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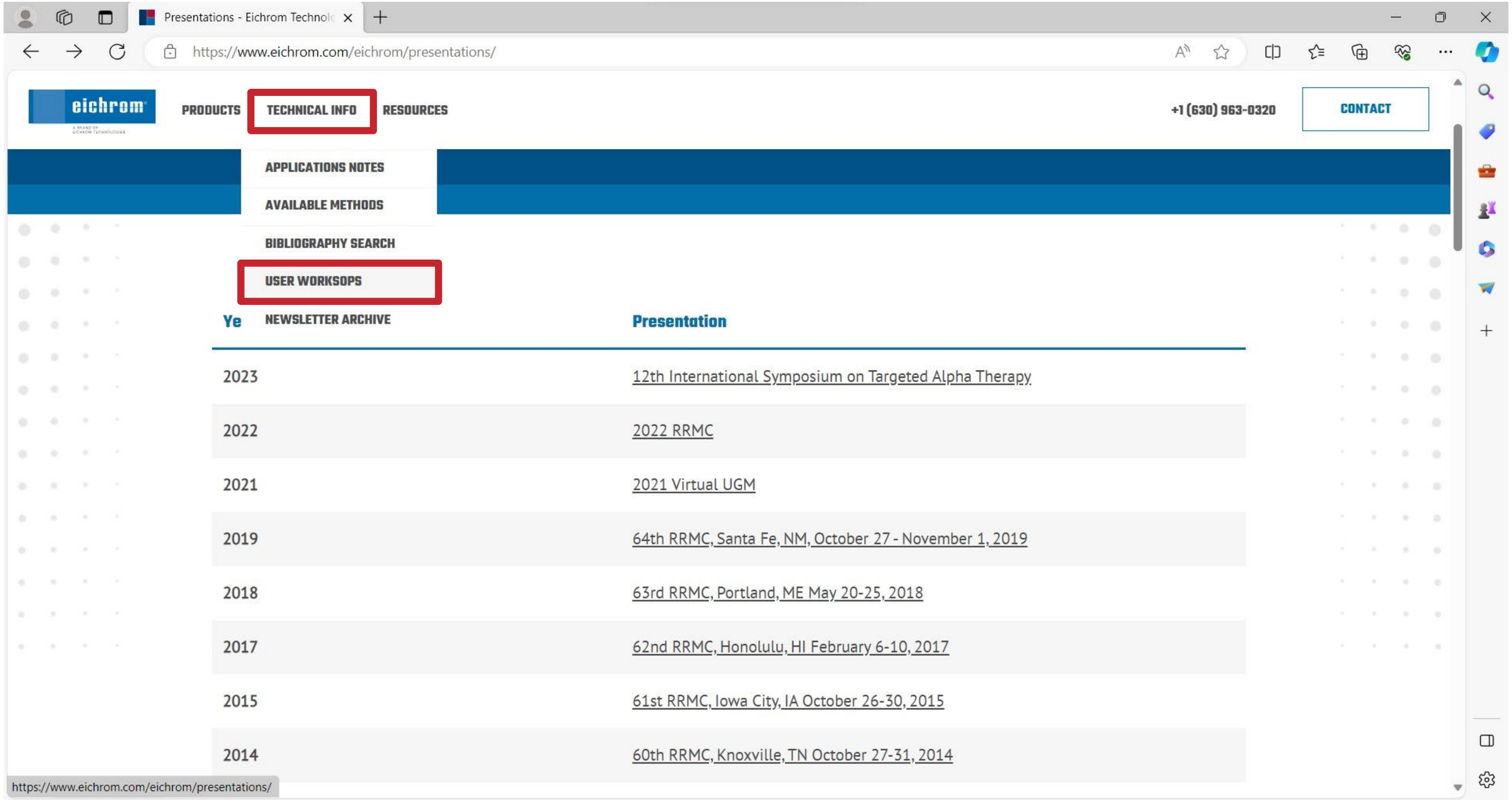
Eichrom 101: Separations Basics

https://www.eichrom.com/eichrom/presentations



Separation Types

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

Elements or groups of elements or compounds

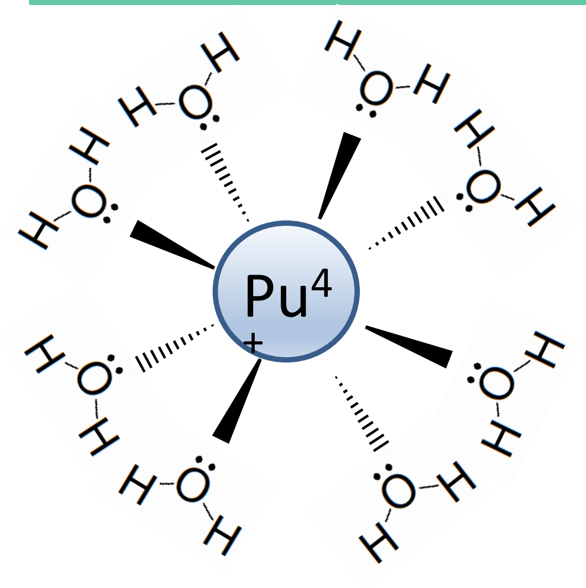
Separation Types

F^-

Cl^-

HO^-

H^+



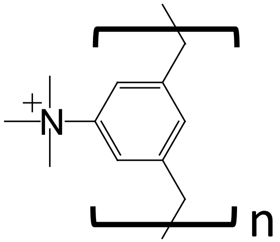
NO_3^-

Phase Boundary

PuF_4 (s)

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

$[Pu(NO_3)_5]^-$



Aqueous Phase

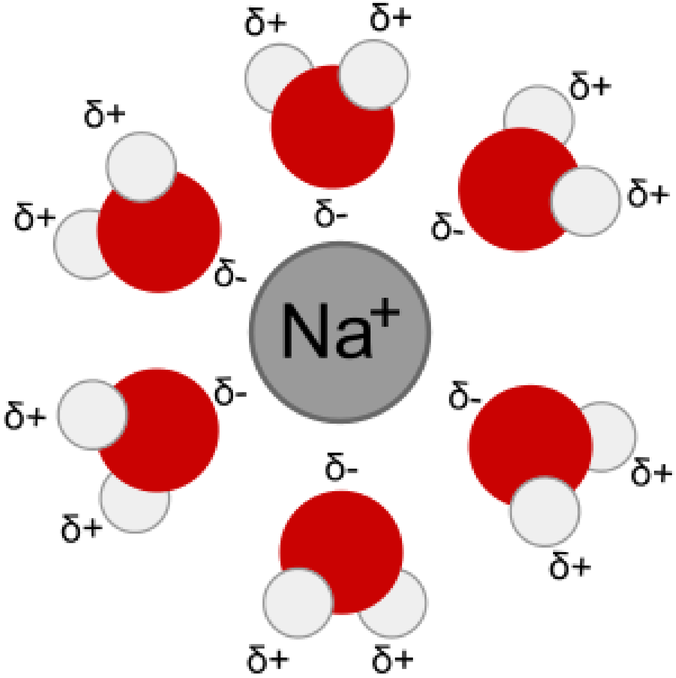
Non-Aqueous Phase

Aqueous Phase

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

M = metal ion
n = solvation number
z = charge

Solublity related to strength of solvation vs interaction between cations and anions



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

Hydrolysis

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

$$m\ UO_2^{2+} + x\ H_2O \quad <---> \quad (UO_2)_m(OH)_x^{2m-x} + x\ H^+$$

more U

more hydrolysis

equilibrium

more H^+

less hydrolysis

Choppin 2013

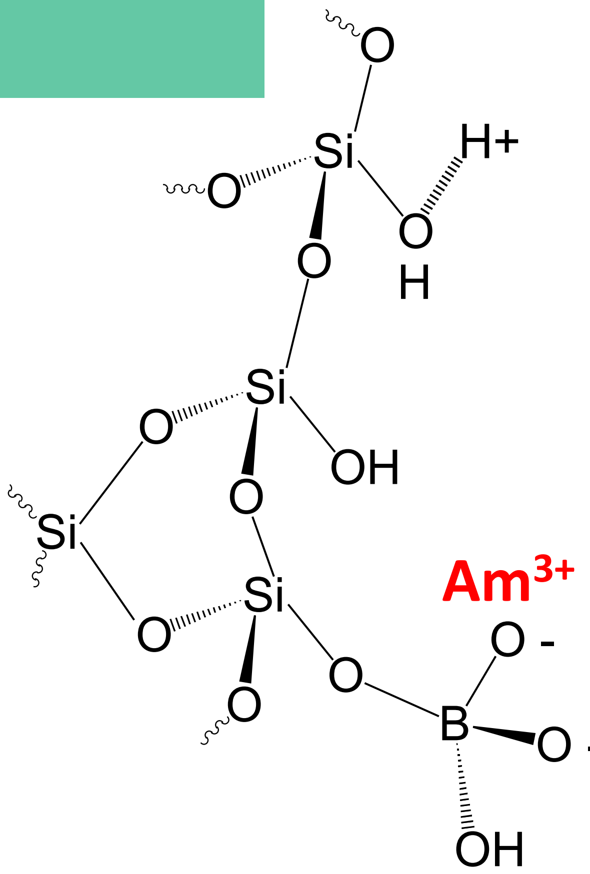
ADSORPTION

Point of zero charge – pH at which surface charge is 0.

At higher pH
- Surface charge is negative/Cations adsorb

At lower pH
- Surface charge is positive/Anions adsorb

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



Borosilicate Glass

1L Bottle 10^{-7}-10^{-8} mole H^{+}

Choppin 2013

Storage Conditions

- Aqueous samples often stored in HNO_3 at pH < 2.

- Radioactive tracers may be stored in 0.1 – 3.0 M HNO_3 or HCl to limit hydrolysis and adsorption.

- Glass vs plastic.

- **Carrier** may be added to limit adsorption.

Carrier

Stable element added to a system to provide additional mass.

- Same element or different element with similar chemistry
- prevent adsorption to container walls.
- provide mass to exceed solubility to promote precipitation (Stable Sr/Ca for Sr-89/90)
- gravimetric yield monitor (Stable Sr)
- prevent adsorption to precipitate (hold-back carrier)
  - Adding Co, Cs when precipitating Ni

Common Yield Tracers

Analyte	Tracer	Tracer Measurement
Fe, Ni, Sr, Pb	stable element	Gravimetric, ICP-MS, ICP-AES
^{99}Tc	Stable Re, ^{99m}Tc	Re: ICP-MS, ICP-AES, ^{99m}Tc: Gamma
^{210}Po	^{209}Po, ^{208}Po	Alpha
^{226}Ra	^{133}Ba, ^{225}Ra(^{229}Th)	^{133}Ba: Gamma, ^{225}Ra: Alpha
Th	^{229}Th	Alpha
U	^{232}U (self-cleaning)	Alpha
Np	^{236}Pu, ^{239}Np(^{243}Am)	^{236}Pu: Alpha, ^{239}Np: Gamma
Pu	^{242}Pu, ^{236}Pu	Alpha
Am/Cm	^{243}Am	Alpha

Oxidation State Adjustments

Element	Common Oxidation States in Acidic Aqueous Solution	Adjustments
Ac	Ac(III)	
Th	Th(IV)	High acidity to reduce hydrolysis
Pa	Pa(V)	Complex with F- to reduce hydrolysis
U	U(IV), **$U(VI)O_2^{2+}$**	Reduce to U(IV) with $TiCl_3$
Np	Np(IV), **$Np(V)O_2^{+}$**, $Np(VI)O_2^{2+}$	Reduce to Np(IV) with Fe(II)
Pu	Pu(III), **Pu(IV),** $Pu(VI)O_2^{2+}$	Reduce to Pu(III) with Fe(II) Oxidize to Pu(IV) with NO_2^-
Am/Cm	Am(III)/Cm(III)	

Precipitation

Beginning of methods

- Concentrate large aqueous samples

- Reject unwanted matrix ions

- Easy to dissolve in acidic matrix for further separations

End of methods

- Provide low mass, concentrated sample for efficient measurement

- Reject unwanted interferences

- Difficult to dissolve to make stable sources

Hydroxide precipitates

Actinides form acidic cations in aqueous solution and readily hydrolyze to precipitate as hydroxides.

La(OH)3 and Fe(OH)3 are often used as carriers for actinides in all oxidation states (rejects Sr):

III (ksp ~10E-20)	IV (ksp ~10E-54)
V (ksp ~10E-10)	VI (ksp ~10E-25)

Hydroxides are normally easy to dissolve in acid for further processing.

Nash 2006

Phosphate precipitates

Ca phosphate and Fe(III) phosphate are often used as carriers for actinides in all oxidation states + Sr.

Phosphates are normally easy to dissolve in acid for further processing.

Phosphate may complex actinides (Th/Pu/Np), interfering with further separation steps. Addition of Al(NO3)3 during precipitate dissolution can help reduce the impact of phosphate.

Nash 2006

Fluoride and Oxalate precipitates

Rare earth fluorides and oxalates are often used as carriers for actinides in the III and IV oxidation states.

Oxalates are normally easy to dissolve in acid for further processing.

Fluorides can be dissolved by the addition of Boric acid (complexes F- to form fluoboric acid).

Fluoride precipitates are particularly useful for removal of silicates from soil/rock/concrete samples.

Nash 2006

Rare Earth Fluoride micro. ppt

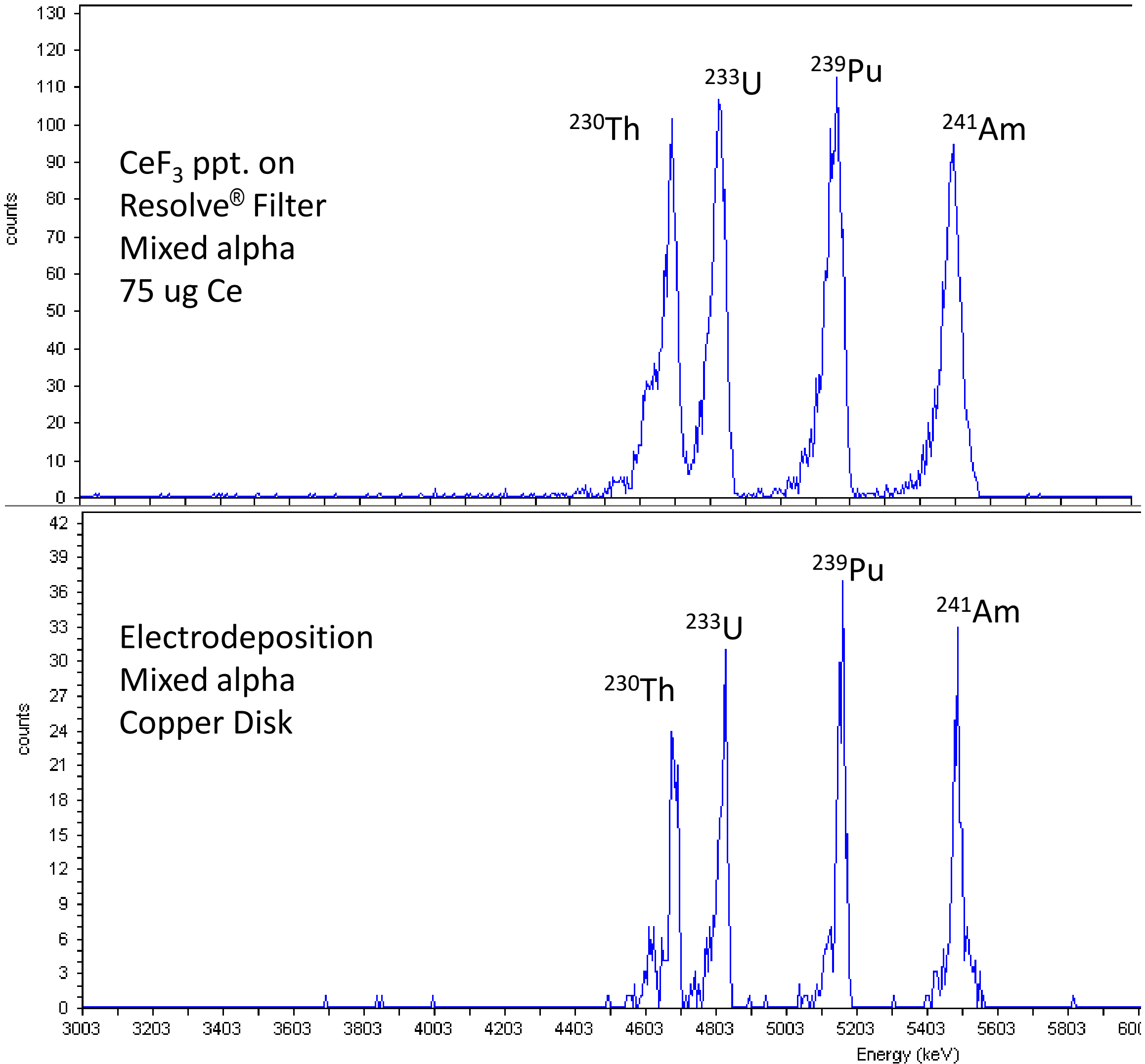
CeF_3 or NdF_3 are alternatives to electrodeposition for alpha source preparation.

CeF_3 or NdF_3 microprecipitates (50-150ug) can be prepared directly from HNO_3 or HCl solution.

CeF_3 or NdF_3 microprecipitates (50-150ug) can be used to provide additional decontamination from U.

- Add H_2O_2, U(VI) not carried on CeF_3
- Add $TiCl_3$, U(IV) carried on CeF_3

Nash 2006



CeF3 filter

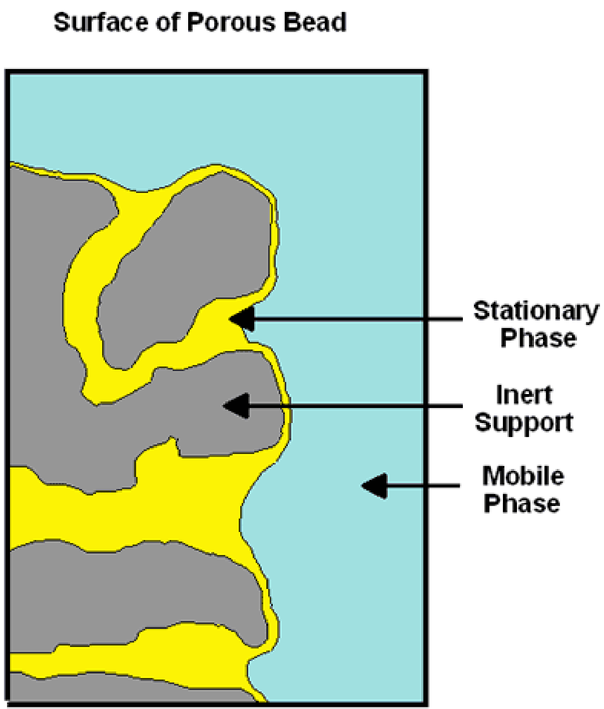
- Faster
- Simpler
- Adequate resolution
- Less durable (contamination)
- Additional U purification

Electrodeposition

- Slower
- More complex
- Superior resolution
- More durable

Extraction Chromatography

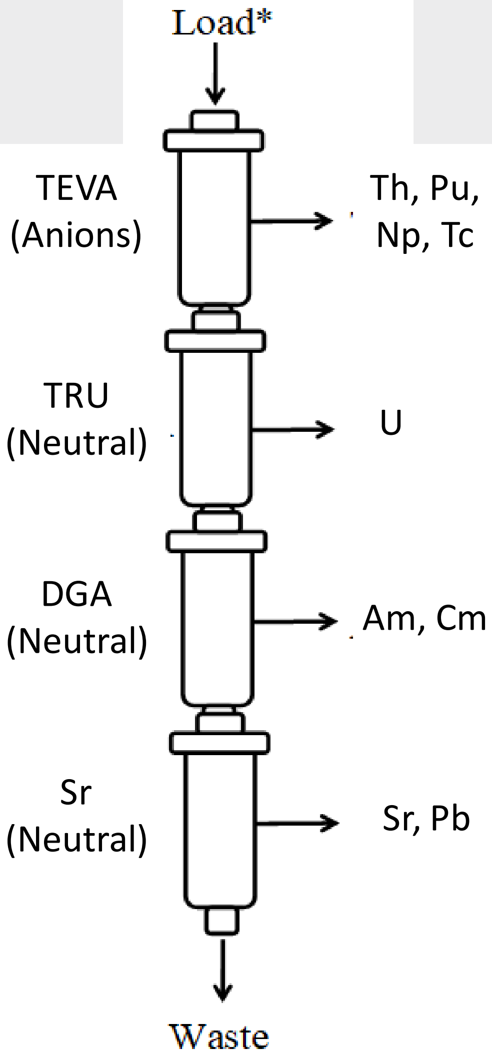
Extraction Chromatographic Resin



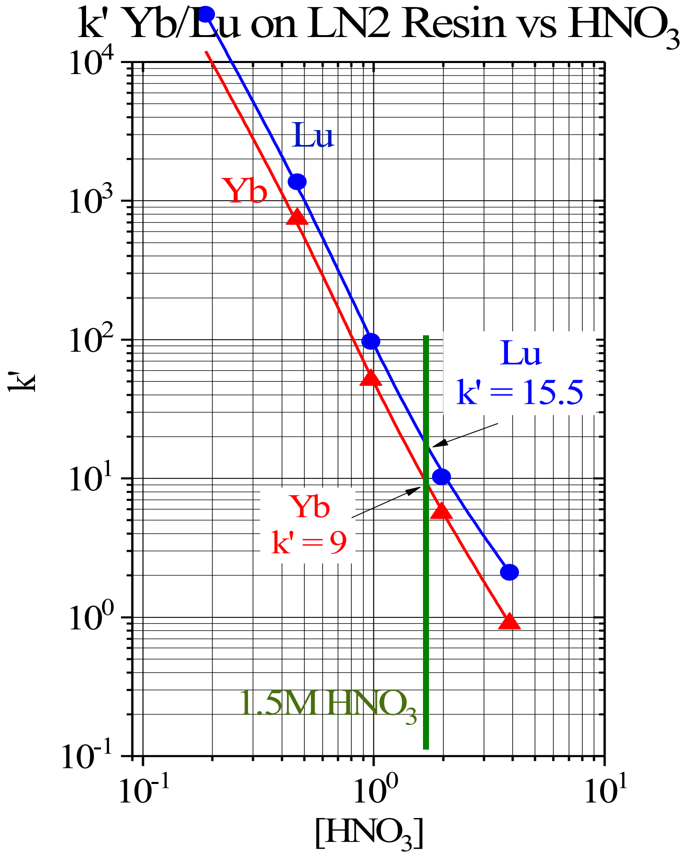
- Solvent extraction reagents on inert chromatographic support.
- High selectivity.
- Less waste.
- Less Labor.
- Rapid.
- Can be applied in glovebox or hot cell.

Multi-dimensional separations

- Different column materials can be stacked
- Analysis of multiple analytes from a single sample preparation

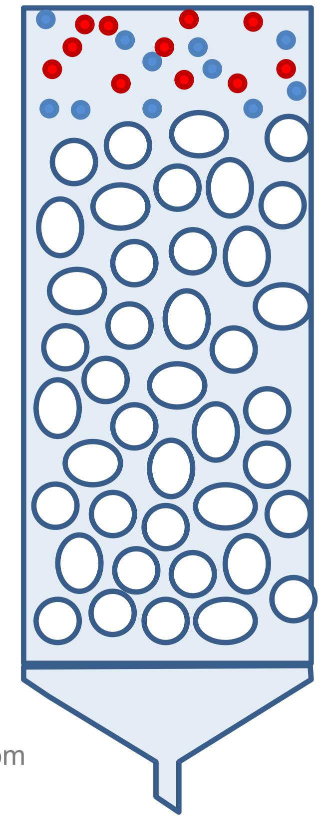


Acid Dependency Curve

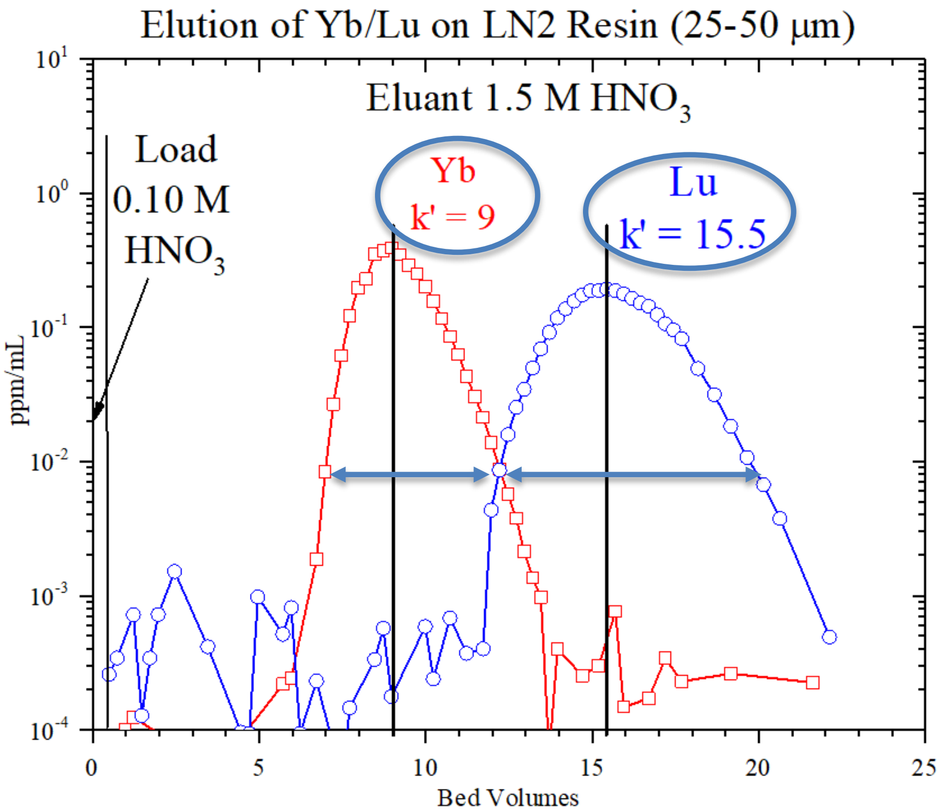


- Data often presented as k' vs acid concentration
- k' = capacity factor
  - Free column volumes to peak maximum
  - Relative retention strength
  - Simple way to view selectivity
  - Δk' is one factor in resolution

Column Chromatography Principles

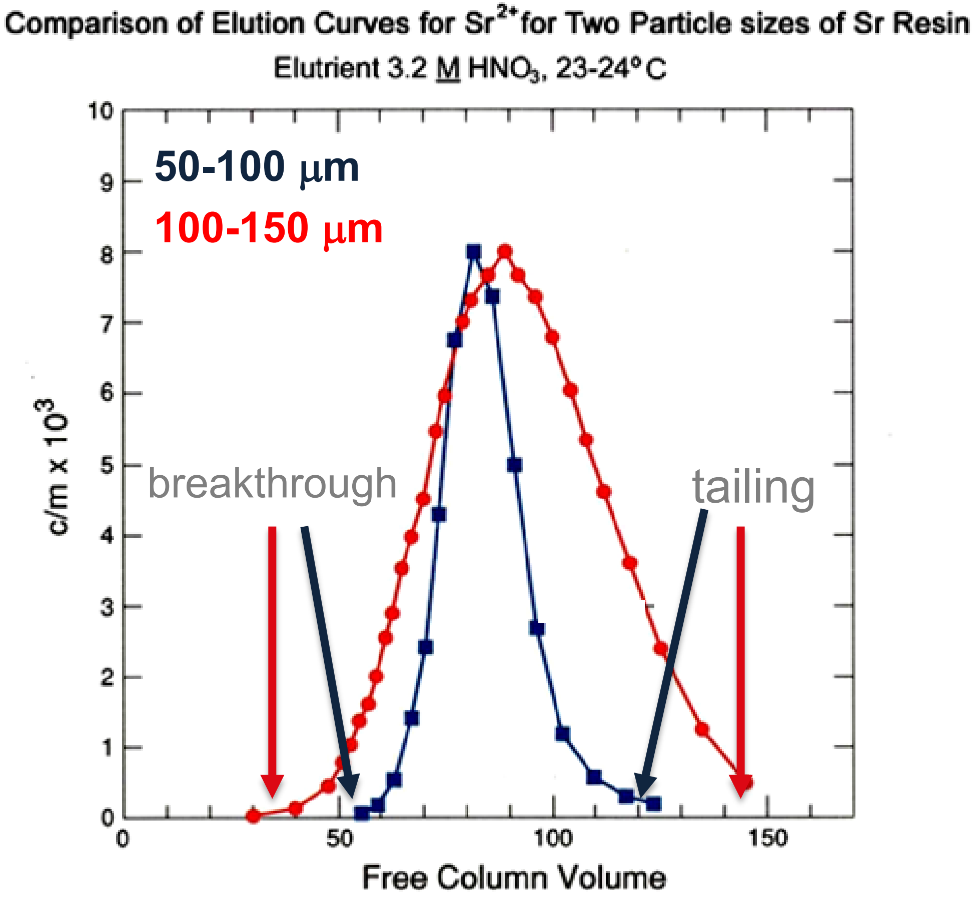


Elution Chromatogram



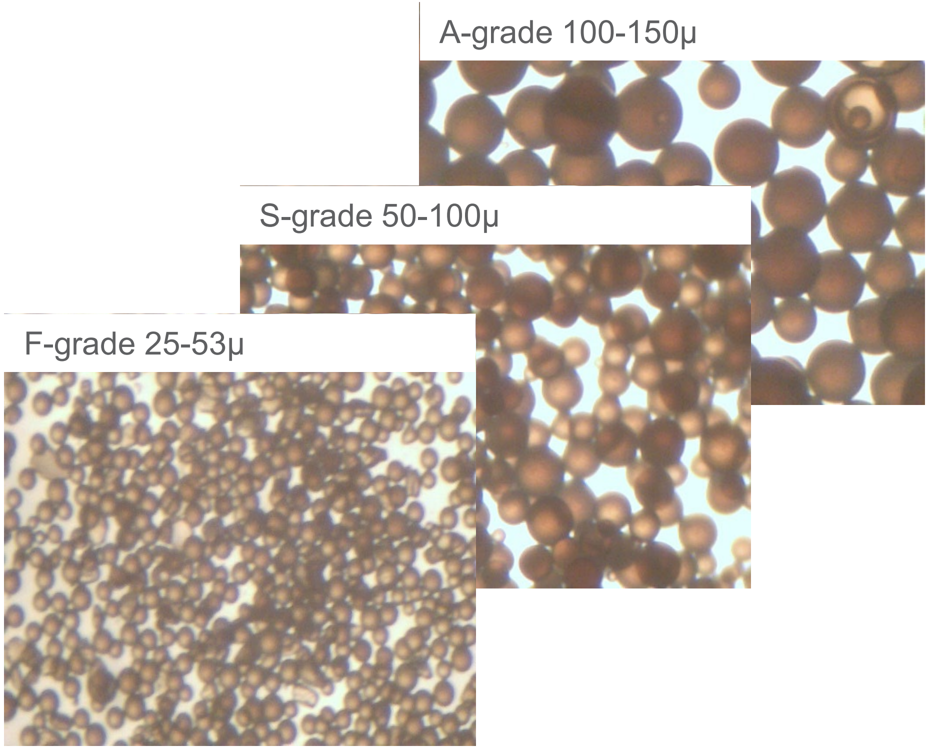
- Δk' is one factor in resolution
  - Resin Type
  - Mobile Phase
- Peak width also affects resolution
  - Particle Size
  - Temperature

Particle Size



- Smaller particle size
  - Narrower elution bands
  - Higher back pressure
- Particle size affects
  - -- Breakthrough
  - -- Tailing

Resin Particle Sizes (Grades)



www.eichrom.com

- Part number: XX-XXX-A
  - Gravity Flow ‘columns’
- Part number: XX-XXX-S
  - Vacuum assisted ‘cartridges’
- Part number: XX-XXX-F
  - Specialty applications
  - Small cartridges
  - Rare Earth separations

Questions????