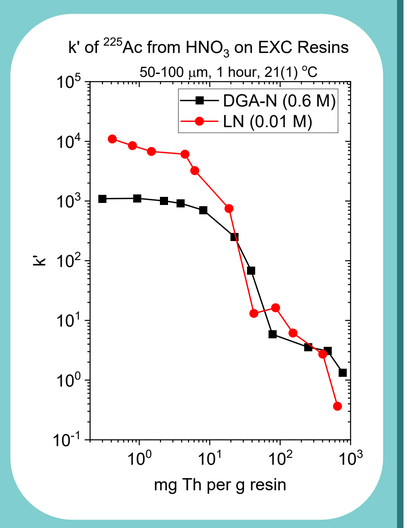


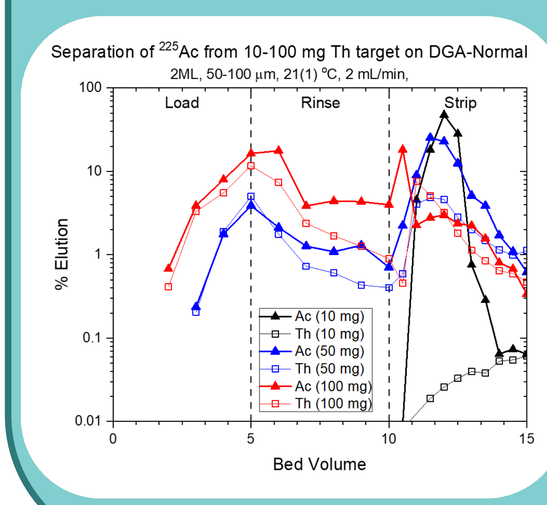


To improve resolution:
- Increase column length (ΔX)
- Optimize mobile phase (ΔX)
- Decrease particle size (σ)
- Increase temperature (σ)

Target Selective:
$^{225}Ac^{3+}$ from Th^{4+} targets

- Target (Th^{4+}) is strongly retained under load solution conditions
  - Saturates the column from top of bed downward
- Product ($^{225}Ac^{3+}$) is eluted first and may be lost if capacity is exceeded
- Some target will likely bleed into isotope product
- *Limited by column capacity*
- **Improve separation by increasing column volume or reducing target mass prior to loading**





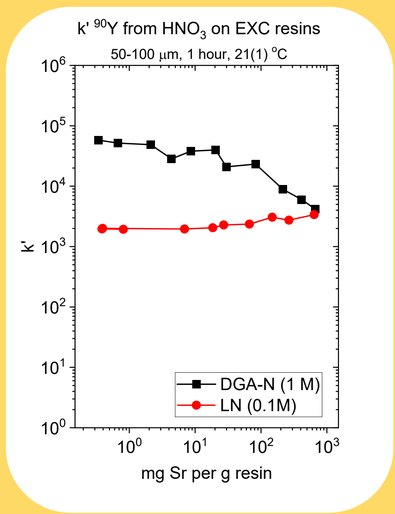
DGA conditions
Load 10 mL 4 M HNO_3,
Rinse 10 mL 4 M HNO_3,
Strip 10 mL 2 M HCl

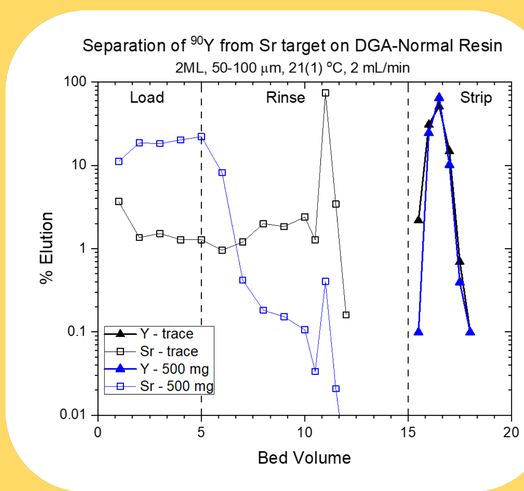
mg Th in Strip	
10 mg	0.03
50 mg	11.1
100 mg	21.1

^{225}Ac in Strip	
10 mg	99.4%
50 mg	84.3%
100 mg	34.3%

Product Selective:
$^{90}Y^{3+}$ from Sr^{2+} targets

- Target (Sr^{2+}) eluted under load solution conditions
- Product (Y^{3+}) strongly retained by resin
  - Usually in a tight band at the top of the column
- Target rinsed away completely
- Isotope product stripped in high-purity
- *Independent of target mass*
- **Decontamination factors of >10^4 typical for target removal**

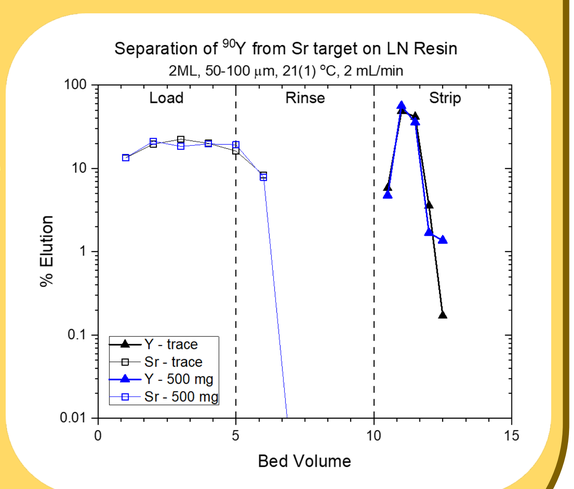




DGA conditions
Load 10 mL 4 M HNO_3,
Rinse 10 mL 4 M HNO_3,
Rinse 10 mL 0.1 M HNO_3,
Strip 10 mL 0.1 M HCl

mg Sr in Strip	
tracer	0.004
500 mg	0.028

^{90}Y in Strip	
tracer	100%
500 mg	100%



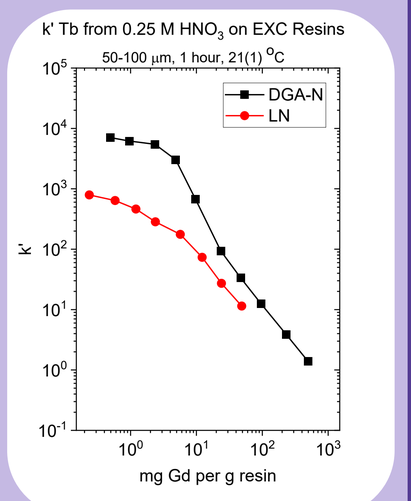
LN conditions
Load 10 mL 0.1 M HNO_3,
Rinse 10 mL 0.1 M HNO_3,
Strip 10 mL 8 M HNO_3

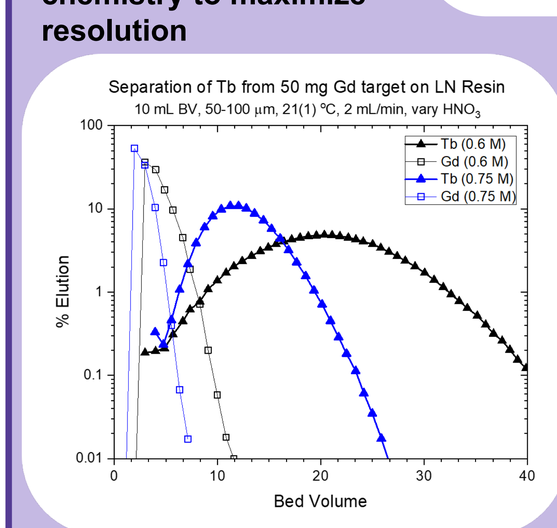
mg Sr in Strip	
tracer	0.000
500 mg	0.026

^{90}Y in Strip	
tracer	100%
500 mg	100%

Low Selectivity:
Tb^{3+} from Gd^{3+} targets

- Target (Gd^{3+}) and product (Tb^{3+}) have nearly identical chemistry
  - Common for adjacent Ln's
- Exploit minor differences in retention to optimize separation efficiency
- *Strongly dependent on target mass and column geometry*
- **Requires fine-tuning to optimize column geometry and elution chemistry to maximize resolution**





Elution Chemistry
0.6 vs 0.75 M HNO_3
Reducing k' of both Tb and Gd to reduce σ

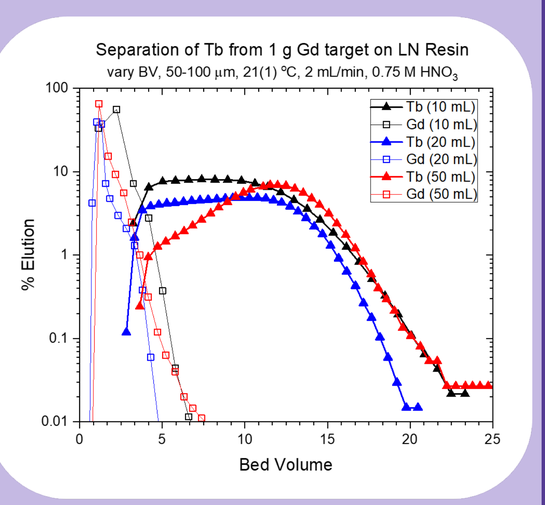
R_s	
0.6 M	0.93
0.75 M	1.00

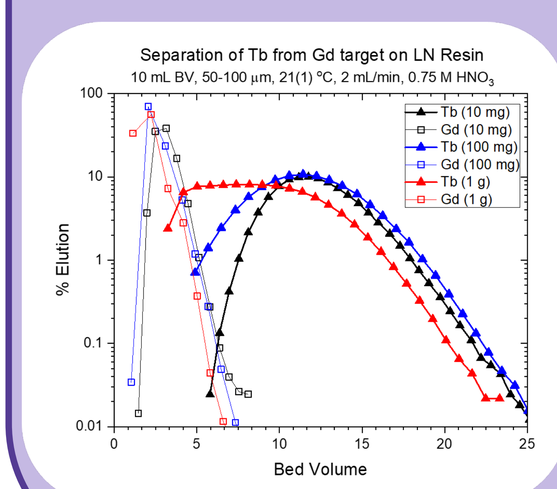
Tb Recovery with < 1 mg Gd	
0.6 M	98.9%
0.75 M	99.4%

Column Geometry
10, 20, 50 mL Columns
Increasing column capacity and increasing X

R_s	
10 mL	0.41
20 mL	0.87
50 mL	1.34

Tb Recovery with < 1 mg Gd	
10 mL	89.5%
20 mL	94.9%
50 mL	96.0%





Optimal Conditions
10 mL BV, 0.75 M HNO_3
Even ideal condition performance heavily dependent on target mass

R_s	
10 mg	1.13
100 mg	0.87
1 g	0.41

Tb Recovery with < 1 mg Gd	
10 mg	100%
100 mg	98.0%
1 g	89.5%

Conclusions

- Product-selective separations result in the highest purity isotopes
  - Essentially independent of target mass
- Target-selective separations break down as soon as the column capacity is exceeded
  - Not ideal – significant product loss
- Low selectivity separations are strongly dependent on column chemistry, column geometry, and target mass
  - Careful optimization is necessary

References

1. Giddings, J. C. Unified Separation Science; Wiley-Interscience: New York, 1991
2. Eddy, M.; Rush, R.; McAlister, D. R. *Solvent Extr. Ion Exch.* **2024,** *42*(6-7), 519-542.
3. Mcalister, D.; Howritz, E. *Solvent Extr. Ion Exch.* **2005,** *23*(4), 579-606.
4. Apostolidis, C.; et al. *J. Radioanal. Nucl. Chem.* **2015,** *305*, 493-499.
5. Poorbaygi, H.; et al. *J. Radioanal. Nucl. Chem.* **2021,** *327,* 985-990.
6. Aziz, A.; Artha, W. T. *Indones. J. Chem.* **2016,** *16*(3), 283-288.