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Separations of M^{2+} with DGA and SR Resins

Daniel McAlister, Ed Rush and Madeleine Eddy

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RRMC
Radiobioassay & Radiochemical Measurements Conference

Goals

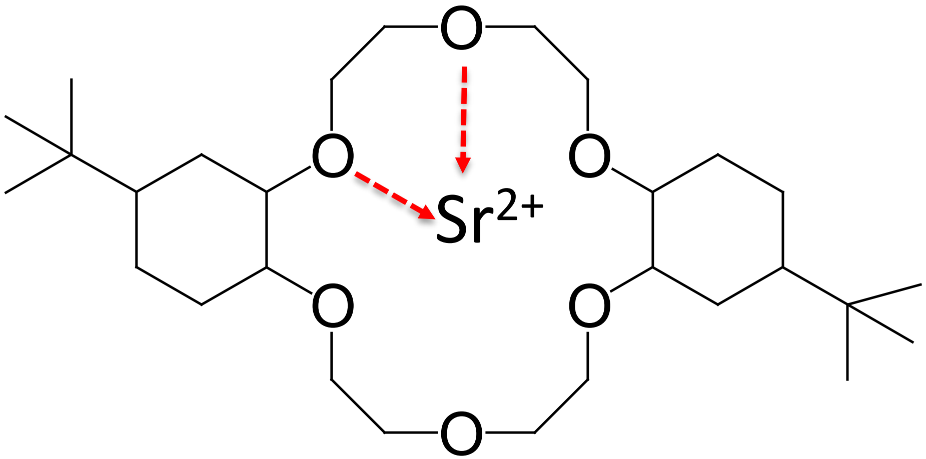
1) Gain additional insights into extraction of M^{2+} into crown ethers and DGAs

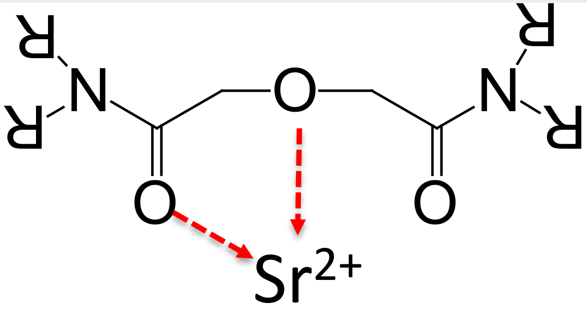
2) Impart unique selectivity for M^{2+} (Pb, Ra, Sr, Ca) or REE

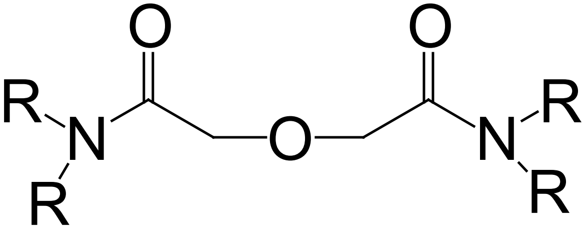
3) Develop materials with improved physical properties (stability, shelf-life, etc…)

How
- Modify SR resin with different diluents
- Synthesize DGAs with different R-groups
  - Neat (40% mass loading)
  - 28% loading with 12% diluent (solids)

D*t*BCH18C6 and DGA







$M^{2+}(aq) + 2NO_3^-(aq) \leftarrow\rightarrow M(NO_3)_2CE + xH_2O$

1.0M in 1-octanol = SR Resin

0.75M in isodecanol = PB Resin

$M^{2+}(aq) + 2NO_3^-(aq) \leftarrow\rightarrow M(NO_3)_2DGA_2 + xH_2O$

$M^{3+}(aq) + 3NO_3^-(aq) \leftarrow\rightarrow M(NO_3)_3DGA_3 + xH_2O$

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D*t*BCH18C6 and DGA

Similarities:

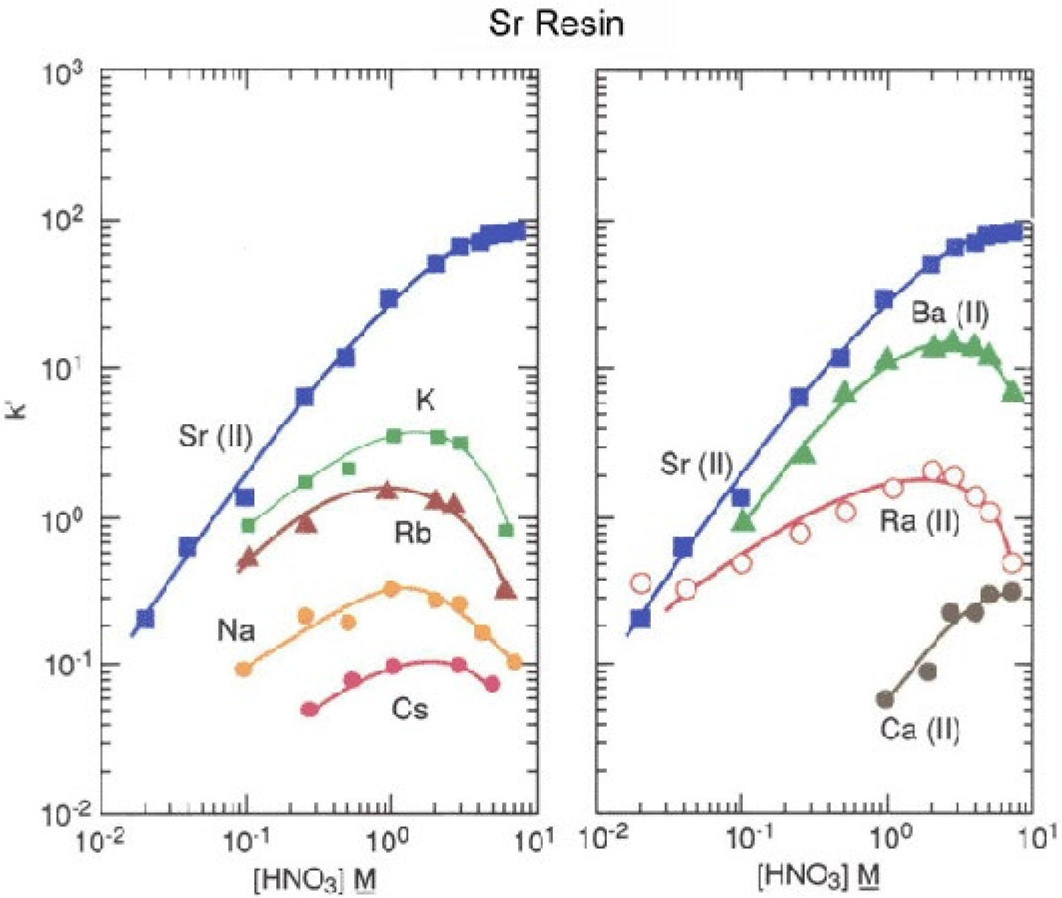
1) Both neutral extractants that require counter anion to neutralize charge of extracted metal ions.
2) Both can extract M^{2+}
3) Both systems in SX co-extract HNO_3 and H_20.
4) Changing substituents on molecules change extraction characteristics
5) Extraction correlates to size of metal ions.

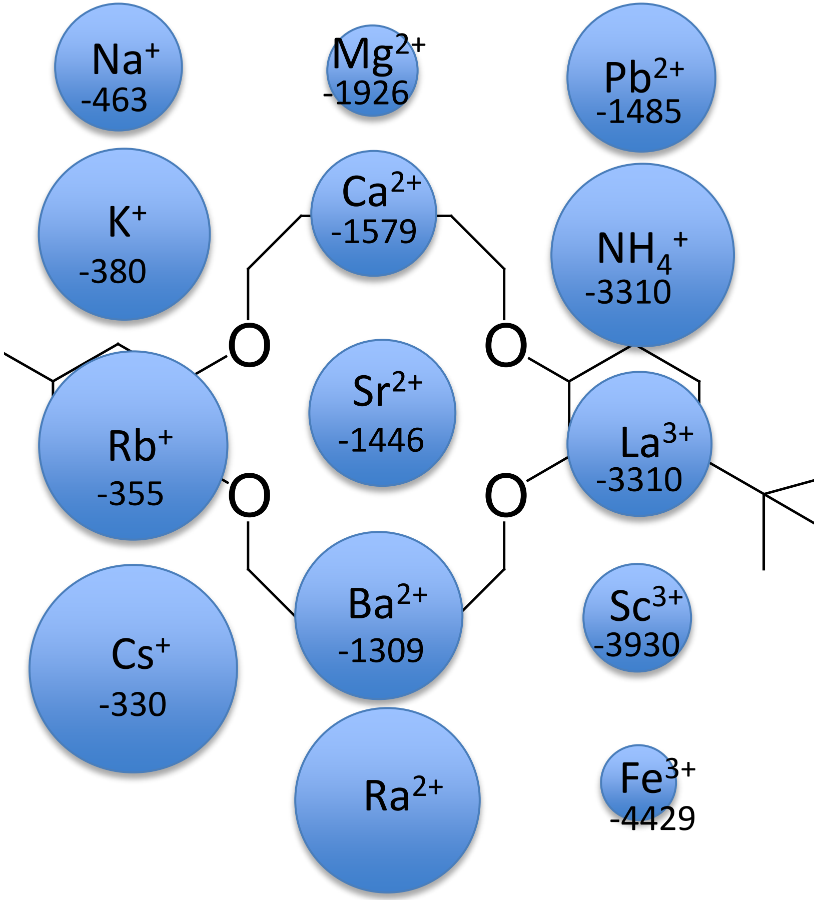
Differences:

1) DGA can also extract M3+, M4+, M(VI)
2) DtBCH18C6 requires polar diluent, DGA can work with polar or non-polar diluents.
3) DtBCH18C6 more sensitive to competition from K+, NH4+, Na+
4) DGA more sensitive to competition from Ca2+
5) Extraction order different.

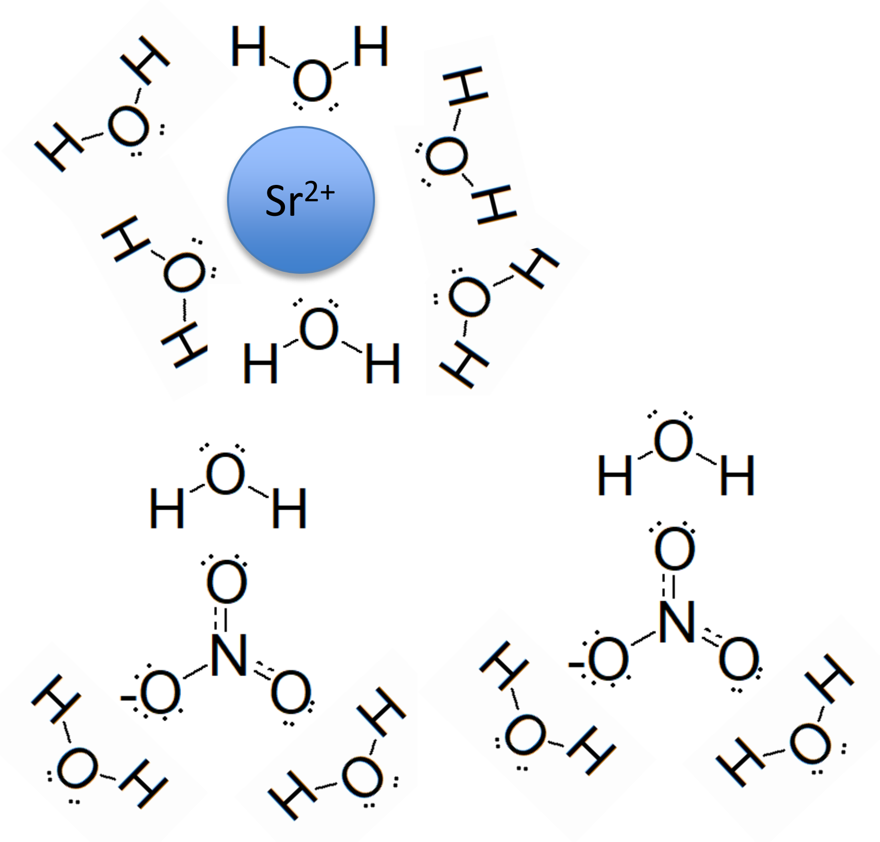
DtBCH18C6:	Pb > Sr > Ba > Ca
DGA:	Ca > Sr ~ Pb > Ba

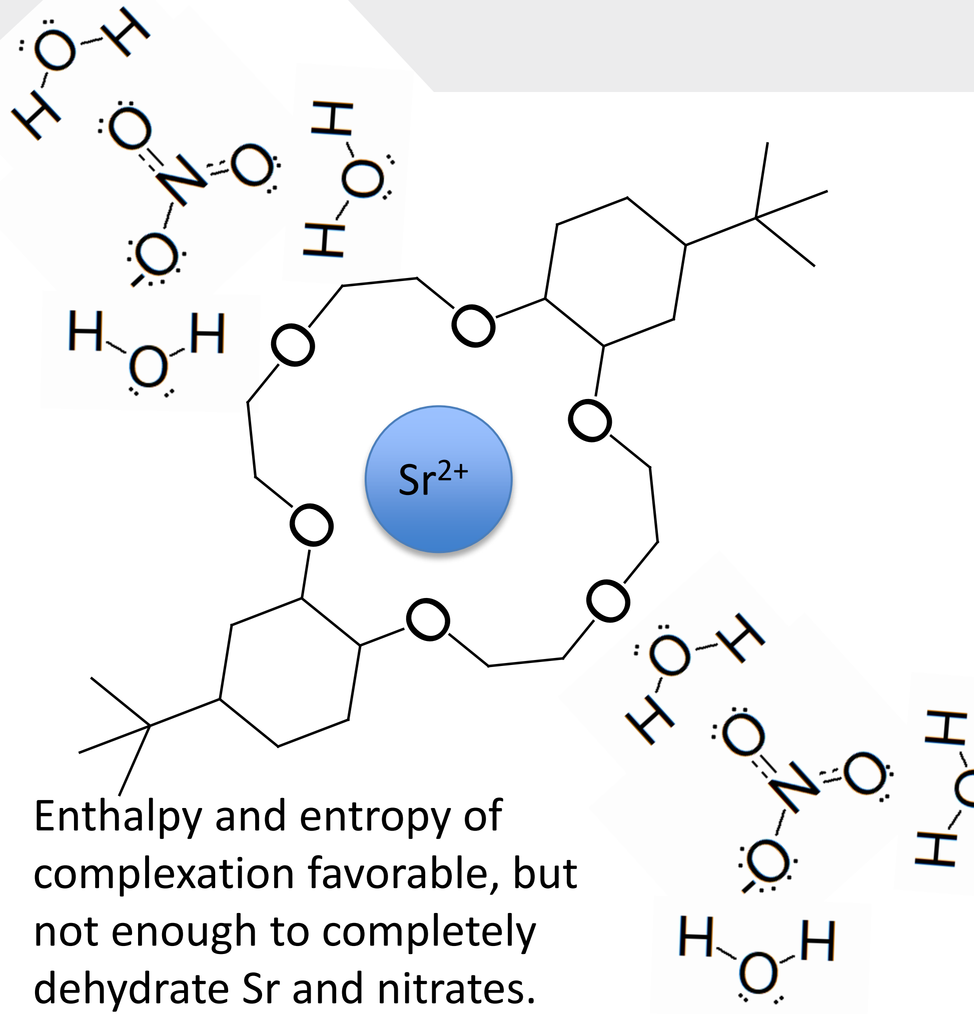
1M D*t*BCH18C6 in 1-octanol





D*t*BCH18C6 Extraction





Enthalpy and entropy of complexation favorable, but not enough to completely dehydrate Sr and nitrates.

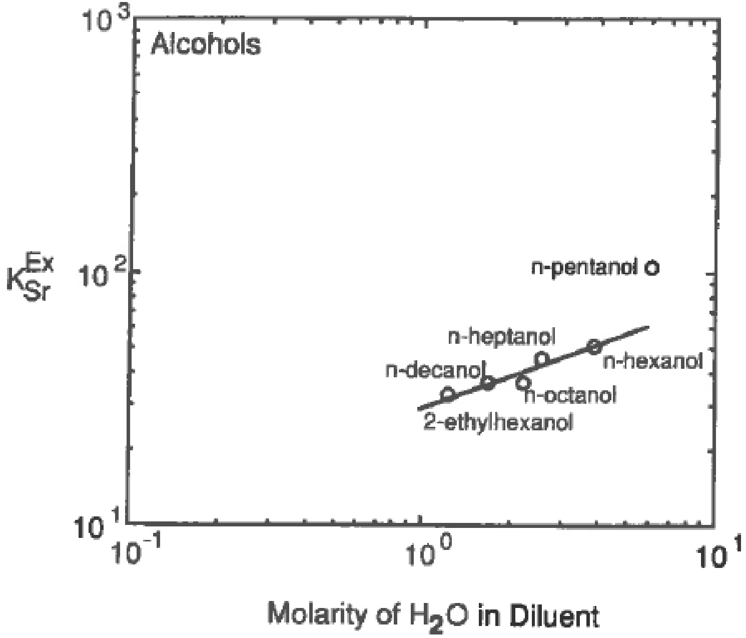
D*t*BCH18C6 Extraction

-Extraction into non-polar diluents requires dehydration of metal-nitrates.

-Extraction of Sr by dtBCH18C6 into alkanes poor.

-Extraction of Sr by dtBCH18C6 into more polar diluents favorable.

E. P. Horwitz, M. L. Dietz, and D. E. Fisher
EXTRACTION OF STRONTIUM FROM NITRIC ACID SOLUTIONS USING DICYCLOHEXANO-18-CROWN-6 AND ITS DERIVATIVES*
SOLVENT EXTRACTION AND ION EXCHANGE, 8(4&5), 557-572 (1990)



Strontium Distribution Ratios Between 0.1 M DtBuCH18C6 in Several Solvents and 3 M HNO_3 (T = 25°C)

Solvent	D_{Sr}
dodecane	0.045
octanoic acid	2.2
2-octanone	3.4
n-octyl alcohol	6.5
n-decyl alcohol	5.9

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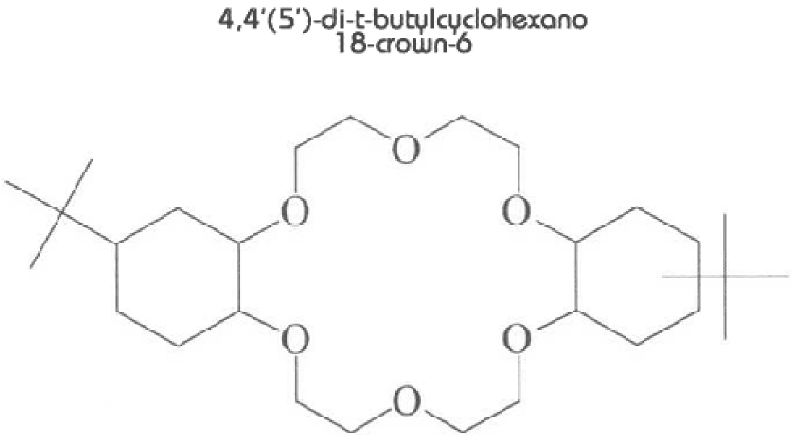
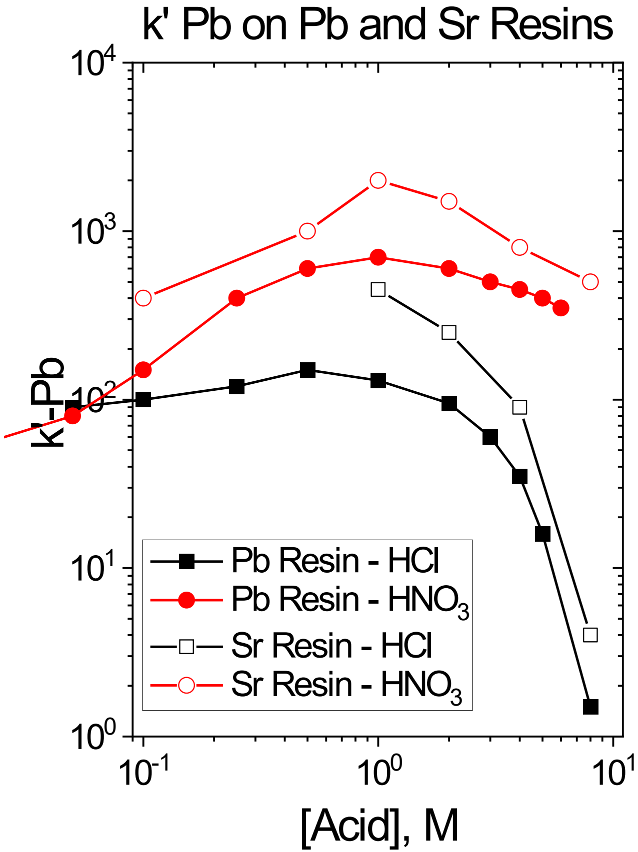
Pb Resin vs Sr Resin

$$Pb^{2+}_{(aq)} + 2X^{-}_{(aq)} \leftrightarrow Pb(Crown)X_{2(org)}$$

Sr Resin:

- d*t*BuCH18C6 in 1-octanol

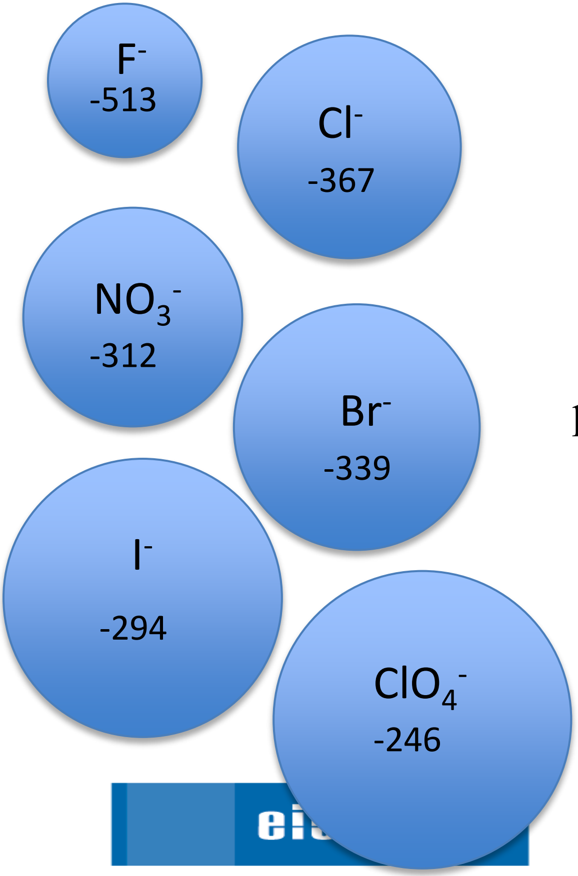


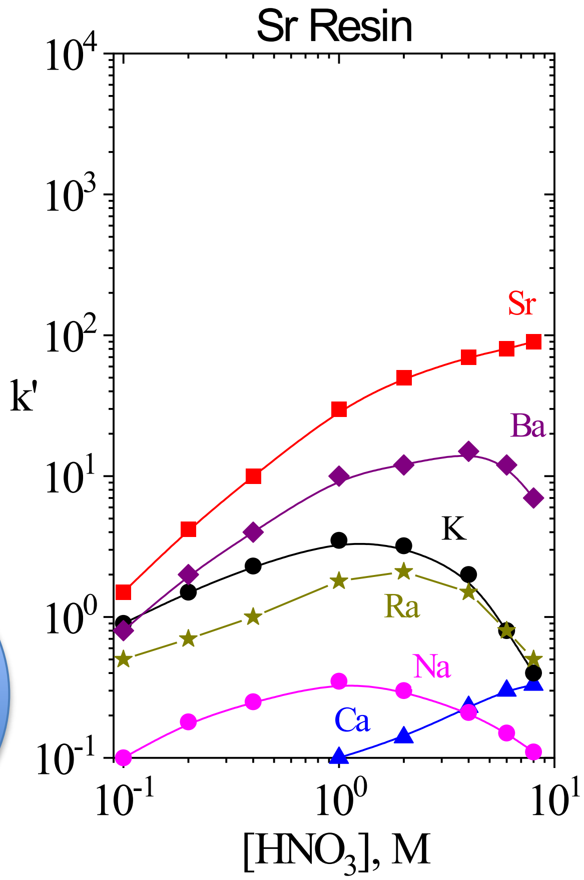


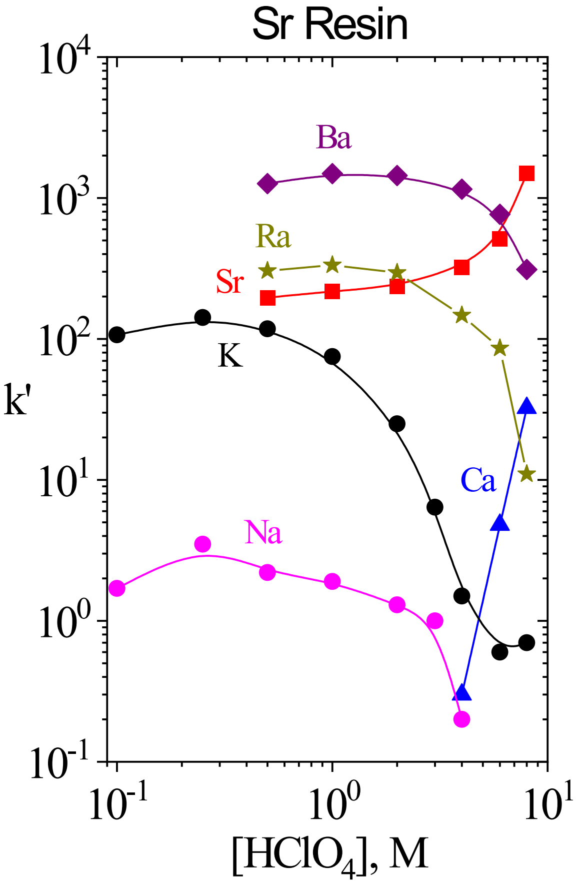
Pb Resin:

-25% less d*t*BuCH18C6 in isodecanol

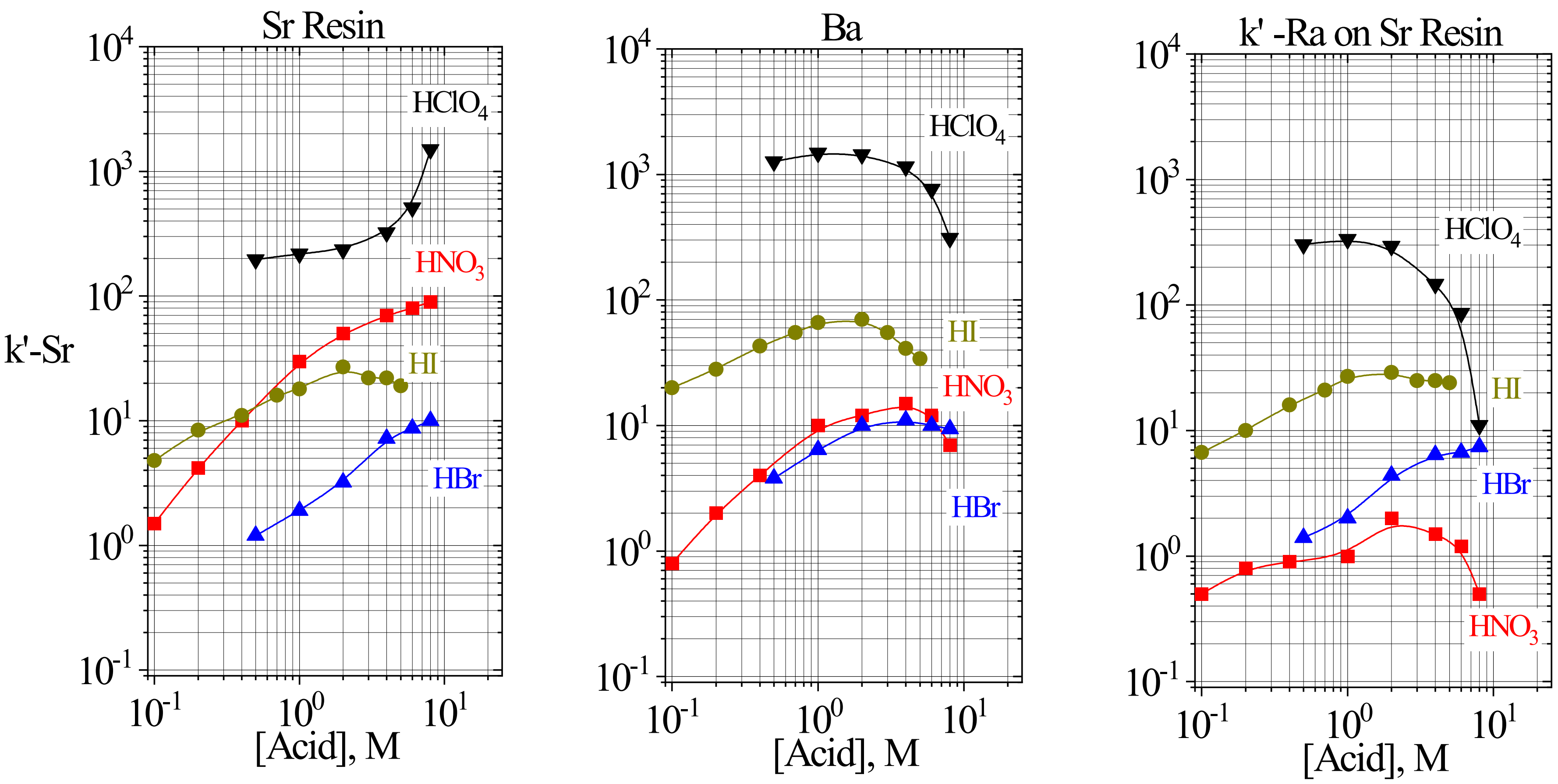
Anion can change selectivity



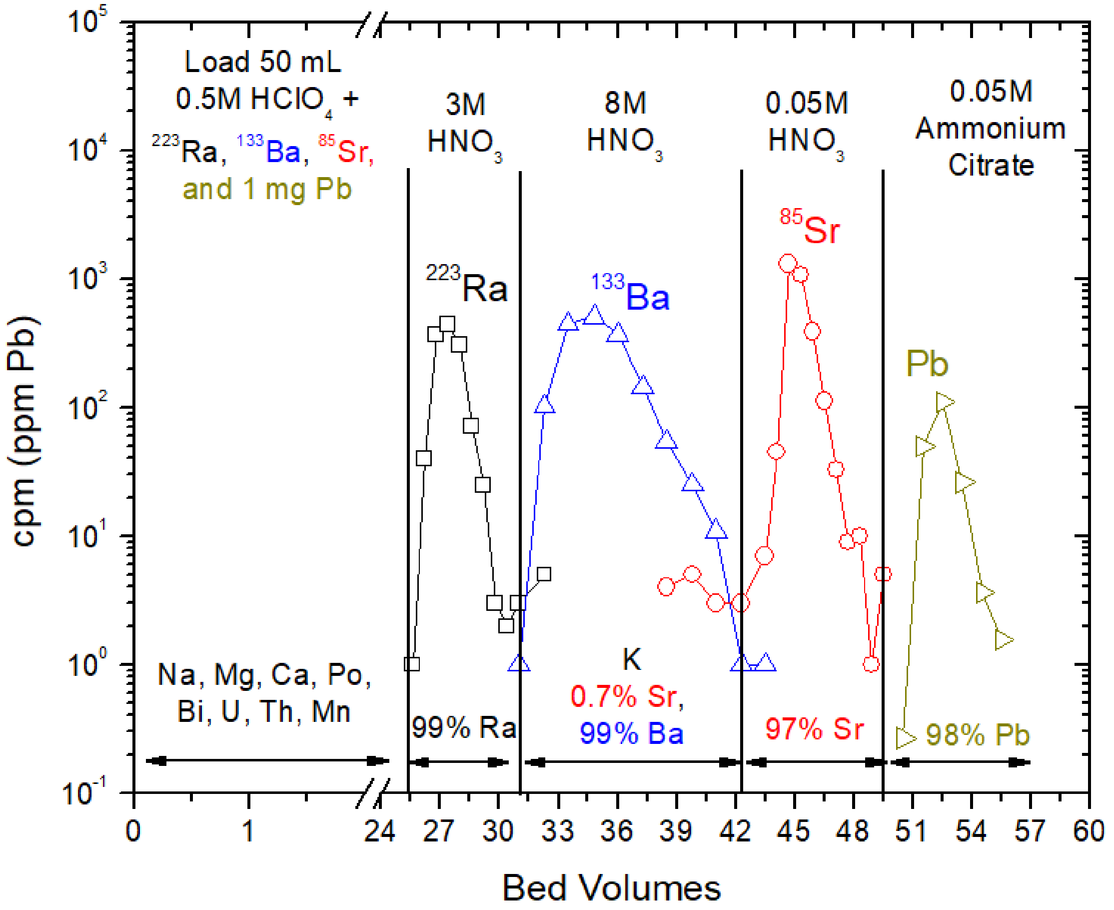




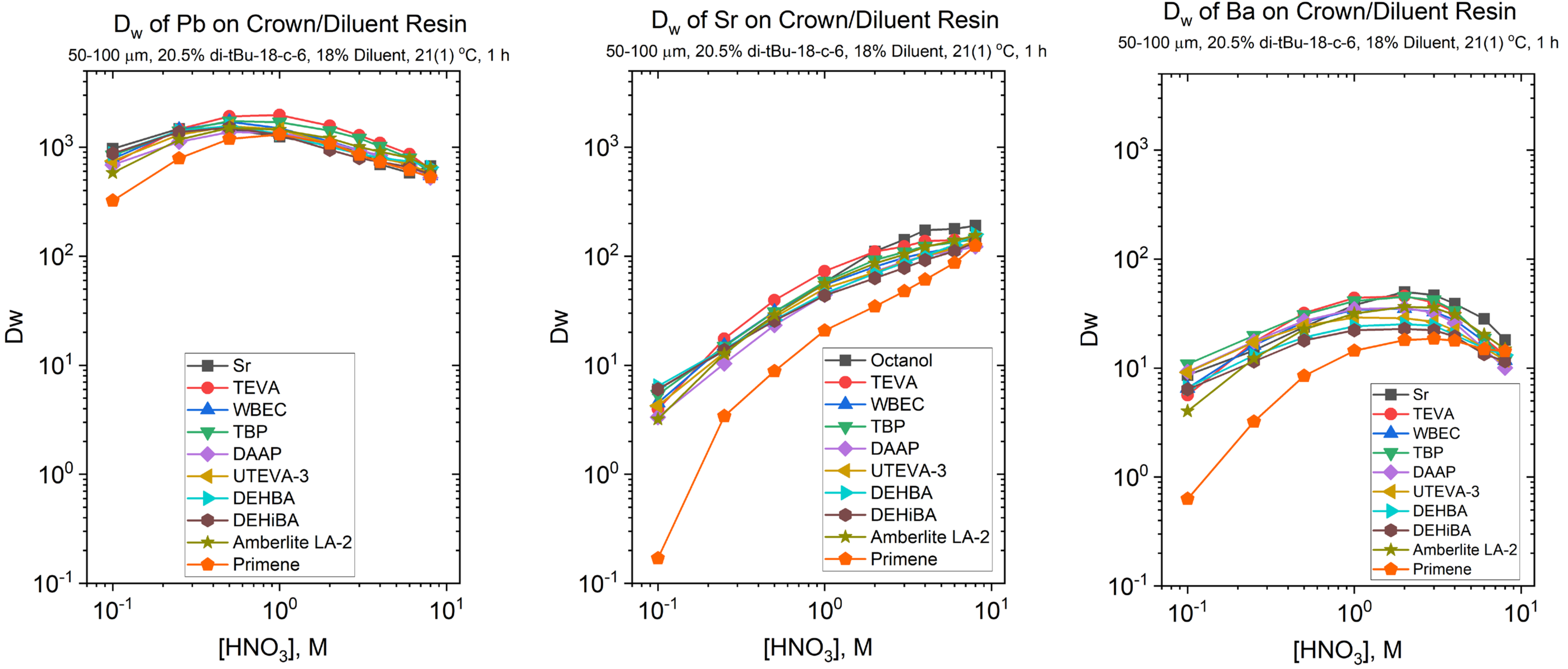
D*t*BCH18C6 (Hofmeister $Cl^- < Br^- < NO_3^- < I^- < ClO_4^- < SCN^-$)



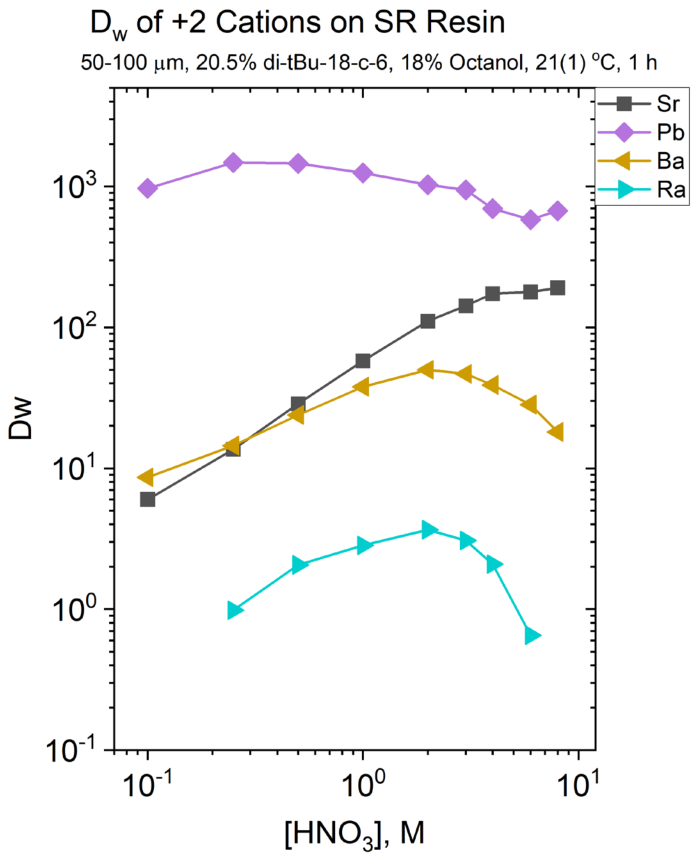
Chromatogram on Sr Resin from HClO4

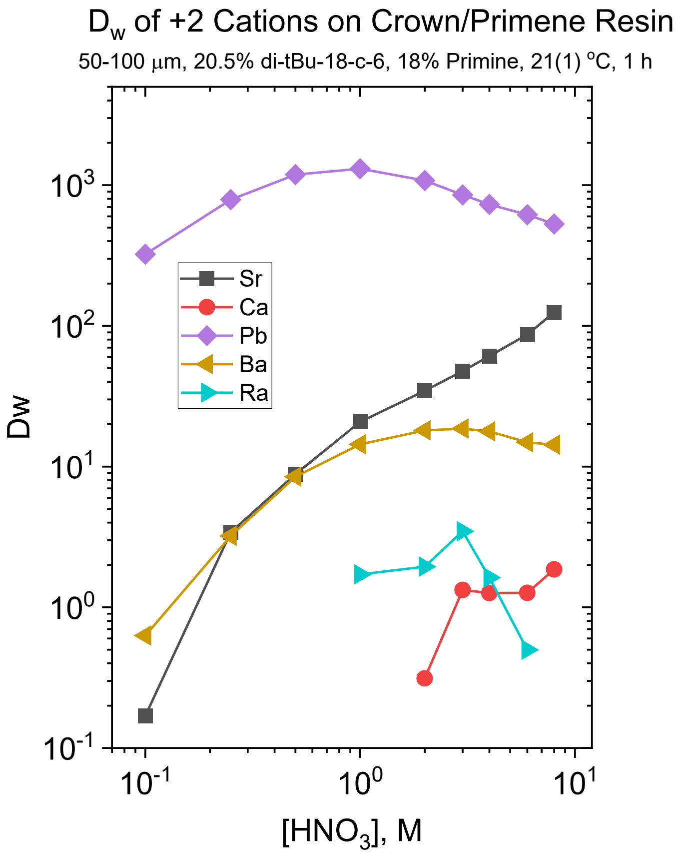


D*t*BCH18C6 vs diluent (amines, amides, organophosphorus)

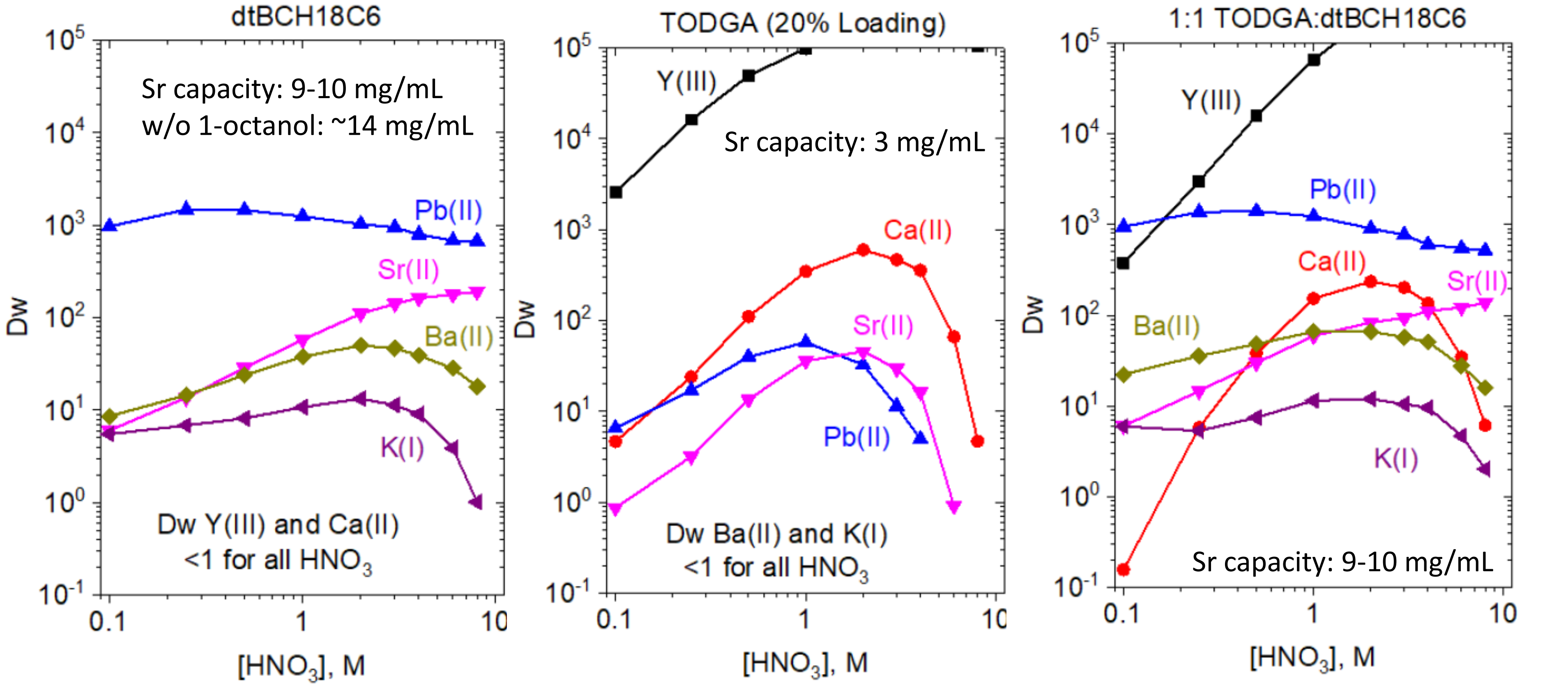


D*t*BCH18C6 (diluent changes magnitude, but not selectivity)



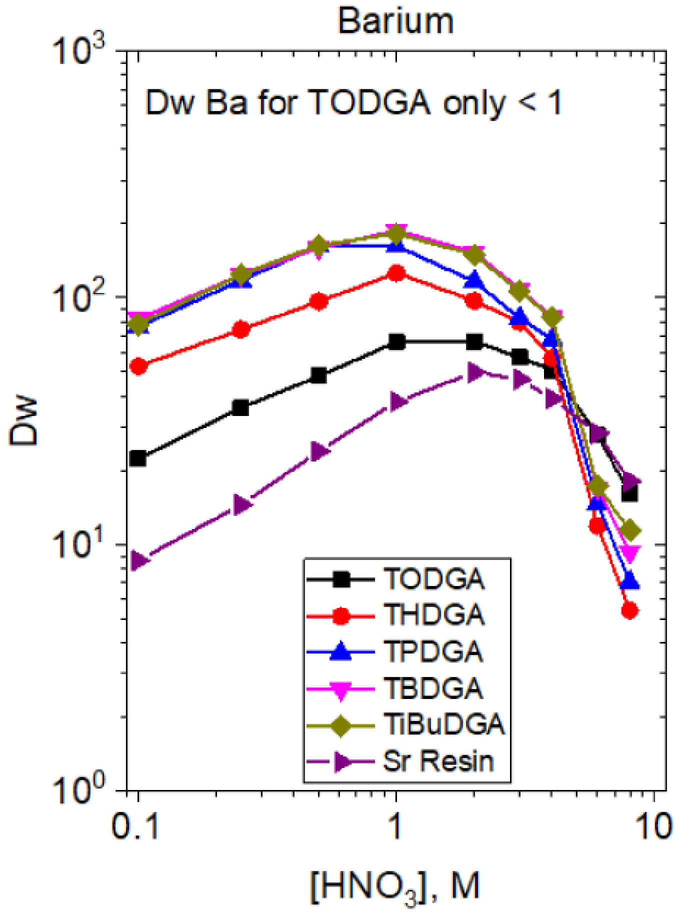


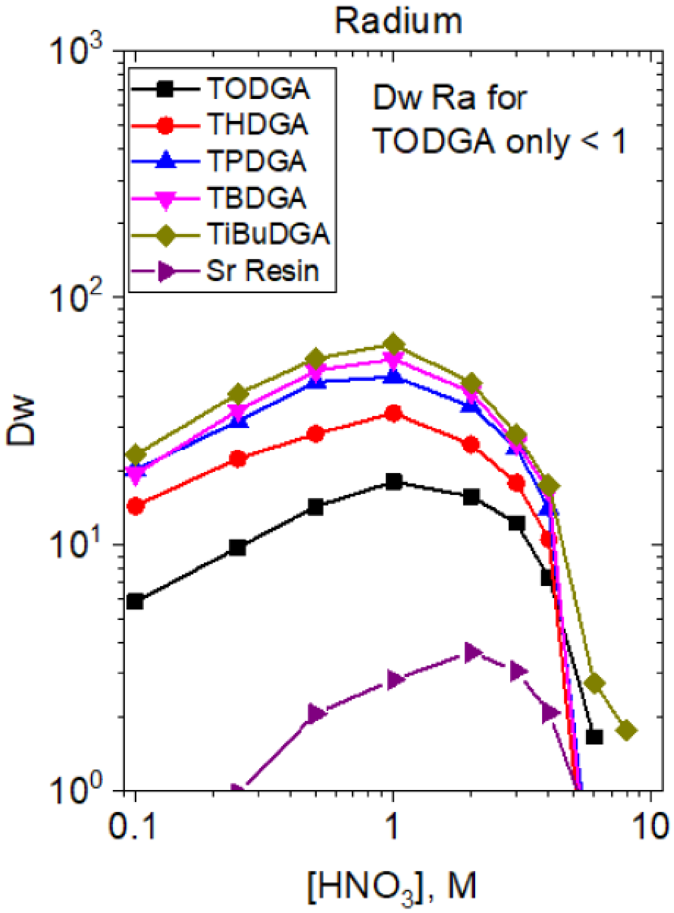
DtBCH18C6 + DGA (diluent/phase modifier/extractant/~~synergism~~)



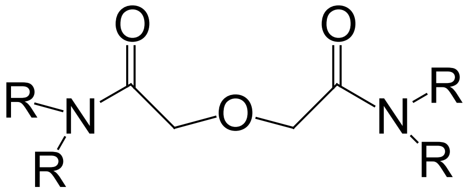
D.R. McAlister, D. Silvestri, E. Rush, E.P. Horwitz, "Extraction of Selected Metal Ions by Mixtures of Diglycolamides and Crown Ethers," *Solv. Extr. Ion Exch.*, 39(2), 184-203 (2021).

DtBCH18C6 + DGA vs R-group (magnitude + / selectivity -)

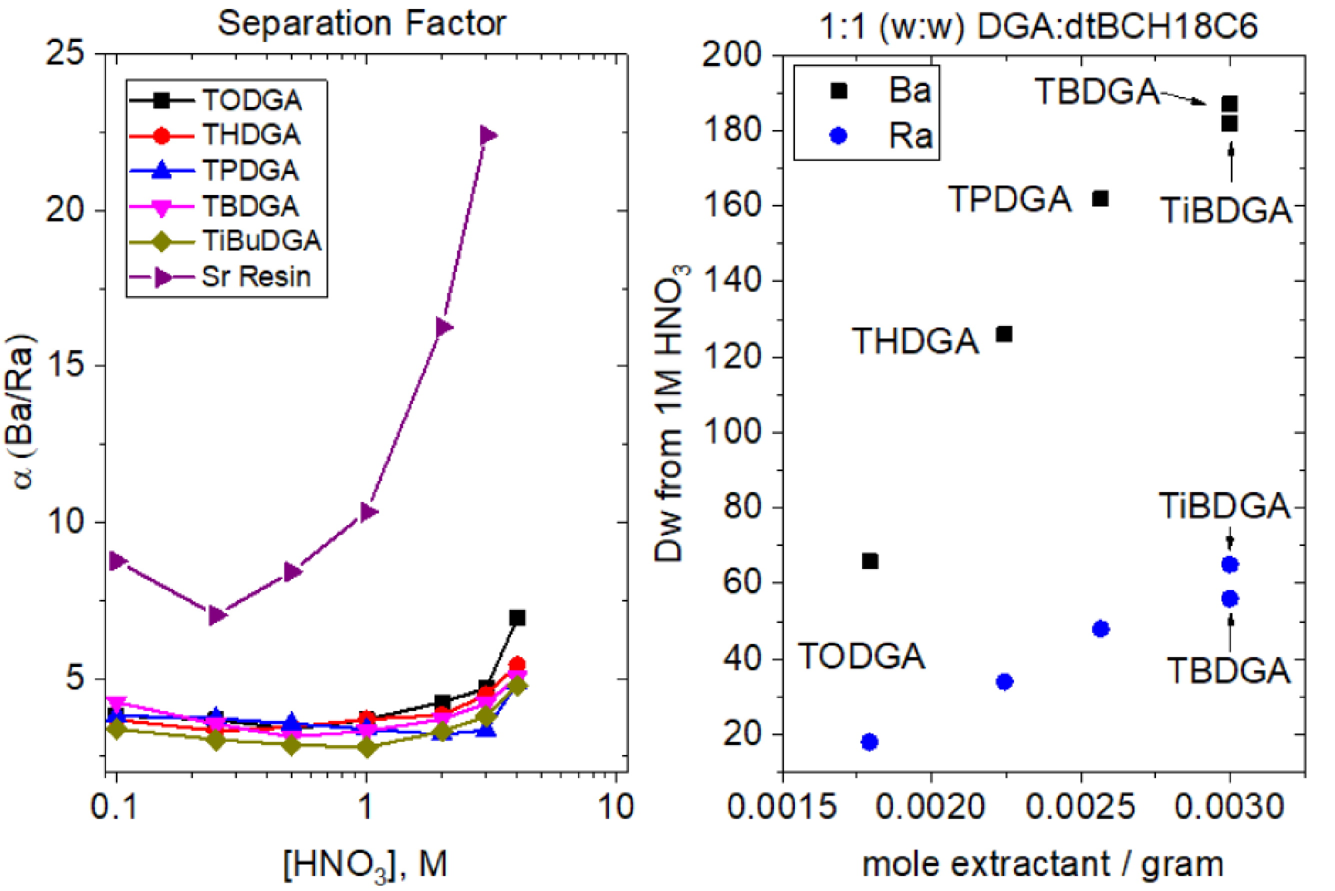




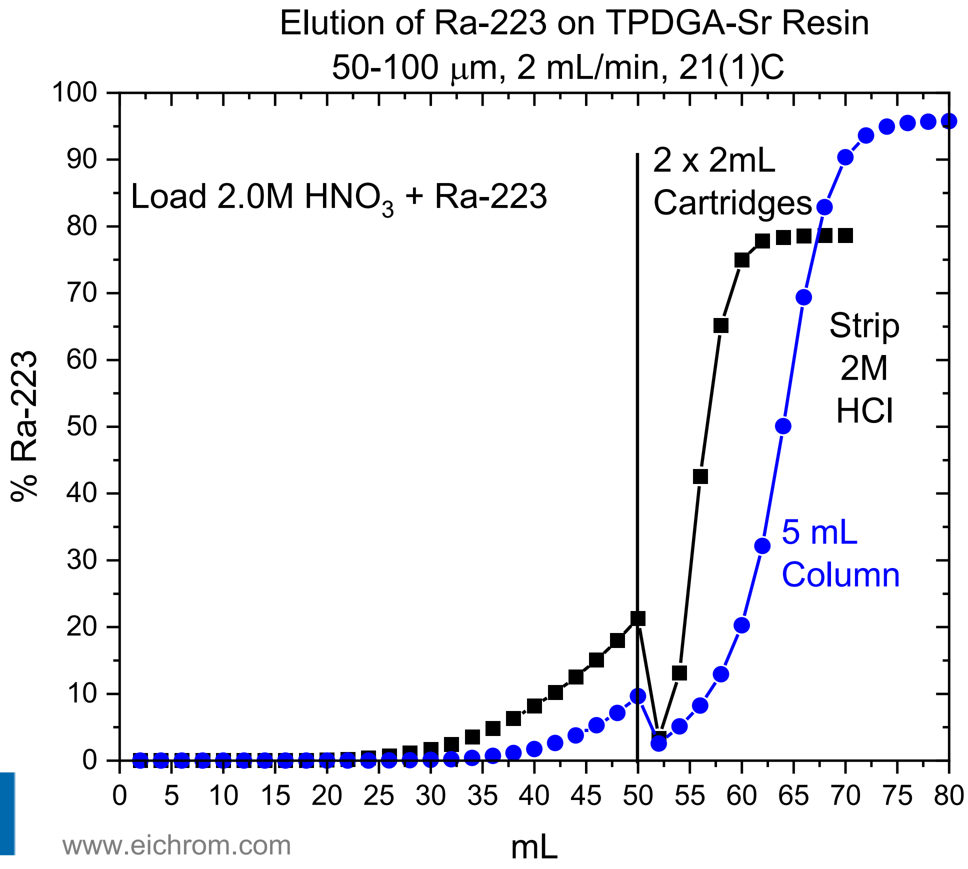
Octyl = TO
Hexyl = TH
Pentyl = TP
Butyl = TB
iButyl = TiB
1-octanol



Ra/Ba Separation (shorter R-group = more DGA/gram resin)



Radium concentration on TPDGA-Sr



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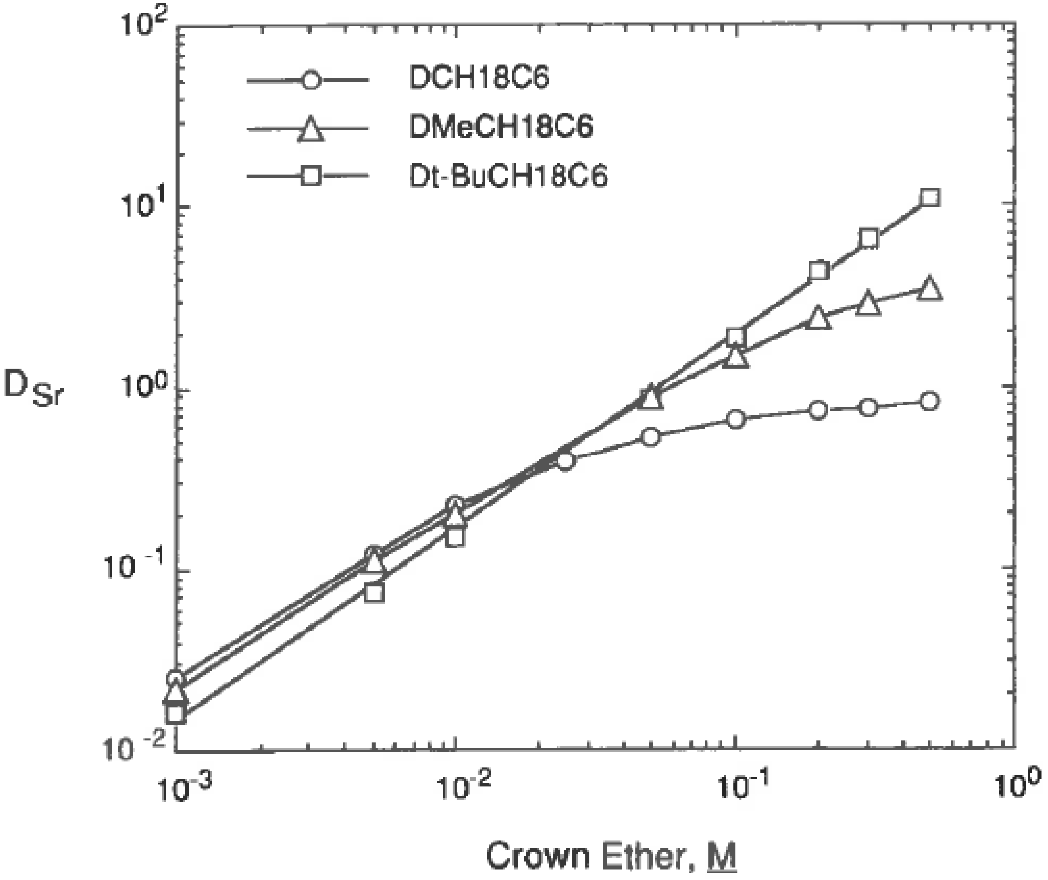
DtBCH18C6 steric hinderance

D_{Sr} extractant dependencies for three 18-crown-6 derivatives in n- octanol. ([HNO_3] = 1 M).



Less steric hinderance

More aggregation at high CE concentration.

Lowers effective concentration of CE and D_{Sr}.

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Extraction of M^{2+} with DGAs

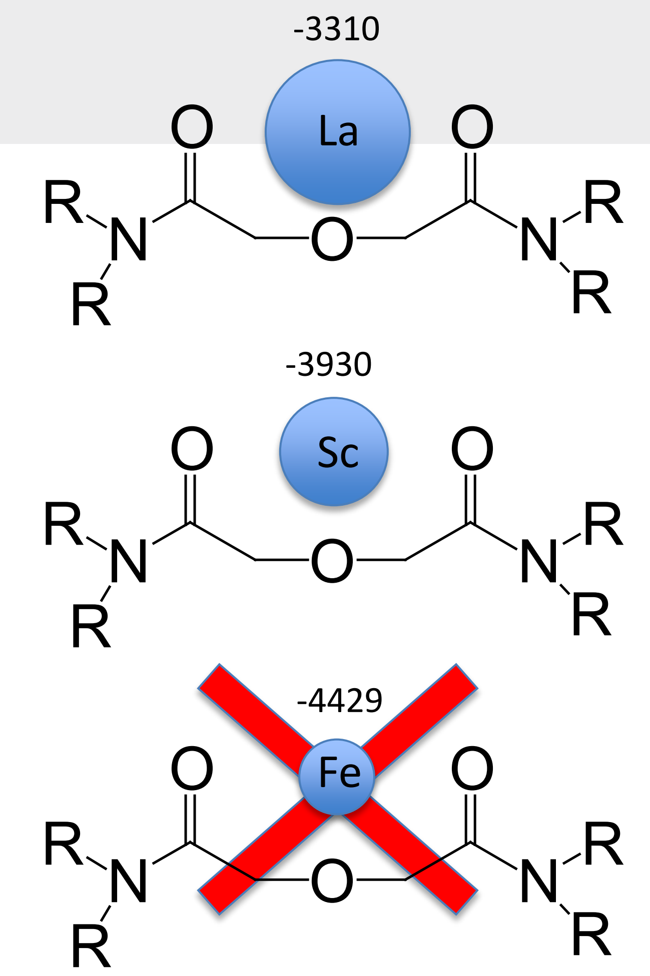
	-3310	-3365	-3410	-3445		-3490
Ionic Radius (CN =8)	1.160	1.143	1.126	1.109	1.093	1.079
Element	**La**	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**
Z	57	58	59	60	61	62

(Am = 1.090)

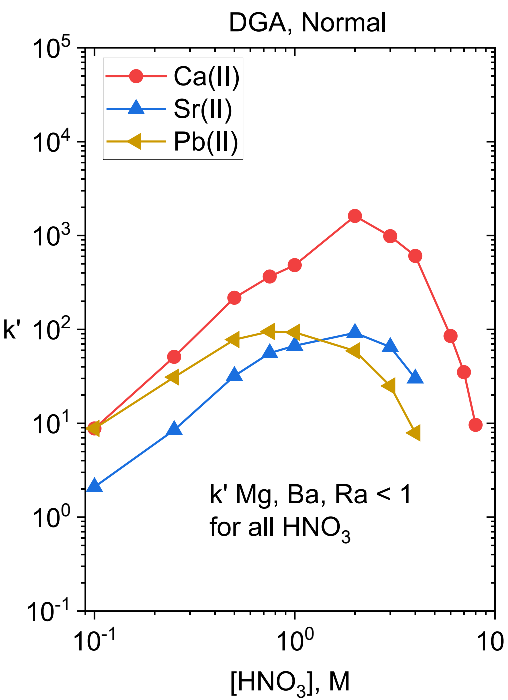
	-3535	-3545	-3580	-3600	-3635	-3670
Ionic Radius (CN =8)	1.066	1.053	1.040	1.027	1.015	1.004
Element	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**
Z	63	64	65	66	67	68

	-3695	-3740	-3695	-3930	-4105	
Ionic Radius (CN =8)	0.994	0.985	0.977	0.870	1.019	1.120
Element	**Tm**	**Yb**	**Lu**	**Sc**	**Y**	**Ac (CN=6)**
Z	69	70	71	21	39	89

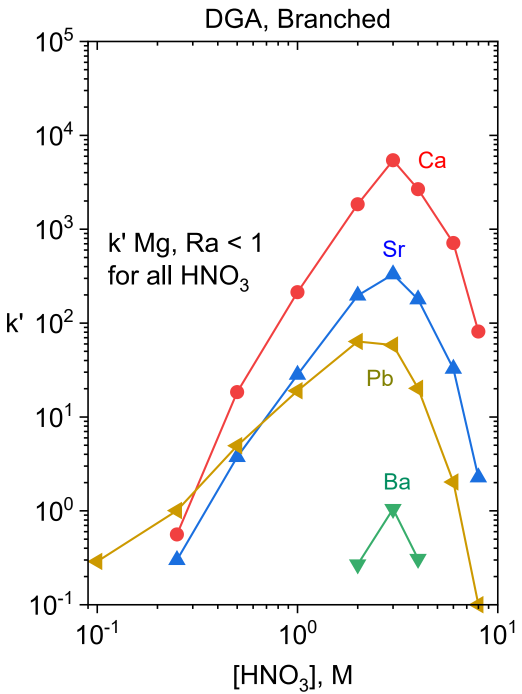
La(6) = 1.032



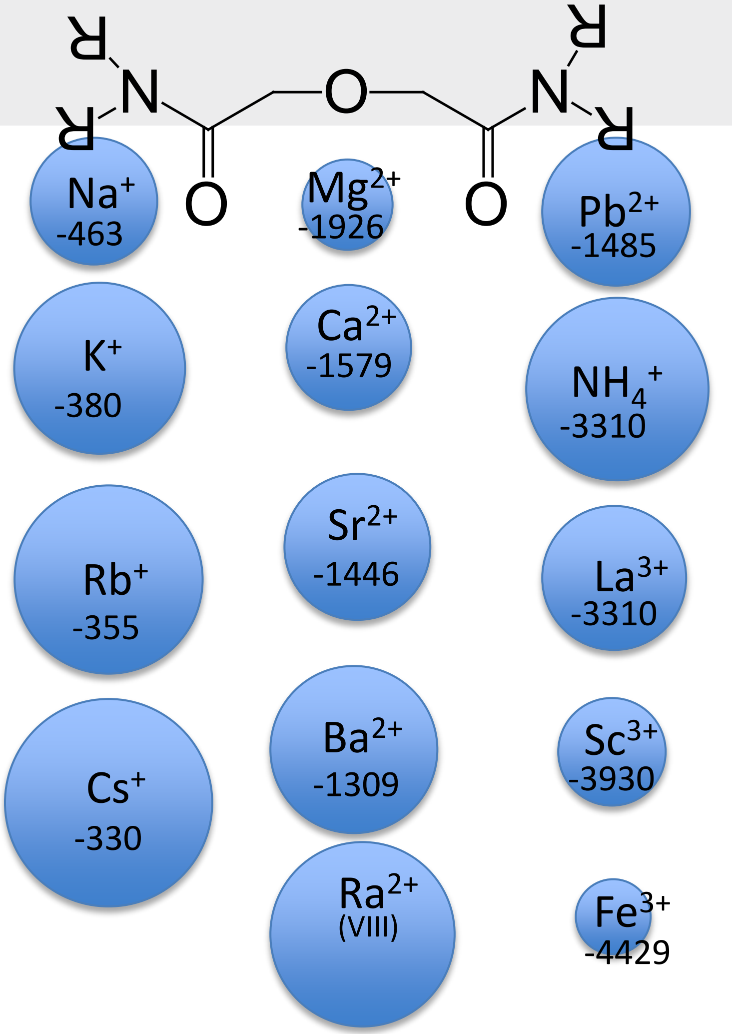
DGA



DGA, Normal
Ca(II)
Sr(II)
Pb(II)
k'
[HNO3], M
k' Mg, Ba, Ra < 1
for all HNO3

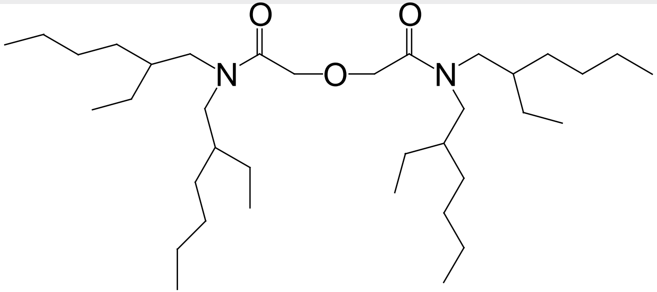


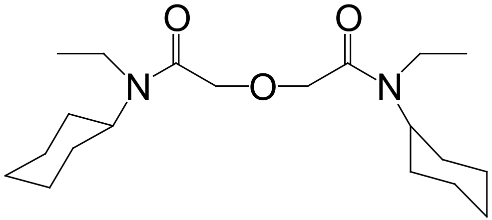
DGA, Branched
Ca
Sr
Pb
Ba
k'
[HNO3], M
k' Mg, Ra < 1
for all HNO3

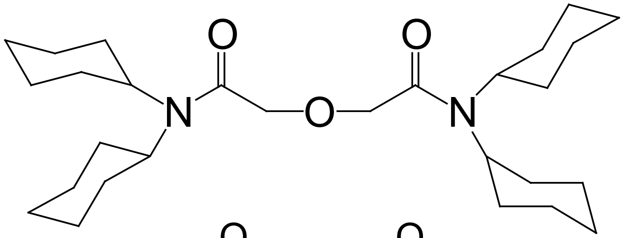


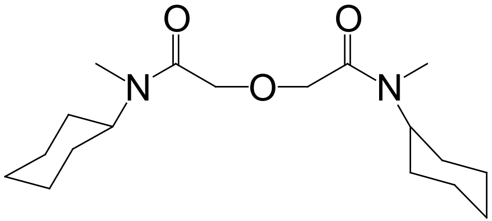
R
N
O
Na+ -463
Mg2+ -1926
Pb2+ -1485
K+ -380
Ca2+ -1579
NH4+ -3310
Rb+ -355
Sr2+ -1446
La3+ -3310
Cs+ -330
Ba2+ -1309
Sc3+ -3930
Ra2+ (VIII)
Fe3+ -4429

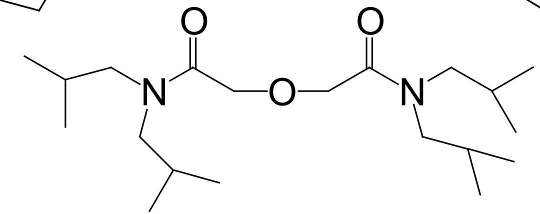
DGAs (R-group)

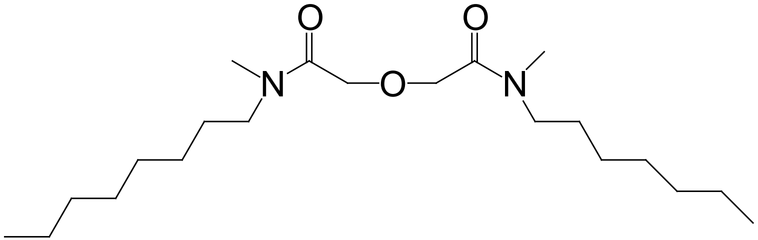


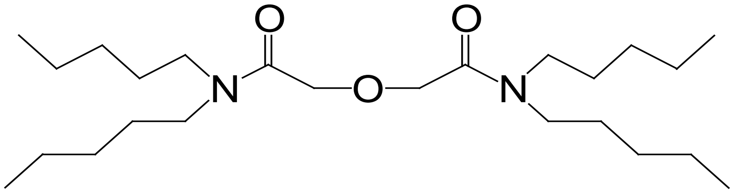




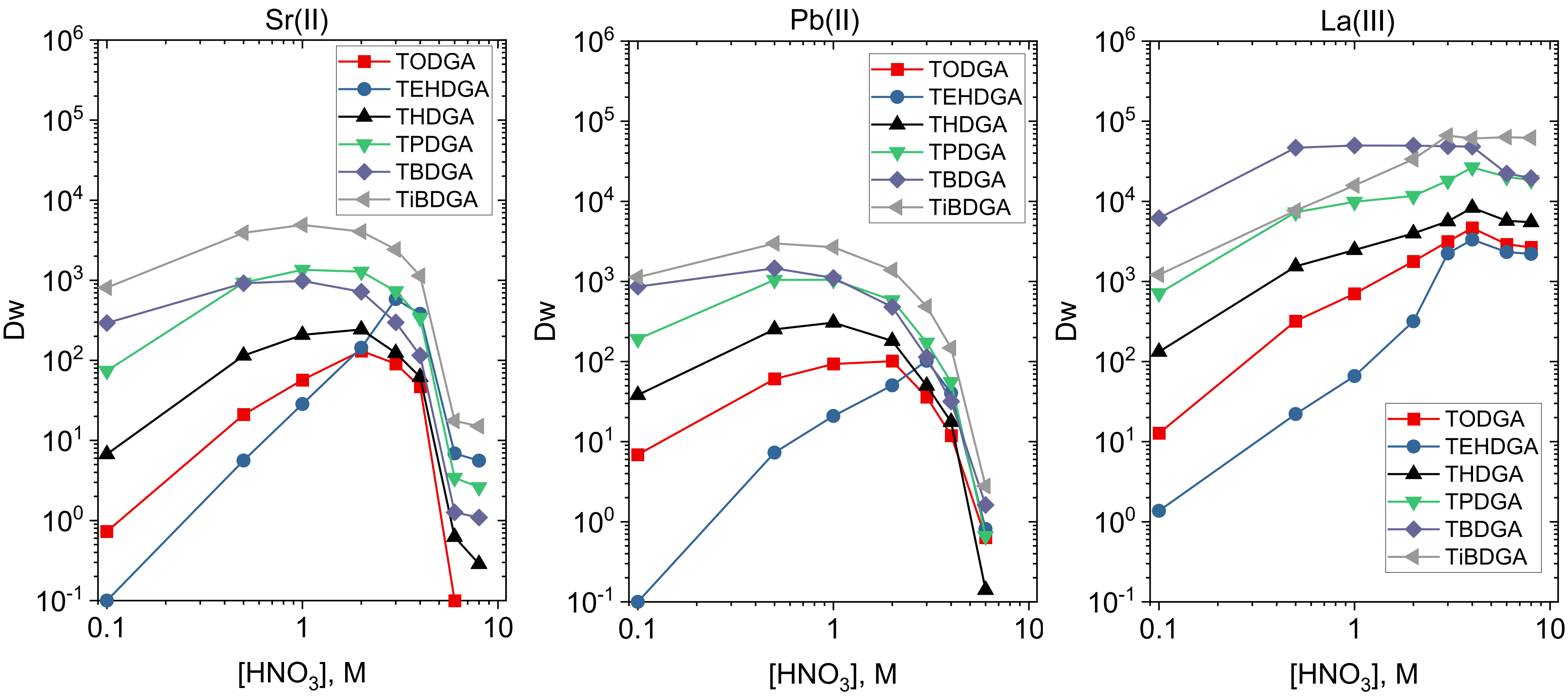




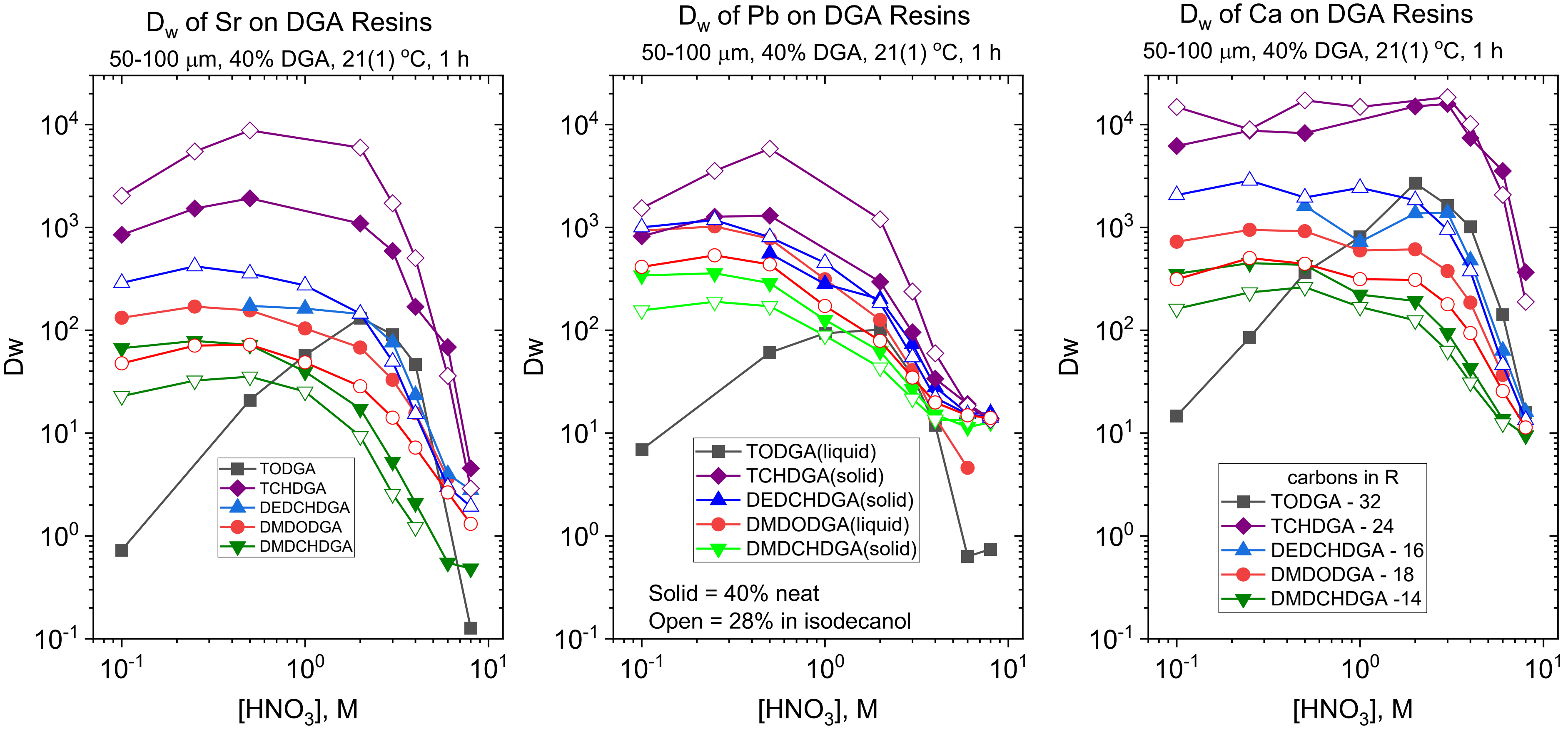




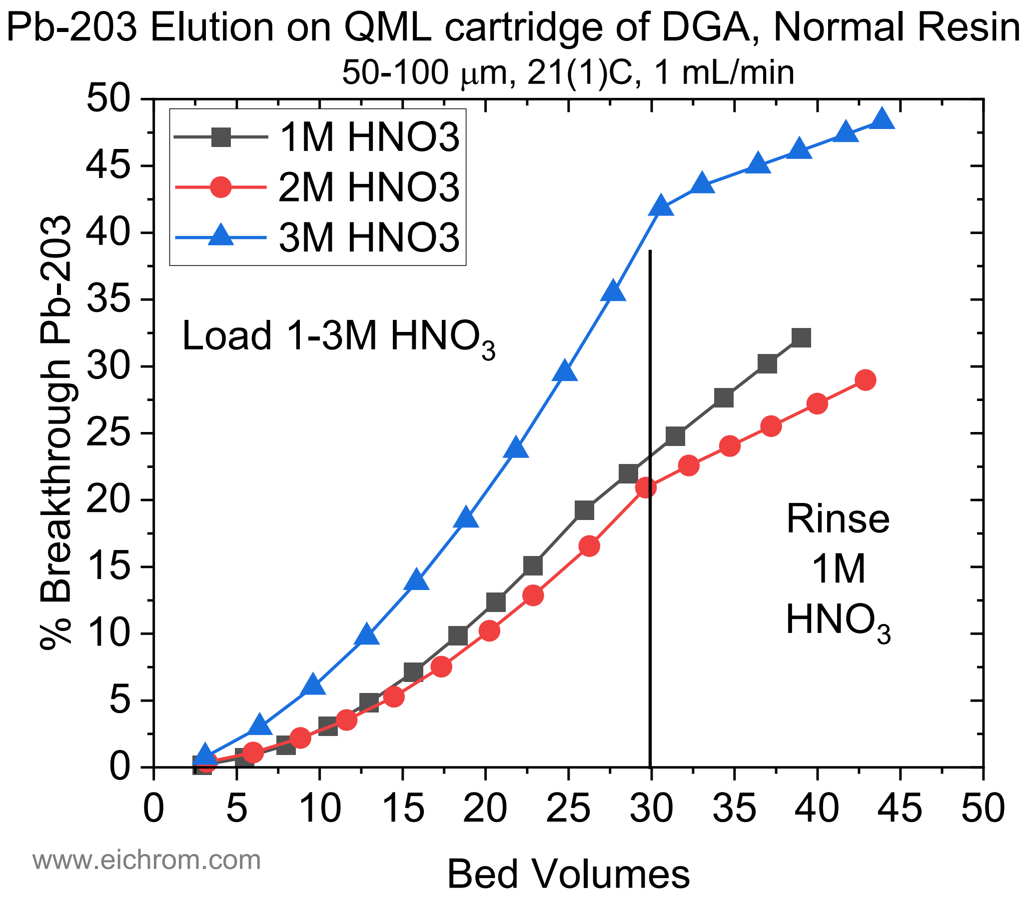
DGAs (Size of R-group, straight chain)



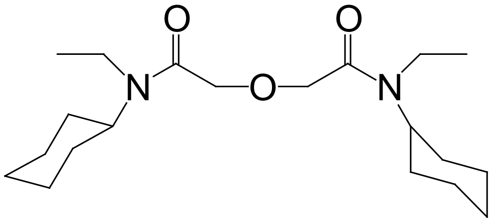
DGAs (asymmetrical/branching)



Pb on DGAs (DGA-N = octyl)



Pb on DGAs (ethyl cyclohexyl)



Less Pb breakthrough

Good selectivity over Ra

Poor recovery in 0.05M HCl (large volume)

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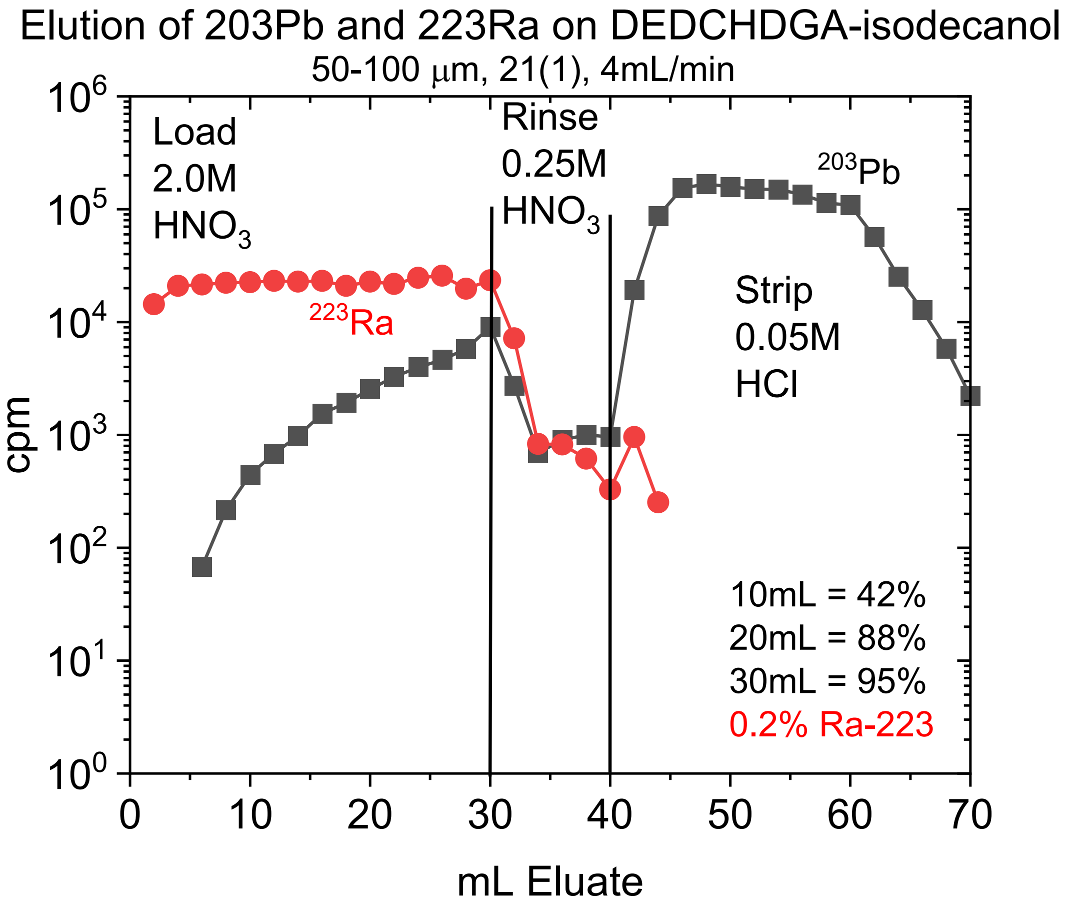
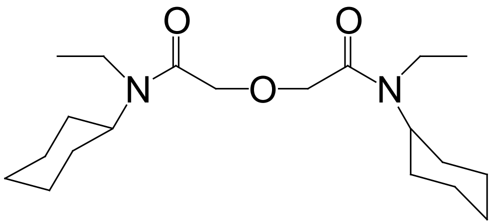


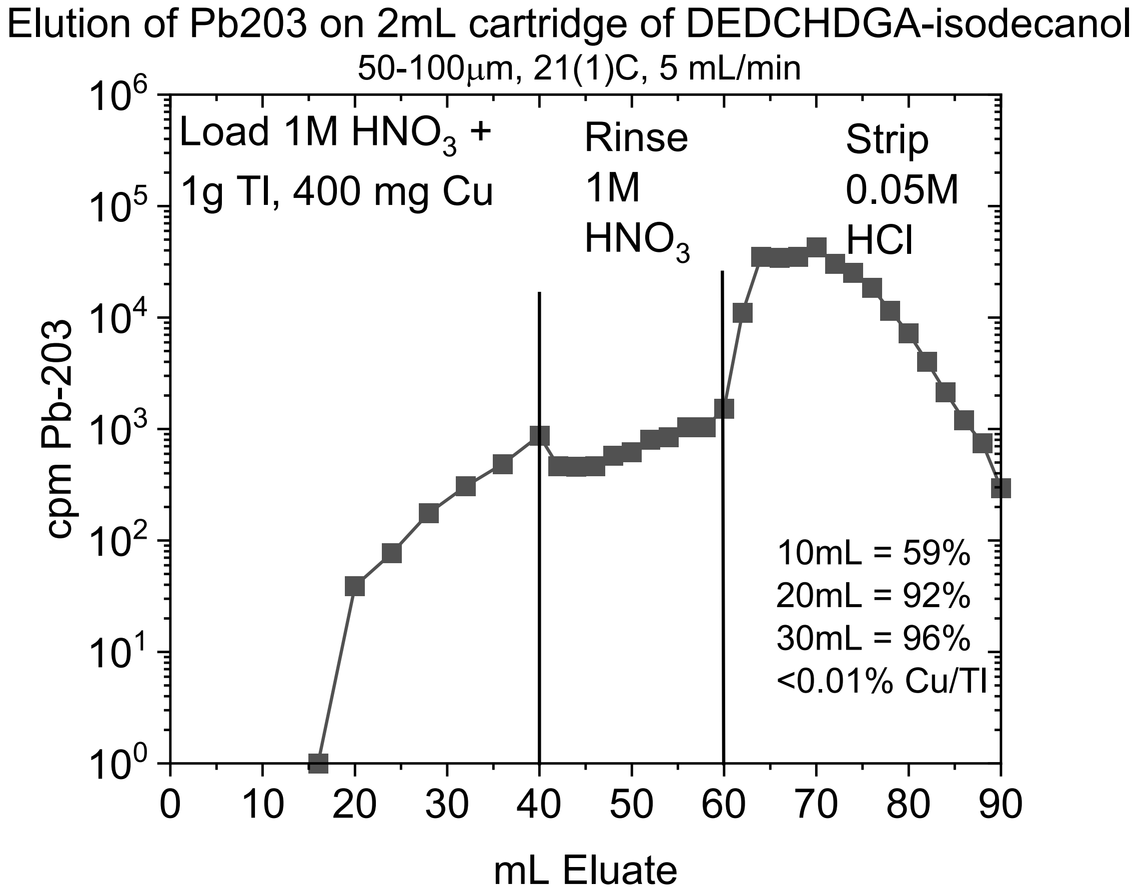
DGA (ethyl cyclohexyl)



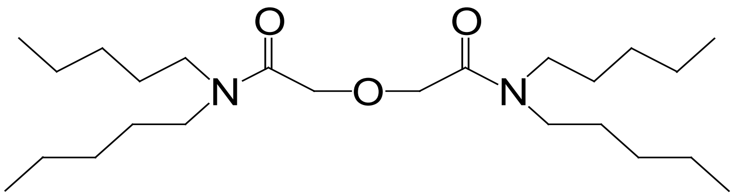
Simulated separation of Pb203 from Tl target.

Low Pb breakthrough

Same recovery as from pure HNO3/HCl.



Pb on DGAs (octyl vs pentyl)



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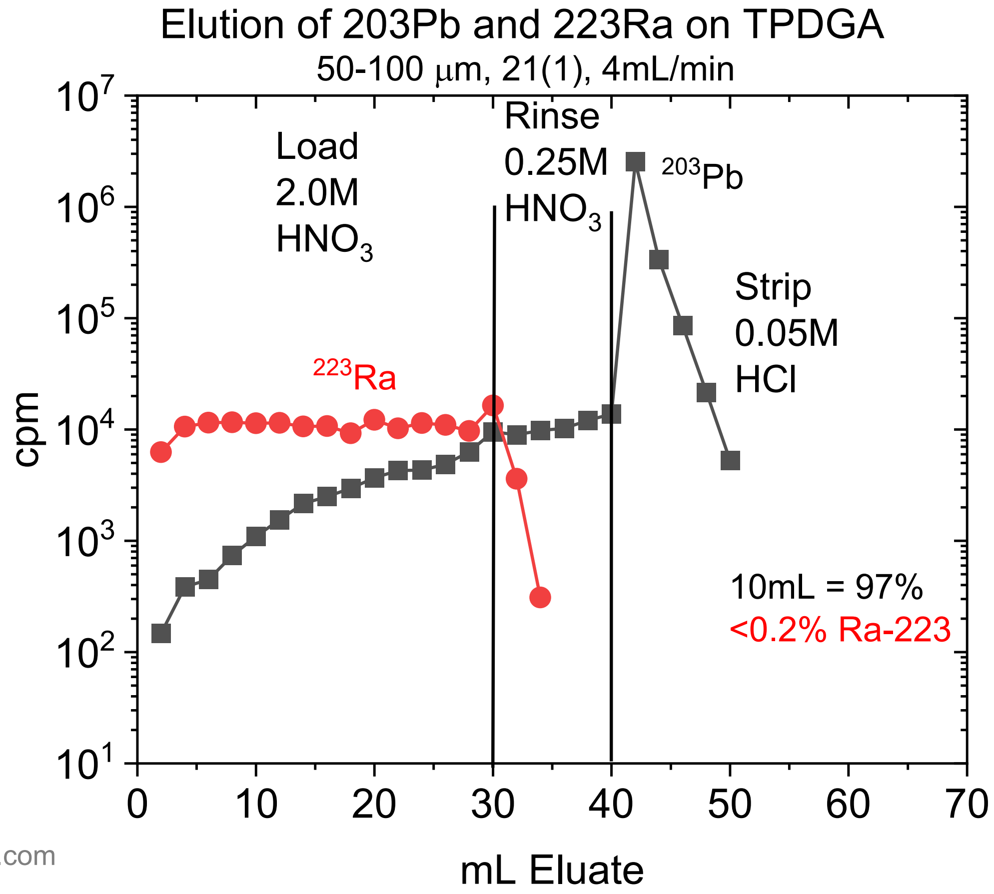
(small volume)



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Future work

- Further characterize new resins/extractants
    - Sr Resins w/ different diluents
    - DGAs w/ different R-groups (REE, Th/U selectivity, HCl system)
    - DGAs w/ different anions (HBr, HI, SCN^-, ClO_4^-)