The Science of Radiochemical Separations

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## Outline

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

## 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

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

## **Particle Separation Methods**

Filtration	Particle Electrophoresis
Sedimentation	Electrostatic Precipitation
Elutriation	Flotation
Centrifugation	Screening

#### Radiochemical vs. non-radiochemical separations: When is there a difference?

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

## Solvent Extraction (SX)

### Single Stage Liquid-Liquid Extraction

Before After Distribution Ratio (D) =  $C_0 / C_a$ Phase Ratio (R) =  $V_o / V_a$ Organic  $M_1 \bullet E^{+n}$ Ε Phase  $Q_0 = C_0 V_0$ ,  $Q_a = C_a V_a$ Aqueous  $M_1^{+n}, M_2^{+n}$  $M_2^{+n}$ Phase Fraction of M<sup>+n</sup> Extracted  $= \frac{Q_o}{Q_o + Qa} = \frac{RD_o}{RD_o + 1}$ Extraction Factor (E) = RD

## Continuous Counter-Current Liquid-Liquid Extraction Scheme



### % Extraction As a Function of the Number of Stages

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

Number of Stages	Φ	% Extracted
2	2.3 x 10 <sup>-2</sup>	97.7
4	6.4 x 10 <sup>-4</sup>	99.9
6	1.8 x 10 <sup>-5</sup>	99.998

 $\Phi$  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:

$$X_{w} = Xf \frac{E-1}{[(E)^{n+1}-1]}$$

Where  $X_w$  and  $X_f$  are the concentration in the feed and raffinate, respectively.

For a stripping unit: 
$$Y_w = Yf \frac{[(E)^{-1}-1]}{[(E)^{-(n+1)}-1]}$$

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

 $= \frac{(E_1 - 1)(E_2^m - 1)}{(E_1^{m+1} - 1)(E_2 - 1)(E_2^{m-1}) + (E_2^{m-1} - 1)(E_1 - 1)}$ 

## Did You Know?

Some of the largest differences in chemical equilibrium constants are achieved by forcing ions to transfer from an aqueous into a nonaqueous (organic) environment.

## Example

Example of a simple extraction equilibrium between cations (M<sup>3+</sup>) and anions (A<sup>-</sup>) in an aqueous phase and a neutral extractant (E) in an organic phase:

 $\mathsf{M}^{3+\bullet} (\mathsf{H}_2\mathsf{O})_{\mathsf{x}} + 3\mathsf{A}^{-\bullet} (\mathsf{H}_2\mathsf{O})_{\mathsf{y}} + \overline{\mathsf{nE}} \cdot (\mathsf{solvent})_{\mathsf{z}} \rightleftarrows \overline{\mathsf{ME}}_{\mathsf{n}} \mathsf{A}_3^{\bullet} (\mathsf{solvent})_{\mathsf{z}} + (\mathsf{x}+\mathsf{y}) \mathsf{H}_2\mathsf{O}$ 

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  $\alpha = K_{2}/K_{1}$  = Separation Factor

To Change α by	Requires (k cal/mol)	
104	5.4	
10 <sup>2</sup>	2.7	
10	1.4	
2	0.41	

## 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





### **Dialkyl Phosphoric Acid Extractants**



acidity constants (pKa) measured in 75% ethyl alcohol.

### Ionic Radii, Ionic Volumes and Calculated Hydration Energies of Selected Cations

Cation	Ionic Radii (nm)	Vol (nm <sup>3</sup> )	Hydration Energy (k cal/mol)
Al <sup>3+</sup>	0.055	6.2 X 10 <sup>-4</sup>	1304
Fe <sup>3+</sup>	0.065	1.2 X 10 <sup>-3</sup>	1096
La <sup>3+</sup>	0.105	4.9 X 10 <sup>-3</sup>	739
Pu <sup>3+</sup>	0.114	6.2 X 10 <sup>-3</sup>	763
Pu <sup>4+</sup>	0.093	3.4 X 10 <sup>-3</sup>	1377

## **Comparison of Ionic Volume**



**ΔI**<sup>3+</sup>



Pu<sup>3+</sup>

# 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 
$$\left( Pu4+\cdots 0 = P \left( Pu4+\cdots 0 \right) \right)$$

- dipole dipole hydrogen bond
- dipole induced dipole  $P = O C_{12}H_{26}$
- induced dipole induced dipole liquid inert gases





\* 0.5M extractants in isopropyl benzene / 4M HNO<sub>3</sub>

### The Carbamoylphosphoryl Moiety and Substituents



### Single Stage Liquid-Liquid Extraction



### Phase Modification of CMPO by TBP



0.25M CMPO In decalin as a function of added TBP, 25°C

## Types of Extractants

<u>Acidic</u>

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

**Neutral** 

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

<u>Basic</u>

$$R_{3}N + HX \rightleftharpoons R_{3}NH^{+}X^{-}$$
$$R_{3}NH^{+}X^{-} + MX_{3} \rightleftharpoons R_{3}NH^{+}MX_{4}^{-}$$

 $X^{-} = NO_{3}^{-}, Cl^{-}$ 



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





Mono-Thio Phosphinic Acid Di-Thio Phosphinic Acid

HO OH,

Alkylbisphosphonic Acid



DinonyInaphthalene Sulfonic Acid (DNNSA)



Oximes  $R_1 = H, CH_3, C_6H_6$  $R_2 = C_9H_{18}, C_{12}H_{25}$ 

 $M^{2+} + 2HL \leftrightarrow ML_2 + 2H^+$ 

### Example (Neutral Extractants)







TBP Phosphate  $R = C_4H_9$  DAAP Phosphonate  $R = C_5H_{11}$  Trialkyl Phosphine Oxide  $R = C_8 H_{17}$ Or mixtures Of C<sub>6</sub> and C<sub>8</sub>

### 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)



 $\begin{array}{c} R_{1} \\ R_{2} \\ R_{3} \\ R_{3} \end{array} + Cl^{-} Cl^{-} \\ R_{3} \\ R_{3} \end{array}$ 

Primary Ammonium

 $R_1 + R_2 = C_{15}$  to  $C_{21}$   $R = C_8$  or  $C_{10}$ 

Tertiary Ammonium  $\begin{array}{c} R_{1} \\ R_{2} \\ R_{2} \\ R_{3} \end{array} \xrightarrow{\text{Cl}} CH_{3} \\ R_{3} \end{array}$ 

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

#### 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





#### **Resolution Equations**

1. Definition of Resolution

- $R_{S} = \frac{(V_{max})_{1} (V_{max})_{2}}{\frac{1}{2}(W_{1} + W_{2})}$
- 2. Number of Theoretical Plates



- 3. Capacity Factor
- 4. Separation Factor

5. Condition of Separation

- $k' = \frac{V_{max} v_m}{v_m}$
- $\alpha = \frac{k'_2}{k'_1}$
- $R_{S} = \frac{1}{4} (\alpha 1) \sqrt{N} \left( \frac{k'}{1 + k'} \right)$

## The Achievement of Separation

Separation Gap  $\Delta V_{max} = (V_{max})_1 - (V_{max})_2$ Bandwidth  $W = 1/2(W_1 + W_2)$ 



## Column Permeability K°

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

Where v is the interstitial flow velocity, K° is specific column pereability,  $\Delta P$  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 $$\rm R_s$ Values of 0.8 to 1.25





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 microshperes.

 $T = 50^{\circ}C$ , v = 2 cm/min.



**FCV of Eluate** 

## Calculation of Elution Curve

#### Using the equations of Glueckauf {1}

$$(C)_{v} = C_{\max} \exp{-\frac{N(V_{\max} - V)^{2}}{2V_{\max} \bullet V}}$$

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

{1} Glueckauf, E Trans, Faraday Society 51, 34 (1955)

## Short Break

#### "The mind can only absorb

## what the bottom can endure."

Phil



















Ammonium Phosphomolybdate (AMP)

Zeolite

## Extraction Chromatography

## Depiction of Extraction Chromatography (EXC)

Surface of Porous Bead



## Relationship Between SX and EXC

$$\mathbf{k'} = \mathbf{D}_{\mathbf{v}} \bullet \frac{\mathbf{v}_{\mathbf{s}}}{\mathbf{v}_{\mathbf{m}}}$$

- k' = retention volume(FCV to peak maximum)
- $D_v$  = volume distribution ratio
- v<sub>s</sub> = volume of stationary phase
- $v_m$  = volume of mobile phases

#### **Dry Weigh Distribution Ratio**



## 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 station phase to the mobile phase or number of free column volumes to peak maximum for a column.

$$\therefore \frac{1-R}{R} = k' \tag{1}$$

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.

$$\frac{R}{1-R} = \frac{C_m Vm}{C_s Vs}$$
(2)

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

$$\therefore \frac{R}{1-R} = \frac{V_m}{D_w Vs} = \frac{1}{k'}$$
(3)

$$\therefore \mathbf{k}' = \mathbf{D}\mathbf{v} \bullet \mathbf{v}_{\mathrm{s}} / \mathbf{v}_{\mathrm{w}}$$
(4)

## Relationship between k' and D<sub>w</sub>

$$D_{w} = \frac{A_{o} - A_{s}}{\text{Weight of Resin(g)}} / \frac{A_{s}}{\text{Volume of Solution (mL)}}$$
(5)  
$$D_{v} = \frac{A_{o} - A_{s}}{\text{Volume of Ext on Resin (V_{e})}} / \frac{A_{s}}{\text{Vol of Sol (mL)}}$$
(6)

Where  $D_{\rm w}$  equals weight distribution ratio and  $D_{\rm v}$  equals volume distribution ratio.

$$D_{\rm w} = D_{\rm v} \bullet V_{\rm e}/g \tag{7}$$

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 
$$D_v = D_w \times 2.5$$
 (8)

Assuming  $v_s/v_v = 1/5$  which is close to the value obtained from packed column, substitute in eq. 4.

Then 
$$k' = D_w \bullet 0.5$$
. (9)

# Comparison of K' Calculated from D<sub>w</sub> and K' Obtained from Elution Curves

Element	[HNO <sub>3</sub> ], M	k' Calculated from D <sub>w</sub>	k' from Elution Curve
Nd	0.25	6.5 ± 0.8	6.0 ± 0.3
Pm	0.25	11 ± 1	13 ± 0.7
Sm	0.40	7.0 ± 0.8	6.5 ± 0.3
Eu	0.40	13 ± 2	14 ± 0.7
Gd	0.40	25 ± 3	23 ± 1

# Comparison of K' Calculated from D<sub>w</sub> and K' Obtained from Elution Curves

Element	[HNO <sub>3</sub> ], M	k' Calculated from D <sub>w</sub>	k' from Elution Curve
Dy	0.50	8.0 ± 1.0	8.7 ± 0.4
Но	0.50	18 ± 2	21 ± 1
Yb	1.5	11 ± 1	11 ± 0.6
Lu	1.5	20 ± 2	20 ± 1

#### Factors Affecting Band Spreading in EXC

Flow phenomena:

$$H = \frac{1}{1/2\lambda_i d_p + D_m/\omega_i d_p^2 v}$$
### Factors Affecting Band Spreading in EXC

Stationary phase diffusion:

$$H = q \bullet \frac{k'}{(1+k')^2} \bullet \frac{d_\ell^2 v}{D_s}$$

- H = plate height (HETP)
- q = geometrical configuration factor
- k' = FCV to peak maximum
- $d_{\ell}$  = depth of stationary phase
- D<sub>s</sub> = diffusion coefficient in the stationary phase
- v = interstitial flow velocity

### Factors Affecting Band Spreading in EXC

Extraction kinetics:

$$H = 2 \bullet \frac{k'}{(1+k')^2} \bullet \frac{v}{k_{oa}}$$

- H = plate height (HETP)
- k' = FCV to peak maximum
- v = interstitial flow velocity
- k<sub>oa</sub> = aqueous to organic rate constant

Reference for all equations: E.P. Horwitz and C.A.A. Bloomquist,
 J. Inorg. Nucl. Chem., 1972, Vol. 34, pp. 3851-3871.
 J.C. Giddings, Dynamics of Chromatography
 Principles and Theory. Marcel Dekker, New York (1965)

# Types of EXC Resins

$$\frac{\text{Acidic}}{M^{3+} + 3\text{HY}} \rightleftharpoons MY_3 + 3\text{H}^+ M^{3+} + 3(\text{HY})_2 \rightleftharpoons M(\text{HY}_2)_3 + 3\text{H}^+ M^{3+} + 3(\text{HY})_2 \rightleftharpoons M(\text{HY}_2)_3 + 3\text{H}^+ MX_3$$

$$\frac{\text{Neutral}}{M^{3+} + nE + 3X^-} \rightleftarrows ME_n \bullet X_3$$

$$\frac{\text{Basic}}{R_3\text{N} + nE + 3X^-} \rightleftarrows ME_n \bullet X_3$$

$$\frac{\text{Basic}}{R_3\text{N} + HX} \rightleftarrows R_3\text{NH}^+X^- MX_3 \rightleftharpoons R_3\text{NH}^+MX_4^- MX_4^- MX_5 \rightleftharpoons R_3\text{NH}^+MX_4^- MX_5 \rightleftharpoons R_3\text{NH}^+MX_4^- MX_5 \rightleftharpoons R_3\text{NH}^+MX_4^- MX_5 \oiint R_3\text{NH}^+MX_5 \oiint R_3\text{NH}^+MX_4^- MX_5 \oiint R_3\text{NH}^+MX_5 \H R_3\text{NH}^+MX_5 \H$$

## Anionic Extraction Chromatographic Resins

Resin	Туре	Extractant	Major Applications
TEVA	Basic	Quaternary Amine	Pu, Tc, Th, Np, Am/Ln
Weak Base EC	Basic	Tertiary Amine	Tc, Np, Pu

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



Quaternary Ammonium Extractant



Tertiary Ammonium Extractant



#### Mean Activity Coefficients vs. Molarity



# UTEVA Resin

Diamyl Amylphosphonate (DAAP) a.k.a. Dipentyl Pentylphosphonate (DPPP)





# Structure/Extracted Species



Am<sup>3+</sup> + 3X<sup>-</sup> + 
$$\overline{3E}$$
 ↔  $\overline{AmE_3X_3}$   
X = Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>

# Uptakes of Actinides on TRU vs DGA



# Uptakes of Actinides on TRU vs DGA

**TRU Resin** 

DGA Resin, Normal

#### DGA Resin, Branched





# **Cationic Extractants**





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# **Coupled Column Applications**



\*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



#### Proposed <sup>213</sup>Bi Generator for Medical Uses



# Separations at Curie Levels

Water-Radiolysis Equation from 5.3MeV Alpha Particles from <sup>210</sup>Po

$$\begin{split} H_2 OM &\to [0.05] OH + [X] e^-{}_{aq} + [0.06] H \\ &+ [0.15] H_2 O_2 + [X] H_3 O^+ + [0.16] H_2 \end{split}$$

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

Equations from Mincher, et al. Solvent Extraction and Ion Exchange 27, 1 (2009)

#### Radiolytic Degradation Products of CMPO



#### Radiolytic Degradation Products of TODGA



# 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 sever 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 ?





**RRMC 2011** Sandestin, Florida October 31 - November 4, 2011

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#### 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 acthoring place reminiscent of an old world fishing village. The Village

