

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

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

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TECHNOLOGIES

A GCI COMPANY

A banner for the ACS Spring 2024 meeting. The text "ACS SPRING 2024" is in large, bold, blue letters. Below it, "MARCH 17-21 | NEW ORLEANS, LA" is in smaller, blue letters. The background is a light blue grid pattern.

ACS SPRING 2024
MARCH 17-21 | NEW ORLEANS, LA

A blue banner with the tagline "Many Flavors of Chemistry" in a white, cursive font.

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

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~~

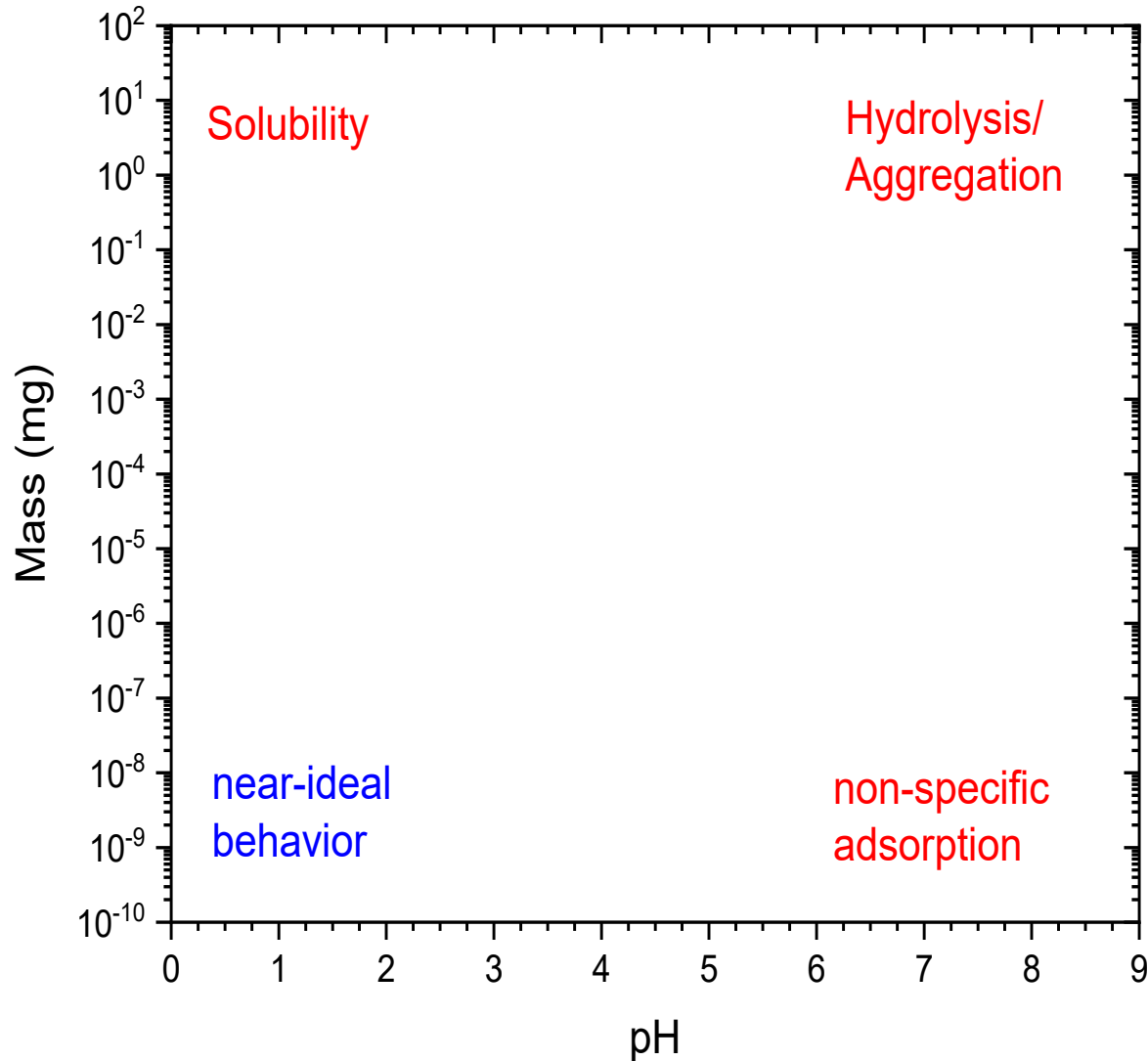
~~Cyclotron~~

Radiol isotopes may be:
Unavailable

~~Nuclear Reactor~~

Expensive
Short-lived
Complex decay scheme
(ALARA)

Surrogates: Stable elements vs Radionuclides



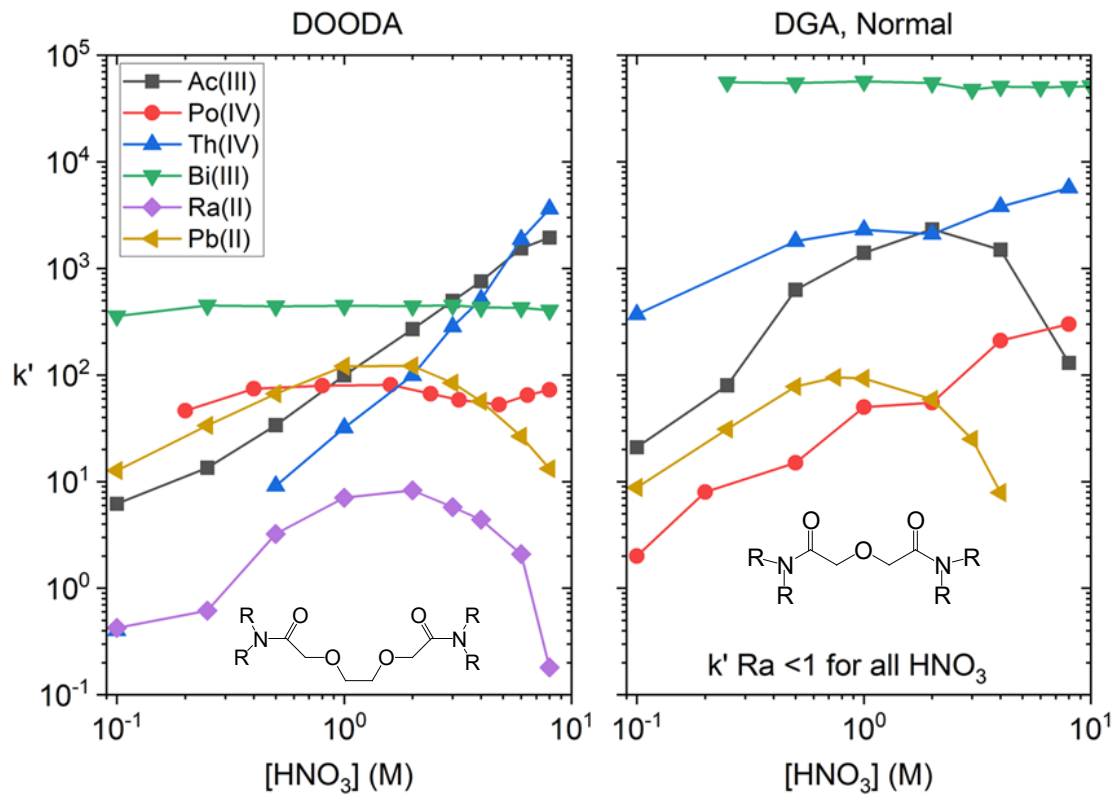
Stable Elements (μg):

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

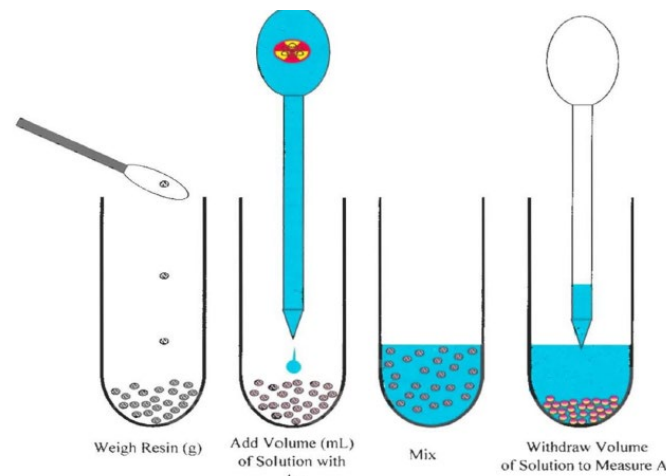
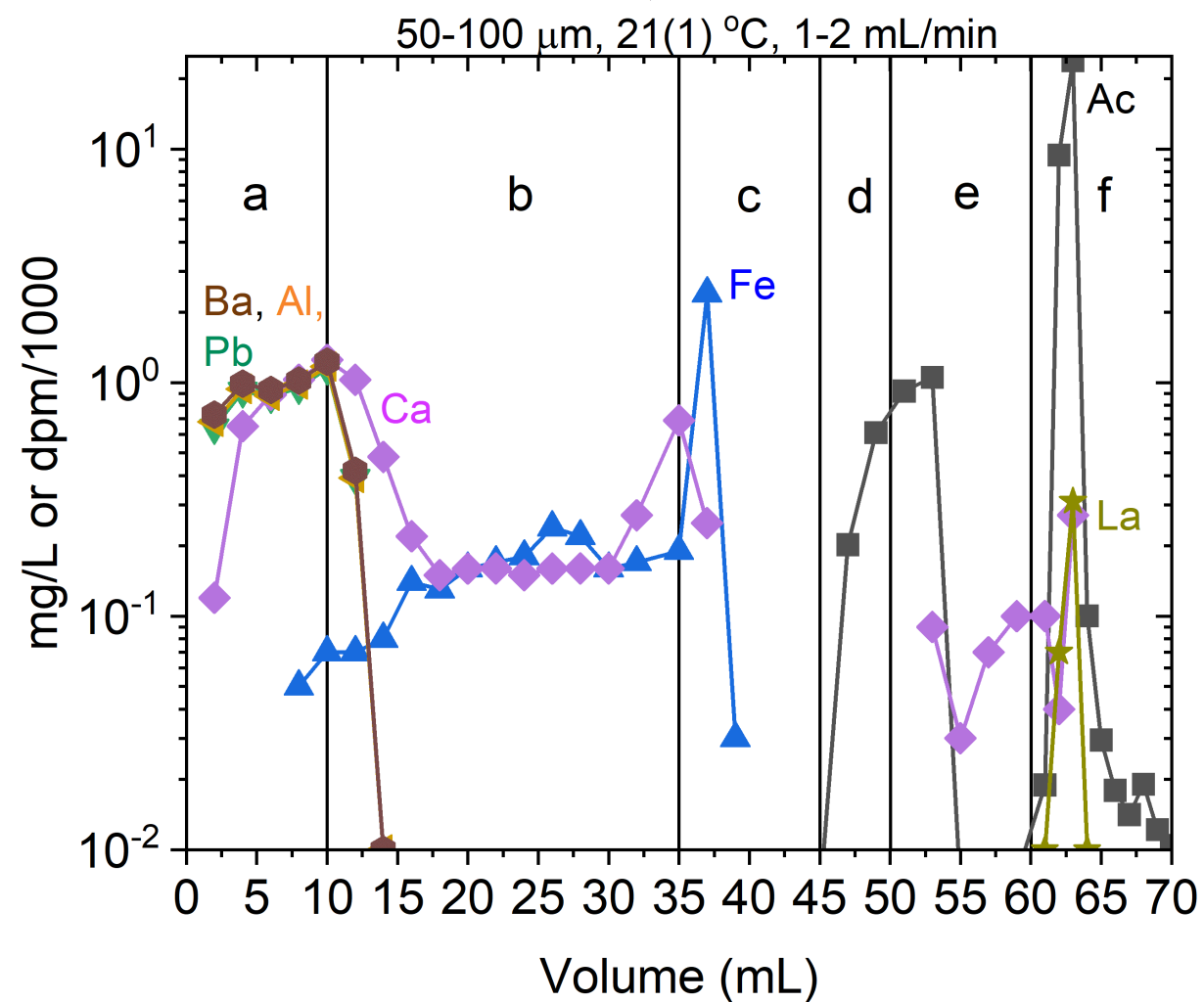
Radionuclides:

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

When does mass help/hurt?



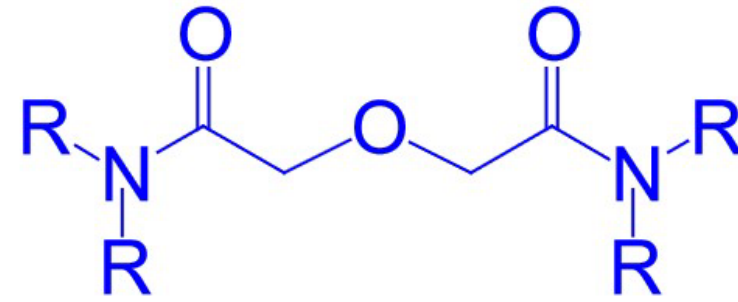
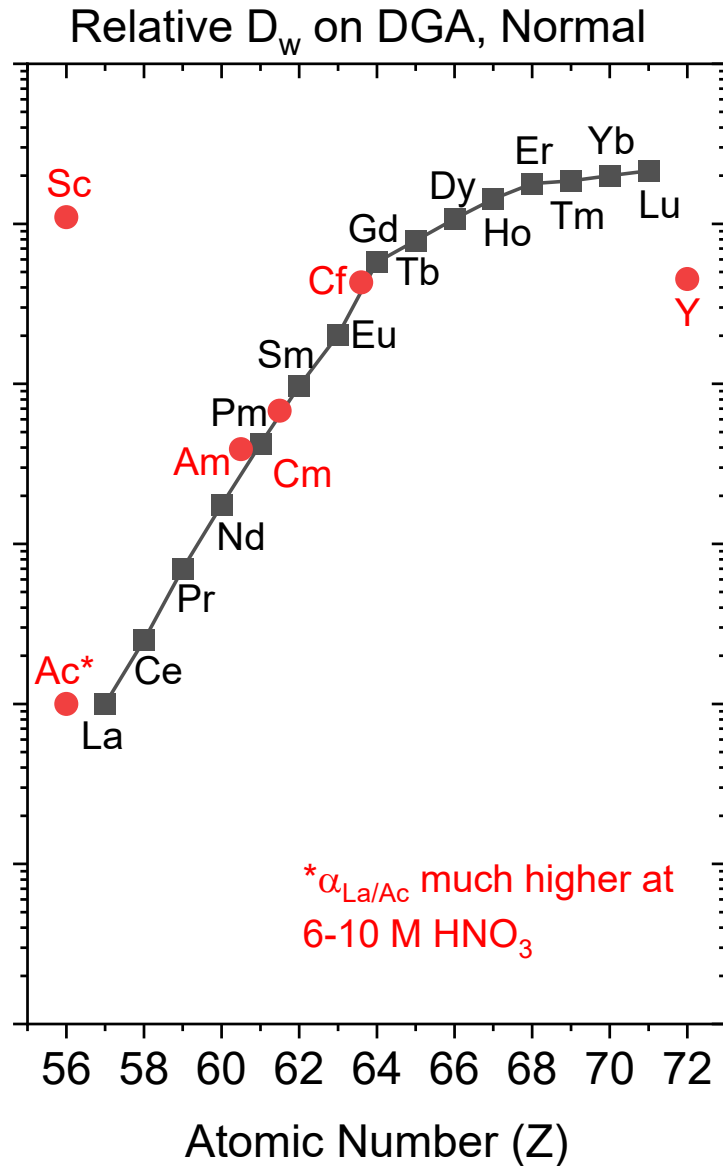
Elution on 0.5mL DGA, Normal and 2 mL DOODA



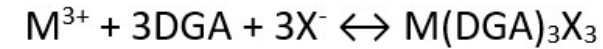
$$D_w = \frac{A_0 - A_s}{w(g)} \bigg/ \frac{A_s}{v(mL)}$$

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

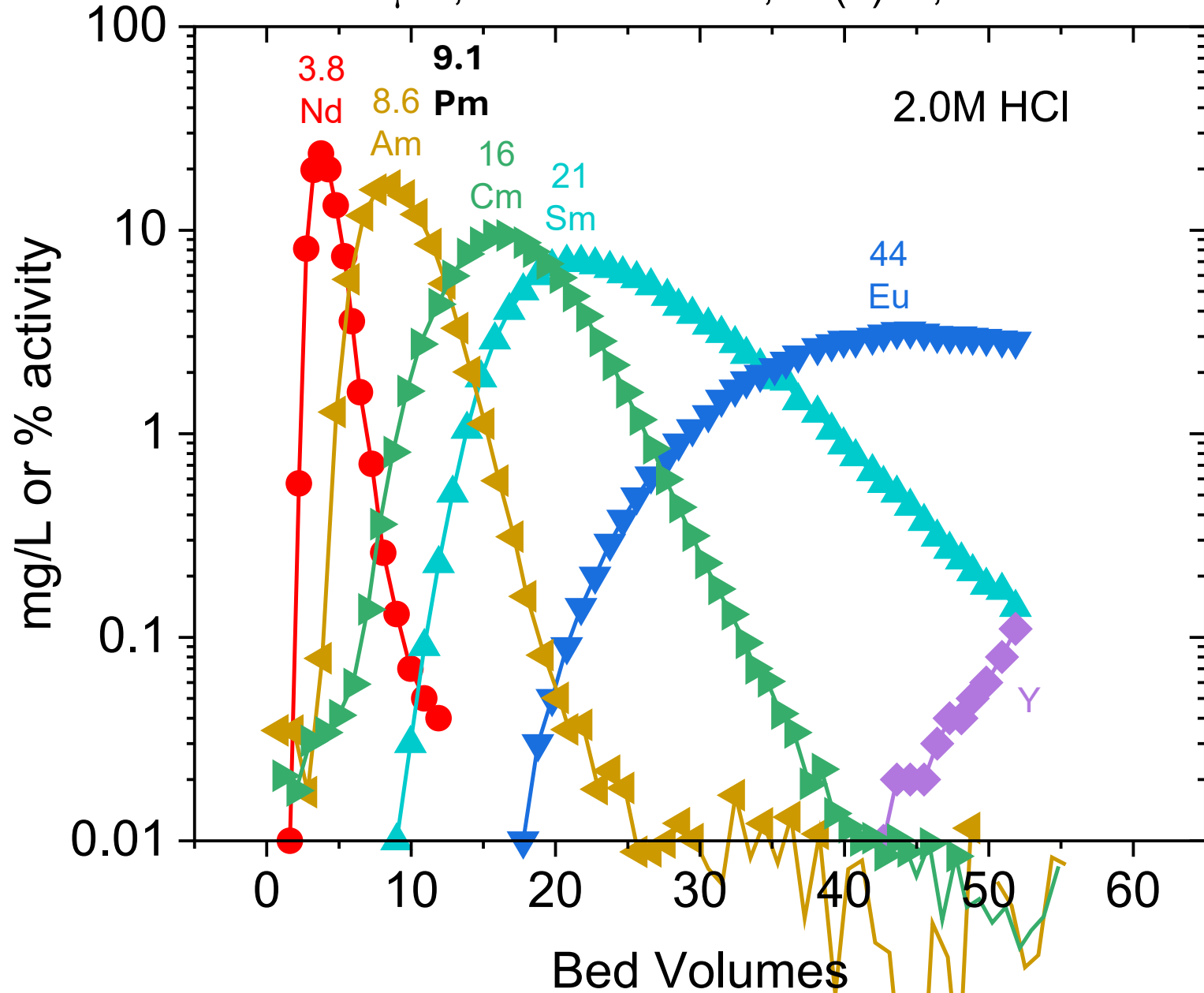


M = Ln(III) or An(III), X = NO_3^- or Cl^-

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



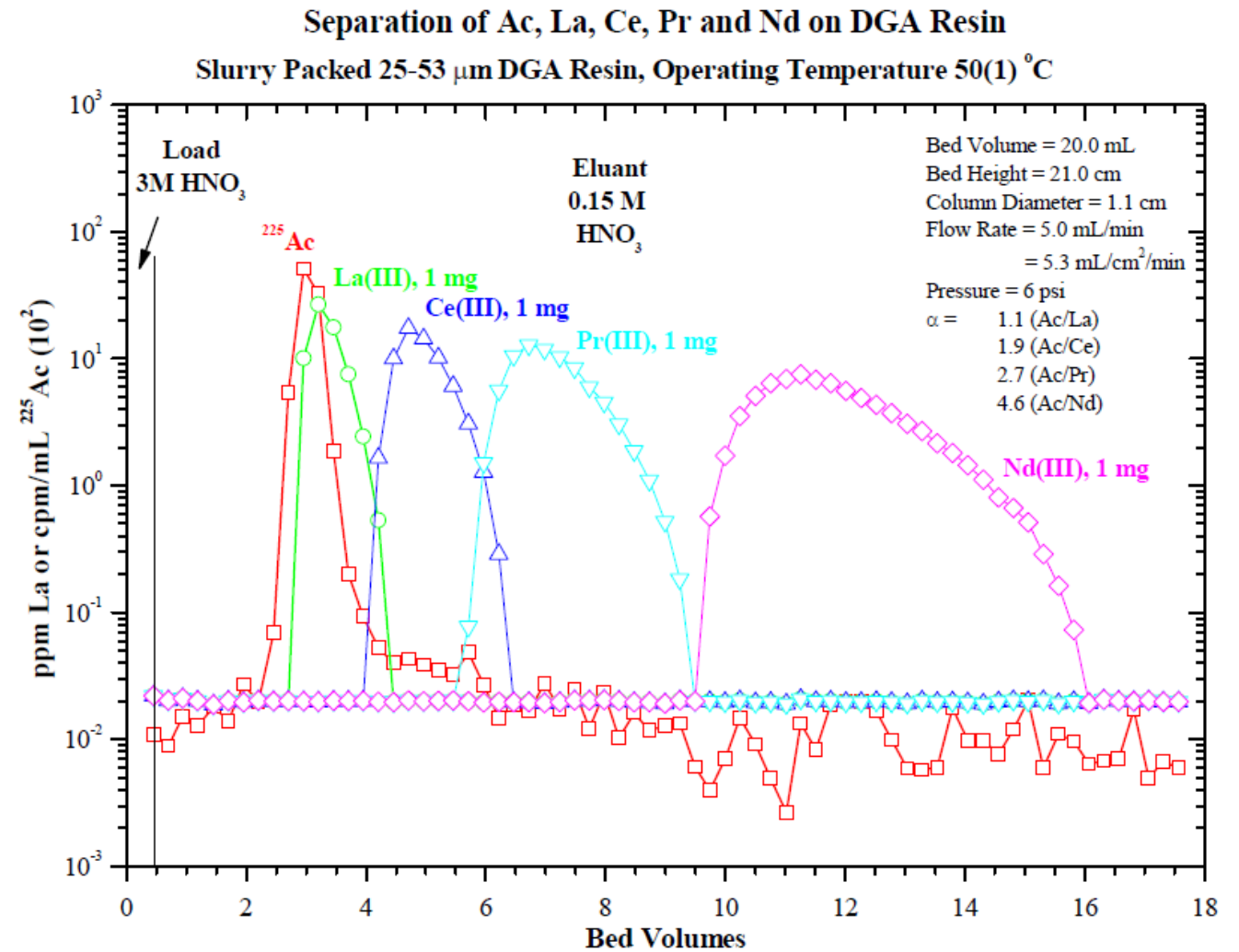
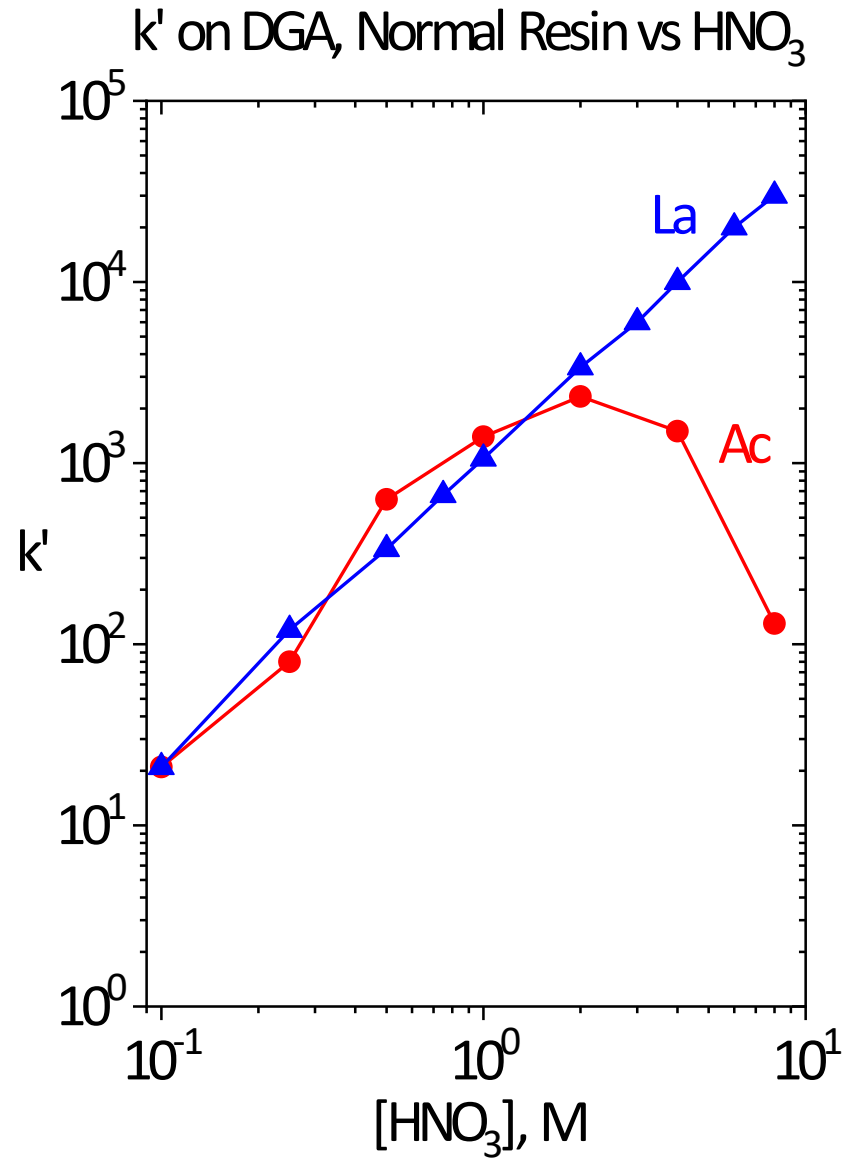
M^{3+}	Separation factor (M/Nd)	Predicted BV (Nd = 3.8)
Nd	1.0	3.8
Am	2.2	8.4
Pm	2.4	9.1
Cm	3.9	15
Sm	5.5	21

Nd/Sm bracket Am/Cm

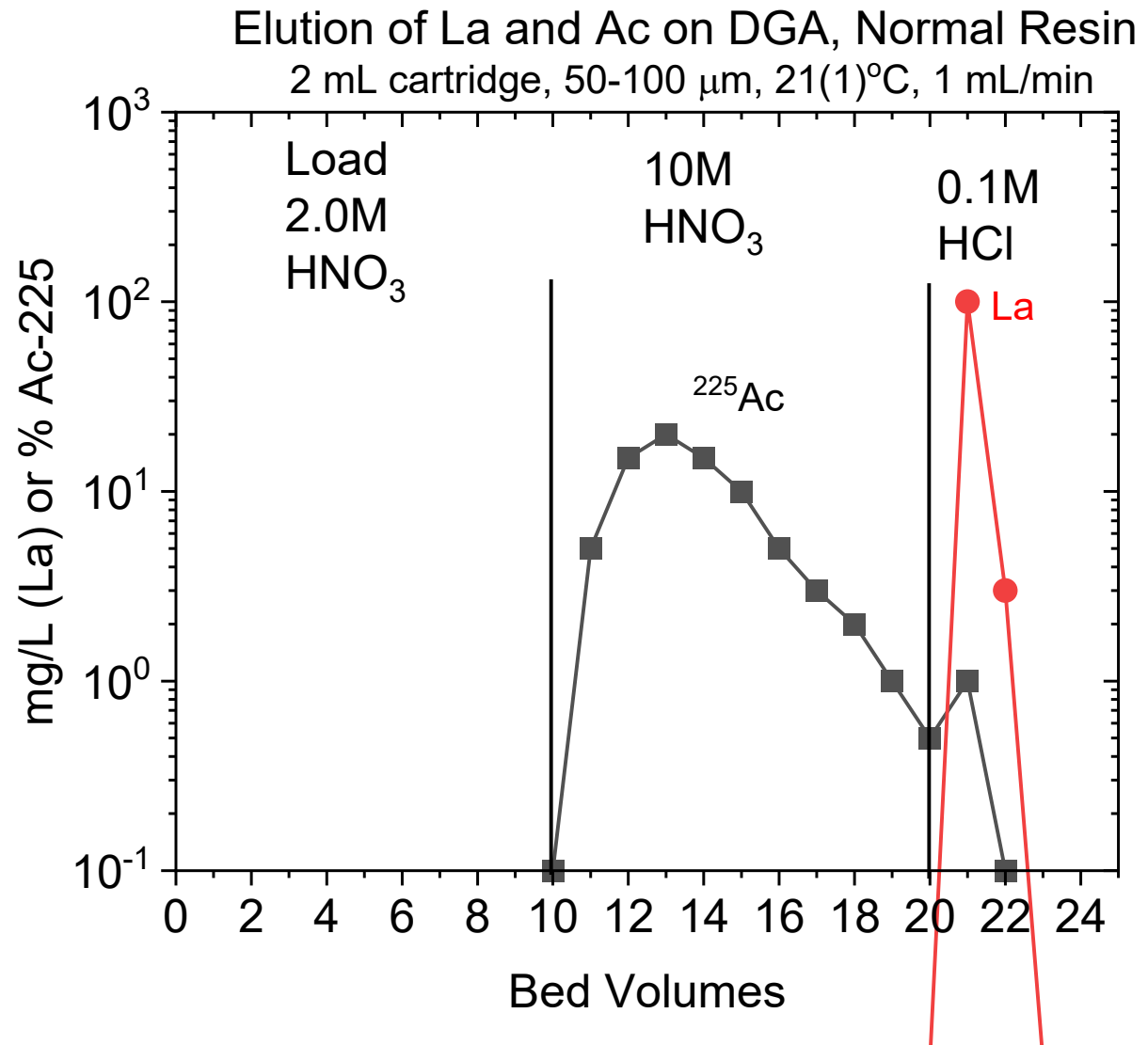
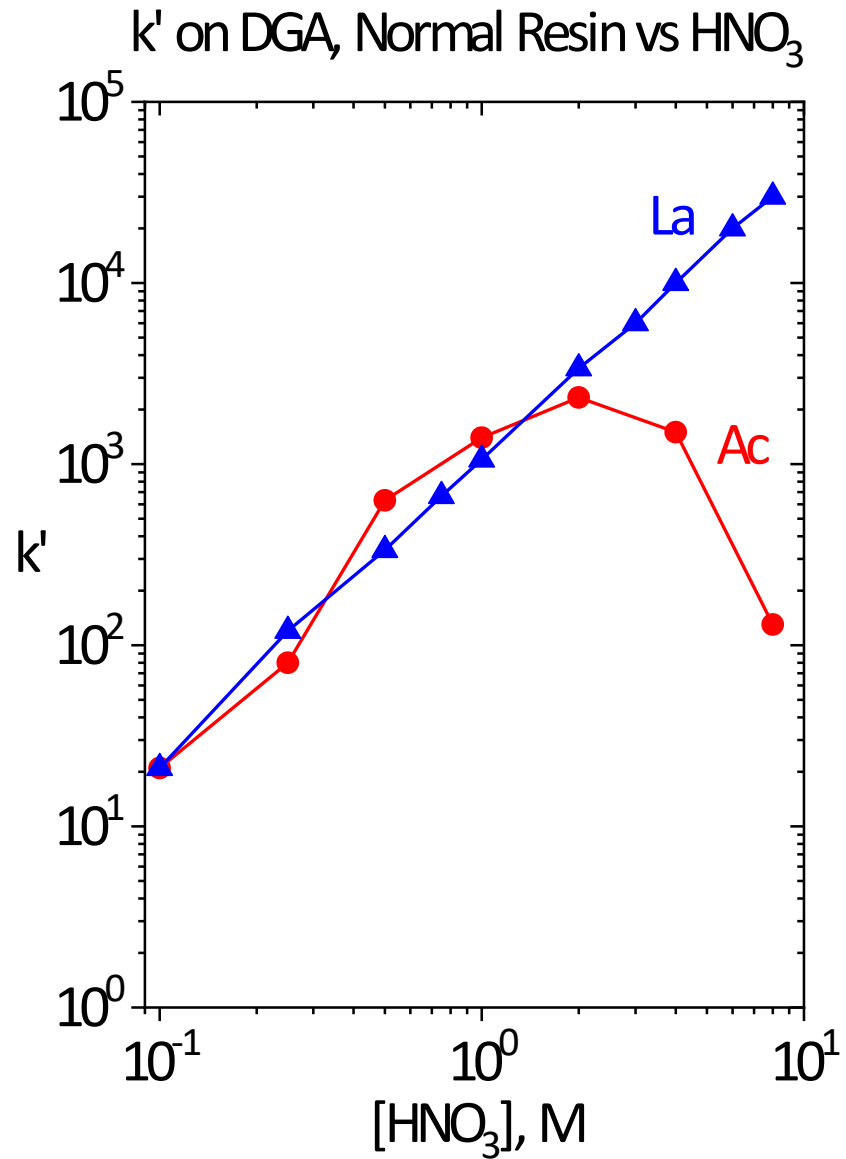
$^{147}\text{Pm} \leftrightarrow ^{241}\text{Am}$

Sm \rightarrow Cm

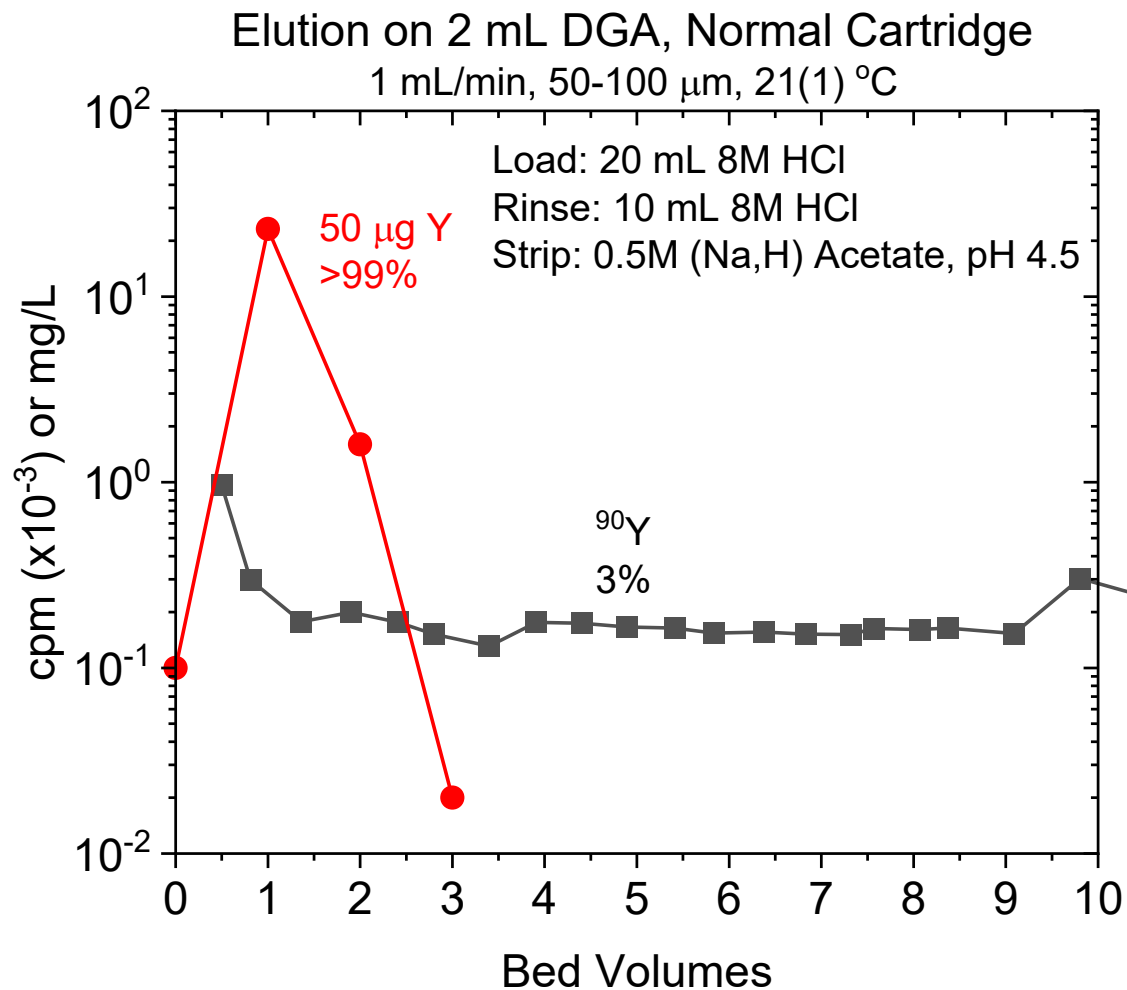
La for Ac-225 (DGA-dilute HNO₃)



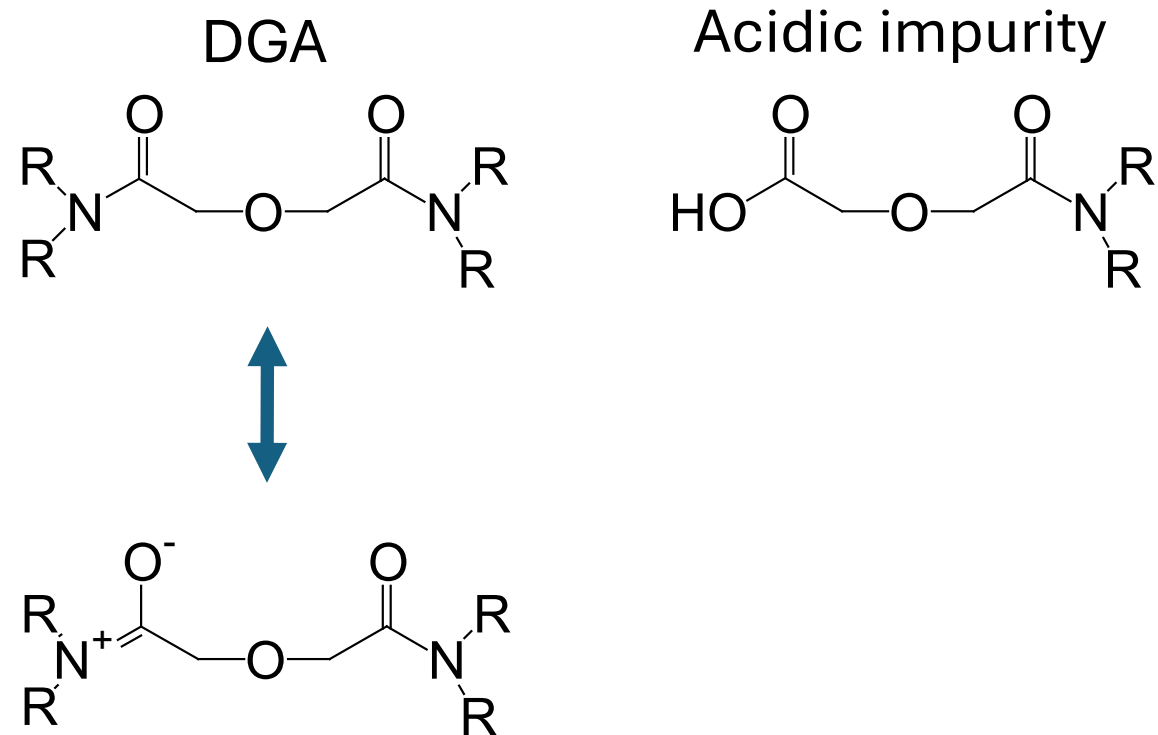
La for Ac-225 (DGA – 10M HNO₃)



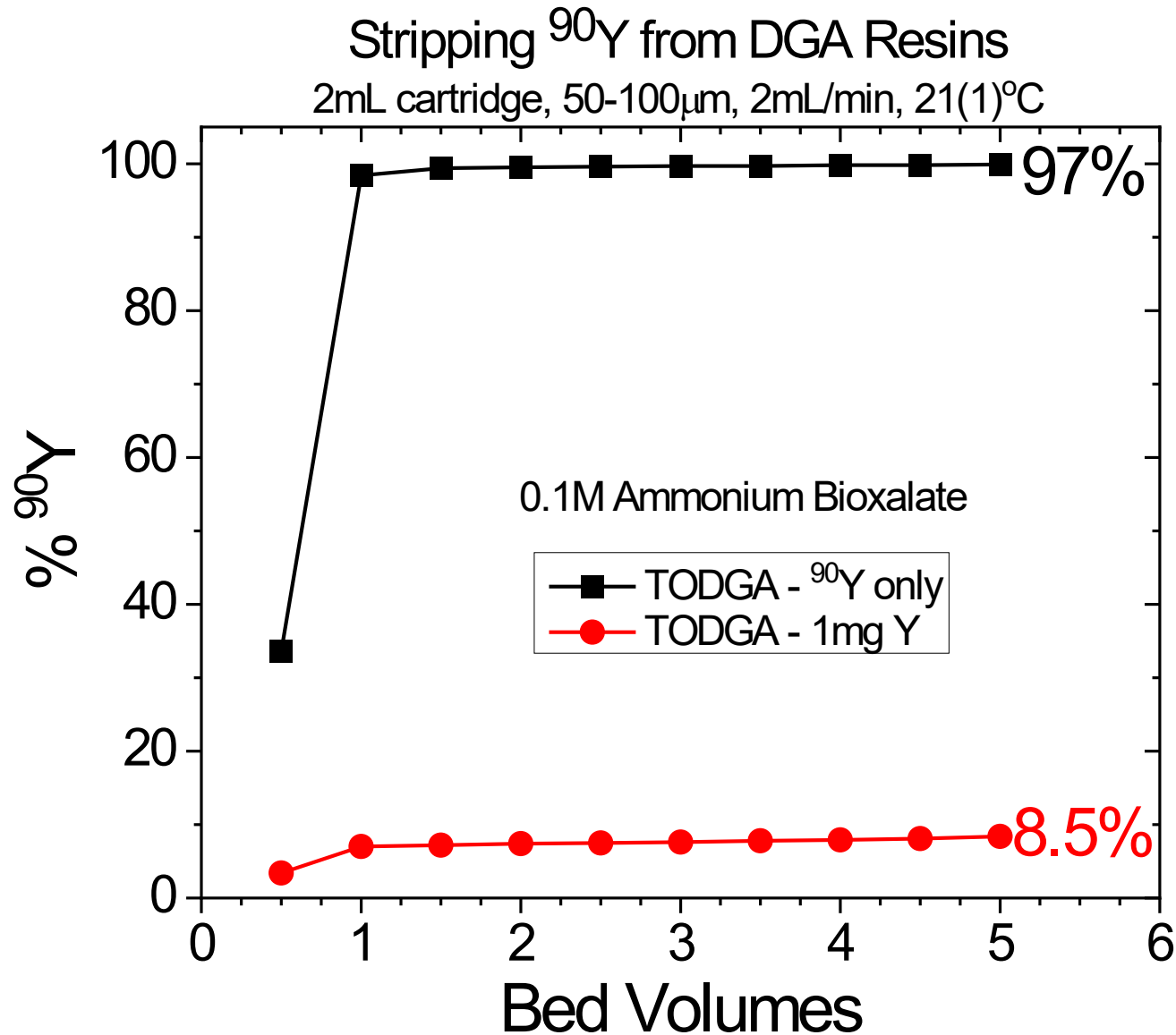
^{90}Y vs Y (Elution from DGA Resin)



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



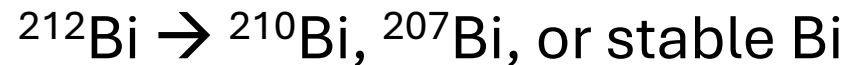
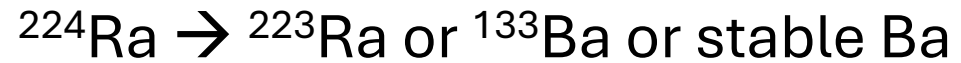
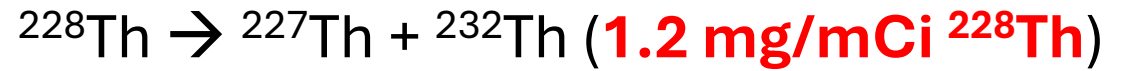
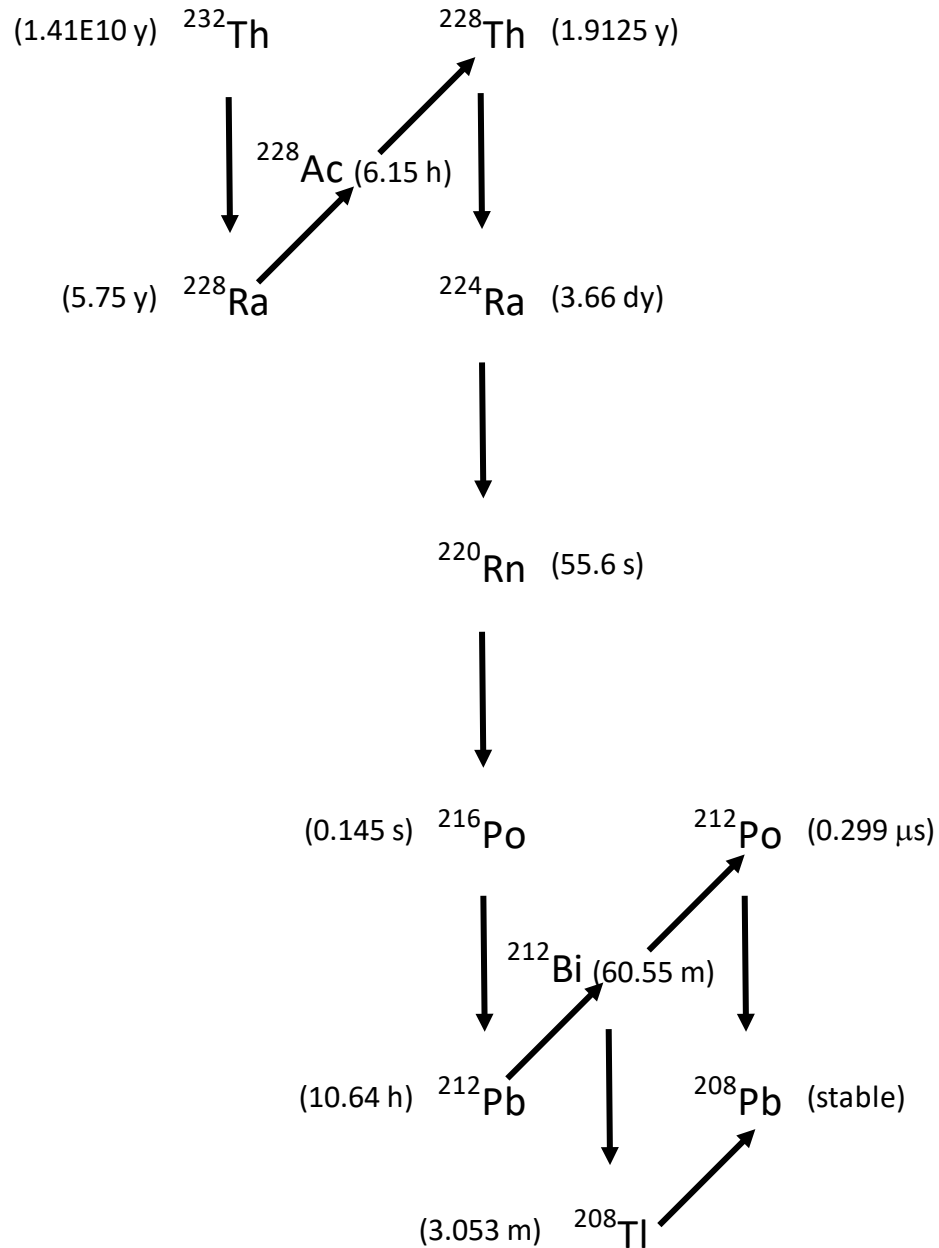
^{90}Y vs Y (Elution from DGA Resin)



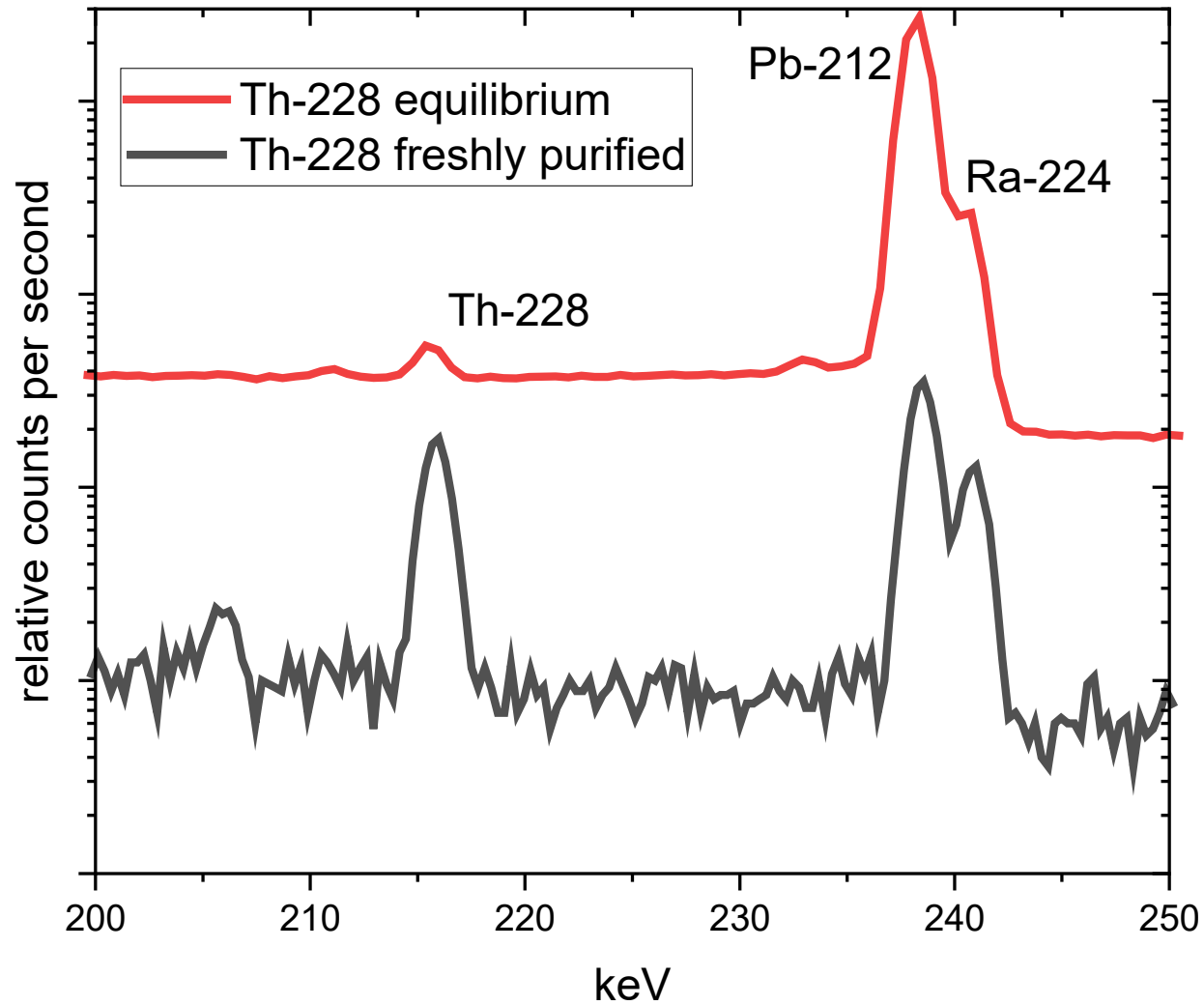
Load: 20 mL 0.25M HNO_3
Rinse: 10 mL 8M HNO_3
Strip Y: 10 mL 0.1M ammonium
bioxalate

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%)

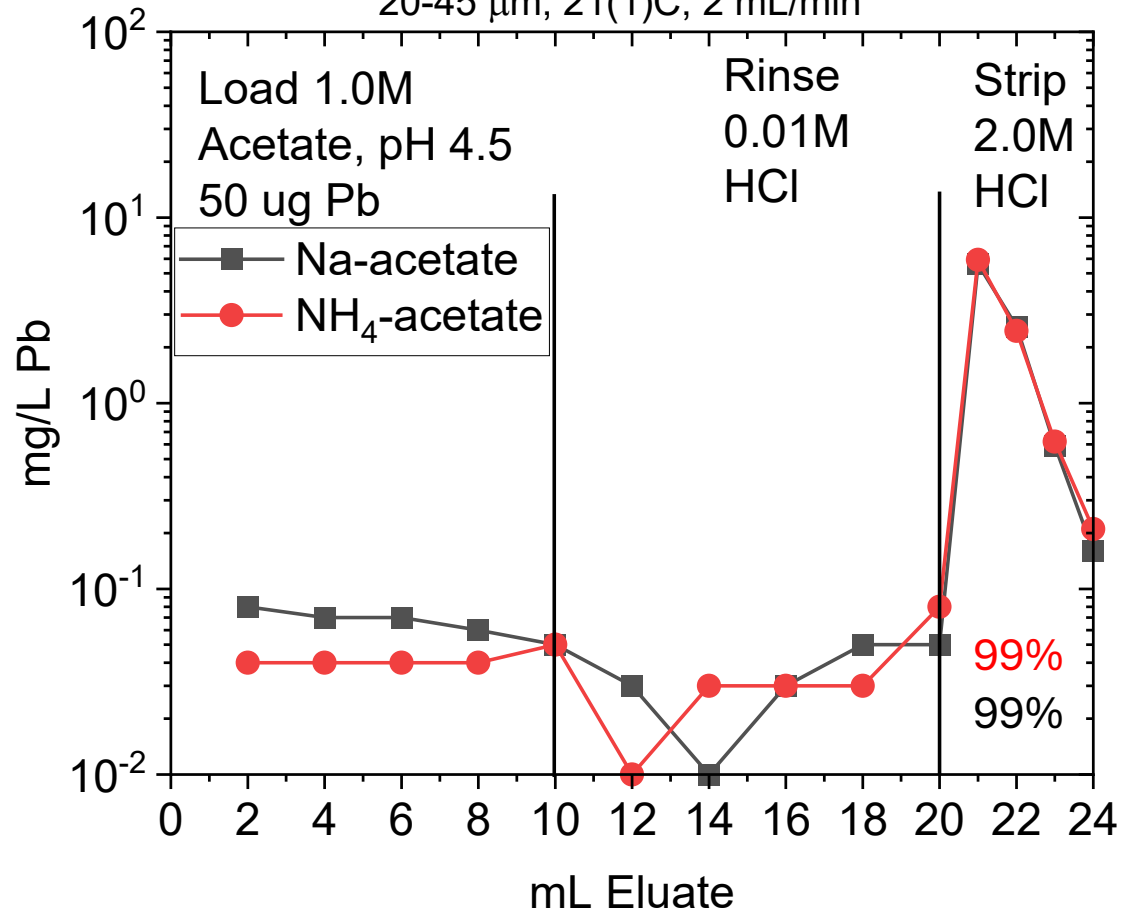
^{208}Tl 510.75 keV (22.5%)

583.187 keV (85.0%)

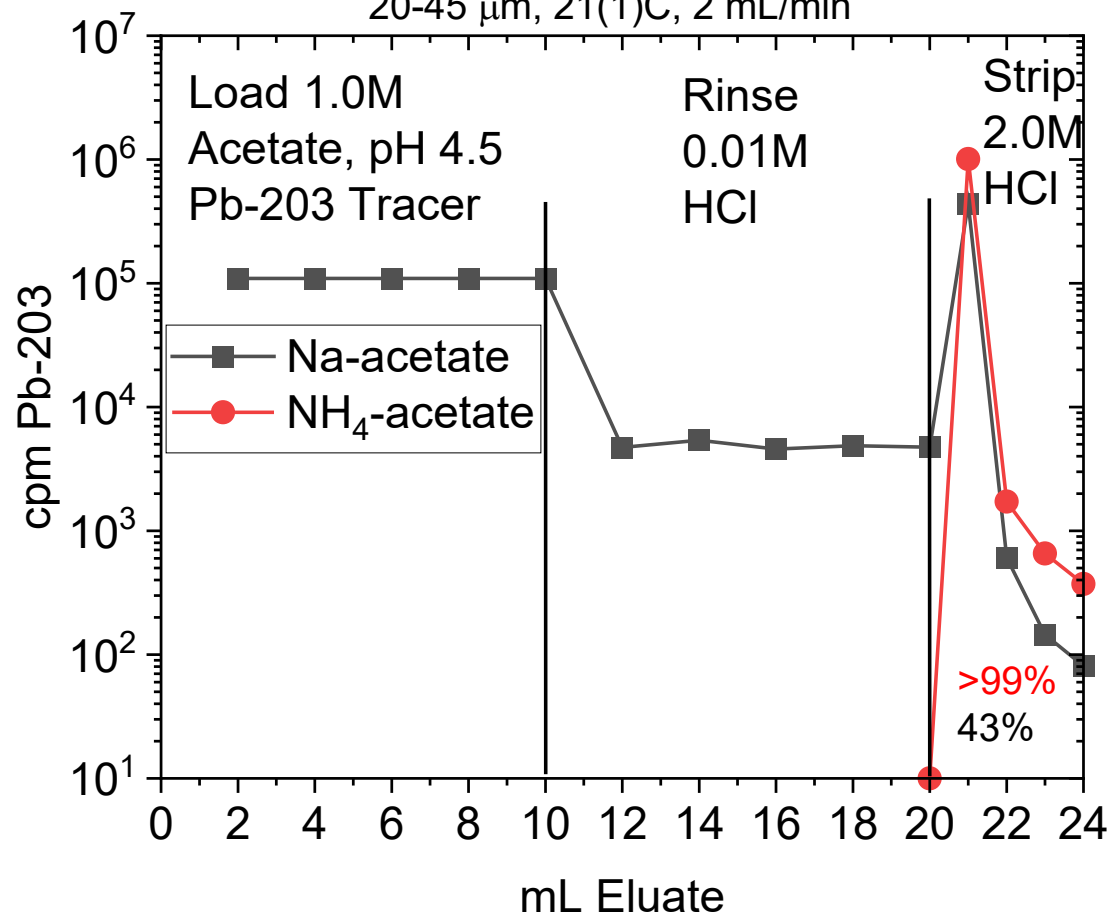
2614.511 keV (99.775%)

^{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

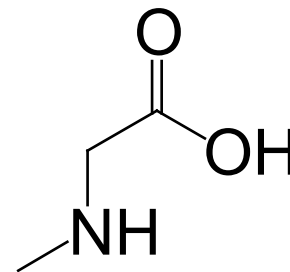


Pb elution on QML cartridge of CM-silica
20-45 μm , 21(1)C, 2 mL/min



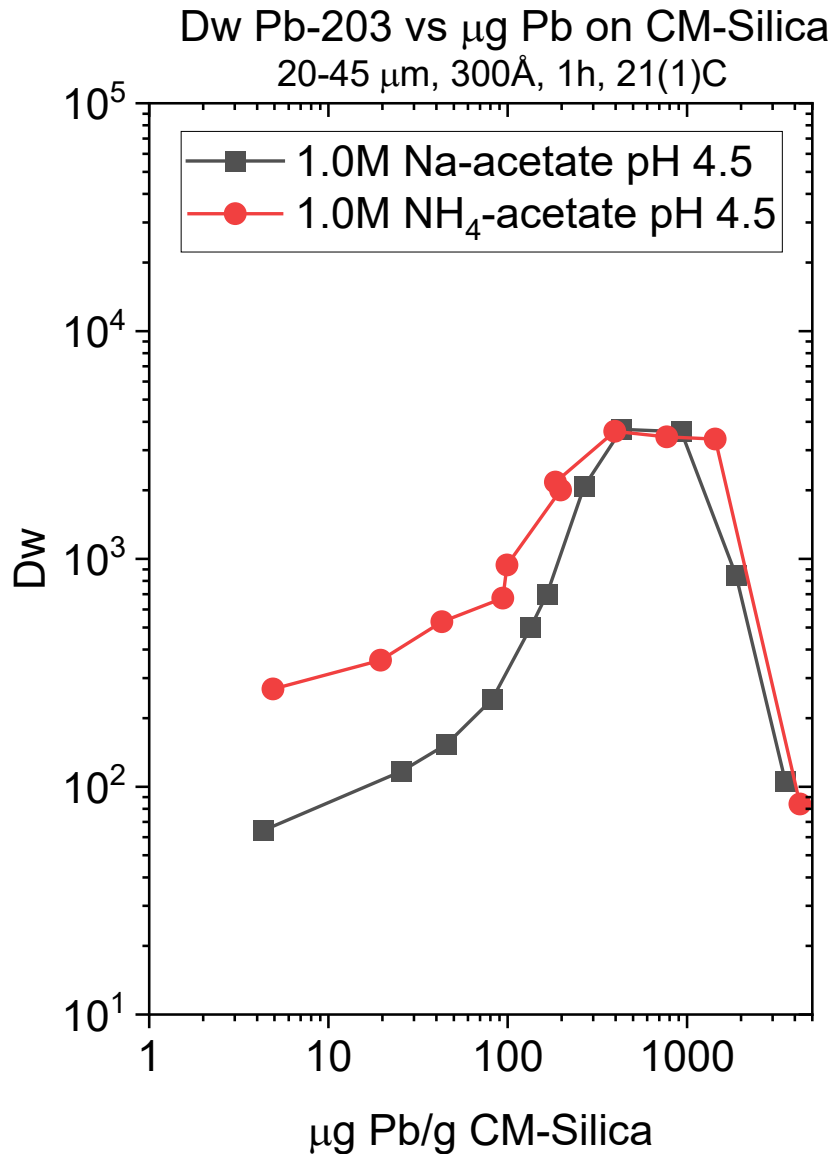
Weak cation exchange silica.

NH_4^+ vs Na^+ to reduce impact on stable element measurements by AES.



$\text{pK}_a \sim 2$

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

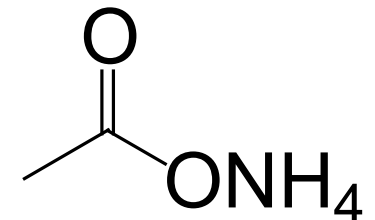
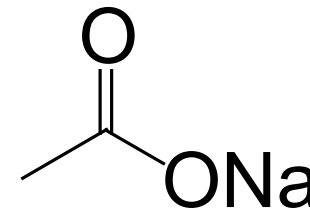
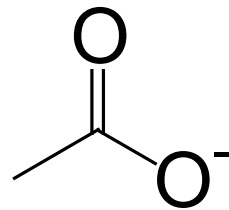


Some difference expected between Na^+ and NH_4^+ based on competition for IX sites.

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???

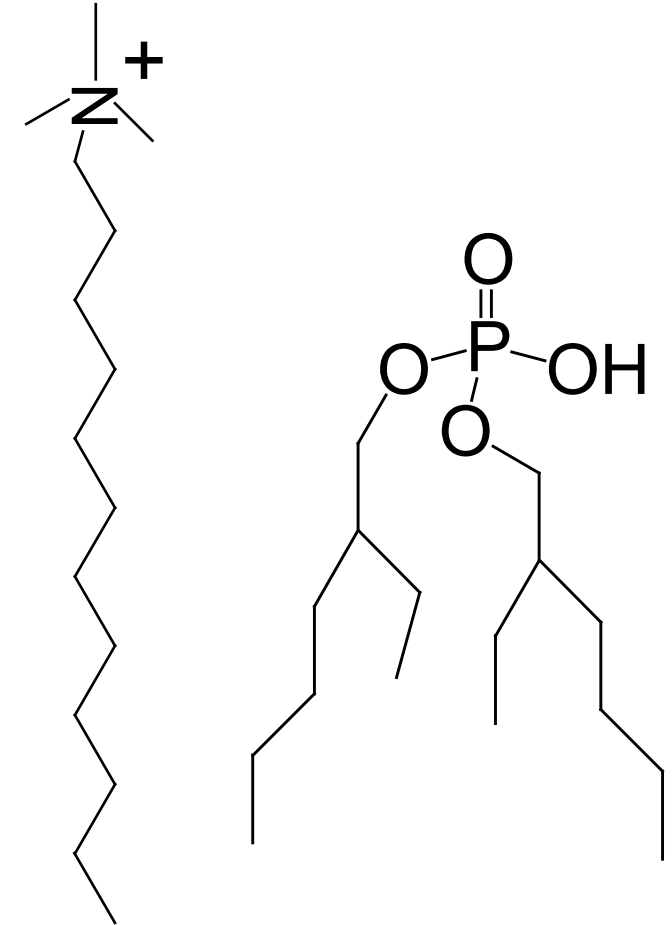
Answers???

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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)

