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DGA, Beryllium and the Ln Series of Resins, an applications update

RRMC

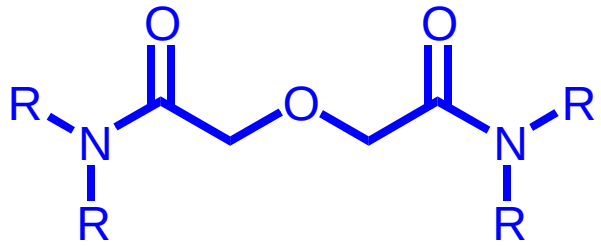
October 25, 2005

Outline

- DGA Resin
  - Formats- Branched and Normal
  - Fe-55/Eu-154
  - Radium/Actinium
  - Actinides in Soil (presented by Sherrod Maxwell)
- Ln Series of Resins
  - Lu-177
- Beryllium Resin
  - Be metal by ICP-AES (Chronic Beryllium Disease)

Diglycolamide (DGA) Resin

Extractant:



N,*N*,*N*',*N*'-tetraoctyldiglycolamide- (DGA Resin, Normal or TN-DGA)

N,*N*,*N*',*N*'-tetrakis-2-ethylhexyldiglycolamide (DGA Resin, Branched or TB-DGA)

Extraction Equilibrium:

$$M^{3+} + 3NO_3^- + 3\overline{E} \rightleftharpoons \overline{M(NO_3)_3 \bullet E_3}$$

$$M = Ln, An$$

DGA Reference

NOVEL EXTRACTION CHROMATOGRAPHIC RESINS BASED ON TETRAALKYLDIGLYCOLAMIDES: CHARACTERIZATION AND POTENTIAL APPLICATIONS

E. P. Horwitz, D. R. McAlister, A. H. Bond
and R. E. Barrans, Jr.

Solvent Extr. Ion Exch. 23, 319-344 (2005)

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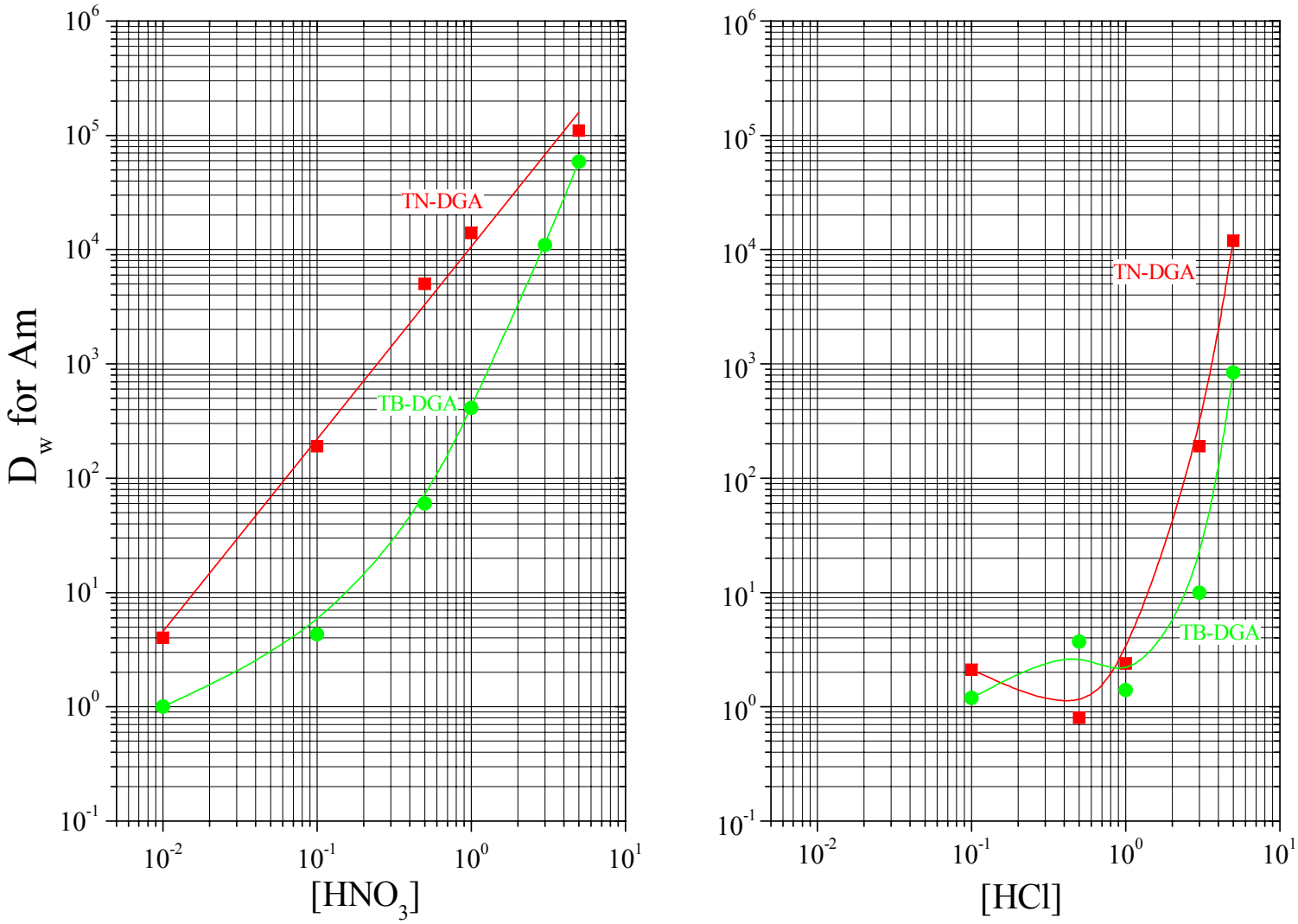
Comparison of TN-DGA and TB-DGA Resins



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Elution of selected cations on TN-DGA resin.

Fraction	Bed Vols.	Percent of Total					
		Ba(II)	Cd(II)	Cu(II)	Fe(III)	Y(III)	Zr(IV)
Load (4 M HNO_3)	20	90	93	95	92	0	0.9
Rinse	2.0	10	7	3.5	7	0	0.2
(0.5 M HNO_3)	2.0	< 0.1	< 0.1	0.4	0.6	0	0
	2.0	< 0.1	0	0.4	< .1	0	0
	2.0	0	0	0.4	0.4	0	0
	2.0	0	0	< 0.1	0	0	0
Strip	2.0	0	0	0	0	71	5
(0.01 M HCl)	2.0	0	0	0	0	27	10
	2.0	0	0	0	0	1	11
	2.0	0	0	0	0	0.7	10
	2.0	0	0	0	0	0.3	10

Column bed volume = 0.5 mL, flow rate = 0.5 mL/minute for load and

0.25 mL/minute for wash and strip

Eu-154 interference with Fe-55

- West Valley Nuclear Services Company
  - Spent nuclear fuel analysis
- Craig Maddigan- Spring 2004 Users' Group
- Fe-55 main photon at 5.9 KeV- Eu-154 has an 8% probable photon at 6.1 KeV
  - 8 M nitric acid load on TRU Resin Fe and Eu retained
  - TRU+DGA, Branched for 2 M nitric acid strip
  - Eu retained, Fe stripped

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Ac-228 on DGA Resin (Maxwell, Spring ’05)

- Ln Resin (2 mL) + DGA-Normal (2mL) stacked
  - Ln resin (U,Th removal) and DGA (Ac-228 retention)
  - loaded 12 mL 4 M HCl 1.5%H2O2 strip solution from MnO2 resin on LN-DGA
  - collect load + 5 mL 4M HCL rinse for Ra-226
  - 10 mL 4M HCL rinse-discard
  - Save LN Resin
  - Strip Ac-228 from DGA with 10 mL 0.5M HCl
  - 100 uL Ce and 1 mL con. HF

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Ra-228 in Groundwater

	% Recovery Ba-133	% Recovery Ra-228
BLK	90%	N/A
LCS (spiked DI H2O)	95%	99.7%
GRNDWATER smp	100%	N/A
GRNDWATER smp	89%	N/A
GRNDWATER smp	97%	N/A
GRNDWATER SPK	95%	101.2%
Avg =	94%	100.4%

1 L samples

Ba-133=1040 pCi; Ra-226 spk= 5 pCi: Ra-228 spk= 20 pCi

waited 36 hr/used Ln-DGA

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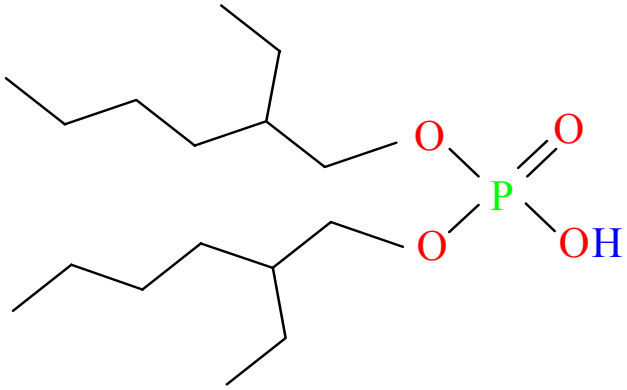
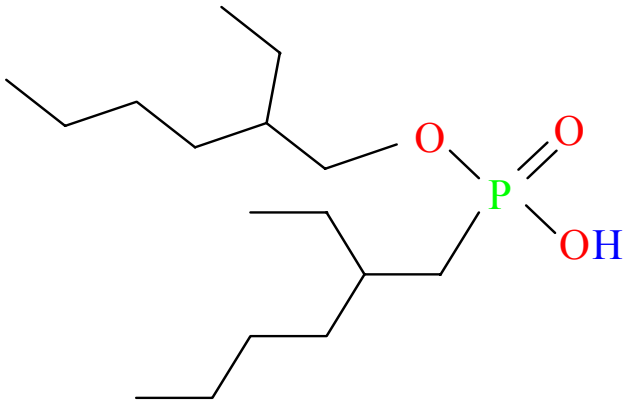
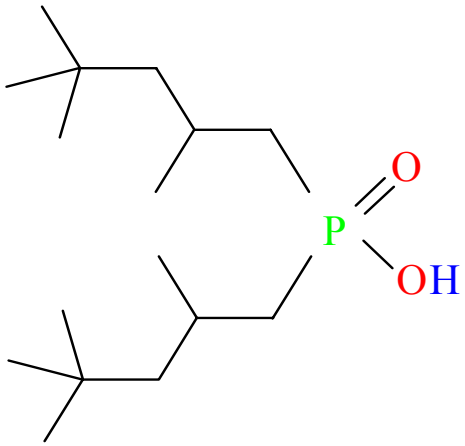
The LN Series of Resins



HDEHP (LN)



HEH[EHP] (LN2)



H[DTMPeP] (LN3)

$$M^{3+} + 3\overline{(HY)_2} \leftrightarrow \overline{M(HY_2)_3} + 3H^+$$

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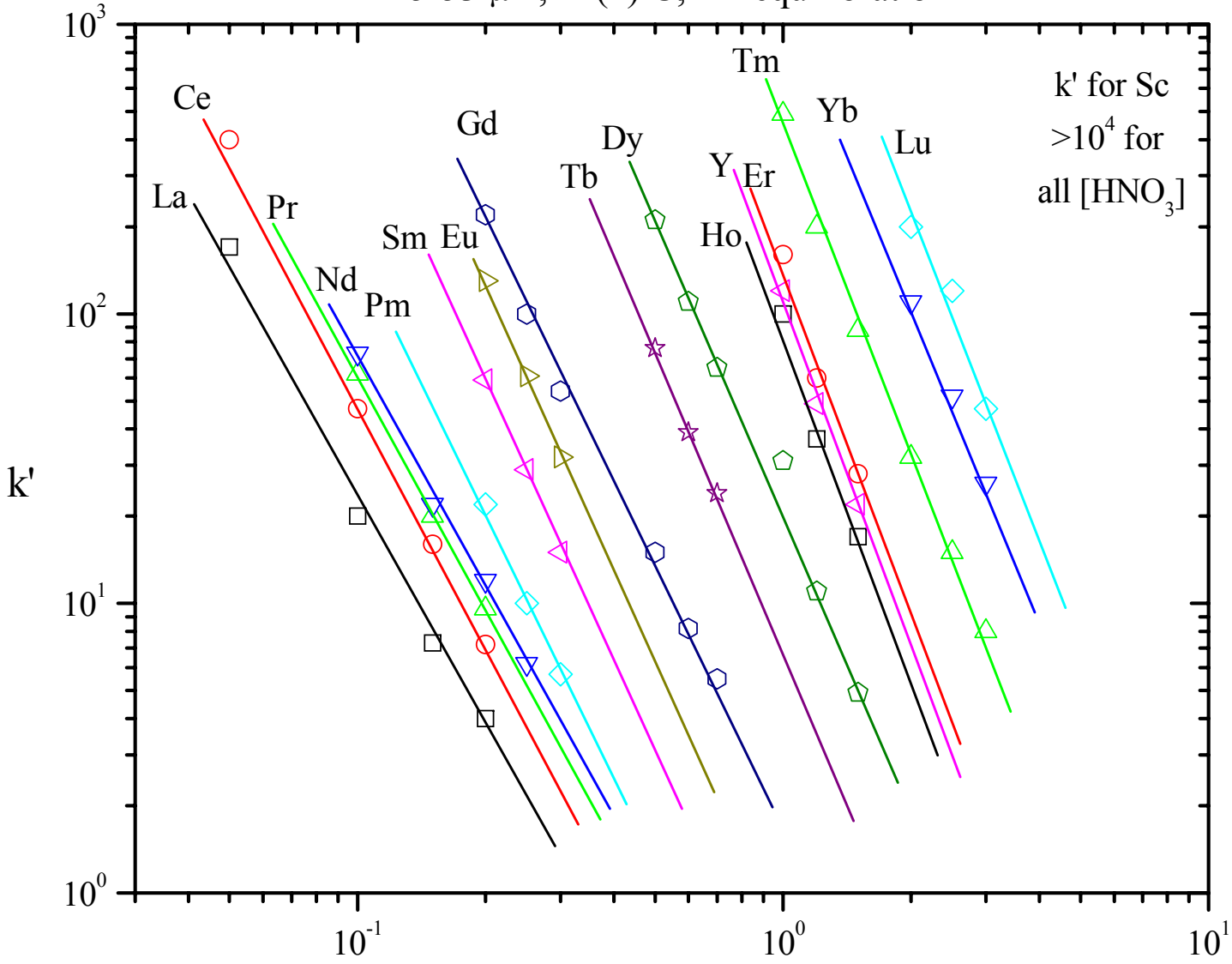
k' for Ln(III), Y(III) and Sc(III) on LN Resin vs. HNO_3

25-53 μm, 22(1)°C, 1 h equilibration



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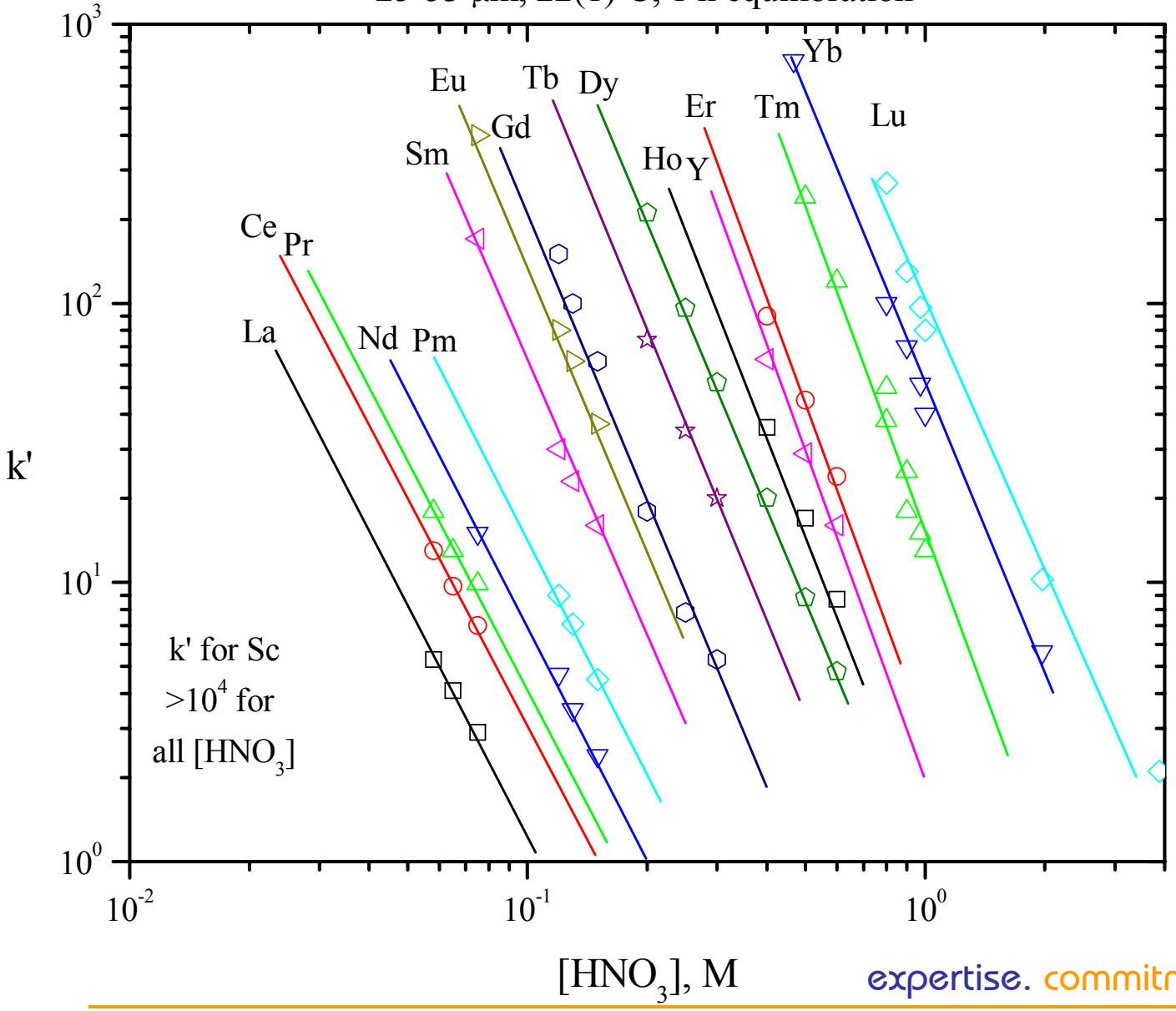
k' for Ln(III), Y(III) and Sc(III) on LN2 Resin vs. HNO_3

25-53 µm, 22(1)°C, 1 h equilibration



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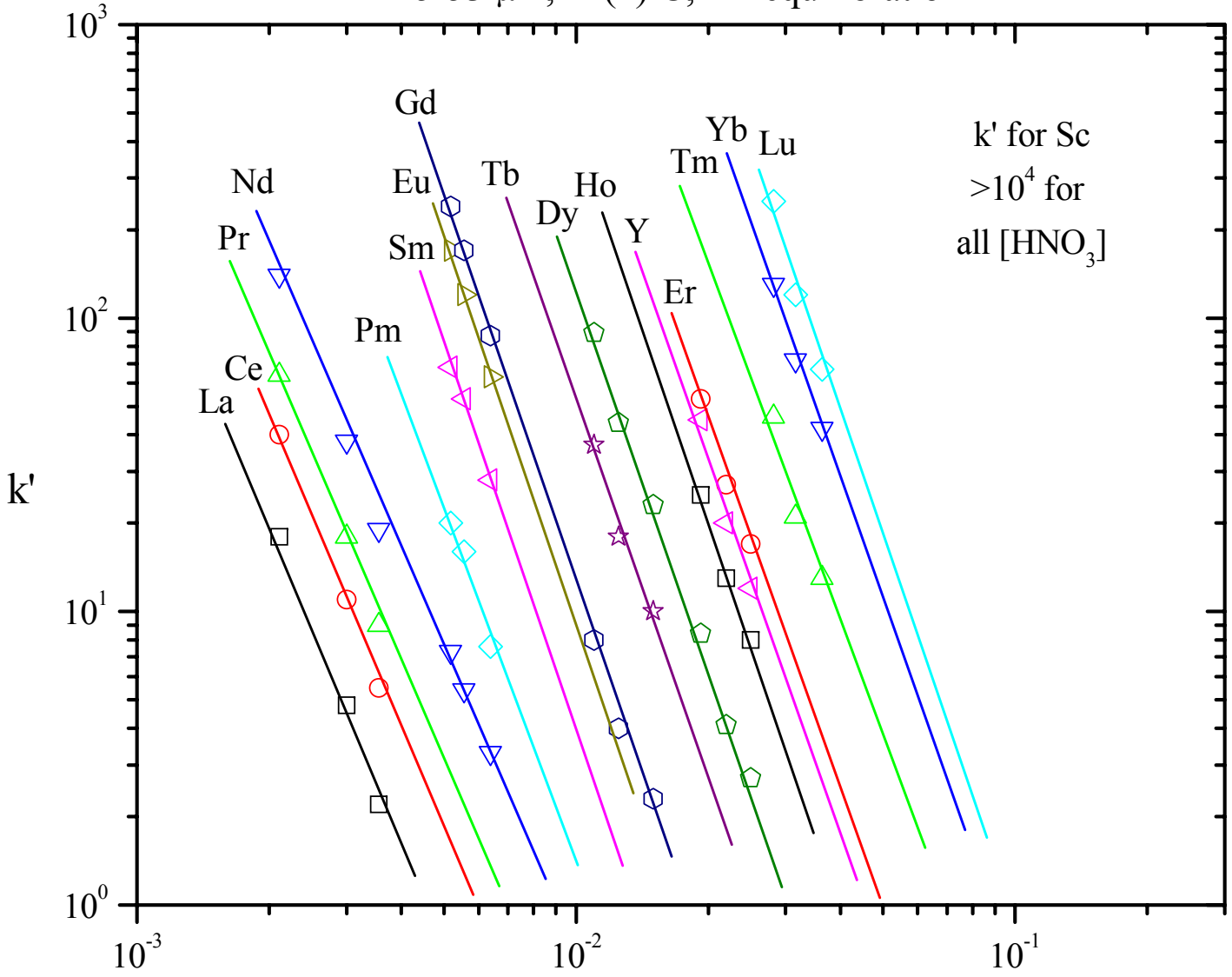
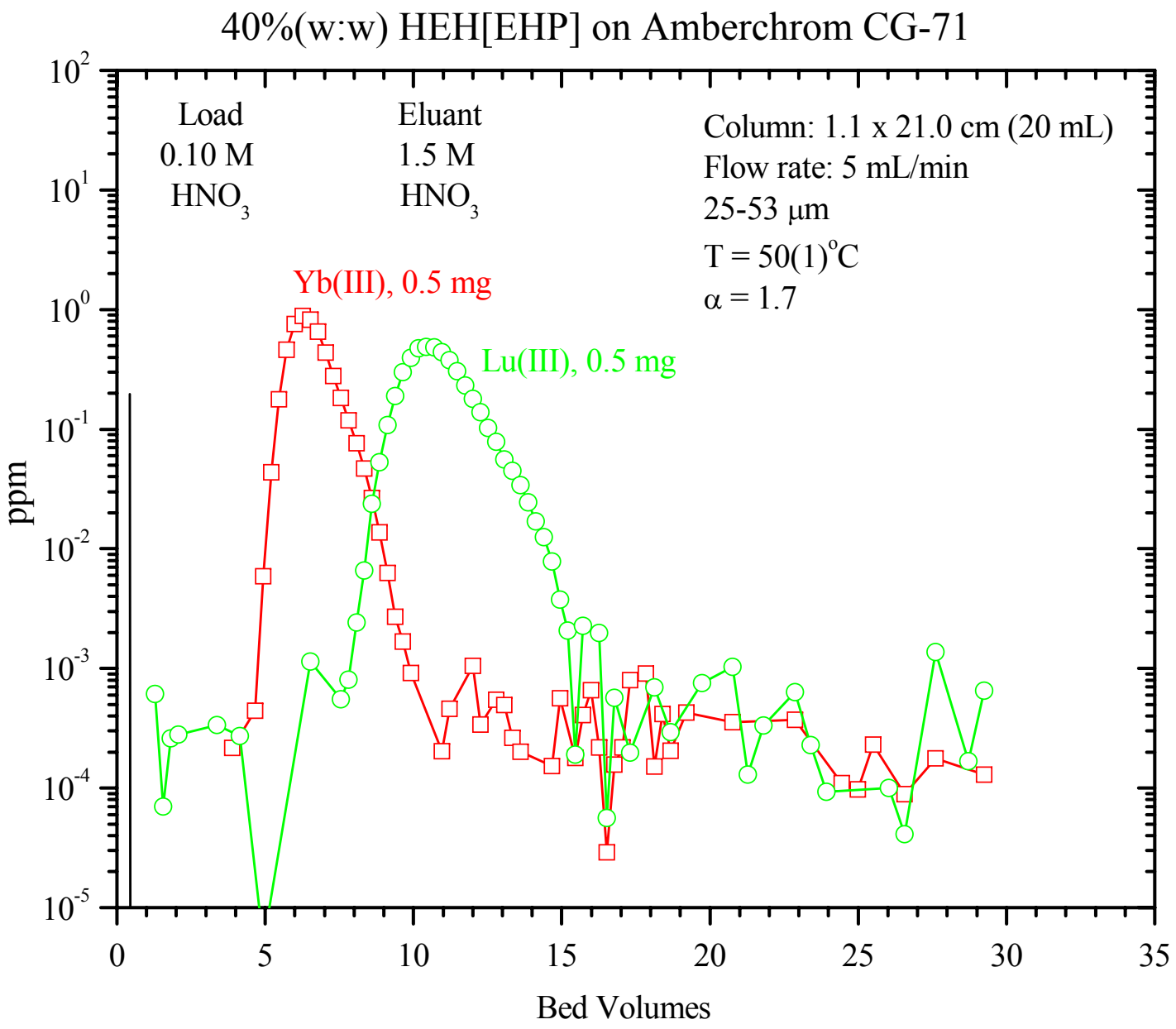
k' for Ln(III), Y(III) and Sc(III) on LN3 Resin vs. HNO_3

25-53 μm, 22(1)°C, 1 h equilibration




40%(w:w) HEH[EHP] on Amberchrom CG-71
Load
0.10 M
HNO3
Eluant
1.5 M
HNO3
Column: 1.1 x 21.0 cm (20 mL)
Flow rate: 5 mL/min
25-53 μm
T = 50(1)°C
α = 1.7
Yb(III), 0.5 mg
Lu(III), 0.5 mg
ppm
Bed Volumes

Lu-177 Reference

A Process For The Separation of ^{177}Lu From Neutron Irradiated ^{177}Yb Targets

E.P. Horwitz, D.R. McAlister, A.H. Bond, R.E. Barrans, Jr., and J. M. Williamson

Appl. Radiat. Isotopes 63, 23-36 (2005)

Be program at Y-12 National Security Complex

- Controlled by US Dept. of Energy's Chronic Beryllium Disease Prevention Program
  - 10 CFR Part 850
  - Promulgated in 1999 to protect DOE workers from CBD
  - Requires Be surface and air monitoring to determine health risk
  - Rule greatly increased the need for Be analysis in the DOE complex
  - Current analytical methods include ICPOES and GFAA

The Problem? (Darrin Mann Users' Group '05)

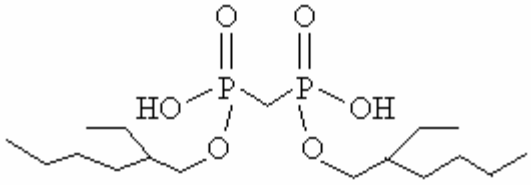
- **The Internal Standard (IS) works great correcting interferences to a point**:
  - High Concentrations of Interfering Elements
    - Some elements are very spectral rich
      - Uranium
        - » Shift depends on enrichment
  - Some elements overlap spectrally
    - Vanadium, Cesium and Zirconium are examples
    - Dilution not useful for these elements
- **Possible Solutions**
  - Dilution
    - May lose Be signal
    - Increase in MDL
  - Run samples by ICPMS
    - Expensive (relative to an OES)
    - Not as rugged as OES (can't handle 500 samples/day)
  - Remove/Concentrate Be

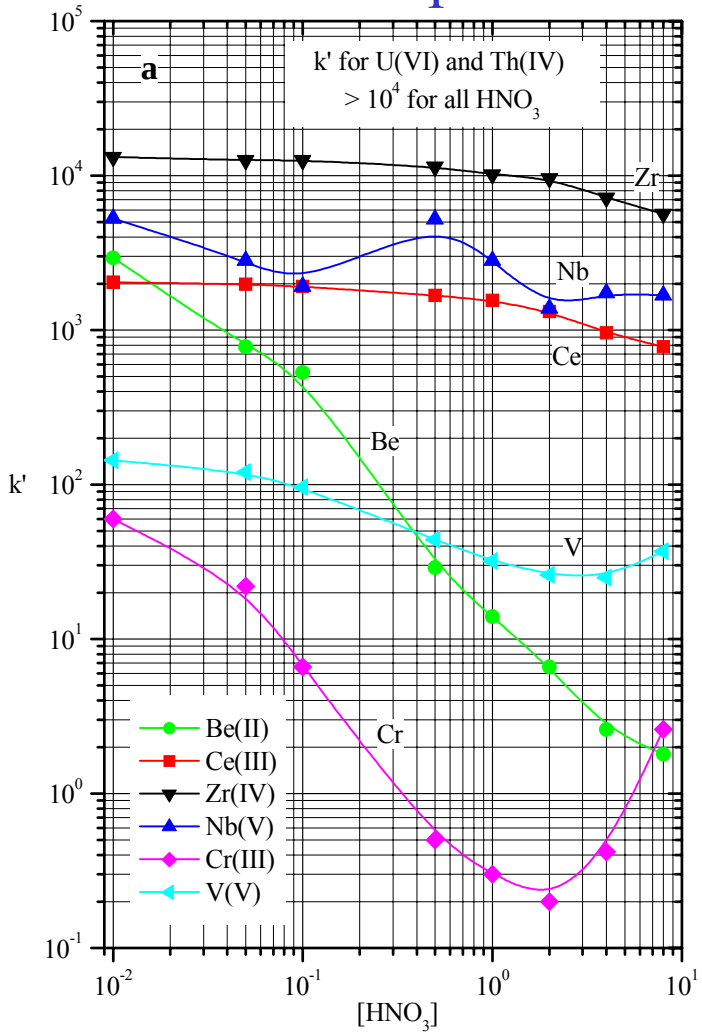
Uptake of Selected Elements on Beryllium Resin

(also referred to as Dipex ® Resin)

Several EXC materials evaluated

Dipex Extractant offered the most promising beryllium retention characteristics





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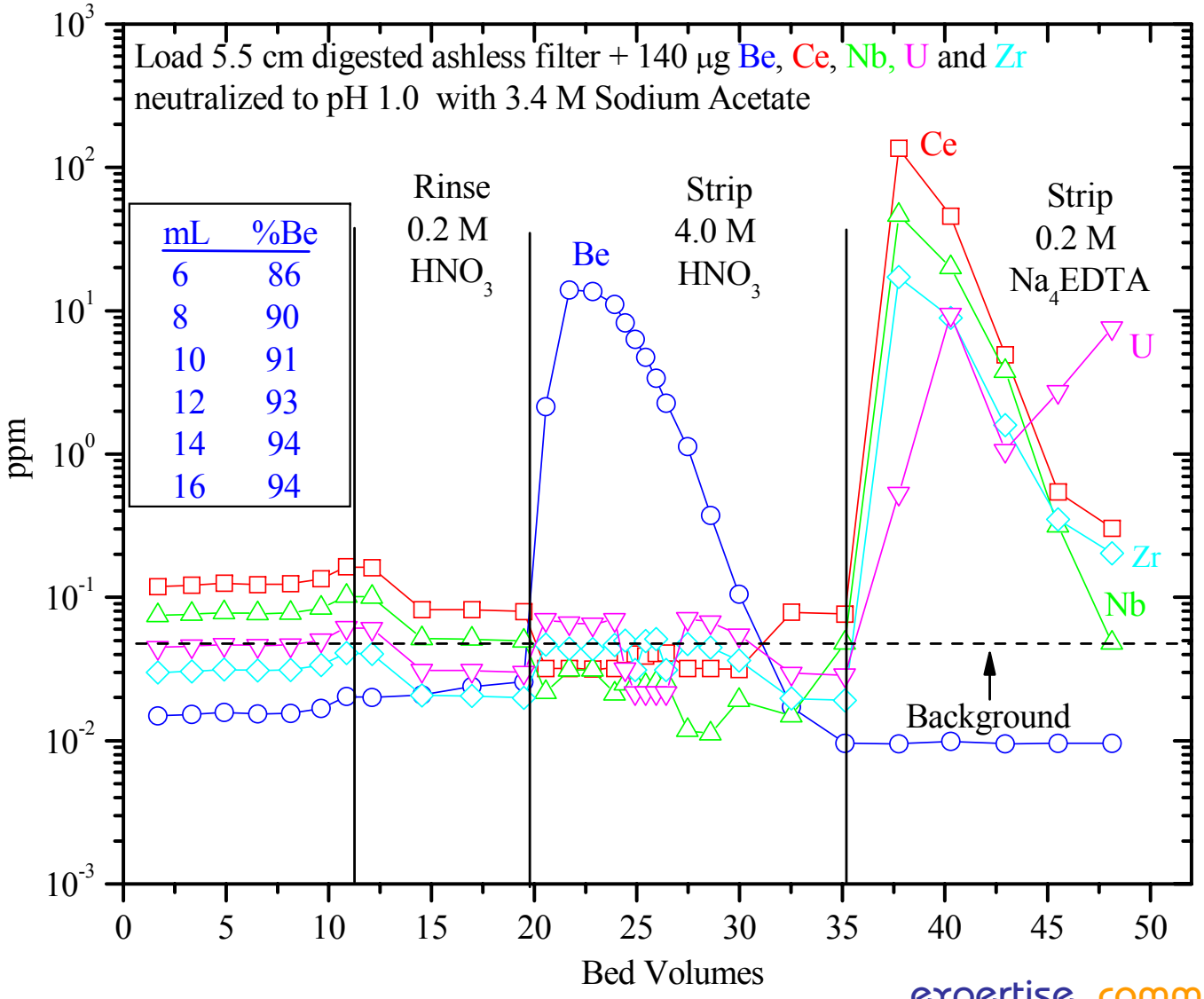
Elution of Be and Selected Elements on Dipex Resin



Y-12 Method using Eichrom Be Resin

- Elegantly simple
- Usually use 5 ml of sample left over from ICPOES analysis
- Adjust sample pH to between 1-2 with 4 M Sodium Acetate
- 2% Crystal Violet used as indicator (3-4 drops)
- Load sample onto Be cartridge (usually 10 mL) and pass through at 2 ml/min
- Rinse cartridge with 10 ml of 0.2 M HNO_3 at 2 ml/min
- Elute Be with 10 ml of 4M HNO_3 at < 1 ml/min
- Sample can be re-run within a few hours.

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Separation of Be from Large Amounts of Interferences

Capacity of Dipex® Resin for Selected Metal Ions

Metal Ion	Dipex® capacity mg/2 mL bed	mg to reduce Be yeild to 90%[c]
Cr(VI)	N/A	> 100
Mo(VI)	N/A	25
U(VI)	102.6[a]	25
Ti(IV)	12.5[b]	7.5
Th(IV)	60.6[a]	10
Fe(III)	22.6[a]	10
Pb(II)	53.8[b]	50
Ca(II)	10.4[a]	>100
Be(II)	0.9[b]	0.5

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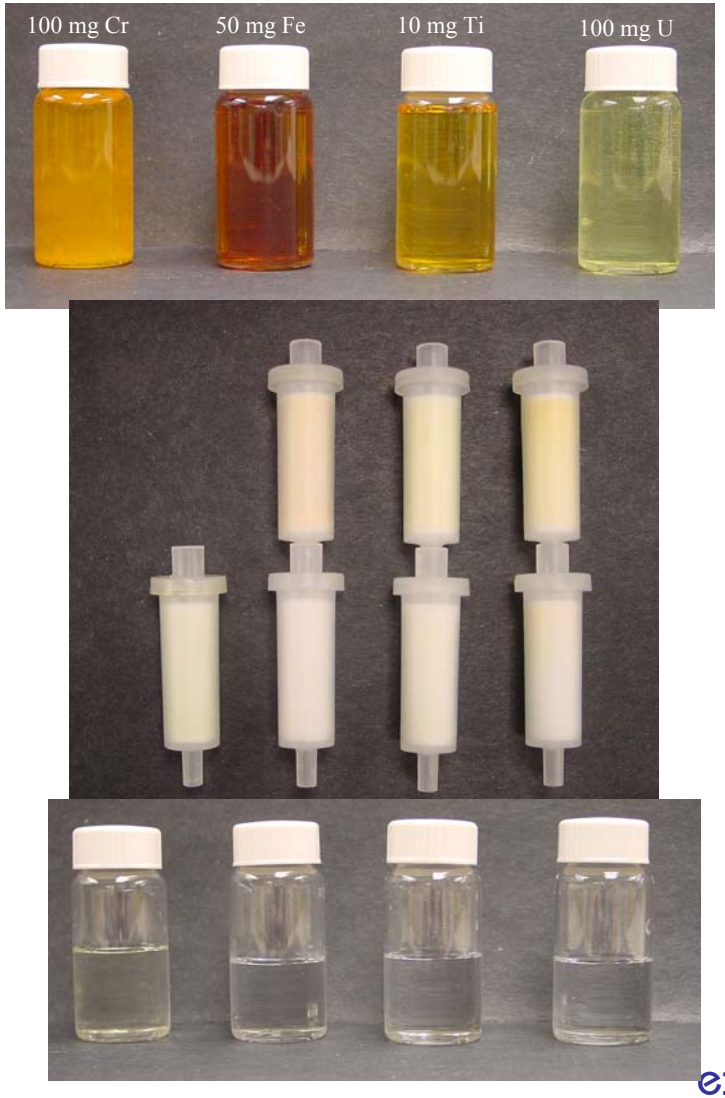
Separation of Be from Large Amounts of Interferences



More Difficult Matrices

- 100 mg Fe
- + 25 mg Cr
- + 20 mg Ni
- + 25 mg Mo
- + 25 mg V
- + 15 mg Ti
- + 7.5 mg Ce

- Requires multiple cartridges
- Oxalic acid useful (0.1 M)
- 85% Ave. Be recovery
  - 12 mL anion column +
  - 2 mL LN cartridge +
  - 2 mL Beryllium cartridge

Beryllium Reference

Separation of Beryllium From Selected Elements Using Dipex ® Extraction Chromatographic Resin

E. P. Horwitz and D. R. McAlister

Solvent Ext. Ion Exchange. 23, 611-629 (2005)

A second paper is in press in Talanta

Conclusion

- More and more metal separations can be performed more efficiently using different EXC Resin
- Phil Horwitz and PGRF are still firing on all cylinders
- Share with us your needs and together we will share success