The Science of Radiochemical Separations

Phil Horwitz*

Director, PG Research Foundation
Founder and Senior Consulting Scientist
Eichrom Technologies LLC

*Formerly Senior Scientist, Argonne National Laboratory,
Group Leader of Chemical Separation Group, Chemistry Division,
Section Chief of Heavy Element Group, Chemistry Division
• Introduction
• Solvent Extraction
• Chromatography
• Achievement of Separation
• Ion Exchange
• Extraction Chromatography
• Separations at Curie Levels
Introduction
What is Separation?

In general, separation is an operation by which a mixture is divided into at least two fractions having different compositions.

In radiochemical separations, the ratio of the initial concentration of one or more components in the original mixture to their concentrations in the final mixture is the decontamination factor (DF).
## Separation Methods Based on Phase Equilibria

<table>
<thead>
<tr>
<th>Gas – Liquid</th>
<th>Gas – Solid</th>
<th>Liquid – Liquid</th>
<th>Liquid – Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disk</td>
<td>Adsorption</td>
<td>Solvent Extraction</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Gas Chromatograph</td>
<td>Sublimation</td>
<td>Exclusion</td>
<td>Fractional Crystallization</td>
</tr>
<tr>
<td>Molecular Sieves</td>
<td></td>
<td></td>
<td>Ion Exchange</td>
</tr>
<tr>
<td>Gas Chromatograph</td>
<td></td>
<td></td>
<td>Extraction Chromatography</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Adsorption</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ion Exclusion</td>
</tr>
<tr>
<td>Particle Separation Methods</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filtration</td>
<td>Particle Electrophoresis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sedimentation</td>
<td>Electrostatic Precipitation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elutriation</td>
<td>Flotation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centrifugation</td>
<td>Screening</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Radiochemical vs. non-radiochemical separations: When is there a difference?

<table>
<thead>
<tr>
<th>Alpha and Beta Radiation Level in mCi/mL</th>
<th>Effect on solids and liquids</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; $10^{-3}$</td>
<td>Negligible</td>
</tr>
<tr>
<td>$10^{-3}$ to 1</td>
<td>Negligible for short-term exposure, discoloration for long-term exposure</td>
</tr>
<tr>
<td>1 to $10^3$</td>
<td>Definite effect on oxidation-reduction processes. Noticeable decomposition of organic substances</td>
</tr>
<tr>
<td>&gt; $10^3$</td>
<td>Profoundly affects all aqueous and organic solution processes</td>
</tr>
</tbody>
</table>
Solvent Extraction (SX)
Single Stage Liquid-Liquid Extraction

Before

Organic Phase

Aqueous Phase

M$_1^{+n}$, M$_2^{+n}$

E

After

M$_1 \cdot$ E$^{+n}$

M$_2^{+n}$

Distribution Ratio (D) = C$_o$ / C$_a$

Phase Ratio (R) = V$_o$ / V$_a$

Q$_o$ = C$_o$V$_o$ , Q$_a$ = C$_a$V$_a$

Fraction of M$^{+n}$ Extracted

= \frac{Q_o}{Q_o + Q_a} = \frac{RD_o}{RD_o + 1}$

Extraction Factor (E) = RD
Continuous Counter-Current Liquid-Liquid Extraction Scheme

Barren Aqueous Phase

Feed Solution

Scrub Solution

Product Stream

Strip Solution

Organic Extractant Recycle
% Extraction
As a Function of the Number of Stages

\[D = 2, \ R = 3, \ E = 6\]

<table>
<thead>
<tr>
<th>Number of Stages</th>
<th>(\phi)</th>
<th>% Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(2.3 \times 10^{-2})</td>
<td>97.7</td>
</tr>
<tr>
<td>4</td>
<td>(6.4 \times 10^{-4})</td>
<td>99.9</td>
</tr>
<tr>
<td>6</td>
<td>(1.8 \times 10^{-5})</td>
<td>99.998</td>
</tr>
</tbody>
</table>

\(\phi\) is the fraction of species remaining in aqueous phase
Calculation of the Number of Stages Needed in Extraction and Stripping

For an extraction section with n stages:

\[ X_w = X_f \frac{E-1}{((E)^{n+1}-1)} \]

Where \( X_w \) and \( X_f \) are the concentration in the feed and raffinate, respectively.

For a stripping unit:

\[ Y_w = Y_f \frac{[(E)^{-1}-1]}{[(E)^{-(n+1)}-1]} \]

Where \( Y_f \) and \( Y_w \) are the organic feed and aqueous raffinate, respectively, and \( E = RD \).
Schematic of Centrifugal Contactor
Bank of 12 Centrifugal Contactors
BASIC EQUATION FOR COUNTERCURRENT EXTRACTION AND SCRUB

\[ \phi = \frac{(E_1 - 1)(E_2^m - 1)}{(E_1^{n+1} - 1)(E_2 - 1)(E_2^{m-1}) + (E_2^m - 1)(E_1 - 1)} \]

E = extraction factors (D x R) for extraction stages

E = extraction factors for scrub stages

n = number of stages in extraction section

m = number of stages in scrub section

\( \phi \) = fraction of species remaining in the aqueous phase
Did You Know?

Some of the largest differences in chemical equilibrium constants are achieved by forcing ions to transfer from an aqueous into a non-aqueous (organic) environment.
Example of a simple extraction equilibrium between cations ($M^{3+}$) and anions ($A^{-}$) in an aqueous phase and a neutral extractant ($E$) in an organic phase:

$$M^{3+}\cdot (H_2O)_x + 3A^{-}\cdot (H_2O)_y + nE\cdot(solvent)_z \rightleftharpoons ME_nA_3\cdot(solvent)_z + (x+y) H_2O$$

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
Separation Factor and Free Energy

\[ \Delta G^\circ = RT \ln K \]

\[ (\Delta G^\circ)_1 - (\Delta G^\circ)_2 = RT(\ln K_2 - \ln K_1) \]

\[ \Delta(\Delta G^\circ) = RT \ln \alpha \]

where \( \alpha = \frac{K_2}{K_1} = \text{Separation Factor} \)

<table>
<thead>
<tr>
<th>To Change ( \alpha ) by</th>
<th>Requires (k cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^4 )</td>
<td>5.4</td>
</tr>
<tr>
<td>( 10^2 )</td>
<td>2.7</td>
</tr>
<tr>
<td>( 10 )</td>
<td>1.4</td>
</tr>
<tr>
<td>( 2 )</td>
<td>0.41</td>
</tr>
</tbody>
</table>
Mechanism of SX

- All LLE reagents are amphipathic.
- Their amphipathic nature makes them interfacially active at oil/water interfaces.
- 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.
Phase Interface

Neutral Extractants

Acidic Extractants
Dialkyl Phosphoric Acid Extractants

The negative log of $C_{\text{min}}$ values (measured at 25°C for dodecane solutions against 1M HNO$_3$) for the dialkyl phosphoric acids vs. their acidity constants (pKa) measured in 75% ethyl alcohol.
<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic Radii (nm)</th>
<th>Vol (nm$^3$)</th>
<th>Hydration Energy (k cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$</td>
<td>0.055</td>
<td>6.2 X 10$^{-4}$</td>
<td>1304</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.065</td>
<td>1.2 X 10$^{-3}$</td>
<td>1096</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>0.105</td>
<td>4.9 X 10$^{-3}$</td>
<td>739</td>
</tr>
<tr>
<td>Pu$^{3+}$</td>
<td>0.114</td>
<td>6.2 X 10$^{-3}$</td>
<td>763</td>
</tr>
<tr>
<td>Pu$^{4+}$</td>
<td>0.093</td>
<td>3.4 X 10$^{-3}$</td>
<td>1377</td>
</tr>
</tbody>
</table>
Comparison of Ionic Volume
Bonding

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

• Steric factors also play a significant role in determining selectivity.
Examples of Electrostatic Bonds

- cation – anion
- ion – dipole
- dipole – dipole - hydrogen bond
- dipole – induced dipole
- induced dipole – induced dipole

liquid inert gases
\[
\begin{align*}
\text{R} & \quad \text{P} & \quad \text{H} & \quad \text{C} & \quad \text{C} & \quad \text{N} & \quad \text{Et} \\
\text{R'} & \quad \text{H} & \quad \text{C} & \quad \text{C} & \quad \text{N} & \quad \text{Et}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Extractant</th>
<th>( ^*D_{am} )</th>
<th>( \alpha \left( \frac{D_{Am}}{D_{Fe}} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}<em>6\text{H}</em>{13}\text{O} \cdot \text{P} \cdot \text{O} )</td>
<td>2.4</td>
<td>3.0 \times 10^3</td>
</tr>
<tr>
<td>( \text{C}<em>6\text{H}</em>{13}\text{O} \cdot \text{P} \cdot \text{O} )</td>
<td>10</td>
<td>4.2 \times 10^2</td>
</tr>
<tr>
<td>( \text{C}<em>6\text{H}</em>{13}\text{O} \cdot \text{P} \cdot \text{O} )</td>
<td>18</td>
<td>1.0 \times 10^{-1}</td>
</tr>
</tbody>
</table>

* 0.5M extractants in isopropyl benzene / 4M HNO\(_3\)
The 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
Single Stage Liquid-Liquid Extraction

biphasic

M^{+N}

M^{+N}

M^{+N}

triphasic

M^{+N}

M^{+N}
Phase Modification of CMPO by TBP

0.25M CMPO in decalin as a function of added TBP, 25°C
Types of Extractants

**Acidic**

\[ M^{3+} + 3HY \rightleftharpoons MY_3^+ + 3H^+ \]
\[ M^{3+} + 3(HY)_2 \rightleftharpoons M(HY_2)_3 + 3H^+ \]

**Neutral**

\[ M^{3+} + nE + 3X^- \rightleftharpoons ME_n \cdot X_3 \]

**Basic**

\[ R_3N + HX \rightleftharpoons R_3NH^+X^- \]
\[ R_3NH^+X^- + MX_3 \rightleftharpoons R_3NH^+MX_4^- \]

\[ X^- = NO_3^-, Cl^- \]
Example
(Acidic Extractants)

\[
\text{M}^{3+} + 3(\text{HL})_2 \leftrightarrow \text{M(HL}_2)^3 + 3\text{H}^+
\]
Example
(Acidic Extractants)

Mono-Thio Phosphinic Acid

Di-Thio Phosphinic Acid
Example
(Acidic Extractants)

Alkylbisphosphonic Acid

Dinonylnaphthalene Sulfonic Acid (DNNSA)
Example
(Acidic Extractants)

**Oximes**

\[ R_1 = H, \text{CH}_3, C_6\text{H}_6 \]
\[ R_2 = C_9\text{H}_{18}, C_{12}\text{H}_{25} \]

\[ M^{2+} + 2\text{HL} \rightleftharpoons \text{ML}_2 + 2\text{H}^+ \]
Example
(Neutral Extractants)

TBP Phosphate
R = C₄H₉

DAAP Phosphonate
R = C₅H₁₁

Trialkyl Phosphine Oxide
R = C₈H₁₇
Or mixtures
Of C₆ and C₈
Example
(Neutral Extractants)

Carbamoylphosphine oxide

Diglycolamide
R = n-octyl, 2-ethylhexyl

Triisobutylphosphine Sulfides
TIBPs
Example
(Neutral Extractants)

Di-\(t\)-butylcyclohexano-18-crown-6

Nonamethyl-14-crown-4
Example
(Neutral Extractants)

Calix[4]arene-bis(t-octylbenzo-crown-6)
Example
(Basic Extractants)

Primary Ammonium

$$R_1 + R_2 = C_{15} \text{ to } C_{21}$$

Tertiary Ammonium

$$R = C_8 \text{ or } C_{10}$$

Quaternary Ammonium

$$R = C_8 \text{ or } C_{10}$$

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_8H_{17})_3N$</td>
<td>26%</td>
</tr>
<tr>
<td>$(C_{10}H_{21})(C_8H_{17})_2N$</td>
<td>46%</td>
</tr>
<tr>
<td>$(C_{10}H_{21})<em>2(C_8H</em>{17})N$</td>
<td>26%</td>
</tr>
<tr>
<td>$(C_{10}H_{21})_3N$</td>
<td>2%</td>
</tr>
</tbody>
</table>
Summary of Features of Solvent Extractions

- Capable of high selectivity
- Has high capacity for targeted constituent
- Usually achieves rapid attainment of equilibrium
- Can be carried out in a batch or continuous multistage mode
- Can achieve a high level of decontamination
- Ideal for large-scale operations
Potential Problems and Difficulties

• Aqueous and solvent entrainment, which lowers stage efficiency
• Third phase or emulsion formation
• Crud at the interface
• Difficulty with back-extraction
• Difficulty with solvent cleanup, especially from radiolytic degradation
Chromatography
Achievement of Separation
Movement of Two Analytes Through a Resin Bed
Contribution to Band Spreading in EXC

Eddy Diffusion

Mobile Phase Mass Transfer

Stationary Phase and Interfacial Mass Transfer
Separation by Elution Chromatography
$N = 16 \left( \frac{V_{\text{max}}}{W'} \right)^2$

$N = 238$ plates

$N = \left( \frac{V_{\text{max}}}{\sigma} \right)^2 = 236$

HETP = $L / N$
Resolution Equations

1. Definition of Resolution
   \[ R_s = \frac{(V_{\text{max}})_1 - (V_{\text{max}})_2}{\frac{1}{2}(W_1 + W_2)} \]

2. Number of Theoretical Plates
   \[ N = \frac{16 V_{\text{max}}^2}{W^2} \]

3. Capacity Factor
   \[ k' = \frac{V_{\text{max}} - \nu_m}{\nu_m} \]

4. Separation Factor
   \[ \alpha = \frac{k'_2}{k'_1} \]

5. Condition of Separation
   \[ R_s = \frac{1}{4} (\alpha - 1) \sqrt{N} \left( \frac{k'}{1+k'} \right) \]
The Achievement of Separation

Separation Gap \[ \Delta V_{\text{max}} = (V_{\text{max}})_1 - (V_{\text{max}})_2 \]

Bandwidth \[ W = \frac{1}{2}(W_1 + W_2) \]
Column Permeability $K^\circ$

$$v = \frac{K^\circ \cdot \Delta P}{\eta \cdot f \cdot L}$$

Where $v$ is the interstitial flow velocity, $K^\circ$ is specific column permeability, $\Delta P$ is the pressure drop of the column, $\eta$ is the viscosity coefficient of the mobile phase, $f$ is the total column porosity and $L$ is the column length.

$$K^\circ \propto d_p^2$$
Standard Resolution Curves for Band Size Ratio of 1
$R_s$ values of 0.5 to 1.25
Standard Resolution Curves for Band Size Ratio of 10/1 and 100/1
$R_s$ Values of 0.8 to 1.25
Separation of Yb and Lu on LN2 Resin
Slurry Packed 25-53 μm LN2 Resin, Operating Temperature 50(1) °C

Bed Volume = 20.0 mL
Bed Height = 21.0 cm
Column Diameter = 1.1 cm
Flow Rate = 5.0 mL/min
\( \alpha = 5.3 \text{ mL/cm}^2/\text{min} \)
Pressure = 6 psi

Lu(III), 0.5 mg
Yb(III), 5 mg

99.4% Lu in 6 BV
0.2% Yb

Lu(III), 0.5 mg
Separation of Ce, Bk and Cf on a 2 cm column containing 30 weight percent of 1.5 F HDEHP in dodecane on 5 µm porous silica microspheres. T = 50°C, v = 2 cm/min.
Calculation of Elution Curve

Using the equations of Glueckauf \{1\}

\[
(C)_v = C_{\text{max}} \exp \left( - \frac{N(V_{\text{max}} - V)^2}{2V_{\text{max}} \cdot V} \right)
\]

Where \((C)_v\) is the concentration of solute at the corresponding elution volume \((V)\), \((C_{\text{max}})\) is the peak concentration, \((V_{\text{max}})\) is the elution volume at \((C_{\text{max}})\) and \(N\) is the number of theoretical plates.

\{1\} Glueckauf, E Trans, Faraday Society 51, 34 (1955)
“The mind can only absorb what the bottom can endure.”

Phil
Ion Exchange
Commercial Ion Exchange and Absorbent Resins

Strong Acid

Weak Acid
Commercial Ion Exchange and Absorbent Resins

**Strong Base**

- \( \text{C} - \text{C} - \text{CH}_2\text{N}^+\text{CH}_3 \)
- \( \text{CH}_3 \)
- \( \text{Cl}^- \)

- \( \text{H} - \text{C} - \text{H}_2 \)
- \( \text{CH}_2\text{N}^+\text{CH}_3 \)
- \( \text{CH}_3 \)
- \( \text{Cl}^- \)

- \( \text{H} - \text{C} - \text{H}_2 \)
- \( \text{CH}_2\text{N}^+\text{CH}_3 \)
- \( \text{CH}_2\text{CH}_2\text{OH} \)

- \( \text{HC} - \text{CH}_2 \)
- \( \text{N}^+\text{CH}_3 \)
- \( \text{Cl}^- \)

**Weak Base**

- \( \text{C} - \text{C} - \text{CONH(CH}_2\text{)_nN}^-\text{CH}_3 \)
- \( \text{CH}_3 \)

- \( \text{H} - \text{C} - \text{H}_2 \)
- \( \text{CONH(CH}_2\text{)_nN}^-\text{CH}_3 \)

- \( \text{H} - \text{C} - \text{H}_2 \)
- \( \text{CH}_2\text{NH(CH}_2\text{CH}_2\text{NH})_n\text{H} \)

- \( \text{H} - \text{C} - \text{H}_2 \)
- \( \text{CH}_2\text{N}^-\text{CH}_3 \)
Commercial Ion Exchange and Absorbent Resins

Chelating

\[
\text{CH}_2\text{NCH}_2(\text{CH}_2)_4\text{CH}_2\text{OH} \\
\text{CH}_3 \quad \text{OH}
\]
<table>
<thead>
<tr>
<th>Chelating</th>
<th>Commercial Ion Exchange and Absorbent Resins</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Chemical Structure 1" /></td>
<td><img src="image2.png" alt="Chemical Structure 2" /></td>
</tr>
<tr>
<td><img src="image3.png" alt="Chemical Structure 3" /></td>
<td><img src="image4.png" alt="Chemical Structure 4" /></td>
</tr>
</tbody>
</table>
Commercial Ion Exchange and Absorbent Resins

<table>
<thead>
<tr>
<th>Absorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Absorbent Structure 1]</td>
</tr>
<tr>
<td>![Absorbent Structure 3]</td>
</tr>
</tbody>
</table>

\( n = 50 \)
Commercial Ion Exchange and Absorbent Resins

Zeolite

Ammonium Phosphomolybdate (AMP)

Monosodium Titanate (MST)

\[
\text{HO Ti O– O}^- \quad \text{Na}^+
\]
Extraction Chromatography
Depiction of Extraction Chromatography (EXC)
Relationship Between SX and EXC

\[ k' = D_v \cdot \frac{v_s}{v_m} \]

- \( k' \) = retention volume (FCV to peak maximum)
- \( D_v \) = volume distribution ratio
- \( v_s \) = volume of stationary phase
- \( v_m \) = volume of mobile phases
Dry Weigh Distribution Ratio

\[ D_w = \frac{A_0 - A_s}{w(g)} \times \frac{A_s}{v(mL)} \]
Relationship between $k'$ and $D_v$

$R =$ equilibrium fraction of solute in the mobile phase
$1-R =$ equilibrium fraction of solute in the stationary phase

$k' =$ ratio of solute in the stationary phase to the mobile phase or number of free column volumes to peak maximum for a column.

\[ \therefore \frac{1-R}{R} = k' \quad (1) \]

Assume $C_m$ and $C_s$ are the concentrations in the mobile and stationary phase, receptivity and $V_m$ and $V_s$ are the corresponding volumes of these phases.

\[ \frac{R}{1-R} = \frac{C_m V_m}{C_s V_s} \quad (2) \]

$C_s / C_m$ is the volume distribution ratio $D_w$

\[ \therefore \frac{R}{1-R} = \frac{V_m}{D_w V_s} = \frac{1}{k'} \quad (3) \]

\[ \therefore k' = D_v \cdot \frac{v_s}{v_w} \quad (4) \]
**Relationship between k′ and D_w**

\[ D_w = \frac{A_0 - A_s}{\text{Weight of Resin (g)}} / \frac{A_s}{\text{Volume of Solution (mL)}} \]  

\[ D_v = \frac{A_0 - A_s}{\text{Volume of Ext on Resin (V_e)}} / \frac{A_s}{\text{Vol of Sol (mL)}} \]  

Where \( D_w \) equals weight distribution ratio and \( D_v \) equals volume distribution ratio.

\[ D_w = D_v \cdot V_e / g \]  

Assume extractant loading is 40 weight percent. Then one gram of resin contains 0.4g of extractant. Assume the extract has a density of 1 g/cc.

Then \( D_v = D_w \times 2.5 \)

Assuming \( V_s / V_v = 1/5 \) which is close to the value obtained from packed column, substitute in eq. 4.

Then \( k' = D_w \cdot 0.5. \)
### Comparison of K’ Calculated from $D_w$ and K’ Obtained from Elution Curves

<table>
<thead>
<tr>
<th>Element</th>
<th>[HNO₃], M</th>
<th>$k'$ Calculated from $D_w$</th>
<th>$k'$ from Elution Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>0.25</td>
<td>$6.5 \pm 0.8$</td>
<td>$6.0 \pm 0.3$</td>
</tr>
<tr>
<td>Pm</td>
<td>0.25</td>
<td>$11 \pm 1$</td>
<td>$13 \pm 0.7$</td>
</tr>
<tr>
<td>Sm</td>
<td>0.40</td>
<td>$7.0 \pm 0.8$</td>
<td>$6.5 \pm 0.3$</td>
</tr>
<tr>
<td>Eu</td>
<td>0.40</td>
<td>$13 \pm 2$</td>
<td>$14 \pm 0.7$</td>
</tr>
<tr>
<td>Gd</td>
<td>0.40</td>
<td>$25 \pm 3$</td>
<td>$23 \pm 1$</td>
</tr>
</tbody>
</table>
Comparison of $K'$ Calculated from $D_w$ and $K'$ Obtained from Elution Curves

<table>
<thead>
<tr>
<th>Element</th>
<th>$\text{[HNO}_3\text{], M}$</th>
<th>$k'$ Calculated from $D_w$</th>
<th>$k'$ from Elution Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>0.50</td>
<td>8.0 ± 1.0</td>
<td>8.7 ± 0.4</td>
</tr>
<tr>
<td>Ho</td>
<td>0.50</td>
<td>18 ± 2</td>
<td>21 ± 1</td>
</tr>
<tr>
<td>Yb</td>
<td>1.5</td>
<td>11 ± 1</td>
<td>11 ± 0.6</td>
</tr>
<tr>
<td>Lu</td>
<td>1.5</td>
<td>20 ± 2</td>
<td>20 ± 1</td>
</tr>
</tbody>
</table>
Factors Affecting Band Spreading in EXC

Flow phenomena:

\[ H = \frac{1}{1/2\lambda_i d_p + D_m/\omega_i d_p^2 v} \]

- \( H \): plate height (HETP)
- \( d_p \): particle diameter
- \( D_m \): mobile phase diffusion coefficient
- \( v \): interstitial flow velocity
- \( \lambda_i, \omega_i \): geometrical constants related to particle size and shape
Factors Affecting Band Spreading in EXC

Stationary phase diffusion:

\[ H = q \cdot \frac{k'}{(1 + k')^2} \cdot \frac{d_\ell^2 v}{D_s} \]

- \( H \) = plate height (HETP)
- \( q \) = geometrical configuration factor
- \( k' \) = FCV to peak maximum
- \( d_\ell \) = depth of stationary phase
- \( D_s \) = diffusion coefficient in the stationary phase
- \( v \) = interstitial flow velocity
Factors Affecting Band Spreading in EXC

Extraction kinetics:

\[ H = 2 \cdot \frac{k'}{(1 + k')^2} \cdot \frac{v}{k_{oa}} \]

- \( H \) = plate height (HETP)
- \( k' \) = FCV to peak maximum
- \( v \) = interstitial flow velocity
- \( k_{oa} \) = aqueous to organic rate constant

J.C. Giddings, Dynamics of Chromatography Principles and Theory. Marcel Dekker, New York (1965)
Types of EXC Resins

**Acidic**

\[ \text{M}^{3+} + 3\text{HY} \Leftrightarrow \text{MY}_3 + 3\text{H}^+ \]
\[ \text{M}^{3+} + 3(\text{HY})_2 \Leftrightarrow \text{M}([\text{HY}_2])_3 + 3\text{H}^+ \]

**Neutral**

\[ \text{M}^{3+} + n\text{E} + 3\text{X}^- \Leftrightarrow \text{ME}_n \cdot \text{X}_3 \]

**Basic**

\[ \text{R}_3\text{N} + \text{HX} \Leftrightarrow \text{R}_3\text{NH}^+\text{X}^- \]
\[ \text{R}_3\text{NH}^+\text{X}^- + \text{MX}_3 \Leftrightarrow \text{R}_3\text{NH}^+\text{MX}_4^- \]

\[ \text{X}^- = \text{NO}_3^-, \text{Cl}^- \]
Anionic Extraction Chromatographic Resins

<table>
<thead>
<tr>
<th>Resin</th>
<th>Type</th>
<th>Extractant</th>
<th>Major Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEVA</td>
<td>Basic</td>
<td>Quaternary Amine</td>
<td>Pu, Tc, Th, Np, Am/Ln</td>
</tr>
<tr>
<td>Weak Base EC</td>
<td>Basic</td>
<td>Tertiary Amine</td>
<td>Tc, Np, Pu</td>
</tr>
</tbody>
</table>

\[ R = C_8 \text{ or } C_{10} \]

Quaternary Ammonium Extractant

\[ \text{Quaternary Ammonium Extractant} \]

Tertiary Ammonium Extractant

\[ \text{Tertiary Ammonium Extractant} \]
Acid dependency of $k'$ for various ions at 23°C.

TEVA Resin

$[\text{HNO}_3] \text{ M}$ vs. $k'$

$[\text{HCl}] \text{ M}$ vs. $k'$
Mean Activity Coefficients vs. Molarity

The graph shows the dependency of activity coefficients $2x^-$ on molarity. Different compounds (HCl, LiCl, LiNO$_3$, HNO$_3$) have distinct curves indicating their behavior in solutions with varying molarity.
Diamyl Amylphosphonate (DAAP)
a.k.a. Dipentyl Pentylphosphonate (DPPP)
Acid dependency of $k'$ for various ions at 23-25°C.

UTEVA Resin
Structure/Extracted Species

\[
\text{CMPO}
\]

\[
\text{DGA}
\]

\[
\text{Am}^{3+} + 3\text{X}^- + 3\overline{E} \leftrightarrow \overline{\text{AmE}_3\text{X}_3}
\]

\[
\text{X} = \text{Cl}^- \text{ or NO}_3^-
\]
Uptakes of Actinides on TRU vs DGA

TRU Resin

DGA Resin, Normal

DGA Resin, Branched

\[ k' \sim [\text{HNO}_3] \]

- Pu(IV)
- Th(IV)
- U(VI)
- Am(III)
Uptakes of Actinides on TRU vs DGA

TRU Resin

DGA Resin, Normal

DGA Resin, Branched

k' vs [HCl]

Pu(IV)

Th(IV)

U(VI)

Am(III)

Pu

Th

U

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

$k'_{\text{Bi}} < 0.4$
$k'_{\gamma} < 0.4$
Cationic Extractants

HDEHP (LN)       HEH[EHP] (LN2)

H[TMPeP] (LN3)

\[ M^{3+} + 3(HY)_2 \leftrightarrow M(HY_2)_3 + 3H^+ \]
Coupled Column Applications

Load* → TEVA → Th, Np
UTEVA → U
TRU → Am, Pu
Waste

*Load = Nitric acid solutions of water, bioassay, or leached or dissolved soil samples.
Coupled Column Applications

*Load = Nitric acid solutions of water, bioassay, or leached or dissolved soil samples.
Generic Multicolumn Selectivity Inversion Generator

- Parent & Daughter Solution
- Shielding
- Strip Solution
- Resin Selective for Daughter
- Parent Solution
- Purified Daughter Solution
- Resin Selective for Parents
Proposed $^{213}\text{Bi}$ Generator for Medical Uses

Parents & $^{213}\text{Bi}$ in 0.1 M HCl

Shielding

Strip Solution:

$$0.5 \text{ M (Na,H)OAc} + 0.75 \text{ M NaCl at pH = 4}$$

UTEVA Resin Retains

$[\text{H}_3\text{O}][\text{BiCl}_4]$  

Sulfonic Acid Cation Exchange Resin Retains Parents

$^{213}\text{Bi}$ Solution for Labeling uses
Separations at Curie Levels
Water-Radiolysis Equation from 5.3MeV Alpha Particles from $^{210}$Po

$$H_2OM \rightarrow [0.05]OH + [X]e^-_{aq} + [0.06]H + [0.15]H_2O_2 + [X]H_3O^+ + [0.16]H_2$$

Where the values in brackets are the individual yield of each species (the G values) in umol/J.

Radiolytic Degradation Products of CMPO

\[ G = 0.22 \frac{\text{molecules}}{100 \text{ eV}} \]
\[ G = 2.3 \times 10^{-3} \frac{\mu\text{mol}}{\text{joule}} \]
Radiolytic Degradation Products of TODGA

\[
\begin{align*}
G &= 8.2 \frac{\text{molecules}}{100 \text{ eV}} \\
G &= 8.3 \times 10^{-1} \frac{\mu\text{mol}}{\text{joule}}
\end{align*}
\]
Trans-plutonium and lanthanide fission products separation by anion exchange with lithium chloride
Trans-plutonium and lanthanide fission products separation by anion exchange with lithium chloride
Separation of Cm-242 (24 Ci) from Am-241
Before and after Cm-242 separation
Phil before and after
Summary of Features of IX and EXC

- Capable of high resolution and selectivity
- Modest to low capacities
- Attainment of equilibrium is slower than SX, but EXC is more rapid than IX
- Both IX and EXC are ideal techniques for laboratory-scale radiochemical separations,
  But
- EXC is much easier to manipulate than IX
- IX is ideal for water treatment and cleanup
Potential problems and difficulties

• Capacities are lower than SX and therefore can easily be exceeded.

• Both IX and EXC can suffer severe radiolytic damage because of the way columns concentrate activity and the difficulty of removing hydrolytic and radiolytic degradation products.

• Resin swelling with IX resins.
Questions?

You sure he's absorbing all of this?
Welcome to RRMC

The Organizing Committee is proud to announce the 57th Annual Radiobioassay and Radiochemical Measurements Conference will be held October 31 through November 4, 2011 at the Sandestin Golf and Beach Resort in Destin, Florida.

We know many of you will enjoy re-visiting the site of the 54th Annual RRMC. Join with your colleagues in presenting and learning about new work, both completed and in progress, in radiobioassay and radiochemistry at this premier Conference. As usual, there will be workshops and vendor exhibits in addition to the oral and poster technical papers.

Sandestin is nestled on 2,400 spectacular acres between the Gulf of Mexico and the Choctawhatchee Bay located in Northwest Florida 8 miles east of Destin. The Village at Baytowne Wharf, a pedestrian village opened in May of 2002, provides Sandestin guests a central gathering place reminiscent of an old-world fishing village. The Village