# INFLUENCE OF LARGE UNIVALENT ANIONS ON LIGAND SELECTIVITY

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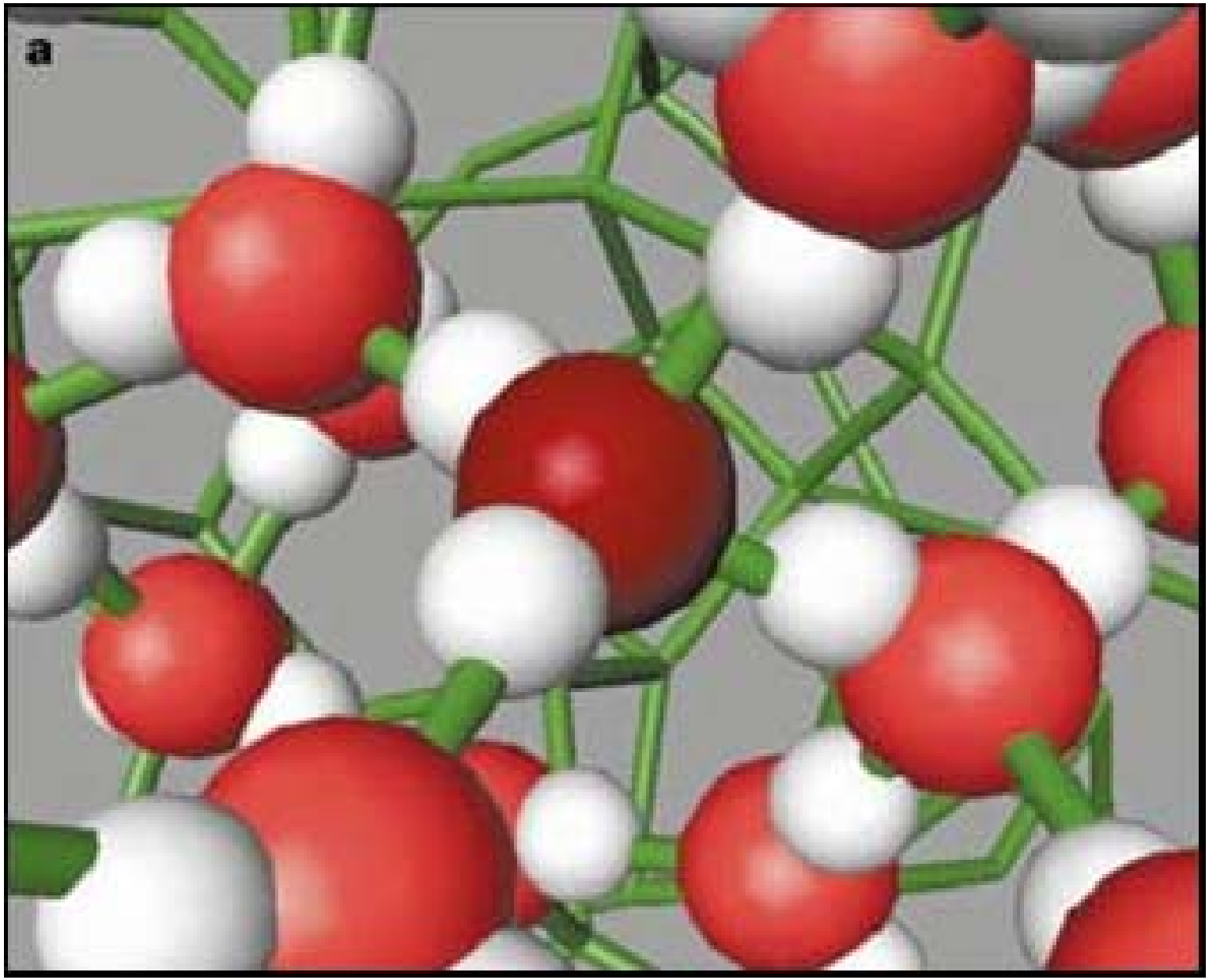
REALIZING THE FUTURE

Example of a simple extraction equilibrium between cations ($M^{3+}$) and anions ($A^-$) in an aqueous phase and a neutral extractant (E) in an organic phase:

$$M^{3+}\cdot(H_2O)_x + 3A^-\cdot(H_2O)_y + \overline{nE\cdot(solvent)_z} \leftrightarrow \overline{ME_nA_3\cdot(solvent)_z} + (x+y)H_2O$$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## Ionic Radii, Ionic Volumes, and Calculated Hydration Energies of Selected Anions

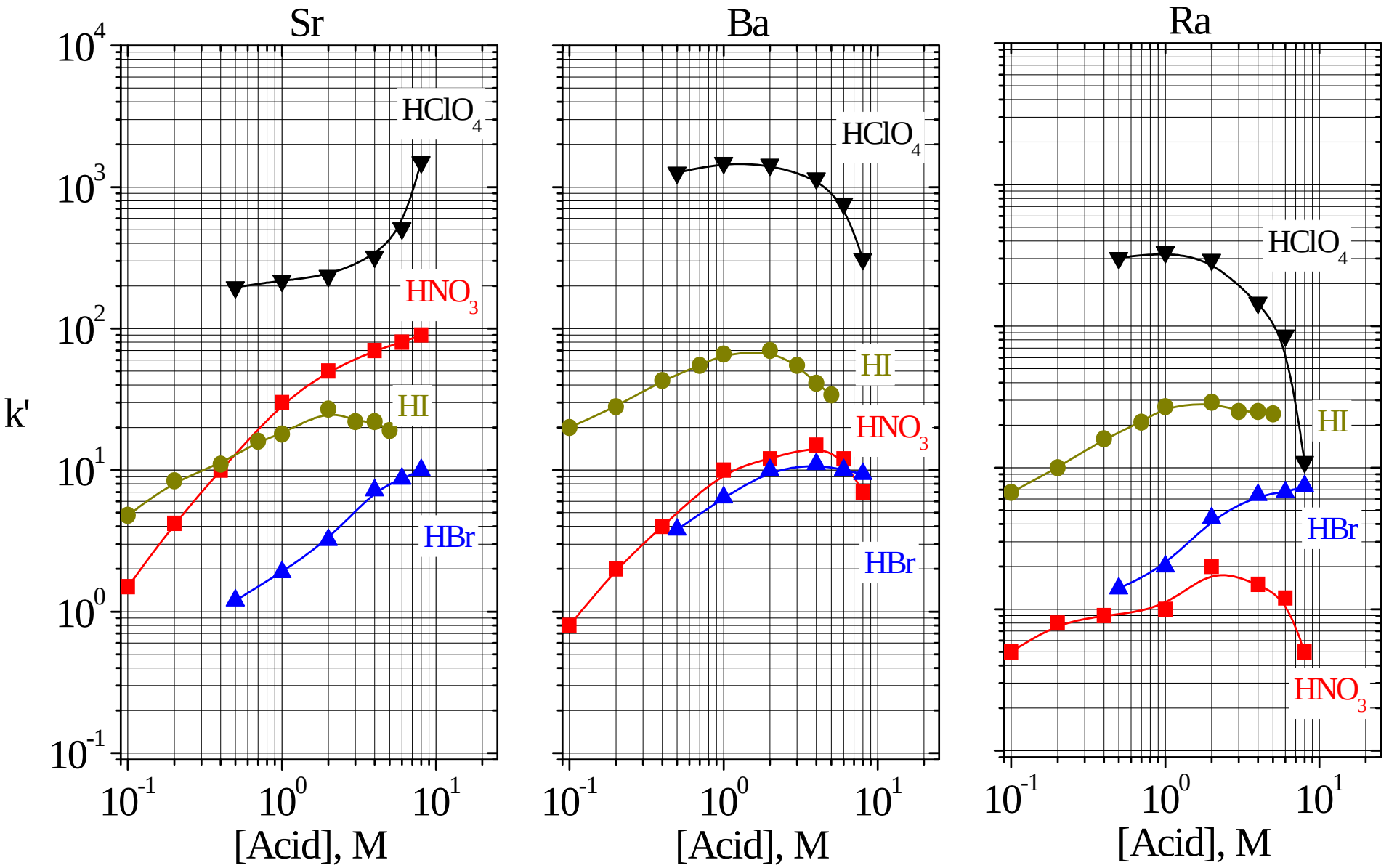
| Anion | Ionic Radius (nm) | Volume ($nm^3$) | Hydration Energy (kcal/mol) |
|---|---|---|---|
| $F^-$ | 0.133 | 9.9E-03 | 88 |
| $Cl^-$ | 0.181 | 2.5E-02 | 65 |
| $Br^-$ | 0.196 | 3.2E-02 | 60 |
| $I^-$ | 0.220 | 4.5E-02 | 53 |
| | | | |
| $NO_3^-$ | 0.179 | 2.4E-02 | 66 |
| $ClO_4^-$ | 0.250 | 6.6E-02 | 43 |
| $MnO_4^-$ | 0.240 | 5.8E-02 | 47 |
| | | | |
| $O^{2-}$ | 0.140 | 1.2E-02 | |

$F^-$

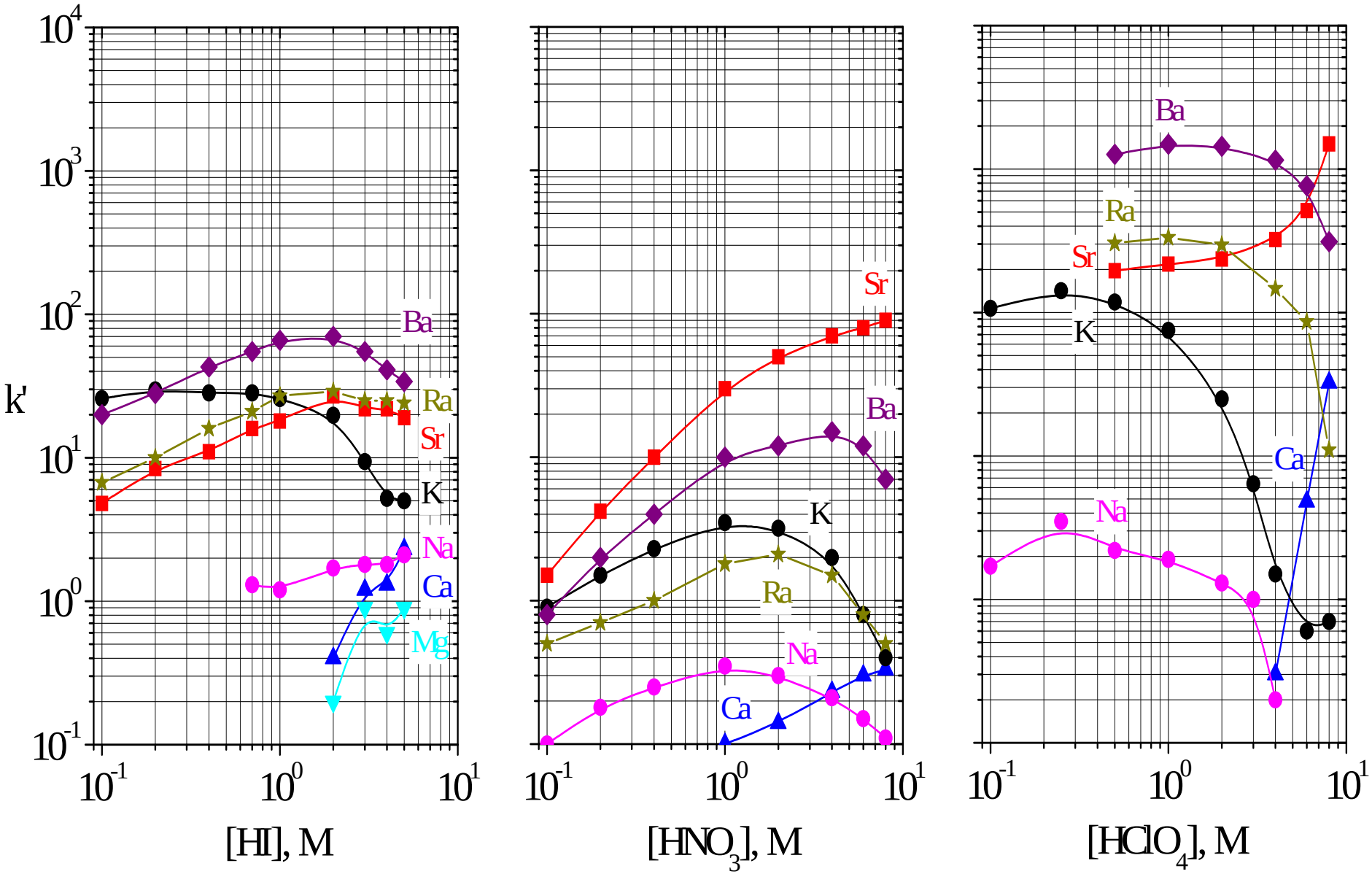
$NO_3^-$

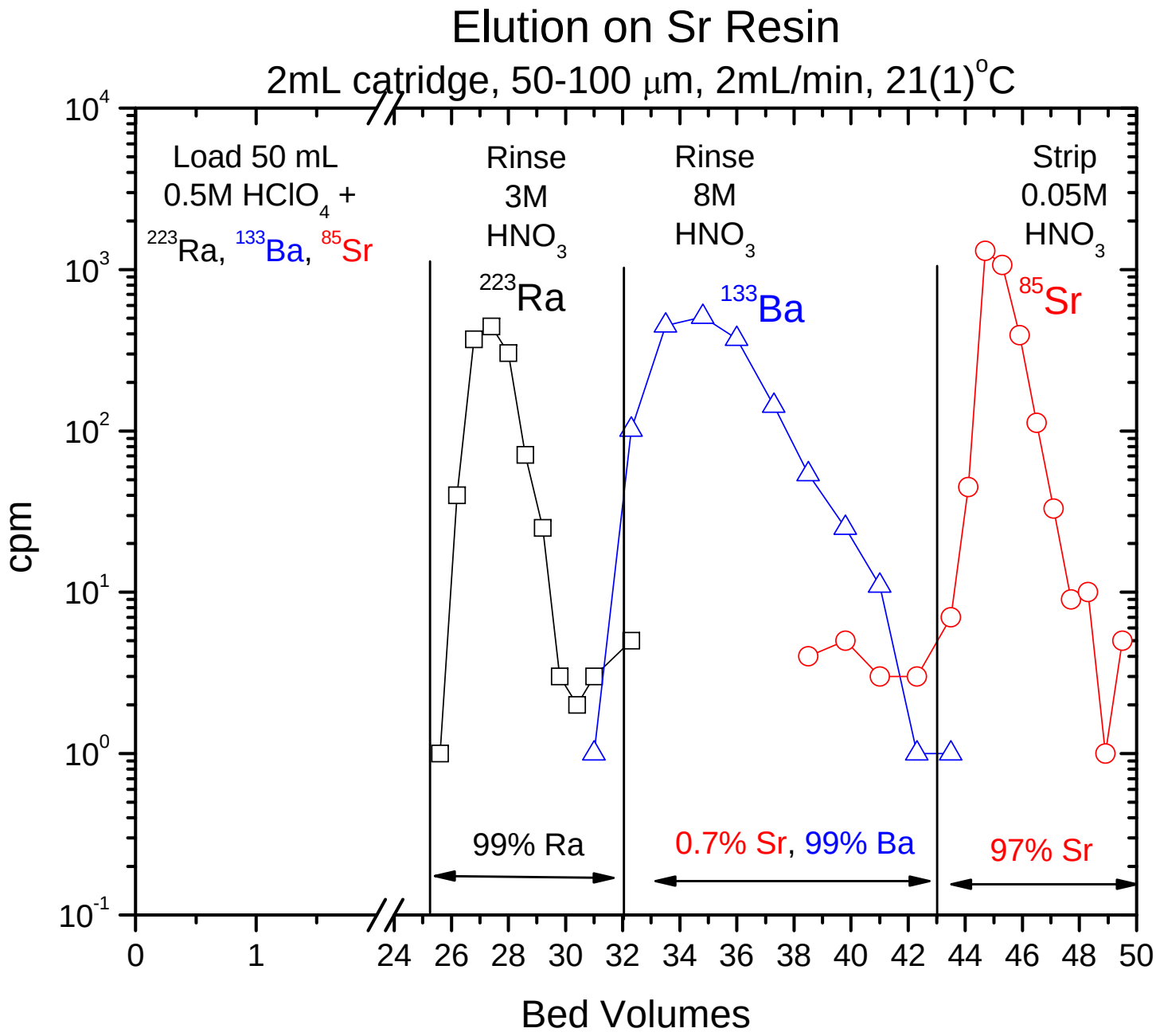
$ClO_4^-$

# Uptake of Metal Ions on Sr Resin vs Anion

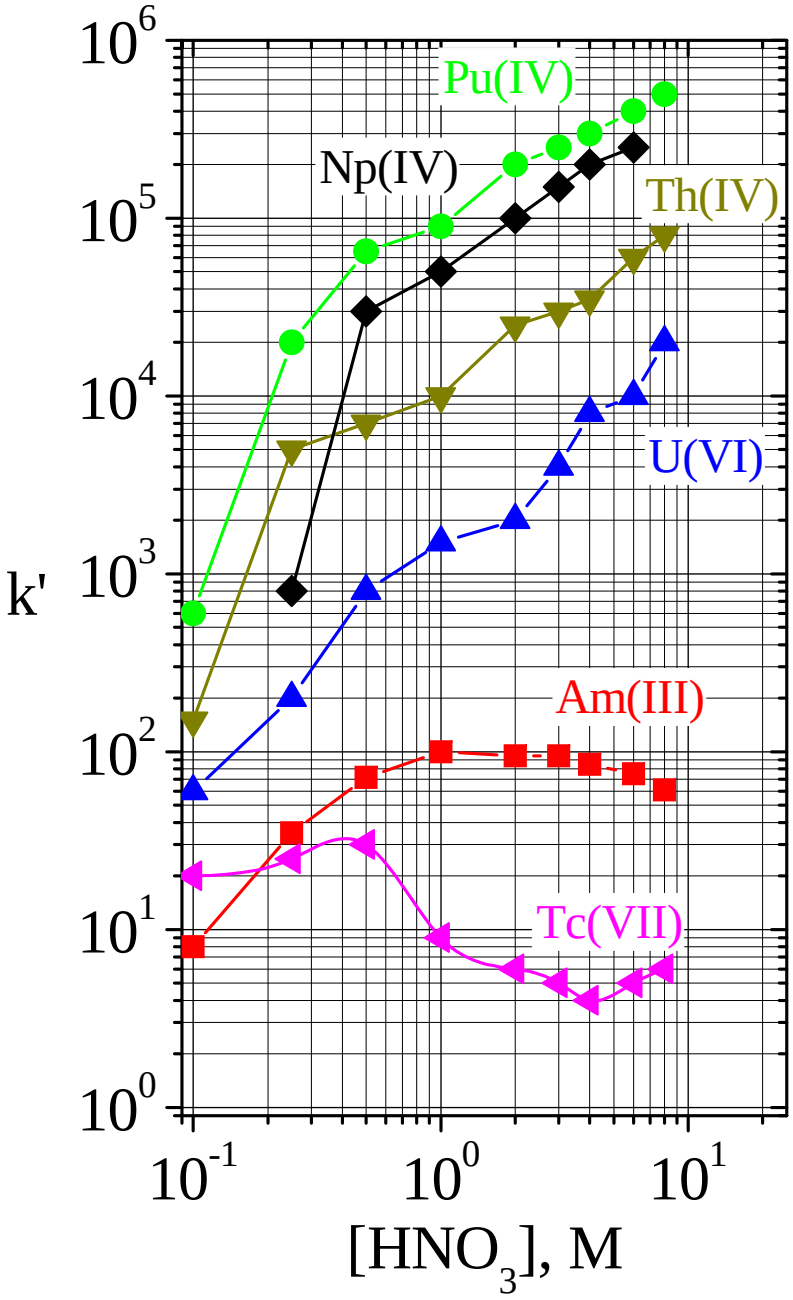


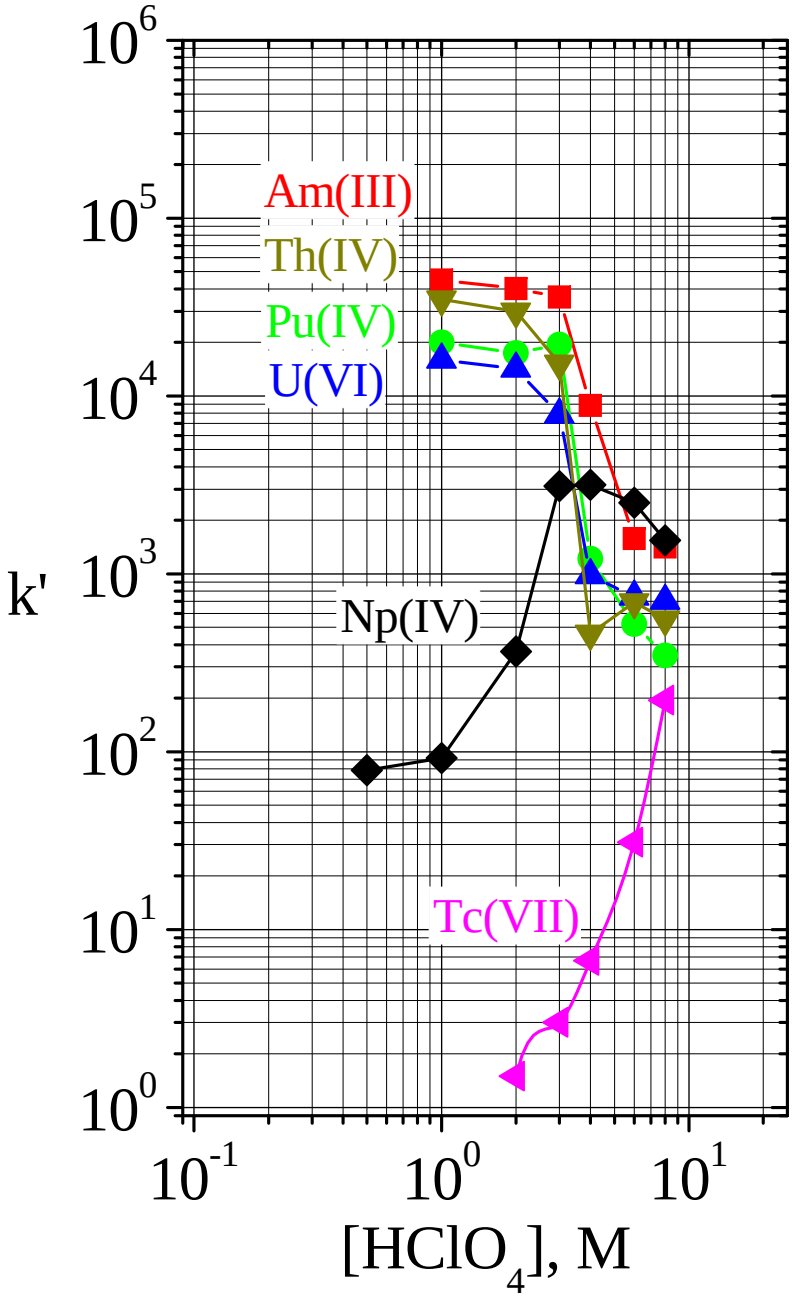
# Uptake of Metal Ions on Sr Resin



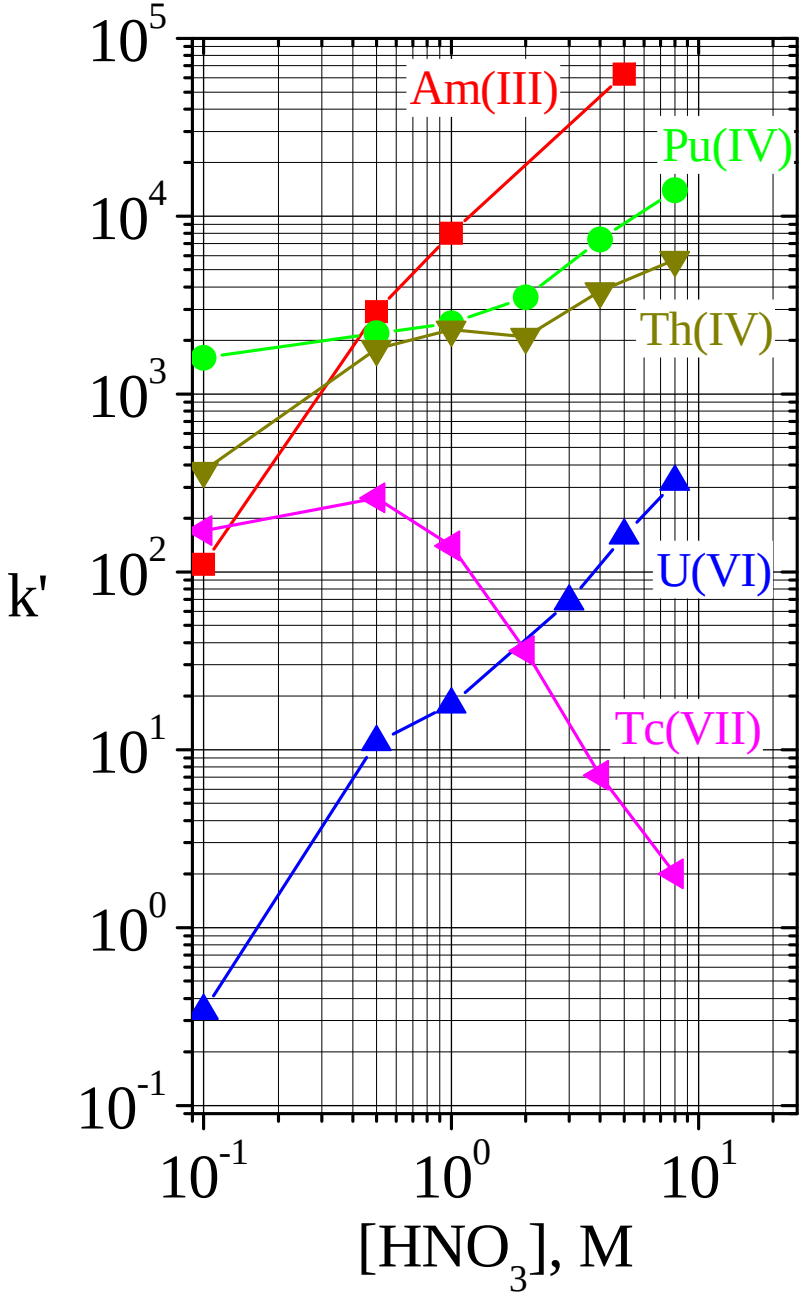

Elution on Sr Resin
2mL catridge, 50-100 μm, 2mL/min, 21(1)°C
Load 50 mL
0.5M HClO4 +
223Ra, 133Ba, 85Sr
Rinse
3M
HNO3
223Ra
Rinse
8M
HNO3
133Ba
Strip
0.05M
HNO3
85Sr
99% Ra
0.7% Sr, 99% Ba
97% Sr
cpm
Bed Volumes

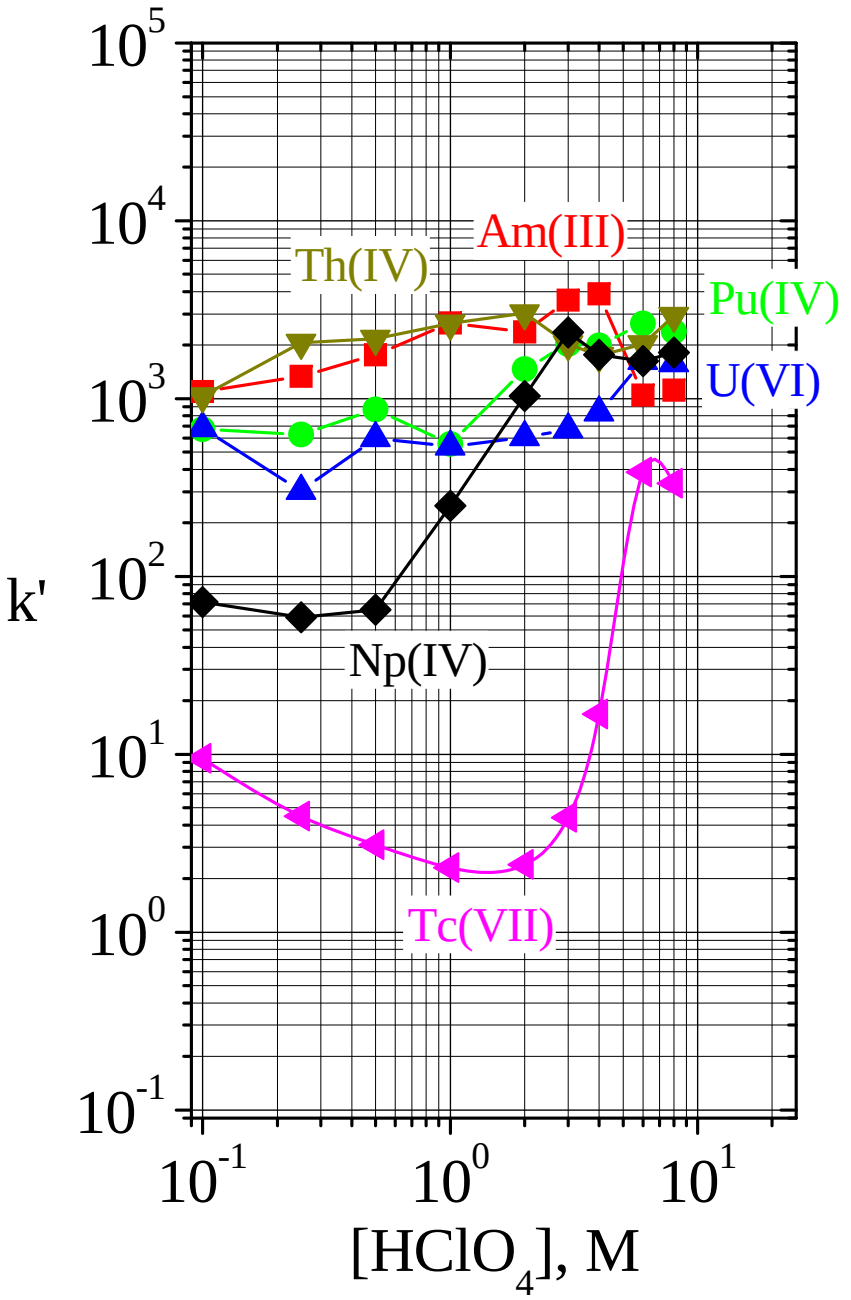
# Uptake of Metal Ions on TRU Resin



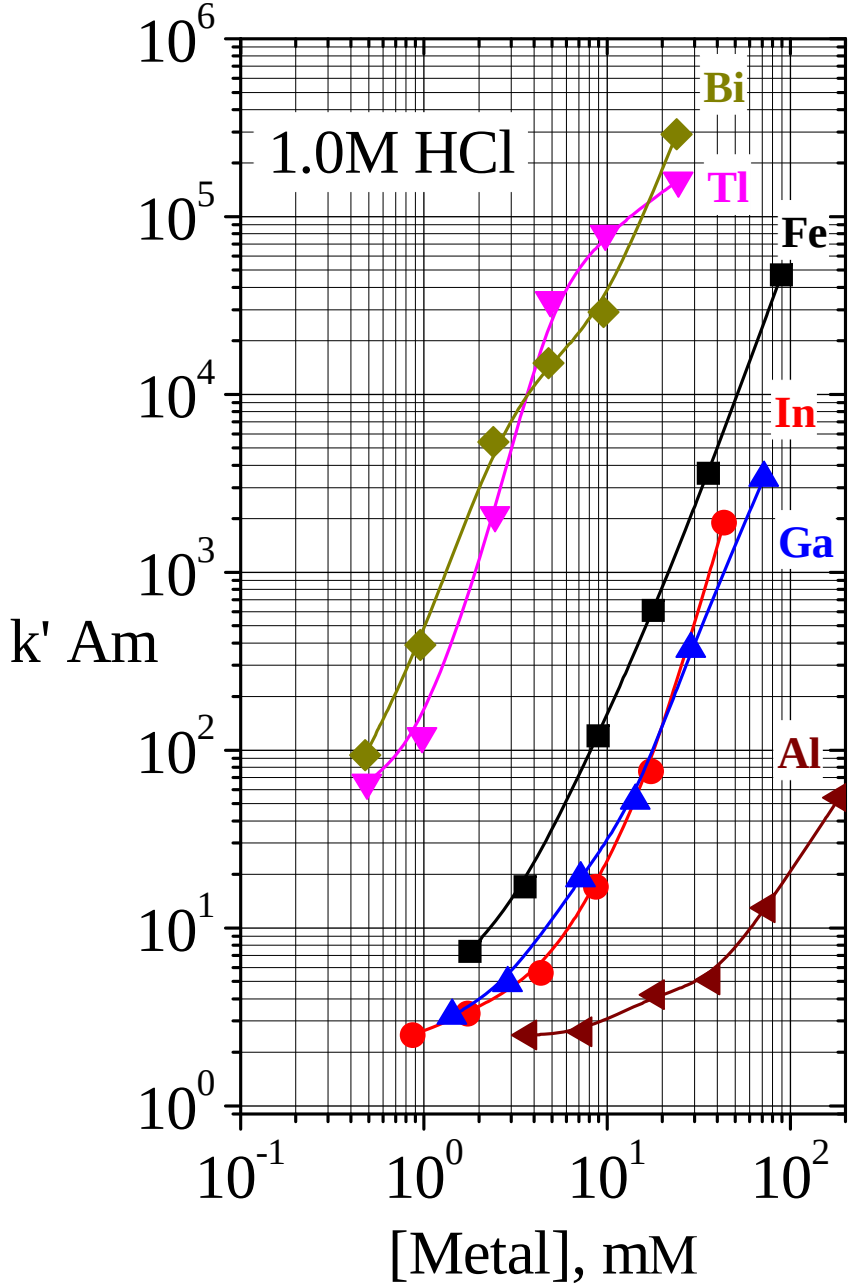



# Uptake of Metal Ions on DGA Resin, Normal



# Uptake of Am(III) on DGA Resin, Normal



# Equations for Metal Ion Uptake for DGA/Metal/Cl System

$$\overline{\text{TODGA}} + x\text{HCl} \leftrightarrow \overline{\text{TODGA(HCl)}_x} \qquad (1)$$

$$\overline{\text{TODGA}} + \text{H}^+ + \text{MCl}_4^- \leftrightarrow \overline{\text{TODGA(HMCl}_4\text{)}} \qquad (2)$$

$$\overline{3\text{TODGA}} + \text{Am}^{3+} + 3\text{MCl}_4^- \leftrightarrow \overline{\text{Am(TODGA)}_3(\text{MCl}_4)_3} \qquad (3)$$

# The Science of Radiochemical Separations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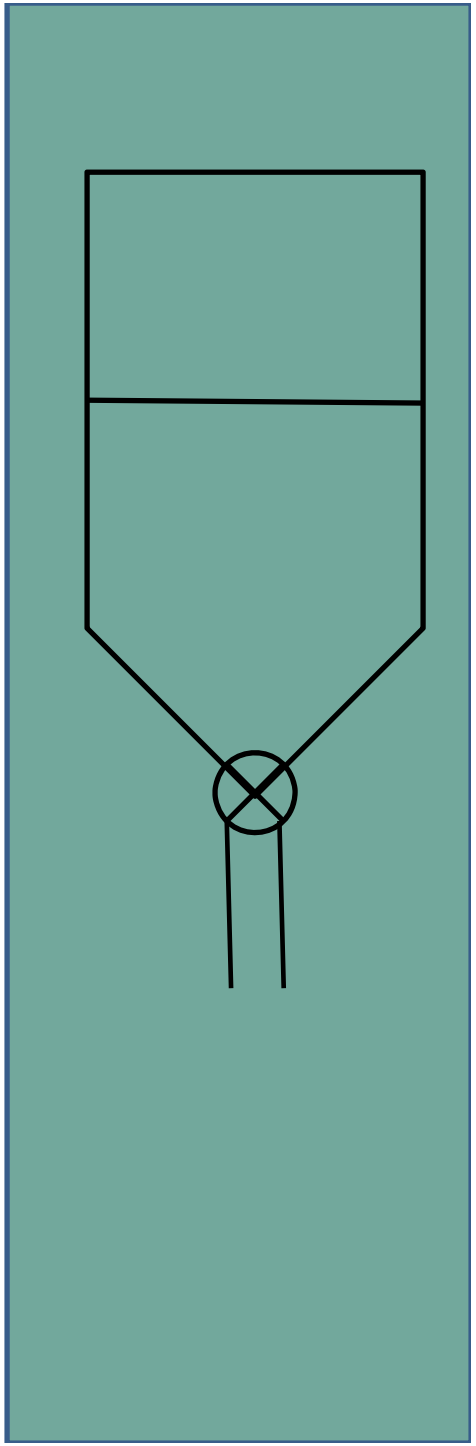

# Outline

- Introduction
- Solvent Extraction
- Chromatography
- Achievement of Separation
- Ion Exchange
- Extraction Chromatography
- Separations at Curie Levels