How EXC Resins Work

(How to make EXC Resins Work)

Daniel McAlister, Ph.D.

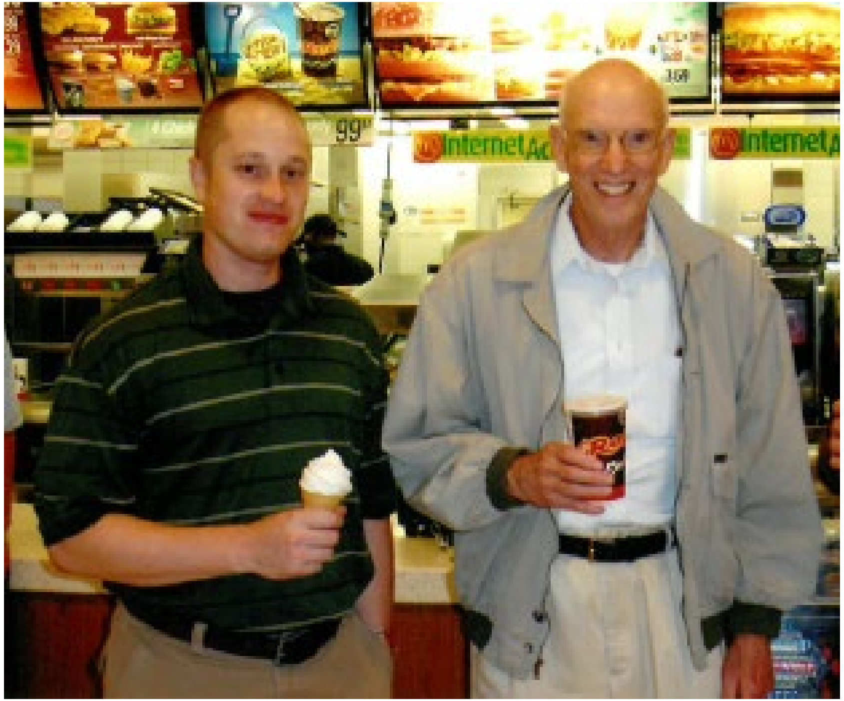
2022 RRMC, Atlanta, Georgia

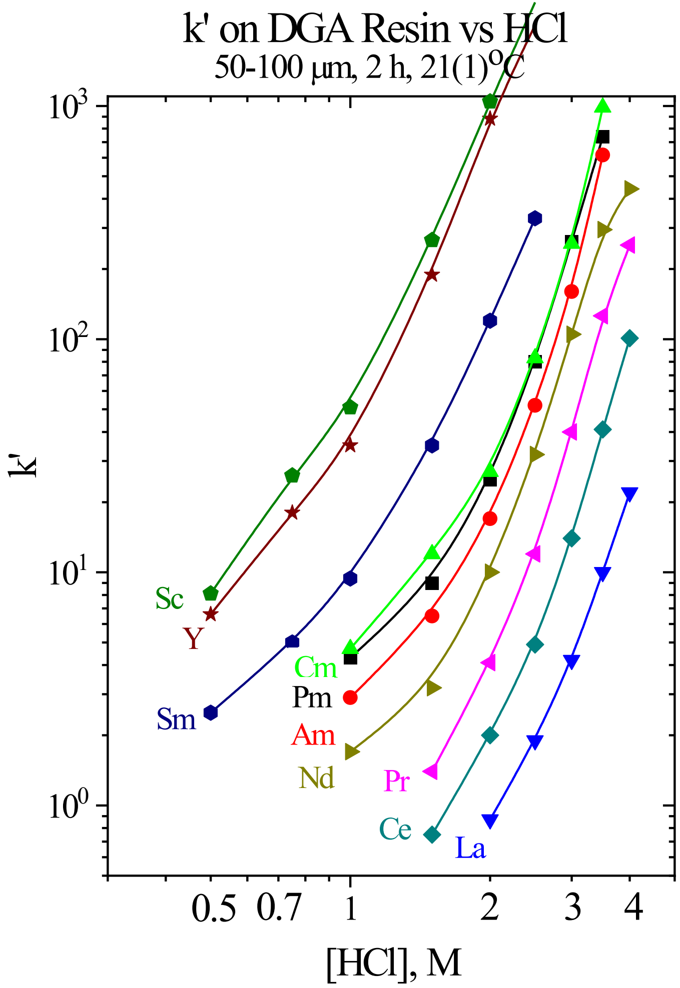
Outline

Basics of Chromatography

Basics of metal ion extraction

Applied separations
- Sr Resin
- Pb Resin
- DGA/Sr Resin





Peak maximum positions:

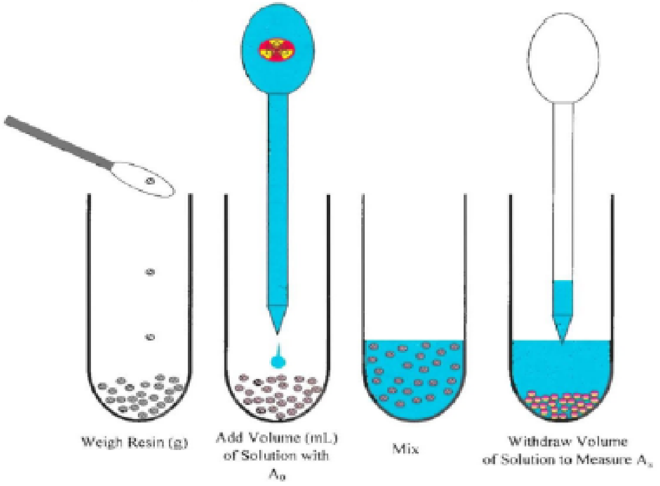
Dw = mL eluate/grams resin (measured by batch contact)

Dv = mL eluate/mL resin

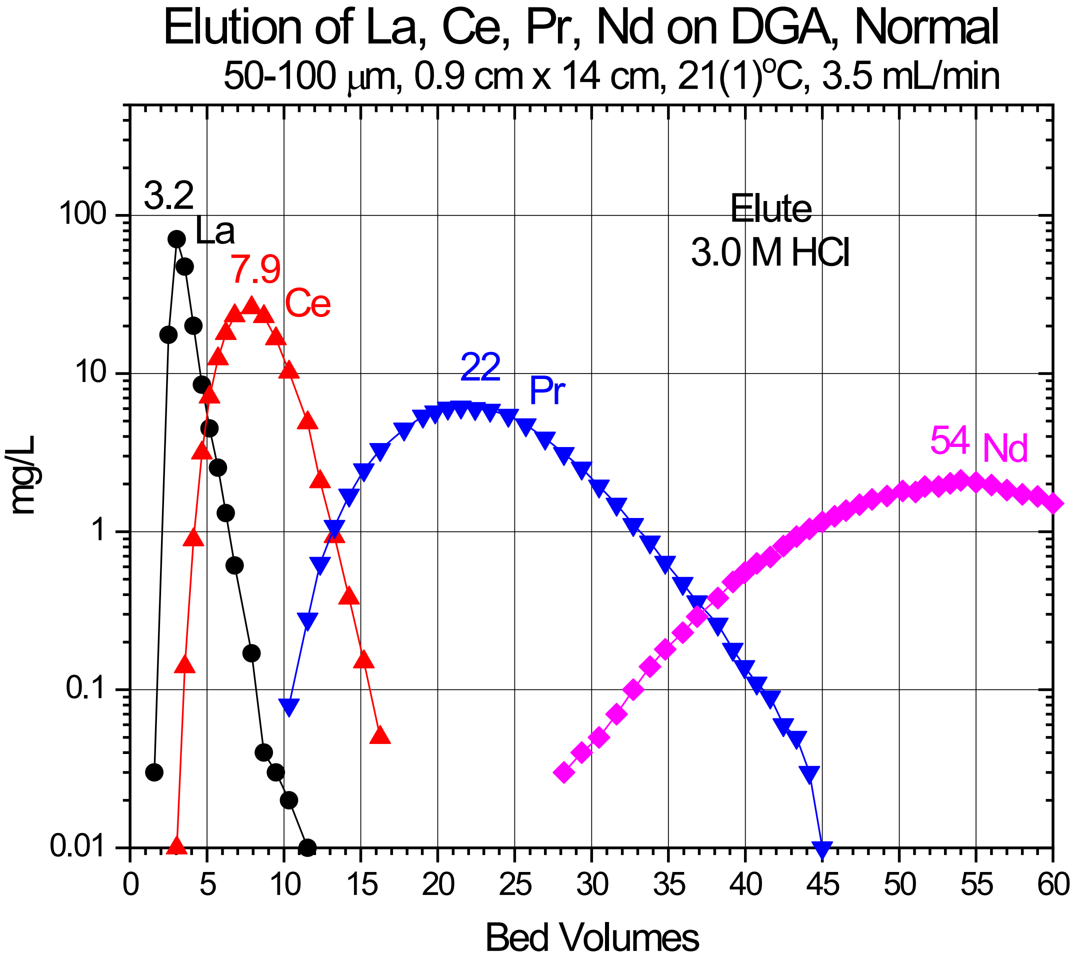
k' = free column volumes

Calculated from Dw using:

- Bed density
- Resin density
- Extractant density
- Extractant loading



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



Dw, Dv, or k' gives information about the position of the peaks……

but not the peak widths.

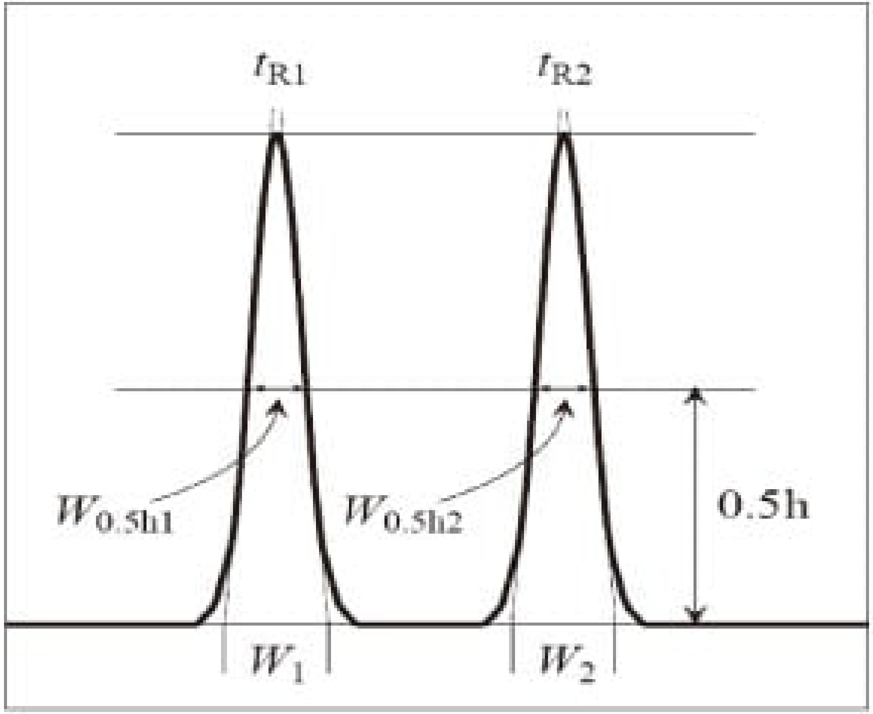
Separation (Resolution) is dependent on

1) the separation factor…..

2) The peak widths

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).

Resolution



t_{R1}, t_{R2} : Retention time for each peak ($t_{R1} < t_{R2}$)

$W_{0.5h1}$, $W_{0.5h2}$: Full width at half maximum (FWHM) of each peak

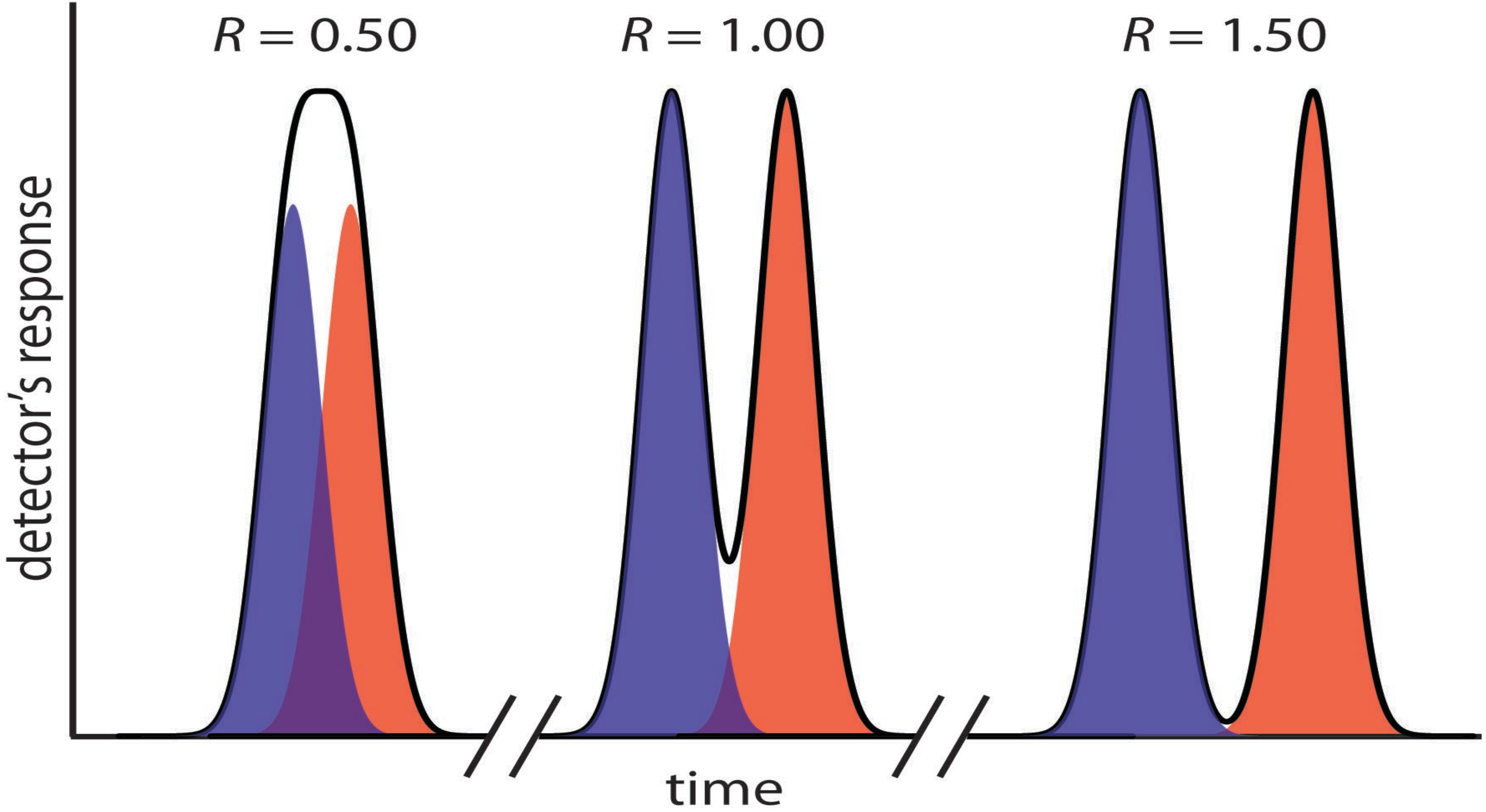
W_1, W_2 : Width of each peak

Fig. 1 Two Adjacent Peaks

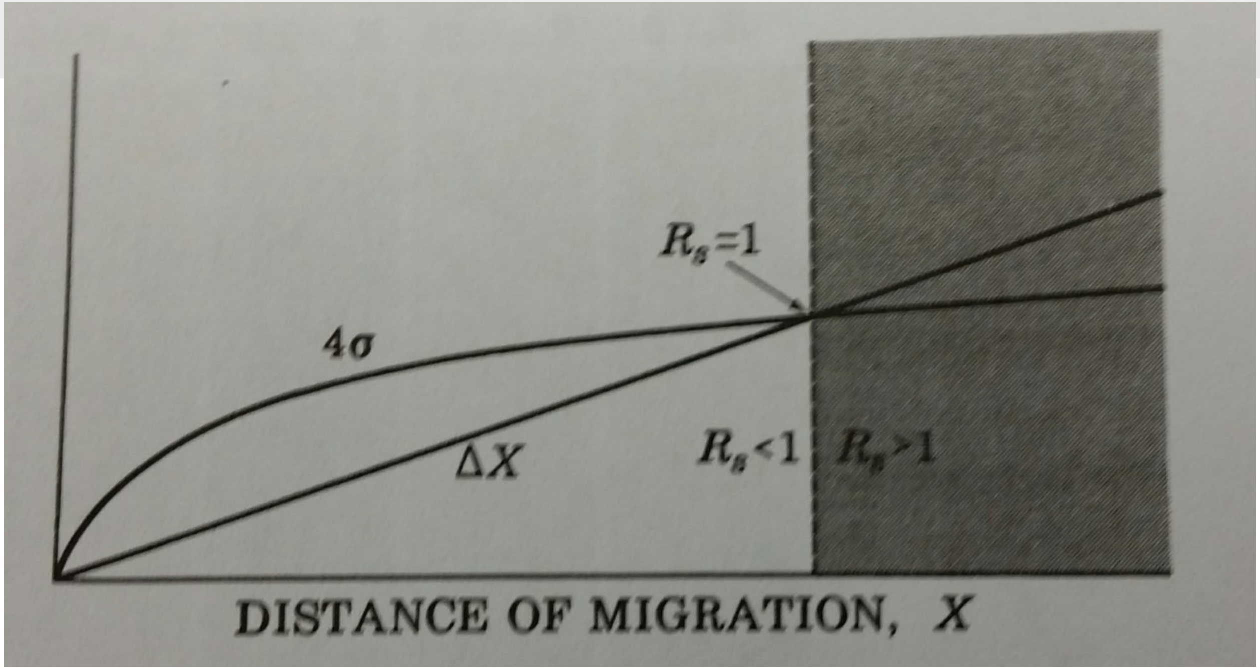
$$R = \frac{t_{R2} - t_{R1}}{\frac{1}{2}(W_1 + W_2)} \quad \cdots (1)$$

$$R = 1.18 \times \left(\frac{t_{R2} - t_{R1}}{W_{0.5h1} + W_{0.5h2}} \right) \quad \cdots (2)$$

Resolution



Resolution improves with longer columns!



For longer columns (larger X):

ΔX (difference in peak positions) increases linearly

4σ (peaks width) increases as the square root of X

EXC Resin

Eichrom EXC resins typically have very high separation factors (ΔX) for key metal ions.

Large ΔX allows:

1) Small columns/cartridges
2) Large particle size resins
3) Gravity or low-pressure flow

Small ΔX require:

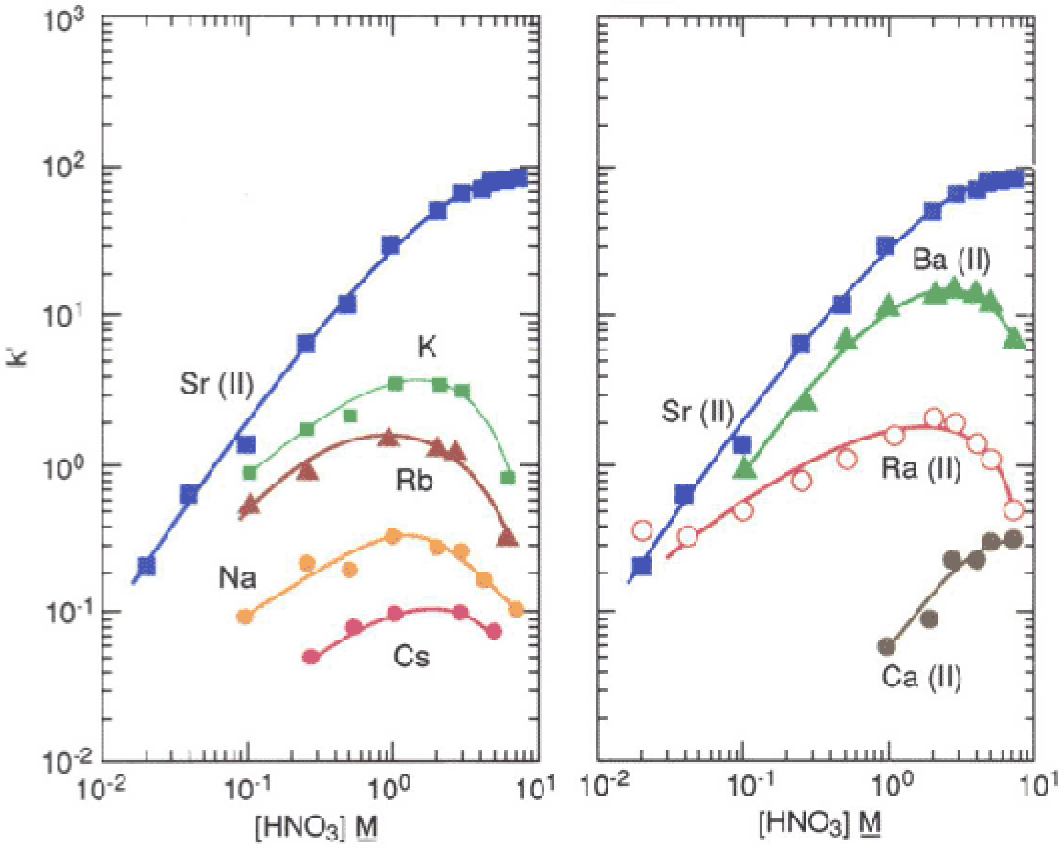
1) Longer columns
2) Small particle size
3) High temperature/pressure

www.eichrom.com

Figures 2 and 3

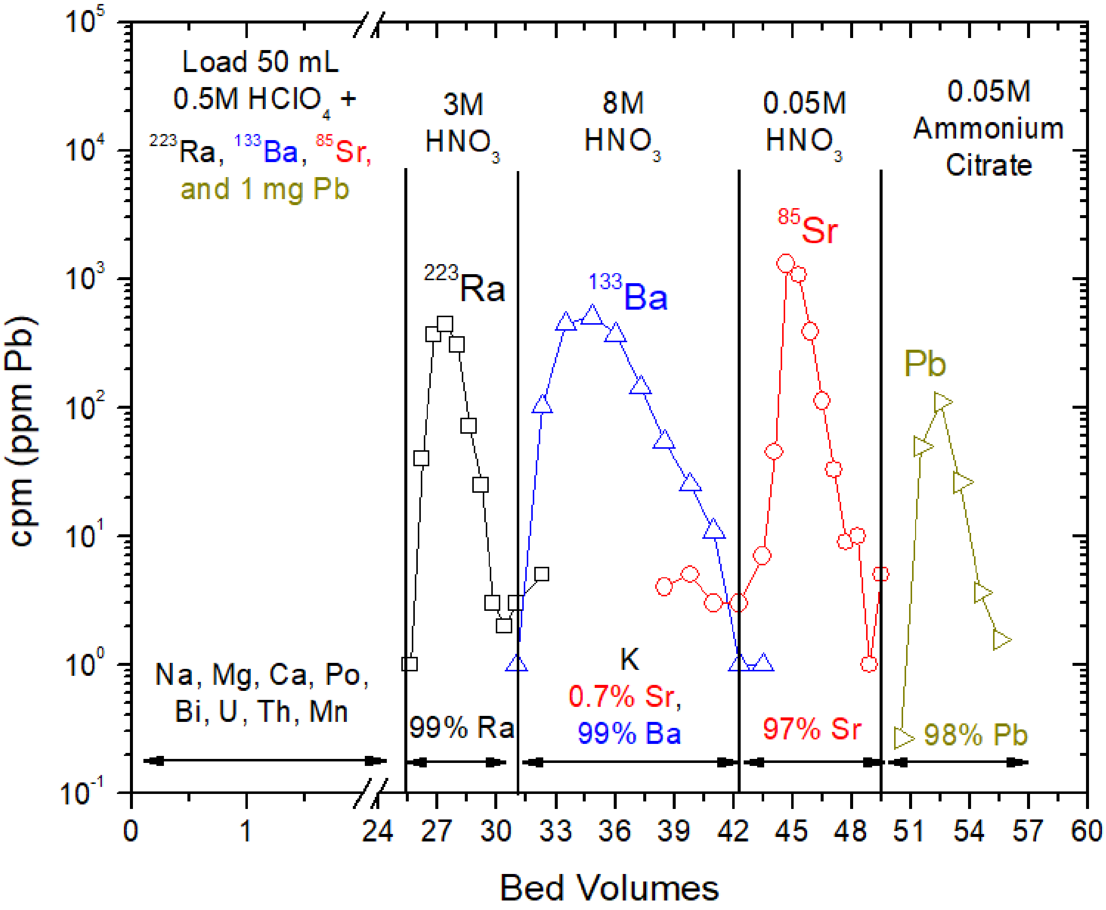
Acid dependency of k' for various ions at 23-25°C.

Sr Resin



Horwitz, et al., (HP292)

EXC Chromatogram (Sr Resin, 50-100 μm, i.d. 0.8 cm, length 3.2 cm, b.v. = 1.6 mL)



2 mL/min

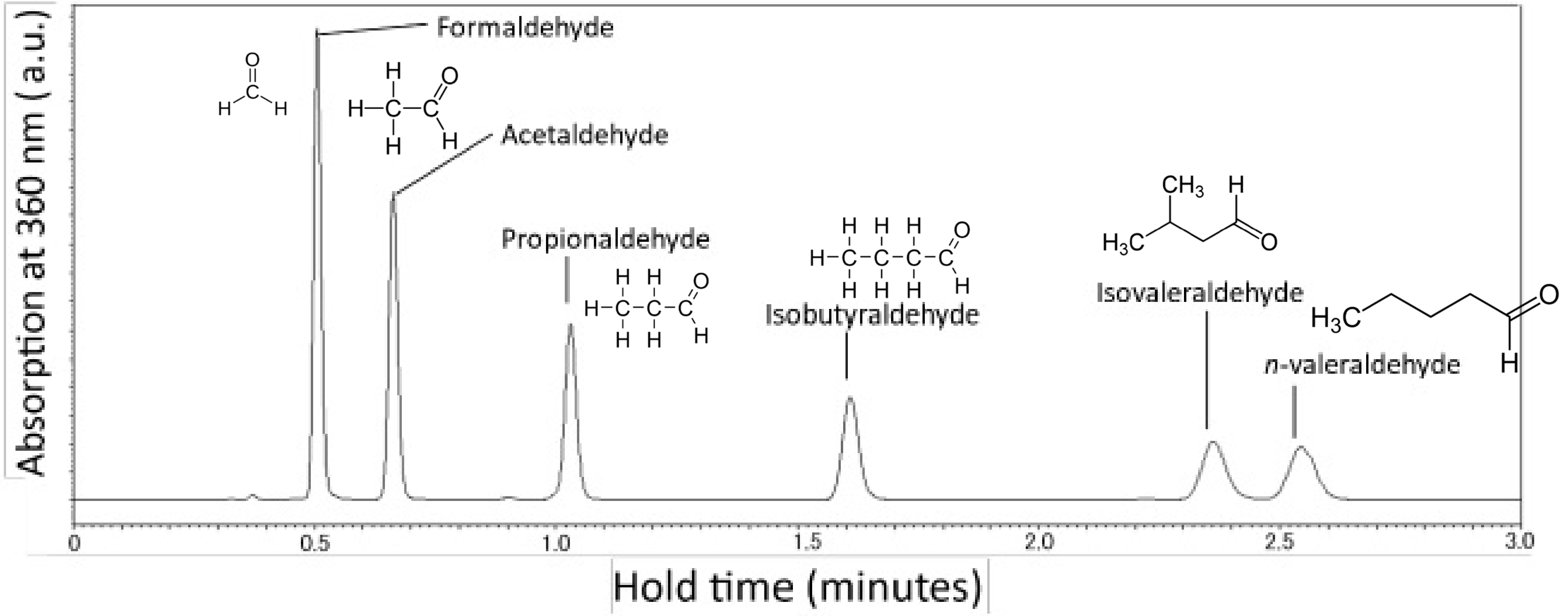
60 mL

30 minutes

Gradient elution

21°C

HPLC Chromatogram (c18 silica, 2 μm, i.d. 0.5 cm, length 15 cm, b.v. = 3 mL)

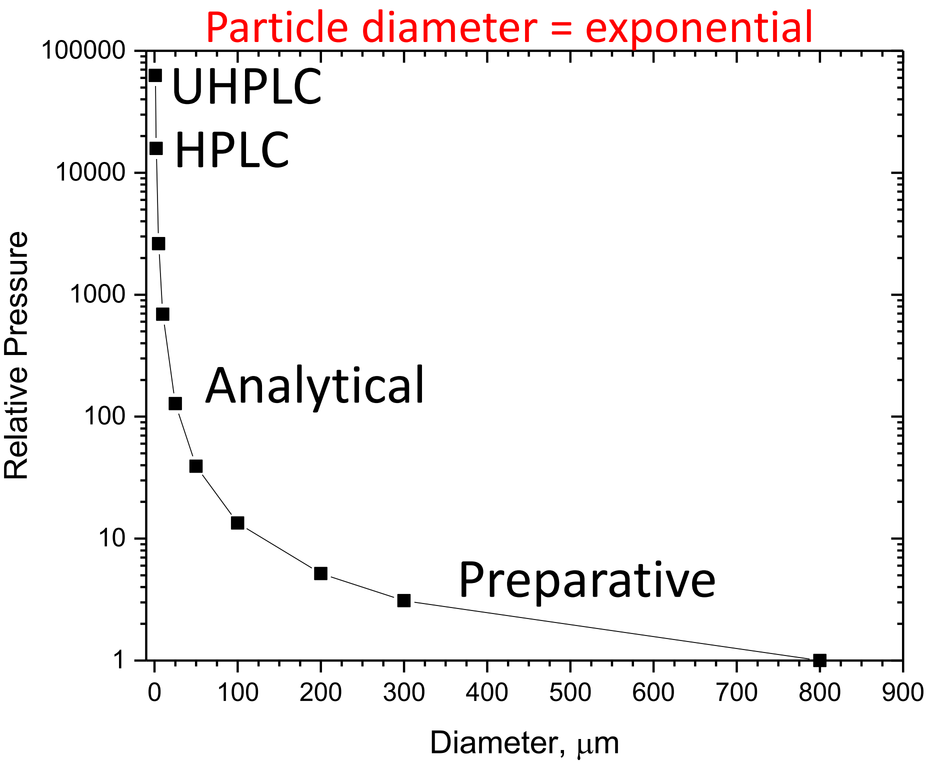


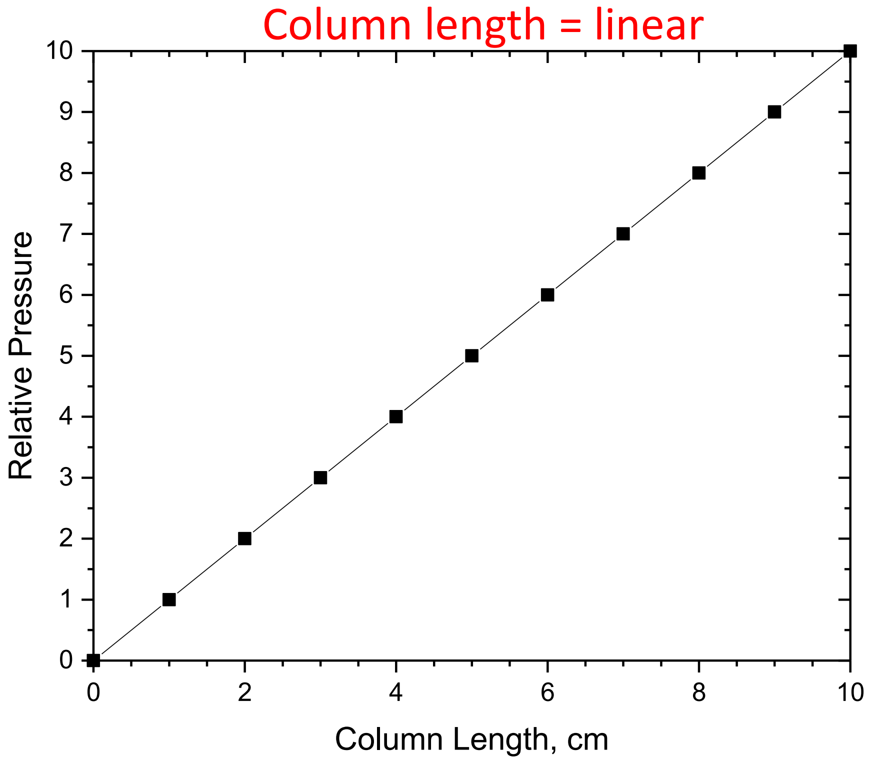
1.4 mL/min x 3 minutes = 4.2 mL, isocratic elution, 40ºC

eichrom

www.eichrom.com

Relative pressure drop through packed bed





Fundamentals of Extraction

Sr Resin vs Pb Resin

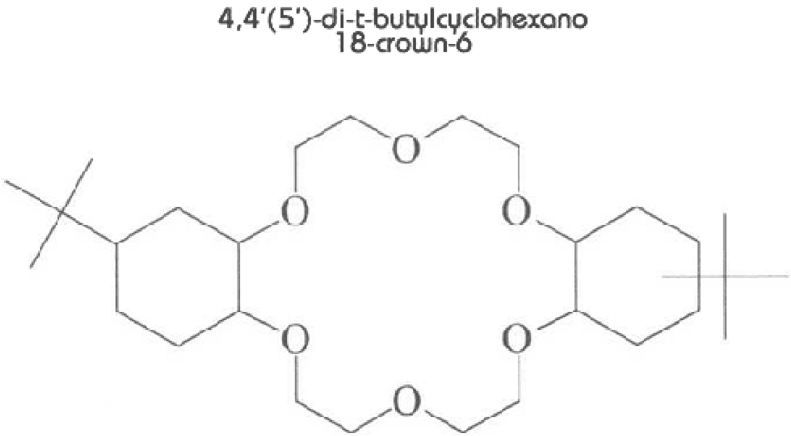
Factors that effect selectivity and k’

Pb Resin vs Sr Resin

$Pb^{2+}_{(aq)} + 2X^{-}_{(aq)} \leftrightarrow Pb(Crown)X_{2(org)}$

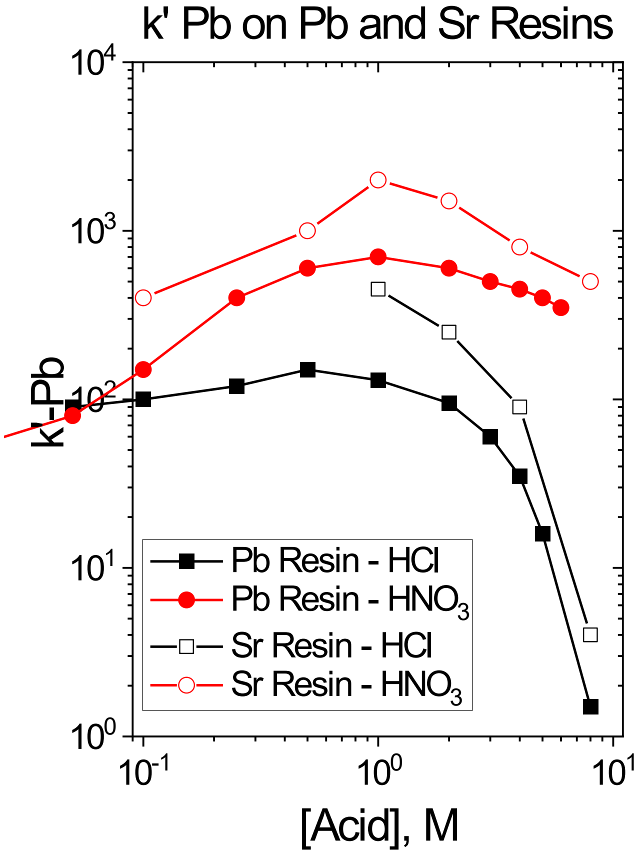
Sr Resin:

- d*t*BuCH18C6 in 1-octanol



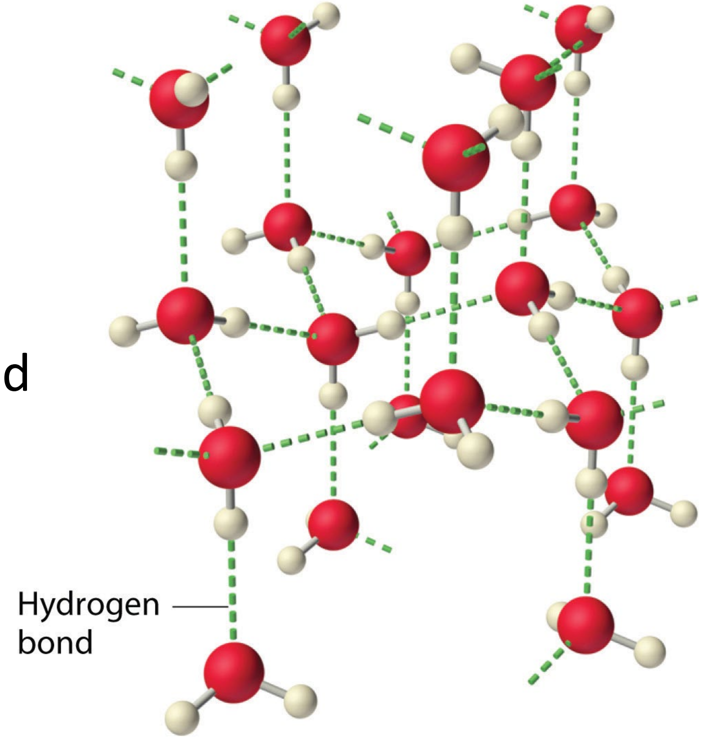
Pb Resin:

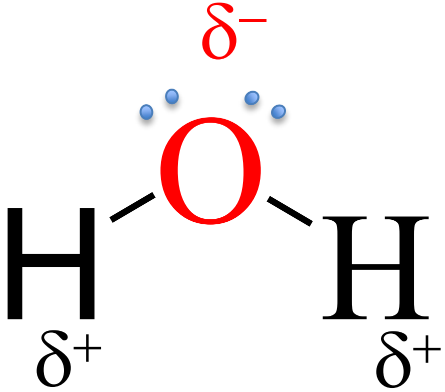
-25% less d*t*BuCH18C6 in isodecanol



Aqueous phase water structure

Water H-Bond Structure





Adding ions to the water disrupts the hydrogen bonded structure.

eichrom

Aqueous phase solvation (hydration)

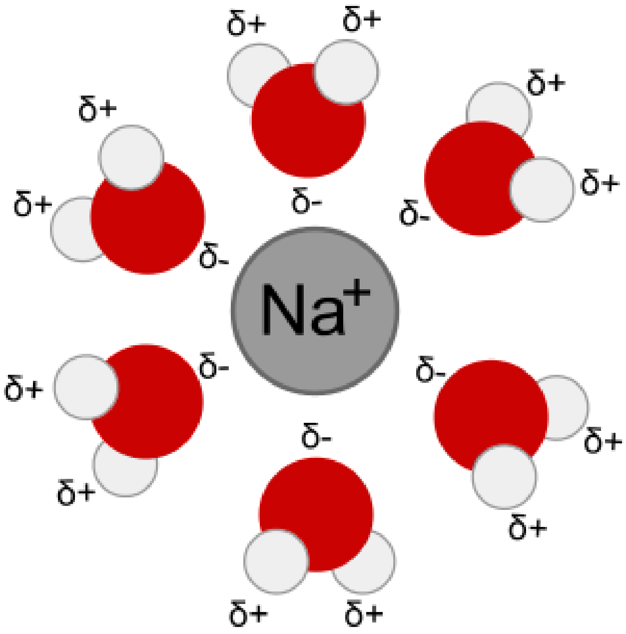
$[M(H_2O)_n]^{z+}$

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

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

Actinides and lanthanides n ~ 8-9

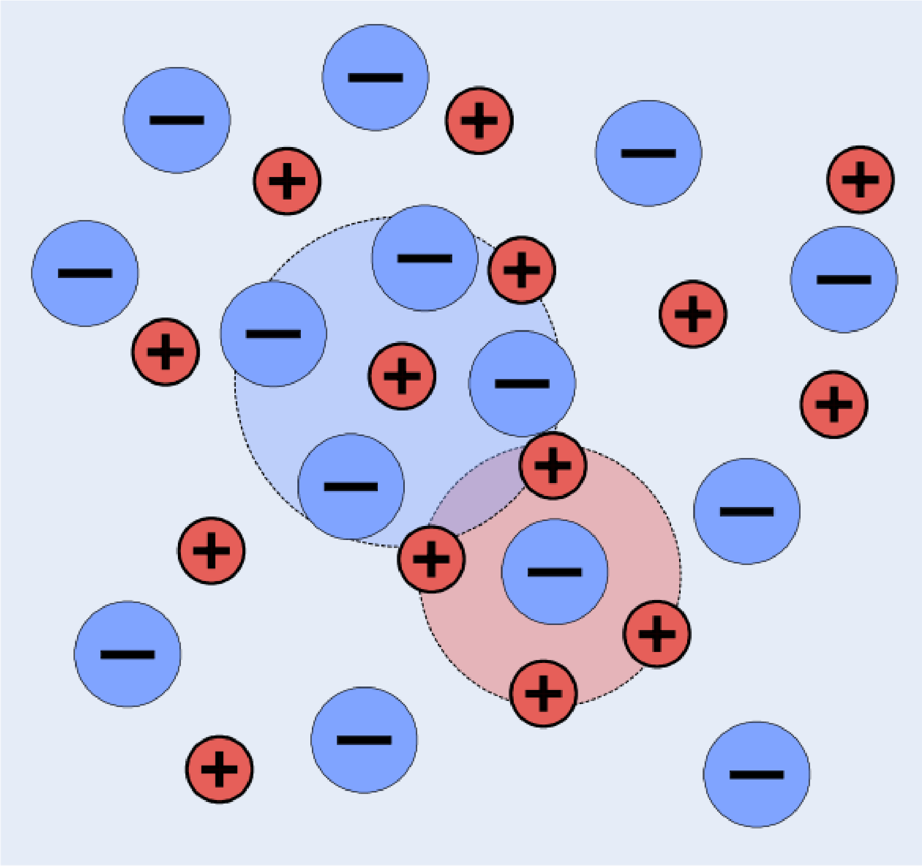
n = primary hydration/coordination
H = total hydration/solvation (secondary)



Coordinate covalent bonding is ubiquitous.[7] In all metal aquo-complexes $[M(H_2O)_n]^{m+}$, the bonding between water and the metal cation is described as a coordinate covalent bond. Metal-ligand interactions in most organometallic compounds and most coordination compounds are described similarly.

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

Aqueous phase activities as electrolyte concentrations increase



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

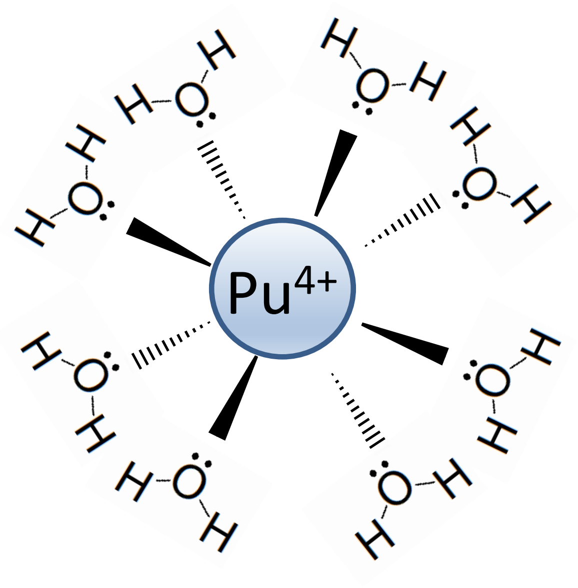
Aqueous activity/coefficients.

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

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

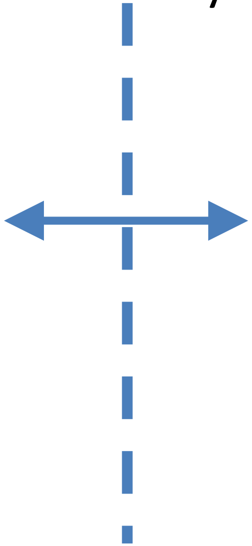
Transfer from aqueous to non-aqueous phase

Sekine 1977



Aqueous Phase

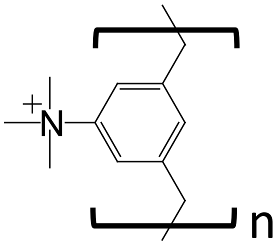
Phase Boundary



PuF_4 (s)

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

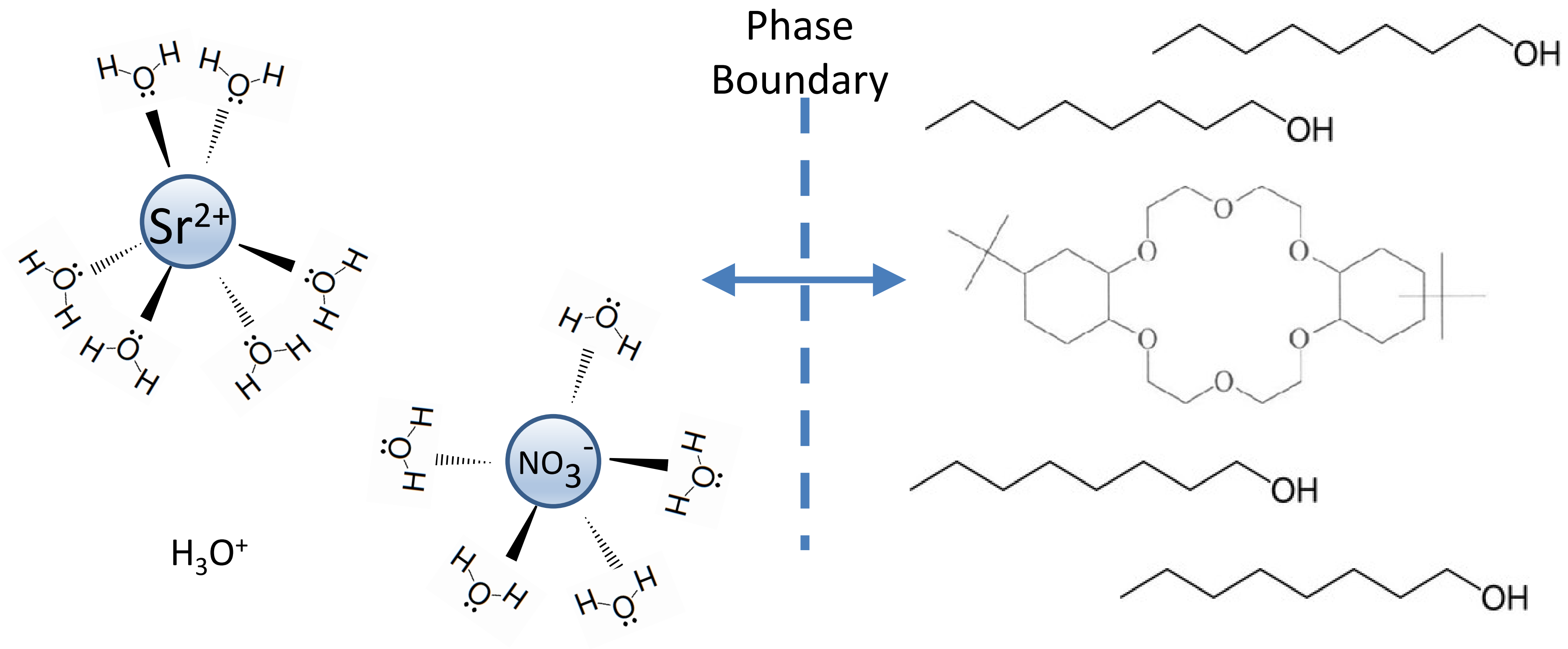
$[Pu(NO_3)_5]^-$



Non-Aqueous Phase

eichrom

Sr Extraction from HNO3 into crown ether in 1-octanol



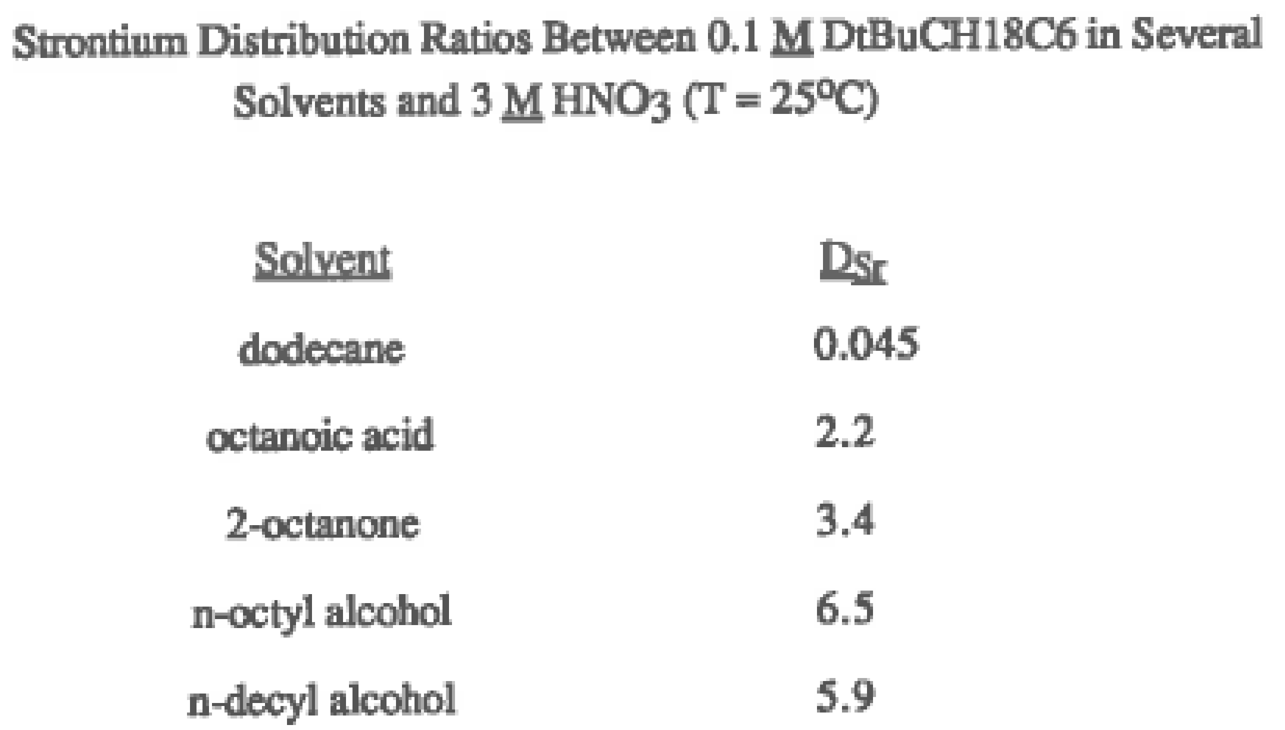
Phase Boundary

H_3O^+

Aqueous Phase

Resin Phase

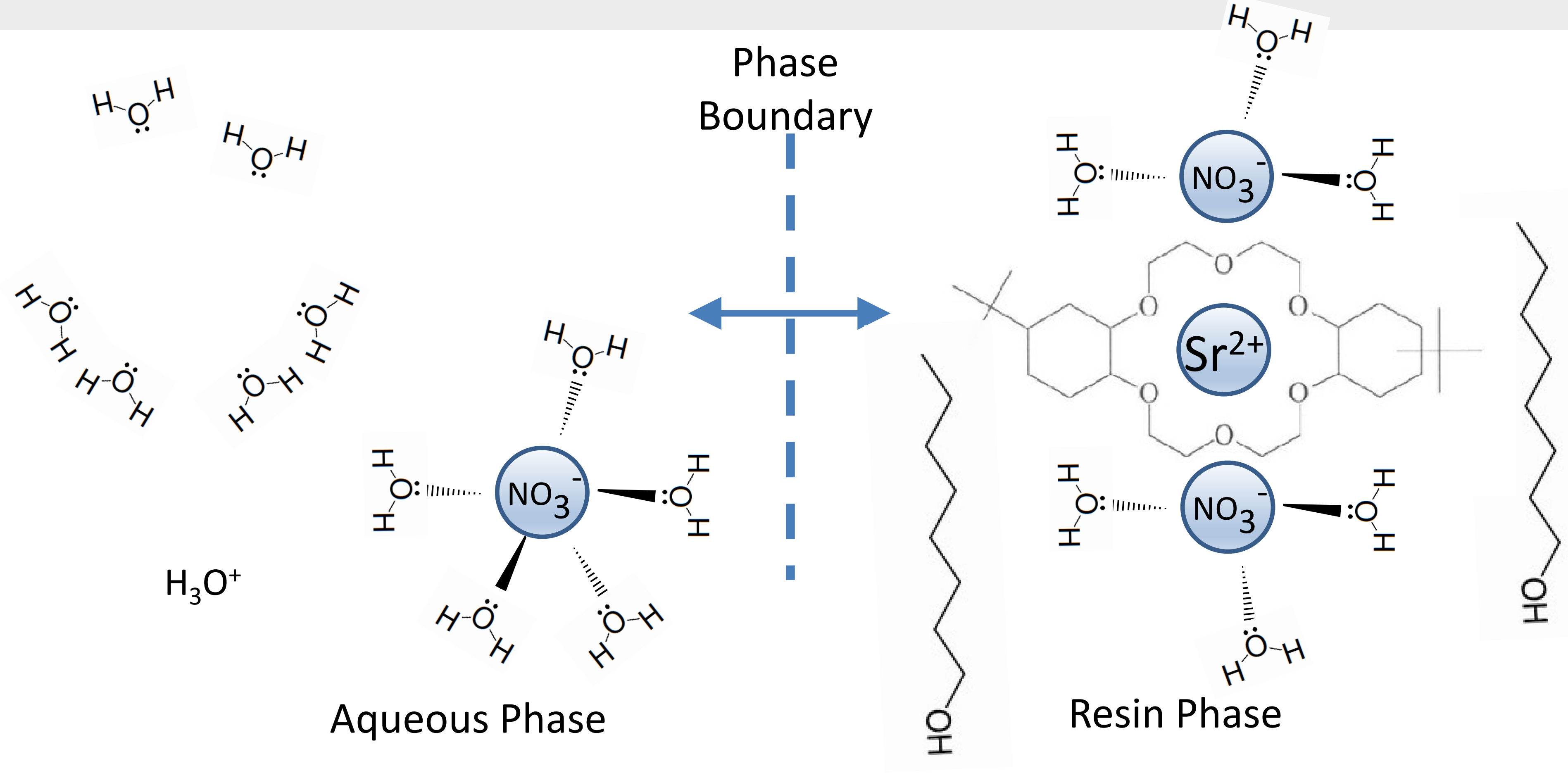
Pb Resin vs Sr Resin



Strontium Distribution Ratios Between 0.1 M DtBuCH18C6 in Several Solvents and 3 M HNO_3 (T = 25°C)

Solvent	D_{Sr}
dodecane	0.045
octanoic acid	2.2
2-octanone	3.4
n-octyl alcohol	6.5
n-decyl alcohol	5.9

Sr Extraction from HNO3 into crown ether in 1-octanol



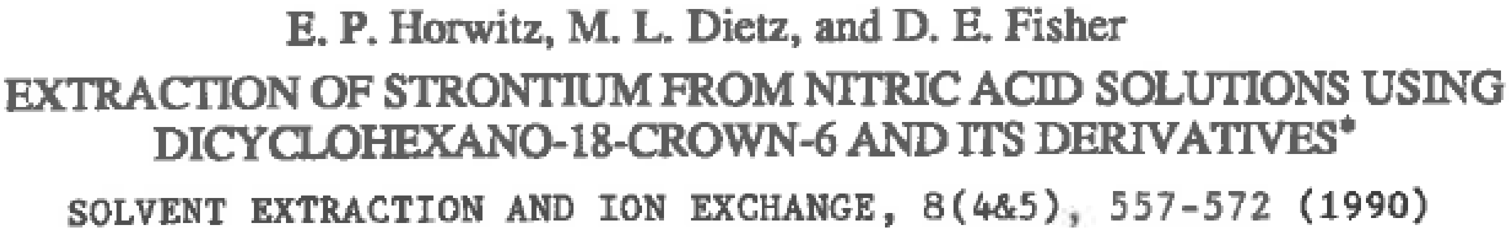
Phase Boundary

H_3O^+

Aqueous Phase

Resin Phase

Extractant, Acid, Temperature, Diluent in Sr Extraction



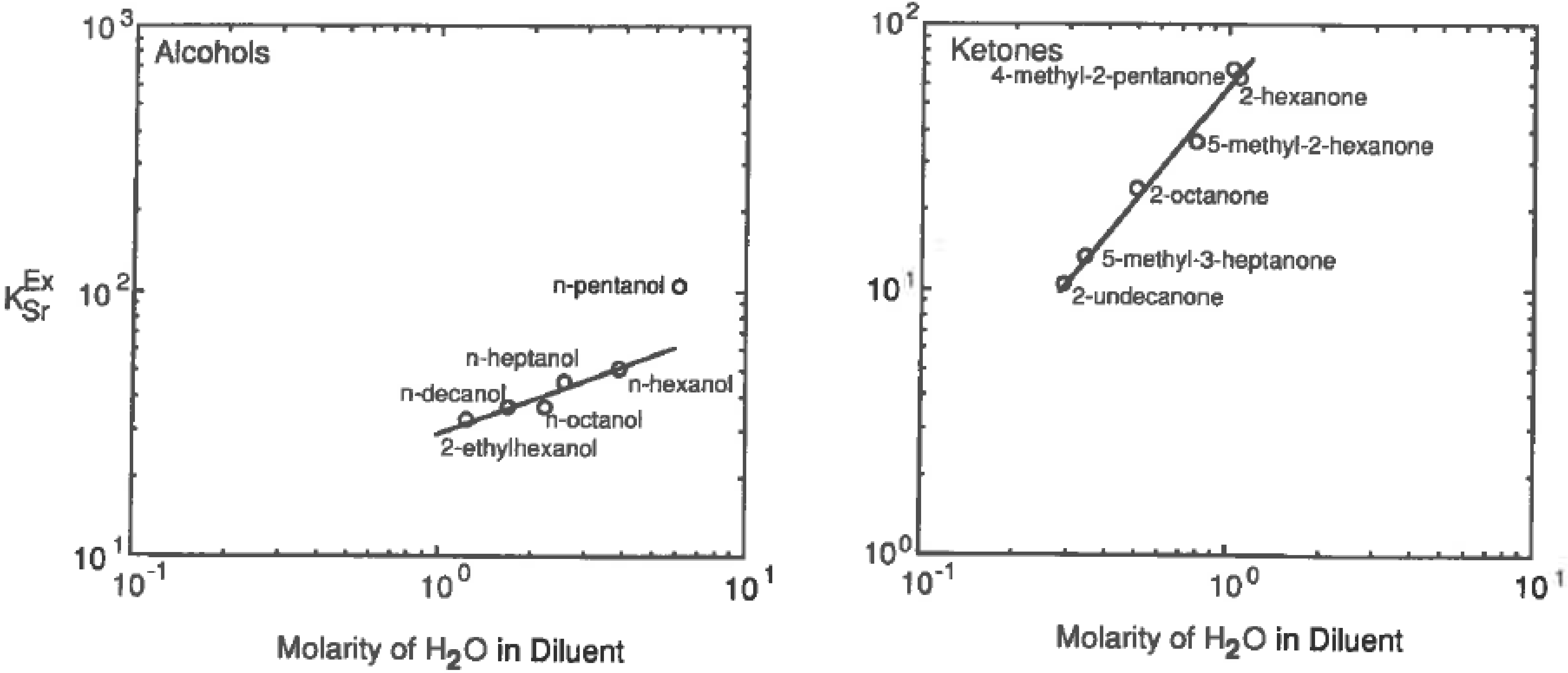
E. P. Horwitz, M. L. Dietz, and D. E. Fisher

EXTRACTION OF STRONTIUM FROM NITRIC ACID SOLUTIONS USING DICYCLOHEXANO-18-CROWN-6 AND ITS DERIVATIVES*

SOLVENT EXTRACTION AND ION EXCHANGE, 8(4&5), 557-572 (1990)

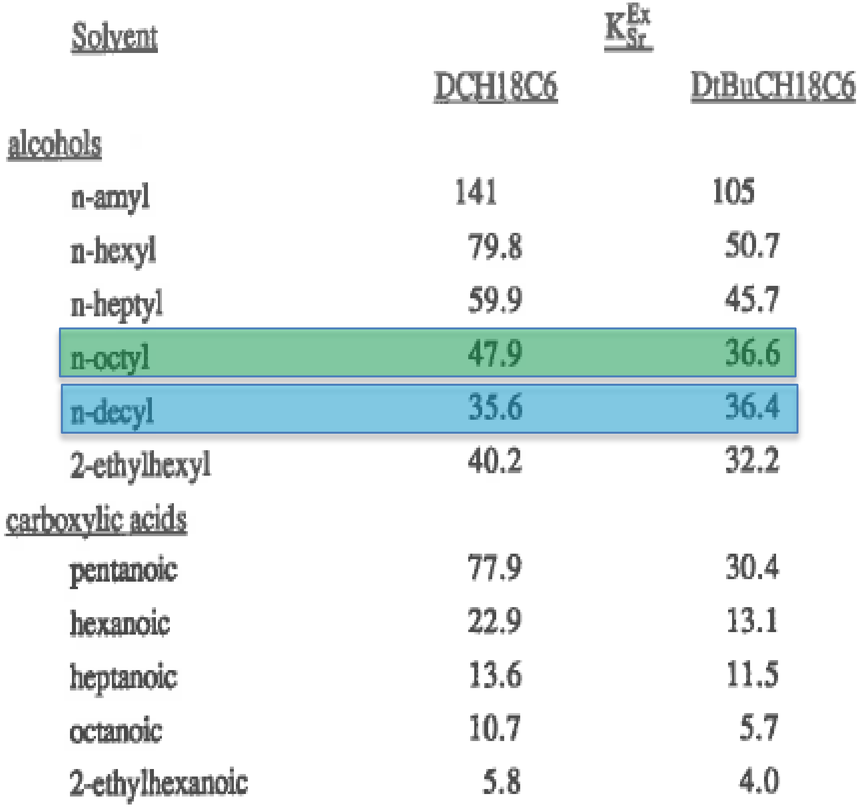
Diluent (polarity/water-nitrate accepting/aggregation)

Extraction constants for strontium nitrate (K_{Sr}^{Ex}) by DtBuCH18C6 in various diluents versus the water concentration in the organic phase.

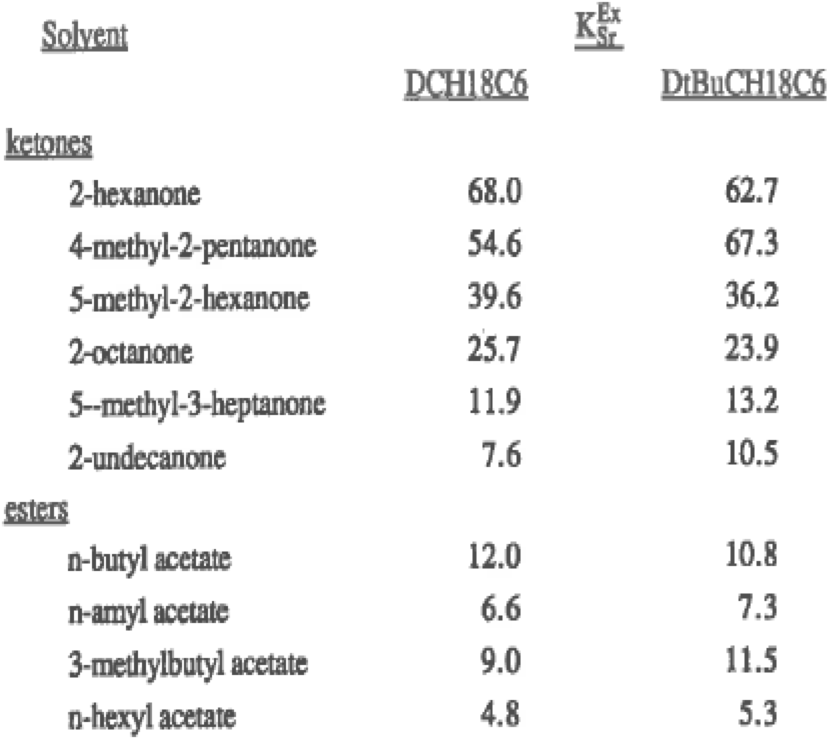


Comparison of Strontium Extraction Constants for DCH18C6 and DtBuCH18C6 in Various Diluents (T = 25°C)

Remove DCH18C6, add boiling points, water solubility



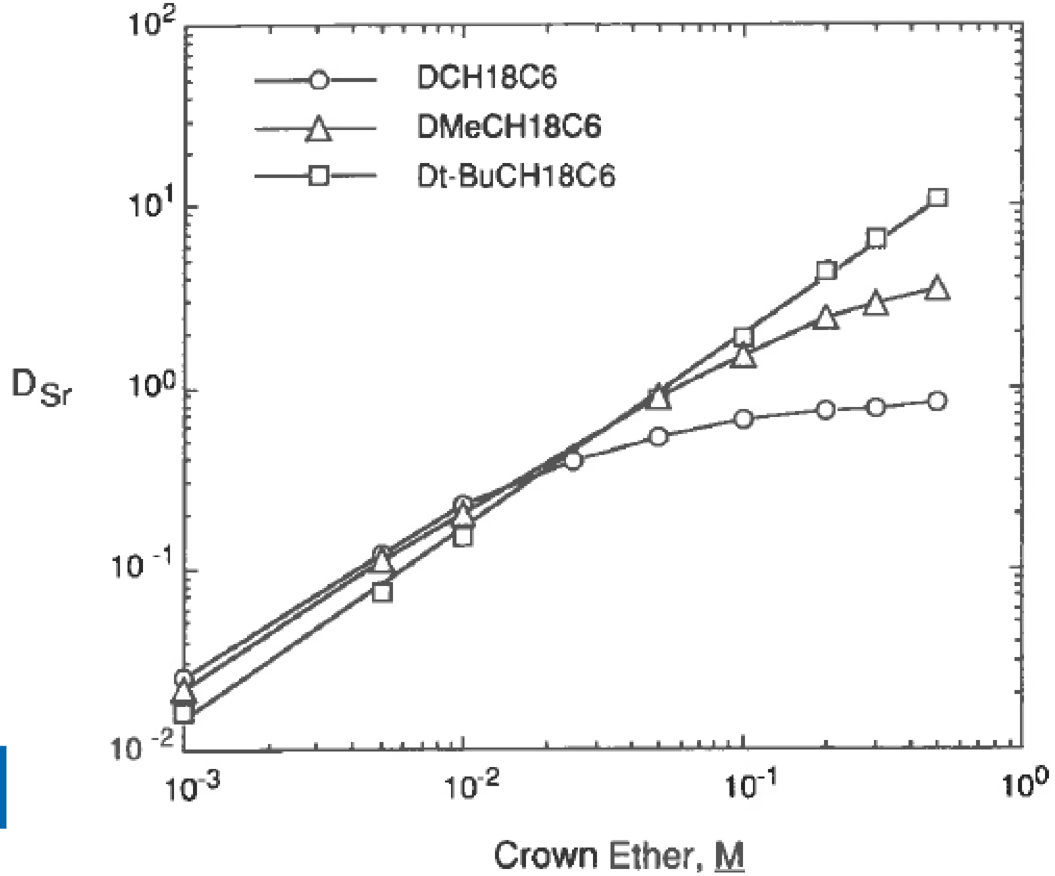
Solvent	K_{Sr}^{Ex} DCH18C6	K_{Sr}^{Ex} DtBuCH18C6
alcohols		
n-amyl	141	105
n-hexyl	79.8	50.7
n-heptyl	59.9	45.7
n-octyl	47.9	36.6
n-decyl	35.6	36.4
2-ethylhexyl	40.2	32.2
carboxylic acids		
pentanoic	77.9	30.4
hexanoic	22.9	13.1
heptanoic	13.6	11.5
octanoic	10.7	5.7
2-ethylhexanoic	5.8	4.0



Solvent	K_{Sr}^{Ex} DCH18C6	K_{Sr}^{Ex} DtBuCH18C6
ketones		
2-hexanone	68.0	62.7
4-methyl-2-pentanone	54.6	67.3
5-methyl-2-hexanone	39.6	36.2
2-octanone	25.7	23.9
5--methyl-3-heptanone	11.9	13.2
2-undecanone	7.6	10.5
esters		
n-butyl acetate	12.0	10.8
n-amyl acetate	6.6	7.3
3-methylbutyl acetate	9.0	11.5
n-hexyl acetate	4.8	5.3

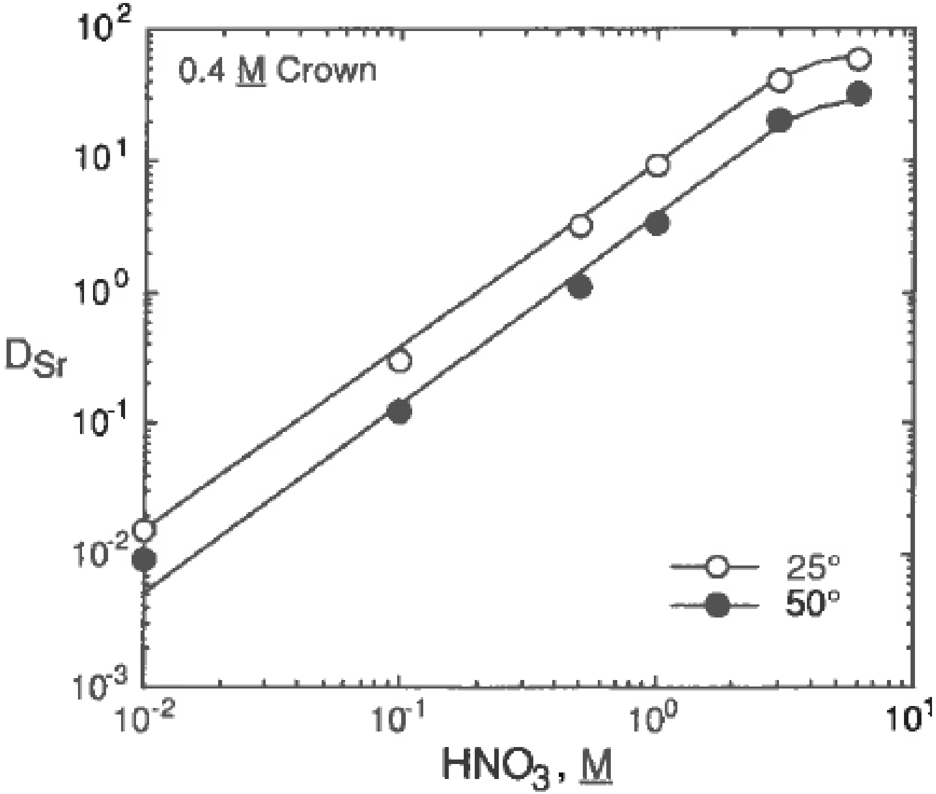
Extractant Concentration (Aggregation)

D_{Sr} extractant dependencies for three 18-crown-6 derivatives in n- octanol. ($[HNO_3] = 1$ M).



Acid Concentration (counter ion)

D_{Sr} acid dependencies for DtBuCH18C6 in n- octanol at two temperatures.



Counter ion/steric effect and dehydration energy

F^-

88 kj/mol

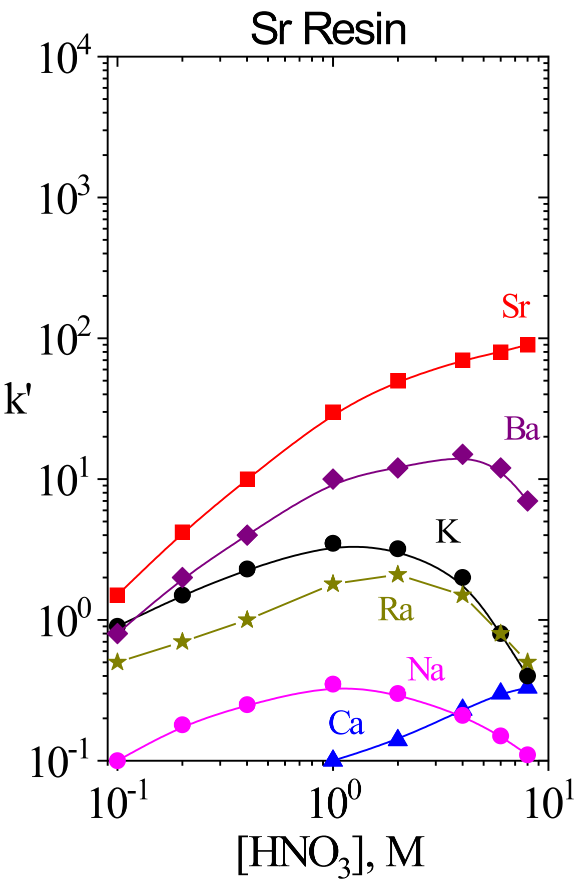
NO_3^-

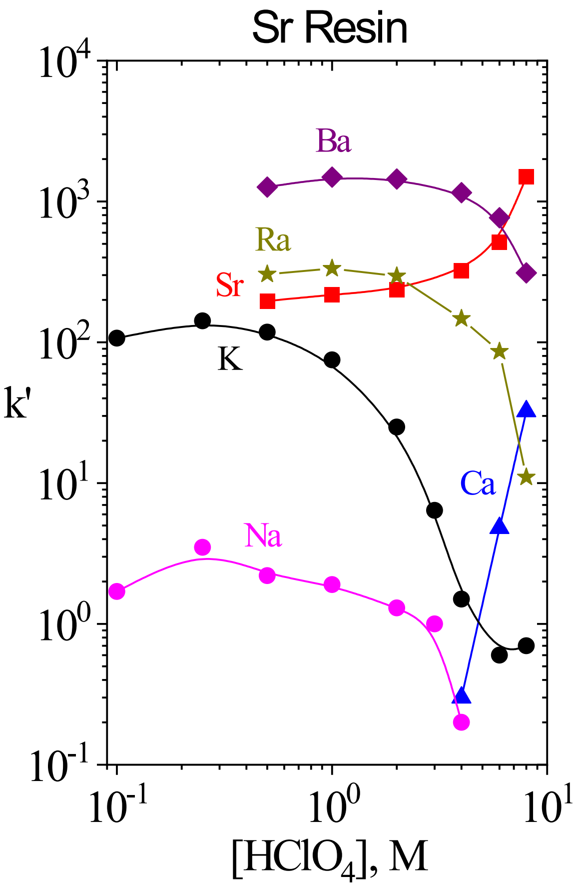
66 kj/mol

ClO_4^-

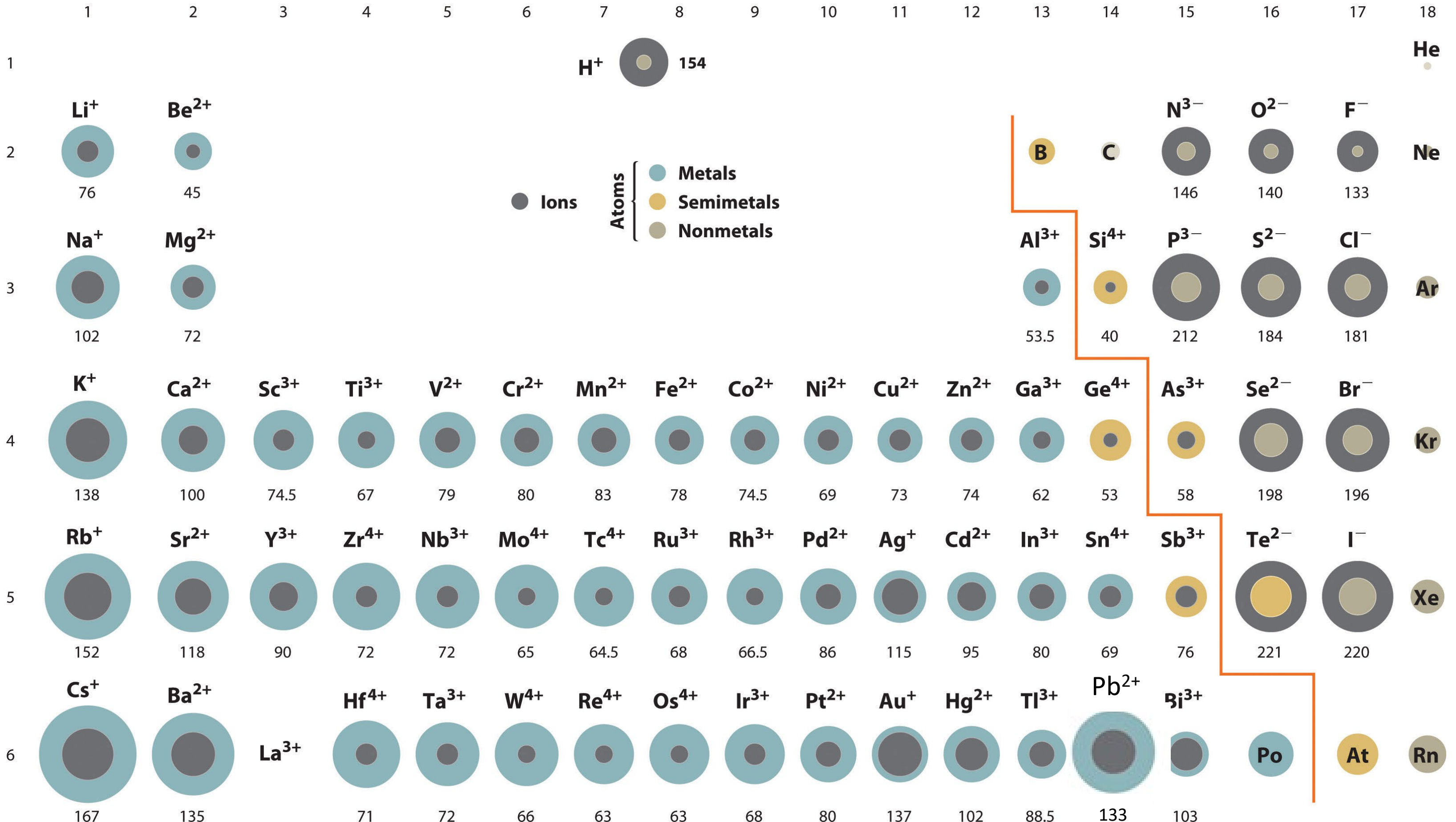
43 kj/mol

Anion can change selectivity



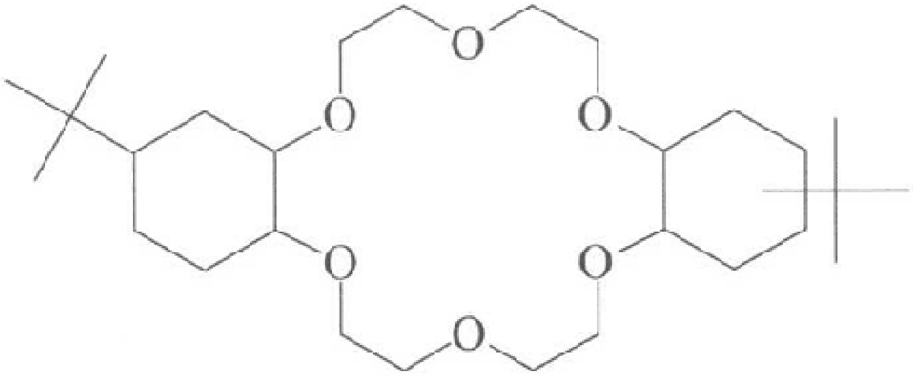


Ionic radii

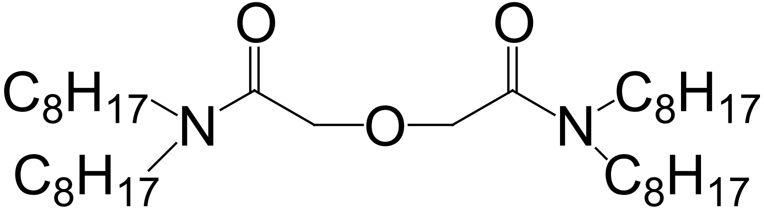

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
1
H+ 154
He
2
Li+ 76
Be2+ 45
B
C
N3− 146
O2− 140
F− 133
Ne
Ions
Atoms
Metals
Semimetals
Nonmetals
3
Na+ 102
Mg2+ 72
Al3+ 53.5
Si4+ 40
P3− 212
S2− 184
Cl− 181
Ar
4
K+ 138
Ca2+ 100
Sc3+ 74.5
Ti3+ 67
V2+ 79
Cr2+ 80
Mn2+ 83
Fe2+ 78
Co2+ 74.5
Ni2+ 69
Cu2+ 73
Zn2+ 74
Ga3+ 62
Ge4+ 53
As3+ 58
Se2− 198
Br− 196
Kr
5
Rb+ 152
Sr2+ 118
Y3+ 90
Zr4+ 72
Nb3+ 72
Mo4+ 65
Tc4+ 64.5
Ru3+ 68
Rh3+ 66.5
Pd2+ 86
Ag+ 115
Cd2+ 95
In3+ 80
Sn4+ 69
Sb3+ 76
Te2− 221
I− 220
Xe
6
Cs+ 167
Ba2+ 135
La3+
Hf4+ 71
Ta3+ 72
W4+ 66
Re4+ 63
Os4+ 63
Ir3+ 68
Pt2+ 80
Au+ 137
Hg2+ 102
Tl3+ 88.5
Pb2+ 133
Bi3+ 103
Po
At
Rn

Other diluents/phase modifiers

4,4'(5')-di-t-butylcyclohexano
18-crown-6



DGA



- Helps transfer H_2O and HNO_3
- Extracts Sr and Pb at 1-3M HNO_3
- Extracts REE (Y)
- Liquid, miscible w/dtBCH18C6
- Very high boiling point/hydrophobic

D.R. McAlister, D. Silvestri, E. Rush, E.P. Horwitz, "Extraction of Selected Metal Ions by Mixtures of Diglycolamides and Crown Ethers," *Solv. Extr. Ion Exch.*, 39(2), 184-203 (2021).

Physical Properties

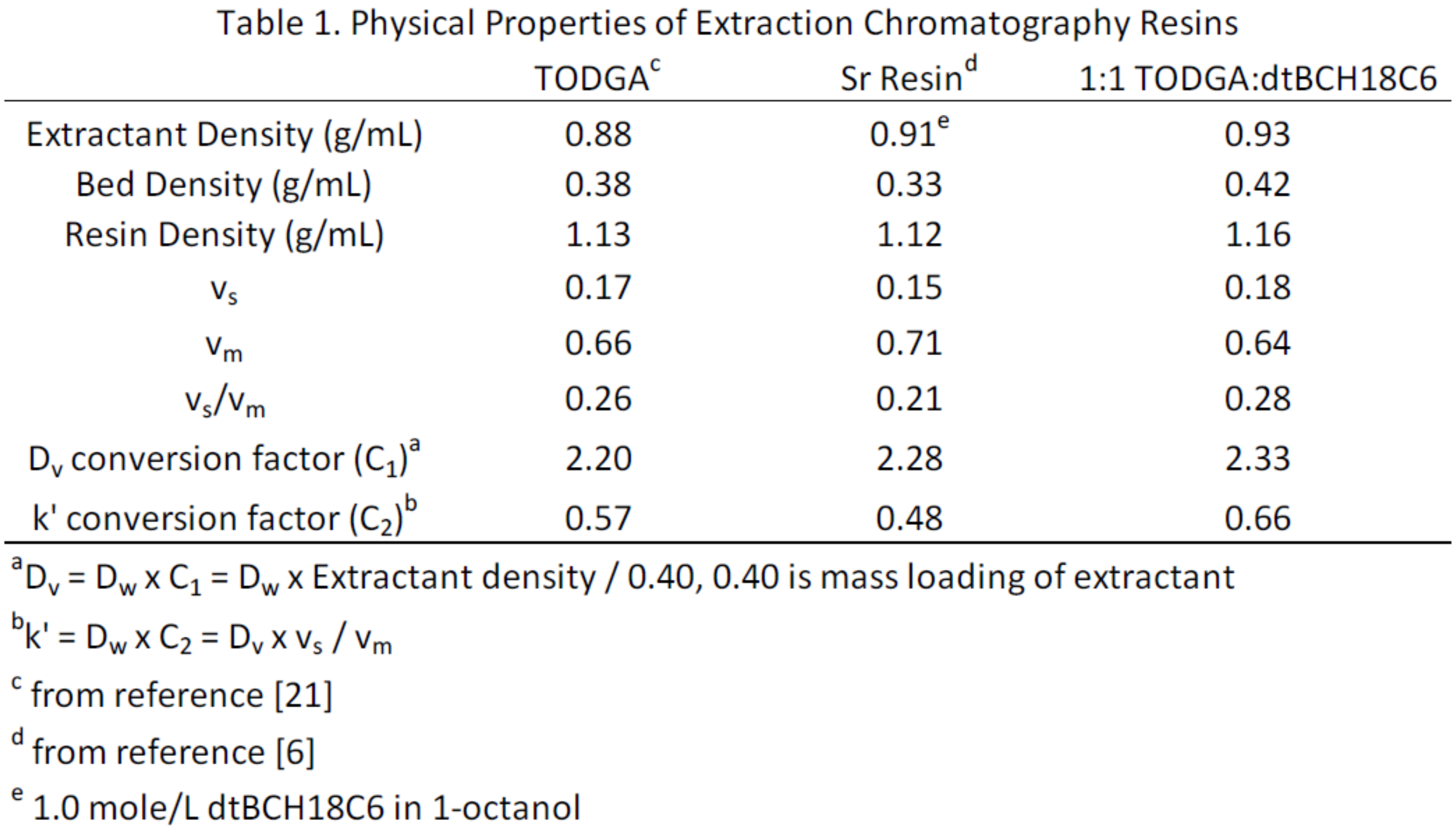


Table 1. Physical Properties of Extraction Chromatography Resins

	TODGA[c]	Sr Resin[d]	1:1 TODGA:dtBCH18C6
Extractant Density (g/mL)	0.88	0.91[e]	0.93
Bed Density (g/mL)	0.38	0.33	0.42
Resin Density (g/mL)	1.13	1.12	1.16
v_s	0.17	0.15	0.18
v_m	0.66	0.71	0.64
v_s/v_m	0.26	0.21	0.28
D_v conversion factor (C_1)[a]	2.20	2.28	2.33
k' conversion factor (C_2)[b]	0.57	0.48	0.66

[a] $D_v = D_w \times C_1 = D_w \times$ Extractant density / 0.40, 0.40 is mass loading of extractant

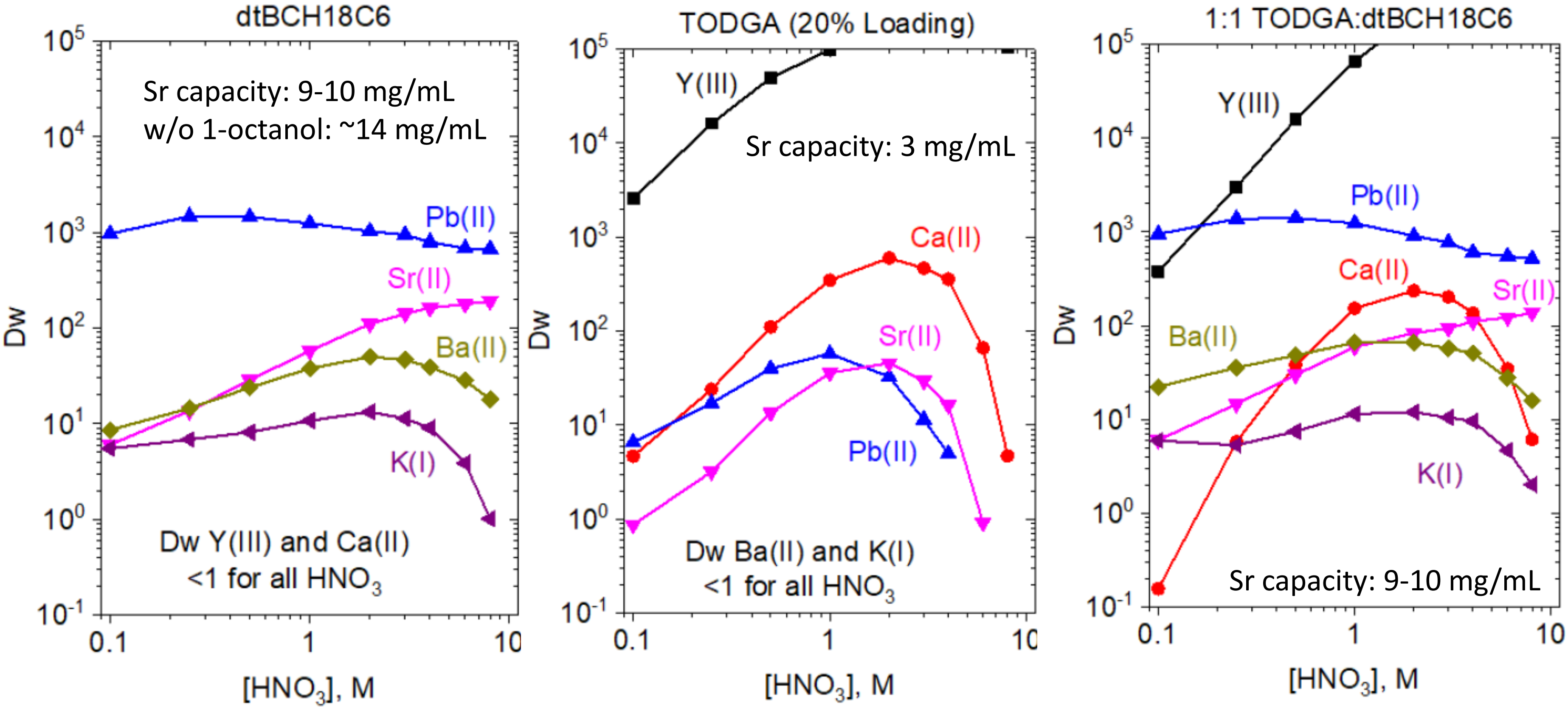
[b] $k' = D_w \times C_2 = D_v \times v_s / v_m$

[c] from reference [21]

[d] from reference [6]

[e] 1.0 mole/L dtBCH18C6 in 1-octanol

Metal Ion Extraction by Crown, DGA and Mixtures



Sr capacity: 9-10 mg/mL
w/o 1-octanol: ~14 mg/mL

Dw Y(III) and Ca(II) <1 for all HNO$_3$

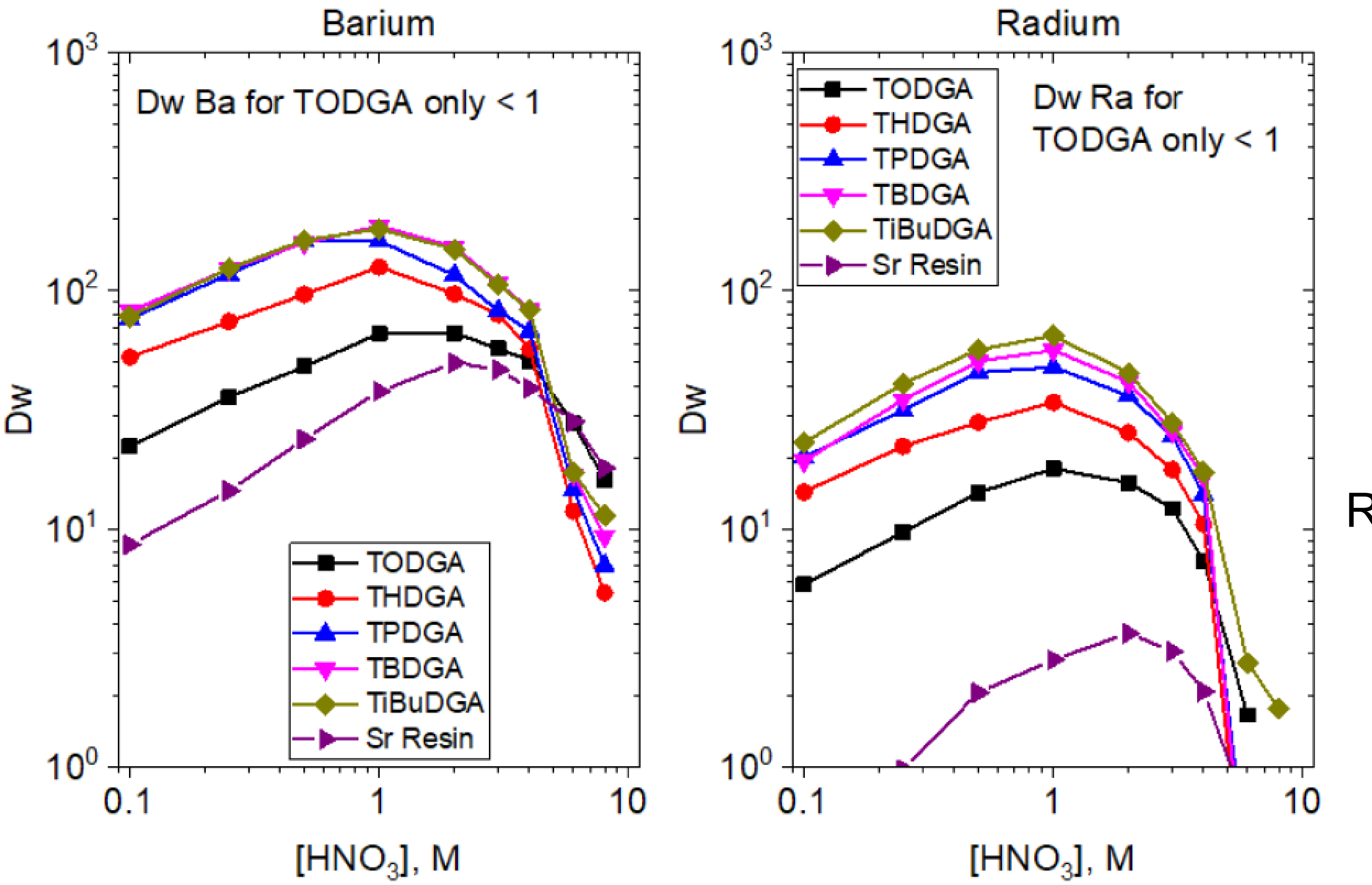
Sr capacity: 3 mg/mL

Dw Ba(II) and K(I) <1 for all HNO$_3$

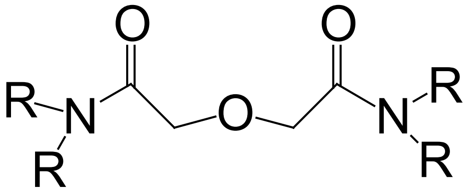
Sr capacity: 9-10 mg/mL

D.R. McAlister, D. Silvestri, E. Rush, E.P. Horwitz, "Extraction of Selected Metal Ions by Mixtures of Diglycolamides and Crown Ethers," *Solv. Extr. Ion Exch.*, 39(2), 184-203 (2021).

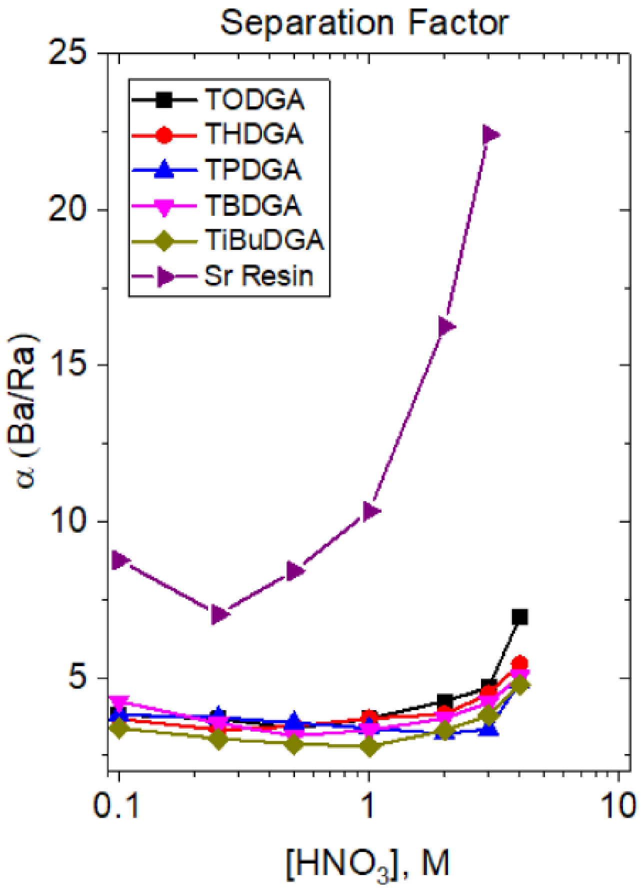
Effect of length of DGA R-group

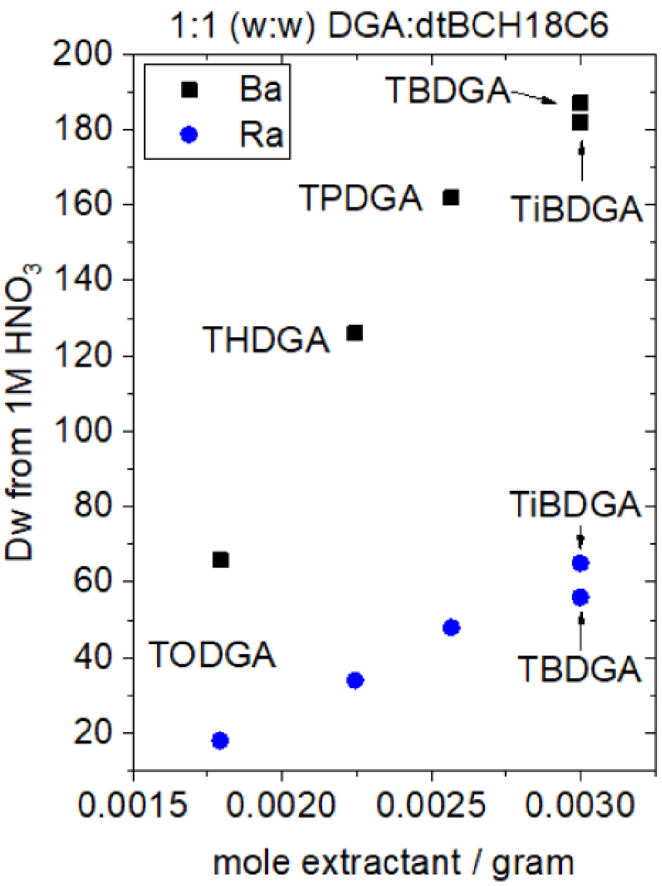


Octyl = TO
Hexyl = TH
Pentyl = TP
Butyl = TB
iButyl = TiB
1-octanol

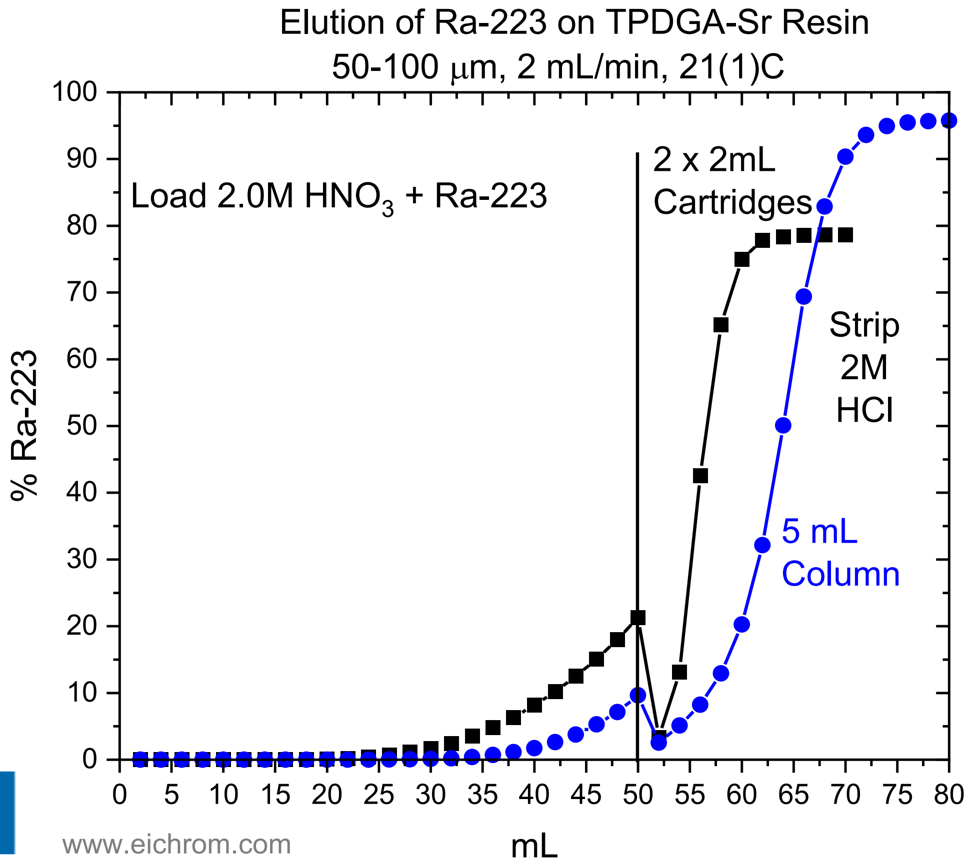


Ra/Ba Separation

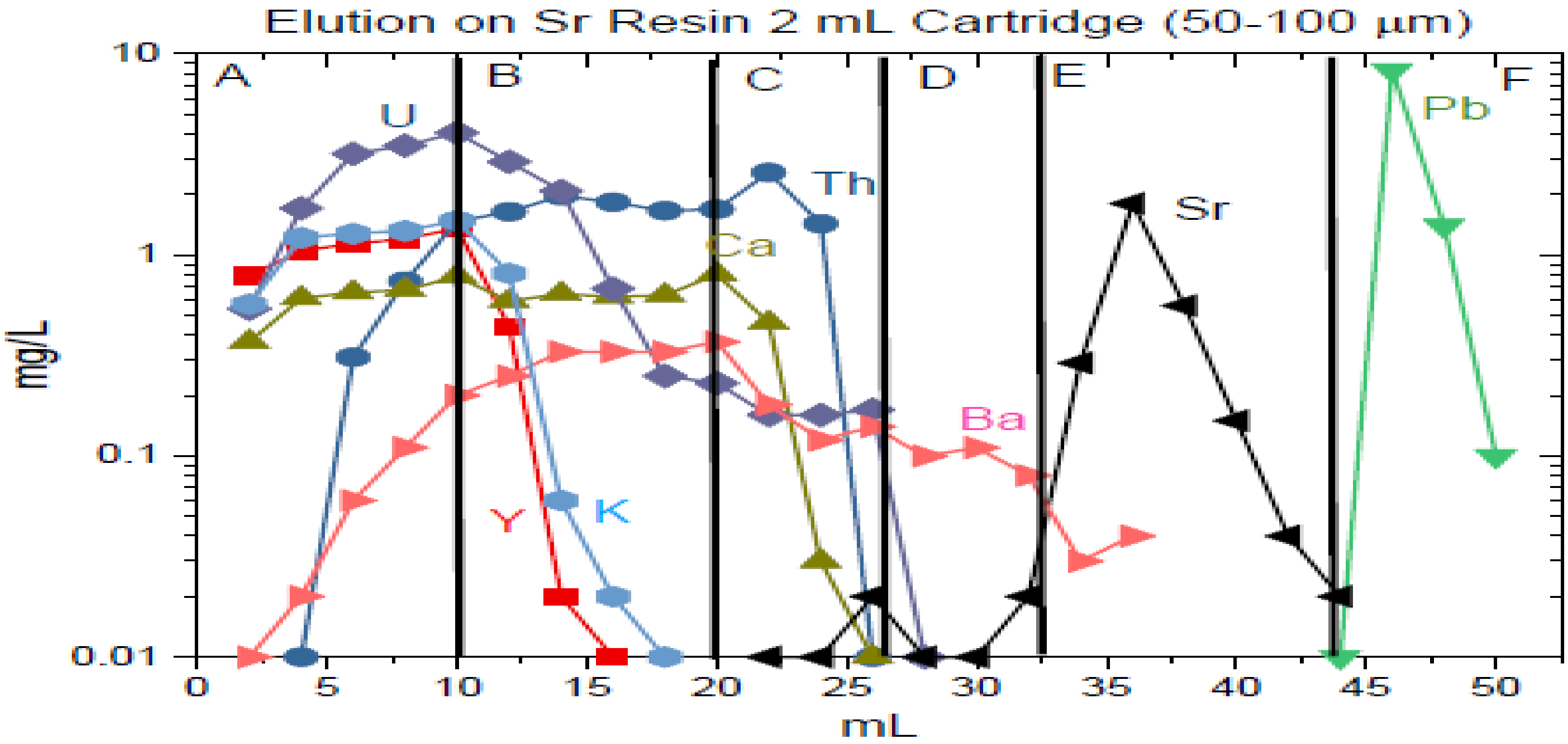




Ra Concentration from 2M HNO_3



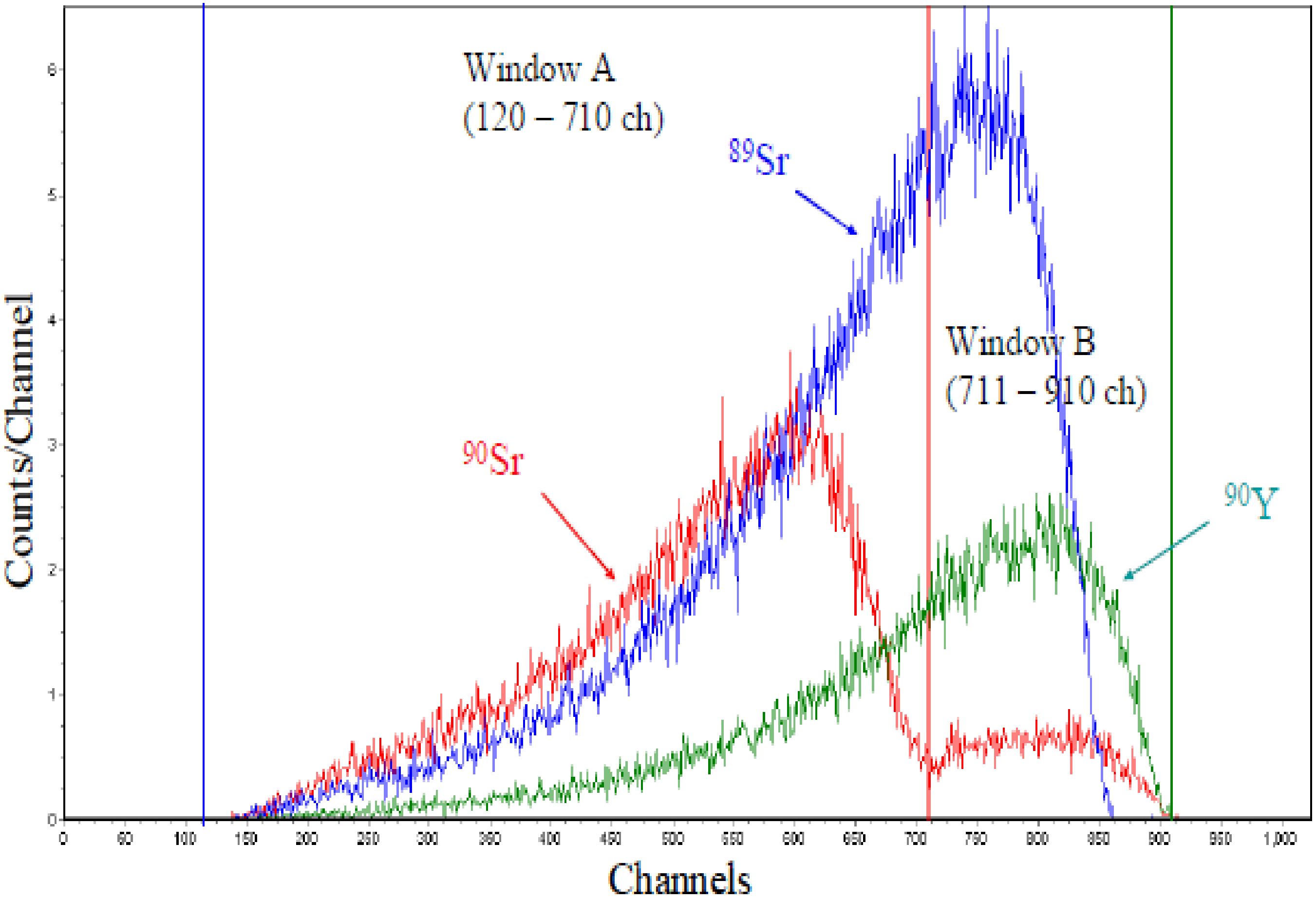
Sr-90/Y-90 Separation (Sr Resin)

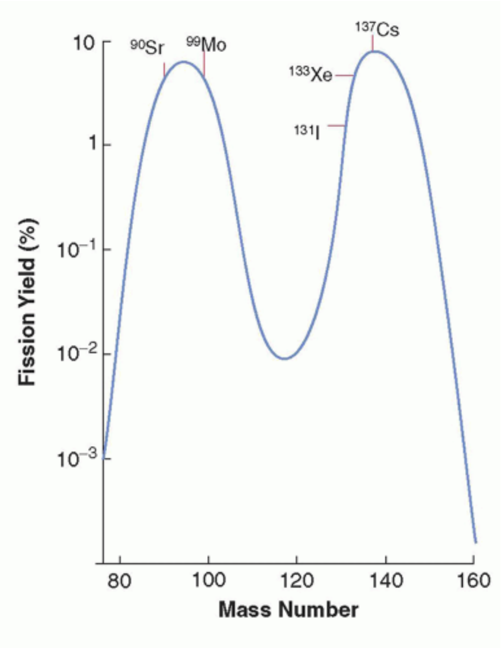


A: Load 8M HNO_3 B: 8M HNO_3 C: 3M HNO_3-0.05M Oxalic acid

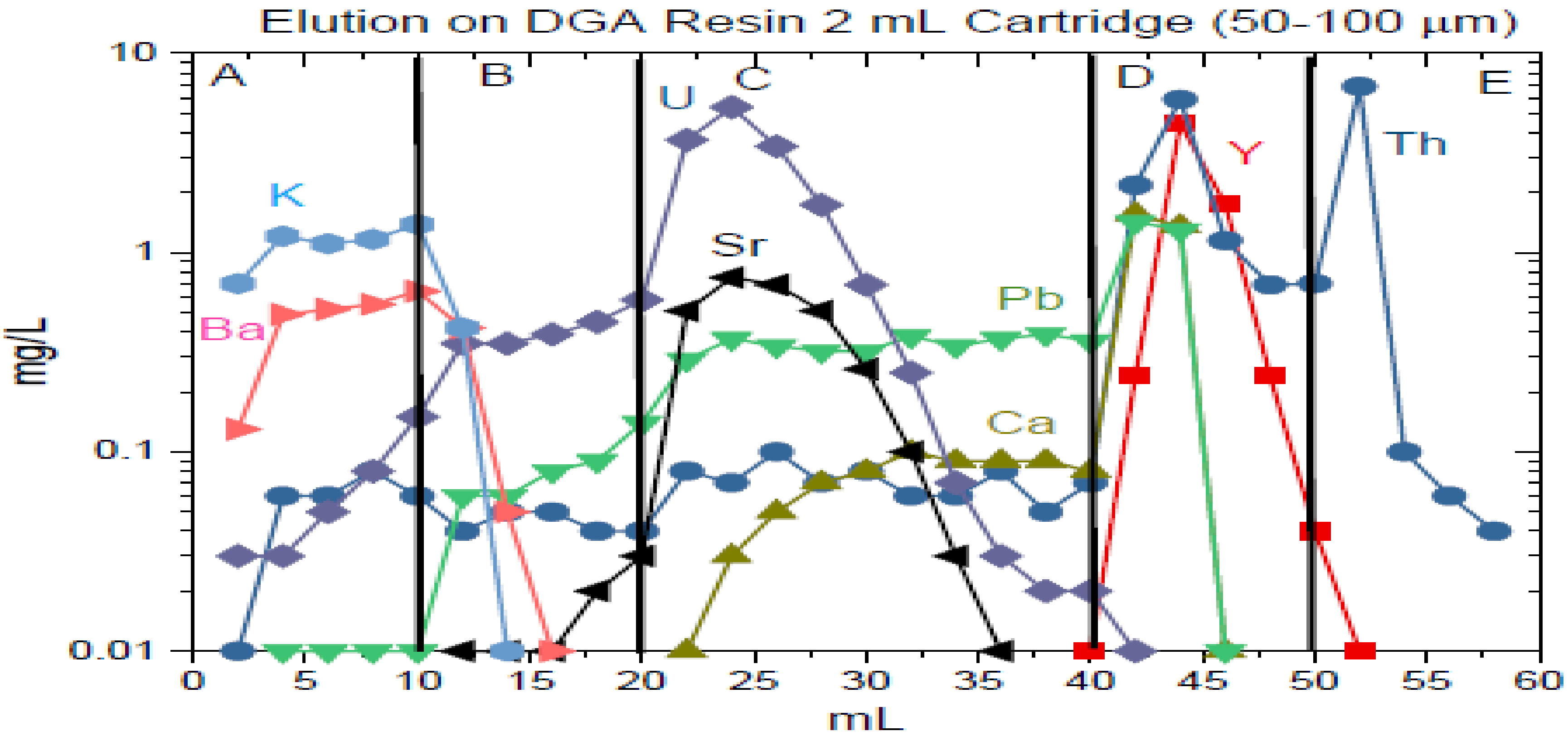
D: 8M HNO_3 E: 0.05M HNO_3 F: 0.10M Ammonium Citrate

Sr-90/Y-90 Separation for analysis





Sr-90/Y-90 Separation (DGA, Normal Resin)

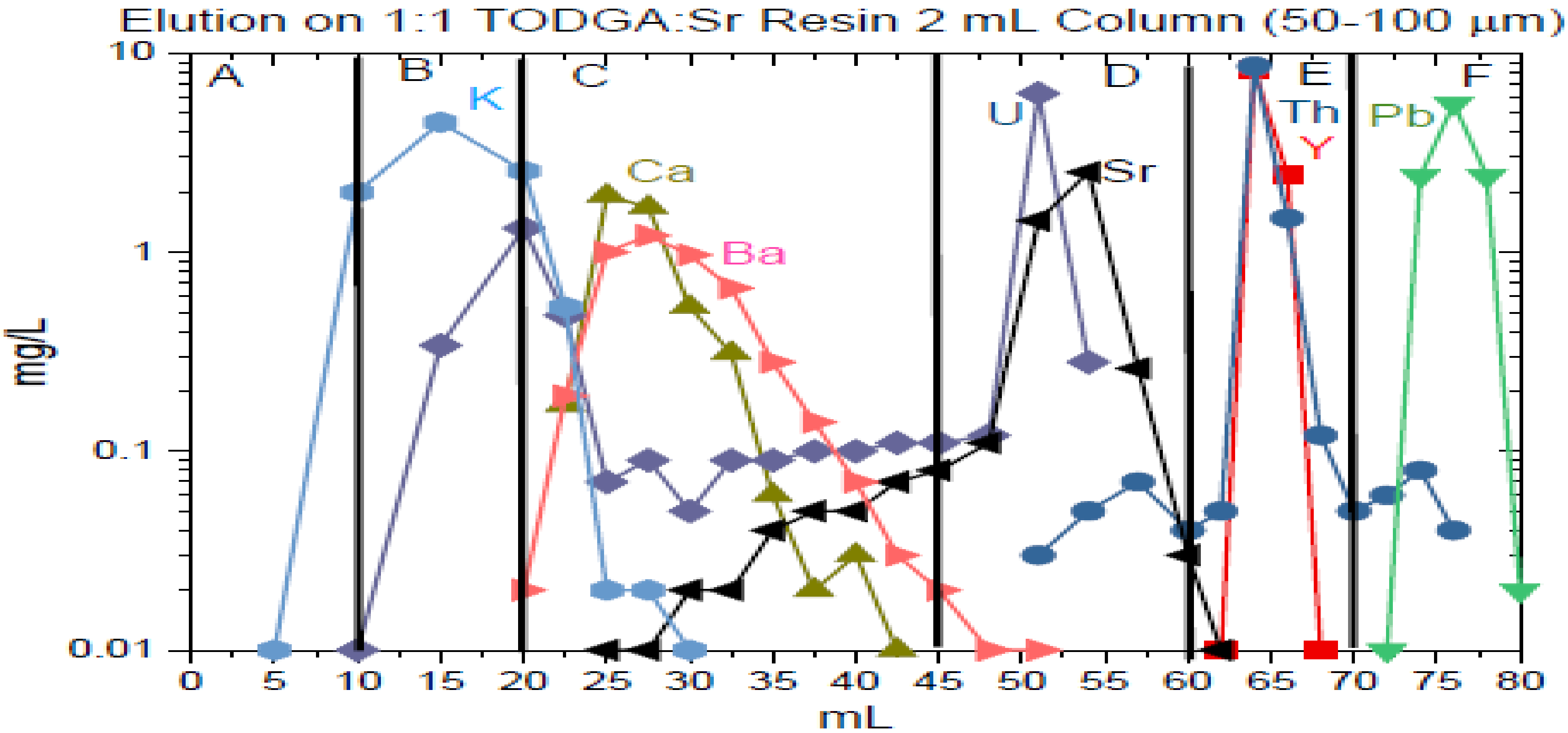


Elution on DGA Resin 2 mL Cartridge (50-100 µm)

A: Load 2M HNO_3 B: 2M HNO_3 C: 0.2M HNO_3

D: 0.1M HCl E: 0.1M Ammonium Bioxalate

Sr-90/Y-90 Separation (DGA-Sr Resin)



A: Load 2M HNO_3 B: 2M HNO_3 C: 8M HNO_3 D: 0.05M HNO_3

E: 0.1M HCl F: 0.1M Ammonium Bioxalate

Summary

- EXC resins are effective due to very high separation factors

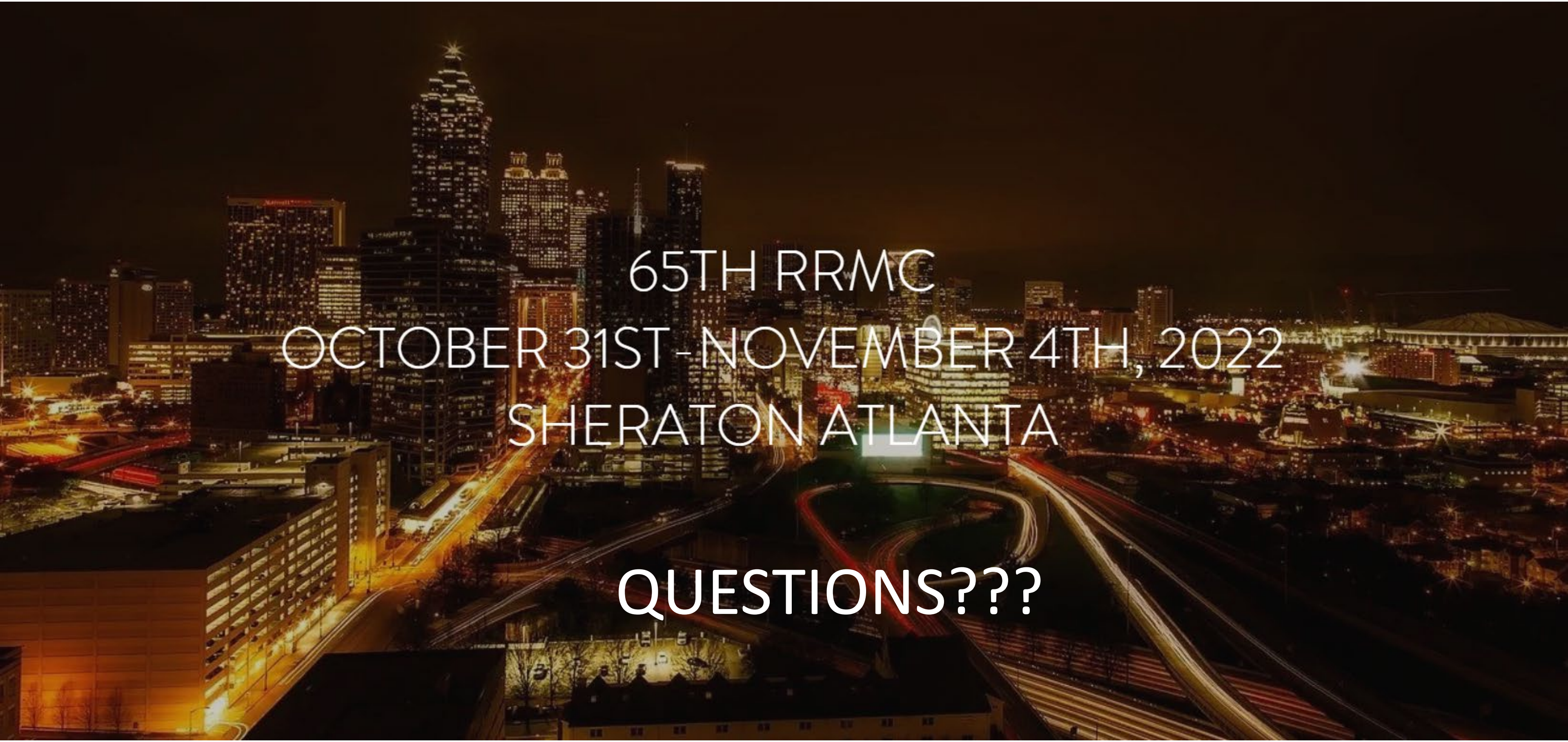
- Extraction of metal ions with crown ether systems depends on many factors
    - Crown ether structure
    - Crown ether concentration
    - Acid Type and concentration
    - Diluent/Phase modifier

- Selectivity can be tuned with different aqueous acids and phase modifiers

Future Work

- Study EXC resins based on DtBCH18C6 in other diluents
  - Ketones, DOODA, Others
  - How does higher water/HNO3 transfer affect the magnitude of extraction and the selectivity for Ca/Sr/Ba/Ra/Pb?
  - Could other diluents lead to more stable Sr Resin formulations?

- Study the properties of DGA-N, DGA-B, and other DGAs
  - REE separations
  - Alkaline earth separations
  - Other applications



65TH RRMC

OCTOBER 31ST - NOVEMBER 4TH, 2022

SHERATON ATLANTA

QUESTIONS???