The use of surrogates in radionuclide separations method development

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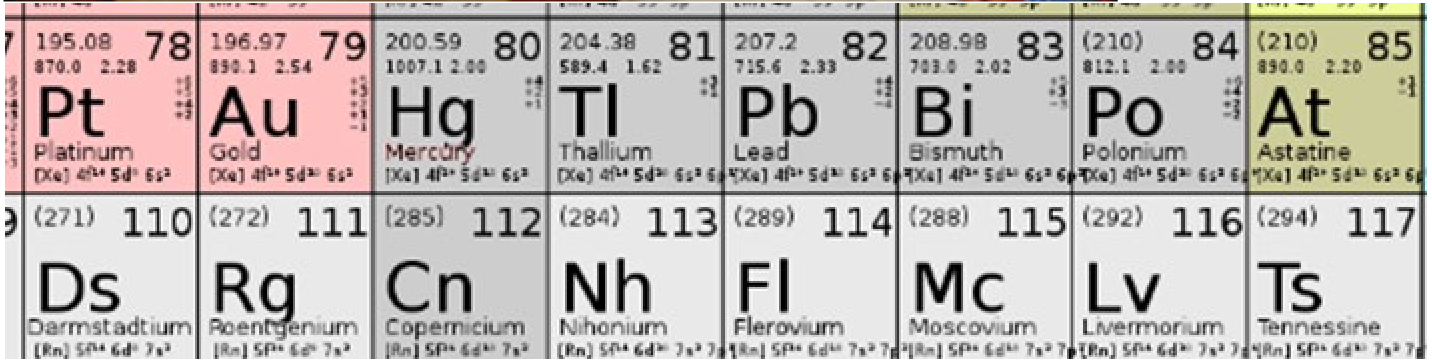
RRMC Radiobioassay & Radiochemical Measurements Conference

Eichrom

Dan and Phil (Oxford McDonalds, 2006)



- Founded in 1990 by Phil Horwitz

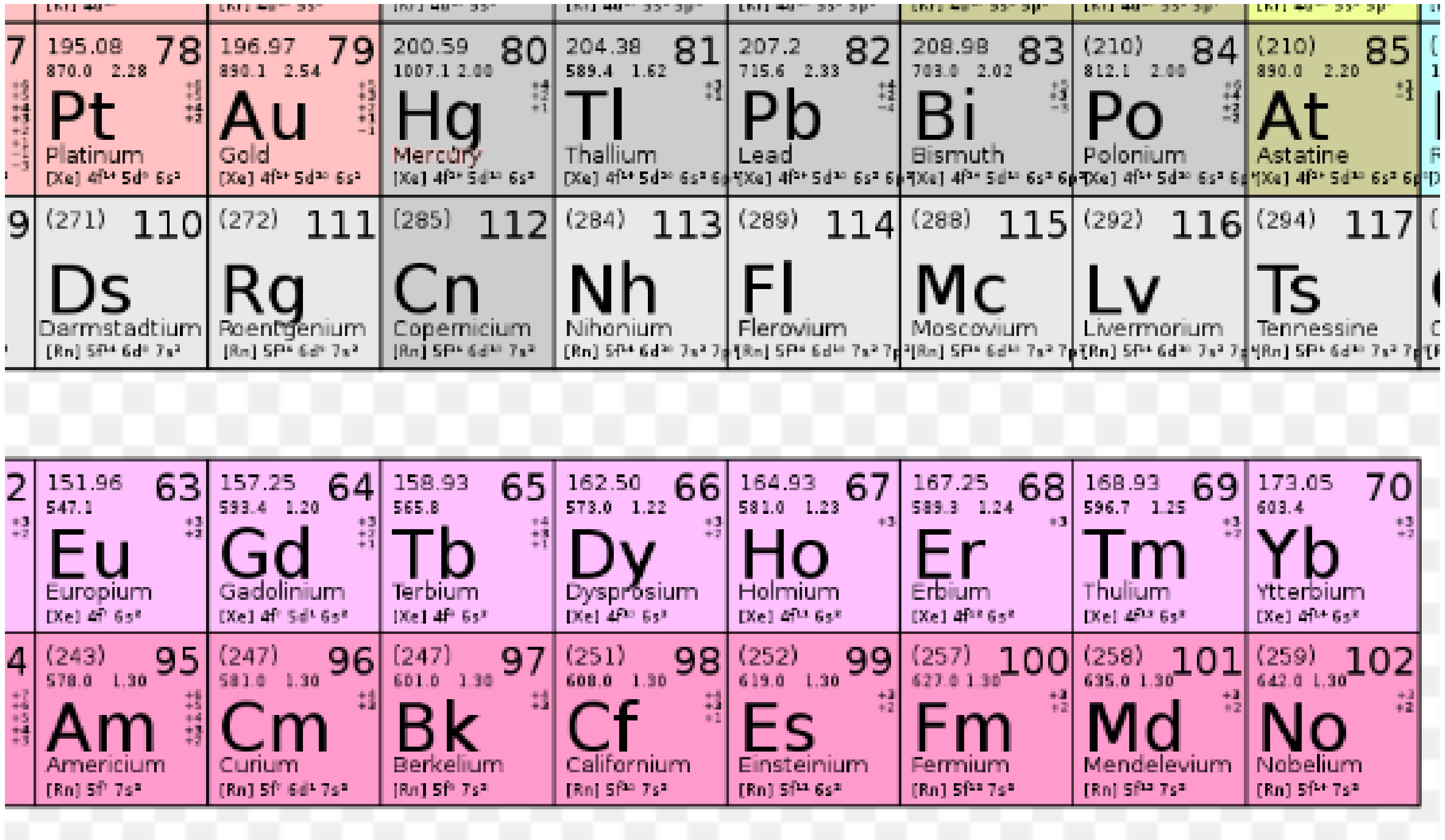
- Commercialized EXC resins developed and characterized at Argonne National Laboratory.

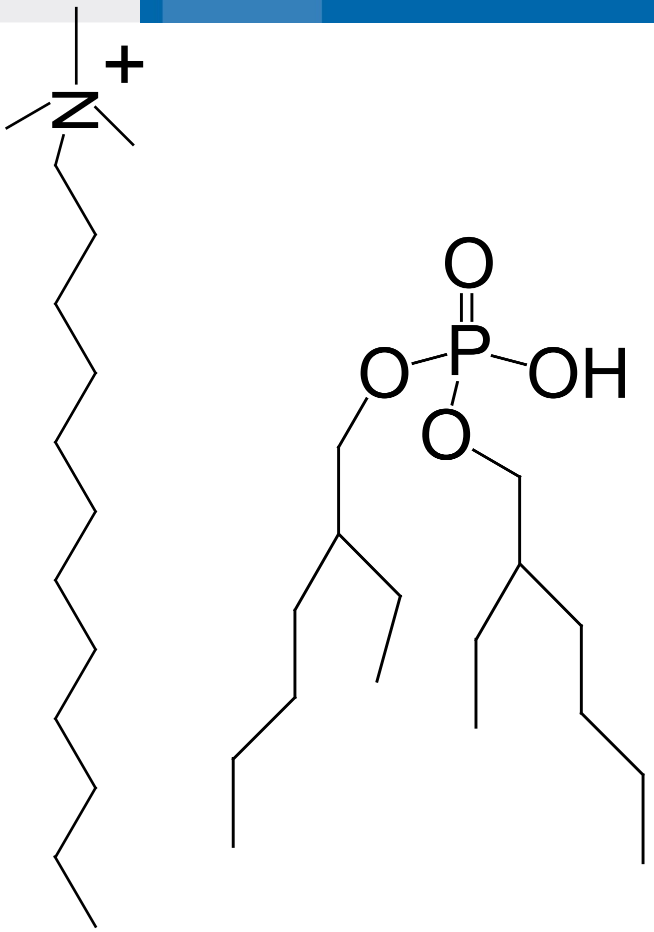
- Low-level environmental monitoring and bioassay to Ci-level production of isotopes for industry and nuclear medicine.

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

No other options

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





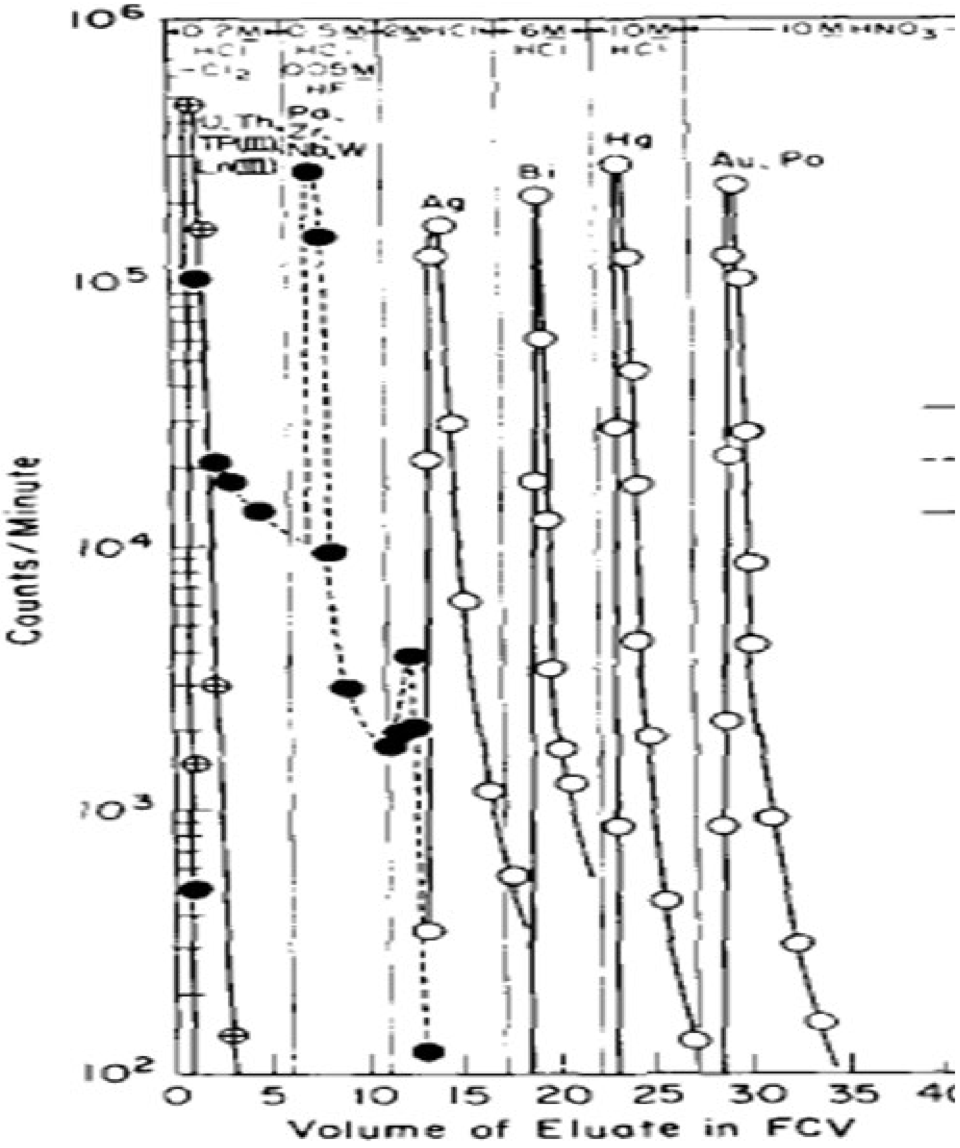
TEVA LN

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).

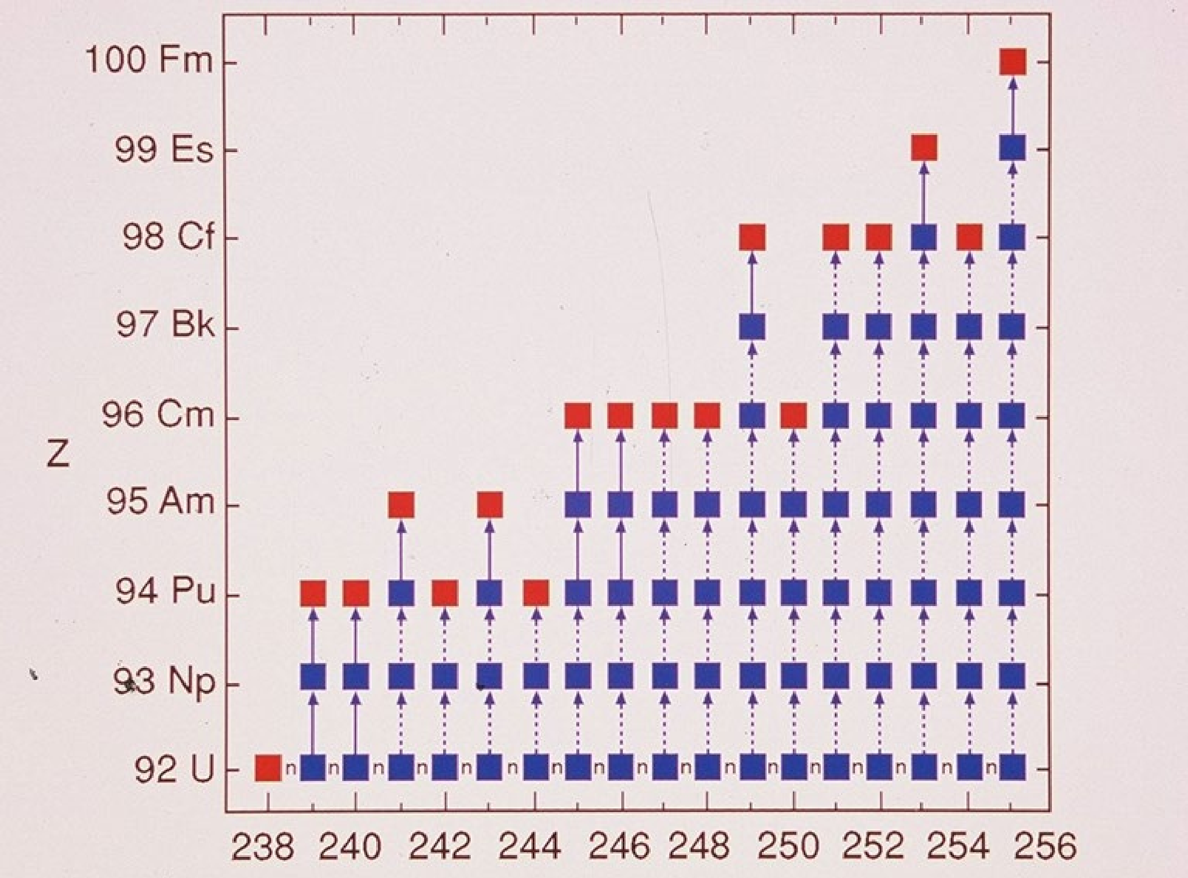
No other options

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.

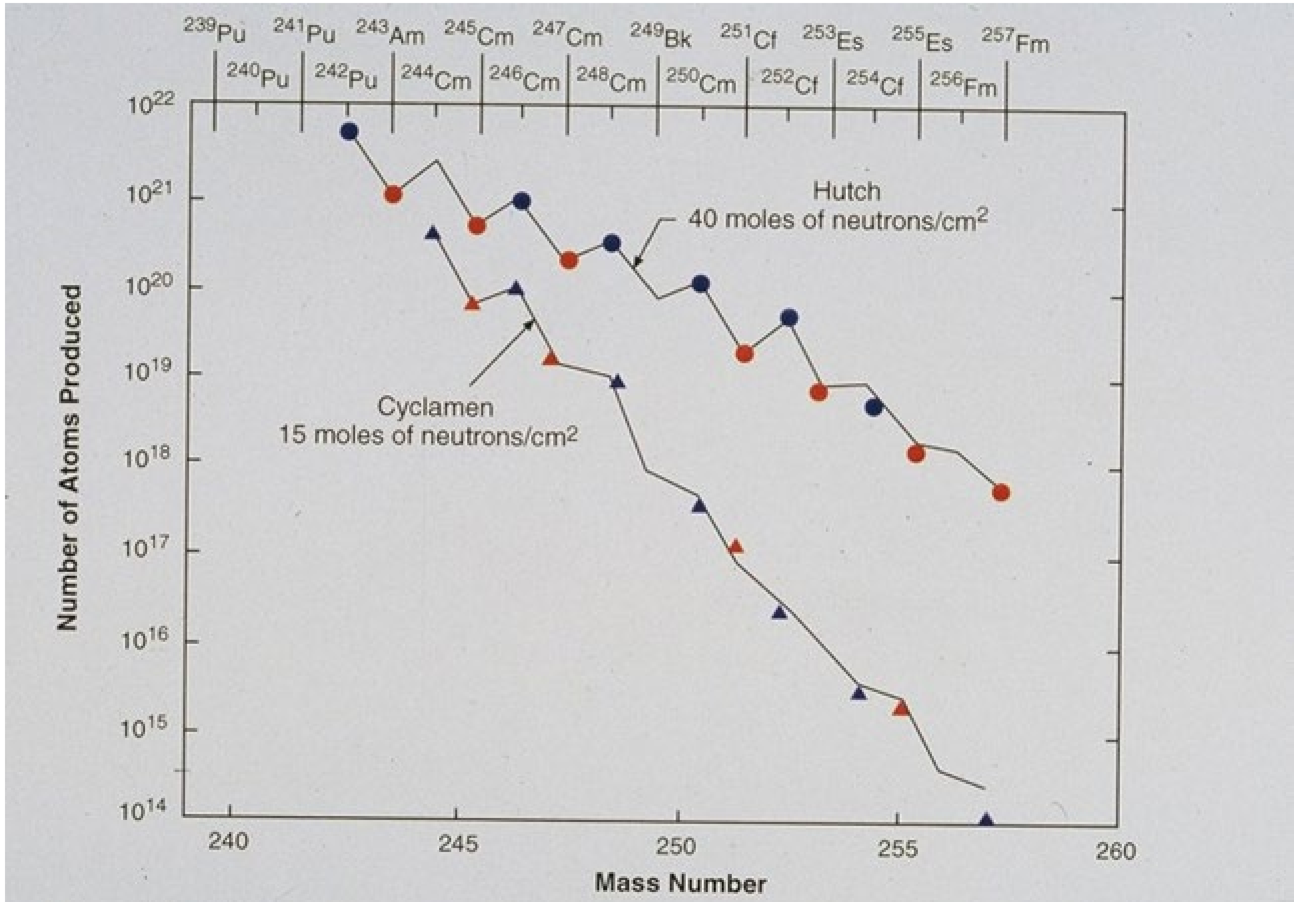
Group	Subgroups	Elements and Oxidation States
Group *A*		
	A_1	Zn(II), Cd(II), Re(VII), Bi(III)
	A_2	Pt(IV), Pb(IV), Hg(II)
	A_3	Sn(IV), Os(IV), Ir(IV), Au(III), Tl(III), Po(IV)
Group *B*		
	B_1	Ag(I), Zr(IV), Nb(V), W(VI)
	B_2	Pa(V)
	B_3	Sb(V), Te(VI), U(VI)
	B_4	Np(IV), Pu(IV)
Group *C*		
	C_1	Th(IV)
	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)



Results



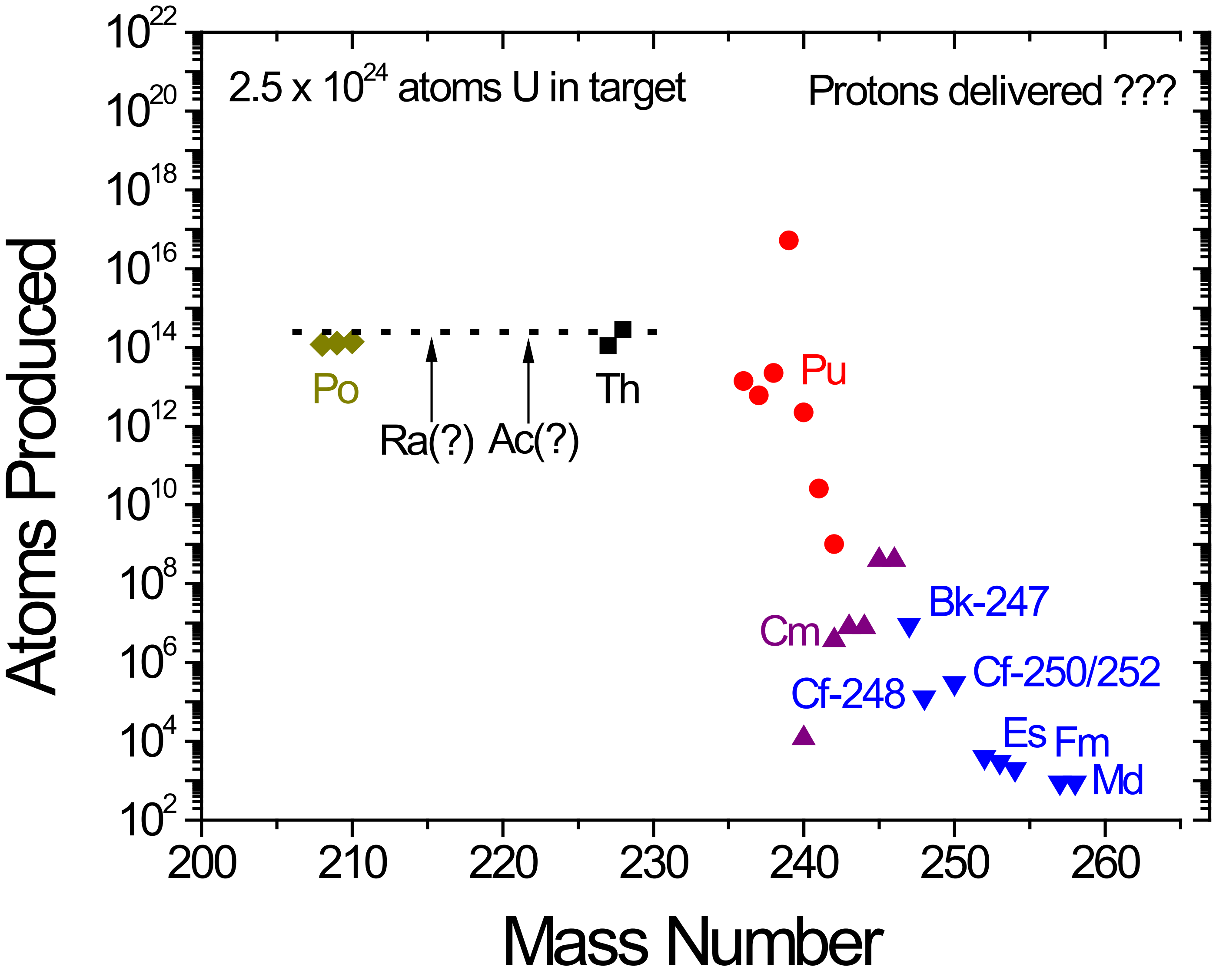
Production of heavy element isotopes in thermonuclear events. ■ beta unstable nuclide. ■ beta stable nuclide.



Mass Yield Curves in the Hutch and Cyclamen Nuclear Explosions.
From UCRL-81566

Results

Spallation Yield for Uranium Beamstop with 12 GeV Protons



Current Resources at Eichrom

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

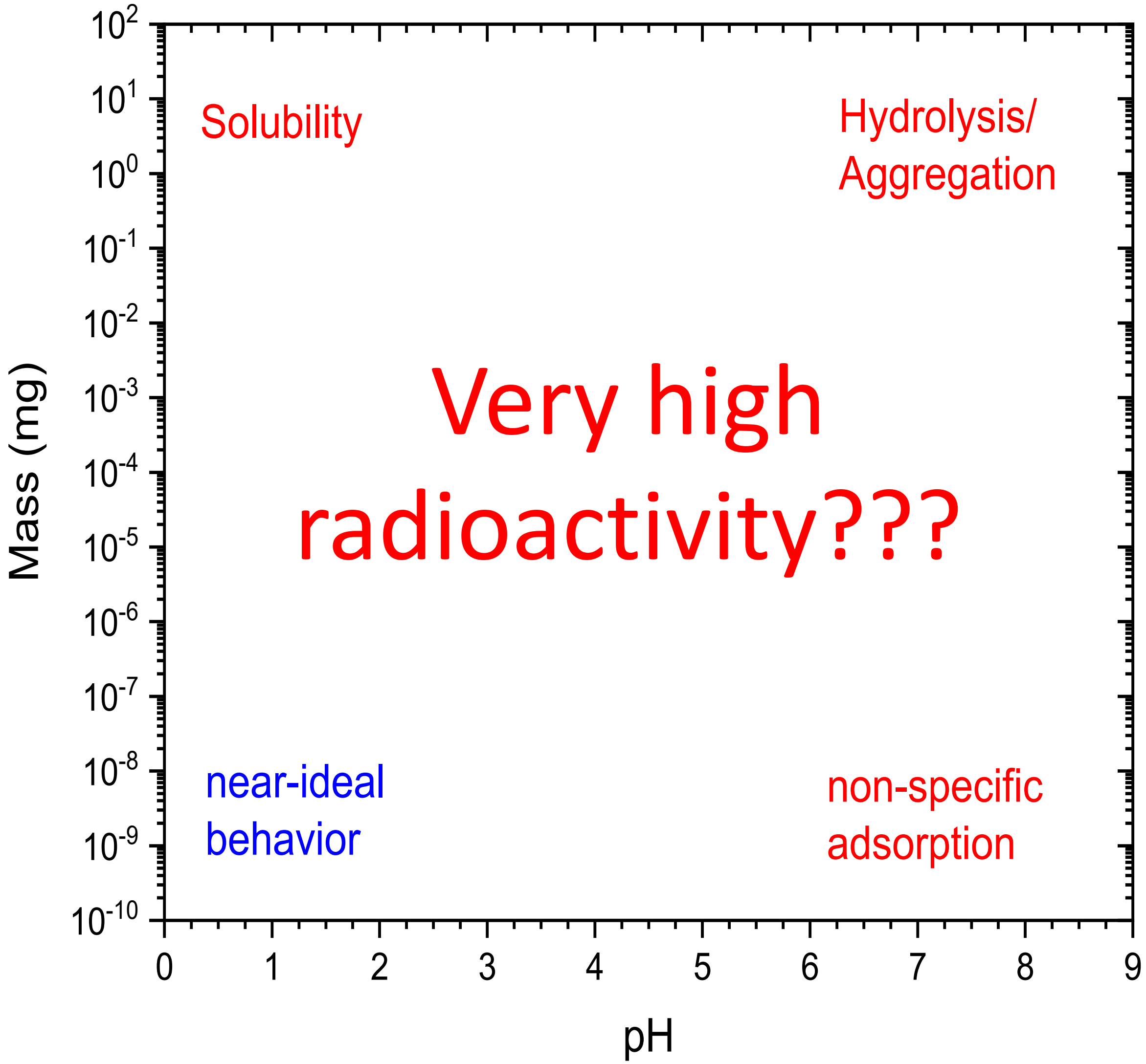
Alpha spectrometry, HPGe gamma, LSC, Na(Tl)I gamma, MP-AES, ~~**ICP-MS**~~

~~**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?

Hydrolysis

Hydrolysis - Splitting of H_2O into ^{-}OH and H^+

$$m\ UO_2^{2+} + p\ H_2O \quad \longleftrightarrow \quad (UO_2)_m(OH)_p^{2m-p} + p\ H^+$$

more U

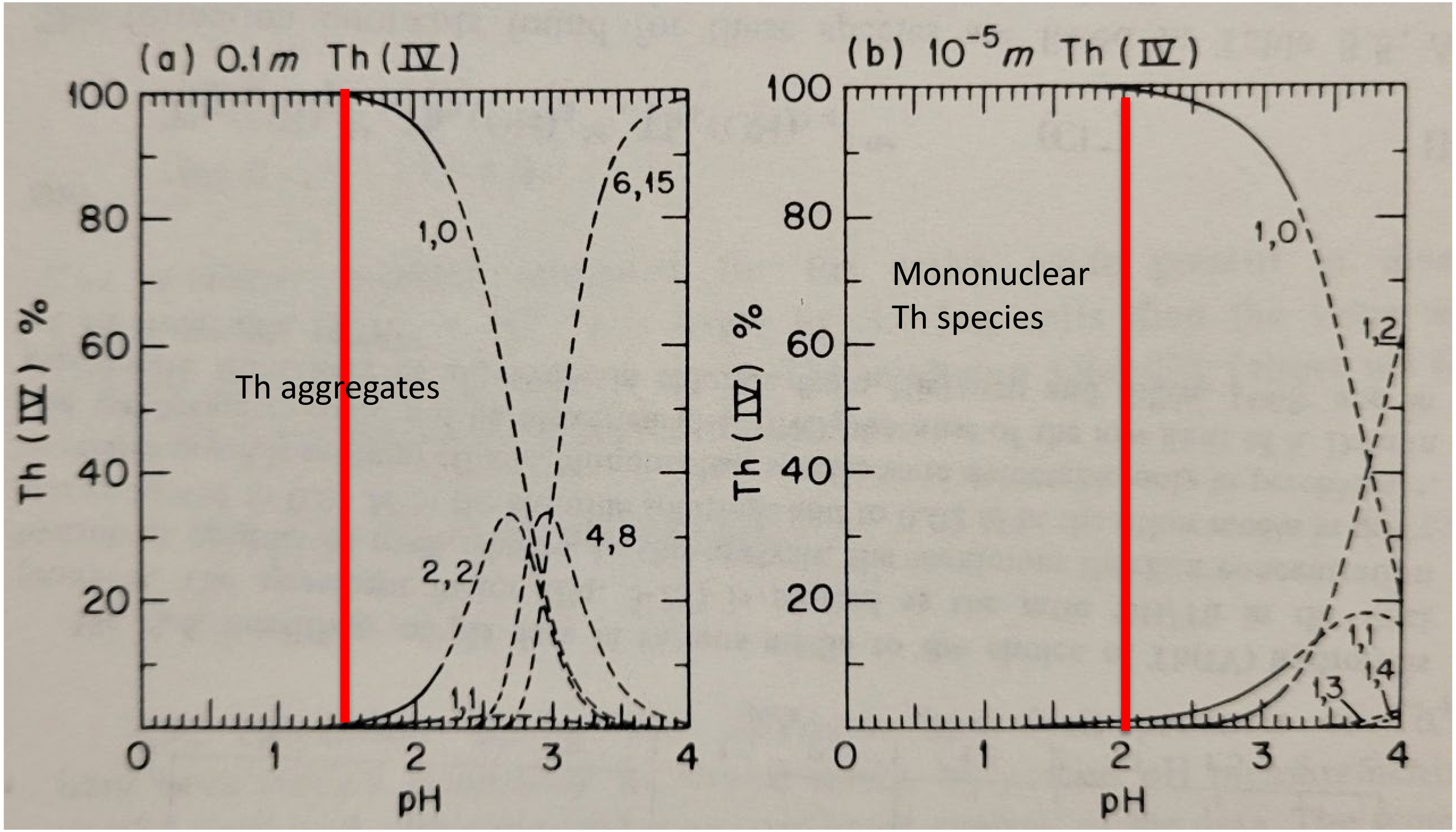
more hydrolysis

equilibrium

more H^+

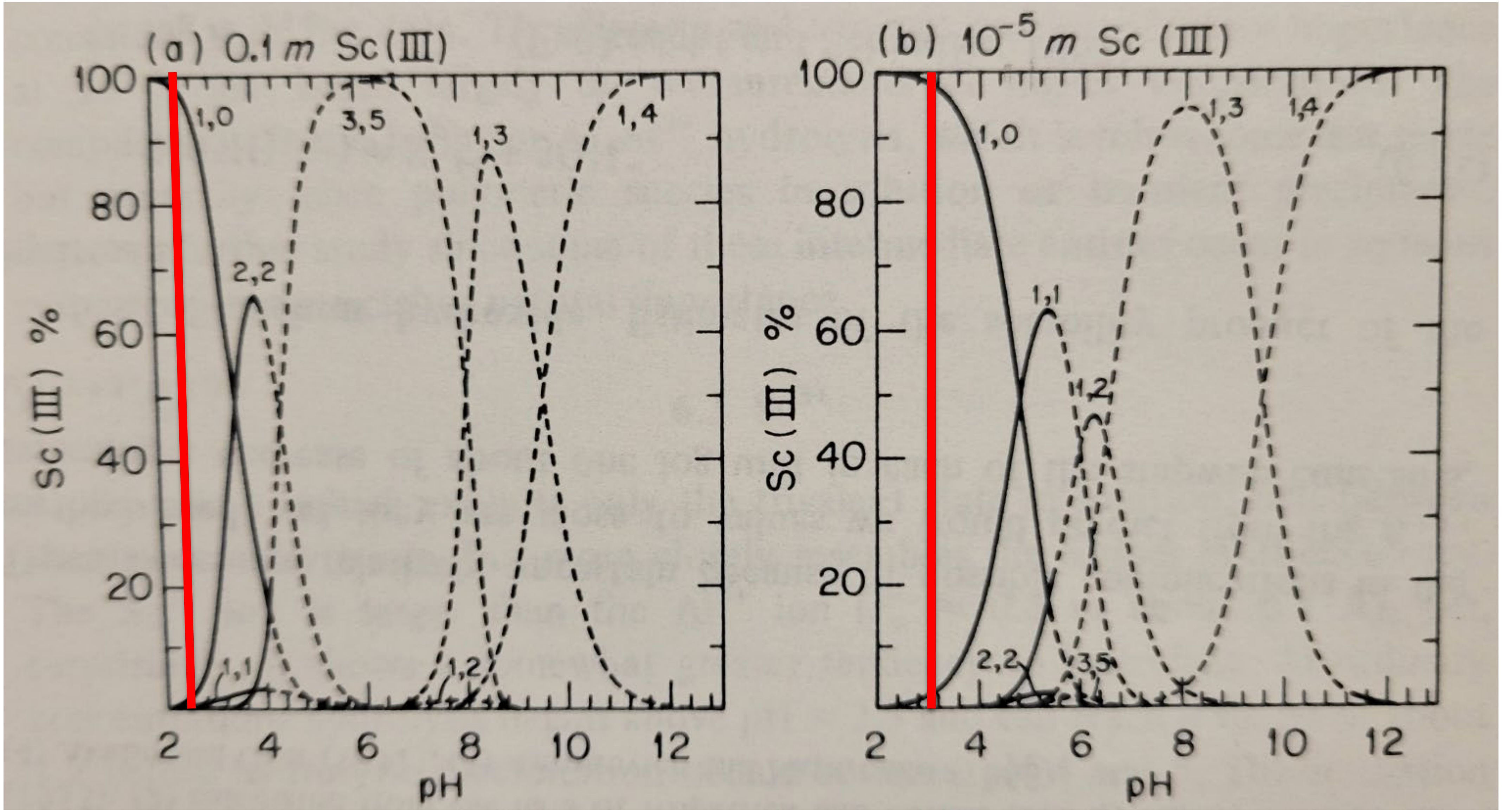
less hydrolysis

Hydrolysis Th(IV)

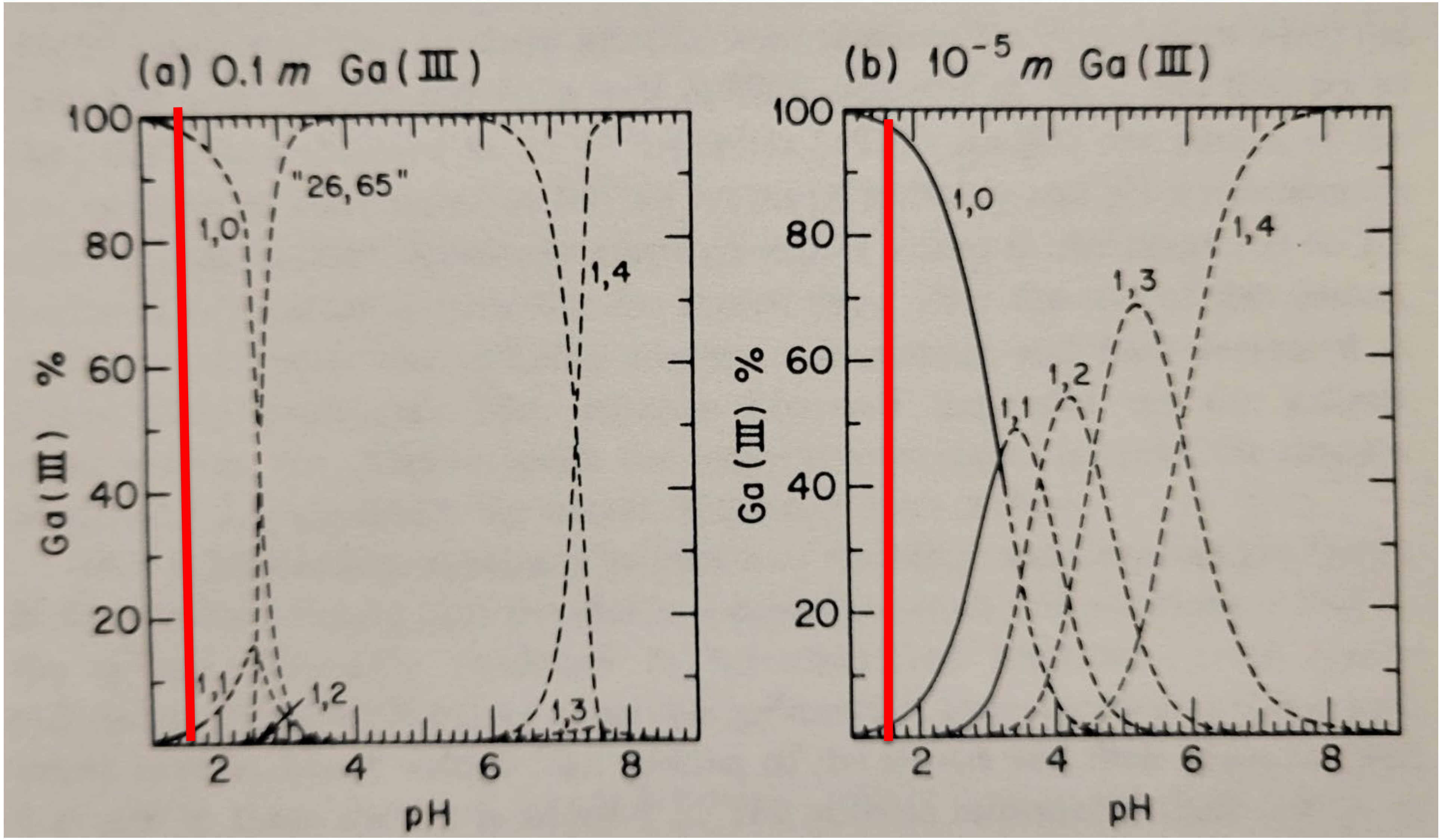


Charles F Baes and Robert E Mesmer “The hydrolysis of cations”, Wiley-Interscience, New York (1976).

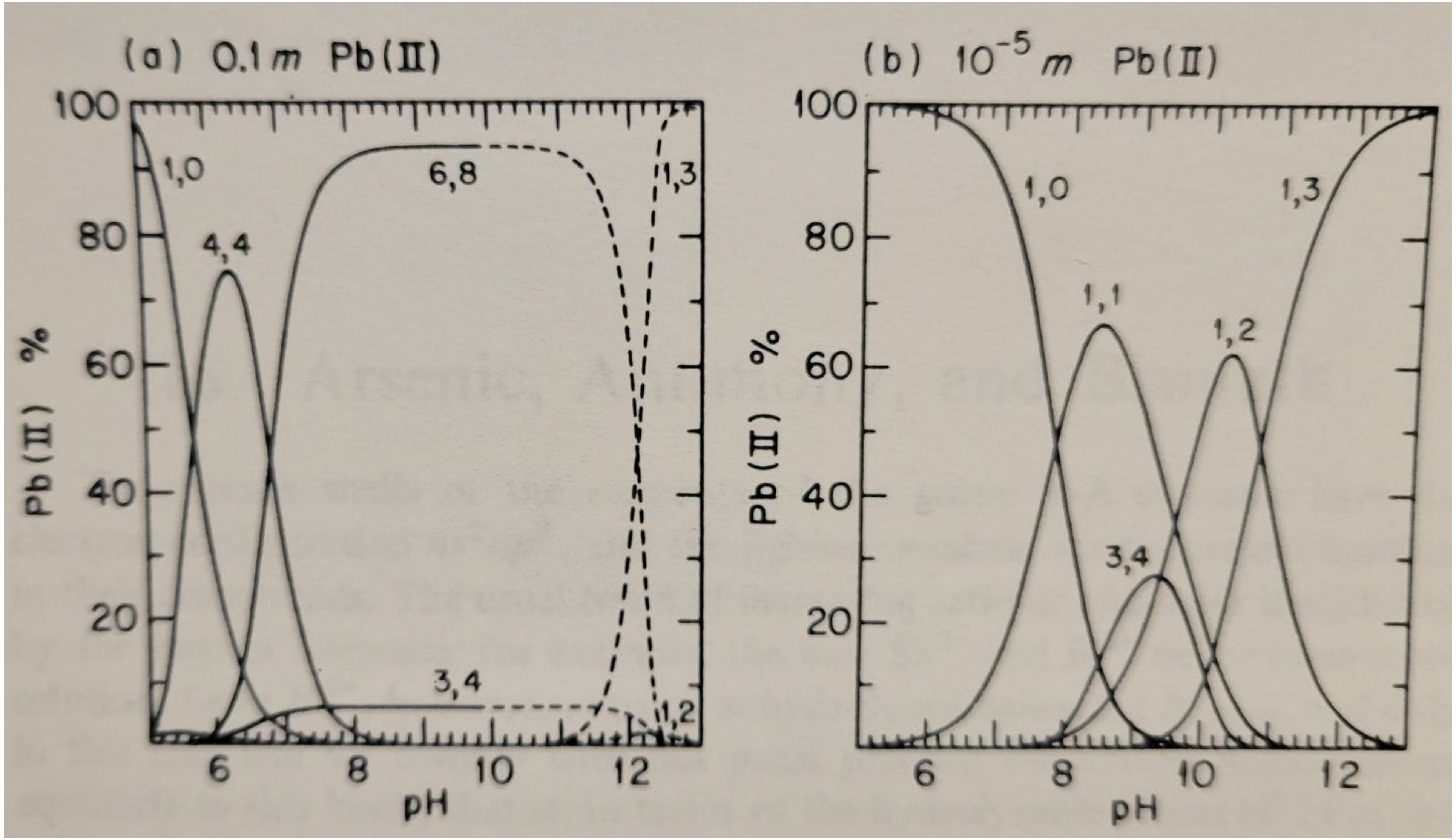
Hydrolysis Sc(III)



Hydrolysis Ga(III)



Hydrolysis Pb(II)



Solubility $Ra(NO_3)_2$ / $Ba(NO_3)_2$

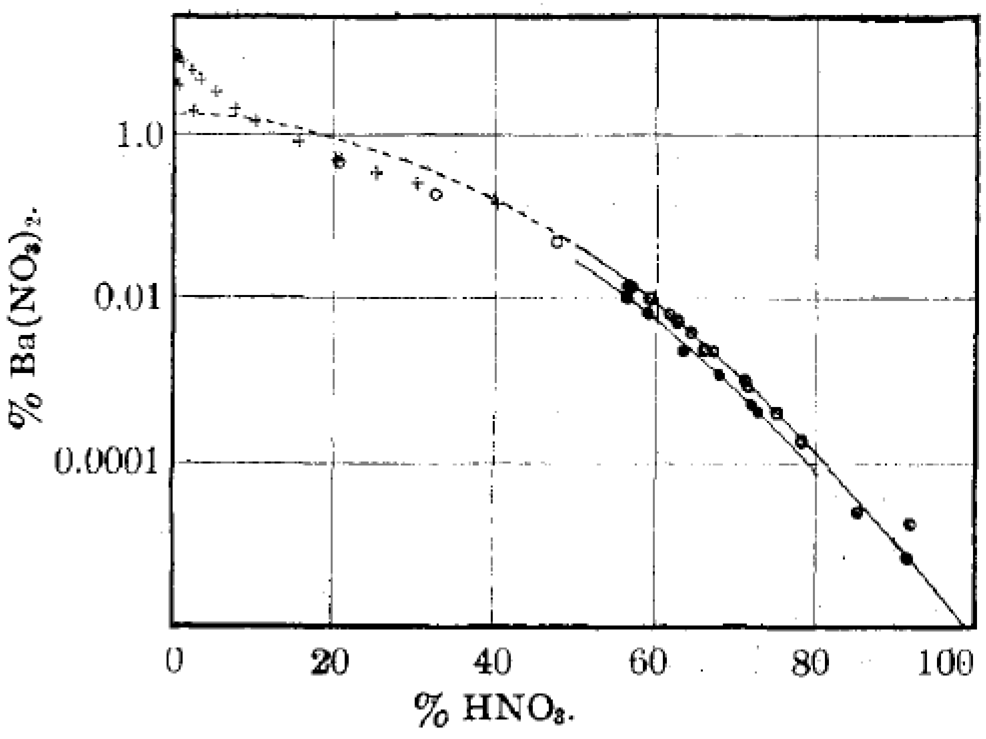


Fig. 1.—The solubility of barium nitrate in nitric acid: ○, experiments at 24.88°; ●, experiments at 0.00°; +, experiments of Tolmachev.[8]

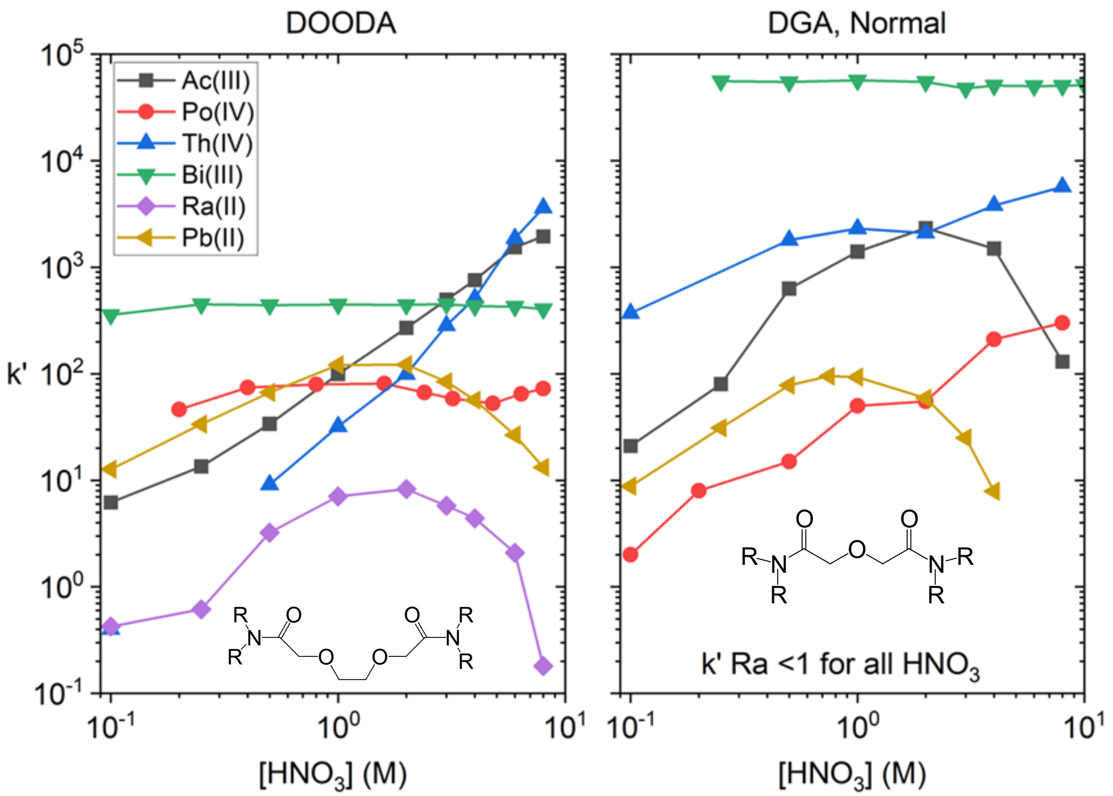
J. Am. Chem. Soc. 1937, 59, 7, 1186–1188

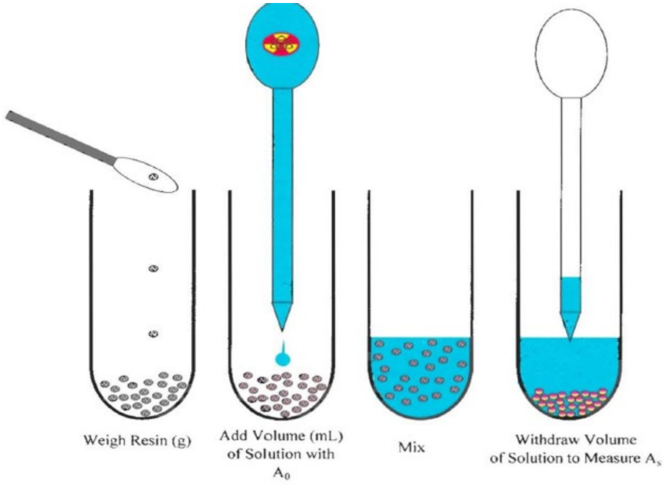
THE SOLUBILITY OF BARIUM NITRATE IN NITRIC ACID

Temperature, 24.88°

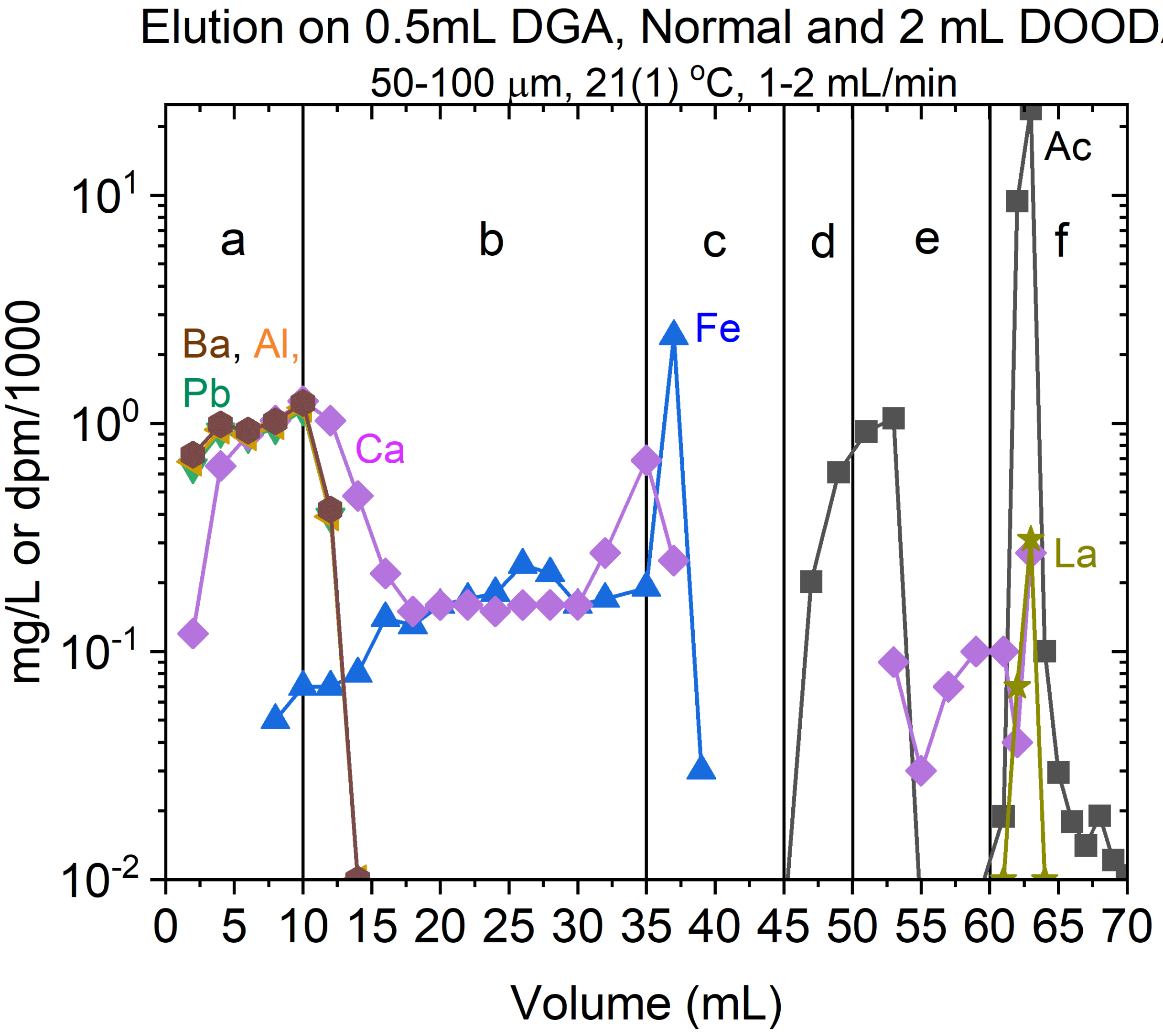
HNO_3, %	Density, g./ml.	$Ba(NO_3)_2$, mg./l.	$Ba(NO_3)_2$, %	6 + log (% $Ba(NO_3)_2$) Exptl.	Calcd.
0.00	1.0769	99,400[b]	9.23	6.97[a]	..
20.65	1.1221	5,560[b]	0.495	5.69[a]	..
32.71	1.1966	2,380[b]	.199	5.30[a]	..
47.60	1.2907	624[b]	.0484	4.68[a]	..
56.60	1.343	197	.0147	4.17	4.18
56.98	1.346	187	.0139	4.14	4.15
59.06	1.355	136	.0100	4.00	3.99
61.67	1.372	87.3	.00636	3.80	3.79
62.77	1.373	72.8	.00532	3.73	3.70
64.36	1.385	51.5	.00372	3.57	3.57
66.05	1.394	33.5	.00241	3.38	3.43
67.12	1.394	31.7	.00228	3.36	3.34
67.30	1.395	31.0	.00223	3.35	3.33
71.15	1.413	14.1	.00100	3.00	2.99
71.45	1.415	12.2	.000865	2.94	2.96
75.14	1.430	5.78	.000404	2.61	2.61
78.29	1.445	2.87	.000199	2.30	2.30
78.51	1.442	2.85	.000197	2.29	2.28
85.37	1.463	0.376	.0000257	1.41[a]	1.56
91.69	1.485	.108	.0000072	0.86[a]	0.85
92.10	1.480	.283	.0000191	1.28[a]	.80

Typical method development at Eichrom





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



f: 10 mL 0.1M HCl

90% Ac-225

<<1% La, Th, Bi, Po

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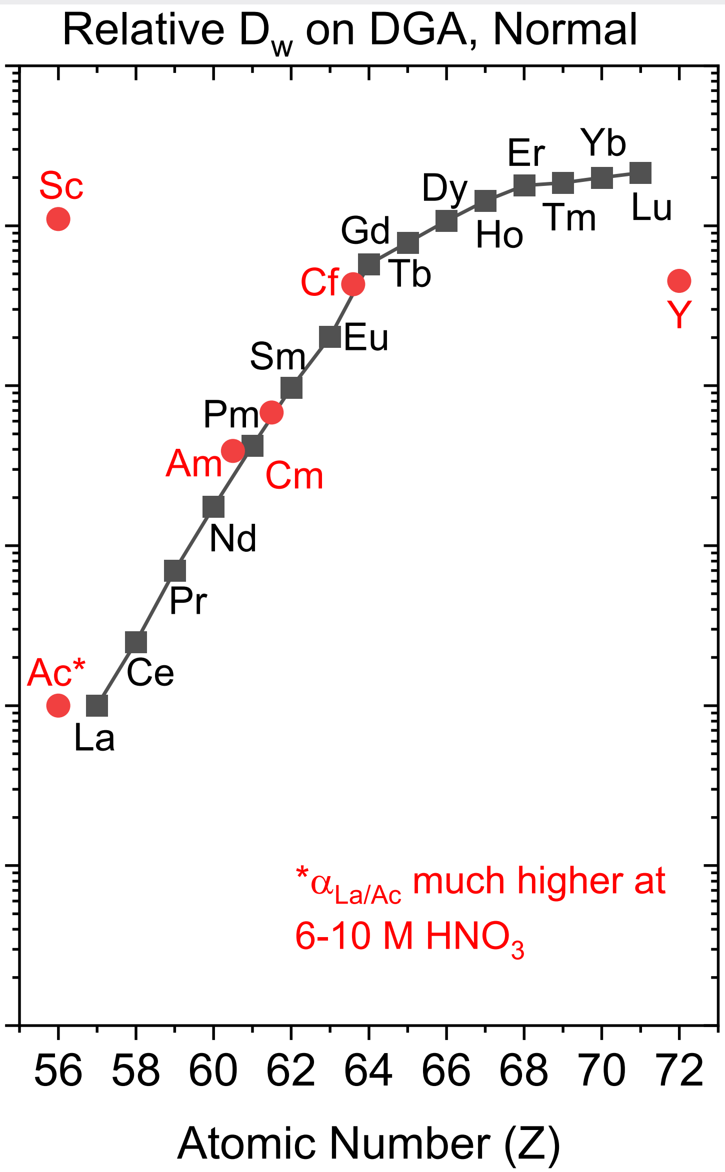
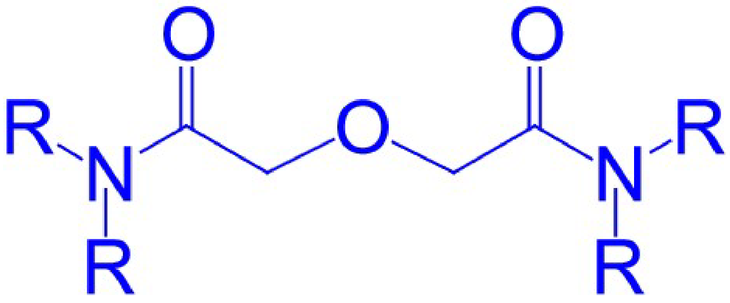
Examples of the use of surrogates

Rare Earths for Minor Actinides

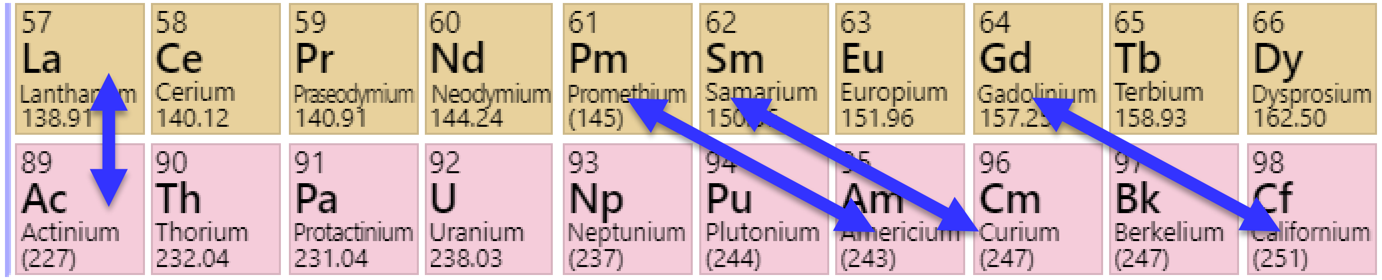




R = n-octyl or 2-ethyl-1-hexyl

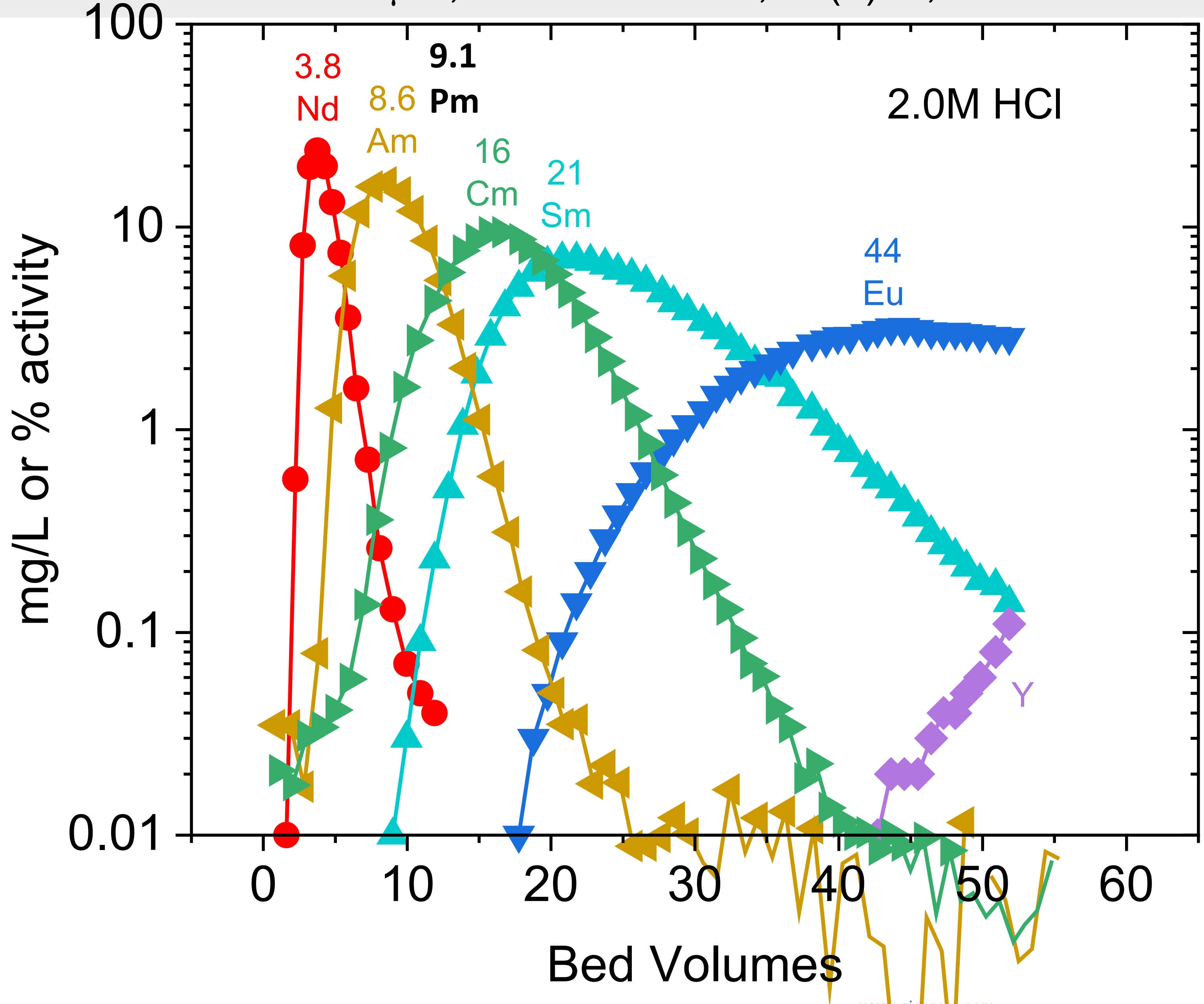
$M^{3+} + 3DGA + 3X^{-} \leftrightarrow M(DGA)_3X_3$

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)

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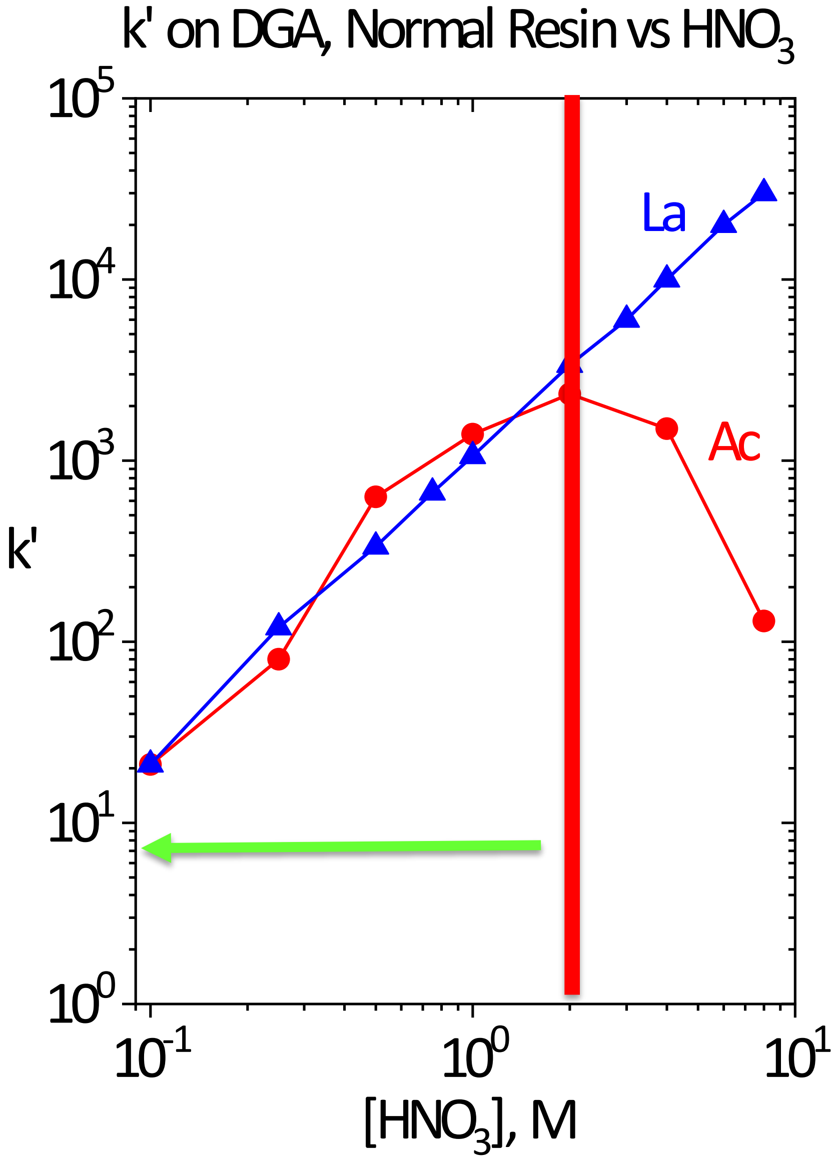
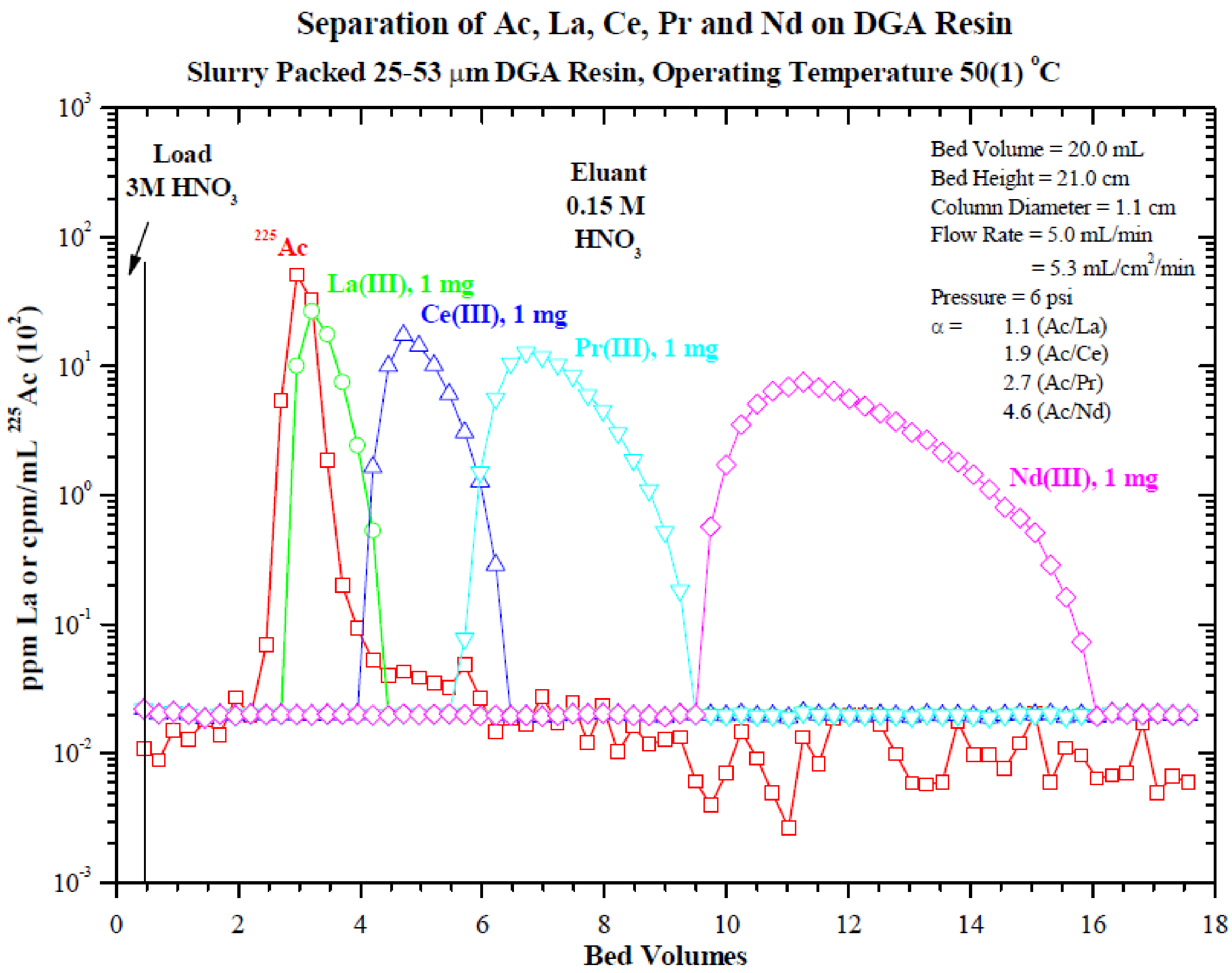
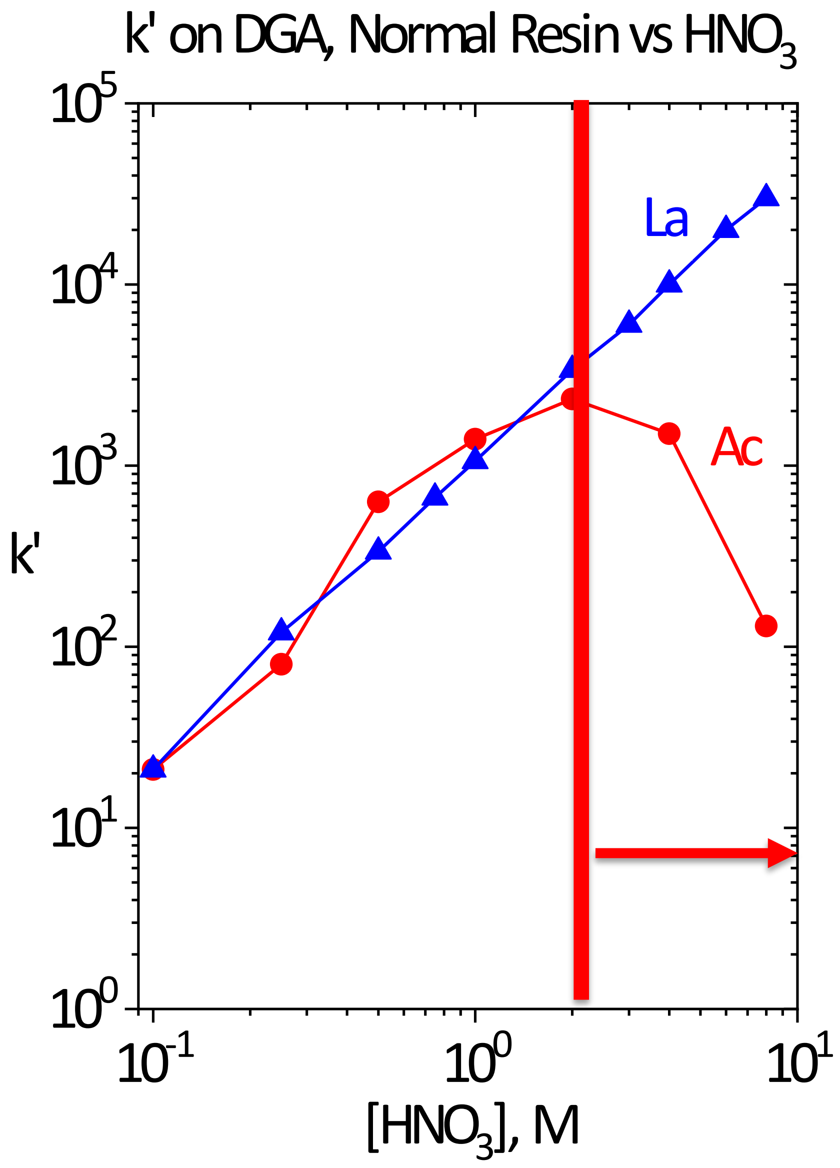
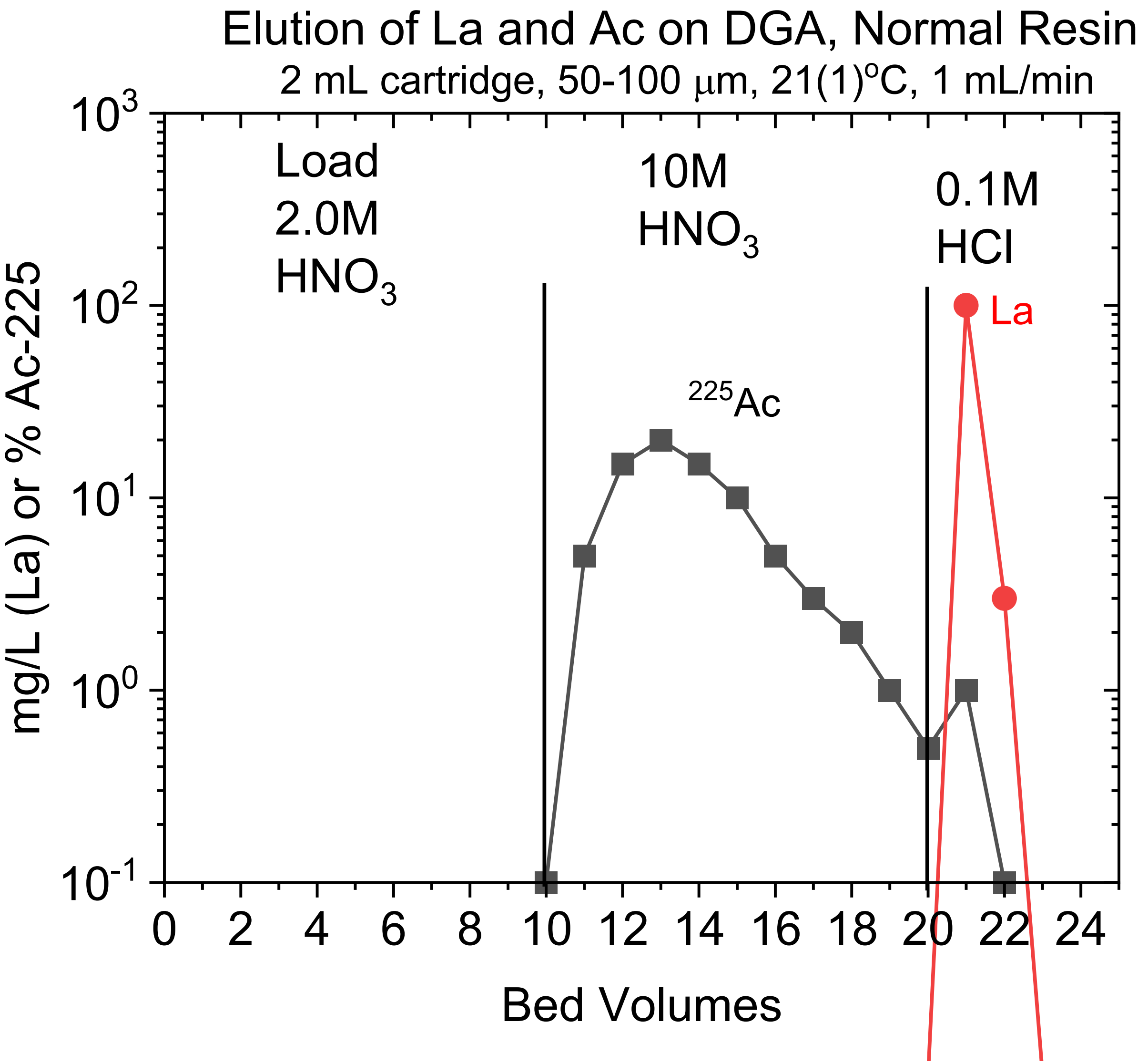




La for Ac-225 (DGA – 10M HNO_3)





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

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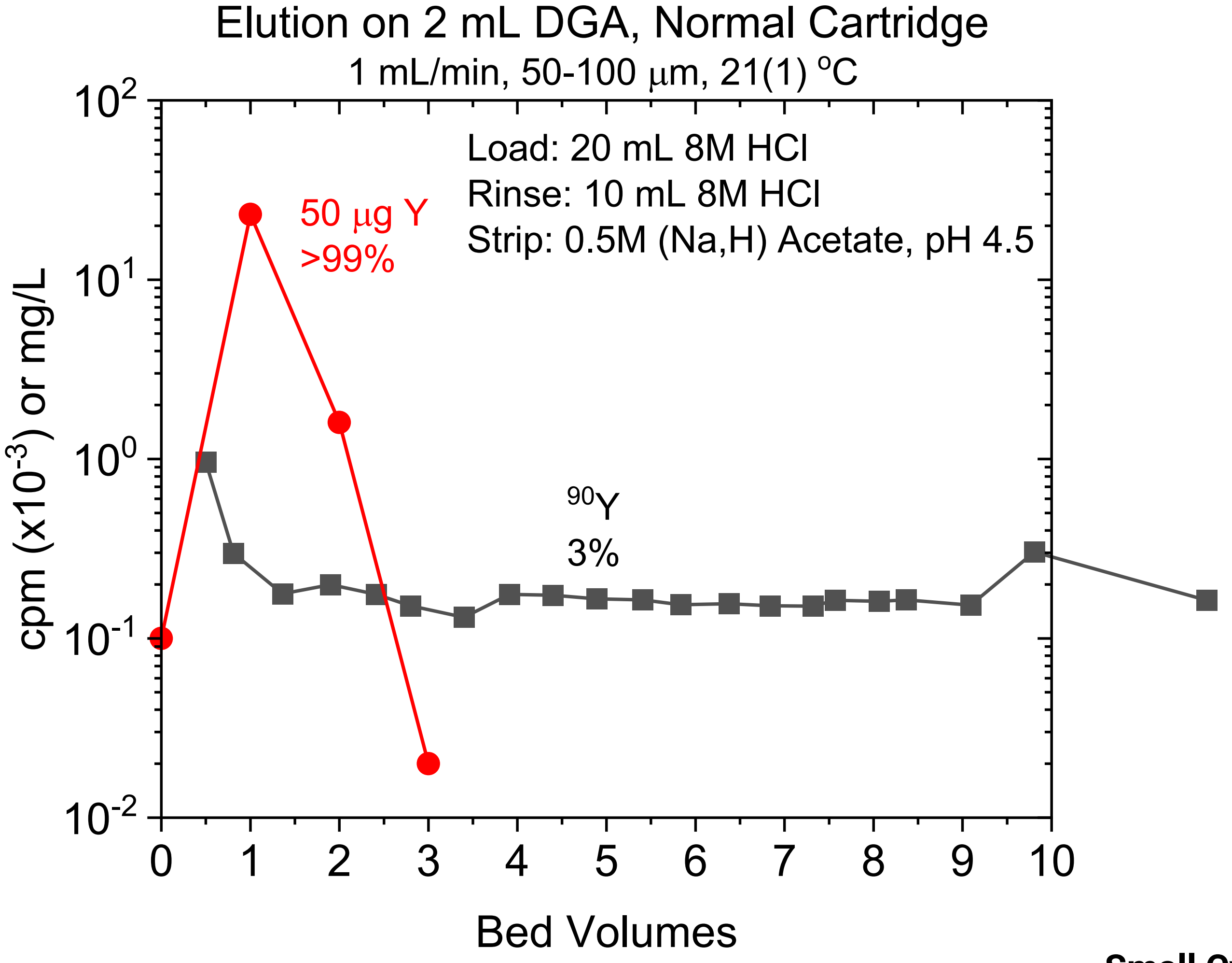

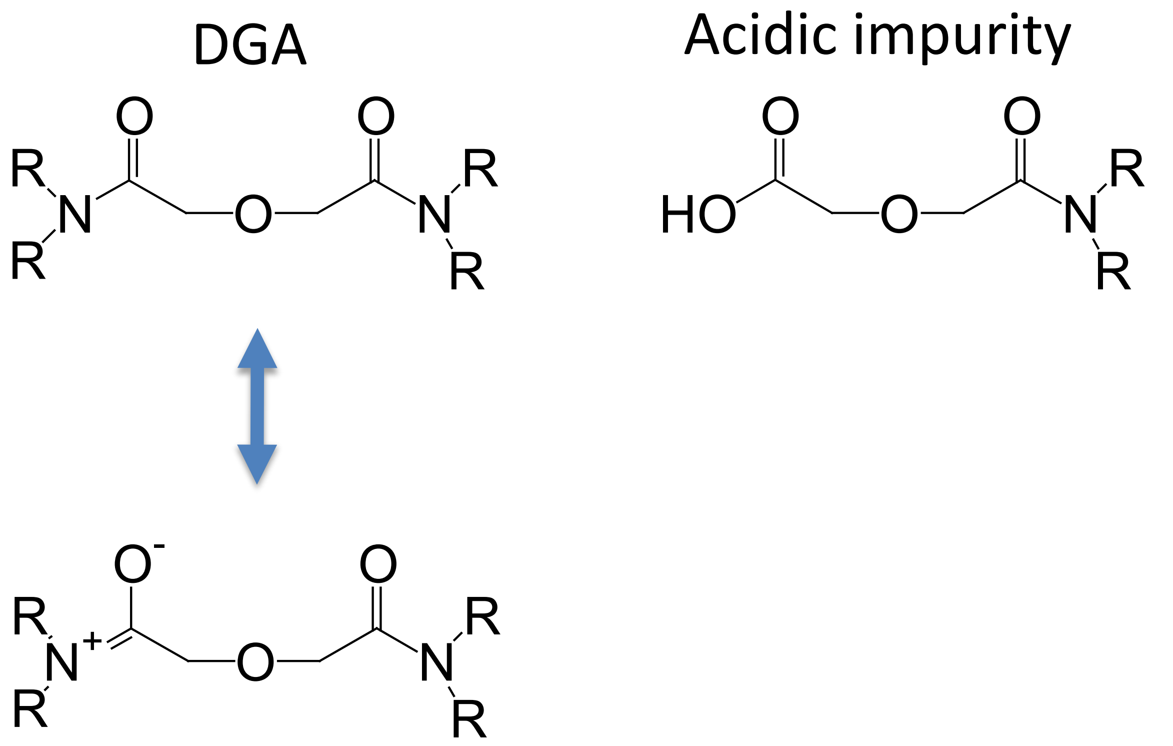

Yield for ^{225}Ac > 95%

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 stable Y (Elution from DGA Resin)

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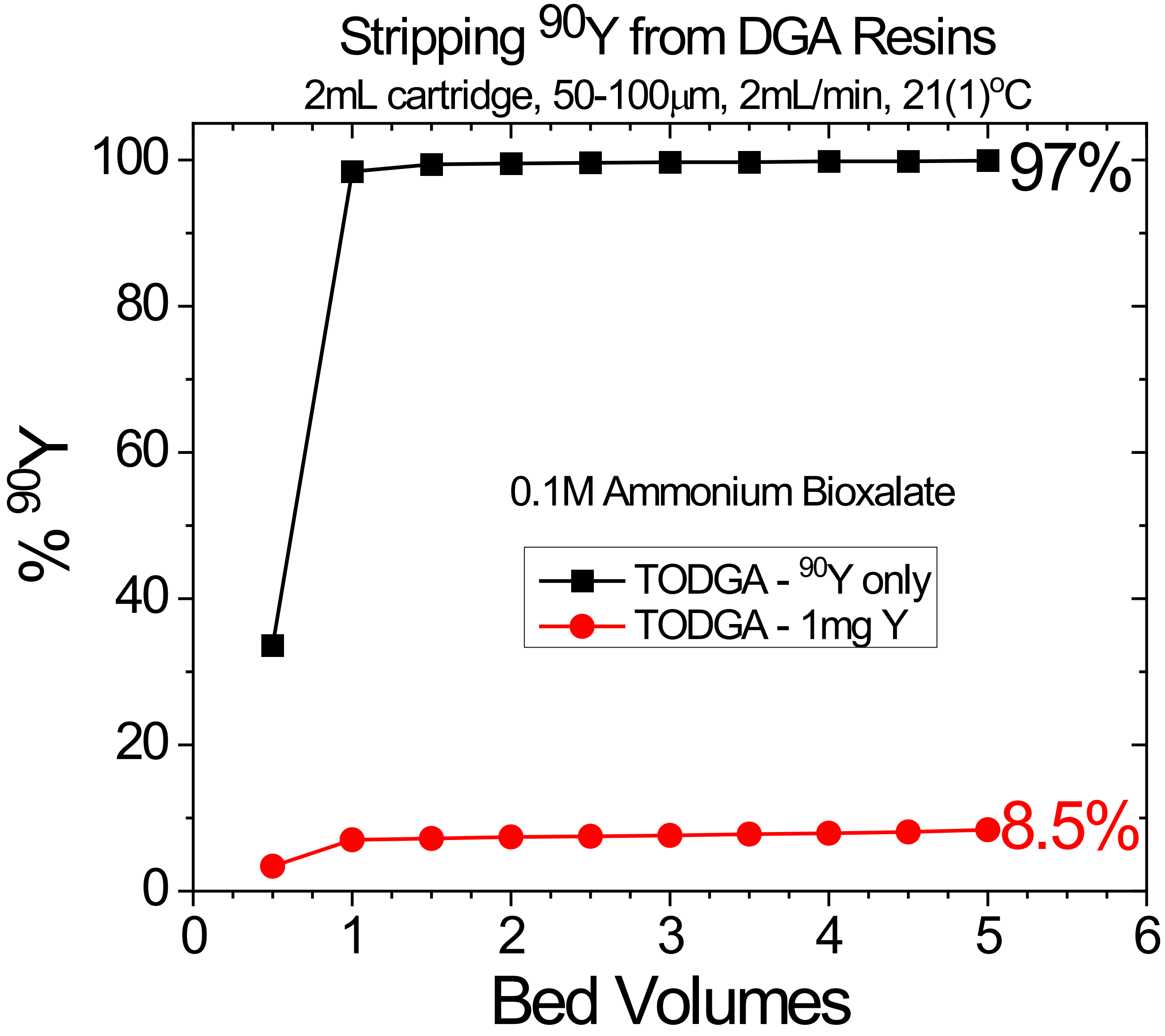

Load: 20 mL 0.25M HNO_3
Rinse: 10 mL 8M HNO_3
Strip Y: 10 mL 0.1M ammonium bioxalate

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

^{228}Th Decay Scheme and surrogate options

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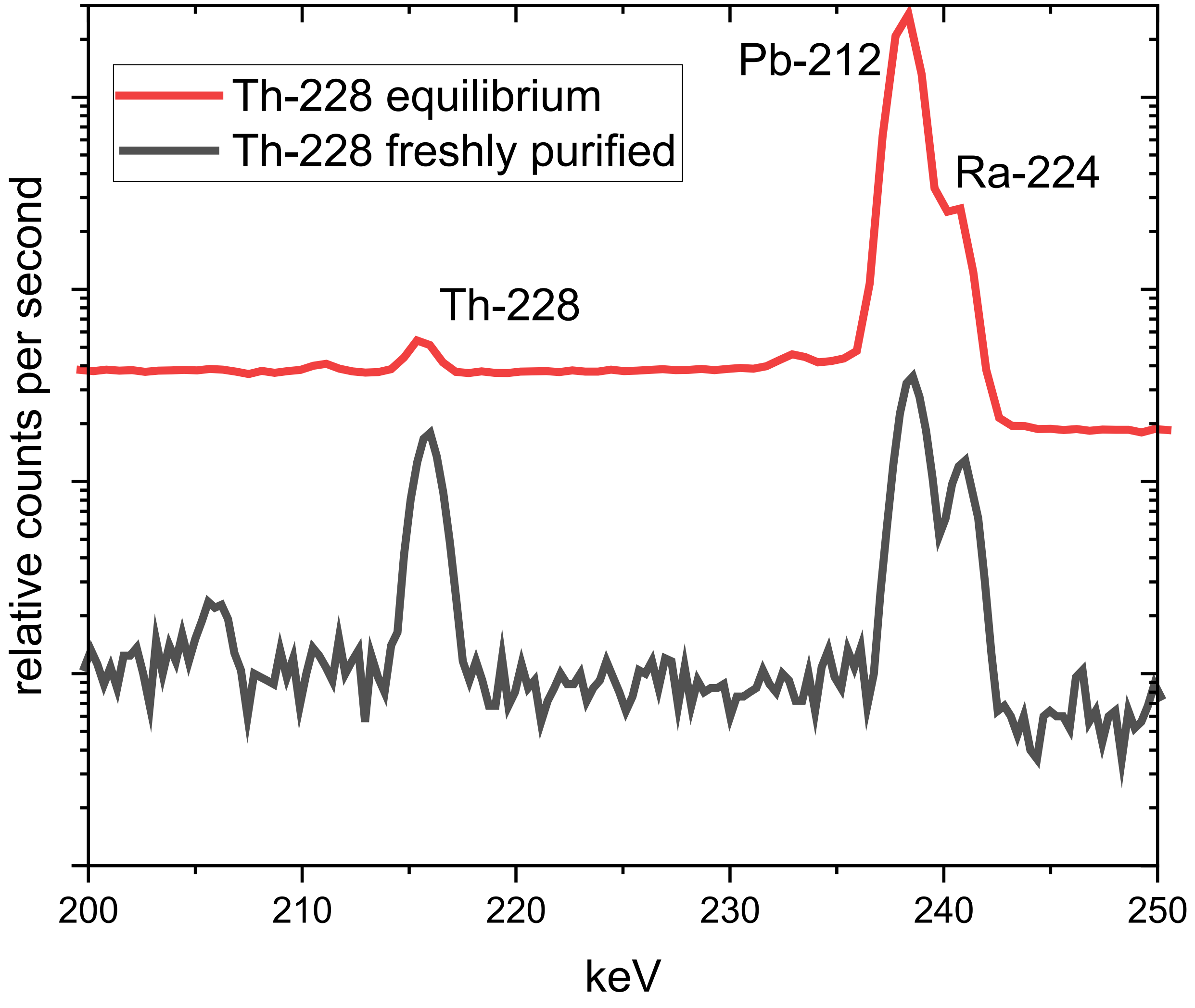


^{228}Th 215.985 keV (0.246%)

^{224}Ra 240.986 keV (4.12%)

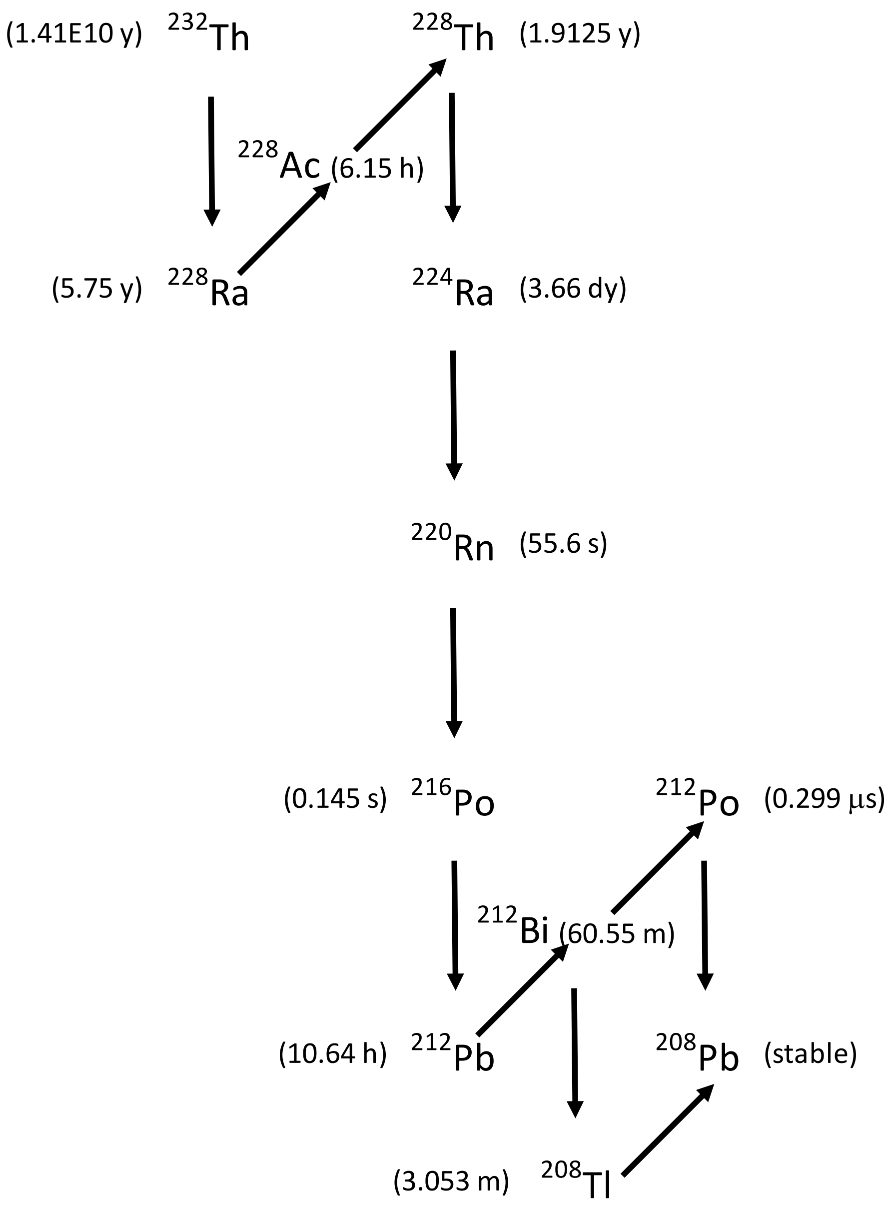
^{212}Pb 238.632 keV (43.6%)

^{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/

^{228}Th 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

^{203}Pb vs Stable Pb for ^{212}Pb (Na^+ vs NH_4^+ acetate)

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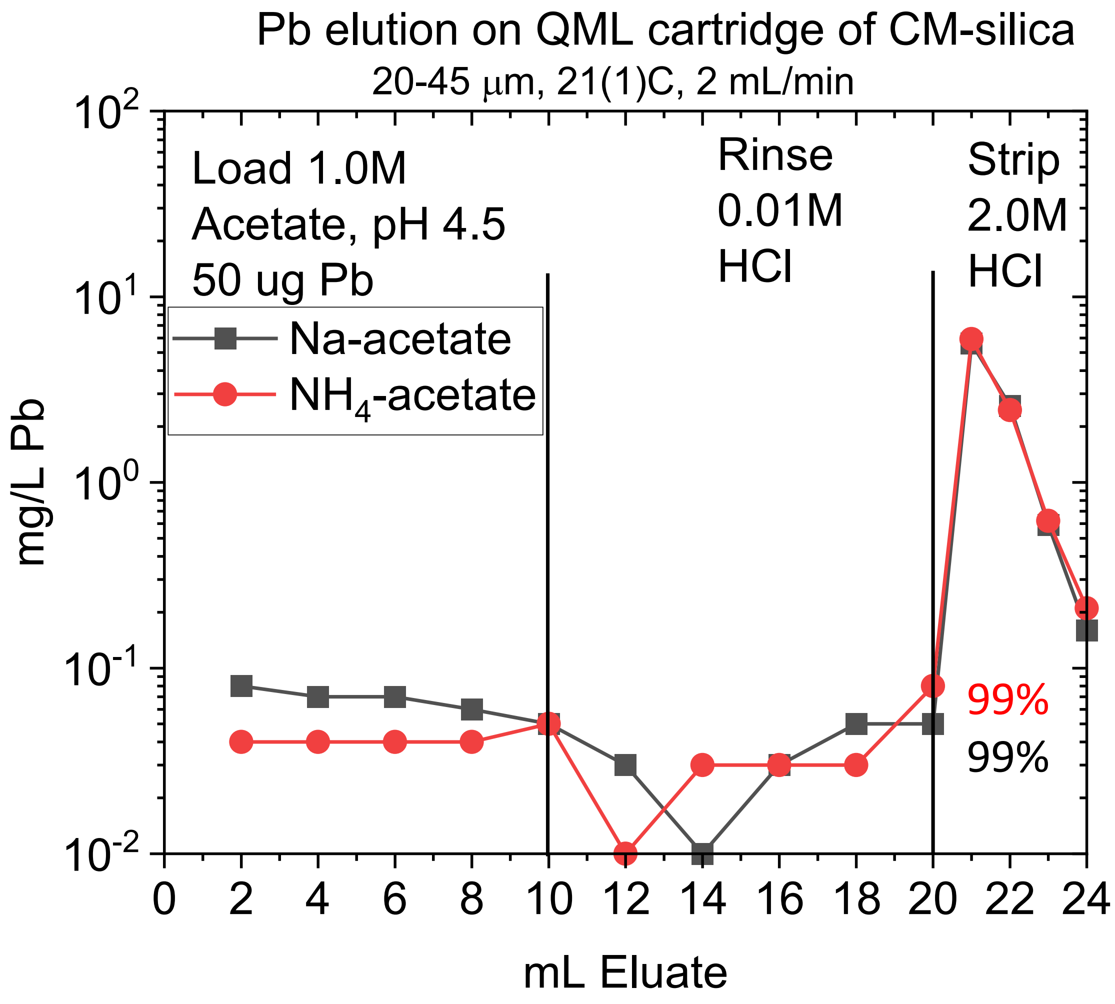
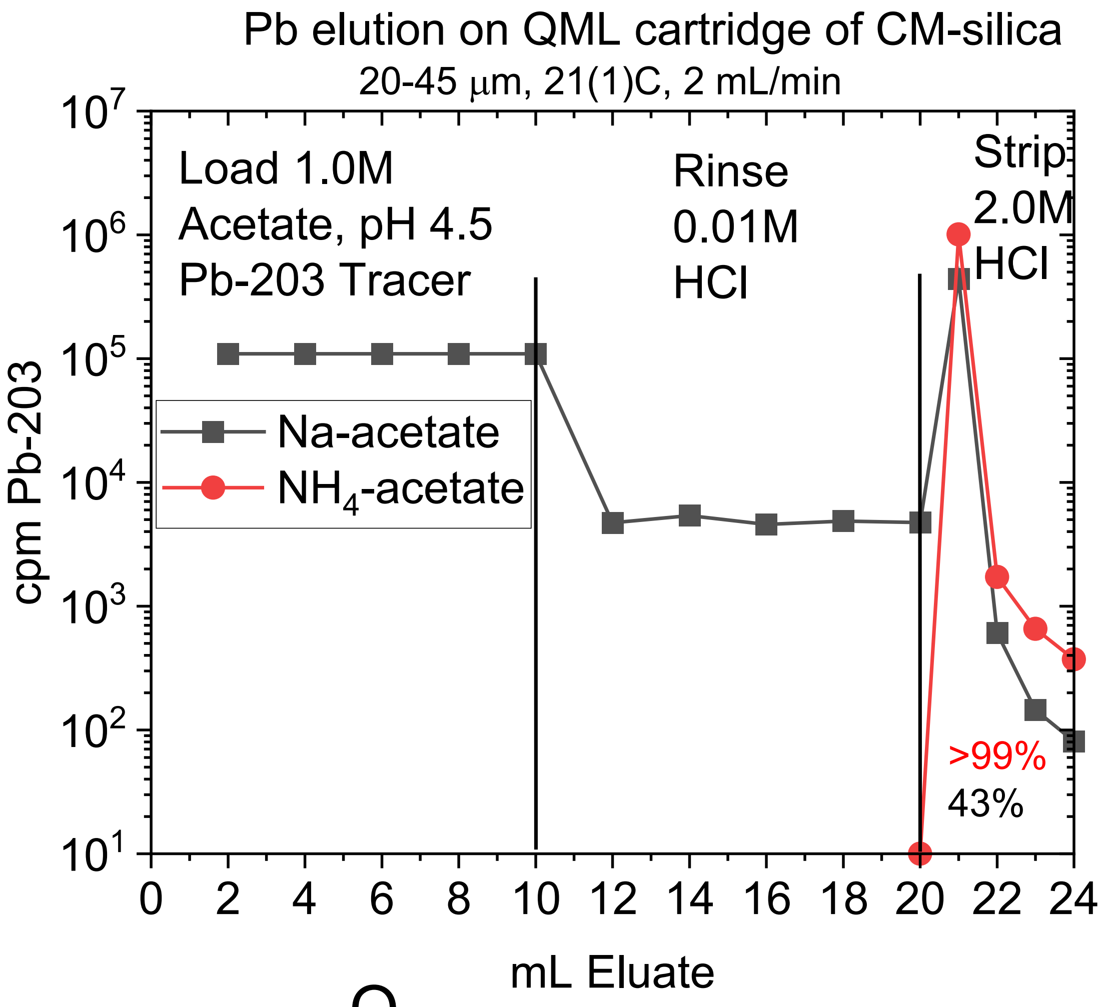
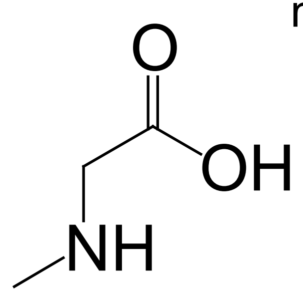


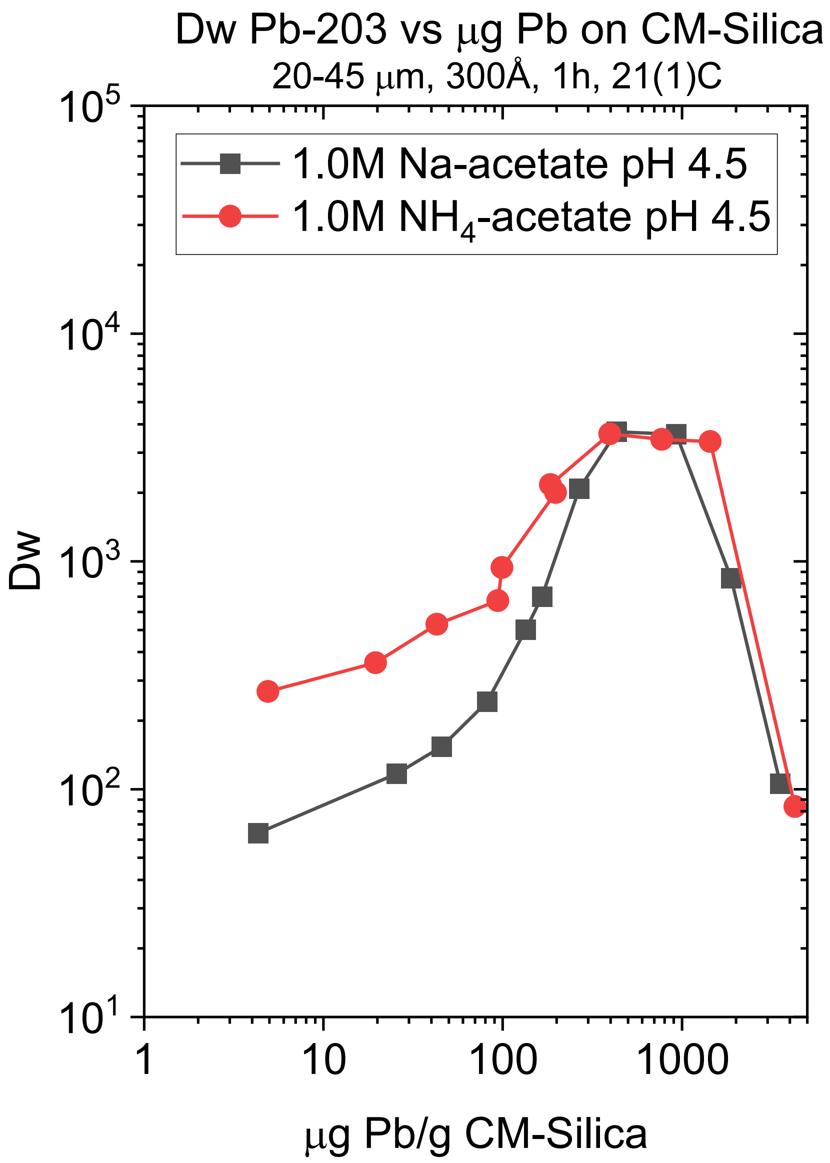


Weak cation exchange silica.
NH_4^+ vs Na^+ to reduce impact on stable element measurements by AES.



pKa ~ 2

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

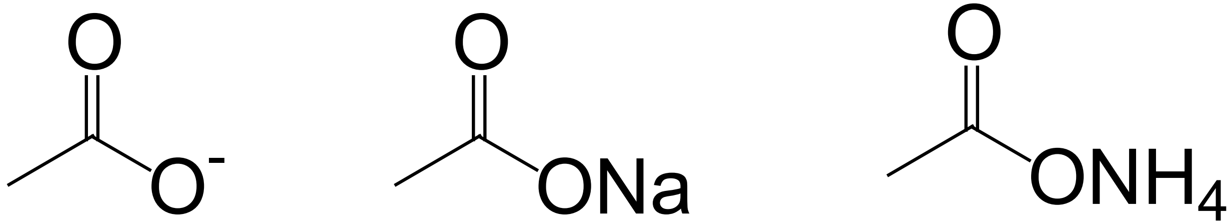


Some difference expected between Na^+ and NH_4^+ based on competition for IX sites.

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???

Applying concepts to develop QC tests

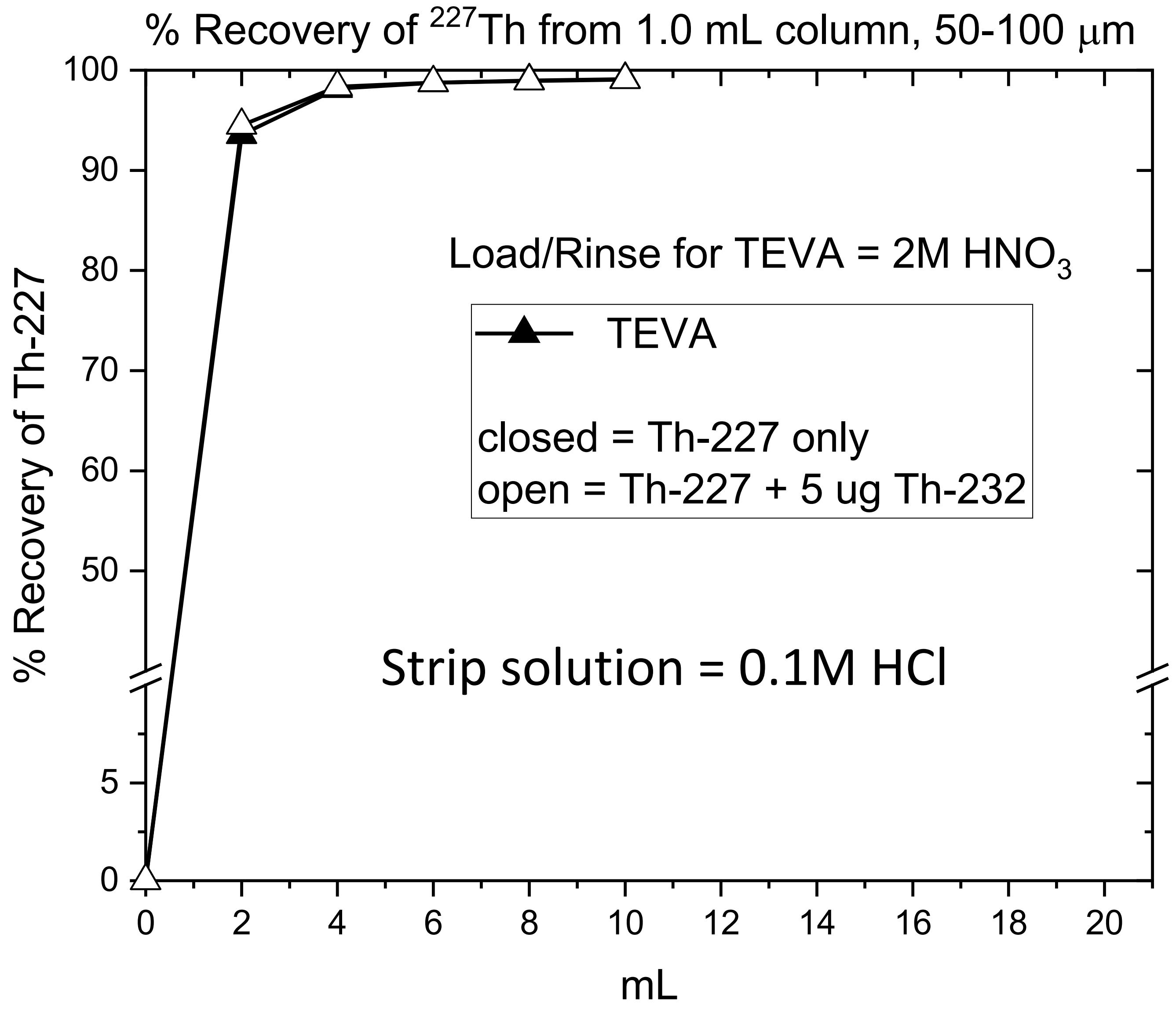
1) High specific activity Th-227 (half life = 18.72 days) to identify acidic impurities in TRU and TEVA resin. (Strip Th with 0.1M HCl)

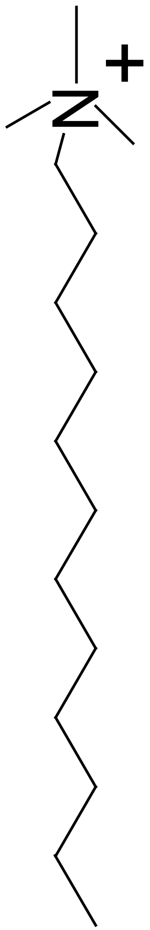
2) High specific activity Po-210 (half life = 138.38 days) to identify acidic impurities and sulfide impurities in DGA. (Strip Po with 0.05M HNO_3).

3) Standard QC for all resins includes separation of relevant radiotracers at dpm levels

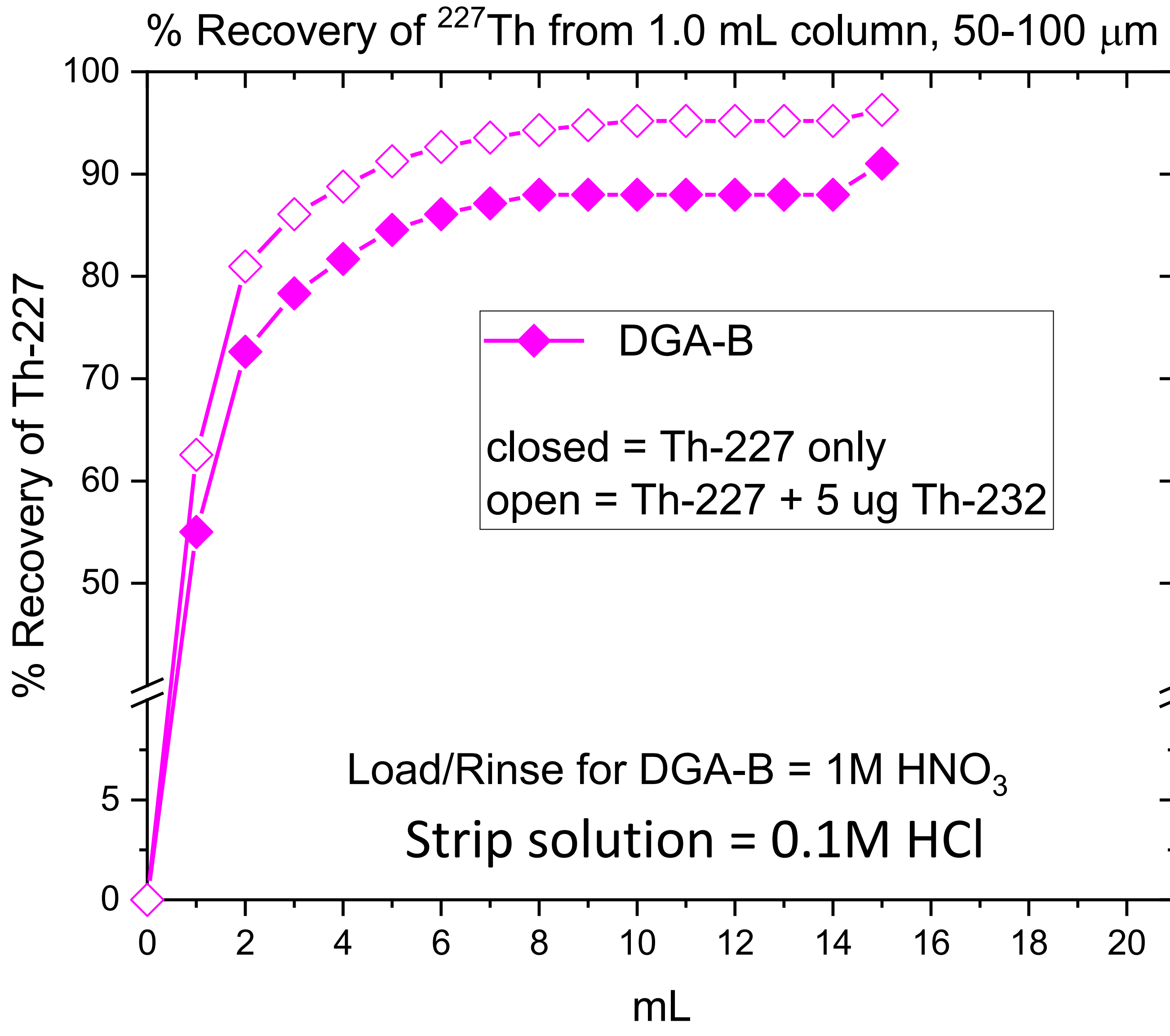
TEVA	Th-230	Pu-239
TRU	Am-241	Pu-239
UTEVA	Th-230	U-233
DGA	U-233	Am-241

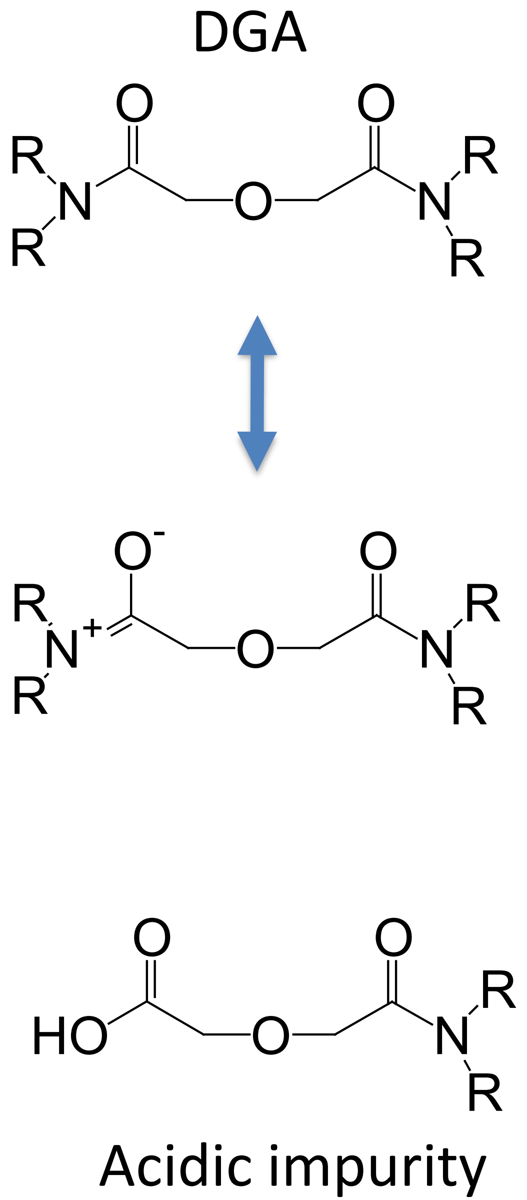
Th mass vs Elution of ^{227}Th



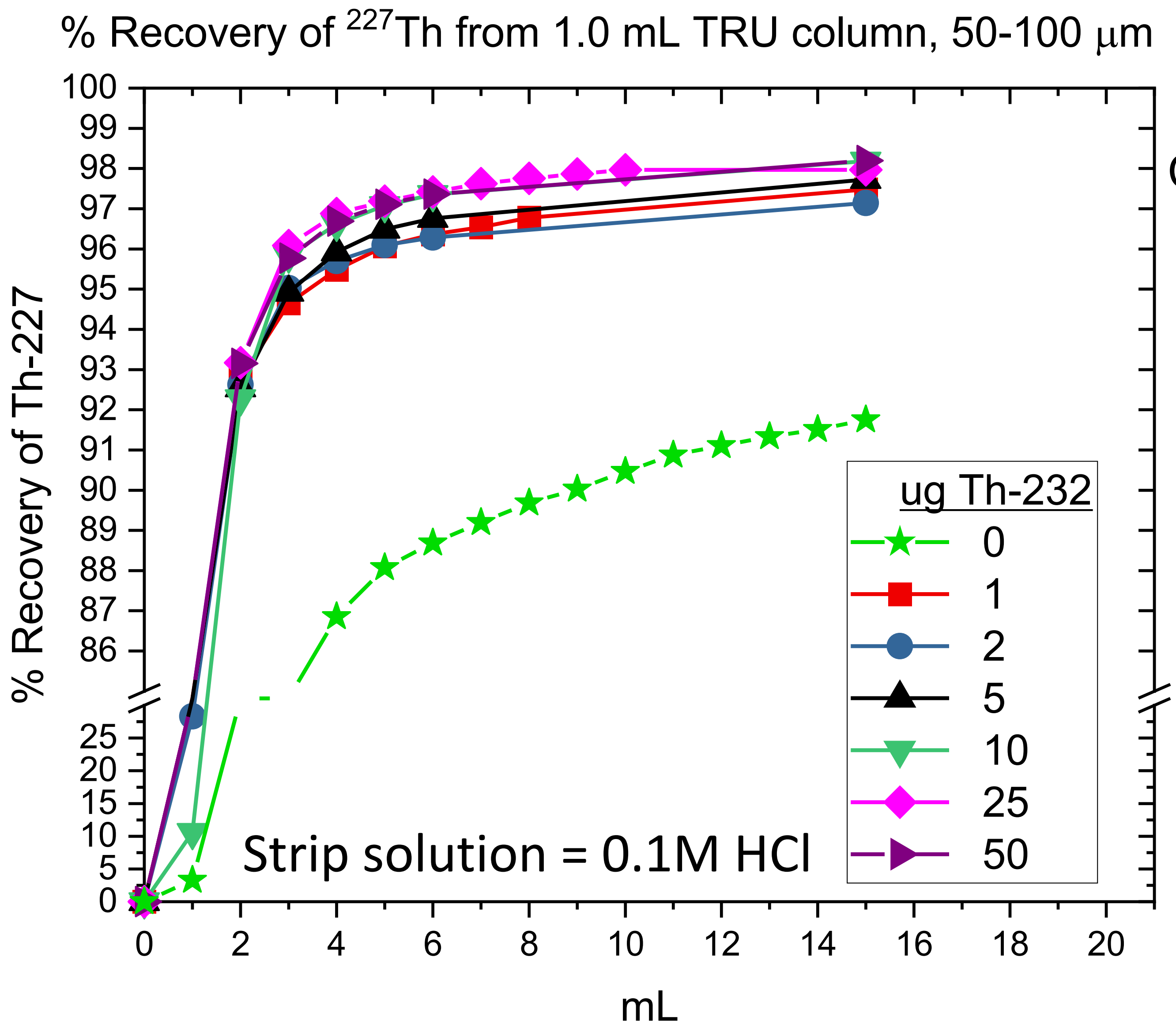


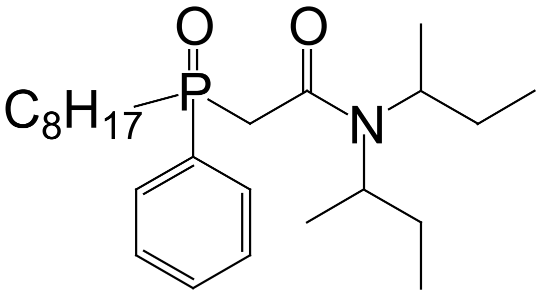
Th mass vs Elution of ^{227}Th



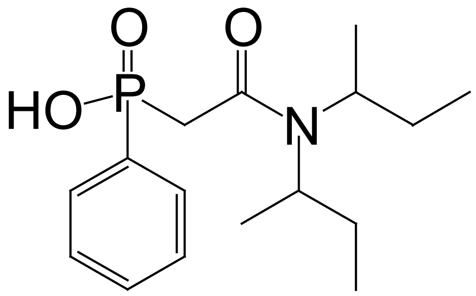


Th mass vs Elution of ^{227}Th

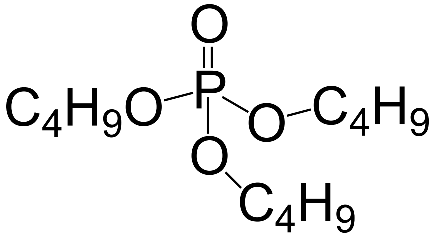




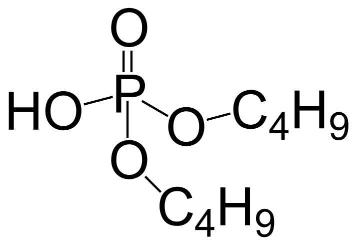
CMPO



Acidic impurity



TBP



Acidic impurity

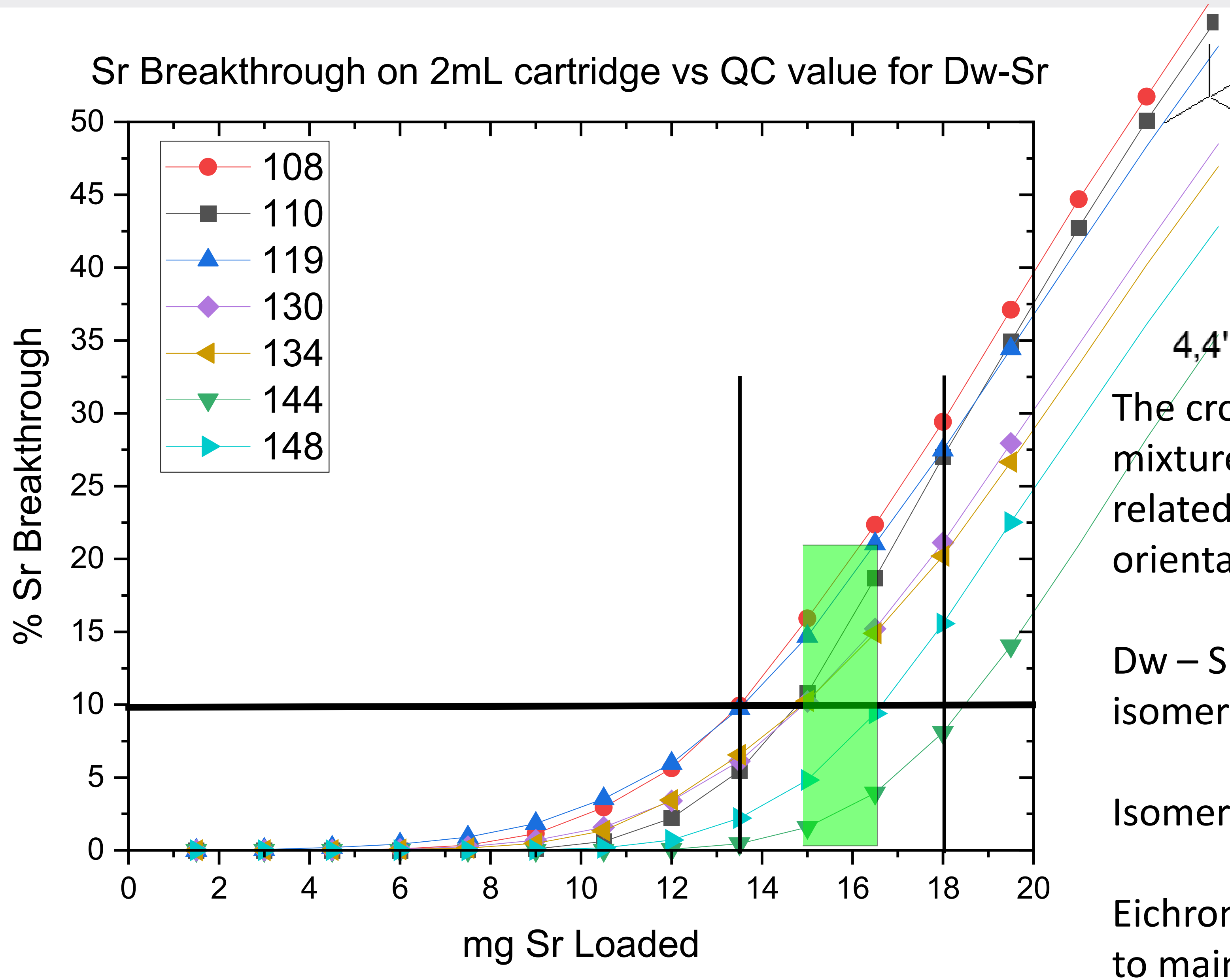
Applying concepts to develop QC tests

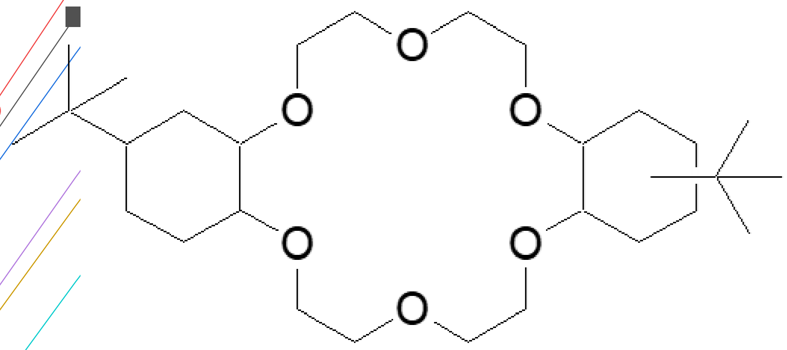
4) Sr Resin, column elution with 5 mg Sr and 50 mg Ca.

5) Pb Resin, column elution with 10 mg Pb.

6) Ni Resin, column elution with 2 mg Ni.

Sr Breakthrough vs Dw-Sr





4,4'(5')-di(t-butylcyclohexano)18-crown-6

The crown ether in Sr/Pb resin is a complex mixture of stereo- and regio- isomers related to the physical and spatial orientation of the *t*-butyl groups.

Dw – Sr is vastly different for the various isomers.

Isomeric mixture can vary from lot to lot.

Eichrom blends crown batches as necessary to maintain a Dw-Sr of 120-130.

Conclusions

1) Surrogates can be used to predict the behavior of radionuclides in separation methods.

2) Surrogates must be chosen carefully to avoid issues with hydrolysis, solubility, and binding to impurities / ion exchange sites.

3) Once separation methods are developed using surrogates, they should be tested with the actual radioisotope to identify any unforeseen complications.

Questions???