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

Daniel McAlister, Ph.D. and Madeleine Eddy, Ph.D.
Eichrom Technologies, LLC 1995 University Lane, Lisle, IL 60532
dmcalister@eichrom.com

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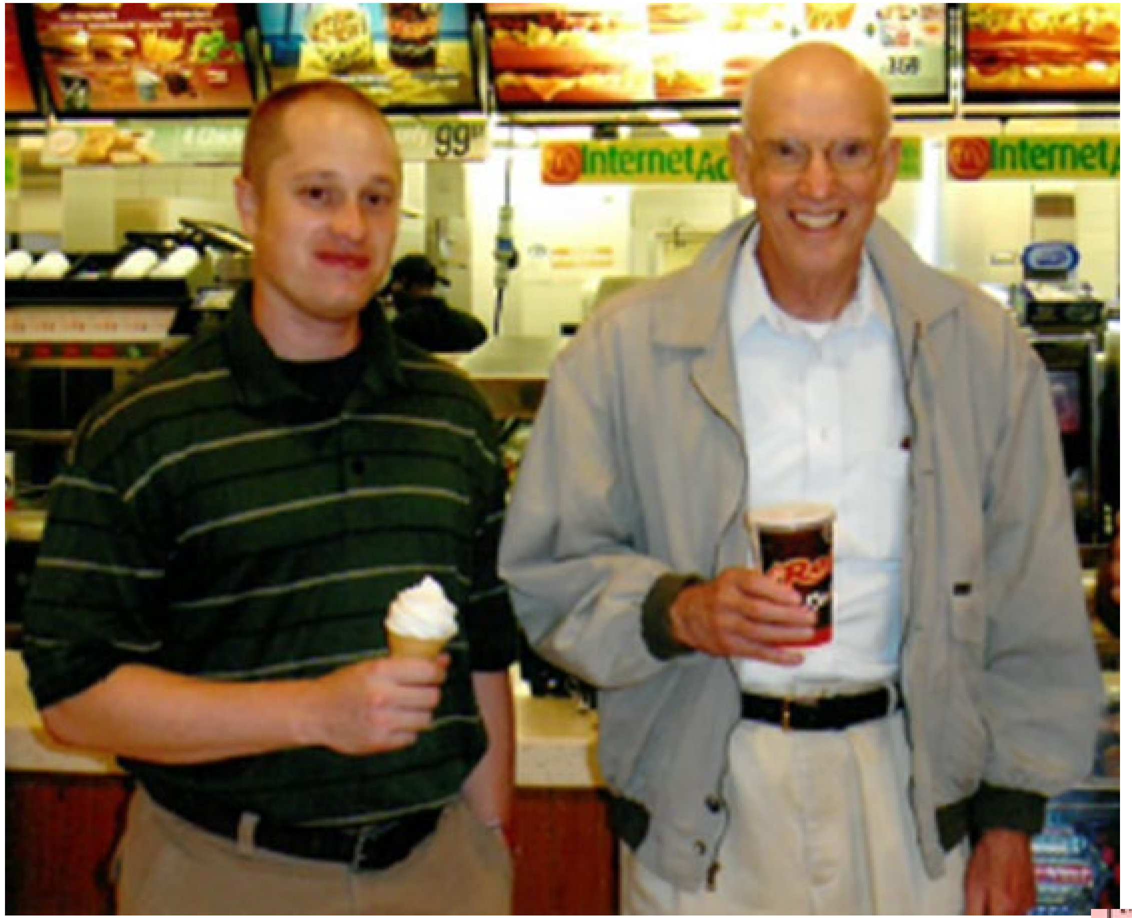
Many Flavors of Chemistry

Eichrom

Dan and Phil (Oxford McDonalds, 2006)



- Founded in 1990 by Phil Horwitz

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

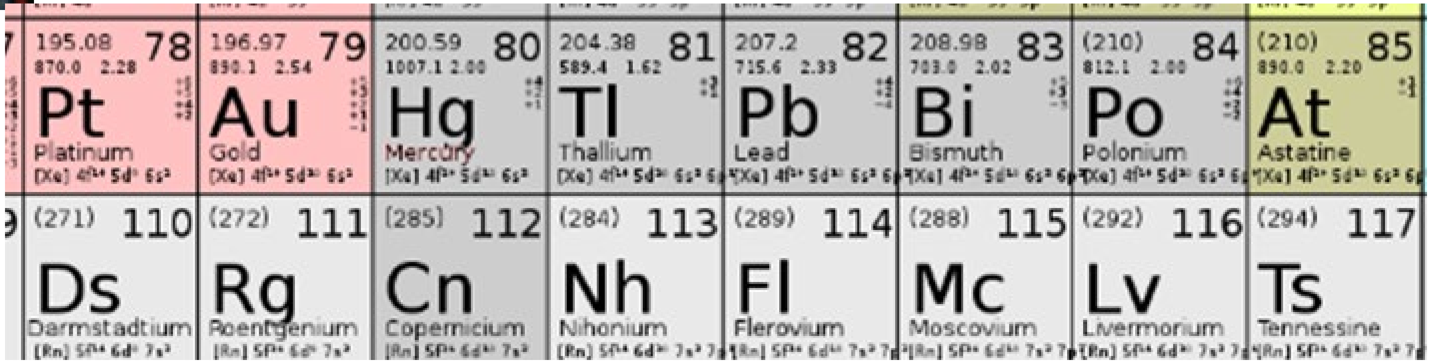
- Low-level environmental monitoring and bioassay to Ci-level production of isotopes for industry and nuclear medicine.

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

Eichrom R&D currently:

2 Ph.D. radiochemists

1 B.S. chemist



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

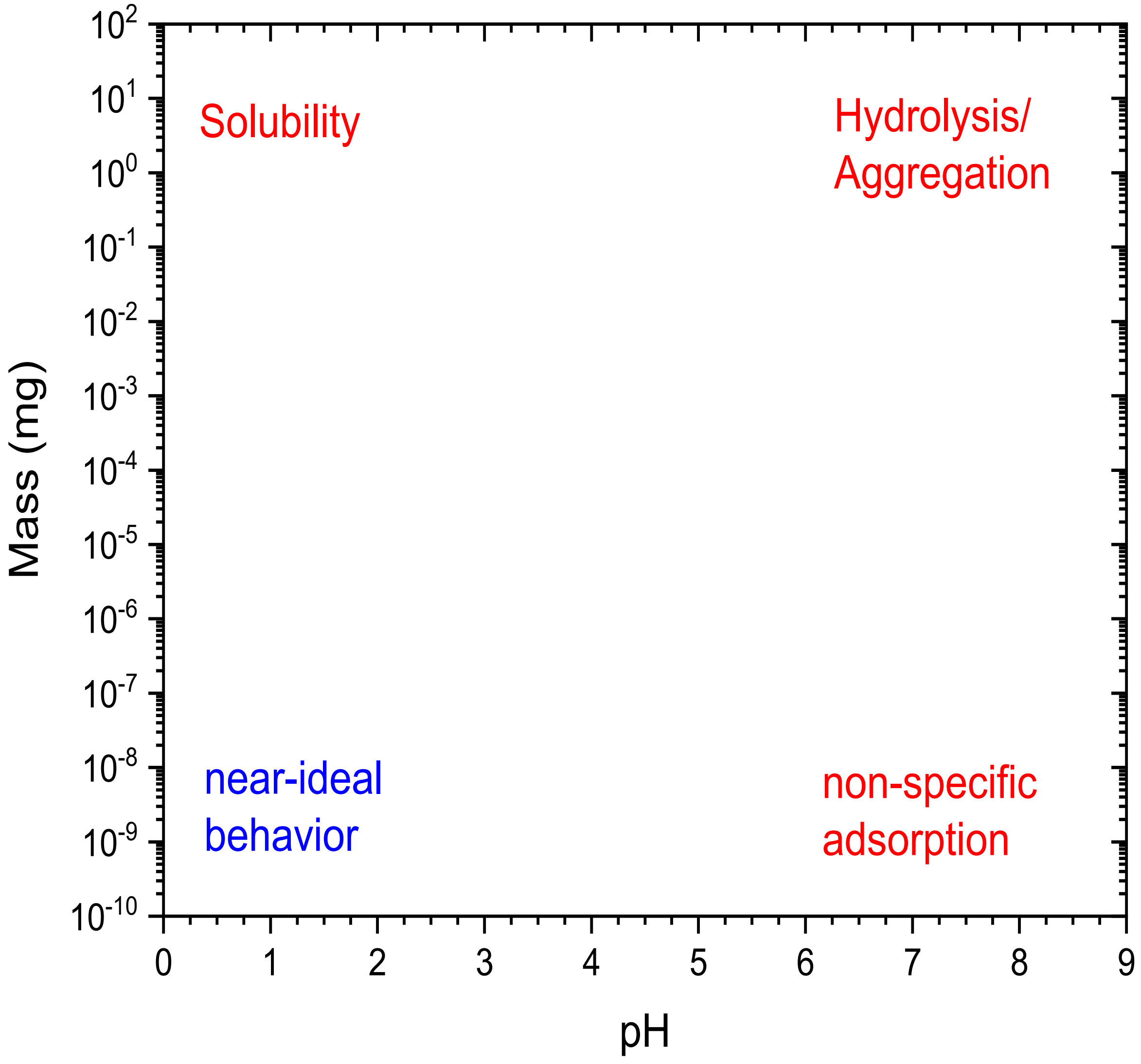
Alpha spectrometry, HPGe gamma, LSC, Na(Tl)I gamma, MP-AES, ~~ICP-MS~~

~~Cyclotron~~

~~Nuclear Reactor~~

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

Surrogates: Stable elements vs Radionuclides



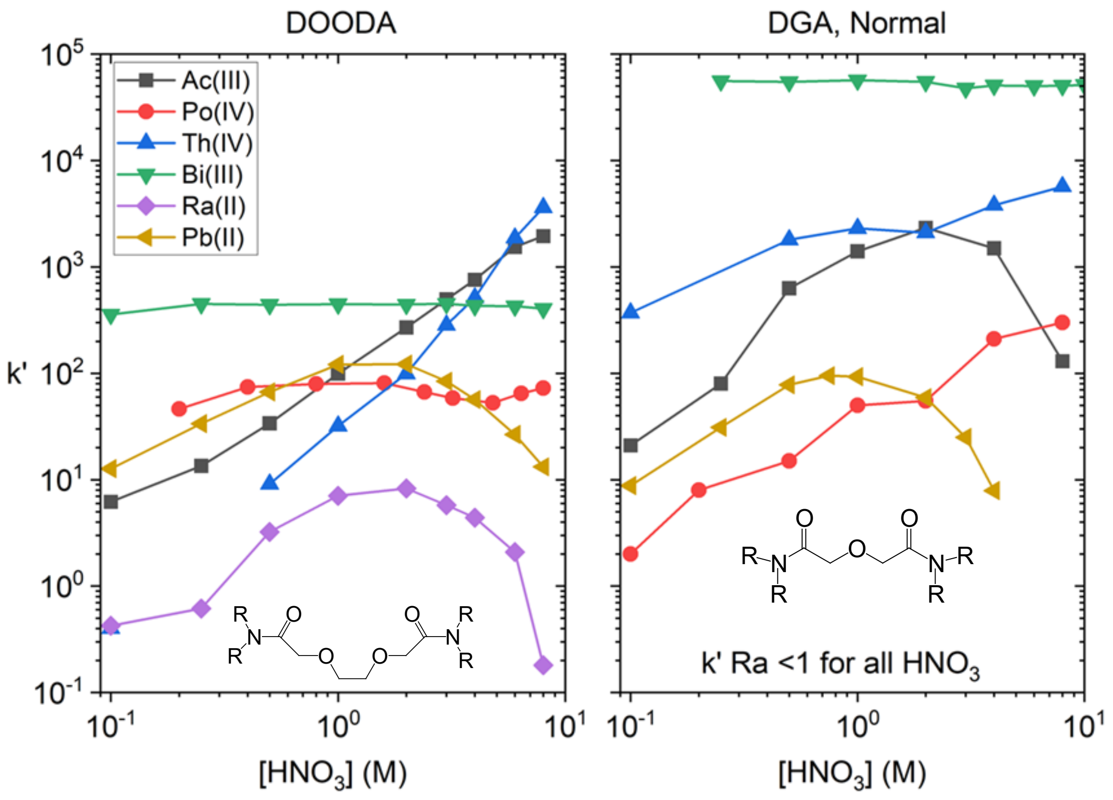
<u>Stable Elements (μg):</u>

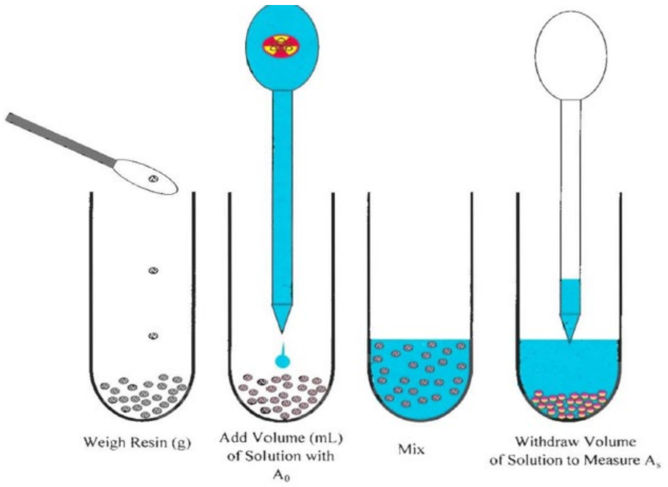
- Readily available
- Measure by AES/MS
- Reasonable Surrogates for elements without stable isotopes

<u>Radionuclides:</u>

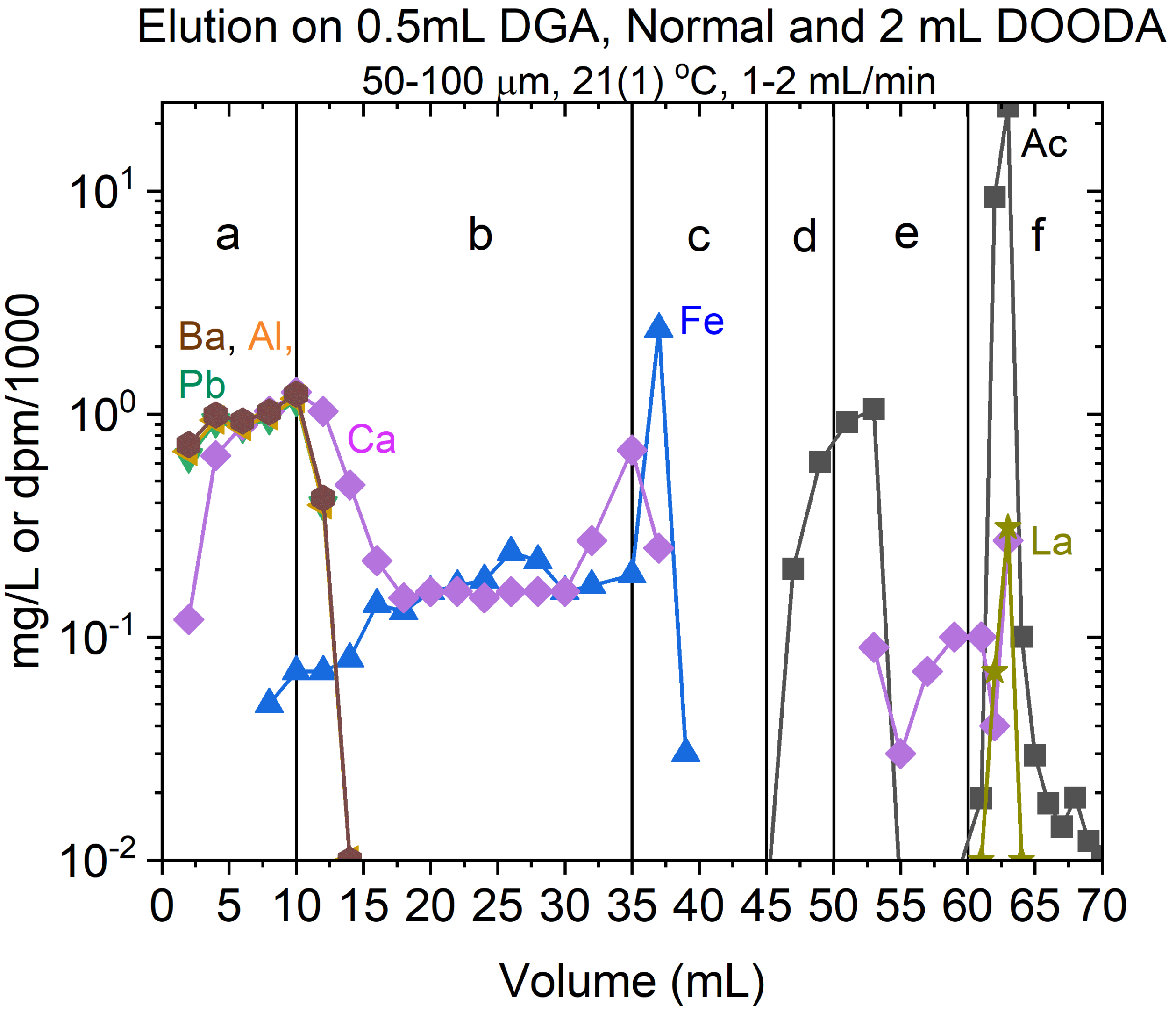
- Require special license
- Waste can be expensive (DIS)
- Can dope with long-lived isotopes to tune specific activity

When does mass help/hurt?





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

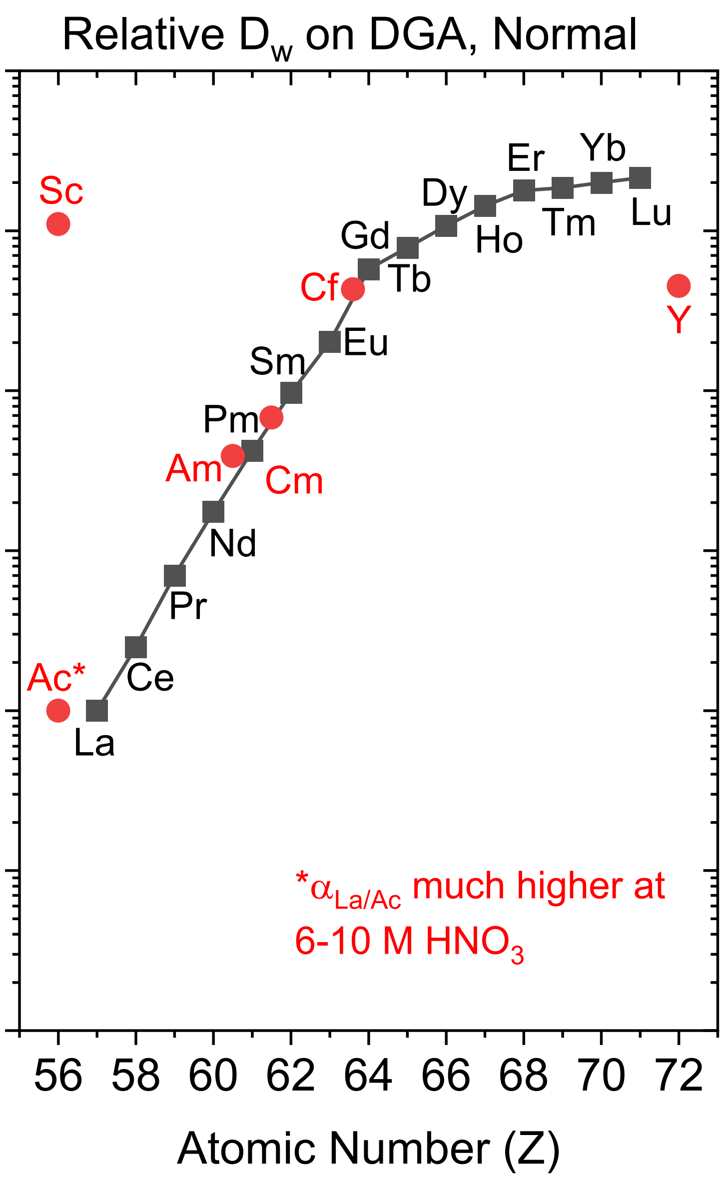


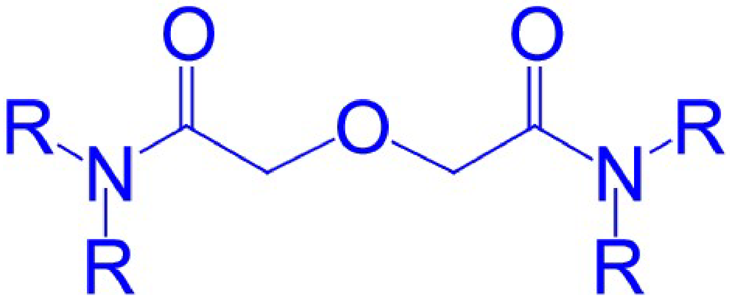
f: 10 mL 0.1M HCl

90% Ac-225

<<1% La, Th, Bi, Po

Rare Earths for Minor Actinides

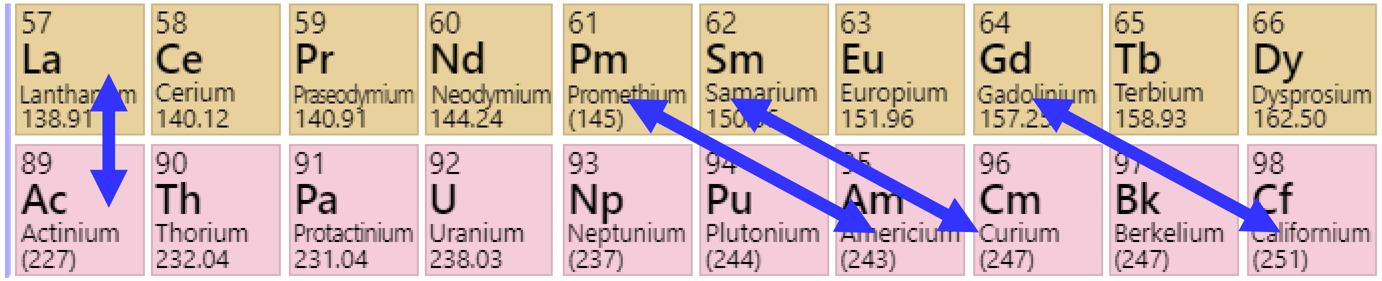




R = n-octyl or 2-ethyl-1-hexyl

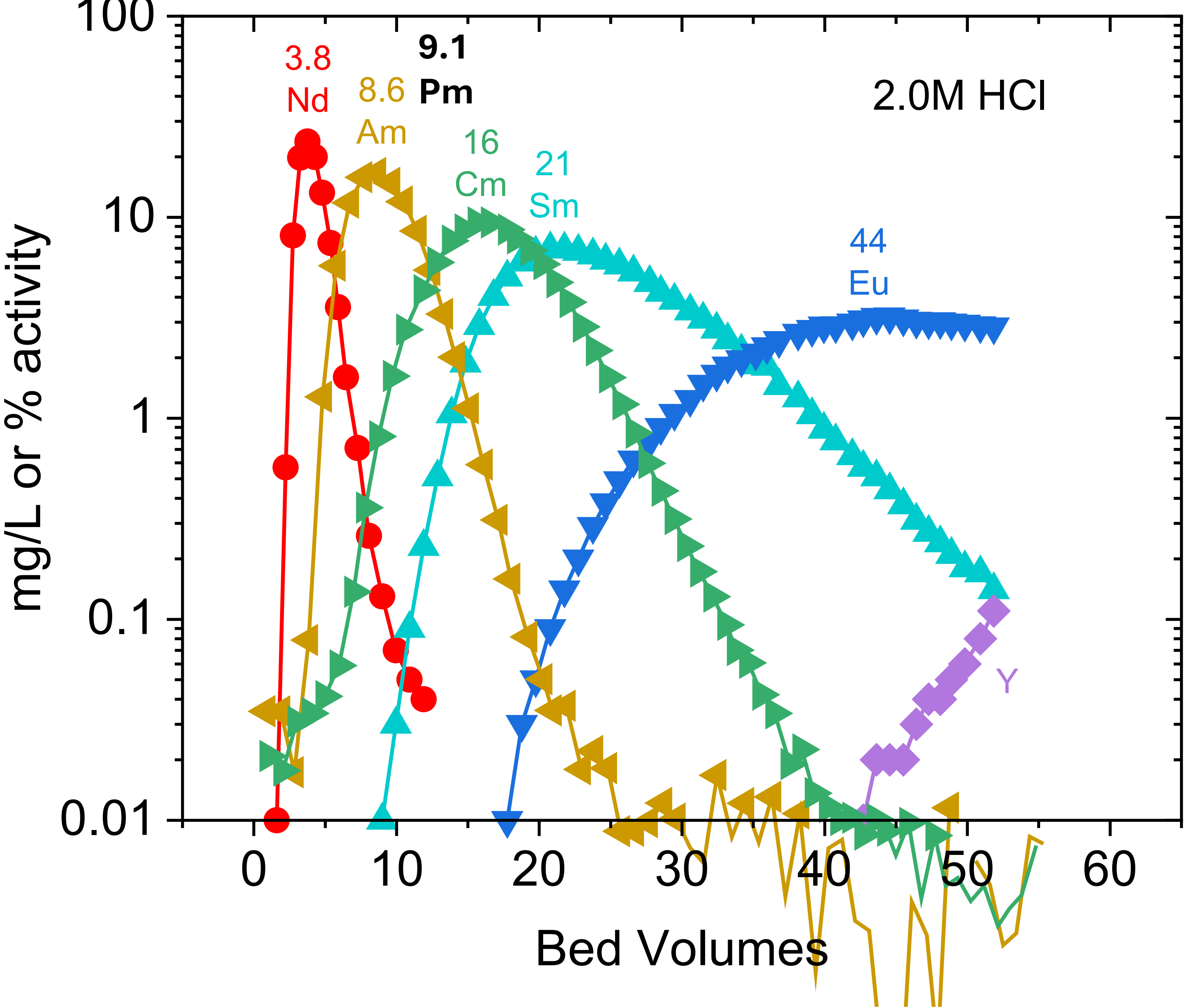
$M^{3+} + 3DGA + 3X^{-} \leftrightarrow M(DGA)_3X_3$

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



Elution on DGA, Normal

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



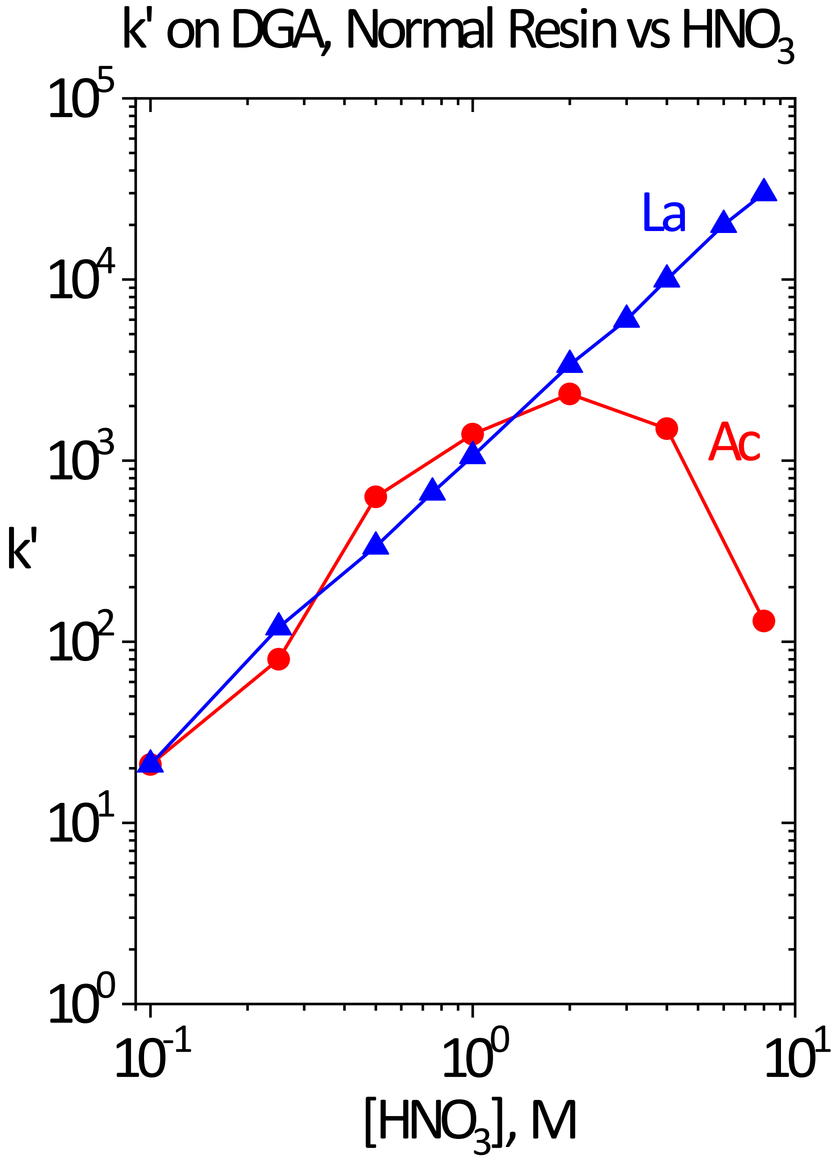
M^{3+}	Separation factor (M/Nd)	Predicted BV (Nd = 3.8)
Nd	1.0	3.8
Am	2.2	8.4
Pm	2.4	9.1
Cm	3.9	15
Sm	5.5	21

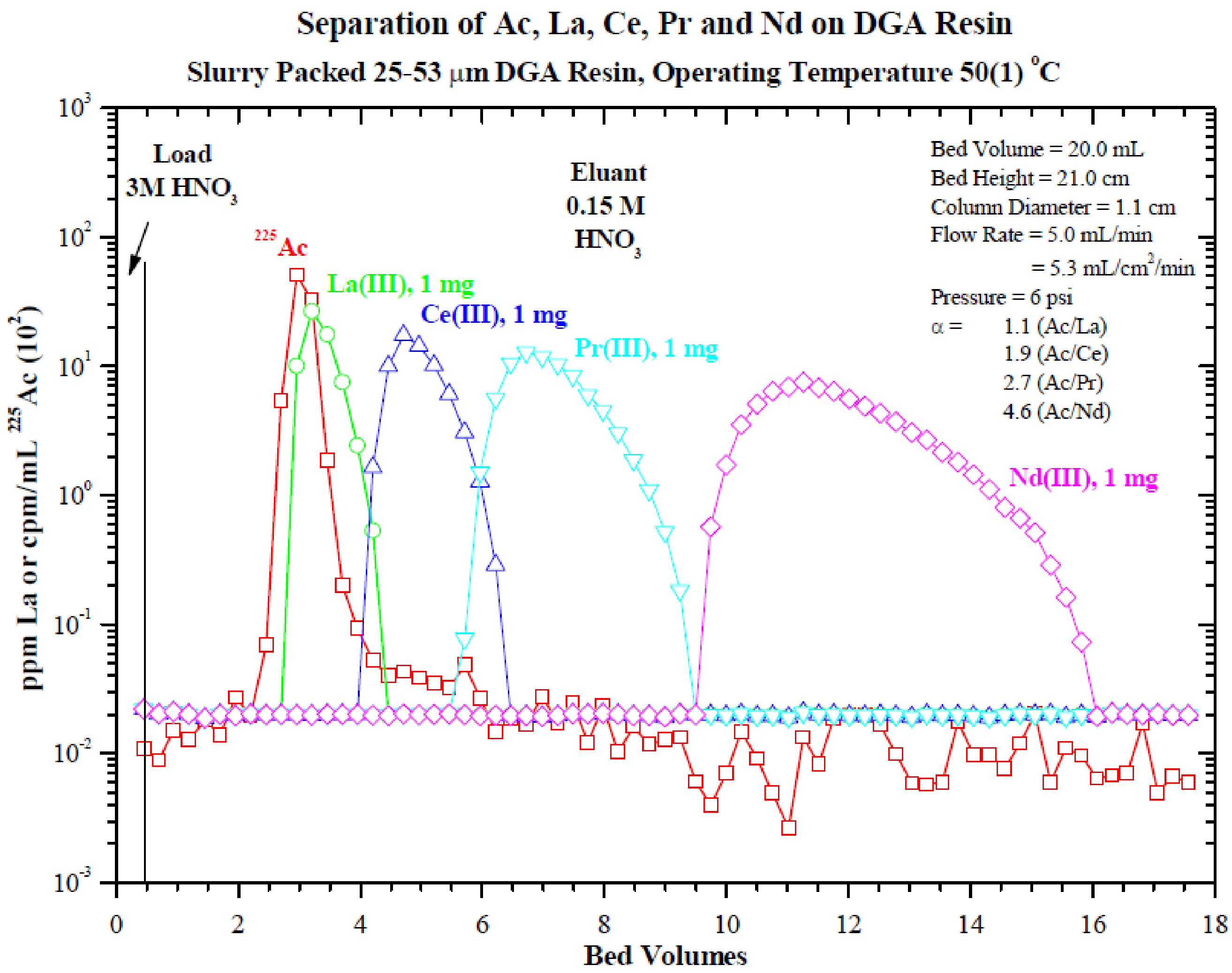
Nd/Sm bracket Am/Cm

^{147}Pm ←→ ^{241}Am

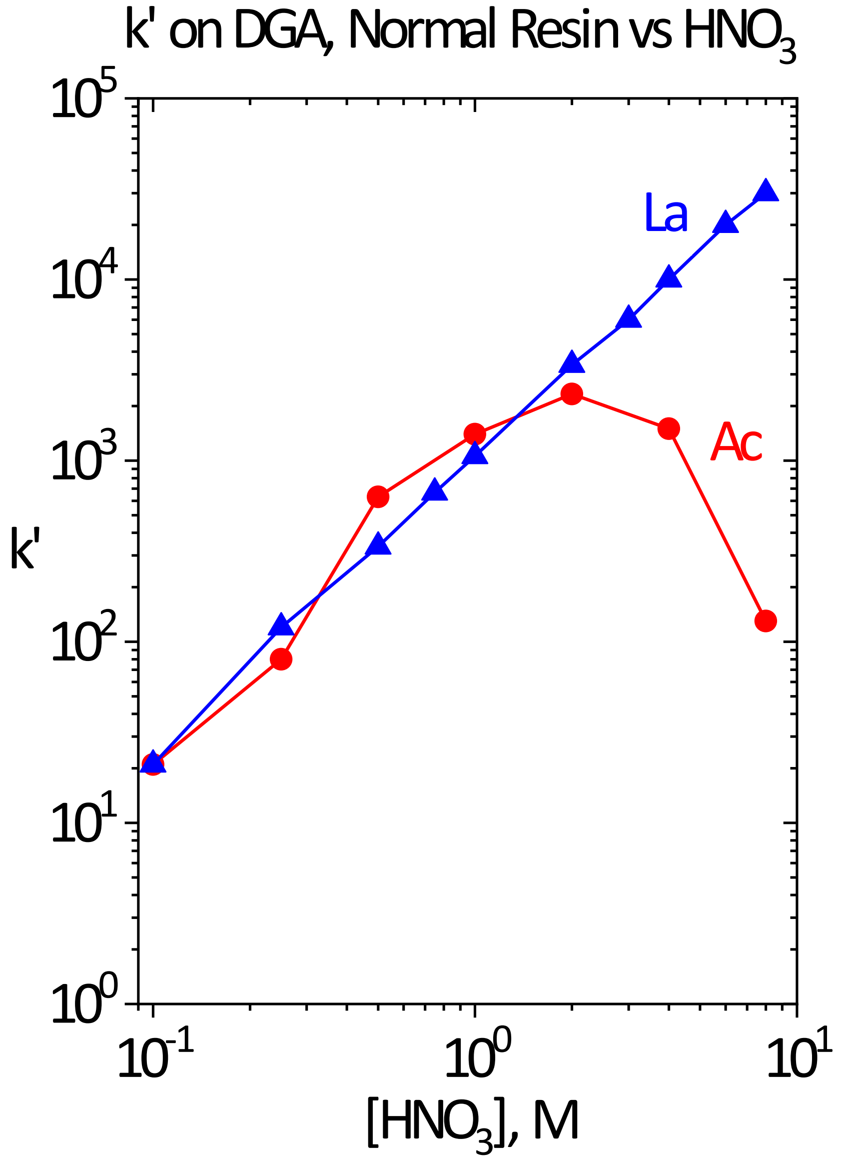
Sm → Cm

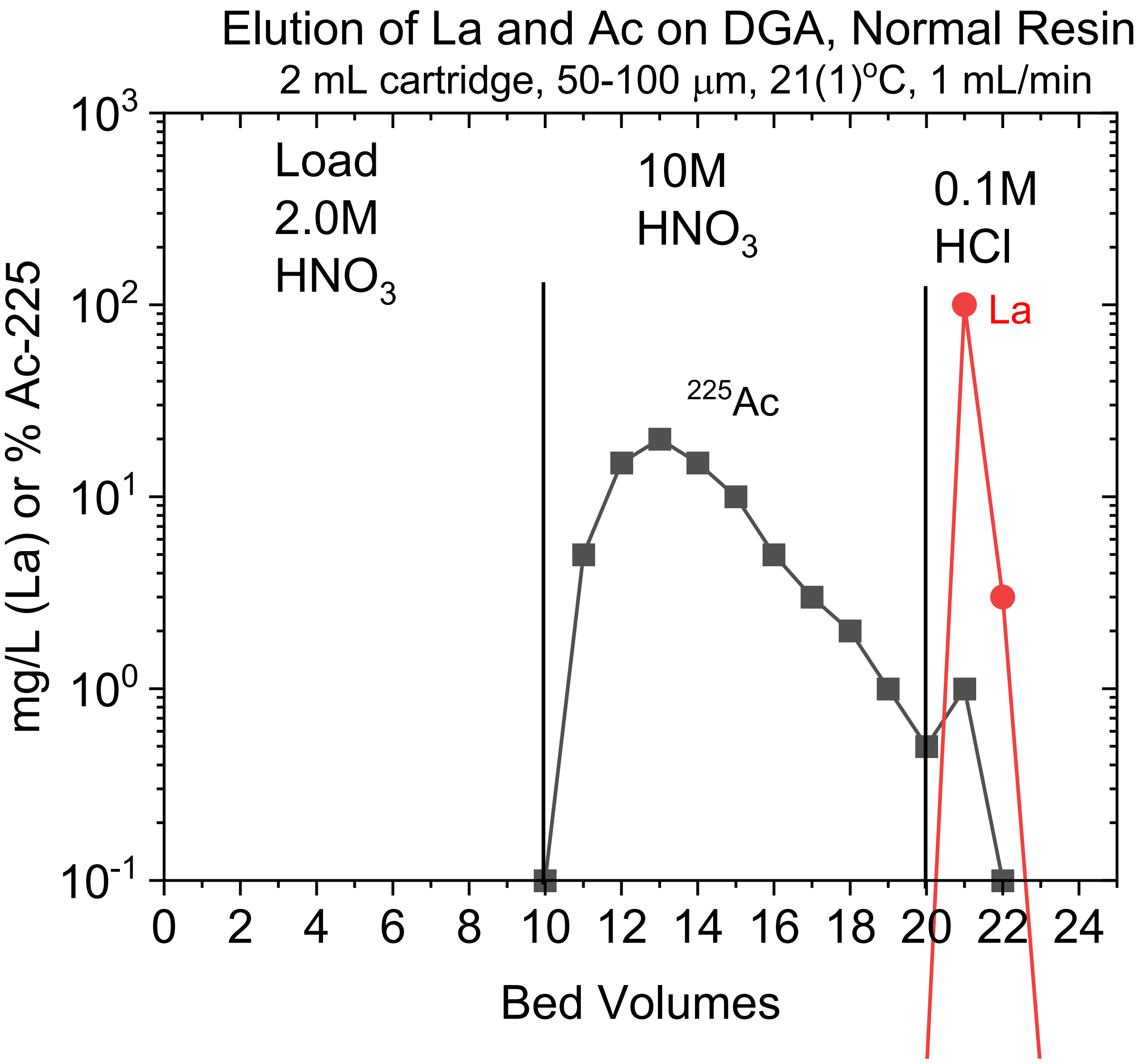
La for Ac-225 (DGA-dilute HNO_3)



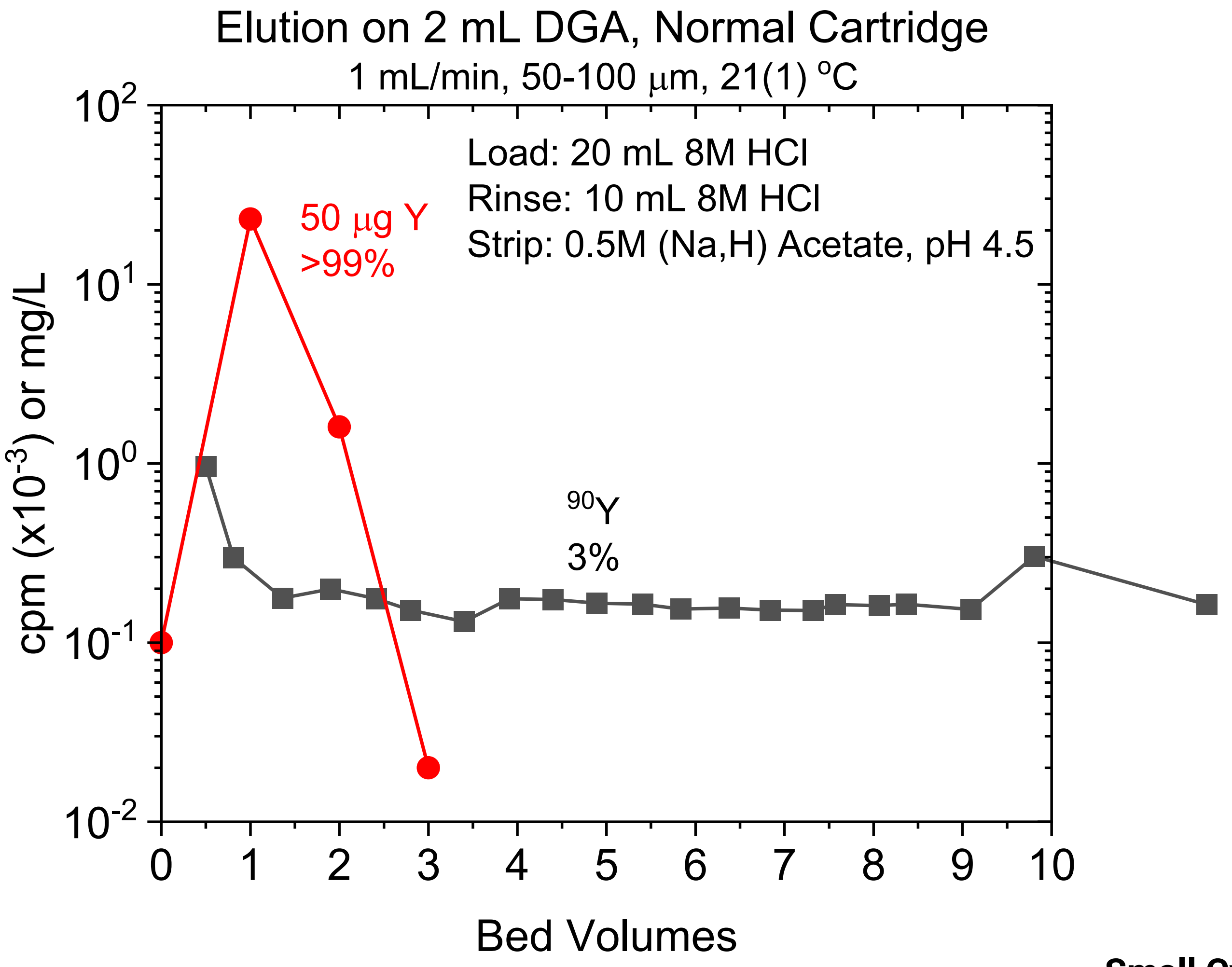


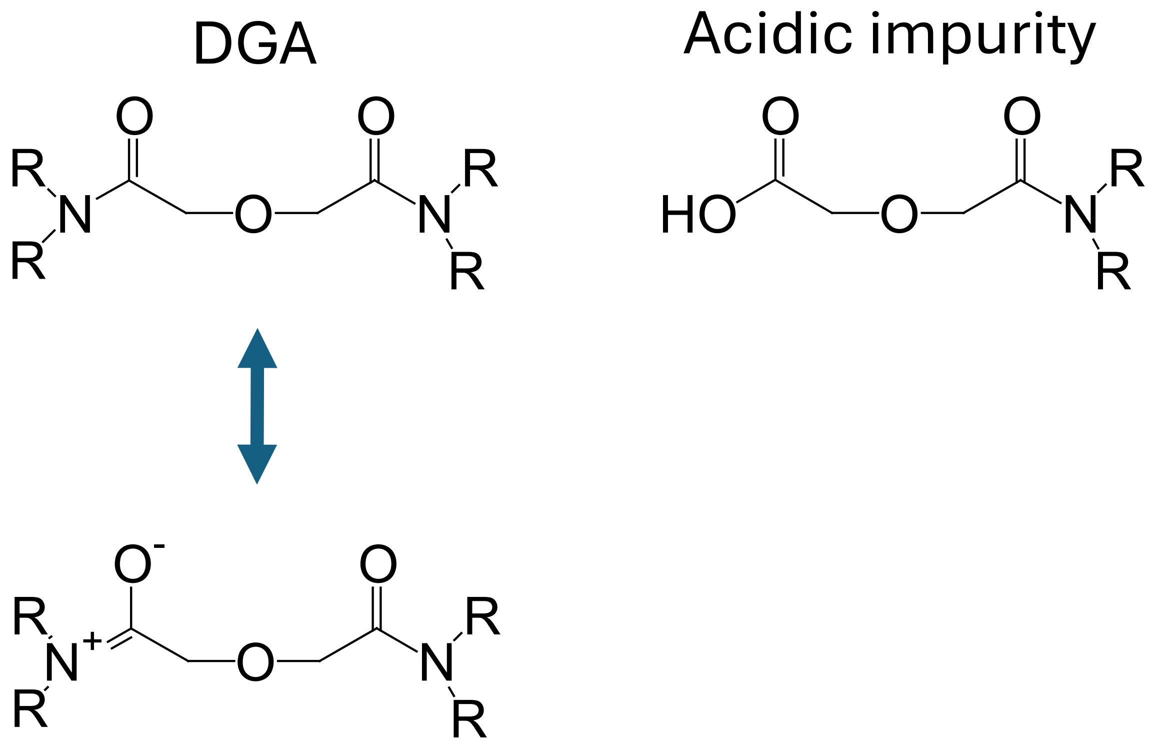
La for Ac-225 (DGA – 10M HNO_3)





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

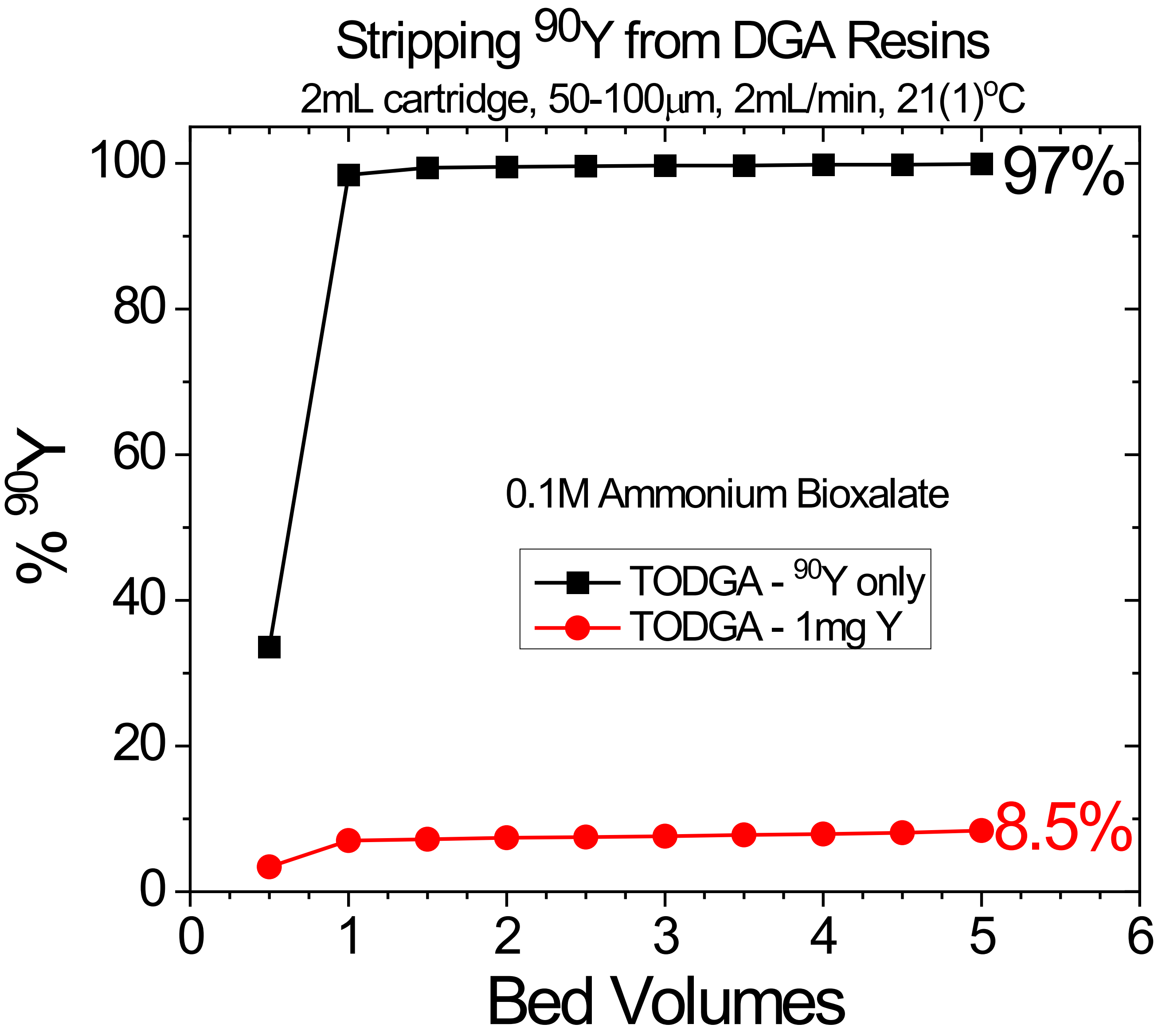




Yield for ^{225}Ac > 95%
Correlates with ionic potential of metal ion.

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

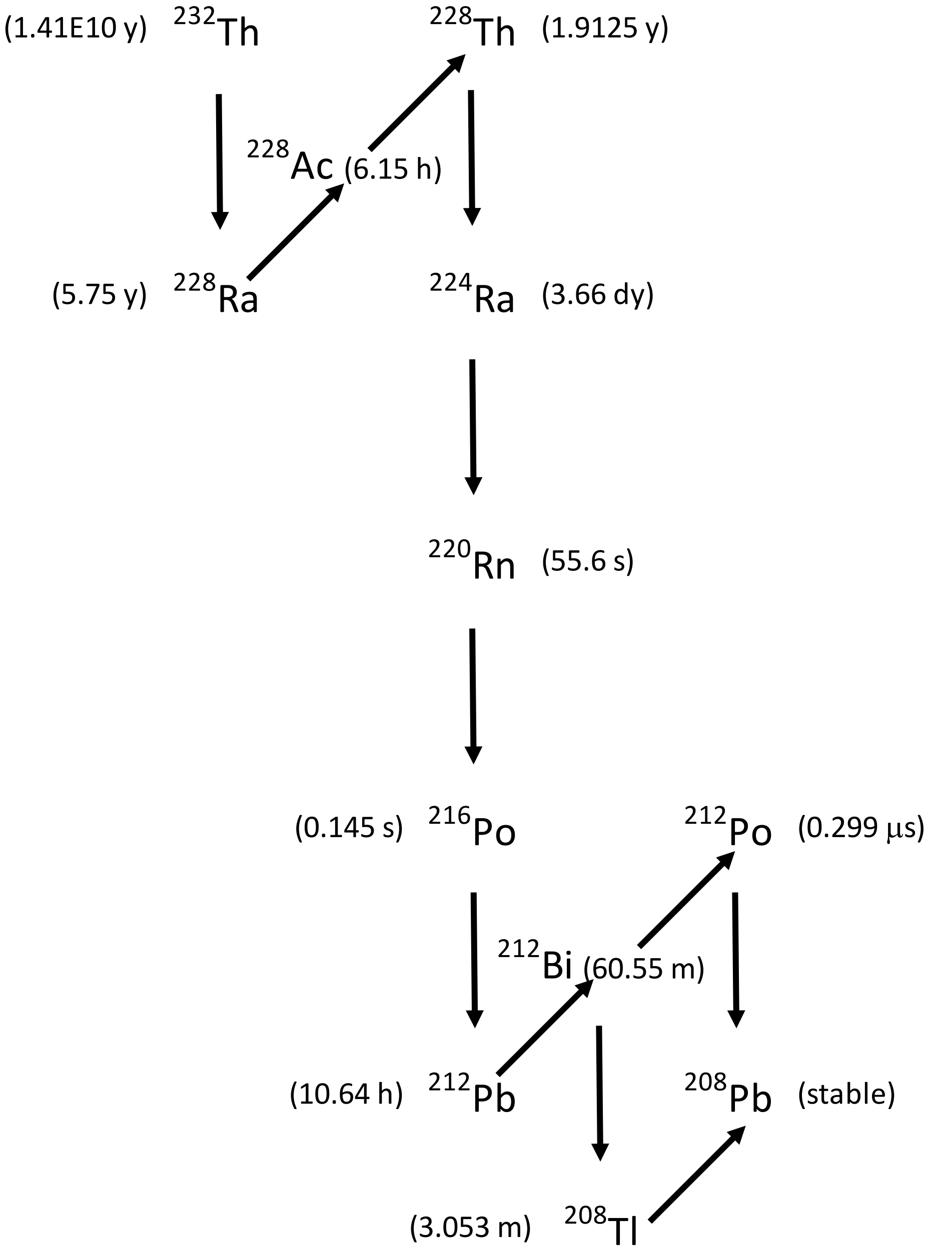
Rinse: 10 mL 8M HNO_3

Strip Y: 10 mL 0.1M ammonium bioxalate

Yttrium oxalate

$K_{sp} = 5.1 \times 10^{-30}$

Th-228 Decay Scheme and surrogate options



$^{228}Th \rightarrow {}^{227}Th + {}^{232}Th$ (**1.2 mg/mCi ^{228}Th**)

$^{224}Ra \rightarrow {}^{223}Ra$ or ^{133}Ba or stable Ba

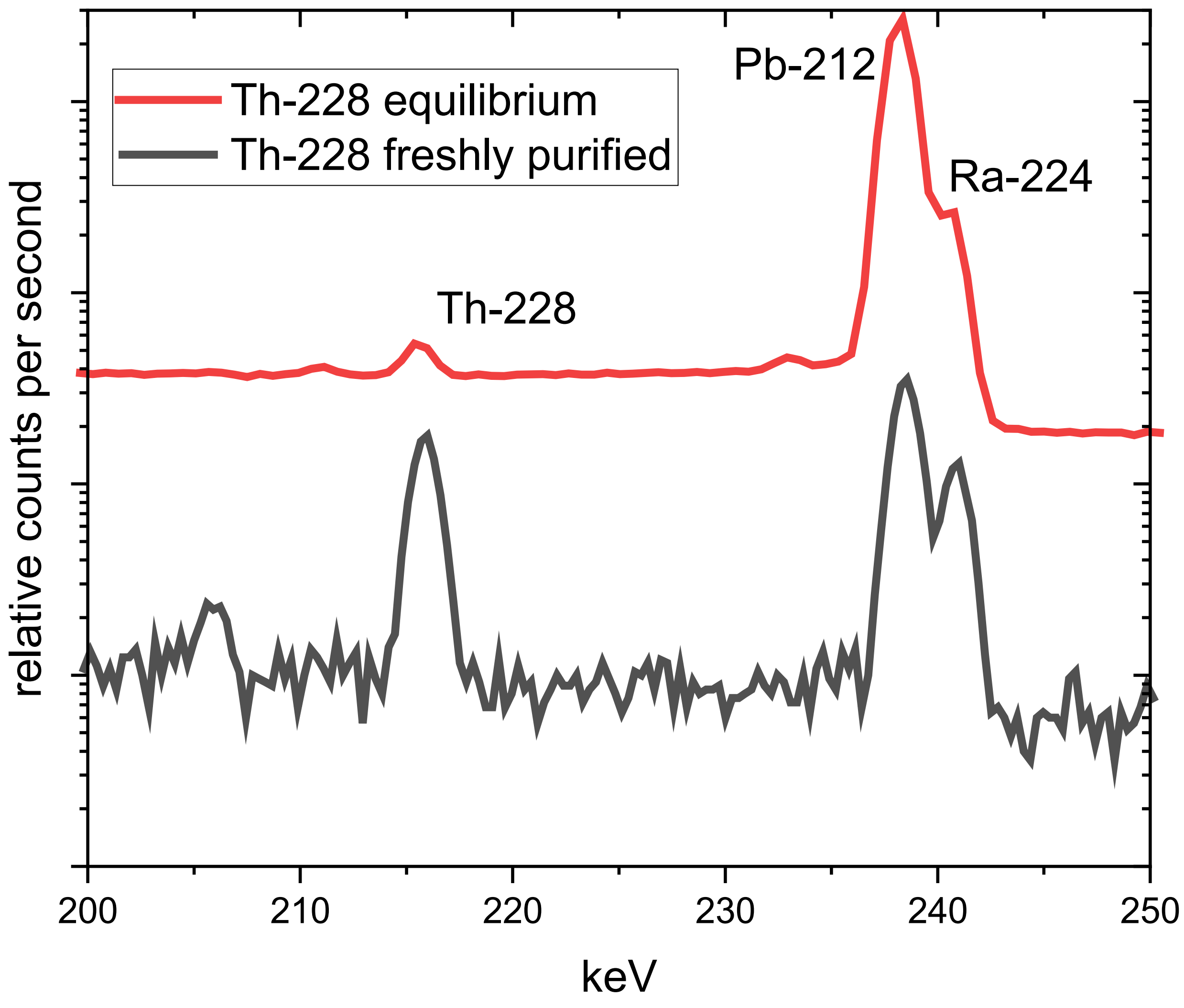
$^{216/212}Po \rightarrow {}^{210}Po$

$^{212}Pb \rightarrow {}^{203}Pb$ or stable Pb

$^{212}Bi \rightarrow {}^{210}Bi$, ^{207}Bi, or stable Bi

$^{208}Tl \rightarrow {}^{204}Tl$ or Stable Tl

Th-228 Decay Scheme and surrogate options



^{228}Th 215.985 keV (0.246%)

^{224}Ra 240.986 keV (4.12%)

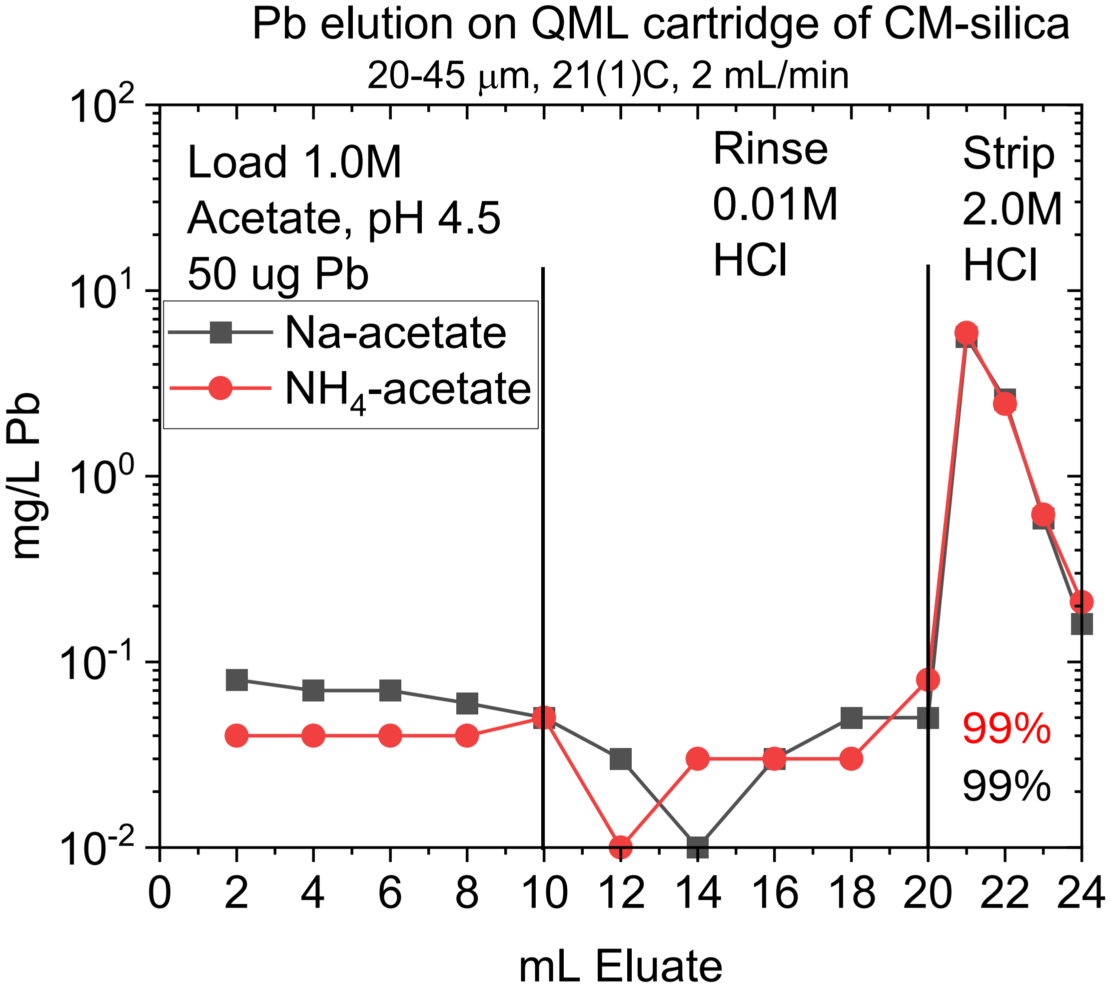
^{212}Pb 238.632 keV (43.6%)

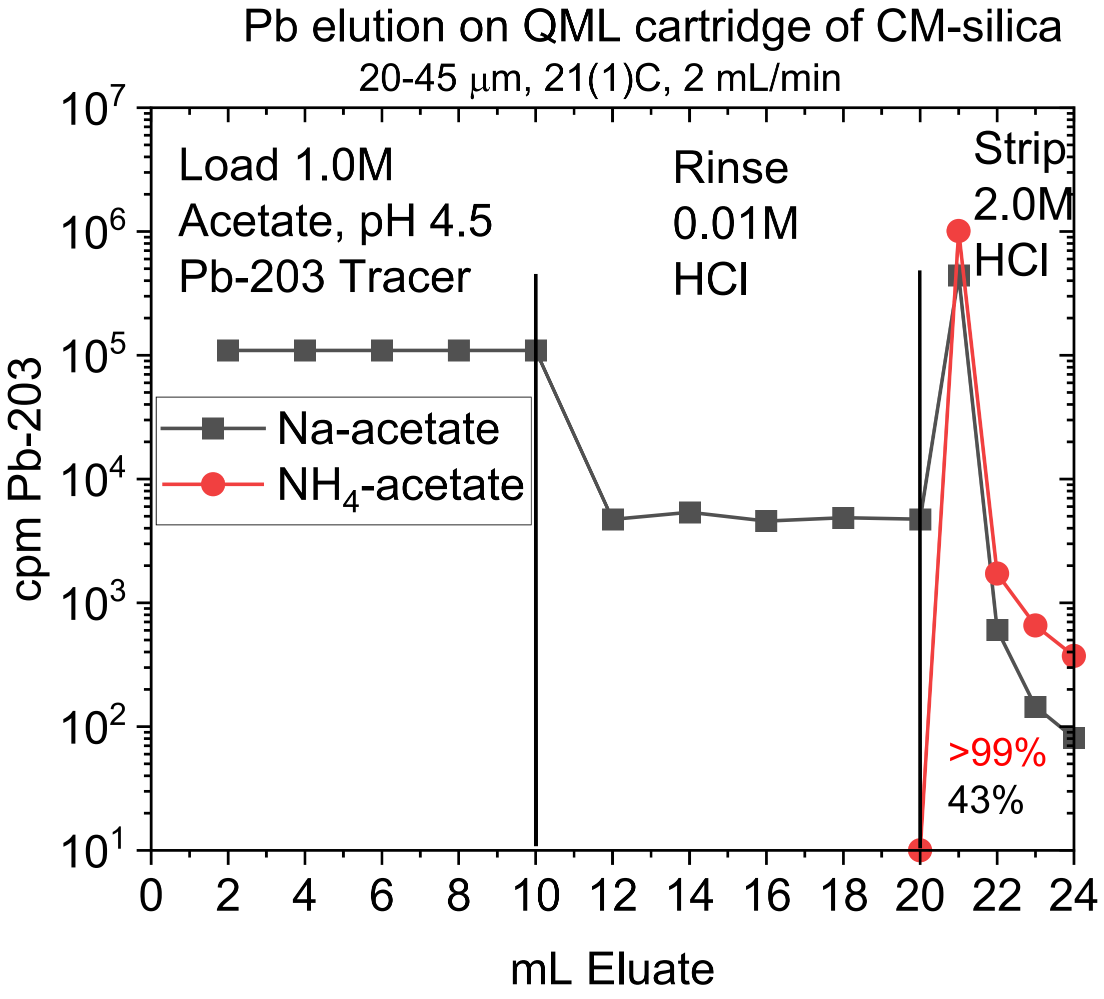
^{212}Bi 727.330 keV (6.65%)

^{208}Tl 510.75 keV (22.5%)
583.187 keV (85.0%)
2614.511 keV (99.775%)

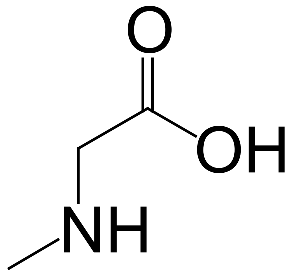
http://www.lnhb.fr/home/nuclear-data/nuclear-data-table/

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



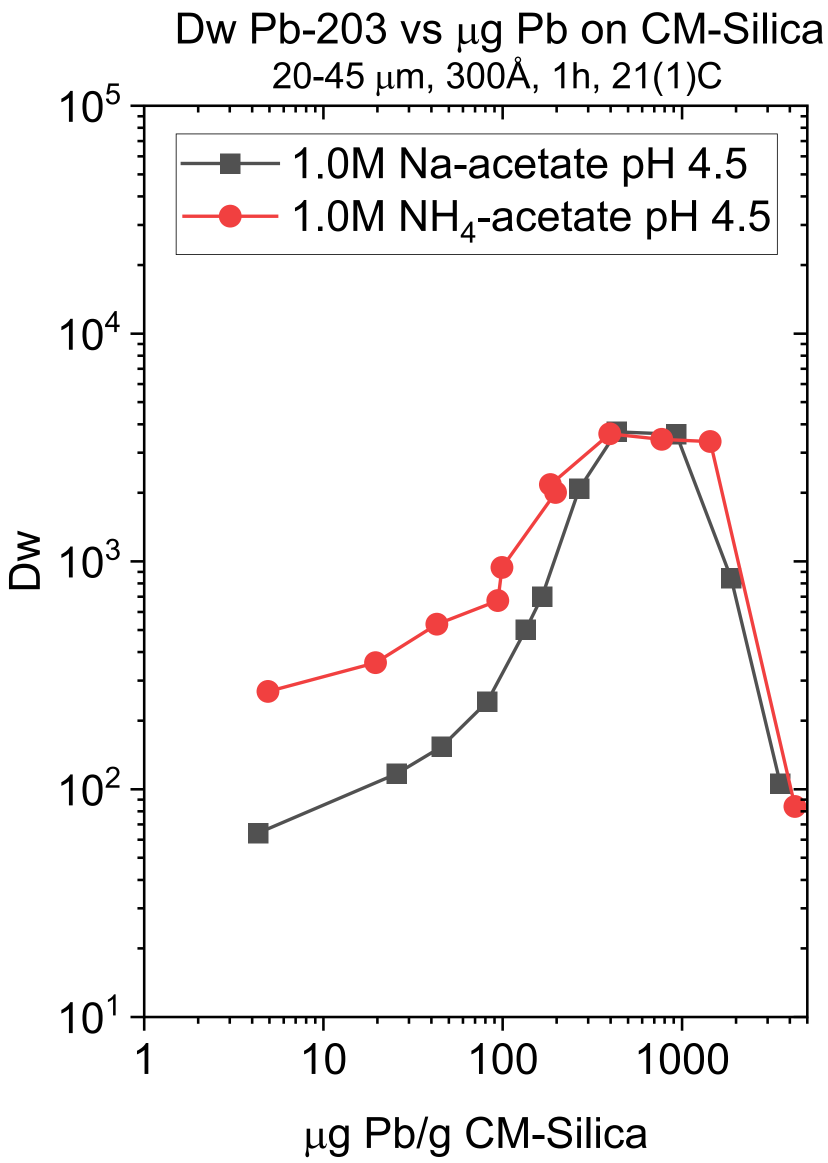


Weak cation exchange silica.
NH_4^+ vs Na^+ to reduce impact on stable element measurements by AES.



pKa ~ 2

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

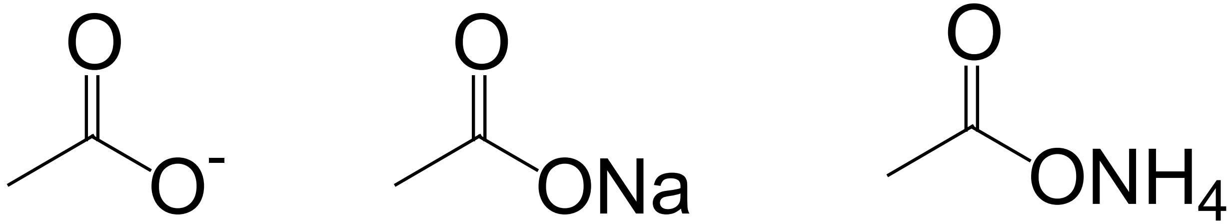


Some difference expected between Na^+ and NH_4^+ based on competition for IX sites.

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

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

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



Dw proportional to µg Pb until resin saturation.

Mechanism unclear???

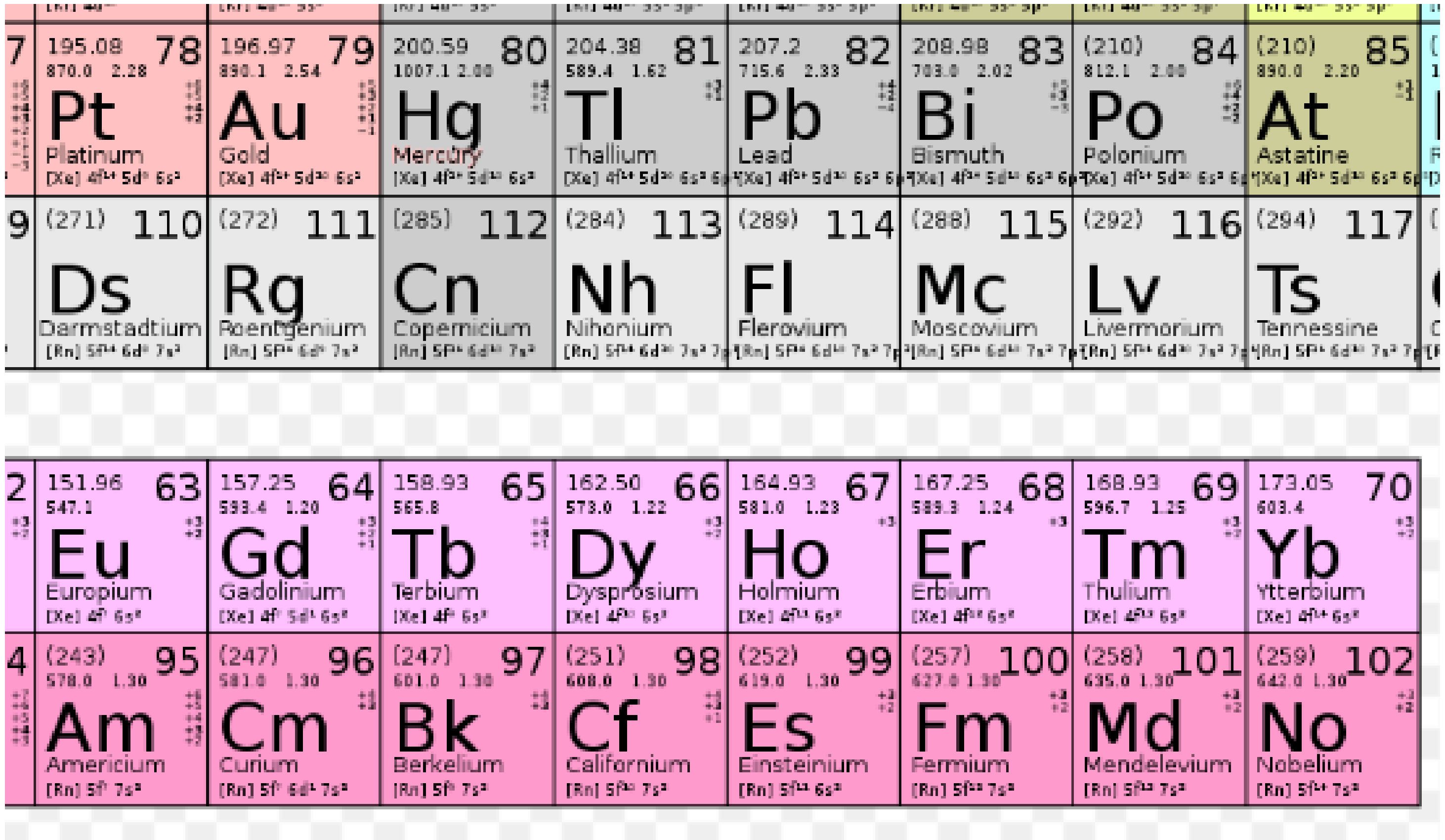
Questions???

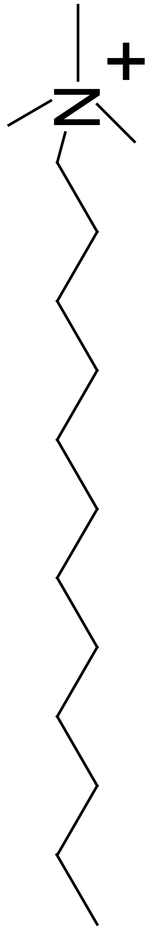
Answers???

dmcalister@eichrom.com

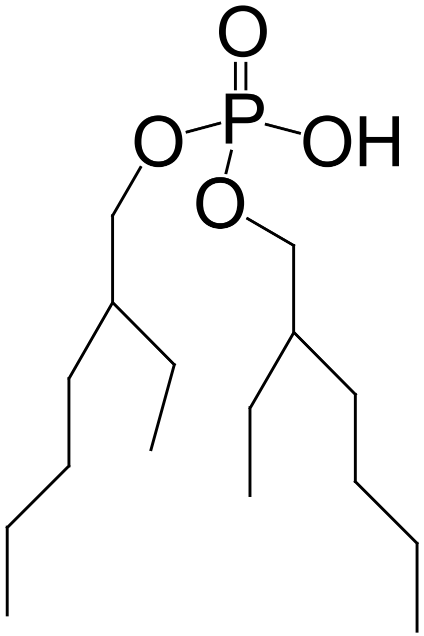
No other options

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.

Group	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)