The use of surrogates in separations method development: advantages and challenges

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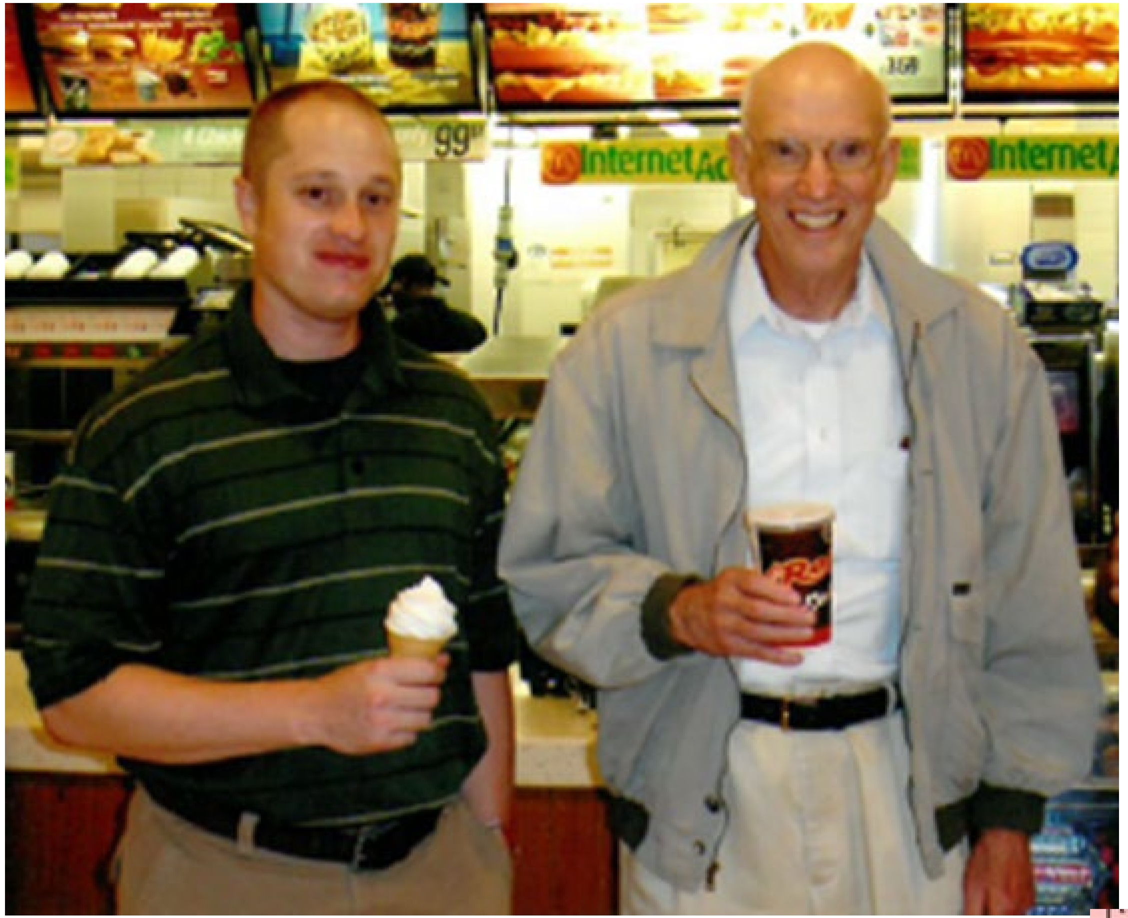
Many Flavors of Chemistry

Eichrom

Dan and Phil (Oxford McDonalds, 2006)



- Founded in 1990 by Phil Horwitz

- Commercialized EXC resins developed and characterized at Argonne National Laboratory.

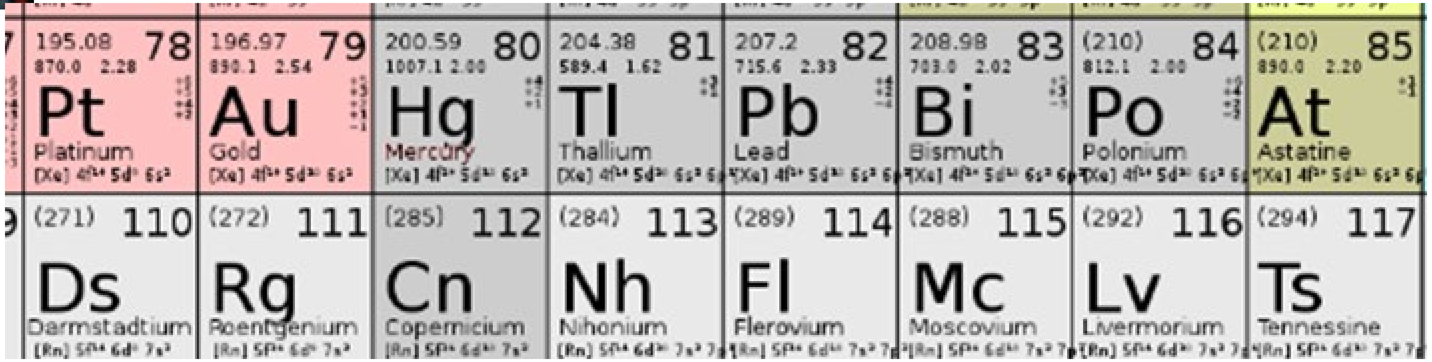
- Low-level environmental monitoring and bioassay to Ci-level production of isotopes for industry and nuclear medicine.

- Pt – Po for Ds – Lv (search for new elements in 1960s/1970s)

Eichrom R&D currently:

2 Ph.D. radiochemists

1 B.S. chemist



195.08 78 870.0 2.28 Pt Platinum	196.97 79 890.1 2.54 Au Gold	200.59 80 1007.1 2.00 Hg Mercury	204.38 81 589.4 1.62 Tl Thallium	207.2 82 715.6 2.33 Pb Lead	208.98 83 703.0 2.02 Bi Bismuth	(210) 84 812.1 2.00 Po Polonium	(210) 85 890.0 2.20 At Astatine
(271) 110 Ds Darmstadtium	(272) 111 Rg Roentgenium	(285) 112 Cn Copernicium	(284) 113 Nh Nihonium	(289) 114 Fl Flerovium	(288) 115 Mc Moscovium	(292) 116 Lv Livermorium	(294) 117 Ts Tennessine

Resources

Radioactive Materials Laboratory

Broad Scope License, any radionuclide of elements 1(H) – 103(Lr), **no Rf, Db, Sg… ☹**

Permitted mCi amounts of Ac-225, Ac-227, Pb-203, F-18, Th-228

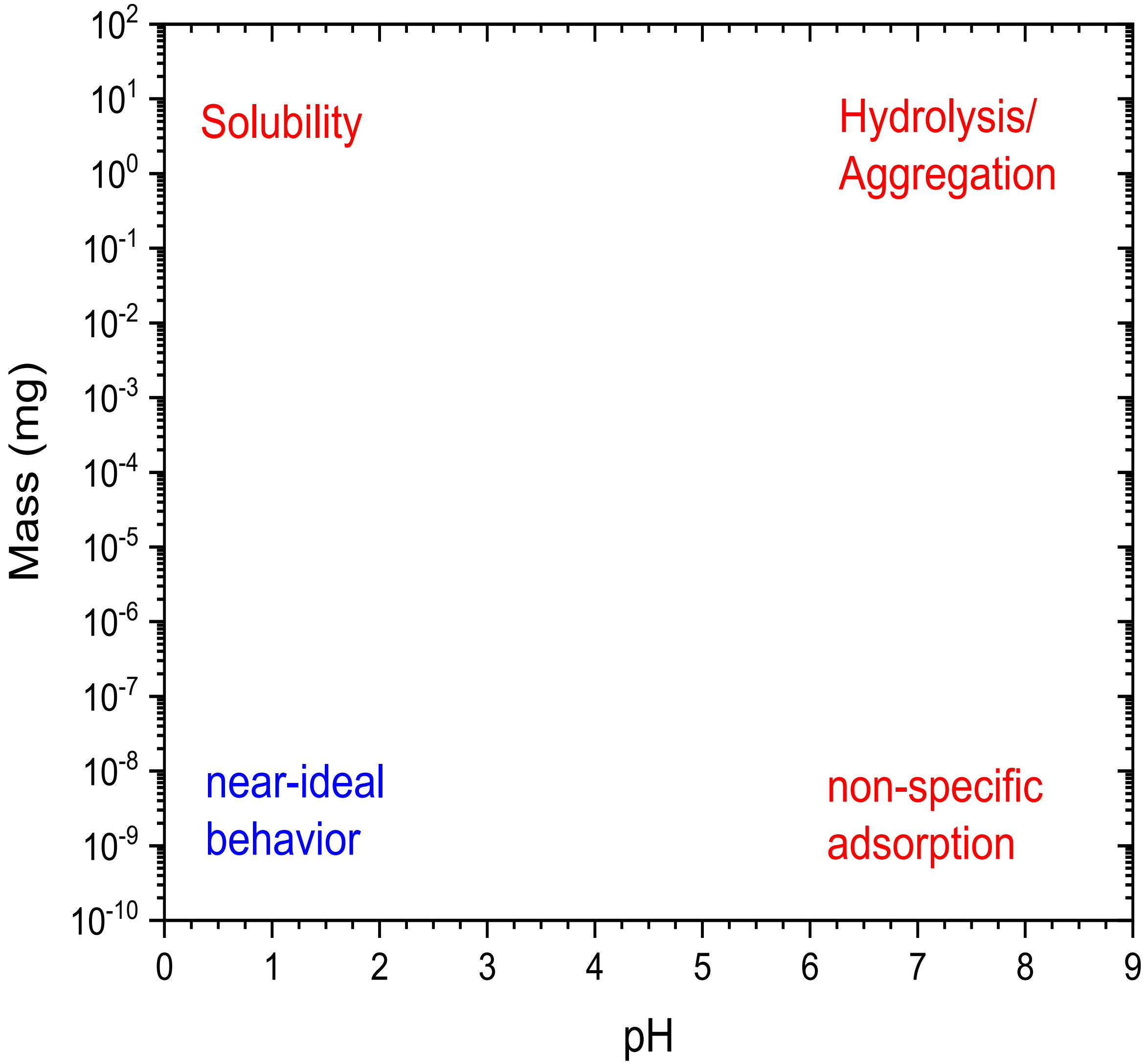
Alpha spectrometry, HPGe gamma, LSC, Na(Tl)I gamma, MP-AES, ~~ICP-MS~~

~~Cyclotron~~

~~Nuclear Reactor~~

RadioIsotopes may be:
Unavailable
Expensive
Short-lived
Complex decay scheme
(ALARA)

Surrogates: Stable elements vs Radionuclides



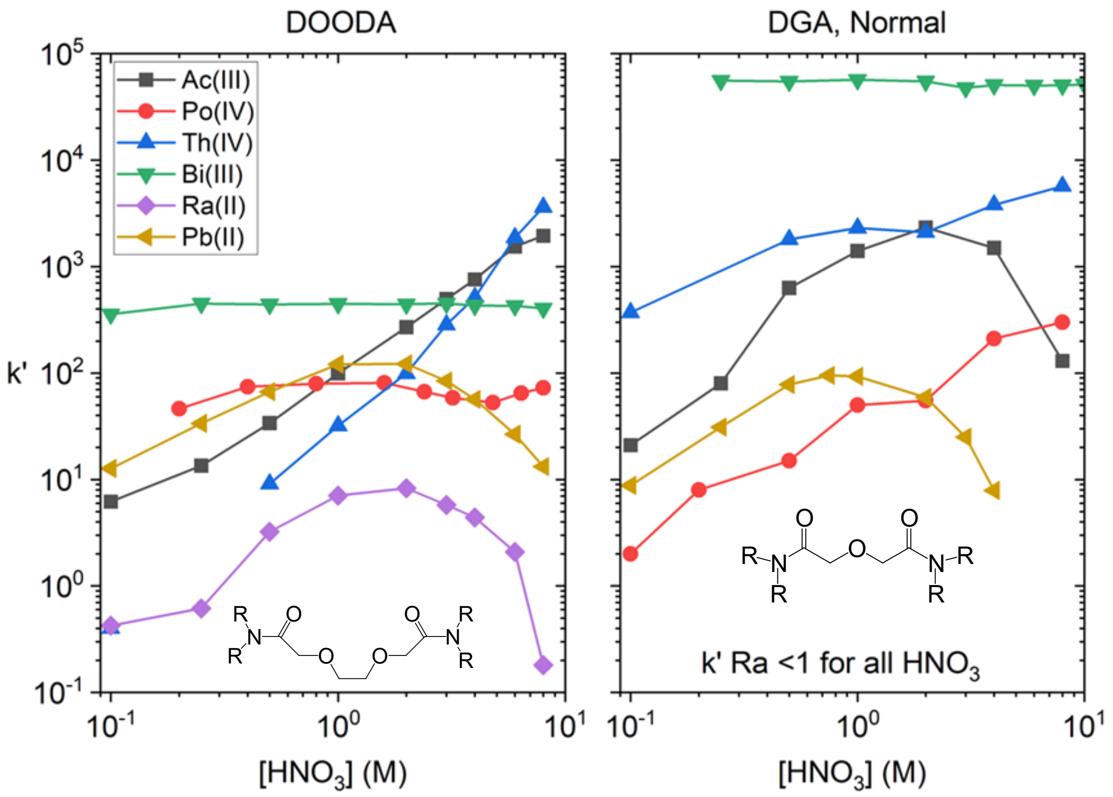
Stable Elements (µg):

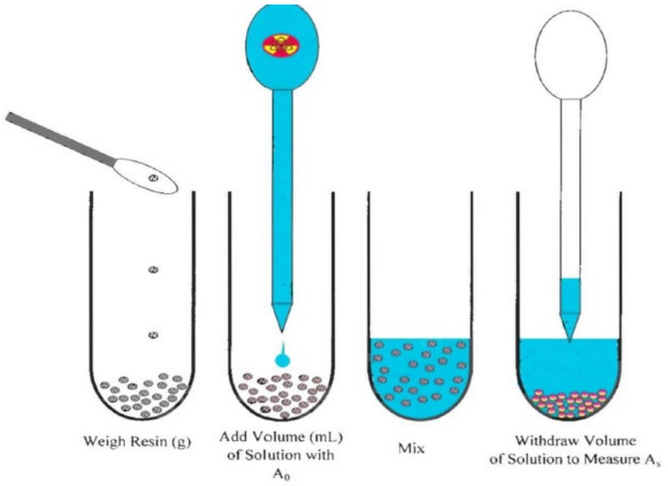
- Readily available
- Measure by AES/MS
- Reasonable Surrogates for elements without stable isotopes

Radionuclides:

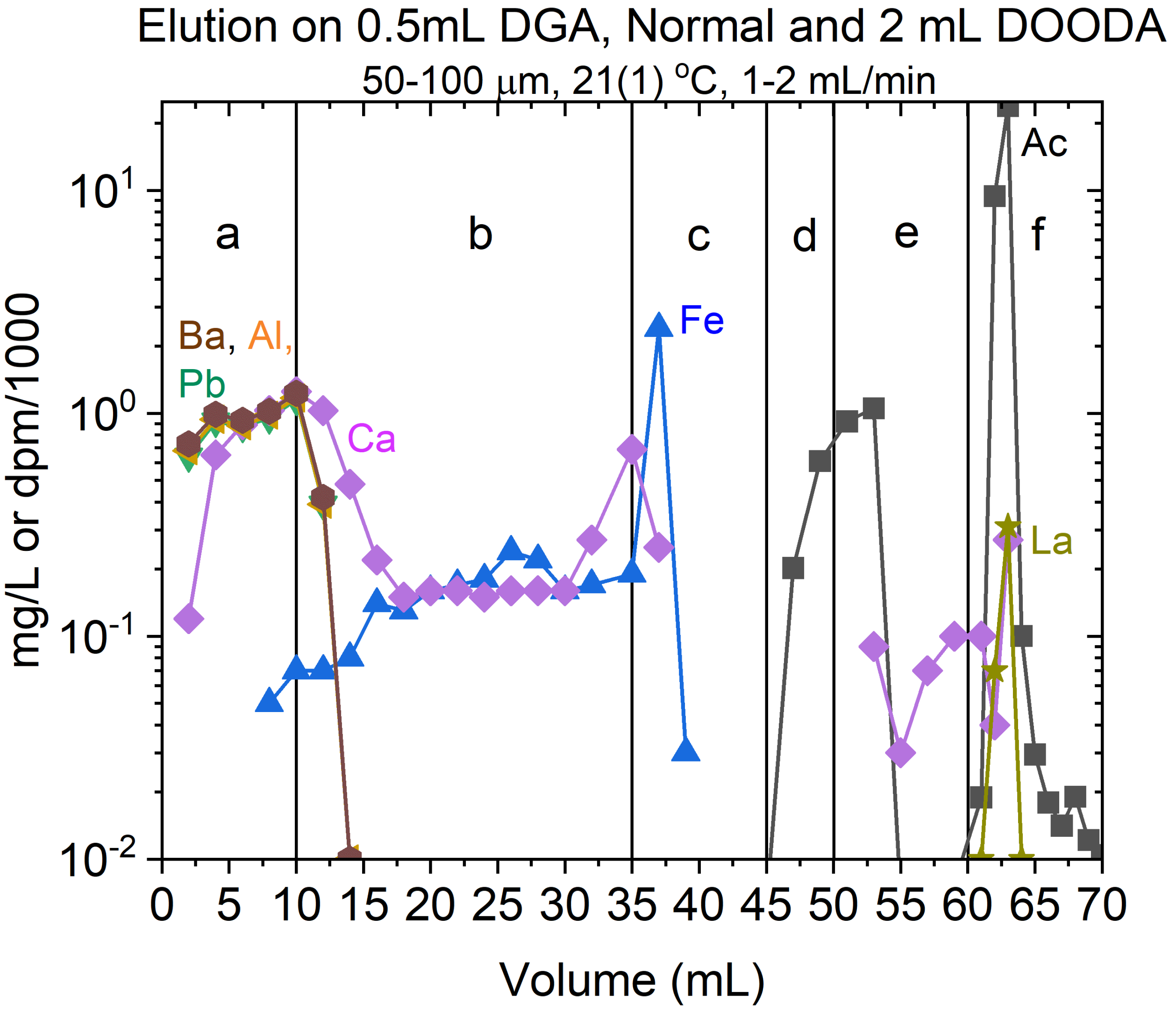
- Require special license
- Waste can be expensive (DIS)
- Can dope with long-lived isotopes to tune specific activity

When does mass help/hurt?





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



Elution on 0.5mL DGA, Normal and 2 mL DOODA

50-100 μm, 21(1) °C, 1-2 mL/min

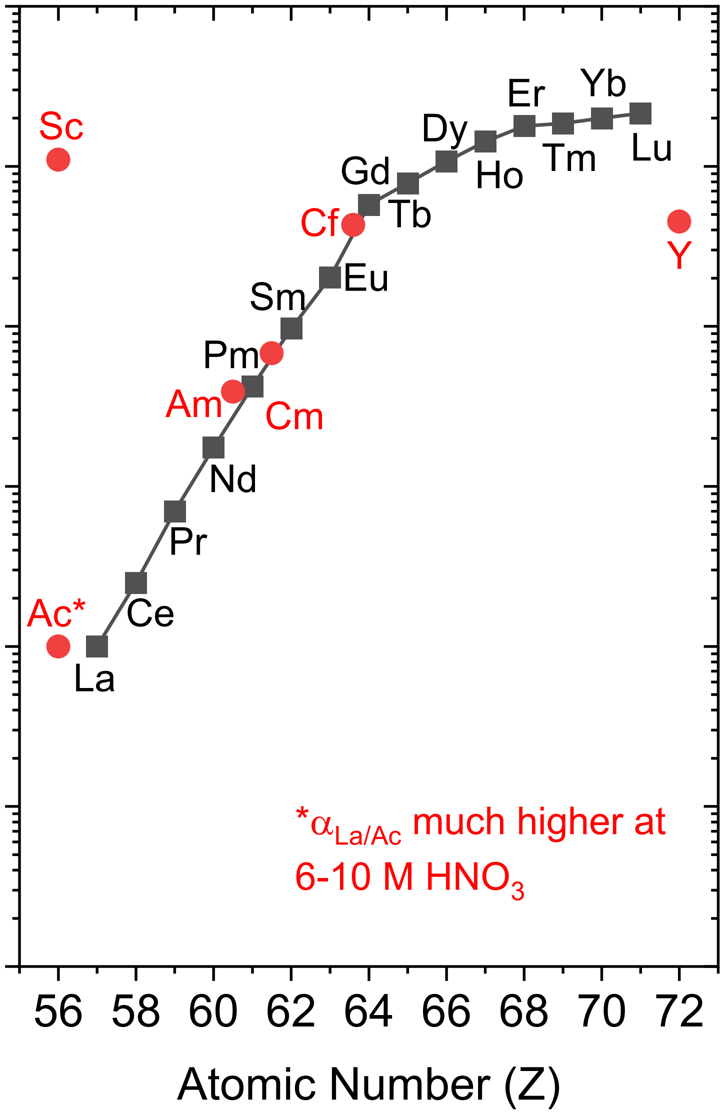
f: 10 mL 0.1M HCl

90% Ac-225

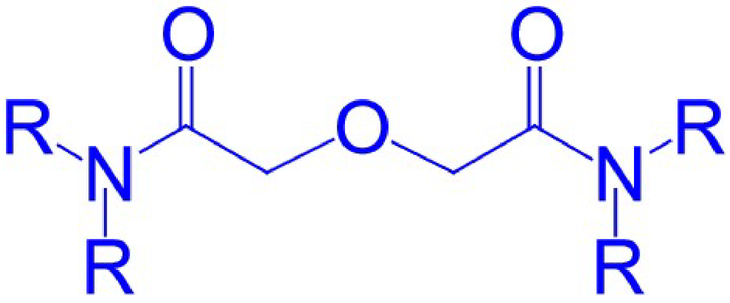
<<1% La, Th, Bi, Po

Rare Earths for Minor Actinides

Relative D_w on DGA, Normal



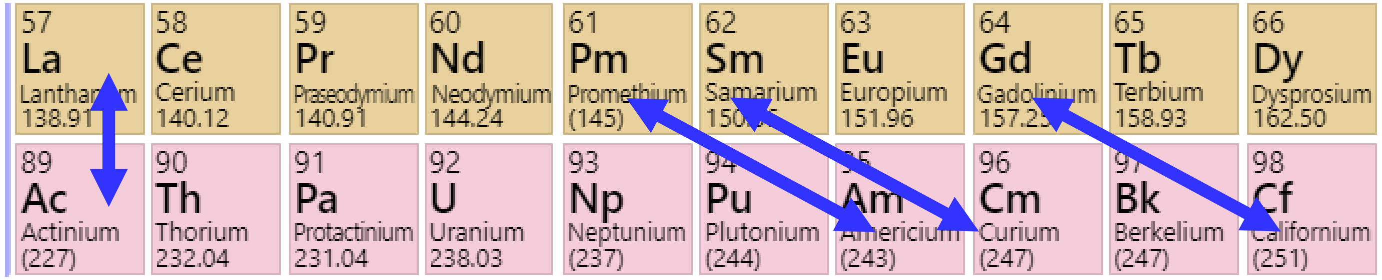
*$\alpha_{La/Ac}$ much higher at 6-10 M HNO_3



R = n-octyl or 2-ethyl-1-hexyl

$M^{3+} + 3DGA + 3X^- \leftrightarrow M(DGA)_3X_3$

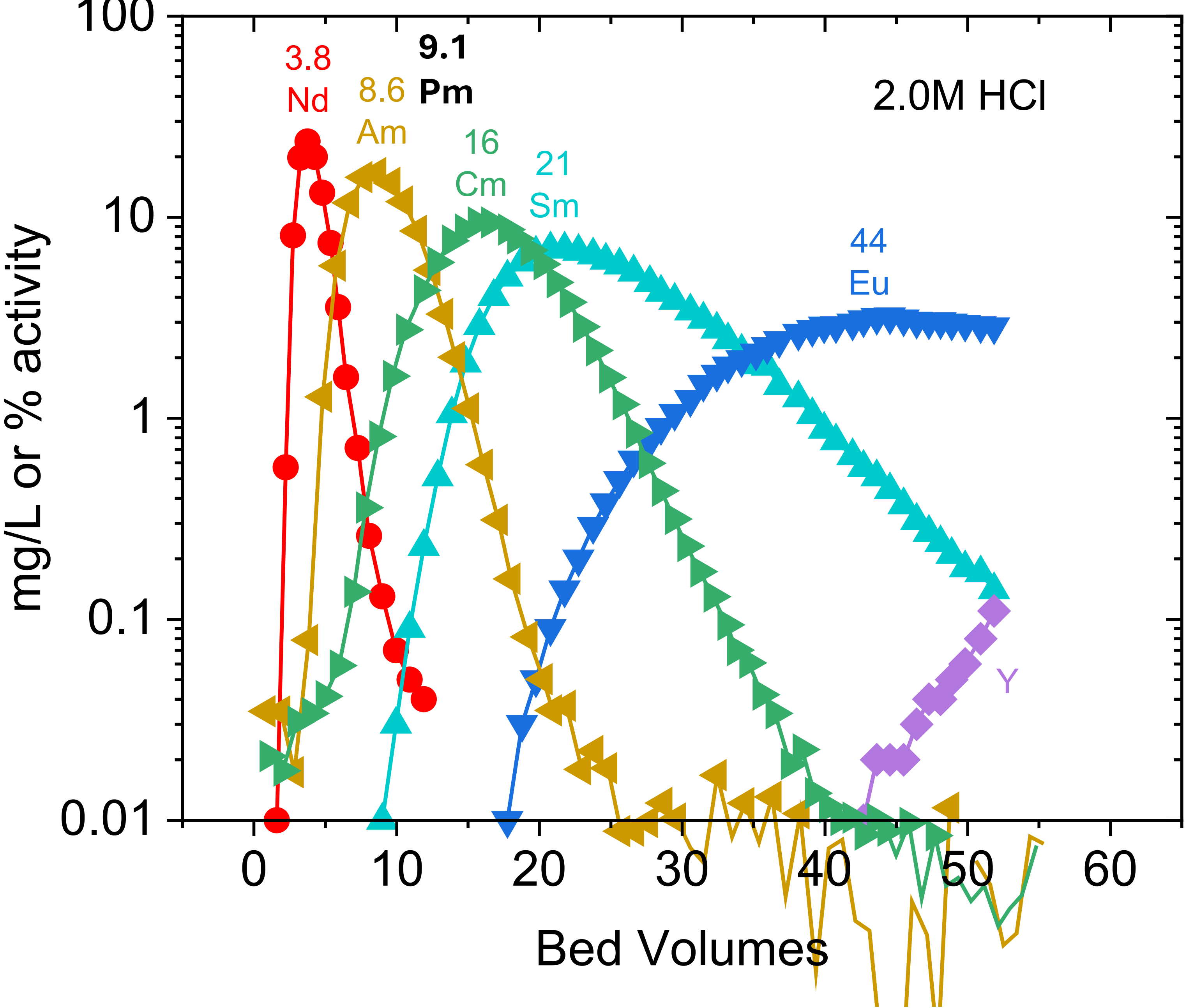
M= Ln(III) or An(III), X = NO_3^- or Cl^-



57 **La** Lanthanum 138.91	58 **Ce** Cerium 140.12	59 **Pr** Praseodymium 140.91	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.96	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.93	66 **Dy** Dysprosium 162.50
89 **Ac** Actinium (227)	90 **Th** Thorium 232.04	91 **Pa** Protactinium 231.04	92 **U** Uranium 238.03	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)

Elution on DGA, Normal

50-100 μm, 0.9 cm x 14 cm, 21(1)°C, 3.5 mL/min



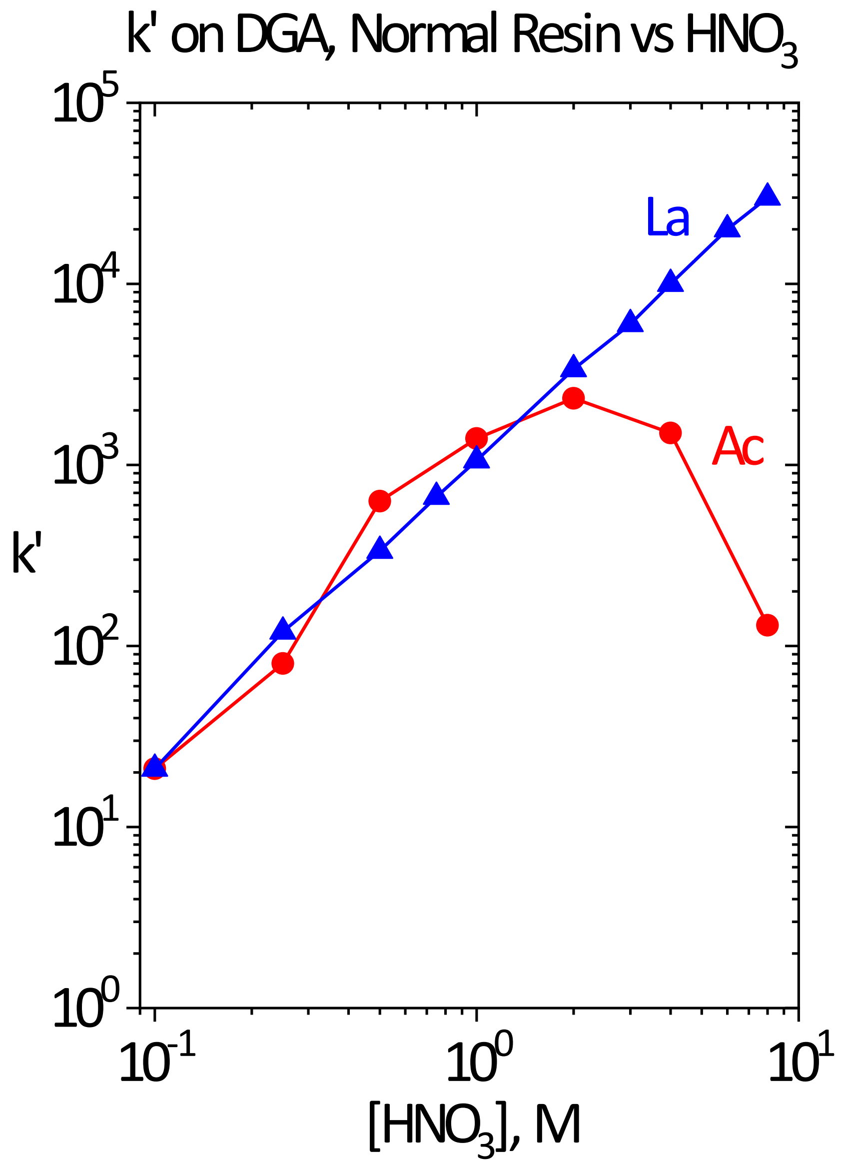
M^{3+}	Separation factor (M/Nd)	Predicted BV (Nd = 3.8)
Nd	1.0	3.8
Am	2.2	8.4
Pm	2.4	9.1
Cm	3.9	15
Sm	5.5	21

Nd/Sm bracket Am/Cm

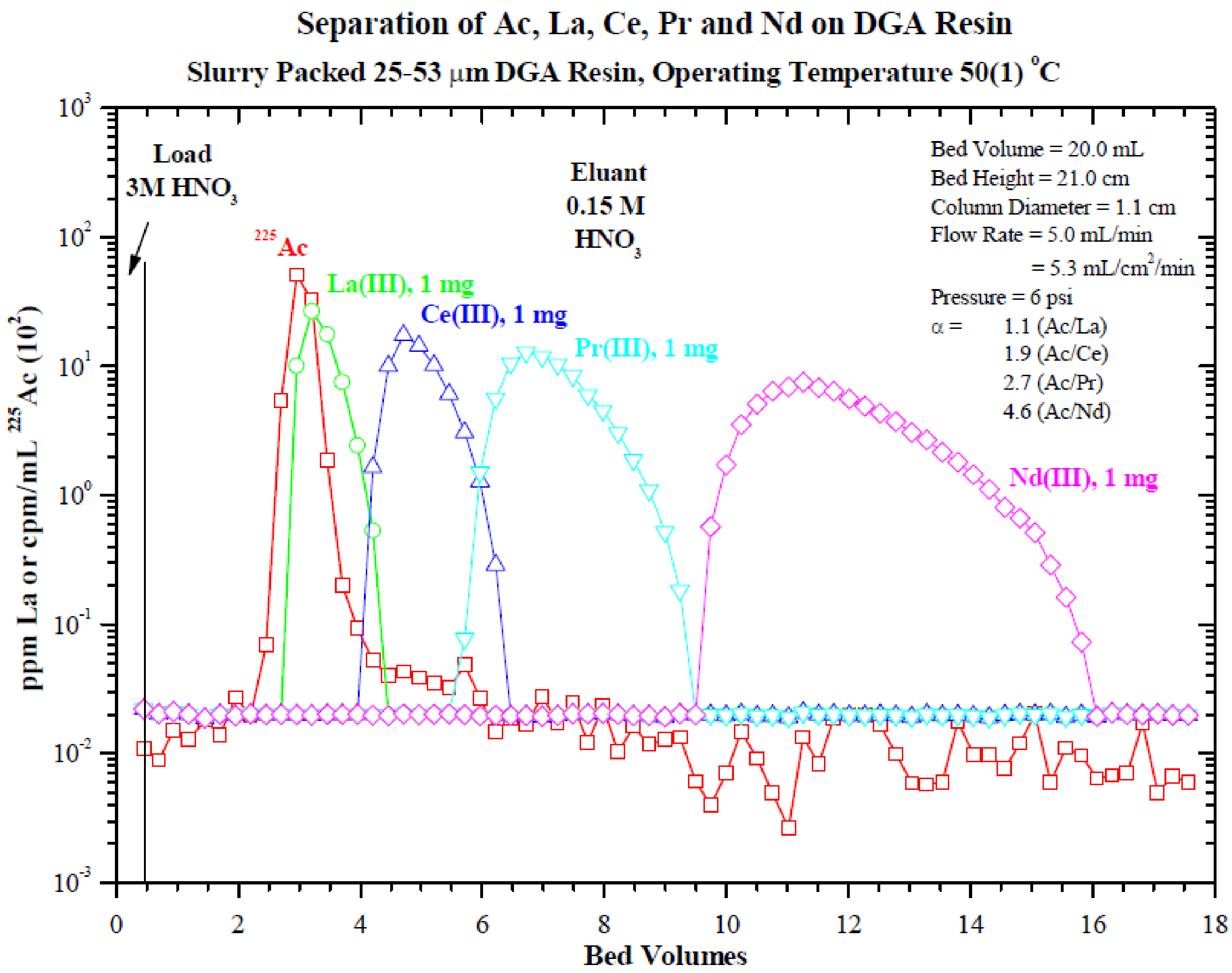
^{147}Pm ←→ ^{241}Am

Sm → Cm

La for Ac-225 (DGA-dilute HNO_3)



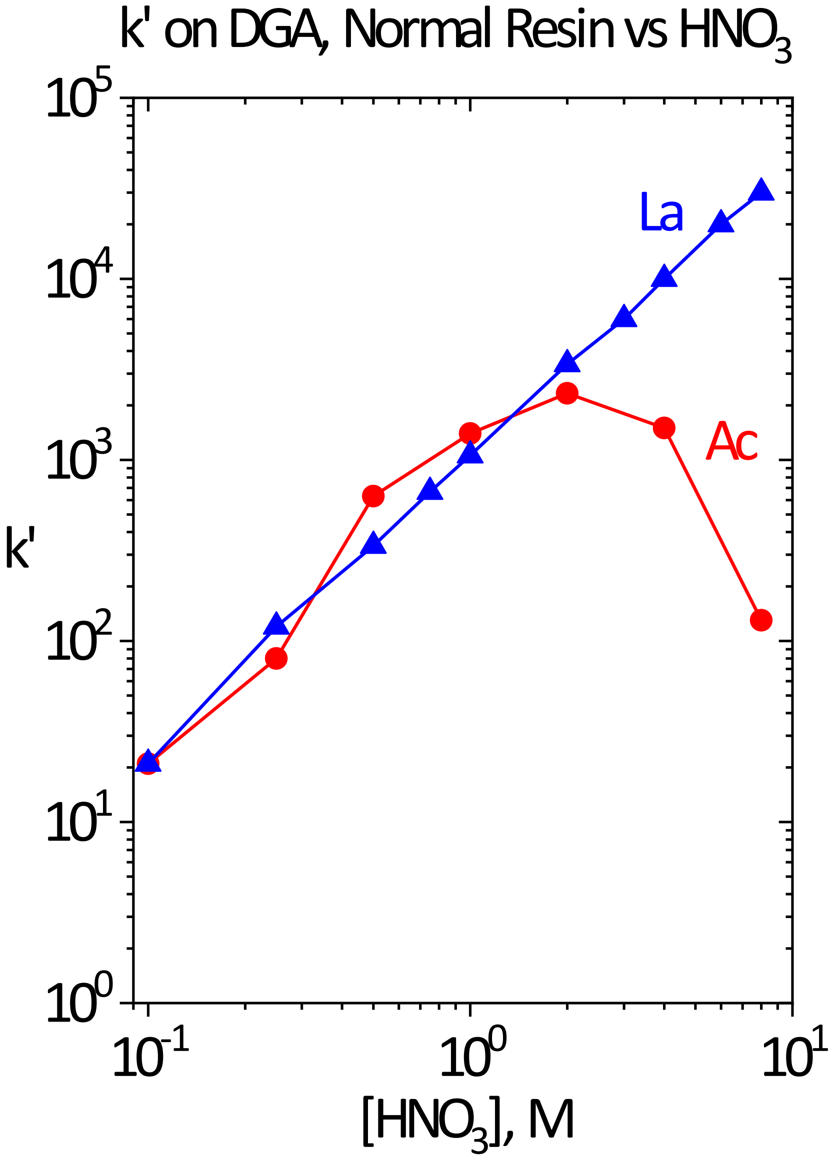
k' on DGA, Normal Resin vs HNO_3



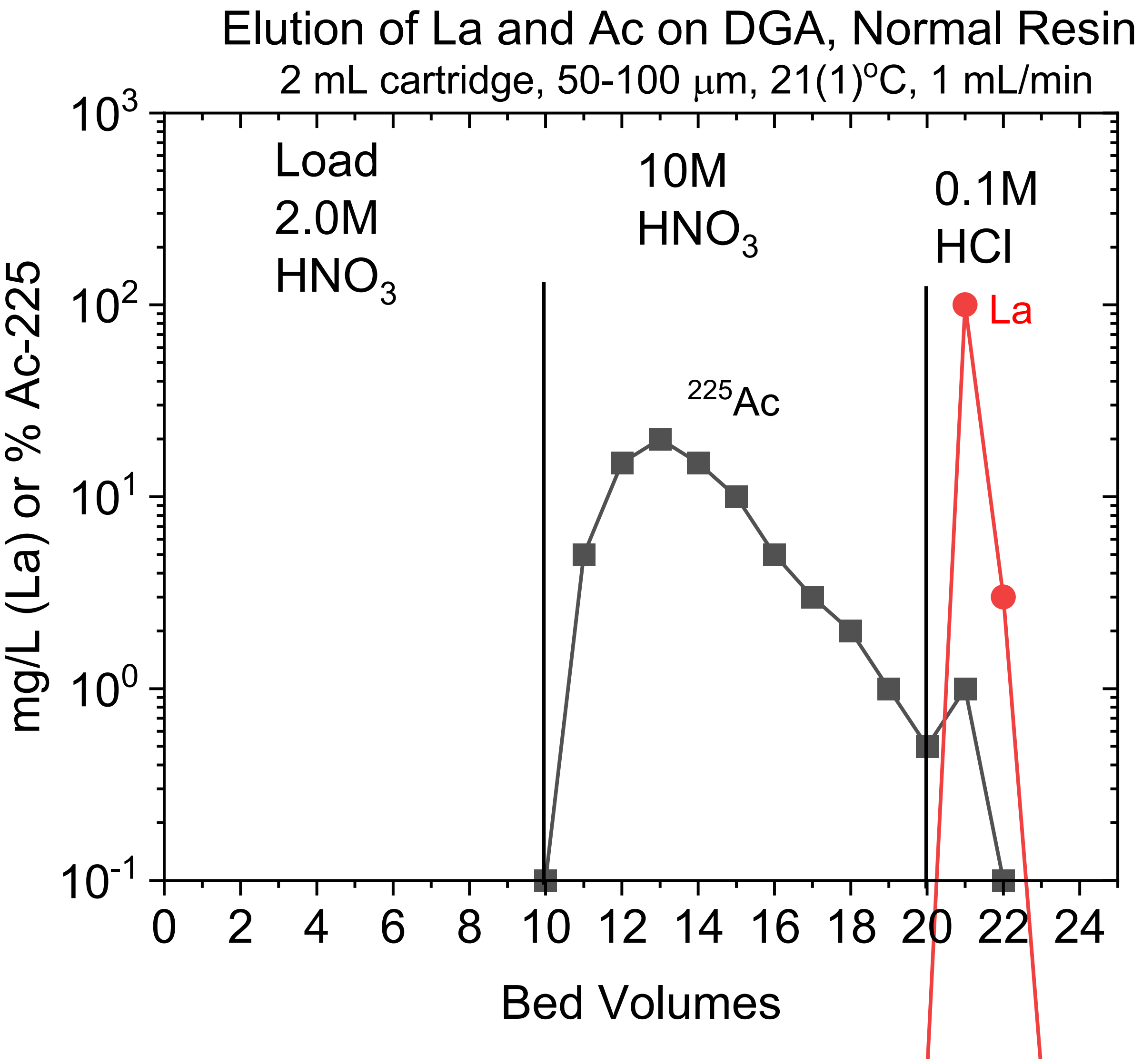
Separation of Ac, La, Ce, Pr and Nd on DGA Resin

Slurry Packed 25-53 μm DGA Resin, Operating Temperature 50(1) °C

La for Ac-225 (DGA – 10M HNO_3)



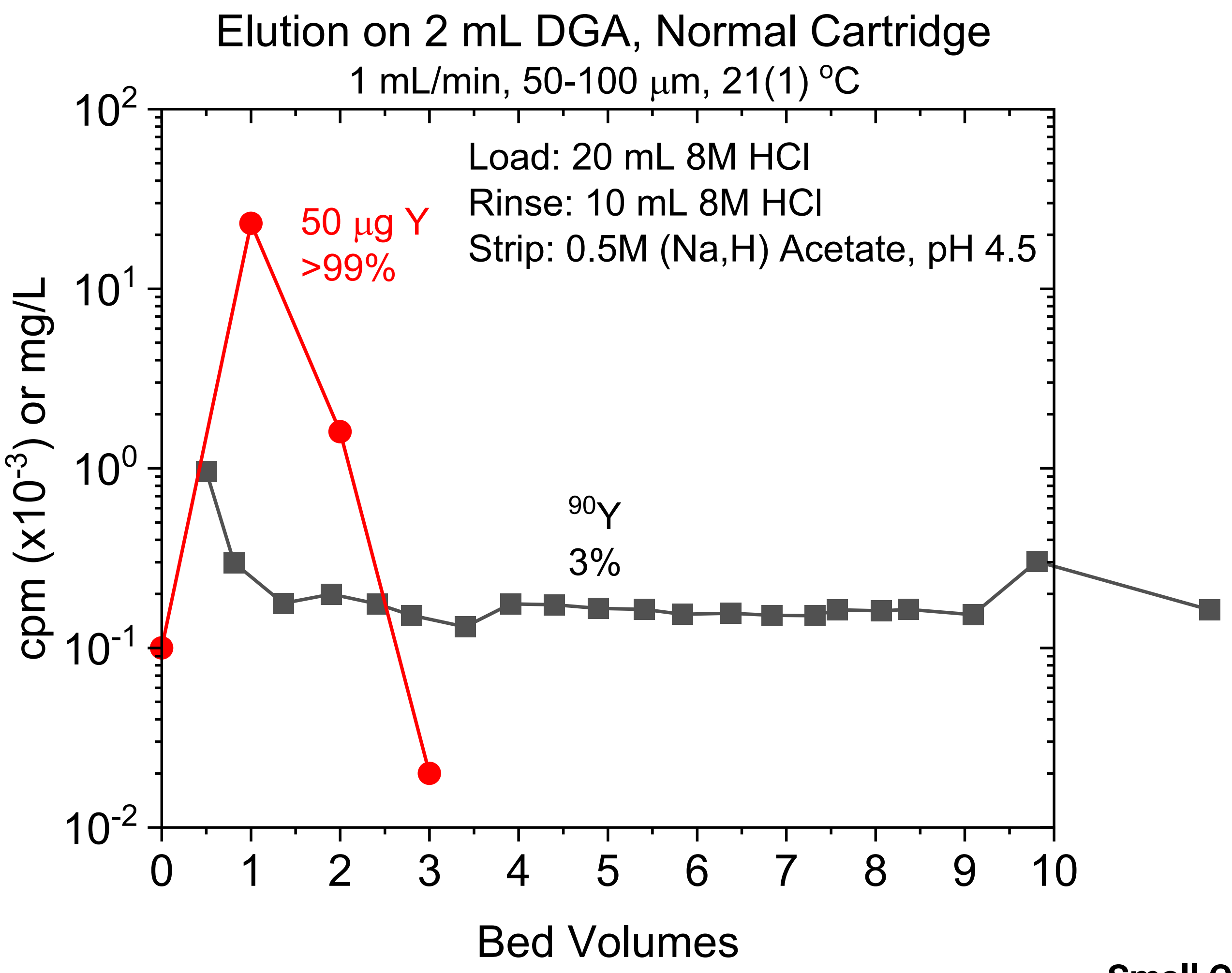
k' on DGA, Normal Resin vs HNO_3



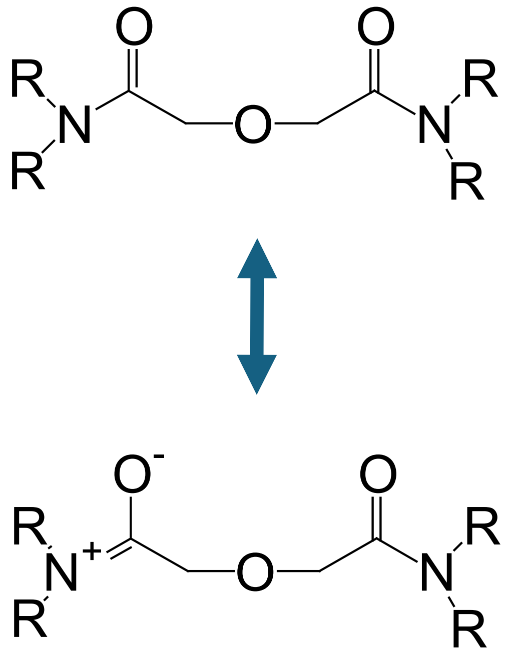
Elution of La and Ac on DGA, Normal Resin

2 mL cartridge, 50-100 μm, 21(1)°C, 1 mL/min

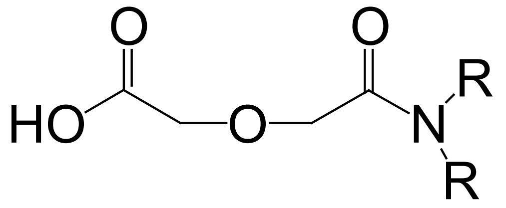
^{90}Y vs Y (Elution from DGA Resin)



DGA



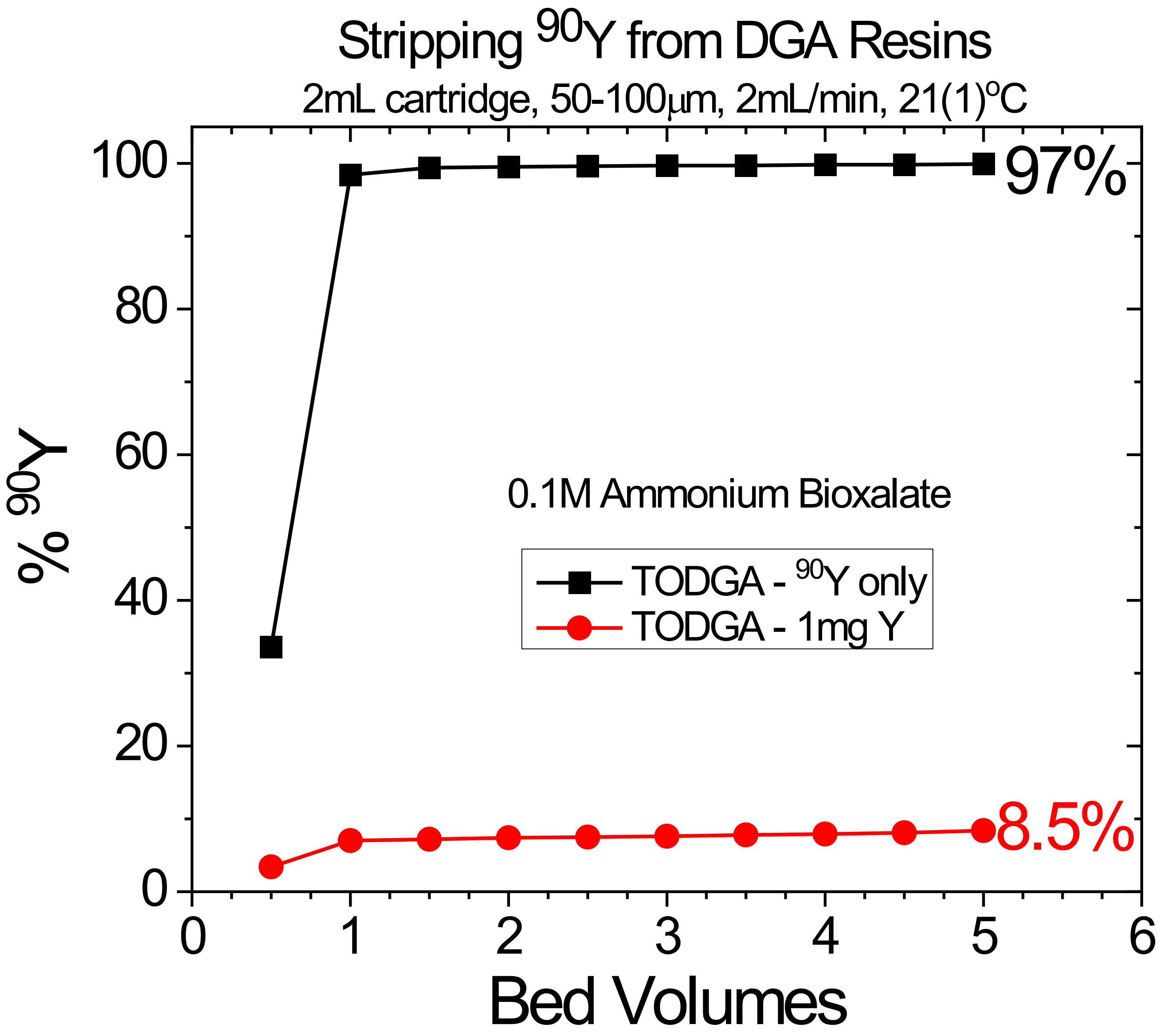
Acidic impurity



Yield for ^{225}Ac > 95%
Correlates with ionic potential of metal ion.

Small Cyclic Diglycolamides: Tautomerism, Solvent Extraction and Coordination with *f*-Elements: One Strain to Rule Them All. Mikhail A. Kalinin, Mariia V. Evsiunina, Paulina Kalle, Konstantin A. Lyssenko, Petr I. Matveev, and Nataliya E. Borisova *Inorganic Chemistry* **2024** *63* (1), 602-612
DOI: 10.1021/acs.inorgchem.3c03488

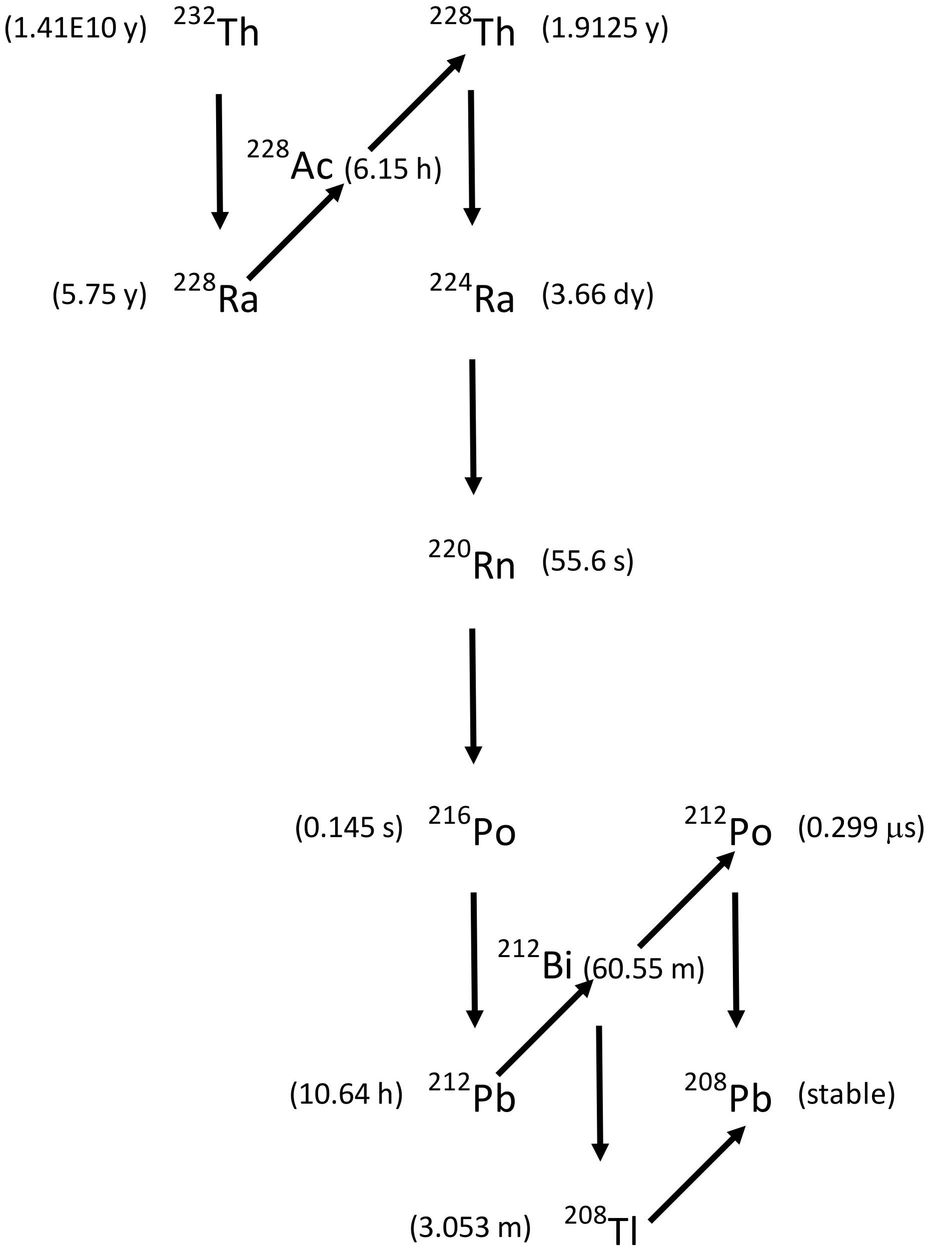
^{90}Y vs Y (Elution from DGA Resin)



Load: 20 mL 0.25M HNO_3
Rinse: 10 mL 8M HNO_3
Strip Y: 10 mL 0.1M ammonium
bioxalate

Yttrium oxalate
Ksp = 5.1×10^{-30}

Th-228 Decay Scheme and surrogate options



^{228}Th → ^{227}Th + ^{232}Th (**1.2 µg/mCi ^{228}Th**)

^{224}Ra → ^{223}Ra or ^{133}Ba or stable Ba

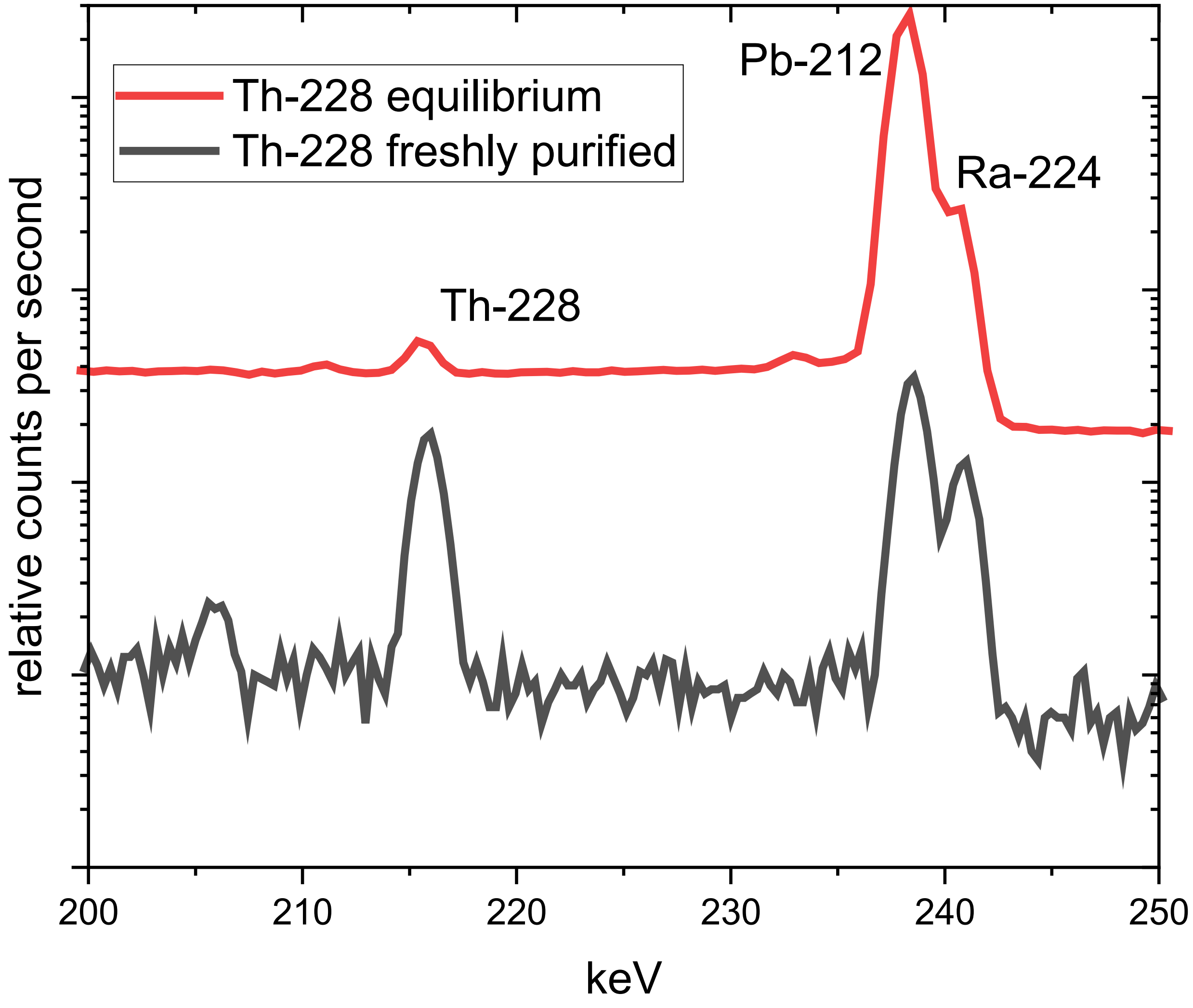
$^{216/212}$Po → ^{210}Po

^{212}Pb → ^{203}Pb or stable Pb

^{212}Bi → ^{210}Bi, ^{207}Bi, or stable Bi

^{208}Tl → ^{204}Tl or Stable Tl

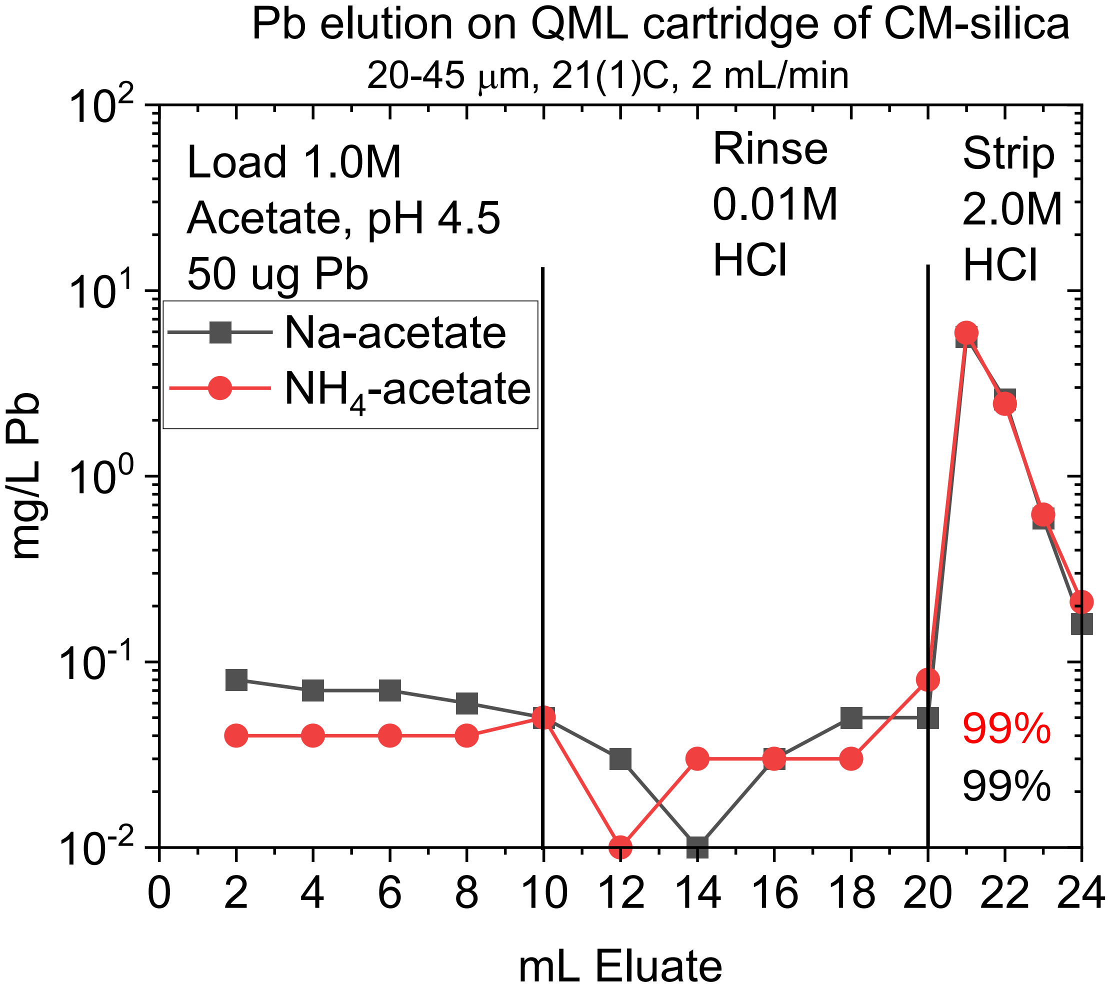
Th-228 Decay Scheme and surrogate options

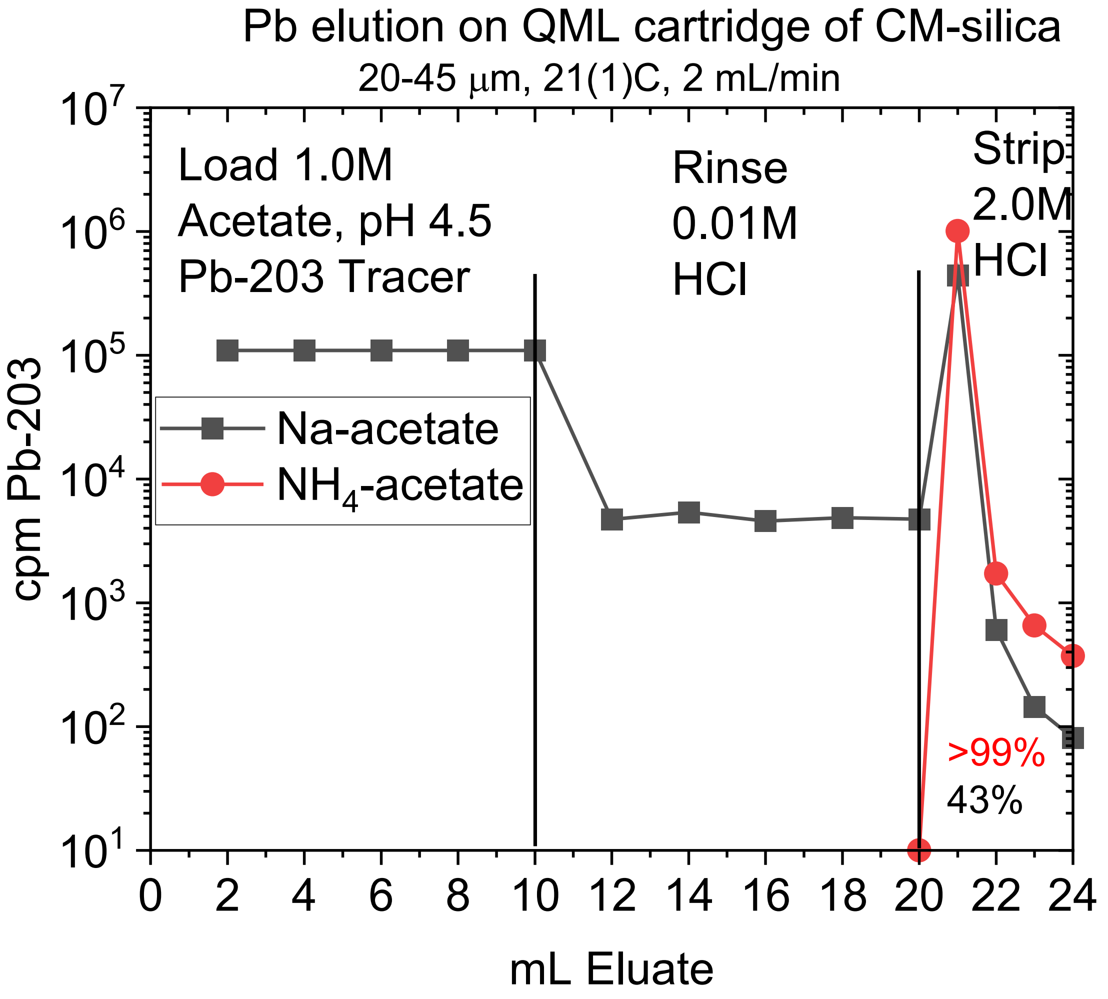


^{228}Th	215.985 keV (0.246%)
^{224}Ra	240.986 keV (4.12%)
^{212}Pb	238.632 keV (43.6%)
^{212}Bi	727.330 keV (6.65%)
^{208}Tl	510.75 keV (22.5%) 583.187 keV (85.0%) 2614.511 keV (99.775%)

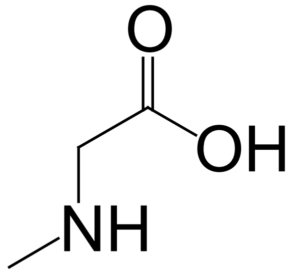
http://www.lnhb.fr/home/nuclear-data/nuclear-data-table/

^{203}Pb vs Stable Pb for ^{212}Pb



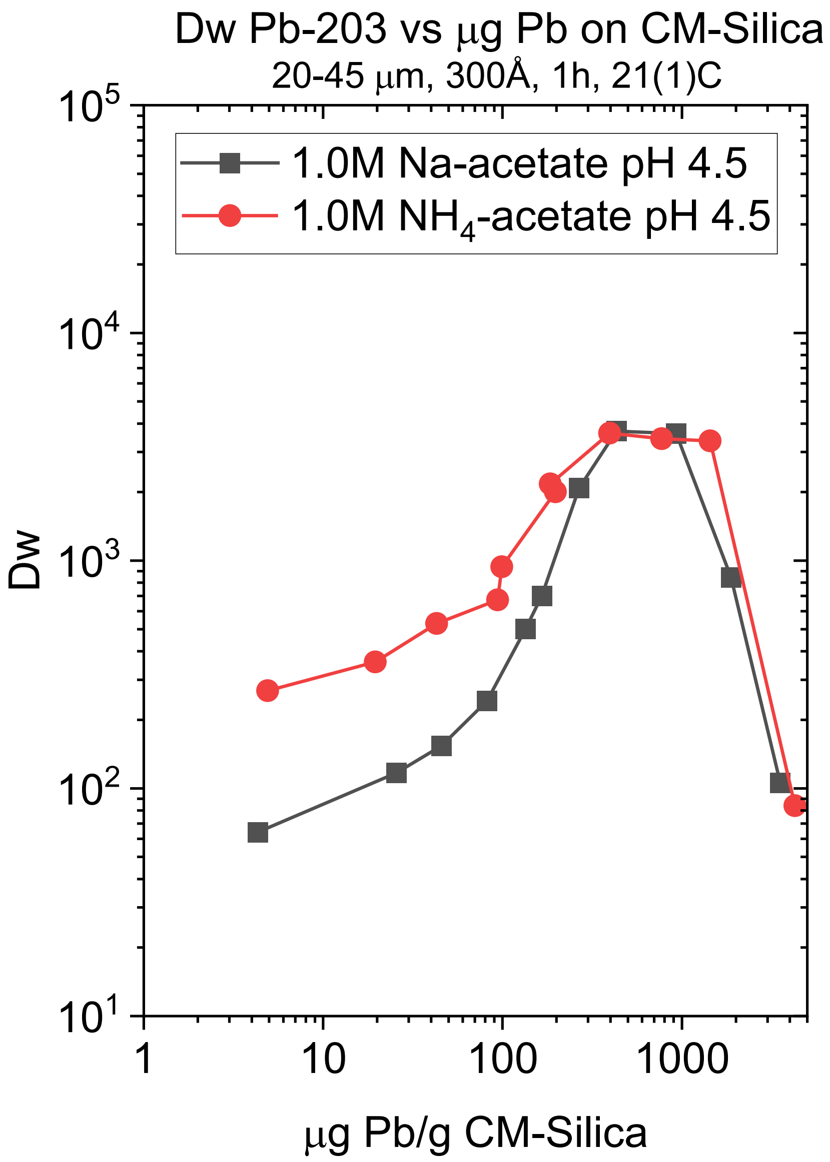


Weak cation exchange silica.
NH_4^+ vs Na^+ to reduce impact on stable element measurements by AES.



pKa ~ 2

^{203}Pb vs Stable Pb for ^{212}Pb

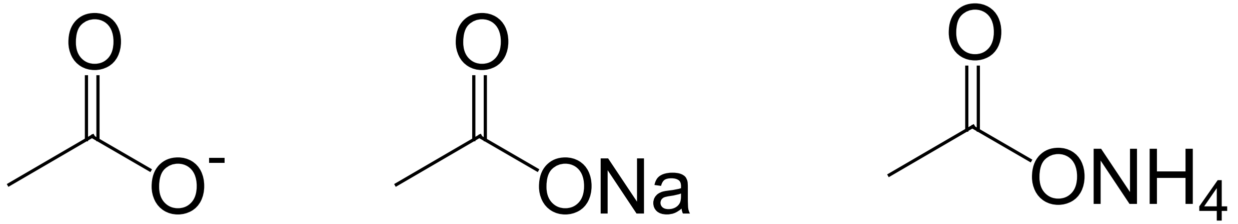


Some difference expected between Na^+ and NH_4^+ based on competition for IX sites.

For **strong acid** cation exchange, selectivity is:

$Li+ < H+ < Na+ < NH_4+ < K+$

$NH_3 + H_2O \leftarrow\rightarrow NH_4^+ + {}^-OH$ (no NH_3 for pH <7)



Dw proportional to µg Pb until resin saturation.

Mechanism unclear???

Questions???

Answers???

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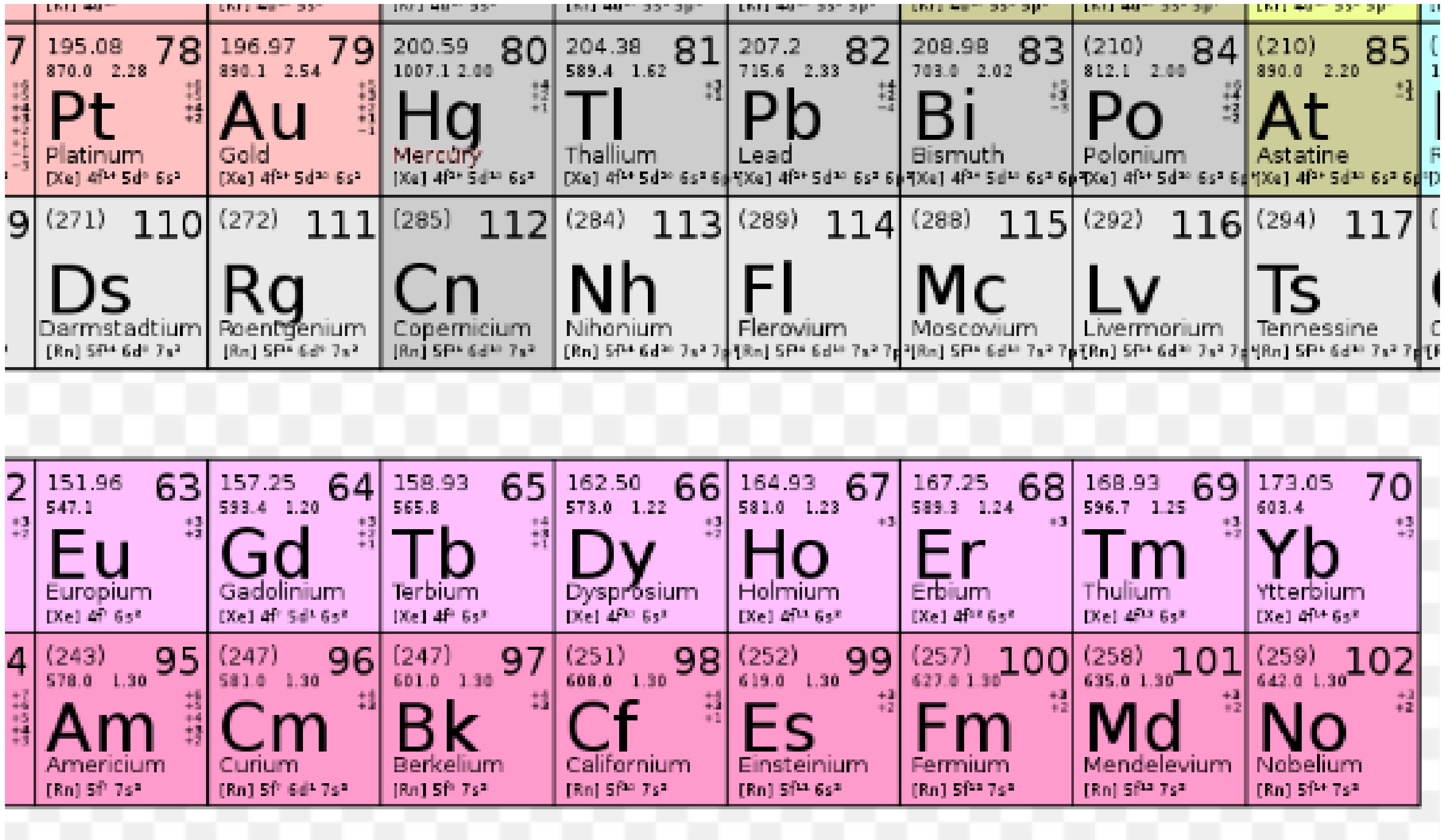
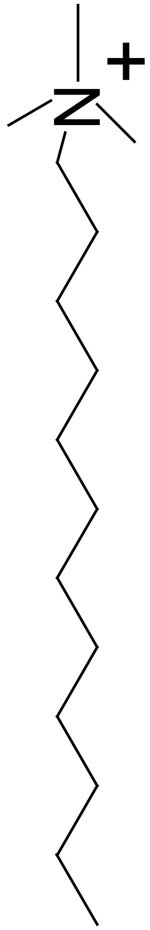
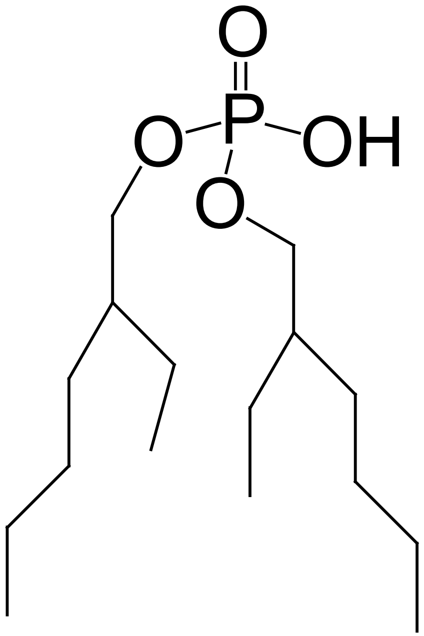
No other options

Long half-lives predicted for neutron rich isotopes of Z=110-114 (Ds-Fl)





TEVA

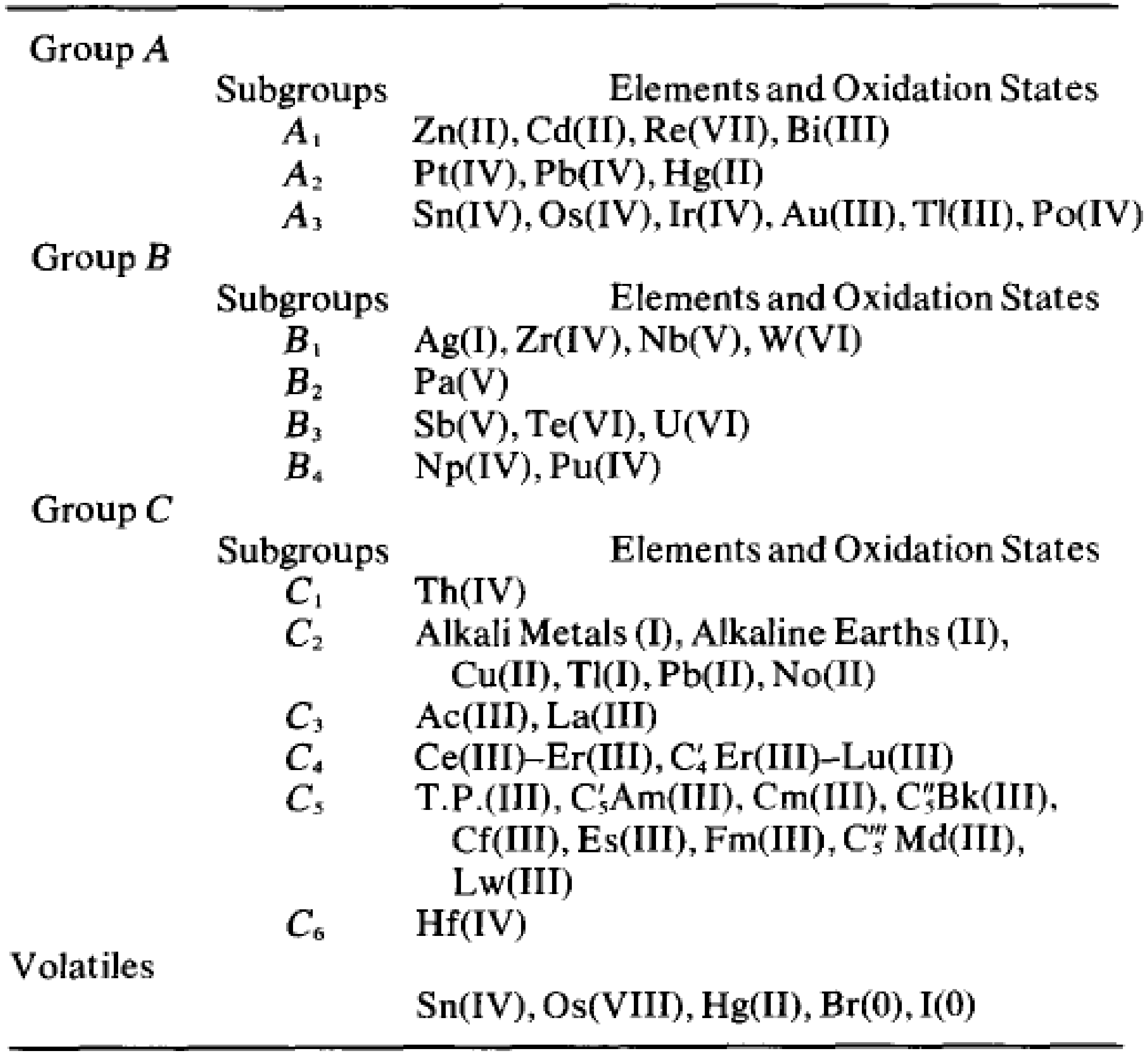


LN

J.P. Unik, E.P. Horwtiz, K.L. Wolf, I. Ahmad, S. Fried, D. Cohen, P.R. Fields, C.A.A. Bloomquist, D.J. Henderson, “Production of Actinides and the Search for Super-Heavy Elements Using Secondary Reactions Induced by GeV Protons,” *Nuclear Physics*, A191, 233-244 (1972).

No other options

TCMA·Cl in o-xylene on Celite (35 μ). Column bed size 0·062 cm × 5 cm; 50°C; v = ~4 cm/min; FCV = 0·19 ml.



	Subgroups	Elements and Oxidation States
Group *A*		
	A_1	Zn(II), Cd(II), Re(VII), Bi(III)
	A_2	Pt(IV), Pb(IV), Hg(II)
	A_3	Sn(IV), Os(IV), Ir(IV), Au(III), Tl(III), Po(IV)
Group *B*		
	B_1	Ag(I), Zr(IV), Nb(V), W(VI)
	B_2	Pa(V)
	B_3	Sb(V), Te(VI), U(VI)
	B_4	Np(IV), Pu(IV)
Group *C*		
	C_1	Th(IV)
	C_2	Alkali Metals (I), Alkaline Earths (II), Cu(II), Tl(I), Pb(II), No(II)
	C_3	Ac(III), La(III)
	C_4	Ce(III)–Er(III), C_4' Er(III)–Lu(III)
	C_5	T.P.(III), C_5'Am(III), Cm(III), C_5''Bk(III), Cf(III), Es(III), Fm(III), C_5''' Md(III), Lw(III)
	C_6	Hf(IV)
Volatiles		Sn(IV), Os(VIII), Hg(II), Br(0), I(0)