eichrom®

A BRAND OF
EICHROM TECHNOLOGIES

RRMC
Radiobioassay & Radiochemical Measurements Conference

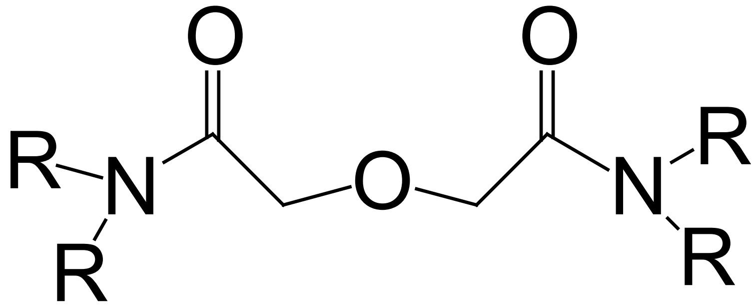
EXC Resin based on the DOODA Extractant

Madeleine Eddy, Ph.D.

Daniel McAlister, Ph.D

2022 RRMC Conference, Atlanta, Georgia

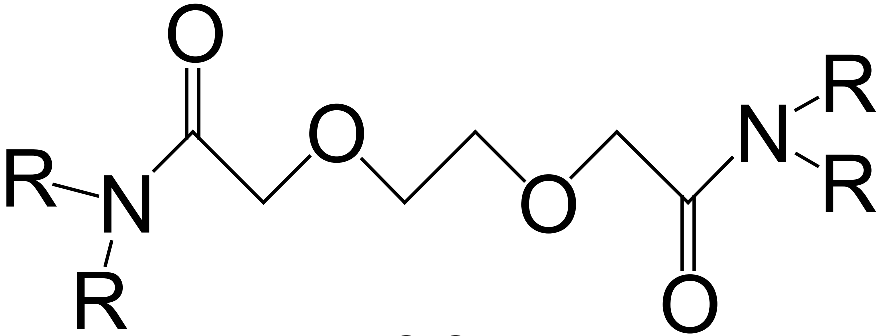
DGA and DOODA Extractants



DGA

Normal = n-octyl

Branched = 1-ethyl-2-hexyl



DOODA

R = n-octyl

References

Solvent Extraction: **(DGA)** **(DOODA)**

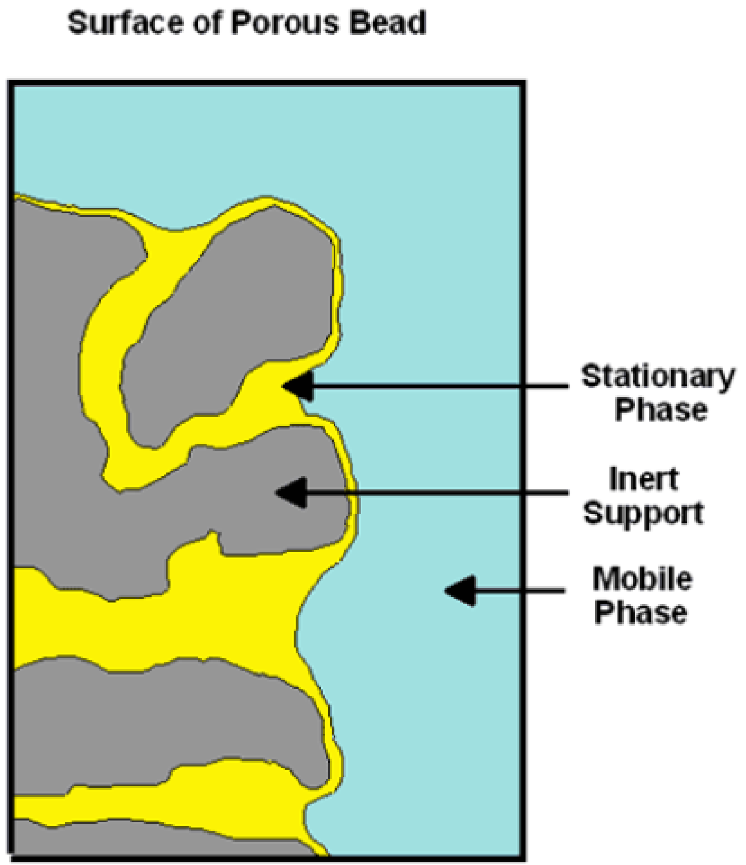
Sasaki, Y.; Sugo, Y.; Suzuki, S.; and Tachimori, S. The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO3-n-dodecane system, Solvent Extr. Ion Exch. 2001, 19, 91-103.

Sasaki, Y.; Tachimori, S. Extraction of actinides(III), (IV), (V), (VI) and lanthanides(III) by structurally tailored diamides, Solvent Extr. Ion Exch. 2002, 20, 21-34.

Tachimori, S.; Suzuki, S.; Sasaki, Y.; Apichaibukol, A. Solvent extraction of alkaline earth metal ions by diglycolic amides from nitric acid solutions, Solvent Extr. Ion Exch. 2003, 21, 707-715.

Sasaki, Y.; Morita,Y.; Kitatsuji, Y.; and Kimura, T. Extraction of Actinides and Fission Products by the New Ligand, N,N,N,,N’-Tetraoctyl-3,6-dioxaoctanediamide, Chemistry Letters, 2009, 38(6), 630-631.

Extraction Chromatographic (EXC) Resins



References

Extraction Chromatography:

E. P. Horwitz, D. R. McAlister, A. H. Bond, R. E Barrans, Jr., "Novel Extraction Chromatographic Resins Based on Tetraalkyldiglycolamides: Characterization and Potential Applications," Solv. Extr. Ion Exch., 23, 319-344 (2005).

Pourmand, A.; Dauphas, N., Distribution coefficients of 60 elements on TODGA resin: Application to Ca, Lu, Hf, U and Th isotope geochemistry, Talanta, 81(3), 741-753 (2010).

D.R. McAlister and E.P. Horwitz, "Synergistic enhancement of the extraction of trivalent lanthanides and actinides by tetra(n-octyl)diglycolamide from chloride media," Solv. Extr. Ion Exch., 26(1), 12-24 (2008).

Usuda, S; Yamanishi, K.; Mimura, H.; Sasaki, Y; Kirishima, A.; Sato, N.; Niibori, Y. Separation of Am and Cm by using TODGA and DOODA(C8) adsorbents with hydrophilic ligand-nitric acid solution, J Radioanal Nucl Chem (2015) 303, 1351–1355.

Physical Properties

Physical Constants for EXC Resins

	DGA, Normal	DGA, Branched	DOODA
Extractant Density (g/mL)	0.88	0.89	0.90
Bed Density (g/mL)	0.39	0.39	0.40
Resin Density (g/mL)	1.13	1.13	1.13
v_s	0.18	0.18	0.18
v_m	0.66	0.66	0.64
v_s/v_m	0.27	0.27	0.28
D_v conversion factor (C_1)[a]	2.22	2.22	2.25
k' conversion factor (C_2)[b]	0.60	0.60	0.63
molecular weight g/mole	580.92	580.92	624.98
capcity Eu (mg/mL)	12.8	12.6	14.8

[1] $D_v = D_w \times C_1$

[1] $k' = D_w \times C_2$

AN-1703
Packing resin columns

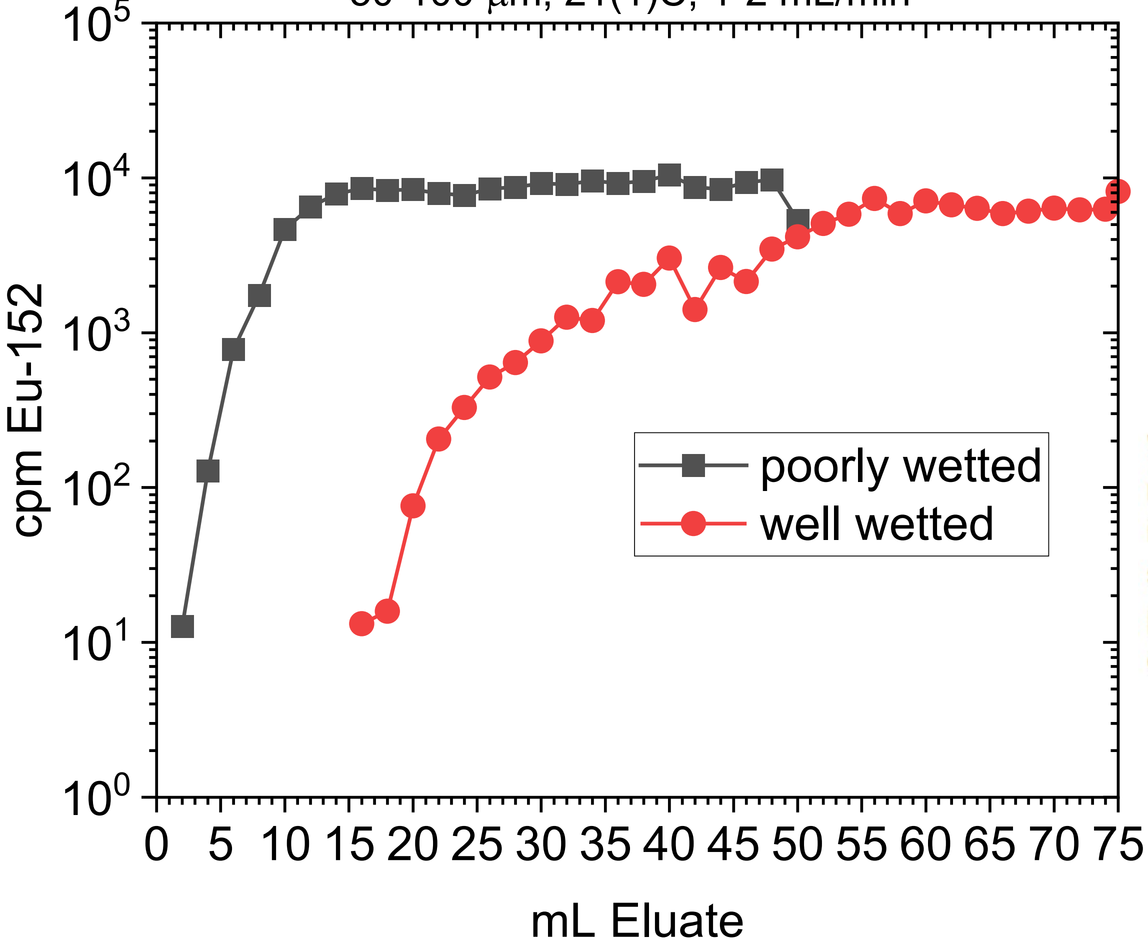
Dw = mL of eluate to peak maximum / gram of resin

Dv = mL of eluate to peak maximum / mL of resin

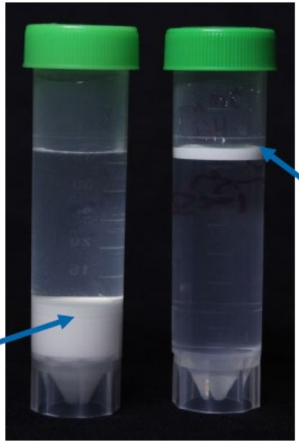
k' = free column volumes to peak maximum

Eu Capacity Measurment on 2 mL Cartridge of DGA, Normal

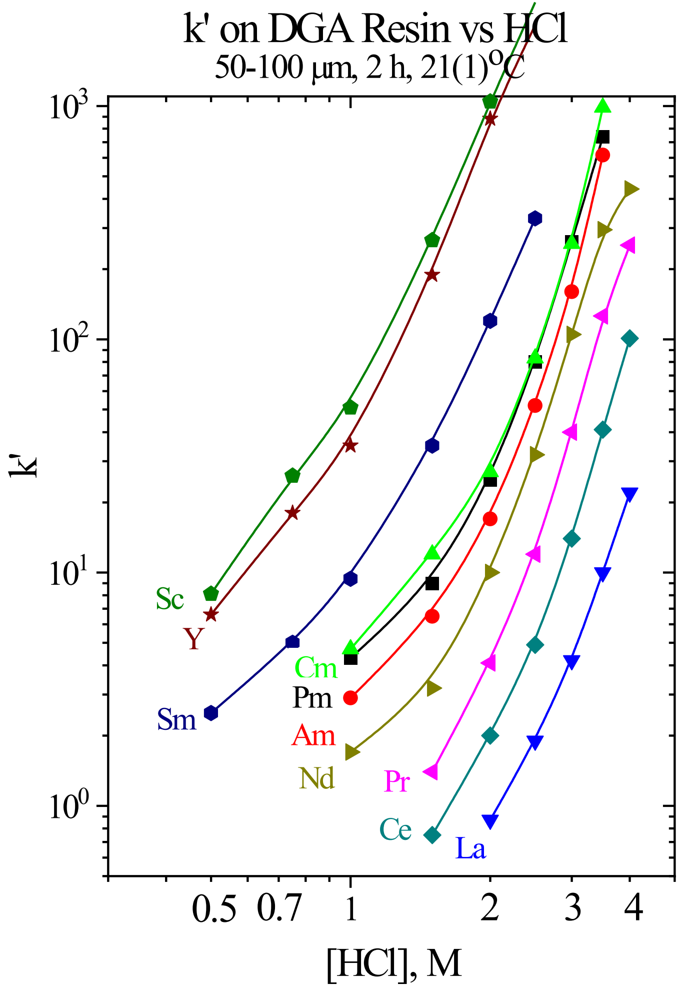
50-100 μm, 21(1)C, 1-2 mL/min



Wetted resin, ideal for slurry packing columns.



Floating or poorly wetted resin, difficult to slurry pack into columns.



Peak maximum positions:

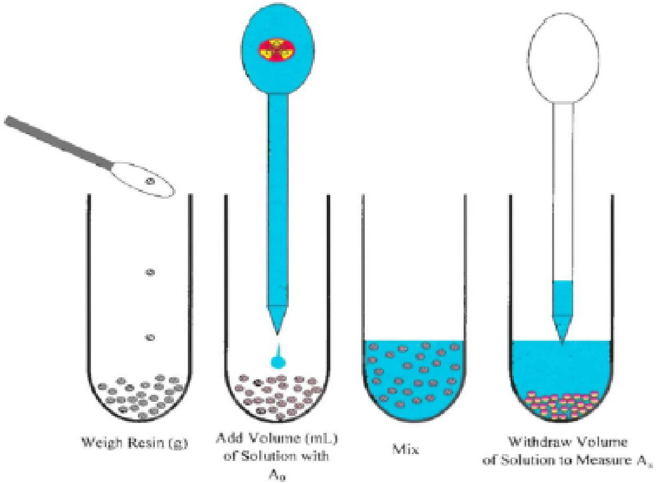
Dw = mL eluate/grams resin (measured by batch contact)

Dv = mL eluate/mL resin

k' = free column volumes

Calculated from Dw using:

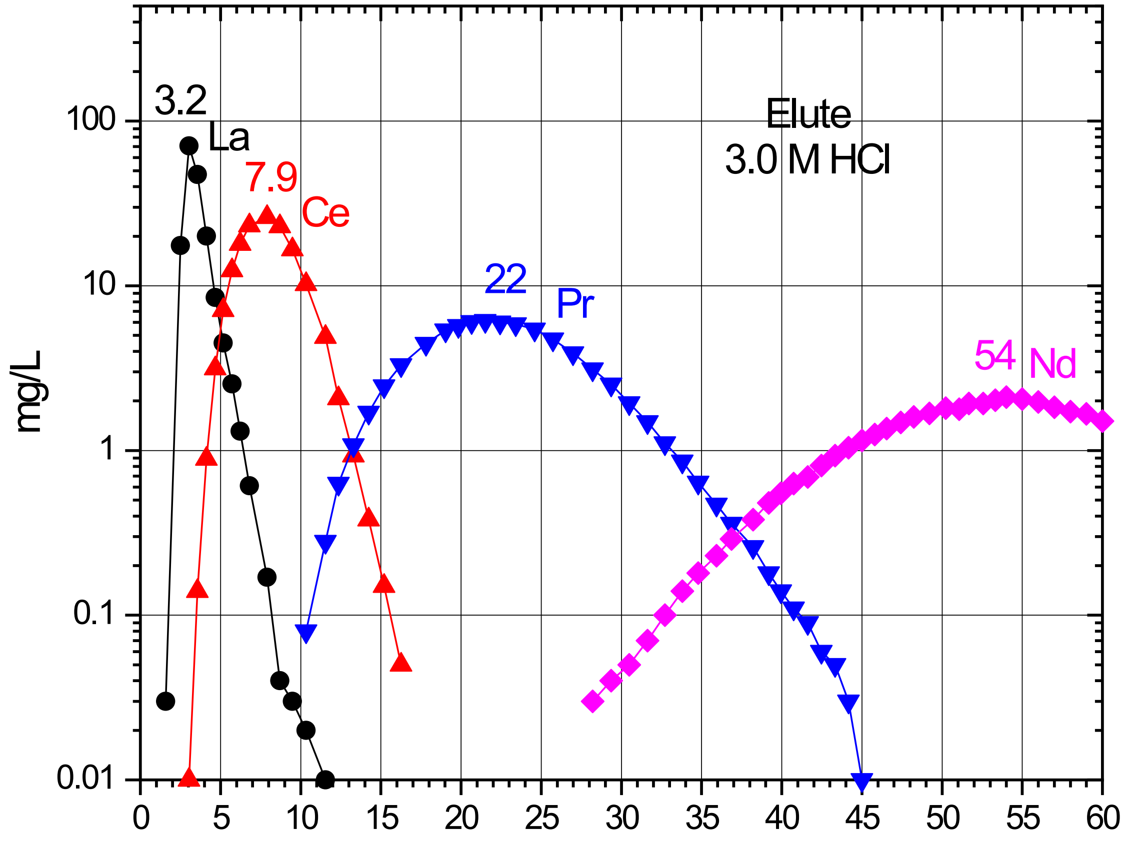
- Bed density
- Resin density
- Extractant density
- Extractant loading



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

Elution of La, Ce, Pr, Nd on DGA, Normal

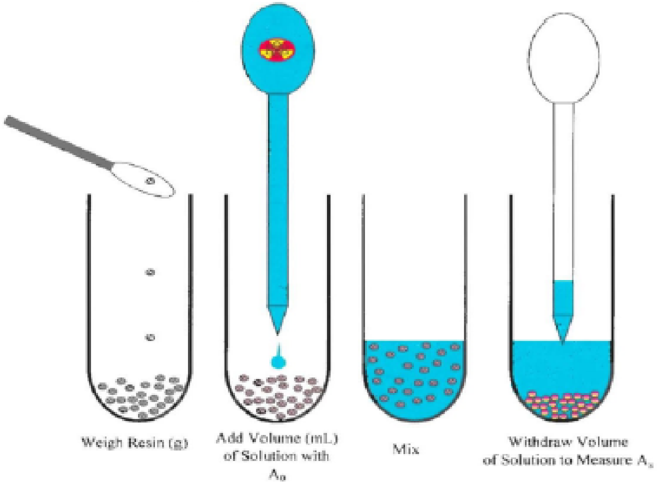
50-100 μm, 0.9 cm x 14 cm, 21(1)^{o}C, 3.5 mL/min



Peak maximum positions:

Dw = mL eluate/grams resin

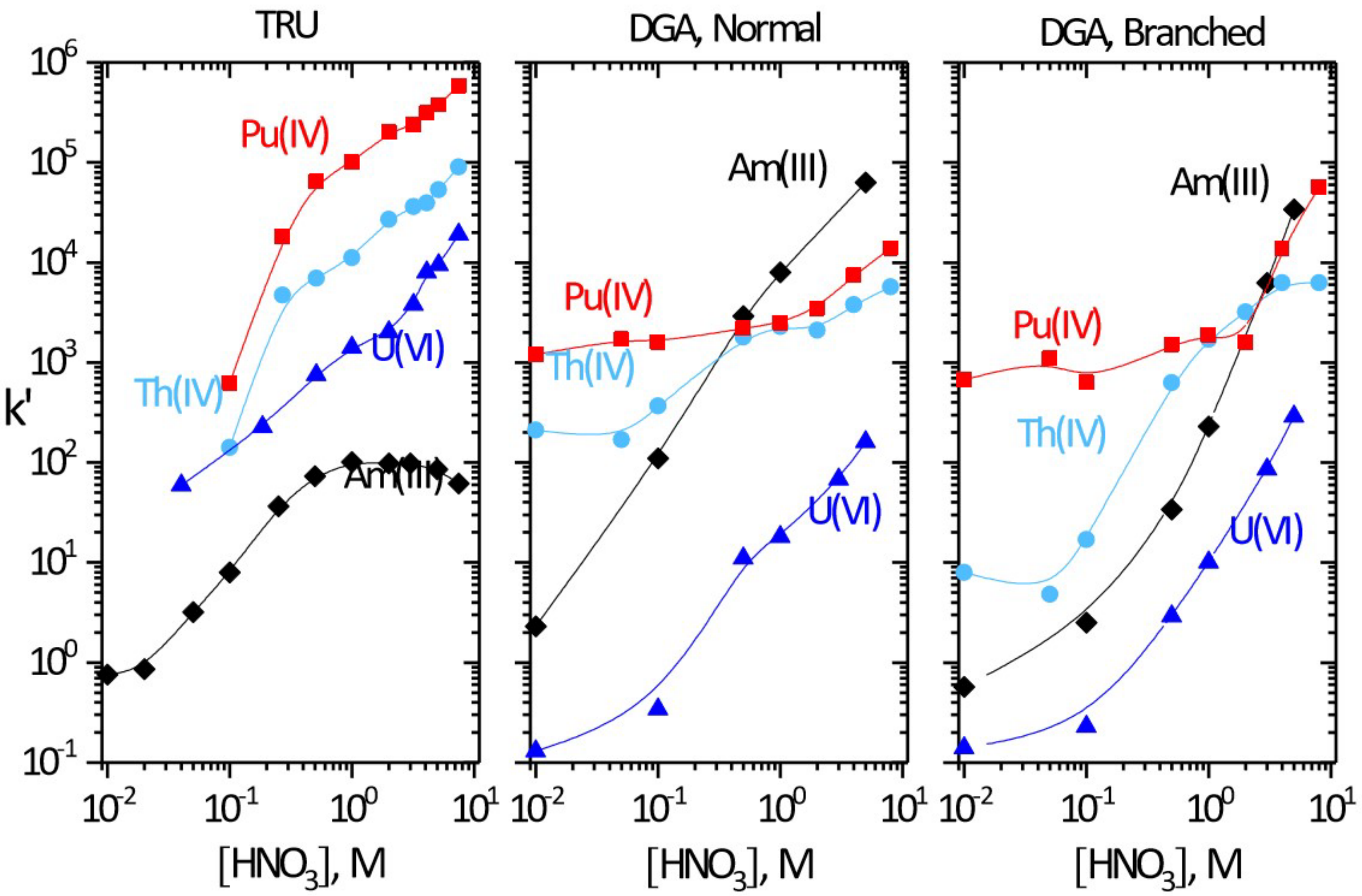
(measured by batch contact)



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

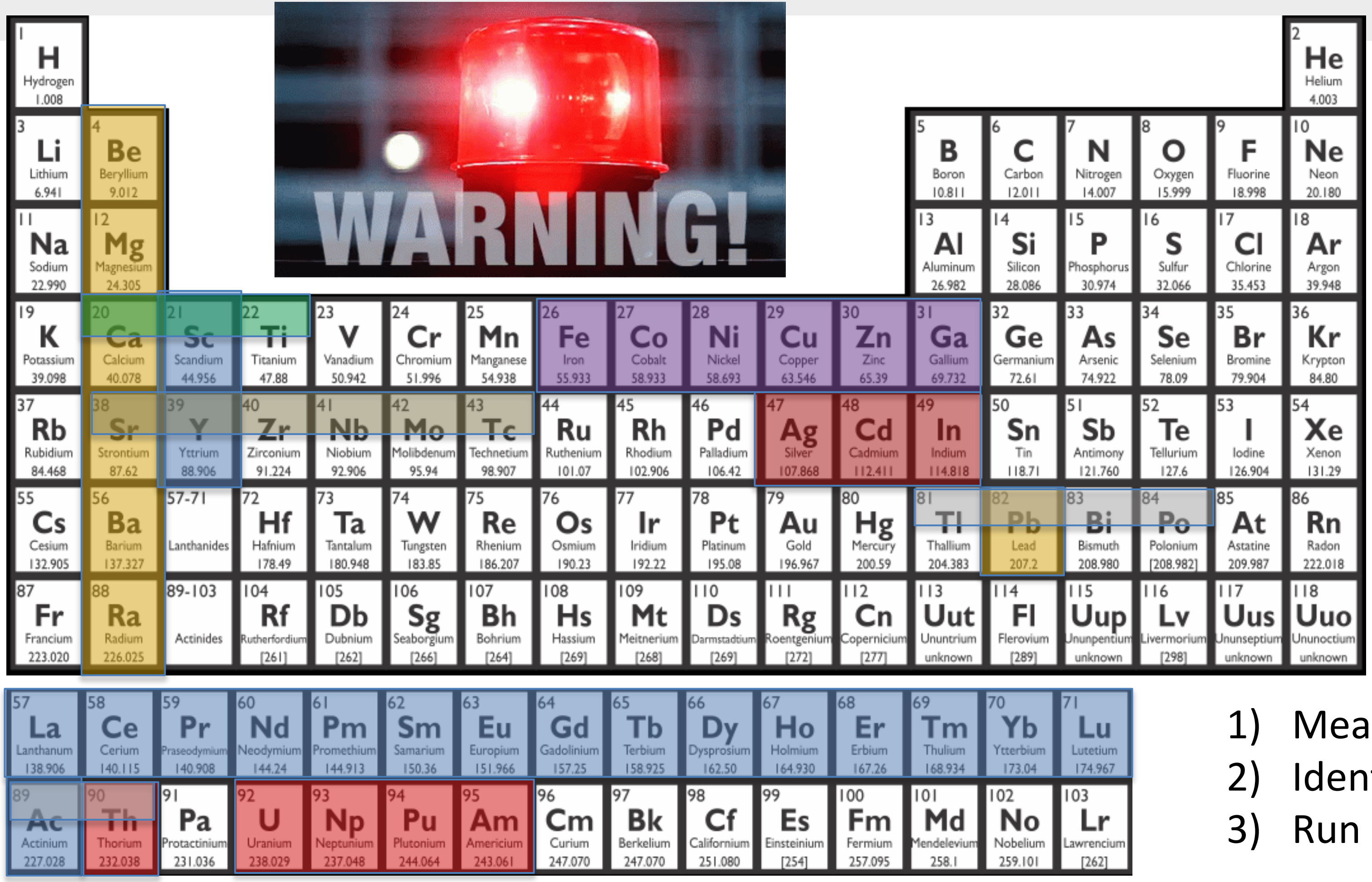
Dv = mL eluate/mL resin

k' = free column volumes



DGA can be used as an alternative or in conjunction with TRU to recover Am/Cm from difficult samples.

DGA Applications (How does DOODA compare?)

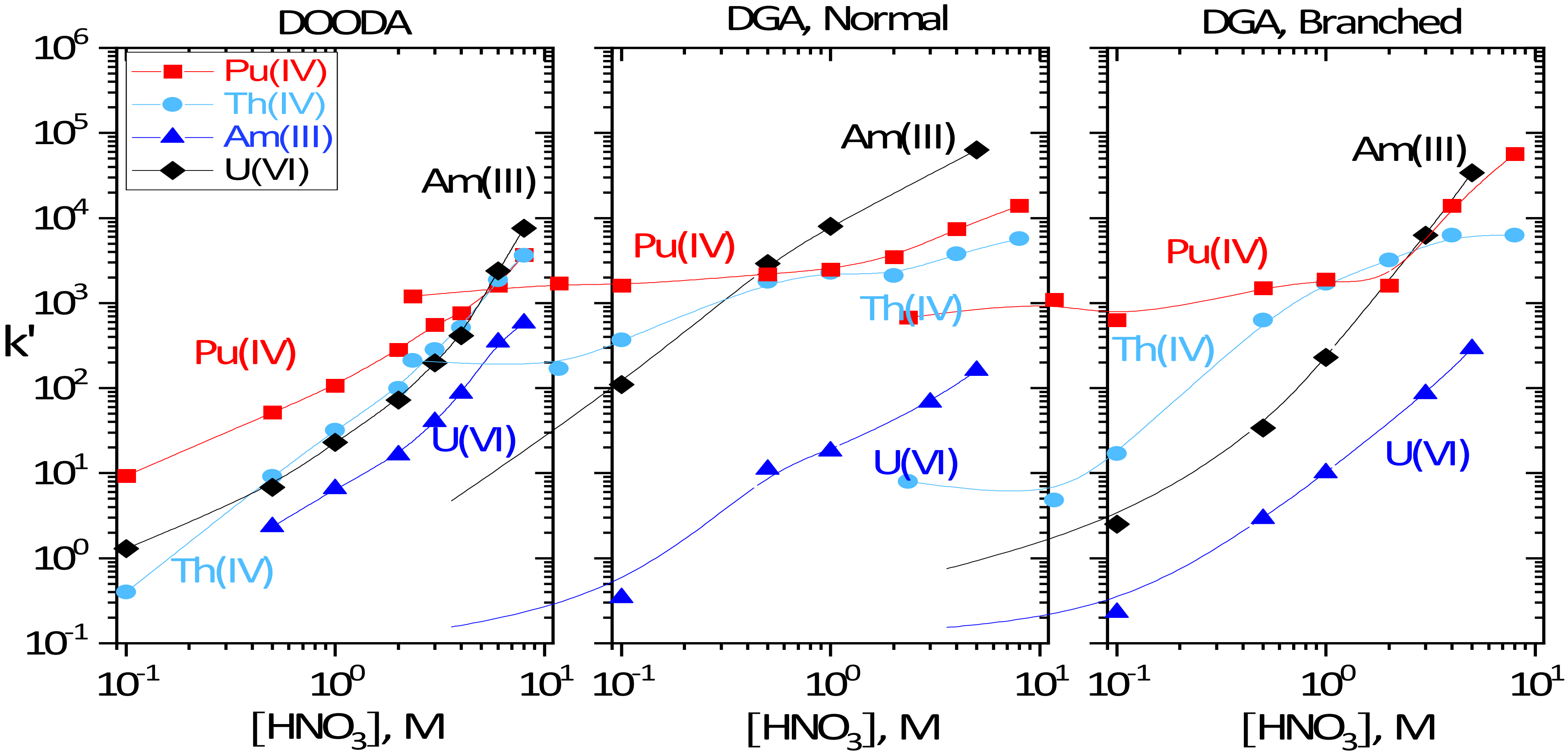


Actinides
Rare Earths
Alkaline Earths + Pb
Ga-68
In-111
Y-90
Sc-44
Zr-89
Ac-225

DGA-N vs DGA-B

1) Measure Dws
2) Identify separations
3) Run columns

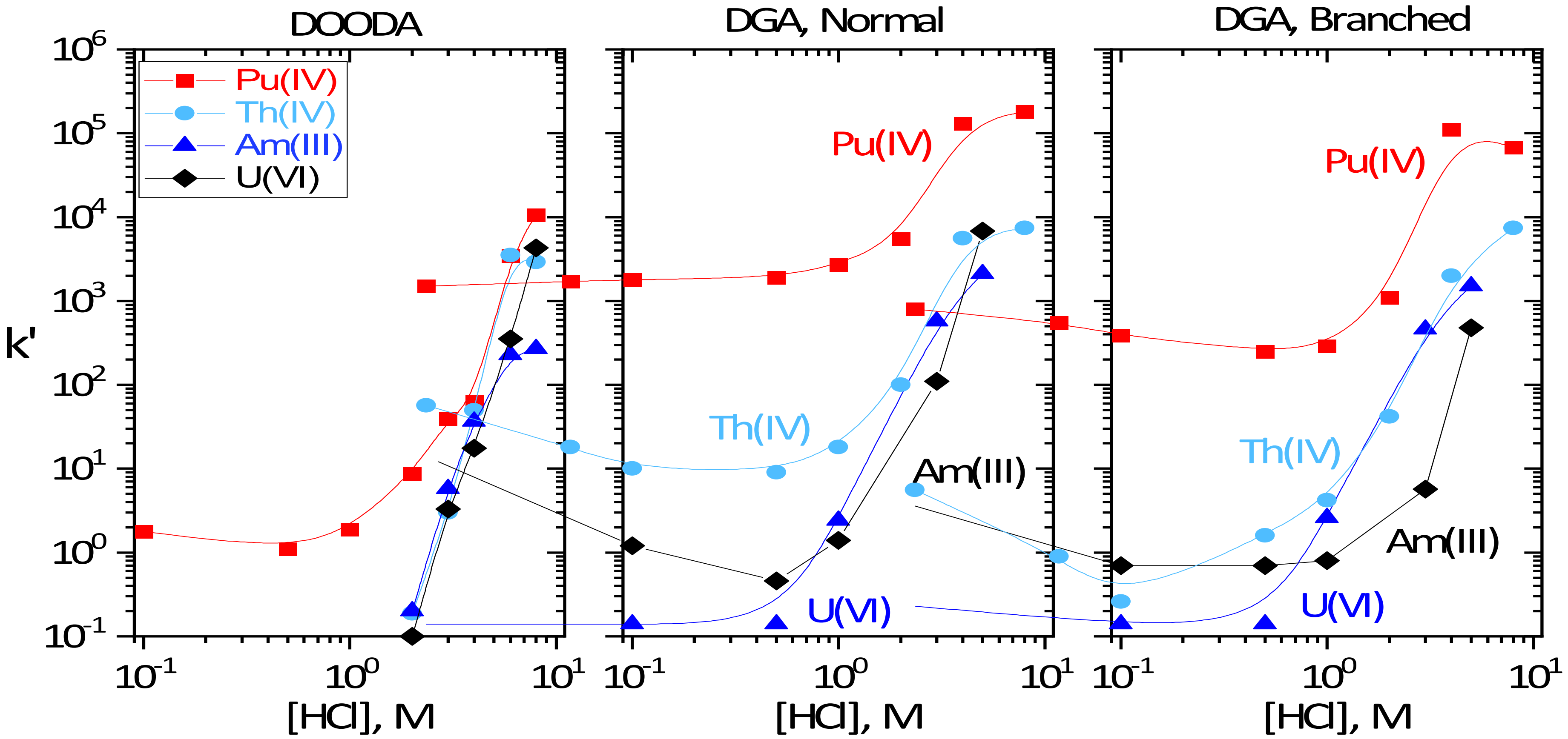
Actinides



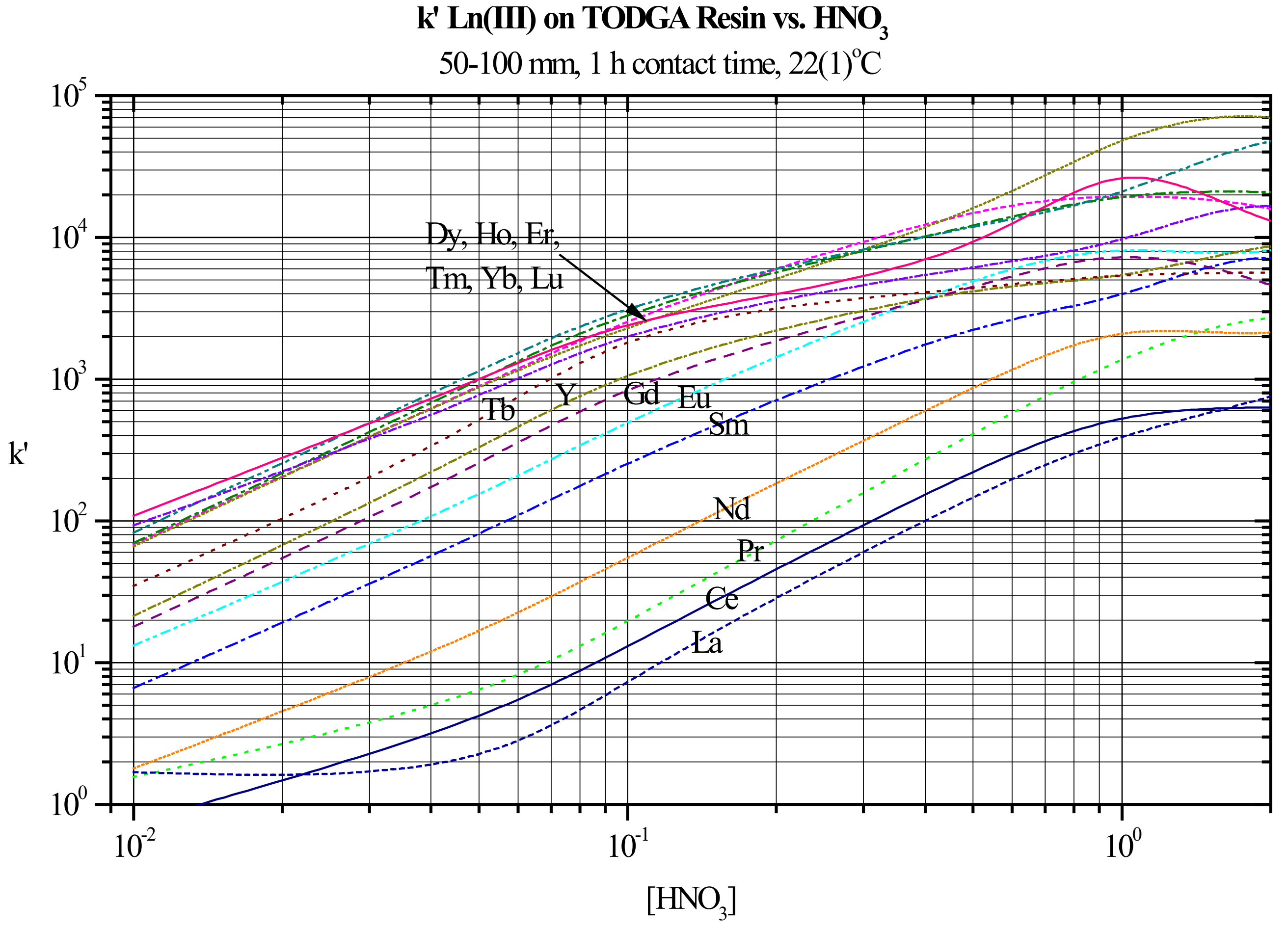
DOODA retains An(III, IV, VI)

Less selectivity for An(III) over An (IV, VI)

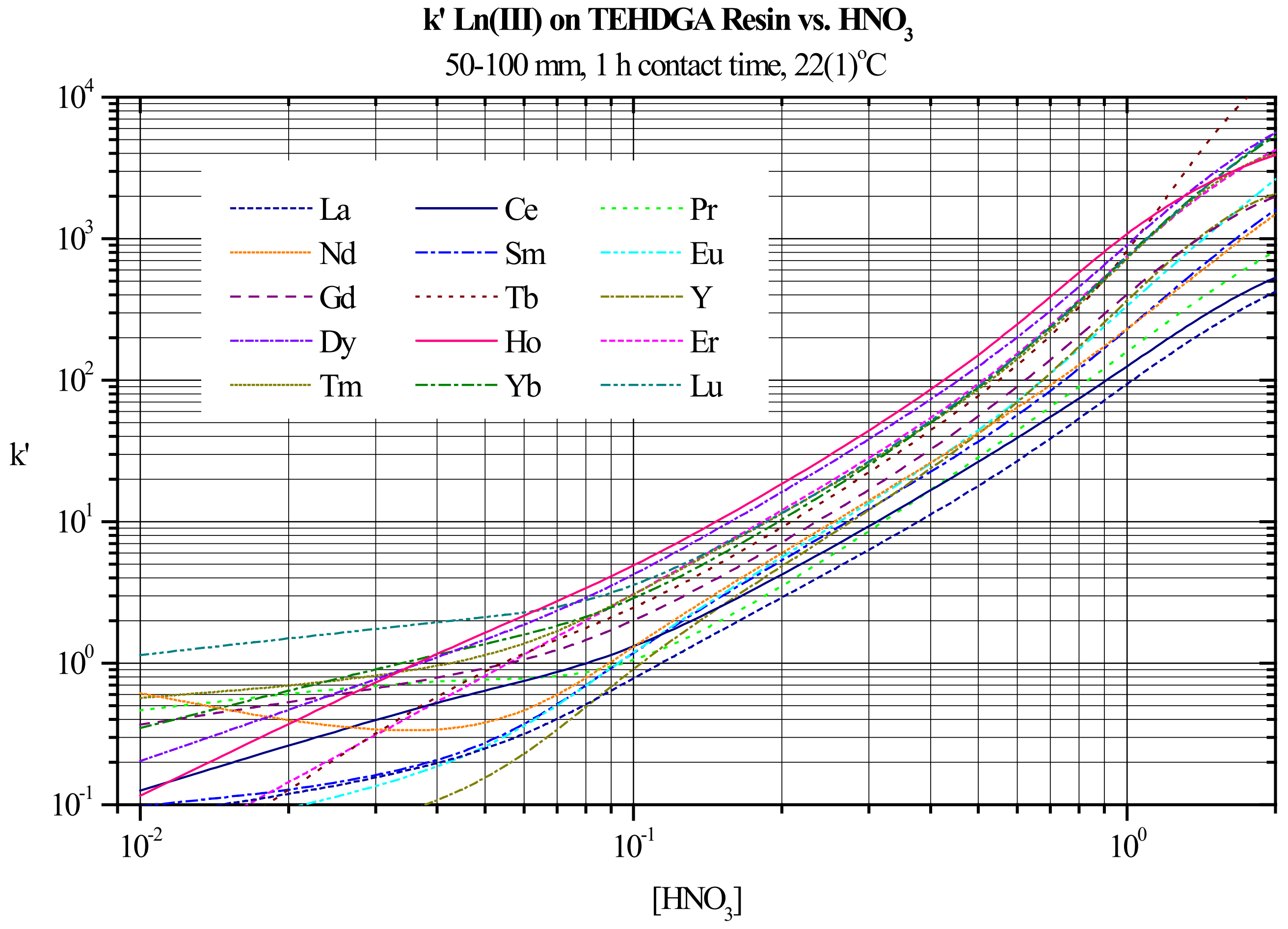
Recovery in dilute HNO3?


DOODA
DGA, Normal
DGA, Branched
k'
Pu(IV)
Th(IV)
Am(III)
U(VI)
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-1}
10^{0}
10^{1}
[HCl], M
Pu(IV)
Th(IV)
Am(III)
U(VI)
Pu(IV)
Th(IV)
Am(III)
U(VI)

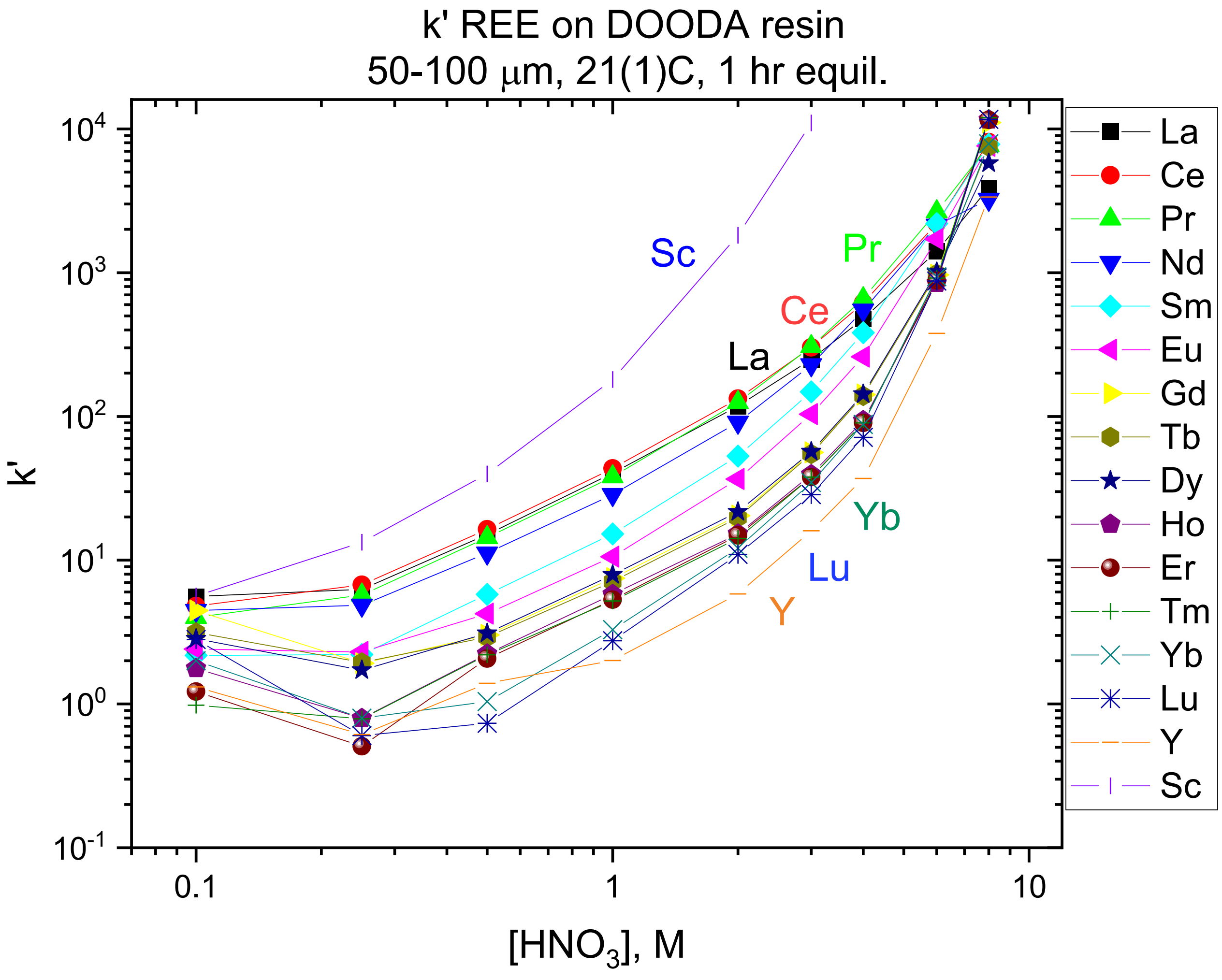
Rare Earths



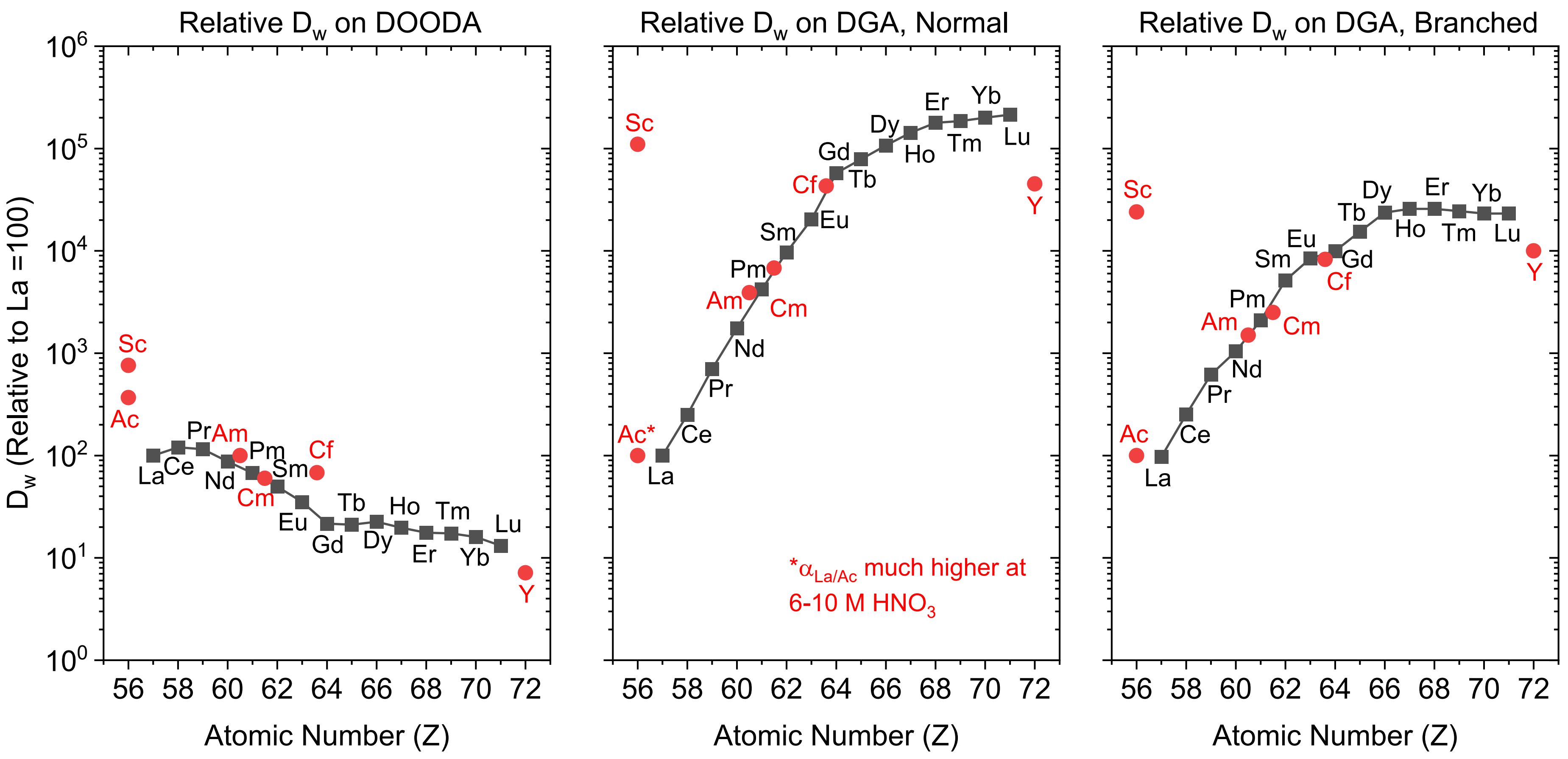
k' Ln(III) on TODGA Resin vs. HNO3
50-100 mm, 1 h contact time, 22(1)°C
k'
[HNO3]
10^5
10^4
10^3
10^2
10^1
10^0
10^-2
10^-1
10^0
Dy, Ho, Er,
Tm, Yb, Lu
Tb
Y
Gd
Eu
Sm
Nd
Pr
Ce
La



k' Ln(III) on TEHDGA Resin vs. HNO3
50-100 mm, 1 h contact time, 22(1)°C
k'
[HNO3]
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-1
10^0
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Y
Dy
Ho
Er
Tm
Yb
Lu



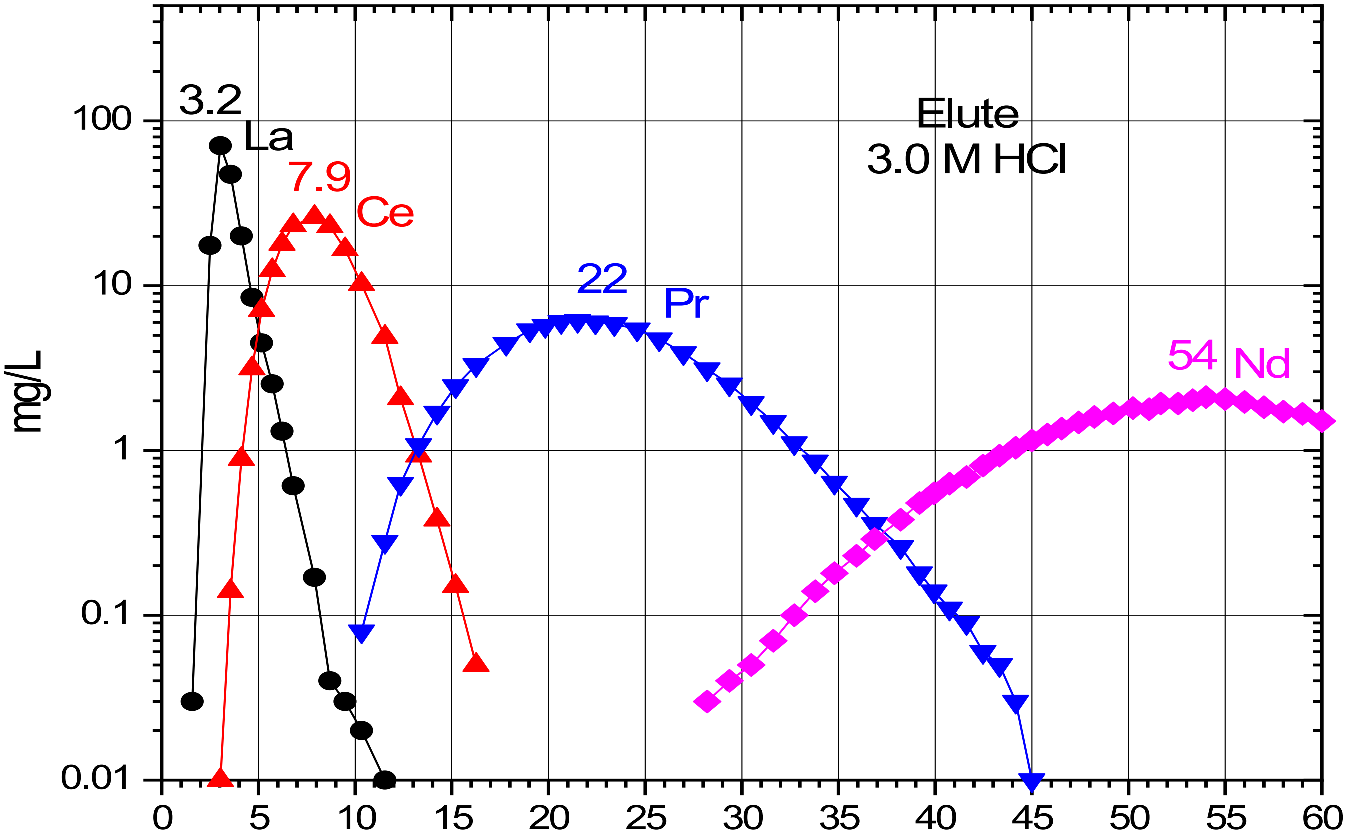
k' REE on DOODA resin
50-100 μm, 21(1)C, 1 hr equil.
k'
[HNO3], M
0.1
1
10
Sc
Pr
Ce
La
Yb
Lu
Y
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Y
Sc



Relative D_w on DOODA
Relative D_w on DGA, Normal
Relative D_w on DGA, Branched
D_w (Relative to La =100)
10^0
10^1
10^2
10^3
10^4
10^5
10^6
Atomic Number (Z)
56 58 60 62 64 66 68 70 72
Sc
Ac
Ac*
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Am
Cm
Cf
Y
*$\alpha_{La/Ac}$ much higher at
6-10 M HNO_3

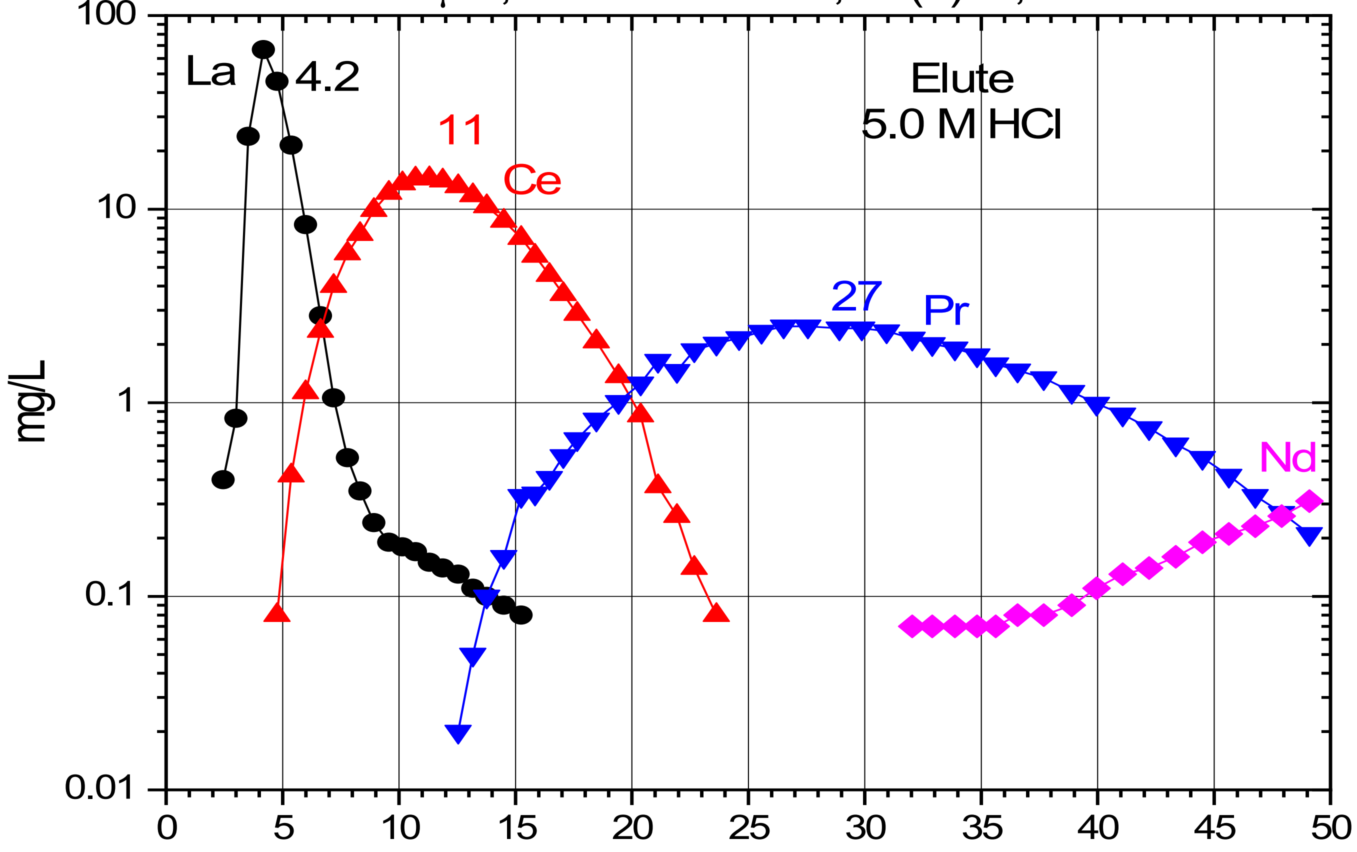
Elution of La, Ce, Pr, Nd on DGA, Normal

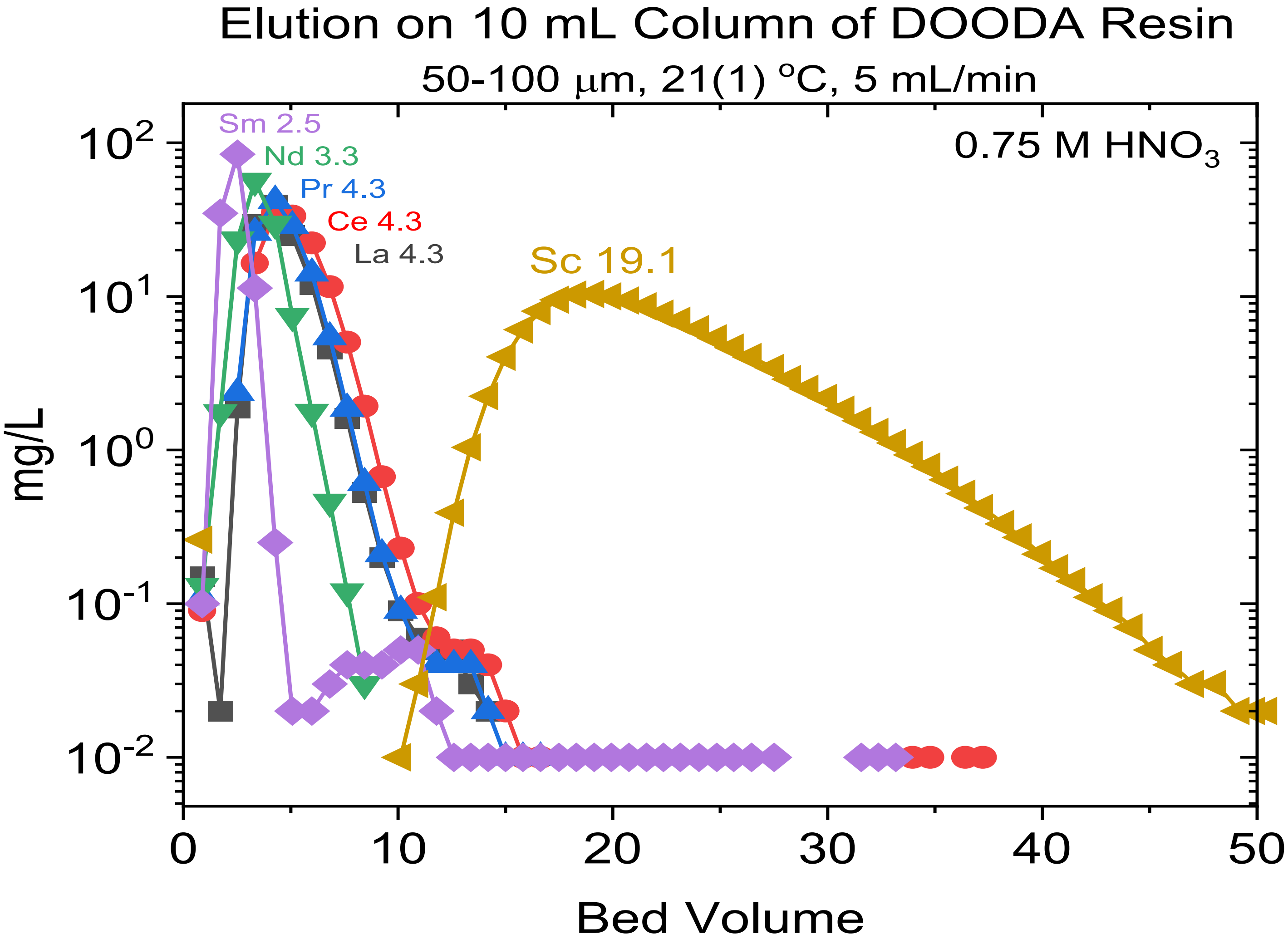
50-100 μm, 0.9 cm x 14 cm, 21(1)°C, 3.5 mL/min



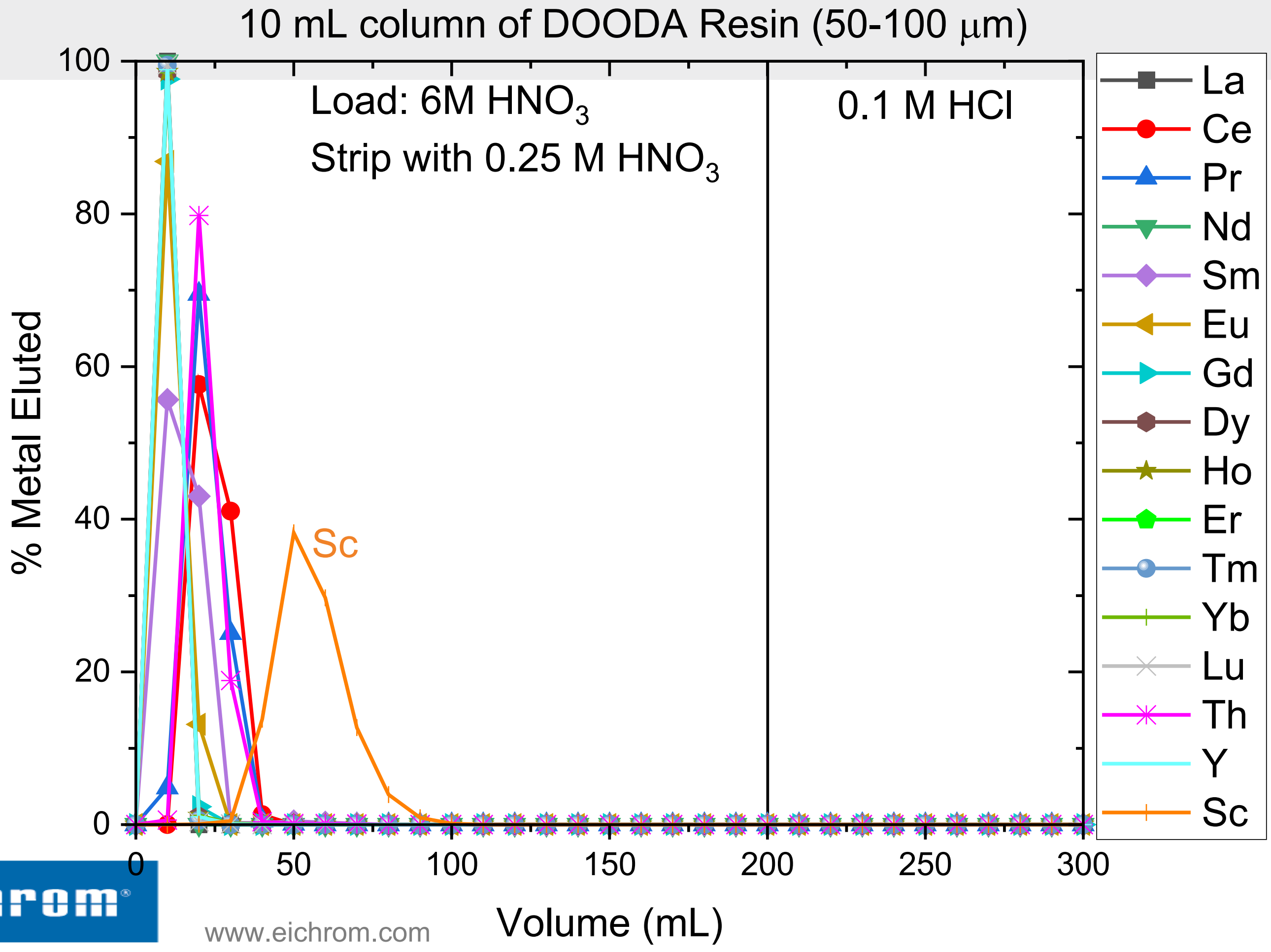
Elution of La, Ce, Pr, Nd on DGA, Branched

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

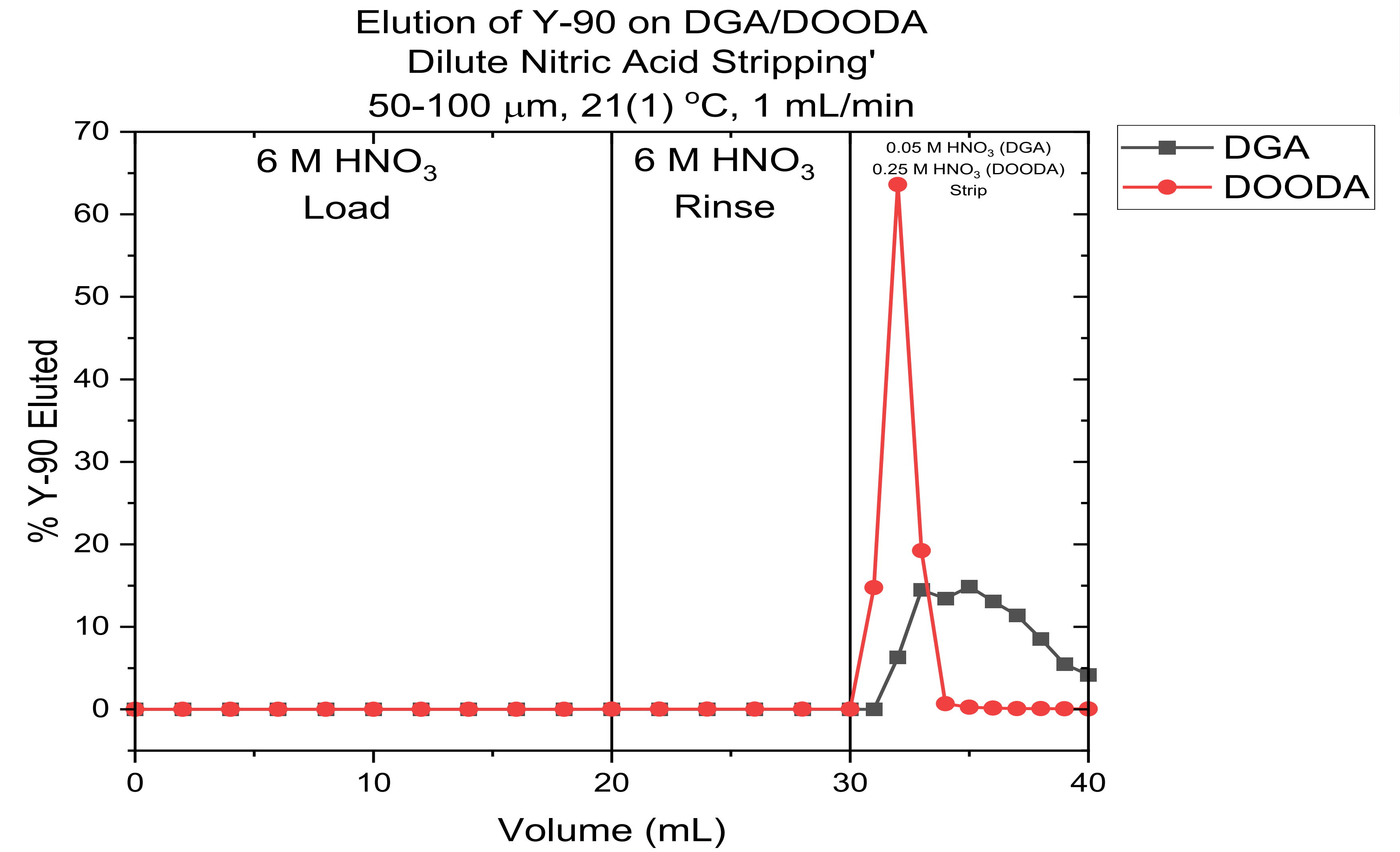




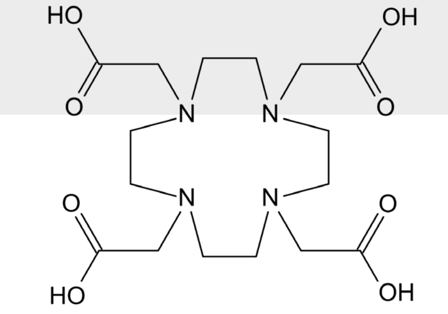
Elution on 10 mL Column of DOODA Resin
50-100 μm, 21(1) °C, 5 mL/min
0.75 M HNO3
Sm 2.5
Nd 3.3
Pr 4.3
Ce 4.3
La 4.3
Sc 19.1
mg/L
10^2
10^1
10^0
10^-1
10^-2
0
10
20
30
40
50
Bed Volume

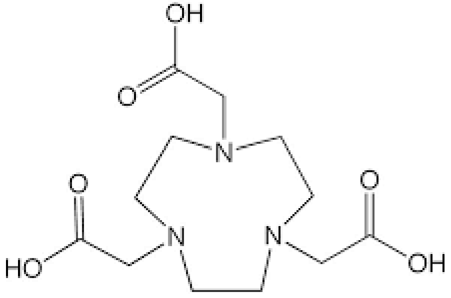


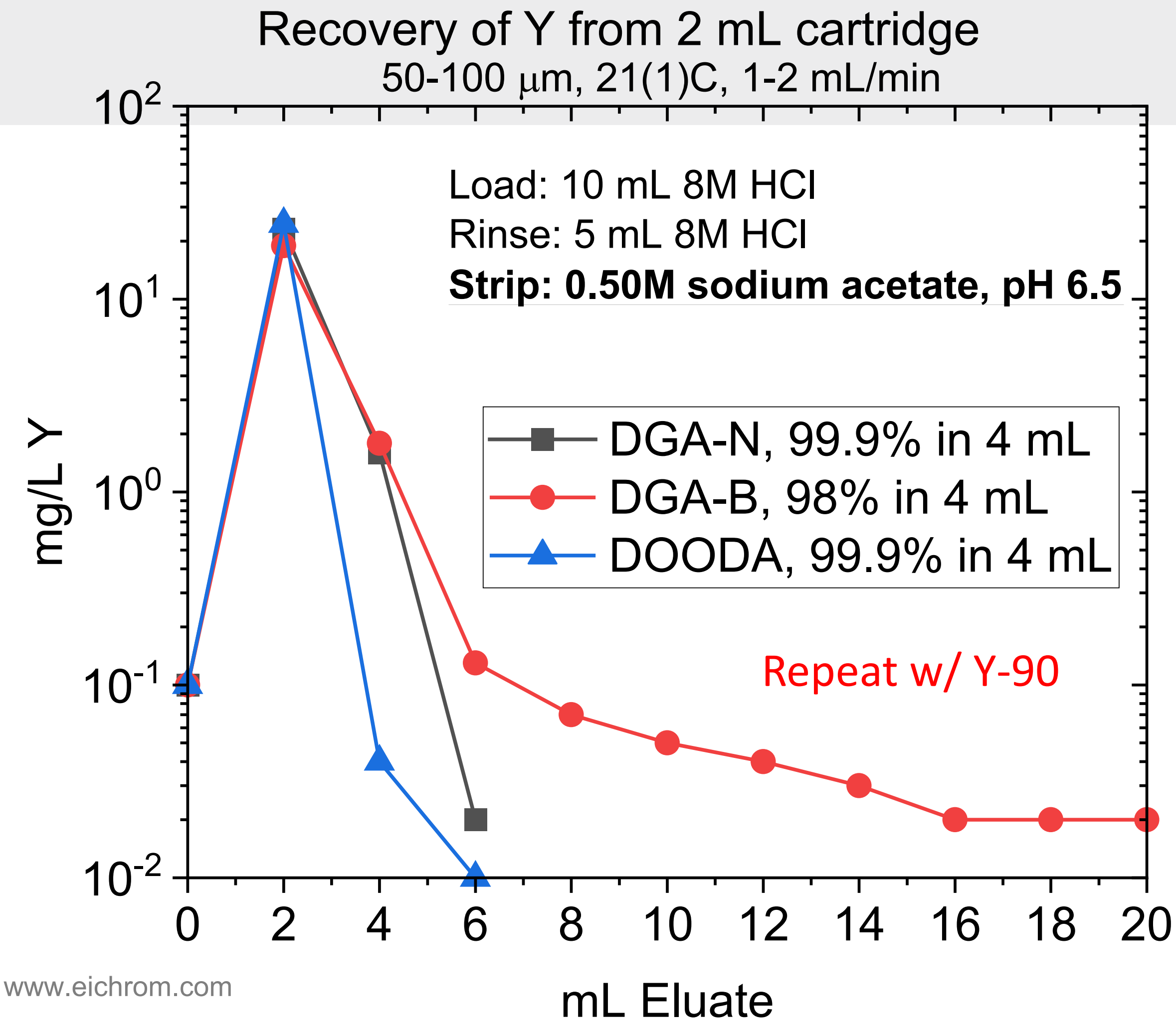
10 mL column of DOODA Resin (50-100 μm)
Load: 6M HNO3
Strip with 0.25 M HNO3
0.1 M HCl
Sc
% Metal Eluted
Volume (mL)
0
20
40
60
80
100
0
50
100
150
200
250
300
La
Ce
Pr
Nd
Sm
Eu
Gd
Dy
Ho
Er
Tm
Yb
Lu
Th
Y
Sc



Elution of Y-90 on DGA/DOODA
Dilute Nitric Acid Stripping'
50-100 μm, 21(1) °C, 1 mL/min
6 M HNO_3
Load
6 M HNO_3
Rinse
0.05 M HNO_3 (DGA)
0.25 M HNO_3 (DOODA)
Strip
DGA
DOODA
% Y-90 Eluted
Volume (mL)
0
10
20
30
40
50
60
70







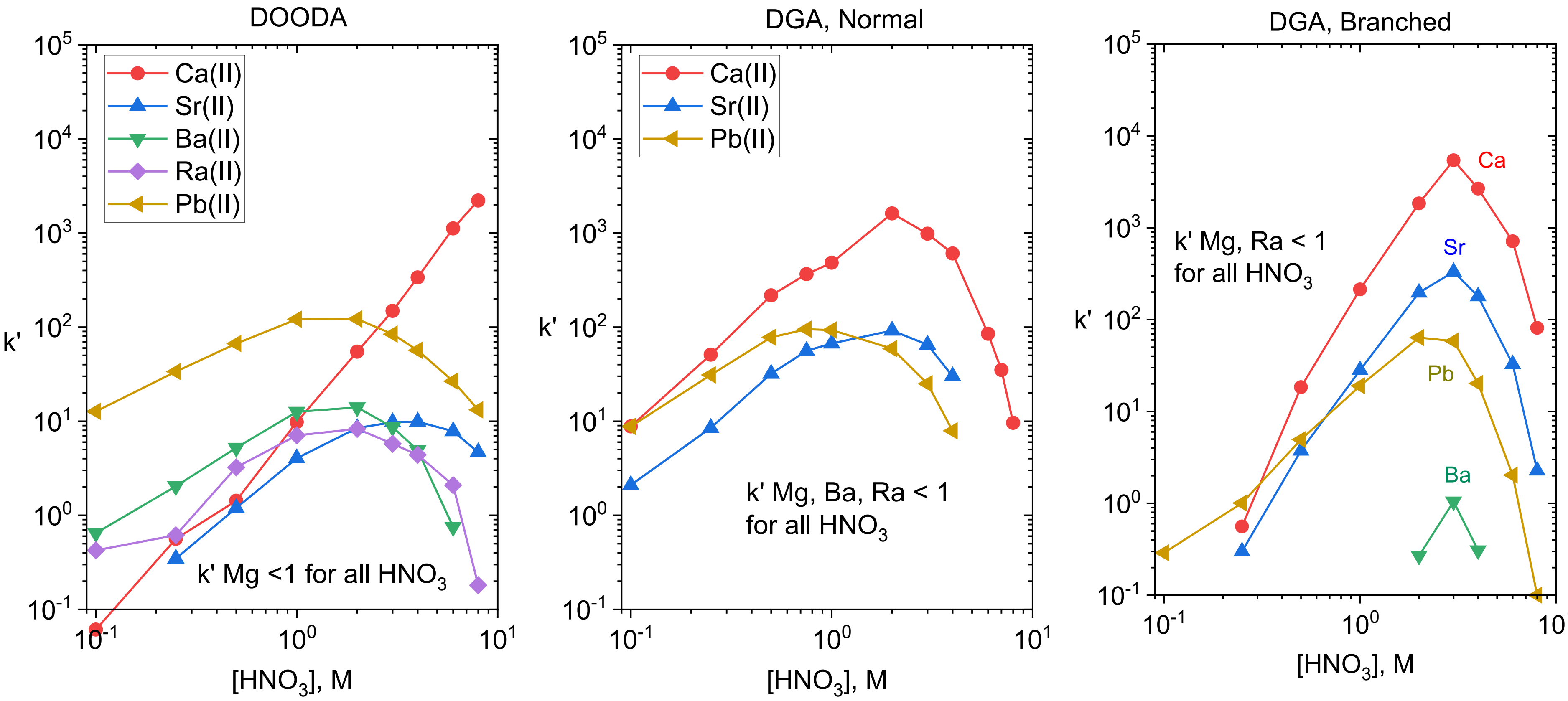
Complexing radiometals to chelators used in nuclear medicine applications.

www.eichrom.com

Half-Way Point

Any Questions???

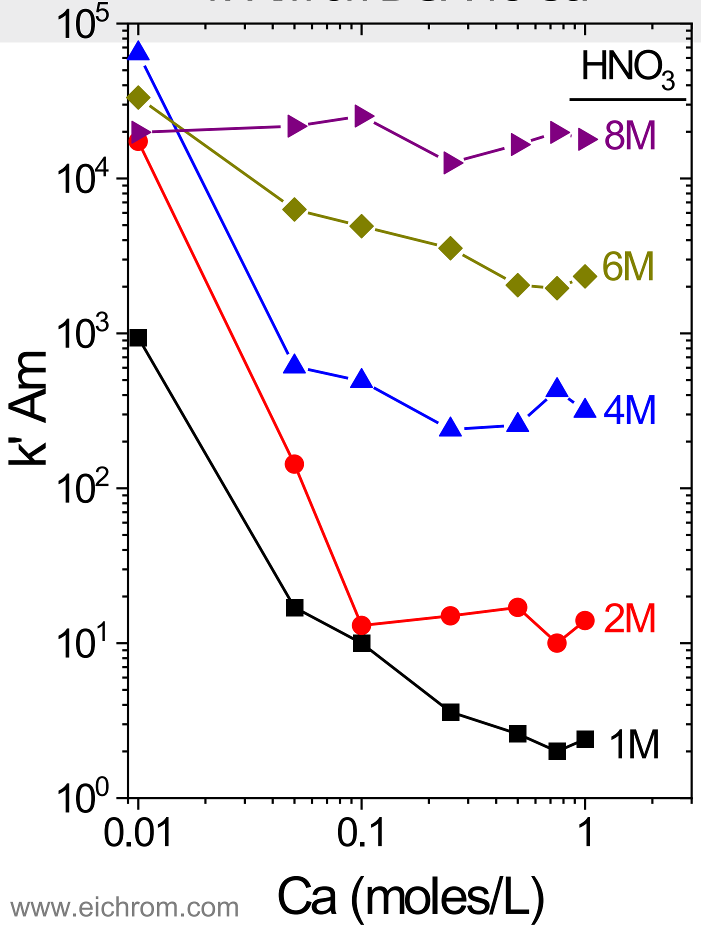
$Metals^{2+}$

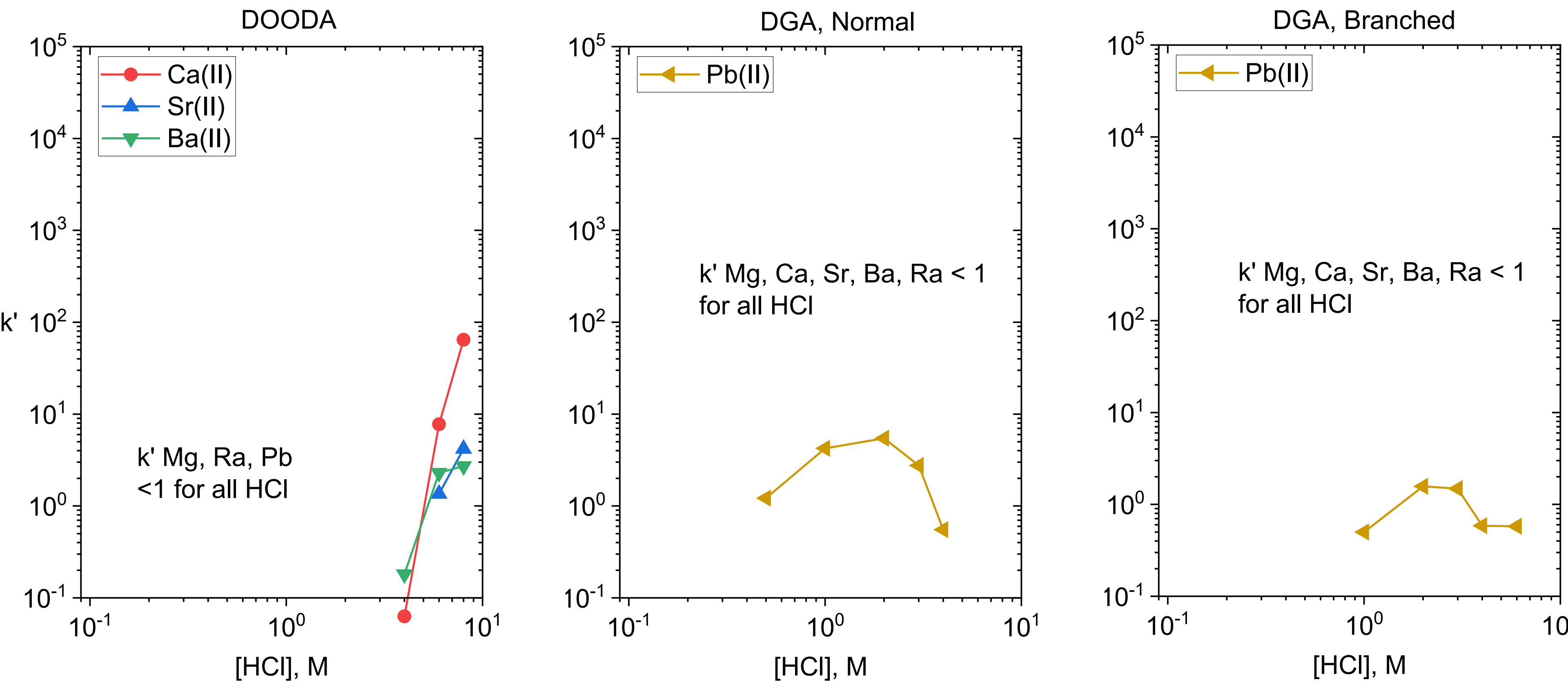


DGA-N, Sr-90 from high K+ samples

Is DGA-B better?

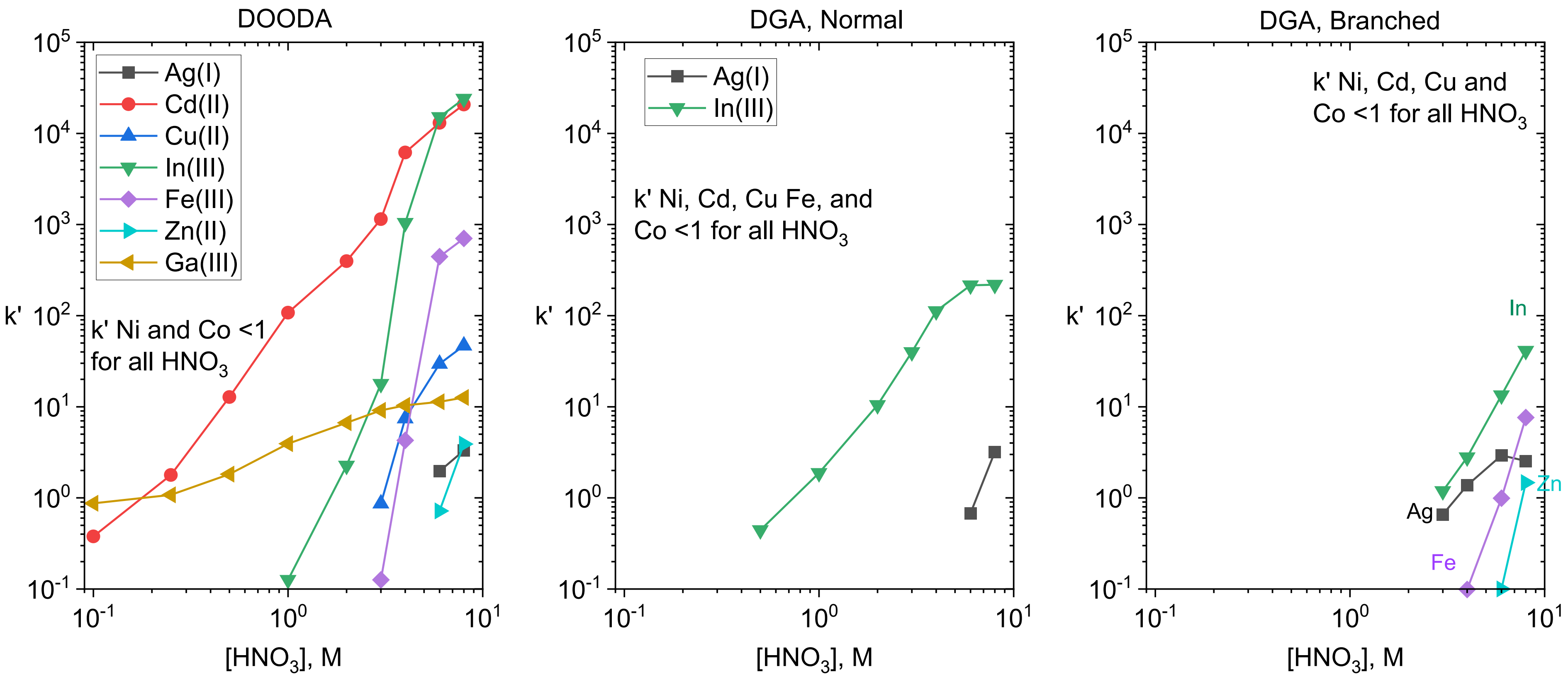
DGA, Normal Resin
k' Am on DGA vs Ca

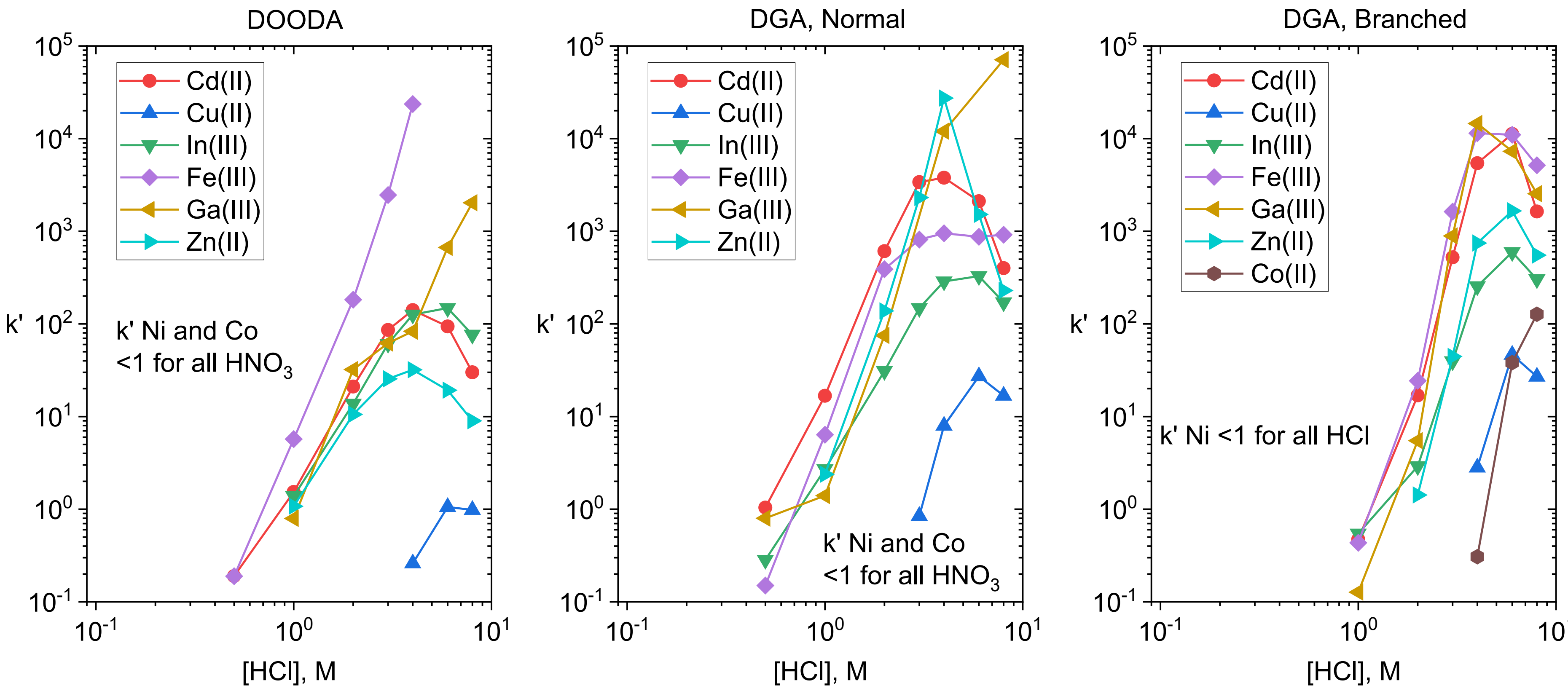



DOODA
Ca(II)
Sr(II)
Ba(II)
k'
k' Mg, Ra, Pb
<1 for all HCl
[HCl], M
DGA, Normal
Pb(II)
k' Mg, Ca, Sr, Ba, Ra < 1
for all HCl
[HCl], M
DGA, Branched
Pb(II)
k' Mg, Ca, Sr, Ba, Ra < 1
for all HCl
[HCl], M

^{111}In

Nuclide	Half Life	Decay	Production
^{111}In	2.8049 d	ε, 100% γ (171.28 keV), 90.61% (245.35 keV), 94.12%	$^{111}Cd(p,n)^{111}In$ $^{112}Cd(p,2n)^{111}In$ $^{nat}Ag(\alpha,xn)^{111}In$

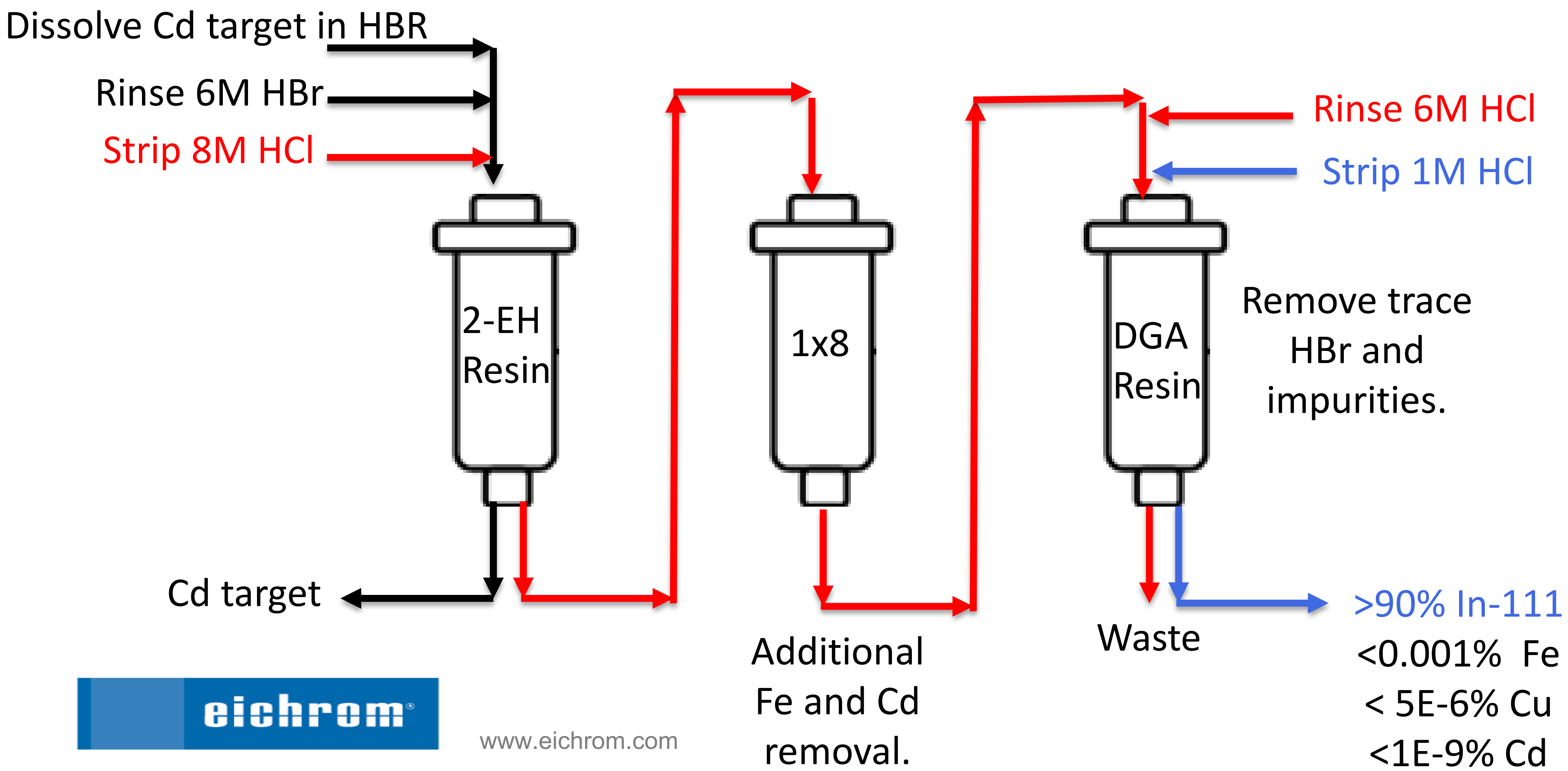

DOODA
Ag(I)
Cd(II)
Cu(II)
In(III)
Fe(III)
Zn(II)
Ga(III)
k' Ni and Co <1 for all HNO_3
k'
[HNO_3], M
DGA, Normal
Ag(I)
In(III)
k' Ni, Cd, Cu Fe, and Co <1 for all HNO_3
k'
[HNO_3], M
DGA, Branched
k' Ni, Cd, Cu and Co <1 for all HNO_3
In
Zn
Ag
Fe
k'
[HNO_3], M



eichrom

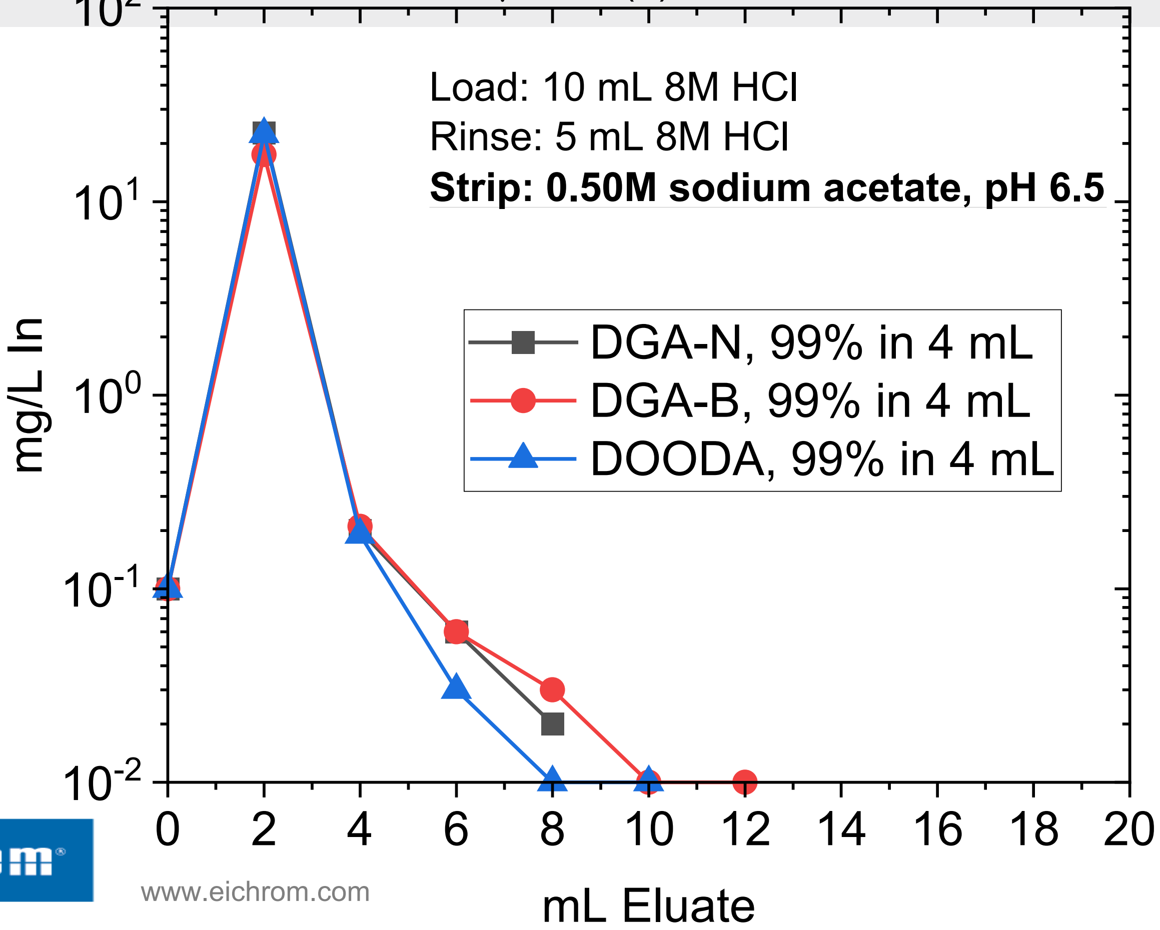
www.eichrom.com

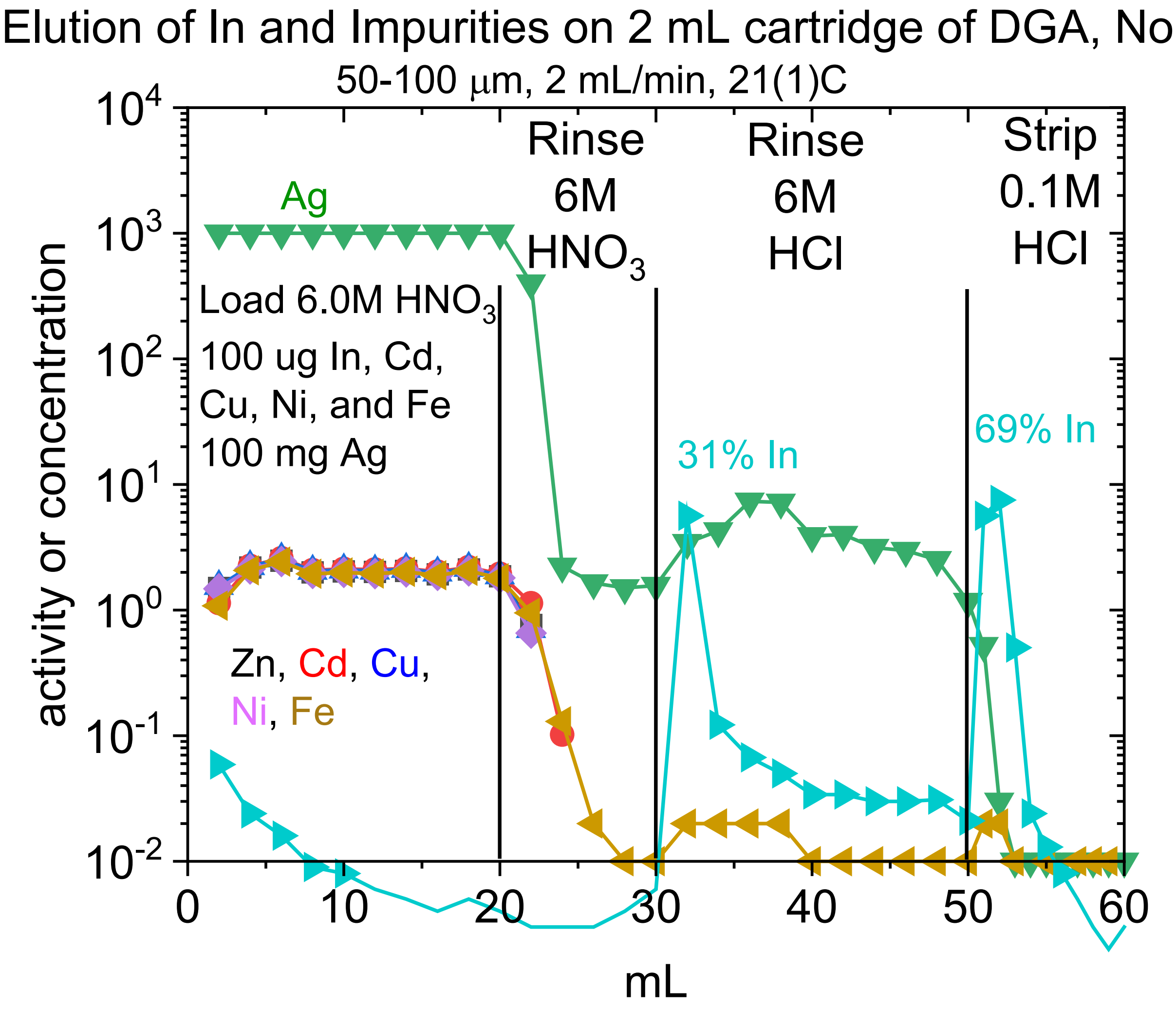
In-111 Separations



Recovery of In from 2 mL cartridge

50-100 μm, 21(1)C, 1-2 mL/min



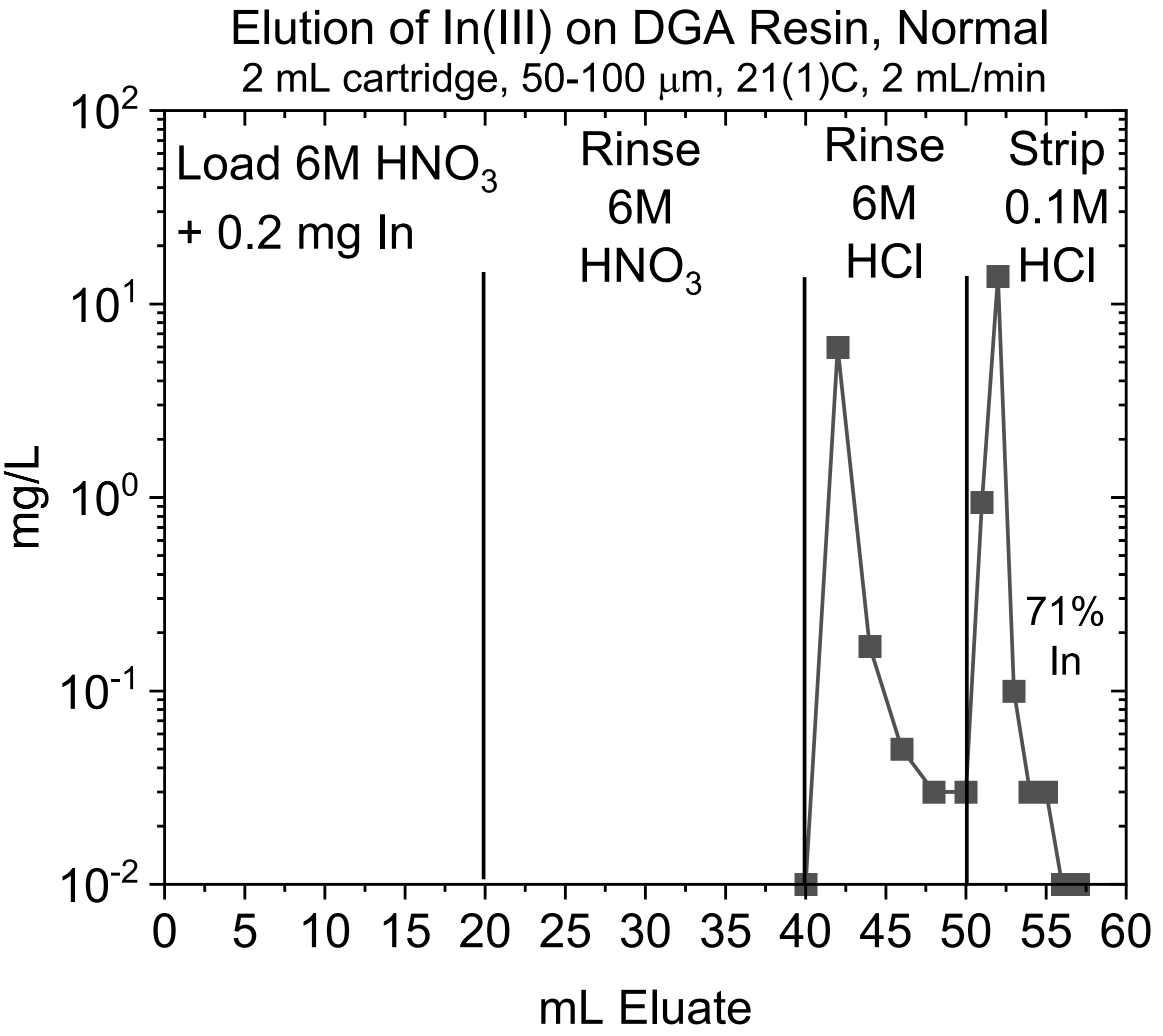


DOODA should work very well.

Preliminary data was promising.

Need to repeat taking care to avoid AgCl ppt, which is very good at clogging AES nebulizers.

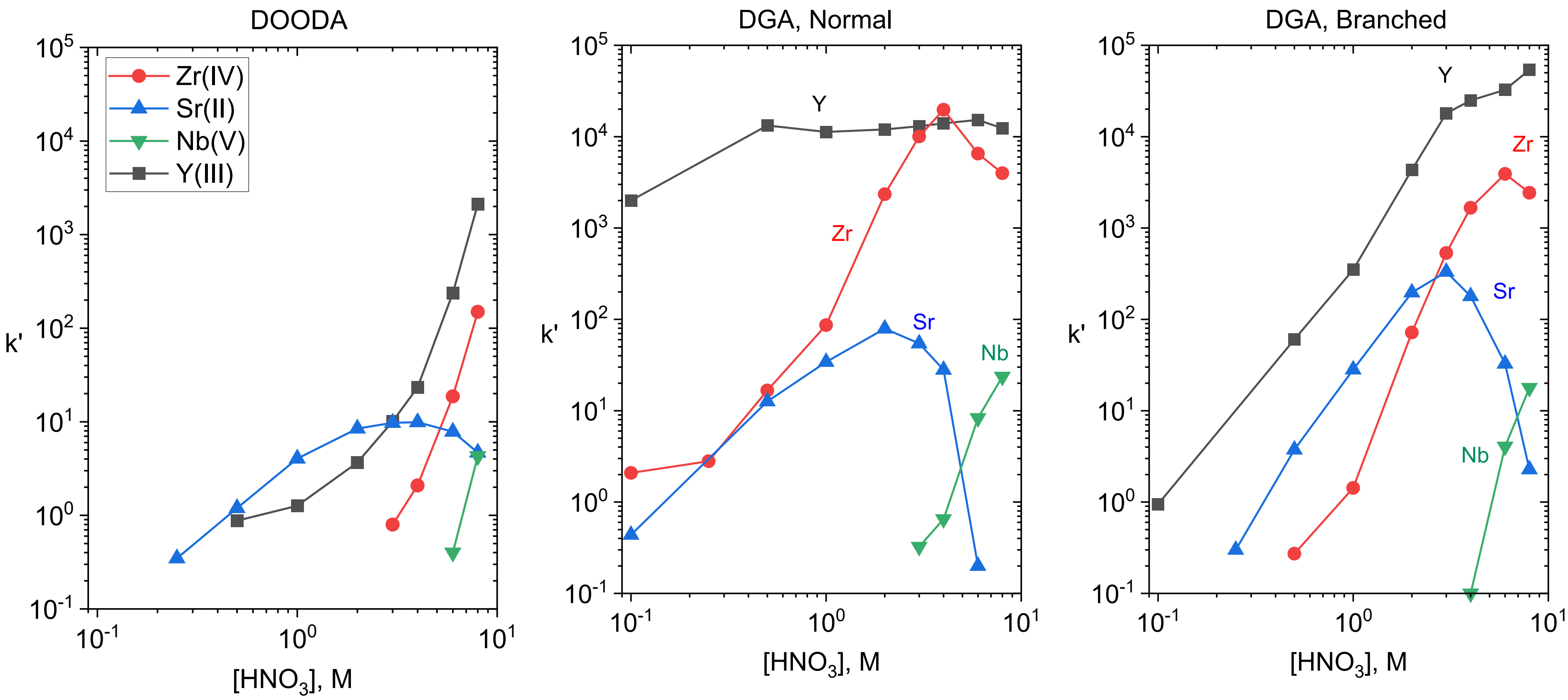
Why is there loss when transitioning from HNO3 to HCl?



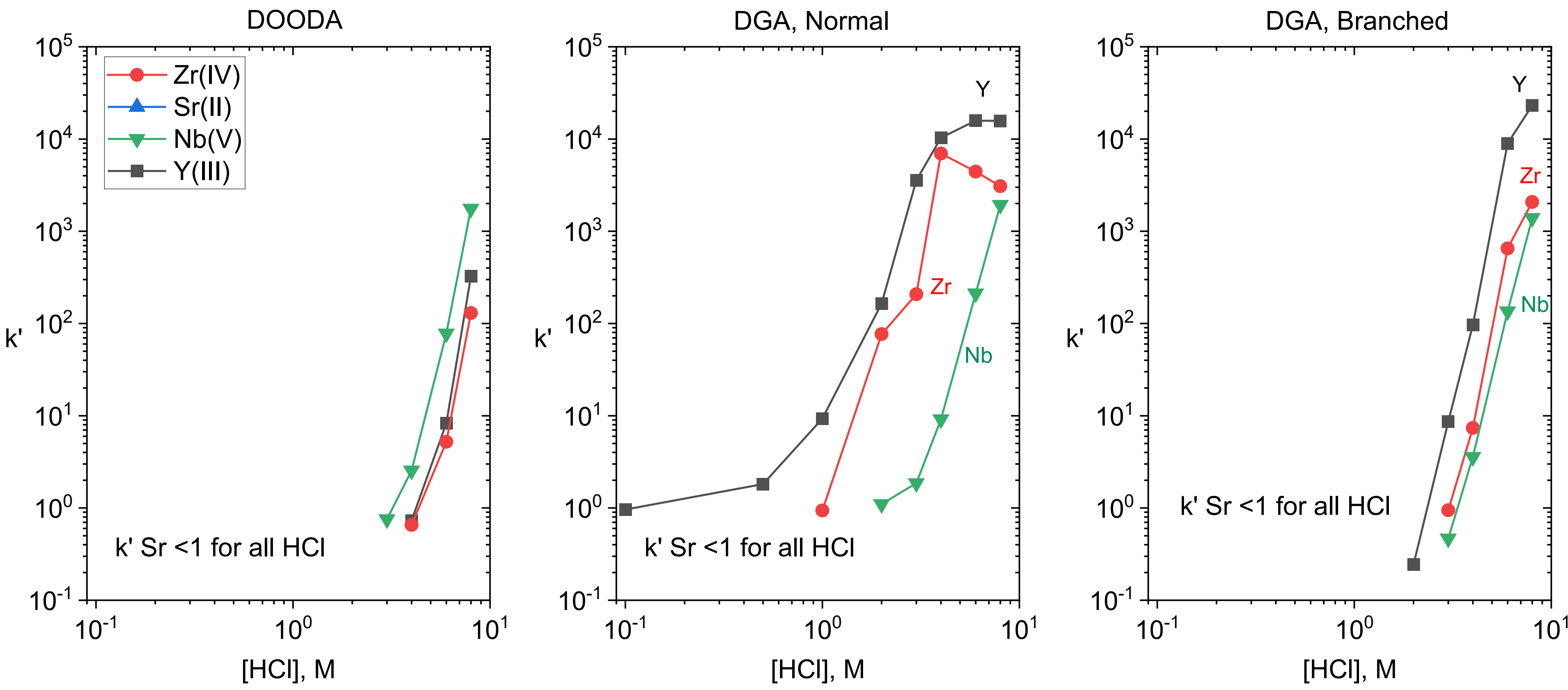
$In(NO_3)_3$ vs $[InCl_4]^-$

Zr-89

Nuclide	Half Life	Decay mode	Photons	Production
^{89}Zr	78.41 h	ε (77%) β^+ (23%) β_{mean} = 397 keV β_{max} = 897 keV	208 keV (10.4%) 113 keV (6.2%)	$^{89}Y(p,n)^{89}Zr$



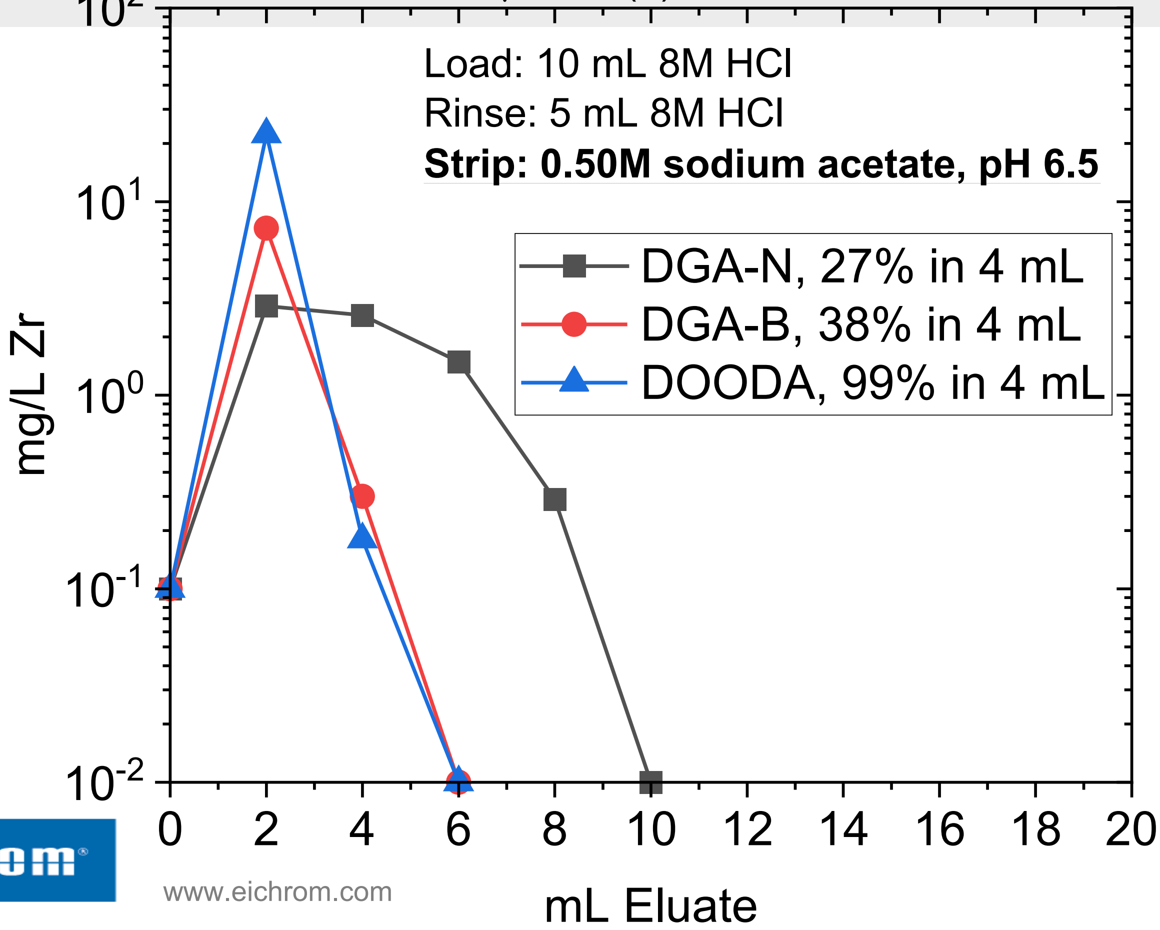
www.eichrom.com



www.eichrom.com

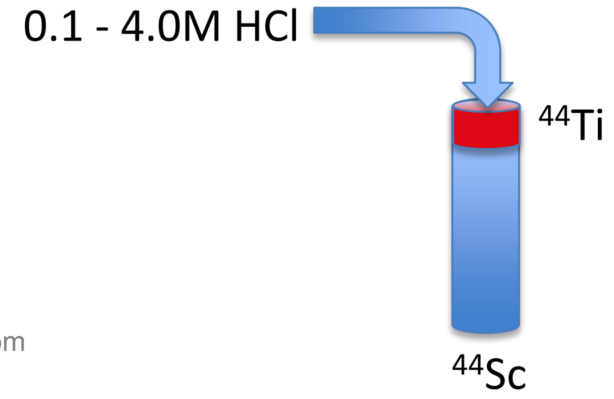
Recovery of Zr from 2 mL cartridge

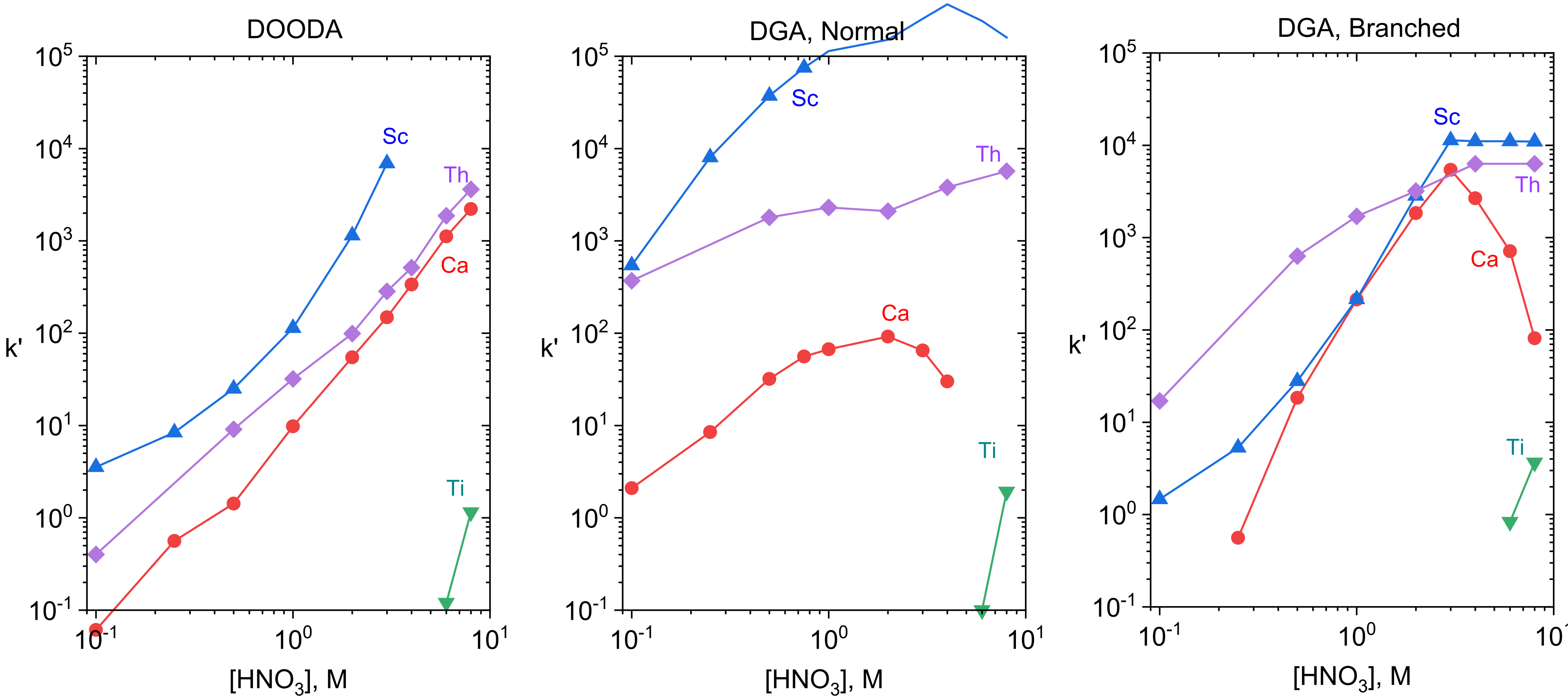
50-100 μm, 21(1)C, 1-2 mL/min

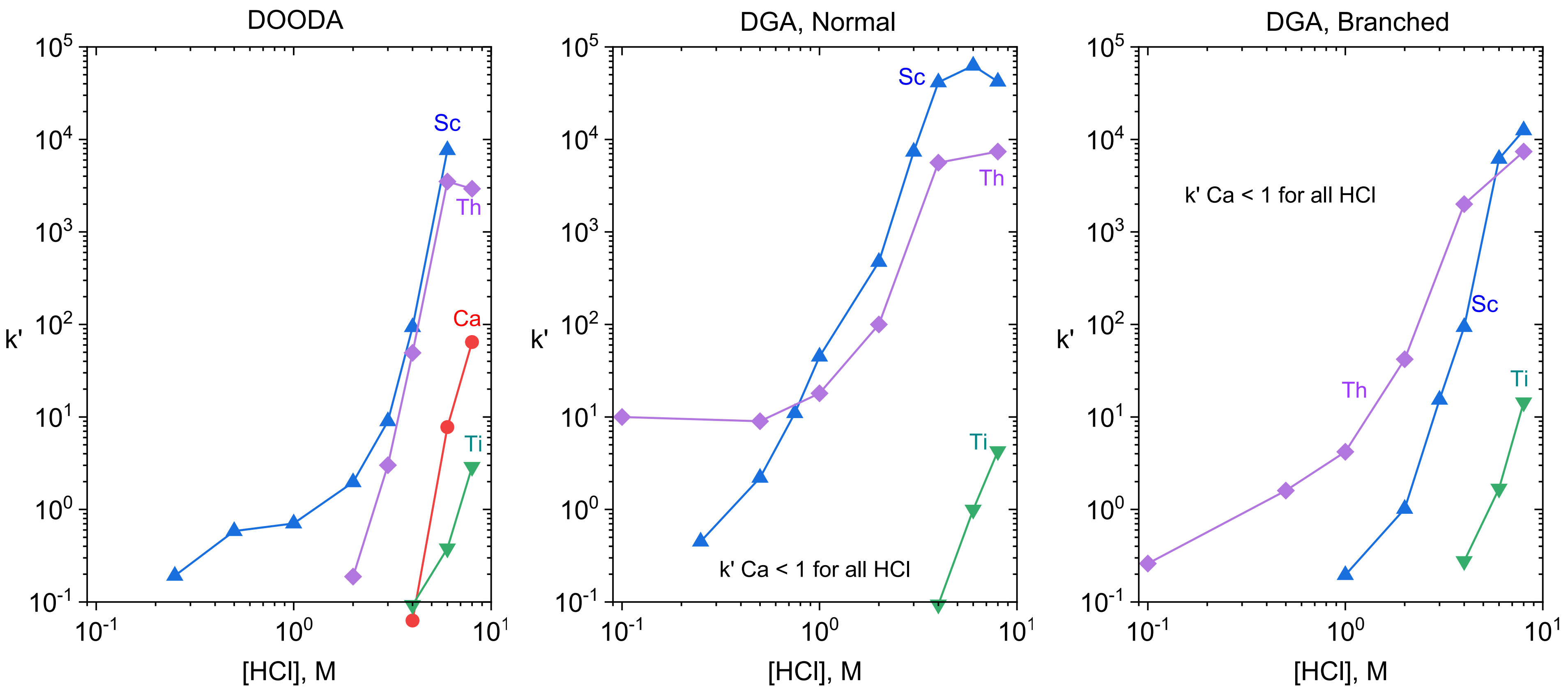


Sc-44

Nuclide	Half Life	Decay	Production
^{44}Sc	3.97 h	β^+ (1.474 MeV), 94.27% ε, 5.73% γ (1.157 MeV), 99.882% (1.499 MeV), 0.908%	$^{44}Ca(p,n)^{44}Sc$ Decay of ^{44}Ti
^{44}Ti	60.0 y	ε, 100%	$^{45}Sc(p, 2n)^{44}Ti$ ^{45}Sc (d, 3n)^{44}Ti

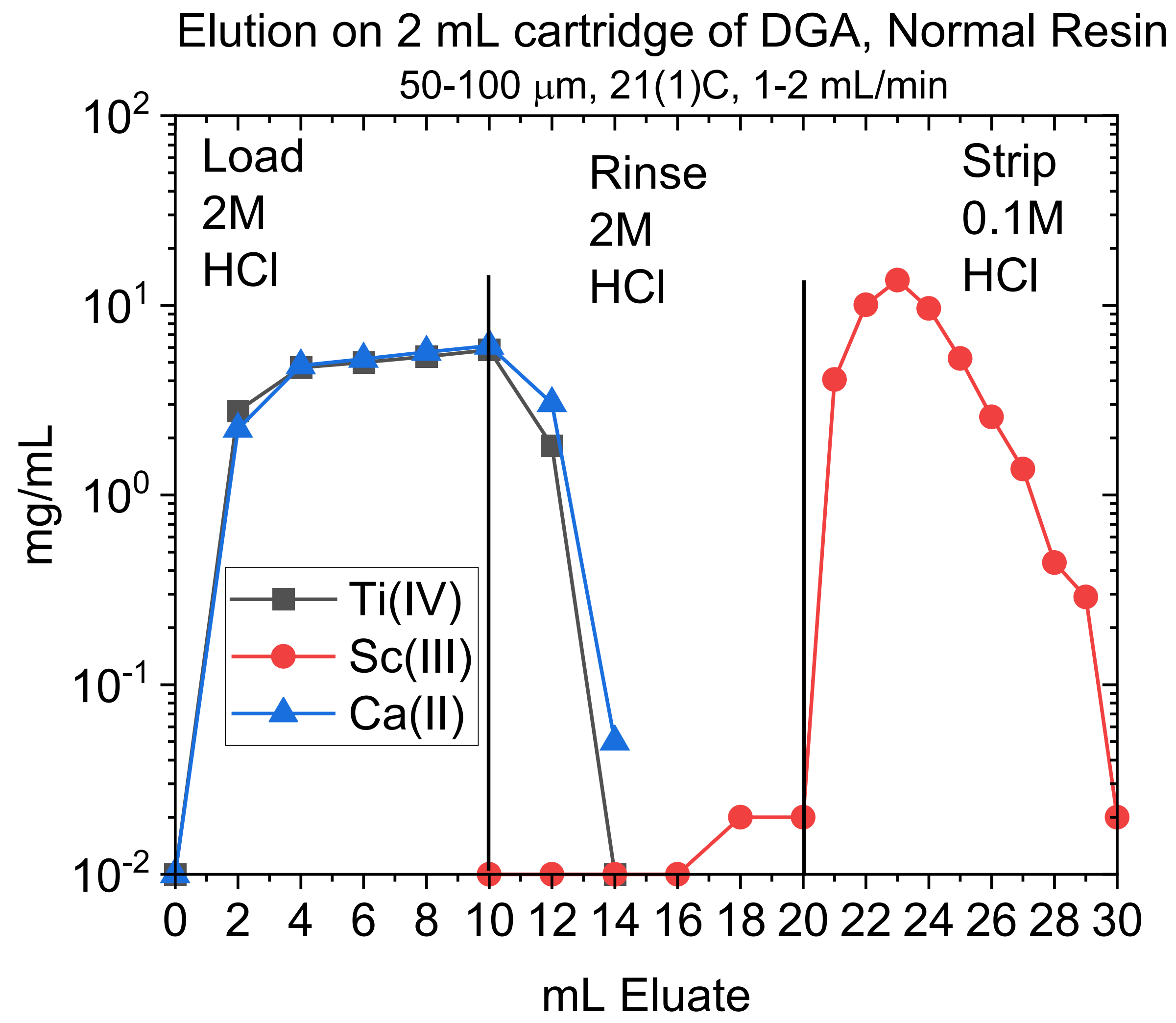



DOODA
DGA, Normal
DGA, Branched
k'
[HNO$_3$], M
Sc
Th
Ca
Ti
10^{-1}
10^0
10^1
10^2
10^3
10^4
10^5

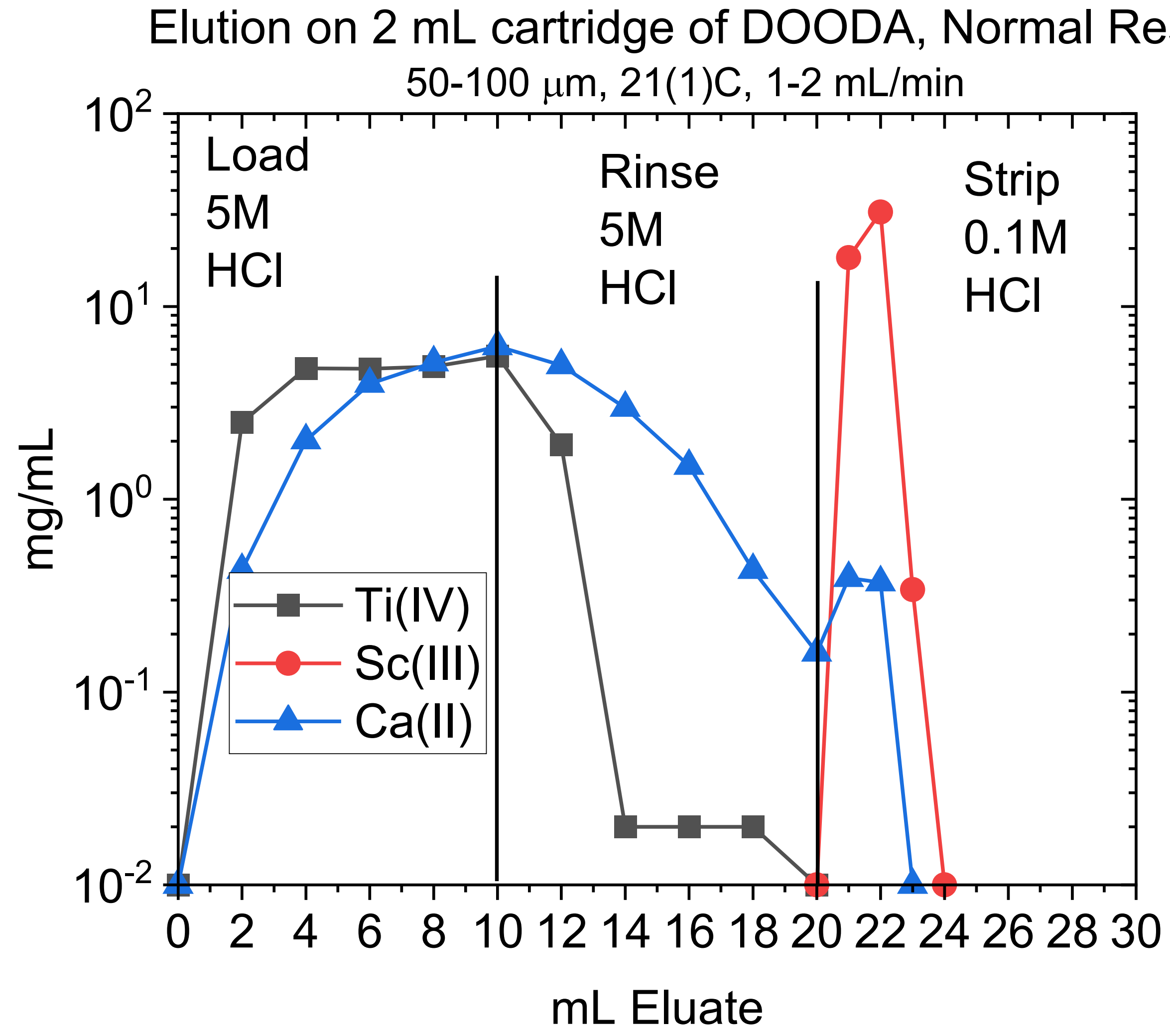


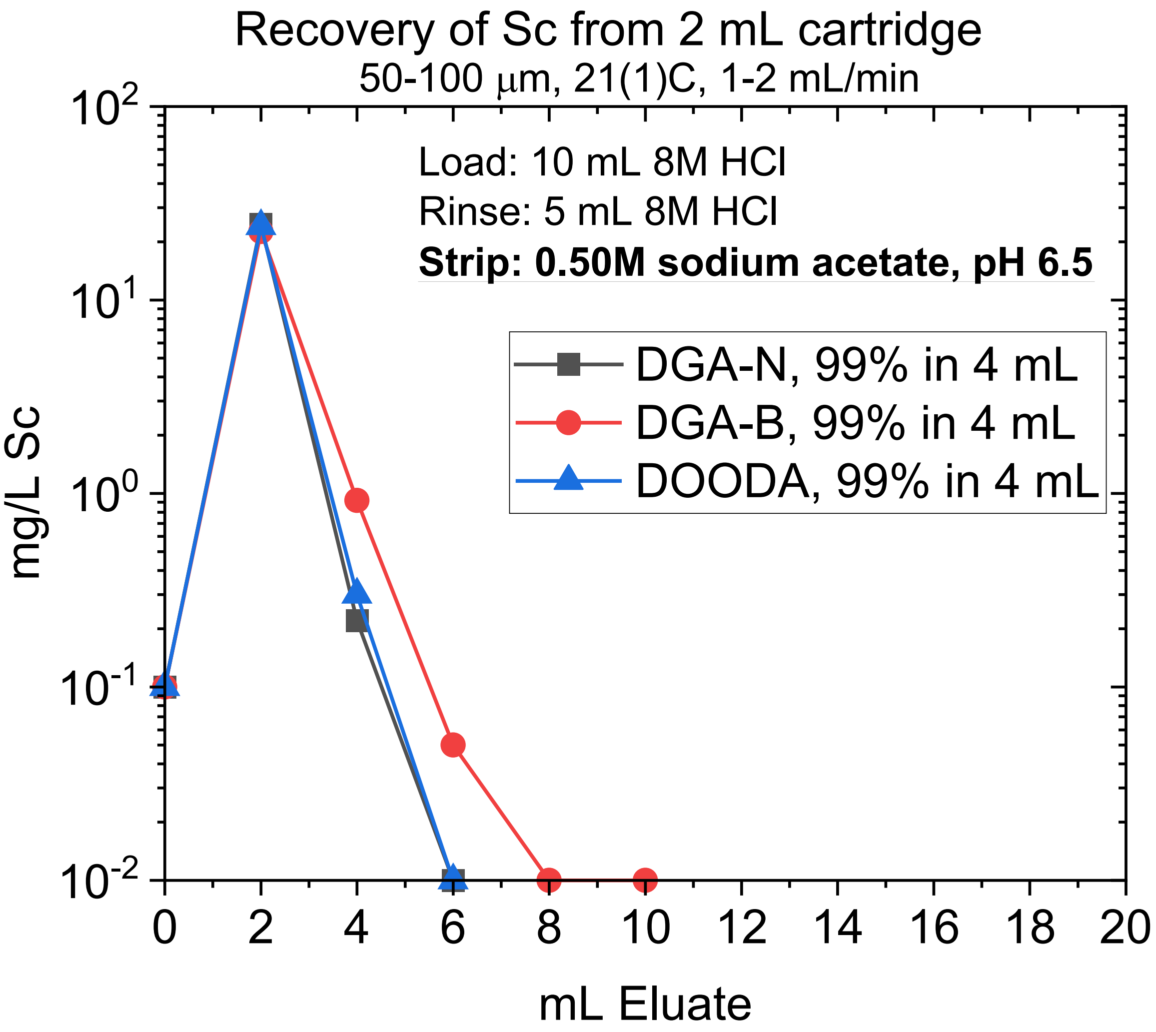
eichrom

www.eichrom.com



Elution on 2 mL cartridge of DGA, Normal Resin
50-100 μm, 21(1)C, 1-2 mL/min
Load
2M
HCl
Rinse
2M
HCl
Strip
0.1M
HCl
Ti(IV)
Sc(III)
Ca(II)
mg/mL
mL Eluate

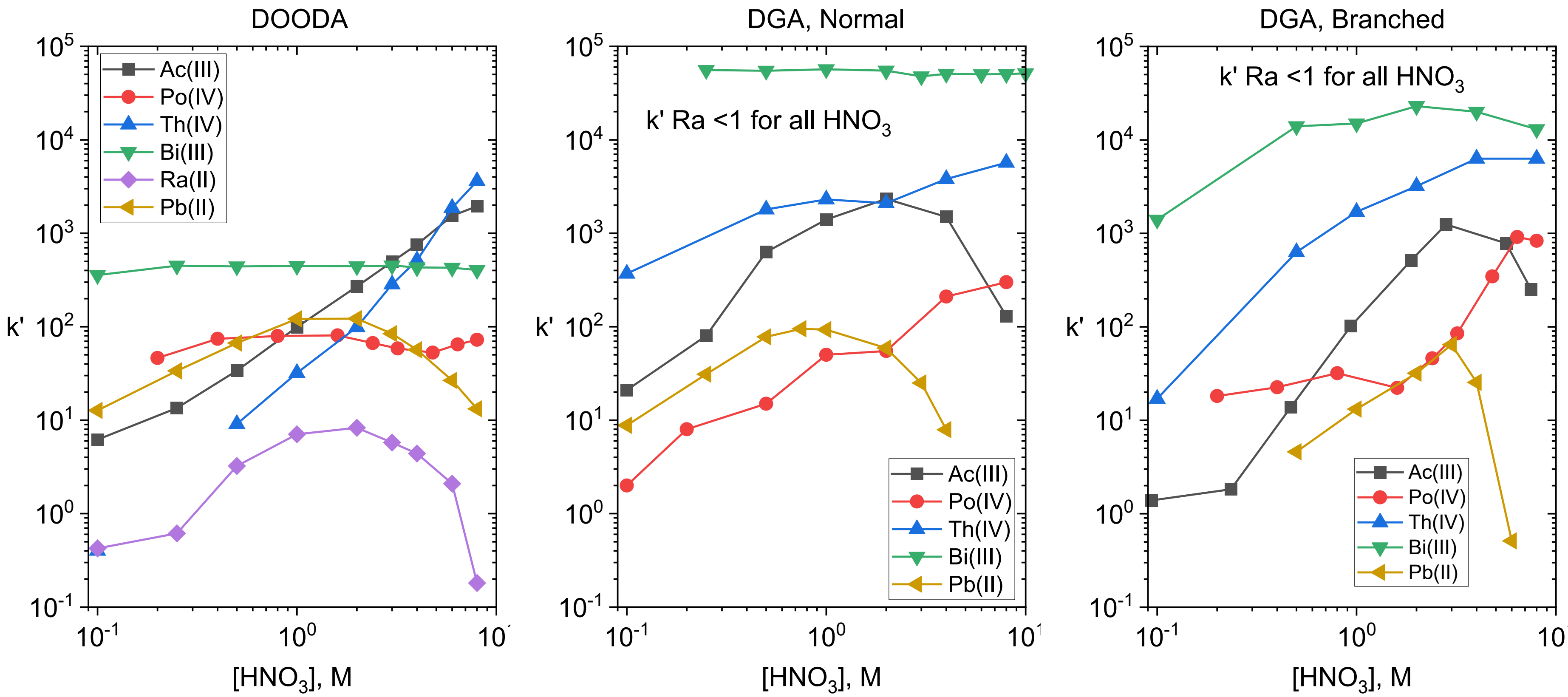

Elution on 2 mL cartridge of DOODA, Normal Resin
50-100 μm, 21(1)C, 1-2 mL/min
Load
5M
HCl
Rinse
5M
HCl
Strip
0.1M
HCl
Ti(IV)
Sc(III)
Ca(II)
mg/mL
mL Eluate
10^2
10^1
10^0
10^-1
10^-2
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30



Recovery of Sc from 2 mL cartridge
50-100 μm, 21(1)C, 1-2 mL/min
Load: 10 mL 8M HCl
Rinse: 5 mL 8M HCl
Strip: 0.50M sodium acetate, pH 6.5
DGA-N, 99% in 4 mL
DGA-B, 99% in 4 mL
DOODA, 99% in 4 mL
mg/L Sc
mL Eluate
10^2
10^1
10^0
10^-1
10^-2
0
2
4
6
8
10
12
14
16
18
20

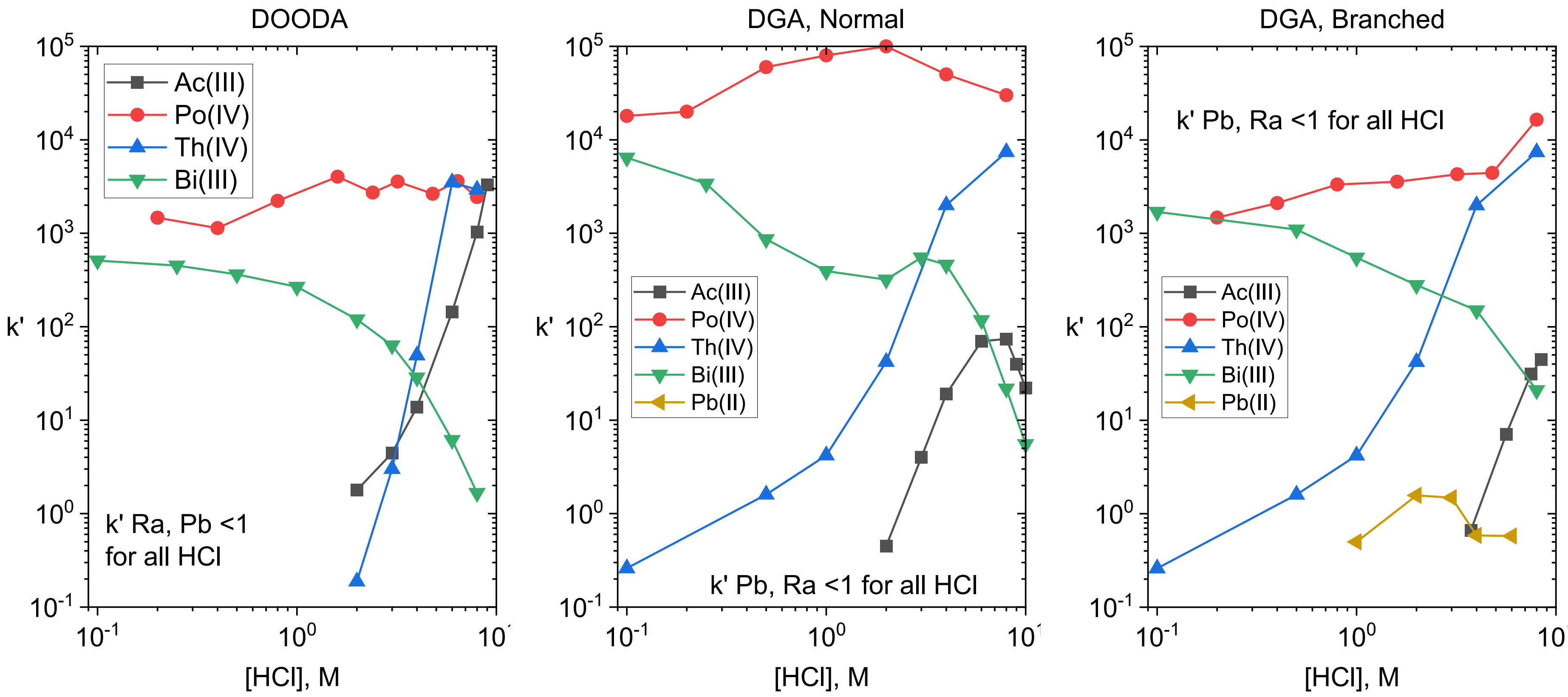
Ac-225

Nuclide	Half Life	Decay	Production
^{233}U	1.592 E5 y	α (4.5 – 4.8 MeV)	Thermal Breeder Reactors: $^{1}n + ^{232}Th \rightarrow ^{233}Th \rightarrow ^{233}Pa \rightarrow ^{233}U$
^{229}Th	7932 y	α (4.5 – 5.1 MeV)	Decay ^{233}U
^{225}Ac	10 d	α (5.0 – 5.8 MeV)	Decay ^{229}Th Proton Spallation ^{232}Th $^{226}Ra(p,2n)^{225}Ac$
^{225}Ra	14.9 d	β^- (356 keV)	Decay ^{229}Th Proton Spallation ^{232}Th
^{213}Bi	45.6 m	α (5.6 – 5.9 MeV), 2.2% β^- (1423 keV), 97.8%	Decay ^{225}Ac
^{227}Ac	21.77 y	α (4.4 – 5.0 MeV), 1.38%	Decay ^{235}U
		β^- (44.8 keV), 98.62%	Proton Spallation ^{232}Th



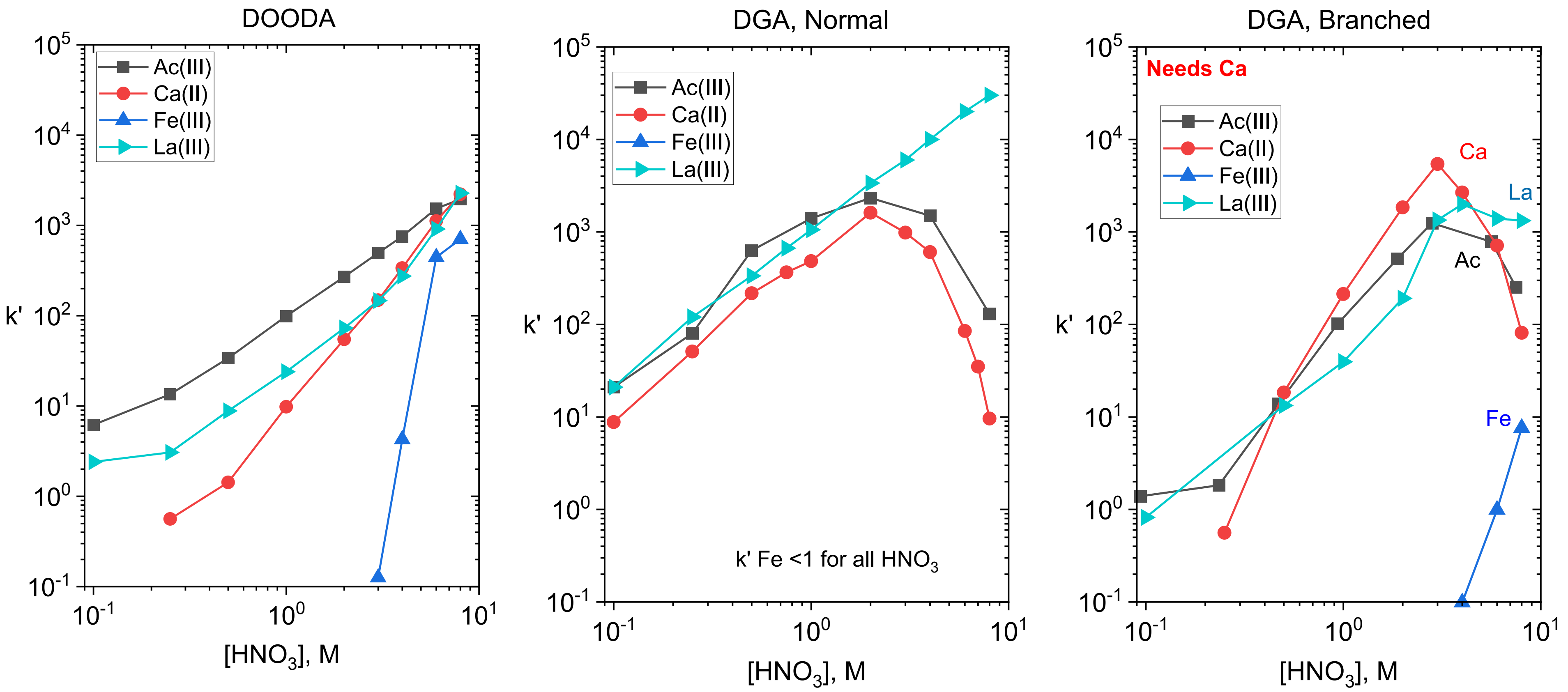
eichrom

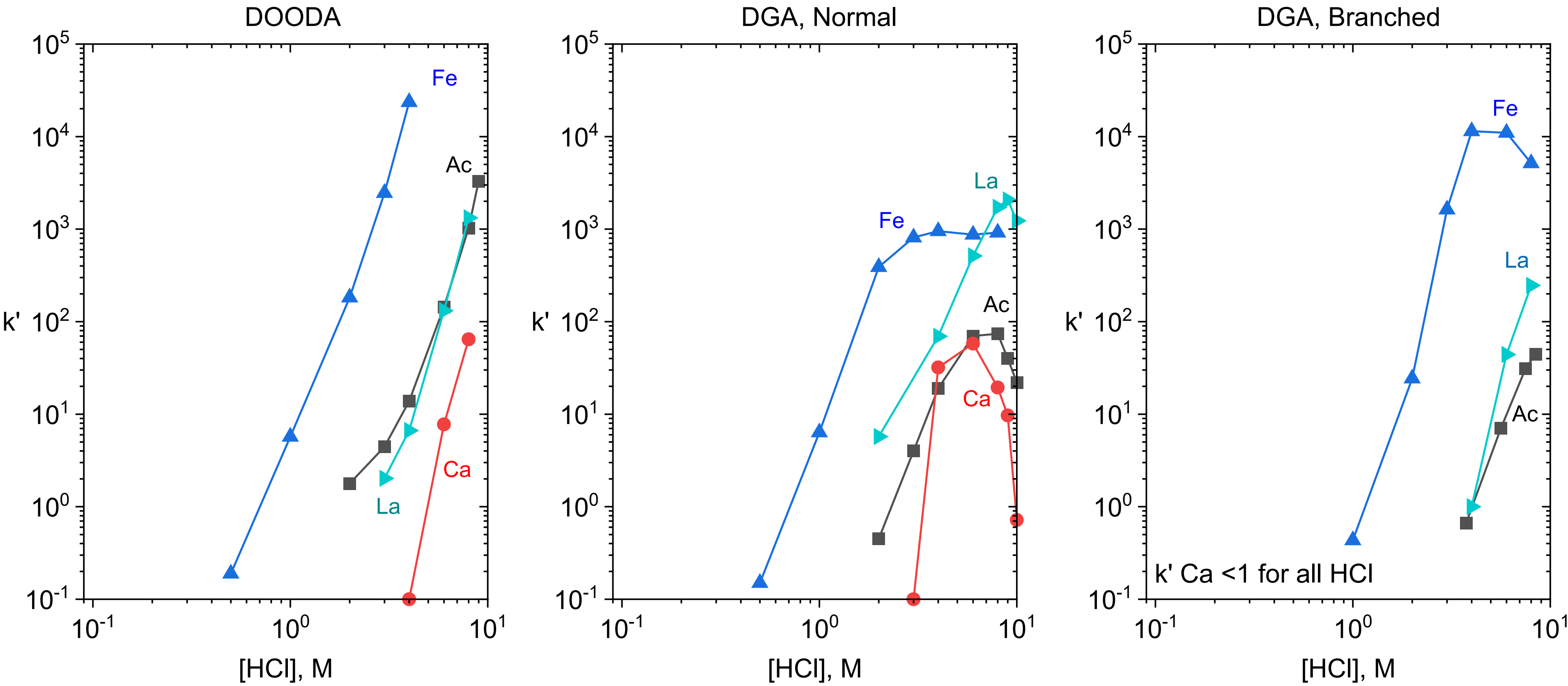
www.eichrom.com

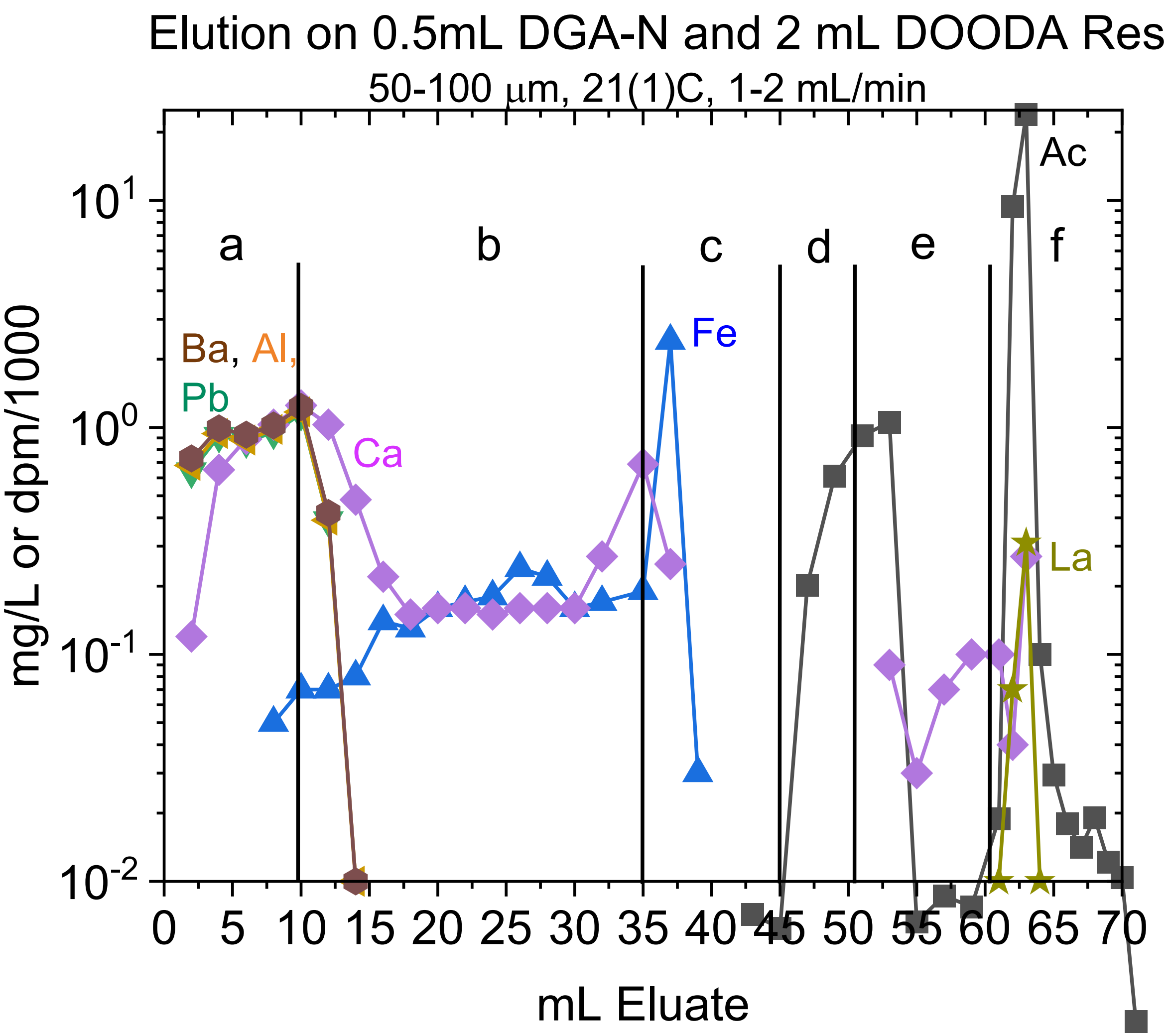


eichrom

www.eichrom.com


DOODA
DGA, Normal
DGA, Branched
Ac(III)
Ca(II)
Fe(III)
La(III)
k'
[HNO3], M
k' Fe <1 for all HNO3
Needs Ca
Ca
La
Ac
Fe


DOODA
DGA, Normal
DGA, Branched
Fe
Ac
La
Ca
k'
[HCl], M
k' Ca <1 for all HCl



a: Load 10 mL 10M HNO3

b: 25 mL 10M HNO3

(remove DGA) [Th, La, Bi, Po]

c: 10 mL 4M HNO3

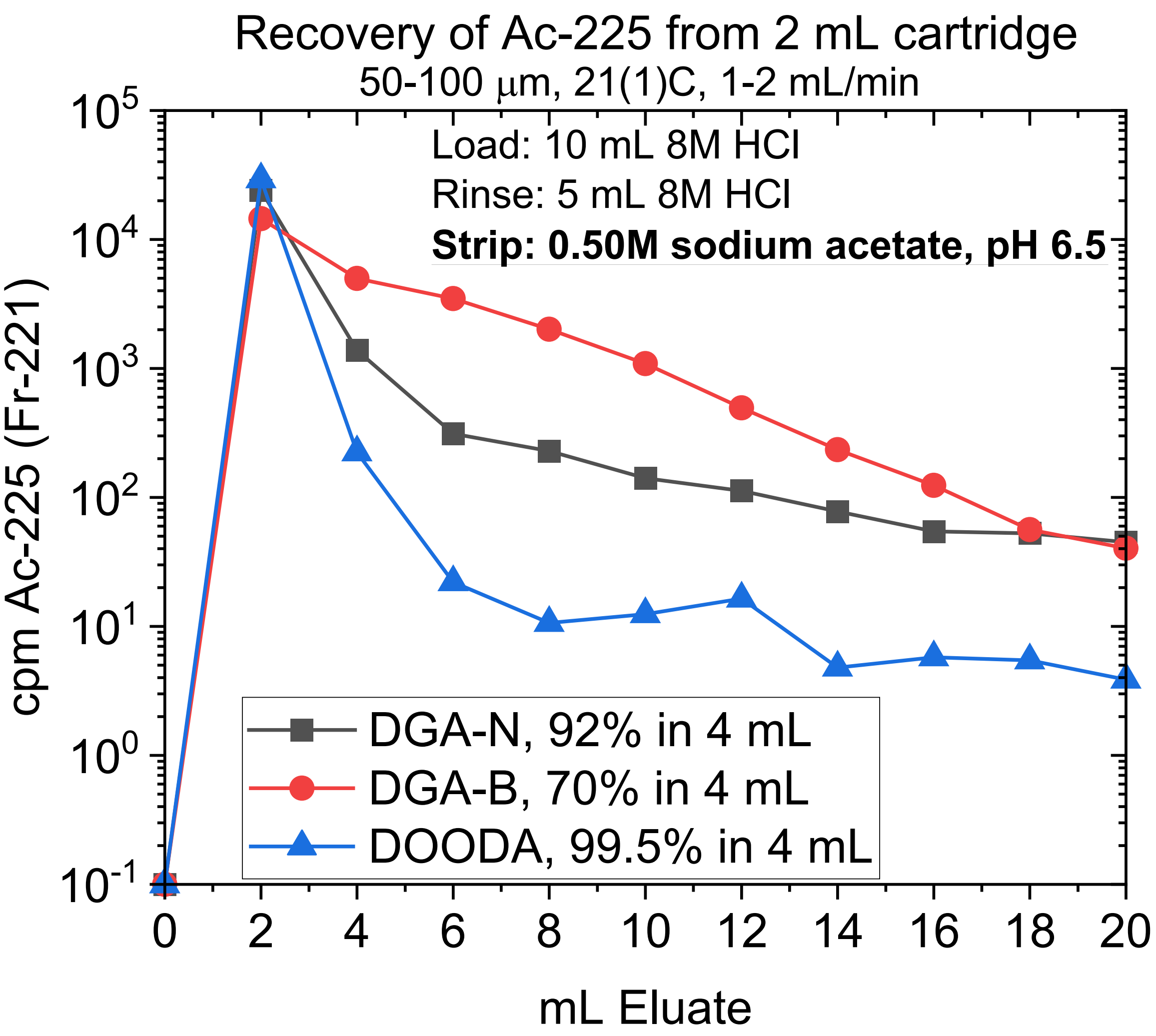
d: 6 mL 0.5M HNO3 (7.5% Ac)

e: 10 mL 8M HCl

f: 10 mL 0.1M HCl

90% Ac-225

<<1% La, Th, Bi, Po

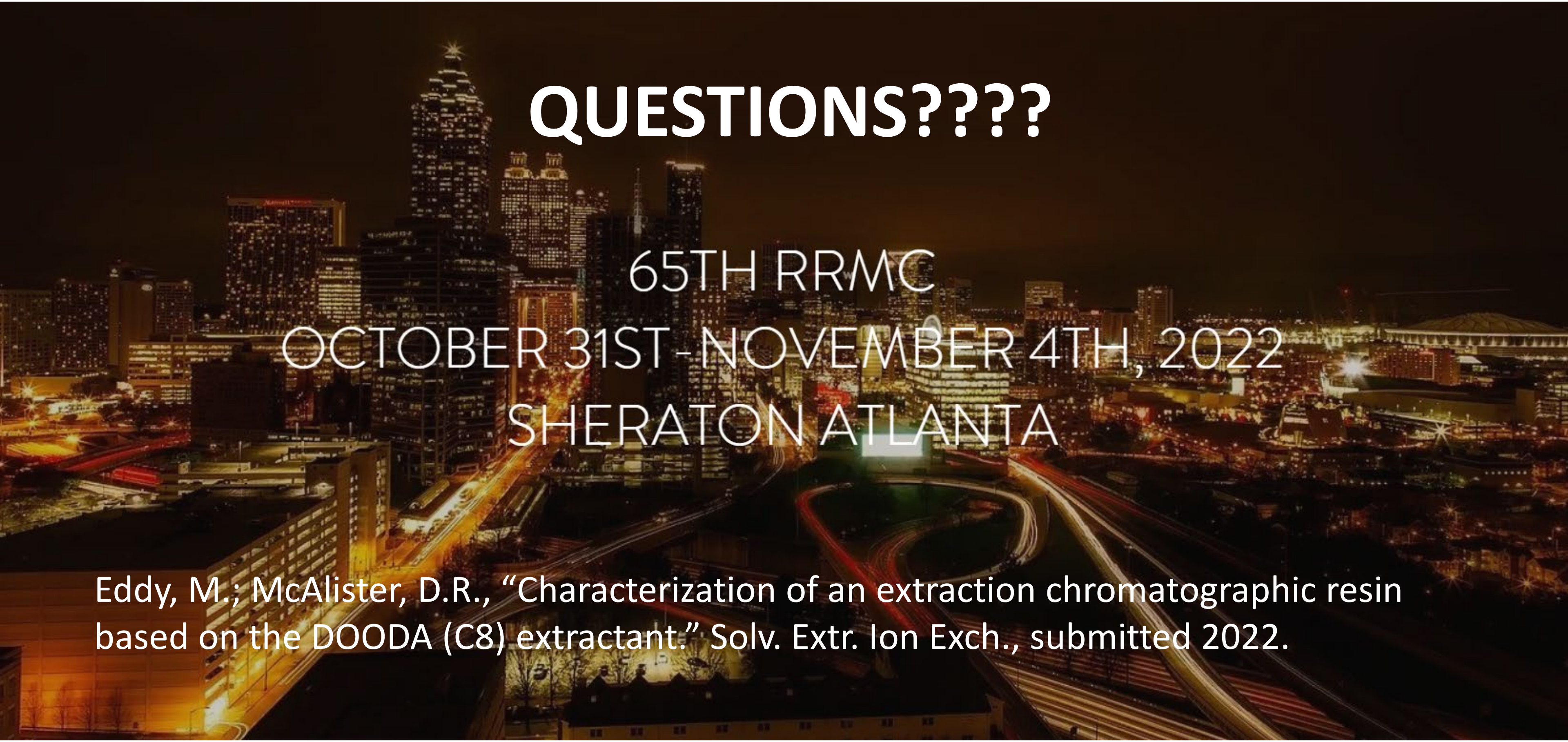


Recovery of Ac-225 from 2 mL cartridge
50-100 μm, 21(1)C, 1-2 mL/min
Load: 10 mL 8M HCl
Rinse: 5 mL 8M HCl
Strip: 0.50M sodium acetate, pH 6.5
DGA-N, 92% in 4 mL
DGA-B, 70% in 4 mL
DOODA, 99.5% in 4 mL
cpm Ac-225 (Fr-221)
mL Eluate

Future Work

- Continue to evaluate data and applications
- Finish writing/publish paper on DOODA EXC resin
- Scale up and optimize synthesis
- More Data available in appendix

Small samples are available



QUESTIONS????

65TH RRMC

OCTOBER 31ST - NOVEMBER 4TH, 2022

SHERATON ATLANTA

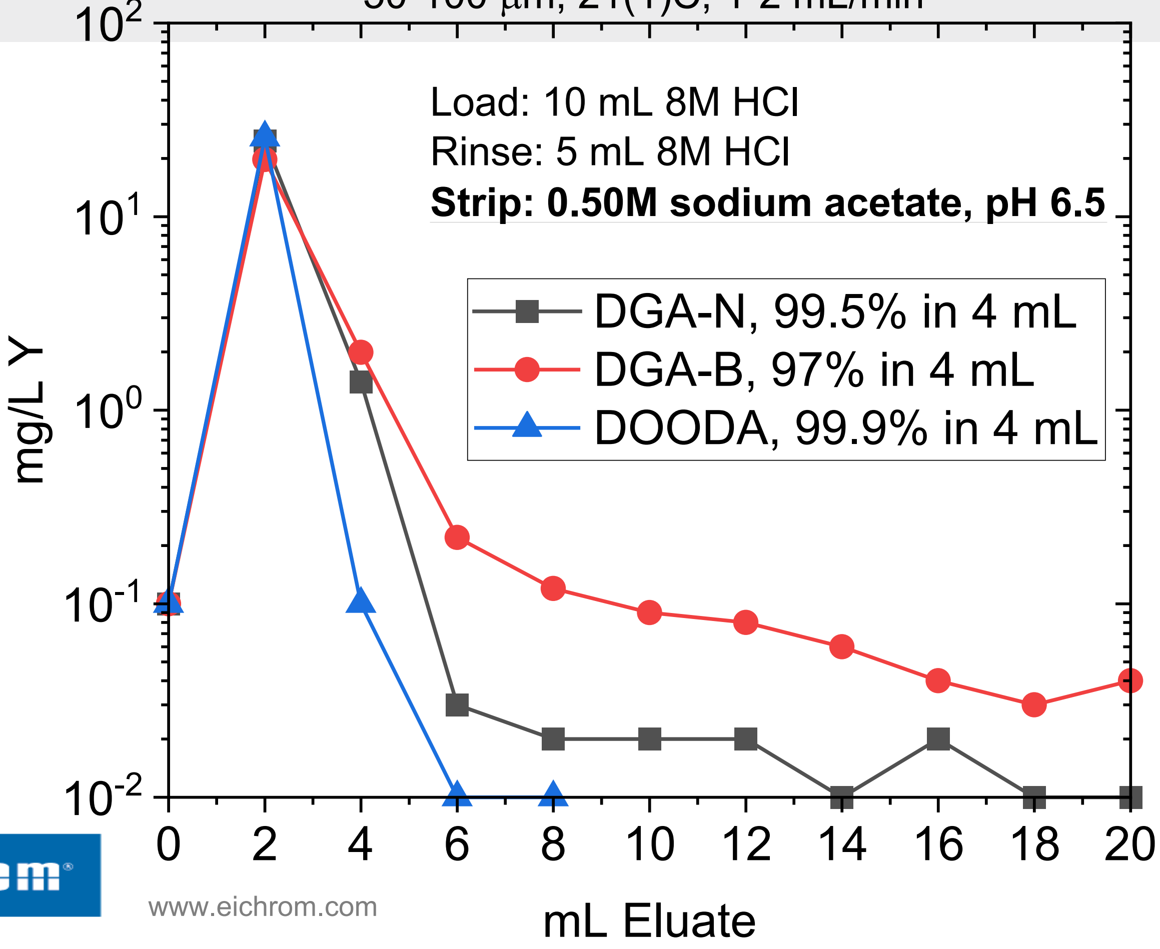
Eddy, M.; McAlister, D.R., “Characterization of an extraction chromatographic resin based on the DOODA (C8) extractant.” Solv. Extr. Ion Exch., submitted 2022.

Appendix

Additional Data

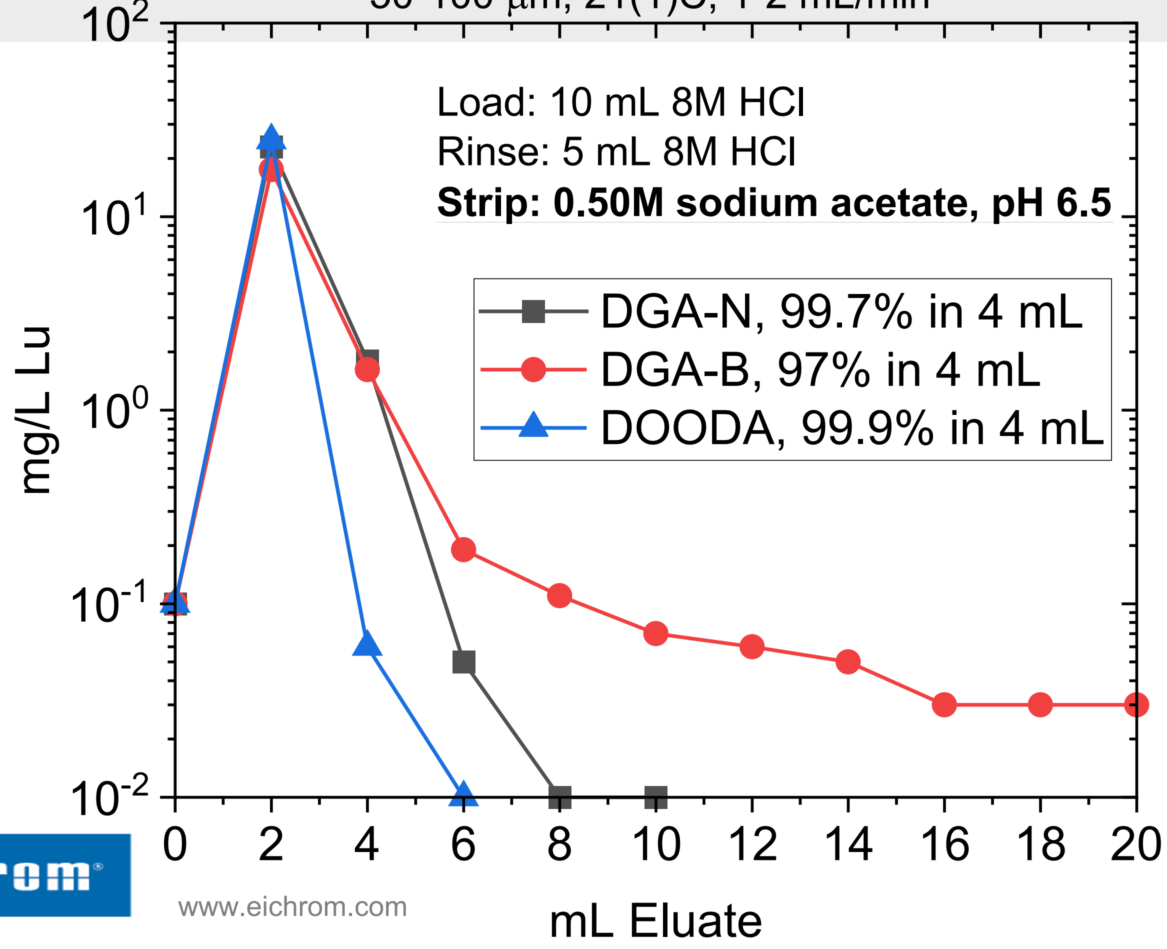
Recovery of Tb from 2 mL cartridge

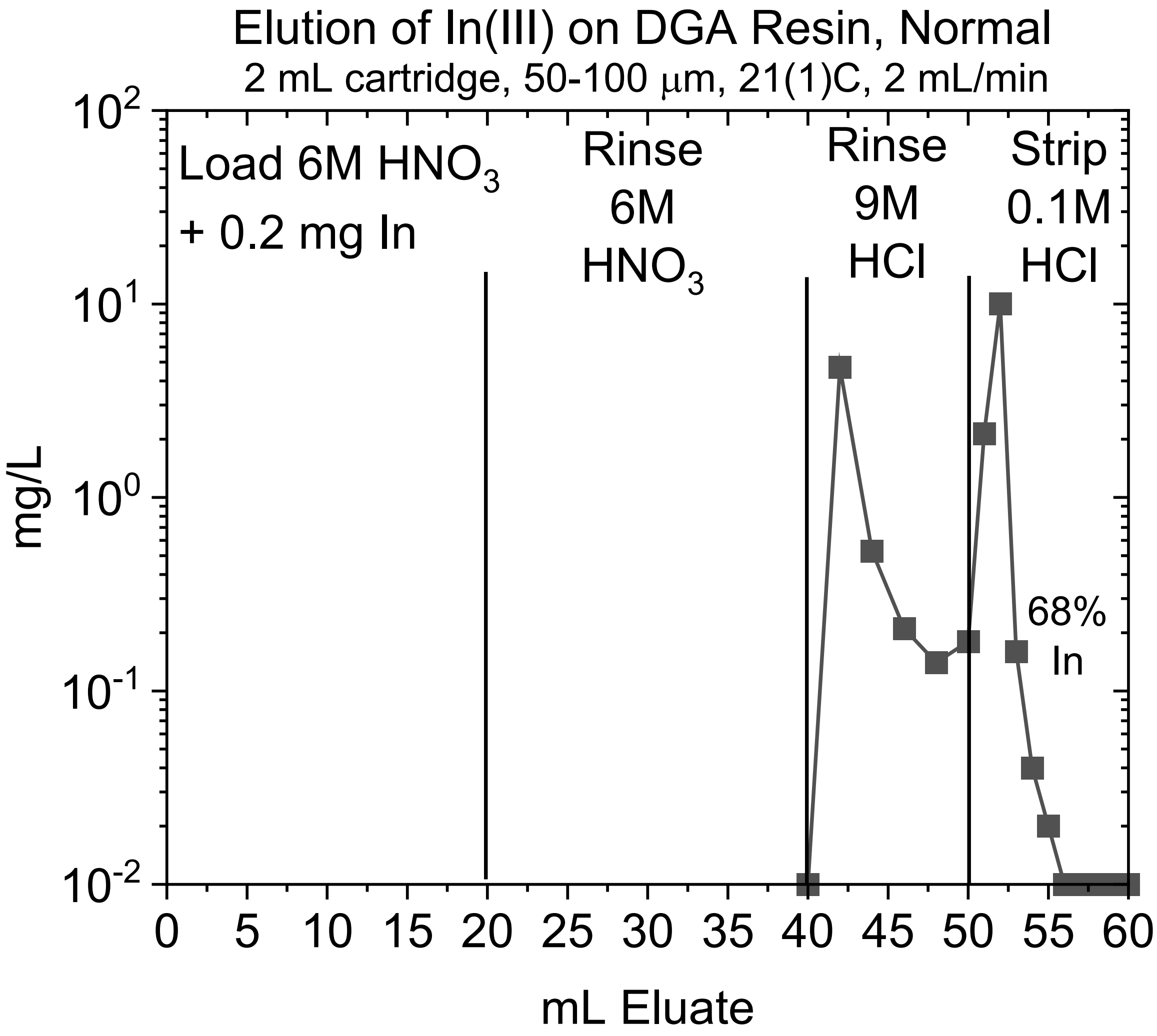
50-100 µm, 21(1)C, 1-2 mL/min



Recovery of Lu from 2 mL cartridge

50-100 μm, 21(1)C, 1-2 mL/min



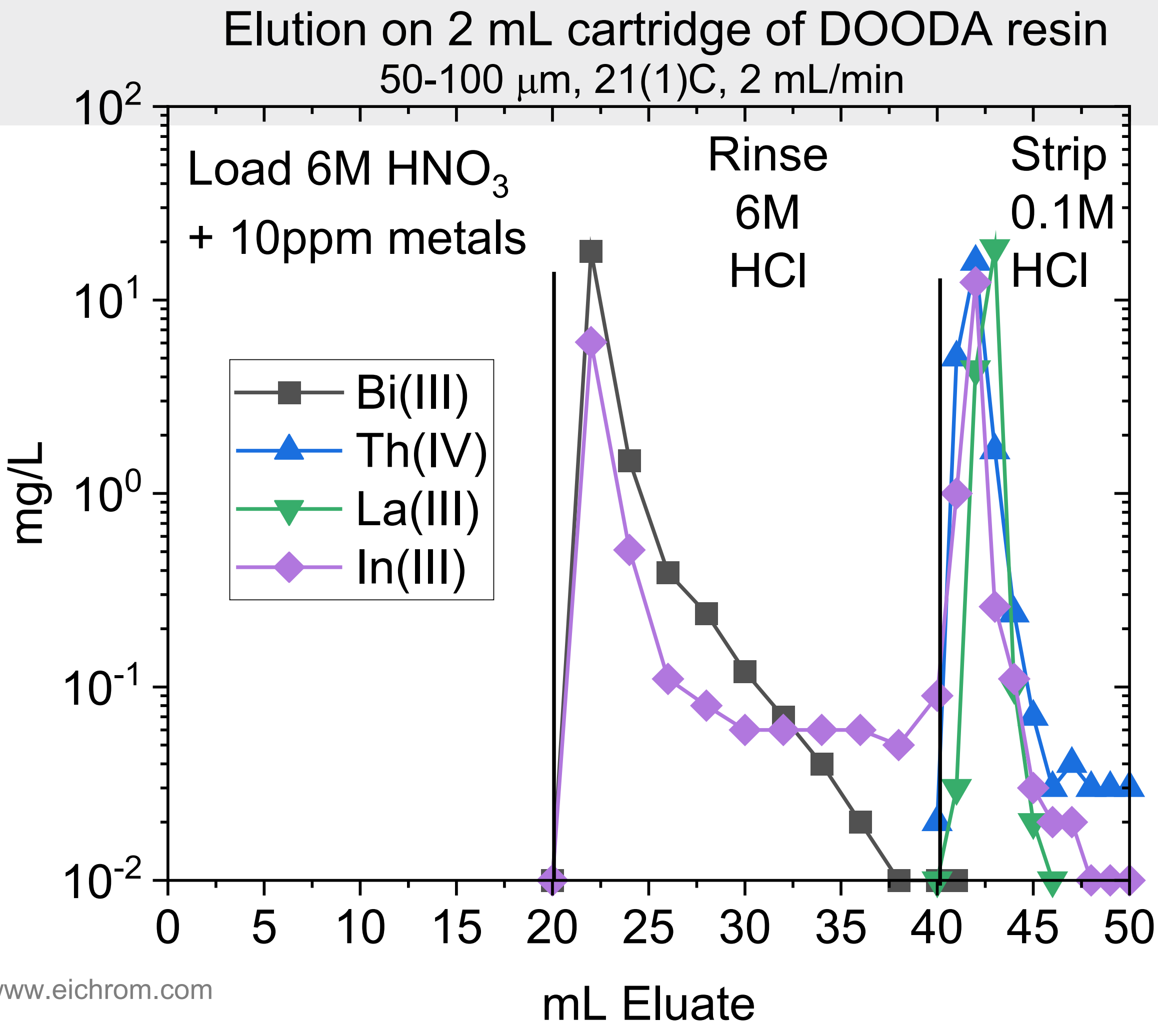


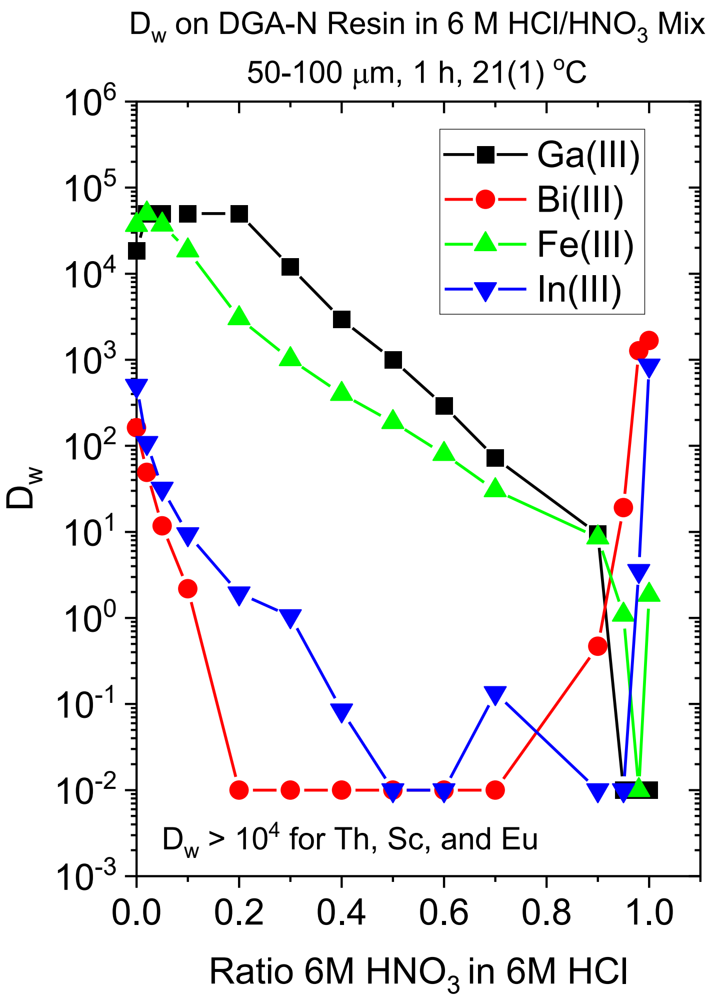
Elution of In(III) on DGA Resin, Normal
2 mL cartridge, 50-100 μm, 21(1)C, 2 mL/min
Load 6M HNO_3
+ 0.2 mg In
Rinse
6M
HNO_3
Rinse
9M
HCl
Strip
0.1M
HCl
68%
In
mg/L
10^2
10^1
10^0
10^{-1}
10^{-2}
0
5
10
15
20
25
30
35
40
45
50
55
60
mL Eluate

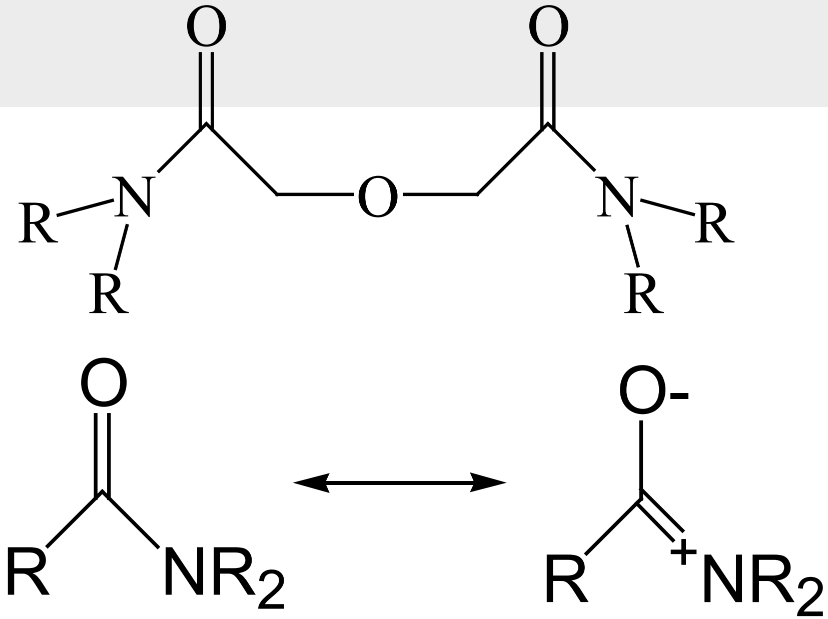
What other metals have retention from HNO3 and HCl?

Does not occur on TEVA or TRU resin.

Bi(NO3)3 vs [BiCl4]-
In(NO3)3 vs [InCl4]-







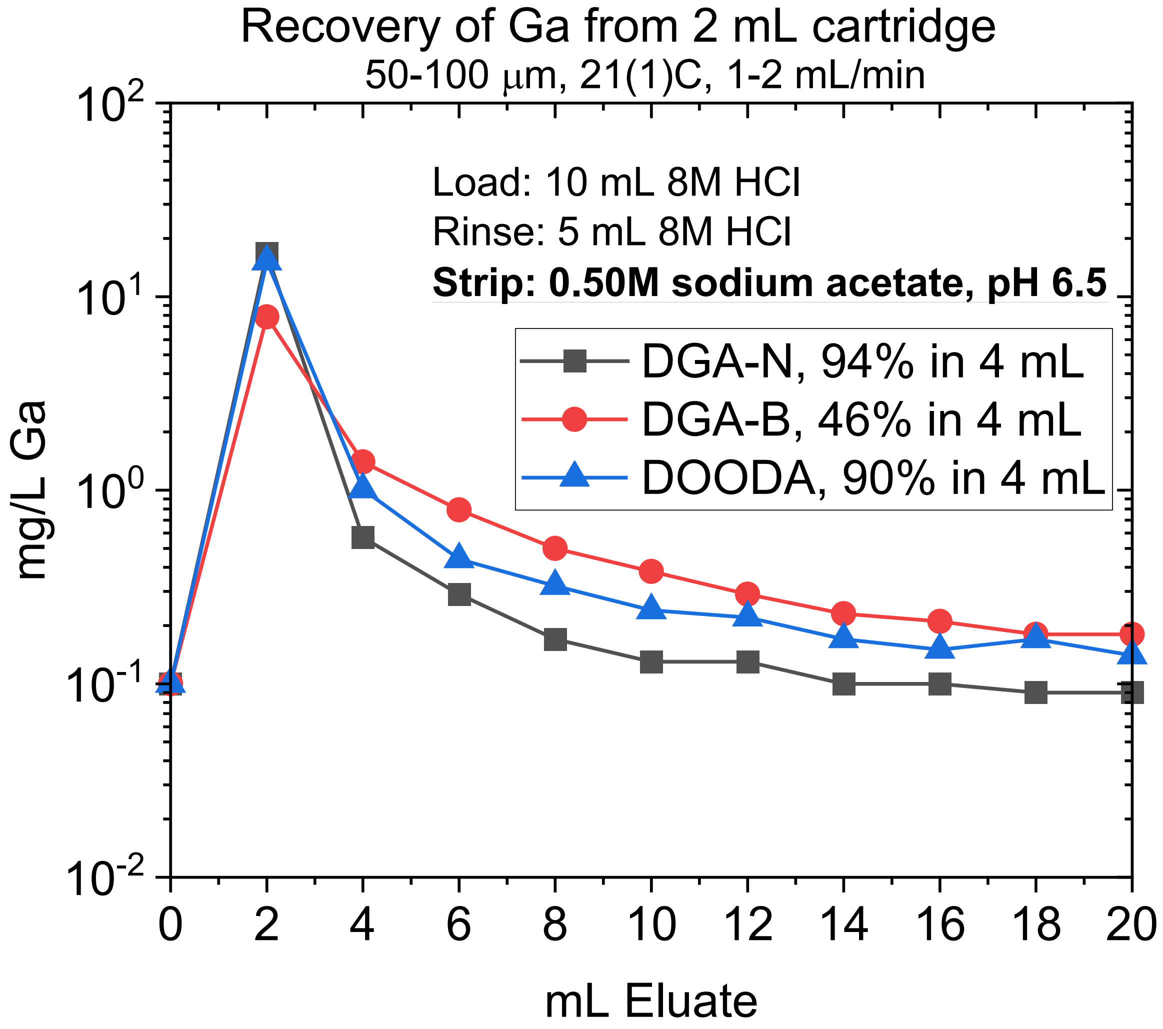
- Amides least reactive of all carboxylic acid derivatives

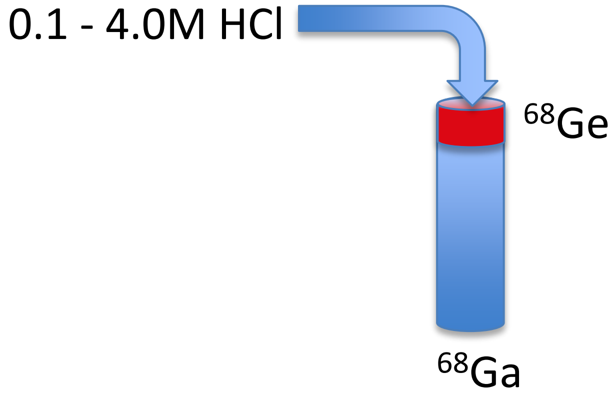
- Resonance form weakens C=O, exhibited by low C=O stretching frequency in IR.

Vollhardt, K.P.; Schore, N.E., Organic Chemistry, 2nd ed. W.H. Freeman and Co., USA, pp.768-780.

^{68}Ga

Nuclide	Half Life	Decay	Production
^{68}Ga	67.83 min	β^+ (0.822 MeV), 1.20% (1.899 MeV), 87.68% ε, 11.11% γ (1.077 MeV), 3.235%	Decay of ^{68}Ge $^{65}Cu(\alpha,n)^{68}Ga$ $^{67}Zn(p,\gamma)^{68}Ga$ $^{68}Zn(p,n)^{68}Ga$ $^{70}Ge(d,\alpha)^{68}Ga$





0.1M HCl (SCX-silica)

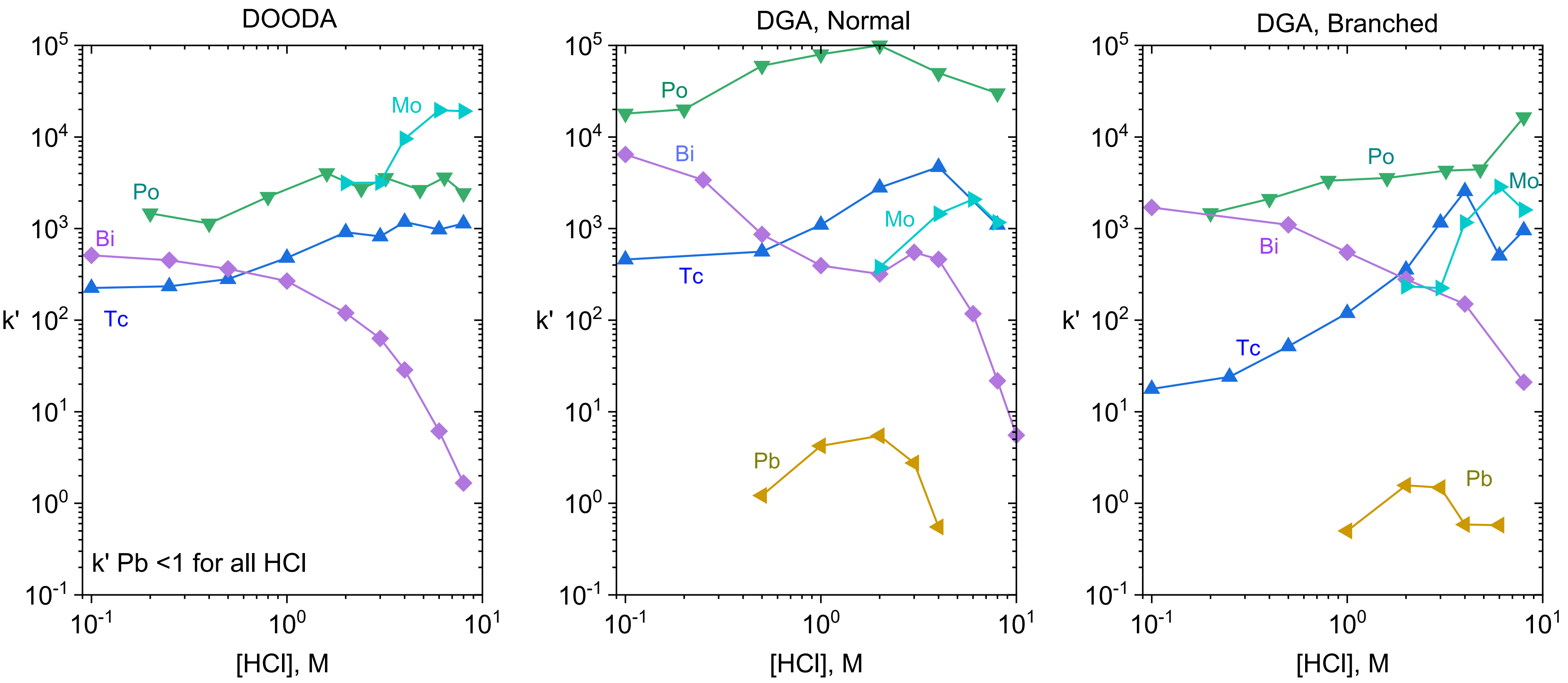
Recover in 5M HCl/0.1M HCl

4M HCl (DGA/DOODA)

Recover in buffer

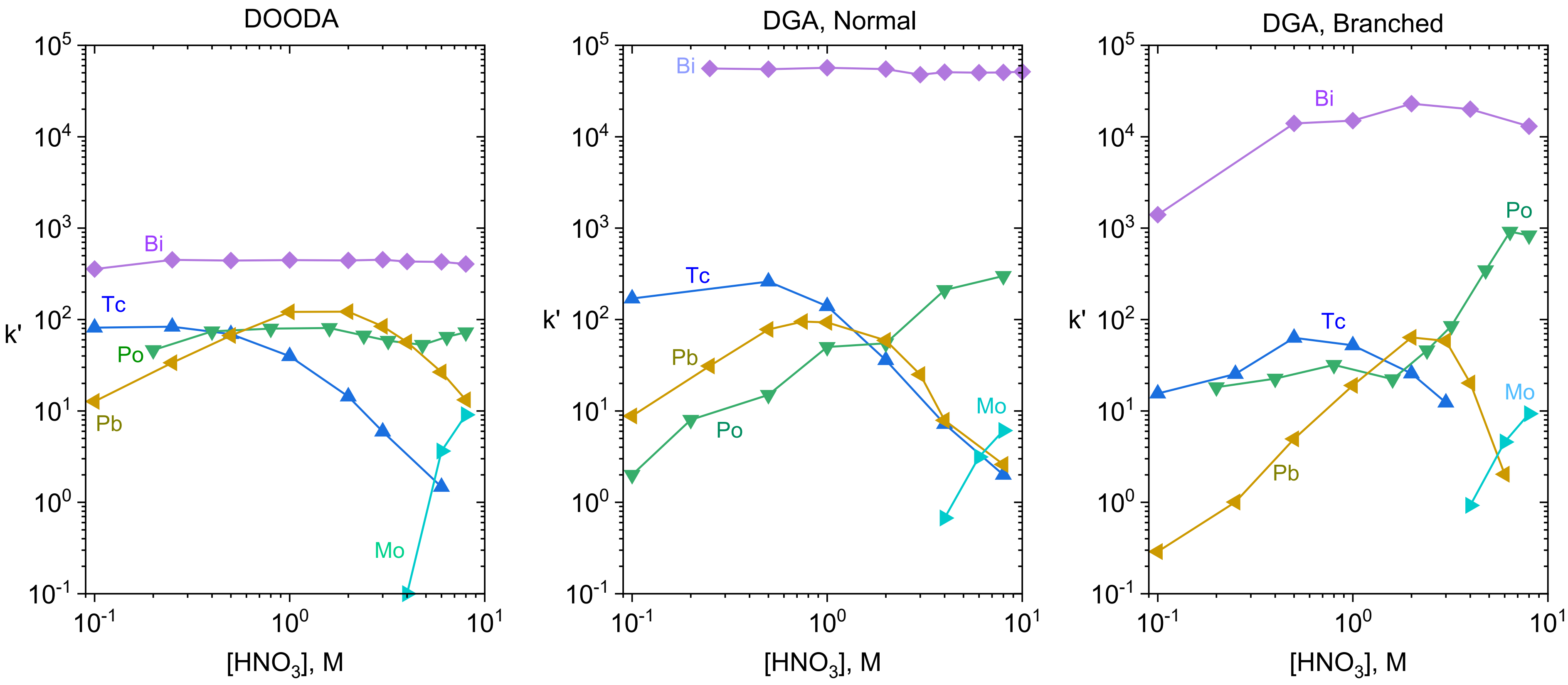
Po-210 Analysis
from difficult matrices

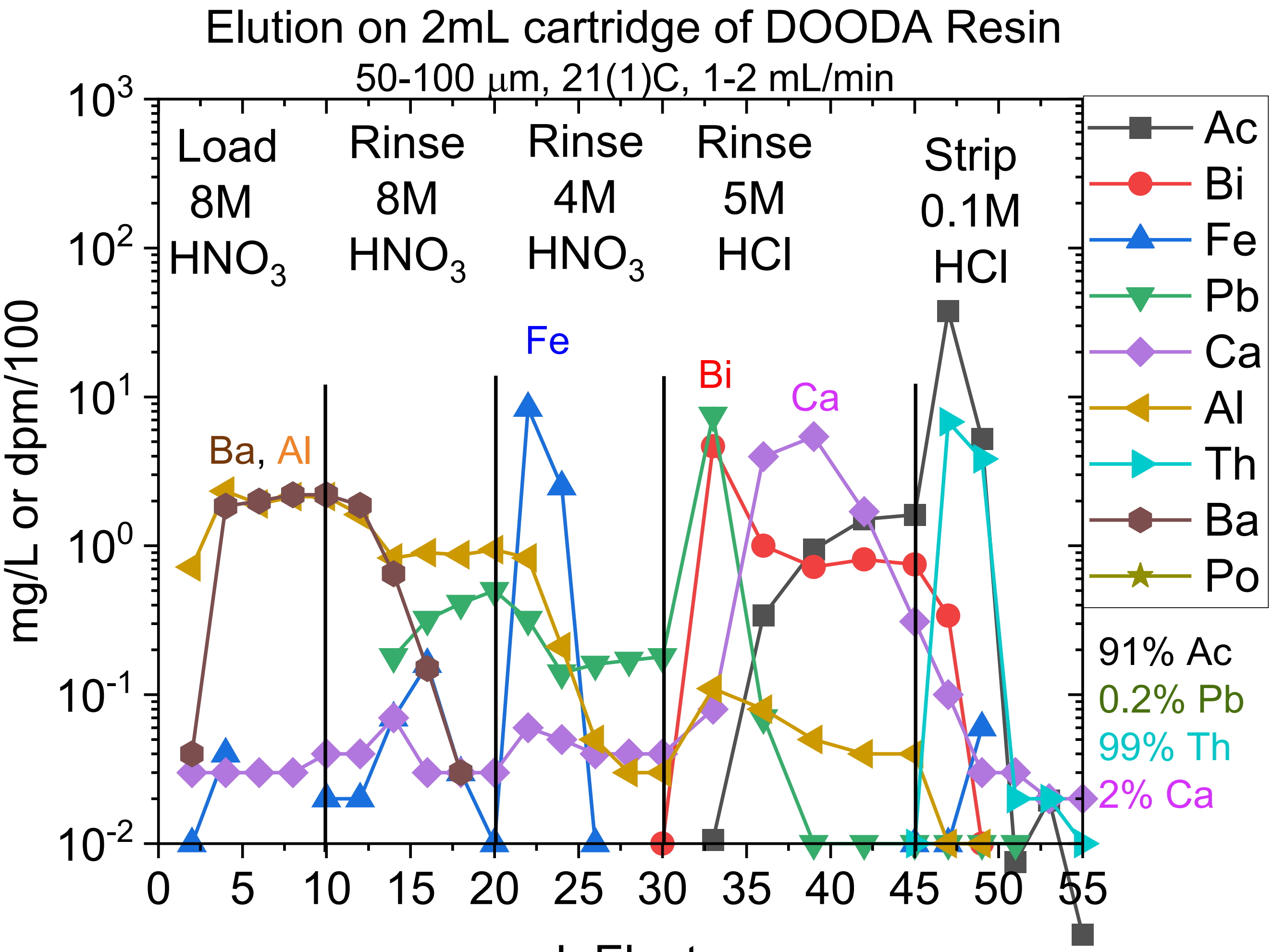
S.L. Maxwell, D.R. McAlister, R. Suldowe, "Rapid Method to Determine Polonium-210 in Urban Matrices," *Applied Radiation and Isotopes,* 148, 270-276 (2019).

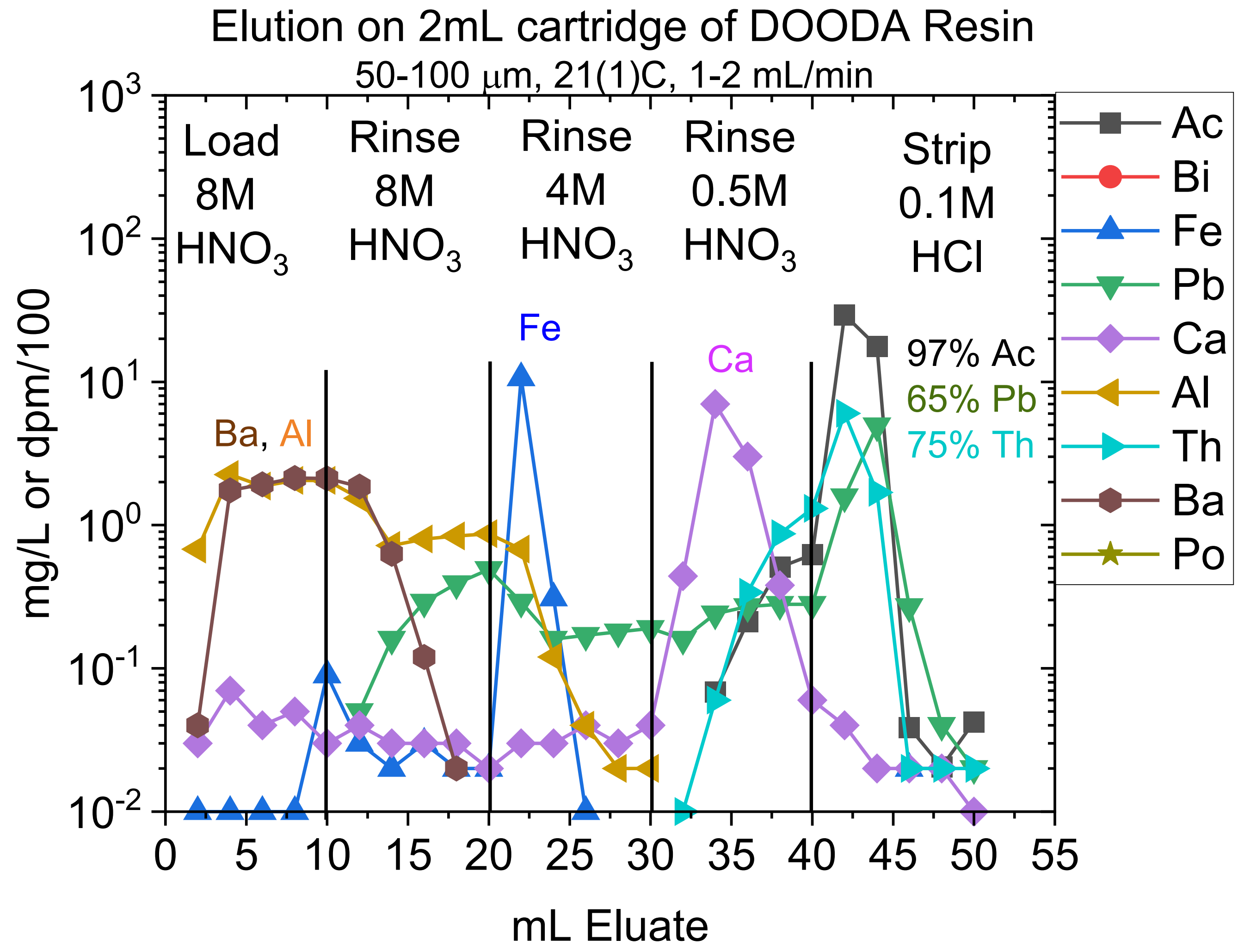


eichrom

www.eichrom.com


DOODA
DGA, Normal
DGA, Branched
k'
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
[HNO_3], M
Bi
Tc
Po
Pb
Mo


Elution on 2mL cartridge of DOODA Resin
50-100 μm, 21(1)C, 1-2 mL/min
Load 8M HNO3
Rinse 8M HNO3
Rinse 4M HNO3
Rinse 5M HCl
Strip 0.1M HCl
Ba, Al
Fe
Bi
Ca
Ac
Bi
Fe
Pb
Ca
Al
Th
Ba
Po
91% Ac
0.2% Pb
99% Th
2% Ca
mg/L or dpm/100
mL Eluate
10^3
10^2
10^1
10^0
10^-1
10^-2
0
5
10
15
20
25
30
35
40
45
50
55


Elution on 2mL cartridge of DOODA Resin
50-100 μm, 21(1)C, 1-2 mL/min
Load 8M HNO3
Rinse 8M HNO3
Rinse 4M HNO3
Rinse 0.5M HNO3
Strip 0.1M HCl
Fe
Ca
Ba, Al
97% Ac
65% Pb
75% Th
Ac
Bi
Fe
Pb
Ca
Al
Th
Ba
Po
mg/L or dpm/100
mL Eluate
10^3
10^2
10^1
10^0
10^-1
10^-2
0
5
10
15
20
25
30
35
40
45
50
55