Matrix and High Loading Effects on Eichrom Resins

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Examples of High Salt Matrices

Sea Water (35 g/L, NaCl, KCl, $MgCl_2$ and $CaCl_2$)

Urine (30-70 g/L, Na^+ (3-4g), K^+ (1-2g), Ca^{2+} (0.1-0.3g), PO_4^{3-} (1-2g), SO_4^{2-} (1-4g), Mg (40-200mg), NH_4^+ (0.3-1g), I (50-250mg), Cl^- (9-16g))

Soil (Na, K, Ca, Mg, Al, Fe, SiO_4^{4-}, SO_4^{2-}, PO_4^{3-}, CO_3^{2-})

Precipitations ($FeOH_3$, $CaHPO_4$, $BaSO_4$, MnO_2)

Uranium Materials

Basic Principle of Metal Ion Extraction

Extractant

Solvent

Organic Phase or Resin

Metal Ion

Counter Ion

Water

Aqueous Phase

The magnitude of the extraction depends on:

a. Hydration Energies of the Cations and Anions

b. Bond Energy Between the Cation and Extractant

c. Solvation Energy of the Extractant and the Complex

d. Activities of ions participating in the extraction

Ways Matrices Can Affect Separations

1) Co-extraction with desired analyte ↓

2) Complexation of the analyte ↓ or ↑

3) Decrease or Increase Solubility ↓ or ↑

4) Complexation of competing species ↑

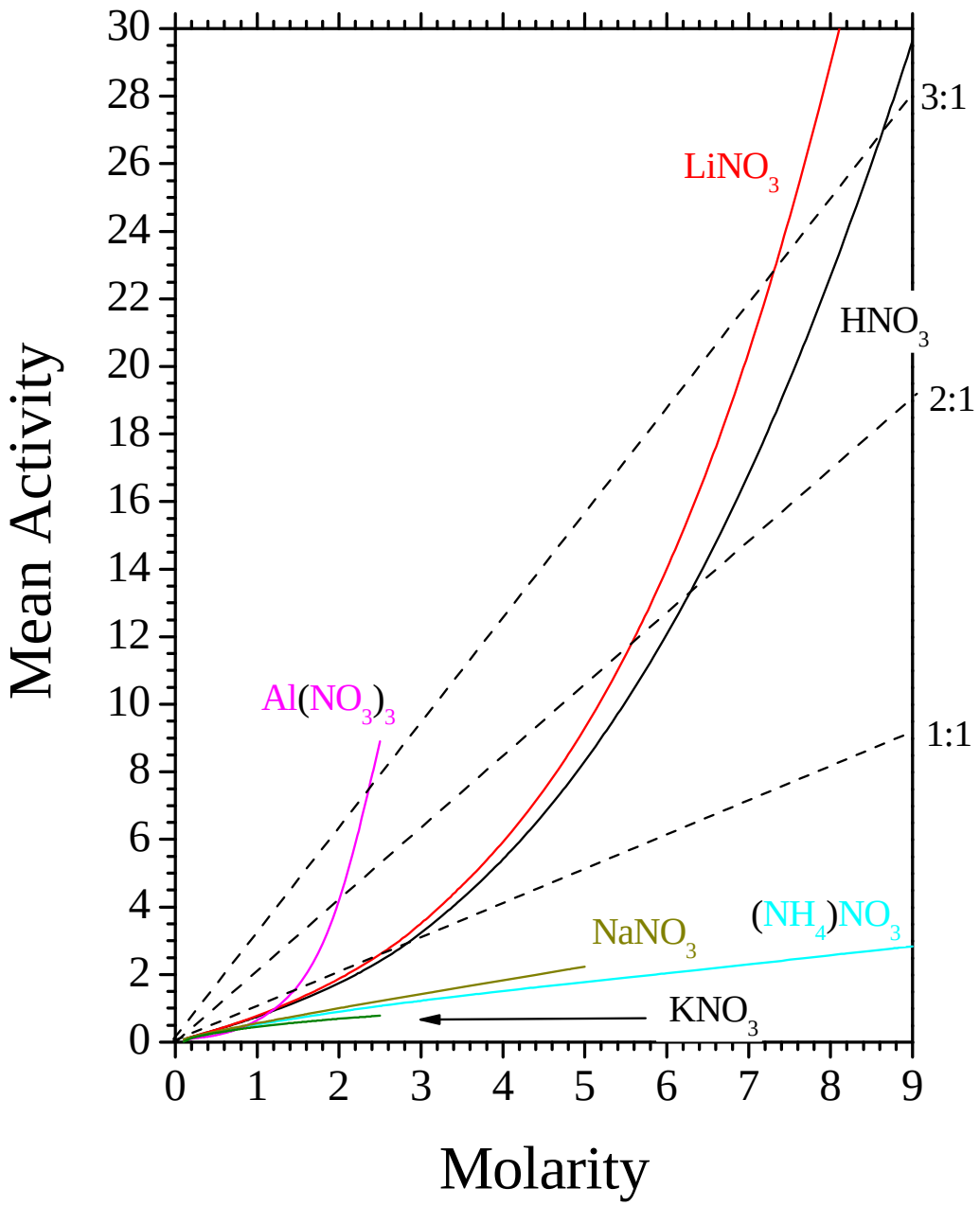
5) Changing the activity of ions ↓ or ↑

6) Masking Impurities in Extractant ↑

Common Matrix Components

H^+ Li^+ Na^+ NH_4^+ K^+

- K^+ on Sr Resin
- Solubility
- Mass following evaporation (NH_4^+)
- Activity of counter ion/magnitude of extraction (Li^+)


Mean Activity
Molarity
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
1
2
3
4
5
6
7
8
9
3:1
2:1
1:1
LiNO3
HNO3
Al(NO3)3
NaNO3
(NH4)NO3
KNO3

Common Matrix Components

Mg^{2+} Ca^{2+} Sr^{2+} Ba^{2+}

- Ca^{2+}, Ba^{2+}, Sr^{2+} on Sr Resin
- Ca^{2+} on DGA
- Solubility
- Activity of counter ion/magnitude of extraction

Common Matrix Components

Fe^{2+}/Fe^{3+} Al^{3+}

- Fe^{3+} on TRU
- Red/Ox states (Fe/Np)
- Bind complexing anions (SO_4^{2-}/PO_4^{3-})
- Activity of counter ion/magnitude of extraction (Al)

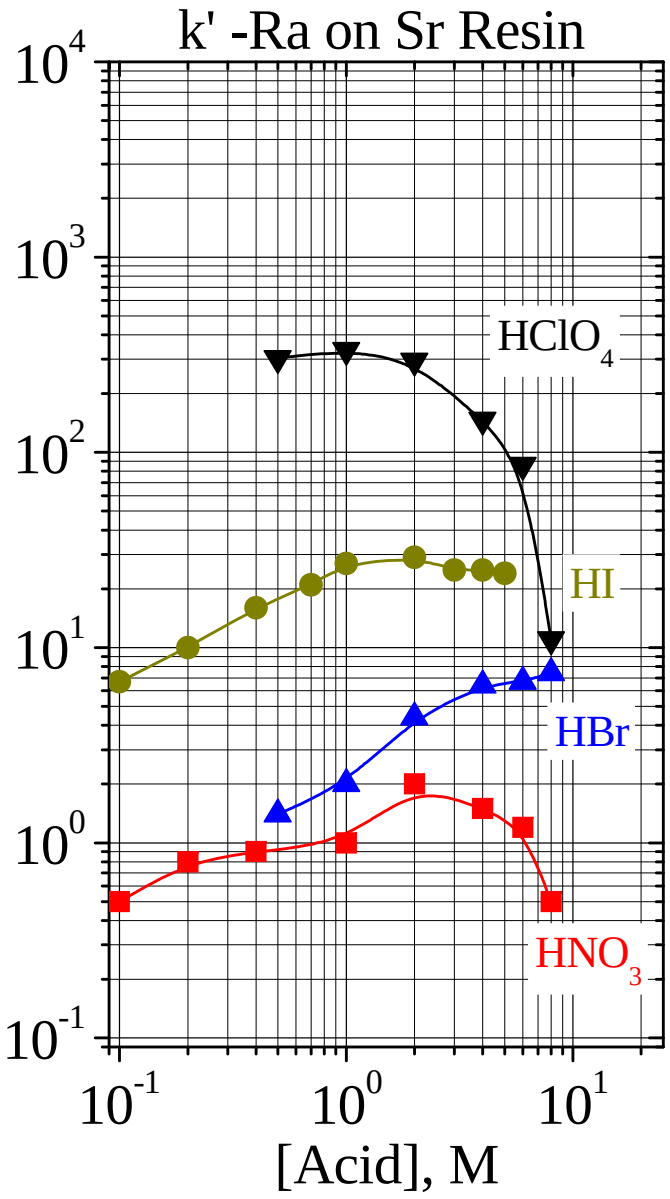
Common Matrix Components

ClO_4^- NO_3^- Cl^- F^- $Oxalate^{2-}$ SO_4^{2-} PO_4^{3-}

- Solubility

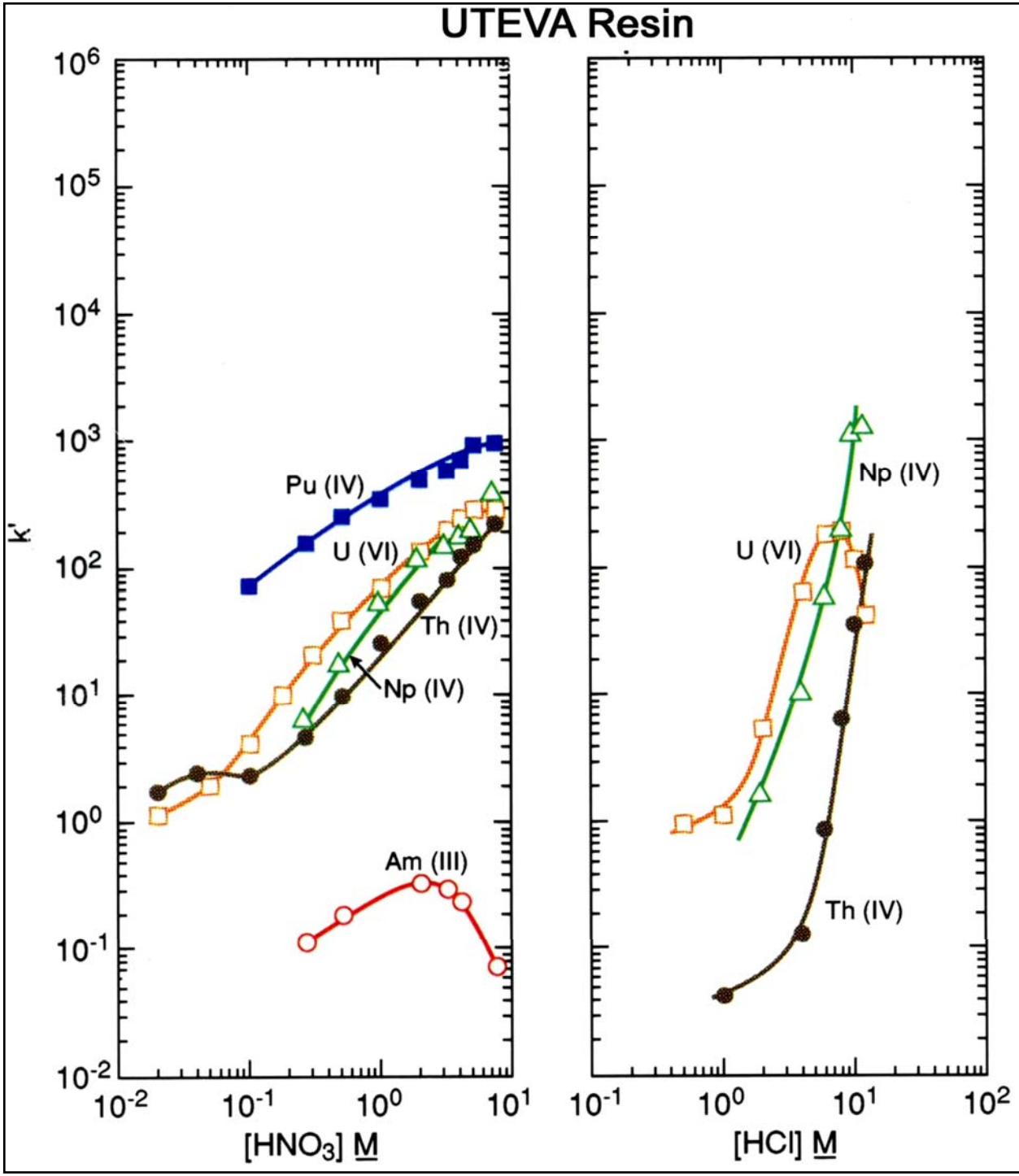
- Extractability of analytes
  - Stoichiometry
  - Charge of complex
  - Hydration Energies

Common Matrix Components



Calculated Hydration Energies of Selected Anions

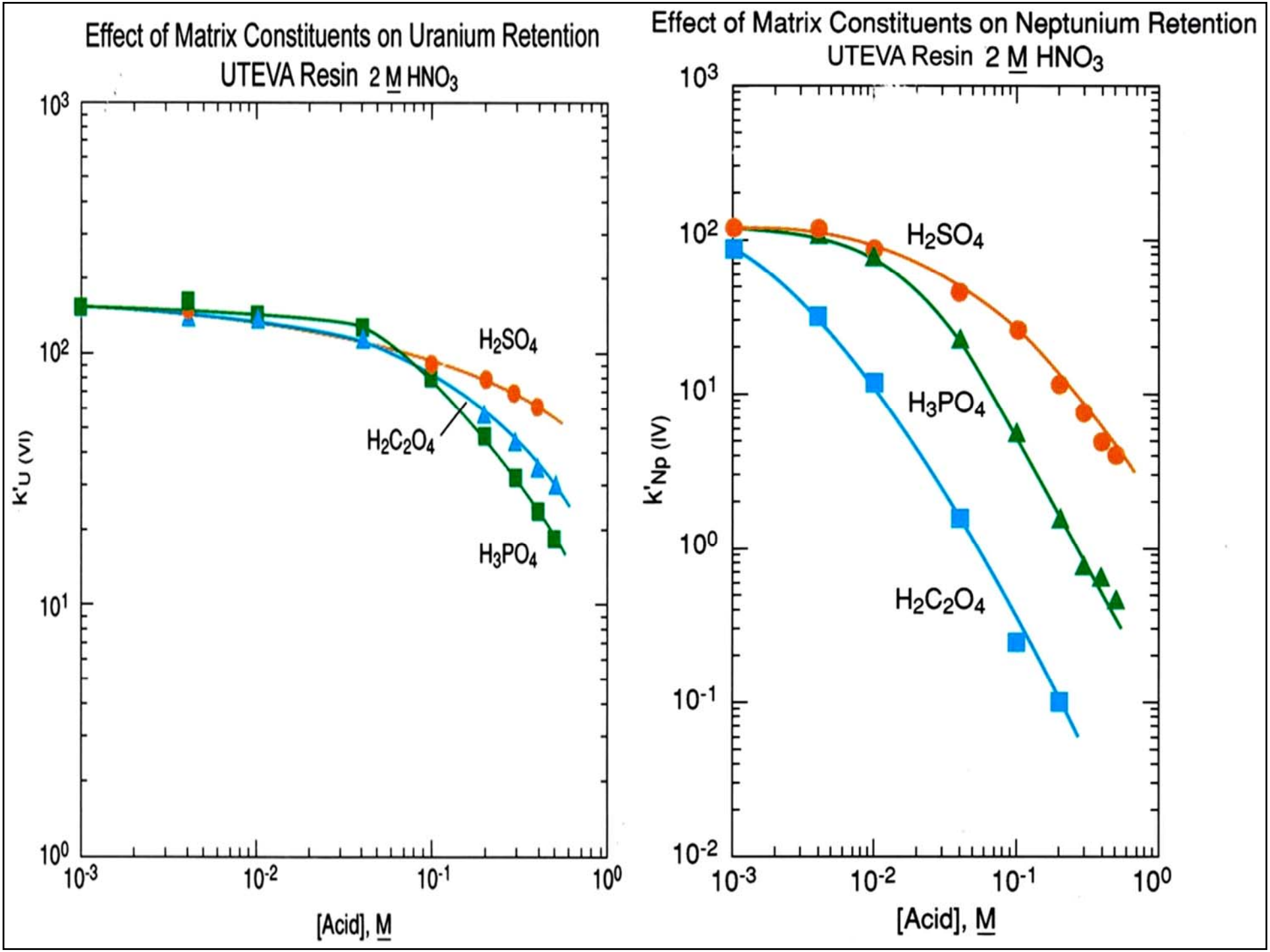
Anion	Hydration Energy (kJ/mol)
ClO_4^-	-180
I^-	-220
SCN^-	-230
Br^-	-250
NO_3^-	-275
Cl^-	-300
F^-	-345
SO_4^{2-}	-1145
CO_3^{2-}	-1300
PO_4^{3-}	-2835

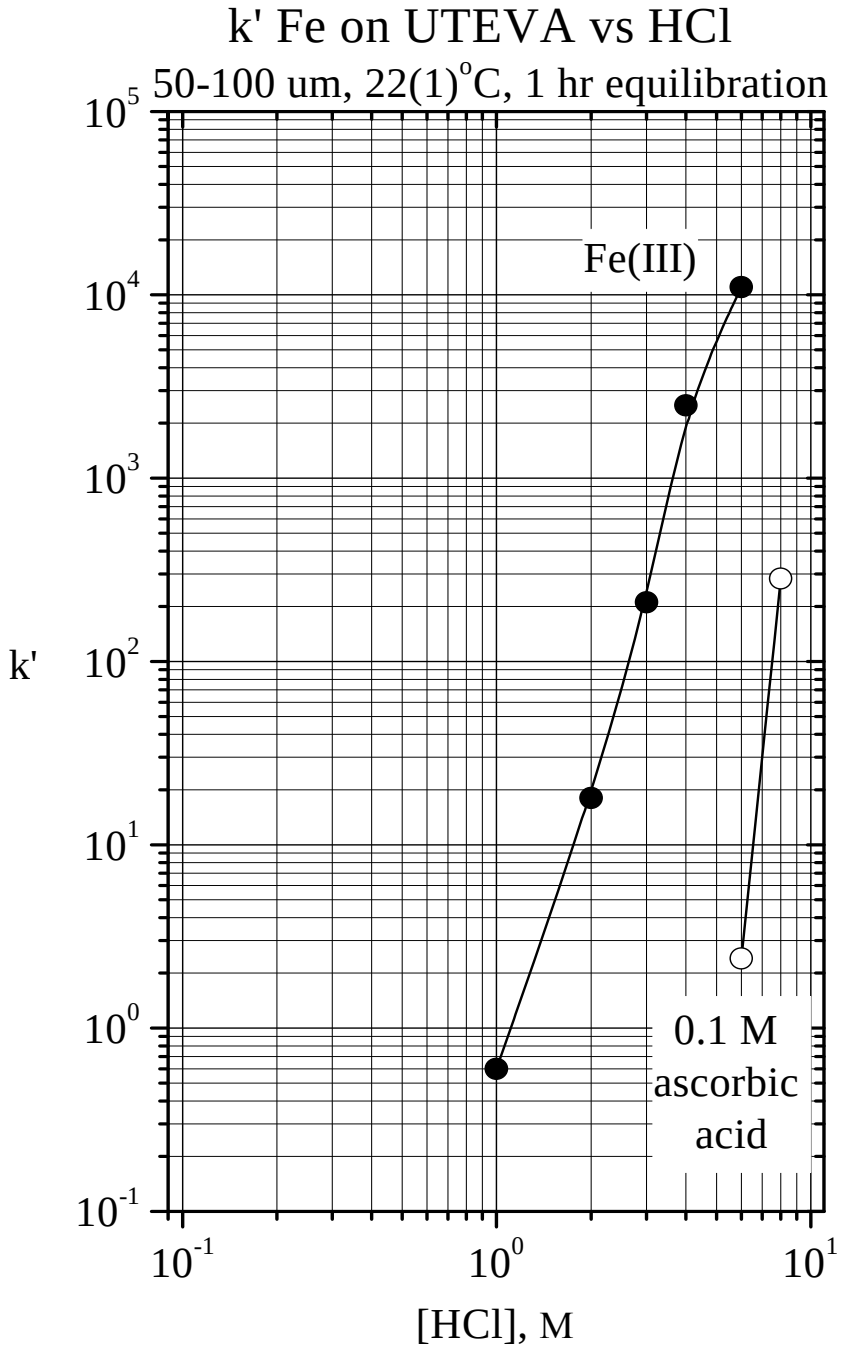


Tolerates High Levels of nearly all matrix cations

High Fe(III) can impact separations in HCl

Complexing anions can reduce uptake of actinides.


Effect of Matrix Constituents on Uranium Retention
UTEVA Resin 2 M HNO3
k'U (VI)
[Acid], M
H2SO4
H2C2O4
H3PO4
Effect of Matrix Constituents on Neptunium Retention
UTEVA Resin 2 M HNO3
k'Np (IV)
[Acid], M
H2SO4
H3PO4
H2C2O4

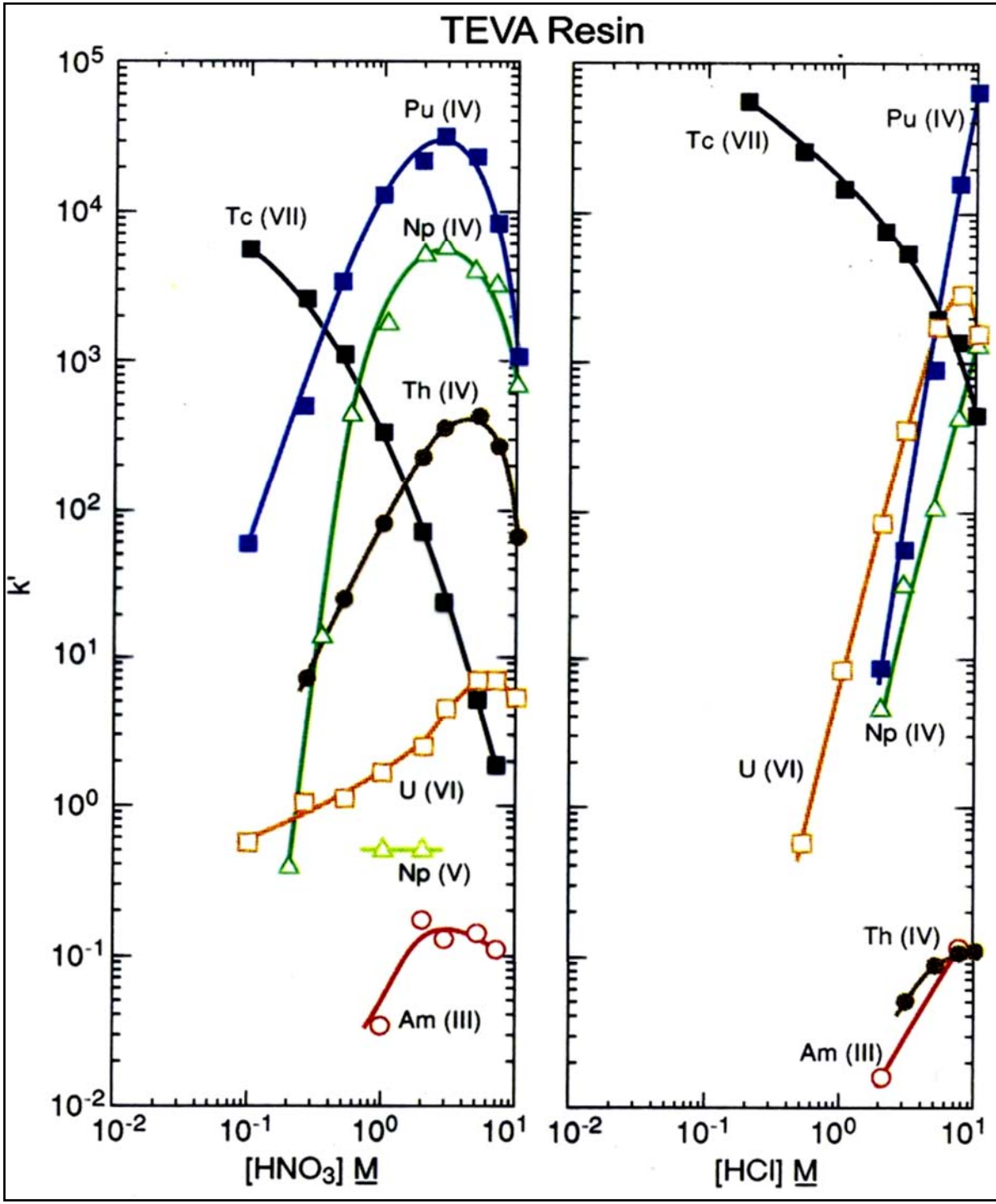


Fe(III) can be extracted from HCl media.

Addition of ascorbic acid reduces Fe(III) to Fe(II).

Fe(II)/ascorbic acid can reduce other analytes

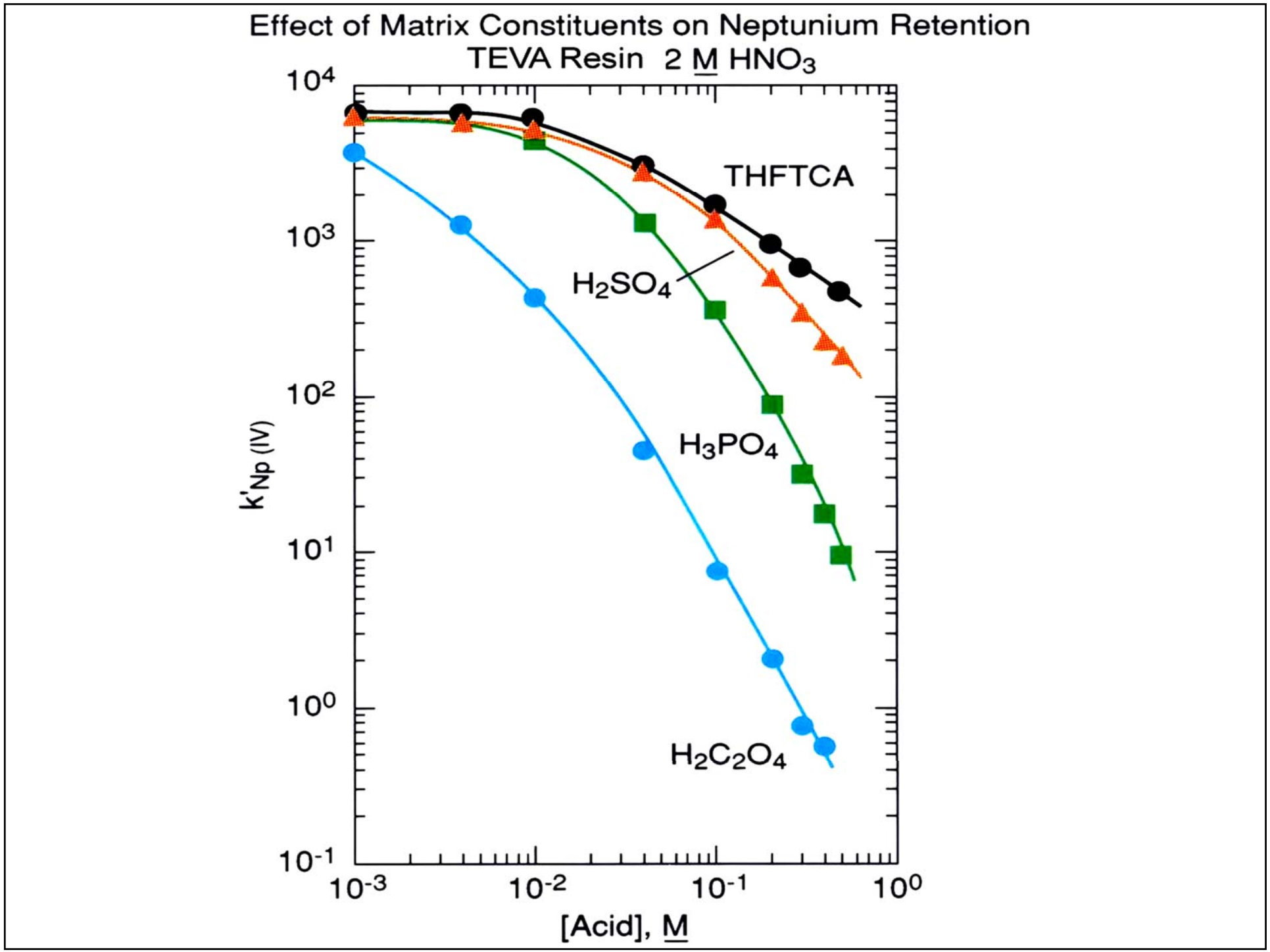
- -Pu(IV) to Pu(III)
- -Np(V)/(VI) to Np(IV)

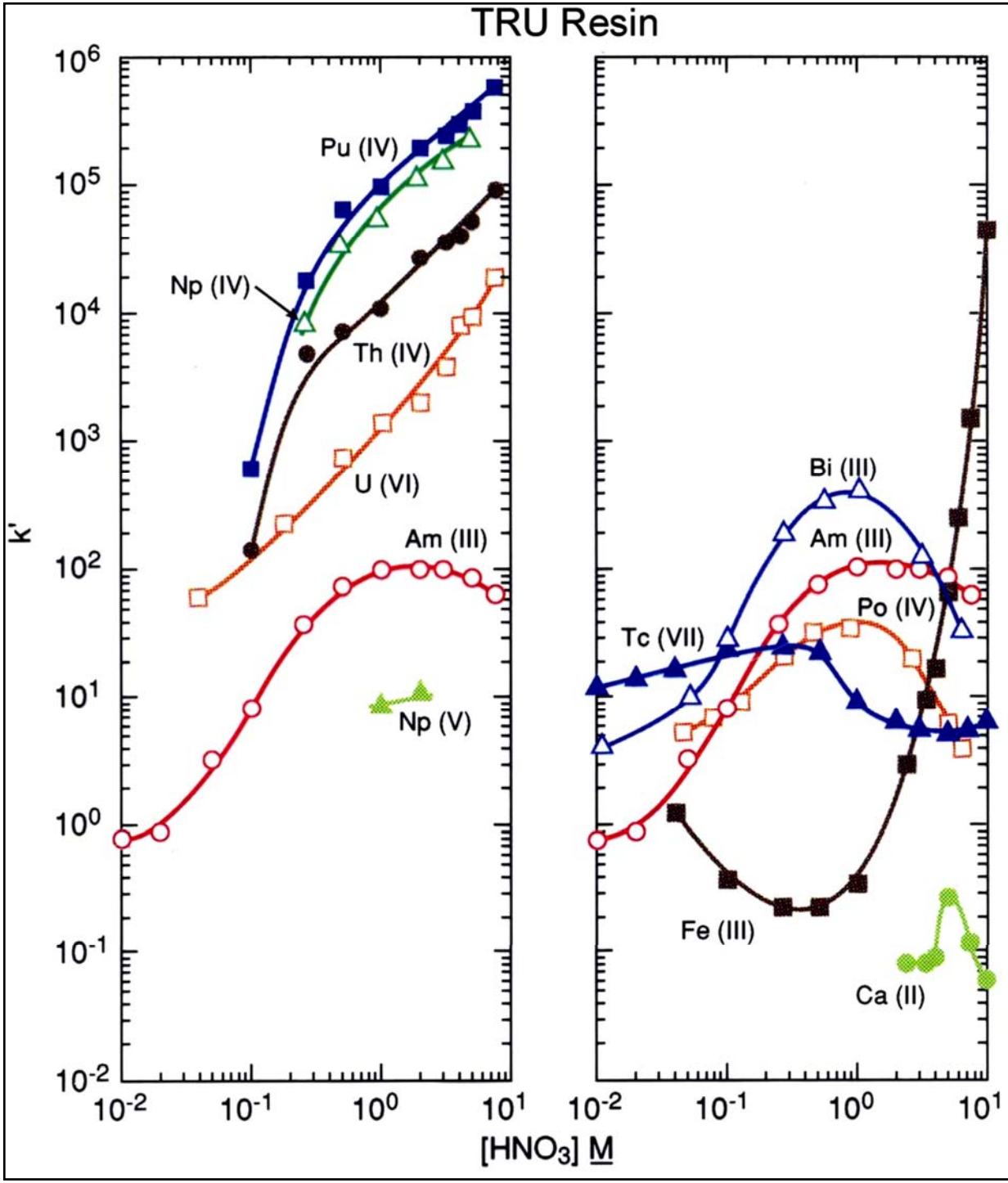


Tolerates High Levels of nearly all matrix cations

High Fe(III) can impact separations particularly in HCl

Complexing anions can reduce uptake of actinides.


Effect of Matrix Constituents on Neptunium Retention
TEVA Resin 2 M HNO3
THFTCA
H2SO4
H3PO4
H2C2O4
k'Np (IV)
[Acid], M
10^4
10^3
10^2
10^1
10^0
10^-1
10^-3
10^-2
10^-1
10^0

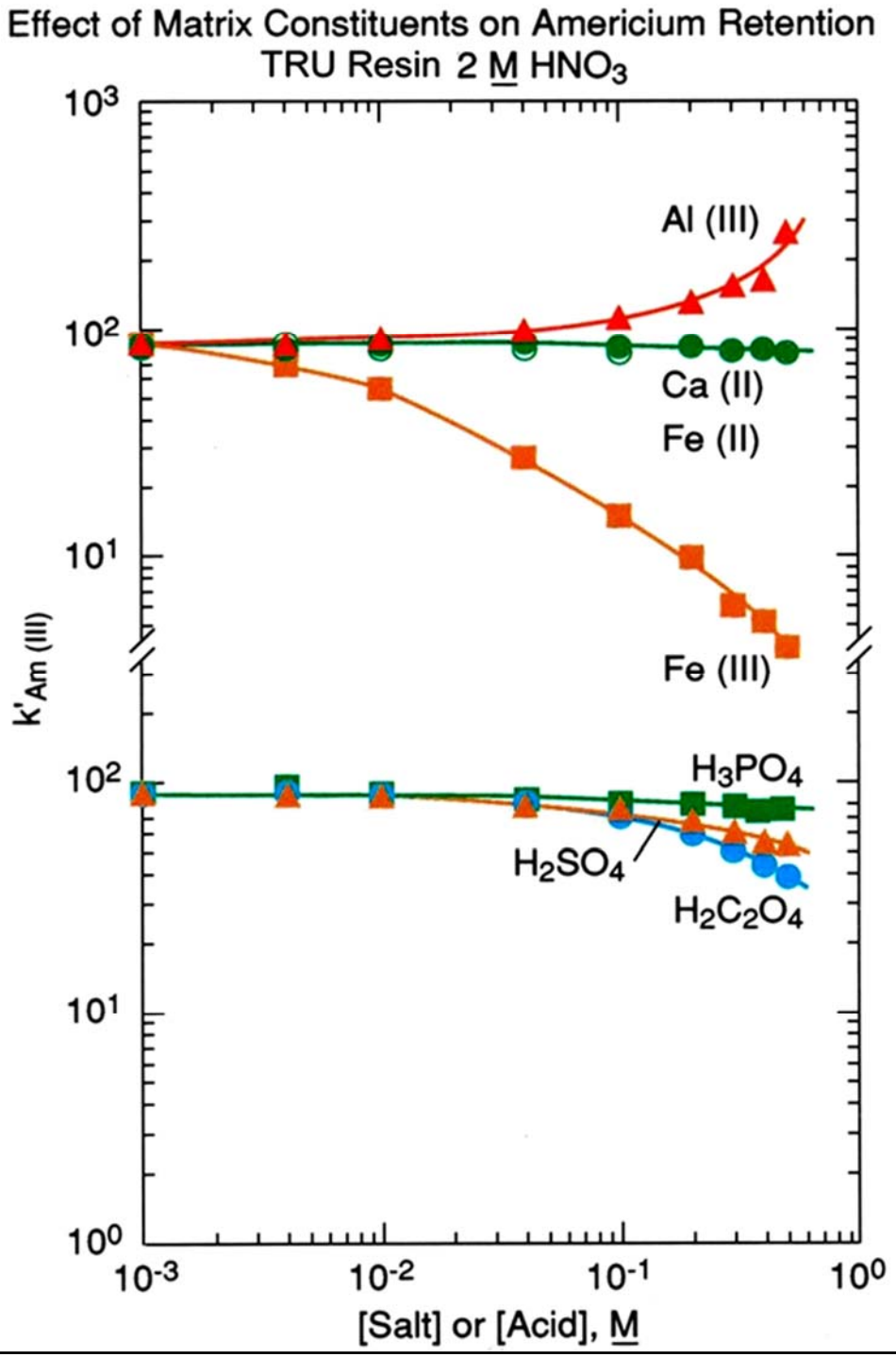


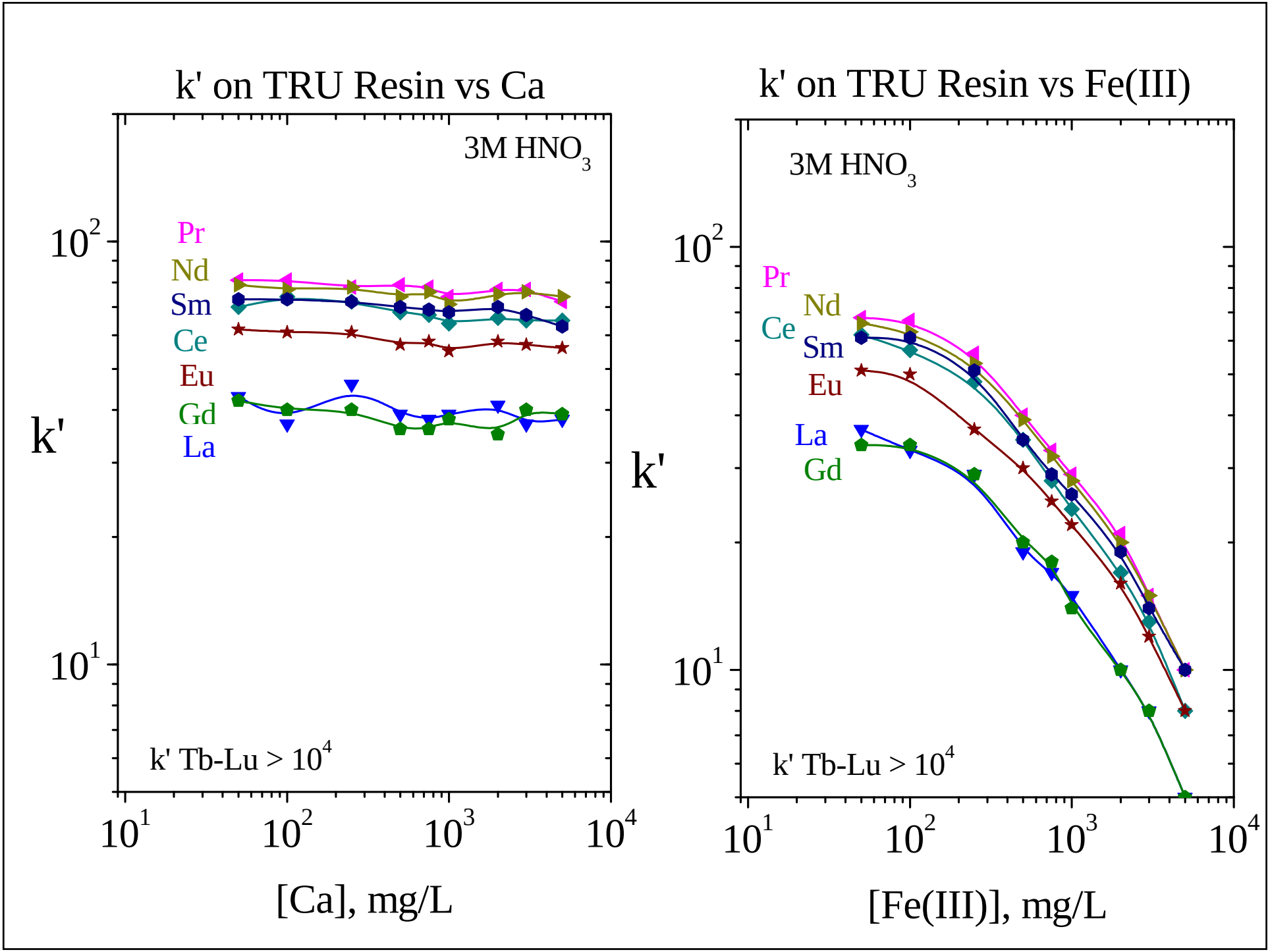
Tolerates High Levels of:

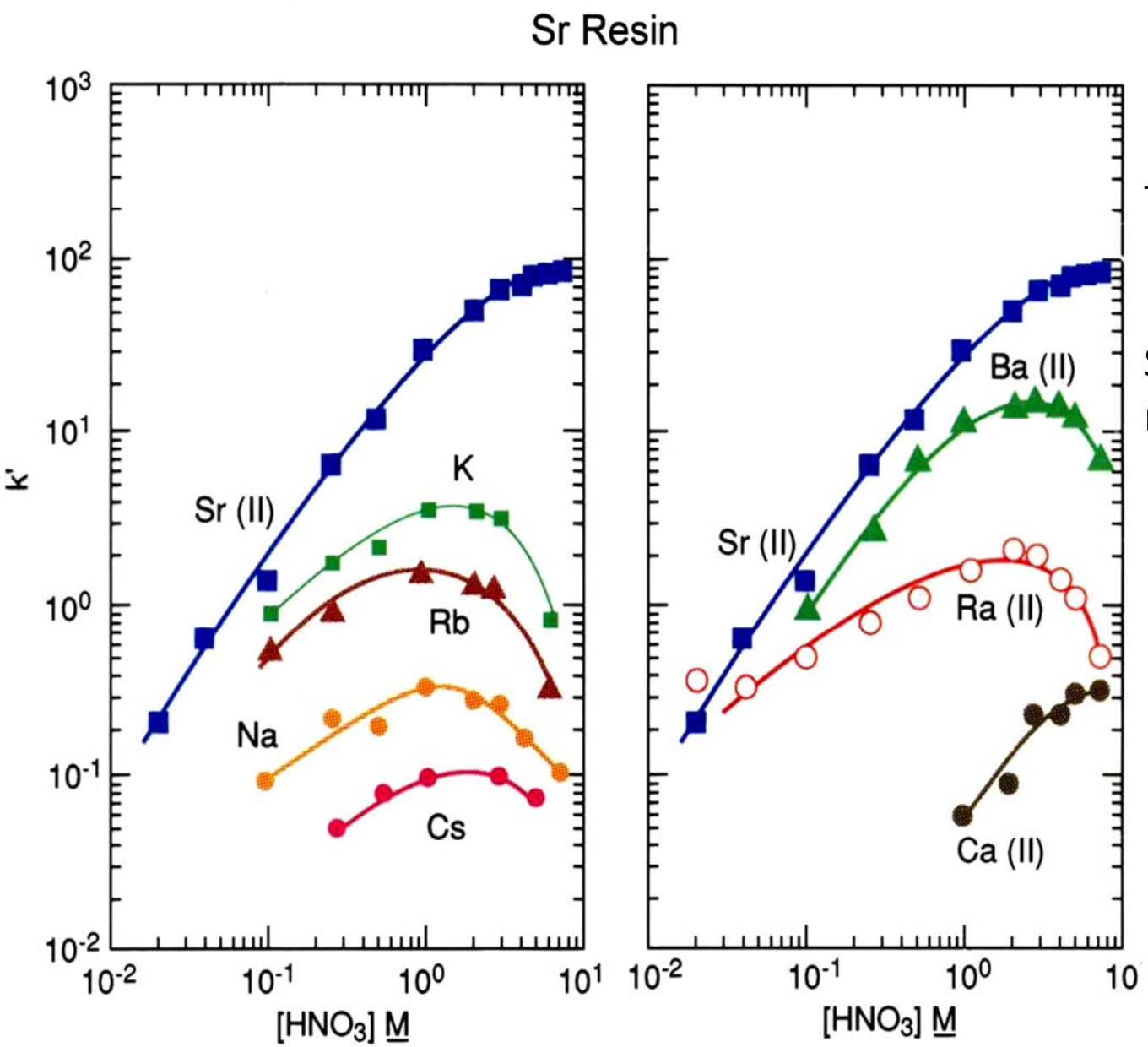
- -Alkalai metals
- -Alkaline earths
- -Aluminum

Am/Cm(III) uptake can be reduced by high:

- -Fe(III)
- -Lanthanides(III)
- -Sulfate
- -Oxalate


Effect of Matrix Constituents on Americium Retention
TRU Resin 2 M HNO3
k'Am (III)
10^3
10^2
10^1
10^2
10^1
10^0
10^-3
10^-2
10^-1
10^0
[Salt] or [Acid], M
Al (III)
Ca (II)
Fe (II)
Fe (III)
H3PO4
H2SO4
H2C2O4


k' on TRU Resin vs Ca
3M HNO3
Pr
Nd
Sm
Ce
Eu
Gd
La
k'
10^2
10^1
k' Tb-Lu > 10^4
10^1
10^2
10^3
10^4
[Ca], mg/L
k' on TRU Resin vs Fe(III)
3M HNO3
Pr
Nd
Ce
Sm
Eu
La
Gd
k'
10^2
10^1
k' Tb-Lu > 10^4
10^1
10^2
10^3
10^4
[Fe(III)], mg/L



Tolerates High Levels of:

-Na, Fe, Al, Mg

Sr uptake can be reduced by high:

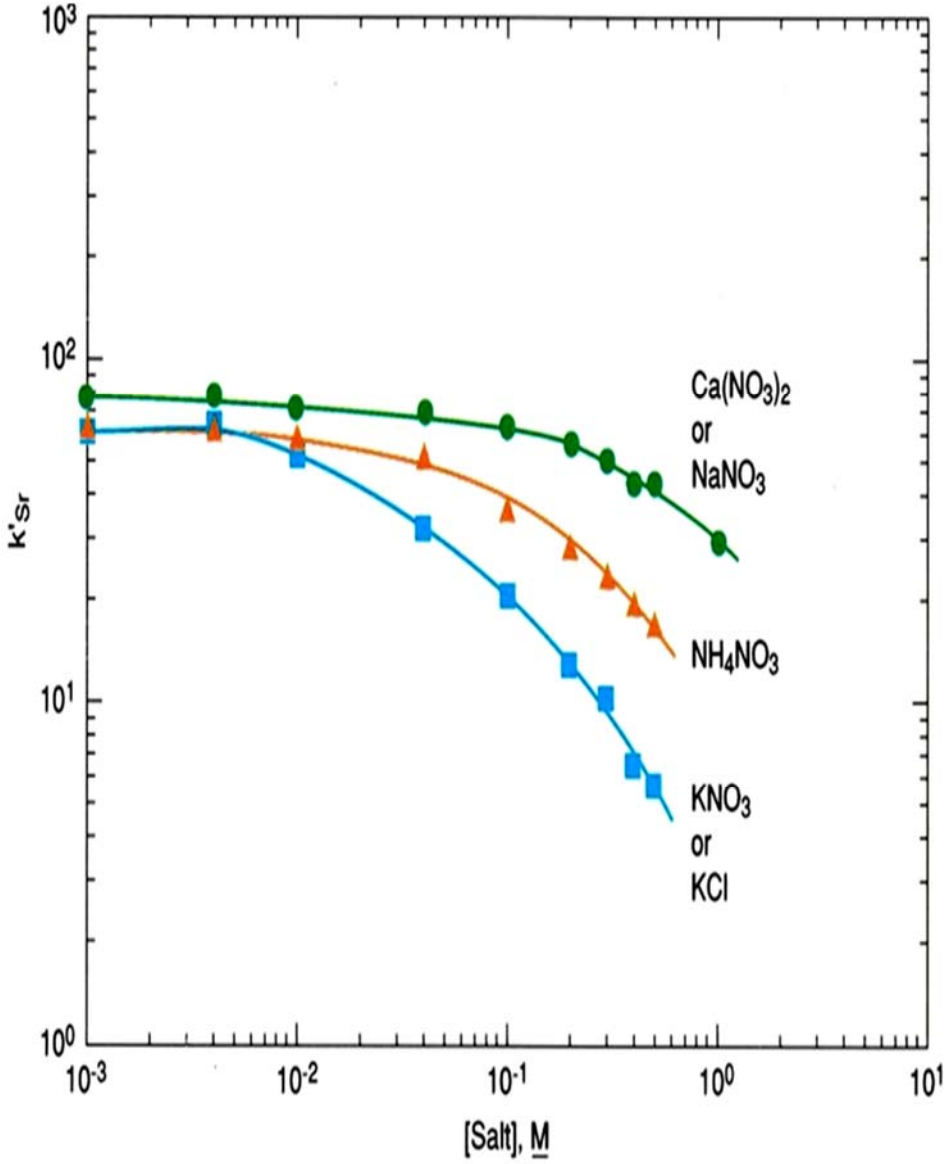
-K

-Ca

-Sr (>5mg)

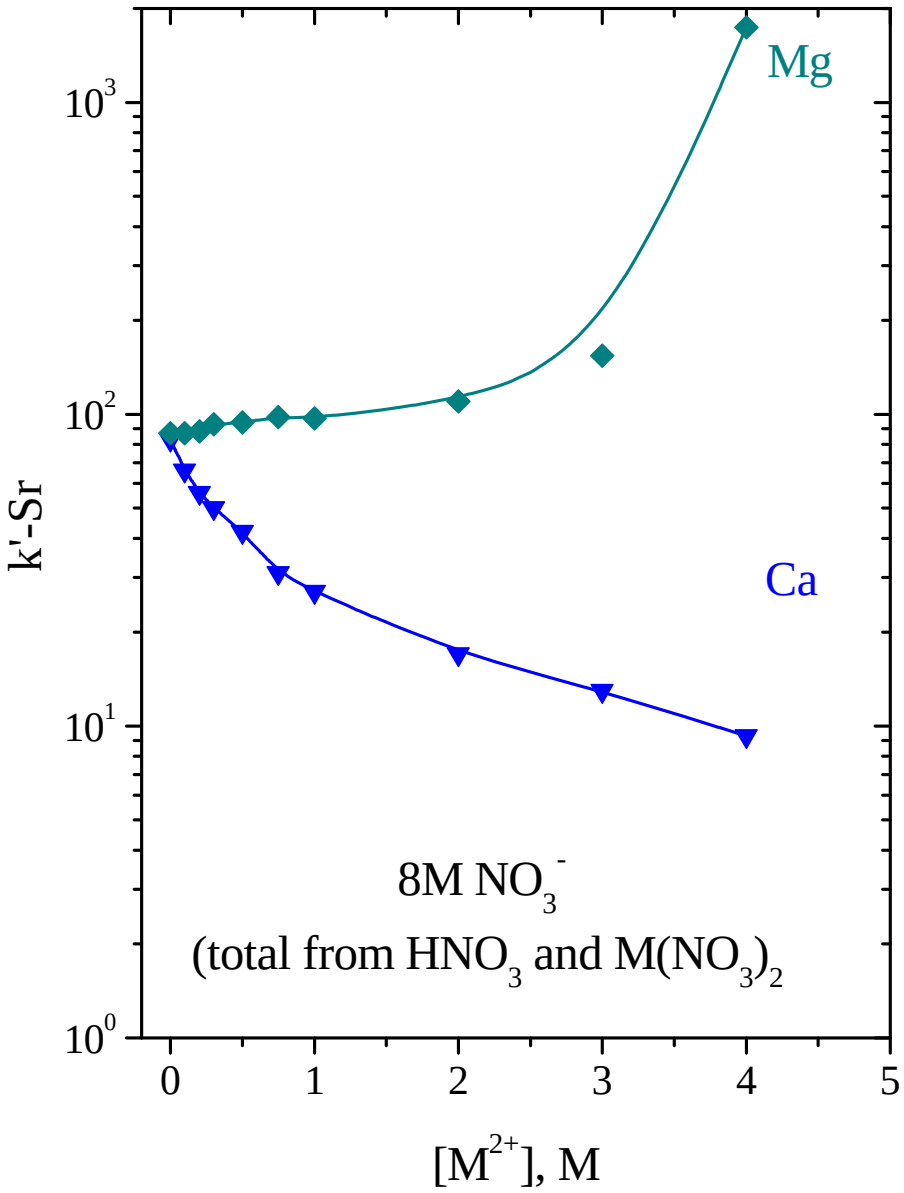
Effect of Matrix Constituents on Strontium Retention

Sr Resin 3 M HNO_3

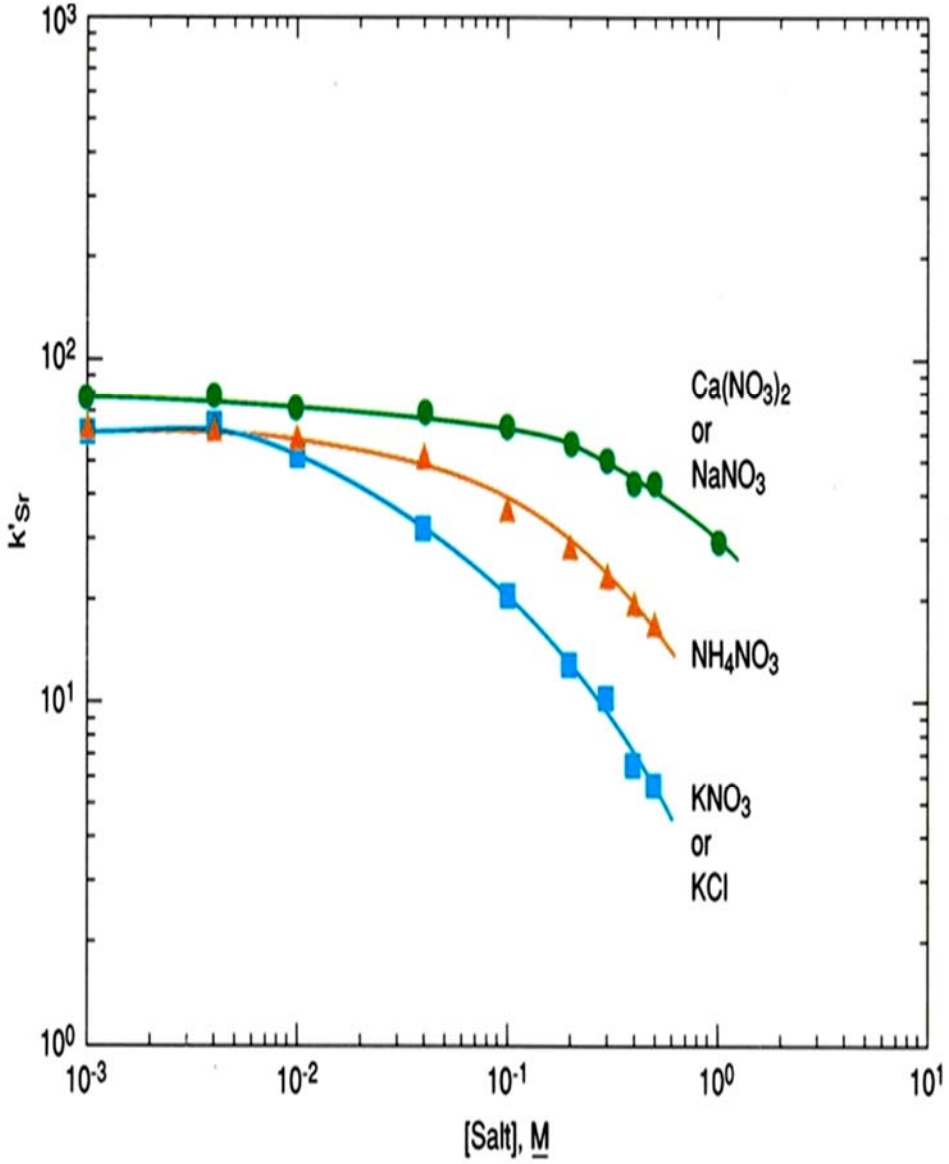


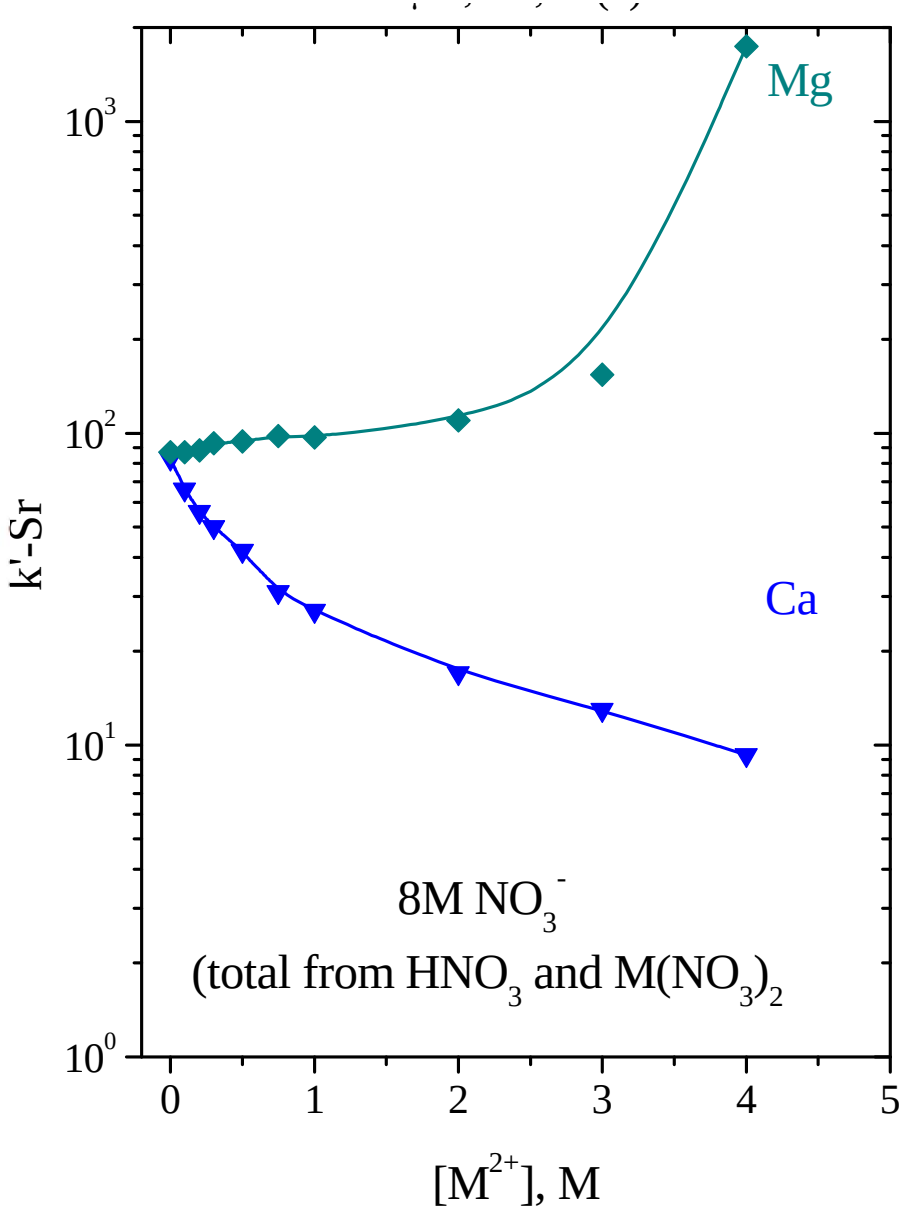
k' Sr on Sr Resin vs Ca and Mg

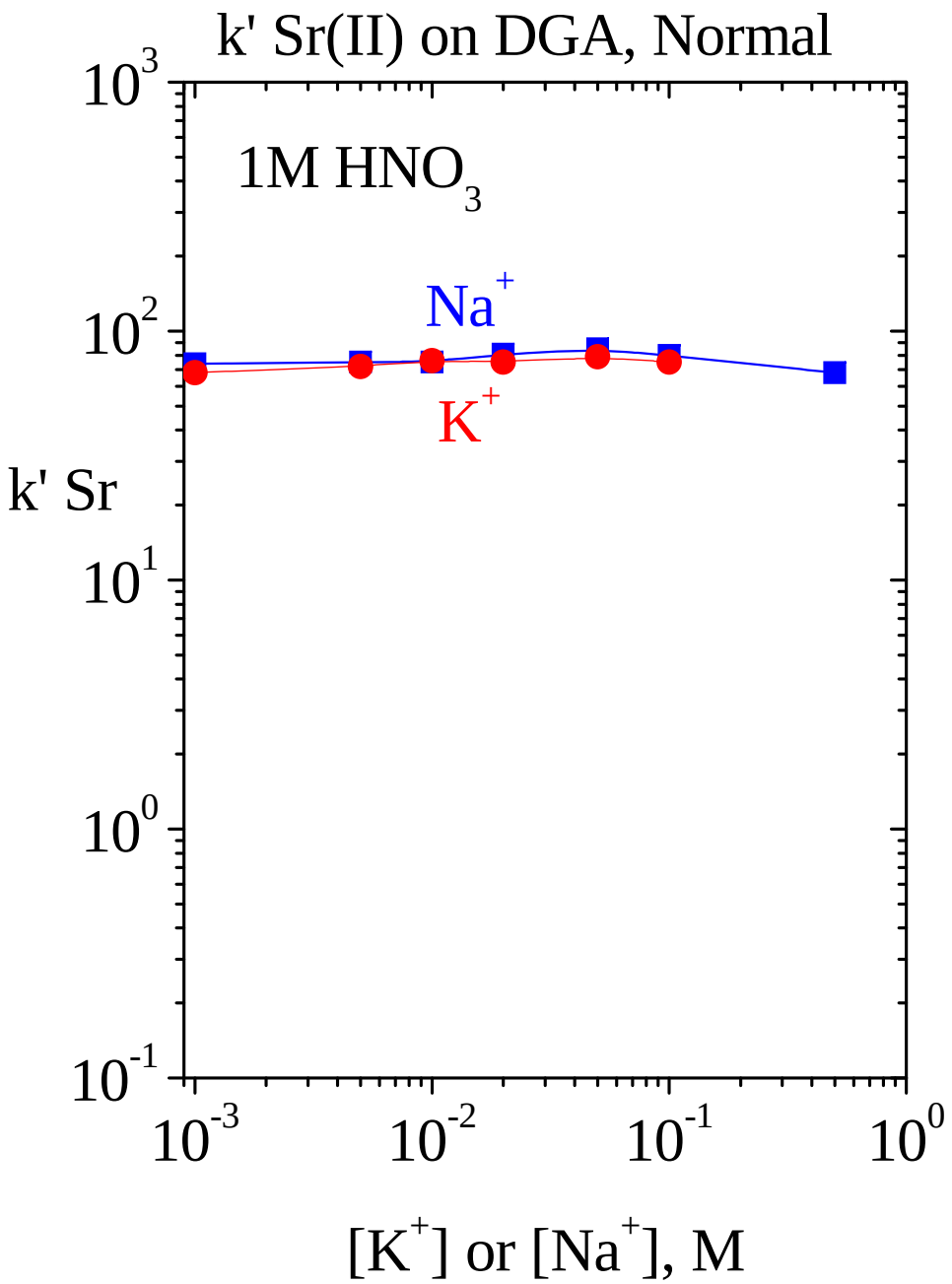
50-100 μm, 2 h, 21(1)°C



Ionic Radii(Å)				
	Sr^{2+}(1.18)	Pb^{2+}(1.19)	Ca^{2+}(1.00)	Mg^{2+}(0.72)
	Na^{+}(1.02)	K^{+}(1.38)	NH_4^{+}(1.44)	H_3O^{+}(1.43)

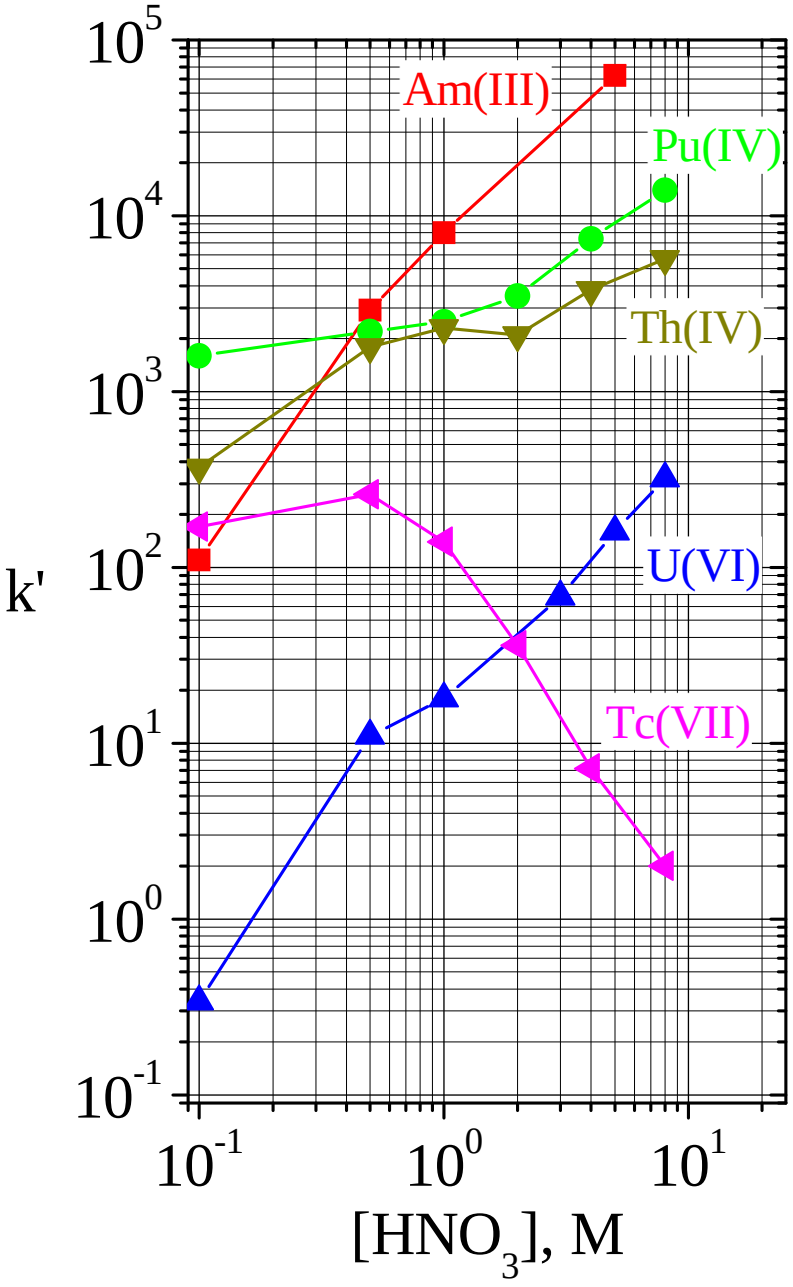


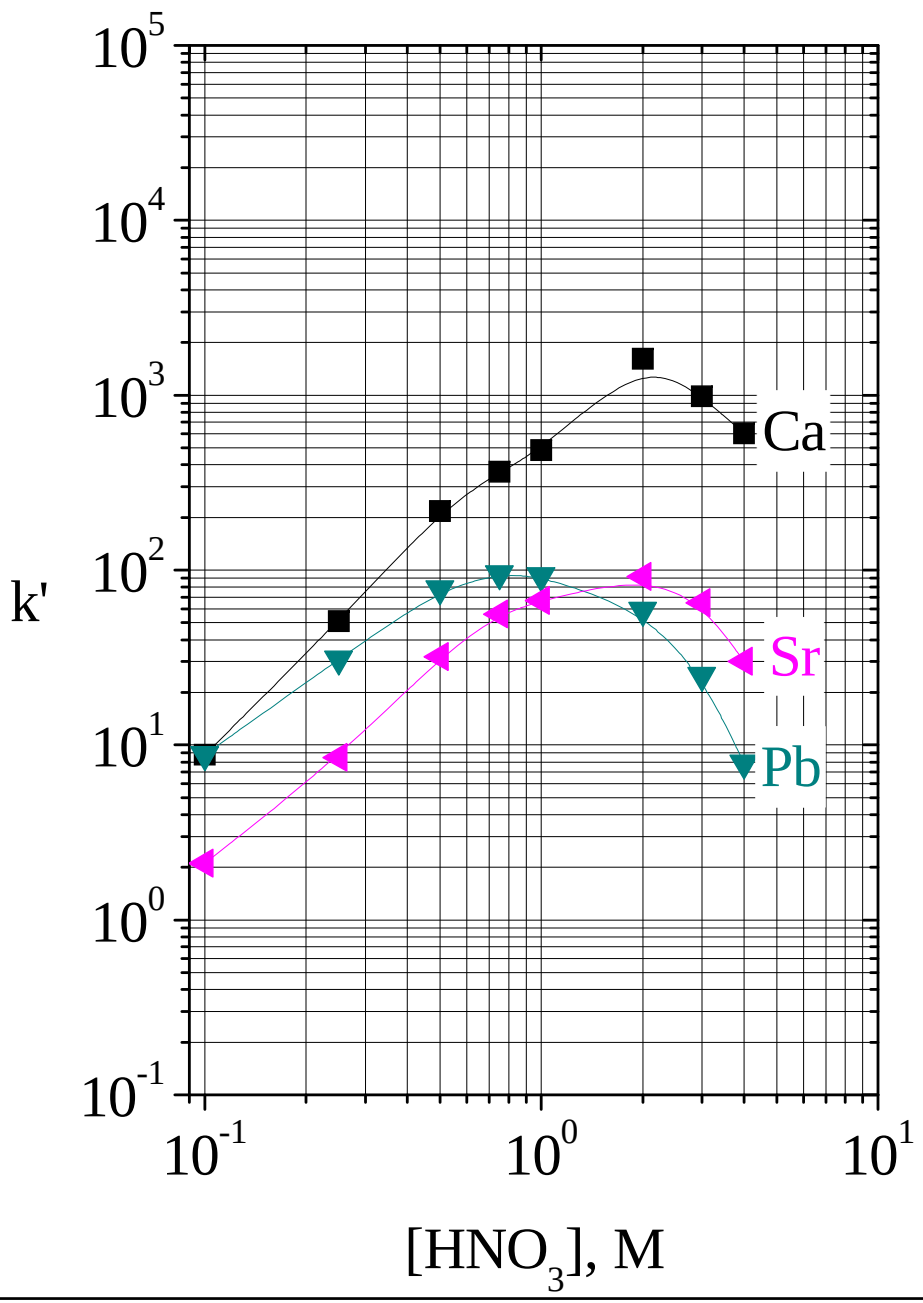


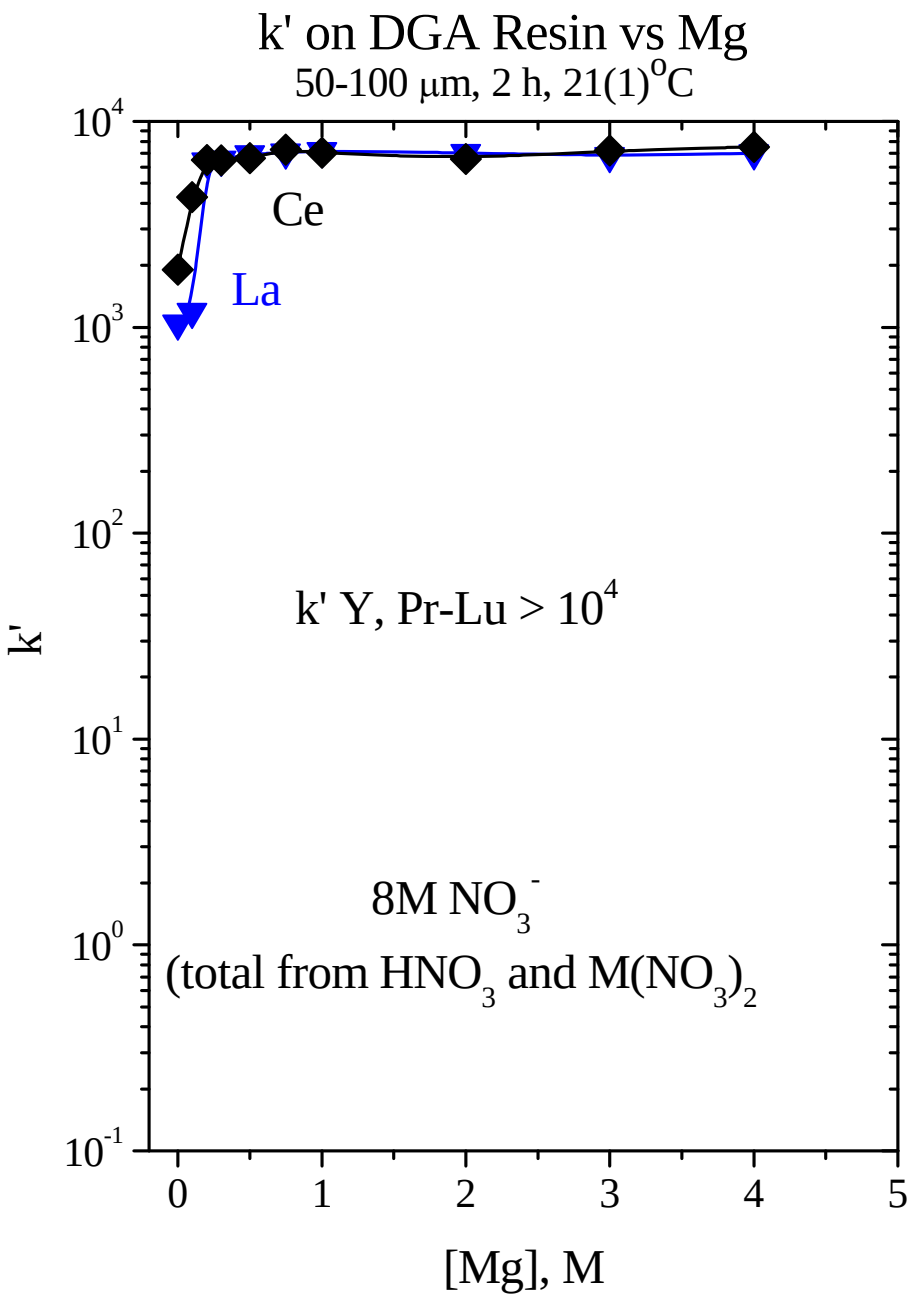


DGA Resin is an alternative for Sr Separation from high potassium samples

k’ on DGA Resin, Normal







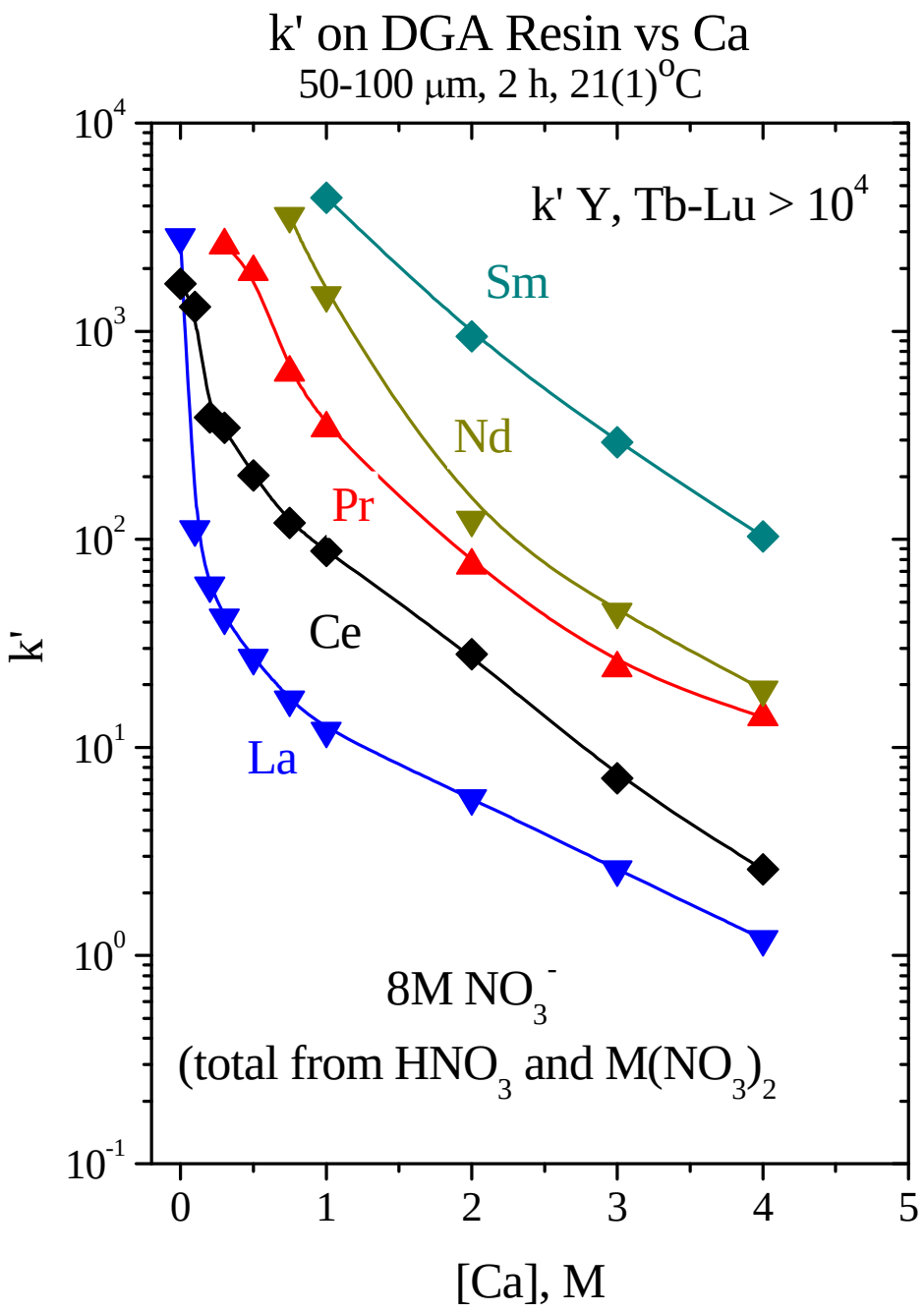
Tolerates High Levels of:

- -Na, K
- -Mg
- -Fe(II)/Fe(III)
- -Al

Uptake of Ac, U(VI) and light lanthanides can be reduced by high:

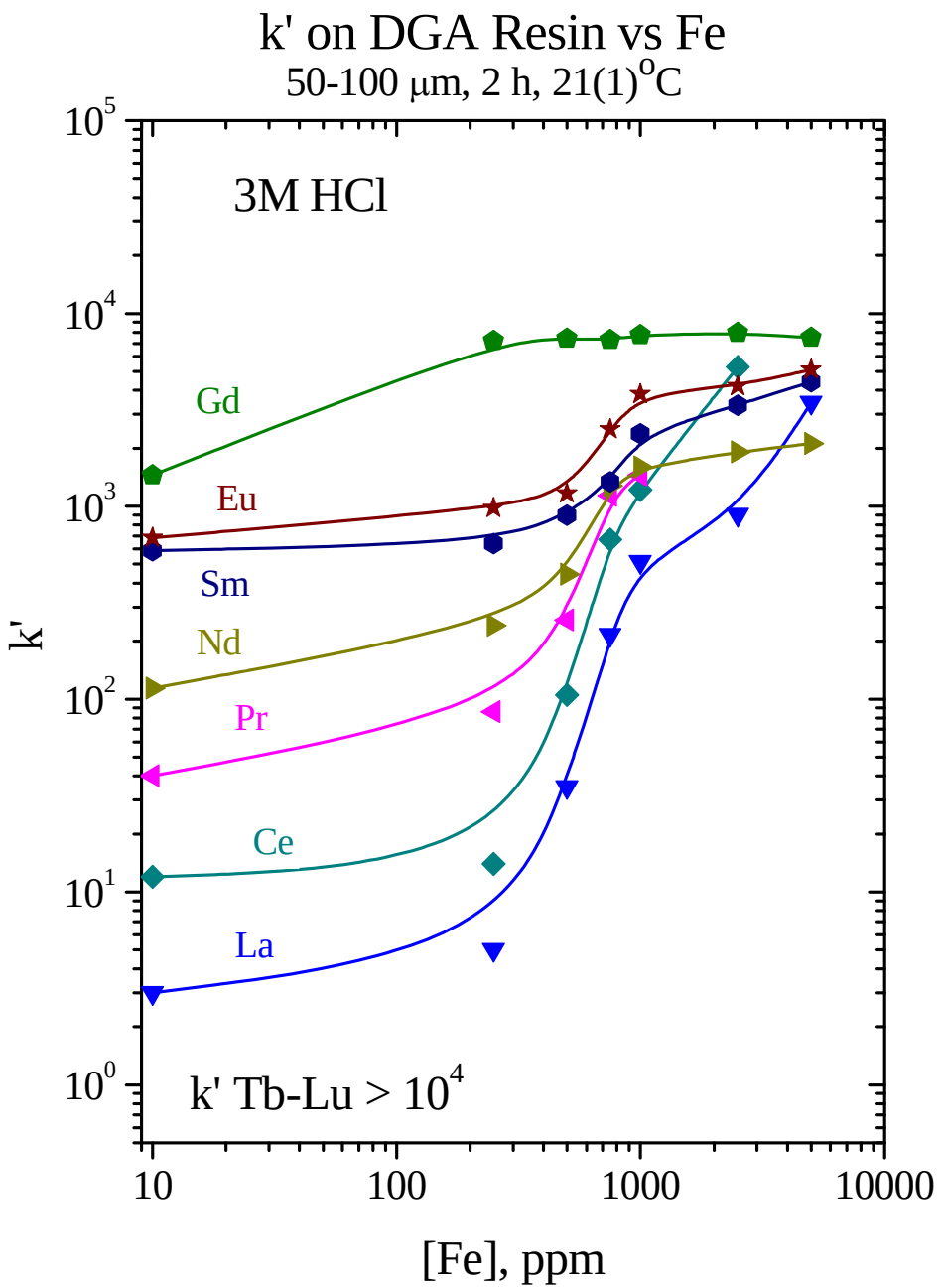
- -Ca

High Fe(III) concentrations in HCl and improve uptakes.

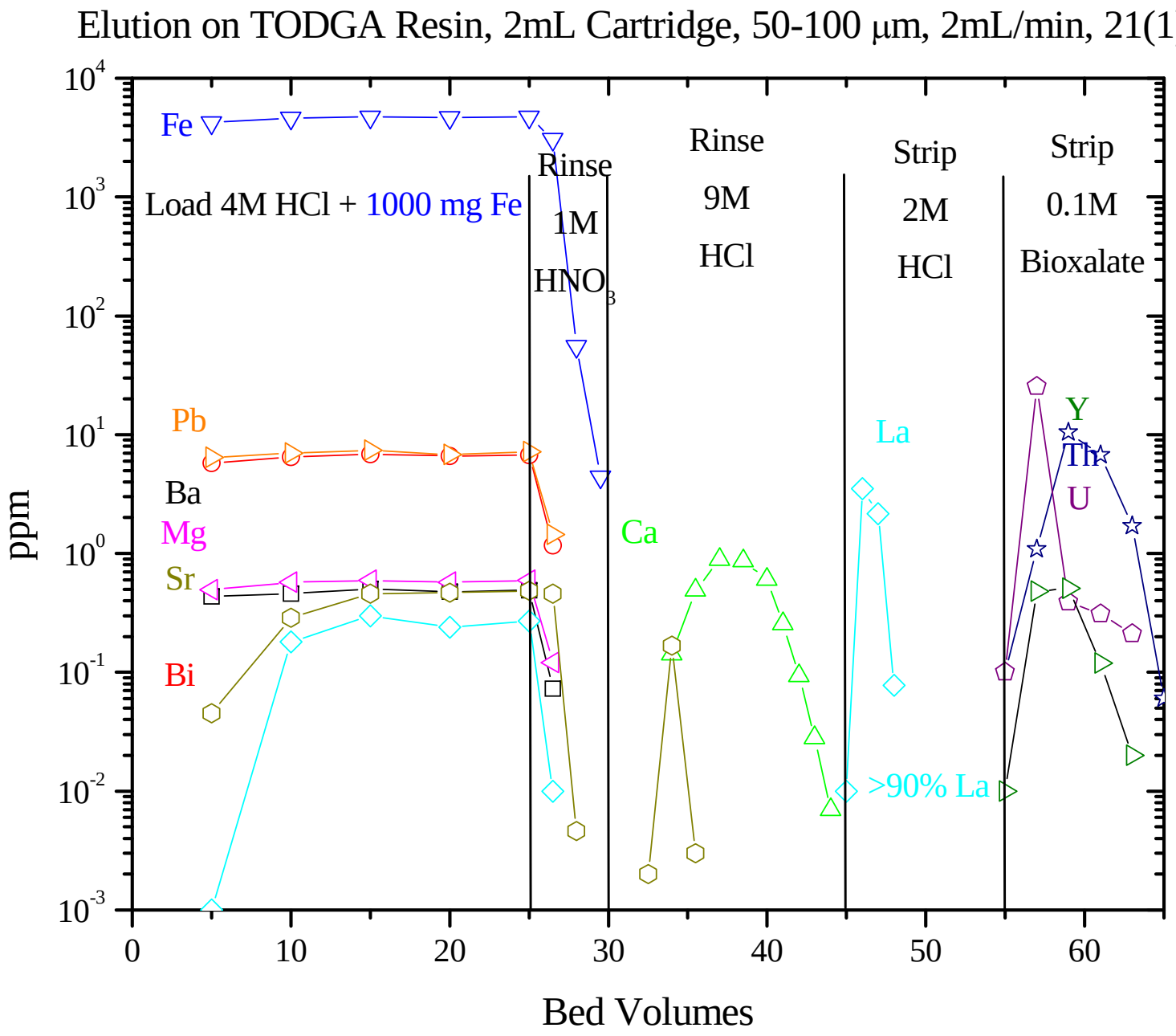


High Ca concentrations in nitrate media significantly reduce the uptake of Ac, La-Sm, U(VI).

Am/Cm uptake still remain >10^3 for Ca concentrations up to 3M



High Fe(III) concentrations in chloride media significantly can increase the uptake of metal ions on DGA.


Elution on TODGA Resin, 2mL Cartridge, 50-100 μm, 2mL/min, 21(1)°C
ppm
Bed Volumes
Load 4M HCl + 1000 mg Fe
Rinse
1M
HNO3
Rinse
9M
HCl
Strip
2M
HCl
Strip
0.1M
Bioxalate
Fe
Pb
Ba
Mg
Sr
Bi
Ca
La
>90% La
Y
Th
U