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EICHROM TECHNOLOGIES

Fundamentals of Metal Ion Separations and History of EXC development

Outline

1: Fundamentals of Separation Methods

- Aqueous metal ions
- Metal ion complexation

2: Separation Types (from aqueous)

- Precipitation
- Solvent Extraction
- Chromatography

3: Development of Eichrom EXC Resins (Historical context)

- Combining precipitations, solvent extraction, chromatography (EXC)

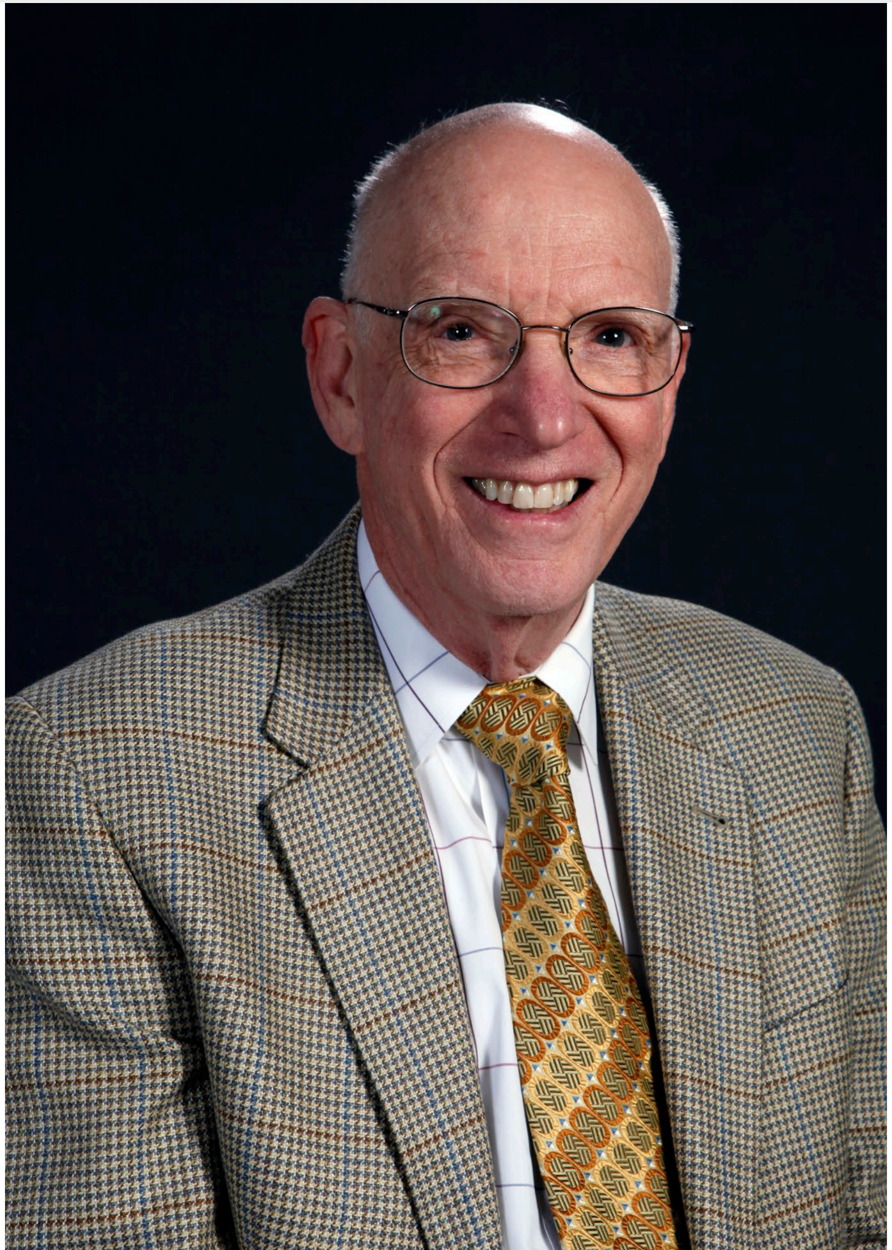
4: Analytical Method

- Eichrom Method ACW17-VBS
- Am/Cm, Pu/Np, Th, U, Sr in water

Friday: Application to separation of nuclear medicine radioisotopes.


eichrom
eichrom
eichrom
1000 mL
KIMAX
KIMBLE USA
140 ml
eichrom
eichrom
eichrom
eichrom

Founded by Phil Horwitz in 1990 to commercialize materials developed at Argonne National Laboratory



Chemist at Argonne National Laboratory from 1959 – 1998.

Group leader of the Chemical Separations Group from 1972 – 1996

Section Chief Heavy Element Research in Chemistry Division 1991-1996

Consulting Scientist, Eichrom Technologies, 1990 – 2019.

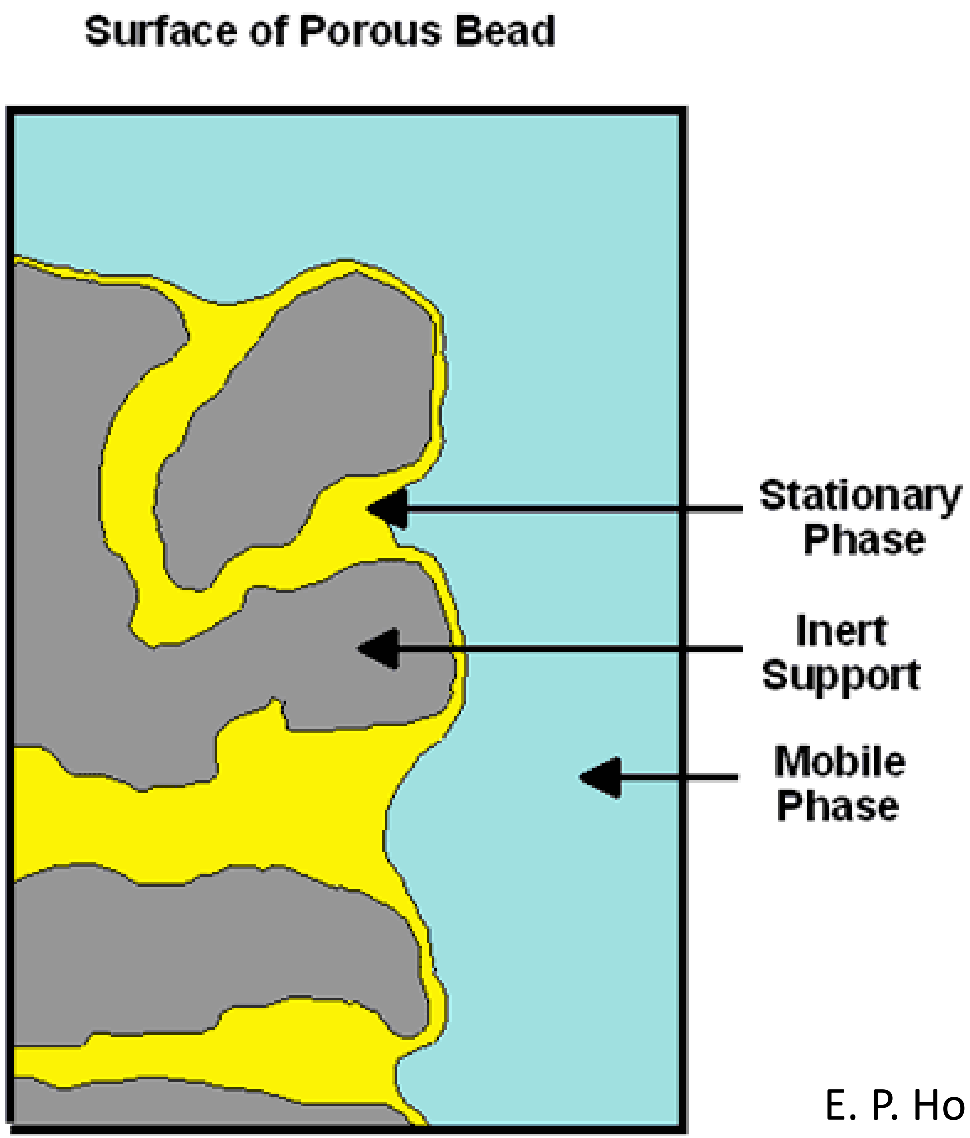
Director and President, PG Research Foundation, 1998 – 2019.

D.R. McAlister, H. Kurosaki, S. Happel, E.P. Horwitz, "Development of EXC Resins for Metal Ion Separations," Bunseki, 2, 44-50, (2020).

(Contact speaker for English language version.)

E.R. Bertelsen, J.A. Jackson, J.C. Shafer, "A Survey of Extraction Chromatographic f-Element Separations Developed by E. P. Horwitz," Solv. Extr. Ion Exch., 38(3), 251-289,(2020).

Extraction Chromatographic (EXC) Resins



Inert support = **Macroporous Acrylic Resin**

Functional Groups = **Hydrophobic Extractants**
Held in pores of support
Not covalently bonded

Mobile Phase = **Aqueous**

Maintains selectivity of solvent extraction with the convenience and resolution of chromatography.

Wide application in analytical radiochemistry and radioisotope production.

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).

References (Section 1: Fundamentals of Separations)

1) Gregory Choppin, Jan-Olov Liljenzin, Jan Rydberg, Christian Ekberg, “Radiochemistry and Nuclear Chemistry,” Elsevier, New York, 2013.

2) J. Calvin Giddings, “Unified Separation Science,” John Wiley and Sons, Inc. New York, 1991.

3) Gregory Choppin and Mark Jensen, “Actinides in Solution: Complexation and Kinetics” In The Chemistry of the Actinide and Transactinide Elements, 3rd Ed., Volume 4, Edited by Lester Morse, Norman Edelstein, Jean Fuger, Joseph J. Katz, Springer, Netherlands, pp. 2524-2621, 2006.

4) Charles, F. Baes, Jr. and Robert E. Mesmer, “The Hydrolysis of Cations,” John Wiley and Sons, New York, 1976.

5) Gregory Choppin and Alfred Morgenstern, “Thermodynamics of Solvent Extraction,” Solv. Extr. Ion Exch., 18(6), 1029-1049 (2000).

References (Section 2: Precipitation, Solvent Extraction, Chromatography)

1) Gregory Choppin, Jan-Olov Liljenzin, Jan Rydberg, Christian Ekberg, “Radiochemistry and Nuclear Chemistry,” Elsevier, New York, 2013.

2) J. Calvin Giddings, “Unified Separation Science,” John Wiley and Sons, Inc. New York, 1991.

3) Alan Townshed and Ewald Jackwerth, “Precipitation of Major Constituents for Trace Preconcentration: Potential and Problems,” *Pure and Applied Chemistry*, 61(9), 1643-1656 (1989).

4) Kenneth L. Nash, Charles Madic, Jagdish N. Mathur, Jerome, Lacquement, “Actinide Separation Science and Technology” In The Chemistry of the Actinide and Transactinide Elements, 3rd Ed., Volume 4, Edited by Lester Morse, Norman Edelstein, Jean Fuger, Joseph J. Katz, Springer, Netherlands, pp. 2622-2798 (2006).

5) Tatsuya Sekine and Yuko Hasegawa, “Solvent Extraction Chemistry Fundamentals and Applications,” Marcel Dekker, Inc., New York, 1977.

6) R.M. Diamond and D.C. Whitney, “Resin selectivity in dilute to concentrated aqueous solutions, Chapter 8, in Ion Exchange: A series of Advances, Marcel Deckker, New York, pp 277-351 (1966).

Separation types and basic thermodynamics

There is a cost to perform separations
- heat (distillation)
- motion (centrifugation)
- chemical potential (ppt/SX/IX/EXC)

Separation Types

Separation is a process by which a mixture is divided between at least two phases having different compositions.

Gas – Liquid	Gas – Solid	Liquid – Liquid	Liquid – Solid
Disk	Adsorption	Solvent Extraction	Precipitation
Gas Chromatograph	Sublimation	Exclusion	Fractional Crystallization
	Molecular Sieves		Ion Exchange
	Gas Chromatograph		Extraction Chromatography
			Adsorption
			Ion Exclusion

Phase 1: Aqueous

Phase 2:
Solid or Liquid

Ions or groups of
Ions or compounds

Radioactive

Partition Coefficients

$K = c_i^b / c_i^a$

K = partition coefficient
c = concentration of i
a, b = phases

Precipitation:	Ksp (solubility product constant)
Solvent Extraction:	D (distribution ratio)
Chromatography:	Dw(Kd), Dv, k’

Separation Factors

A separation factor is the ratio of partition coefficients for two different components.

$$\alpha = K_2/K_1 = \text{Separation Factor}$$

High separation factors allow for easier separation of two or more components.

Thermodynamics of complexation (-ΔG is thermodynamically favorable)

$$\Delta G_n^0 = \Delta H_n - T\Delta S_n$$

Standard
free energy of
complexation

Enthalpy of
complexation

- Electrostatic interactions
- Covalent interactions
+ dehydration

-T x Entropy of
complexation

- Dehydration
+ complexation
(increase or
decrease in
randomness)

Choppin 2000

Magnitude of energy to achieve separation

Giddings 1991

$$\Delta G^\circ = RT \ln K$$

Free energy of complexation can also be related to the partition coefficient (K)….

$$(\Delta G^o)_1 - (\Delta G^o)_2 = RT(\ln K_2 - \ln K_1)$$

$$\alpha = K_2/K_1 = \text{Separation Factor}$$

$$\Delta(\Delta G^\circ) = RT \ln \alpha$$

The separation factor ($\alpha = K_2/K_1$) can be expressed as the difference in free energies of complexation.

To Change α by	Requires (k cal/mol)
10^4	5.4
10^2	2.7
10	1.4
2	0.41

C – C Bonds
83 Kcal/mol

Hydrogen Bonds
1-3 Kcal/mol

van der Waals
~0.5 Kcal/mol

Separations and Entropy?

Giddings 1991

Entropy ~ the degree of disorder or uncertainty in a system.

Isolated systems spontaneously evolve towards thermodynamic equilibrium, the state with maximum entropy.

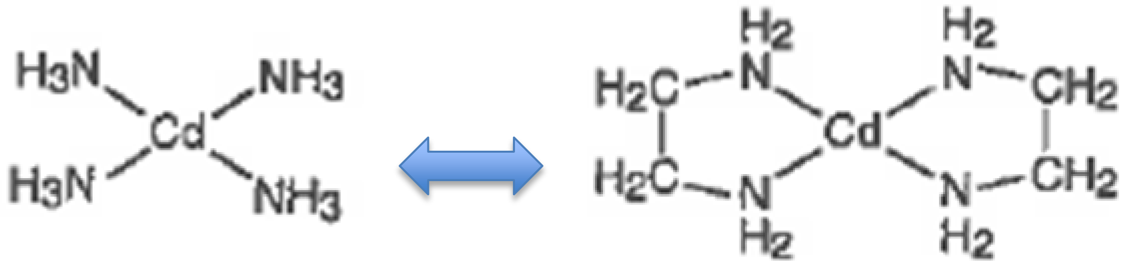
- Mixing and dilution are favored by entropy
- Separation and concentration typically result in unfavorable entropy contributions

Entropy can help drive separations if

- complexation displaces multiple solvating molecules or ions
- multidentate complexation
- chelation (multidentate coordination with additional stabilization of 5-6 member rings.

Chelation can provide favorable entropic contribution

Choppin 2000



Cd $(NH_3)_4^{2+}$ Cd $(NH_2C_2H_4NH_2)_2^{2+}$

Ammonia ⟷ ethylene diamine

(monodentate) (bidendate, chelating)

$$Cd(NH_3)_2^{2+} + en = Cd(en)^{2+} + 2NH_3$$

(2) → (3)

$$Cd(NH_3)_4^{2+} + 2en = Cd(en)_2^{2+} + 4NH_3$$

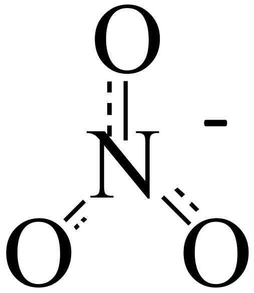
(3) → (5)

Thermodynamic Parameters of Reaction of Cadmium(II)-Ammonia Complex with Ethylenediamine

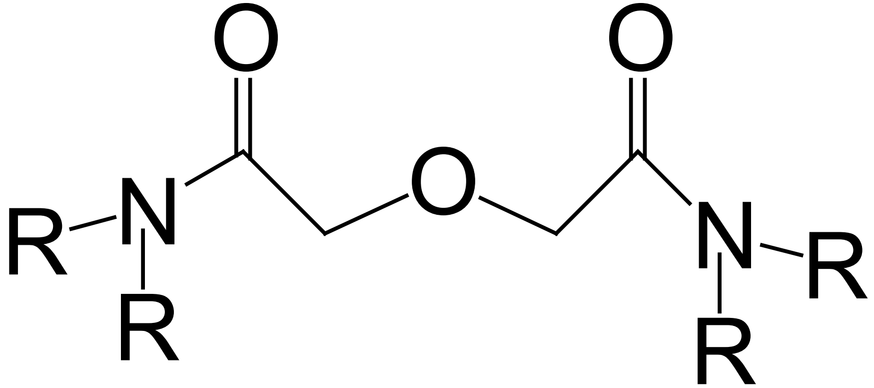
Complex	n	Log K_n^*	ΔH° ($kJ \cdot mol^{-1}$)	ΔS° (J·m·K
$Cd(en)^{+2}$	1	0.9	+0.4	5.4
$Cd(en)_2^{+2}$	2	2.2	- 3.4	+ 15

Strong entropic driver due to liberation of 2x NH_3 for each (en).

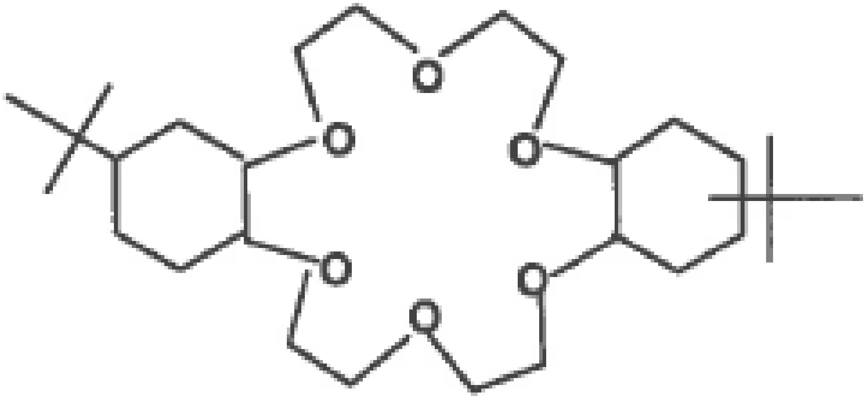
Displacing Multiple Waters of Hydration



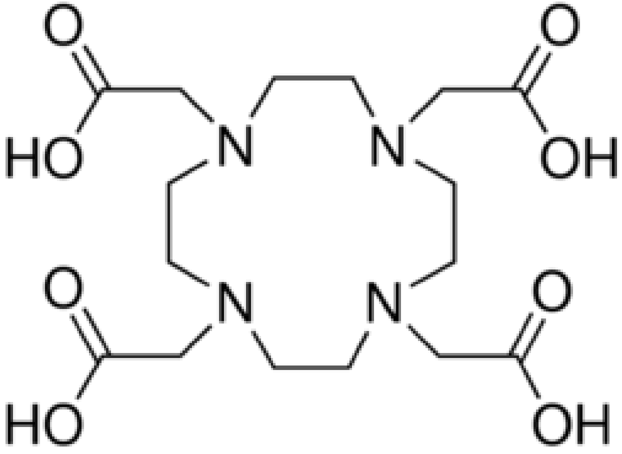
Nitrate
Monodentate
Bidentate
Bridging



DGA
(Tridendate)



18-crown-6
(Up to 6-coordinate)



DOTA
Up to 8 coordinate

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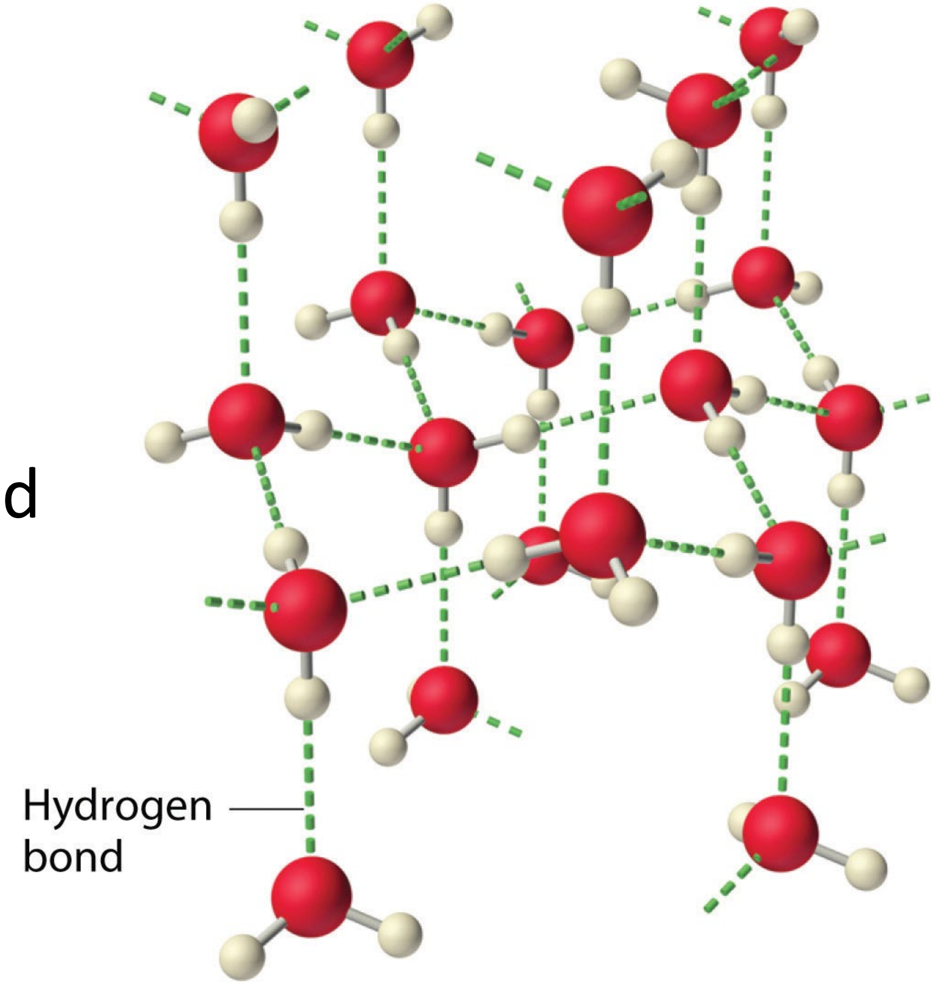
Fundamentals of Metal Ion Separations: Aqueous chemistry of metal ions

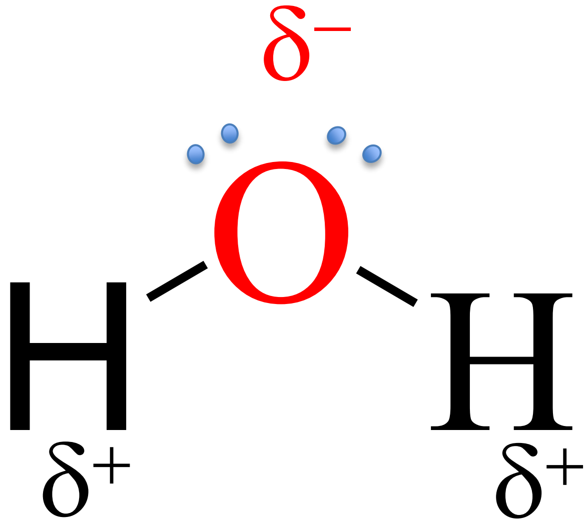
Daniel McAlister, Ph.D.

16 October 2020

Aqueous phase water structure

Water H-Bond Structure





Adding ions to the water disrupts the hydrogen bonded structure.

Aqueous phase solvation (hydration)

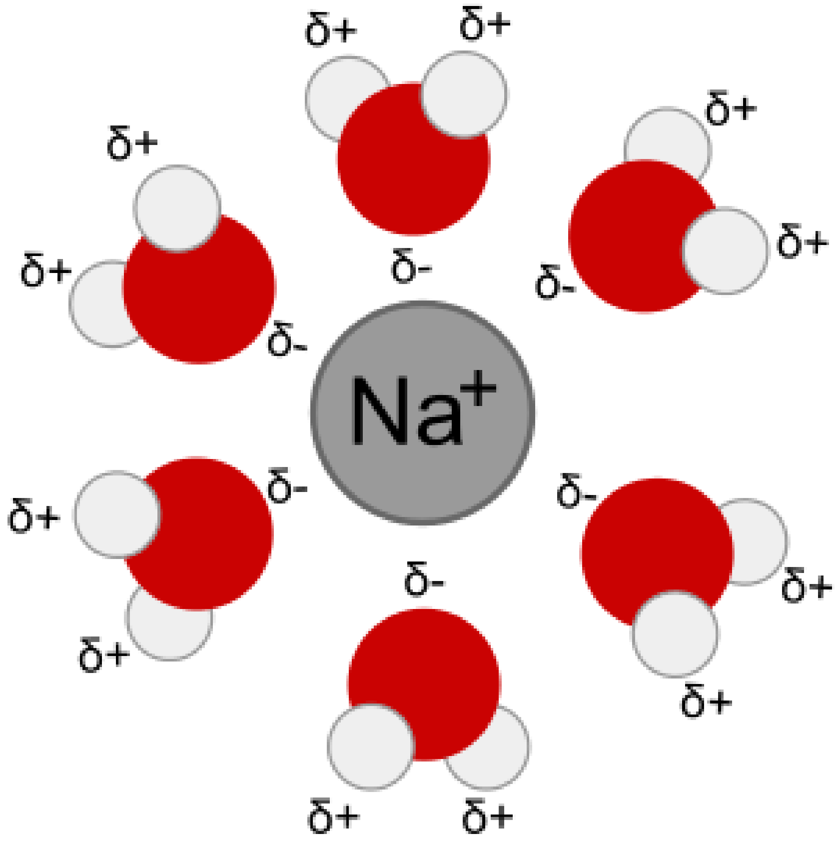
$[M(H_2O)_n]^{z+}$

M = metal ion
n = hydration/solvation number
z = charge

Alkali, alkaline earth and transition metals n~3-6

Actinides and lanthanides n~8-9

n = primary hydration/coordination
H = total hydration/solvation (secondary)



John Burgess, "Metal ions in solution," Ellis Hortwood, Ltd., Chichester, Sussex, England, 1978.

Aqueous phase activities

Choppin 2006

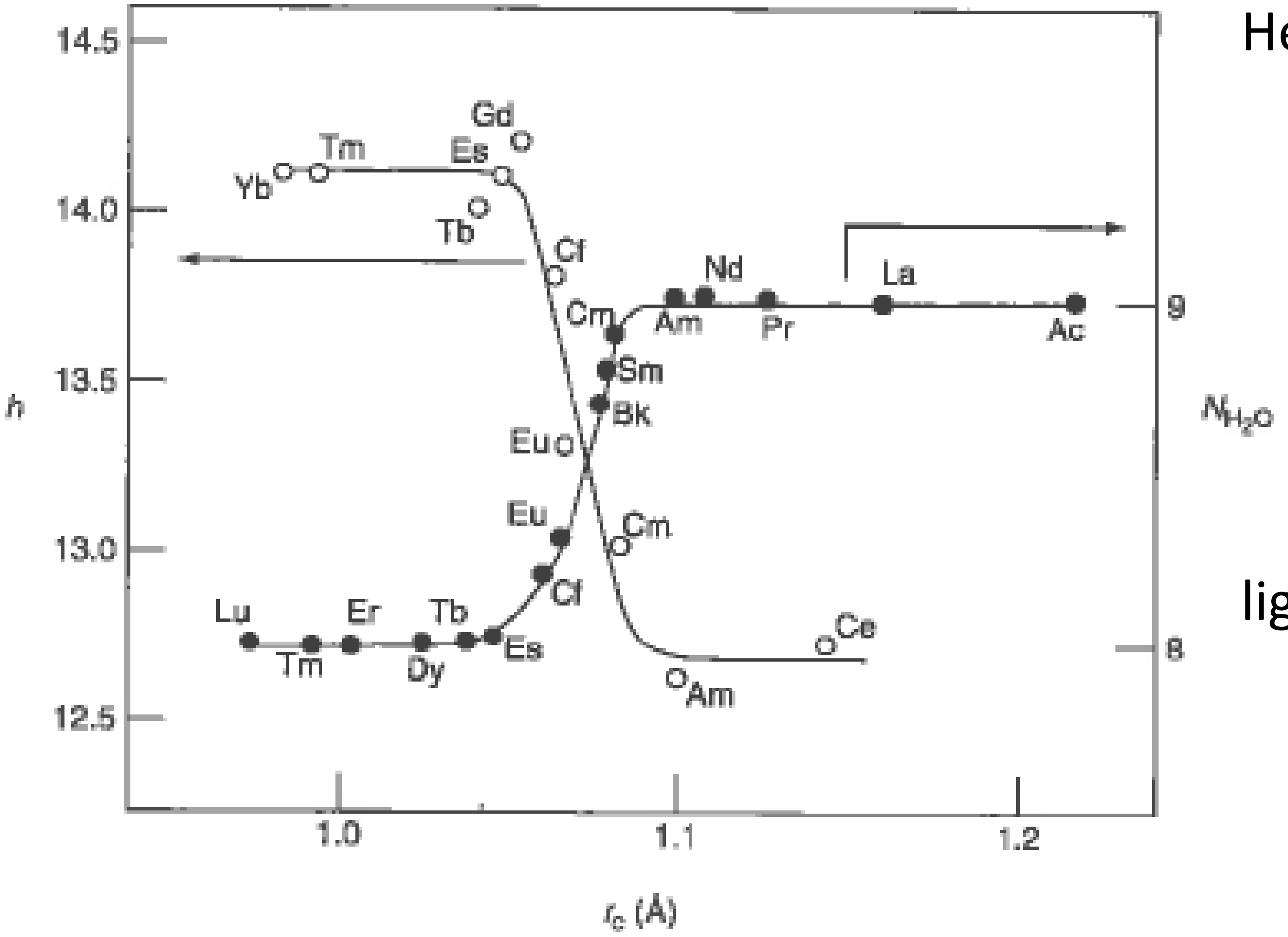


Fig. 23.2 *Total hydration (h) and number of water molecules in the primary coordination sphere (N_{H_2O}) of Ln^{3+} and An^{3+} cations (Rizkalla and Choppin, 1994).*

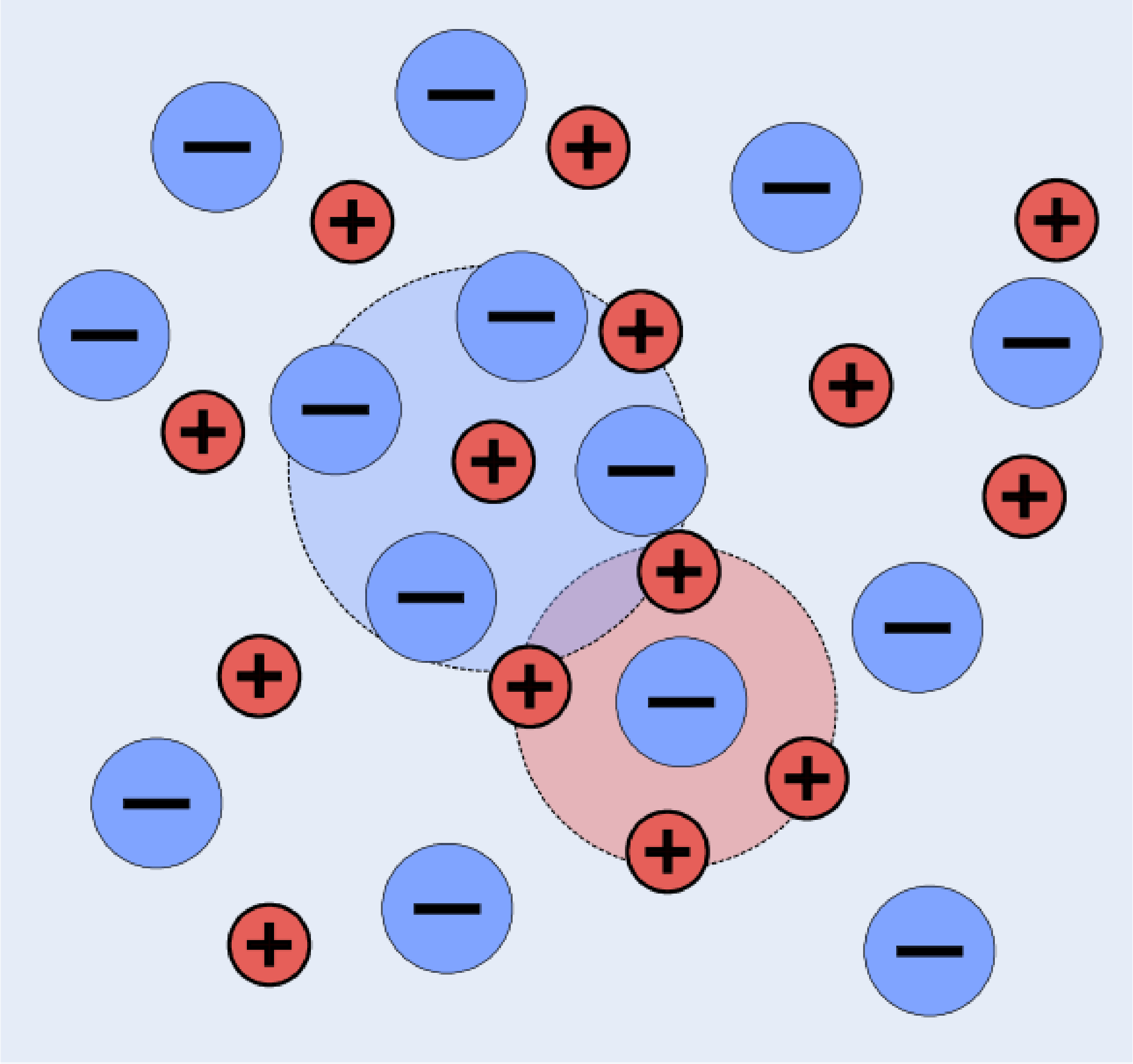
Heavy rare earths

- smaller / more localized 3+
- lower primary hydration (geometry)
- higher total hydration (charge density)

light rare earths

- larger / less localized 3+
- higher primary hydration (geometry)
- lower total hydration (charge density)

Aqueous phase activities as electrolyte concentrations increase



As electrolyte concentrations increase, interactions between ions becomes more important.

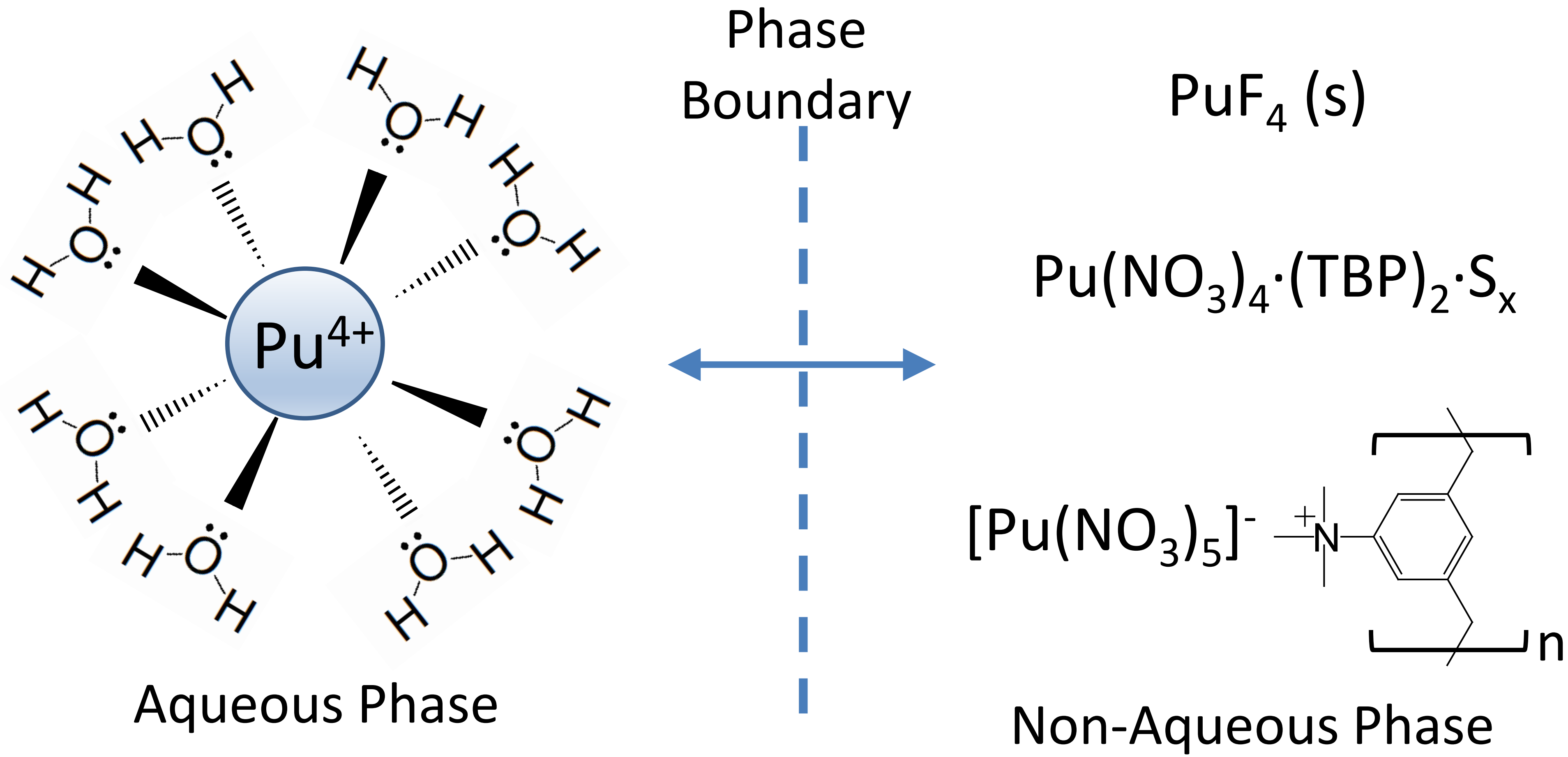
Aqueous activity/coefficients.

$$a_C = \gamma \frac{[C]}{[C^\ominus]}$$

Water activity decreases, solvation decreases, and ion-pairs may form.

Transfer from aqueous to non-aqueous phase

Sekine 1977



Phase Boundary

PuF_4 (s)

$Pu(NO_3)_4 \cdot (TBP)_2 \cdot S_x$

$[Pu(NO_3)_5]^-$

Aqueous Phase

Non-Aqueous Phase

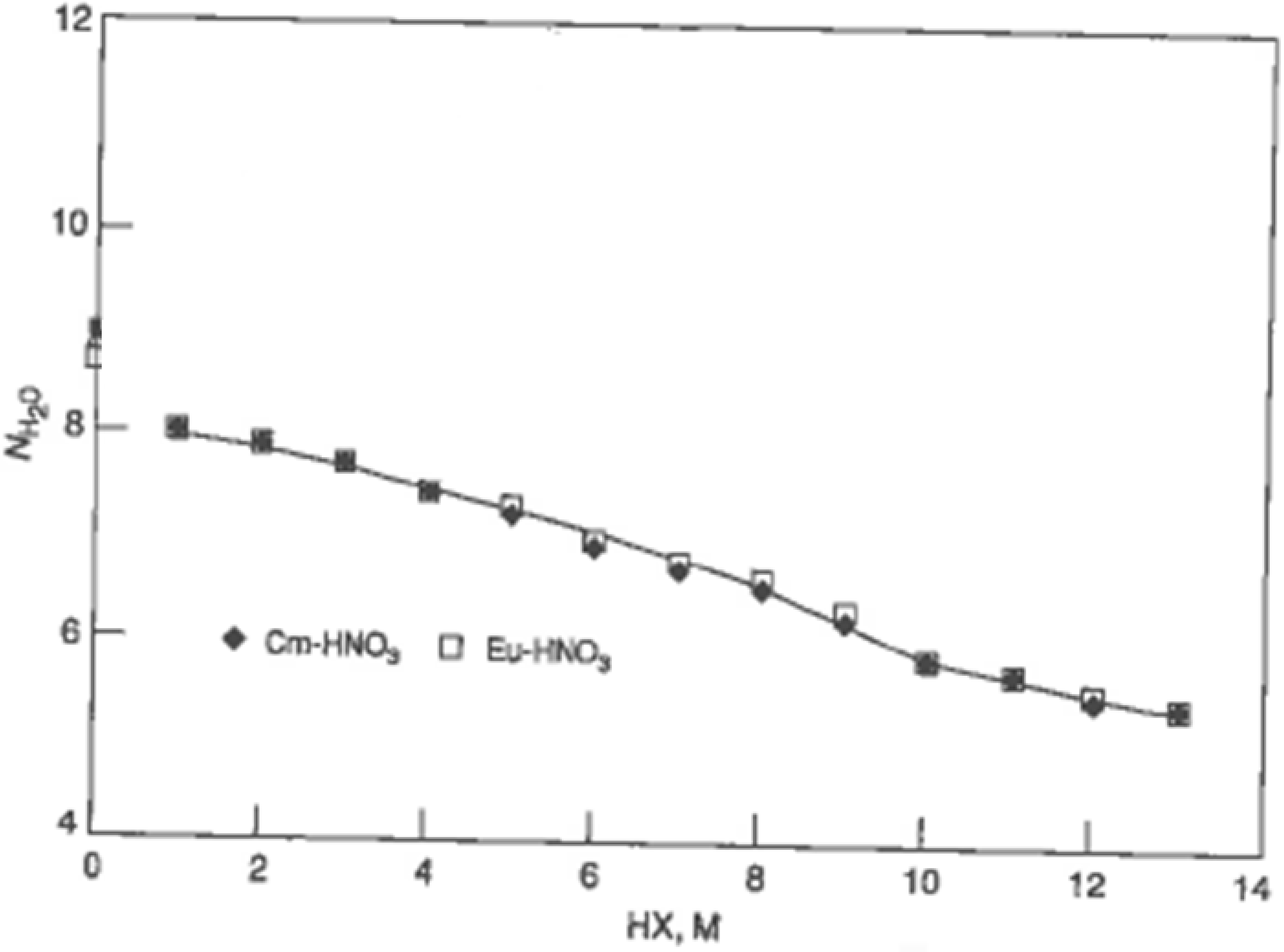
Full/partial dehydration
Complexation by neutral ligands

ion pair formation/ion exchange
Solvation in non-aqueous phase

Electrostatic interactions (Hard)
Covalent interactions (Soft)
Steric limits

Hydration vs acid concentration

Choppin 2006



. 23.4 *Variation of the number of water molecules in the primary hydration sphere of alent europium and curium ions as determined by TRLF.*

Ion pairs form, replacing waters of hydration with anionic counter ions

$$Cm(OH_2)_n + mX^- \rightarrow Cm(OH_2)_{n-m}X_m + mH_2O$$

Some ligands can displace multiple waters (chelate/multidentate)

Some ligands interact more strongly with metal ions, displacing waters at lower concentrations.

Hard and Soft Acids/Bases

Choppin 2000

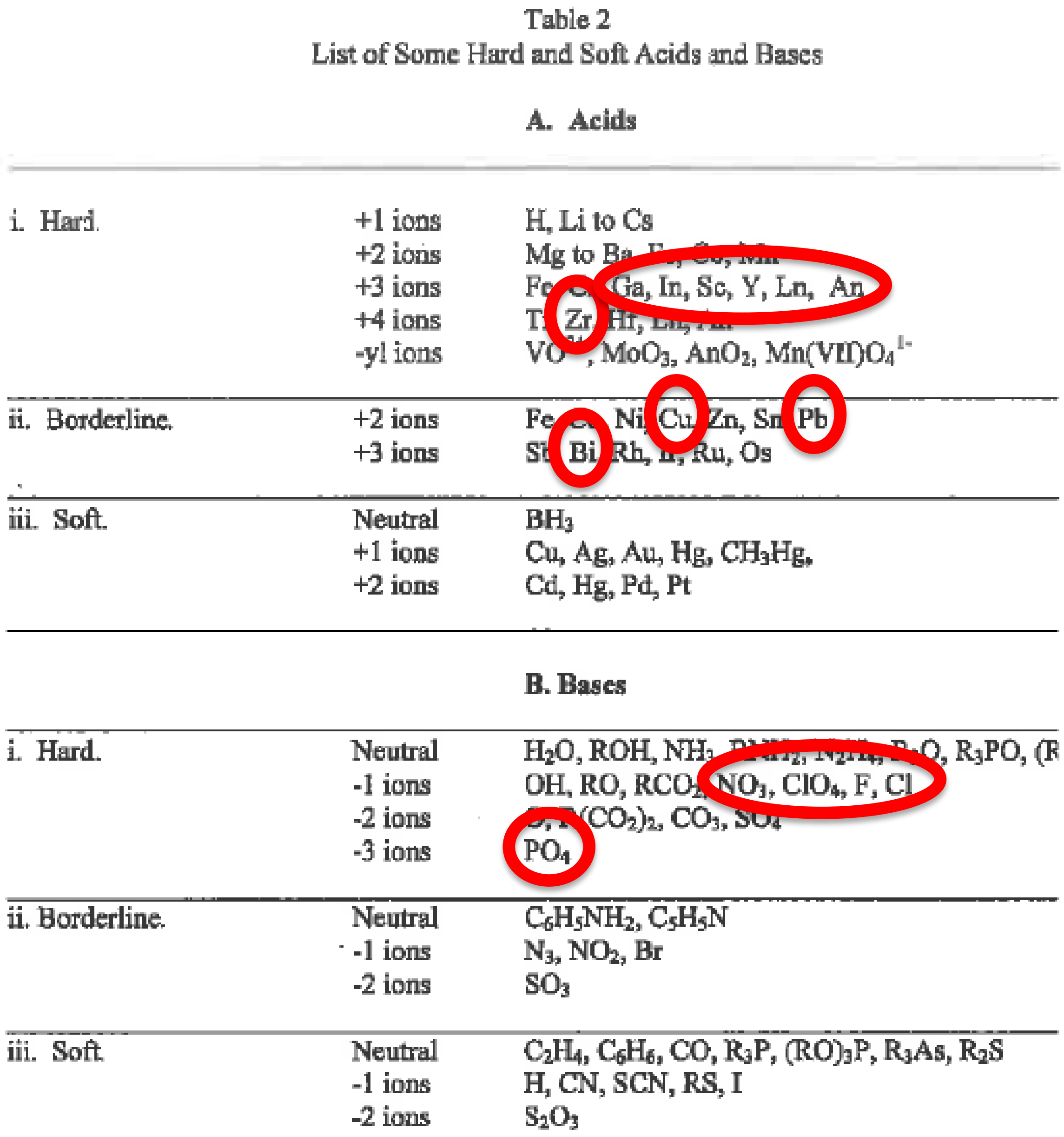


Table 2
List of Some Hard and Soft Acids and Bases

A. Acids

i. Hard.	+1 ions	H, Li to Cs
	+2 ions	Mg to Ba, [illegible], Co, Mn
	+3 ions	Fe, Cr, Ga, In, Sc, Y, Ln, An
	+4 ions	Ti, Zr, Hf, Ln, An
	-yl ions	VO^{2+}, MoO_3, AnO_2, $Mn(VII)O_4^{1-}$
ii. Borderline.	+2 ions	Fe, Co, Ni, Cu, Zn, Sn, Pb
	+3 ions	Sb, Bi, Rh, Ir, Ru, Os
iii. Soft.	Neutral	BH_3
	+1 ions	Cu, Ag, Au, Hg, CH_3Hg,
	+2 ions	Cd, Hg, Pd, Pt

B. Bases

i. Hard.	Neutral	H_2O, ROH, NH_3, RNH_2, N_2H_4, R_2O, R_3PO, (R
	-1 ions	OH, RO, RCO_2, NO_3, ClO_4, F, Cl
	-2 ions	O, $R(CO_2)_2$, CO_3, SO_4
	-3 ions	PO_4
ii. Borderline.	Neutral	$C_6H_5NH_2$, C_5H_5N
	-1 ions	N_3, NO_2, Br
	-2 ions	SO_3
iii. Soft.	Neutral	C_2H_4, C_6H_6, CO, R_3P, $(RO)_3P$, R_3As, R_2S
	-1 ions	H, CN, SCN, RS, I
	-2 ions	S_2O_3

M(+) = electron pair acceptor (acid)
L(-) = electron pair donor (base)

Hard acid/base favors ionic bonding (+ ← -)
βn values correlate with pKa of ligand (acid)

Soft acid/base favors covalent bonding (+ <-> -)
βn values correlate with redox/ionization potential of the ligand.

Strongest interactions between Hard-Hard and Soft-Soft.

Hardness scale NO_3- > Cl- > Br- > SCN-

Hydration vs acid concentration

Choppin 2006

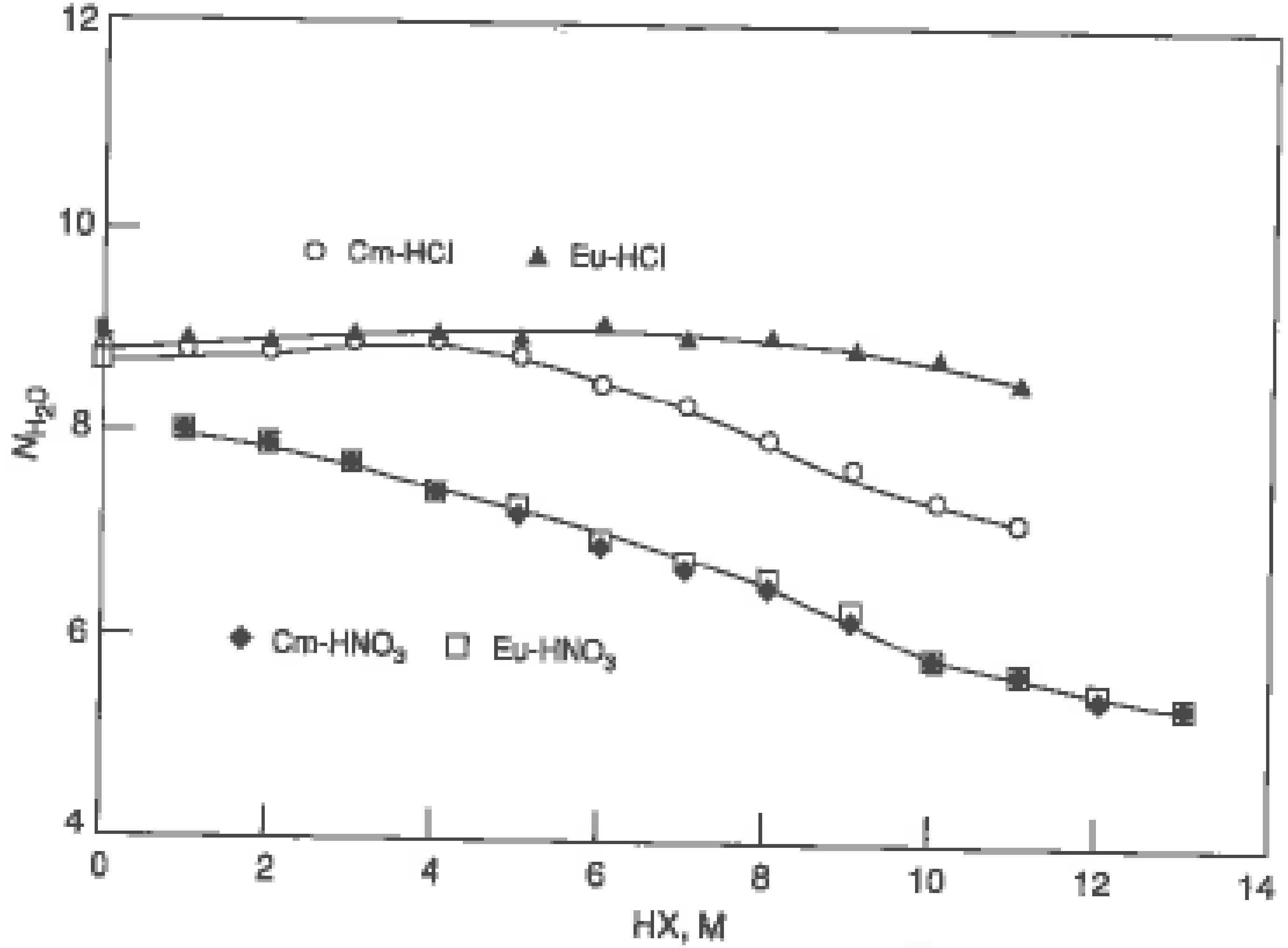


Fig. 23.4 *Variation of the number of water molecules in the primary hydration sphere of trivalent europium and curium ions as determined by T.R.L.F.*

Ion pairs form, replacing waters of hydration with anionic counter ions

$Cm(OH_2)_n$ + mX- →

$Cm(OH_2)_{n-m}X_m$ + mH_2O

Some ligands can displace multiple waters (chelate/multidentate)

Chloride displaces H_2O less than nitrate.

Chloride displaces H_2O more in Cm(III) than in Eu(III).

Mass, concentration, and pH effects

Mass and radioactivity (both can affect solution properties)

Radioactivity vs Mass

Nuclide	Half-Life*	Radioactivity	Mass
^{238}U	4.468×10^9 y	0.373 Bq	30 μg
^{241}Am	432.6 y	37,000 Bq	0.3 μg
^{18}F	2.1×10^{-4} y	37,000,000 Bq	0.01 μg

$$N(t) = N_o e^{-\lambda t}$$

$$dN/dt = -\lambda N$$

*https://www.nndc.bnl.gov/nudat2/

Adsorption to glass

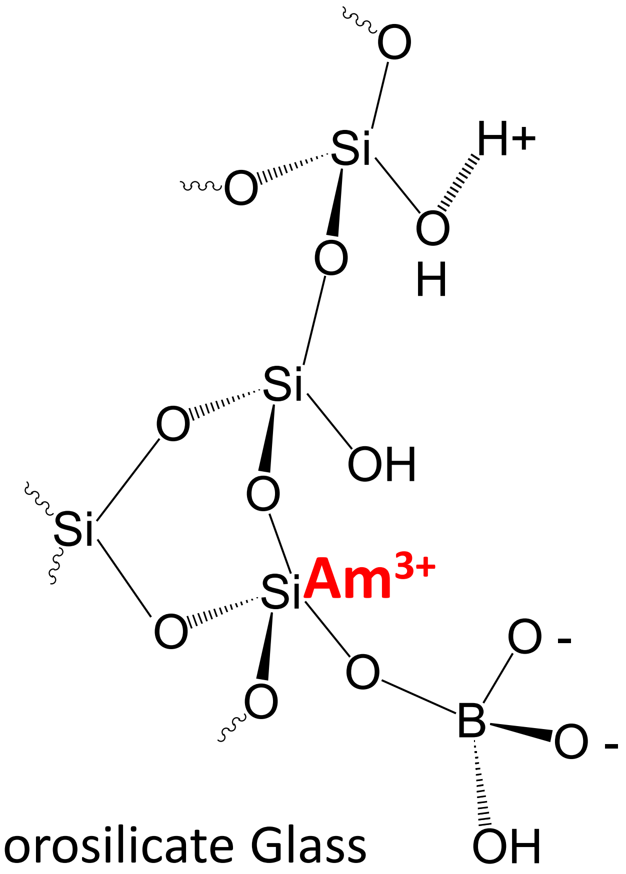
Choppin 2013

At higher pH
- Surface charge is negative/Cations adsorb

At lower pH
- Surface charge is positive/Anions adsorb

Adsorption normally increases with charge
$M^{+} < M^{2+} < M^{3+} < M^{4+}$

Choose conditions to avoid unwanted adsorption or utilize adsorption to achieve separations on silica gel or alumina.



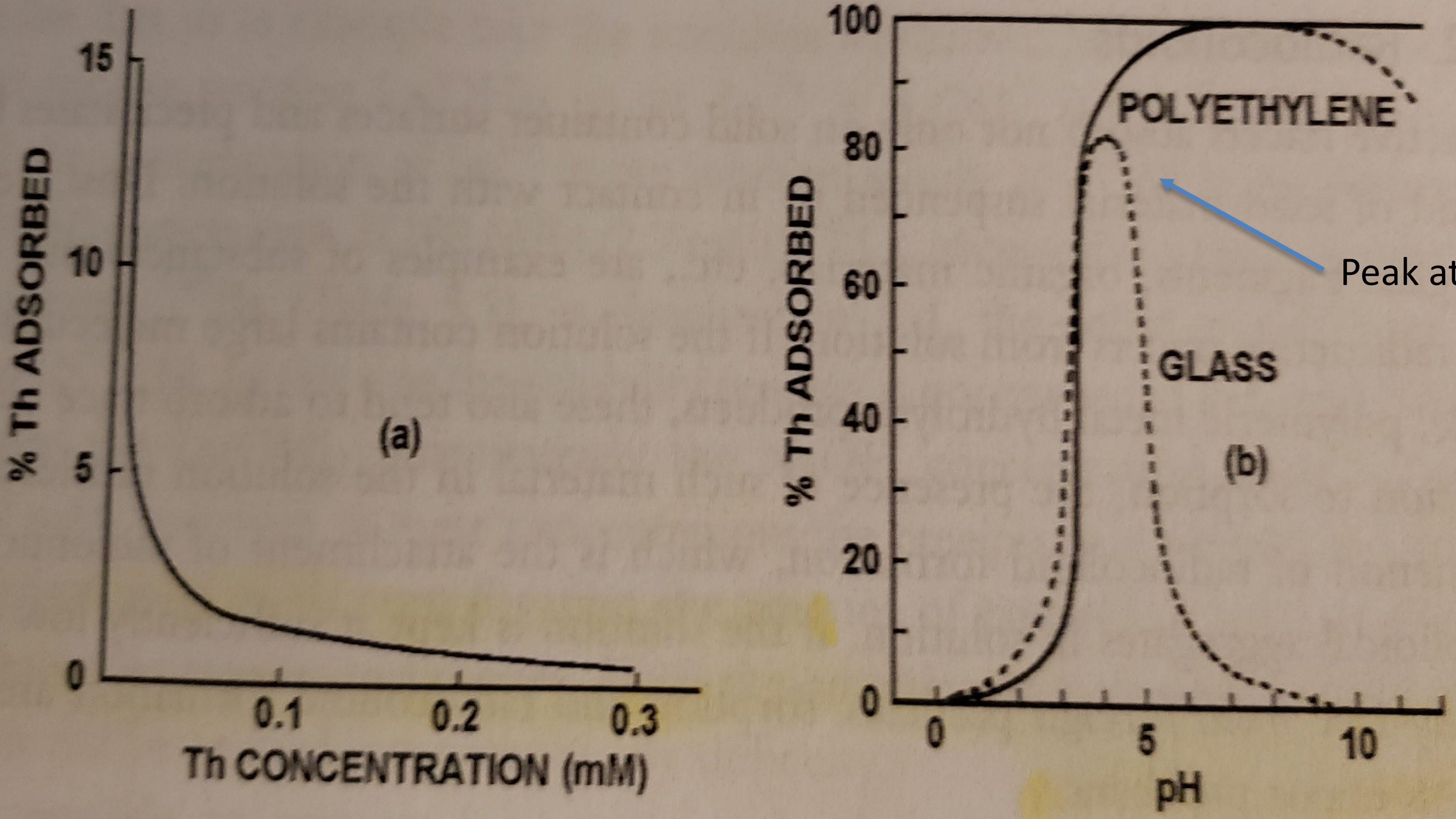
Borosilicate Glass

1L Bottle 10^{-8}-10^{-7} mole H^{+}
(2.4ug / 8 uCi Am-241)

Store Am in 1M HCl or HNO_3.
Add stable Eu(III) carrier.

Adsorption of Th onto glass and polyethylene

Choppin 2013



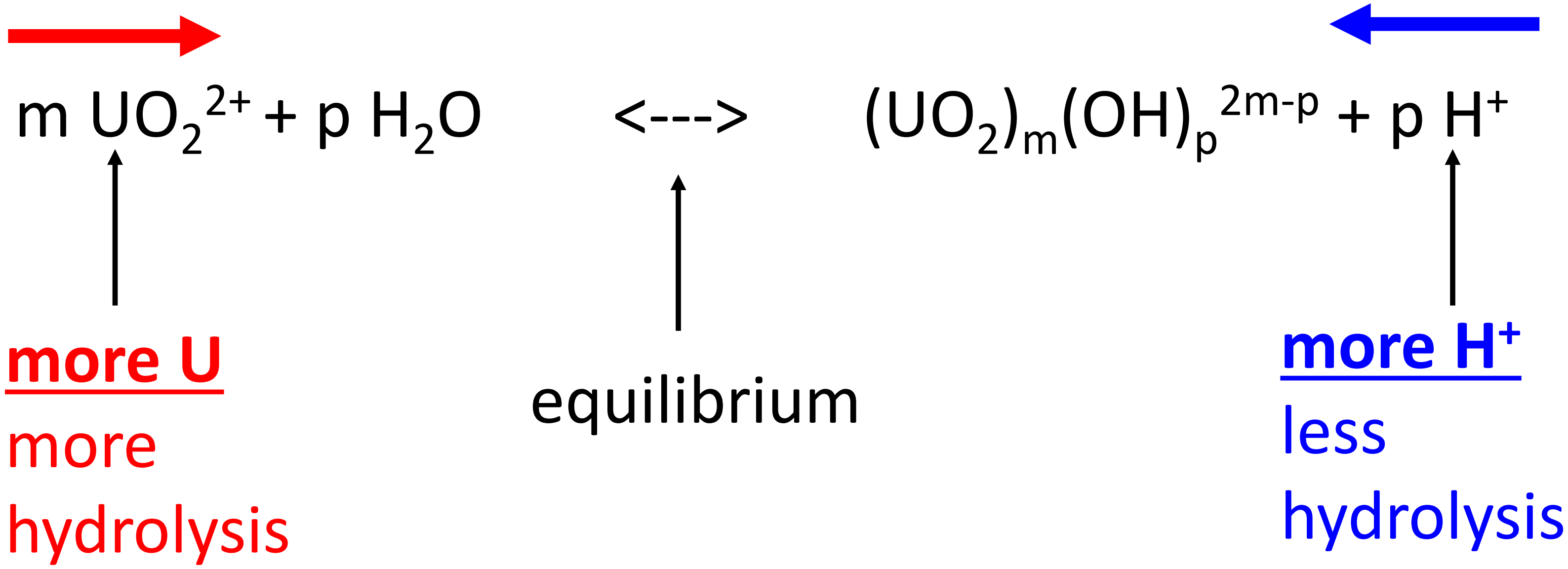
Peak at pH 4-5?

Figure 18.1 Adsorption of Th (a) in a 10 ml pipette at different Th concentrations, (b) from 2×10^{-8} M $Th(ClO_4)_4$ solution on different surfaces and pH's. *(From Rydberg and Rydberg.)*

Hydrolysis

Choppin 2013

Hydrolysis - Splitting of H_2O into ^{-}OH and H^+



$$m\ UO_2^{2+} + p\ H_2O \quad \text{<--->} \quad (UO_2)_m(OH)_p^{2m-p} + p\ H^+$$

more U

more

hydrolysis

equilibrium

more H^+

less

hydrolysis

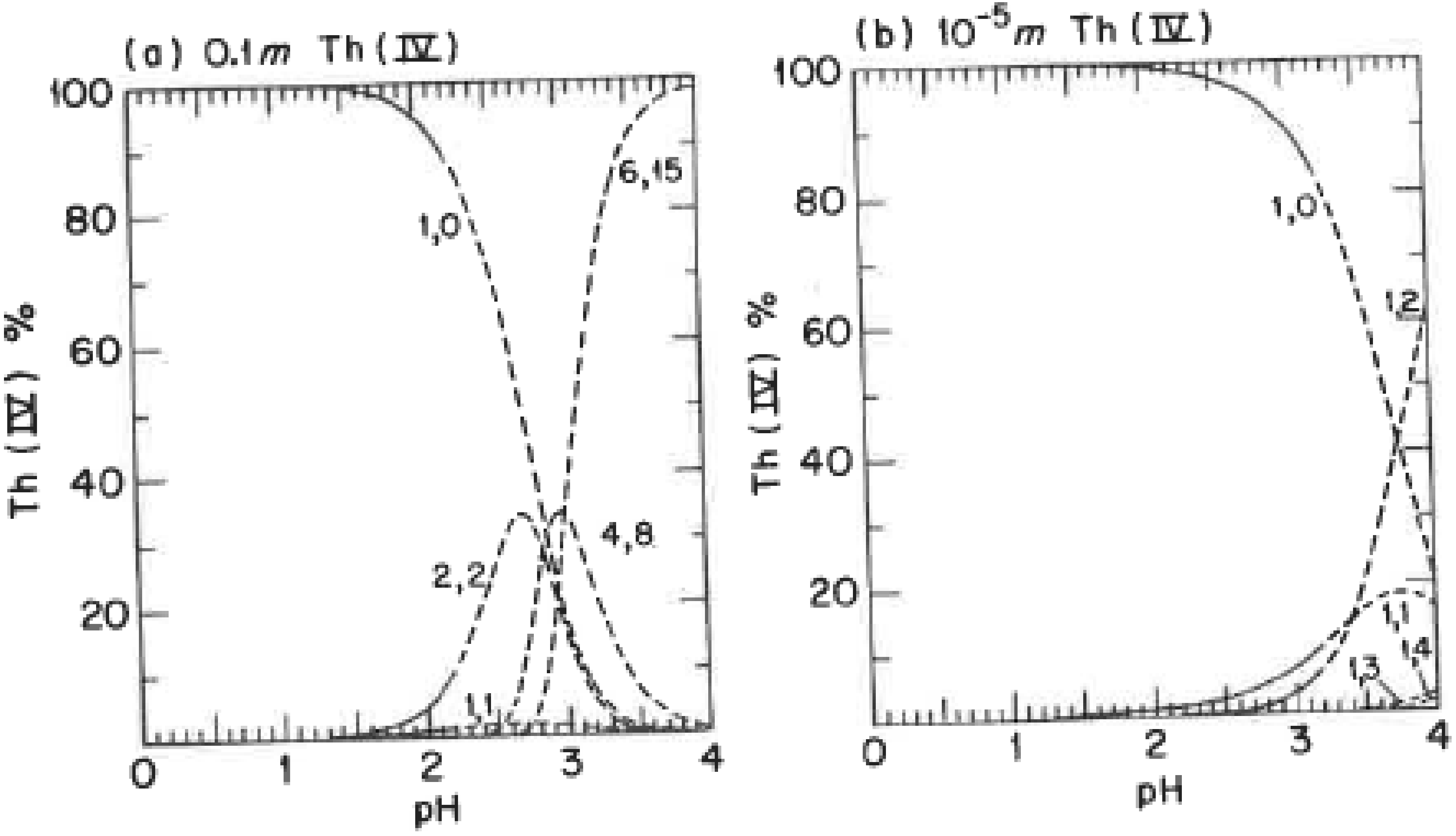
Hydrolysis normally increases with charge

$M^+ < M^{2+} < M^{3+} < M^{4+} < M^{5+}$……

Prevent with low pH and/or complexing agents

Hydrolysis

Baes, 1976



$[Th(OH_2)_9]^{4+}$

Disproportionation

Choppin 2006

$$2\ NpO_2^{+} + 4\ H^{+} \quad \text{<--->} \quad Np^{4+} + NpO_2^{2+} + 2\ H_2O$$

- Higher concentrations of actinides are more difficult to fix in a single oxidation state.
- Disproportionation reaction driven at higher actinide and acid concentrations.
- Higher pHs stabilize higher oxidation states (V, VI, VII).

High radioactivity

- The radioactive nature of nuclides does not fundamentally change the physical or chemical properties of the system, until…….

Alpha and Beta Radiation Level in mCi/mL	Effect on solids and liquids
$< 10^{-3}$	Negligible
10^{-3} to 1	Negligible for short-term exposure, discoloration for long-term exposure
1 to 10^{3}	Definite effect on oxidation-reduction processes. Noticeable decomposition of organic substances
$> 10^{3}$	Profoundly affects all aqueous and organic solution processes

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Fundamentals of metal ion separations: Precipitation, Solvent Extraction, Chromatography

Daniel McAlister, Ph.D.
16 October 2020

9:30

Early radiochemical separations (Precipitations and Fractional Crystalization)

Henri Becquerel

Selective precipitation of β-/γ radioactivity from Uranium samples with carbonate precipitations.

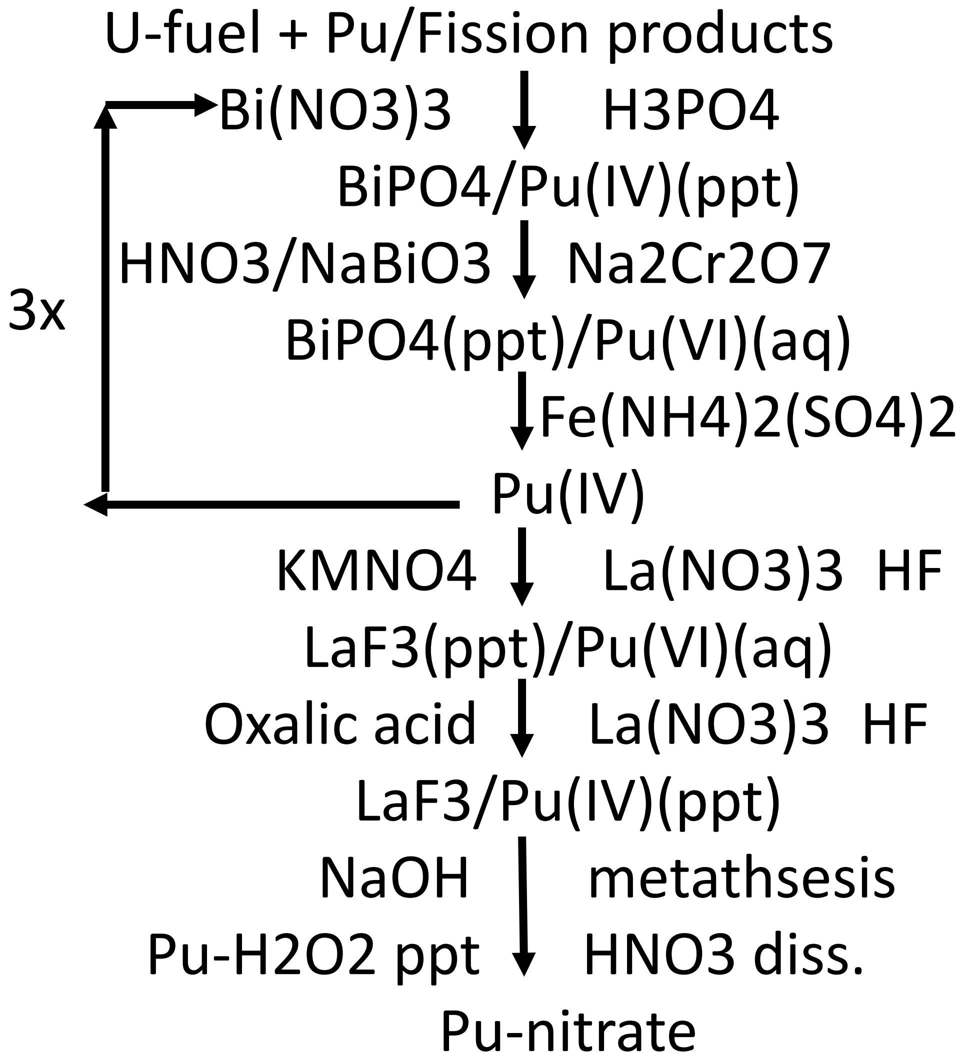
Pierre and Marie Curie

Selective precipitation of Po and Ra from uranium pitchblende ore. Po carried with Bi, while Ra carried with Ba.

Glenn Seaborg and S.G. Thompson

Selective precipitation of Pu(IV) from U(VI) with BiPO4 process.

Plutonium production by the BiPO4 process



U-fuel + Pu/Fission products

Bi(NO3)3 ↓ H3PO4

BiPO4/Pu(IV)(ppt)

HNO3/NaBiO3 ↓ Na2Cr2O7

BiPO4(ppt)/Pu(VI)(aq)

↓ Fe(NH4)2(SO4)2

Pu(IV)

3x

KMNO4 ↓ La(NO3)3 HF

LaF3(ppt)/Pu(VI)(aq)

Oxalic acid ↓ La(NO3)3 HF

LaF3/Pu(IV)(ppt)

NaOH metathsesis

Pu-H2O2 ppt ↓ HNO3 diss.

Pu-nitrate

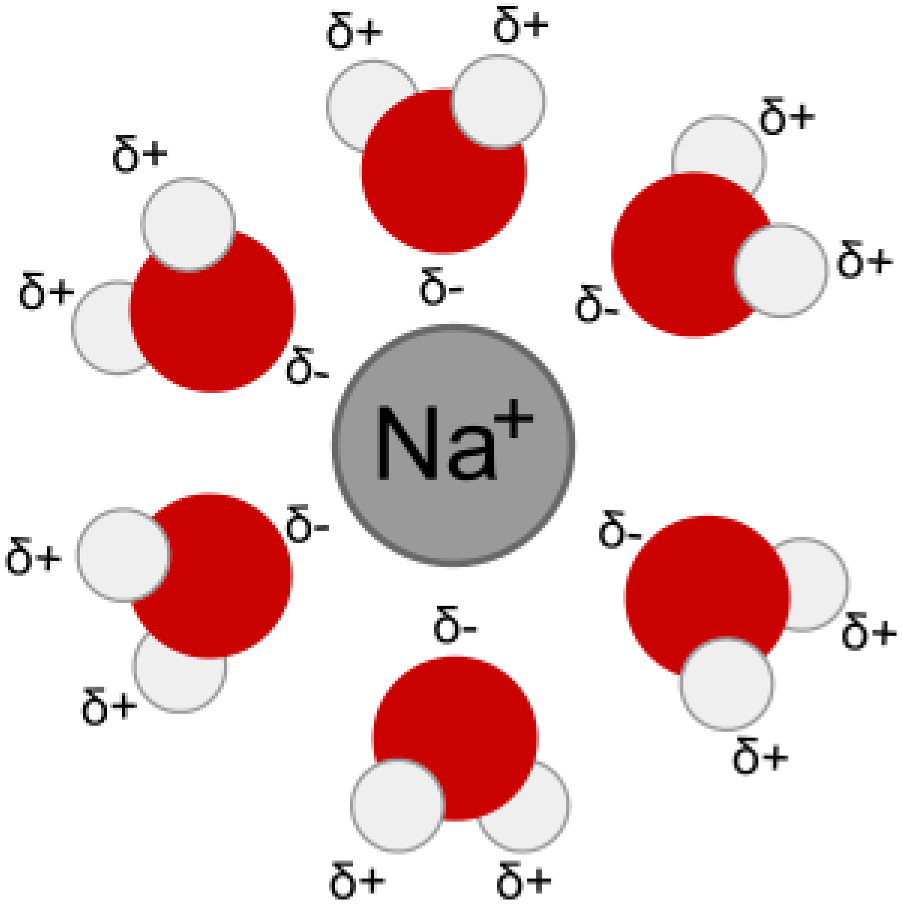
Worked well enough.

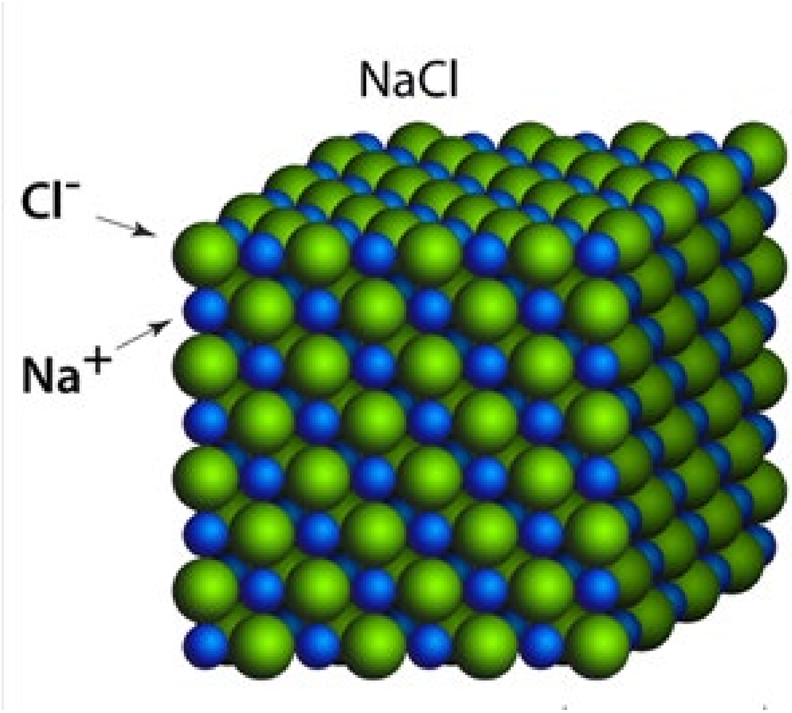
Large waste stream with hazardous metals, hydrofluoric acid, nitric acid, etc…

Batch process, not easily adaptable to a continuous process.

Eventually replaced by SX.

Precipitate Formation





Solute-Solvent vs Solute-Solute

Precipitation vs Crystallization

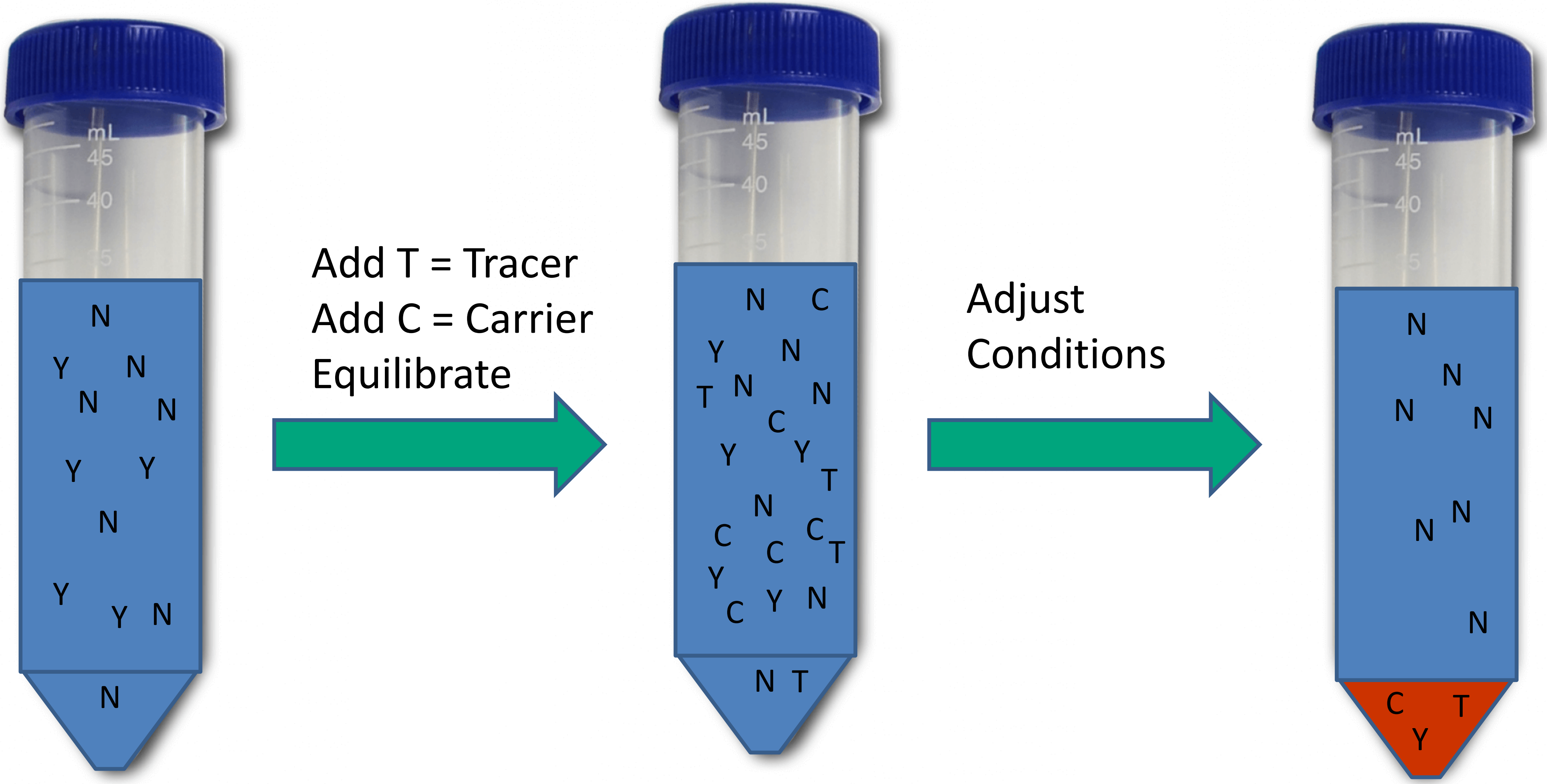
Purity of precipitate greatly affected by speed of formation

- Slow formation from homogeneous, particulate free solution may lead to high purity crystalline precipitate (large particles).

- Rapid formation likely leads to amorphous precipitates with more impurities (smaller particles).

Townshed 1989

Precipitation in analytical radiochemistry



Add T = Tracer
Add C = Carrier
Equilibrate

Adjust
Conditions

Commonly used precipitates

precipitate	**Hydroxide**	**Phosphate**	**Fluoride**	**Carbonate**	**Sulfate**	**Oxalate**	**MnO2**
common carrier(s)	Fe(III), La(III)	Ca(II), Fe(III)	La(III), Ca(II), Ce(III), Nd(III)	Ca(II), Ba(II)	Ba(II), Pb(II)	Ca(II)	MnCl2
other additives	none	NaHPO4	HF or NH4FHF	Na2CO3	(NH4)2SO4	oxalic acid	KMnO4
initiation	Add NaOH or NH4OH to increase to pH 8-10	Add NaOH or NH4OH to increase to pH 8-10	addtion of HF or NH4FHF	Add NaOH or NH4OH to increase to pH 8-10	Addition of (NH4)2SO4, optional addition of isopropanol	Add NaOH or NH4OH to increase to pH 8-10	Add NaOH or NH4OH to increase to pH 8-9 or addition of KMnO4
common ions co-precipitated	Rare earths, Actinides in (III, IV, V, and VI) oxidation states	Rare earths, Actinides in (III, IV, V, and VI) oxidation states, Sr(II), Ba(II), Ra(II)	Rare earths, Actinides in (III, IV) oxidation states, Sr (if very high F- concentration)	Sr(II), Ba(II), Ra(II)	Ra(II)	Rare earths, Actinides in (III, IV) oxidation states	Ra(II), Po(IV)
important ions rejected*	Alkali metals, alkaline earths	Alkali metals	U(VI), Fe(III), Ti(IV)		U(VI)		Alkali metals
dissolution	HNO3 or HCl	HNO3 or HCl, Al(NO3)3 or AlCl3	HNO3 and boric acid	HNO3 or HCl	NaOH/EDTA or metathesis in Na2CO3	HNO3 or HCl	HCl/H2O2

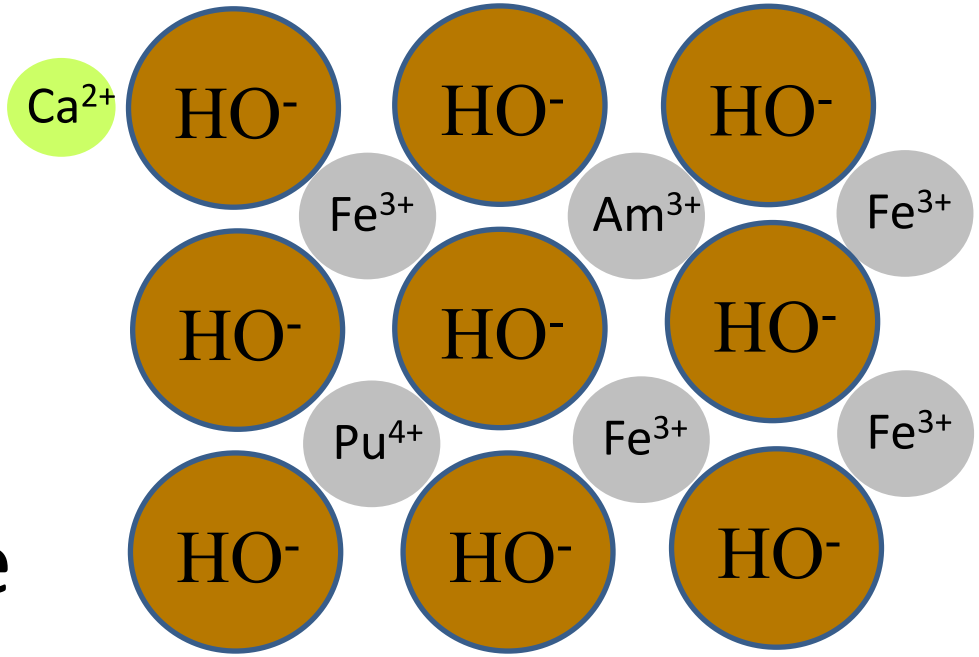
*Some ions may loosely adhere to the precipitation and can be rejected more effectively by the additon of hold-back carriers

Adsorption - Precipitates

Townshed 1989

Point of zero charge

– conditions (pH, ion concentrations) at which surface charge is 0.



Excess Anions

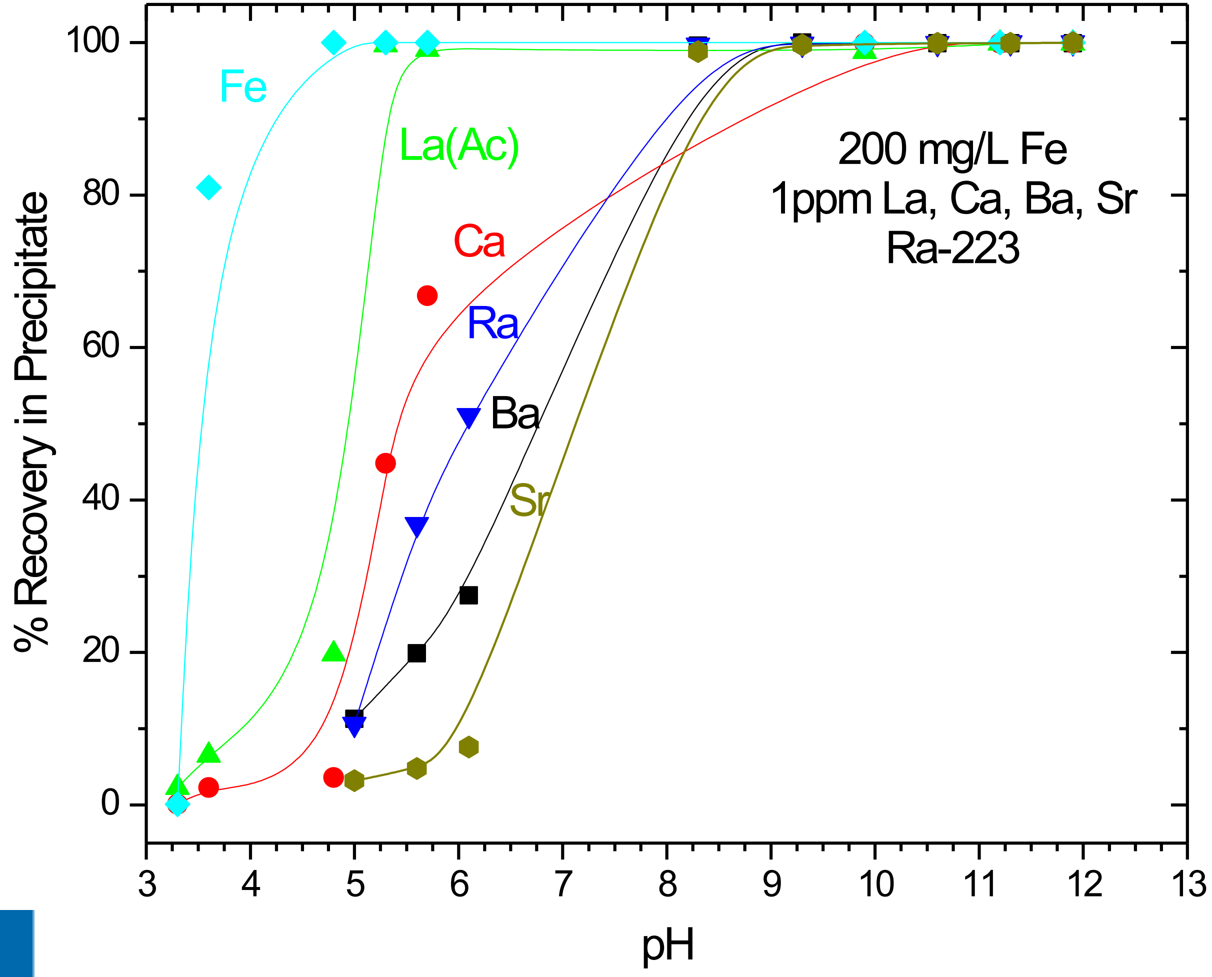
- Surface charge negative
- Cations adsorb

Excess Cations

- Surface charge positive
- Anions adsorb

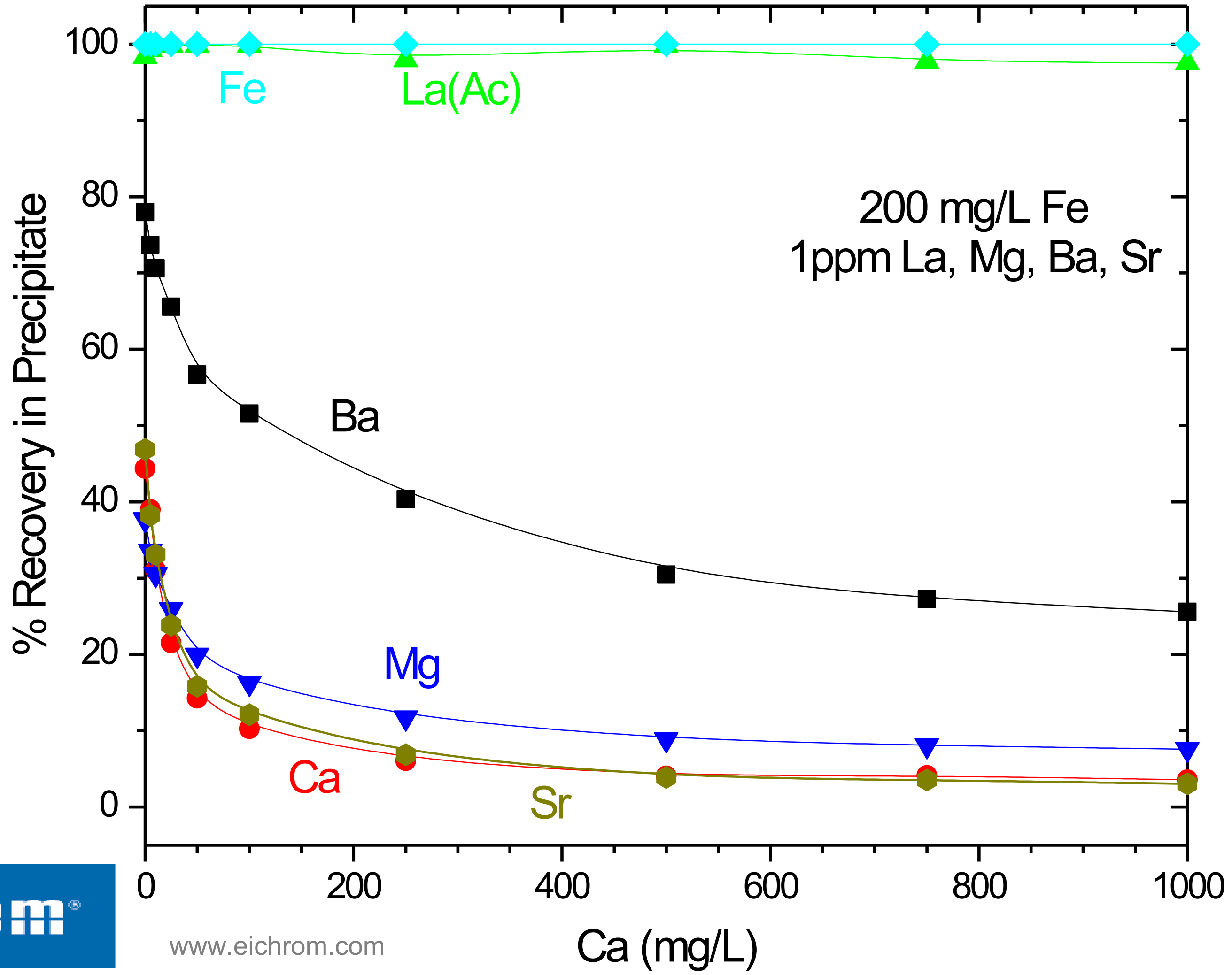
Adsorption - Precipitates

$Fe(OH)_3$ Precipitation Recoveries vs pH (NaOH)



Adsorption – Precipitates (Hold-back carriers)

$Fe(OH)_3$ Precipitation Recoveries vs Ca (pH 9.0)



To reject unwanted ions adsorbing to $Fe(OH)_3$ ppt.:

- Keep pH 8-9 (using NH_4OH instead of NaOH helps)

- Use as little Fe as practical.

- Add holdback carrier (saturates exchange sites)

Ksp and common ion effect (forcing precipitation)

Solubility described by solubility product constant (K_{sp})

$$M_yA_{z(s)} \longleftrightarrow yM^{n+}_{(aq)} + zA^{x-}_{(aq)}$$

$$K_{sp} = [M^{n+}]^y[A^{x-}]^z$$

Common Ion Effect

A. W. Sr = 87.62

5 mg Sr in 50 mL = 1.10E-03 moles/L

Initial [Sr], mole/L	[F-], mole/L	Sr2+ solubility mole/L	% Sr precipitate
1.10E-03	0.10	2.30E-02	0.0
1.10E-03	0.25	3.68E-03	0.0
1.10E-03	0.50	9.20E-04	16.4
1.10E-03	0.75	4.09E-04	62.8
1.10E-03	1.0	2.30E-04	79.1
1.10E-03	2.0	5.75E-05	94.8
1.10E-03	3.0	2.56E-05	97.7
1.10E-03	4.0	1.44E-05	98.7
1.10E-03	5.0	9.20E-06	99.2

$$K_{sp} = 4.3E\text{-}9 = [Sr][F]^2$$

$$4.3E\text{-}9/[F]^2 = [Sr]$$

Increase F- by adding HF (Sr solubility decreases due to the common ion effect)

$$\%Sr\ ppt = 100\% * \frac{(Initial\text{-}Soluble)}{Initial}$$

Alpha Spectrometry Source Preparation

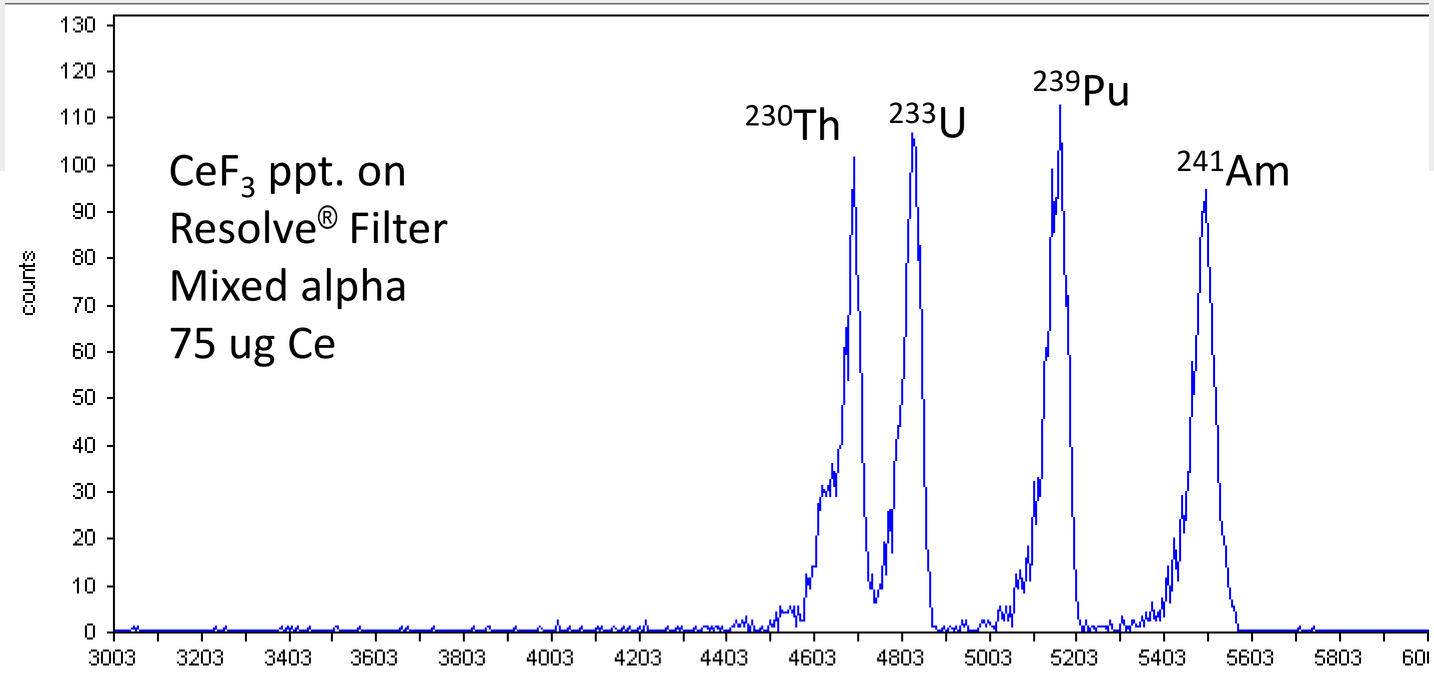
Microprecipitation	Electrodeposition
Adequate resolution	Superior resolution
Rapid/Many Samples	Slower
Direct Prep. from Column Strip Solution	Requires evaporation to remove HNO_3/HCl.
Most Routine Analytical Sources	Calibration Sources Nuclides with difficult to resolve peaks

Need Geometry Match to Calibration Source

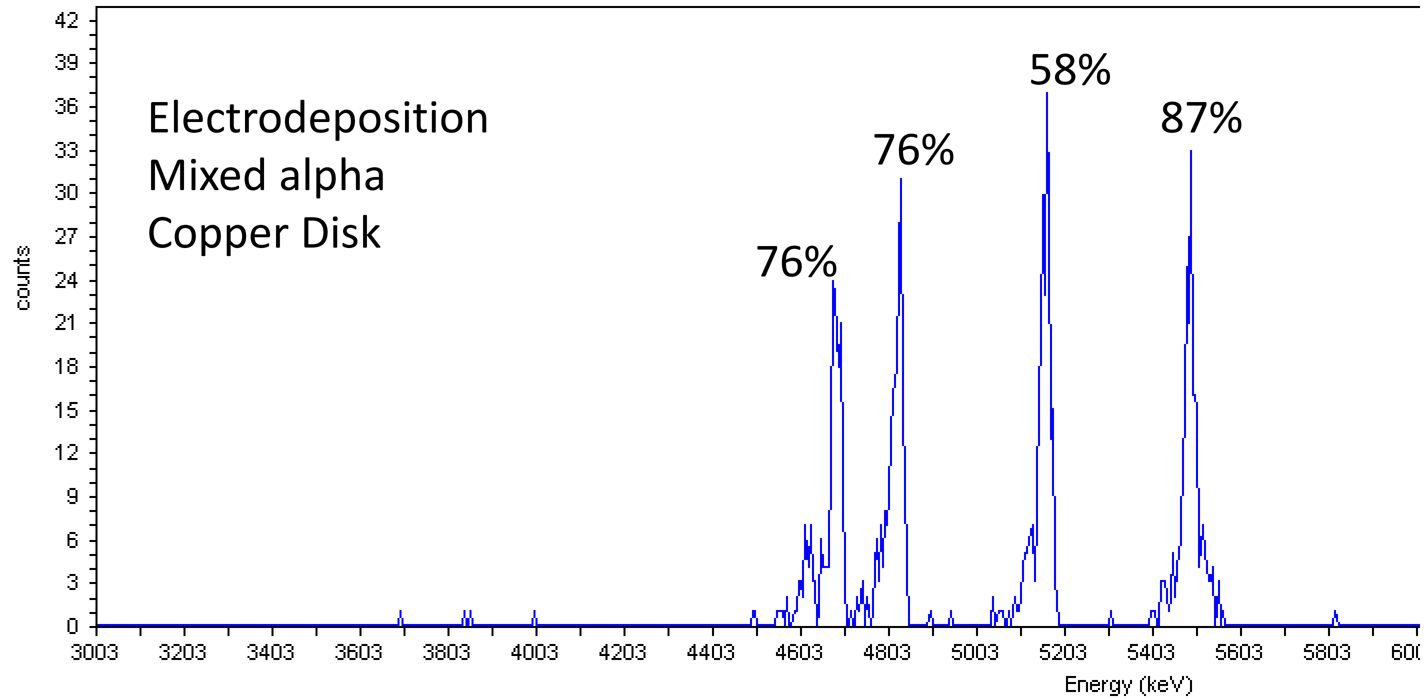
M. Schultz, NAMP Actinide Chemistry Webinar Series, “Source Preparation for alpha spectrometry,” https://www.icln.org/default/assets//File/Source%20Prep%20Alpha%20Spec%20Final_1-21-13%20slide%20deck.pdf

ASTM Method C1284-10 “Standard Practice for Electrodeposition of the Actinides for Alpha Spectrometry”

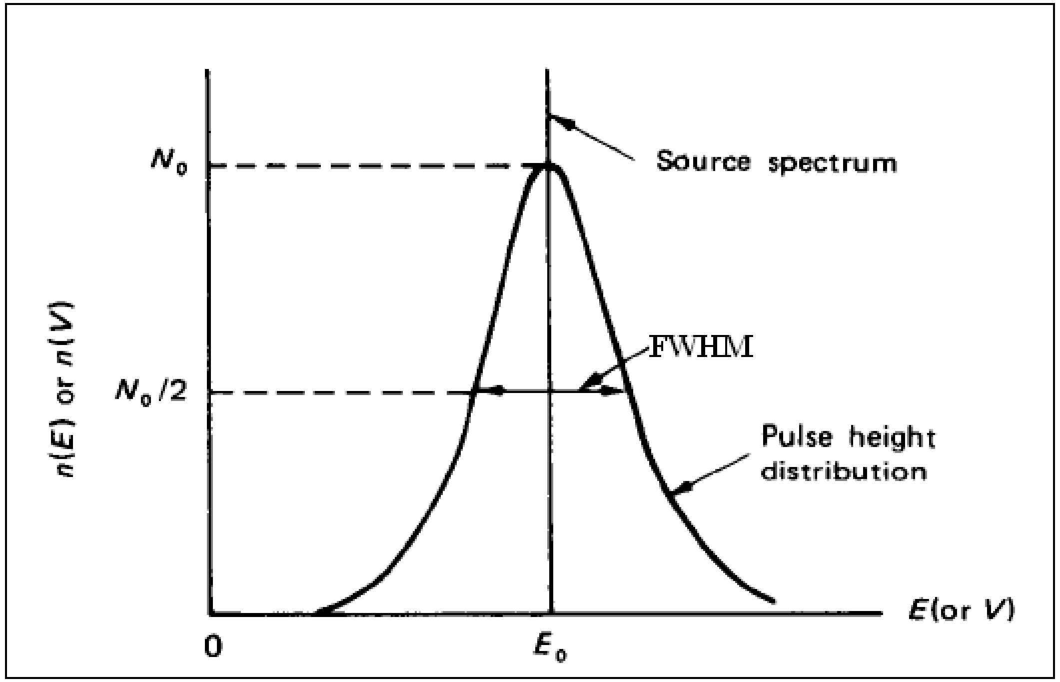
C. W. Sill, “Precipitation of actinides as fluorides or hydroxides for high-resolution alpha spectrometery,” *Nuclear and Chemical Waste Management*, 7, 201-215 (1987).



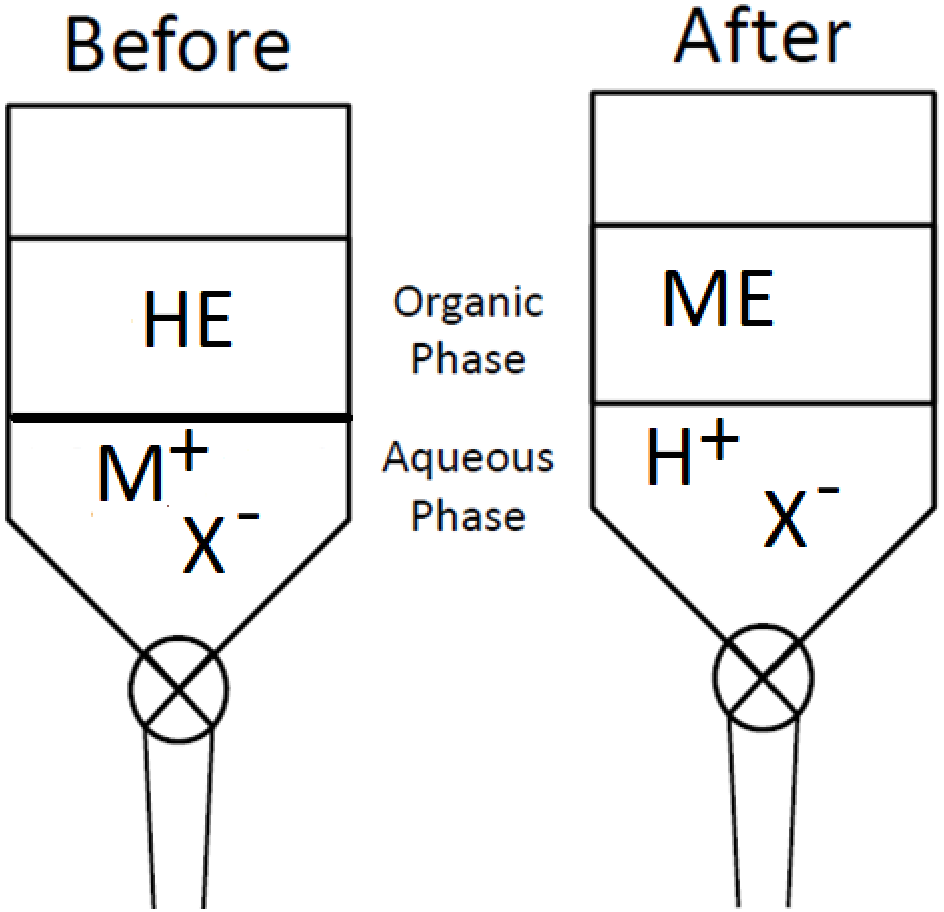
CeF_3 ppt. on
Resolve® Filter
Mixed alpha
75 ug Ce



Electrodeposition
Mixed alpha
Copper Disk



Solvent Extraction



$$D = \frac{[Org]}{[Aq]}$$

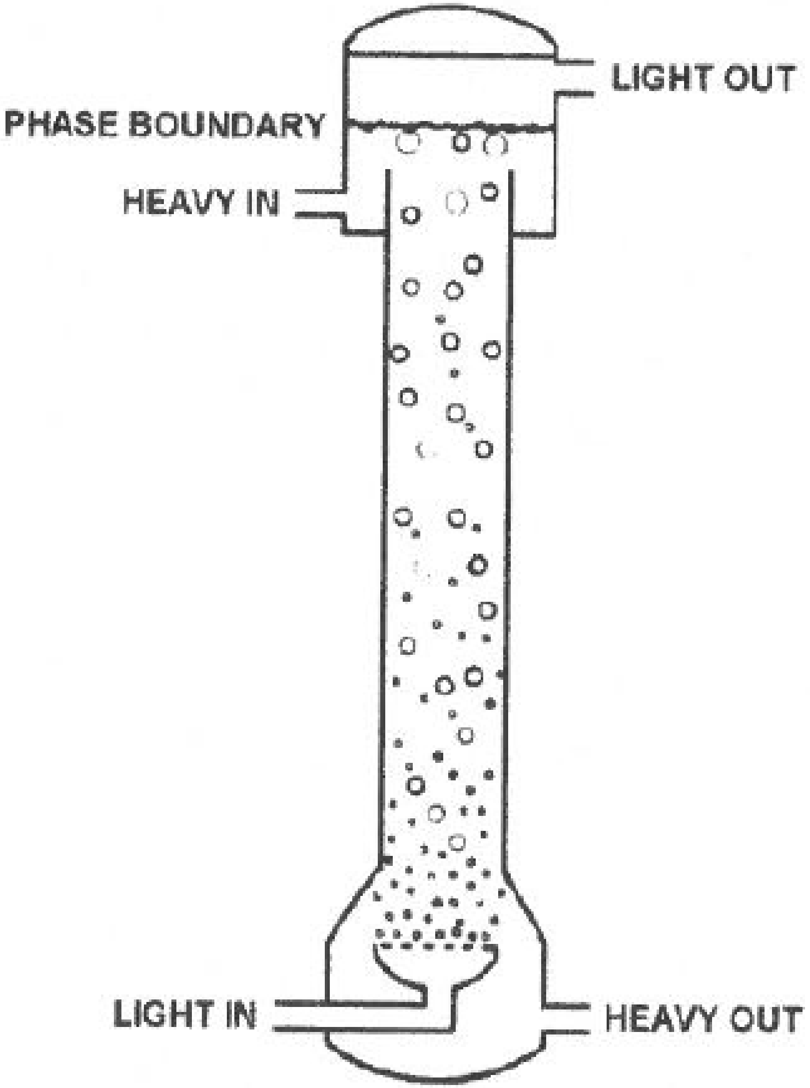
D = 1 = 50% in org

D = 2 = 66% in org

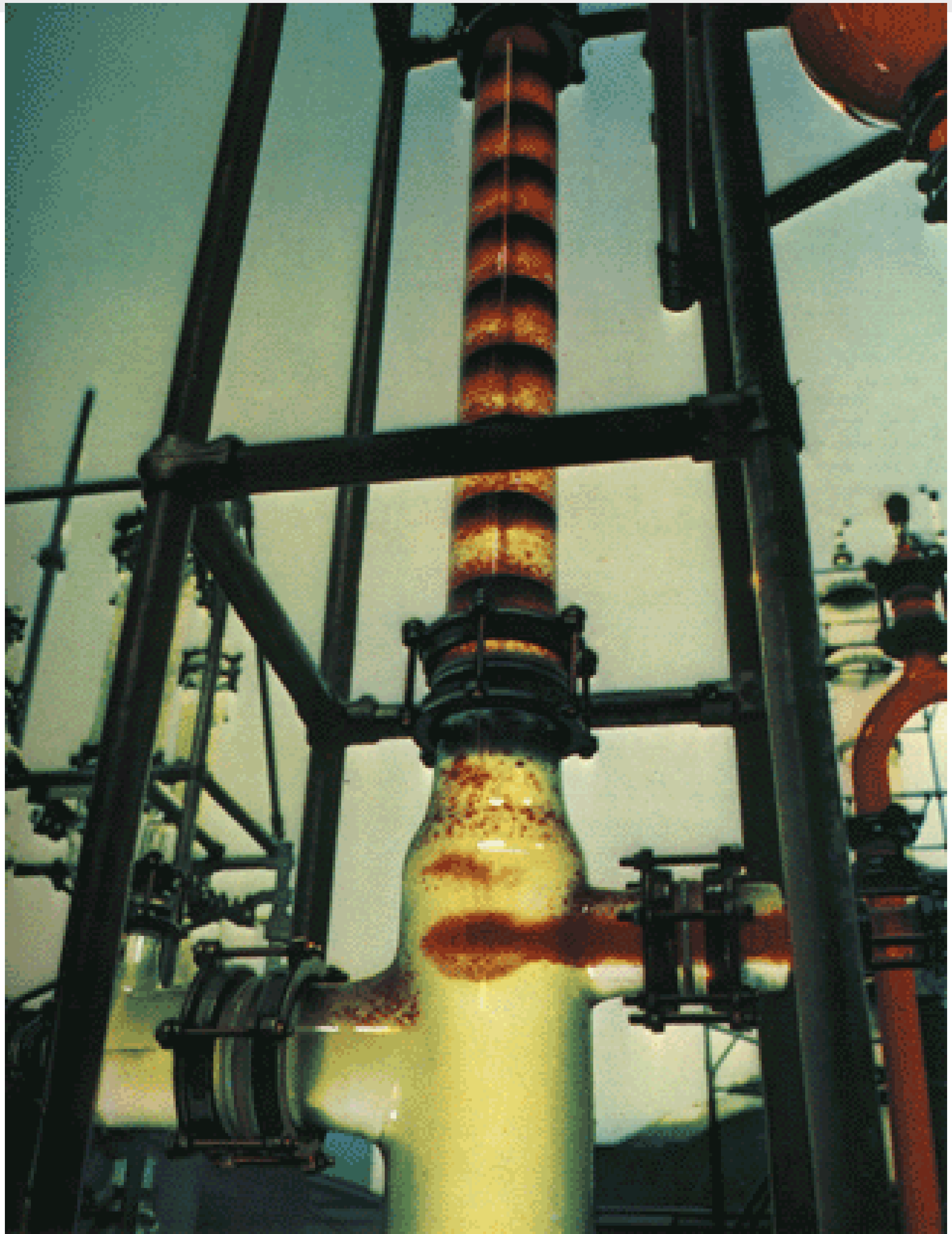
D = 3 = 75% in org

- Two immiscible phases
  - Heavy phase (bottom, usually aqueous)
  - Light phase (top, usually organic)
- Distribution ratio (D)
  - Ratio of concentrations of a component in the organic phase to aqueous phase
- Efficient for large scale separations
- Can be labor intensive for large sample batches in analytical applications.
- Highly selective extractants can lead to high recoveries and decontamination factors using multiple extraction, scrub and stripping stages.

Solvent Extraction Equipment

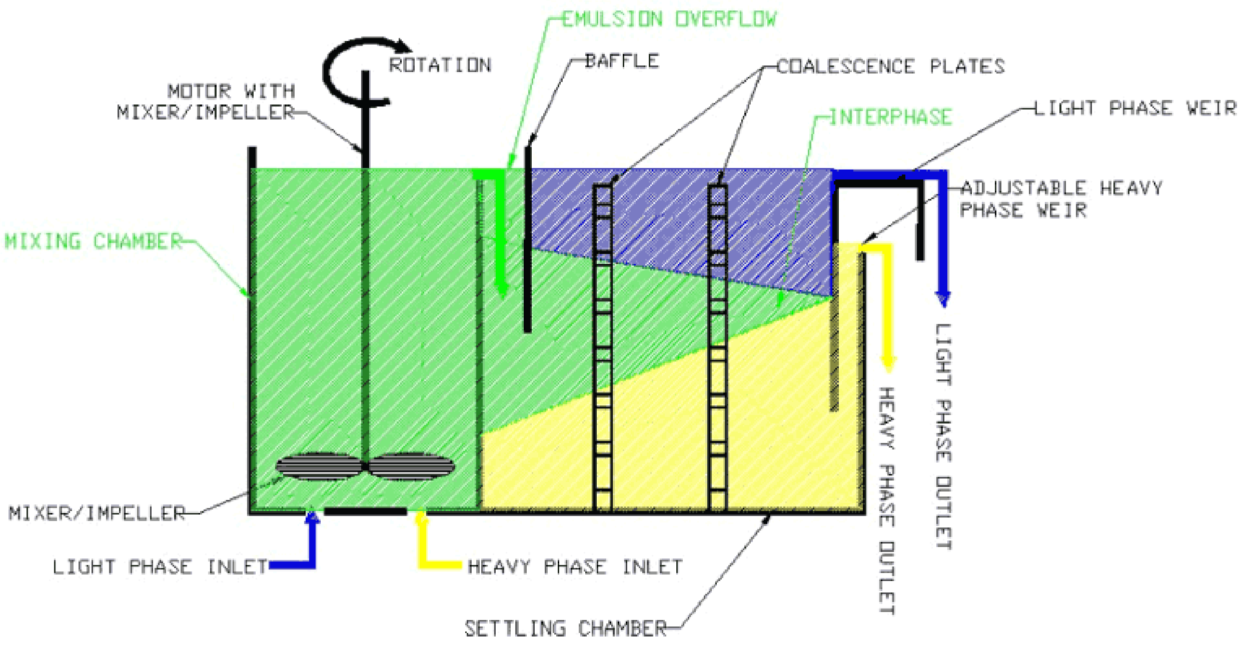


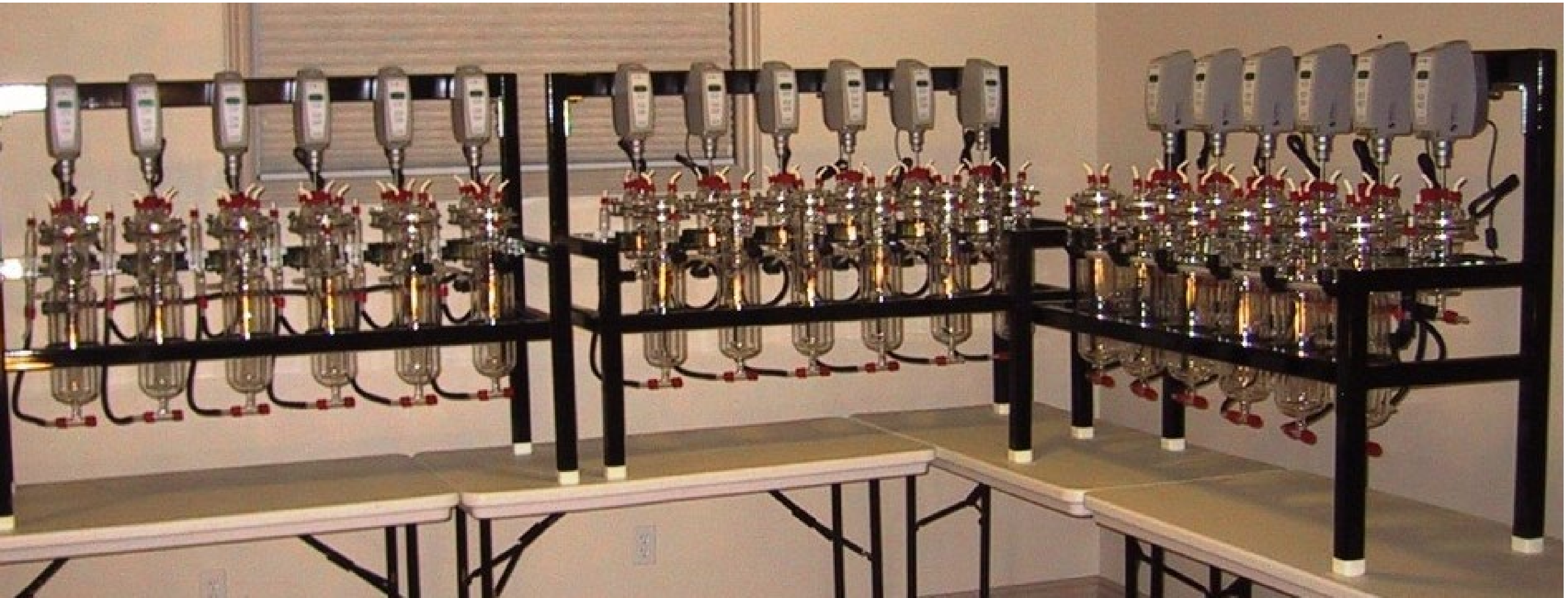
(b)



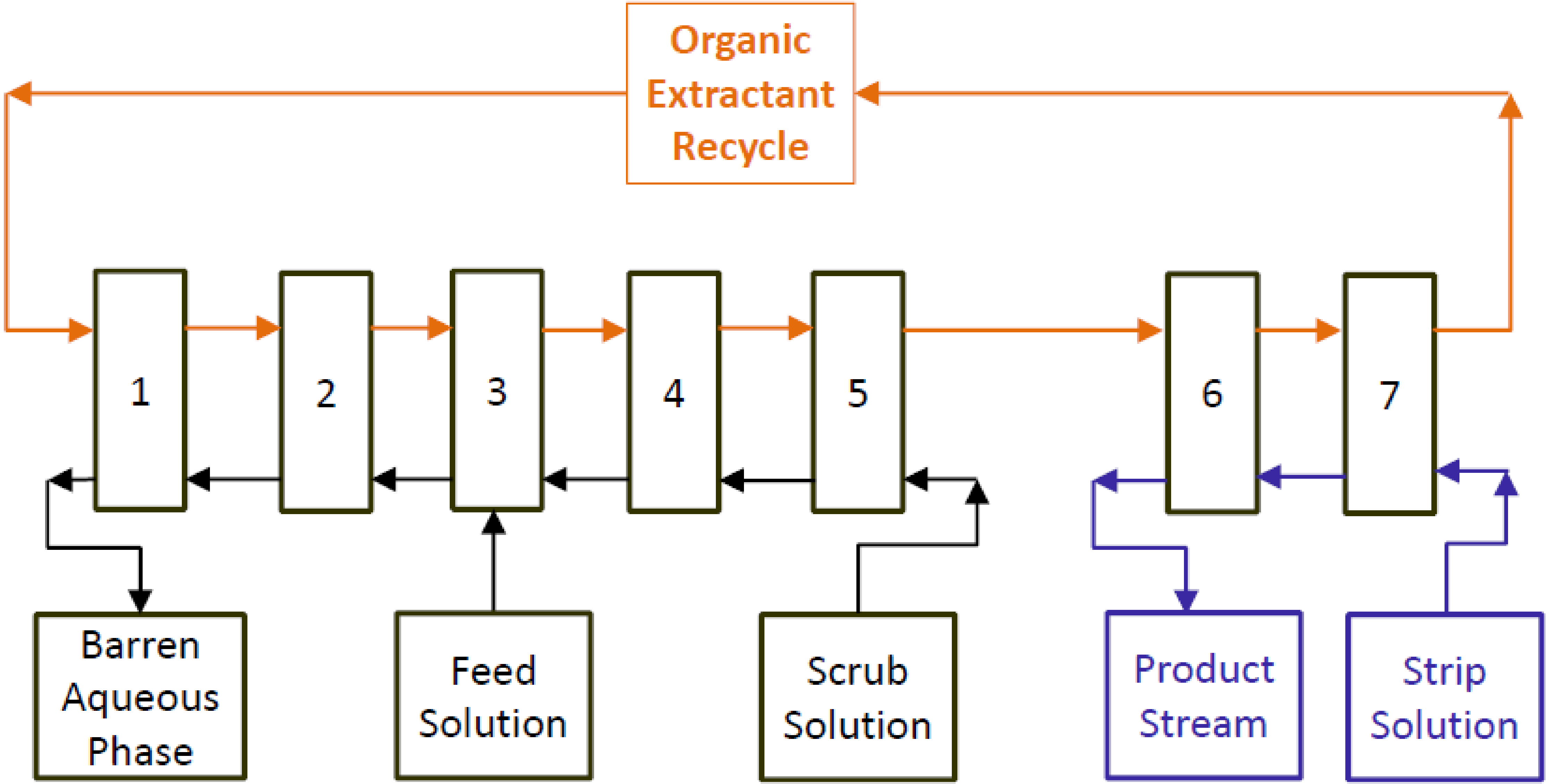
Solvent Extraction Equipment

LABORATORY MIXER-SETTLERS:





Multiple Stage Counter Current Solvent Extraction



Organic Extractant Recycle

1

2

3

4

5

6

7

Barren Aqueous Phase

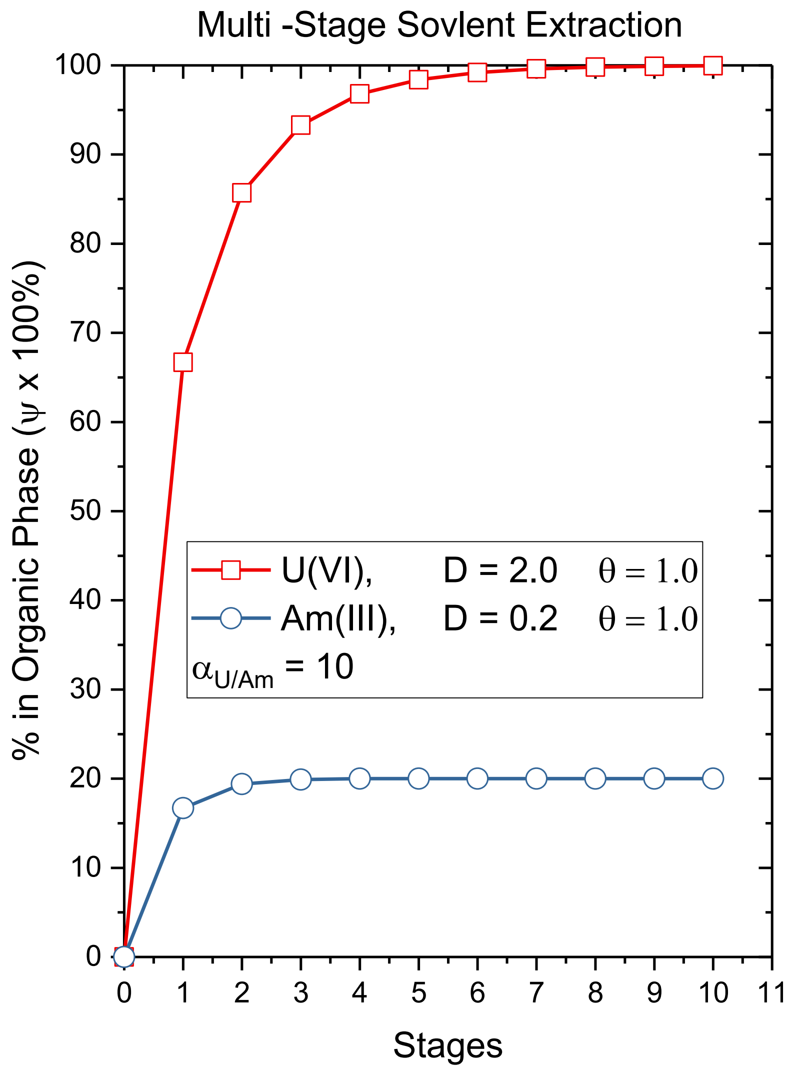
Feed Solution

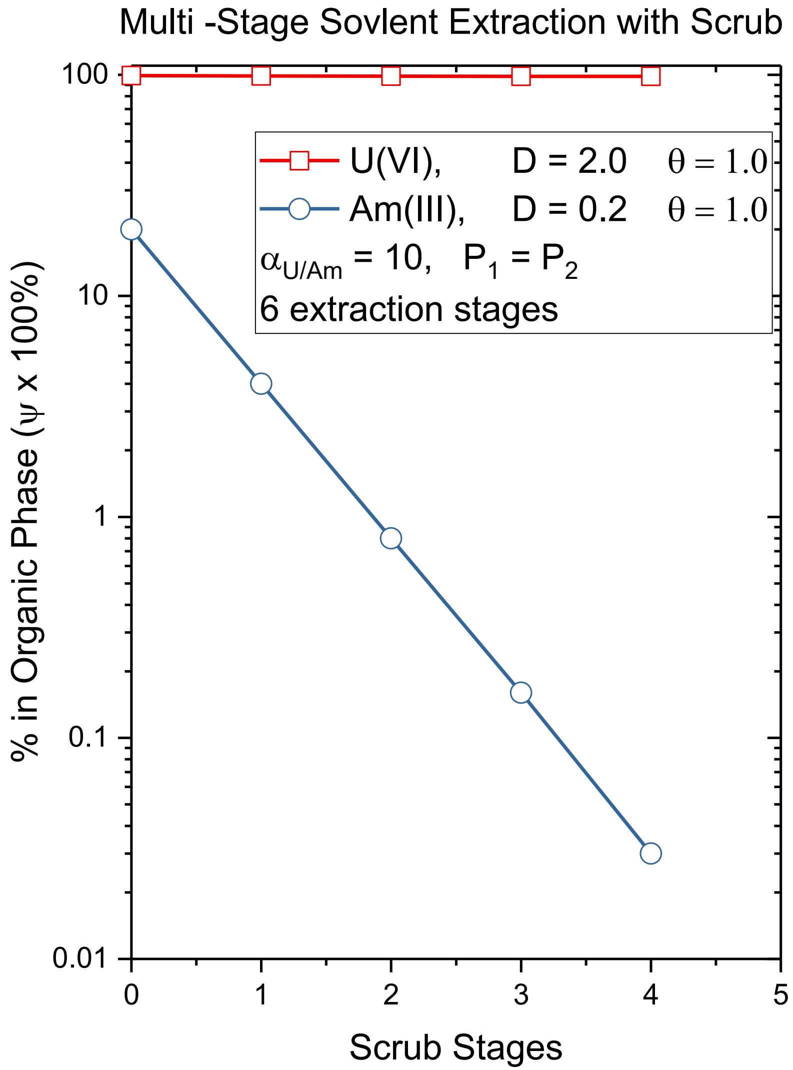
Scrub Solution

Product Stream

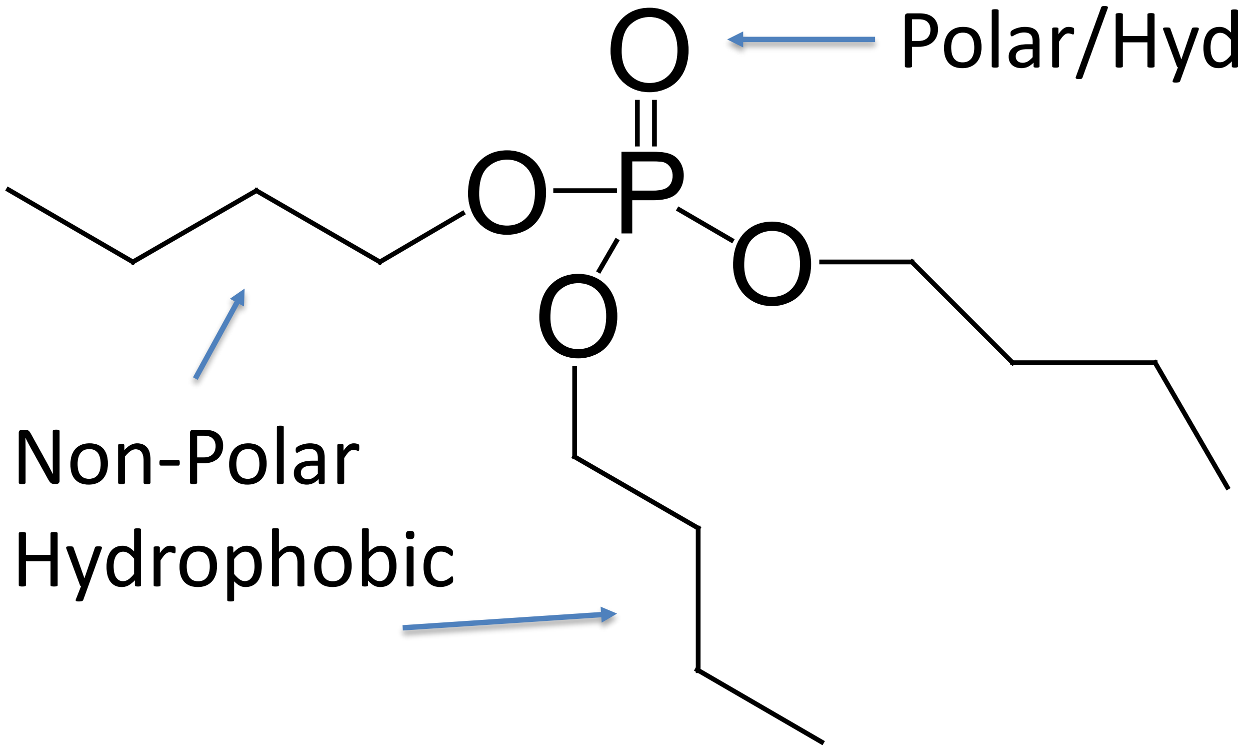
Strip Solution

Effect of Multiple Stages





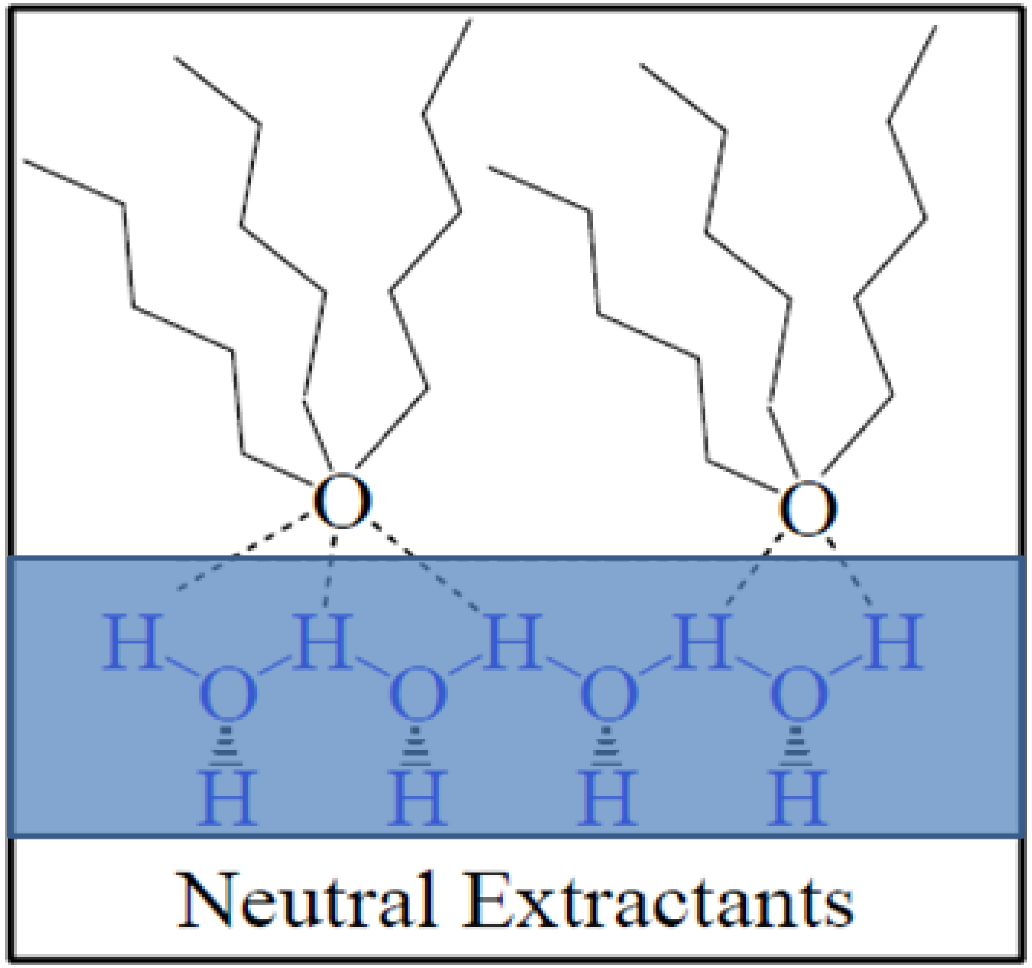
Mechanism of Solvent Extraction

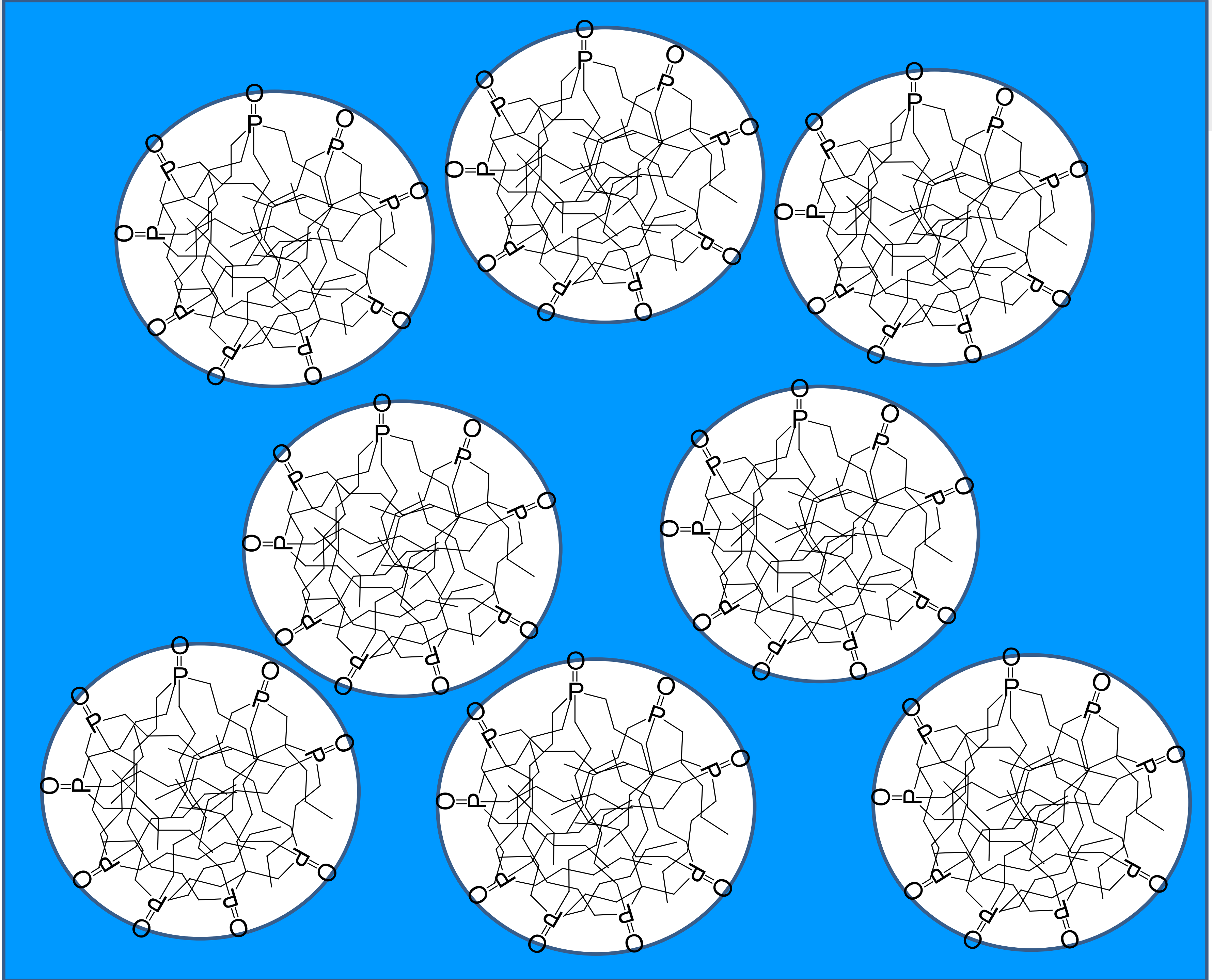


Polar/Hydrophilic

Non-Polar
Hydrophobic

Extractants are amphiphatic and therefore interfacially active (surfactants).





Dispersion of organic phase droplets in aqueous phase after mixing.

Polar head groups orient towards aqueous/organic interface.

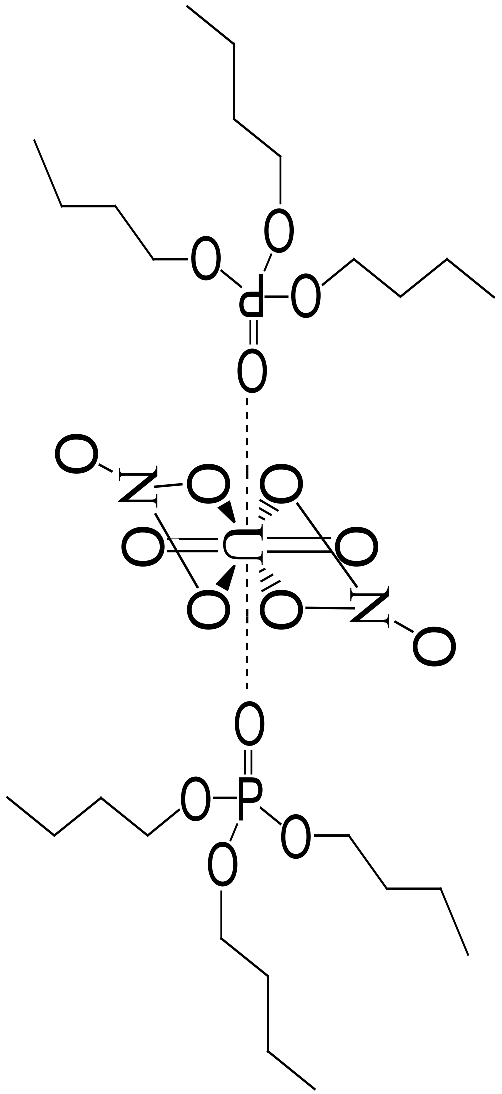
Extractant molecules may also aggregate or form reverse-micelles in organic phase.

Mechanism of SX

$[UO_2(OH_2)_5]^{2+}$

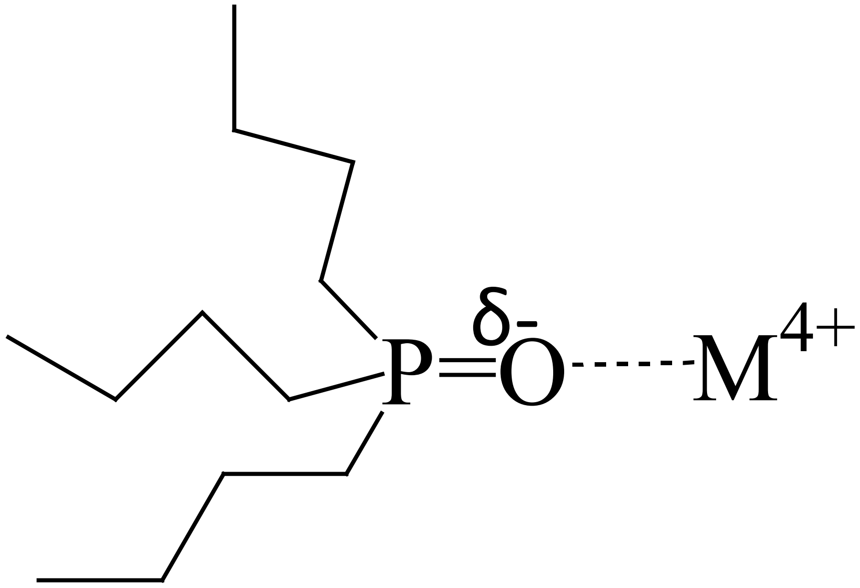
- In LLE, the polar phosphorous-oxygen or carbon-oxygen head of the extractant complexes the metal ion from its aqueous environment at the interface.

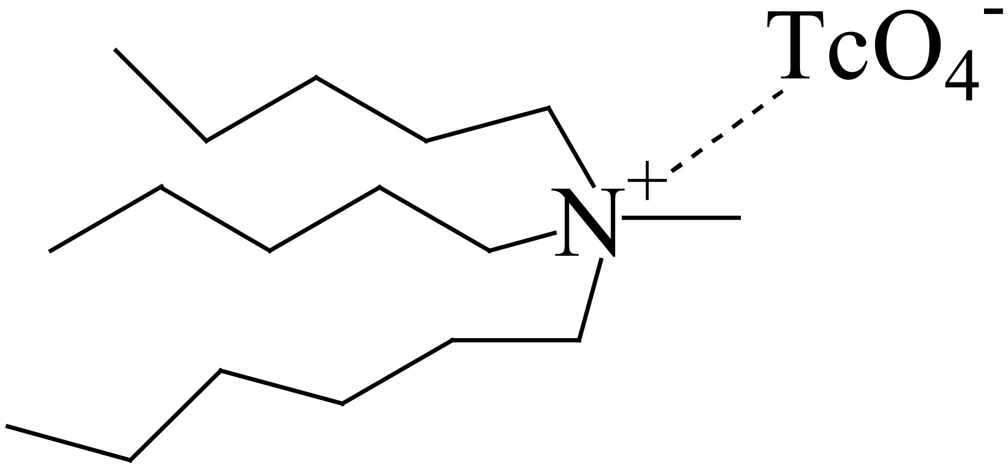
- The non-polar alkyl groups surround the metal complex and act to solubilize it into the organic phase.



Bonding

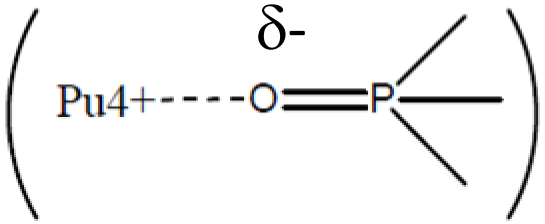
- Bonding between extractants and actinides, lanthanides and most fission products is due largely to electrostatic forces.





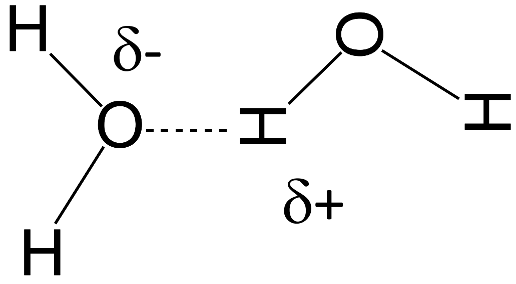
Examples of Electrostatic Bonds

- cation – anion H^+ -- F^-
- ion – dipole

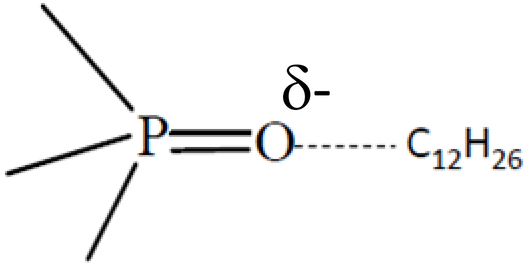


Coordination
Coordinate Covalent

- dipole – dipole - hydrogen bond



- dipole – induced dipole



- induced dipole – induced dipole

van der Waals

Potential Problems

- Aqueous and solvent entrainment, which lowers stage efficiency
- Difficulty with back-extraction
- Difficulty with solvent cleanup, especially from radiolytic degradation
- Third phase or emulsion formation
- Crud at the interface

M. Borkowski, J.R. Ferraro, R. Chiarizia and D.R. McAlister, “FT-IR Study of Third Phase Formation in the U(VI) or Th(IV)/HNO_3, TBP/Alkane Systems,” *Solv. Extr. Ion Exch.*, 20(3), 313-330 (2002).

Advantageous uses of third phase formation

- Purification of acidic organophosphorus extractants (HDEHP)

Hu Zhengshui, Pan Ying, Ma Wanwu & Fu Xun (1995) PURIFICATION OF ORGANOPHOSPHORUS ACID EXTRACTANTS, Solvent Extraction and Ion Exchange, 13:5, 965-976, DOI: 10.1080/07366299508918312

- Enrichment of Sr selective crown ether isomers

MARK L. DIETZ, CLAUDIA FELINTO, SUSAN RHOADS, MAUREEN CLAPPER, JEFFREY W. FINCH, BENJAMIN P. HAY, "Comparison of Column Chromatographic and Precipitation Methods for the Purification of a Macrocyclic Polyether Extractant," SEPARATION SCIENCE AND TECHNOLOGY, 34(15), pp. 2943–2956, 1999.

Solvent Extraction Equilibrium

$$M^{3+}\bullet\,(H_2O)_x + 3A^{-}\bullet\,(H_2O)_y + \overline{nE\cdot(\text{solvent})_z} \rightleftarrows \overline{ME_nA_3\bullet\,(\text{solvent})_z} + (x+y)\,H_2O$$

The magnitude of the extraction depends on:

a. Hydration Energies of the Cations and Anions

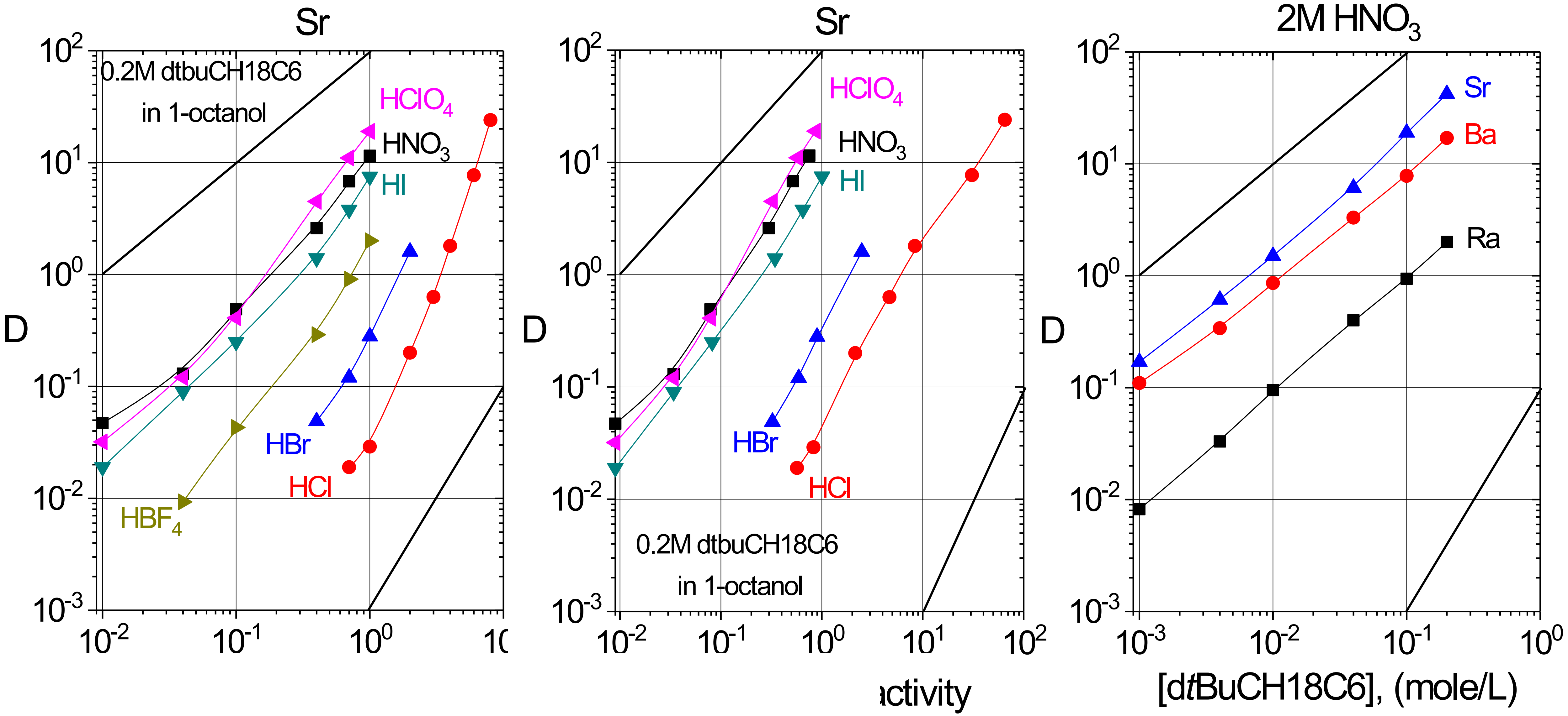
b. Bond Energy Between the Cation and Extractant

c. Solvation Energy of the Extractant and the Complex

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:

Extraction Equilibria

$$Sr^{2+} + 2X^- + \overline{L} \longleftrightarrow \overline{SrX_2L}$$



Chromatography vs Solvent Extraction

Chromatography:

- Lower capacity, higher separation factors for single stage

- Less waste, less labor for multiple simultaneous separations.

- Ideal for analytical and smaller scale preperative separations.

- Can be easier to implement in hot cells and glove boxes.

Liquid Column Chromatography (Reverse Phase)

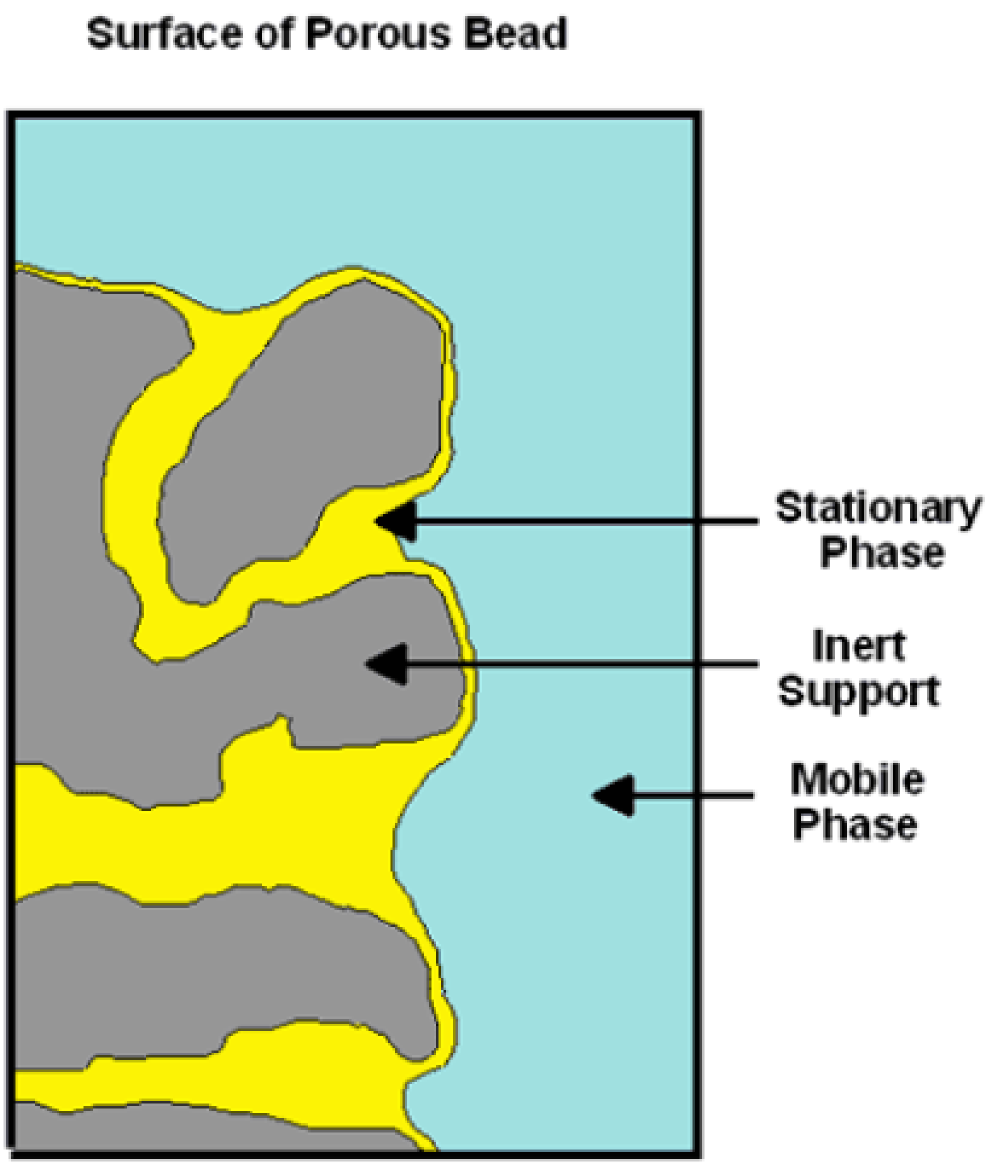
Bonded Phase:

- Stationary phase with covalently attached functional groups
- Polymeric substrates (cross-linked styrene, methacrylate, acrylonitrile)
- Inorganic substrates (Silica)
- Mobile Phase: Aqueous or non-aqueous

Partition Chromatography (Liquid-Liquid or Extraction Chromatography):

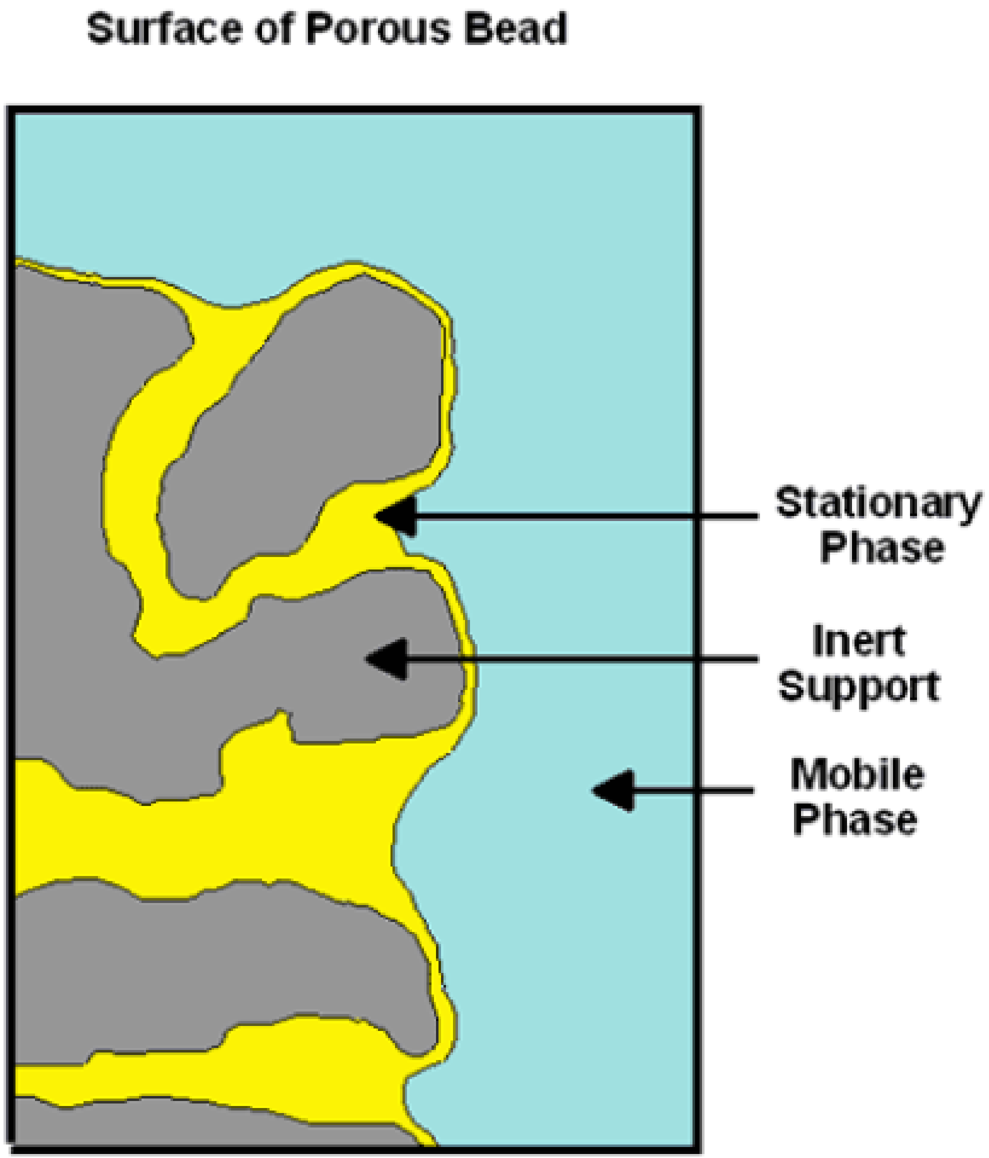
- Stationary Phase: Solvent embedded in the pores/surface of an inert material.
- Mobile Phase: Polar (Aqueous)

Bonded Resins vs EXC



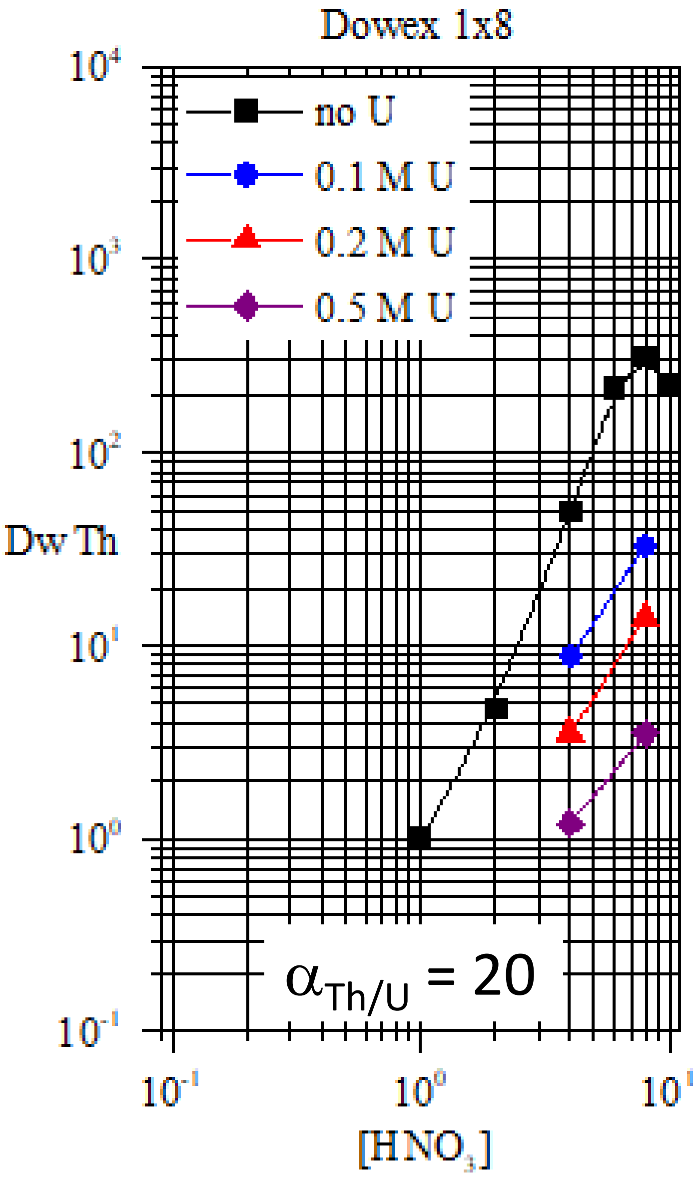
- Resins with covalently bonded functional groups can be more stable than EXC resins allowing the use of non-aqueous mobile phases.
- Covalently bonding the functional groups limits the freedom of the ligands to move and bind multiple ligands to a single metal ion.
- Coating extractants in the pores of an inert support retains the functionality of SX while enabling the functionality of chromatography.

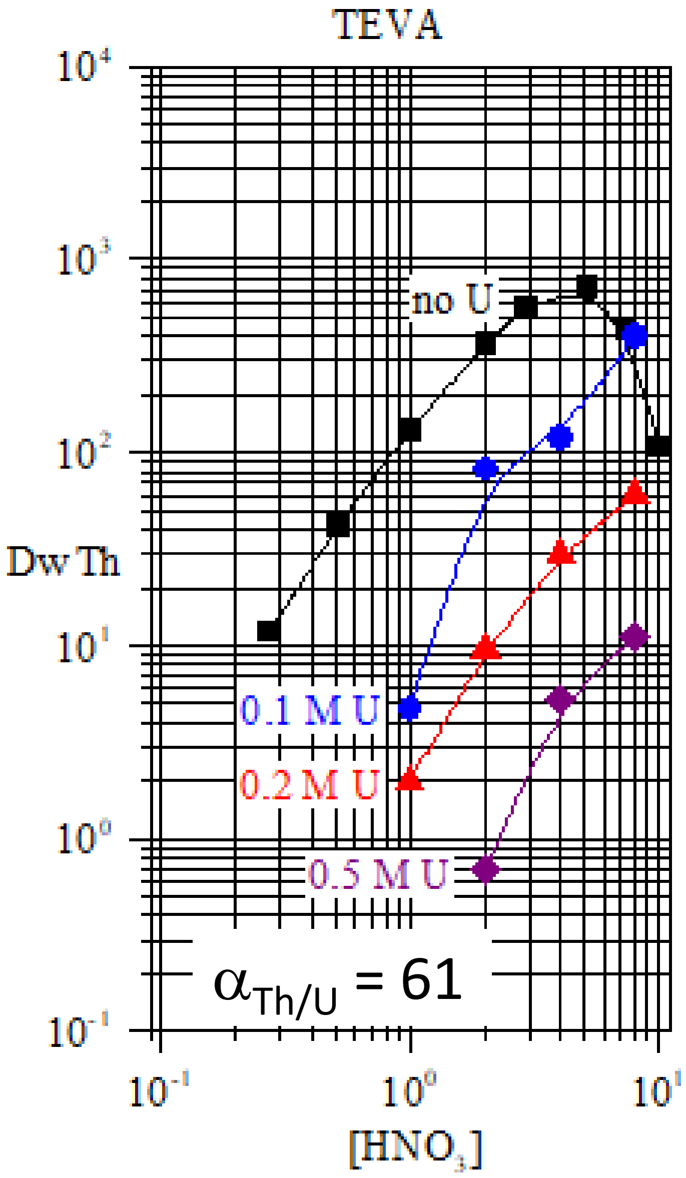
EXC Resins



- Support = Polymeric or Inorganic
- Extractant
  - Hydrophobic balance
  - Neat liquid with relatively low viscosity or dissolved in relatively low viscosity diluent
  - High retention (loading)
  - Low retention (stripping)
- Density, ideally more dense than dilute acid solutions for column packing

Bonded Resins vs EXC





1x8 = bonded polymeric strong anion exchange.

TEVA = EXC strong anion exchange (Aliqat336).

EXC higher Th retention at lower HNO_3.

EXC better selectivity over U, even though capacity is lower than 1x8 (0.13 vs 1.3 meq/mL)

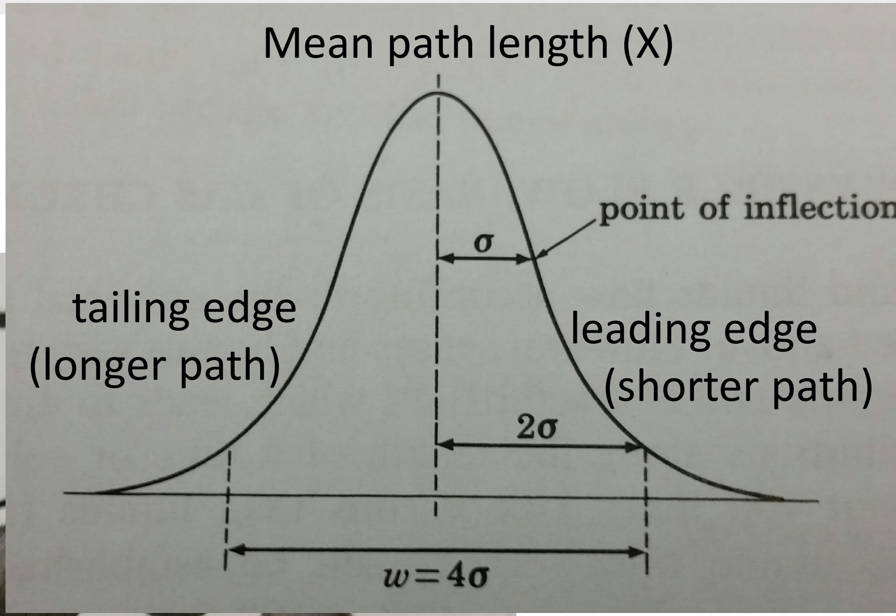
Type	Examples	Advantages	Disadvantages
Inorganic	Silica, Alumina, Zeolite	Physical Stability, Cost, Extractant Purification	Selectivity Fewer Options
Bonded-Polymeric	Cation Exchange, Anion Exchange, Chelex-100	Many Options, Highest Capacity, Stable from pH 0-14, Low to moderate cost,	Shrink in high ionic strength Swell ion low ionic strength and non-aqueous solvents, Lower Selectivity than EXC
Bonded-Silica	C18, tC18, SCX, WCX, SAX, WAX, diol, aminopropyl	Many Options, Physical stability, Relatively low cost,	pH Stability (2-9)*, Low capacity (0.1-1.0 meq/mL)
Partition(EXC)	TEVA, TRU, UTEVA, DGA, WBEC, Sr, Pb, Ni, LN, RE, Cs, Cu, Cl	Superior Selectivity, Many, many options, Acid Stability Can be made on silica	Extractant Bleed, Aqueous mobile phase only, Low Capacity (0.01-0.1 meq/mL), Expensive

*Can be improved with certain bonding chemistries and functional groups

Peak Positions and Shape

Giddings, 1991.

Rule of thumb: column width should be >30x particle size of stationary phase to minimize wall effects/streaming.



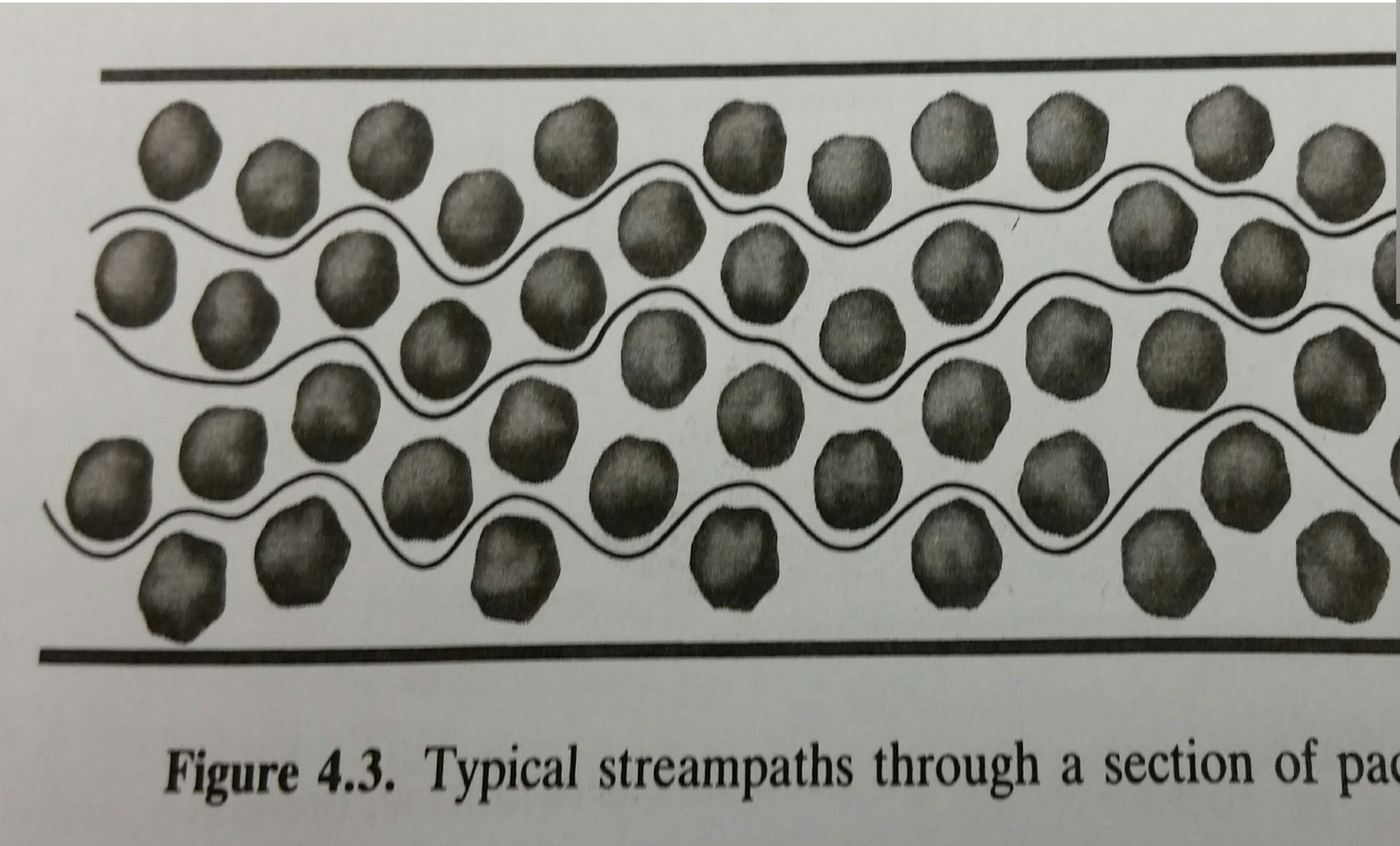
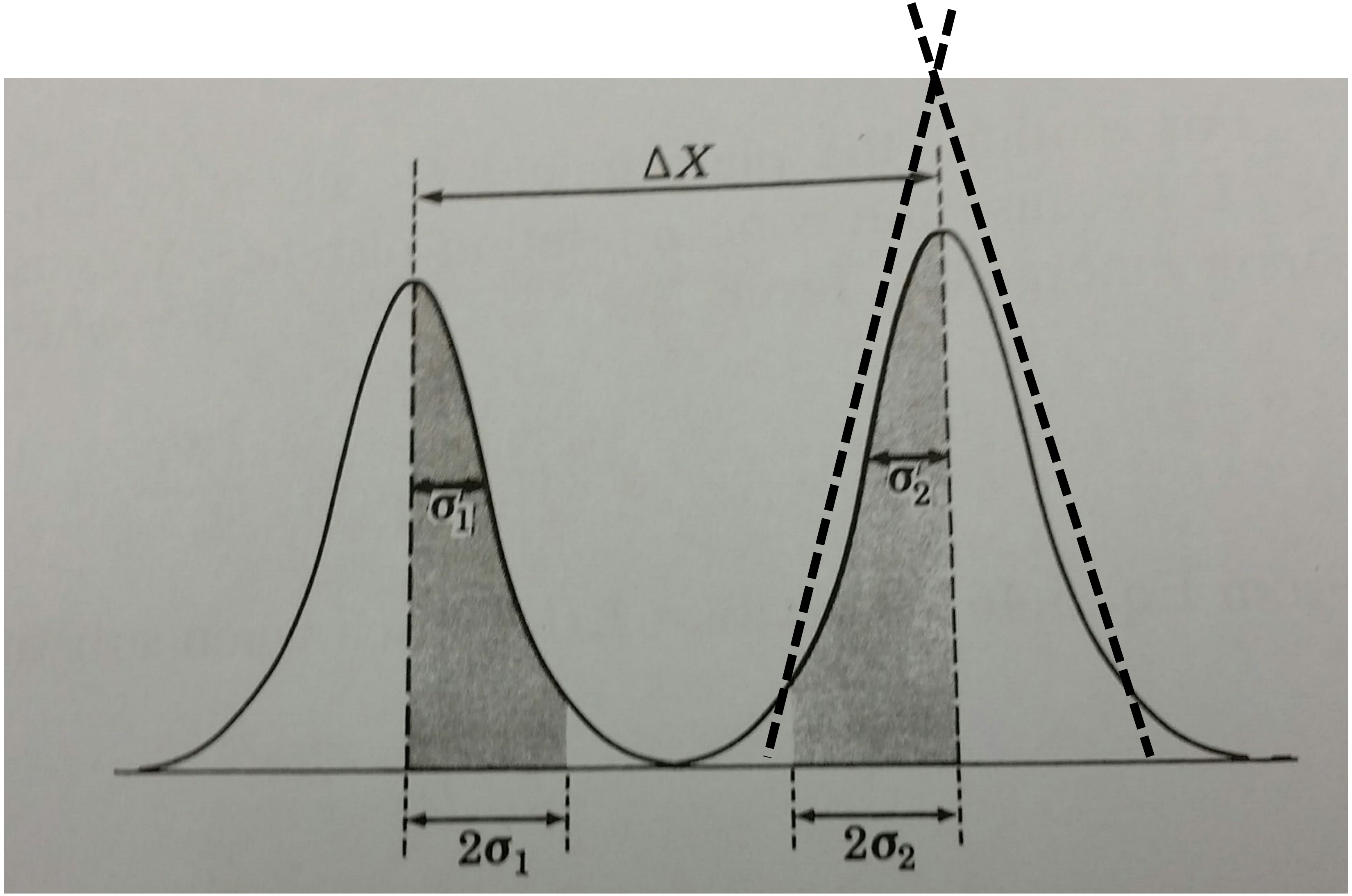


Figure 4.3. Typical streampaths through a section of packed column.

Resolution

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



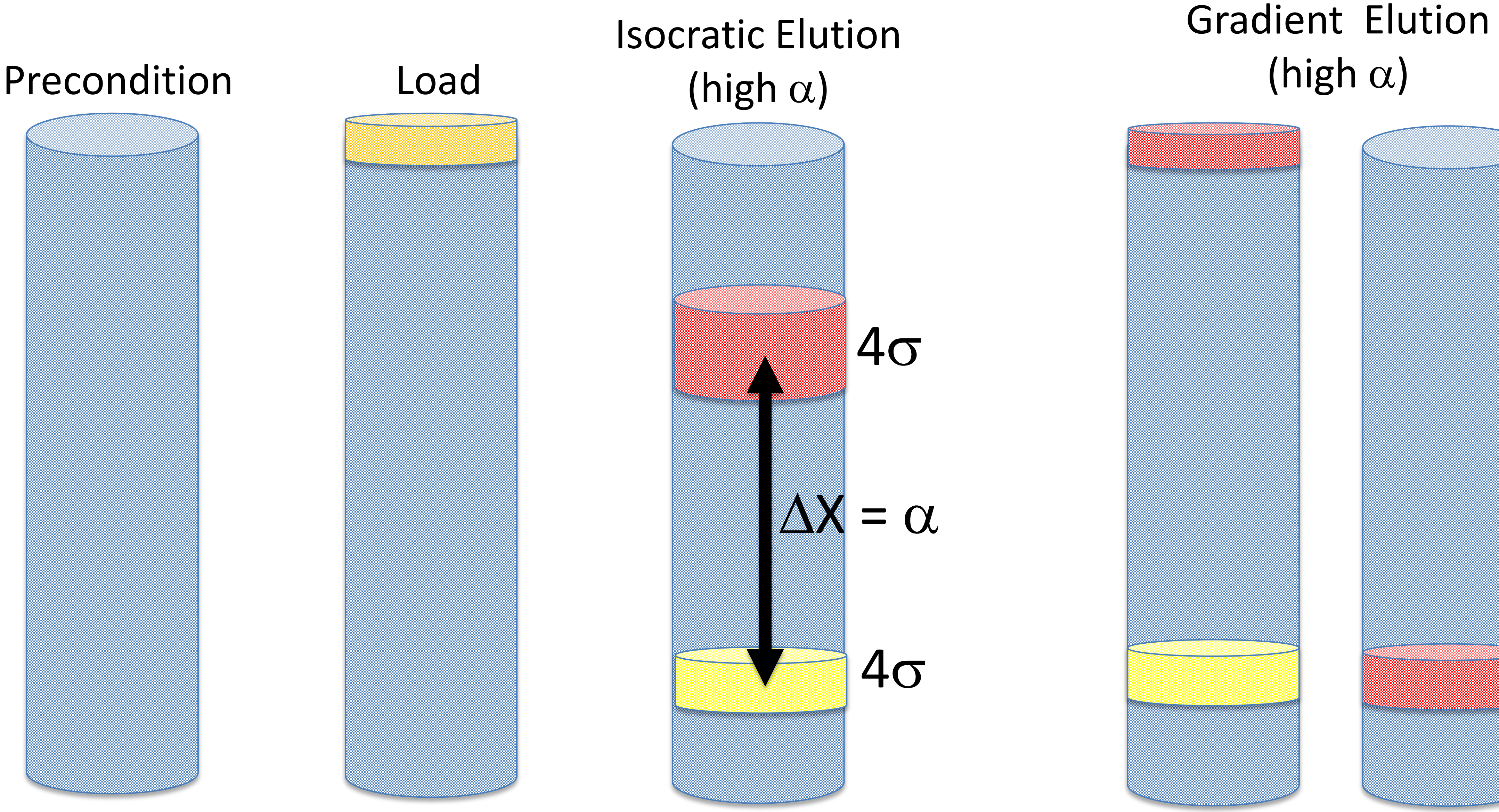
X = peak maximum

2σ = peak width at inflection point

4σ = peak width (W), tangent line through inflection point.

Giddings, 1991.

Mechanics of Chromatography



Precondition

Load

Isocratic Elution (high α)

4σ

$\Delta X = \alpha$

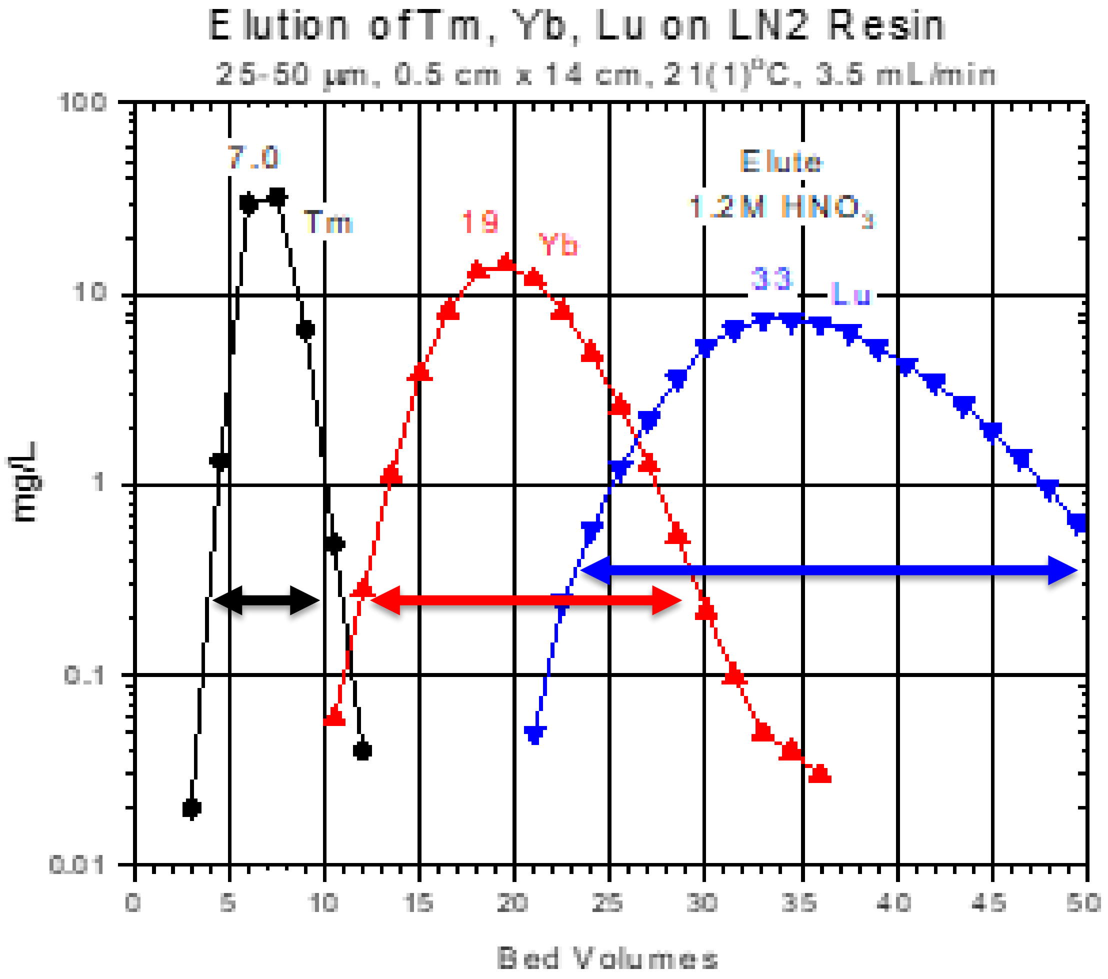
4σ

Gradient Elution (high α)

Isocratic vs Gradient Elution

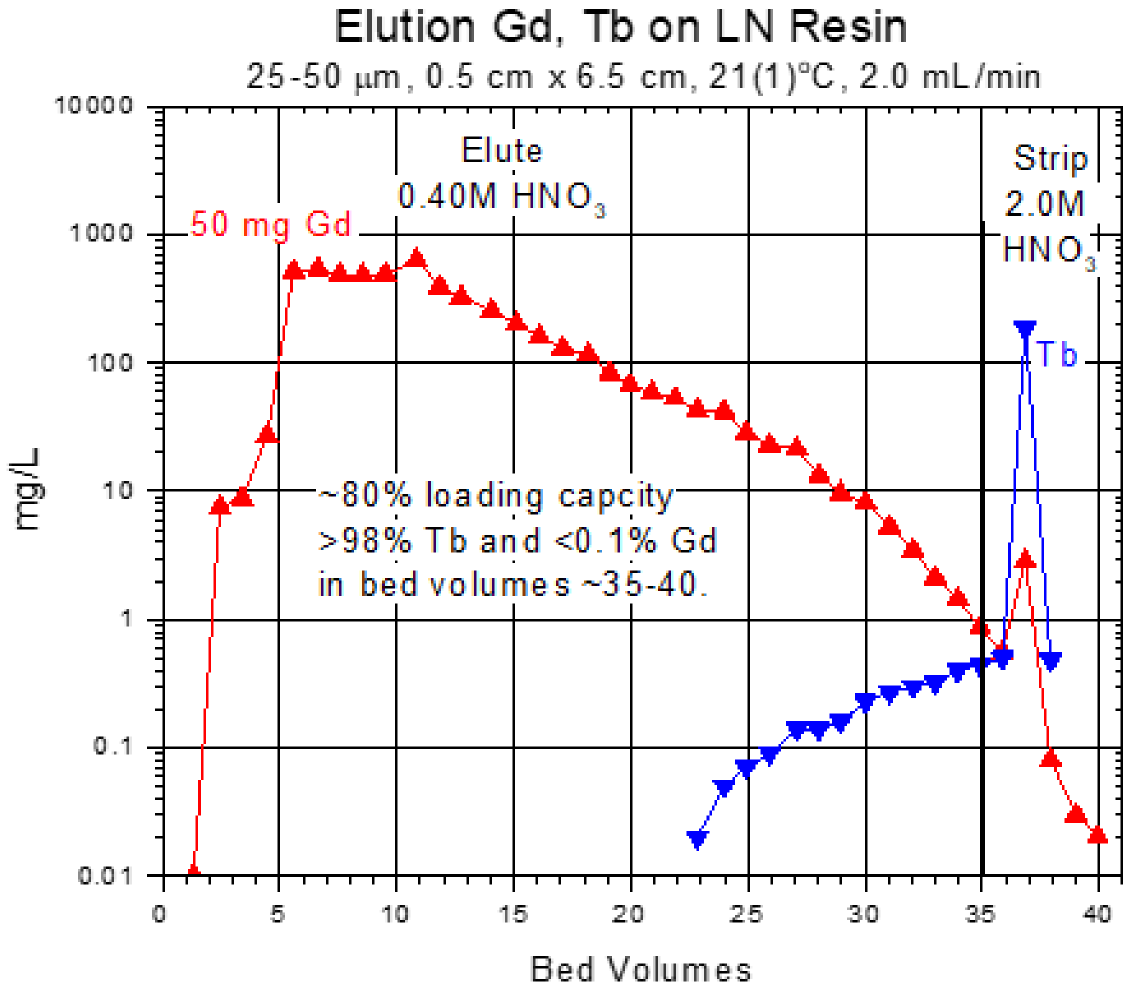
Isocratic elution 1.2M HNO_3

$\alpha < 2$



Gradient elution 0.4 and 2M HNO_3

$\alpha \sim 4.7$



Measurements of peak positions (X)

Retention time (R_T) Need to know column length, width, flow rate.

Dw = mL eluate to peak maximum / gram of resin bed

Dv = mL eluate to peak maximum / mL of resin bed

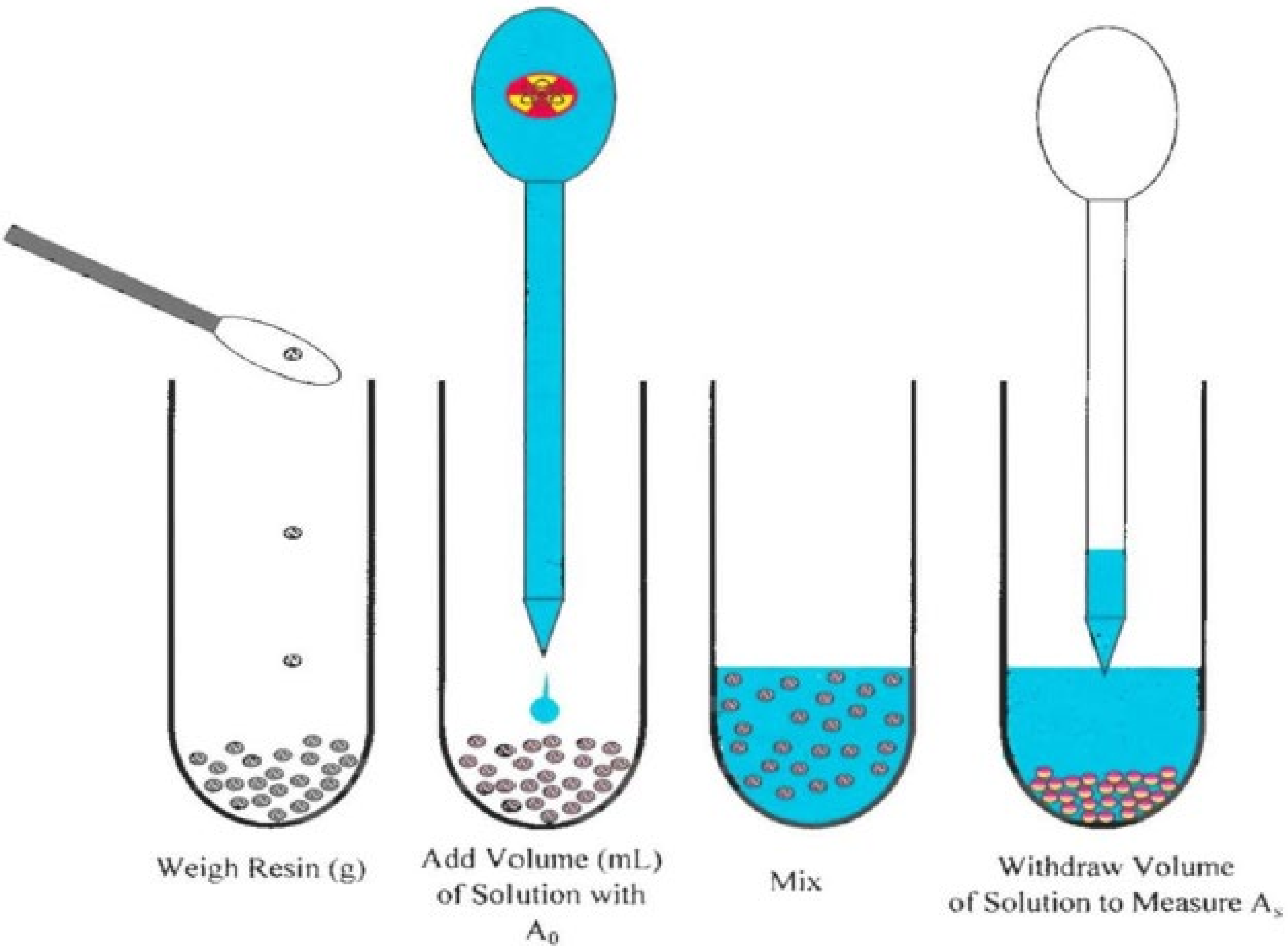
k’ = free column volume to peak maximum

Characterization of stationary phases

1) Measure Dw under a variety of conditions for key metal ions (pH, acid, complexing agents)
2) Measure physical properties of stationary phase (density, bed density, etc..)
3) Calculate Dv or k’ from Dw.
4) Measure elution curves under conditions predicted by 1-3.

Measuring Retention Time/Volume (Batch Dry-weight Distribution, Dw)

D_w = mL of eluate to peak max / g resin bed



1) Add mass of resin (w) into tube.
2) Add volume (v) of aqueous phase with metal ion(s).
3) Equilibrate.
4) Filter/centrifuge to separate liquid/resin.
5) Withdraw aliquot of aqueous.
6) Measure metal ions in initial aqueous phase (A_0) and post equilibration (A_f).

$$D_W = \frac{A_0 - As}{w(g)} \Big/ \frac{A_s}{v(mL)}$$

Dw, Dv and k’

Measurement	Units	Meaning
Dw (Kd)	$\frac{\text{mL mobile phase}}{\text{gram stationary phase}}$	mL mobile phase per gram of stationary phase to peak maximum
Dv	$\frac{\text{mL mobile phase}}{\text{mL stationary phase}}$	mL mobile phase per mL of stationary phase to peak maximum
k’	unitless	Free column volumes to peak maximum

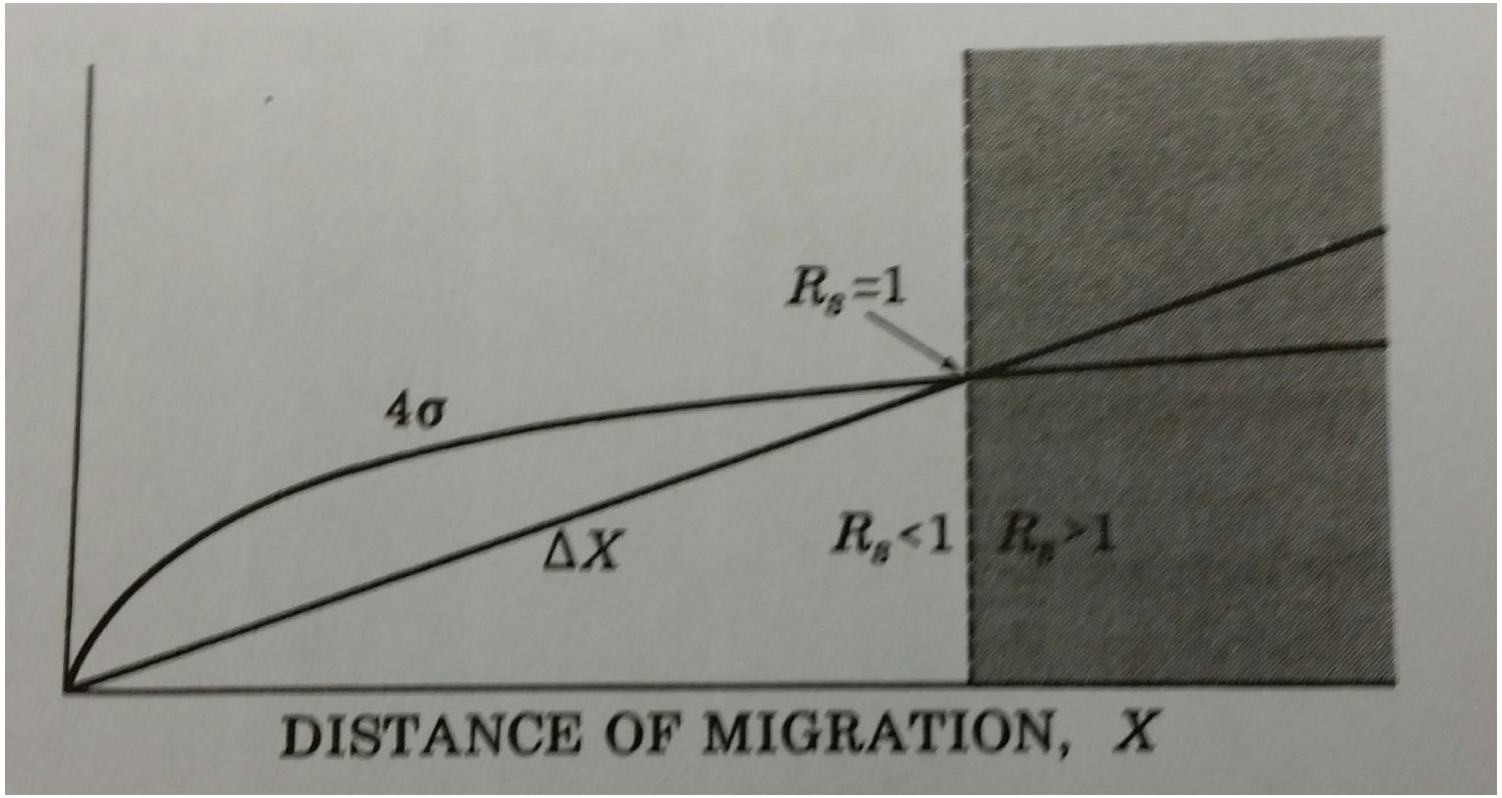
Convert from Dw to Dv and k’ by knowing:

- Bed density (grams resin / mL column volume)
- Physical density of resin (g/mL)
- Mass loading of extractant in EXC resin
- Density of the extractant in EXC resin

Why does chromatography work?

Giddings, 1991.

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



Resolution increases with longer columns!

Separation (ΔX) increases linearly

Peak widths ($2\sigma_1 + 2\sigma_2$) increase as the square root of X

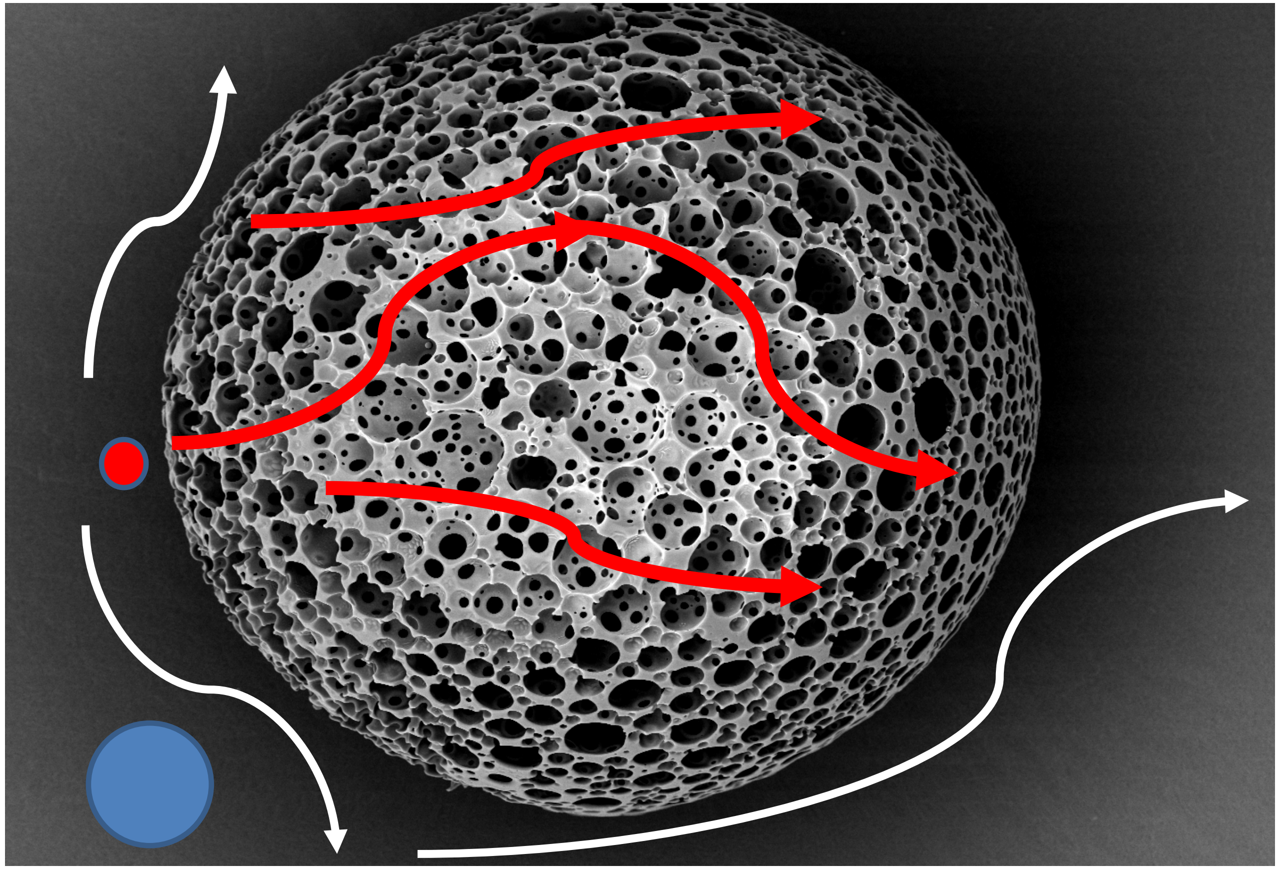
Factors affecting resolution (ΔX)

- Selectivity (α) / Retention (k’)
    - Resin Functionality
    - Mobile Phase Composition
    - Column Length

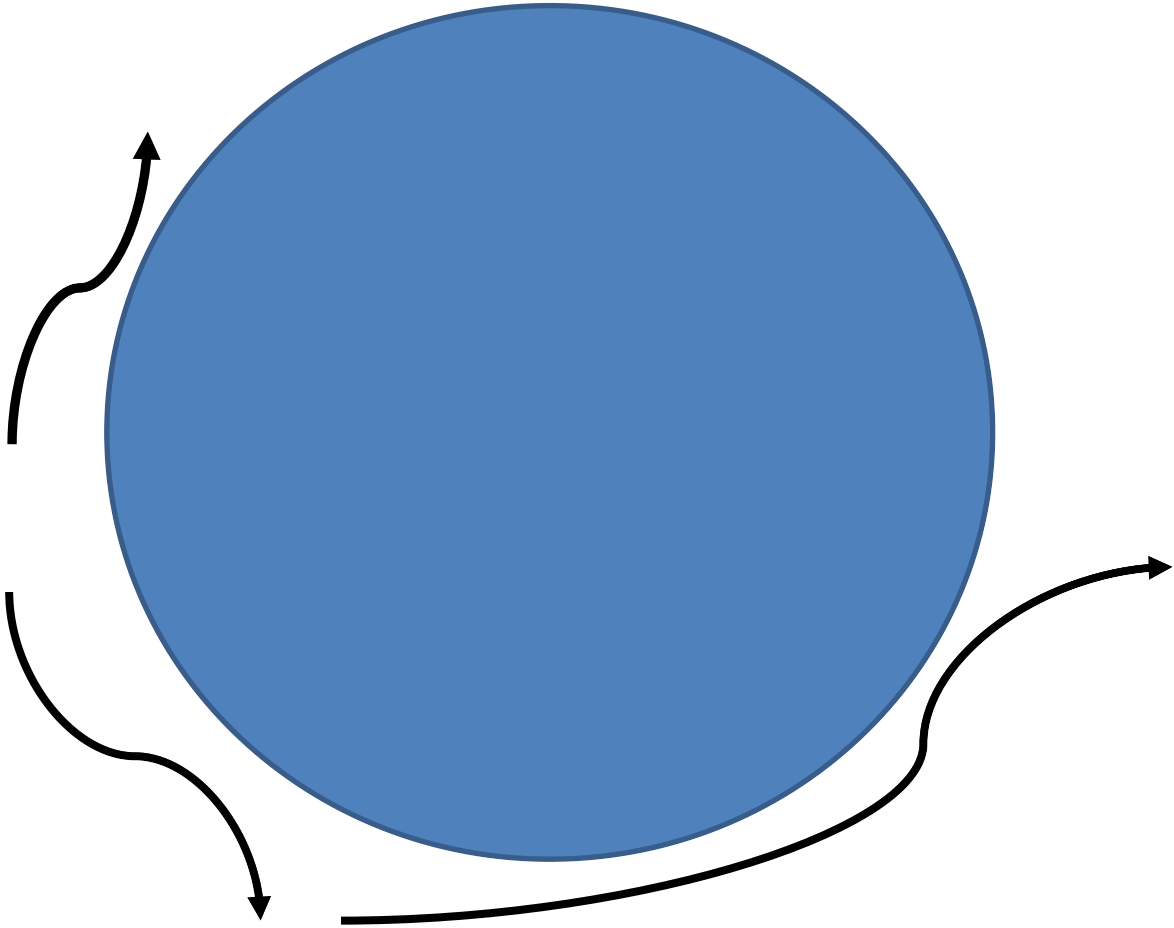
Factors affecting resolution (σ)

- Peak Width/Shape (σ) (Gaussian or non-Gaussian)
  - Particle Size/Shape
  - Porosity
  - Temperature
  - Flow Rate
  - Column Dimensions (length vs width)
  - Column Loading

Porous vs Non-Porous resin (Size Exclusion)



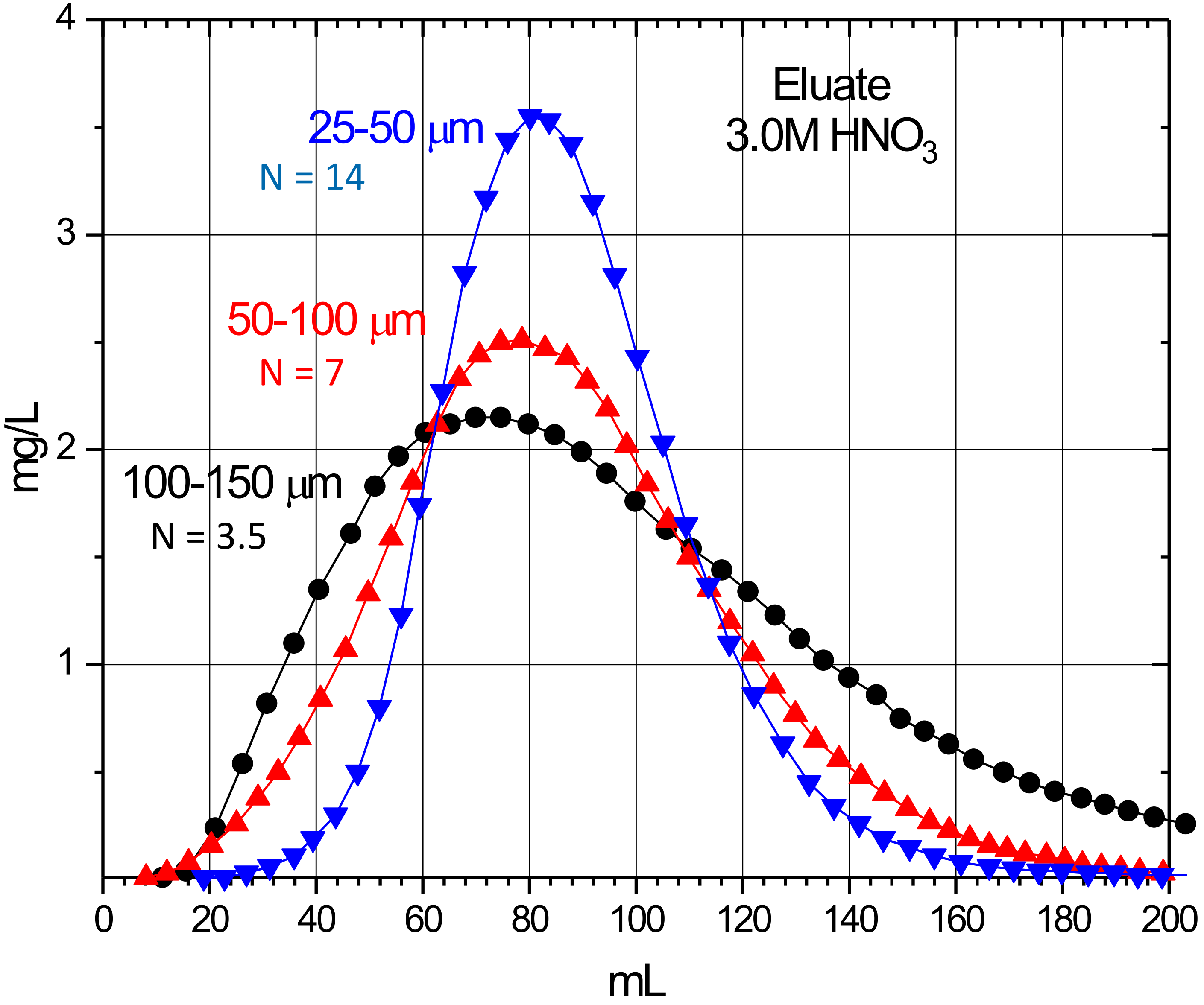
Porous media
Size Exclusion



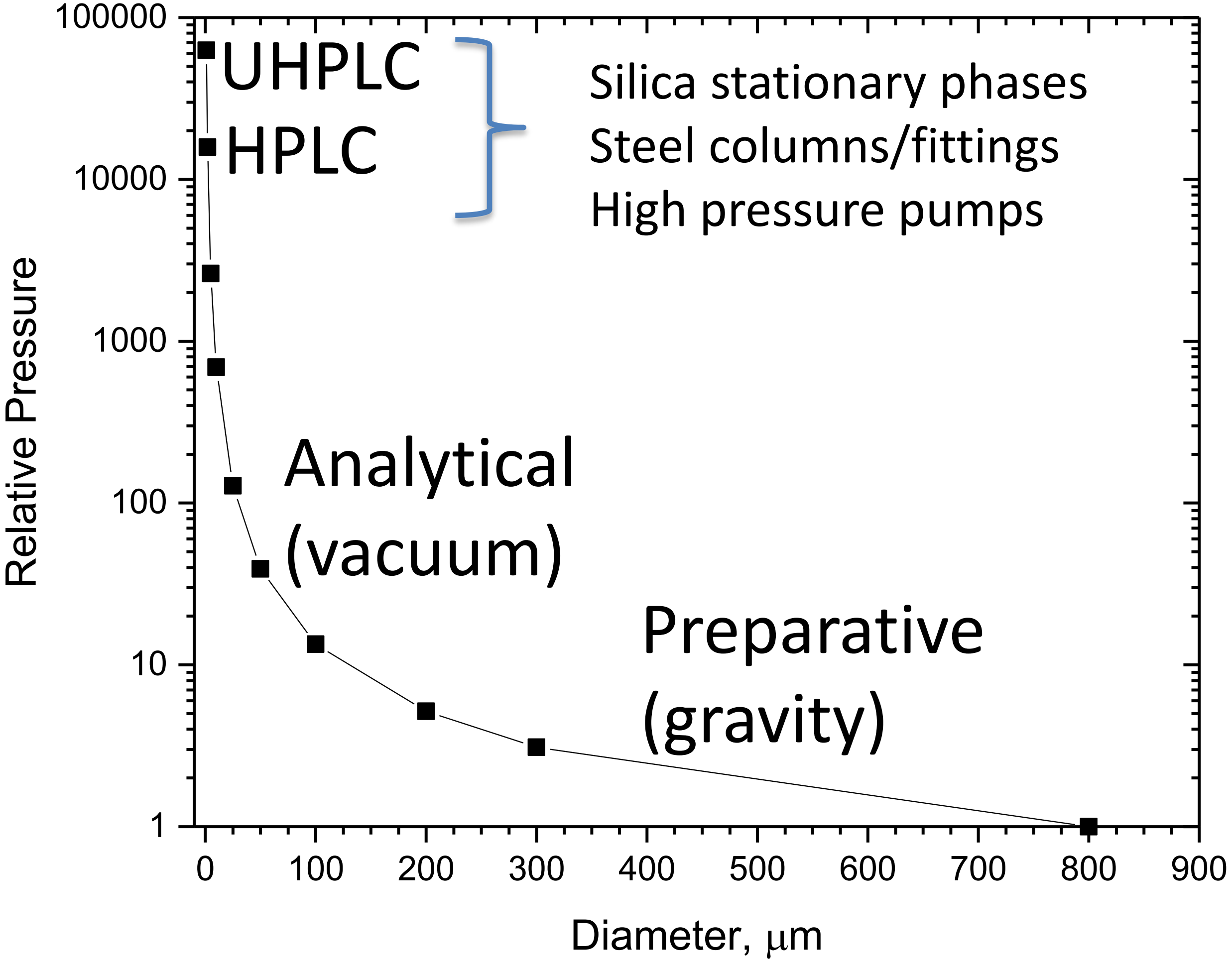
Non-porous media
Narrow peaks, lower capacity

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

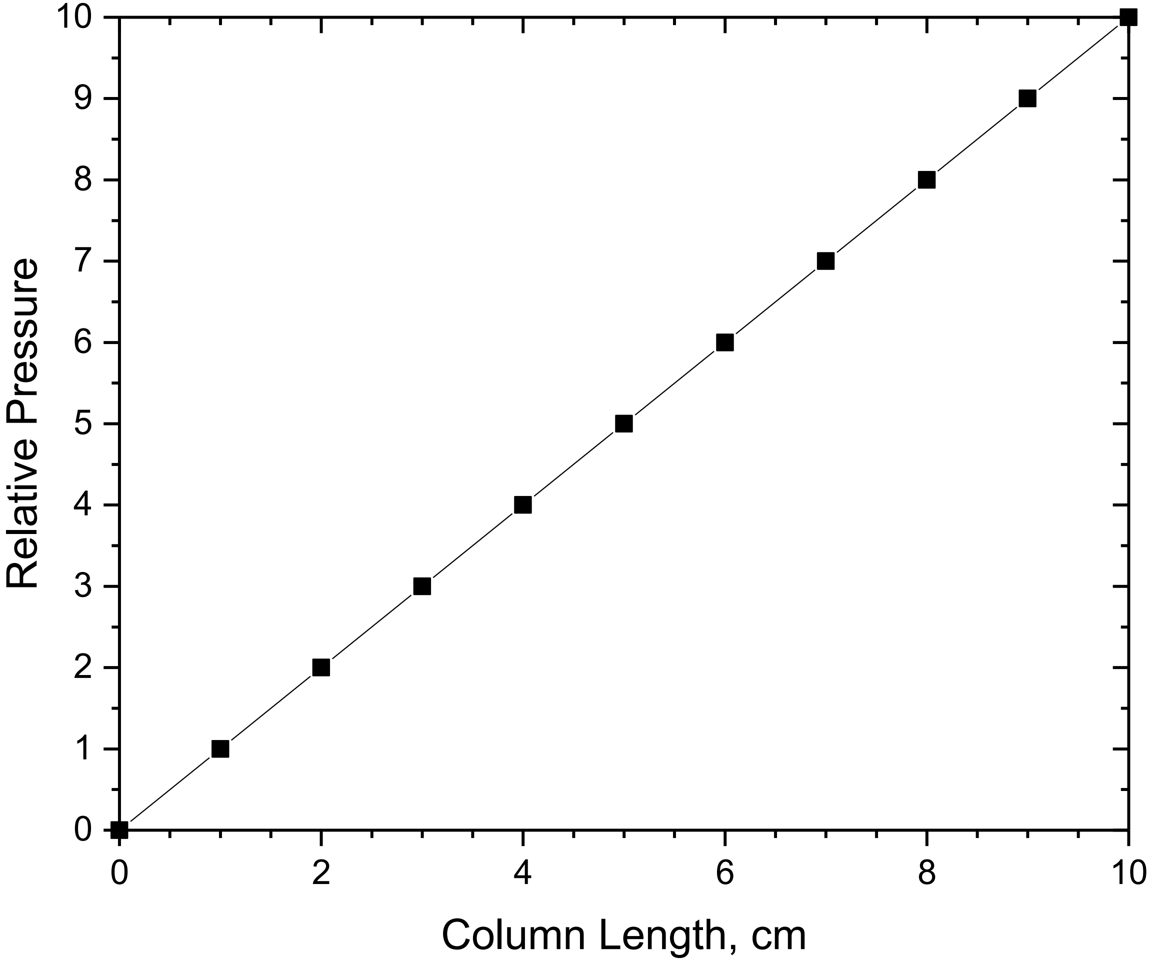
$$N = 5.54(X)^2/(W_{0.5})^2$$



Pressure drop through packed bed



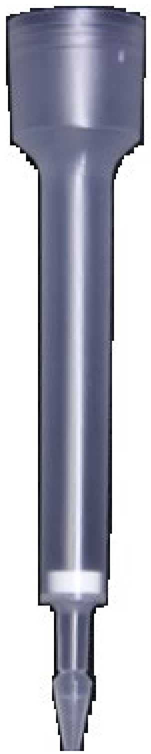
Silica stationary phases
Steel columns/fittings
High pressure pumps



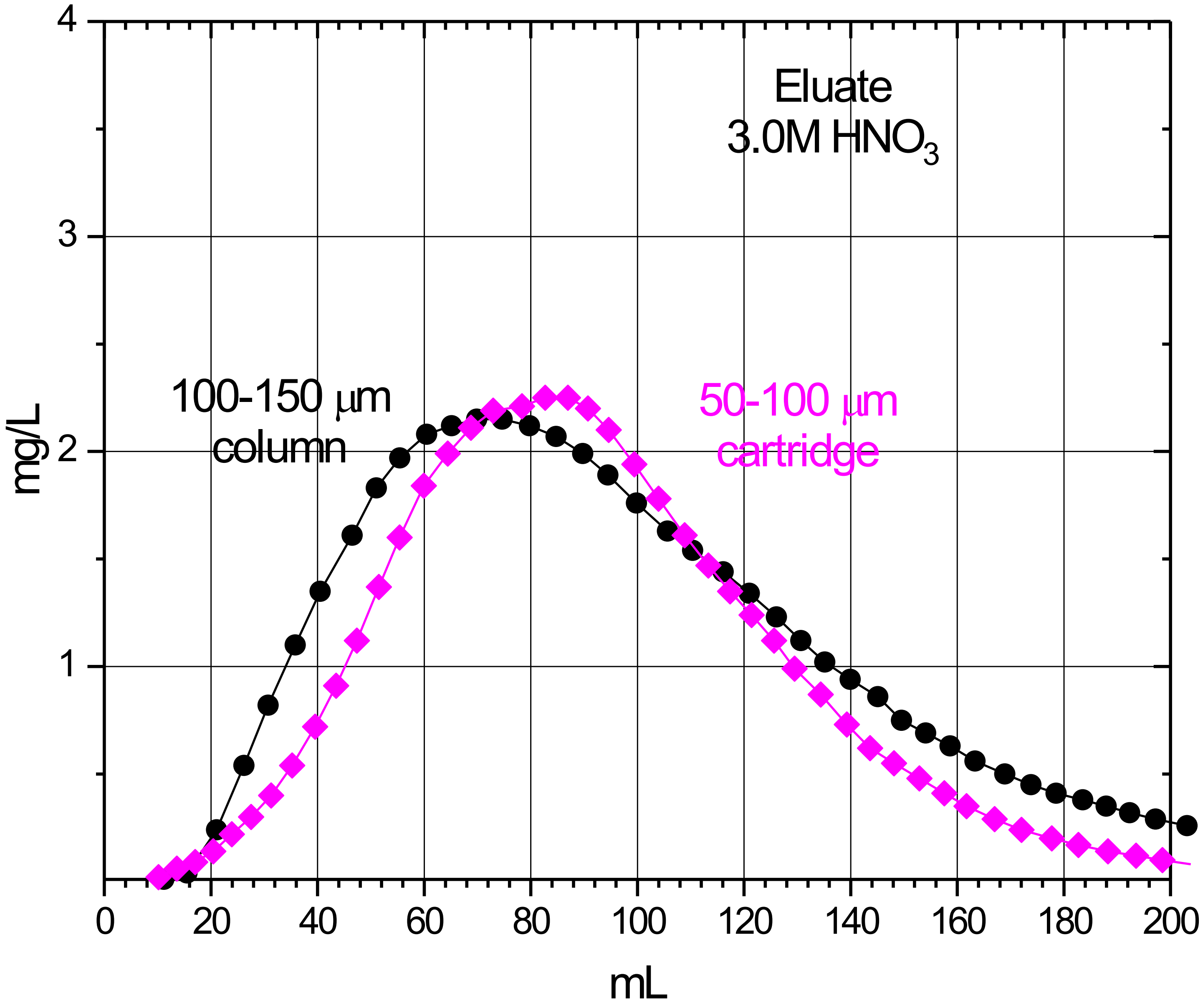
$$\Delta p = \frac{150\mu\, L}{D_p^2}\,\frac{(1-\epsilon)^2}{\epsilon^3}v_s + \frac{1.75\, L\, \rho}{D_p}\,\frac{(1-\epsilon)}{\epsilon^3}v_s\,|v_s|$$

Particle size – inverse second order
Column length - linear

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

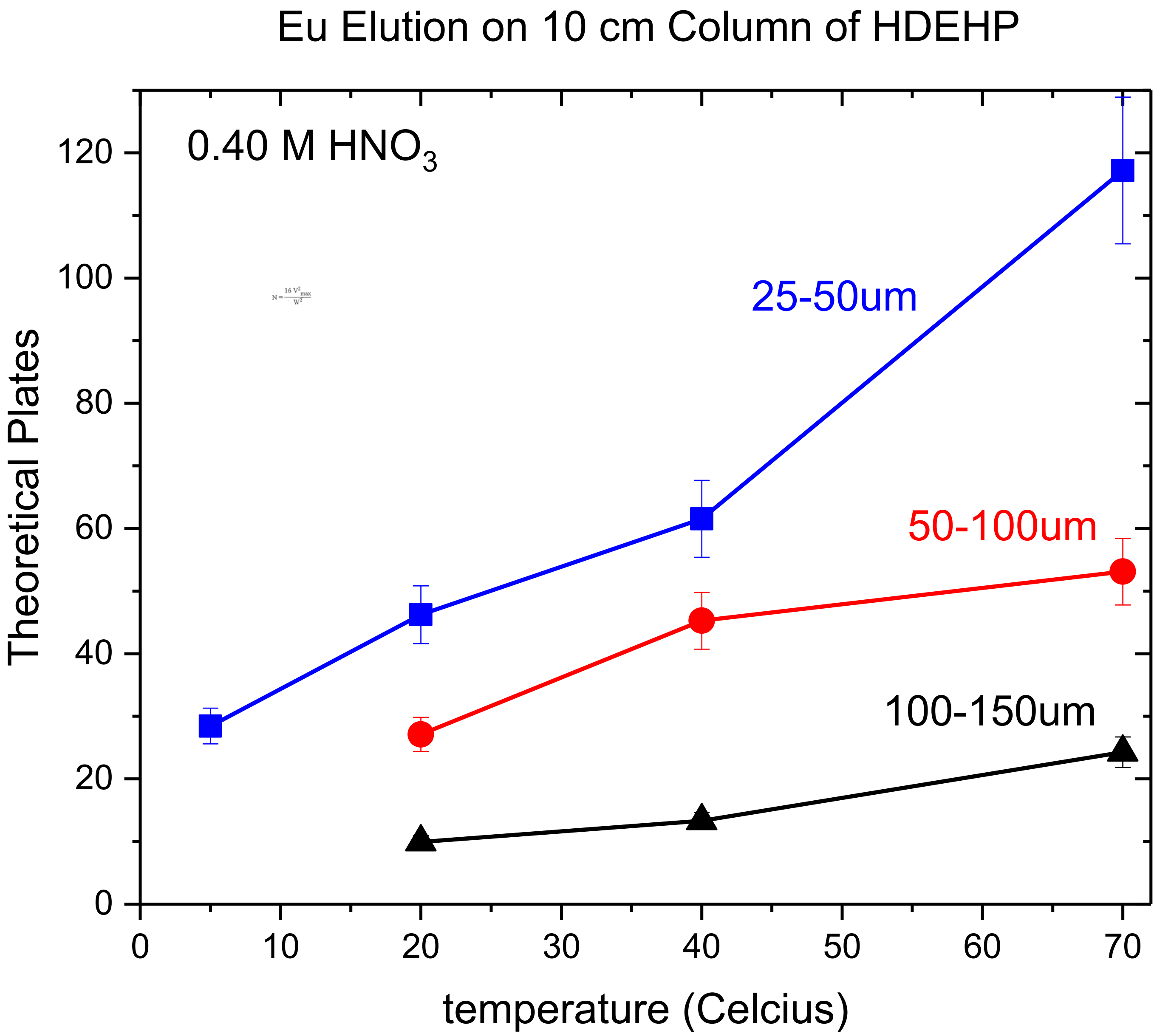


Long
Narrow
Larger particle size
Gravity flow



Shorter
Fat
Smaller particle size
Vacuum flow

Efficiency vs Particle Size/Temperature



Best resolution (good chromatography)***

Long, narrow column*	*will increase back pressure
Small uniform particle size*	*will increase back pressure
Spherical resin particles	
Non-porous**	**will decrease capacity
Elevated temperature	
Low column loading (<1-2%)	

***If you have high k’ (capacity factors) and α (separation factors) you don’t necessarily need good chromatography.

Summary

Precipitations	- concentration - matrix removal - alpha spectrometry sources
Solvent Extraction	- large scale separations - extractant purification - extractant/system characterization
Chromatography	- analytical / preparative scale separations - high resolution - remote handling / automation - bonded phases vs EXC

A BRAND OF
EICHROM TECHNOLOGIES

History of Eichrom EXC resin development

- Why?
- How?

Early applications of EXC (Before Phil)

Howard, G.A., Martin, A.J.P., “The separation of C12-C18 fatty acids by Reversed-Phase Partition Chromatography,” Biochem. J., 46, 532 (1950).

Silk, M.H., Hahn, N.H., “The resolution of mixtures of C16-C24 Normal-Chain fatty acids by Reversed-Phase Partition Chromatography,” Biochem. J. 56, 406 (1954).

Wittenberg, J.B., “The separation of the C6-C12 Fatty Acids by Reversed-Phase Partition Chromatography,” Biochem. J. 65, 42 (1957).

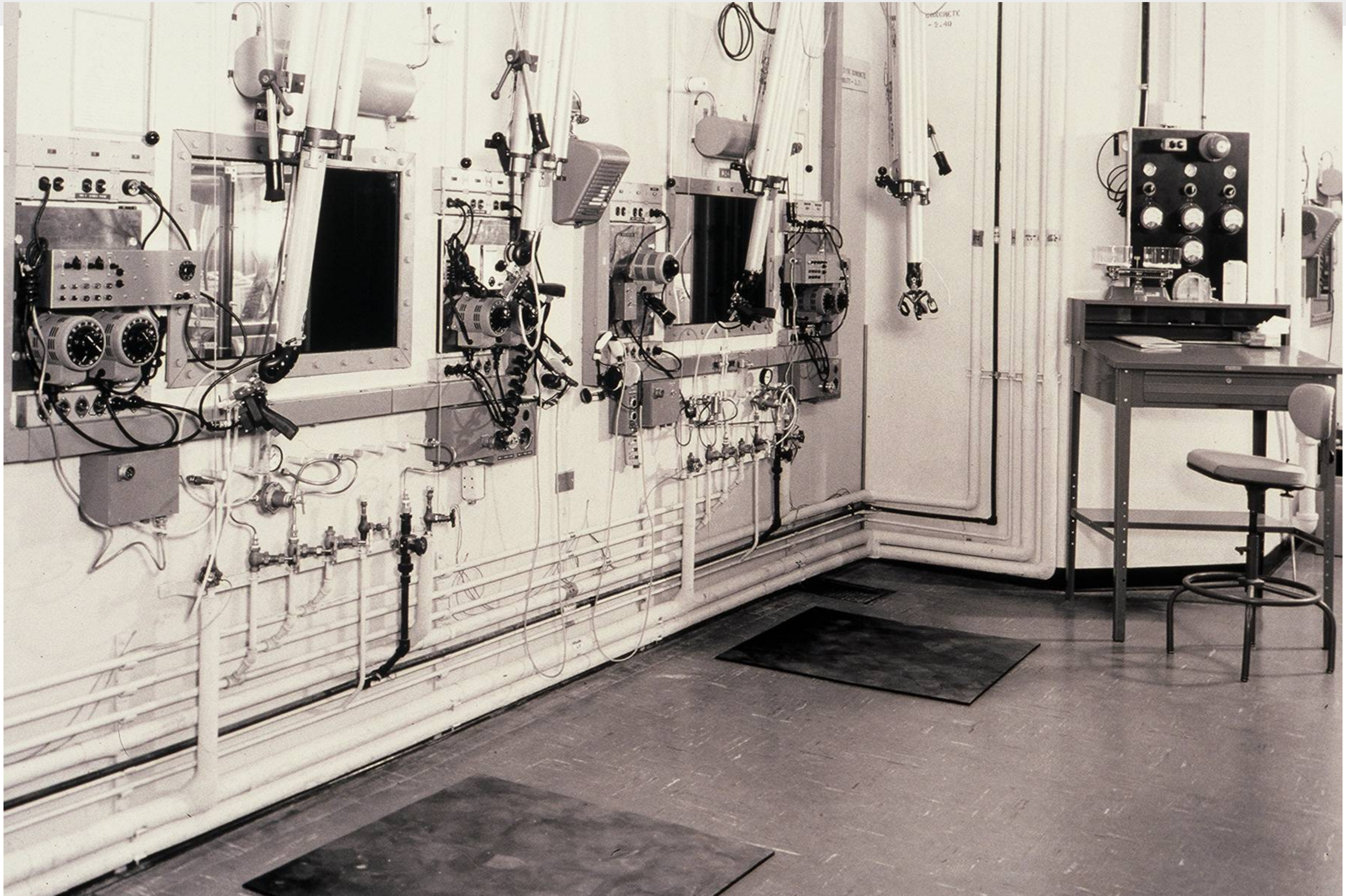
Siekierski, S., Fidelis, I., “Separation of Some Rare Earths by Reversed-Phase Partition Chromatography,” J. Chromatog. 4, 60 (1960).

Fidelis, I., and Siekierski, S., “Separation of Heavy Rare Earths by Reversed-Phase Partition Chromatography, J. Chromatog. 5, 161 (1961).

Gwozdz, R., Siekierski, S., “Separation of Various Oxidation States of Plutonium by Reversed-Phase Partition Chromatography, Nukleonika, 5, 671 (1960).

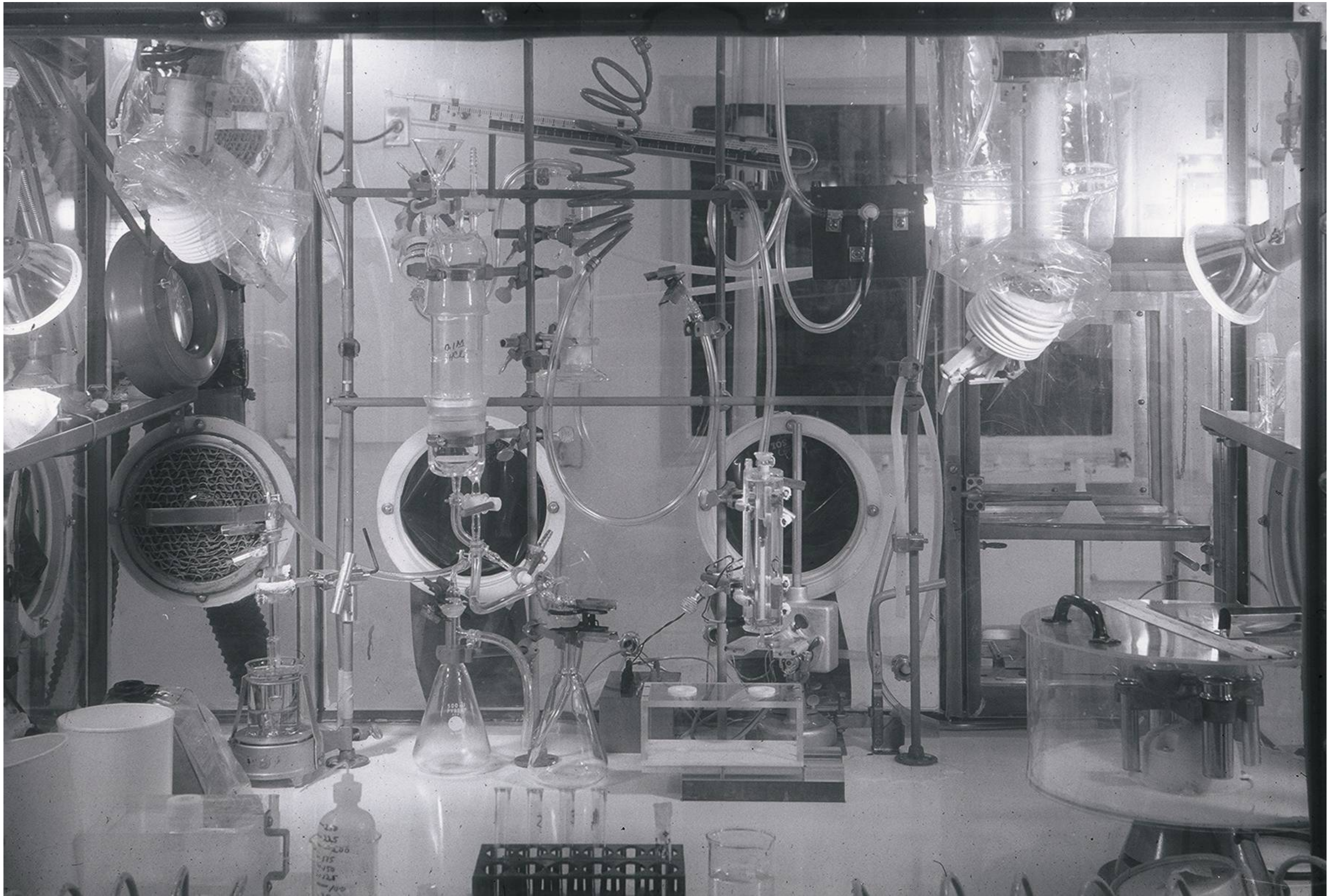
Dietrich, W.C., Caylor, J.D., Johhson, E.E., “Separation of Uranium(VI) from Urine by a Tri-n-octyl-phosphine oxide Column and an **Automation of the Procedure**,” U.S. Atomic Energy Comm. Y-1322, 1 (1960).

Why Does Eichrom Exist?



Solvent extraction was effective, but difficult to manage in a hot cell

Chromatography was easier to implement in the hot cell



Phil’s words of wisdom

“The equipment in the containment box was designed to reduce significantly the causes and spread of radioactive contamination.

The two major causes of contamination in remote-control operations, such as those described below, are in

- the handling and removal of radioactive waste and in
- the evaporation of highly radioactive solutions.”

Goals of method designs: -minimize waste
-eliminate evaporations wherever possible.

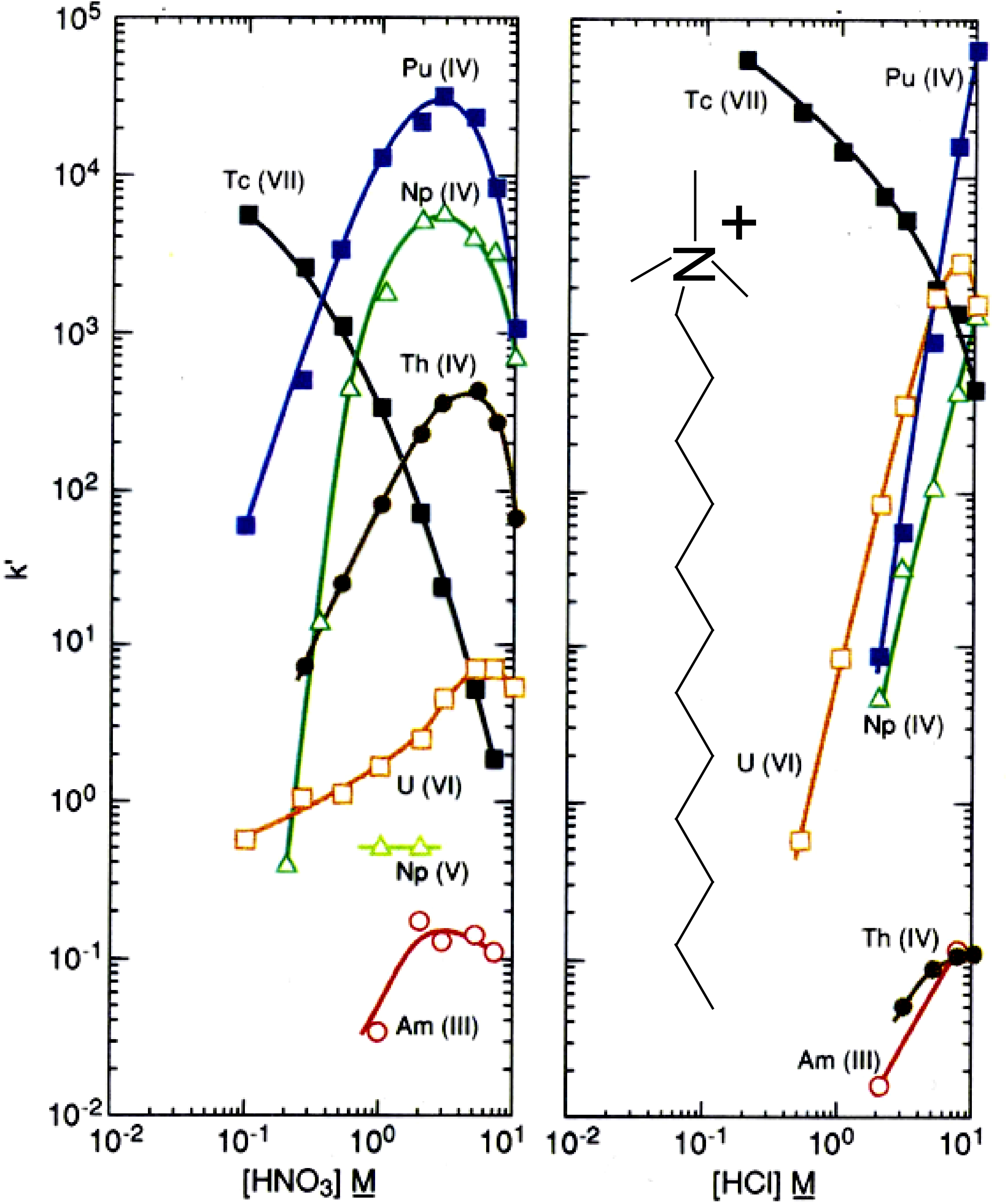
Phil’s 1st commandment of separation science:
“Thou shalt target the minor (valuable) component.”

E.P. Horwtiz, C.A.A. Bloomquist, J.A. Buzzell, H.W. Harvey, “The separation of microgram quantities of 252Cf and 248Cm by EXC in a high-level cave,” AN-7546, February, 1969.

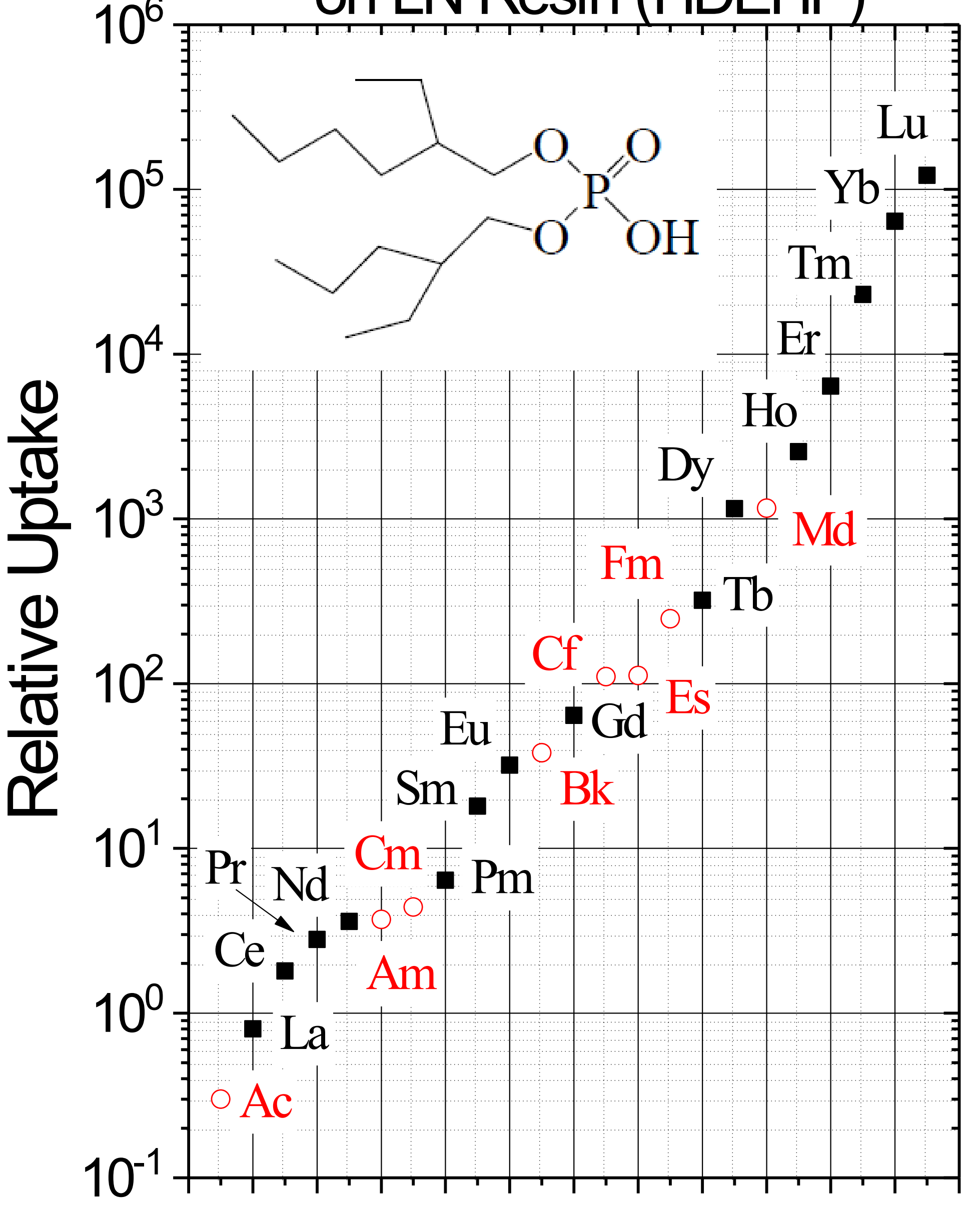
A BRAND OF
EICHROM TECHNOLOGIES

Aliquat336 – TEVA and HDEHP – LN
Cm-242 alpha sources for lunar mission
Search for new elements

Acid dependency of k' for various ions at 23°C.
TEVA Resin



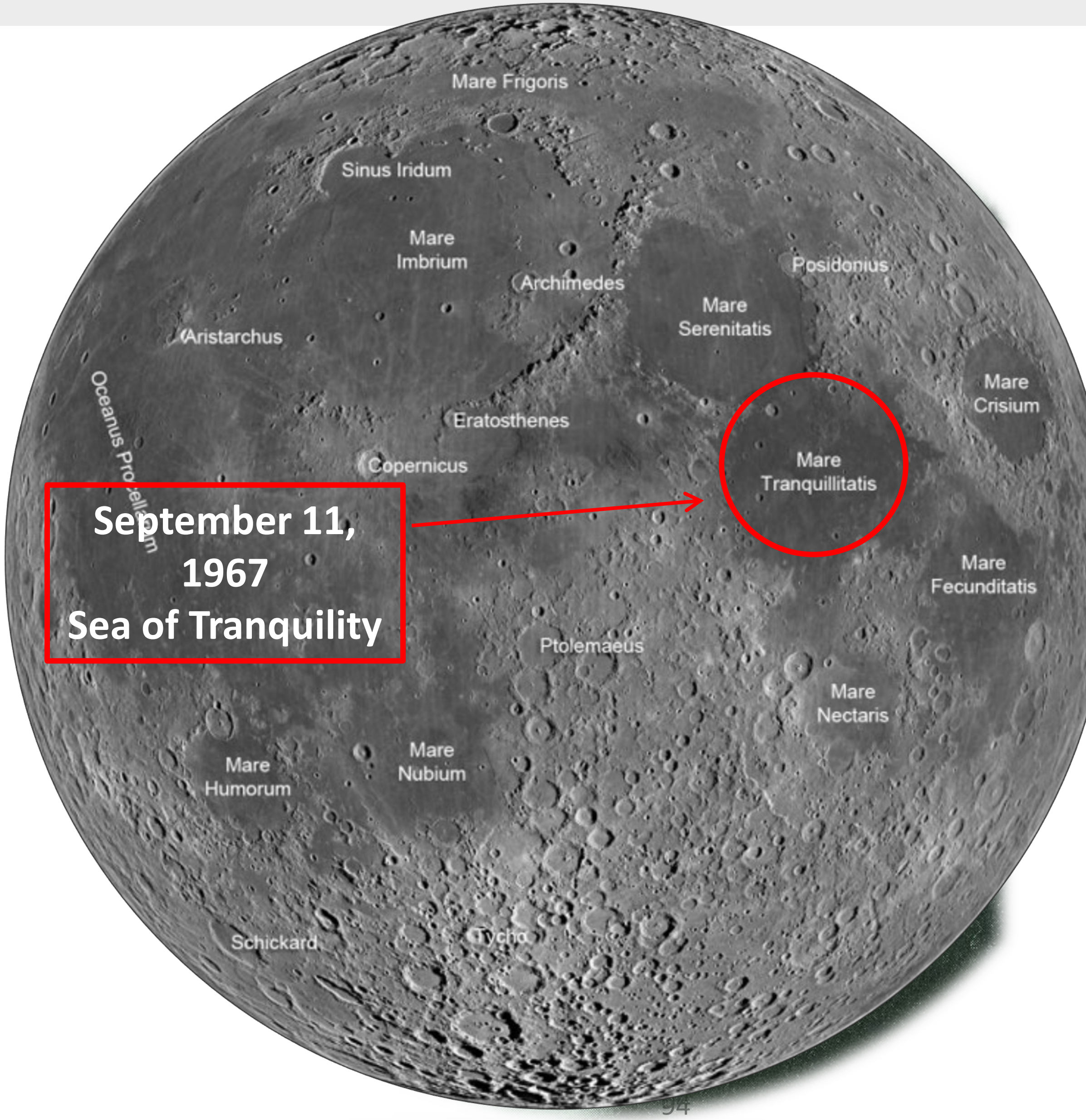
Relative Uptake of Ln(III) and An(III) on LN Resin (HDEHP)



1965-1967

High Purity ^{242}Cm Sources for Alpha Backscatter Spectroscopy (Lunar Surveyor 1-7)

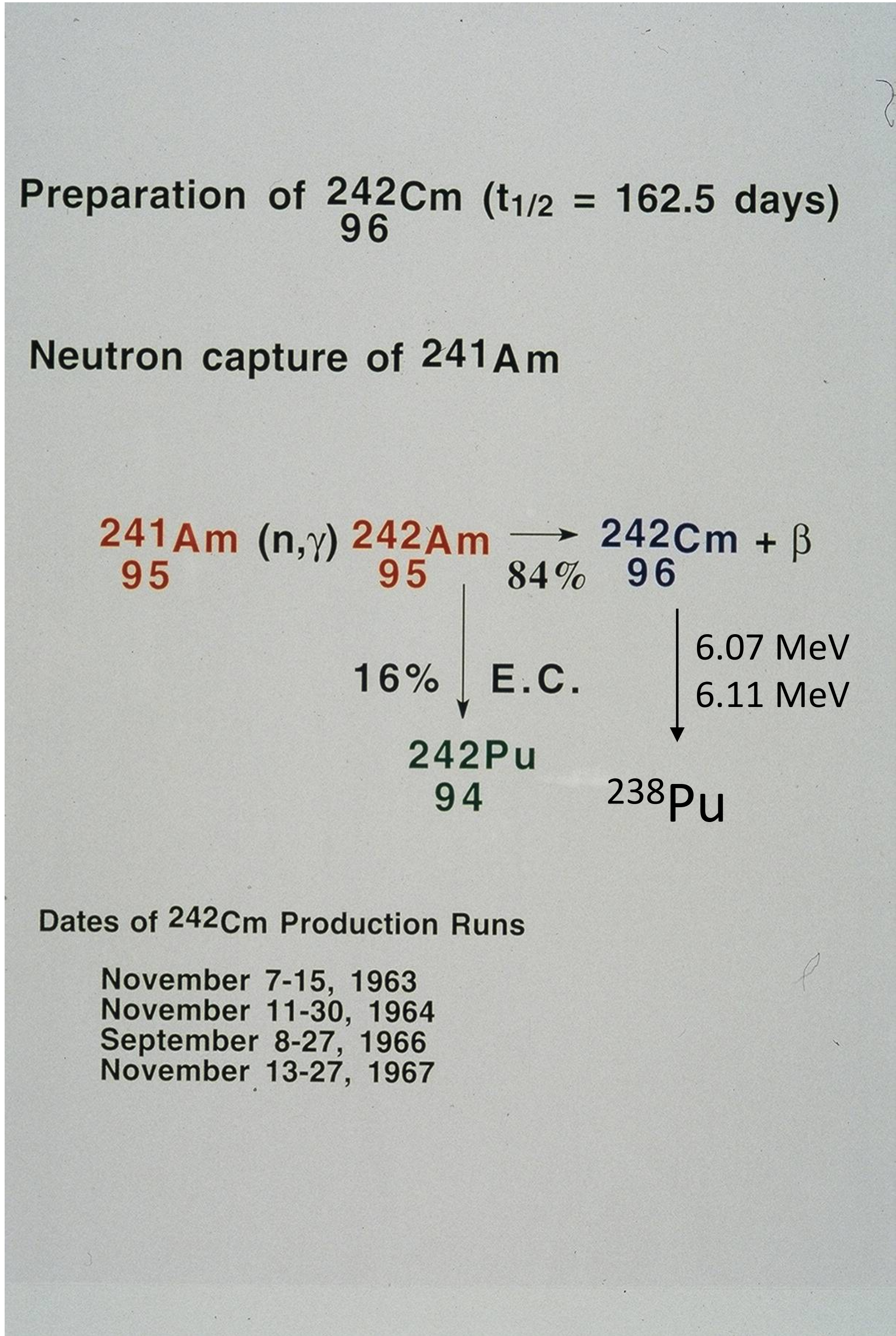
Prior to first lunar landing in July, 1969.



September 11, 1967
Sea of Tranquility

150-250-mg samples 241Am encapsulated in high-purity aluminum

E.P. Horwitz, C.A.A Bloomquist, H.W. Harvey, D. Cohen, L.J. Basile, “Purification of 10 Curies of 242Cm,” Argonne National Laboratory Report ANL-6998, February (1965).



Preparation of $^{242}_{96}$Cm ($t_{1/2}$ = 162.5 days)

Neutron capture of ^{241}Am

$$\begin{tikzcd} {}^{241}_{95}\text{Am}\ (n,\gamma)\ {}^{242}_{95}\text{Am} \arrow[r, "84\%"'] \arrow[d, "16\%"', "\text{E.C.}"] & {}^{242}_{96}\text{Cm} + \beta \arrow[d, "\begin{array}{c}6.07\text{ MeV}\\6.11\text{ MeV}\end{array}"] \\ {}^{242}_{94}\text{Pu} & {}^{238}\text{Pu} \end{tikzcd}$$

Dates of ^{242}Cm Production Runs

November 7-15, 1963
November 11-30, 1964
September 8-27, 1966
November 13-27, 1967

Cm-242 (Original Chemistry) 1965

Am/Cm from Al and byproducts

-35 mg ^{241}Am, 3 mg ^{242}Cm in aluminum capsule

-Dissolve in NaOH/NaNO$_3$

-**Fe(OH)$_3$ ppt** (carries Am/Cm)

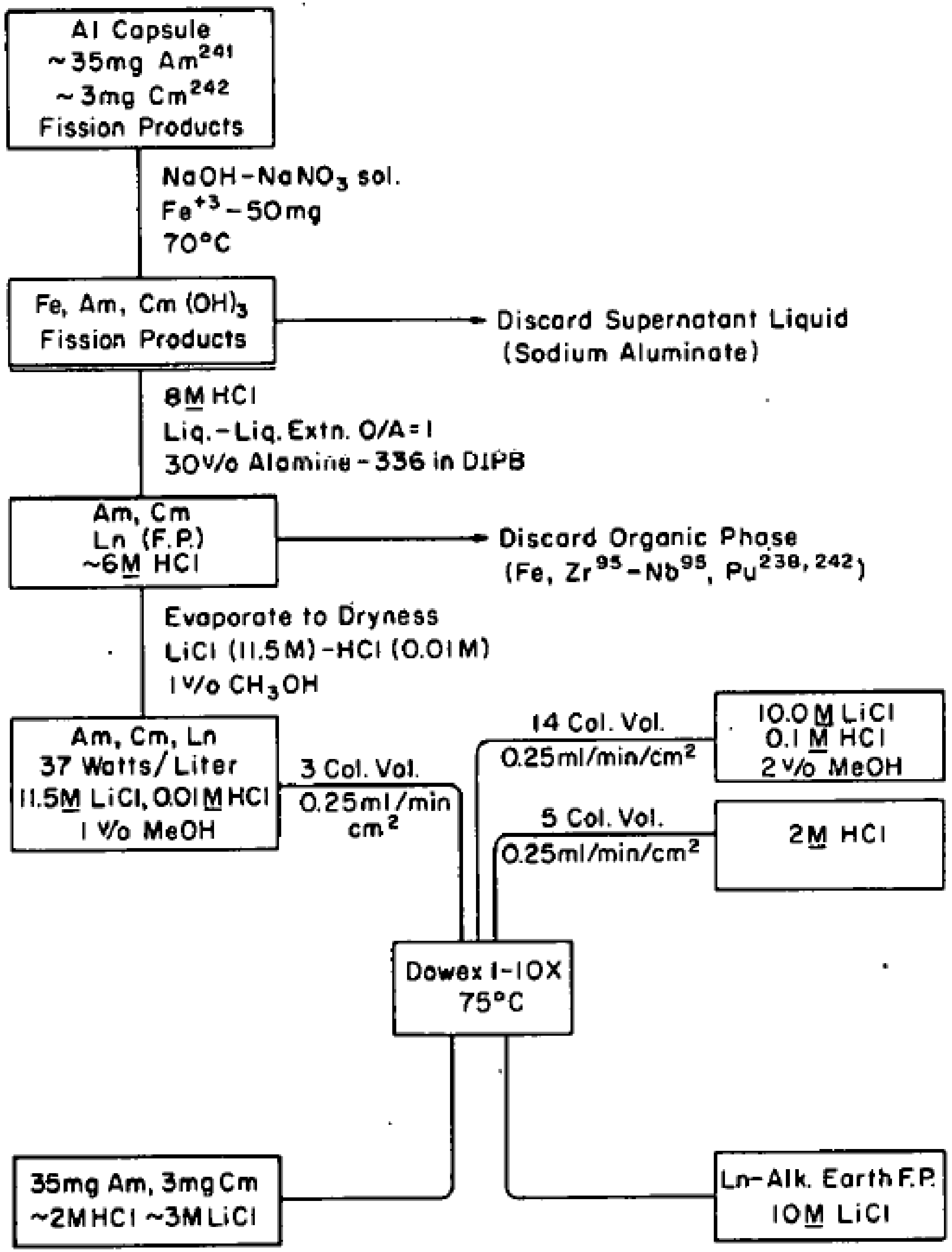
-Dissolve in 8M HCl

-**SX** with **30% alamine 336** (extracts Fe, Zr, Nb, Pu)

-Evaporate, dissolve in 11.5M LiCl-0.01M HCl.

-**Anion exchange** separation (removes rare earths/F.P.)

E.P. Horwitz, C.A.A. Bloomquist, H.W. Harvey, D. Cohen, L.J. Basile, "The purification of 10 Curies of 242Cm," ANL-6998, February 1965



Cm-242 (Original Chemistry) 1965

Cm from Am

-35 mg ^{241}Am, 3 mg ^{242}Cm in 2M HCl-3M LiCl

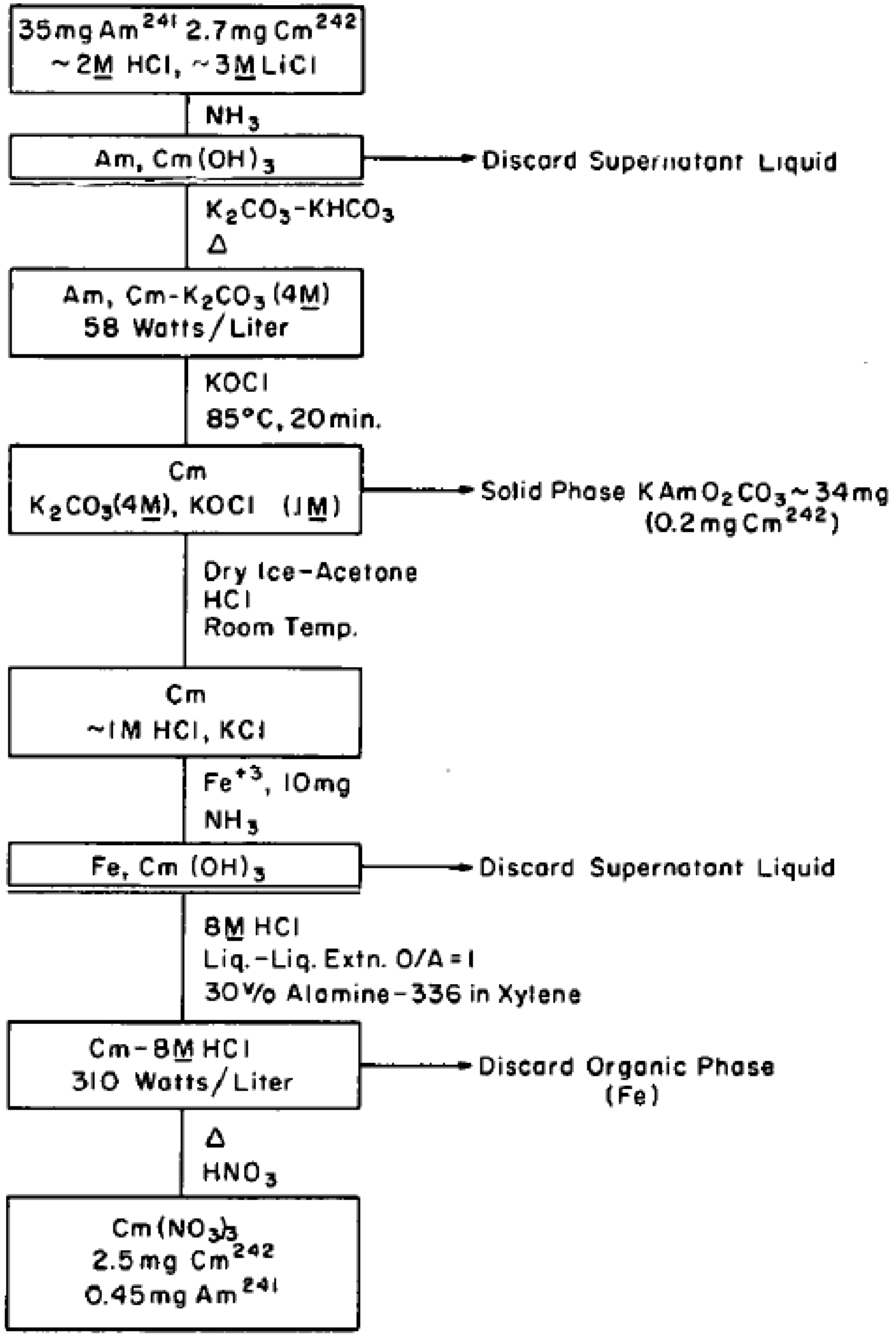
-**Precipitate Am/Cm(OH)$_3$** by adding ammonia.

-Add K_2CO_3-$KHCO_3$. Oxidize to Am(V) with KOCl.

-**Precipitate** $KAm_2O_2CO_3$ **(Am(V) carbonate).**

-Add 1M HCl, KCl, 10 mg Fe, NH_3.

-**Precipitate Fe(OH)$_3$**, carries Cm.
-Dissolve in 8M HCl. **S.X.** with **alamine 336** (Fe removal).
-HNO_3 metathesis. 2.5 mg ^{242}Cm + 0.45 mg ^{241}Am.



Cm-242 (Improved Chemistry) 1969

Am/Cm from Al and byproducts

-222 mg ^{241}Am, 8 mg ^{242}Cm in Al capsule.

-Dissolve in HNO_3 + Hg^{2+}.

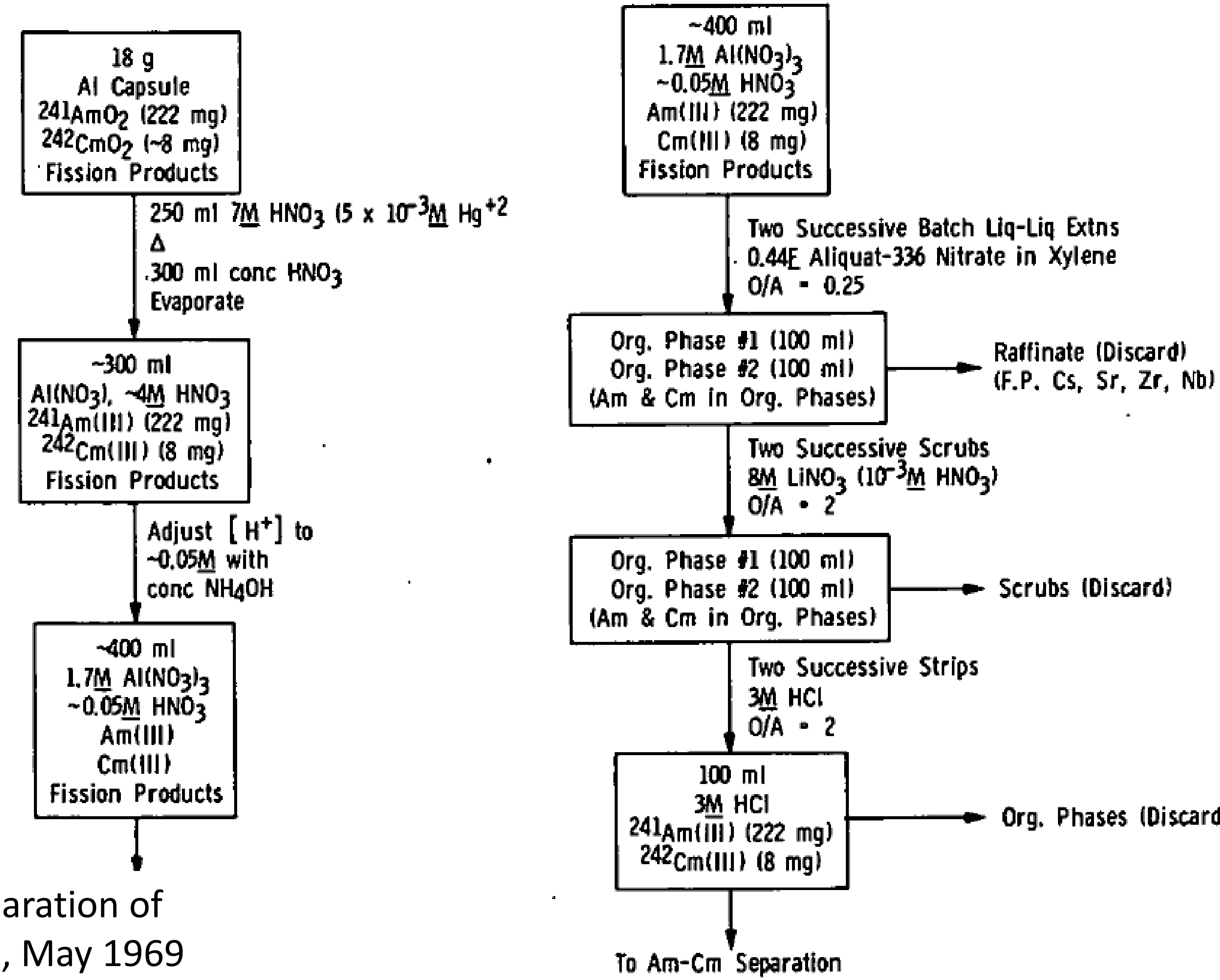
-Evaporate. Dissolve in HNO_3. $Al(NO_3)_3$.

-Dissolve in 8M HCl.

-**SX** with **0.44% aliquat 336** (extracts Am, Cm).

Target Minor Components (222 mg Am/8 mg Cm)

-Recover Am/Cm in 3M HCl.



E.P. Horwitz, C.A.A. Bloomquist, H.E. Griifin, "The preparation of high purity 242Cm in multicurie quantities," ANL-7569, May 1969

Cm-242 (Improved Chemistry) 1969

Cm from Am (Part 1)

-222 mg ^{241}Am, 8 mg ^{242}Cm in 3M HCl.

-**Precipitate Am/Cm(OH)$_3$** by adding ammonia + 5mg La.

-Add K_2CO_3-$KHCO_3$. Oxidize to Am(V) with NaOCl.

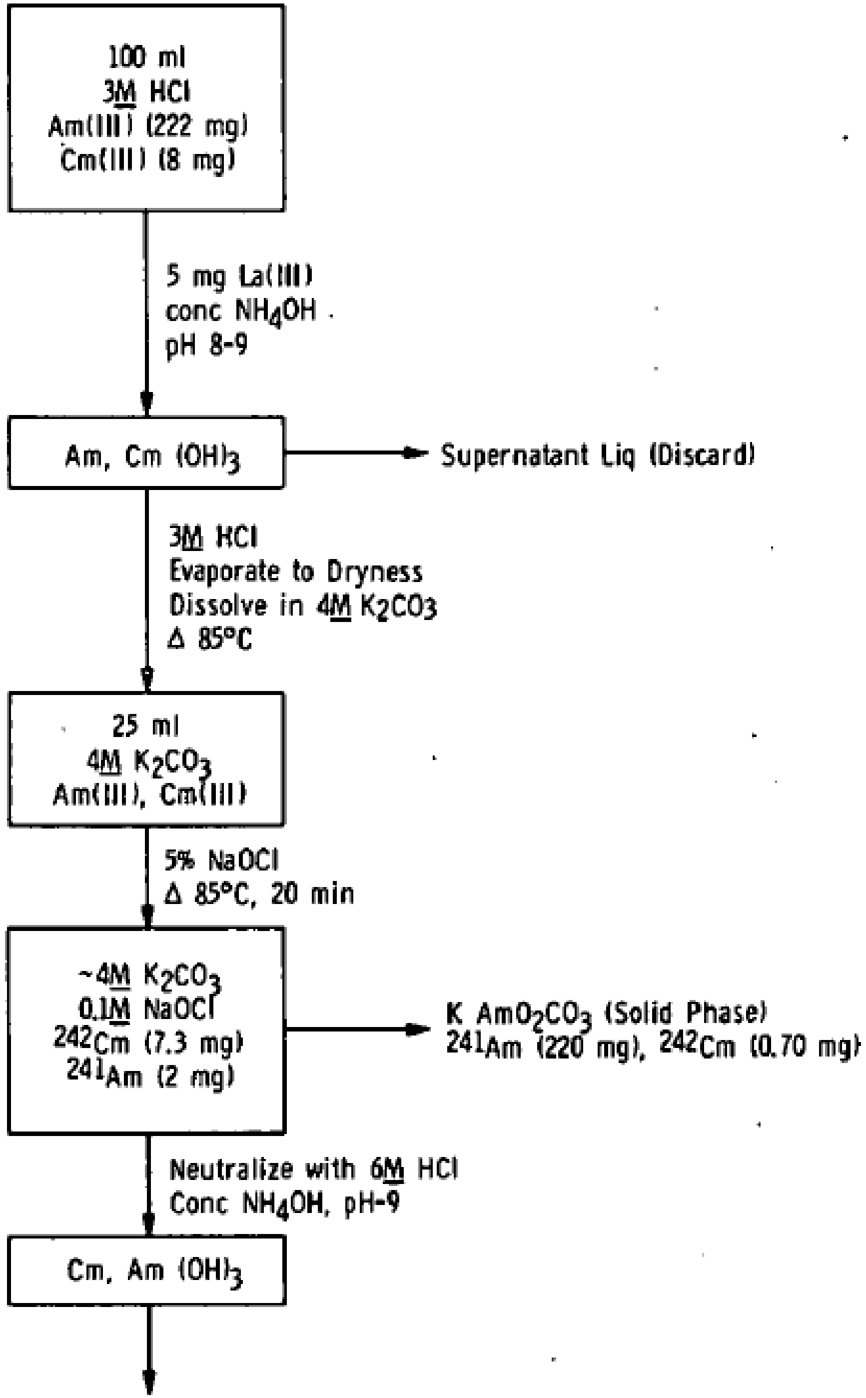
-**Precipitate** $KAm_2O_2CO_3$ **(Am(V) carbonate).**

-Add 1M HCl, KCl, 10 mg Fe, NH_3.

-Dissolve in 6M HCl.

-Neutralize to pH 9 with NH_4OH.

- Precipitate Cm/Am(OH)$_3$: 7.3mg ^{242}Cm + 2 mg ^{241}Am.

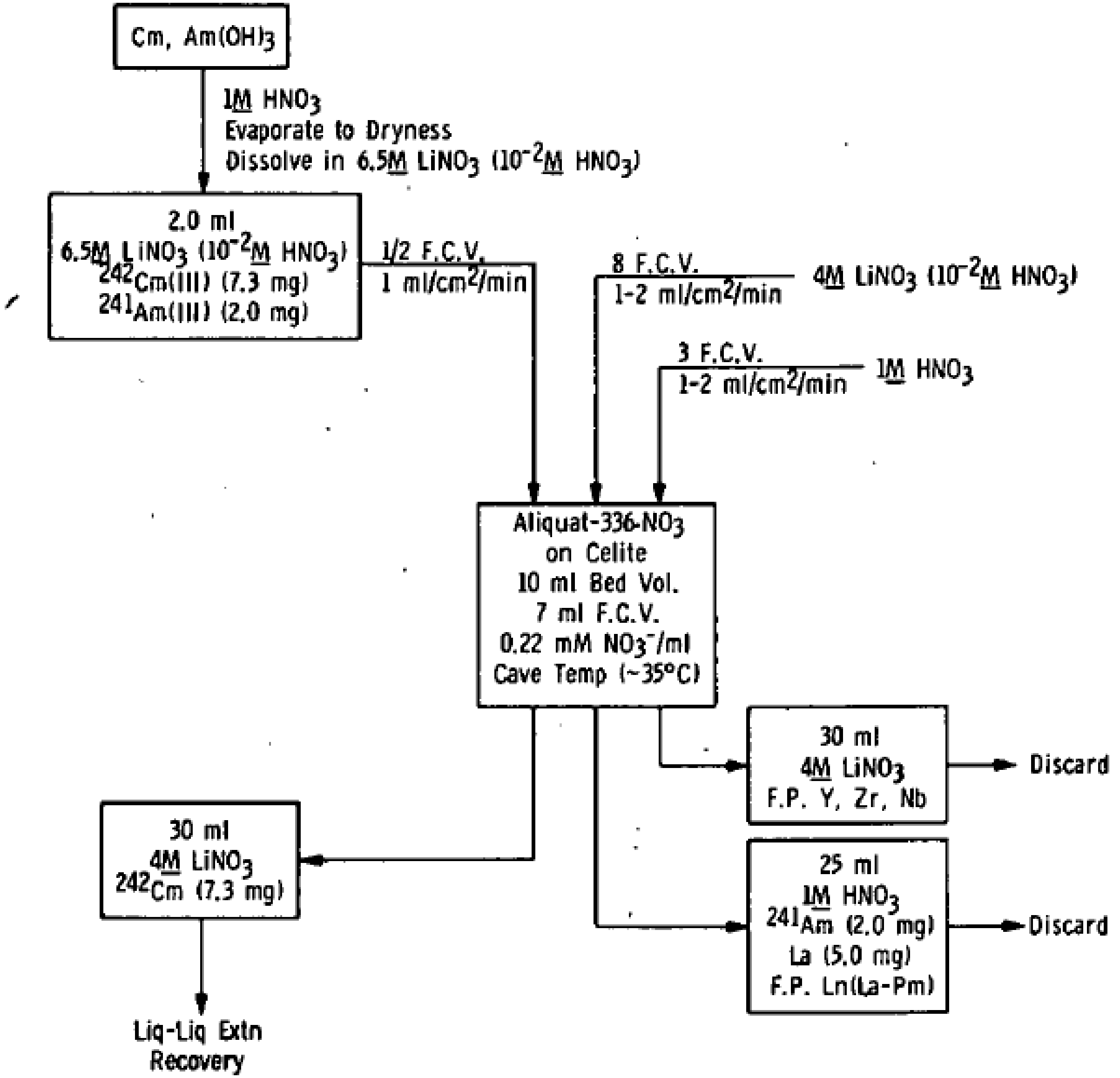


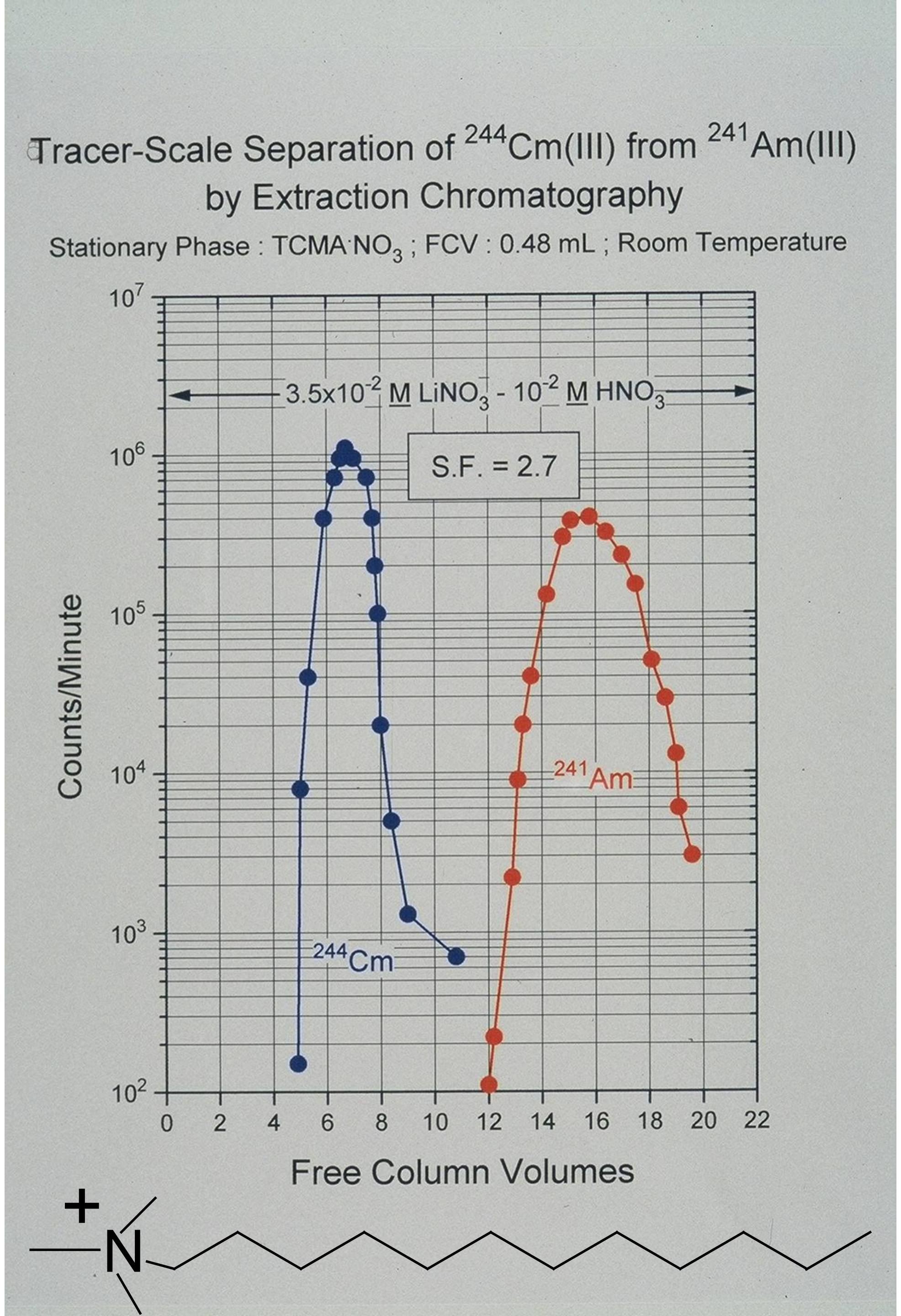
Cm-242 (Improved Chemistry) 1969

Cm from Am (Part 2)

-Add HNO_3. Evaporate to dryness.
-Dissolve in 6M $LiNO_3$-0.01M HNO_3.
-**EXC** on **TEVA**.
-Recover 7.3 mg Cm in 4M $LiNO_3$-0.01M HNO_3.

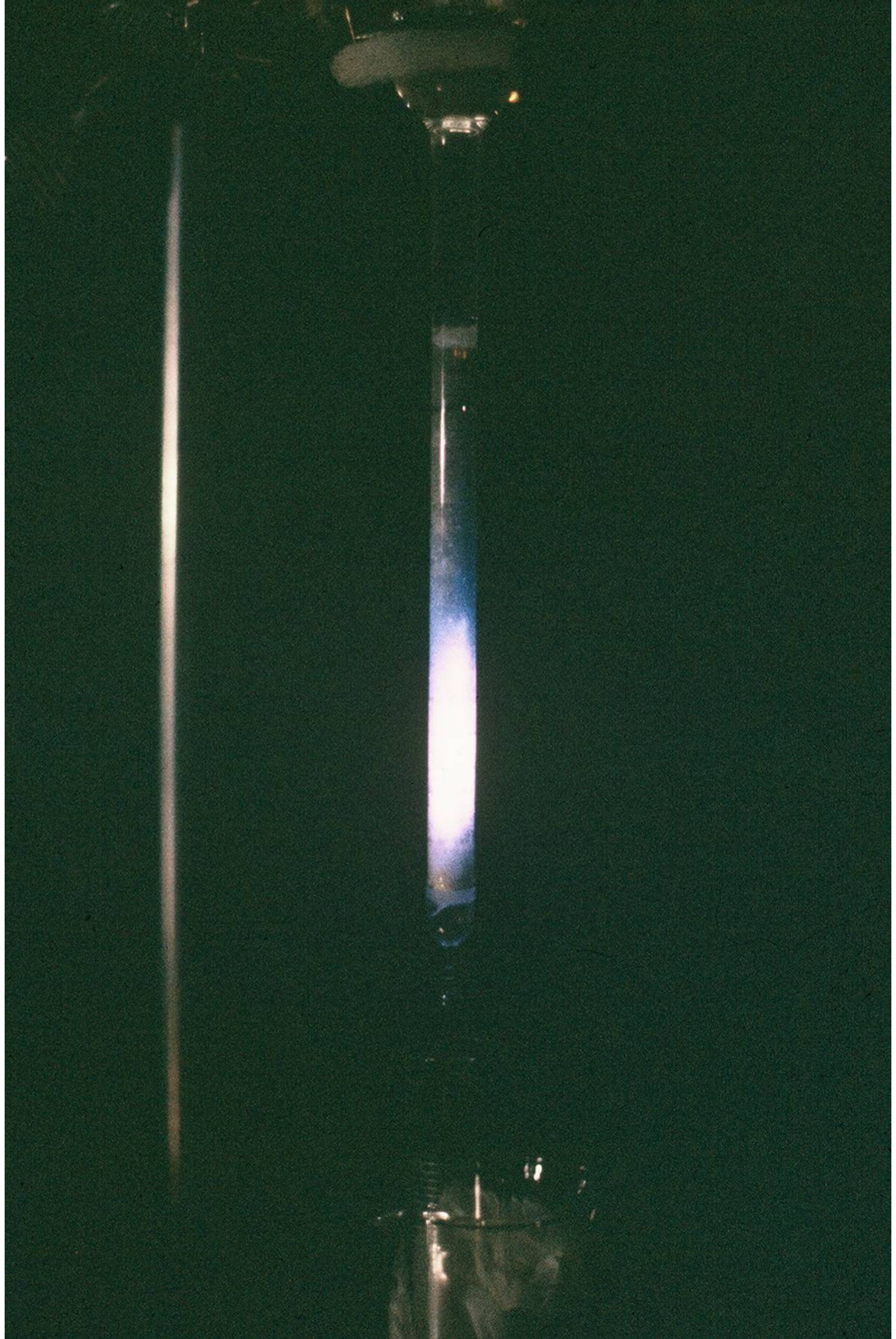
“The intense alpha activity of the ^{242}Cm produced noticeable gas pockets in the column throughout the entire path of the curium band and caused a change in the color of the column from light cream to a light gray.”





Tracer-Scale Separation of ^{244}Cm(III) from ^{241}Am(III) by Extraction Chromatography

Stationary Phase : TCMA·NO_3 ; FCV : 0.48 mL ; Room Temperature



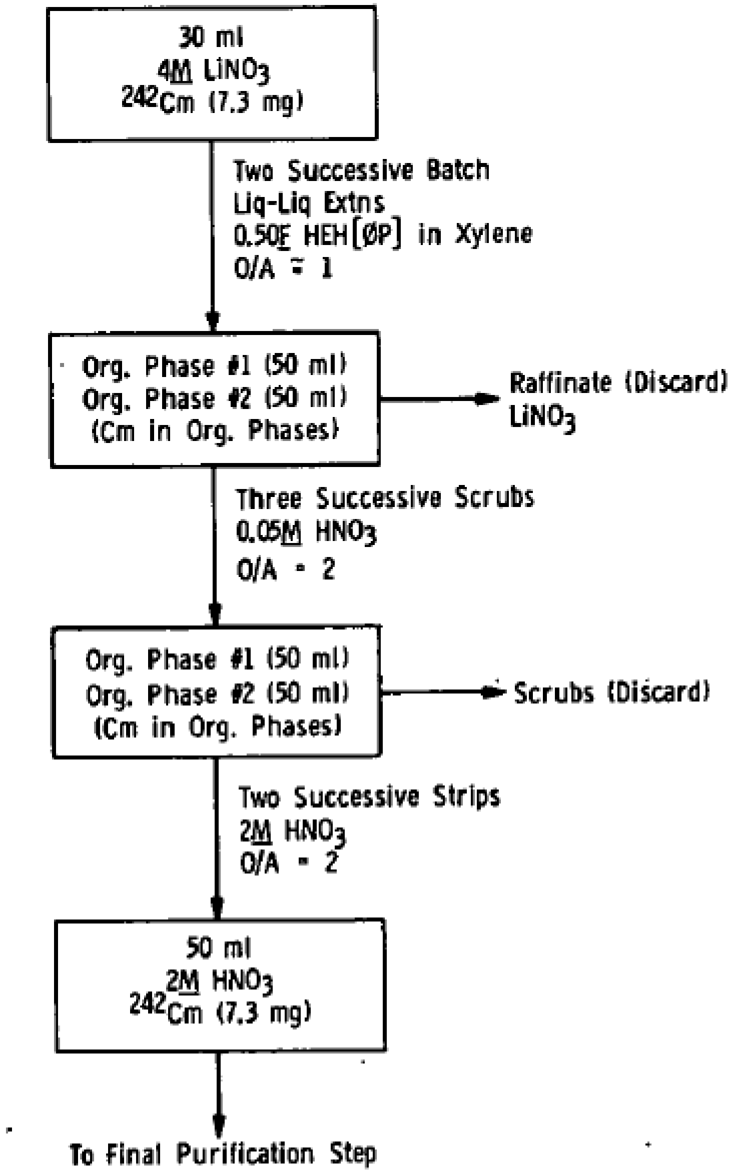
Cm-242 (Improved Chemistry) 1969

Final Purification (Part 1)

-**SX** with **HEH[ΦP]** in o-xylene.

-Scrub with 0.05M HNO_3 to remove Li^+.

-Recover ^{242}Cm with 2M HNO_3.



Cm-242 (Improved Chemistry) 1969

Final Purification (Part 2)

-Evaporate to dryness.

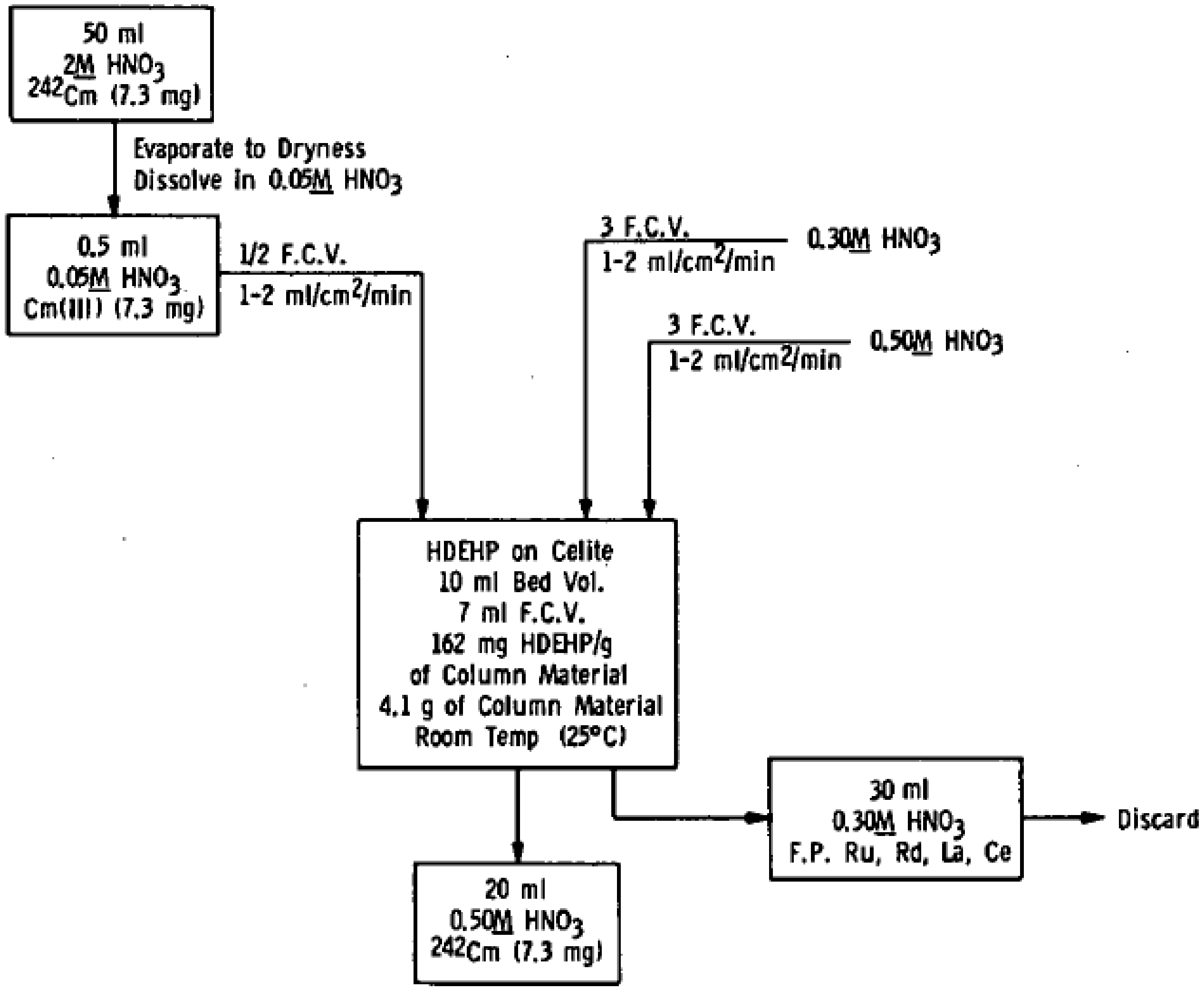
-Dissolve in 0.05M HNO_3.

-**EXC** on **LN Resin**.

- -Additional removal of Li, Na, Ca
- -Additional removal of F.P. (Ru, Rh, La, Ce)

-Recover ^{242}Cm in 0.50M HNO_3.

>90% recovery of ^{242}Cm, <100 ppm ^{241}Am.

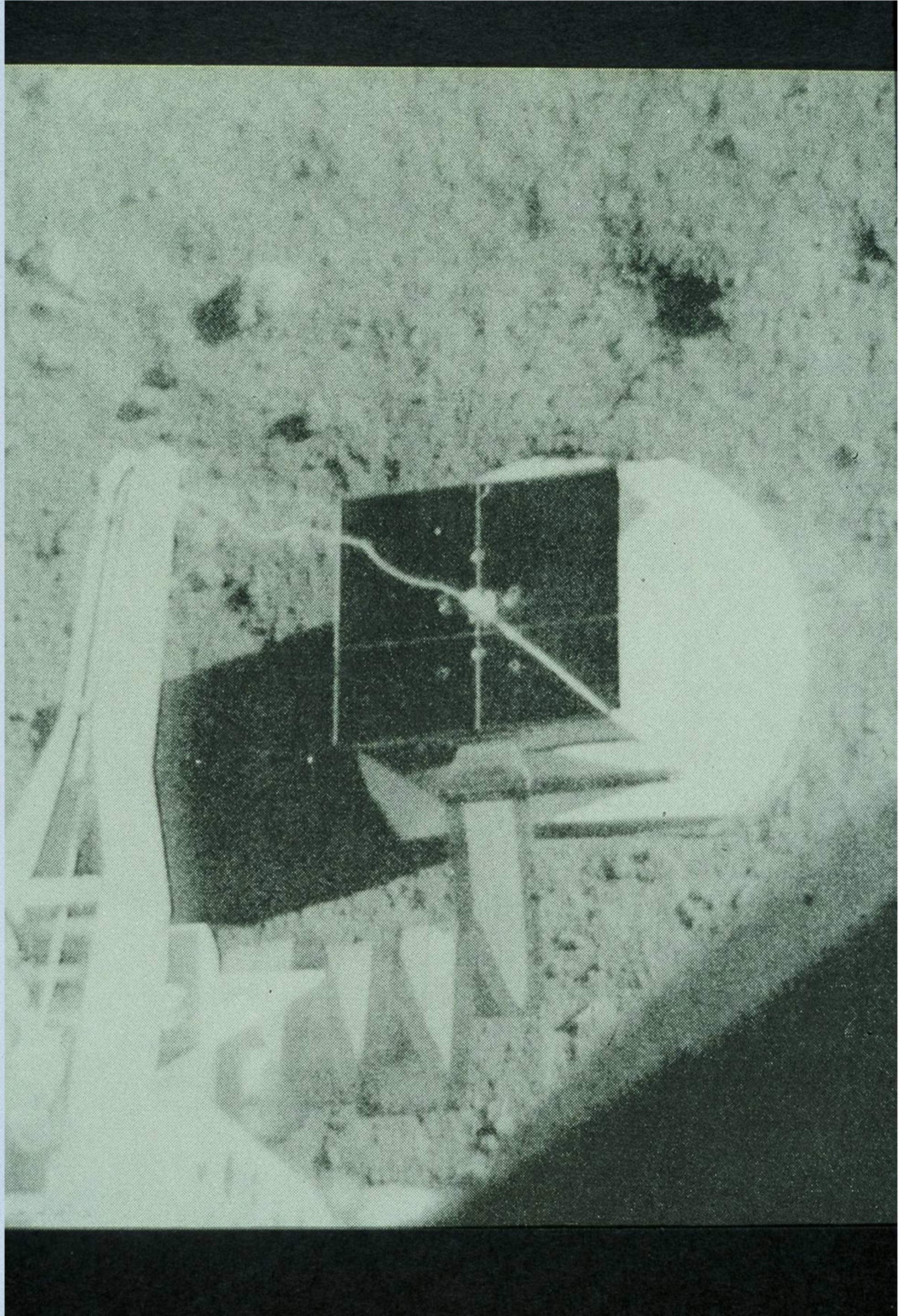


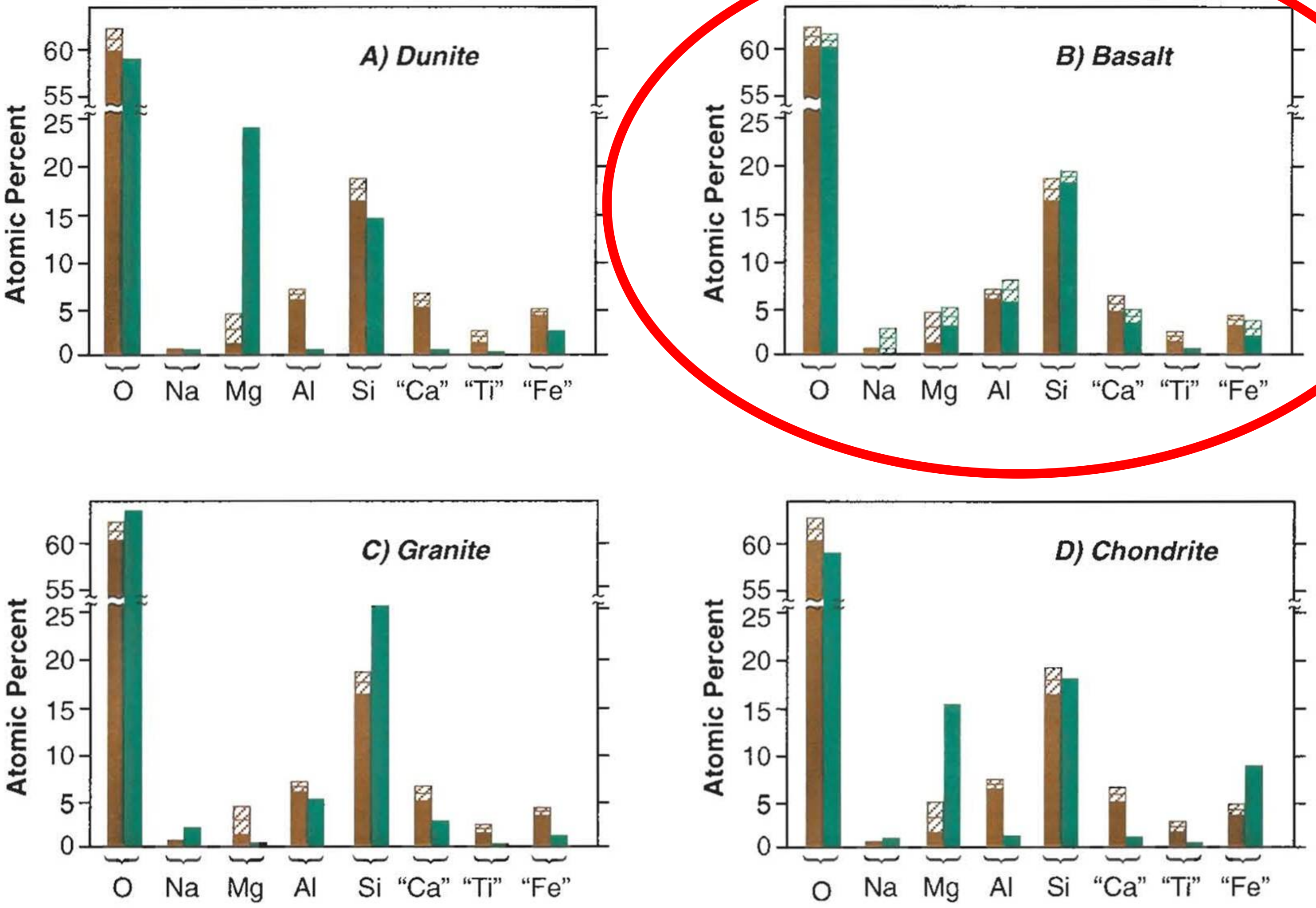
Purity of ^{242}Cm for Use in NASA Surveyor Lunar Program 1963 – 1967

7 – 8 mg ^{242}Cm Stock
(23 to 26 curies)

Fission Products > 10^6 decontamination
Na, Ca, Al and Fe < 0.1 wt. %
Am ~ 100 ppm

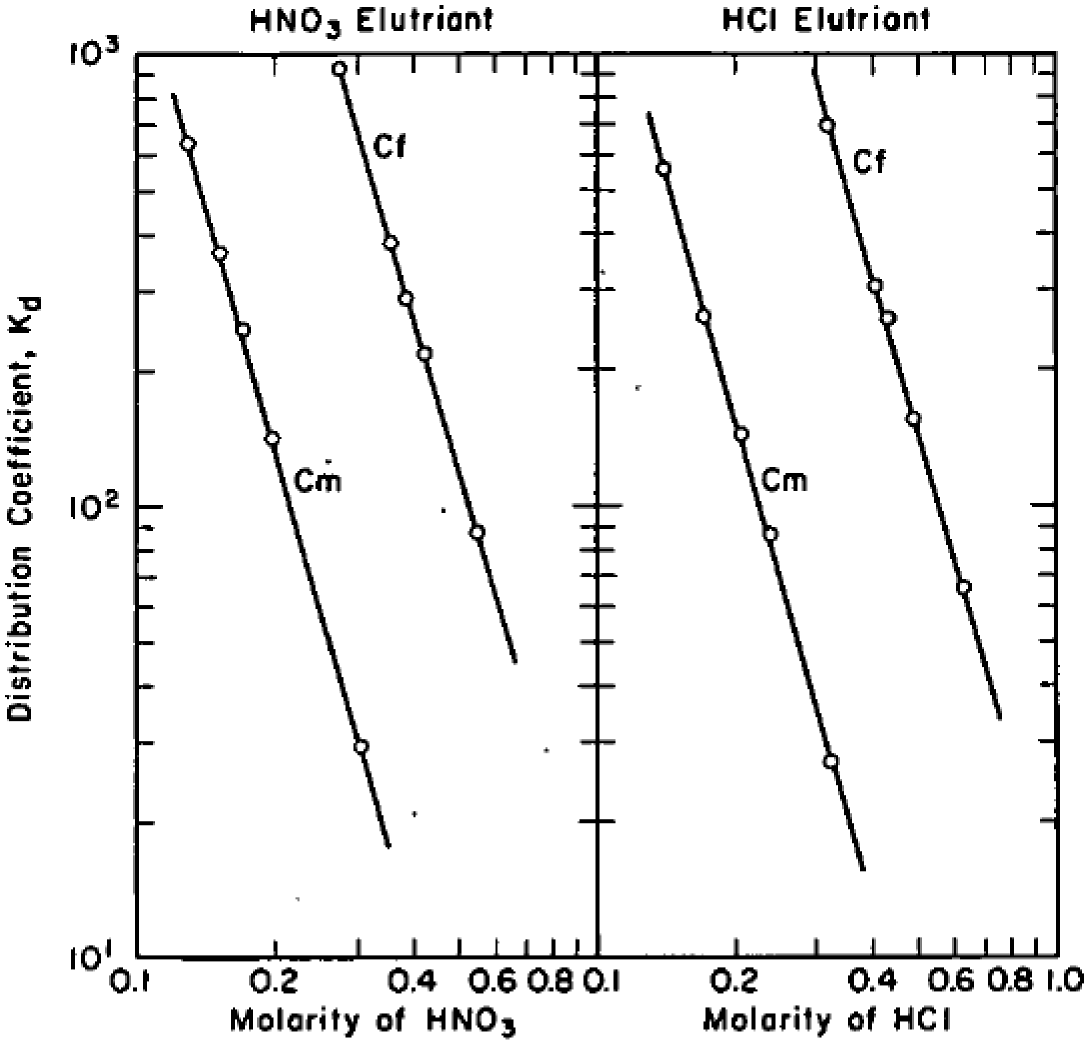
Alpha activity ratio ^{242}Cm / ^{241}Am = 10^7



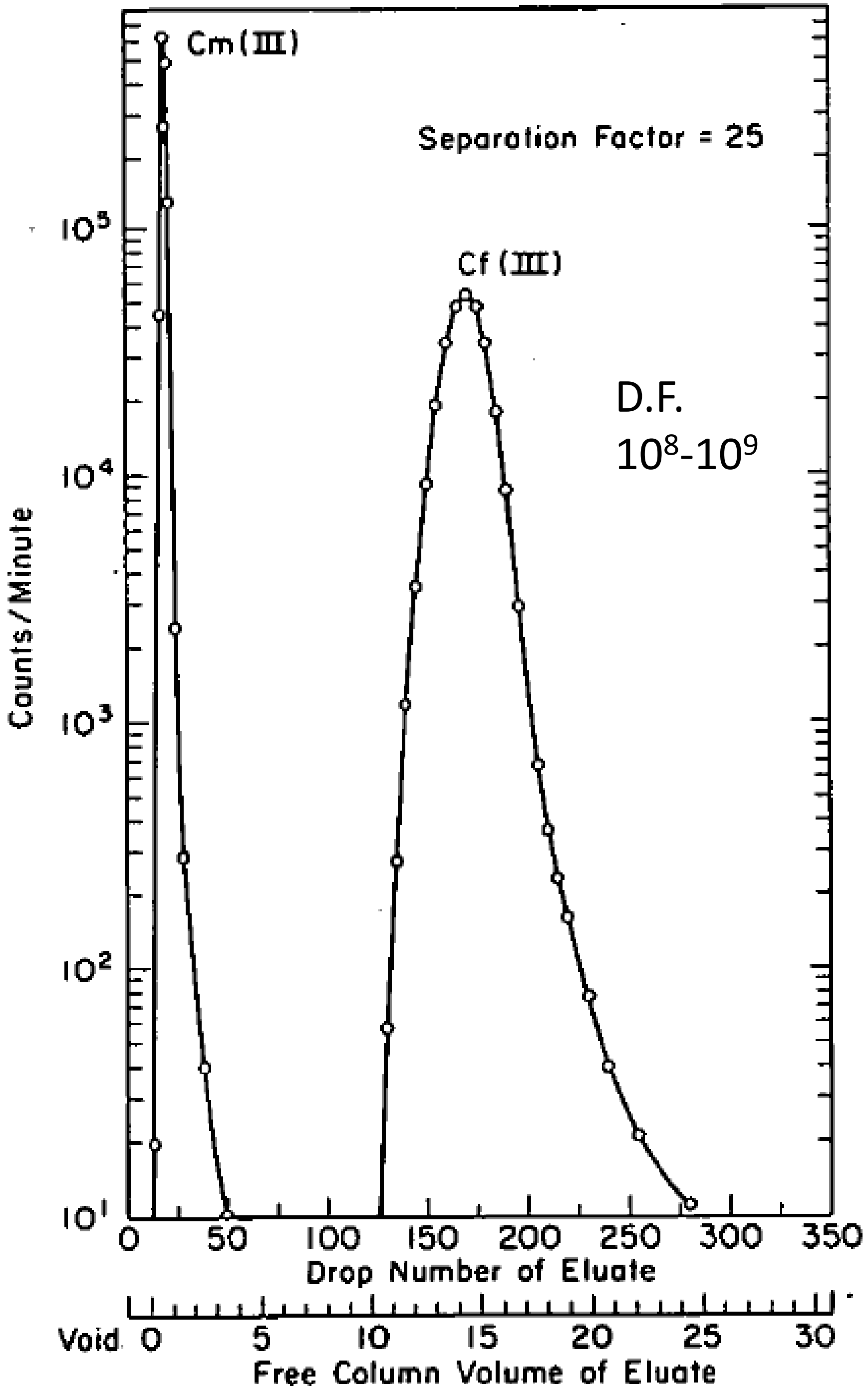


Comparison of the Observed Chemical Composition of the Lunar Sample (Brown Bars) with the Average Composition of Selected Materials (Green Bars)

Separation of micrograms of ^{248}Cm from 100s of micrograms of ^{252}Cf on LN Resin.



E.P. Horwtiz, C.A.A. Bloomquist, J.A. Buzzell, H.W. Harvey, “The separation of microgram quantities of 252Cf and 248Cm by EXC in a high-level cave,” AN-7546, February, 1969.



D.F.
10^8-10^9

1969-1972

Search for new elements

-Underground Nuclear Detonations

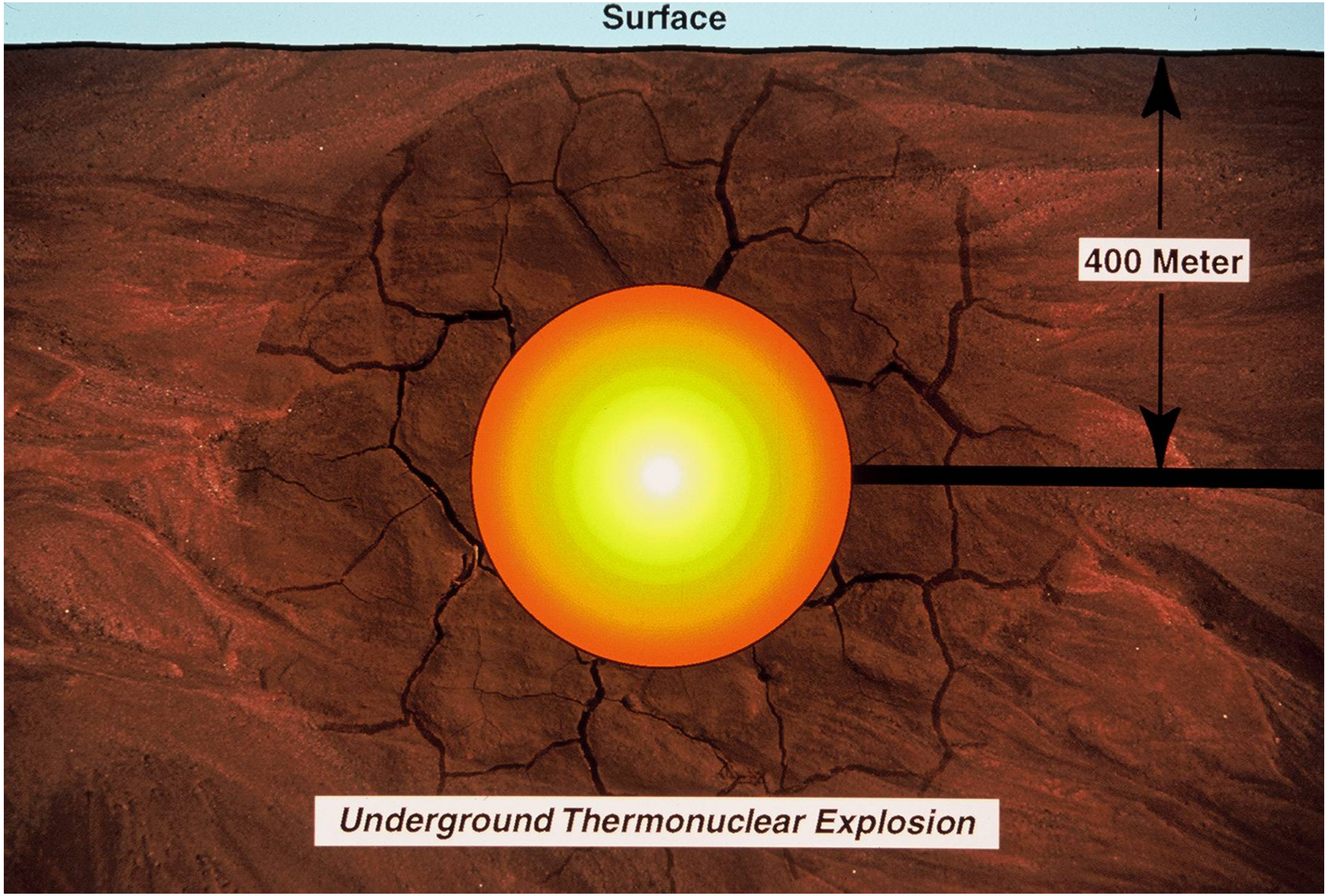
-Uranium and Tungsten Beamstops

in high energy proton accelerators

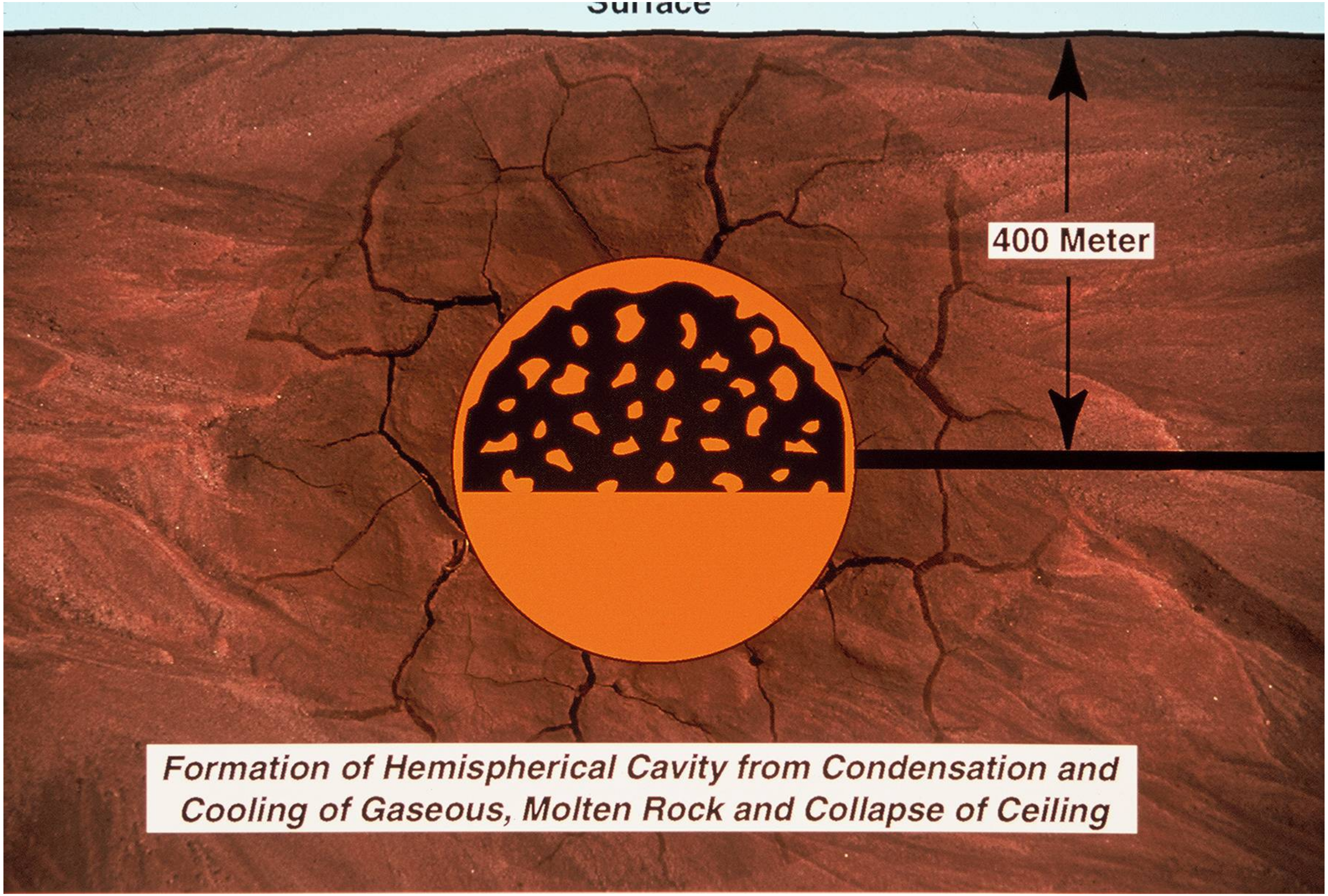
Island of Stability: Half-Lives are predicted to be longer than 1 year for

Z = 110-114 (Ds, Rg, Cn, Nh, Fl)

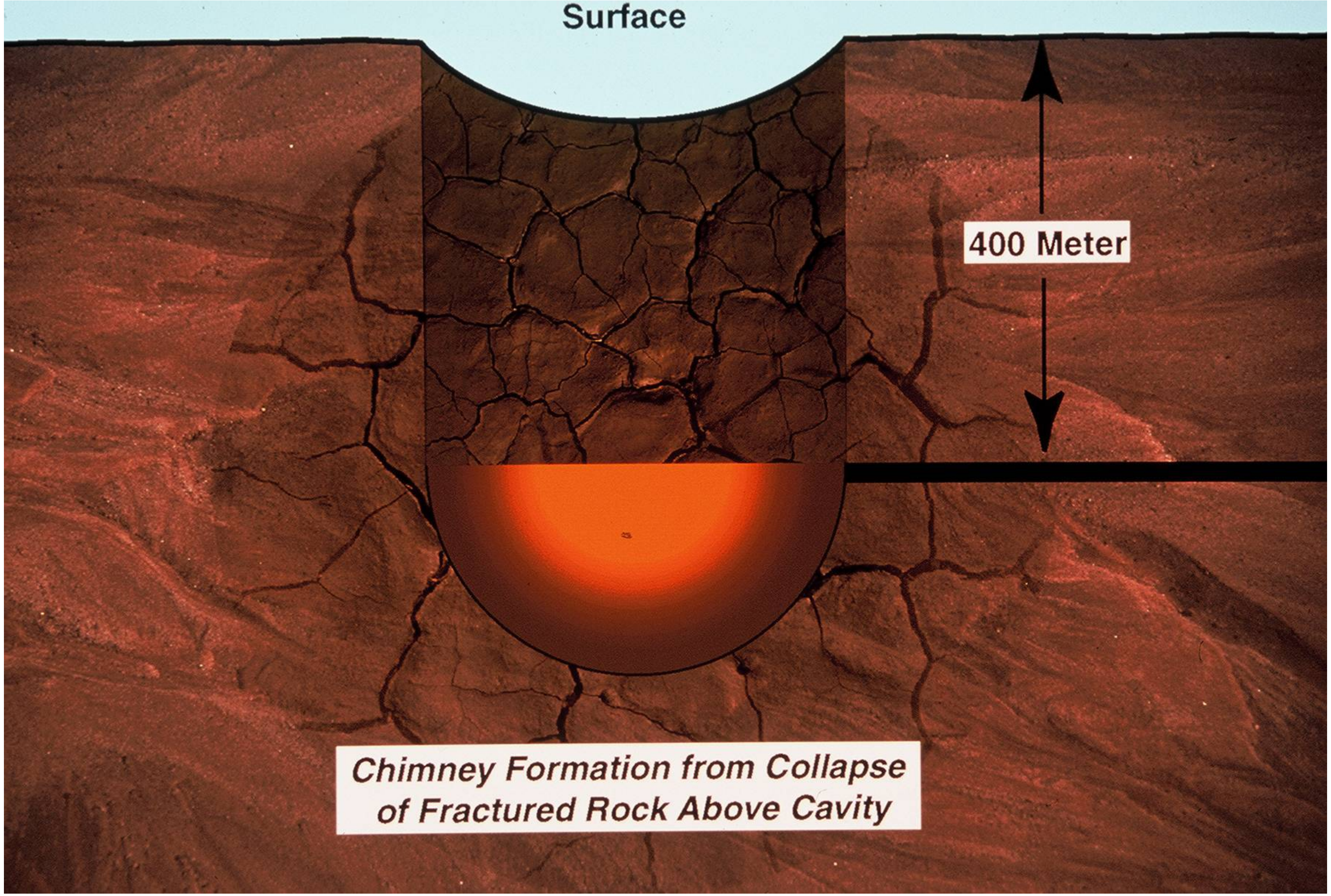
N = 180-184 (Isotopes 290-298)



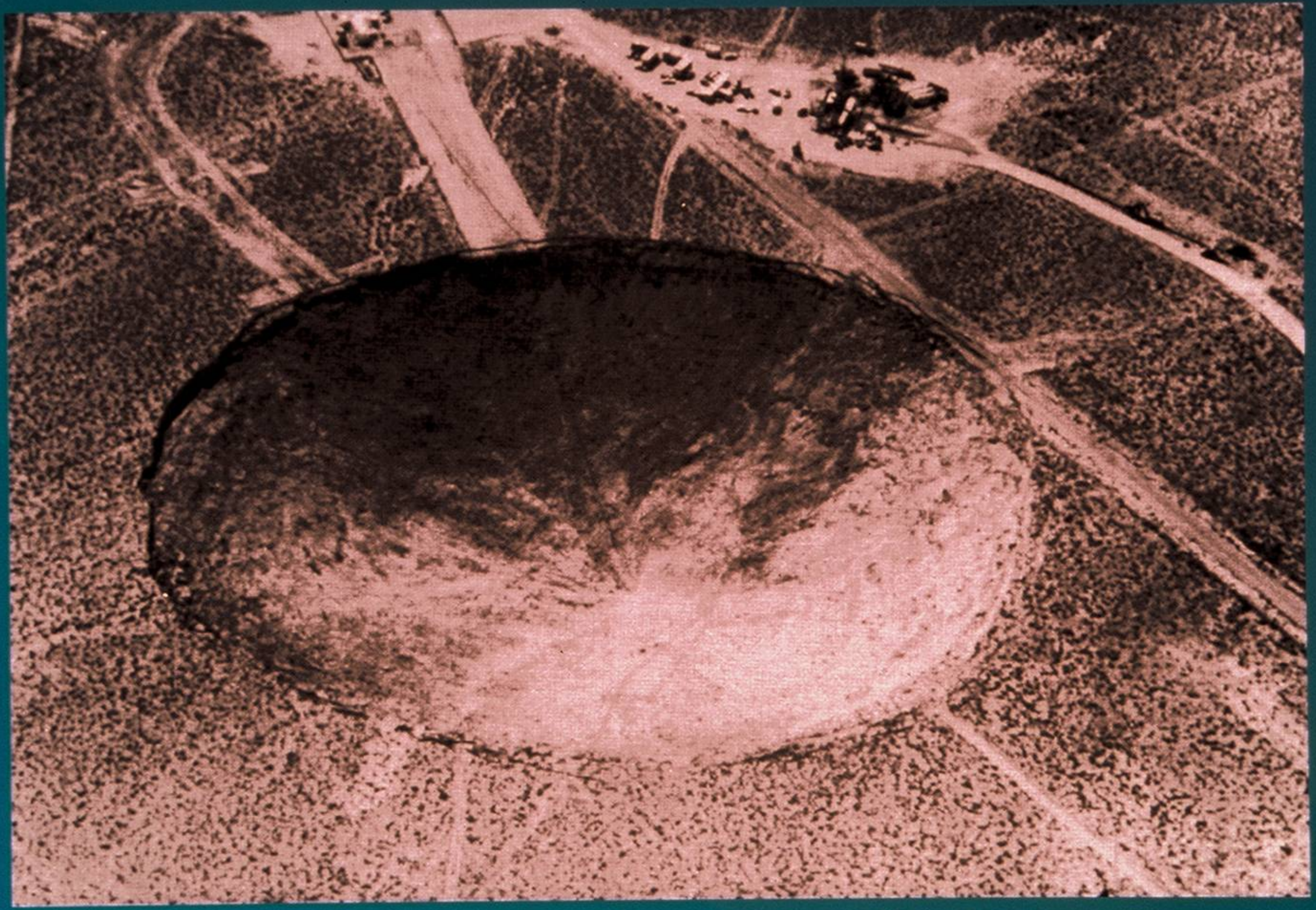
Underground Thermonuclear Explosion



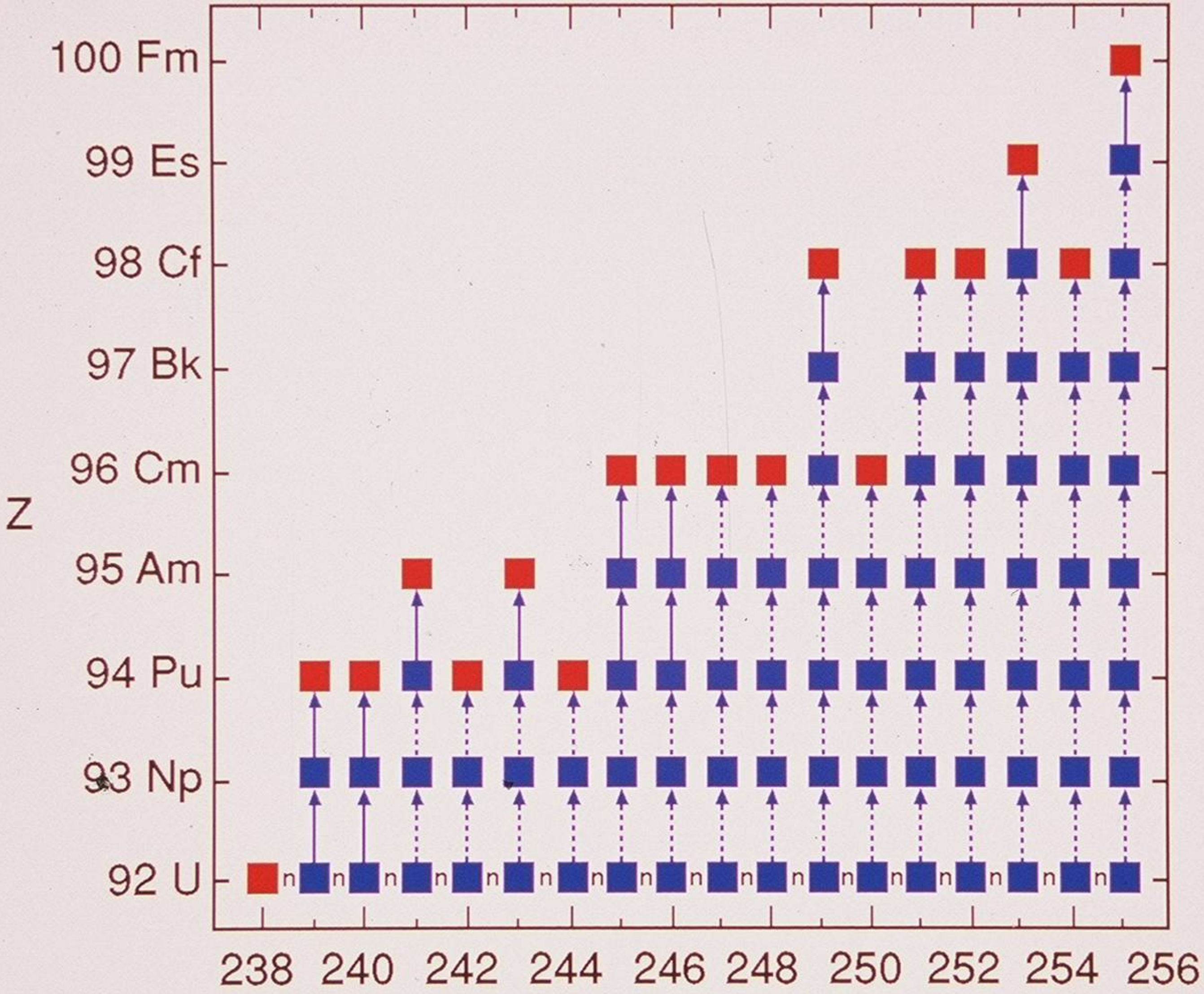
Formation of Hemispherical Cavity from Condensation and Cooling of Gaseous, Molten Rock and Collapse of Ceiling



Chimney Formation from Collapse of Fractured Rock Above Cavity

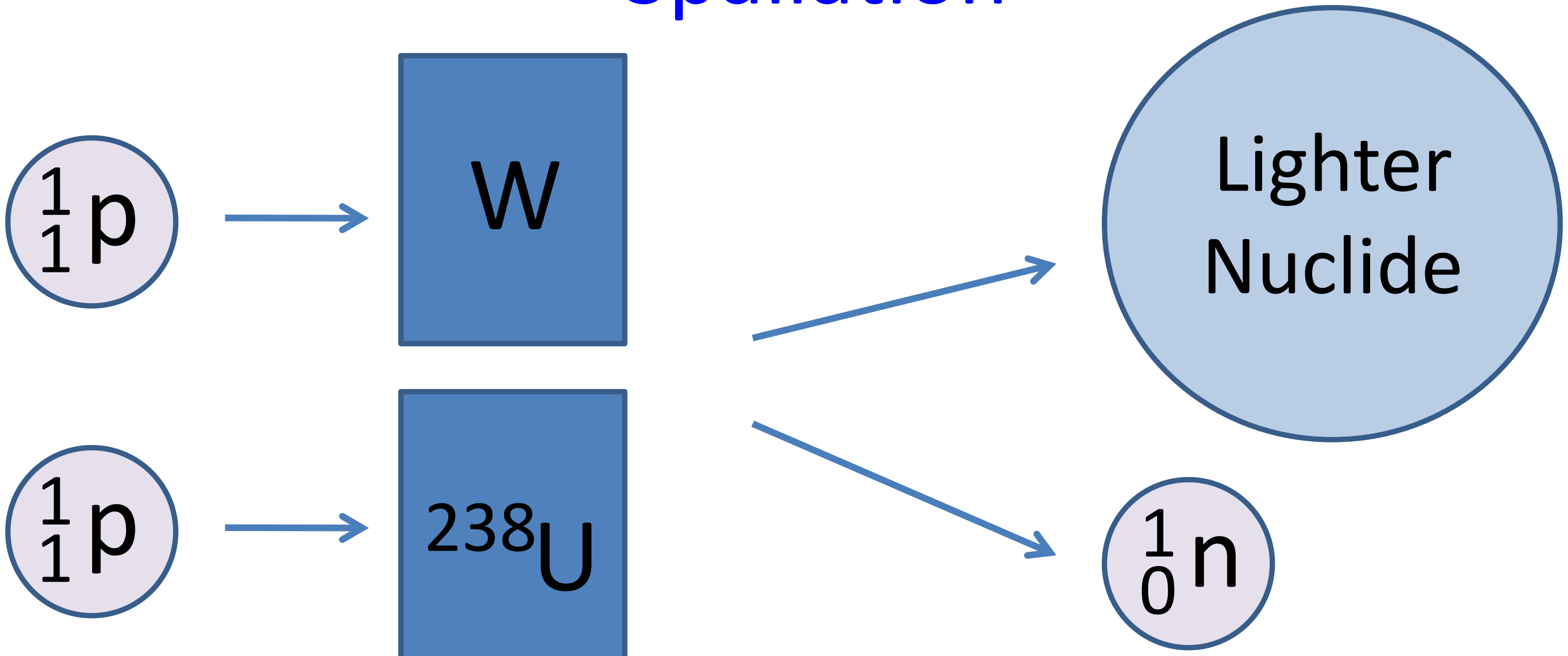


Surface Crater at the Nevada Test Site Produced
by the Hutch Explosion, July 1969



Production of heavy element isotopes in thermonuclear events. 🟦 beta unstable nuclide. 🟥 beta stable nuclide.

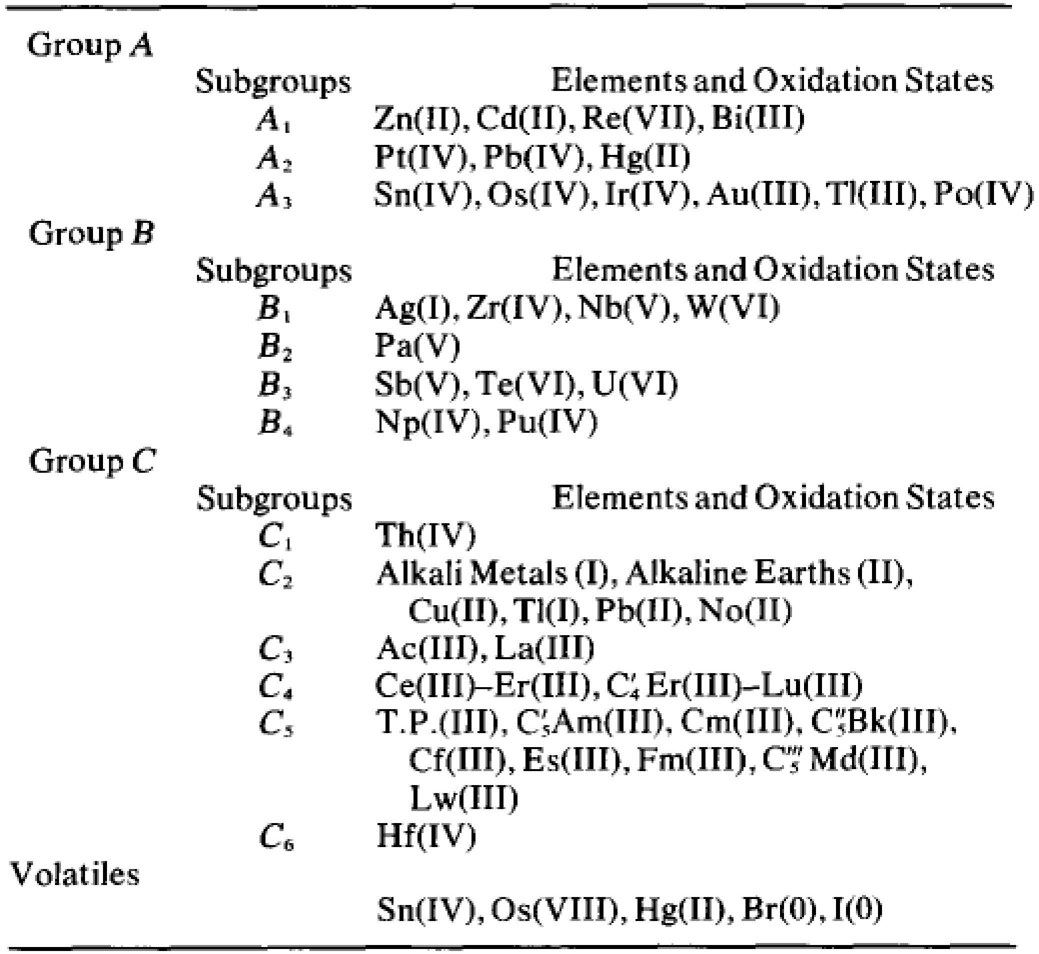
Spallation



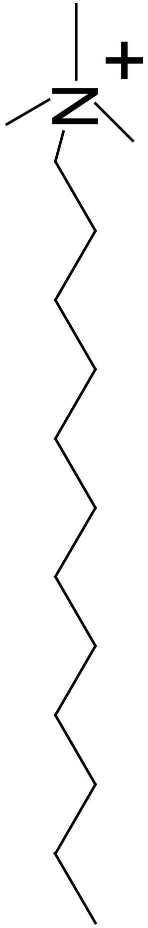
High energy protons strip neutrons and fragments from Uranium forming lighter nuclides.

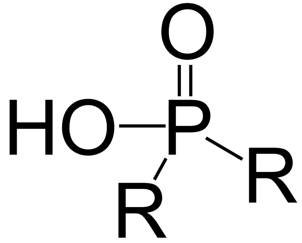
Fragments can also combine with Uranium to form heavier nuclides.

Spallation could yield neutron rich fragments not available in current heavy ion beam line sources.



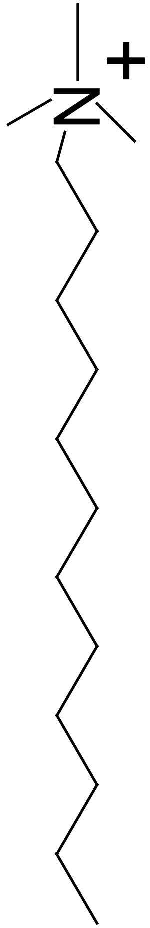
Group *A*		
	Subgroups	Elements and Oxidation States
	A_1	Zn(II), Cd(II), Re(VII), Bi(III)
	A_2	Pt(IV), Pb(IV), Hg(II)
	A_3	Sn(IV), Os(IV), Ir(IV), Au(III), Tl(III), Po(IV)
Group *B*		
	Subgroups	Elements and Oxidation States
	B_1	Ag(I), Zr(IV), Nb(V), W(VI)
	B_2	Pa(V)
	B_3	Sb(V), Te(VI), U(VI)
	B_4	Np(IV), Pu(IV)
Group *C*		
	Subgroups	Elements and Oxidation States
	C_1	Th(IV)
	C_2	Alkali Metals (I), Alkaline Earths (II), Cu(II), Tl(I), Pb(II), No(II)
	C_3	Ac(III), La(III)
	C_4	Ce(III)–Er(III), C'_4 Er(III)–Lu(III)
	C_5	T.P.(III), C'_5Am(III), Cm(III), C''_5Bk(III), Cf(III), Es(III), Fm(III), C'''_5 Md(III), Lw(III)
	C_6	Hf(IV)
Volatiles		
		Sn(IV), Os(VIII), Hg(II), Br(0), I(0)





Horwitz and Bloomquist, "Chemical Separations for Super-Heavy Element Searches in Irradiated Uranium Targets," J. Inorg. Nucl. Chem., 37, 425-434 (1975)

TEVA



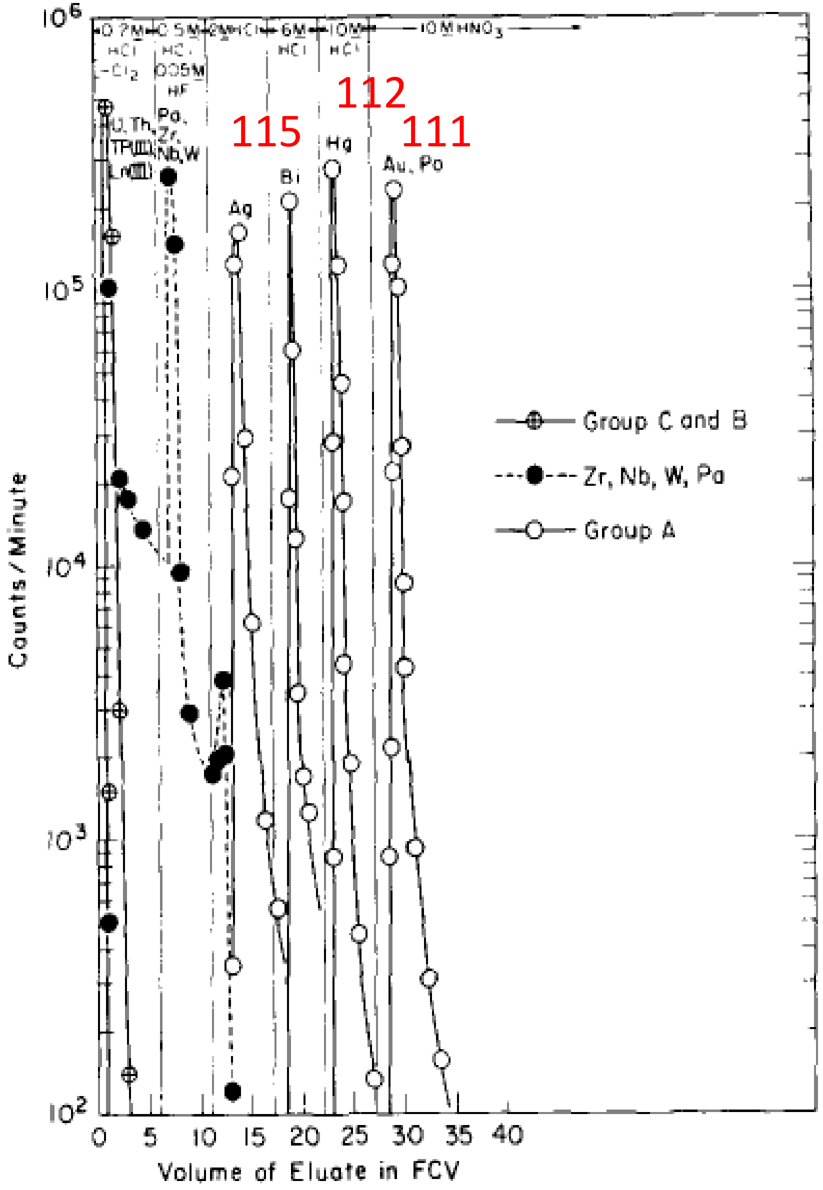


Fig. 6. Separation of groups *C* and *B* from group *A* and the sequential elution of group *A* using 0·04 *F* (2 *v*/*o*) TCMA·Cl in *o*-xylene on Celite (35 μ). Column bed size 0·062 cm × 5 cm; 50°C; *v* = ~4 cm/min; FCV = 0·19 ml.

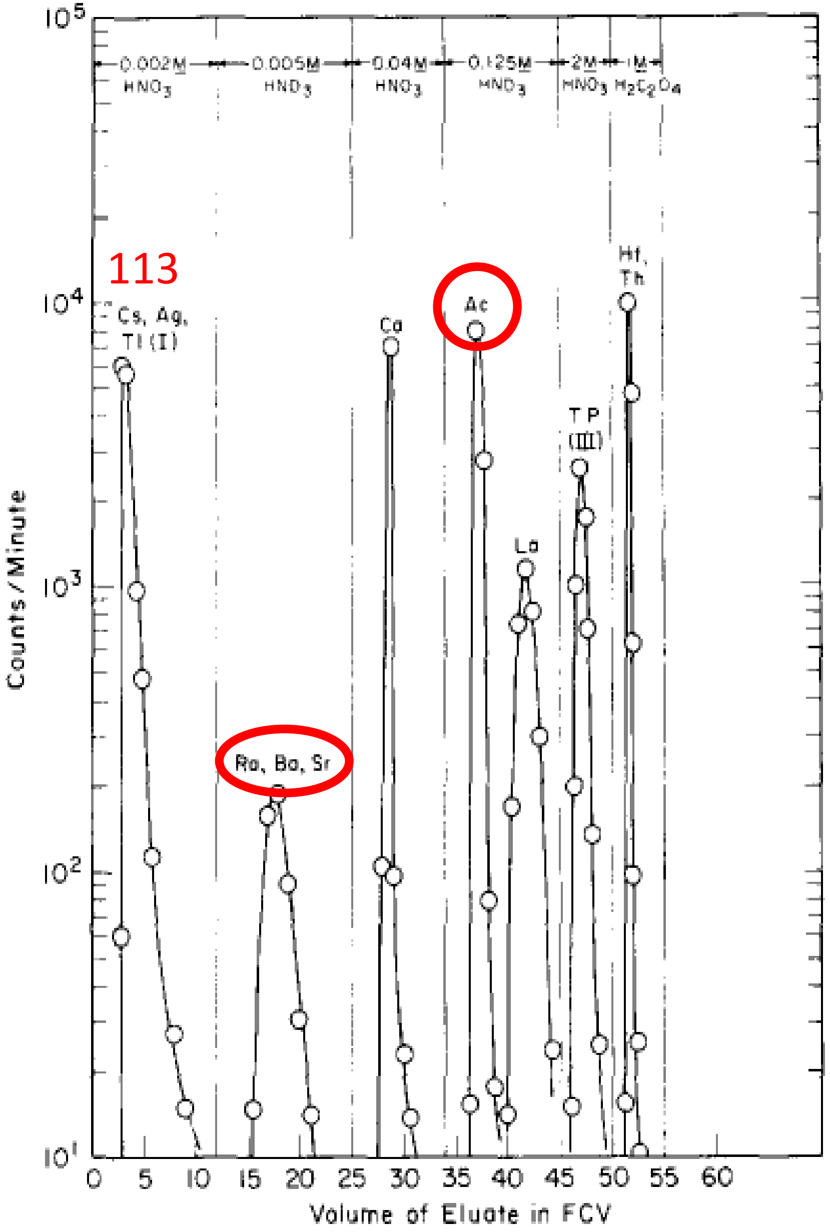
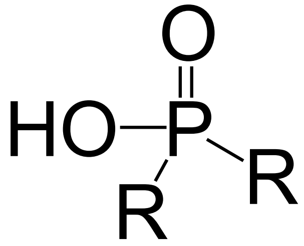
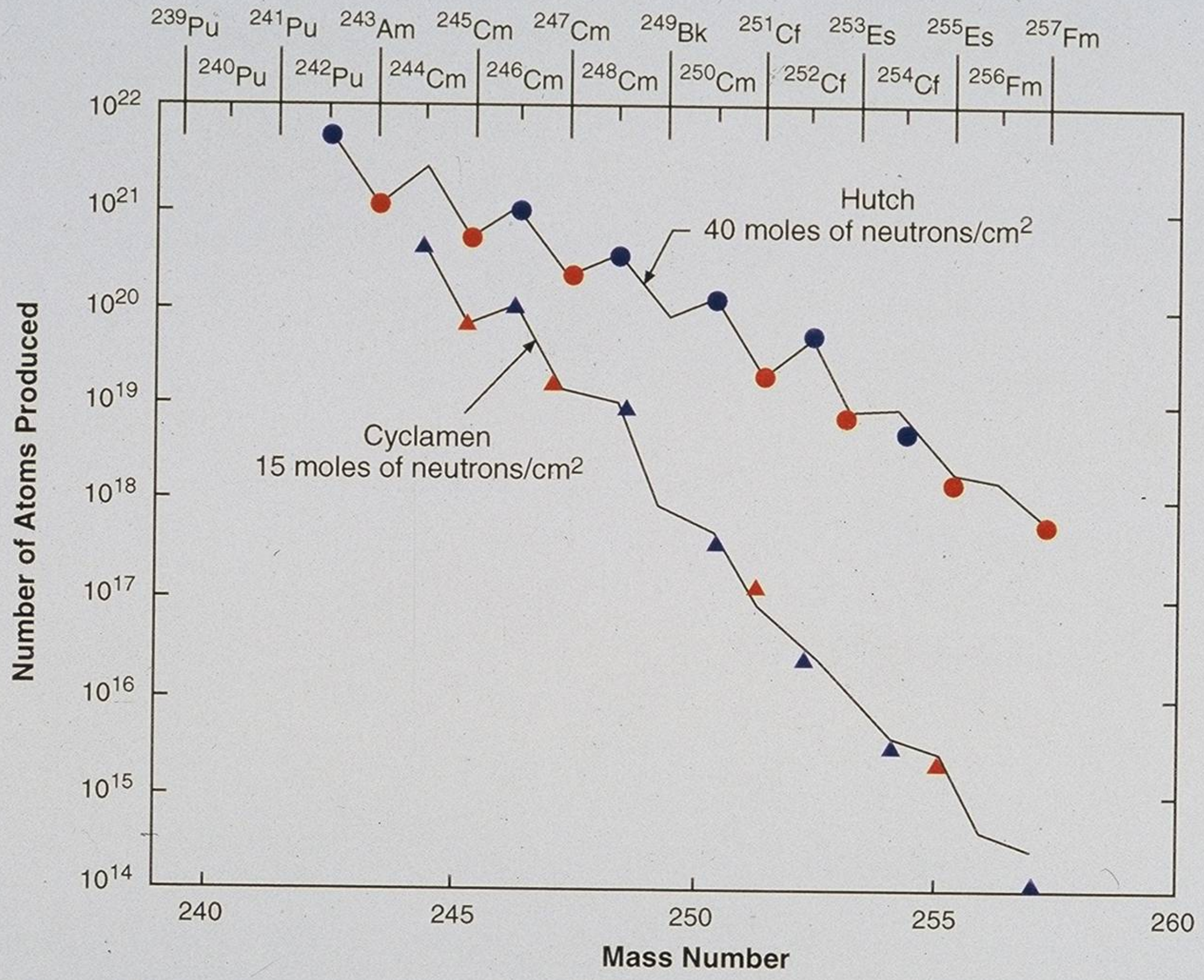


Fig. 9. Sequential separation of group *C* elements using 8·82 *w*/*o* HDEHP on Celite (35 μ). Column bed size 0·062 cm^2 × 5 cm; 50°C; *v* = ~5 cm/min; FCV = 0·22 ml.

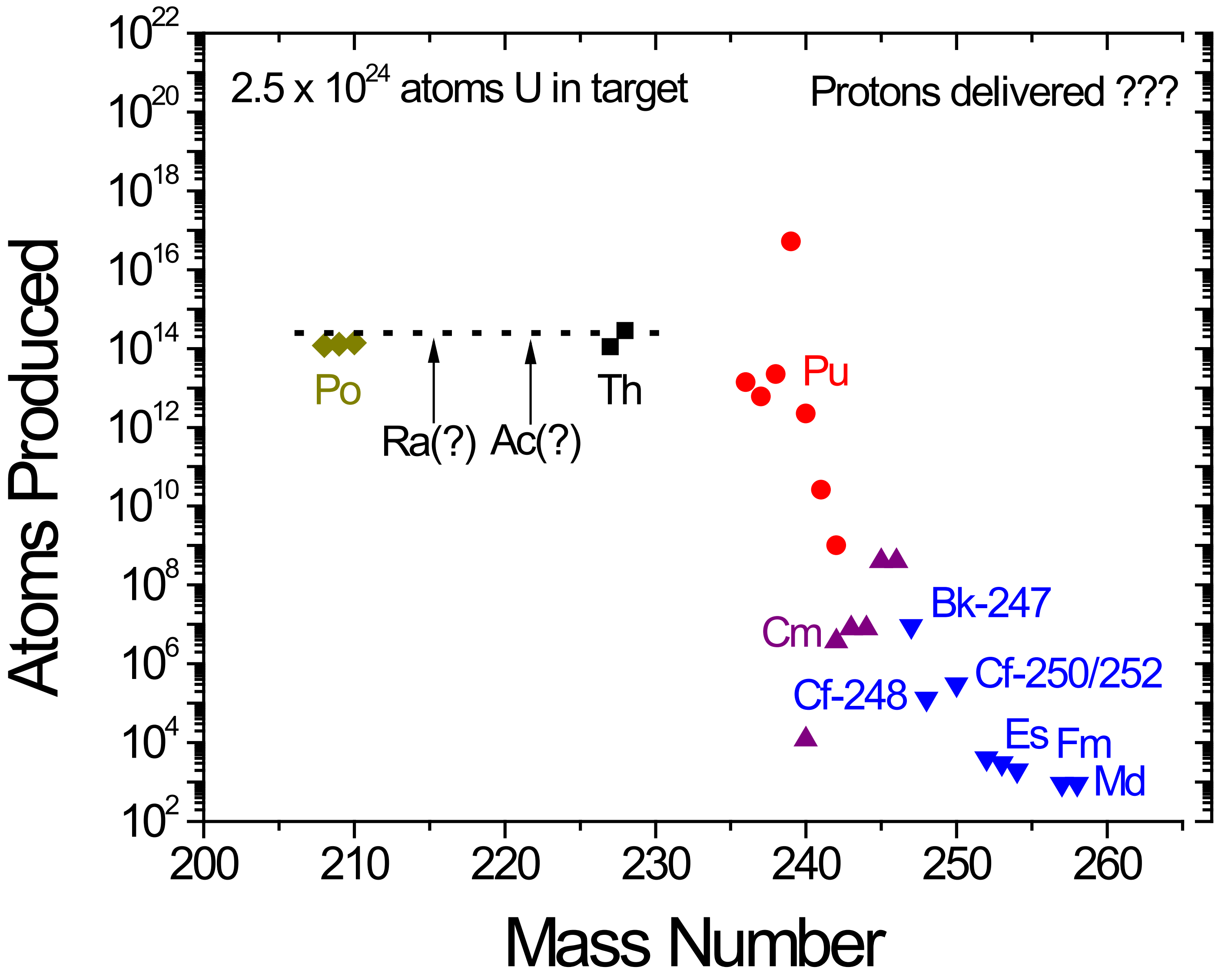
LN Resin





Mass Yield Curves in the Hutch and Cyclamen Nuclear Explosions.
From UCRL-81566

Spallation Yield for Uranium Beamstop with 12 GeV Protons



Elements predicted to have isotopes with long half-lives finally produced in 1994-2004 (Ds-Fl).

However, the neutron-rich isotopes predicted in the island of stability have yet to be produced.

J.P. Unik, E.P. Horwtiz, K.L. Wolf, I. Ahmad, S. Fried, D. Cohen, P.R. Fields, C.A.A. Bloomquist, D.J. Henderson, “Production of Actinides and the Search for Super-Heavy Elements Using Secondary Reactions Induced by GeV Protons,” *Nuclear Physics*, A191, 233-244 (1972).

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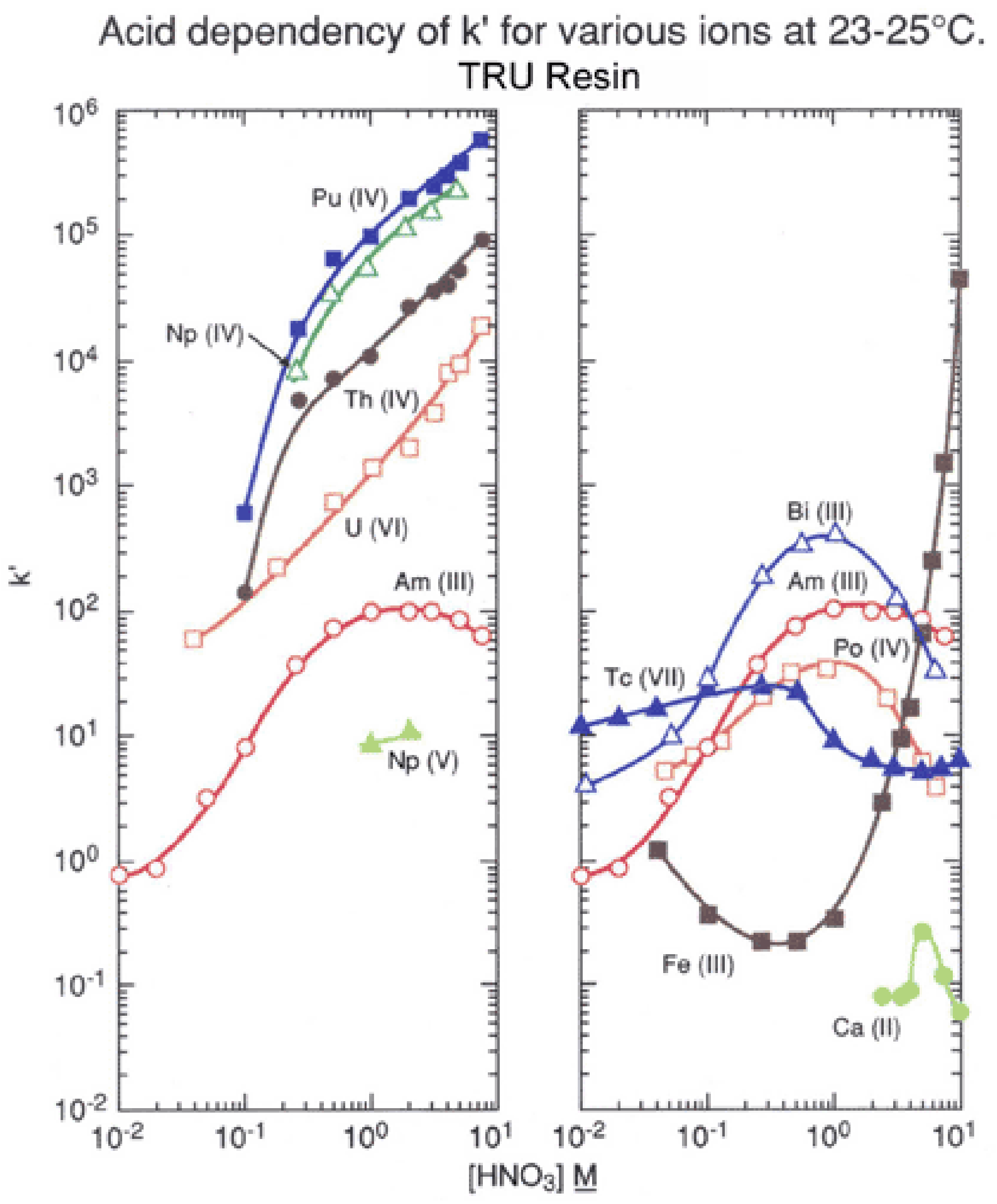
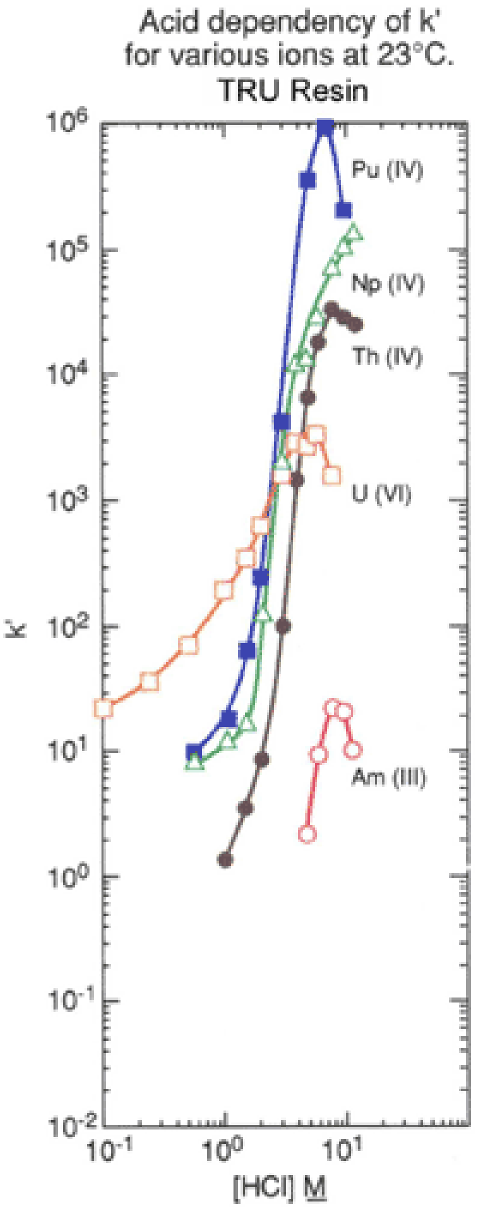
CMPO – TRUEX – TRU and RE Resins
Hanford Waste
Transplutonium processing
Extractant design and phase modifiers

Figure 2

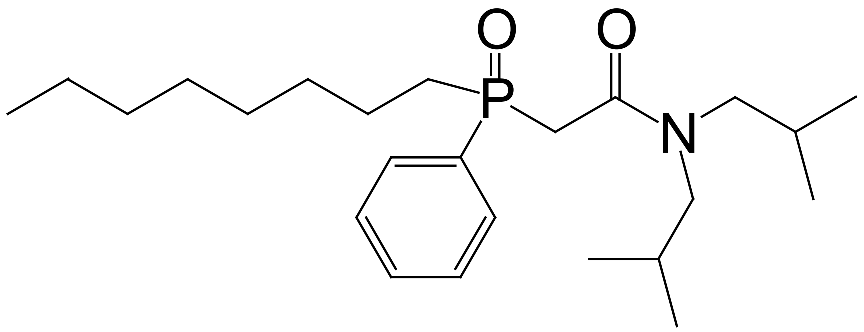


Horwitz, et al. (HP193)

Figure 3



Horwitz, et al. (HP193)



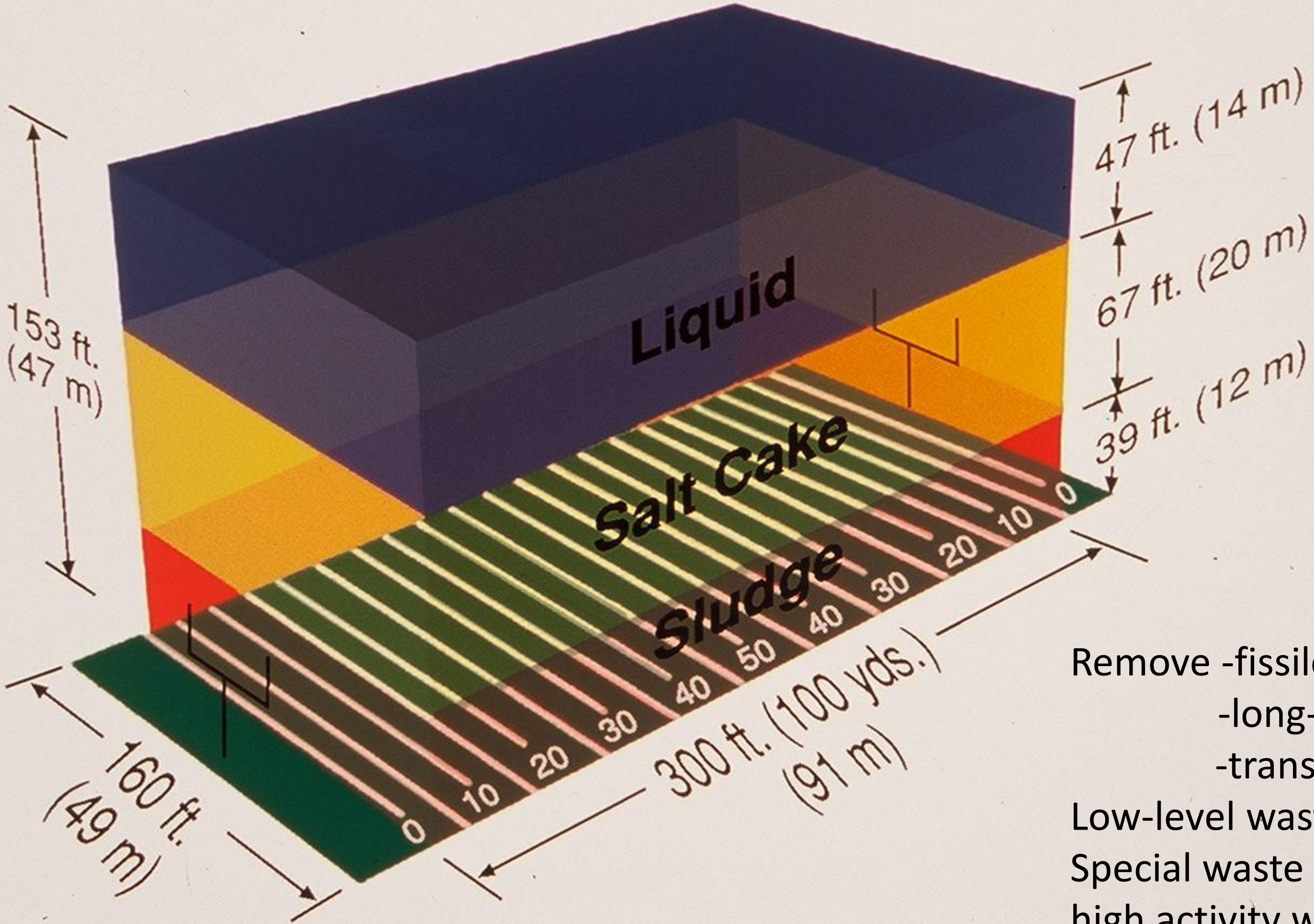
-Developed to extract trivalent actinides (TRUEX) from nuclear waste after removal of U/Pu by PUREX.

-CMPO Extractant

-TBP Phase Modifier

Hanford Waste Processing

The 55 million gallons (208×10^3 cubic meters) of radioactive waste in Hanford's underground storage tanks would fill a football field to a height of about 150 feet.



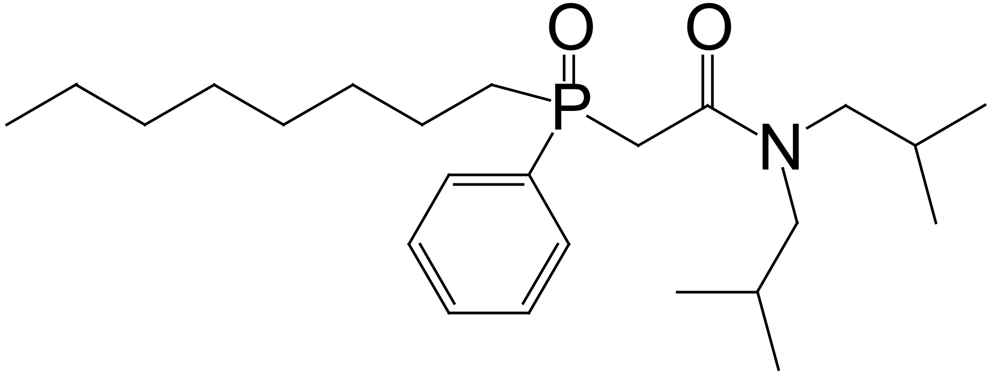
From PNL-10773

Remove -fissile material
-long-lived fission
-transuranics
Low-level waste repository.
Special waste forms for
high activity waste.

CMPO (TRUEX)

W.W. Schulz and E.P. Horwitz, “The TRUEX process and the management of liquid TRU waste,” *Sep. Sci. Tech.*, 23(12-13), 1191-1210 (1988)

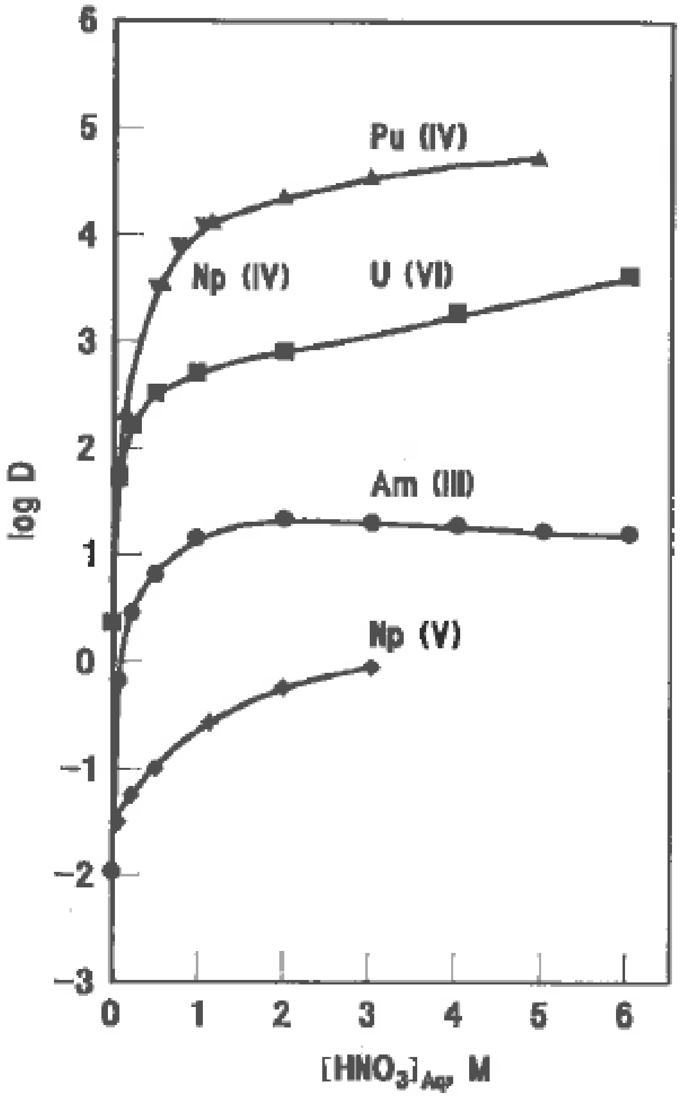
Extraction of transuranics, post PUREX



octylphenyl-N,N-di-isobutylcarbamoylphosphine oxide (CMPO)

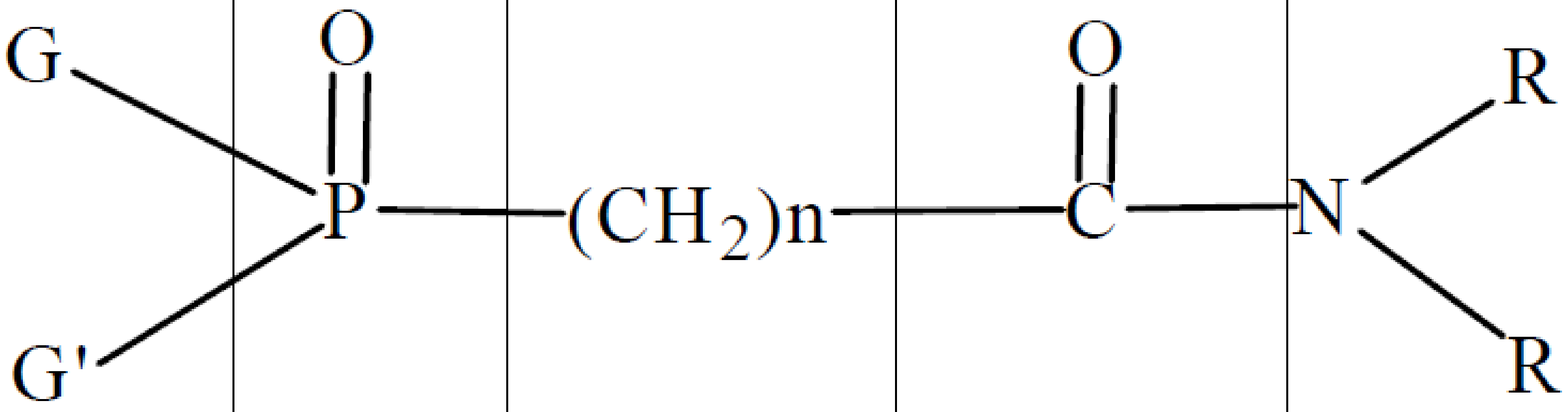
Solvent: 0.25 M CMPO + 1.4 M TBP in Normal parafinnic hydrocarbon (C_{12}-C_{14})

Aqueous: PUREX/UREX raffinate



Distribution ratios of selected actinide ions as a function of the aqueous nitric acid concentration. 0.20 M CMPO – 1.2 M TBP-dodecane. 25°C

Carbamoylphosphoryl moiety and substituents



• Affects basicity of phosphoryl group • Selectivity • Solubility	• Primary donor group	• Affects interaction between donor groups	• Intramolecular buffer • Secondary donor group	• Affects basicity of carbonyl • Solubility

Horwitz, E.P., et al., “Extraction of Am from nitric acid by carbamoyl-phosphoryl extractants: The influence of substituents on the selectivity for Am over Fe and Selected Fission Products,” Solv. Extr. Ion Exch., 4(3), 449-494 (1986)

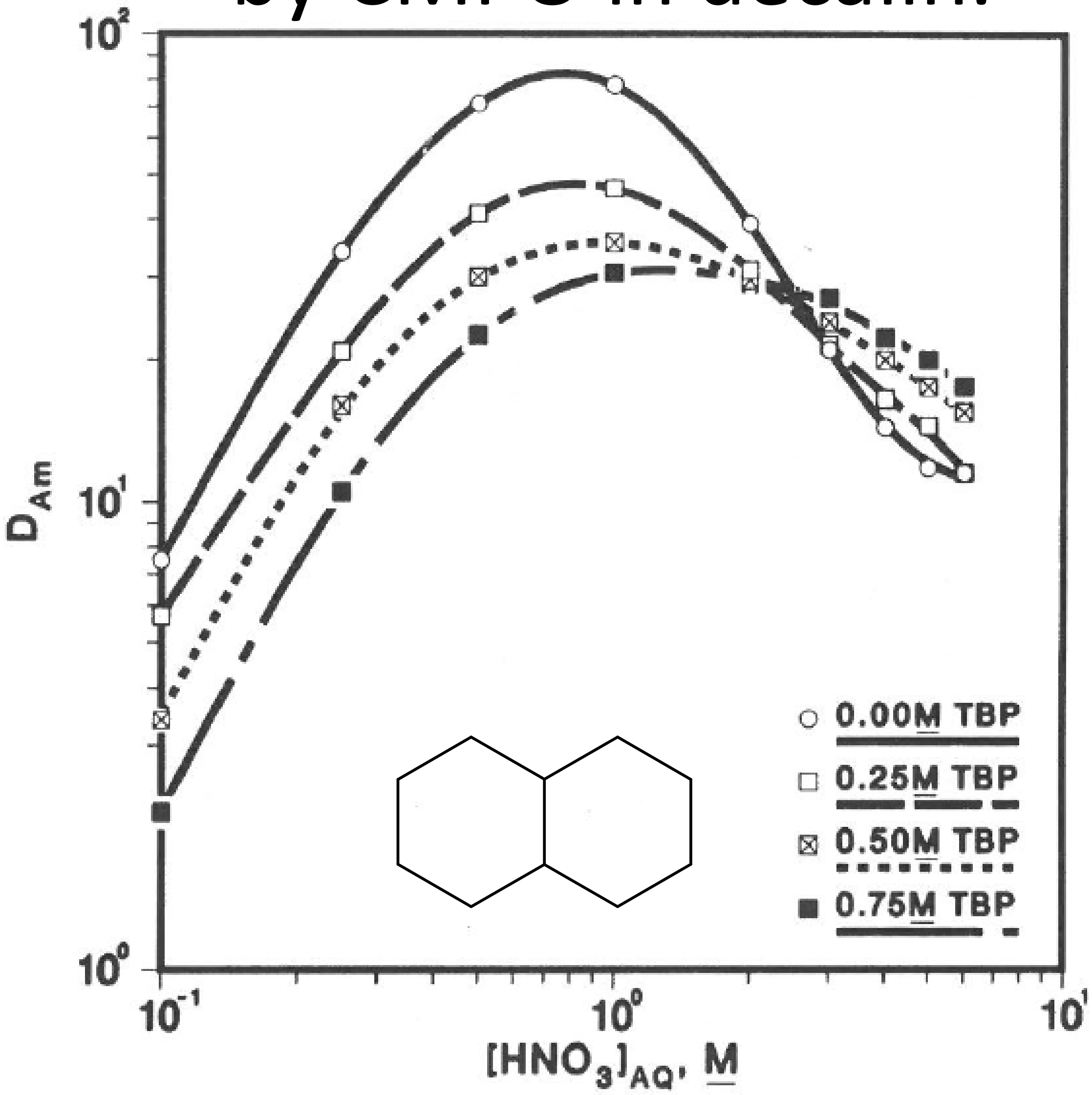
Phase Modifiers (Synergism?)

Increases loading before 3rd phase.

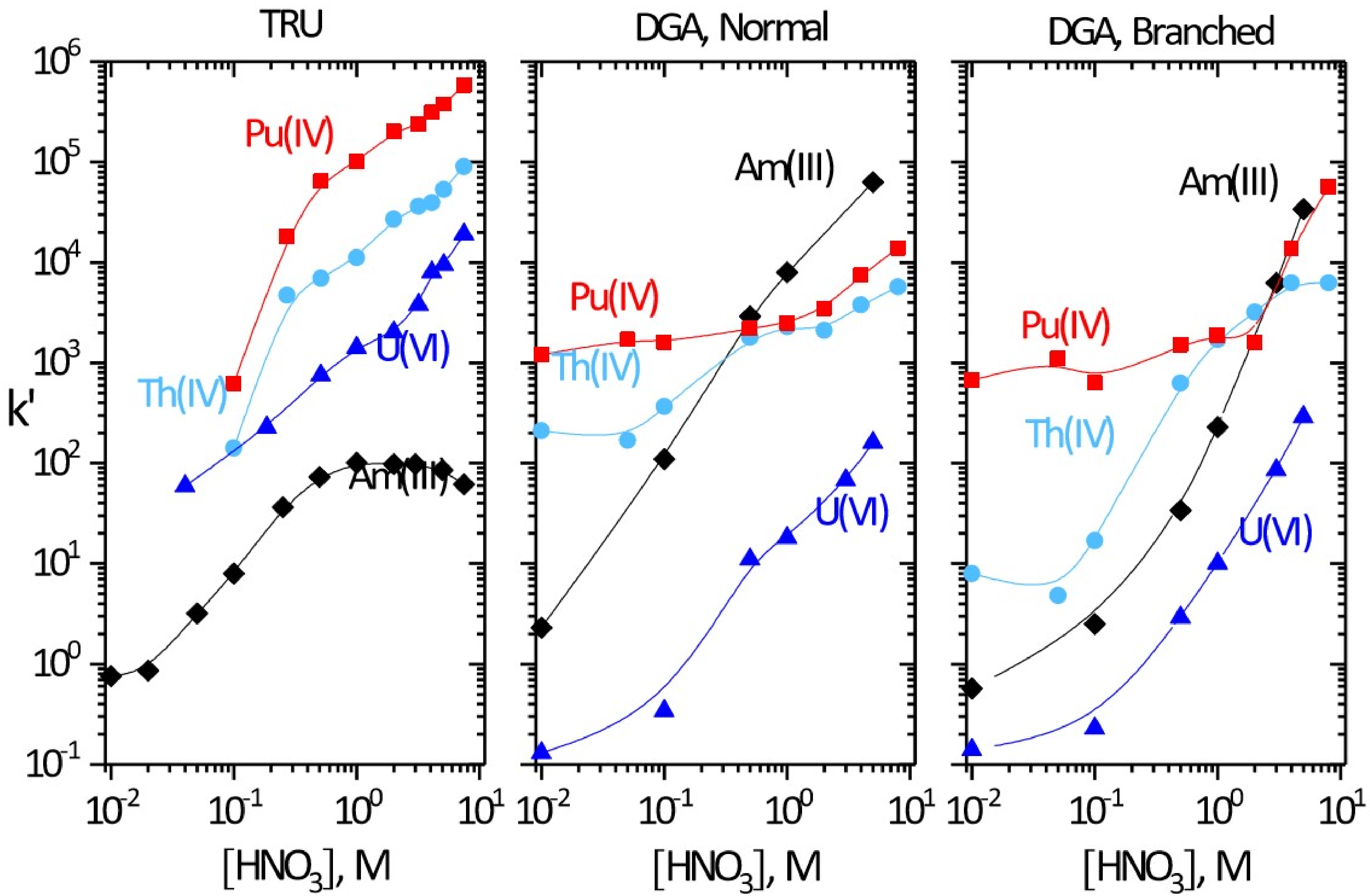
Improves stripping at low acid.

Flattens Am uptake at high HNO_3.

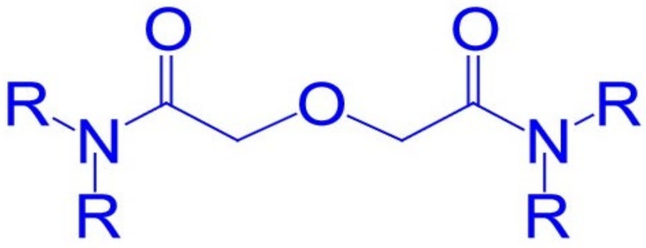
Extraction of Am(III) by CMPO in decalin.



E.P. Horwitz and D.G. Kalina, “The Extraction of Am(III) from nitric acid by octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide - tri-n-butyl phosphate mixtures,” *Solv. Extr. and Ion Exch.*, 2(2), 179-200 (1984).



Sasaki, Y.; Choppin, G.R. Solvent extraction of europium, thorium, uranium, neptunium and americium with N,N′-dimethyl-N,N′-dihexyl-3-oxapentanediamide and its analogous compounds. Anal. Sci. 1996, 12, 225-230.



DGA advantages over TRU.

-Higher retention of trivalent actinides and lanthanides.

-Lower extractant bleed.

-Lower competition from Fe(III).

Disadvantages:
-Wetting difficulty
-Competition from Ca and Pb.

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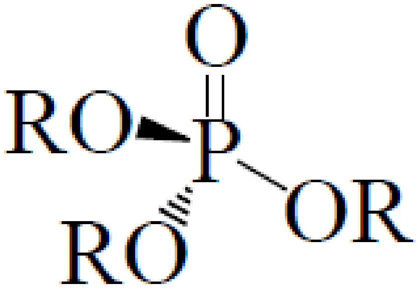
TBP – PUREX and DA[AP] - UTEVA

Improved hydrophobicity
Higher retention at lower HNO3
Selectivity vs steric hindrance

TBP (PUREX or UREX)

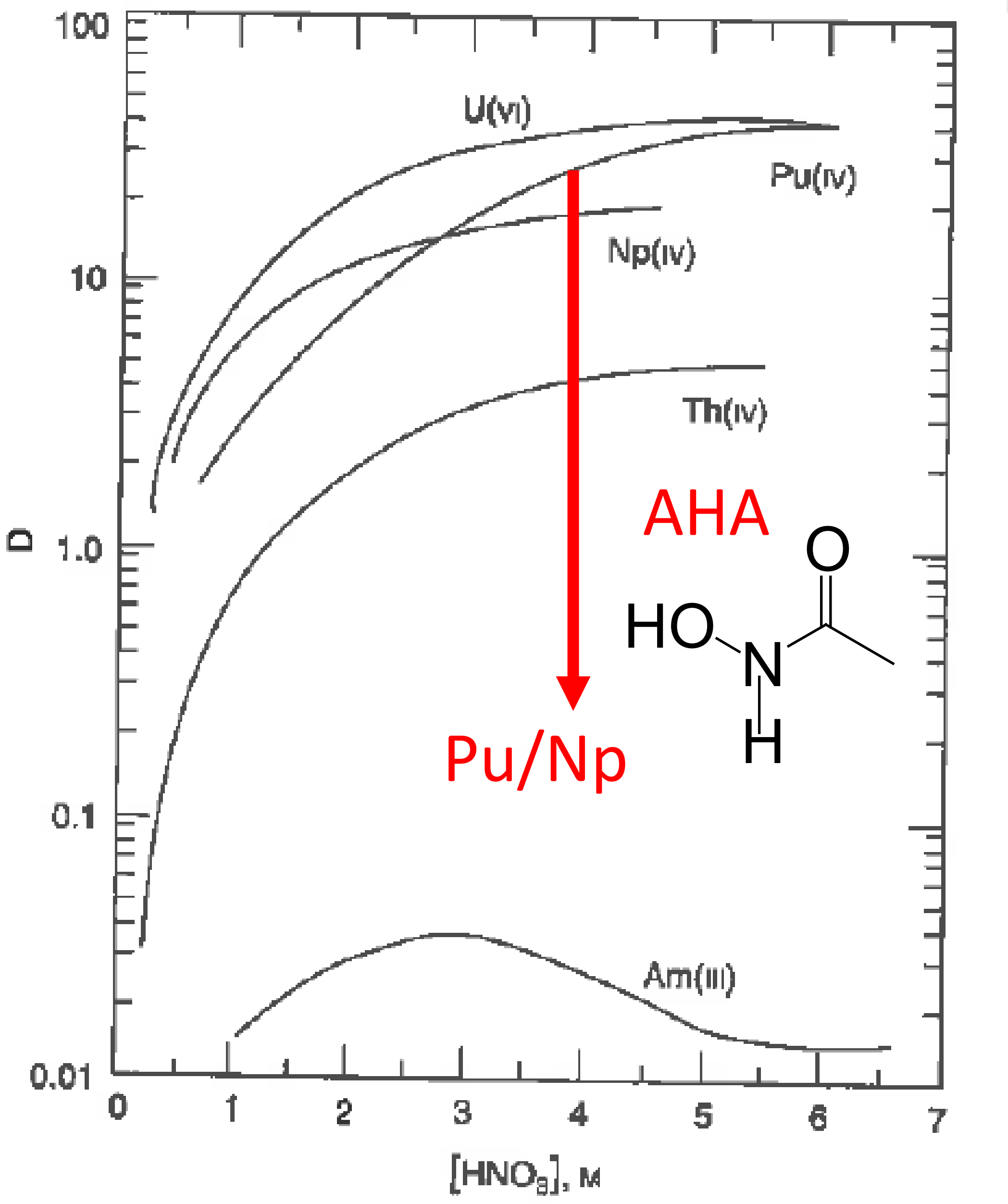
Selective Extraction of U(VI)/Pu(IV)
From spent nuclear fuel



~30% TBP

diluent: Kerosene (C_{11}-C_{12}) or
n-parrifin oil (C_9-C_{17})

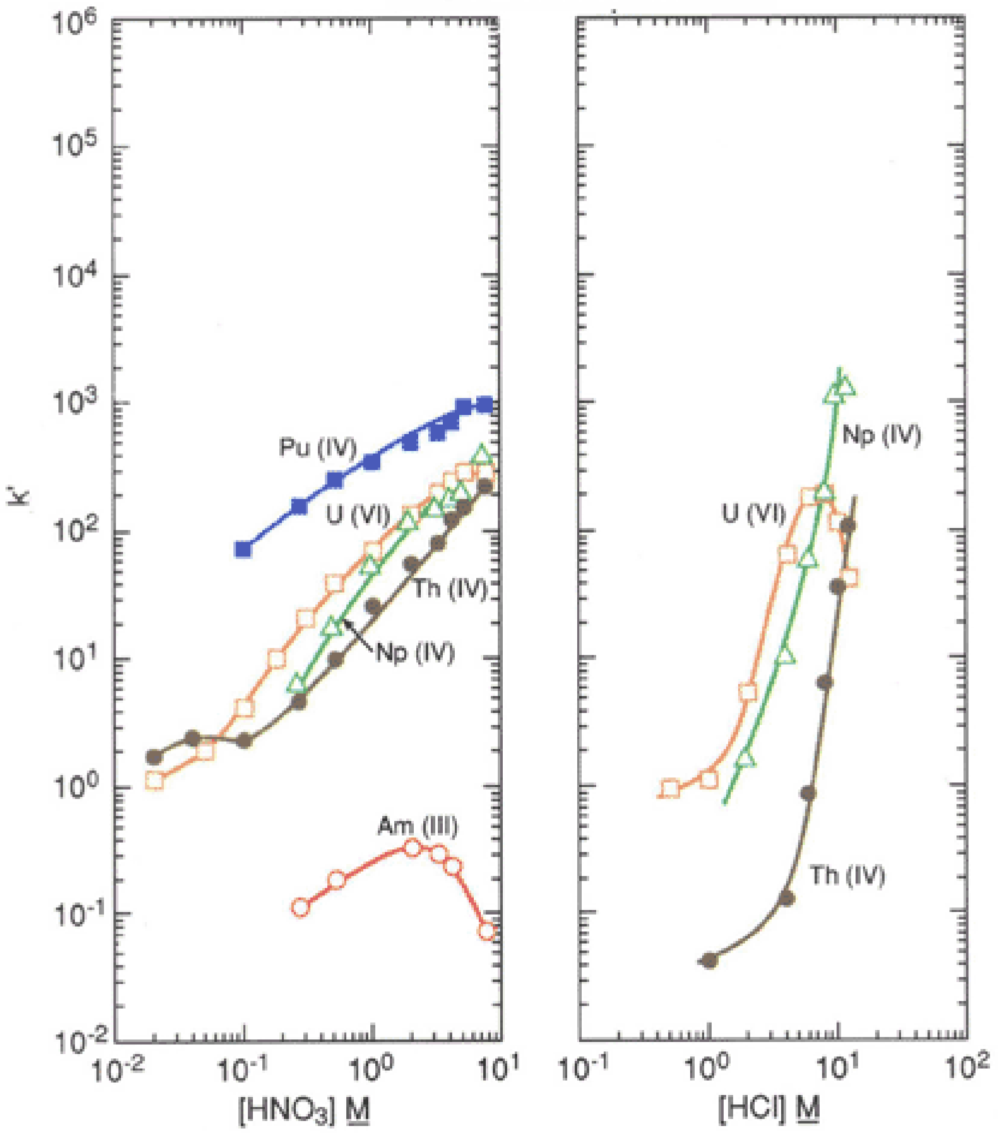
aqueous: ~5 yr cooled nuclear fuel
dissolved in 3-6 M HNO3



Neutral Extractants (Solvating)

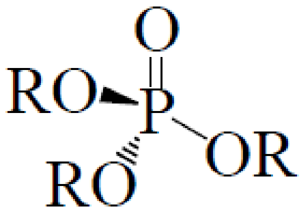
Figures 2 and 3

Acid dependency of k' for various ions at 23-25°C.
UTEVA Resin

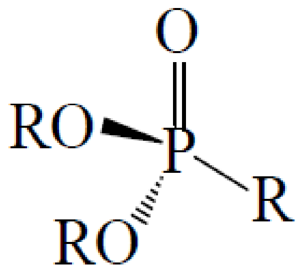


Horwitz, et al. (HP392)

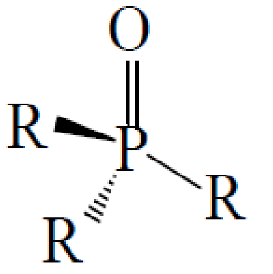
Basicity of P=O



TBP
Phosphate
R = C_4H_9



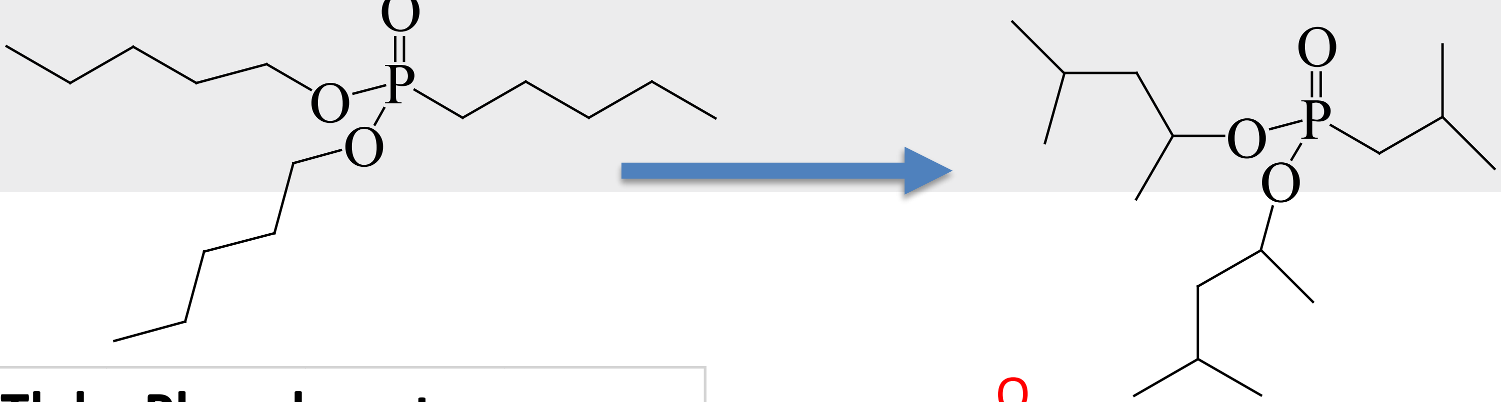
DAAP
Phosphonate
R = C_5H_{11}



Trialkyl
Phosphine Oxide
R = C_8H_{17}
Or mixtures
Of C_6 and C_8

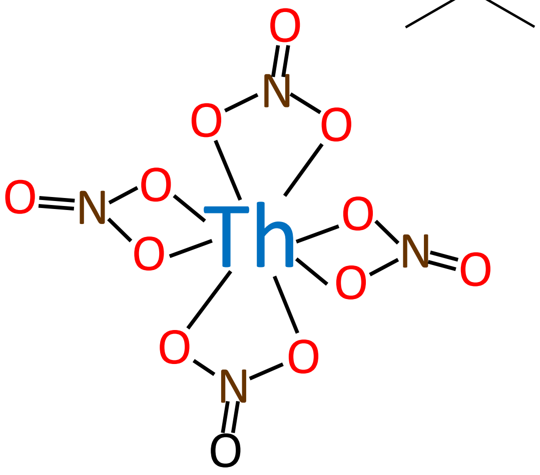
$$M^{3+} + \overline{nE} + 3X^{-} \rightleftarrows \overline{ME_n \bullet X_3}$$

Steric effects

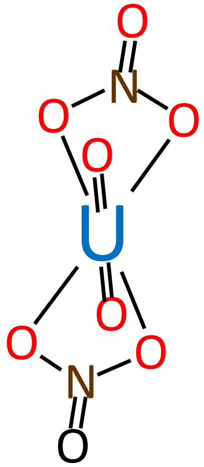


Steric Effects on Extraction of U/Th by Phosphonates

	D		α
Extractant	**U**	**Th**	**U/Th**
dibutyl[butylphosphonate]	249	61	4.1
dipentyl[pentylphosphonate]	295	71	4.2
dibutyl[cyclohexylphosphonate]	245	24	10
di(4-methyl-2-pentyl)[butylphosphonate]	362	3.1	117
di(4-methyl-2-pentyl)[iso-butylphosphonate]	57	0.35	163
Aqueous = 2.0 M HNO3			
Organic = 1.0 M Extractant in Dodecane			



$[Th(OH_2)_9]^{4+}$



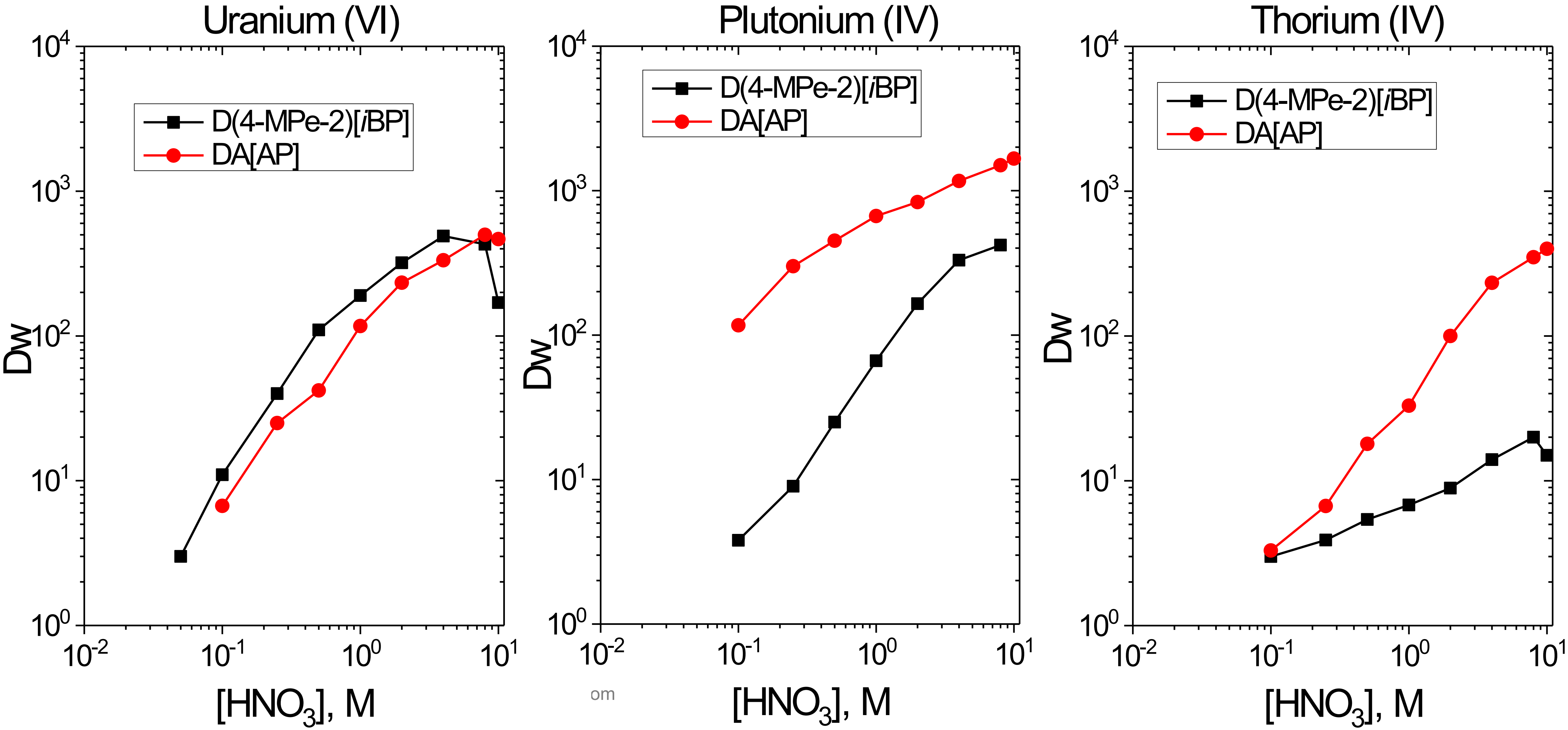
$[UO_2(OH_2)_5]^{2+}$

G.W. Mason and H.E. Griffin, “Demonstration of the potential for designing extractants with preselected extraction properties: Possible application to reactor fuel processing,” in Actinide Separations, ACS Symposium Series, Eds. Jim Navratil and W.W. Shulz, pp 89-99 (1980).

Steric effects (EXC Resins)

UTEVA $\alpha_{U/Th}$ ~1.5

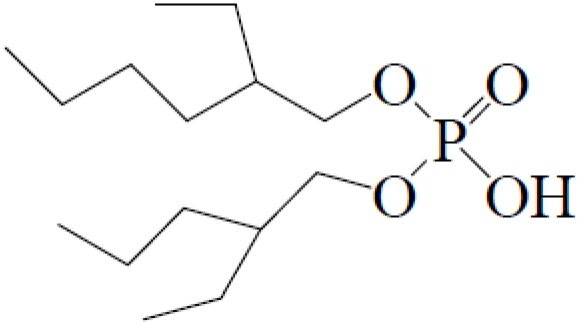
DMP[iBP] $\alpha_{U/Th}$ ~200



om

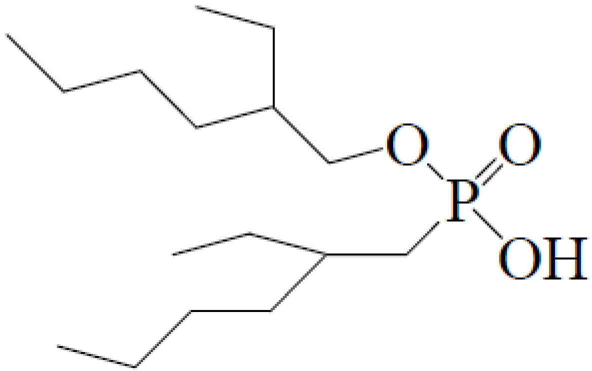
Acidic Phosphorus Extractants (LN Series)

$$M^{3+} + \overline{3(HL)_2} \leftrightarrow \overline{M(HL_2)_3} + 3H^+$$



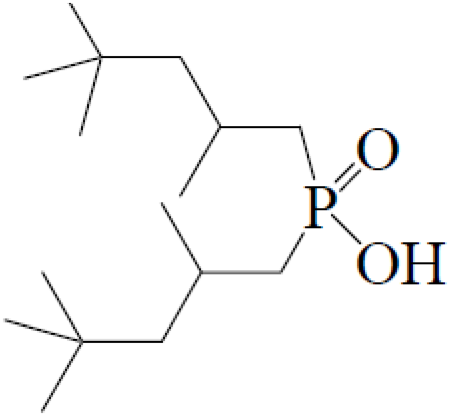
Phosphoric Acid

LN Resin



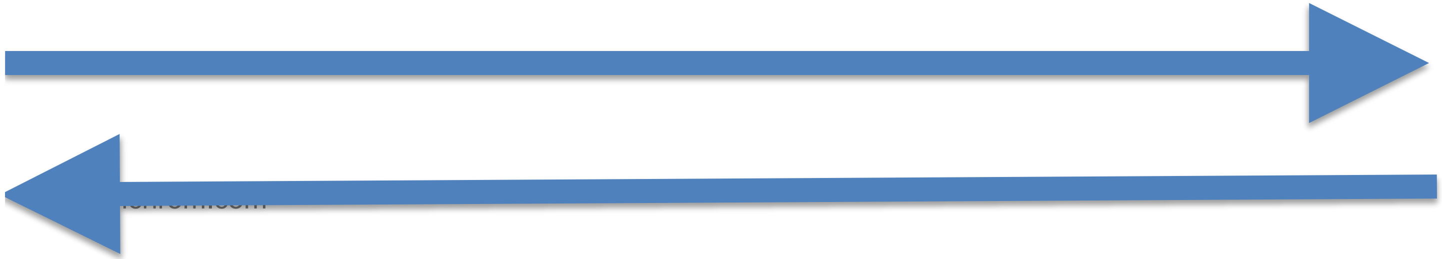
Phosphonic Acid

LN2 Resin



Phosphinic Acid

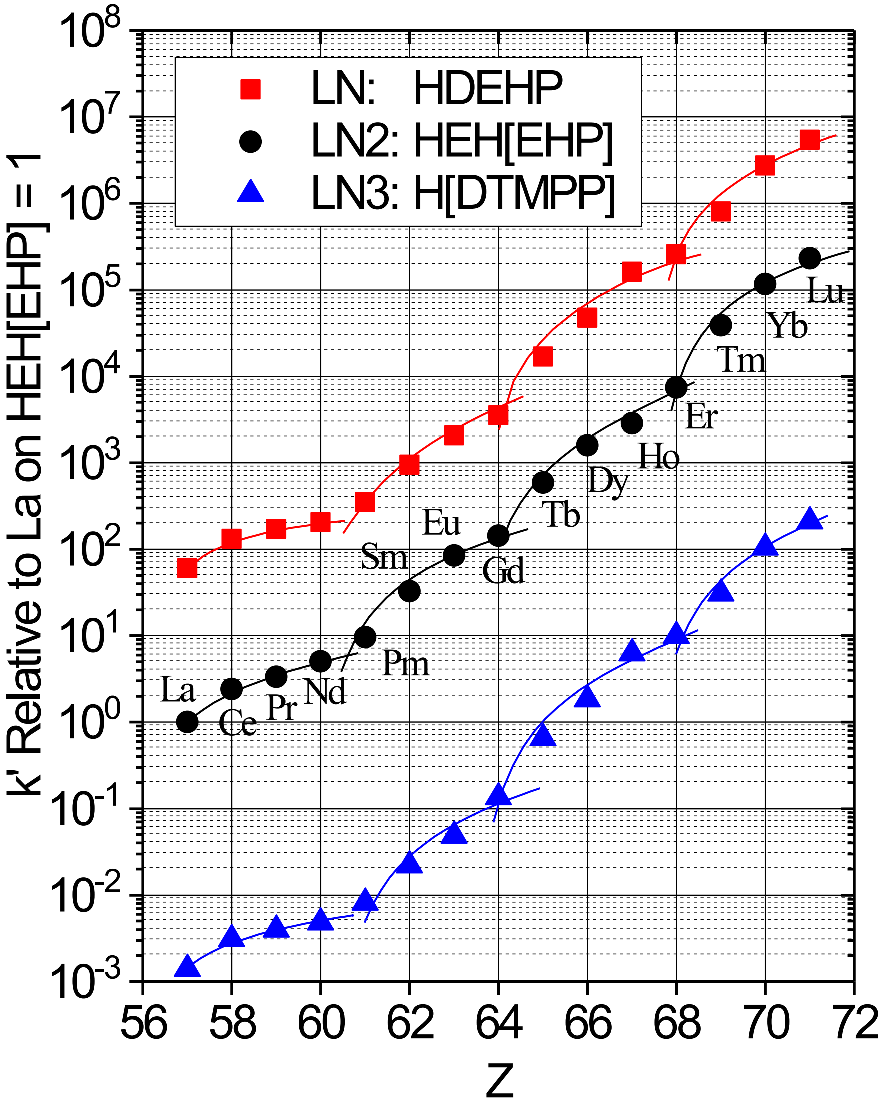
LN3 Resin



Basicity of P=O

Acidity of P-OH

Decreasing acidity of P-OH



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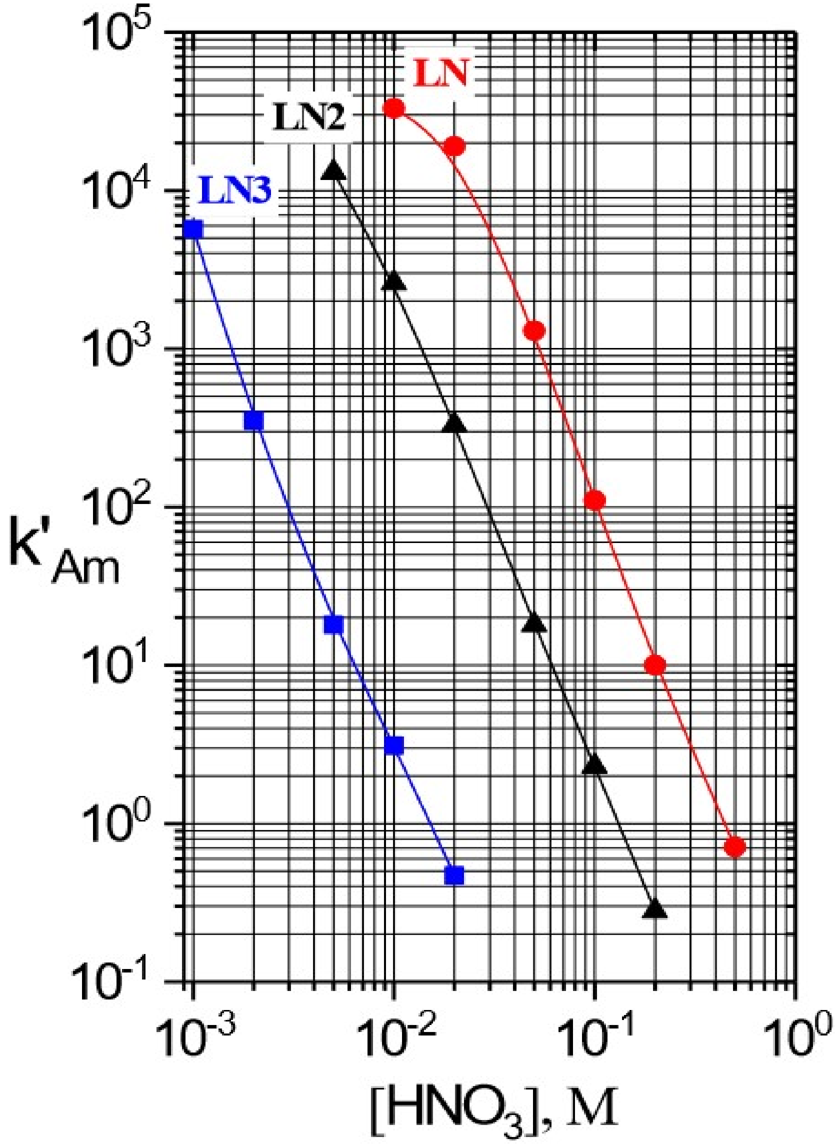
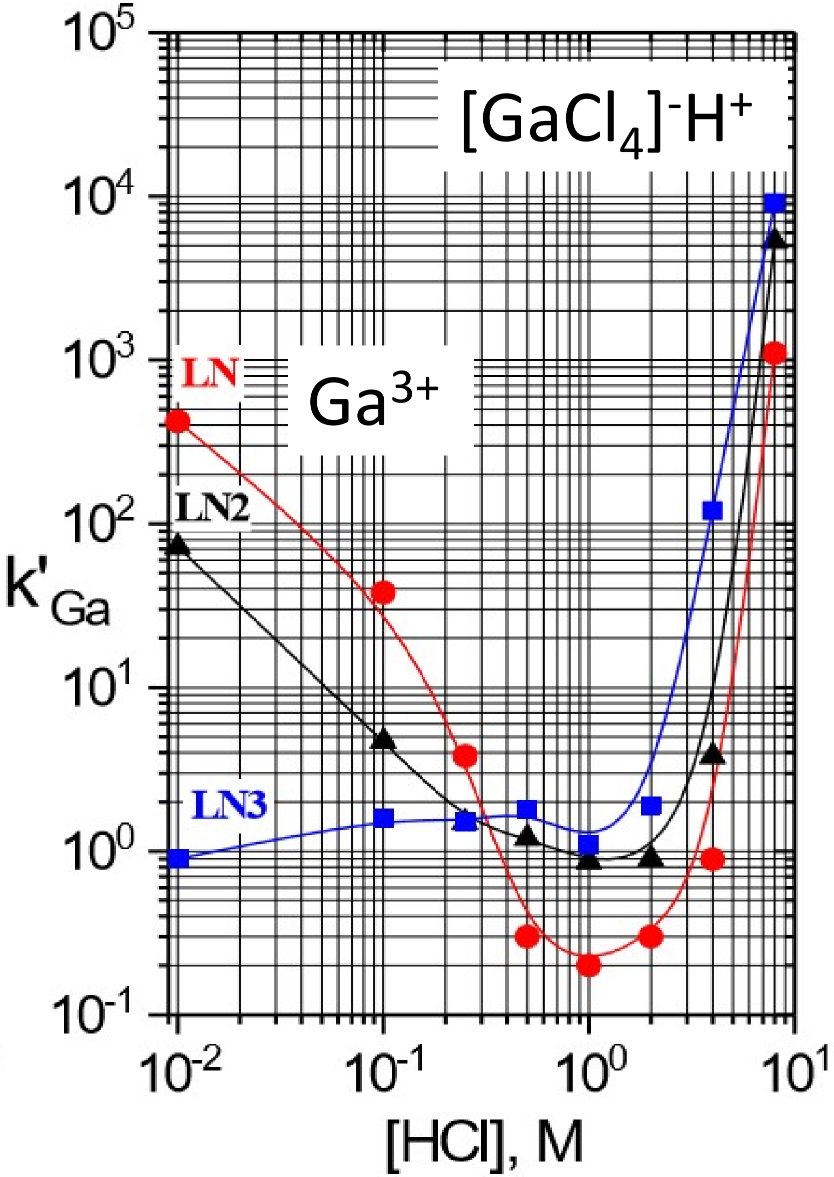
Decreasing acidity of P-OH vs Increasing basicity of P=O





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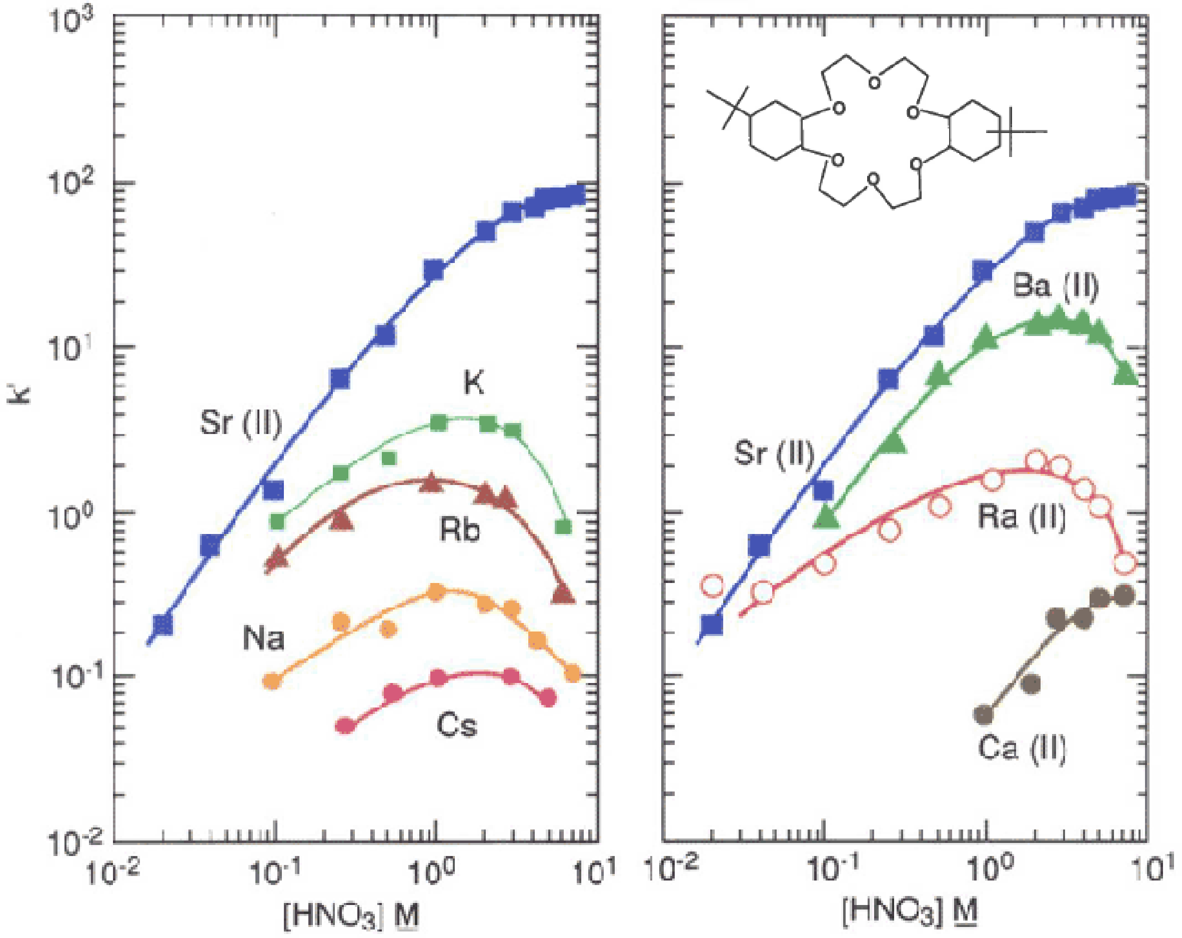
dtBuCH18-crown-6 / SrEx Process / Sr and Pb Resins
Macrocyles
Diluent effects
Importance of hydration energies and counterions

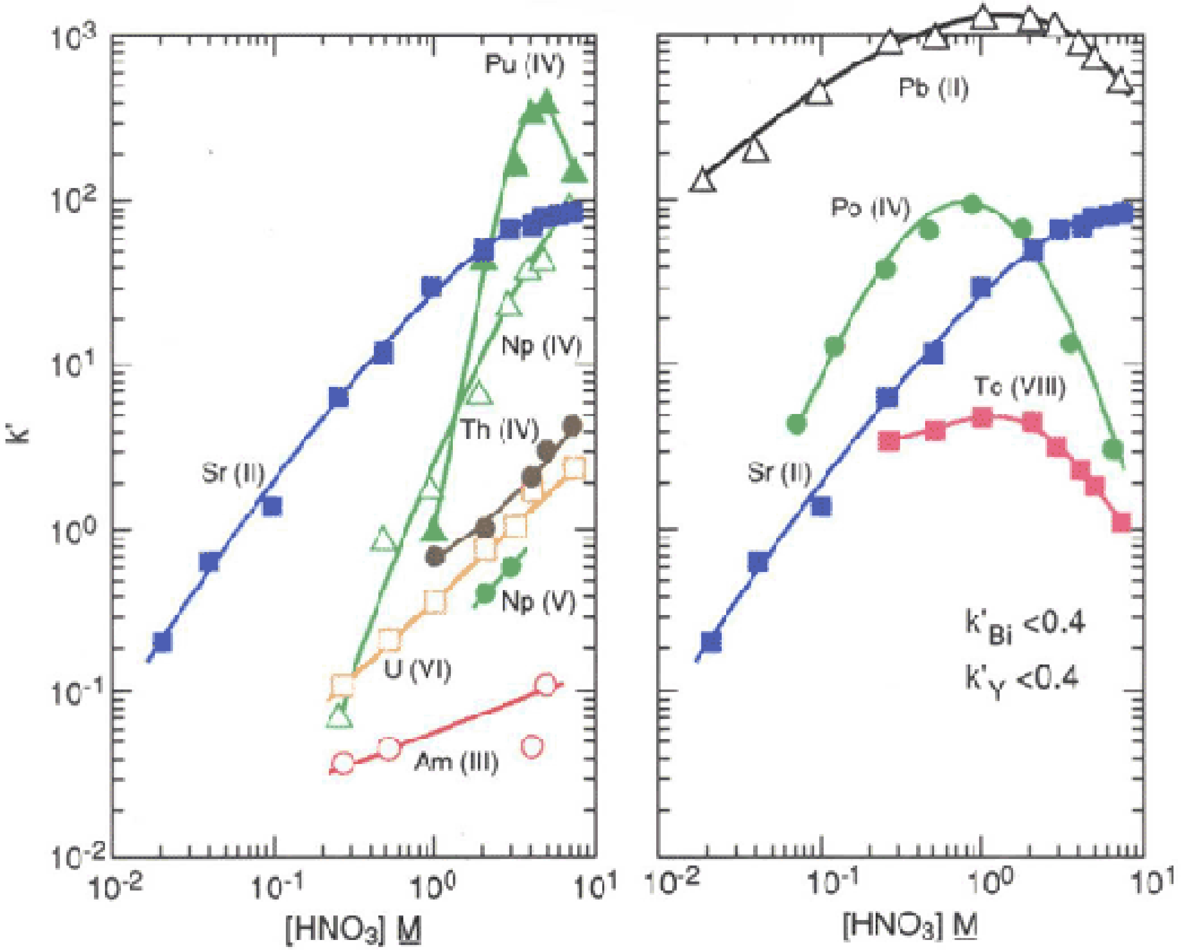
Sr and Pb Resin (concentration and diluent)



Figures 2 and 3

Acid dependency of k' for various ions at 23-25°C.
Sr Resin

Horwitz, et al., (HP292)



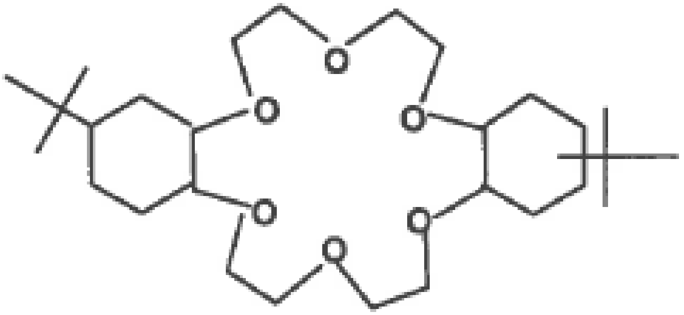
Figures 4 and 5

Acid dependency of k' for various ions at 23-25°C.
Sr Resin

Horwitz (HP199)

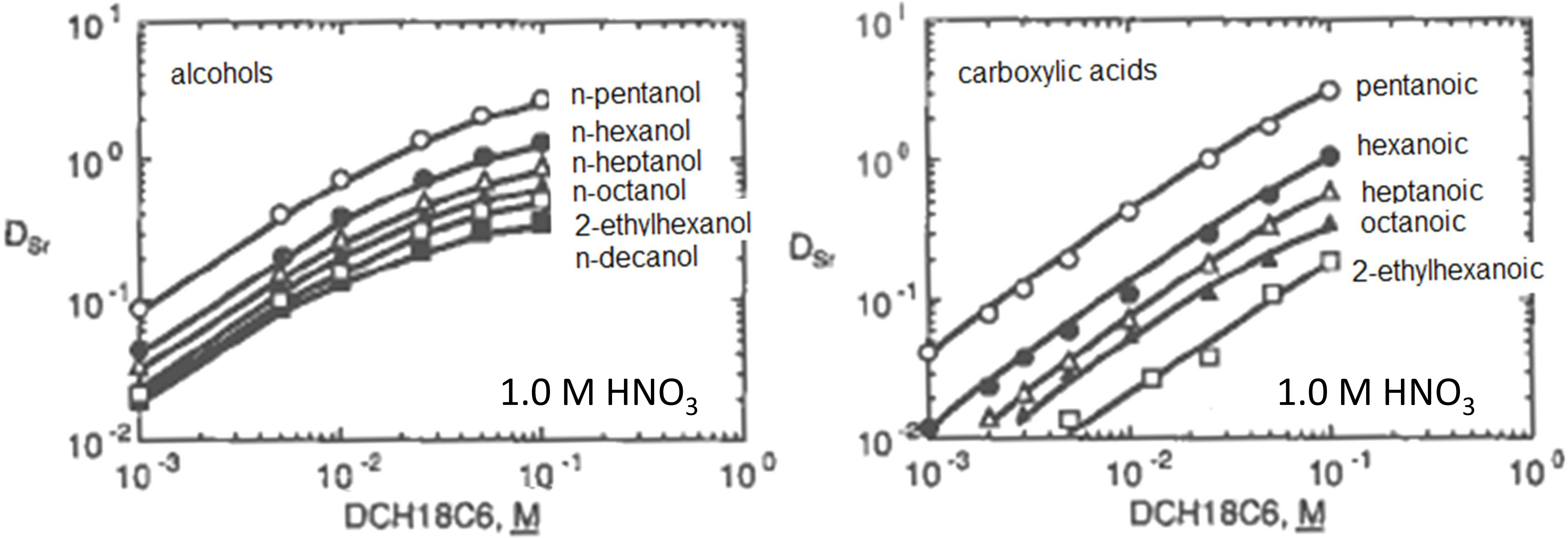
dtBCH18C6 (SREX) – Coextraction of HNO3/H2O

$$Sr^{2+} + 2NO_3^- + \overline{CE} \rightleftharpoons \overline{Sr(CE)(NO_3)_2}$$



Not enough energy from complexation to completely dehydrate and extract into non-polar(hydrophobic) diluents →

Use more polar diluents to promote co-extraction of water and HNO_3. (Also prevents aggregation of crown ether in organic phase)



dtBCH18C6 (SREX) – HNO_3 vs HCl

$$Sr^{2+}(OH_2)_6 + X\text{-}(OH_2)_n + \overline{L} \leftrightarrow \overline{SrLX_2(OH_2)_m} + (6+n-m)H_2O$$

$\Delta G_{hydration}$: NO_3^- = 314 kJ/mol Cl$^-$ = 338 kJ/mol

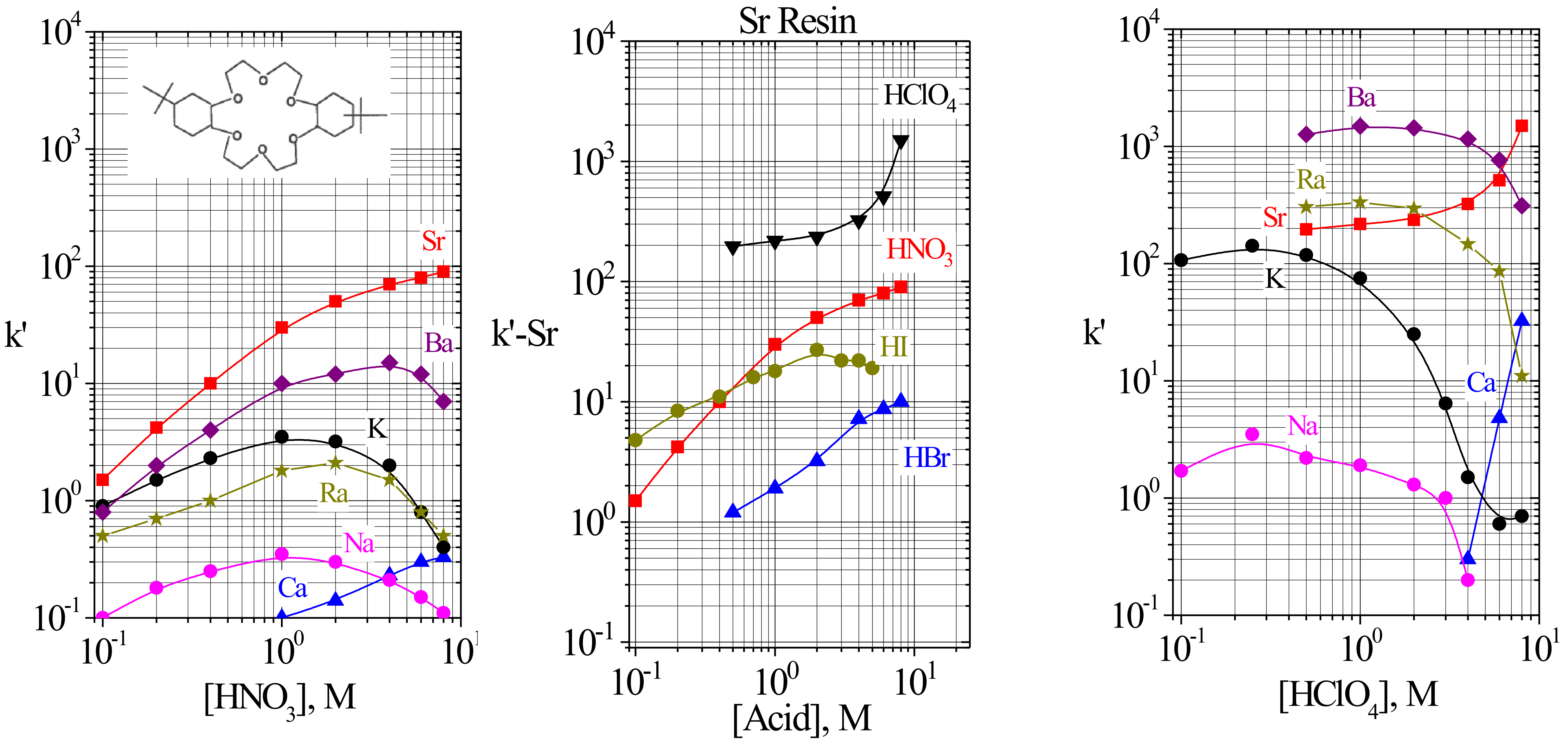
If nitrate chloride completely dehydrated = 24 kJ/mol difference

And **~24,000x** different in K_{ex}^{Sr}

Observed difference only ~**73**

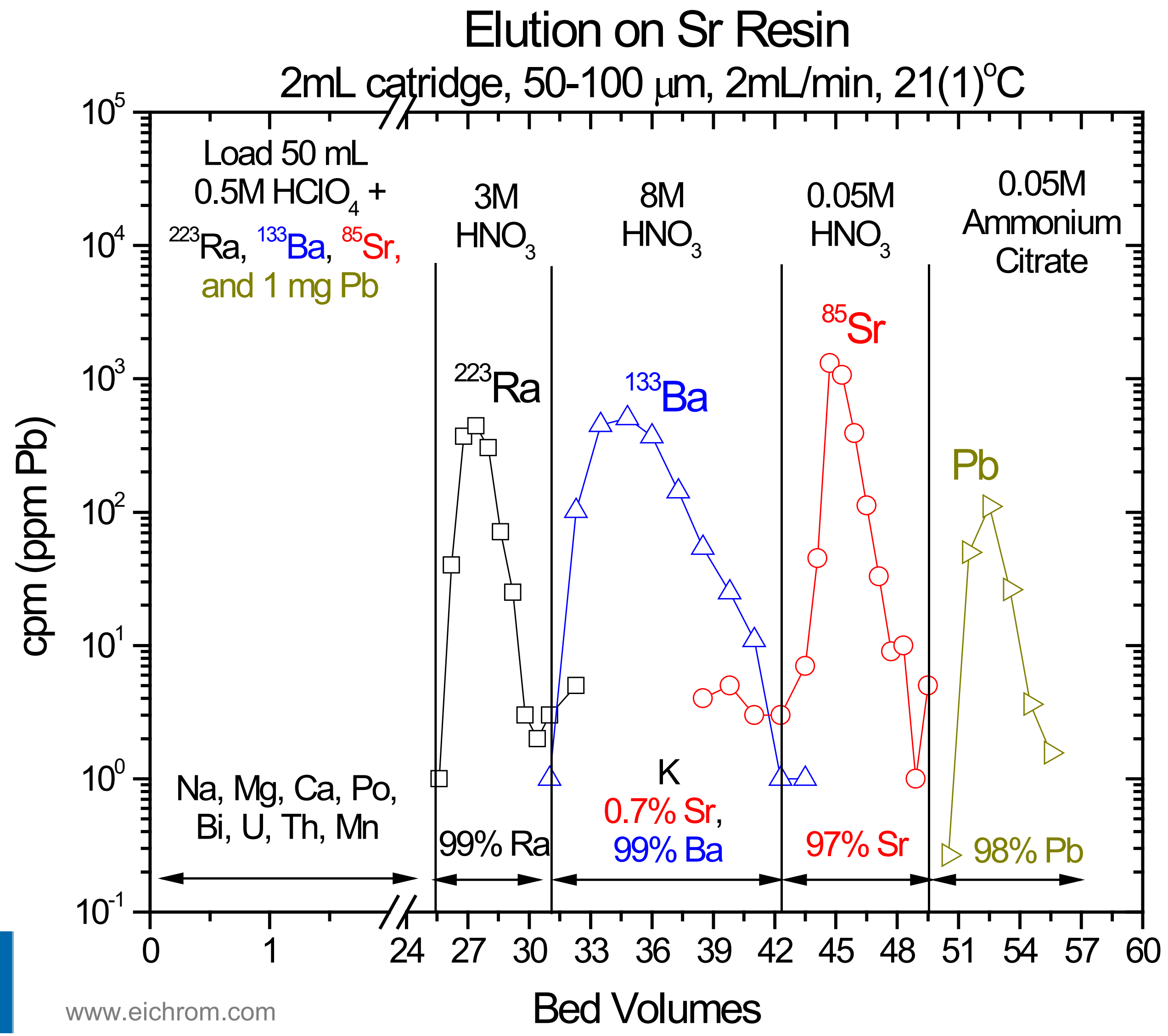
What about other counterions?....

Effect of counterion



Effect of counterion

"Influence of Large Univalent Anions on Ligand Selectivity," E. P. Horwitz, D. R. McAlister, 57th Radiobioassay and Radiochemical Measurement Conference, San Destin, FL, October 31- November 4, 2011.



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1985

Bioassay Emergency

ANL Employee Contaminated

- Accidental Ingestion of Plutonium.

- Bioassay required to prescribe/monitor chelation therapy (DTPA).

- Routine bioassay procedures could take over 1 week to complete.

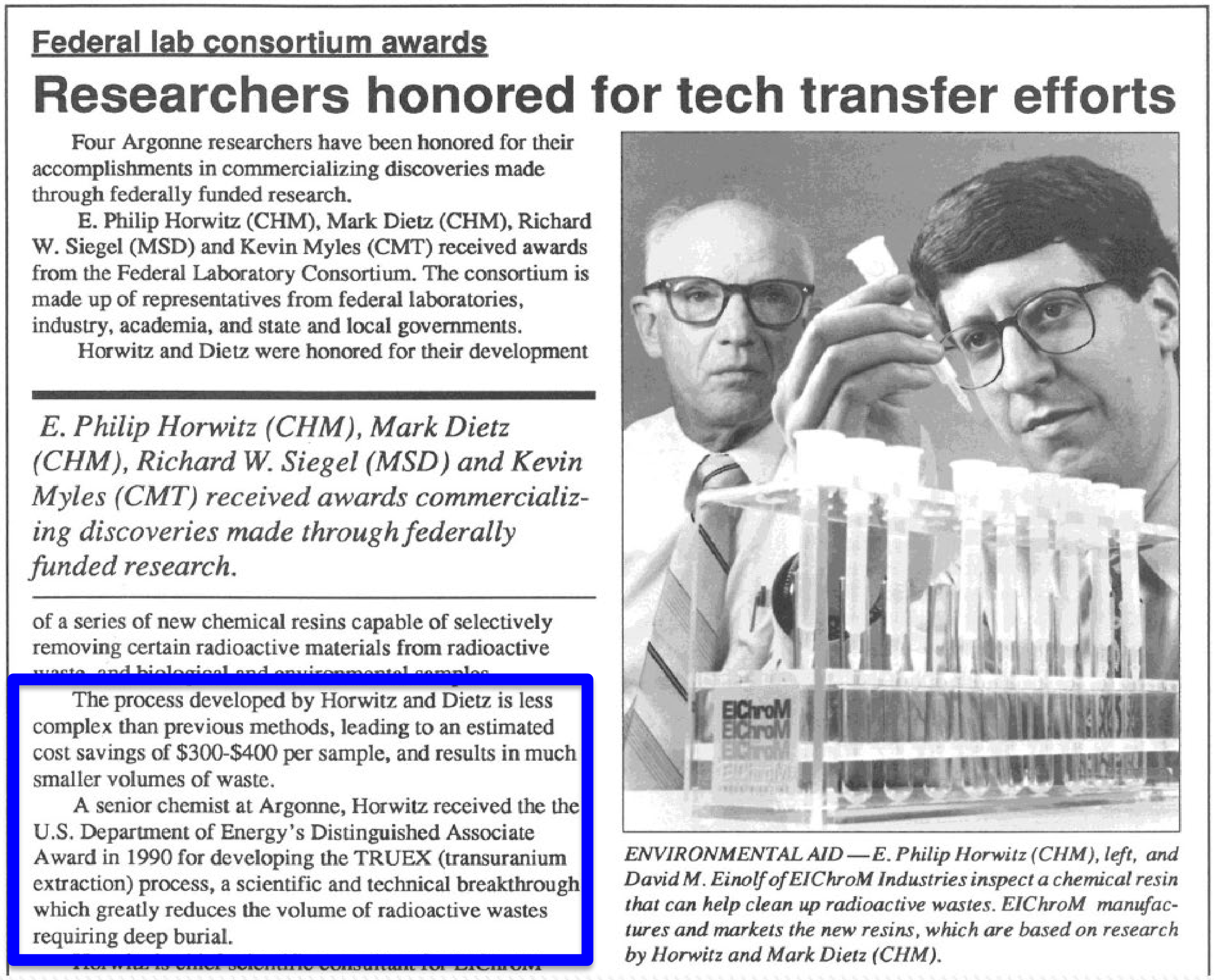
- Chemistry developed by Horwitz group identified as rapid alternative.

- Today: 4-8 hour turnaround for emergency bioassay samples using EXC based methods.

Maxwell, S. and Culligan, B., (2009), Rapid separation method for emergency water and urine samples, J. Radioanal. Nucl. Chem, 279 (No.3), 901

Eichrom Founded to Commercialize Technology

1930
1940
1950
1960
1970
1980
1990
2000
2010



Federal lab consortium awards

Researchers honored for tech transfer efforts

Four Argonne researchers have been honored for their accomplishments in commercializing discoveries made through federally funded research.

E. Philip Horwitz (CHM), Mark Dietz (CHM), Richard W. Siegel (MSD) and Kevin Myles (CMT) received awards from the Federal Laboratory Consortium. The consortium is made up of representatives from federal laboratories, industry, academia, and state and local governments.

Horwitz and Dietz were honored for their development of a series of new chemical resins capable of selectively removing certain radioactive materials from radioactive waste, and biological and environmental samples.

E. Philip Horwitz (CHM), Mark Dietz (CHM), Richard W. Siegel (MSD) and Kevin Myles (CMT) received awards commercializing discoveries made through federally funded research.

The process developed by Horwitz and Dietz is less complex than previous methods, leading to an estimated cost savings of $300-$400 per sample, and results in much smaller volumes of waste.

A senior chemist at Argonne, Horwitz received the the U.S. Department of Energy's Distinguished Associate Award in 1990 for developing the TRUEX (transuranium extraction) process, a scientific and technical breakthrough which greatly reduces the volume of radioactive wastes requiring deep burial.

ENVIRONMENTAL AID — E. Philip Horwitz (CHM), left, and David M. Einolf of EIChroM Industries inspect a chemical resin that can help clean up radioactive wastes. EIChroM manufactures and markets the new resins, which are based on research by Horwitz and Mark Dietz (CHM).

Legacy of Phil’s 60 years at ANL / Eichrom

- Widespread use of extraction chromatography.
- Extensive library of methods combining precipitation, ion exchange and extraction chromatography.
    - Bioassay
    - Environmental Analysis
    - Geochronometry
    - Nuclear Forensics
    - Nuclear Medicine/Isotope Production
- Extensive community of researchers developing new separations to meet current needs.

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Eichrom Method ACW17-VBS
Am/Cm, Pu/Np, Th, U, Sr in water

Steps

Focus on water samples, but methods can be adapted to analyze other liquids and dissolved solid matrices.

- Tracer Equilibration
- Calcium Phosphate Precipitation
- Load Solution and Red/Ox Adjustments
  - Oxidizing: Pu(IV)/Np(IV)
- TEVA/TRU/Sr vs TEVA/TRU/DGA/Sr
- Alpha Source Preparation (CeF3)

Acidification and Tracer Equilibration

Water Sample in glass beaker. Acidify pH 2.

1) Aliquot up to 1000mL of water into glass beaker. (Filter if necessary)

2) Add 5mL concentrated HNO_3 and yield tracers.

^{229}Th, ^{243}Am, ^{232}U*, ^{236}Pu or ^{242}Pu, Stable Sr

*Self-cleaning (Eichrom Method TPO1)

3) Add 2mL of 1.25M $Ca(NO_3)_2$. (100 mg Ca)

4) Heat samples at medium setting for 30-60 minutes.

5) Remove samples from heat.

Calcium Phosphate Precipitation

6) Add 0.75mL of phenolphthalein and 5mL of 3.2M $(NH_4)_2HPO_4$. (excess PO_4^{3-})

7) While stirring sample, slowly add conc. NH_4OH until reaching pH 8-9.

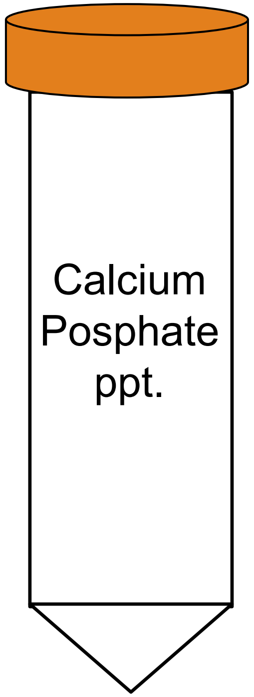
8) Cool to room temperature. Allow precipitate to settle or centrifuge.

9) Decant supernate and discard as waste.

10) Transfer precipitate to centrifuge tube with DI water.

11) Centrifuge ~10minutes at 2000rpm. Decant supernate.

12) Add 10mL DI water to ppt. Mix well. Centrifuge. Decant supernate.



Centrifuge.
Decant Supernate.
Wash ppt with H_2O.
Centrifuge. Decant.

Calcium Phosphate Precipitation

Calcium phosphate - carrier for actinides in all oxidation states, Fe(III) and Sr.

Requires pH adjustment to 8-9. (Higher pH can carry more matrix)

Easy to dissolve in acid for further processing.

Phosphate will strongly affect separation of Th(IV), Pu(IV) and Np(IV) on TEVA and UTEVA.

Addition of $Al(NO_3)_3$ reduces impact by complexing phosphate.

Load Solution and Red/Ox Adjustments

14) Dissolve residue in 16mL 3M HNO_3-1M $Al(NO_3)_3$. (Al complexes PO_4^{3-})

Add 0.5 mL 1.5M Sulfamic Acid, (scavenges NO_2^-)

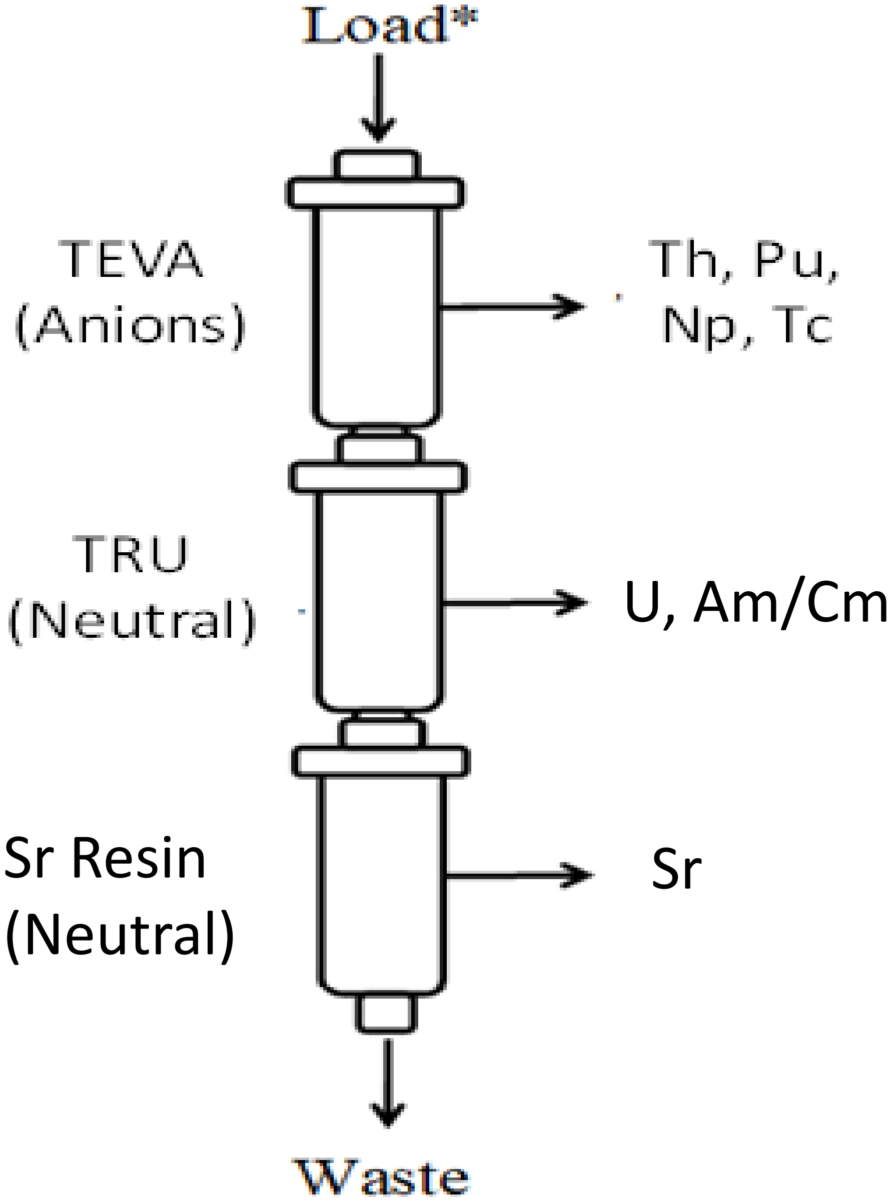
0.2 mL of 5 mg/ mL Fe, (will act as reducing agent)

1.5 mL 1M Ascorbic Acid (reduces to Fe(II) => Pu(III)/Np(IV))

Swirl to mix. Wait 3-5 minutes. (Np(V) to Np(IV) slower, may need more time)

15) Add 1mL 3.5M $NaNO_2$. Swirl to mix. (Pu(III) to Pu(IV), Fe(II) to Fe(III))

Cartridge Separations



Retains (IV) actinides from HNO_3.

Sensitive to phosphate.

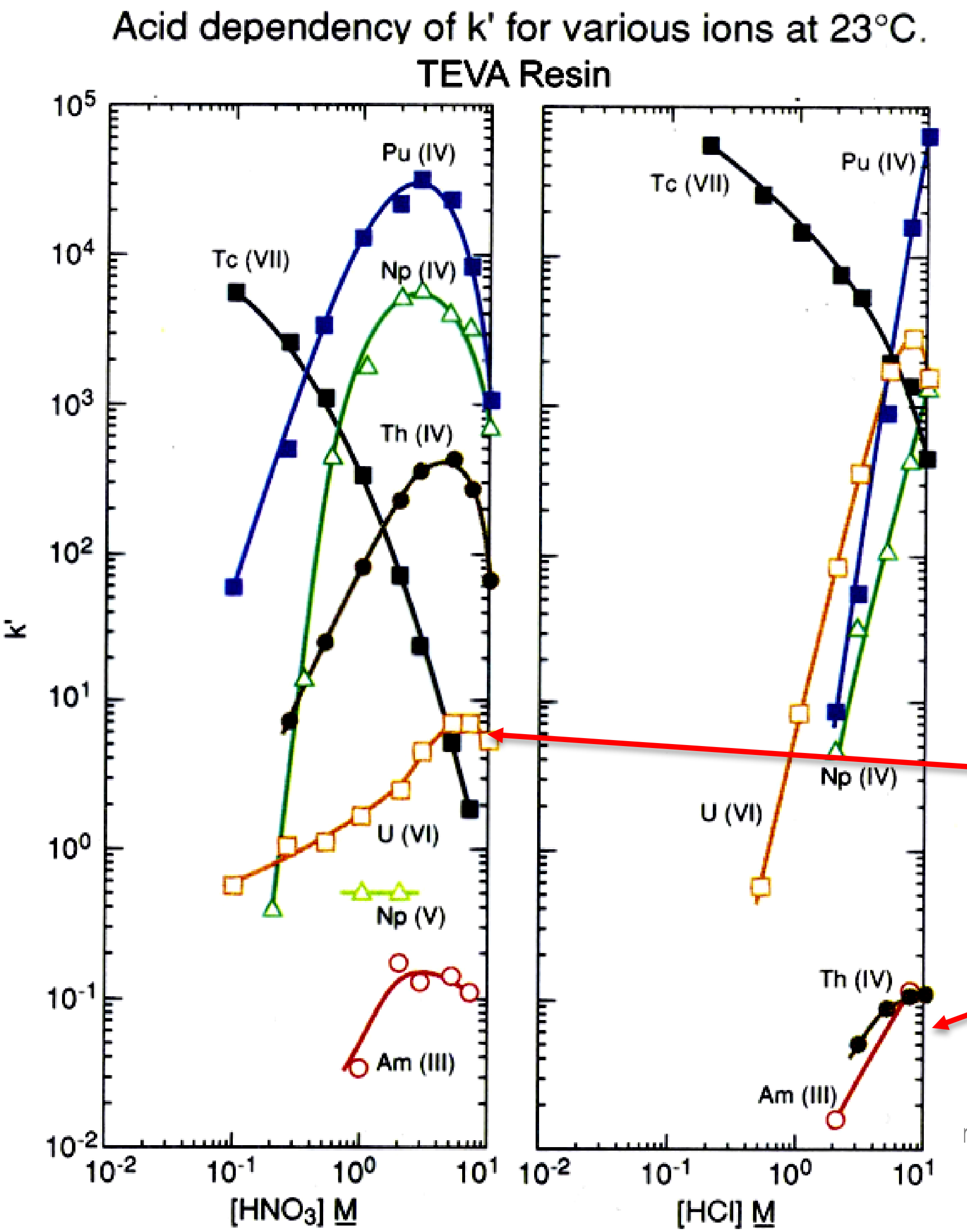
Retains (III), (IV), (VI) actinides from HNO_3.

Am/Cm(III) Sensitive to Fe(III).

Retains Sr(II)

Sensitive to Ba(II), K(I), very large excess of Ca(II).

TEVA Resin


Acid dependency of k' for various ions at 23°C.
TEVA Resin

16) Precondition TEVA-TRU-Sr with 5mL 3M HNO_3.

17) Load sample onto TEVA-TRU-Sr. Allow liquid to drain. TEVA retains Th, Np, Pu. TRU retains Am, Cm, U. SR resin retains Sr.

18) Rinse sample tube with 5mL 3M HNO_3.
Add rinse to TEVA-TRU-Sr. Allow liquid to drain.

19) Rinse TEVA-TRU-Sr with 5mL 3M HNO_3. Allow liquid to drain.

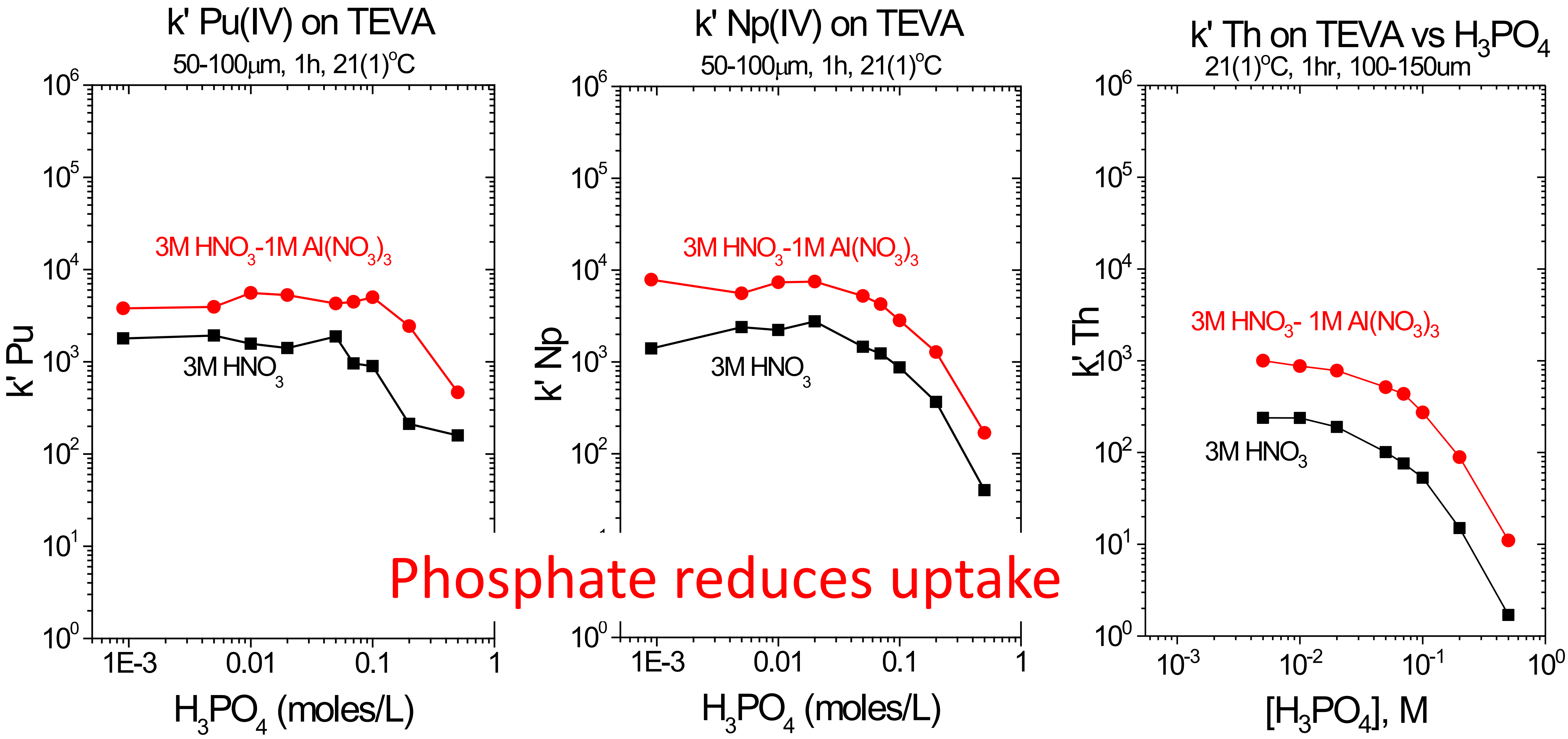
20) Separate TEVA,TRU,Sr cartridges.

21) Rinse TEVA column with 20mL 3M HNO_3.
Remove last traces of U(VI)

22) Place clean centrifuge tube below TEVA.
Strip Th with 15mL 9M HCl.

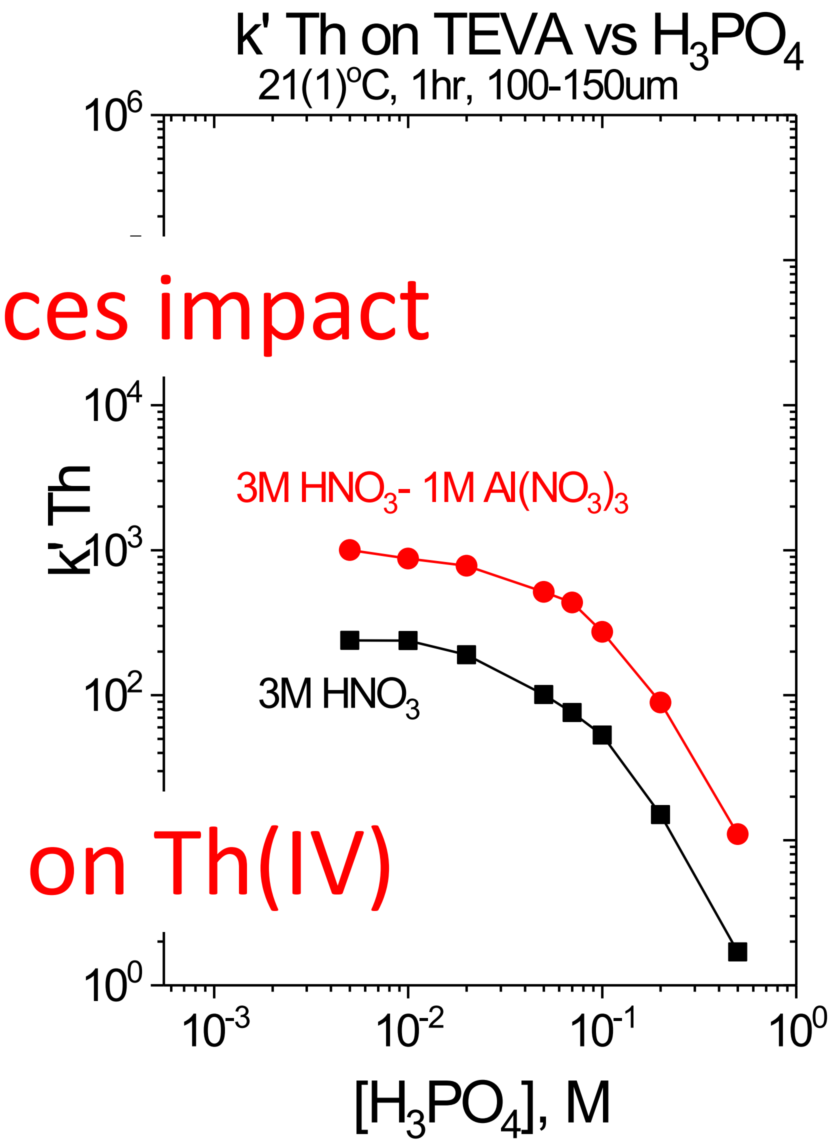
23) Place clean centrifuge tube below each TEVA. Strip Pu-Np with 20mL 0.1M HCl-0.05M HF-0.03M $TiCl_3$.

TEVA Resin (Impact of phosphate)



Phosphate reduces uptake

TEVA Resin (Impact of phosphate)



$Al(NO_3)_3$ reduces impact

High Ca samples may require
20-30 mL 3M HNO_3-$Al(NO_3)_3$

Largest Impact on Th(IV)

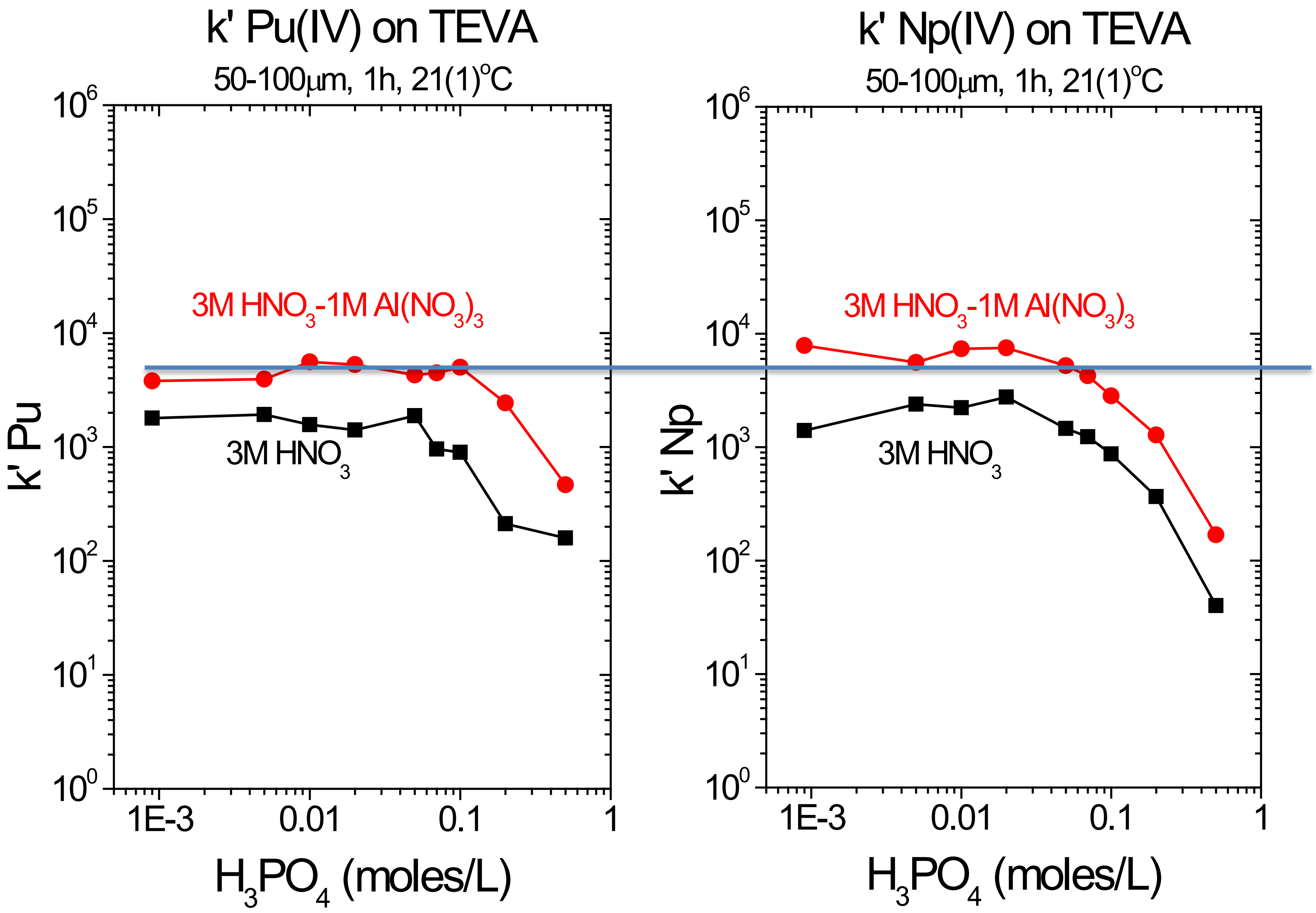
eichrom®

TEVA Resin

Recovery of Th-230 on 2 mL TEVA Cartridge (200 mg Ca)

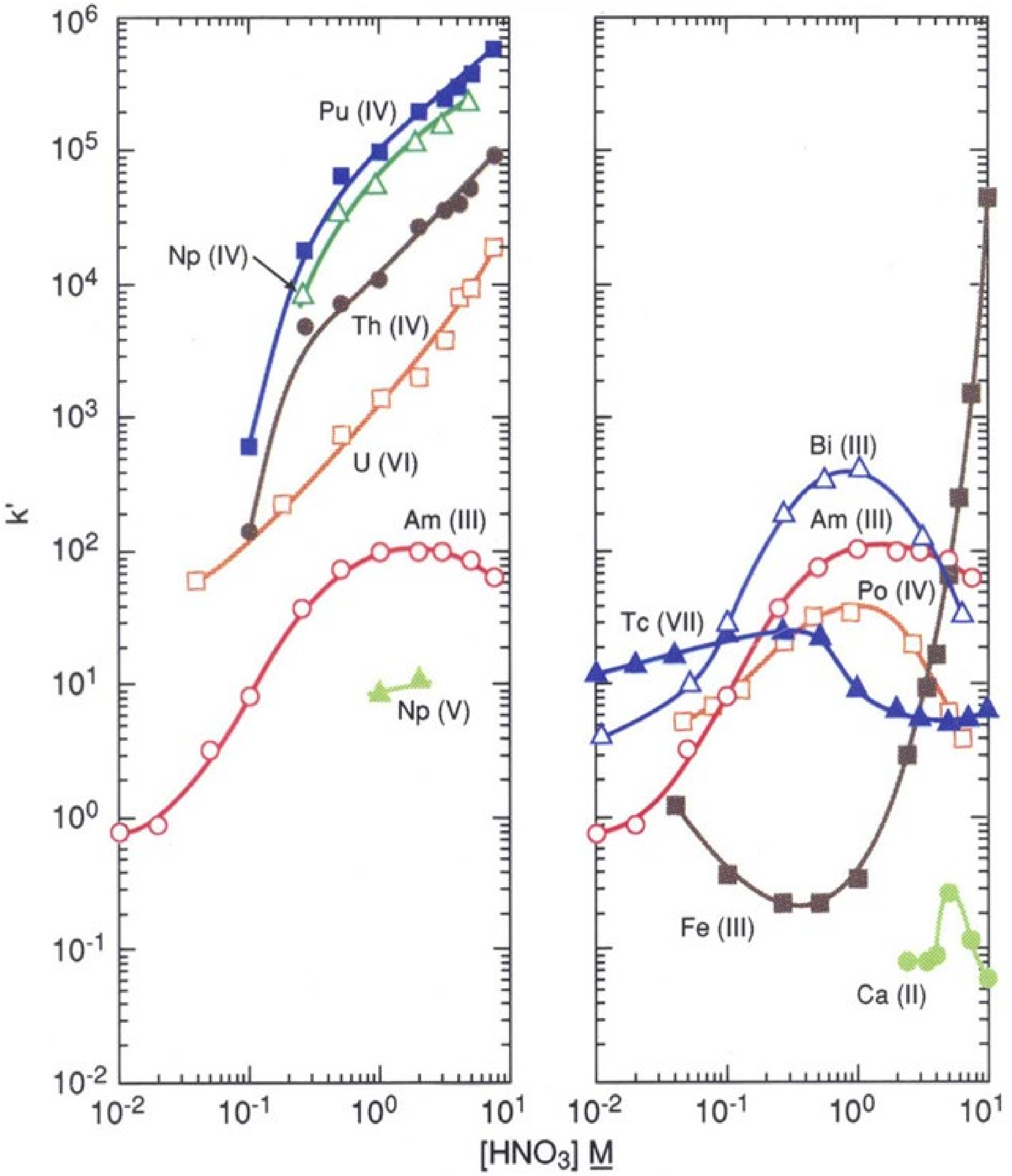
volume (mL)				
3M HNO3	mL	% Th-230		
1M Al(NO3)3	Load Volume	Load	Rinse	Strip
10	18	24.2	6.0	69.8
20	28	3.2	3.1	93.7
30	38	1.5	1.0	97.5
40	48	0.5	0.5	99.0
50	58	0.5	0.1	99.4

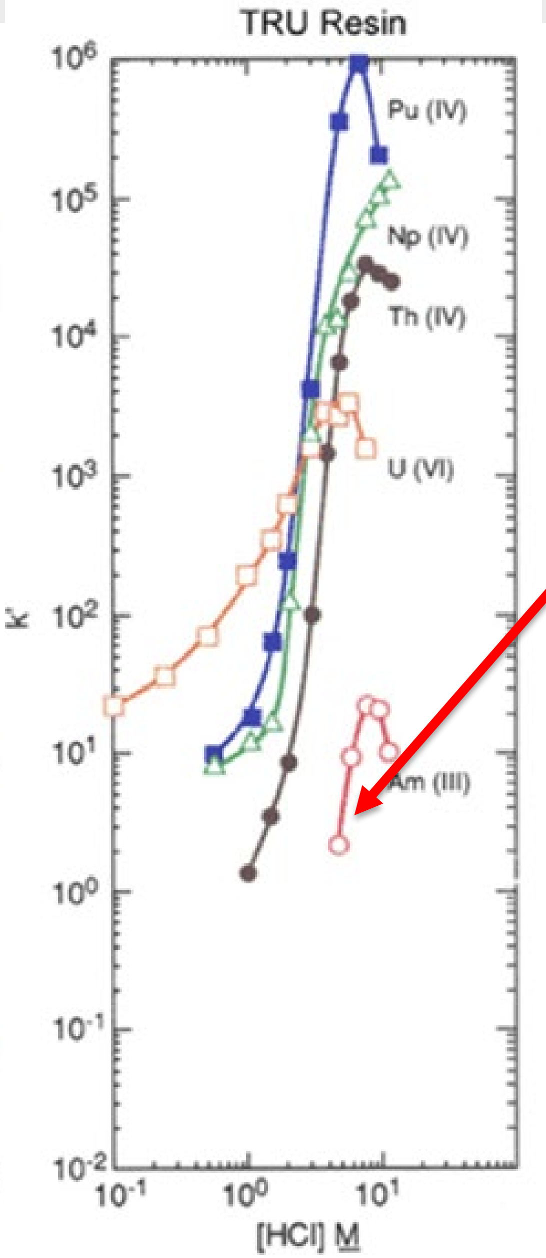
TEVA Resin (Impact of phosphate)



$Al(NO_3)_3$ important to ensure similar recoveries Np(IV)/Pu(IV) when using ^{236}Pu tracer for both.

TRU Resin





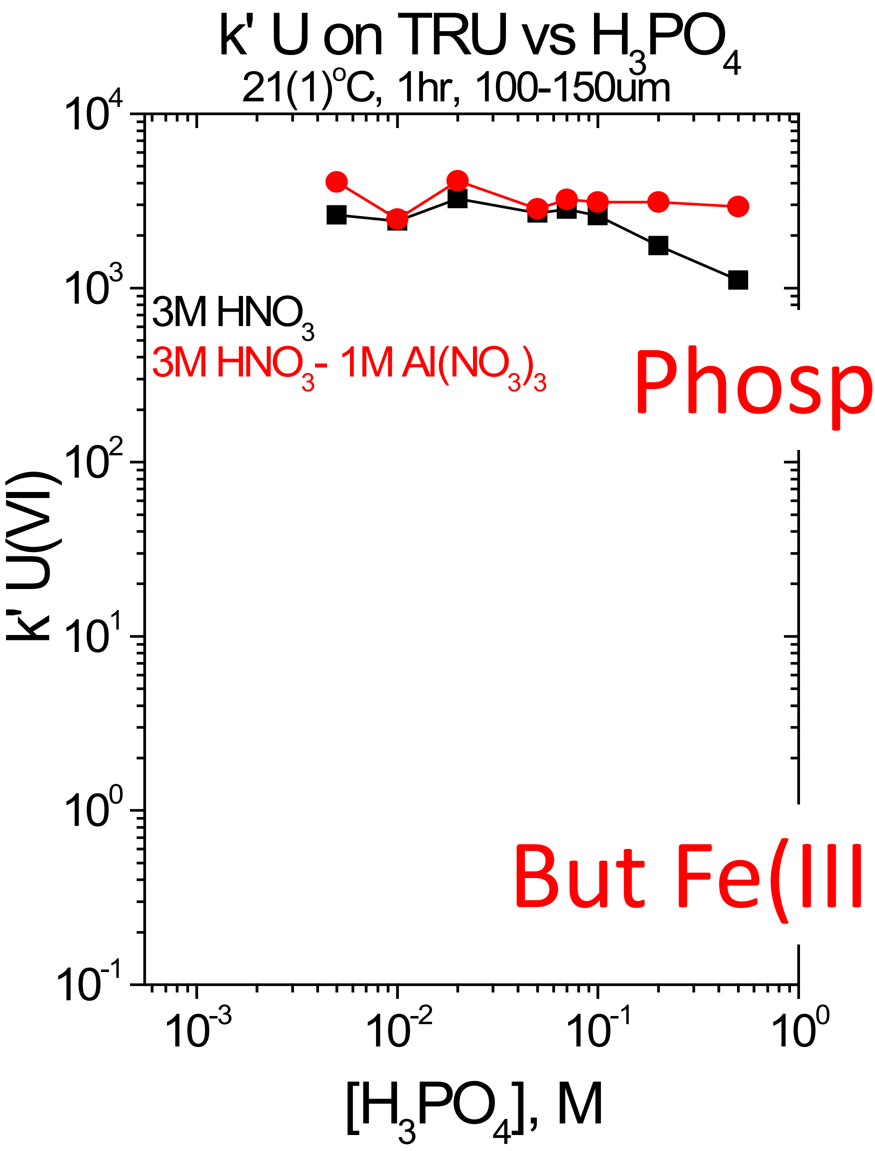
24) Place clean centrifuge tubes below TRU. Strip Am with 15mL of 4M HCl. (DGA)

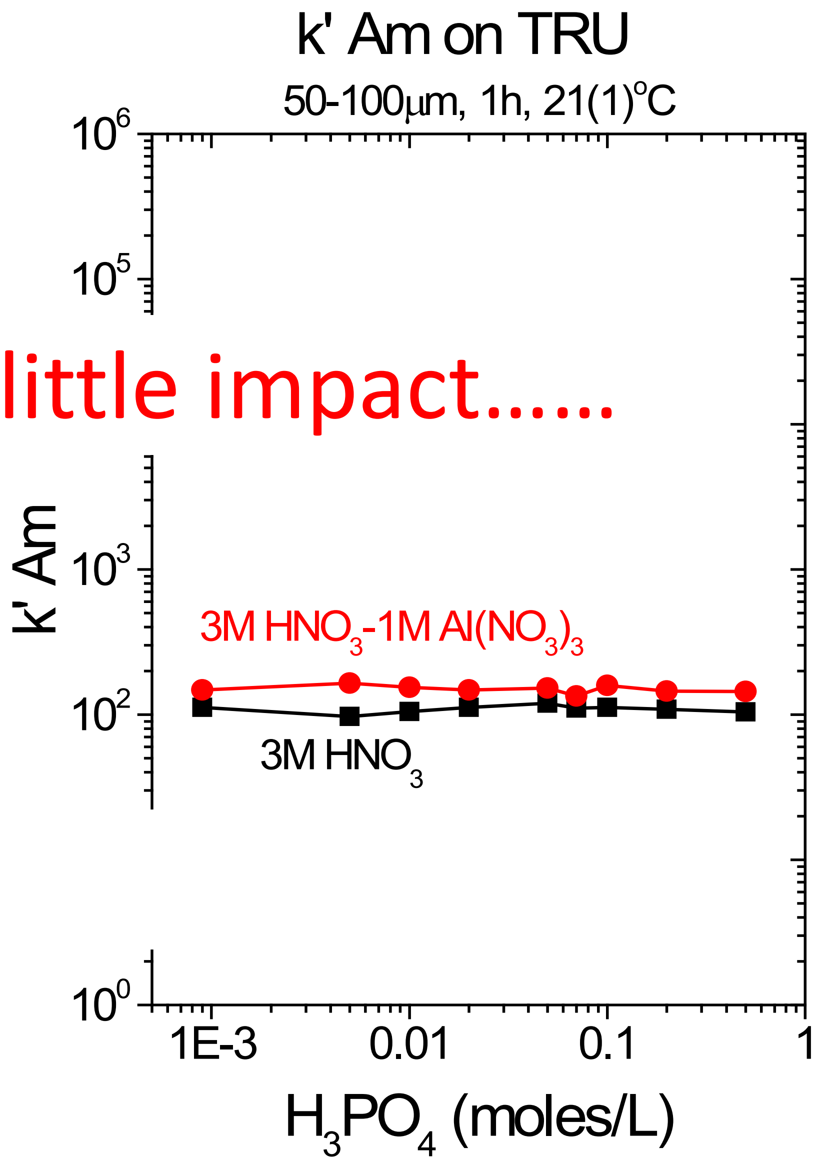
25) Rinse TRU with 12mL 4M HCl-0.1M HF. Discard as waste.

(Removes Th, Pu, Np that may have broken through TEVA)

26) Place a clean centrifuge tube below each cartridge. Strip U with 15mL 0.1M ammonium bioxalate.

TRU Resin

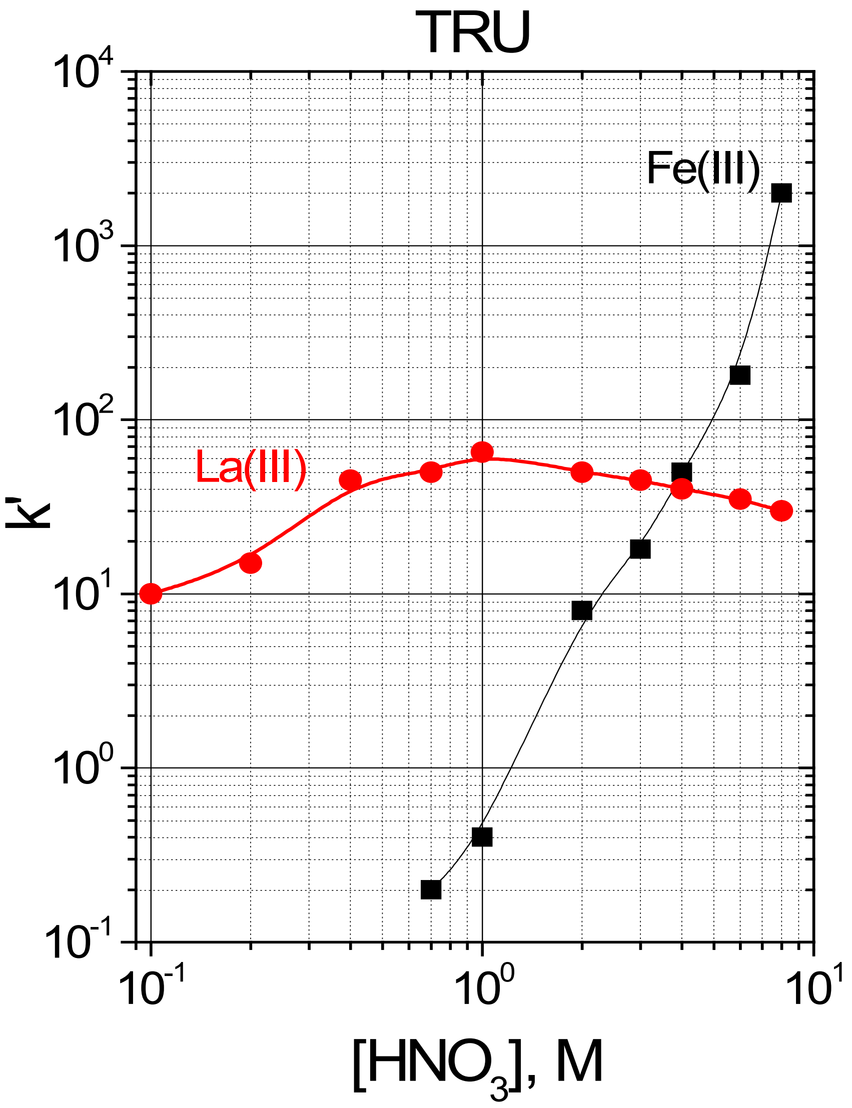


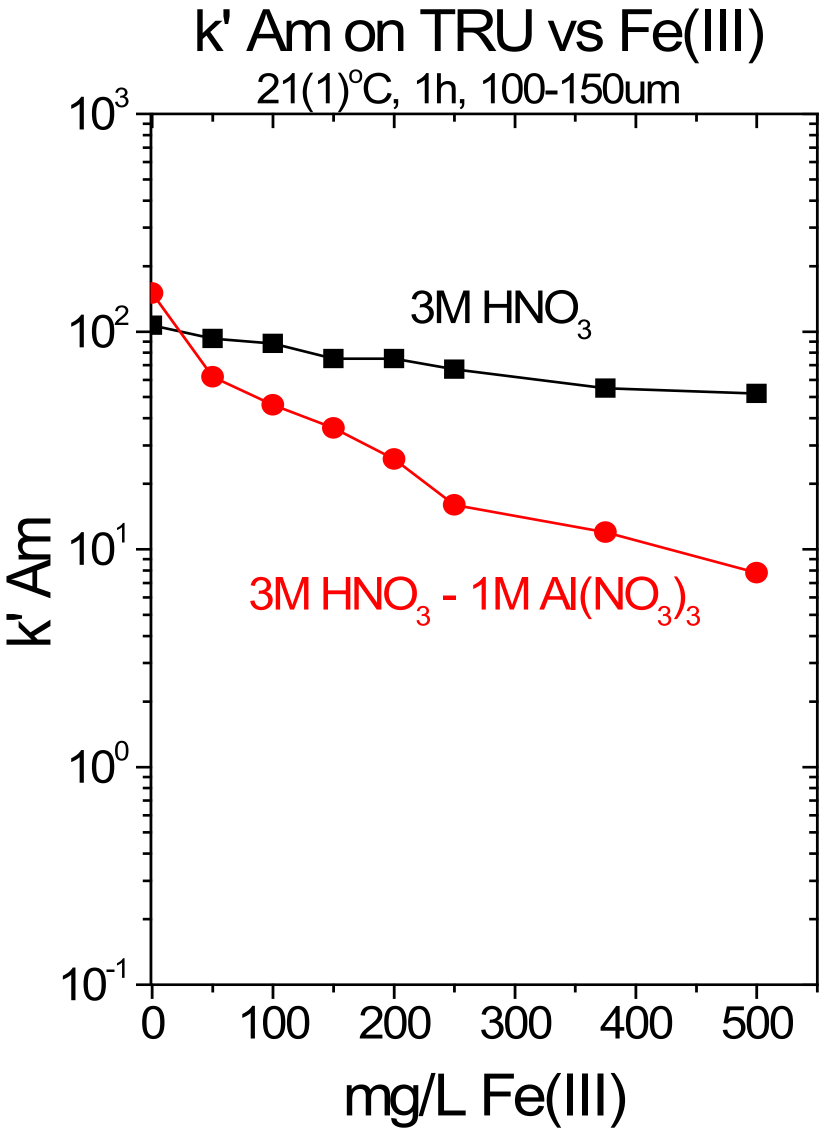


Phosphate has little impact……

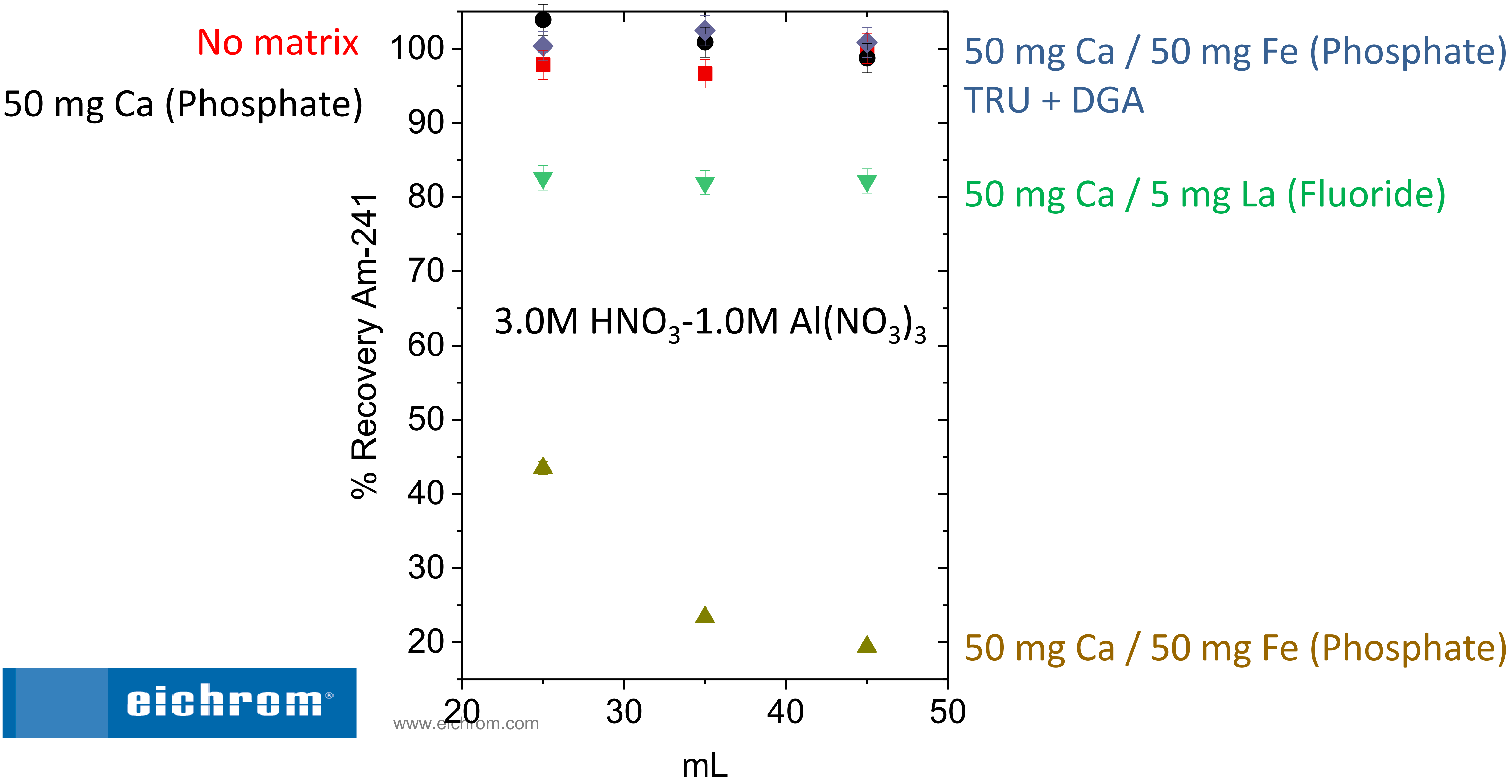
But Fe(III)…….

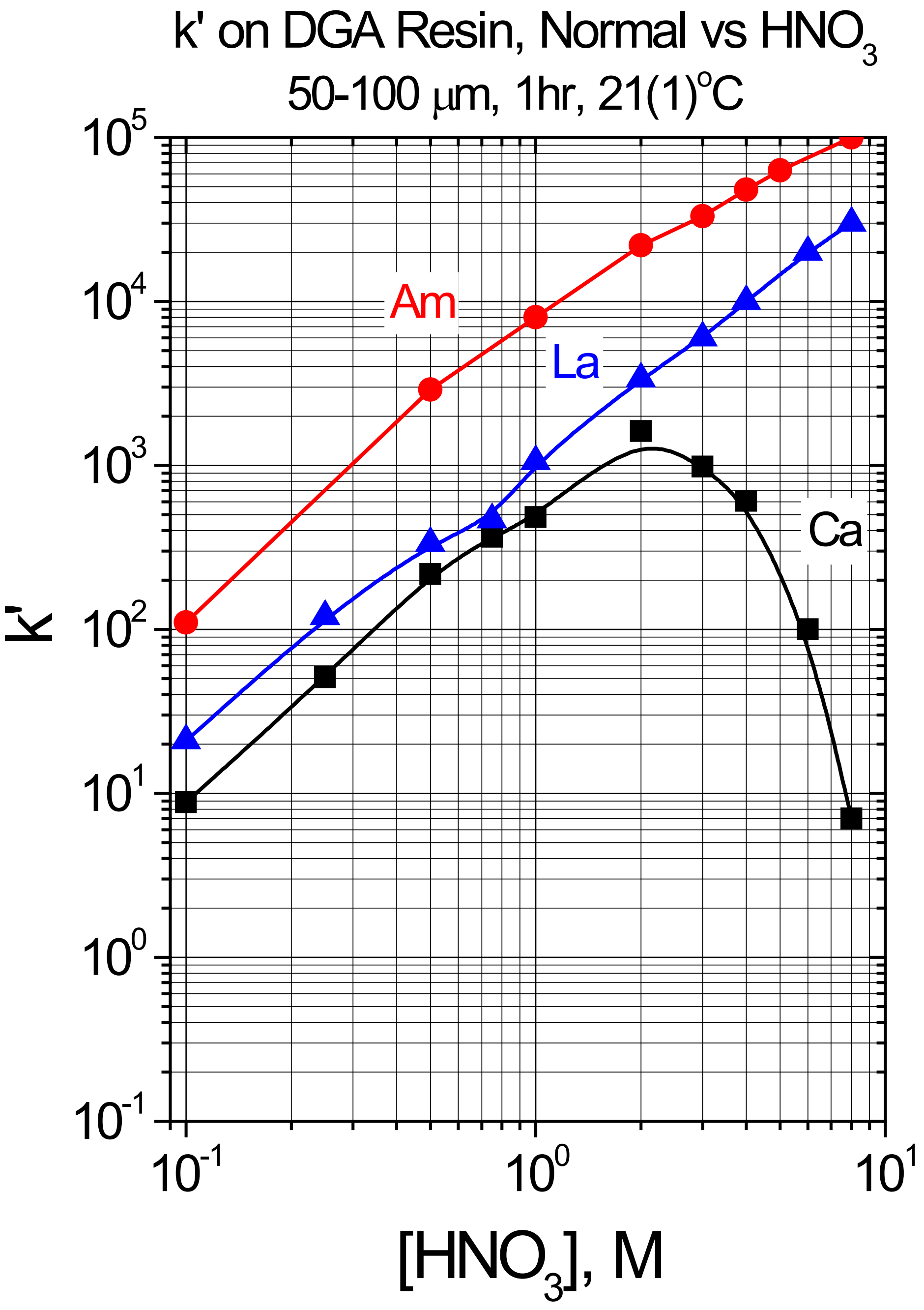
TRU Resin


TRU
Fe(III)
La(III)
k'
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{-1}
10^{0}
10^{1}
[HNO$_3$], M


k' Am on TRU vs Fe(III)
21(1)°C, 1h, 100-150um
3M HNO$_3$
3M HNO$_3$ - 1M Al(NO$_3$)$_3$
k' Am
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
0
100
200
300
400
500
mg/L Fe(III)

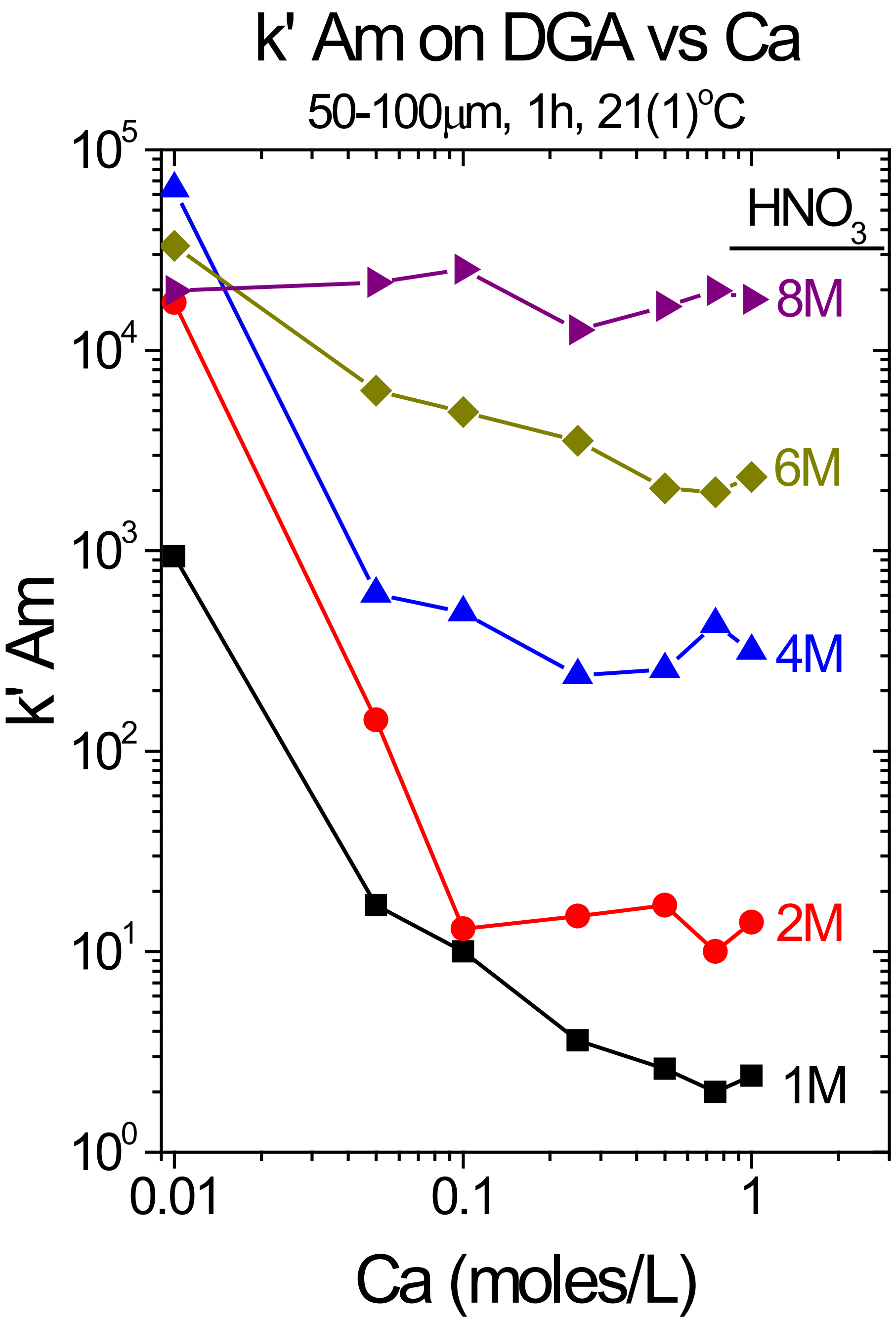
Recovery of Am-241 on 2 mL TRU Resin Cartridge vs volume of load solution





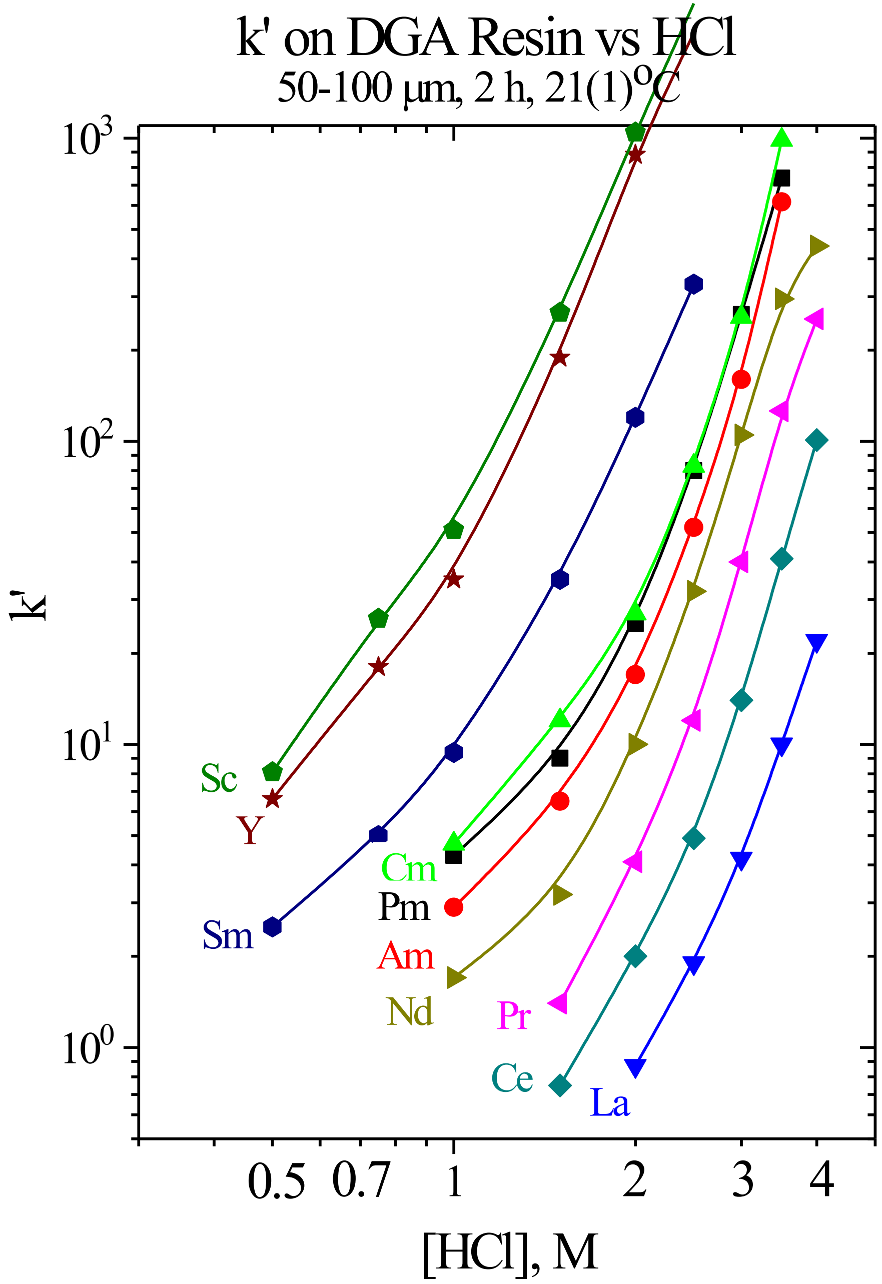
k' on DGA Resin, Normal vs HNO_3

50-100 μm, 1hr, 21(1)°C



k' Am on DGA vs Ca

50-100μm, 1h, 21(1)°C



DGA also allows separation of light REE (La, Ce) from Am/Cm using a 2-3M HCl rinse.

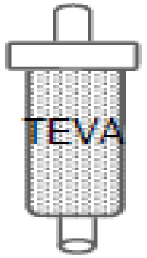
Separation of heavier REE (soils, rocks, etc.) requires TEVA-SCN.

(1) Add 2 mL 70% HNO_3 + 50 uL 10% H_2SO_4 to Am/Cm eluate from TRU or DGA Resin separation. Evaporate to dryness.

(2) Ash to dryness with 3 mL 70% HNO_3 + 2 mL 30% H_2O_2.

(3) Dissolve Am/Cm in 5 mL 4M NH_4SCN -0.1M Formic acid.

(4) Precondition 2 mL TEVA cartridge with 5 mL 4M NH_4SCN -0.1M Formic acid.



(5) Load Am/Cm from step (3) on TEVA.

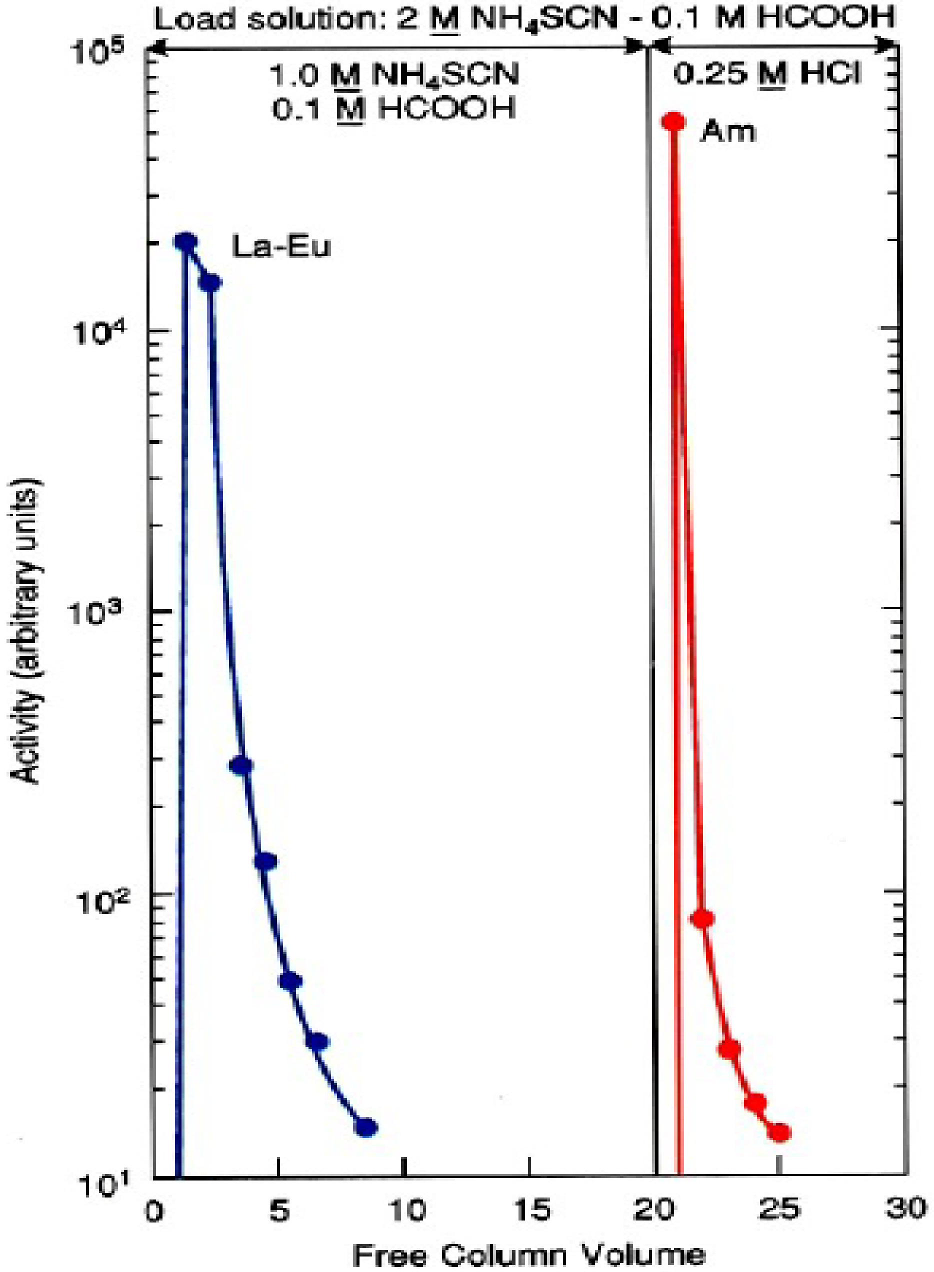
(6) Rinse Am/Cm beaker with 5 mL 4M NH_4SCN-0.1M Formic acid. Add to TEVA.

(7) Rinse TEVA w/ 10 mL 1.5M NH_4SCN-0.1M Formic acid.

(8) Strip Am/Cm from TEVA with 20 mL 1M HCl.

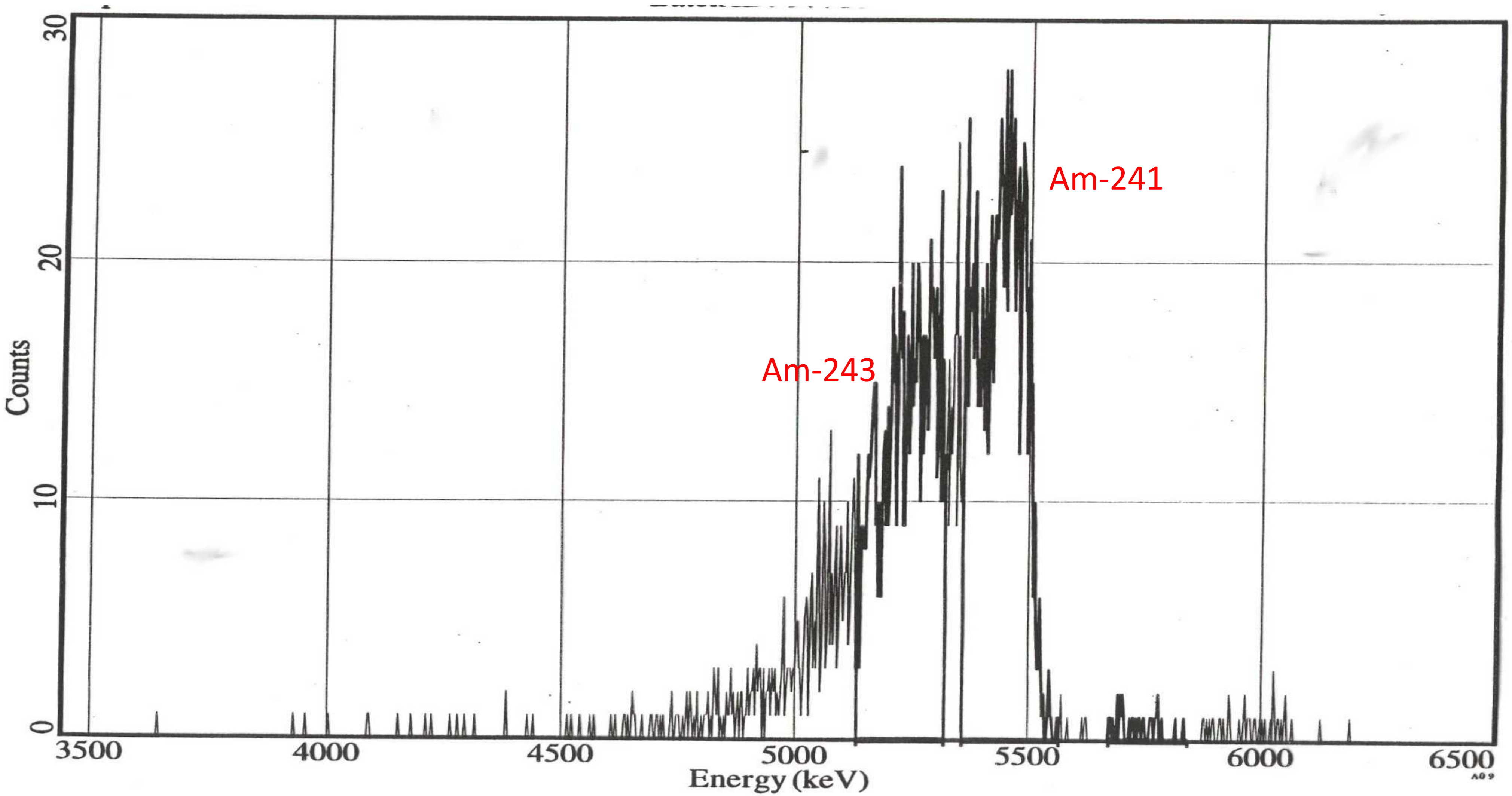
(9) Prepare alpha spectrometry source using rare earth fluoride microprecipitation (AN-1805).

Separation of light lanthanides (La-Eu) from Am using TEVA Resin Column



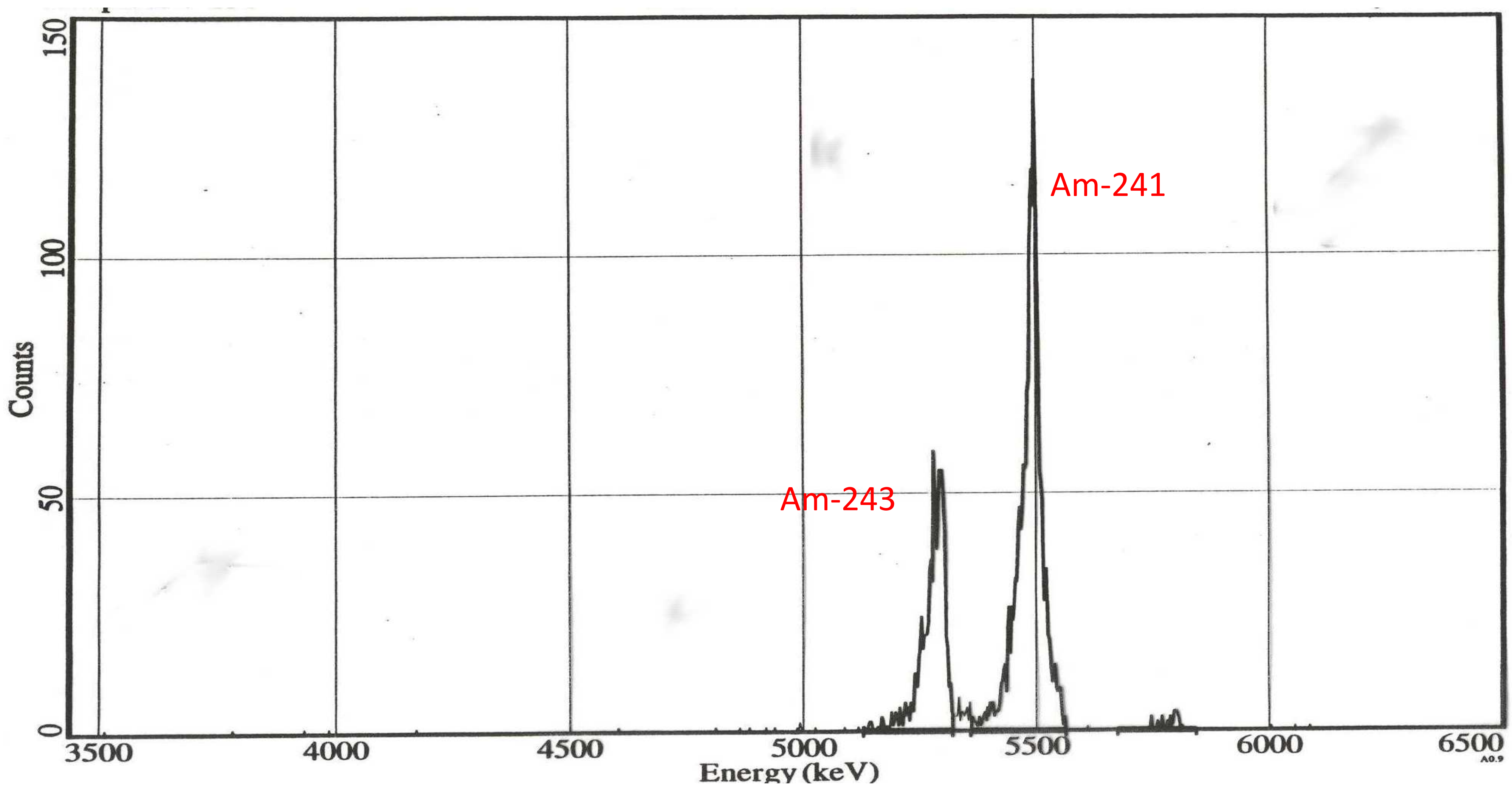
Americium Spectrum after TRU Resin Separation

presence of rare earths degrades spectrum- self absorption issues

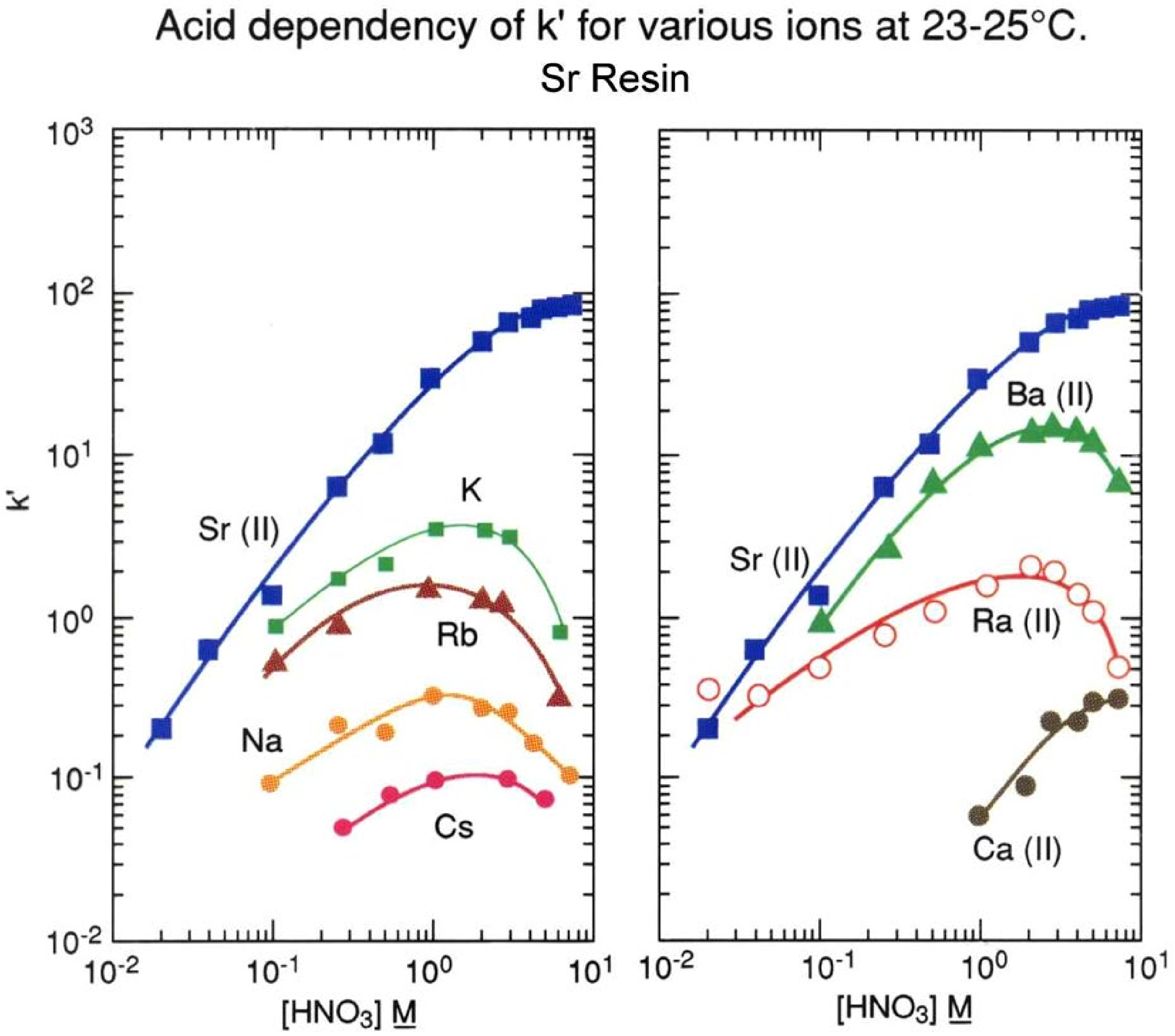


Am Spectrum after TEVA Resin Separation

Lanthanide elements removed - cleaner spectrum



Sr Resin



Acid dependency of k' for various ions at 23-25°C.

Sr Resin

27) Rinse Sr Resin with 5mL 3M HNO_3-oxalic acid.

28) Rinse Sr Resin with 5mL 8M HNO_3.

29) Rinse Sr Resin with 15mL 0.05M HNO_3.

Sr fraction will contain all radio-strontium and stable Sr carrier.

Determine Sr yield from stable Sr via ICP-AES, ICP-MS or gravimetrically.

Count Sr via gas flow proportional counter or LSC for total radiostrontium or follow method for discrimination of 90Sr/89Sr.

Alpha Source Preparation (CeF3)

Rapid method with adequate resolution for most analyses.
- No evaporations
- Additional removal of U(VI)

Add 50-100 ug of Ce

Add $TiCl_3$ to U samples, U(IV) will carry on CeF_3

Add H_2O_2 to non-U samples, U(VI) will not carry on CeF_3

Add HF (or NH_4HF) to all samples

1) Dilute samples as necessary and add Ce Carrier (See Table I).

2) **U Samples**, Add 0.5mL 10% $TiCl_3$

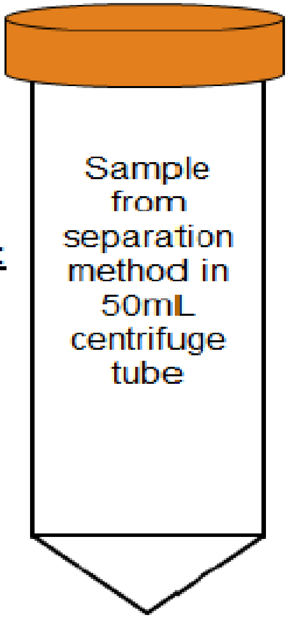
3) **Th, Np, Pu, Am/Cm samples requiring additional U decontamination:** Add 50mL 30% H_2O_2.

4) Swirl to mix.

5) Add 1-3.5mL conc. HF (see Table I).

6) Swirl to mix.

7) Wait 20-30 minutes before filtration.



8) Ensure tight fit of filter assembly.

9) Engage vacuum.

10) Wet filter with 3-5mL 80% ethanol.

11) Wet filter with 3-5mL DI water.

12) Add sample.

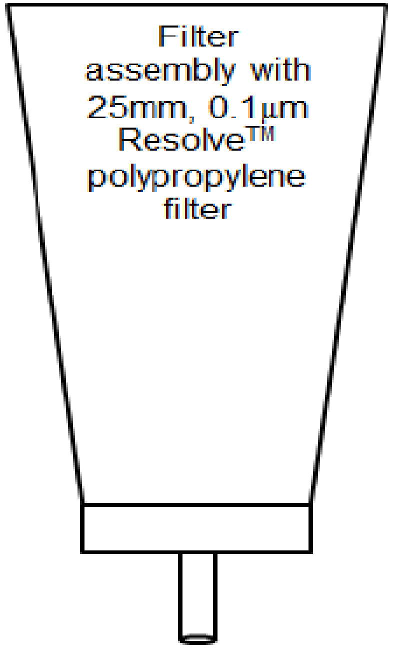
13) Rinse tube with 5mL DI water and add to filter assembly.

14) Allow all fluid to pass through filter.

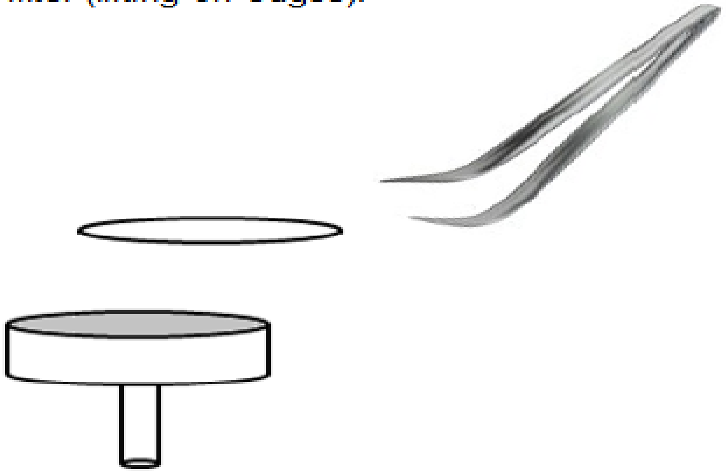
15) Rinse filter funnel with 3-5mL DI Water.

16) Rinse filter funnel with 2-3mL ethanol.

17) Filter until dry.



18) Remove filter (lifting on edges).

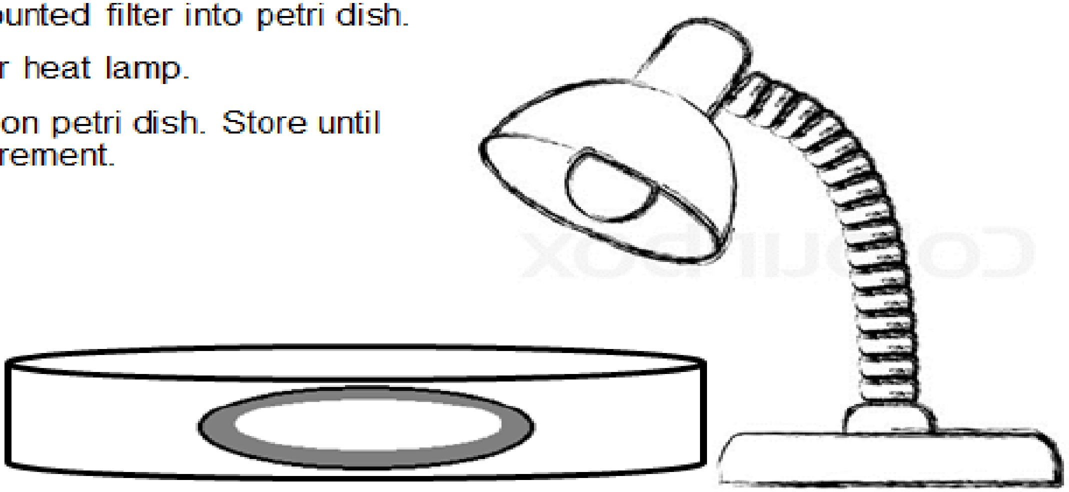


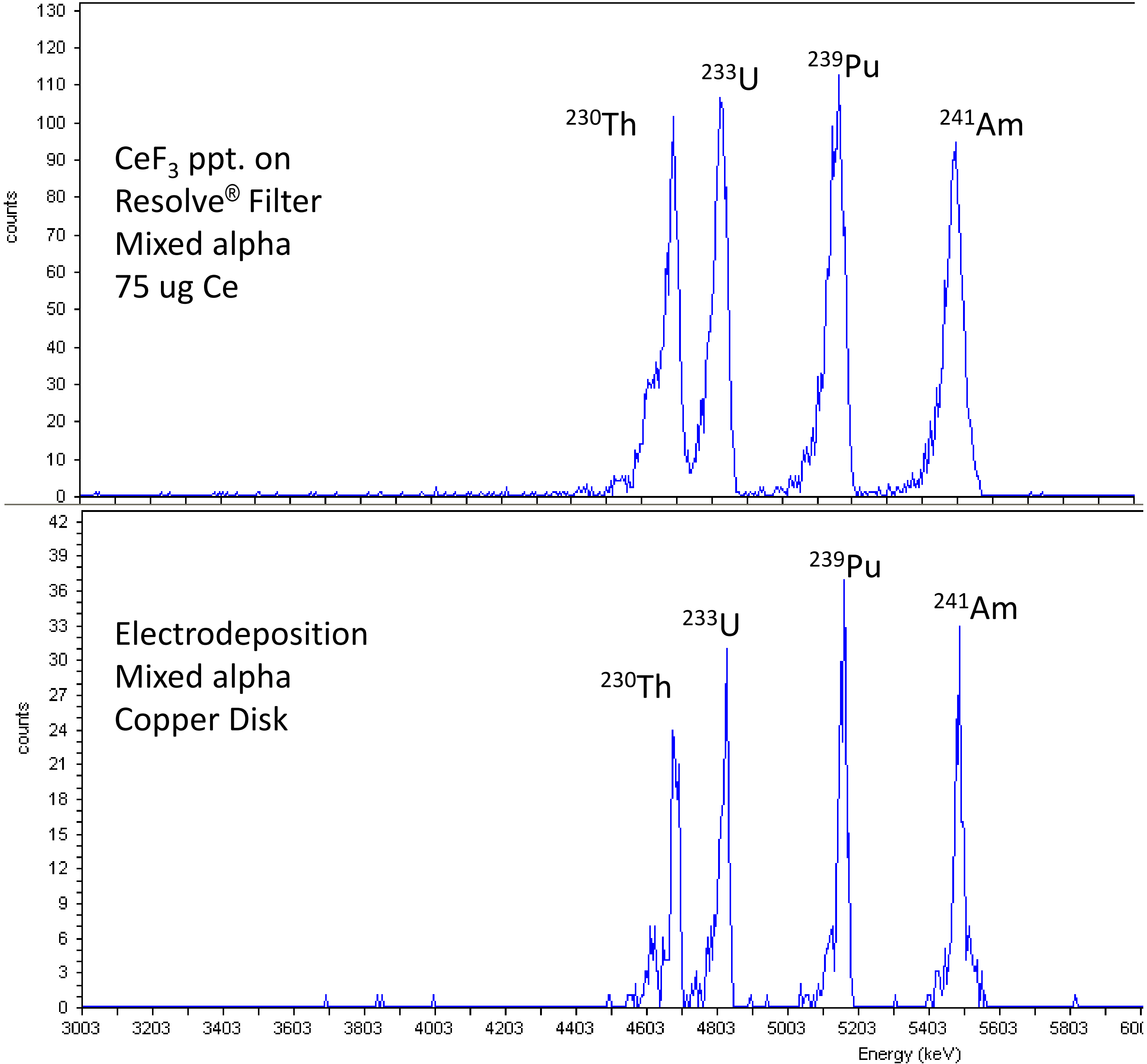
19) Mount filter to stainless steel planchet.

20) Place mounted filter into petri dish.

21) Dry under heat lamp.

22) Place lid on petri dish. Store until alpha measurement.





CeF3 filter

- Faster
- Simpler
- Adequate resolution
- Less durable (contamination)
- Additional U purification

Electrodeposition

- Slower
- More complex
- Superior resolution
- More durable

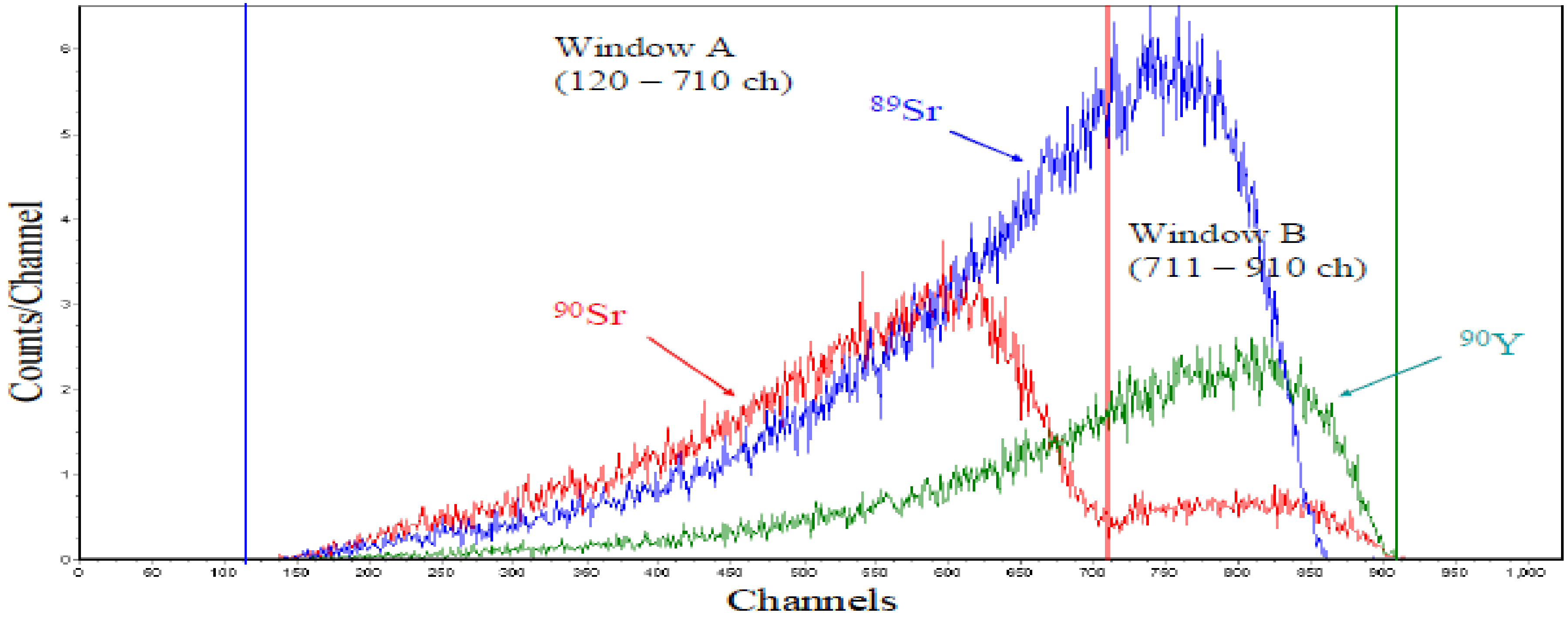
Discrimination of $^{89}Sr/^{90}Sr$

Decay of $^{89}Sr/^{90}Sr$ + Ingrowth ^{90}Y

Pure Beta emitters

Application AN-1624 and RRMC workshop from 2018:

https://www.eichrom.com/wp-content/uploads/2018/07/08.pdf



Questions????

Discrimination of ^{89}Sr and ^{90}Sr

Properties of Selected Nuclides								
		Decay		Detector Suitable for Measurement				
Nuclide	**Half-Life**	**Mode**	**Energy**	**GFPC**	**LSC**	**Cerenkov**	**MS/AES**	**Gamma**
^{82}Sr	25.35 days	ε						
^{82}Rb	1.25 min	β^+	β^+mean = 1479 keV γ = 511 keV (190.4%)					
^{85}Sr	64.849 days	ε/γ	γ = 514 keV (96%)	No	Yes	No	No	Yes
^{88}Sr	Stable			No	No	No	Yes	No
^{89}Sr	50.563 days	β^-	β_{max} = 1500 keV β_{mean} = 587 keV	Yes	Yes	Yes	No	No
^{90}Sr	28.79 years	β^-	β_{max} = 546 keV β_{mean} = 196 keV	Yes	Yes	No	Yes	No
^{90}Y	64 hours	β^-	β_{max} = 2280 keV β_{mean} = 934 keV	Yes	Yes	Yes	No	No

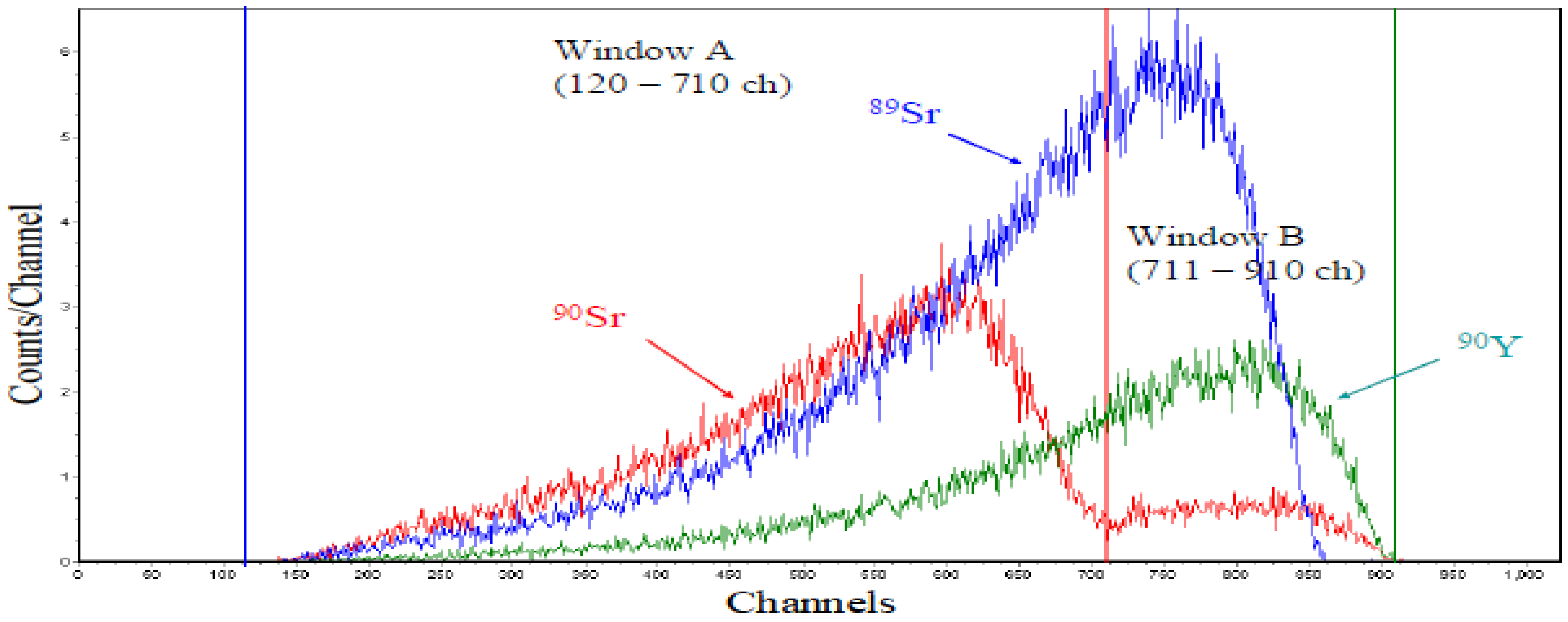
Yield tracers

analytes

Why is $^{89}Sr/^{90}Sr$ Challenging?

Decay of $^{89}Sr/^{90}Sr$ + Ingrowth ^{90}Y

Pure Beta emitters



Cherenkov Spectra

Pros:

No cocktail = No Quench

No luminescence

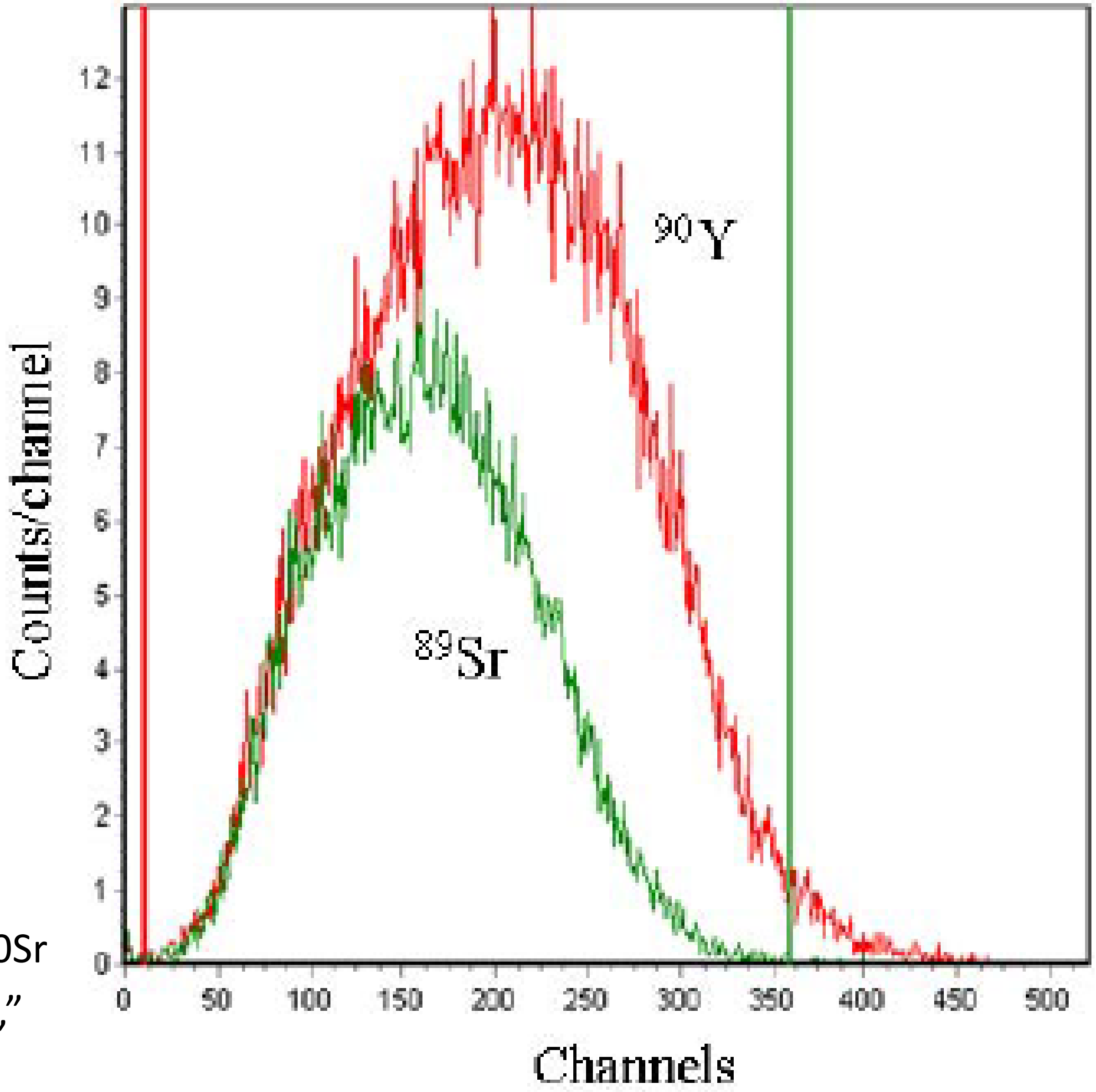
Non-destructive

Selective for high energy β-/β+.

(Measure ^{89}Sr/^{90}Y, reject ^{90}Sr)

Cons:

Lower Efficiency than LSC



IAEA/AQ/27, "Rapid Simultaneous Determination of 89Sr and 90Sr in Milk: a Procedure Using Cherenkov and Scintillation Counting," IAEA Analytical Quality in Nuclear Applications Series No. 27.

Method Options

Following Matrix Removal/Sr Resin Isolation of Sr:

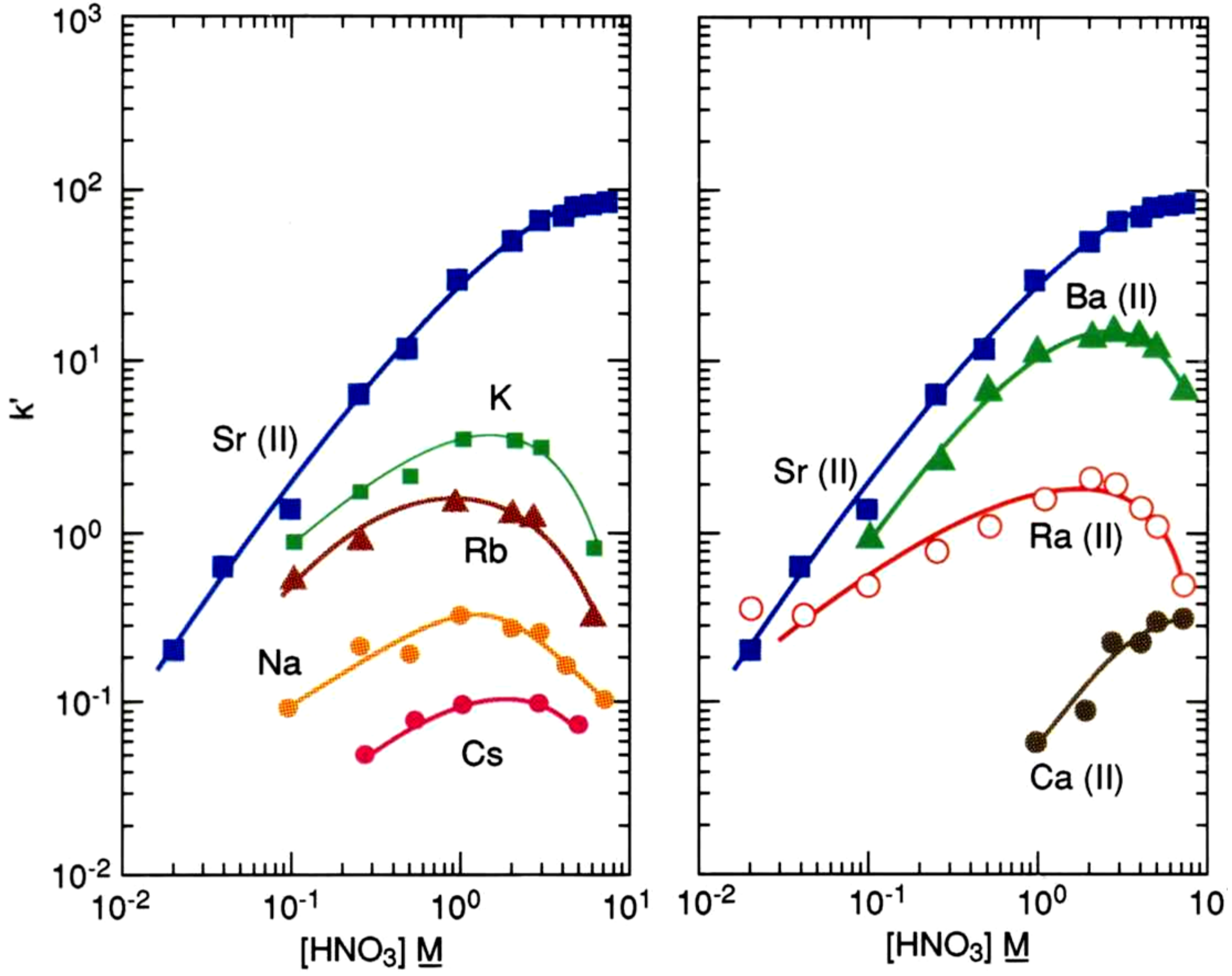
1) MS (^{90}Sr Only)

2) Two count methods
   - Different counting techniques
   - Same technique with period of ingrowth (^{90}Y)

3) Count, ingrowth, Separate ^{90}Y

Described in detail in AN-1624 and Eichrom RRMC workshop 2018

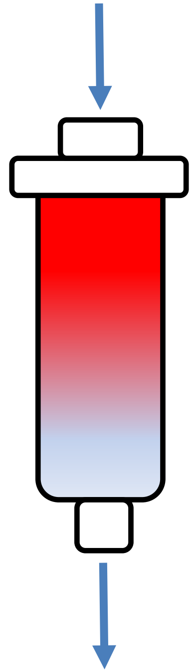
Uptake on Sr Resin



3-8M HNO_3

5 mg Stable Sr

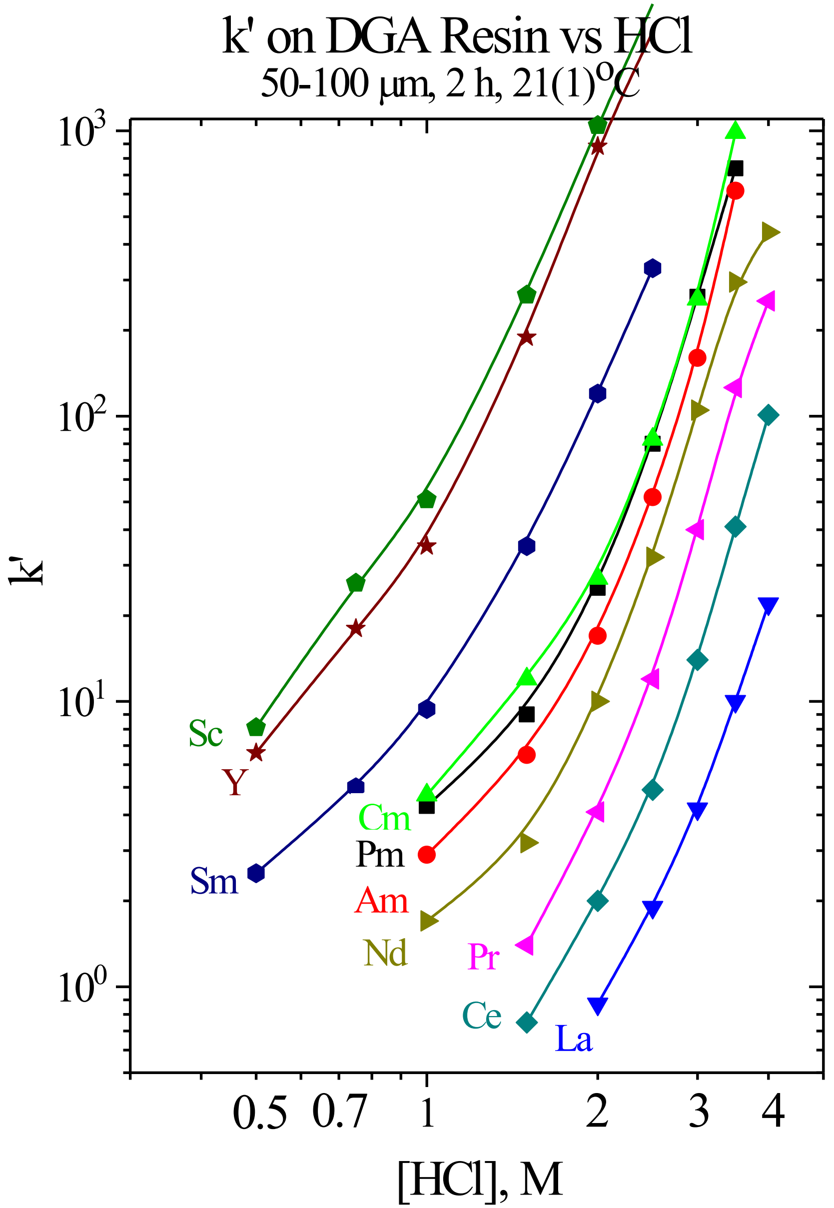
$^{89/90}Sr + ^{90}Y$

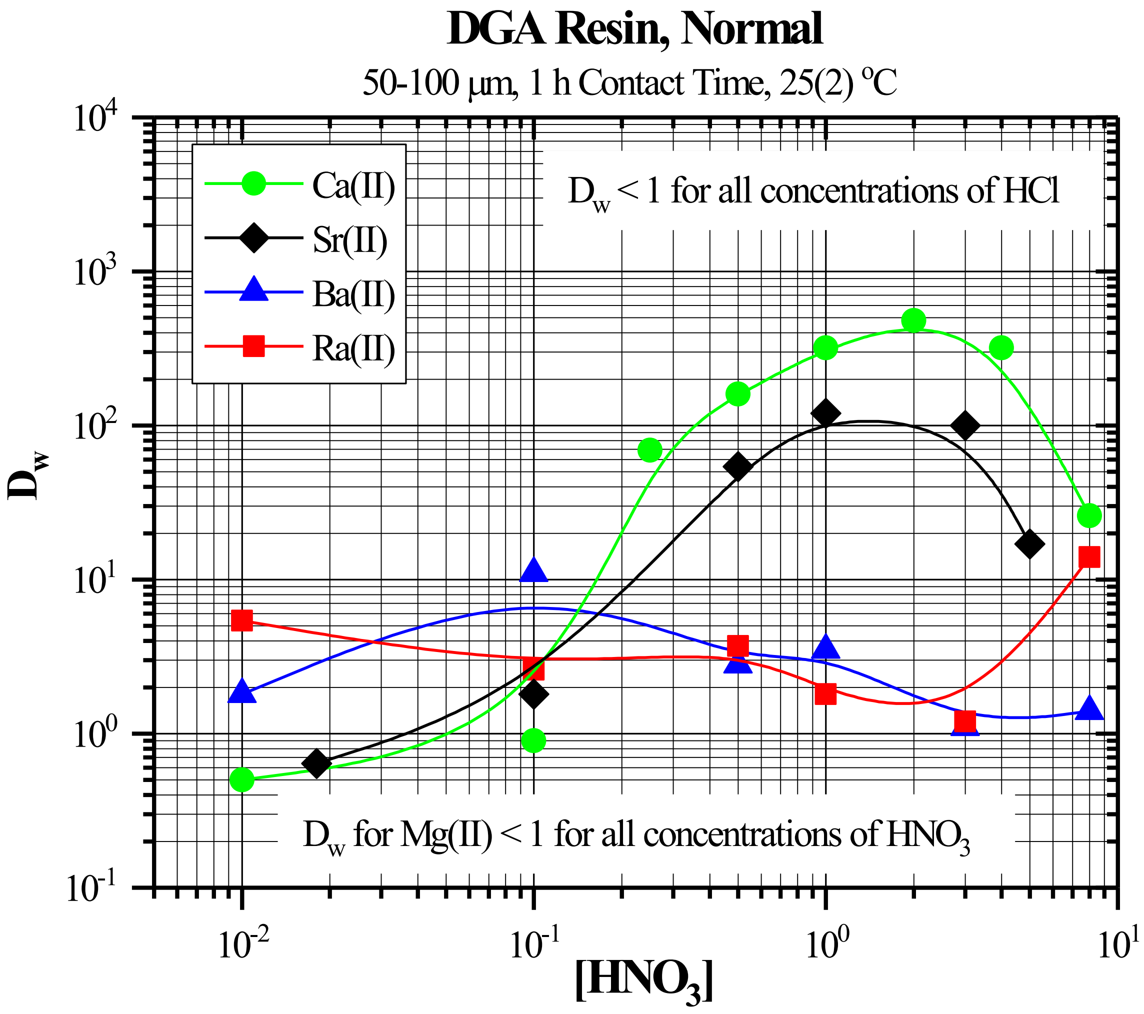


Sr

^{90}Y

Uptake on DGA Resin, Normal

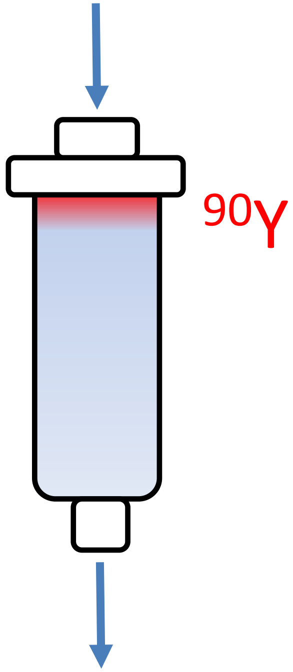




3-8M HNO_3

5 mg Stable Sr

$^{89/90}Sr + ^{90}Y$



Sr

Rinse, Rinse, Rinse!