

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

The logo for Eichrom Technologies, featuring the word "eichrom" in a bold, lowercase, sans-serif font with a registered trademark symbol, and the word "TECHNOLOGIES" in a smaller, uppercase, sans-serif font below it. The logo is set against a dark blue background.

eichrom[®]
TECHNOLOGIES

A GCI COMPANY

A promotional banner for ACS Spring 2024. The top part features the text "ACS SPRING 2024" in large, bold, blue, uppercase letters. Below it, "MARCH 17-21 | NEW ORLEANS, LA" is written in a smaller, blue, uppercase font. The bottom part of the banner has a dark blue background with the tagline "Many Flavors of Chemistry" in a white, cursive script font.

ACS SPRING 2024

MARCH 17-21 | NEW ORLEANS, LA

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

78	79	80	81	82	83	(210)	84	(210)	85
195.08 870.0 2.28	196.97 890.1 2.54	200.59 1007.1 2.00	204.38 589.4 1.62	207.2 715.6 2.33	208.98 703.0 2.02	(210) 812.1 2.00	(210) 890.0 2.20	(210) 890.0 2.20	(210) 890.0 2.20
Pt Platinum [Xe] 4f ¹⁴ 5d ⁹ 6s ²	Au Gold [Xe] 4f ¹⁴ 5d ¹⁰ 6s ²	Hg Mercury [Xe] 4f ¹⁴ 5d ¹⁰ 6s ²	Tl Thallium [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	Pb Lead [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	Bi Bismuth [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	Po Polonium [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	At Astatine [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	Po Polonium [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	At Astatine [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵
(271)	(272)	(285)	(284)	(289)	(288)	(292)	(294)	(294)	(294)
110	111	112	113	114	115	116	117	118	119
Ds Darmstadtium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ²	Rg Roentgenium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ²	Cn Copernicium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ²	Nh Nihonium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	Fl Flerovium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	Mc Moscovium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ³	Lv Livermorium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	Ts Tennessine [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵	Og Oganesson [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶	Uue Ununennium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶

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~~

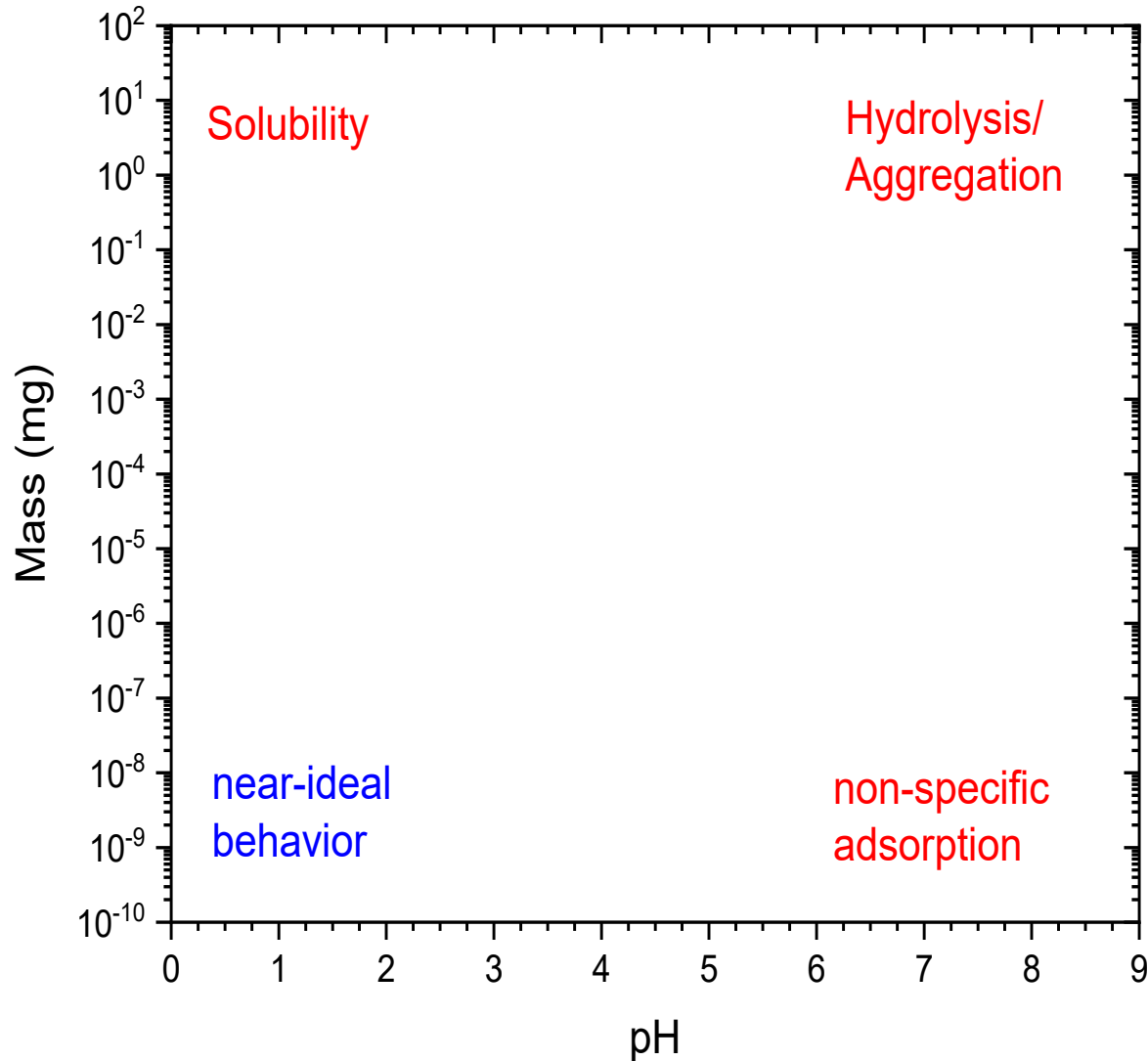
~~Cyclotron~~

Radiol isotopes may be:
Unavailable

~~Nuclear Reactor~~

Expensive
Short-lived
Complex decay scheme
(ALARA)

Surrogates: Stable elements vs Radionuclides



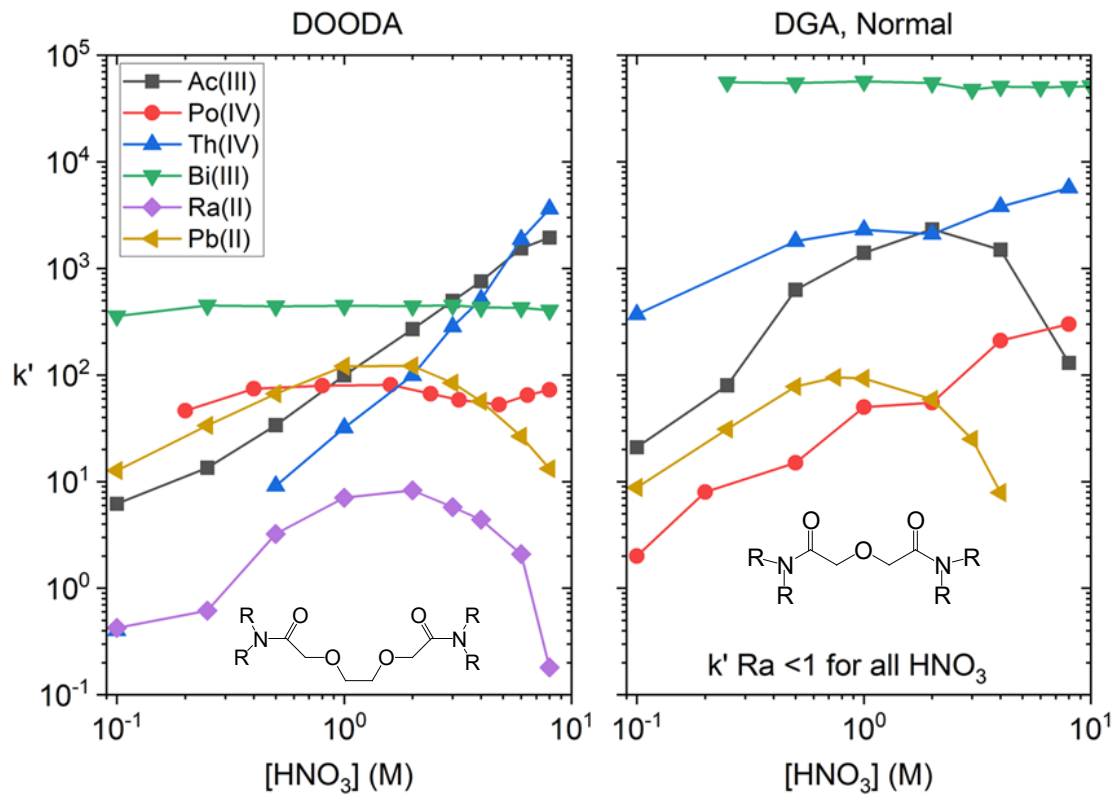
Stable Elements (μg):

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

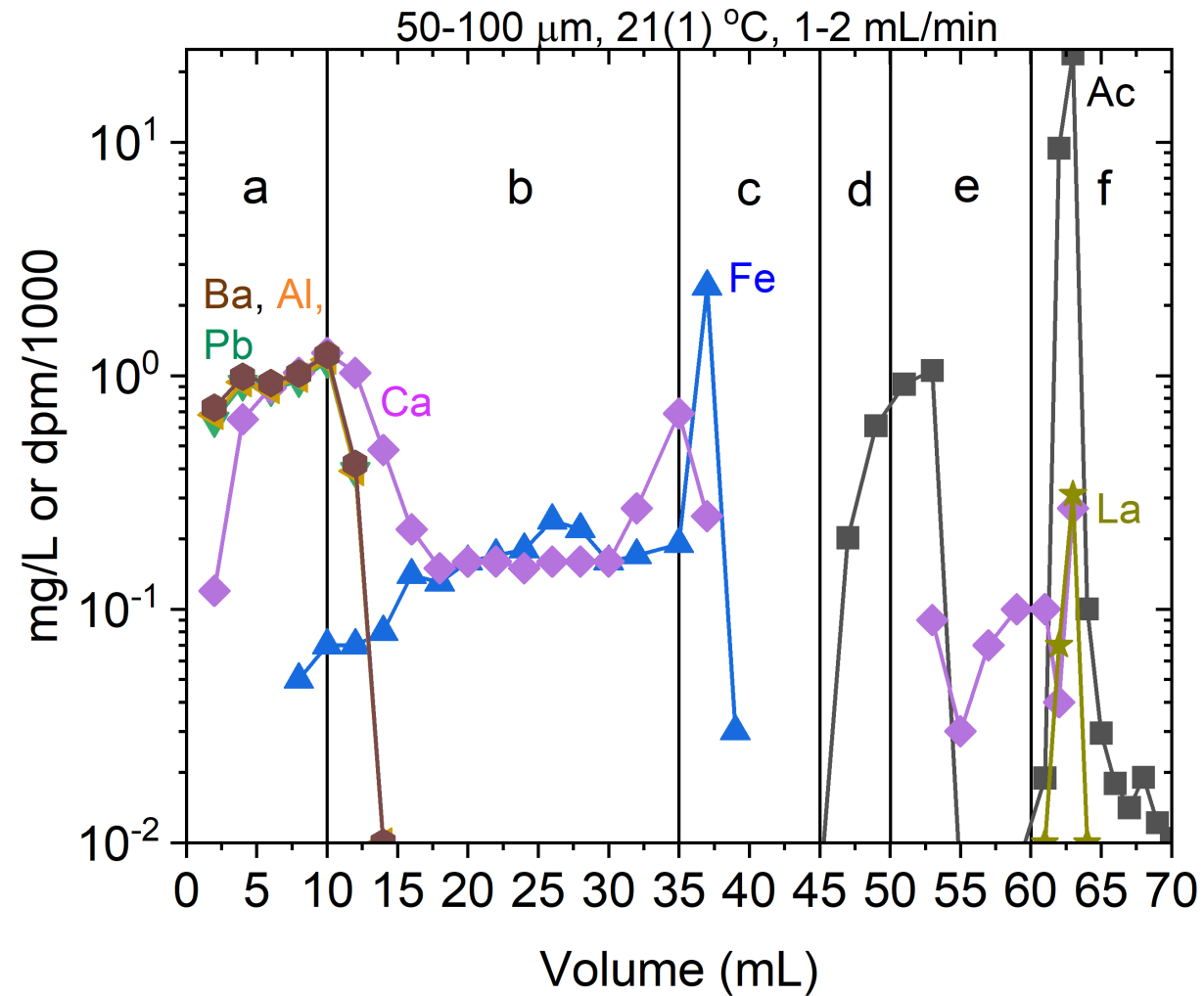
Radionuclides:

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

When does mass help/hurt?



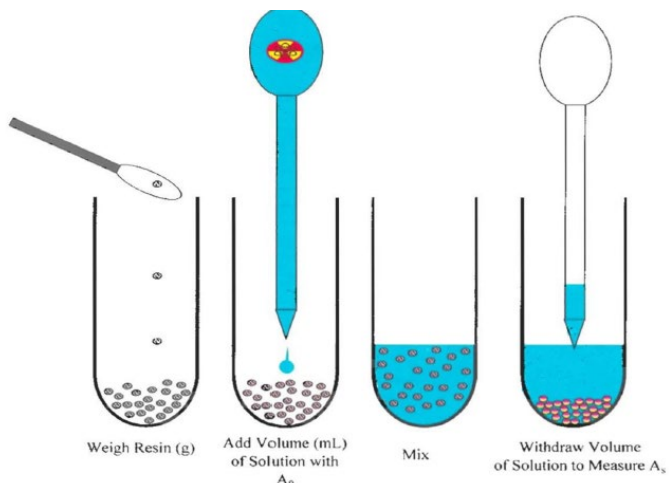
Elution on 0.5mL DGA, Normal and 2 mL DOODA



f: 10 mL 0.1M HCl

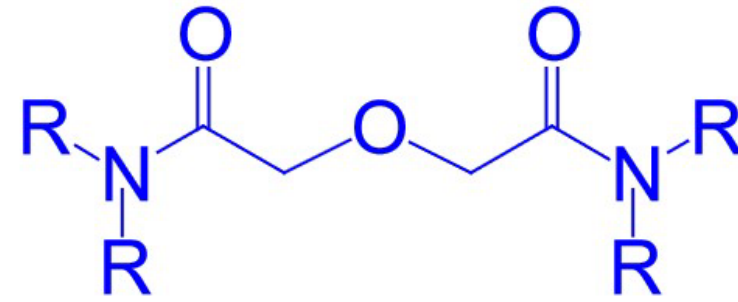
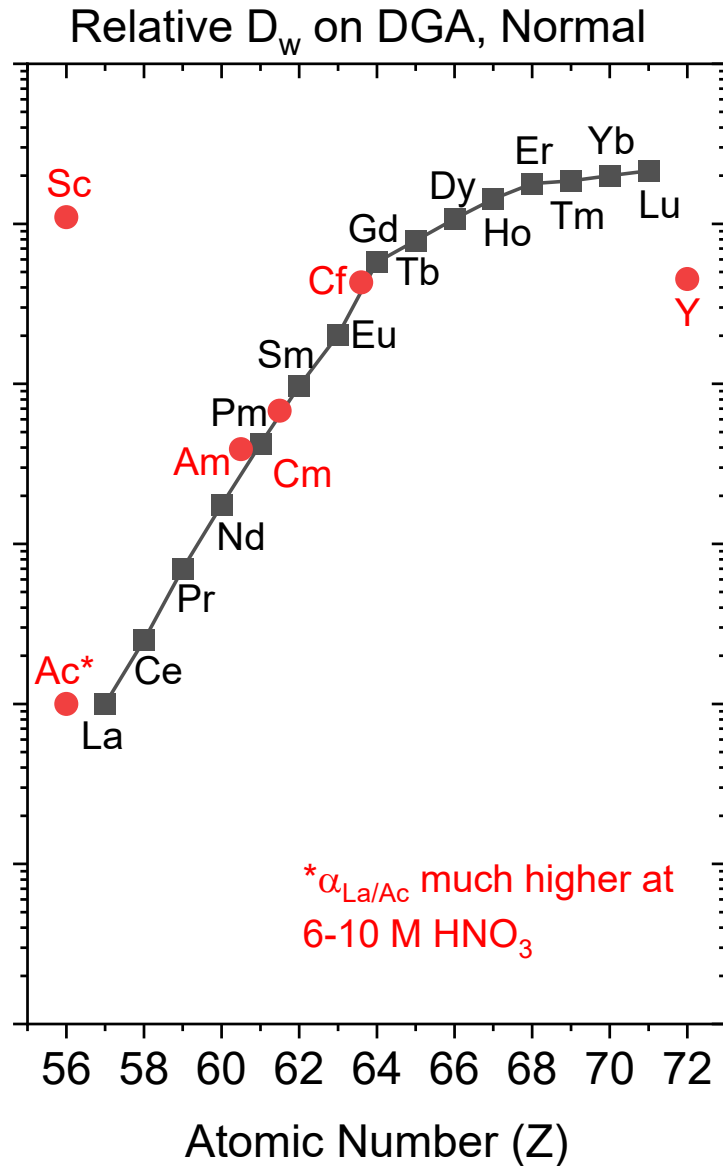
90% Ac-225

$\ll 1\%$ La, Th, Bi, Po

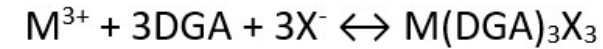


$$D_w = \frac{A_0 - A_s}{w(\text{g})} \bigg/ \frac{A_s}{v(\text{mL})}$$

Rare Earths for Minor Actinides



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

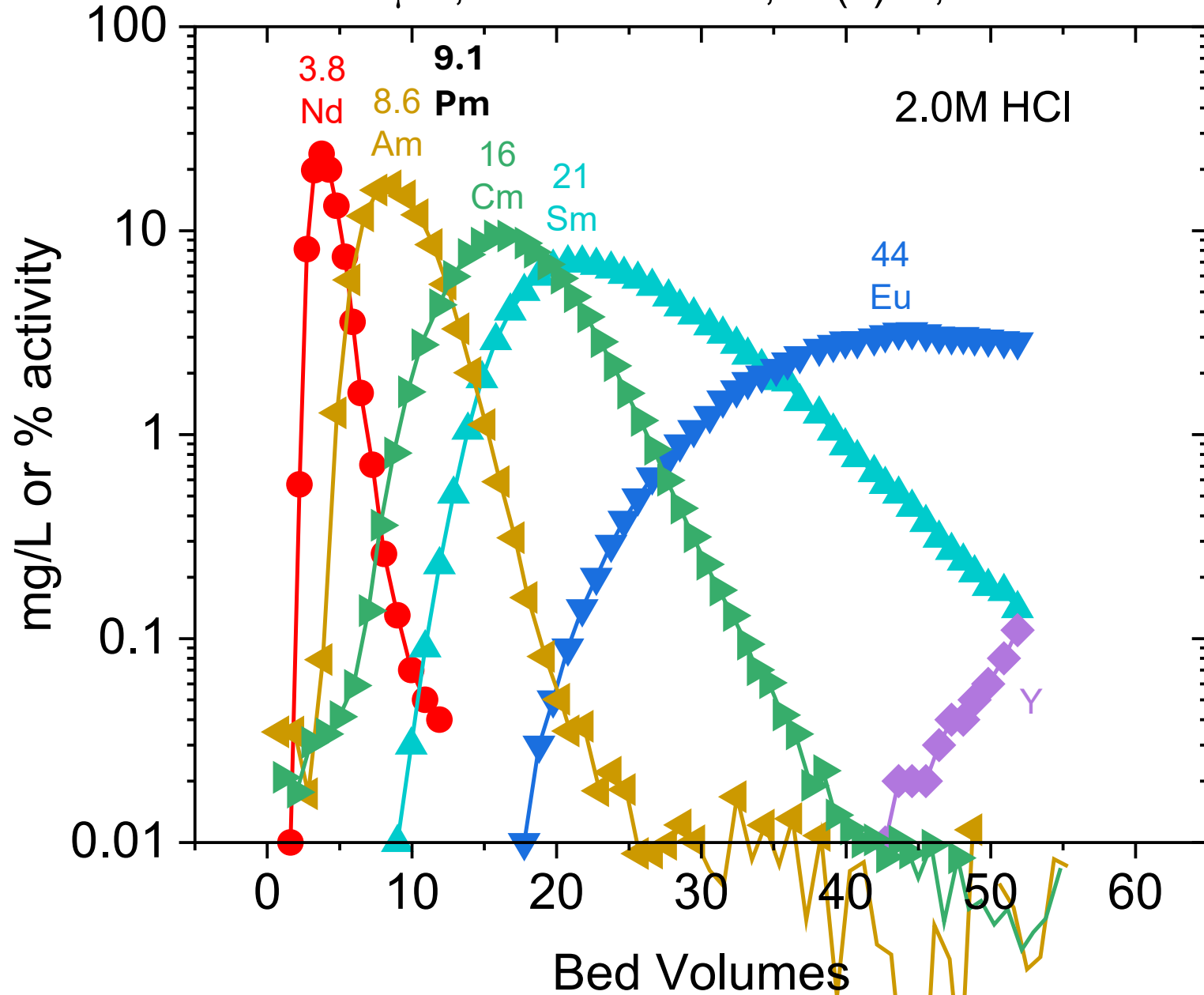


M = Ln(III) or An(III), X = NO_3^- or Cl^-

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) $^{\circ}\text{C}$, 3.5 mL/min



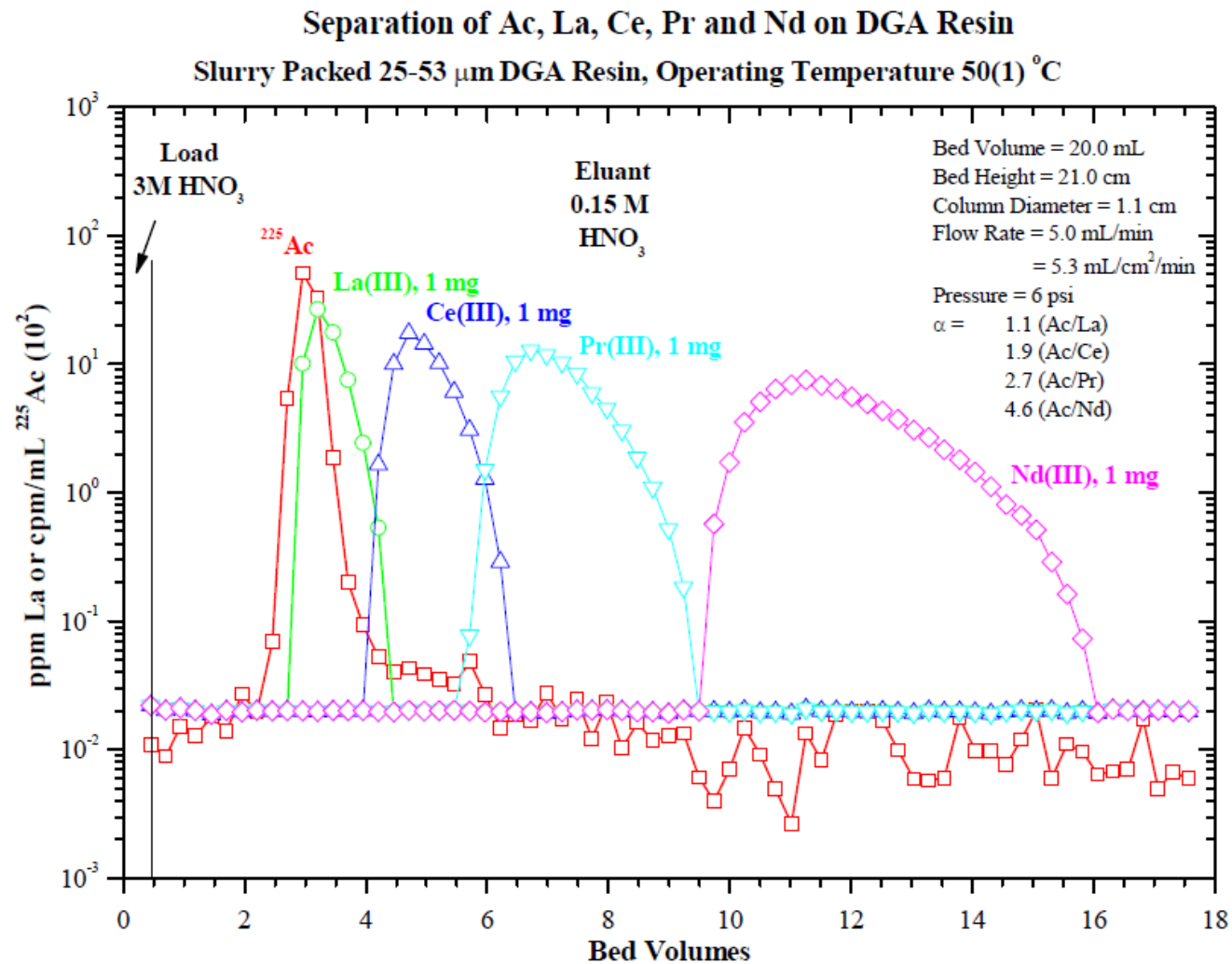
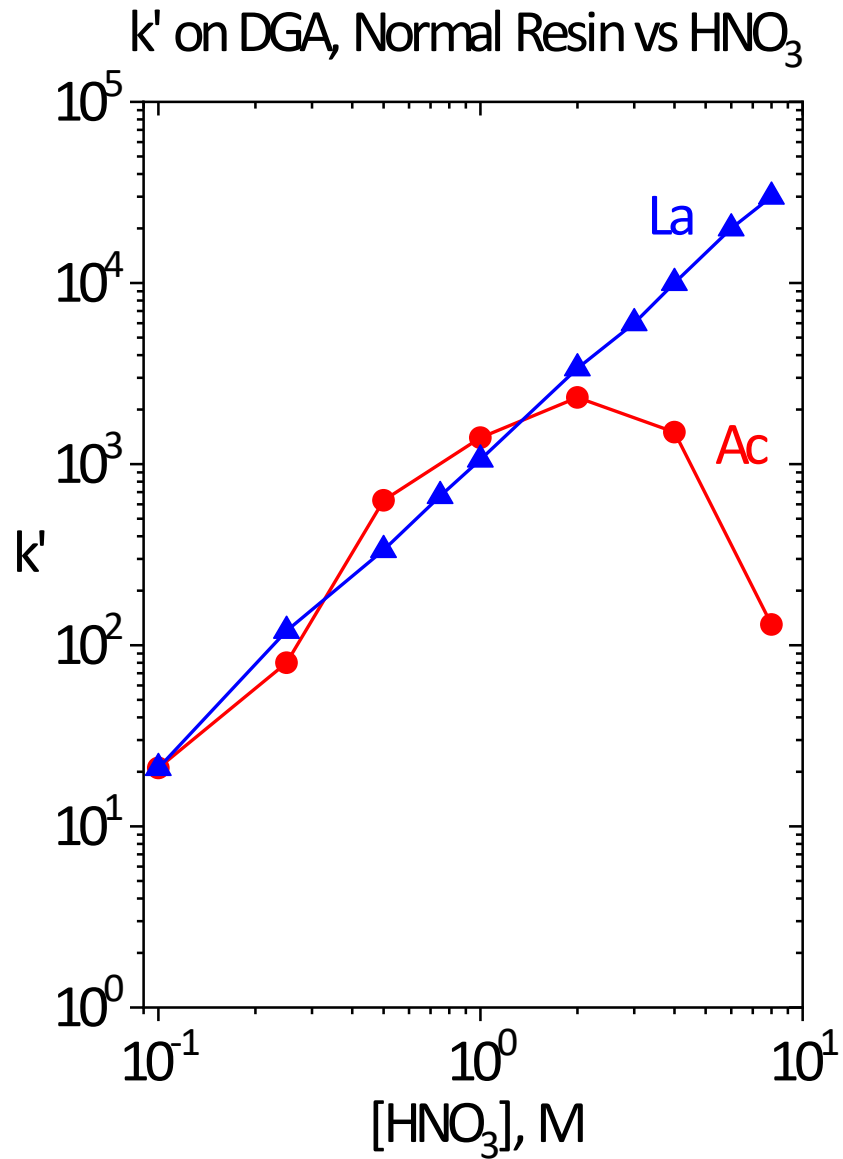
M^{3+}	Separation factor (M/Nd)	Predicted BV (Nd = 3.8)
Nd	1.0	3.8
Am	2.2	8.4
Pm	2.4	9.1
Cm	3.9	15
Sm	5.5	21

Nd/Sm bracket Am/Cm

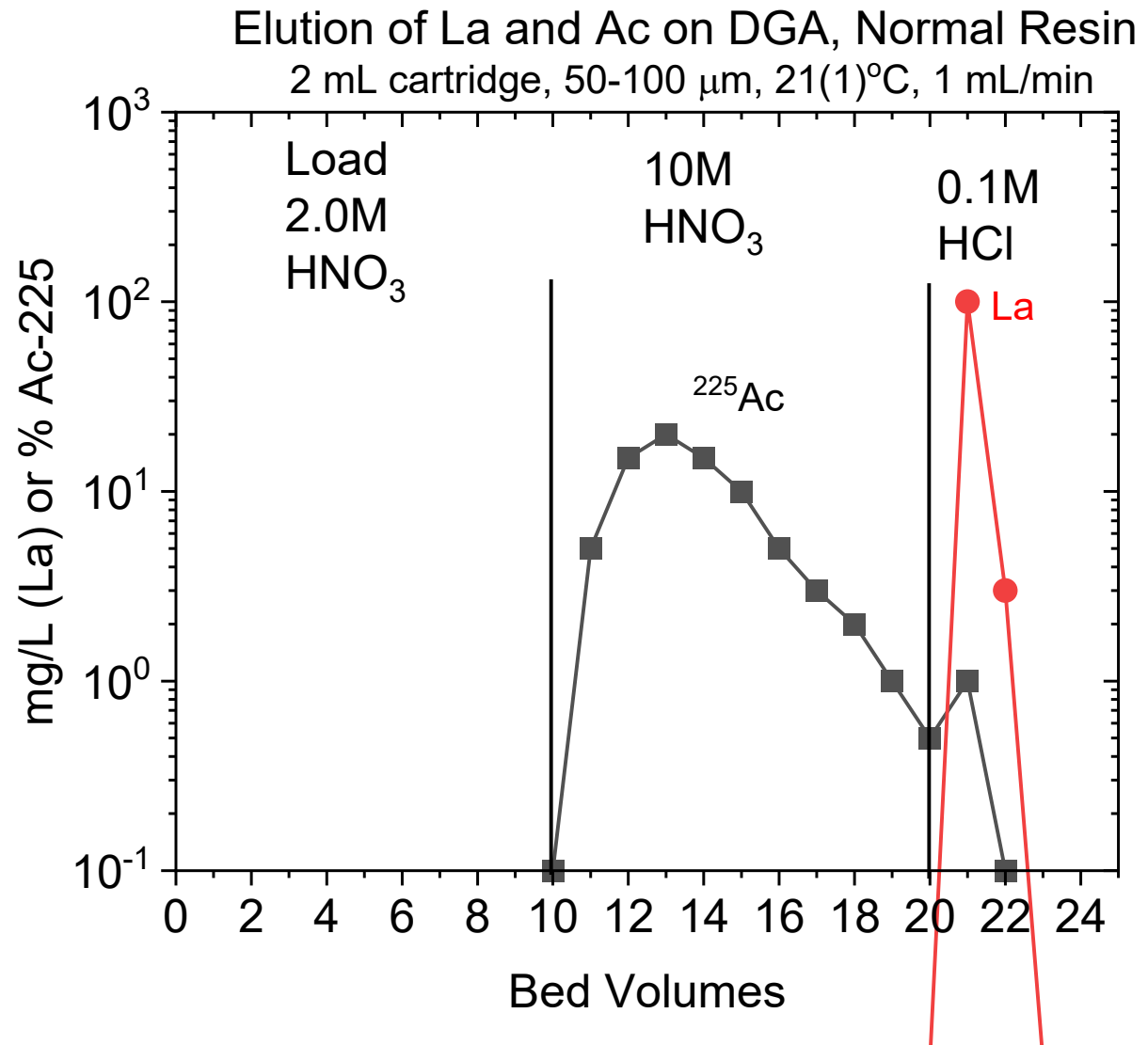
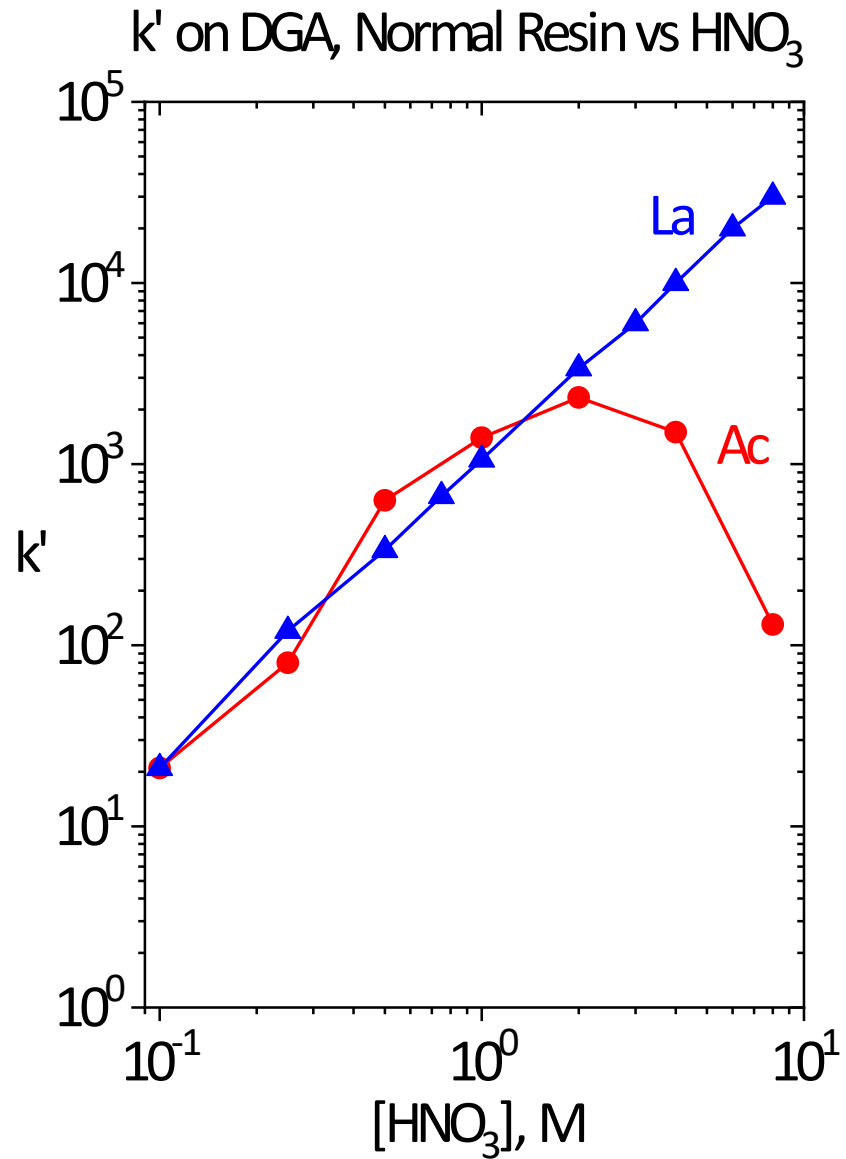
$^{147}\text{Pm} \leftrightarrow ^{241}\text{Am}$

Sm \rightarrow Cm

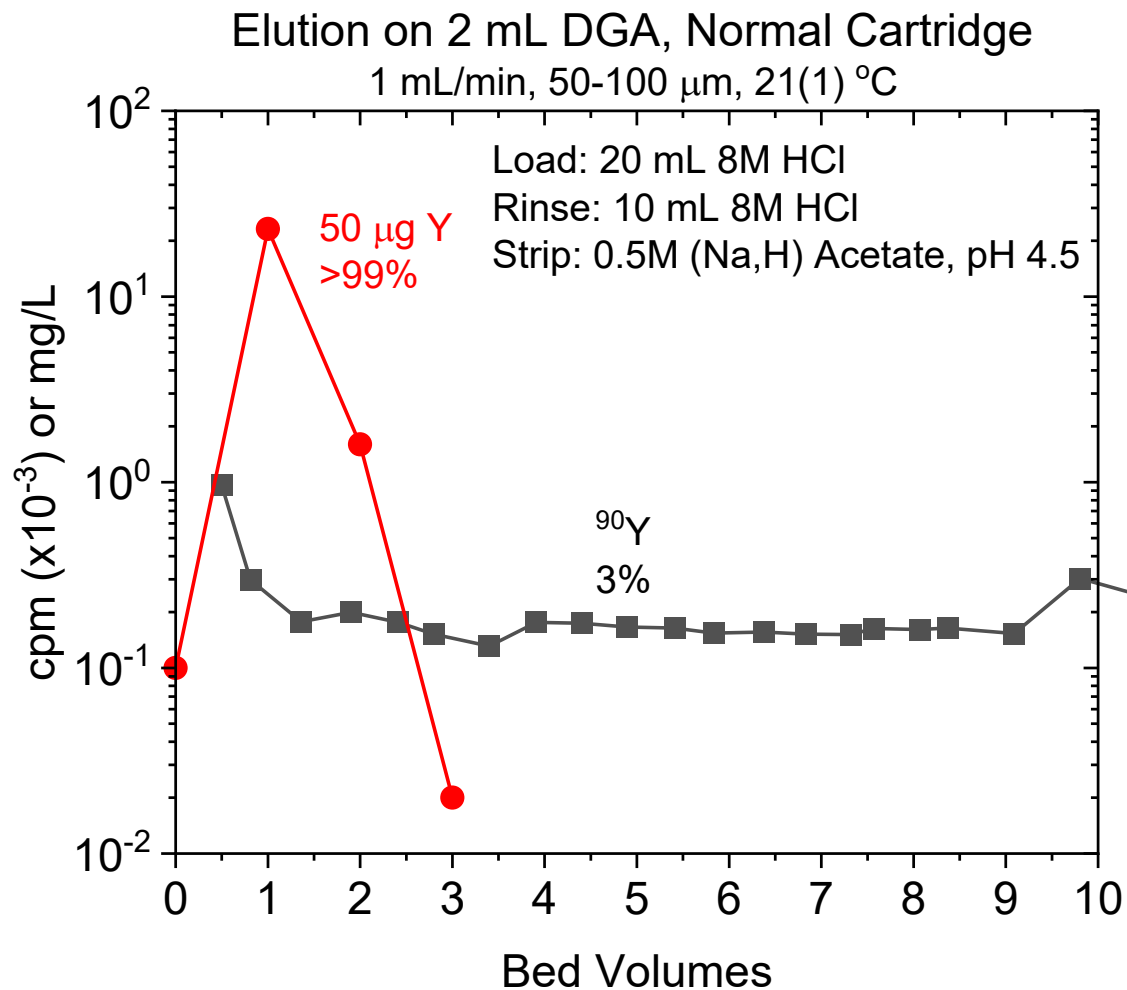
La for Ac-225 (DGA-dilute HNO₃)



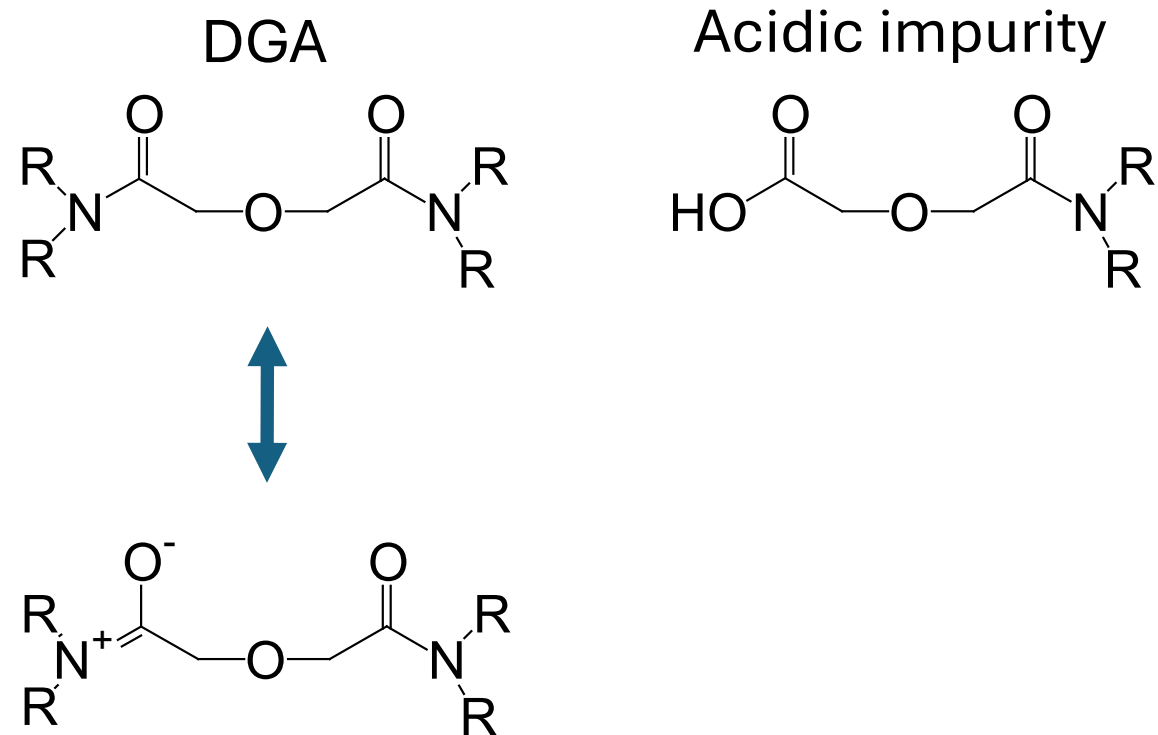
La for Ac-225 (DGA – 10M HNO₃)



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

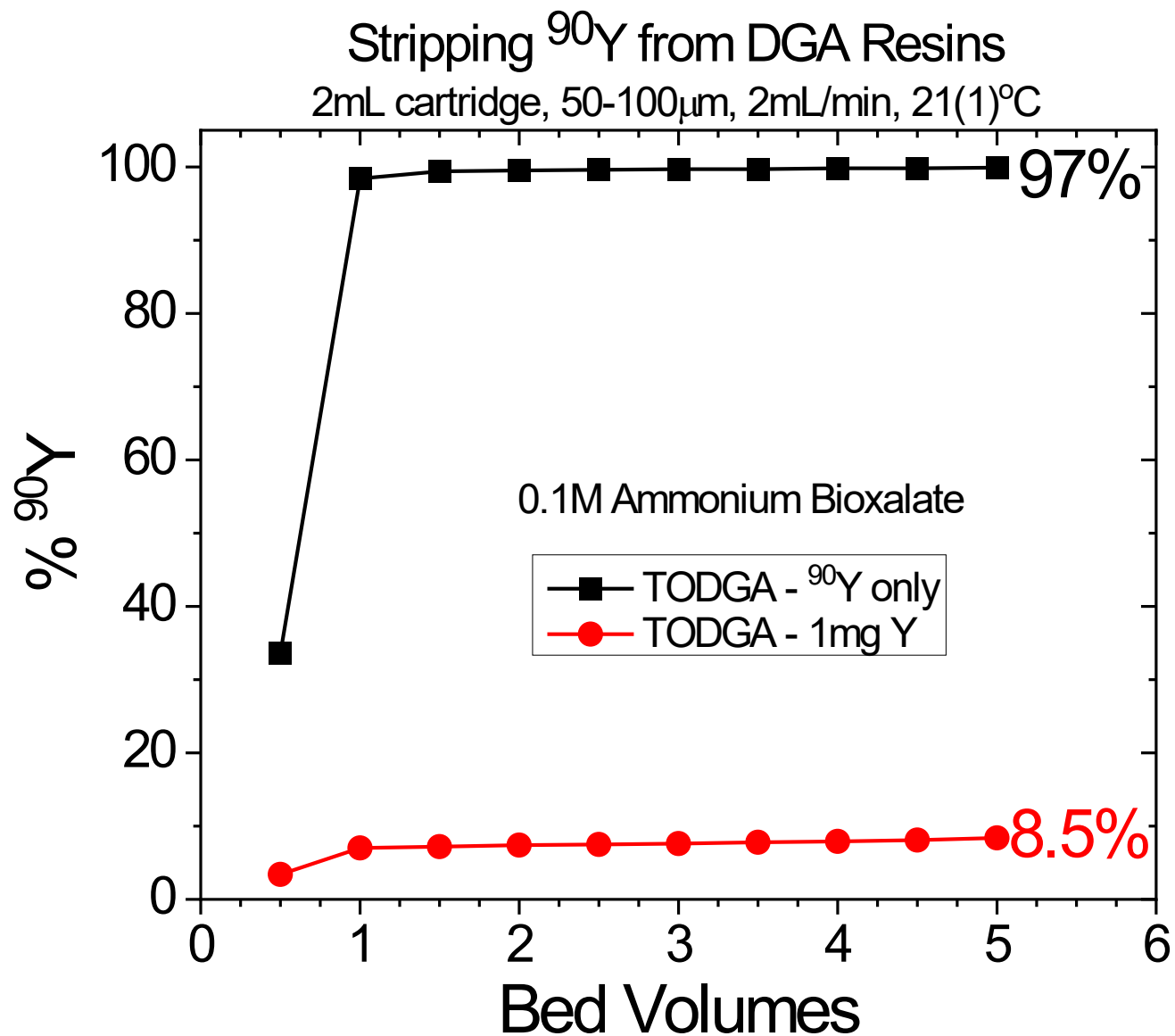


Yield for ^{225}Ac > 95%
Correlates with ionic potential of metal ion.



Small Cyclic Diglycolamides: Tautomerism, Solvent Extraction and Coordination with *f*-Elements: One Strain to Rule Them All. Mikhail A. Kalinin, Mariia V. Evsunina, 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

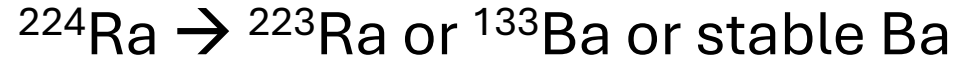
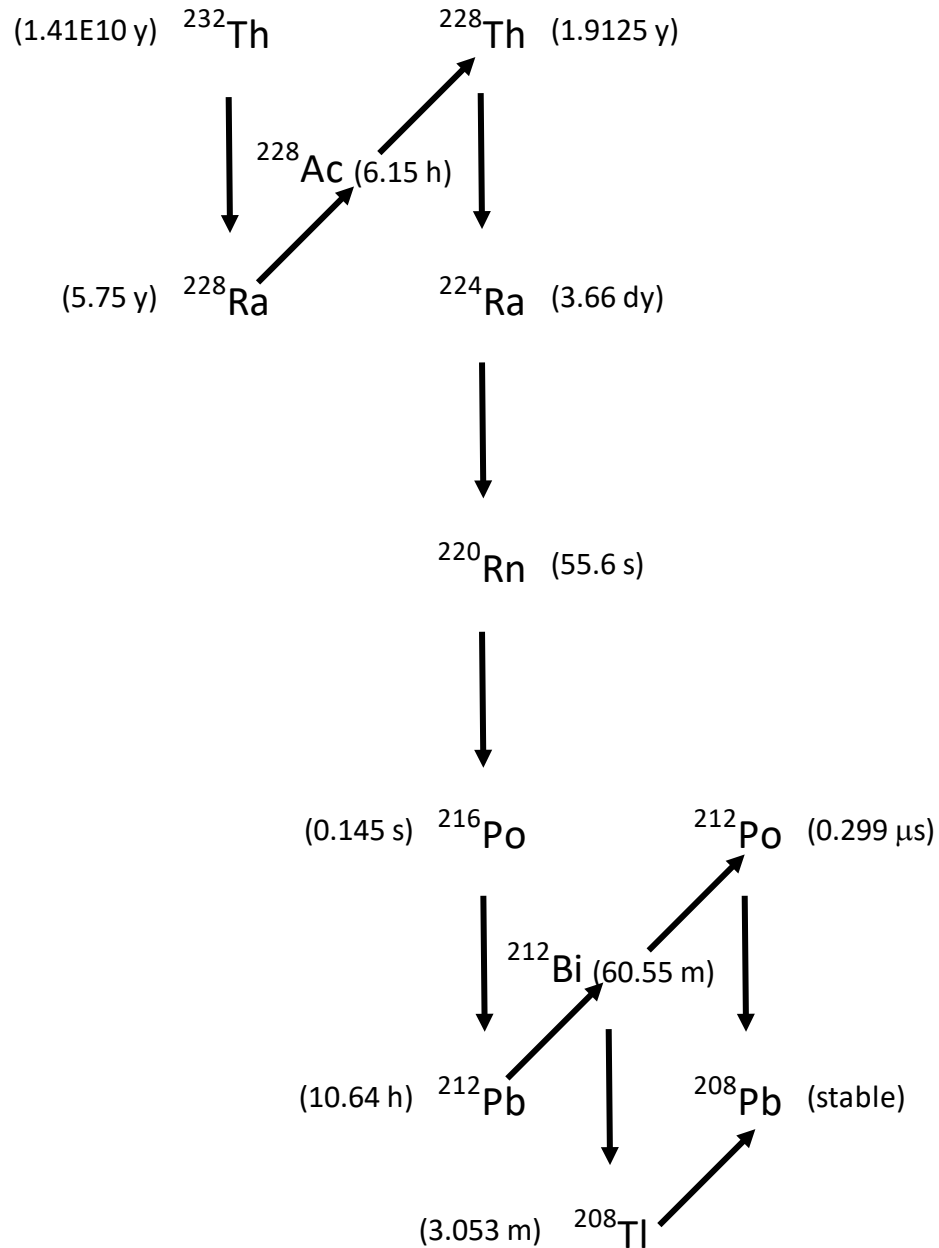
Rinse: 10 mL 8M HNO_3

Strip Y: 10 mL 0.1M ammonium
bioxalate

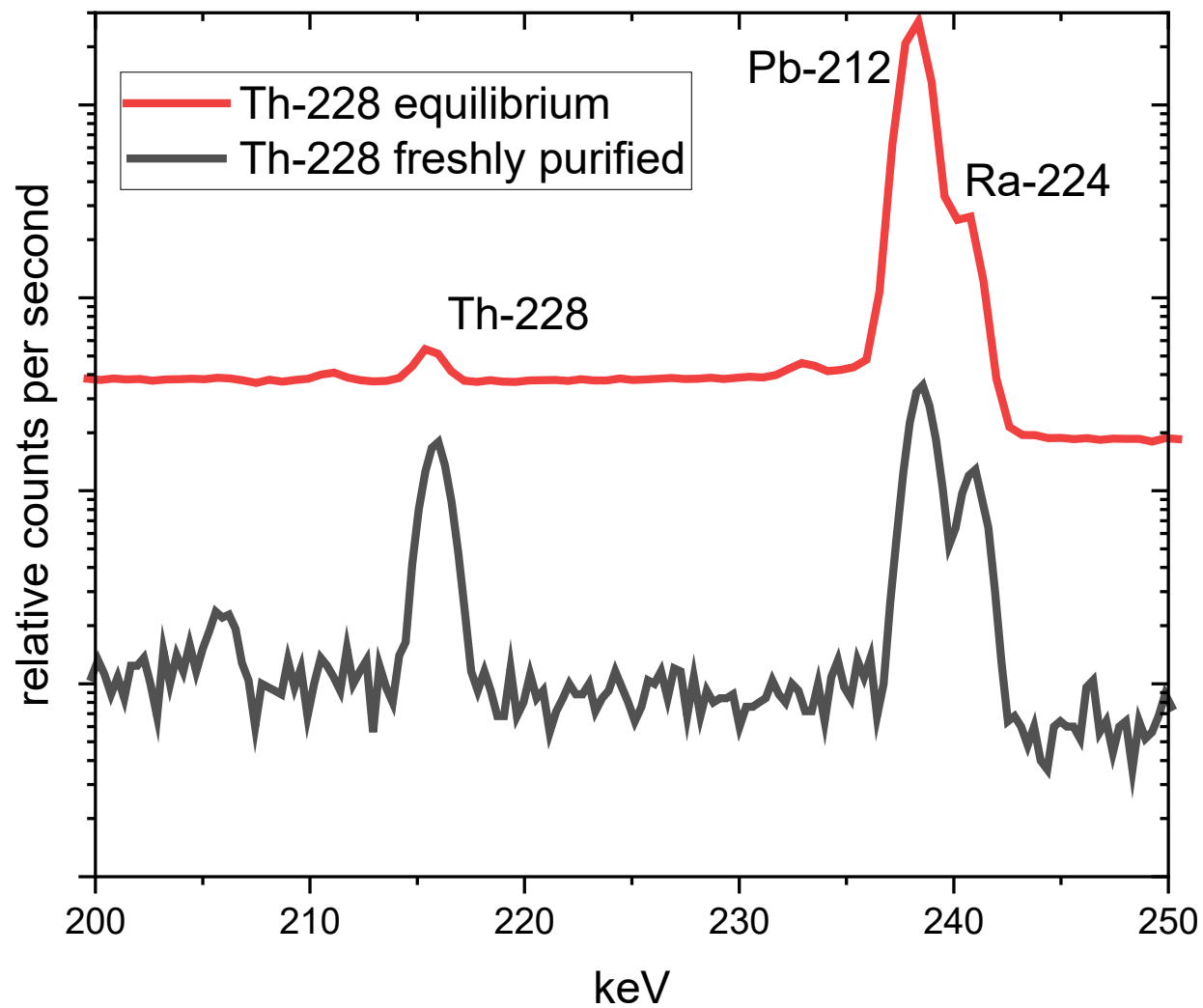
Yttrium oxalate

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

Th-228 Decay Scheme and surrogate options



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%)

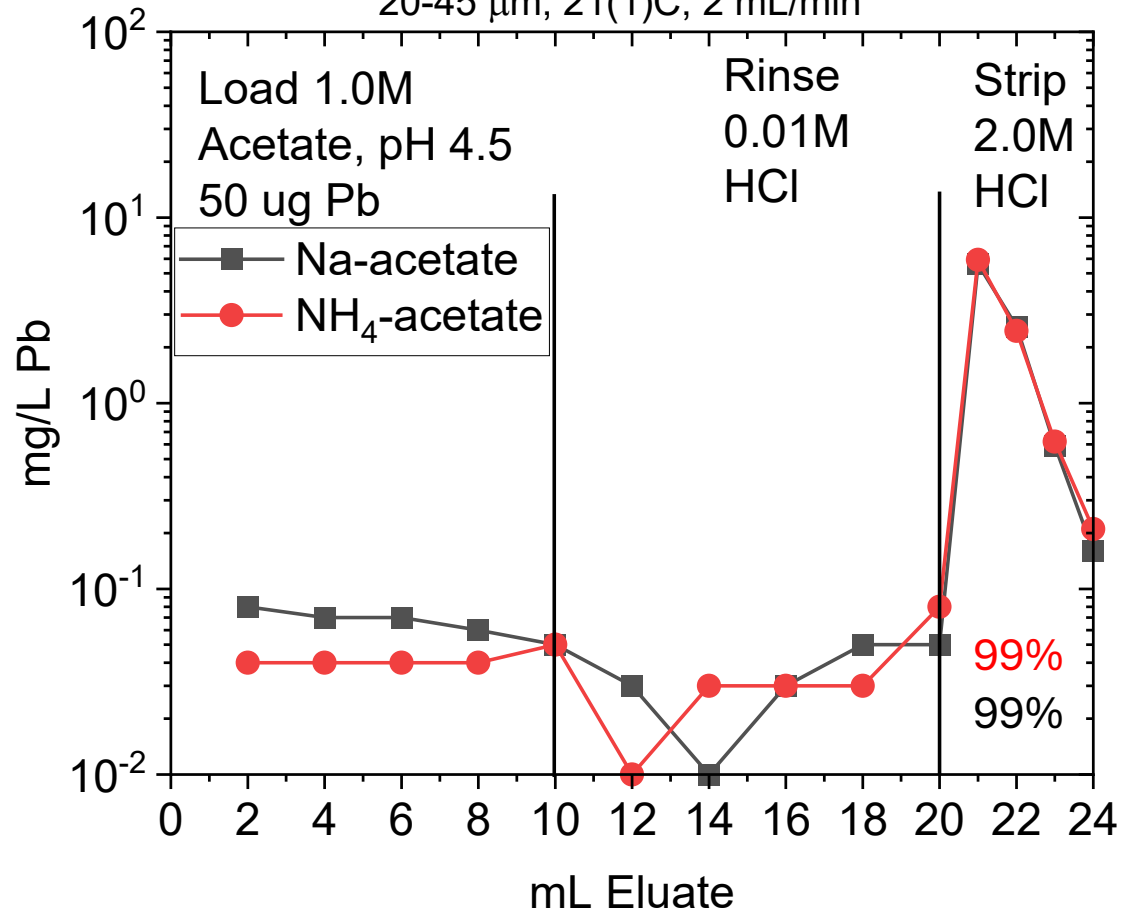
^{208}Tl 510.75 keV (22.5%)

583.187 keV (85.0%)

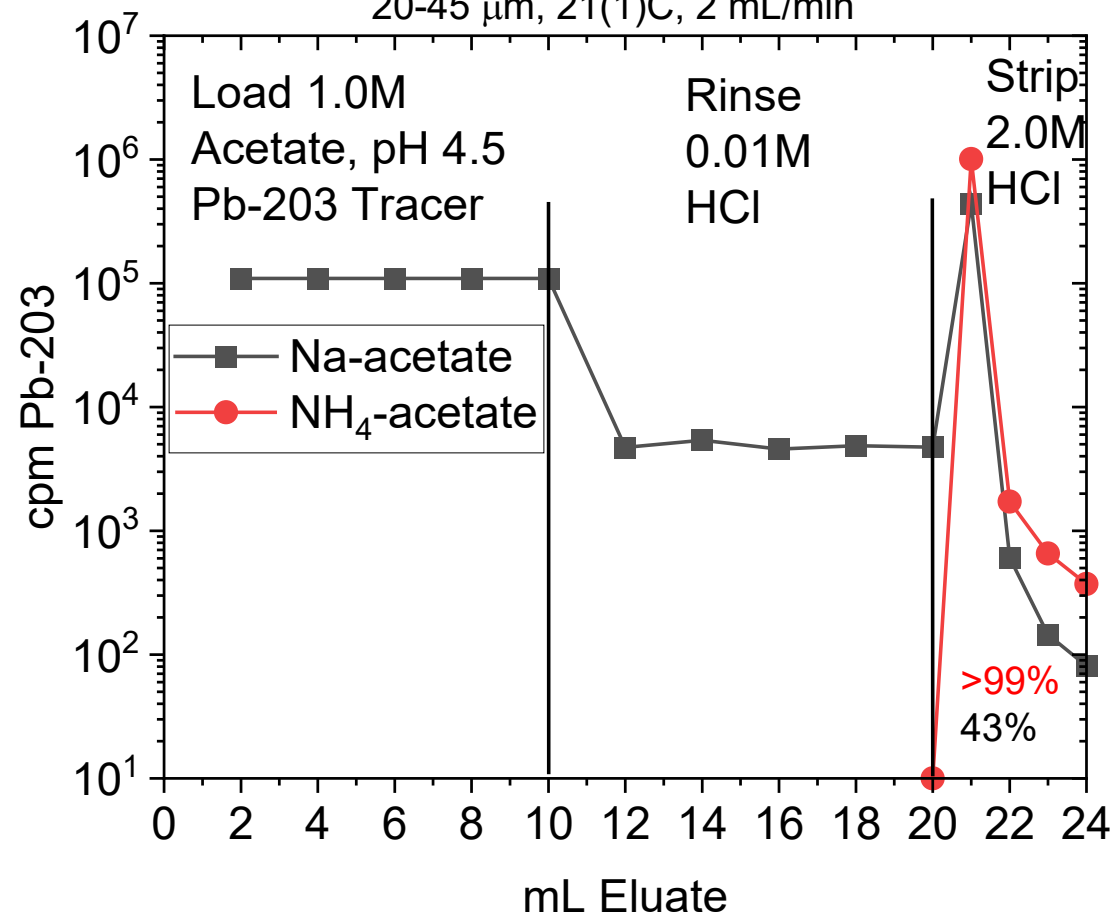
2614.511 keV (99.775%)

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

Pb elution on QML cartridge of CM-silica
20-45 μm , 21(1)C, 2 mL/min

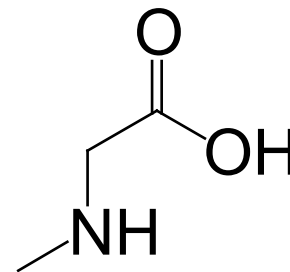


Pb elution on QML cartridge of CM-silica
20-45 μm , 21(1)C, 2 mL/min



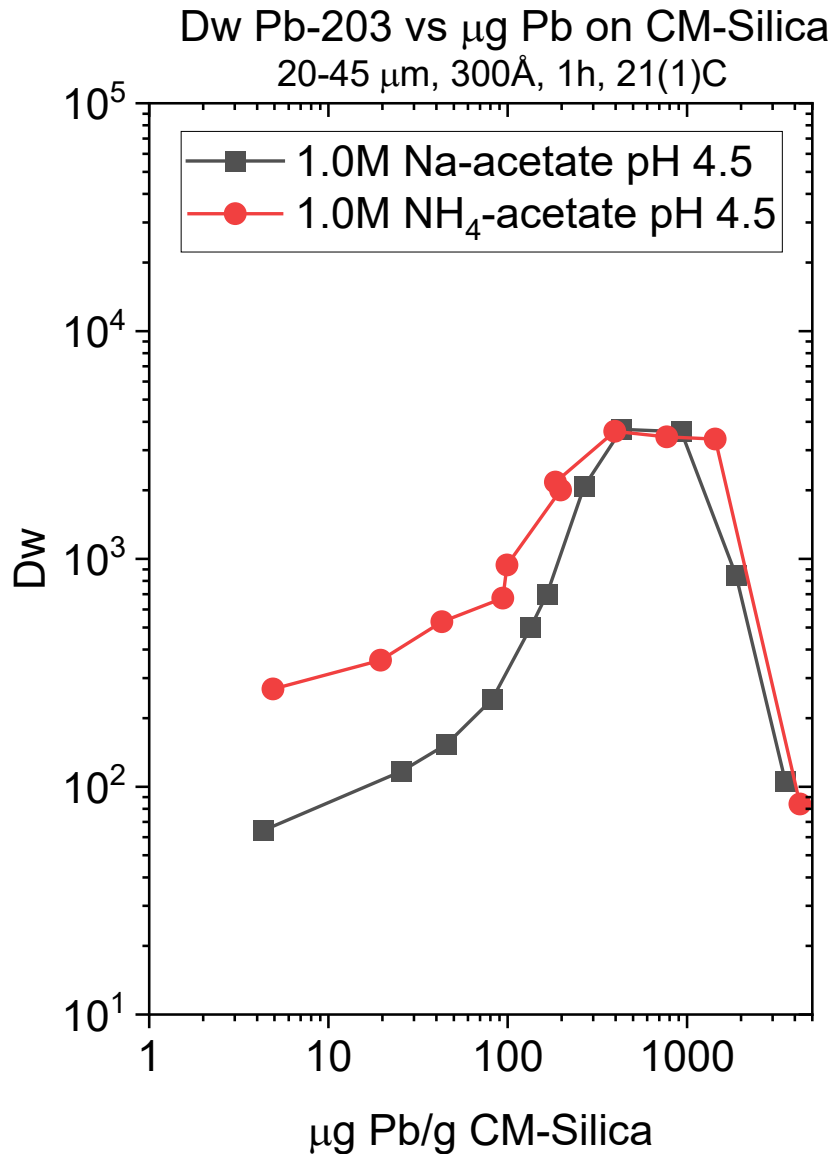
Weak cation exchange silica.

NH₄⁺ vs Na⁺ to reduce impact on stable element measurements by AES.



pKa ~ 2

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

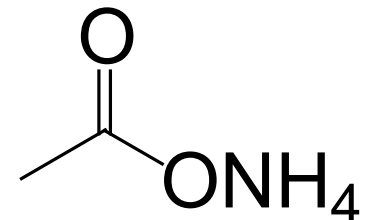
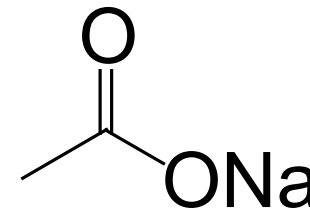
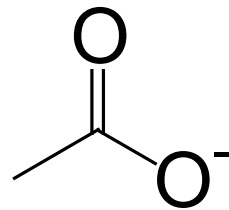


Some difference expected between Na^+ and NH_4^+ based on competition for IX sites.

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

$\text{Li}^+ < \text{H}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+$

$\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + ^-\text{OH}$ (no NH_3 for $\text{pH} < 7$)



Dw proportional to μg Pb until resin saturation.

Mechanism unclear???

Questions???

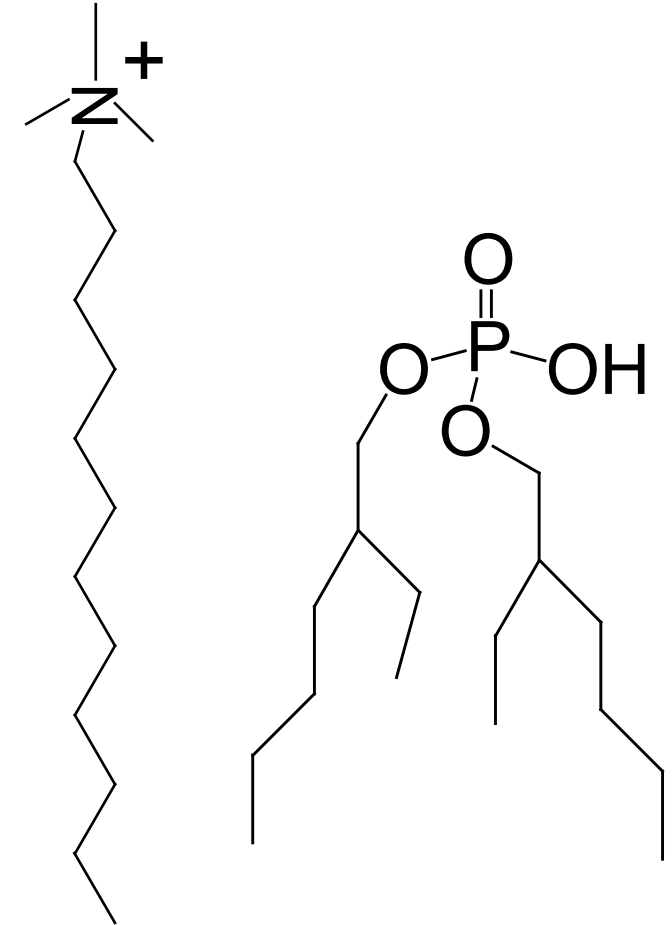
Answers???

dmcalister@eichrom.com

No other options

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

7	195.08 870.0 2.28 Pt Platinum [Xe] 4f ¹⁴ 5d ⁹ 6s ²	196.97 890.1 2.54 Au Gold [Xe] 4f ¹⁴ 5d ¹⁰ 6s ²	200.59 1007.1 2.00 Hg Mercury [Xe] 4f ¹⁴ 5d ¹⁰ 6s ²	204.38 589.4 1.62 Tl Thallium [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	207.2 715.6 2.33 Pb Lead [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	208.98 703.0 2.02 Bi Bismuth [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	(210) 812.1 2.00 Po Polonium [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	(210) 890.0 2.20 At Astatine [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵
9	(271) Ds Darmstadtium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ²	(272) Rg Roentgenium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ²	(285) Cn Copernicium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ²	(284) Nh Nihonium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	(289) Fl Flerovium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	(288) Mc Moscovium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ³	(292) Lv Livermorium [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	(294) Ts Tennessine [Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵
2	151.96 547.1 Eu Europium [Xe] 4f ⁷ 6s ²	157.25 593.4 1.20 Gd Gadolinium [Xe] 4f ⁷ 5d ¹ 6s ²	158.93 565.8 Tb Terbium [Xe] 4f ⁹ 6s ²	162.50 579.0 1.22 Dy Dysprosium [Xe] 4f ¹⁰ 6s ²	164.93 581.0 1.23 Ho Holmium [Xe] 4f ¹¹ 6s ²	167.25 589.3 1.24 Er Erbium [Xe] 4f ¹² 6s ²	168.93 596.7 1.25 Tm Thulium [Xe] 4f ¹³ 6s ²	173.05 603.4 Yb Ytterbium [Xe] 4f ¹⁴ 6s ²
4	(243) 578.0 1.30 Am Americium [Rn] 5f ⁷ 7s ²	(247) 581.0 1.30 Cm Curium [Rn] 5f ⁷ 6d ¹ 7s ²	(247) 601.0 1.30 Bk Berkelium [Rn] 5f ⁹ 7s ²	(251) 608.0 1.30 Cf Californium [Rn] 5f ¹⁰ 7s ²	(252) 619.0 1.30 Es Einsteinium [Rn] 5f ¹¹ 6s ²	(257) 627.0 1.30 Fm Fermium [Rn] 5f ¹² 7s ²	(258) 635.0 1.30 Md Mendelevium [Rn] 5f ¹³ 7s ²	(259) 642.0 1.30 No Nobelium [Rn] 5f ¹⁴ 7s ²



TEVA

LN

J.P. Unik, E.P. Horwitz, 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 \times 5 cm; 50°C; $v = \sim 4$ cm/min; FCV = 0.19 ml.

Group A	Subgroups	Elements and Oxidation States
	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	Subgroups	Elements and Oxidation States
	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	Subgroups	Elements and Oxidation States
	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)

