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Extraction Chromatography; A Presentation of New Resin Characterization Data and Applications

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Outline

- Sample Preparation Objectives
- Introduction to Extraction Chromatography
- Three (3) Case Studies
  - Separation of Lead from Iron and Steel (AAS)
  - Beryllium (ICP-AES)
  - Hafnium/Lutetium (MC-ICP-MS)

Sample Preparation Objectives

- Dilute, Shoot and ask questions later?
  - Sample pre-concentration
  - Removal of spectral or isobaric interferences
    - Isotopic and polyatomic
  - Meet required detection limits and data quality objectives
  - Reduce contamination of spectroscopy equipment
  - Reduce maintenance of spectroscopy equipment

US EPA Method 7000A
ATOMIC ABSORPTION METHODS

3.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering…

Preferably, samples containing high solids should be extracted.

Actinides by ICP-MS: The issues

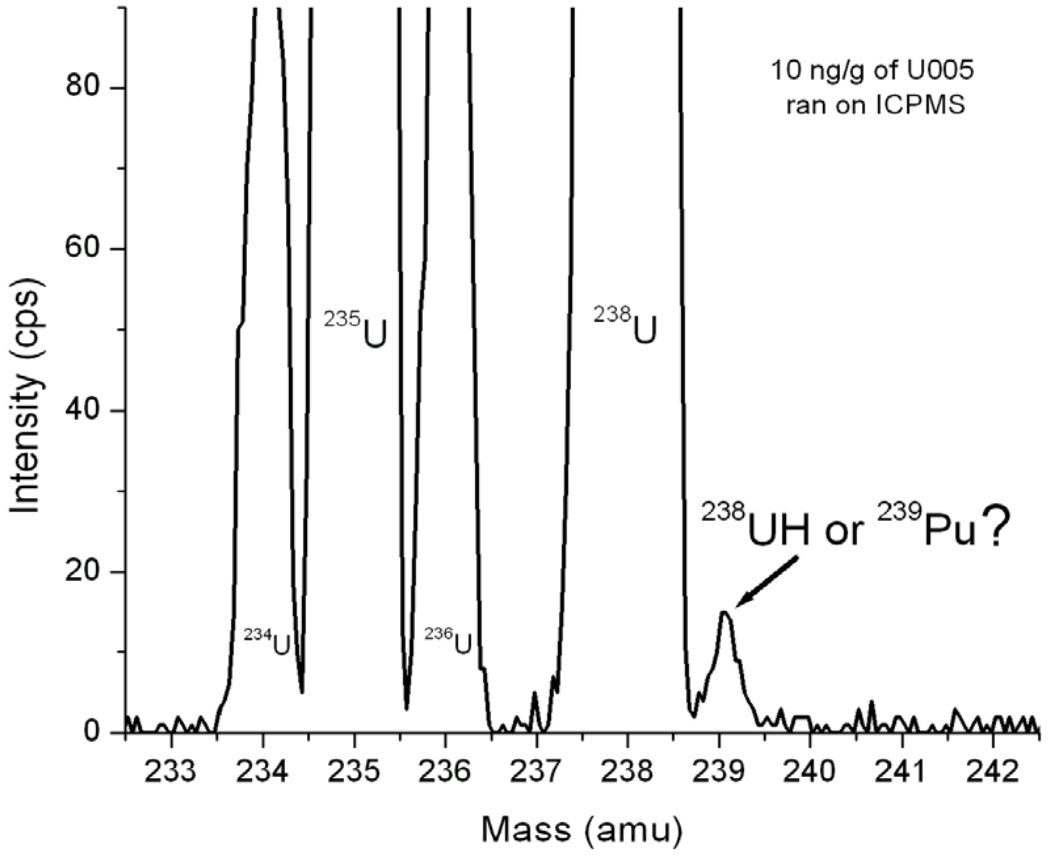
Polyatomic ions

^{230}ThH and ^{231}Pa
^{236}UH and ^{237}Np
^{237}NpH and ^{238}U
^{238}UH and ^{239}Pu
^{240}PuH and ^{241}Am
^{242}PuH and ^{243}Am

Isobars

^{236}U and ^{236}Np
^{238}U and ^{238}Pu
^{241}Pu and ^{241}Am

^{242}Pu and ^{242}Am



THINK IT OVER….

expertise. commitment. results.

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Extraction Chromatography

Solvent Extraction

Column Chromatography

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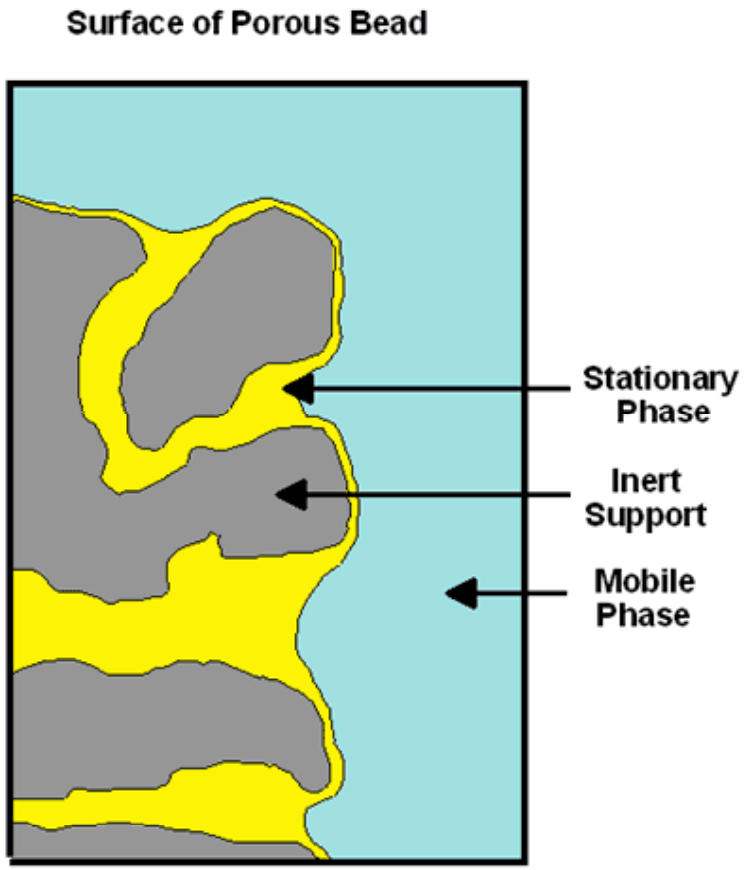
Extraction Chromatographic Resin



Inert support =

Macroporous Acrylic Resin

Example Stationary Phases = Crown Ether, methanediphosponic acid, phosphinic acid, diglycolomide

Make the call…

expertise. commitment. results.

On-line Preconcentration and Determination of Lead in Iron and Steel by Flow Injection-Flame Atomic Absorption

- Tarsuya Seki*, Hiroyuki Takigawa**, Yoshihiro Hirano**, Yoichi Ishibashi*** and Koichi Oguma**
- *Nisan Chemical Industries
- **Chiba University
- ***Kohkankeisoku Corp.

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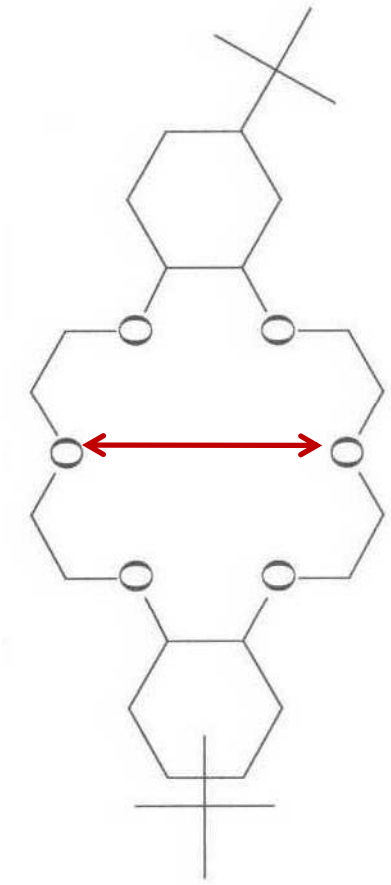
Pb Resin

4, 4', 5' di-t-butylcyclohexano 18-



Elution Behavior of Various Elements on the Lead-Selective Resin[a]

	Percent of Element Found in FCV Number						
	0.1 M HNO_3						0.1 M AOX[b]
Element	1-10	11-20	21-30	31-40	41-50	51-60	61-70
Li	100						
Na	96	<1	<1	1	<1	<1	<1
K	100						
Rb	100						
Cs	100	-	-	-	-	-	-
Mg	100	-	-	-	-	-	-
Ca	100	-	-	-	-	-	-
Sr	100	-	-	-	-	-	-
Ba	100	-	-	-	-	-	-
Al	100	-	-	-	-	-	-
Cr	100	-	-	-	-	-	-
Mn	100	-	-	-	-	-	-
Fe	100	-	-	-	-	-	-
Co	100	-	-	-	-	-	-
Ni	100	-	-	-	-	-	-
Cu	100	-	-	-	-	-	-
Zn	100	-	-	-	-	-	-
Y	100	-	-	-	-	-	-
Zr	100	-	-	-	-	-	-
Mo	100	-	-	-	-	-	-
Ru	100	-	-	-	-	-	-
Rh	100	-	-	-	-	-	-
Pd	58	-	24	18	-	-	-
Ag	100	-	-	-	-	-	-
Cd	100	-	-	-	-	-	-
La-Eu	100	-	-	-	-	-	-

[a] Column parameters: Particle size = 50-100 µm; bed volume = 1.0 mL.; height = 2.5 cm; 1 FCV = 0.66 mL.; Load solution volume = 0.60 mL.; Load solution contained 0.1 M oxalic acid to solubilize zirconium.

[b] AOX = ammonium oxalate

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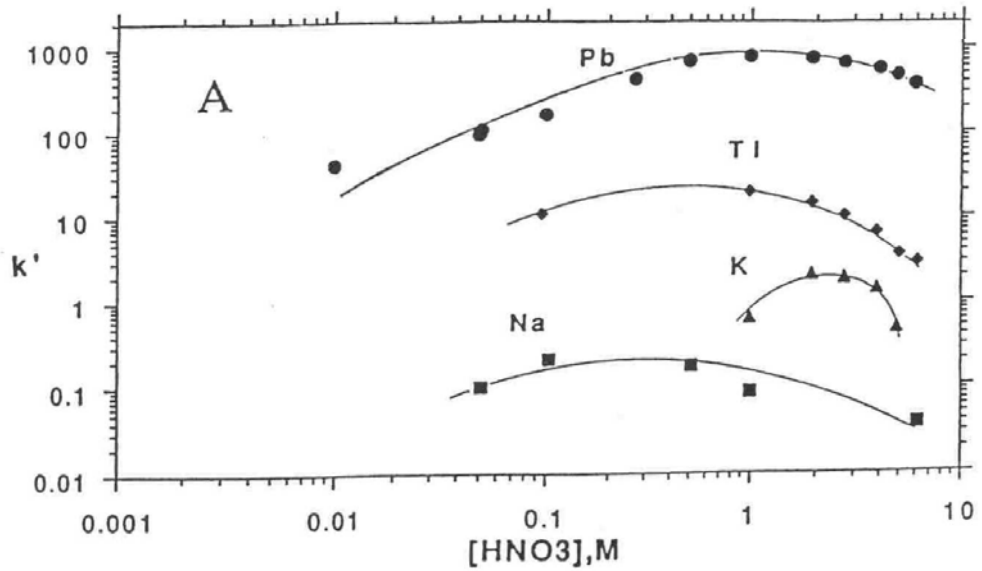
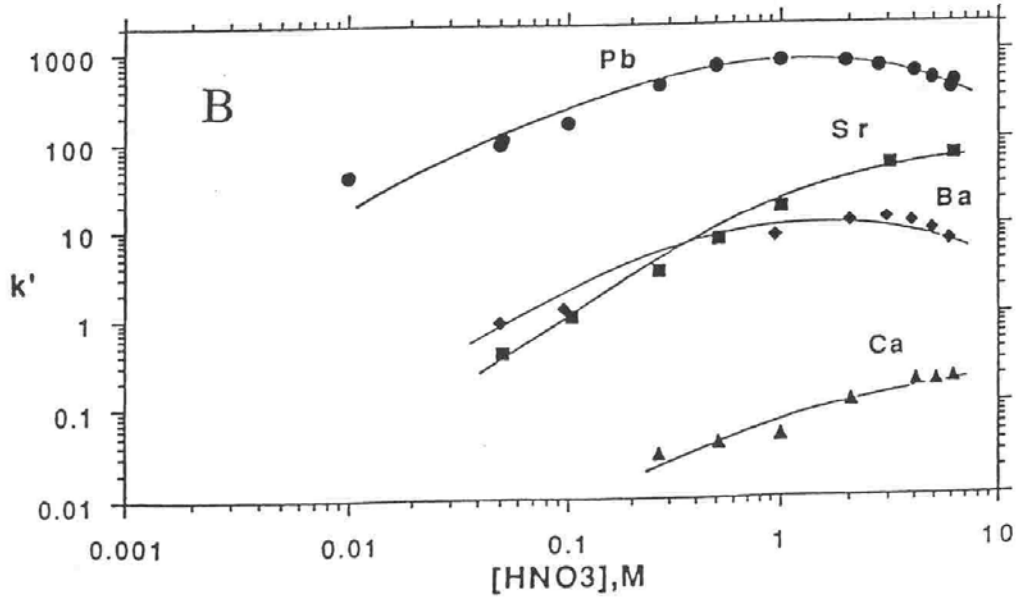

A
Pb
Tl
K
Na
k'
1000
100
10
1
0.1
0.01
0.001
0.01
0.1
1
10
[HNO3],M


B
Pb
Sr
Ba
Ca
k'
1000
100
10
1
0.1
0.01
0.001
0.01
0.1
1
10
[HNO3],M

Lead impurity in iron and steel

Fe(III) added/mg	*Pb(II) added/µg*	*Pb(II) found/µg*
10, 100, or 1000	0	<0.02
10	1.00	1.01
10	1.00	1.01
100	1.00	1.04
100	1.00	1.01
1000	1.00	1.01
1000	1.00	1.01

1. Acid digestion of iron or steel sample
2. Bring up in 30 ml 1 N Nitric acid
3. Load on 7.5 mm i.d. X 100 mm Pb Resin column (flow injection)
4. 6 mL of 1 N Nitric Rinse at 3 mL/min

Sample size/g	Pb found/µg	Pb content	Ref. Value
Pure iron (certified reference material JSS001-4)			
0.7137	0.142	0.20ppm	
1.039	0.20	0.19	
0.8839	0.174	0.20	
0.7991	0.142	0.18	
0.7006	0.136	0.19	
0.9673	0.182	0.19	
	Mean:	**0.19 ± 0.008**	**0.2 ppm**
Lead-free cutting steel (certified reference material JSS519)			
0.1363	130	0.0954%	
0.1303	125	0.0959	
0.1727	163	0.0944	
	Mean:	**0.0952 ± 0.0008**	**0.097%**

5. Elute the Pb with 12 mL of 0.1 M ammonium oxalate solution at 4 ml/min in reverse flow direction
6. Direct measurement by AAS

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Potential Issues with Current Beryllium Method

Interfering elements in the AES spectrum of Beryllium

Table 1. Potential Spectral Interferences for Be determination by ICP-AES[a]

Analyte	Peak (nm)	Intensity	Analyte	Peak (nm)	Intensity
Cr	312.870	15.0	Nb	313.079	2200.0
U	312.879	6.0	Ti	313.080	6.0
Zr	312.918	400.0	Ce	313.087	65.0
Nb	312.964	22.0	Th	313.107	27.0
U	312.973	15.0	Be[b]	313.107	41000.0
Zr	312.976	550.0	Tm	313.126	2300.0
Th	312.997	10.0	U	313.132	8.0
V	313.027	1020.0	Hf	313.181	20.0
OH	313.028	0.0	U	313.199	15.0
Ce	313.033	50.0	Cr	313.206	1000.0
Be[b]	313.042	64000.0	Zr	313.207	7.0
U	313.056	6.0	Th	313.226	5.0
OH	313.057	0.0	Mo	313.259	1800.0
U	313.073	0.0	Ce	313.259	30.0

[a] As listed in Varian Plasma96 software version 1.12

[b] Commonly used peaks for beryllium determination by ICP-AES

Beryllium lines very intense → method is very sensitive for the determination of beryllium

Interfering lines from other elements could lead to false positives.

Spectral shift dependant on unknown uranium enrichment

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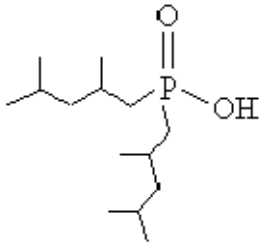
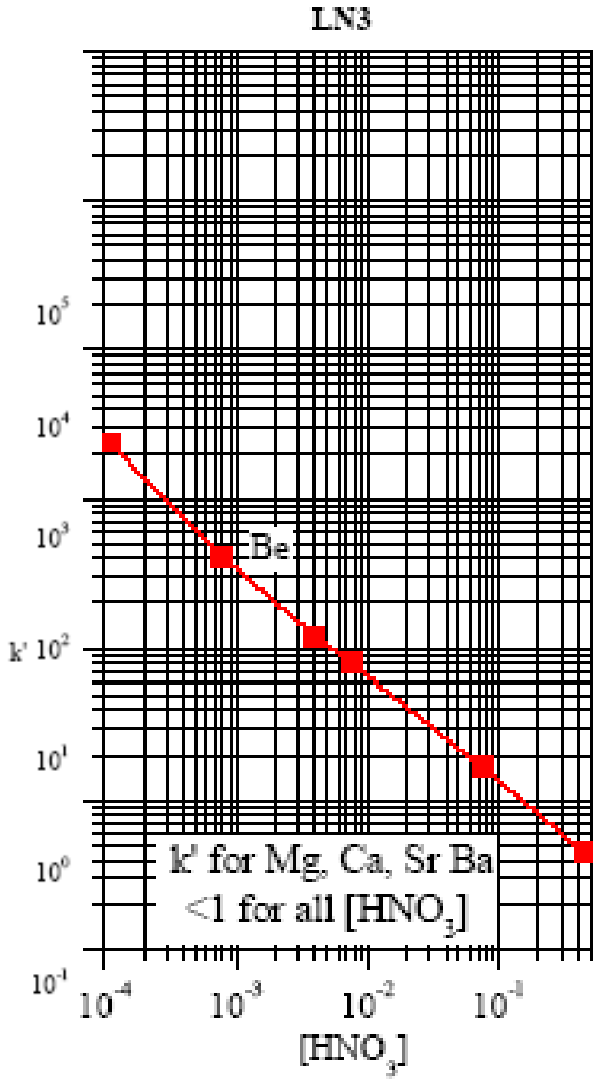
One Step Beryllium Clean Up

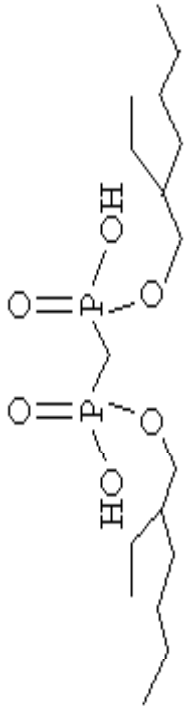
- LN3 Resin (H[TMPP])
  - Retains > 98% U (100 ppm) while passing Be directly from 10% nitric/ 6% sulfuric acid filter digestate
  - One step method/ pass sample through the 2 mL LN3 cartridge and analyze the eluent
  - LN3 retains Mo, Nb and Zr
  - V passes through with the Be

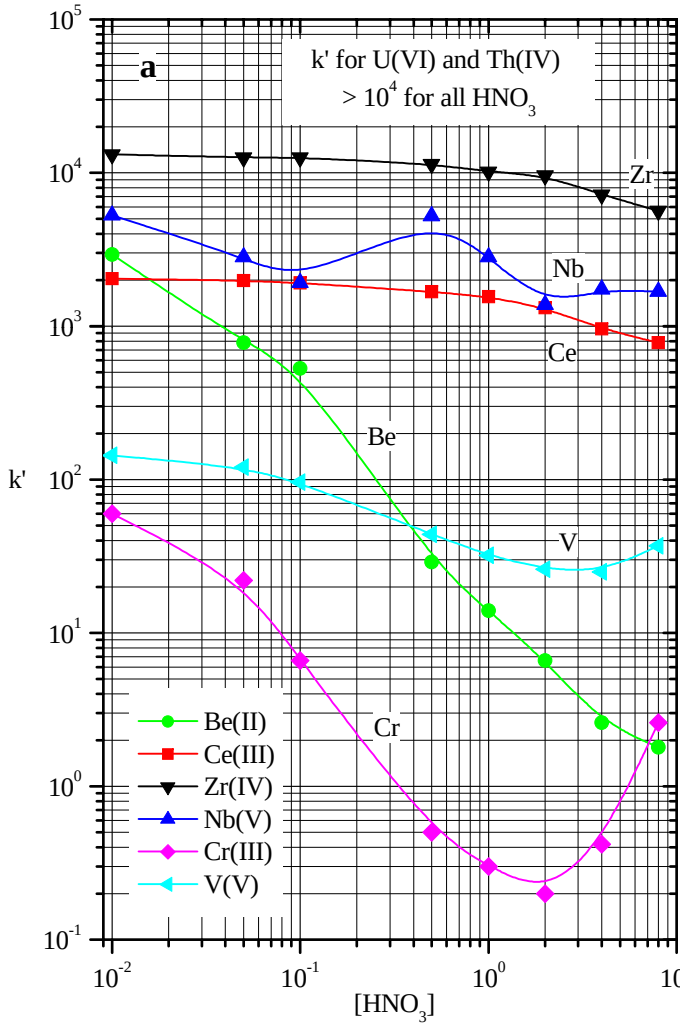


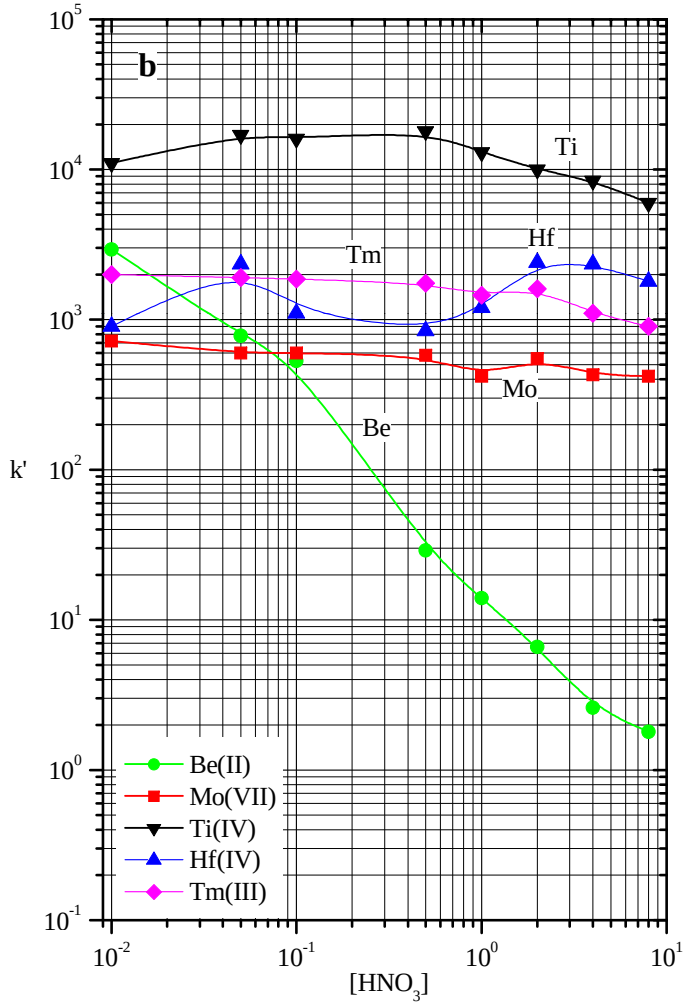


Dipex® Extractant

bis(2-ethylhexyl) methanediphosphonic







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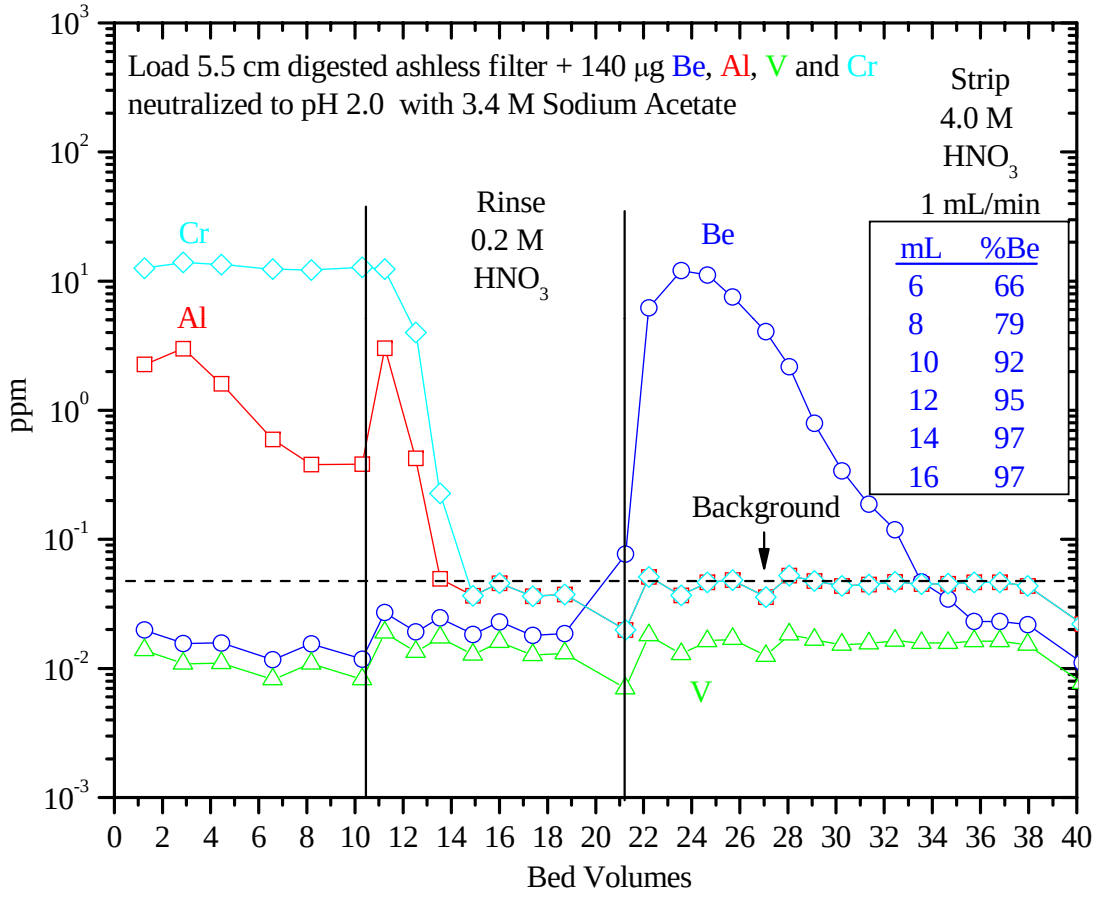
Elution of Be and Selected Elements on Dipex Resin



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Beryllium Separation Method

– Digest sample in any acid
– Adjust pH to 2 w/ sodium acetate
– Add 10 mL 0.3 M oxalic acid
– Load on Beryllium Resin cartridge
– Rinse with 20 mL 0.1 M nitric acid
– Strip with 20 mL 4 M nitric acid strip

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Vacuum System with Beryllium cartridges and 10 ml Reservoirs

eichrom Matrix Challenge- Y-12 Oak Ridge TN

1. Standard 1: 0.001 ppm Be plus 80 ppm V
2. Standard 2: Column Interference Standard containing 0.001ppm Be plus (all in ppm) 400 Cr, 800 Fe, 100 Mo, 100 Nb, 2 Sc, 100 Th, 100 Ti, 100 U, 80 V, 100 Y and 100 Zr.

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Y-12 Results using ICP-OES

	Be (ppm) ICP-OES+ Cartridge	Recovery	Recovery w/o column
Standard 1	0.00099	99.9%	2010%
Standard 2	0.000678	67.8%	4160%

All metals except Cr, V and Y reduced to non-detect. V reduced to 0.08 ppm, Y reduced to 0.24 ppm and Cr reduced to 20.5 ppm.

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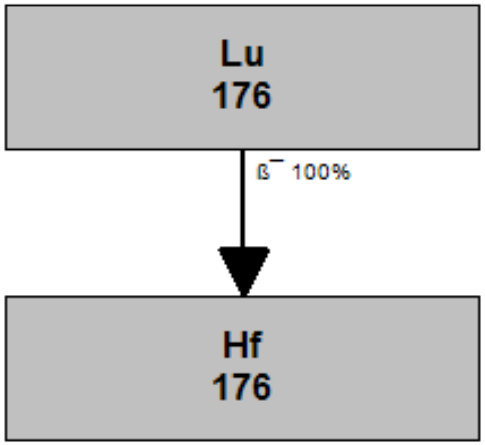
Hf-Lu Separation



Lu-176 half life 37 billion years
Alternative chronometer to the Sm-Nd system.

Advantage of greater variation of parent daughter ratio

Availability of MC-ICP-MS allows better measurement of Hf than with TIMS

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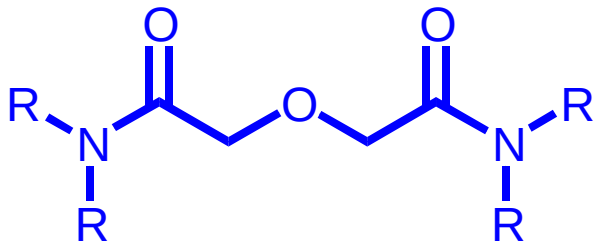
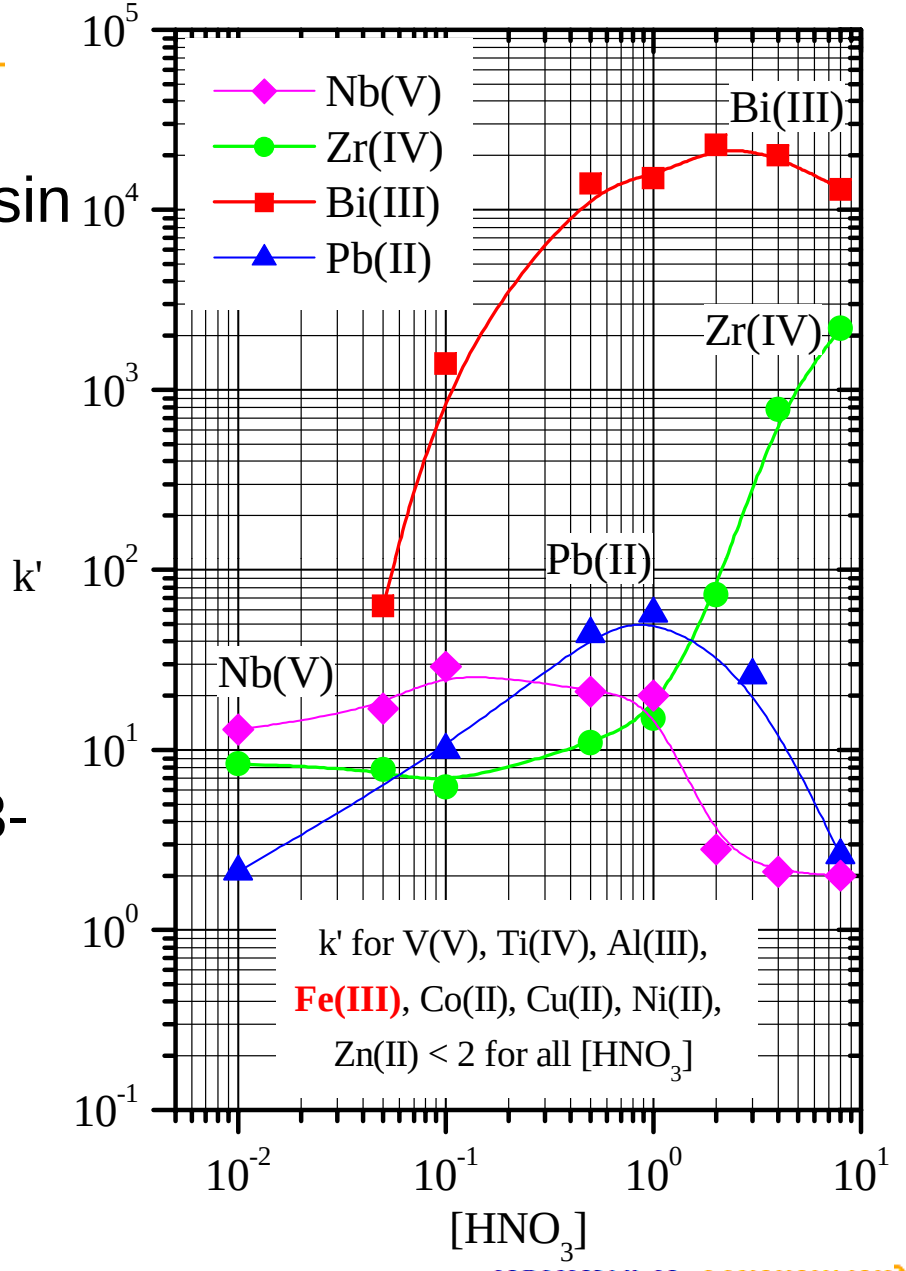
Diglycolamide (DGA) Resin



N,*N*,*N*',*N*'-tetra-*n*-octyl-3-oxopentanediamide (DGA Resin, Normal, TN-DGA, TODGA)



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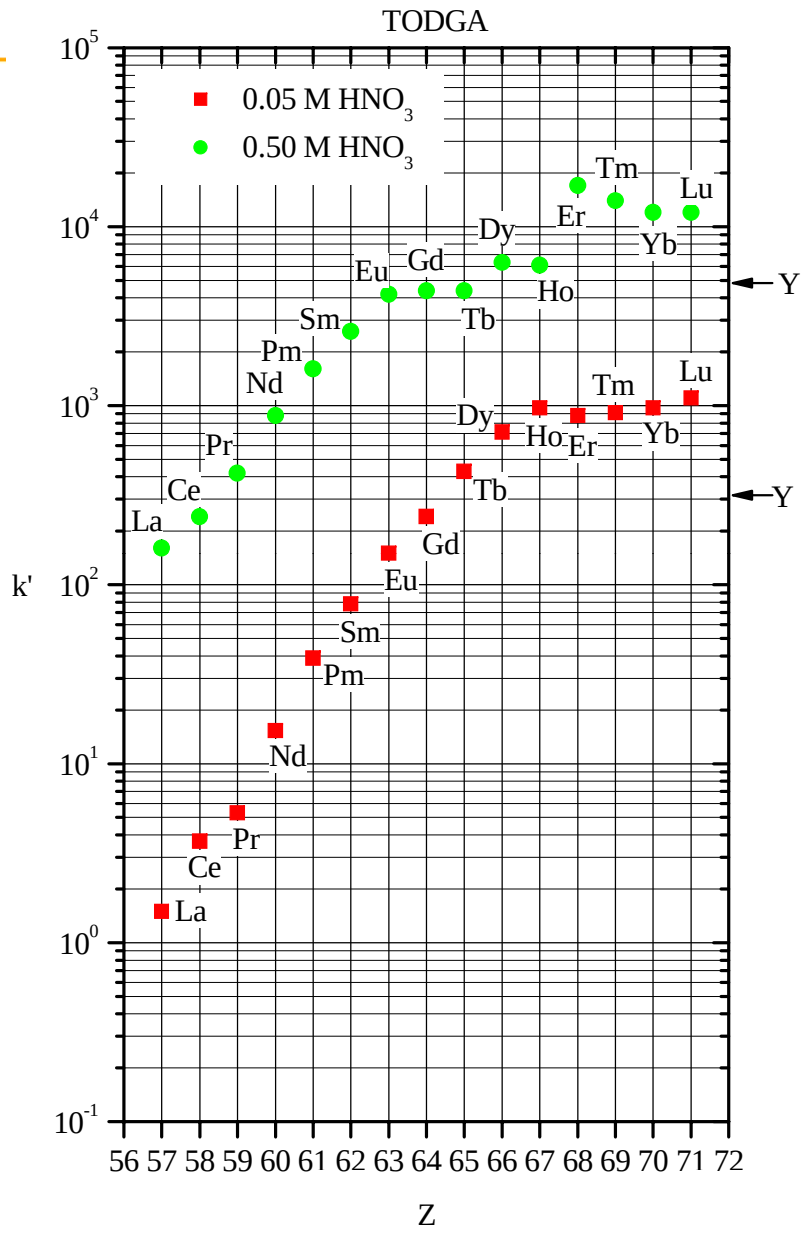
DGA Resin, 50-100µ

Rare Earth Elements including Lutetium



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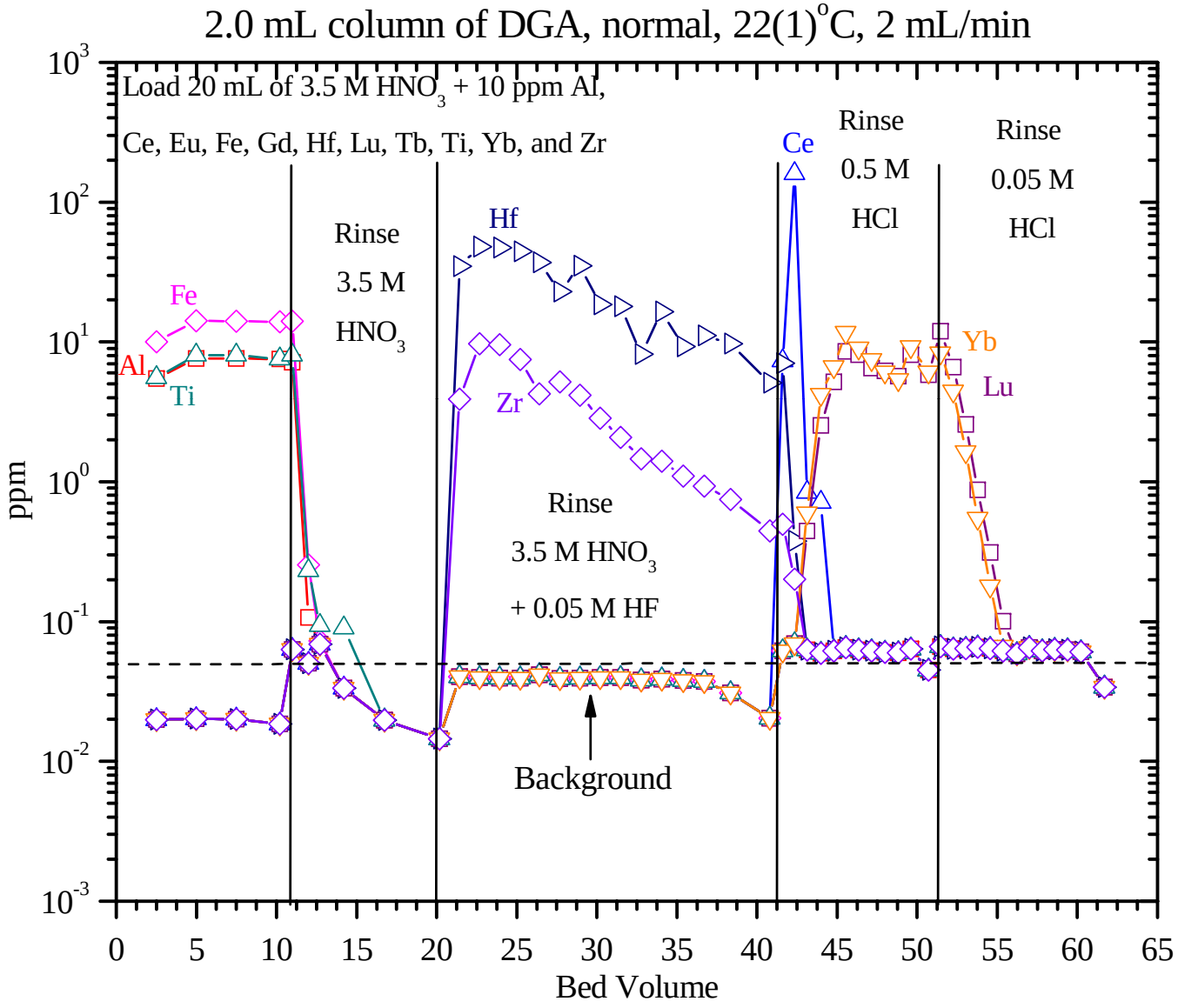
2.0 mL column of DGA, normal, 22(1)°C, 2 mL/min
Load 20 mL of 3.5 M HNO3 + 10 ppm Al,
Ce, Eu, Fe, Gd, Hf, Lu, Tb, Ti, Yb, and Zr
Rinse
3.5 M
HNO3
Rinse
3.5 M HNO3
+ 0.05 M HF
Rinse
0.5 M
HCl
Rinse
0.05 M
HCl
Fe
Al
Ti
Hf
Zr
Ce
Yb
Lu
Background
ppm
Bed Volume

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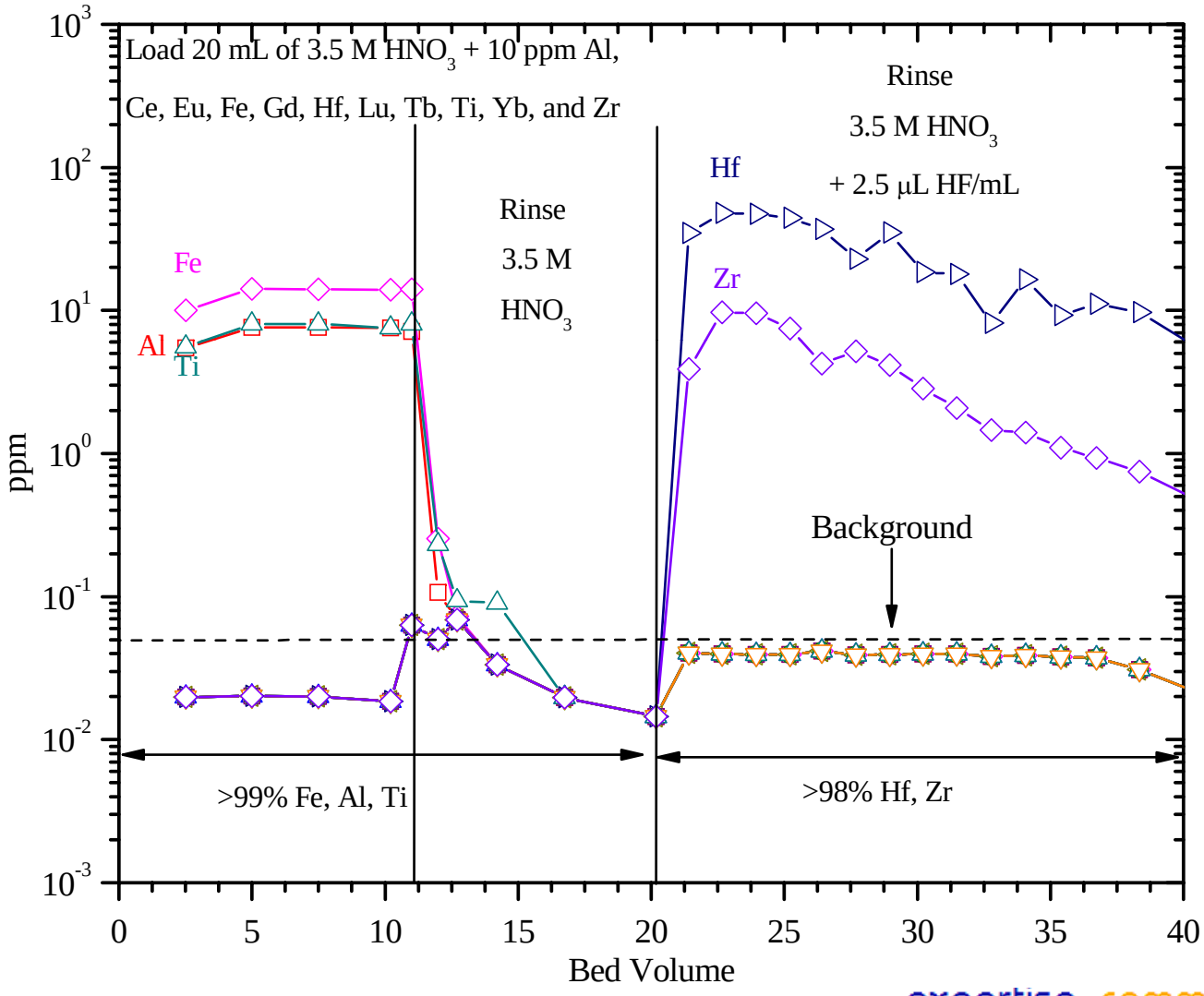
2.0 mL column of DGA, normal, 9.5 cm height x 0.5 cm diameter 22(1)°C, 2 mL/min



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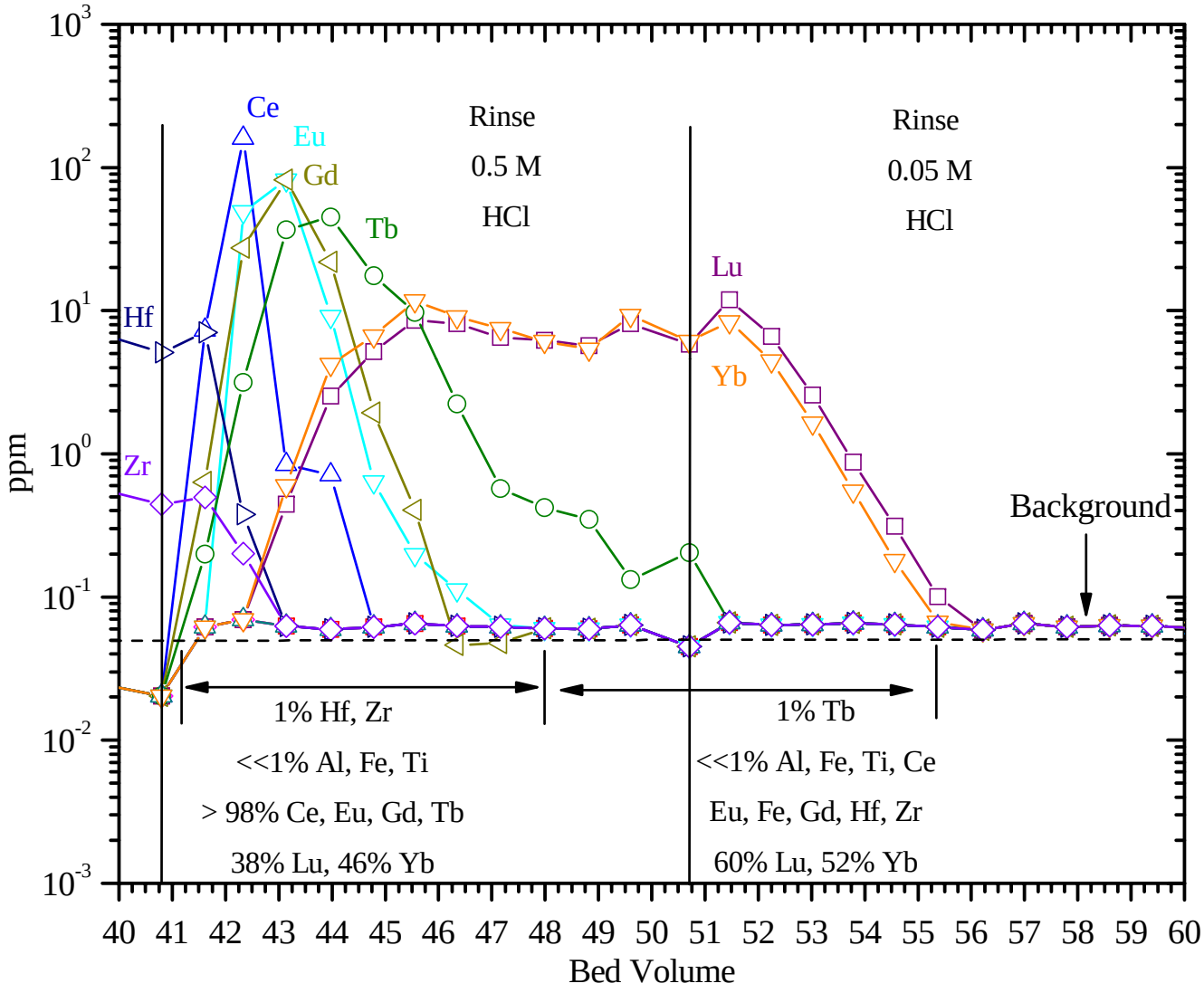
2.0 mL column of DGA, normal, 9.5 cm height x 0.5 cm diameter 22(1)°C, 2 mL/min



Conclusions

- Extraction Chromatography is offers a convenient format to perform sample preparation according to desired objectives
- Substantial literature references available for applications and characterization data
- Applicable to any analytical instrumentation, new or old

References

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