 

What k’ doesn’t tell you

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RRMC 2024
Purdue University
21 October 2024

Introduction

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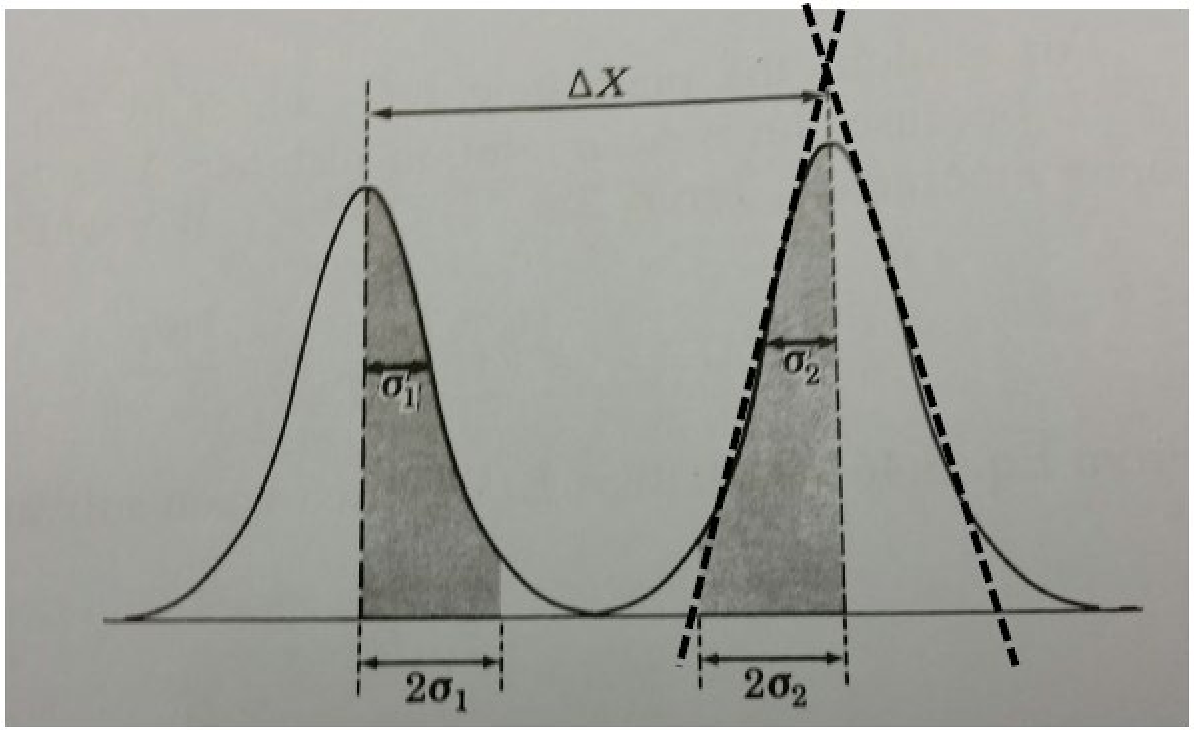
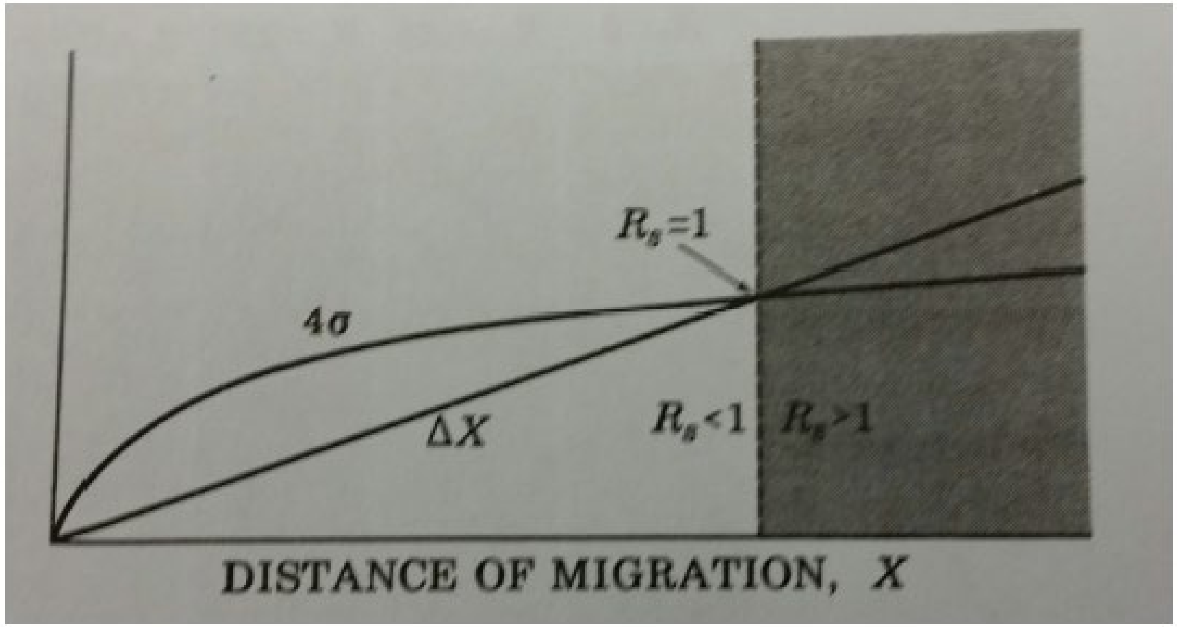
$$\text{Resolution} = R_s = \Delta X / (2\sigma_1 + 2\sigma_2)$$

ΔX increases linearly

$(2\sigma_1 + 2\sigma_2)$ increases as the square root of X

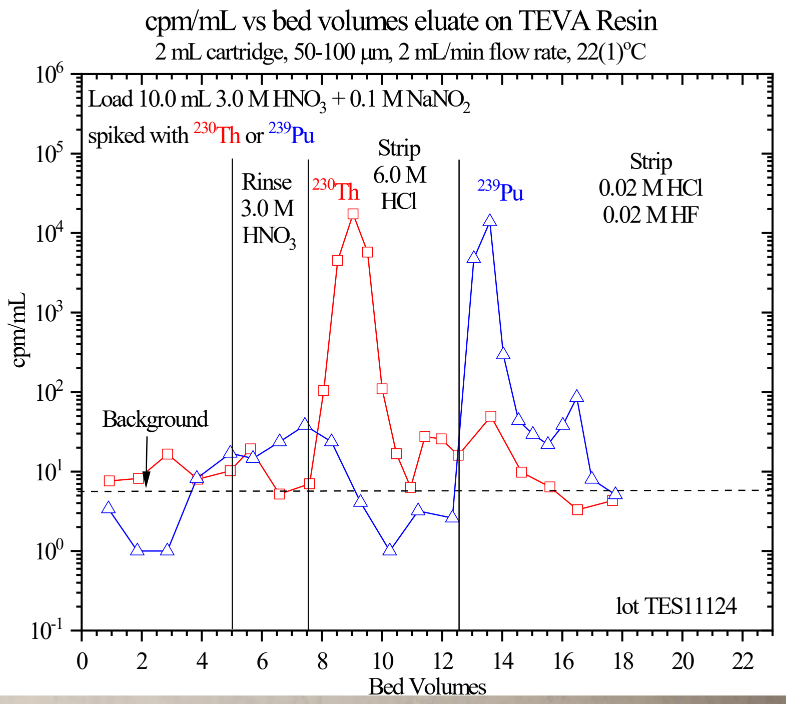
Resolution increases with longer columns!

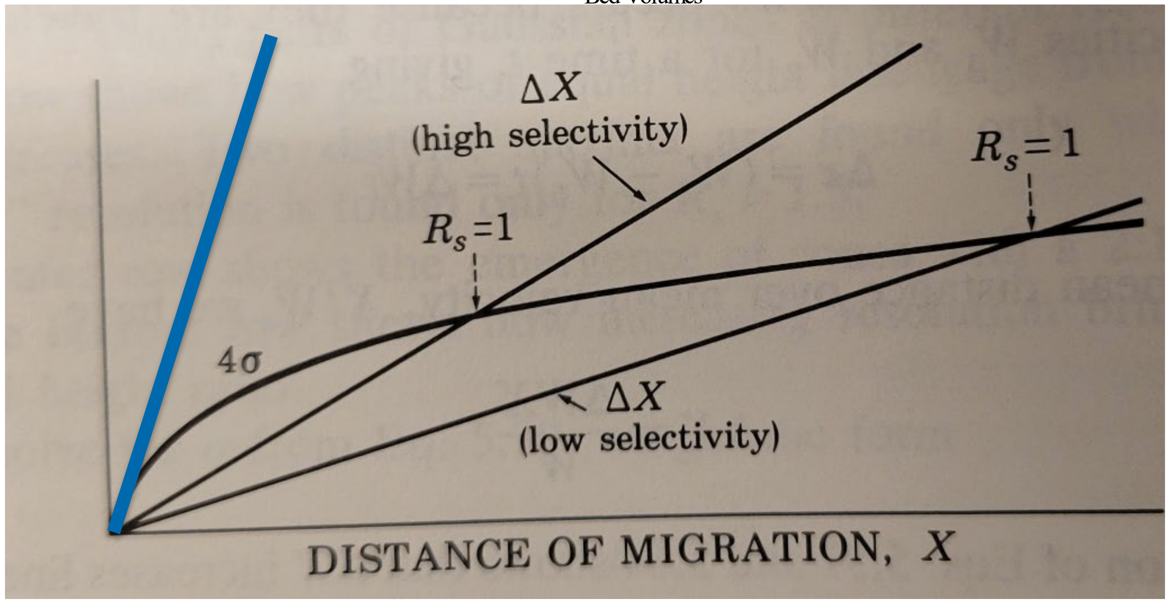


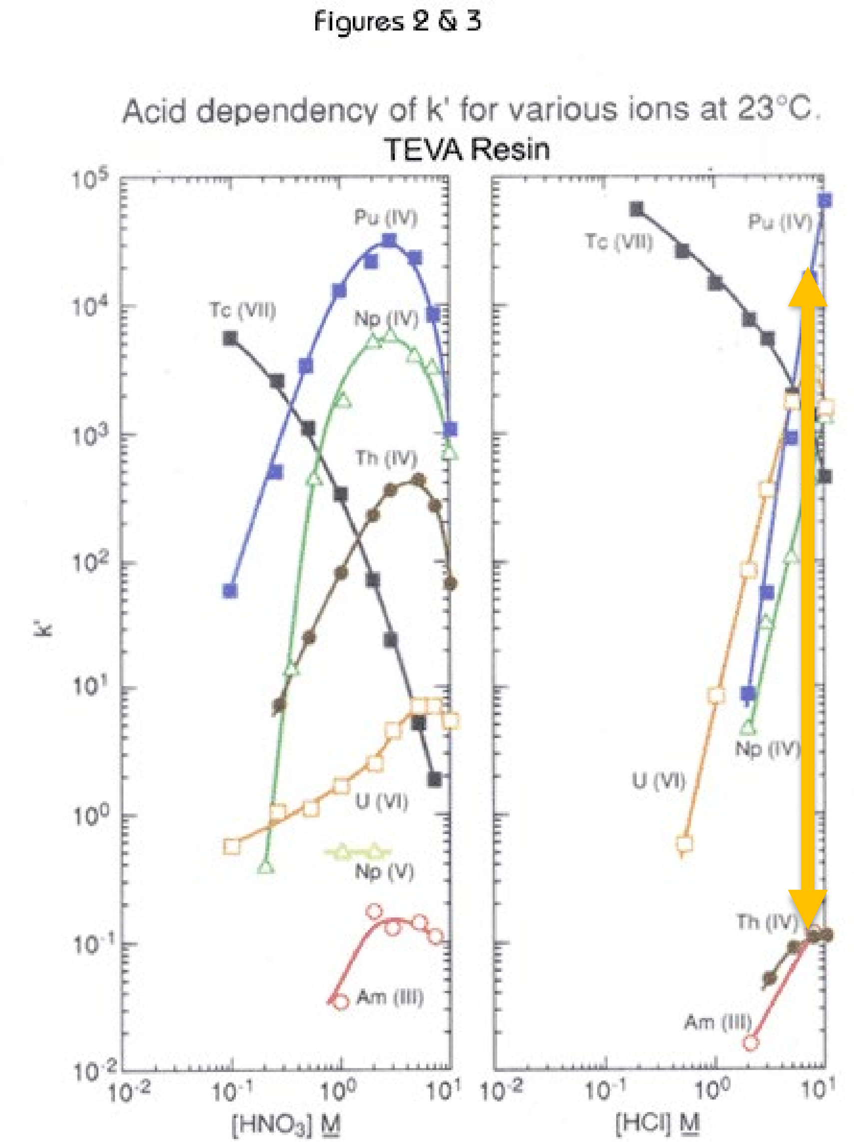


“Unified separation science”, J. Calvin Giddings, J. Wiley and Sons, New York, 1991, pp.102-104.

Introduction (large α = small column)



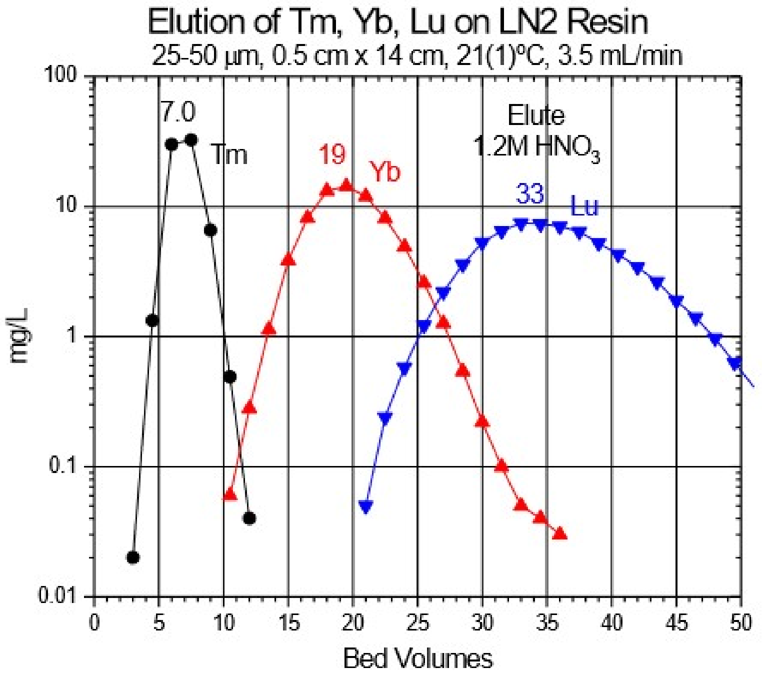


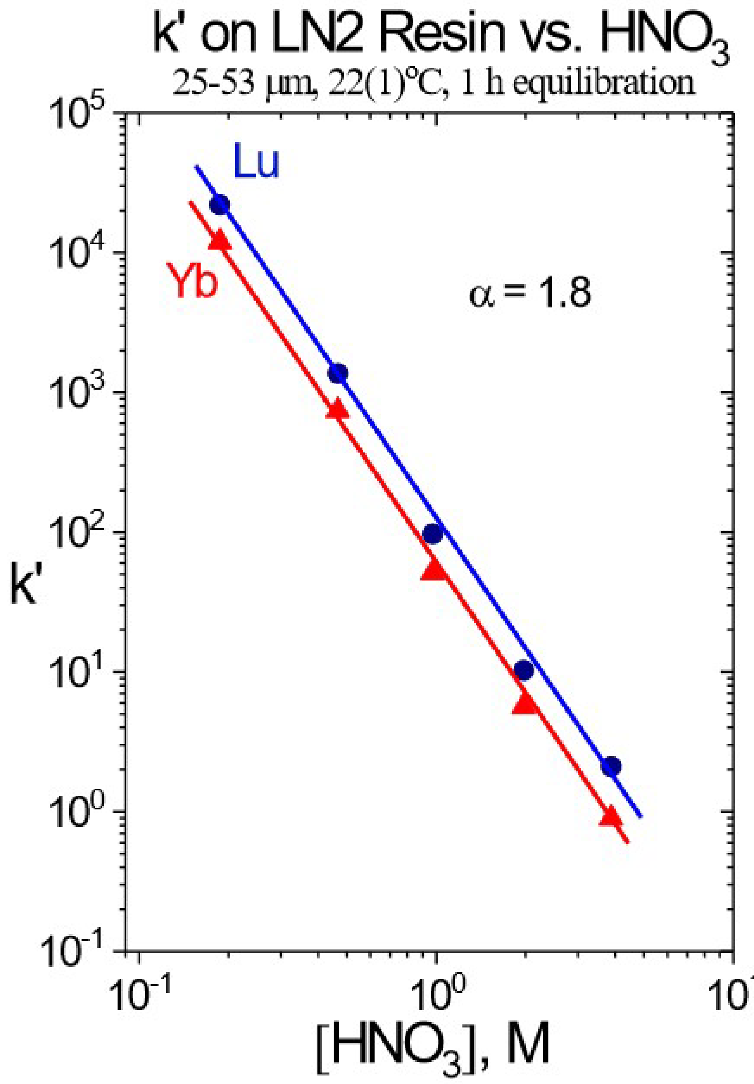


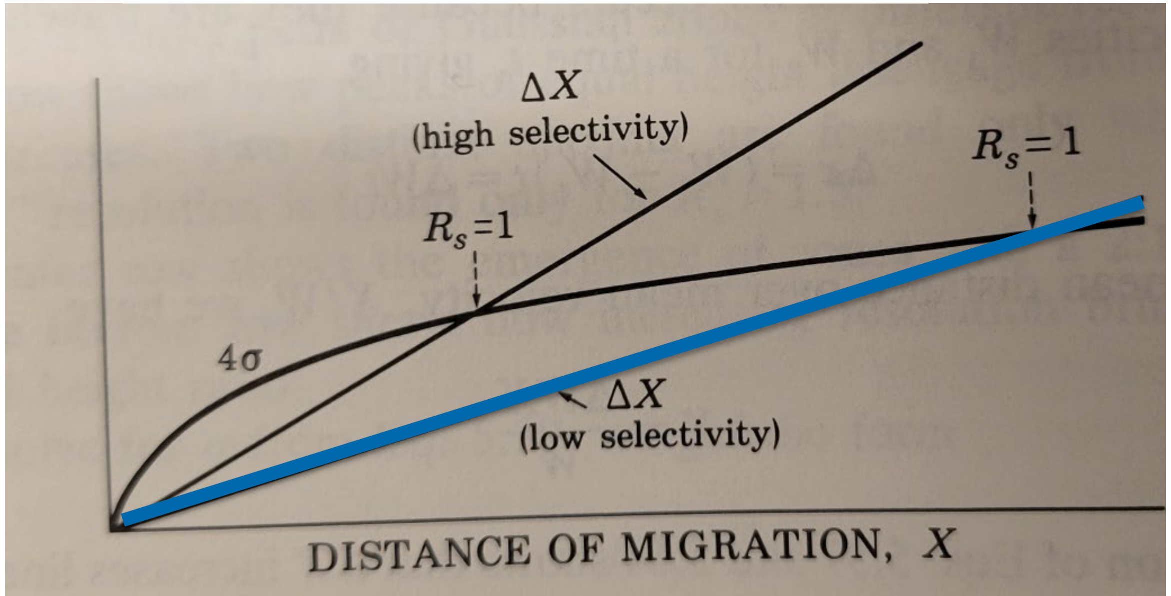
Horwitz, et al. (HP195)

$\alpha_{Pu/Th} = 10^5$

Introduction (small α = large column)







Outline

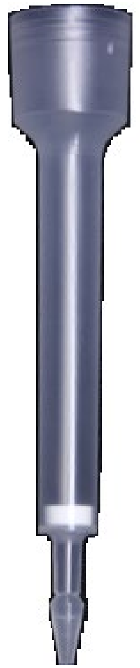
1) Peak shape

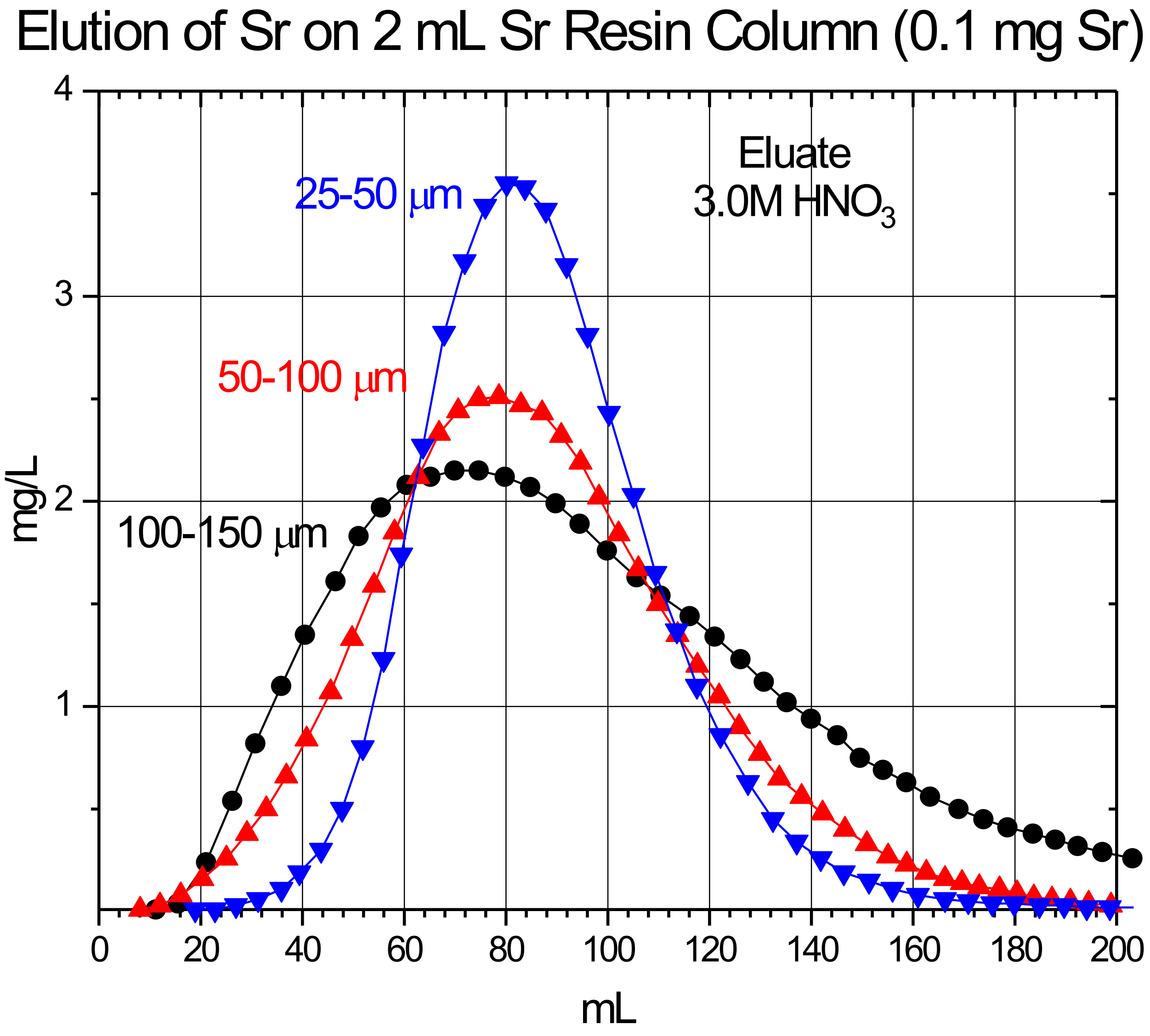
2) Capacity and breakthrough

3) What else could k’ (D) tell you?

4) Additional Data

Particle Size





k' Sr @ 3M HNO_3 = 60

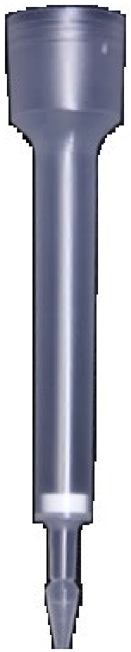
Dw Sr = 122 mL/g Resin

Predicted peak for 2 mL column* = 80 mL

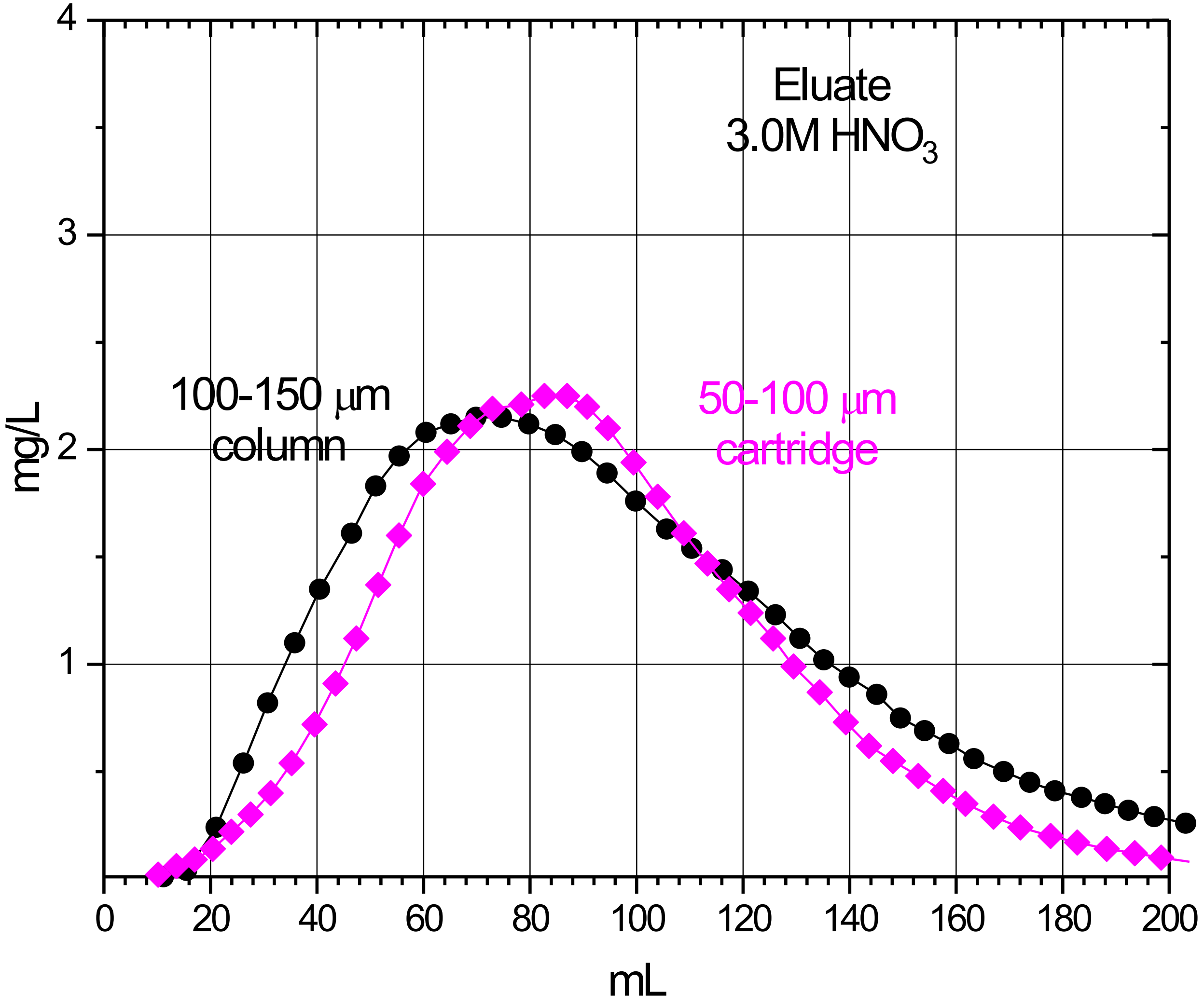
*1.7 mL (0.65 g Resin)

Smaller particle size leads to sharper peaks

Column length



Elution of Sr on 2 mL Sr Resin Column (0.1 mg Sr)



Back-pressure vs particle size

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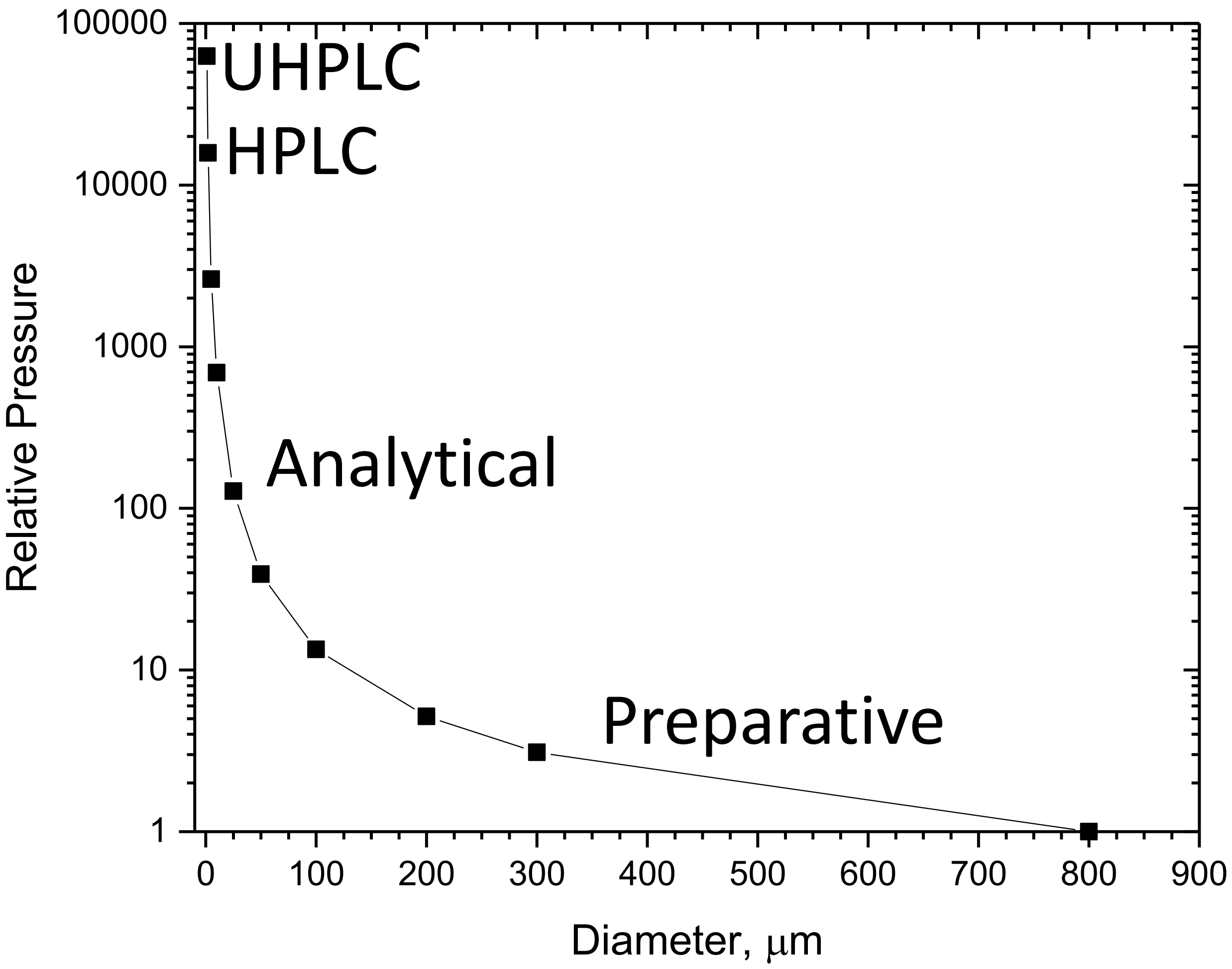
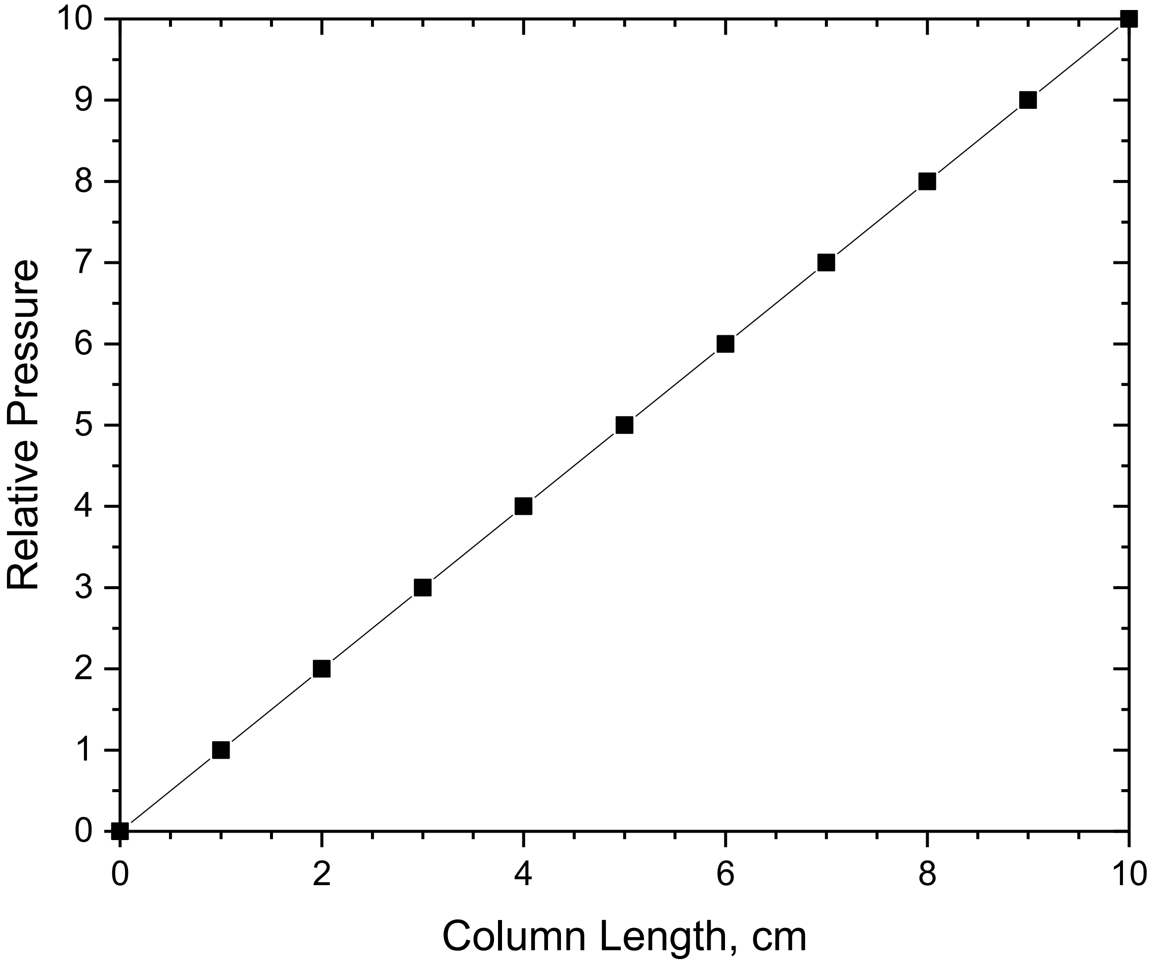
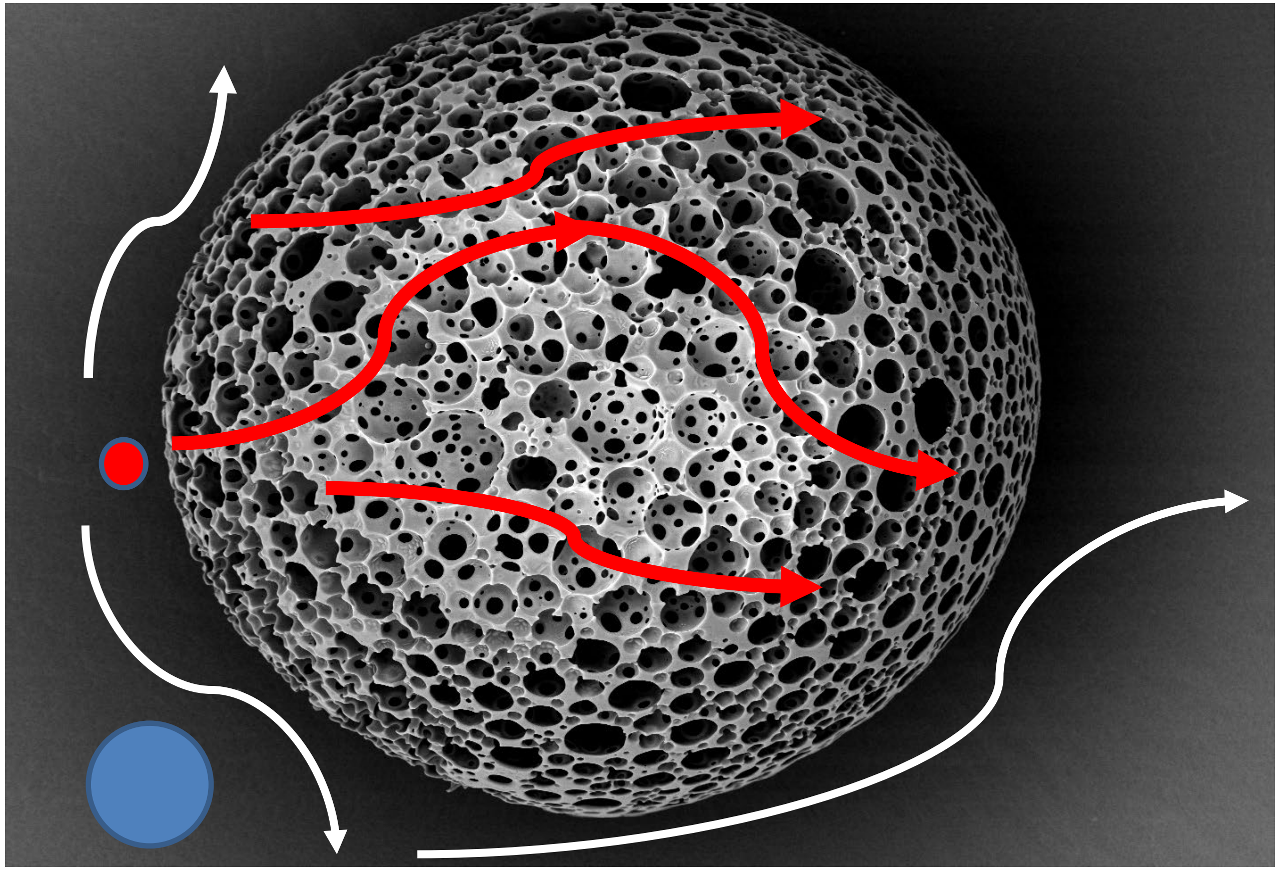
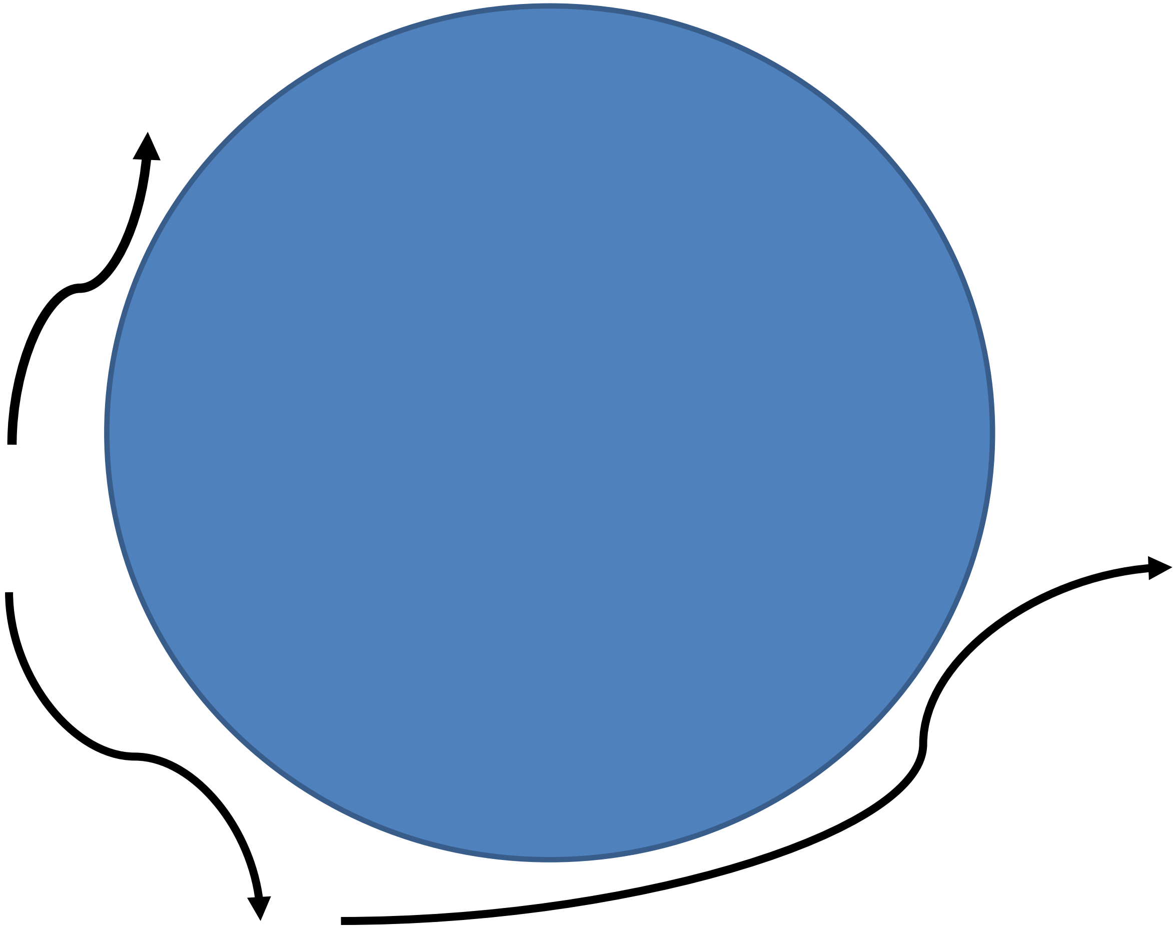




Porosity (capacity vs resolution)



Porous media
Size Exclusion
Highest capacity



Non-porous media
Narrowest peaks

Temperature

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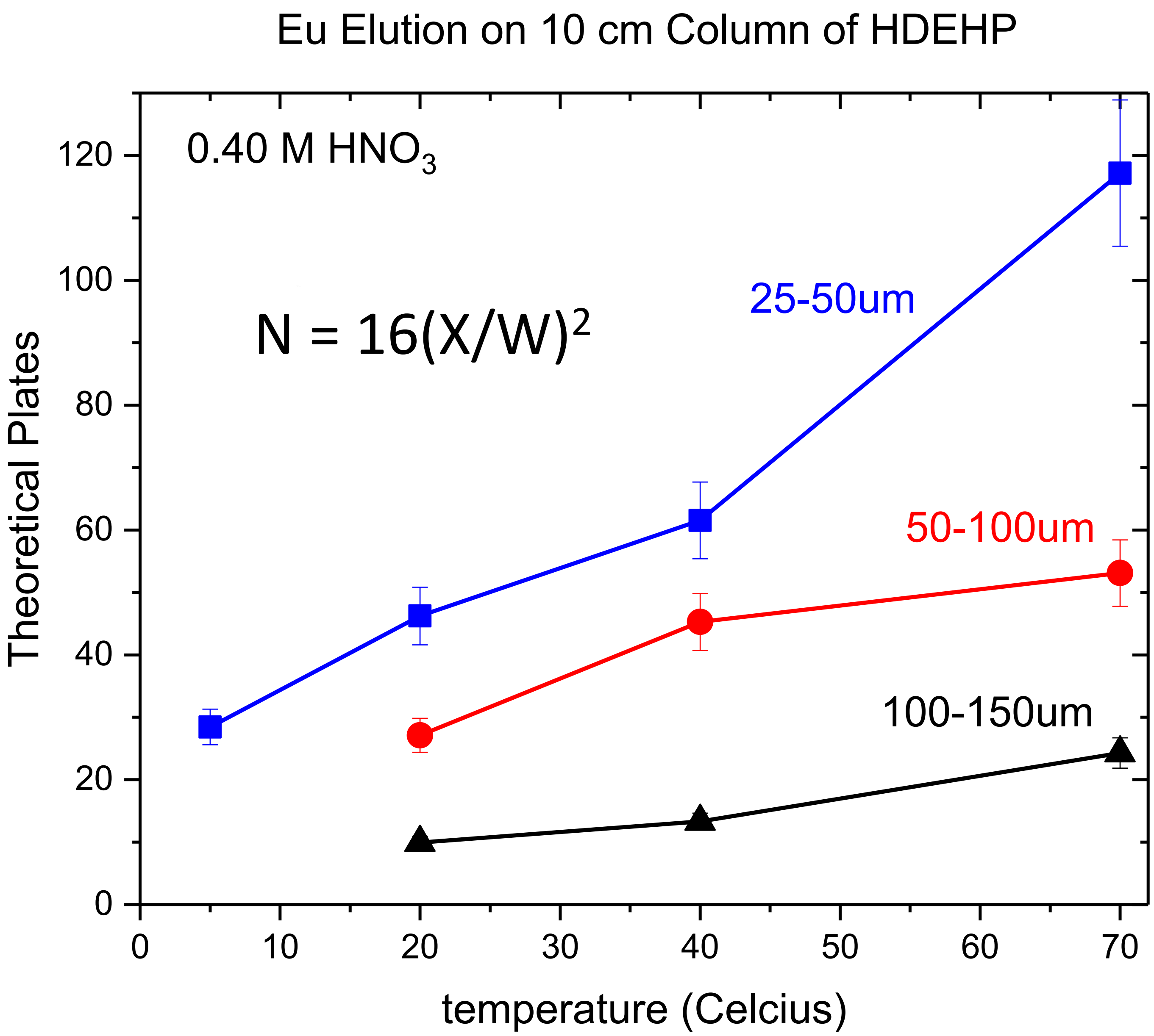
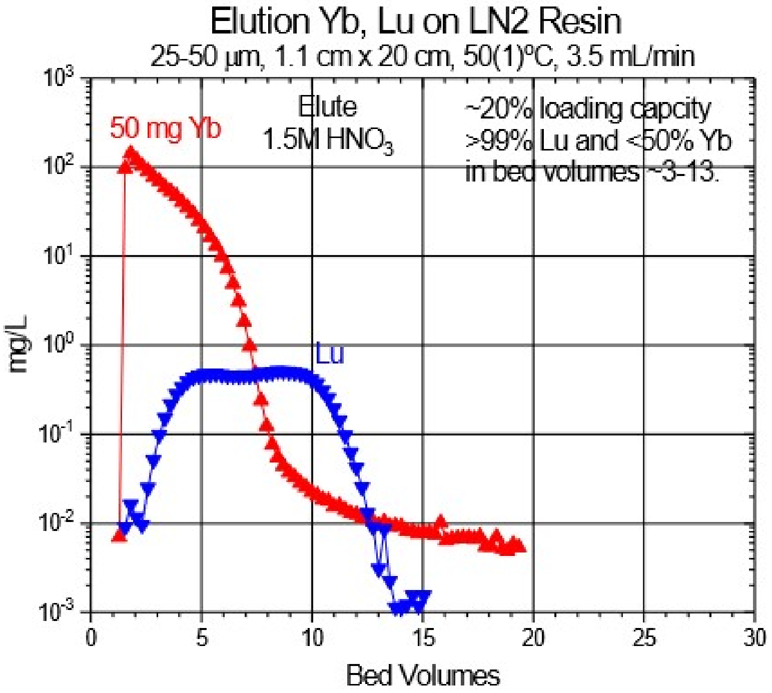


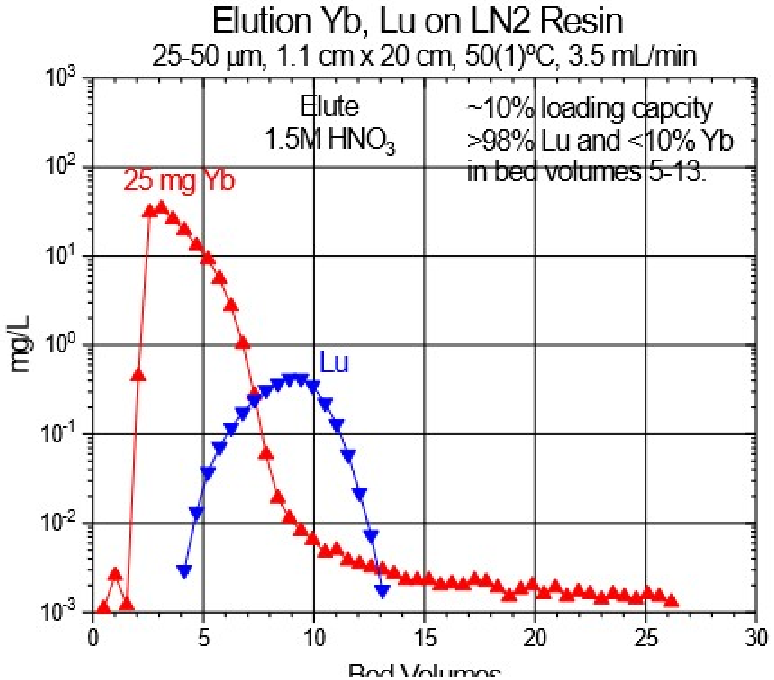
Higher temperature usually improves resolution by decreasing peak widths. (more rapid diffusion through resin pores and inter-bead spaces)

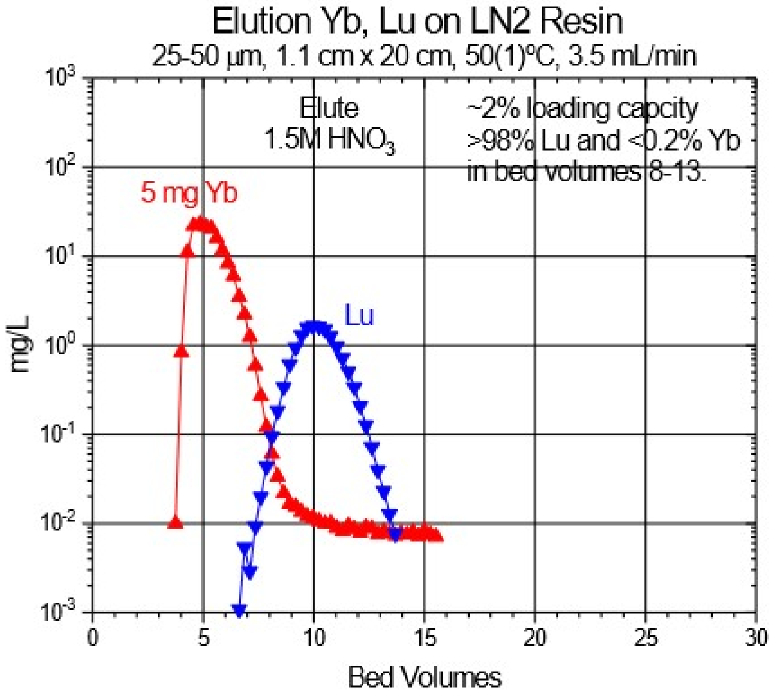
50-100 um material at 70C produces similar resolution to 25-50 um at 20C.

100-150 um material at 70C produces similar resolution to 25-50 um at 5C.

Capacity and Loading







High column loading leads to broader peaks

Capacity Data (Sr Resin)

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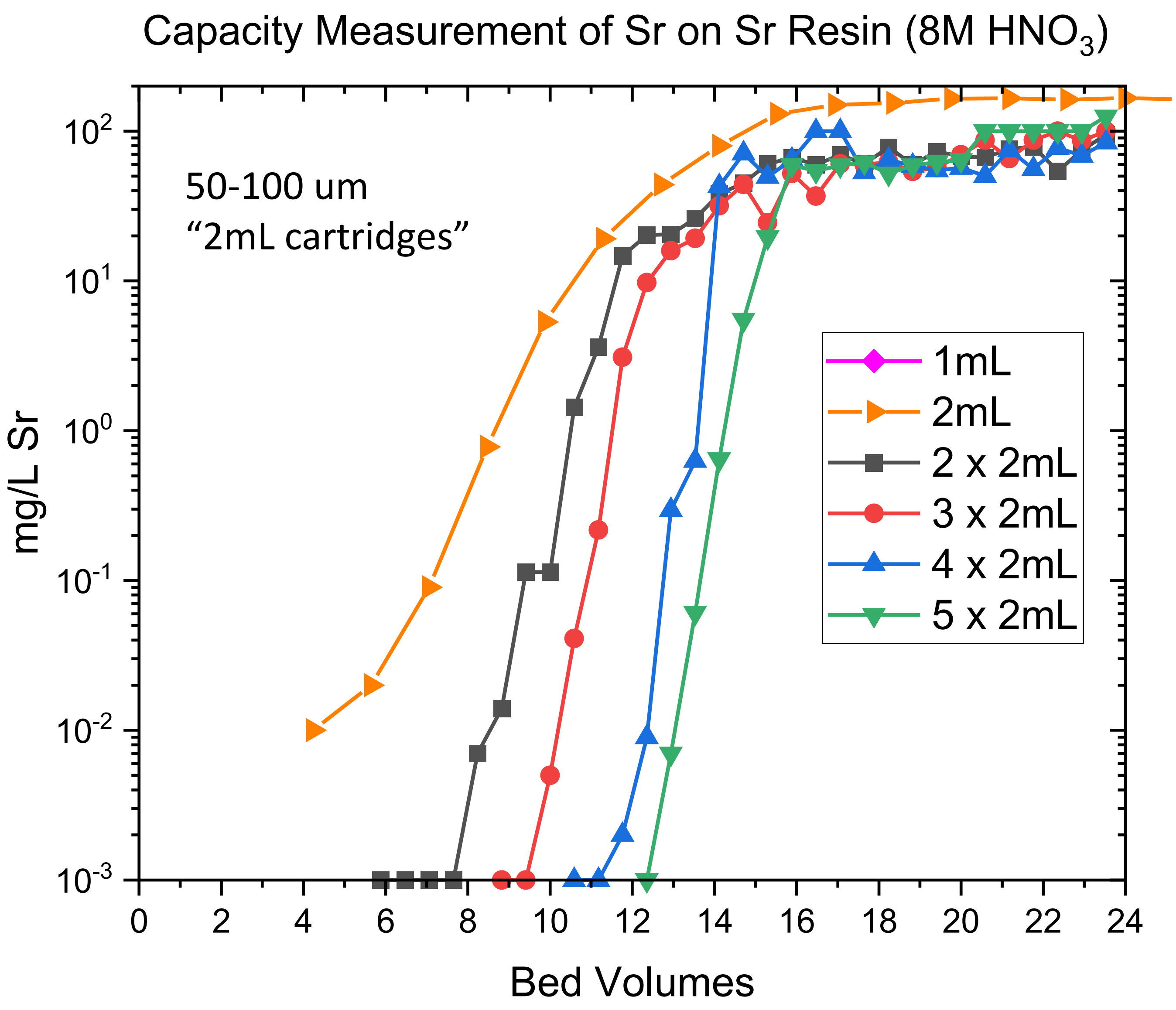


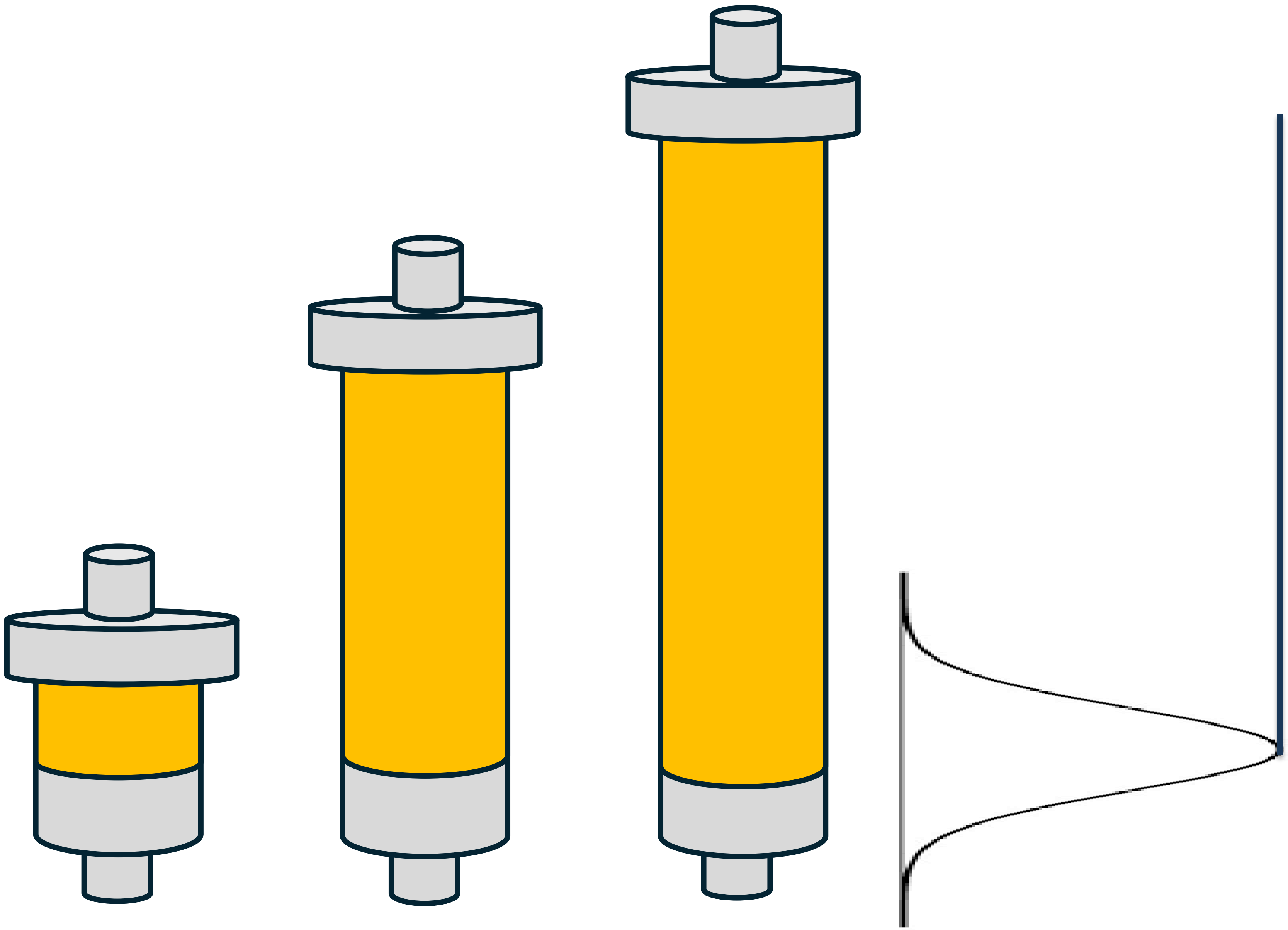
Full capacity (saturated resin):
8.0 ± 0.5 mg Sr / mL resin

Functional capacity (50% loading), >95% recovery
4.0 ± 0.3 mg Sr / mL resin

First breakthrough (<0.1%)
- dependent on column geometry and particle size.

2 mL	~ 3.0 mg Sr / mL resin (5.1 mg Sr)
4 mL	~ 5.5 mg Sr / mL resin (19 mg Sr)
6 mL	~ 6.6 mg Sr / mL resin (34 mg Sr)
8 mL	~ 7.5 mg Sr / mL resin (51 mg Sr)
10 mL	~ 7.6 mg Sr / mL resin (65 mg Sr)

Column Breakthrough



What else could k' (D) tell you?

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1) Mechanism of extraction
    - Stoichiometry through continuous variation

E. P. Horwitz, D. R. McAlister, M. L. Dietz, "Extraction chromatography versus solvent extraction: How similar are they?" *Sep. Sci. and Technol.*, 41(10), 2163-2182 (2006).

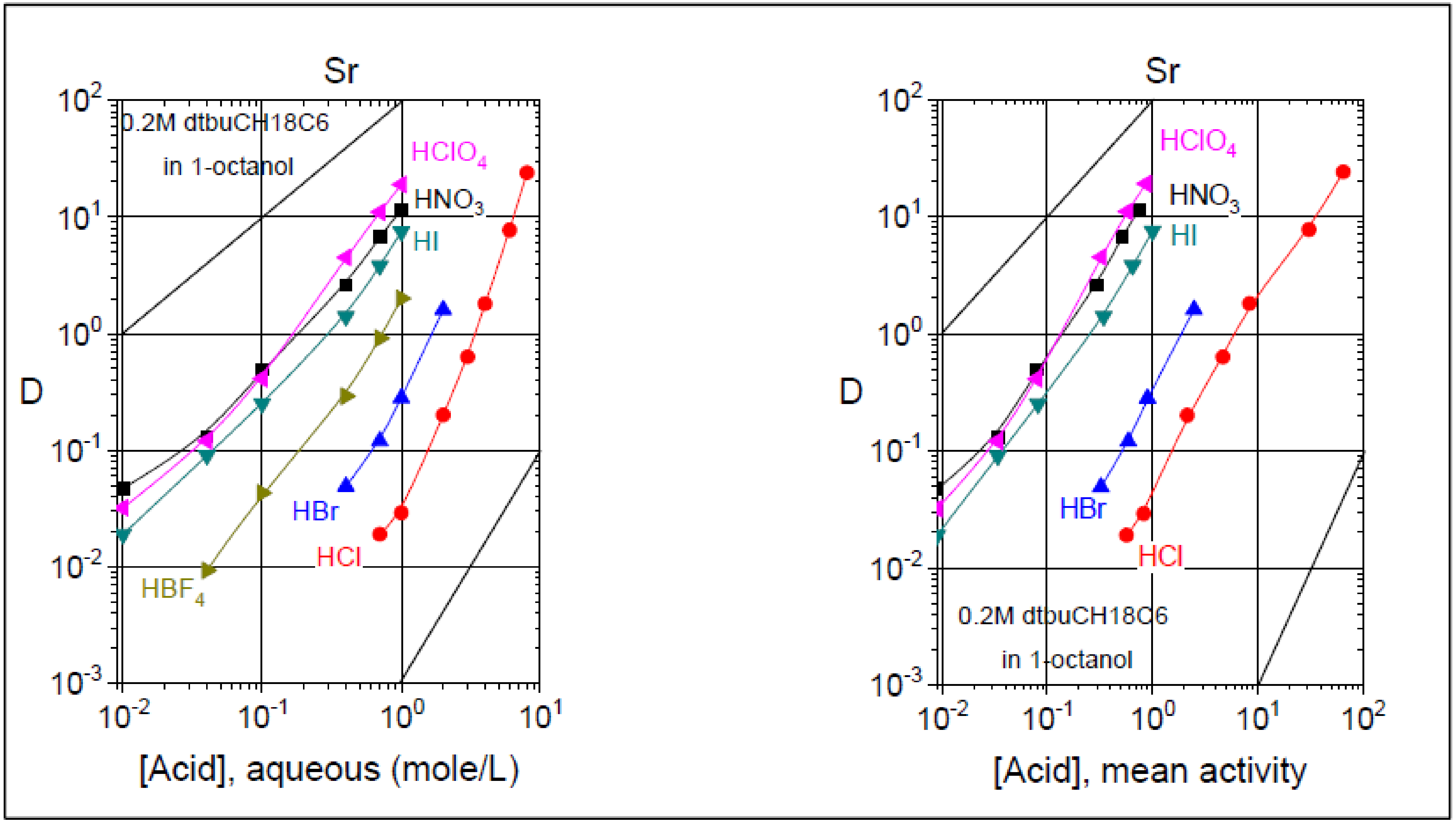
2) Thermodynamics of extraction
    - contribution of enthalpy and entropy of complexation through data collected at different temperatures.

Otu, E. O., & Chiarizia, R. (2001). THERMODYNAMICS OF THE EXTRACTION OF METAL IONS BY DIALKYL-SUBSTITUTED DIPHOSPHONIC ACIDS. II. THE U(VI) AND Sr(II) CASE. *Solvent Extraction and Ion Exchange*, *19*(6), 1017–1036. https://doi.org/10.1081/SEI-100107617

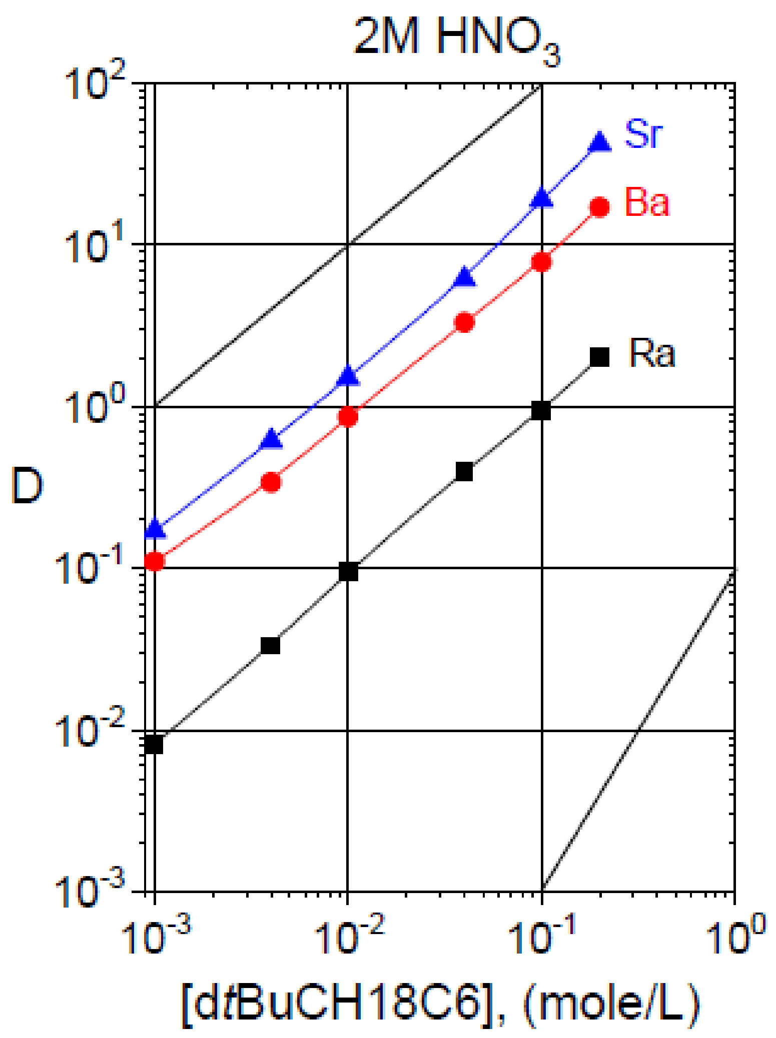
3) Are metal ions/counterions completely dehydrated by collection of data with different counterions (solvating extractants).

Horwitz, E. P., Dietz, M. L., Fisher, D. E. Correlation of the Extraction of Strontium Nitrate by a Crown Ether with the Water Content of the Organic Phase. *Solvent Extractionand Ion Exchange* **8**, 190–208 (1990).

Acid dependency



Extractant dependency



Must account for aggregation of extractants.

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System Stoichiometry by SX

(5) $\log K_d = \log K + \log[X^{m-}]^y[L]^z$ $f(x) = b + mx$

(6) $\log K_d = \log K + \log[L]^z + y\log[X^{m-}]$ (anion dependency)

($\log K + \log[L]^z$: constants; y: slope)

- Use activities, not concentrations

- Non-linear log-log plot may indicate more than one extracted species in equilibrium.

a) Measure K_d for metal M
b) Constant [L]
c) Vary [X]
d) Plot $\log K_d$ vs log[X]
e) Slope of line = y = # of X in the extracted complex.

Questions???

Capacity Data (Pb Resin)

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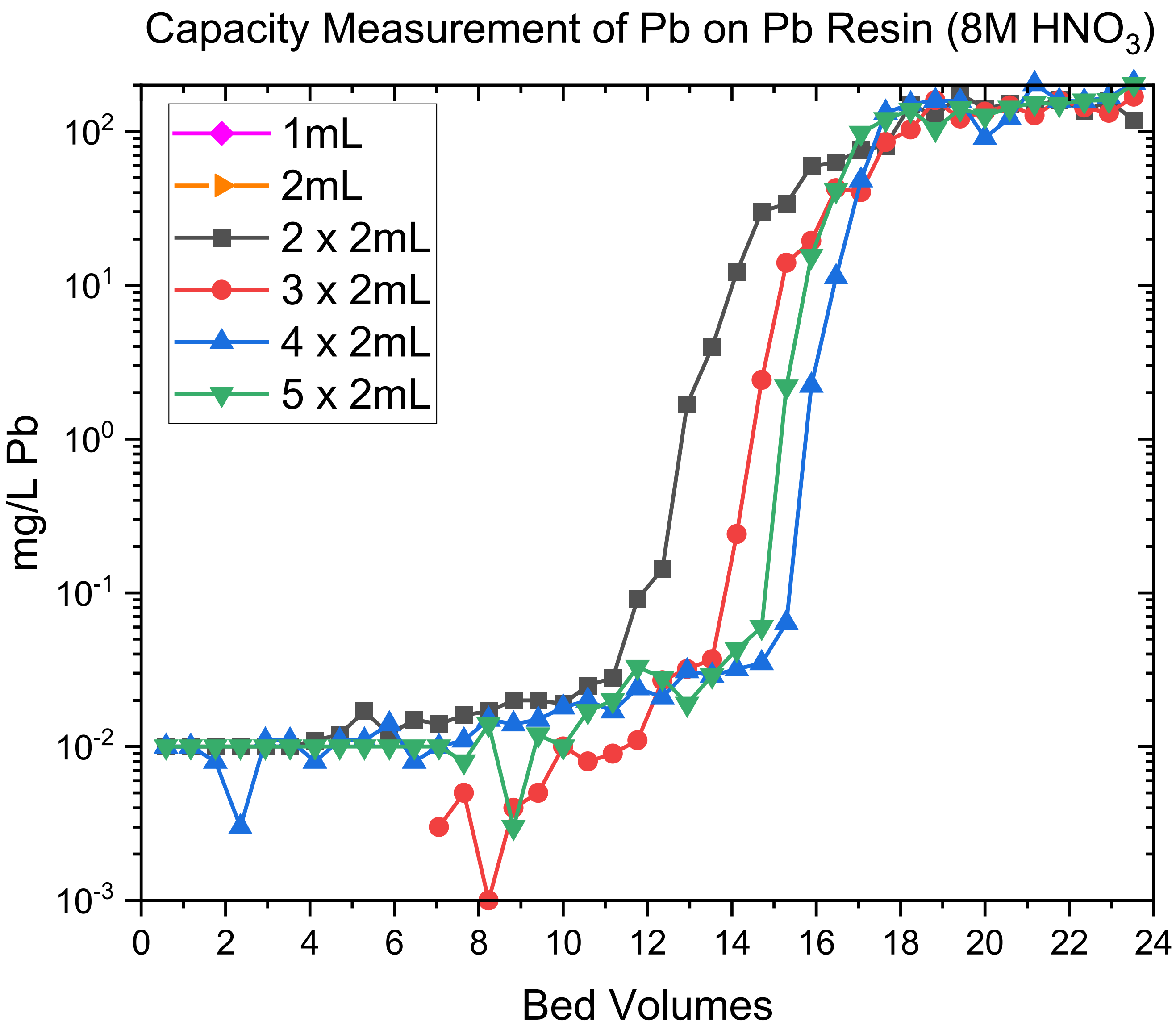


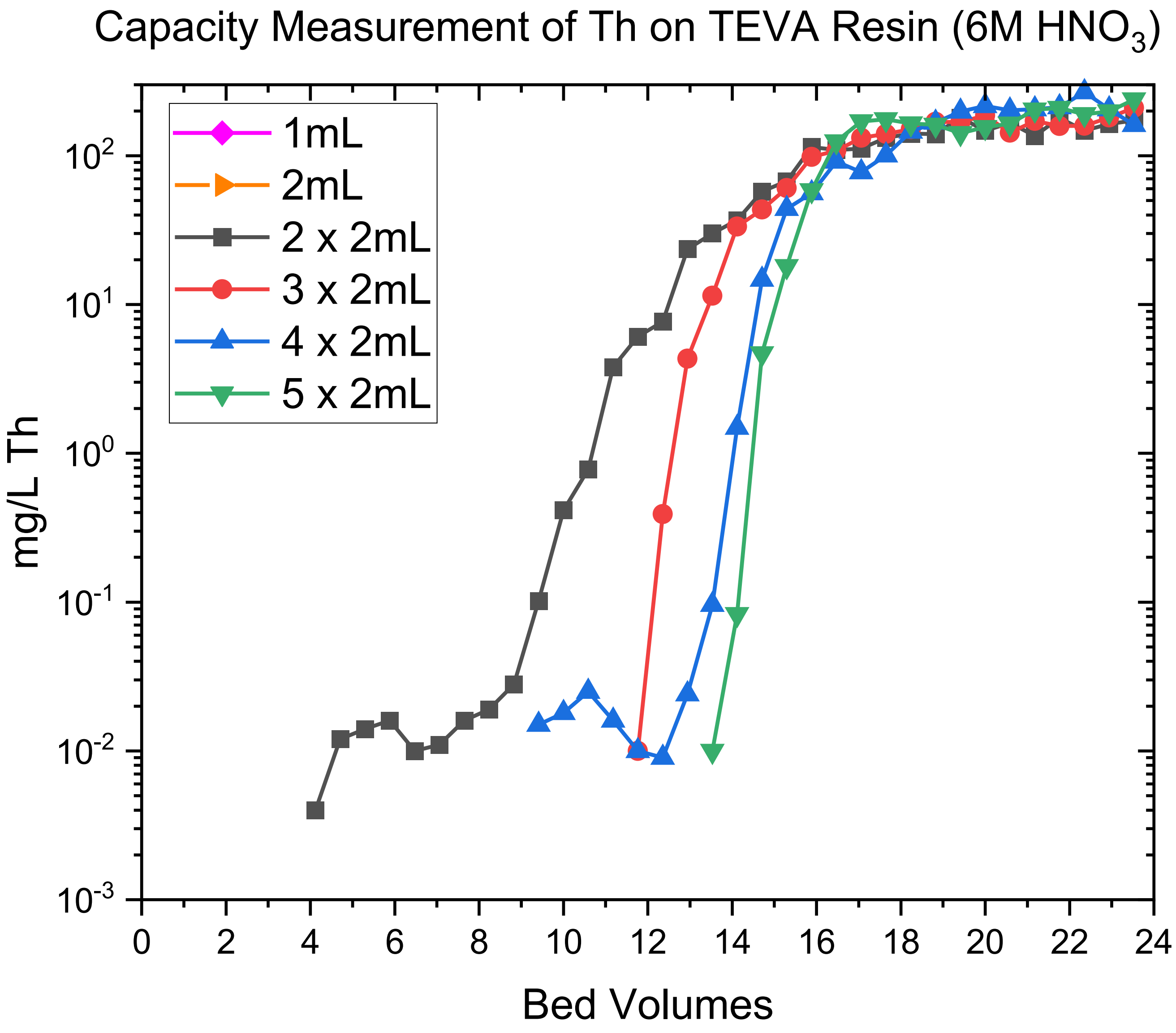
Full capacity (saturated resin):
25 ± 1 mg Pb / mL resin

Functional capacity (50% loading), >95% recovery
12.5 ± 0.5 mg Pb / mL resin

First breakthrough (<0.1%)
- dependent on column geometry and particle size.

2 mL	
4 mL	~ 18 mg Pb / mL resin (61 mg Pb)
6 mL	~ 21 mg Pb / mL resin (108 mg Pb)
8 mL	~ 23 mg Pb / mL resin (156 mg Pb)
10 mL	~ 23 mg Pb / mL resin (196 mg Pb)

Capacity Data (TEVA Resin)



Full capacity (saturated resin):
27 ± 1 mg Th / mL resin

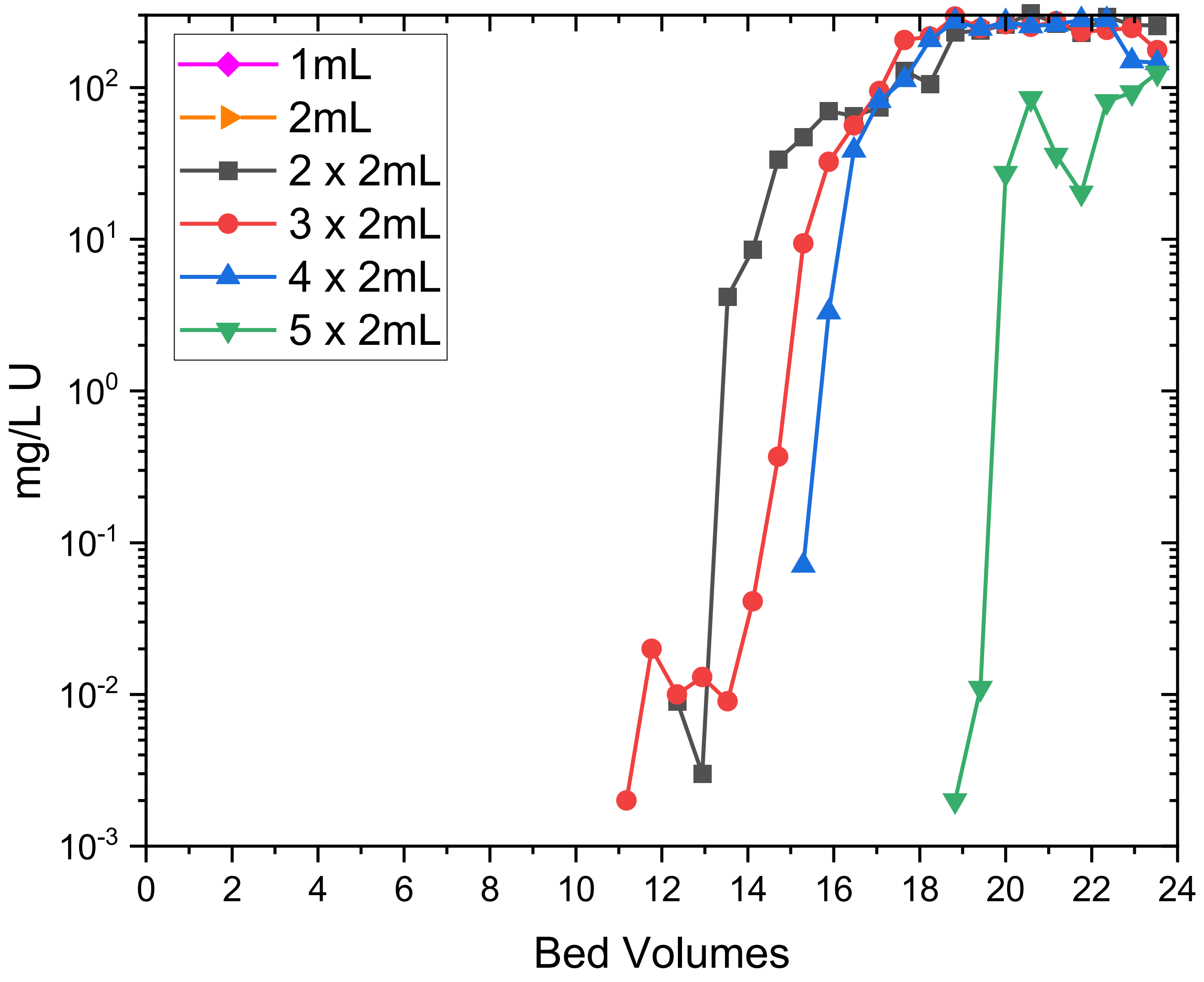
Functional capacity (50% loading), >95% recovery
13.5 ± 0.5 mg Th / mL resin

First breakthrough (<0.1%)
- dependent on column geometry and particle size.

2 mL	
4 mL	~ 17 mg Th / mL resin (58 mg Th)
6 mL	~ 22 mg Th / mL resin (112 mg Th)
8 mL	~ 24 mg Th / mL resin (163 mg Th)
10 mL	~ 25 mg Th / mL resin (212 mg Th)

Capacity Data (UTEVA Resin)

Capacity Measurement of U on UTEVA Resin (6M HNO_3)



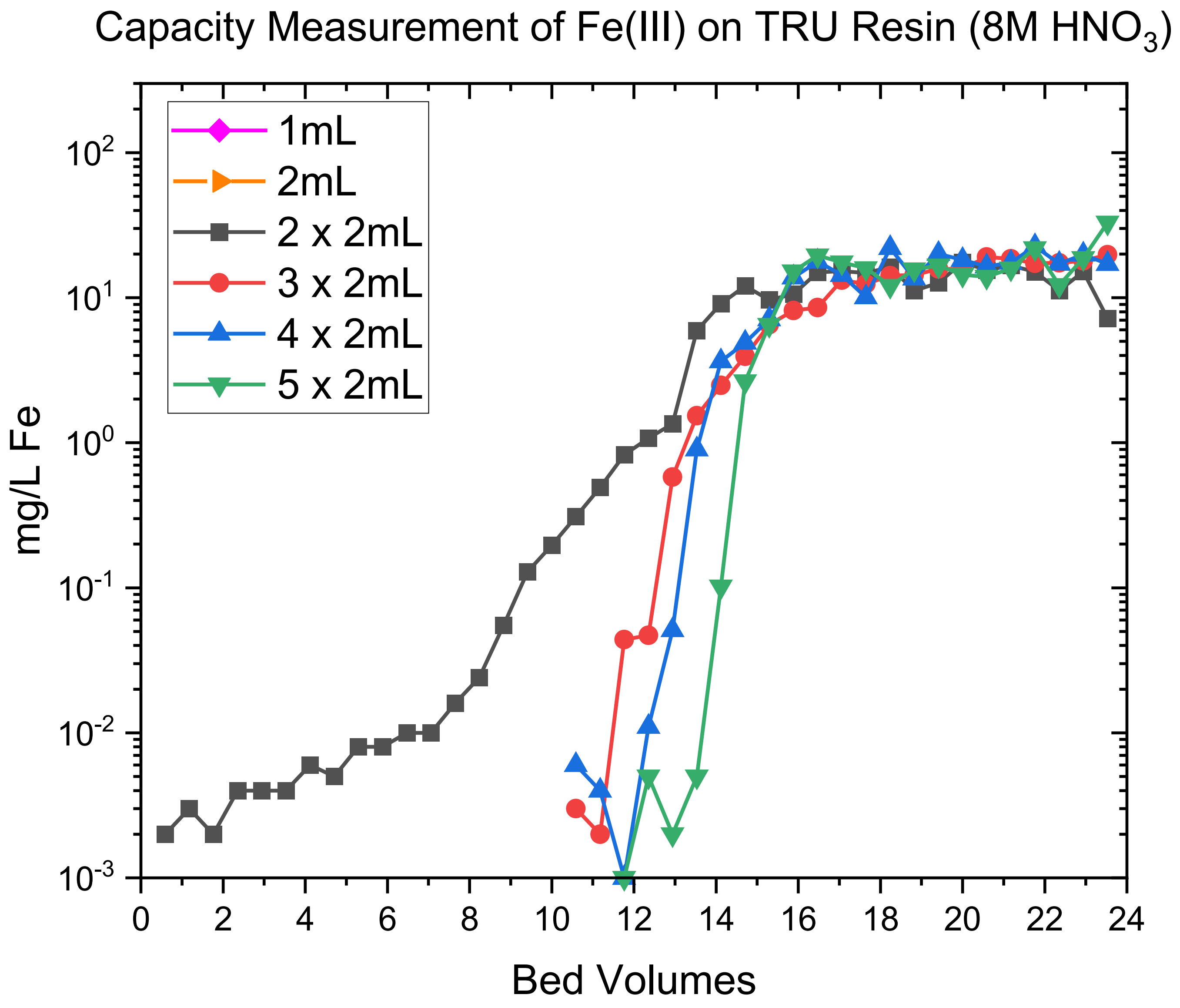
Full capacity (saturated resin):
54 $\pm$ 2 mg U / mL resin

Functional capacity (50% loading), >95% recovery
25 $\pm$ 1 mg U / mL resin

First breakthrough (<0.1%)
- dependent on column geometry and particle size.

2 mL	
4 mL	~ 39 mg U / mL resin (133 mg U)
6 mL	~ 44 mg U / mL resin (224 mg U)
8 mL	~ 46 mg U / mL resin (313 mg U)
10 mL	

Capacity Data (TRU Resin)



Full capacity (saturated resin):
2.2 ± 0.2 mg Fe / mL resin

Functional capacity (50% loading), >95% recovery
1.1 ± 0.1 mg Fe / mL resin

First breakthrough (<0.1%)
- dependent on column geometry and particle size.

2 mL	
4 mL	~ 1.3 mg Fe / mL resin (4.4 mg Fe)
6 mL	~ 1.8 mg Fe / mL resin (9.2 mg Fe)
8 mL	~ 1.9 mg Fe / mL resin (12.9 mg Fe)
10 mL	~ 2.0 mg Fe / mL resin (17.0 mg Fe)

Capacity Data (RE Resin)

Capacity Data (DGA, Normal Resin)

Capacity Data (DGA, Branched Resin)