Optimizing Choice of Preconcentration and Separation Chemistries

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RRMC
Radiobioassay & Radiochemical Measurements Conference

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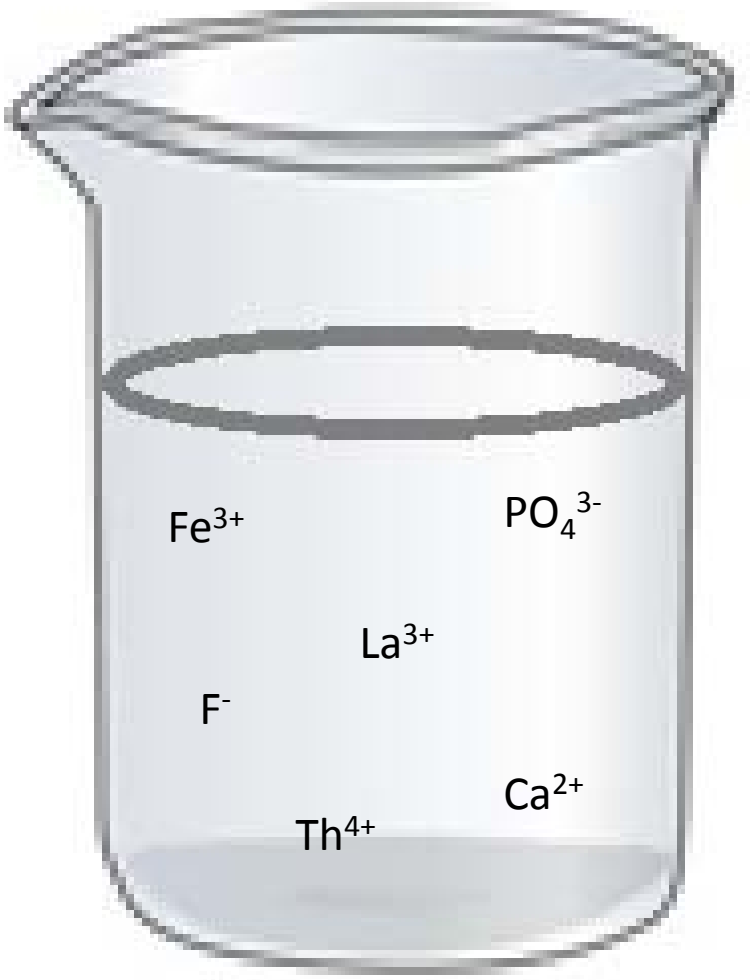
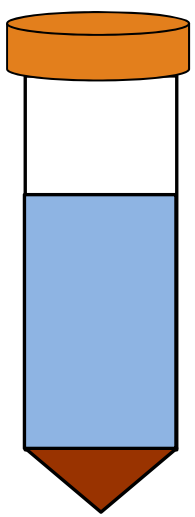
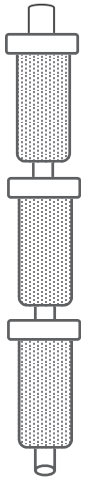
Honolulu, Hawaii

Precipitation + Column Separation







Rapid combination for concentration and matrix removal, while maintaining high yield and large decontamination factors.

Outline

Basics of Some Common Precipitation Carriers

- Solubility
- What do they carry
- Redox?
- Matrix

Impact of carriers on separation chemistry

- Complexation
- Competition
- Th/Phosphate

Methods to reduce impact of carriers

Common Precipitation Chemistries

Precipitate	Ksp	Analytes	Notes
Fe(OH)3	3E-39	Th, Pu, Np, Am, Rare Earths	Rejects Na, K, Mg, Ca if pH 8-9
Ca-phosphate	CaHPO4 = 1E-7 Ca3(PO4)2 = 2E-29	Th, U, Pu, Np, Am, Rare Earths, Sr	U valence adjustment not required, pH 8-9
CaF2	3E-11	Th, U(IV), Np(IV), Pu, Am, Rare Earths	U(IV) valence adjustment required. pH adjustment not required. Good for samples with silicates.
LaF3	2E-19	Th, U(IV), Np(IV), Pu, Am, Rare Earths	
LaF3/CaF2		Th, U(IV), Np(IV), Pu, Am, Rare Earths	

*If $TiCl_3$ is used for valence adjustment, F- is needed to complex Ti(IV)

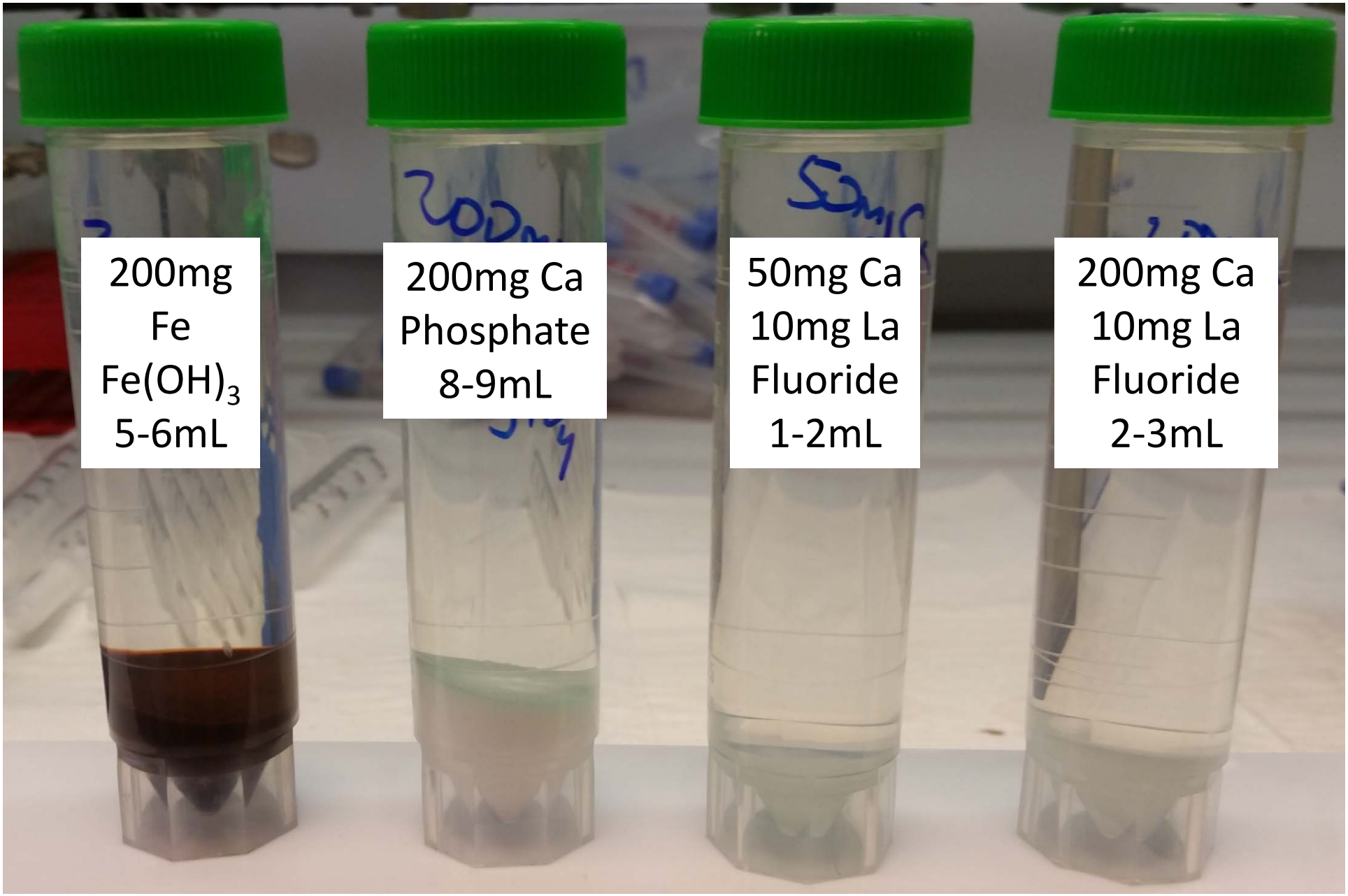
$Ksp = [Sr^{2+}][F^-]^2$ 2.5E-9 [SrF2] = 107mg/L

4.3M F- = 0.02ug/L

Actinide Recoveries with Common Precipitation Chemistries

	% Recovery						
Precipitate	**Th**	**U(VI)**	**U(IV)**	**Np**	**Pu**	**Am**	**Comment**
Fe(OH)3	>99	30	N/A	80	>99	>99	adjust pH 9
Ca-phosphate	>99	98	>99	99	>99	>99	adjust pH 9
CaF2	>99	25	>99	40	>99	>99	pH 2 HNO3
LaF3	>99	15	>99	>99	>99	>99	pH 2 HNO3
LaF3/CaF2	>99	30	>99	90	>99	>99	pH 2 HNO3
100mg/L Fe, Ca or La							

Precipitate Volume

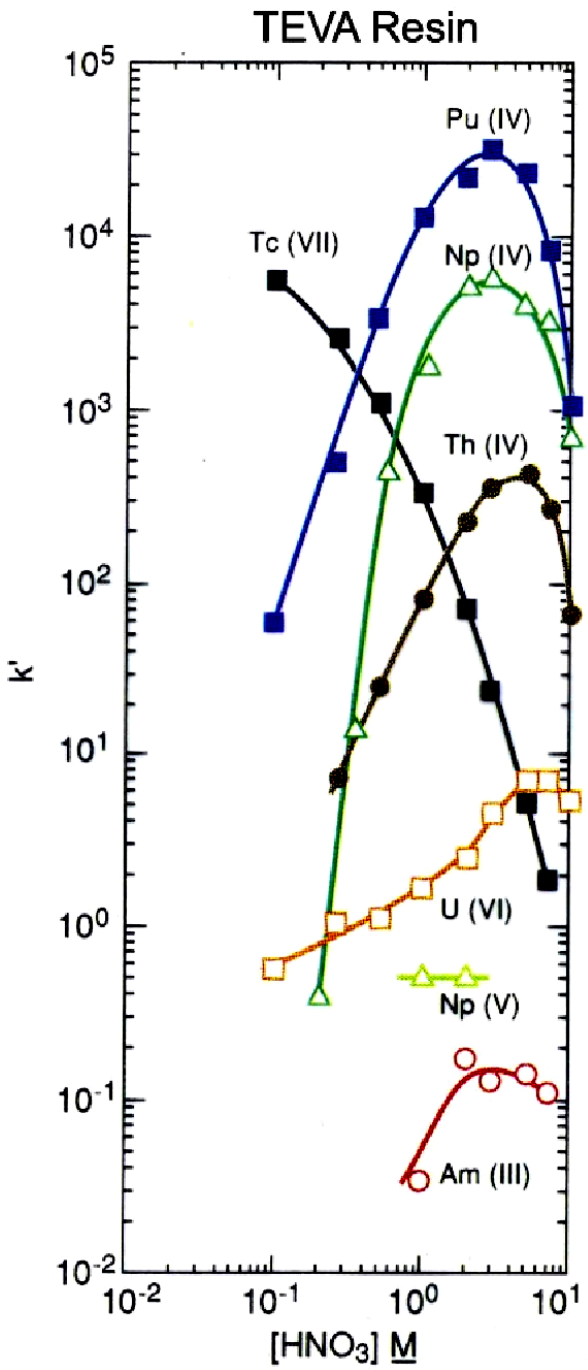


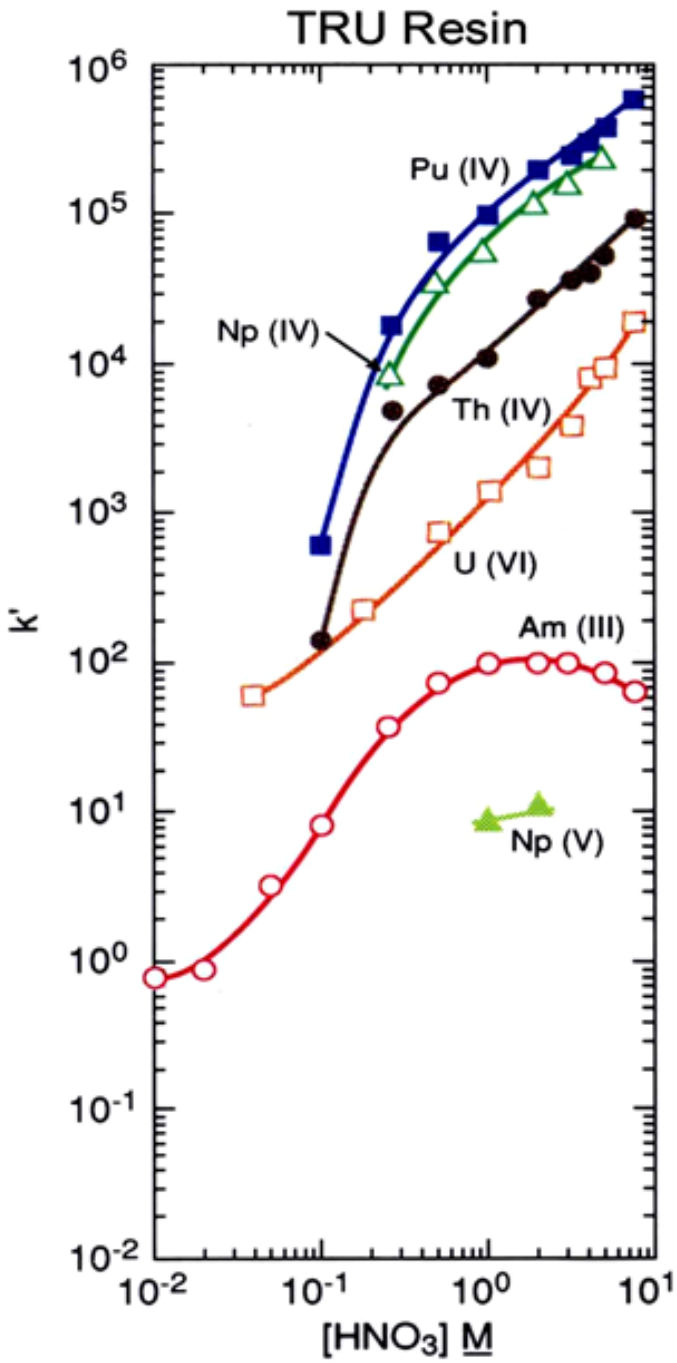
	log formation constant		Impact in HNO3 Load Solution		
Element	**PO43-**	**F-**	**Ca**	**Fe**	**La**
Th(IV)	11, 23, 31 μ = 0.35, HPO4	8, 14, 19, 22 μ = 0			
U(VI)	7.2 μ = 0, HPO4	5.1, 8.6, 10.9, 11.7, 11.5 μ = 0		TRU	TRU
U(IV)		9.3, 16, 22, 26, 27, 29 μ = 0			
Np(IV)		4.8, 7.6, 9.9, 11 μ = 4.0			
Pu(IV)		8.8, 15.7 μ = 0			
Am(III)	24.8 μ = 0, PO4	3.4, 5.8 μ = 0	DGA	TRU	DGA/TRU
"The chemistry of the actinide and transactinide elements," 3rd Edition, Editors Lester R. Morss, Norman M. Edelstein and Jean Fuger, 2006, Springer.					

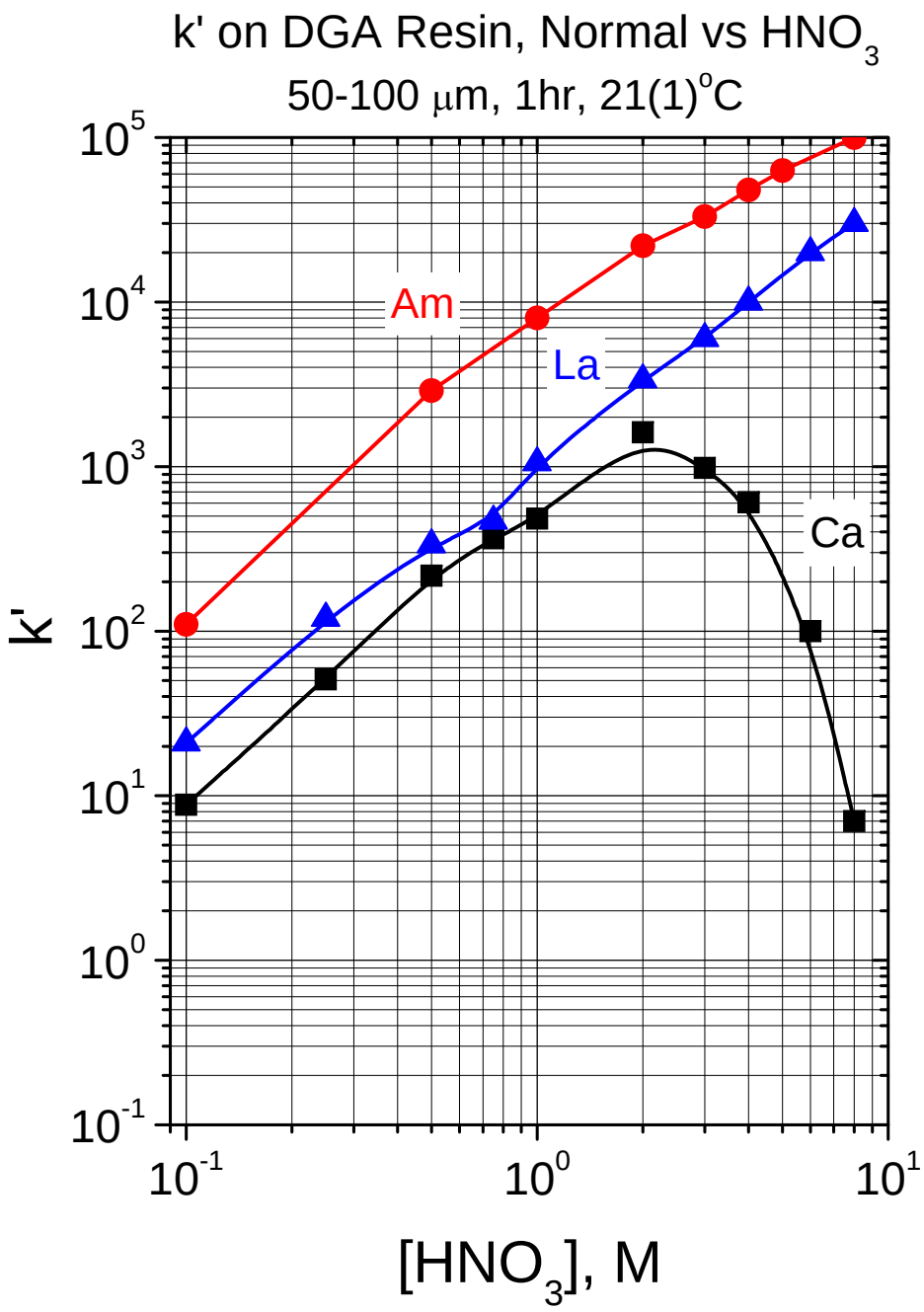
Table 2. Experimental and Calculated Hydration Enthalpies for Anions (in kJ mole^{-1}).

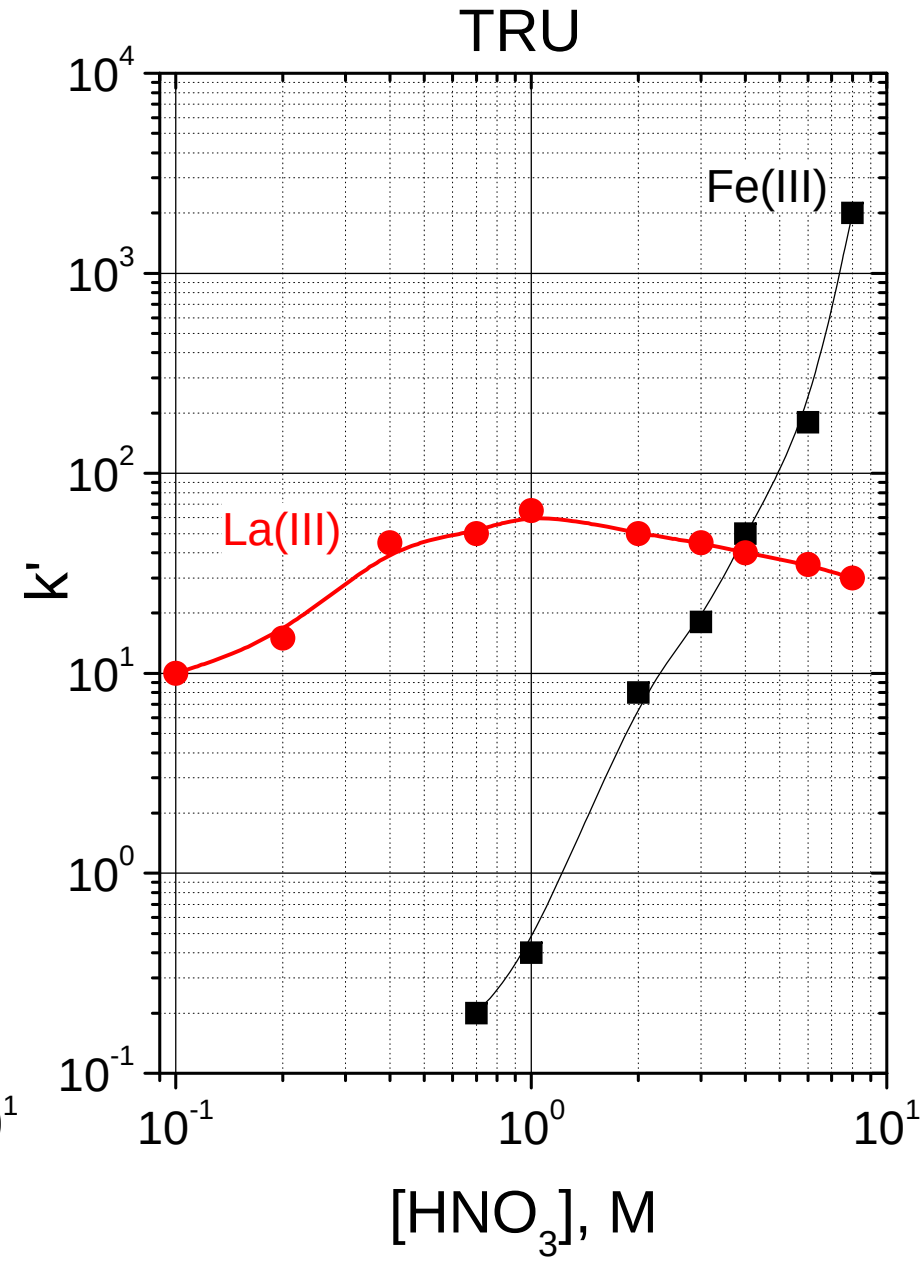
Anion	$-\Delta H^{\circ}_{hyd}$ (expt.)	$-\Delta H^{\circ}_{hyd}$ (calc.)
F^-	515	520
Cl^-	381	390
Br^-	347	360
I^-	305	320
NO_2^-	405	380
NO_3^-	314	320
ClO_3^-	348	310
ClO_4^-	229	260
BrO_3^-	349	320
IO_3^-	326	330
OH^-	460	410
SH^-	333	310
NCO^-	322	370
NCS^-	310	310
CN^-	324	330
N_3^-	352	...
HF_2^-	468	...
BF_4^-	274	270
MnO_4^-	248	260
HCO_3^-	380	360
S^{2-}	1495	1520
SO_4^{2-}	1059	1080
SeO_4^{2-}	998	1030
CO_3^{2-}	1314	1300
CrO_4^{2-}	1103	1040
PO_4^{3-}	2835	

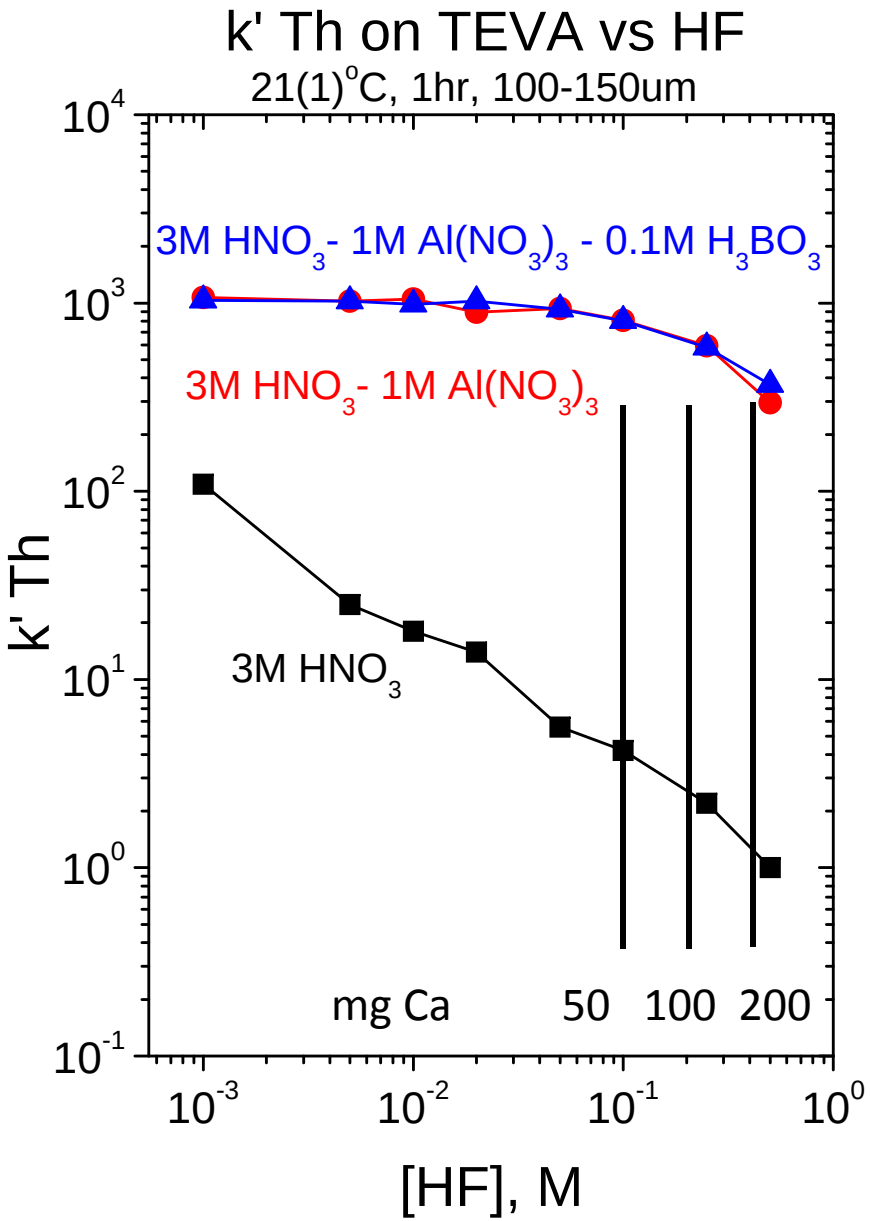
Derek *W.* Smith **Ionic Hydration Enthalpies** Journal *of* Chemical Education
Volume 54, Number 9, September 1977 / 540-542

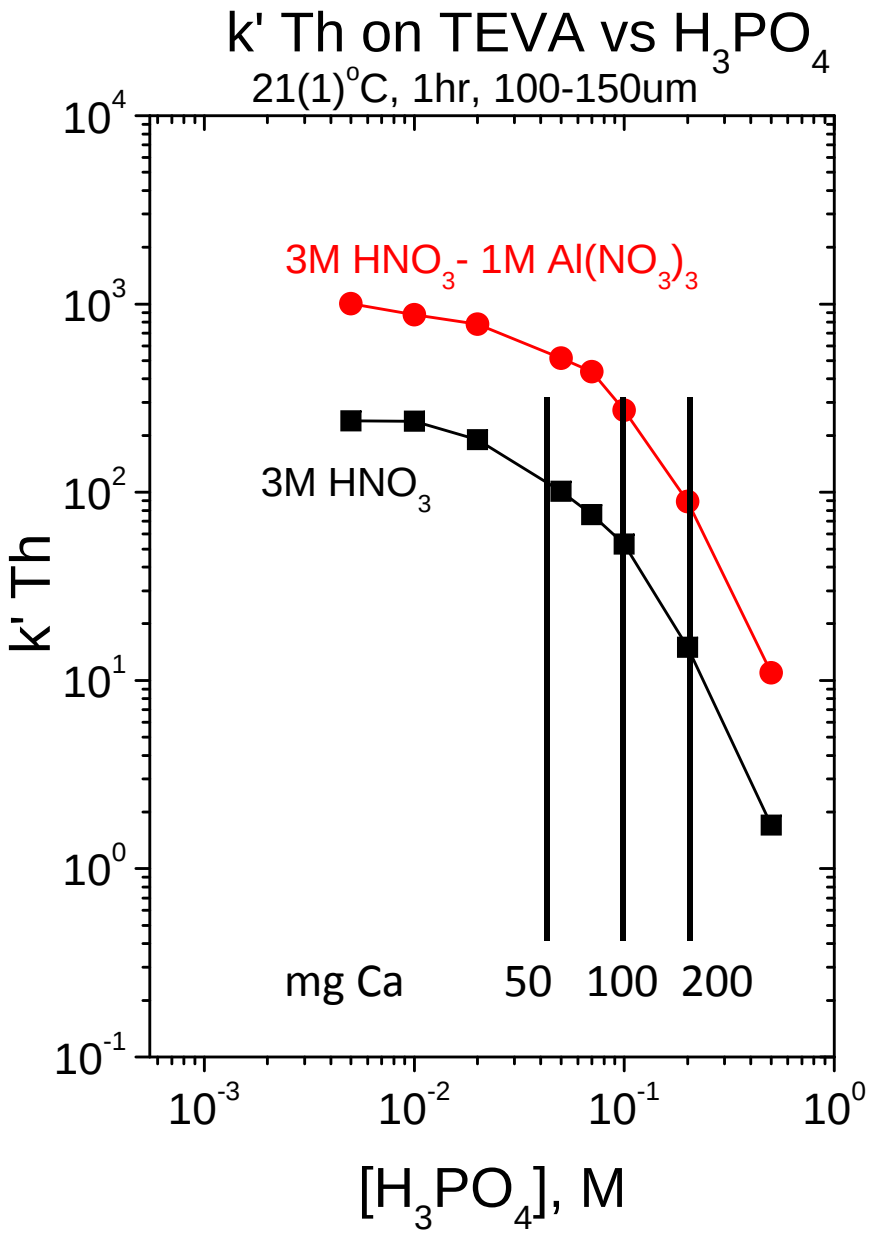

TEVA Resin
k'
[HNO3] M
Pu (IV)
Tc (VII)
Np (IV)
Th (IV)
U (VI)
Np (V)
Am (III)

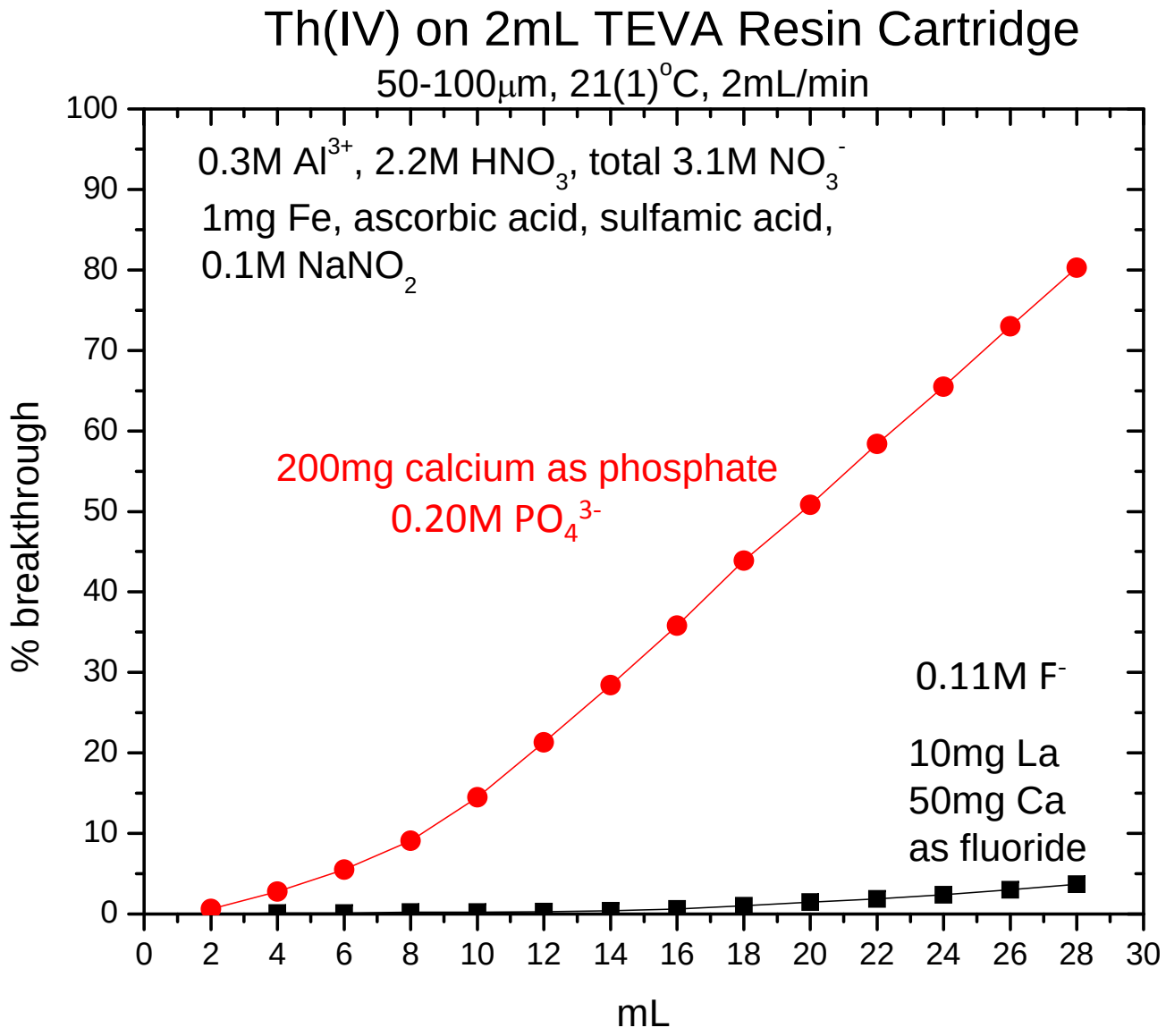

TRU Resin
k'
[HNO3] M
Pu (IV)
Np (IV)
Th (IV)
U (VI)
Am (III)
Np (V)

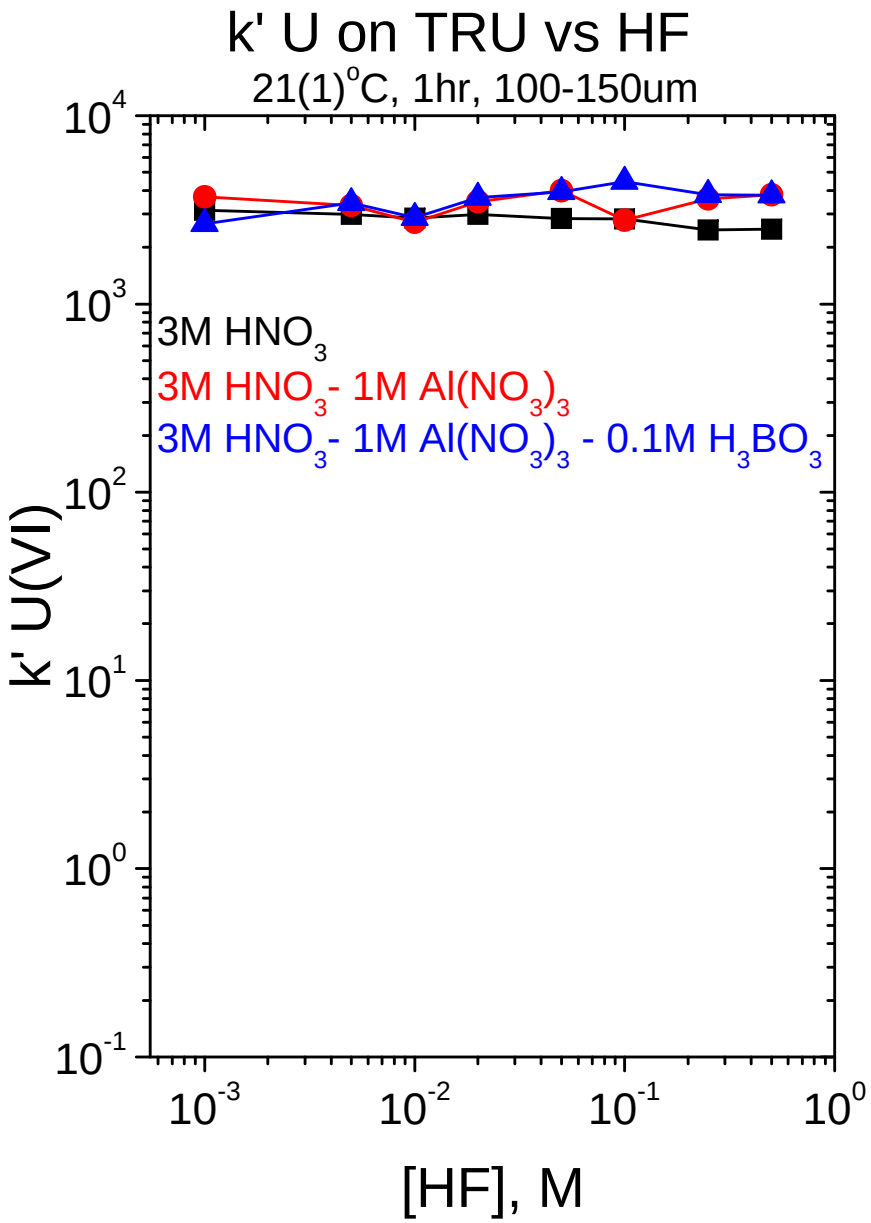

k' on DGA Resin, Normal vs HNO3
50-100 μm, 1hr, 21(1)°C
Am
La
Ca
k'
[HNO3], M

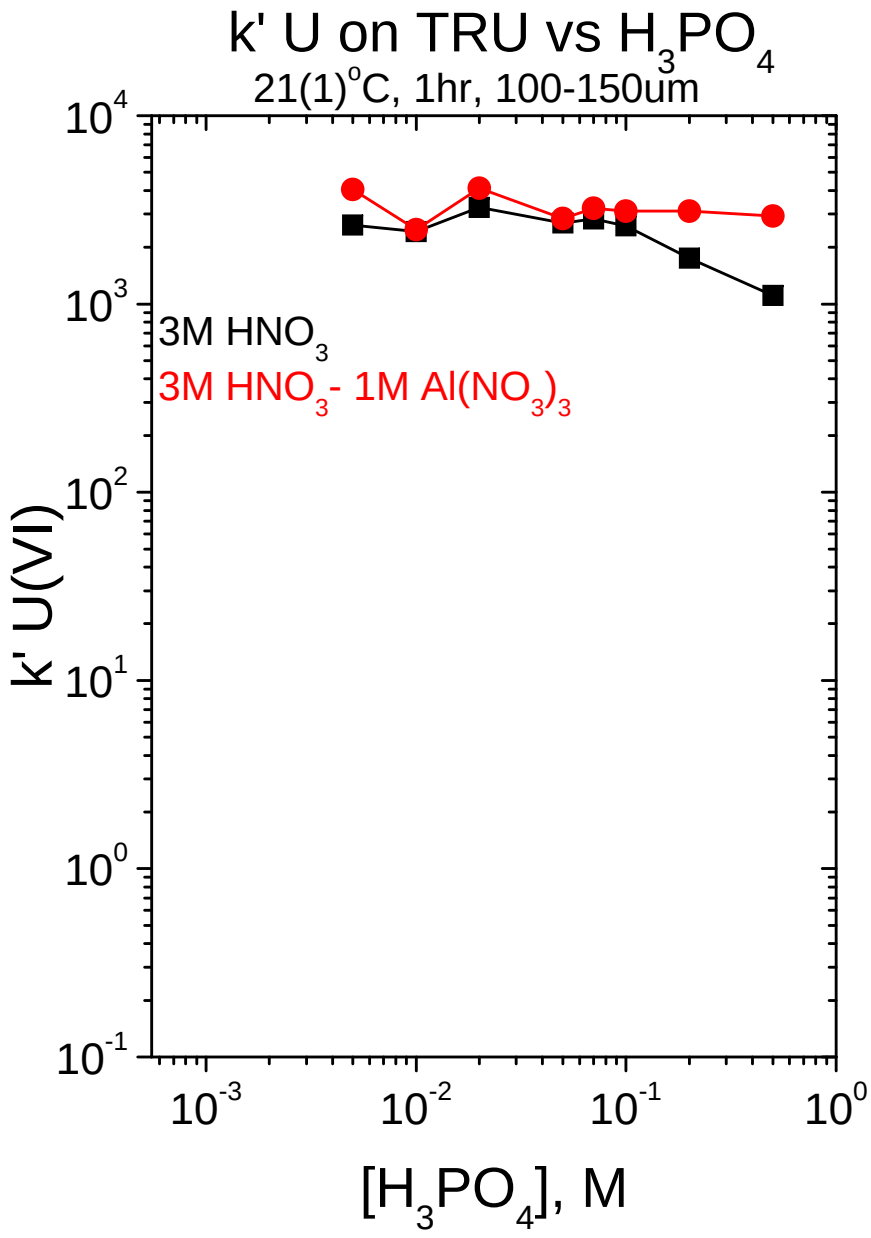

TRU
Fe(III)
La(III)
k'
[HNO3], M

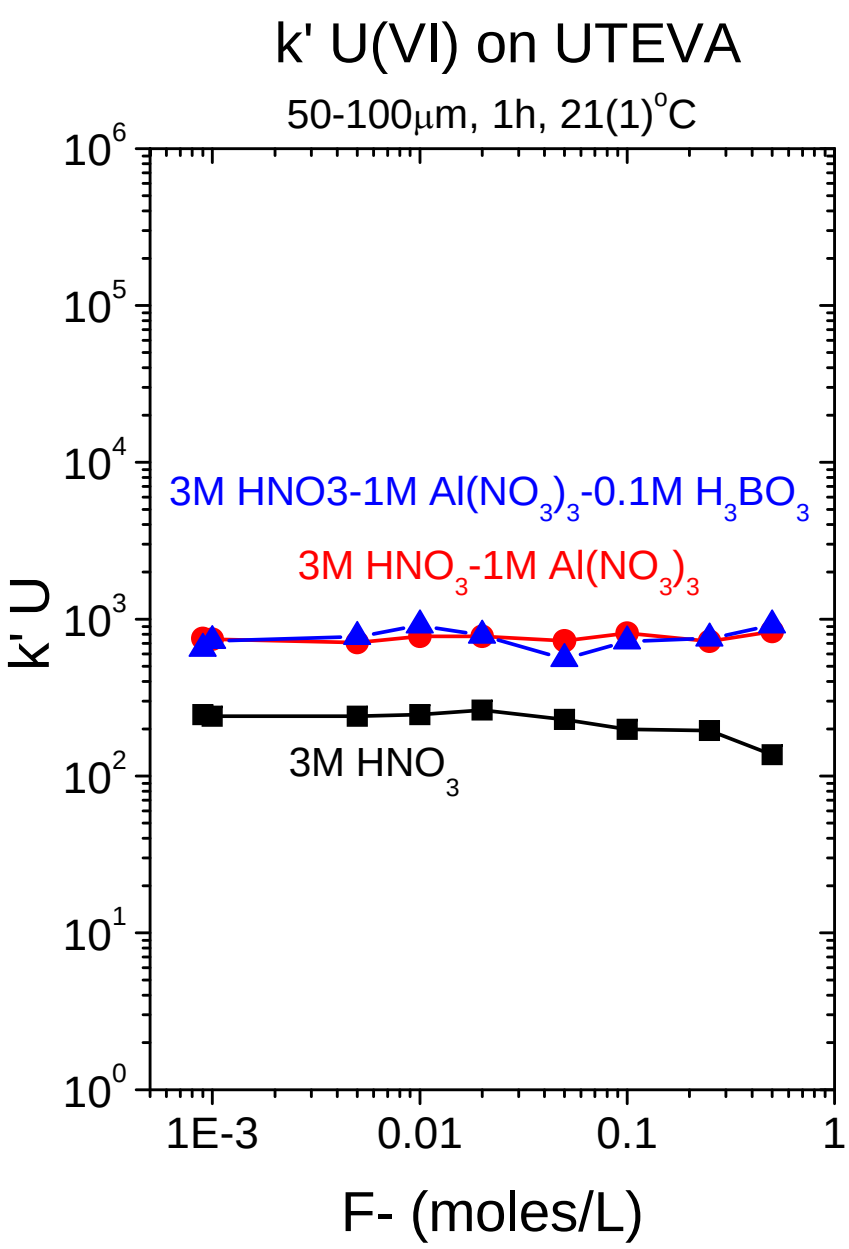

k' Th on TEVA vs HF
21(1)°C, 1hr, 100-150um
3M HNO3- 1M Al(NO3)3 - 0.1M H3BO3
3M HNO3- 1M Al(NO3)3
3M HNO3
mg Ca 50 100 200
k' Th
[HF], M

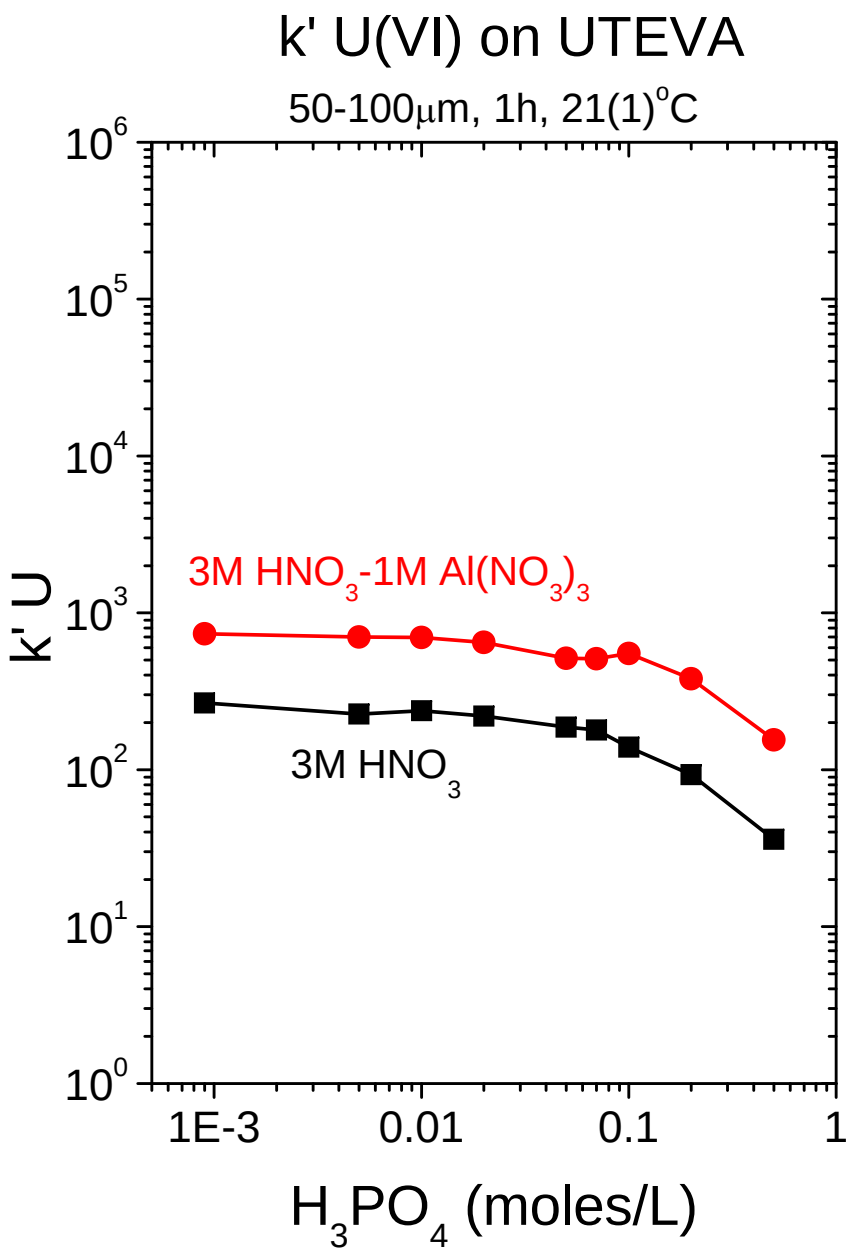

k' Th on TEVA vs H3PO4
21(1)°C, 1hr, 100-150um
3M HNO3- 1M Al(NO3)3
3M HNO3
mg Ca 50 100 200
k' Th
[H3PO4], M

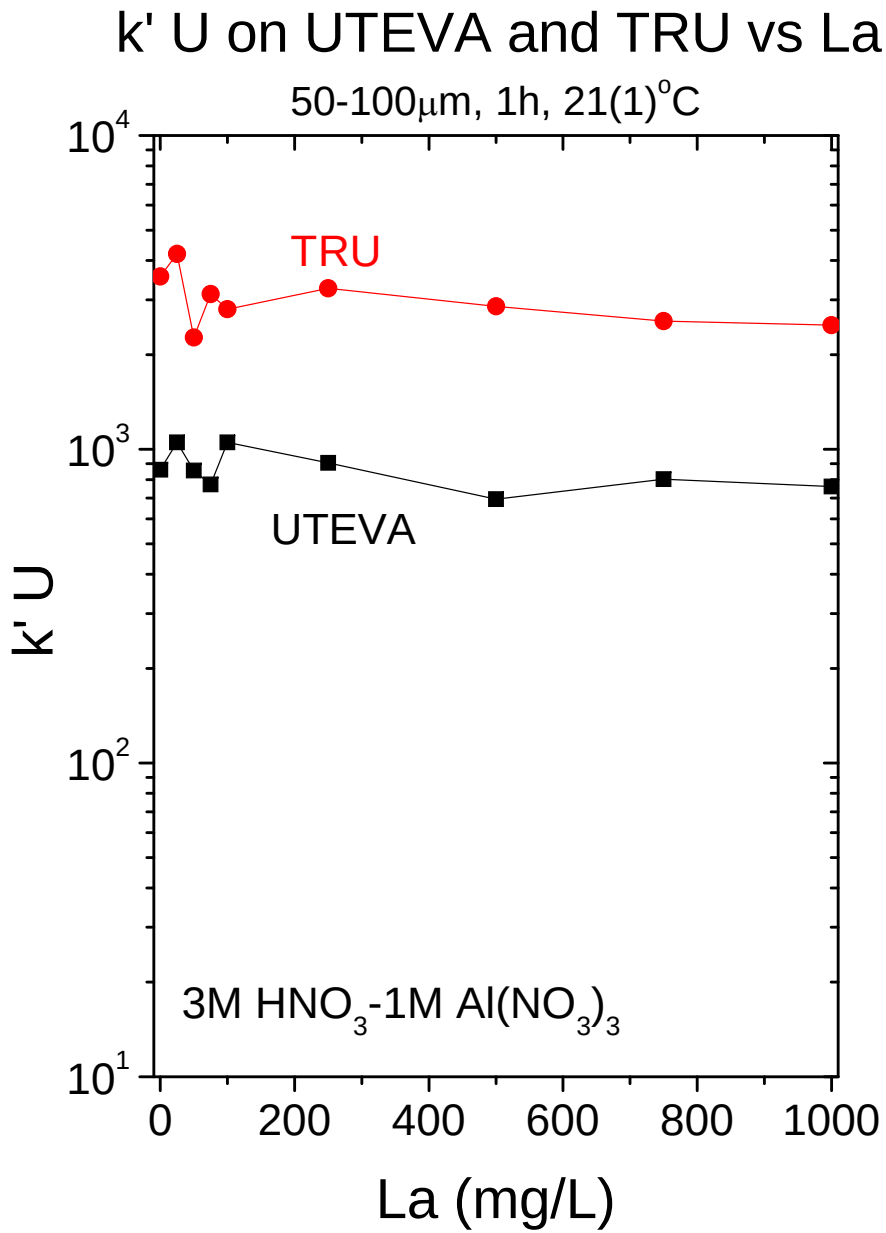

Th(IV) on 2mL TEVA Resin Cartridge
50-100μm, 21(1)°C, 2mL/min
0.3M Al3+, 2.2M HNO3, total 3.1M NO3-
1mg Fe, ascorbic acid, sulfamic acid,
0.1M NaNO2
200mg calcium as phosphate
0.20M PO4 3-
0.11M F-
10mg La
50mg Ca
as fluoride
% breakthrough
mL
0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

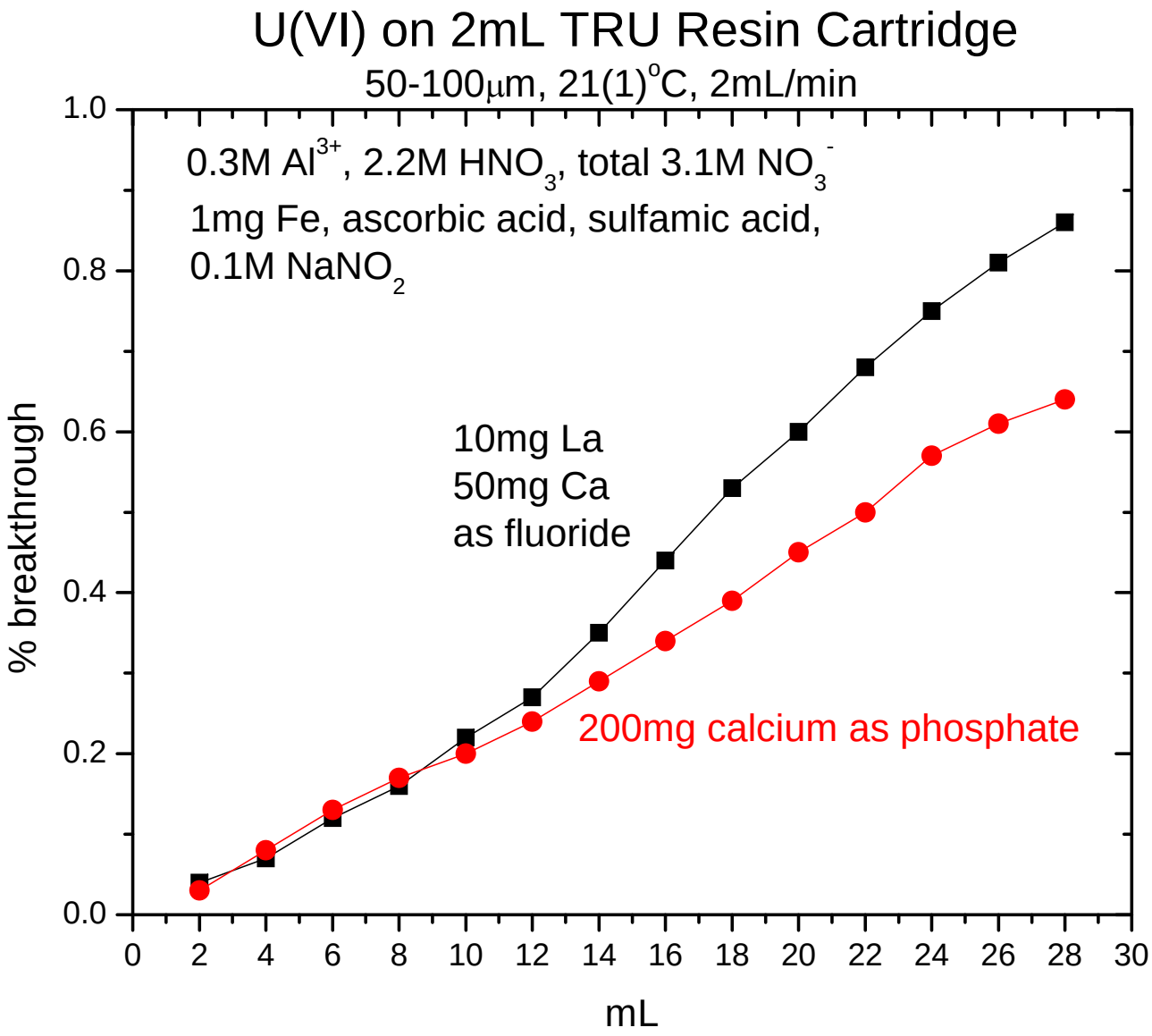

k' U on TRU vs HF
21(1)°C, 1hr, 100-150um
k' U(VI)
[HF], M
3M HNO3
3M HNO3- 1M Al(NO3)3
3M HNO3- 1M Al(NO3)3 - 0.1M H3BO3

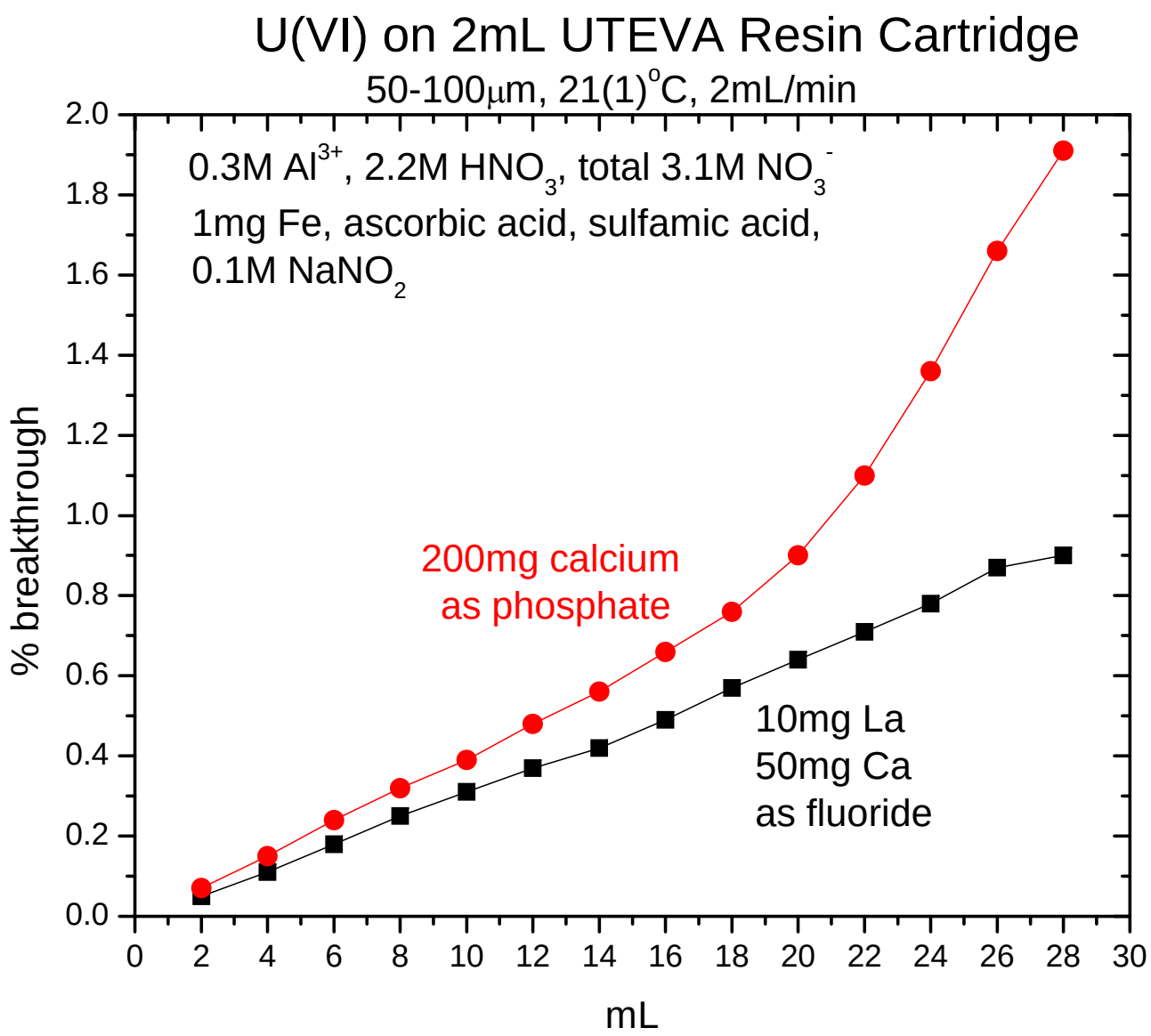

k' U on TRU vs H3PO4
21(1)°C, 1hr, 100-150um
k' U(VI)
[H3PO4], M
3M HNO3
3M HNO3- 1M Al(NO3)3


k' U(VI) on UTEVA
50-100μm, 1h, 21(1)°C
k' U
10^6
10^5
10^4
10^3
10^2
10^1
10^0
3M HNO3-1M Al(NO3)3-0.1M H3BO3
3M HNO3-1M Al(NO3)3
3M HNO3
1E-3
0.01
0.1
1
F- (moles/L)


k' U(VI) on UTEVA
50-100μm, 1h, 21(1)°C
k' U
10^6
10^5
10^4
10^3
10^2
10^1
10^0
3M HNO3-1M Al(NO3)3
3M HNO3
1E-3
0.01
0.1
1
H3PO4 (moles/L)


k' U on UTEVA and TRU vs La
50-100μm, 1h, 21(1)°C
TRU
UTEVA
3M HNO3-1M Al(NO3)3
k' U
La (mg/L)
10^4
10^3
10^2
10^1
0
200
400
600
800
1000


U(VI) on 2mL TRU Resin Cartridge
50-100μm, 21(1)°C, 2mL/min
0.3M Al3+, 2.2M HNO3, total 3.1M NO3-
1mg Fe, ascorbic acid, sulfamic acid,
0.1M NaNO2
10mg La
50mg Ca
as fluoride
200mg calcium as phosphate
% breakthrough
mL
0.0
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30


U(VI) on 2mL UTEVA Resin Cartridge
50-100μm, 21(1)°C, 2mL/min
0.3M Al3+, 2.2M HNO3, total 3.1M NO3-
1mg Fe, ascorbic acid, sulfamic acid,
0.1M NaNO2
200mg calcium
as phosphate
10mg La
50mg Ca
as fluoride
% breakthrough
mL
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0
2
4
6
8
10
12
14
16
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22
24
26
28
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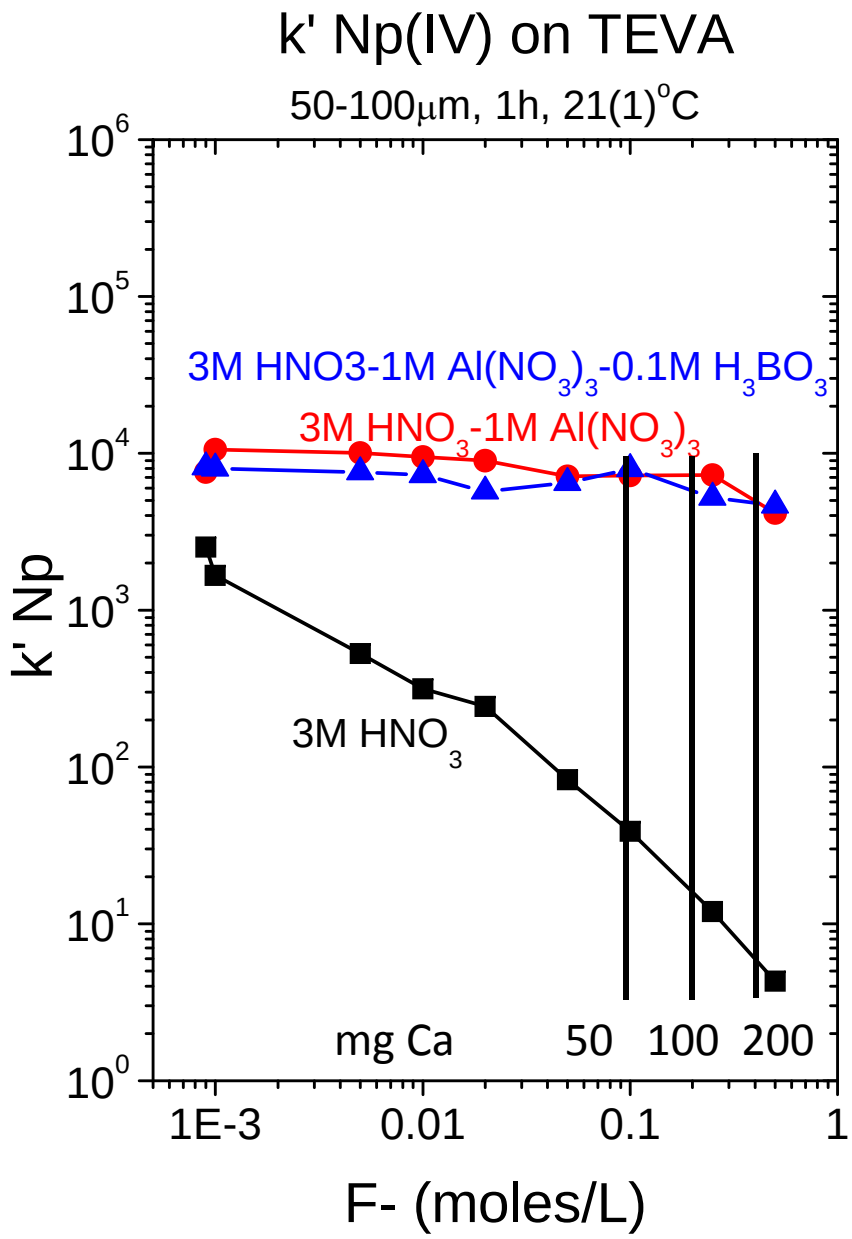
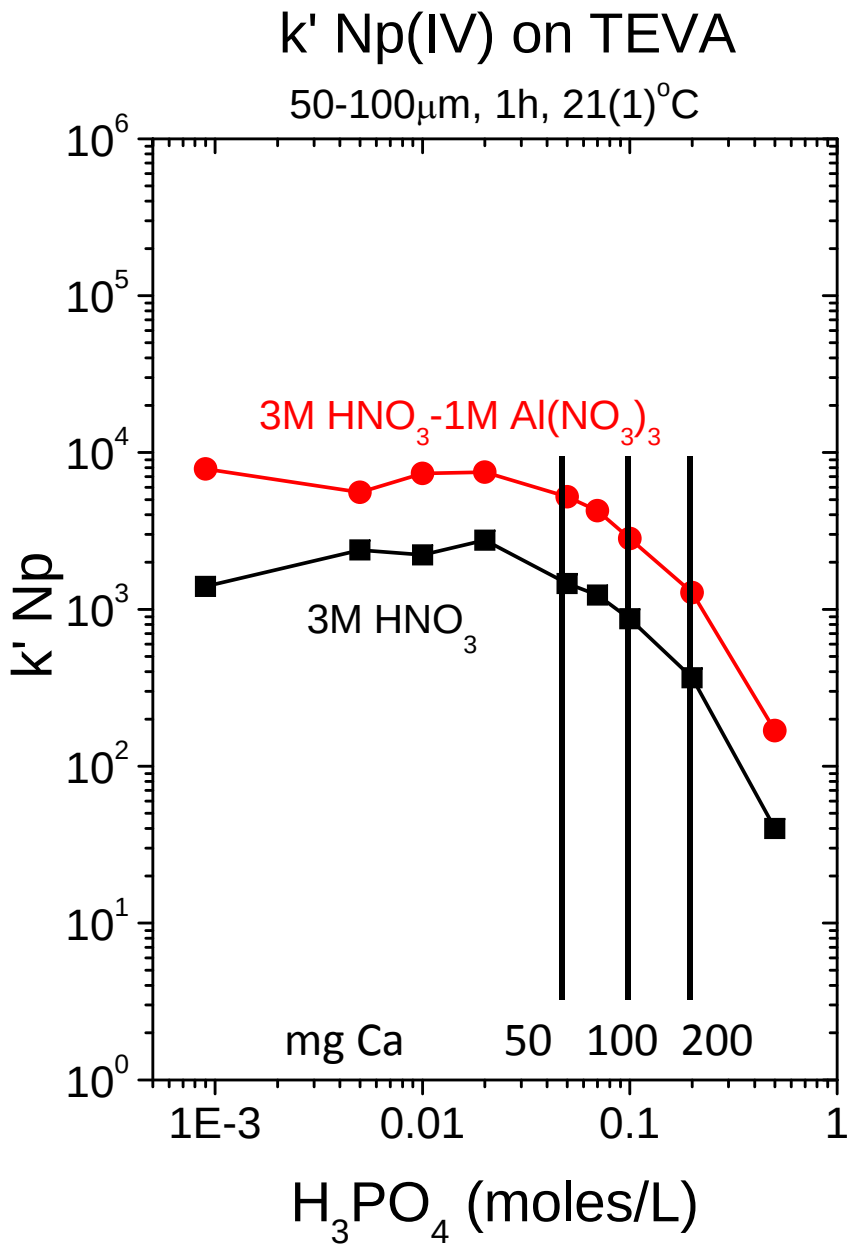
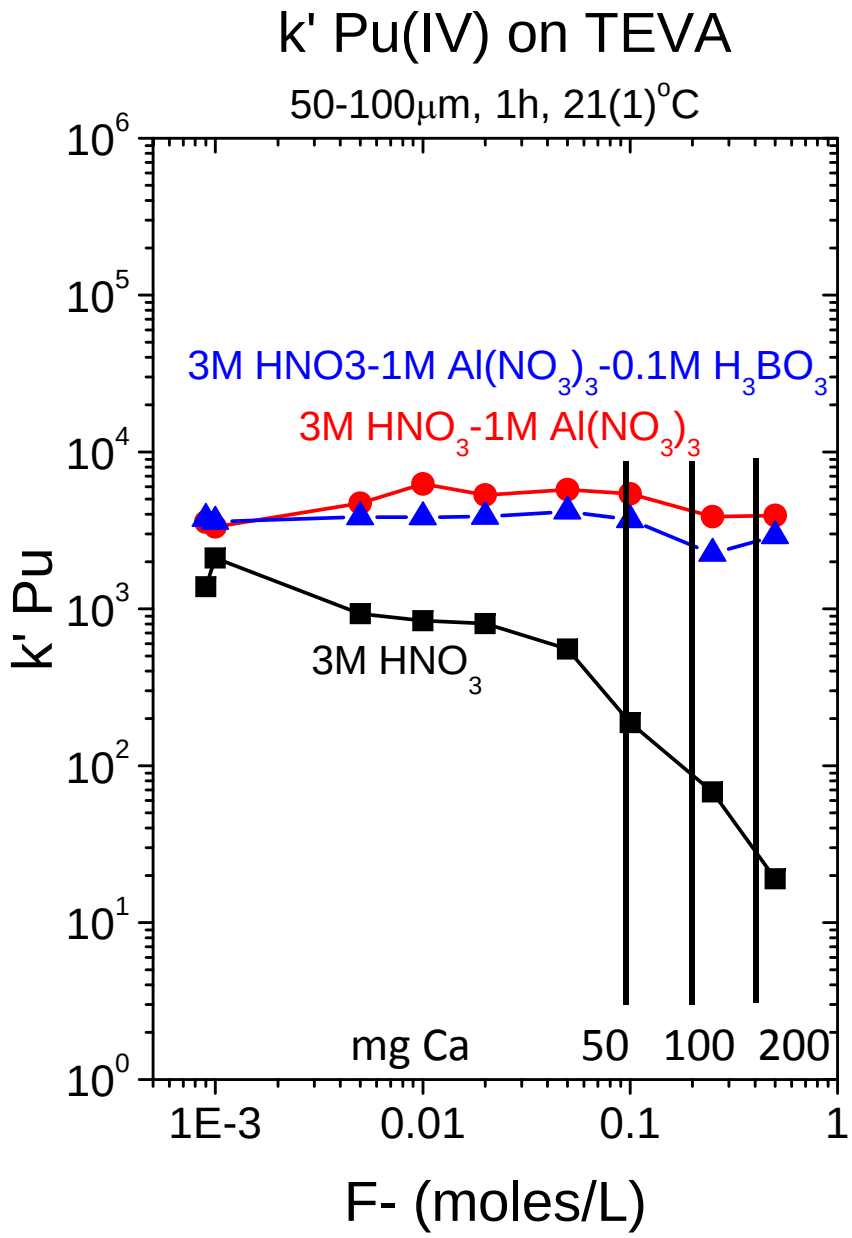
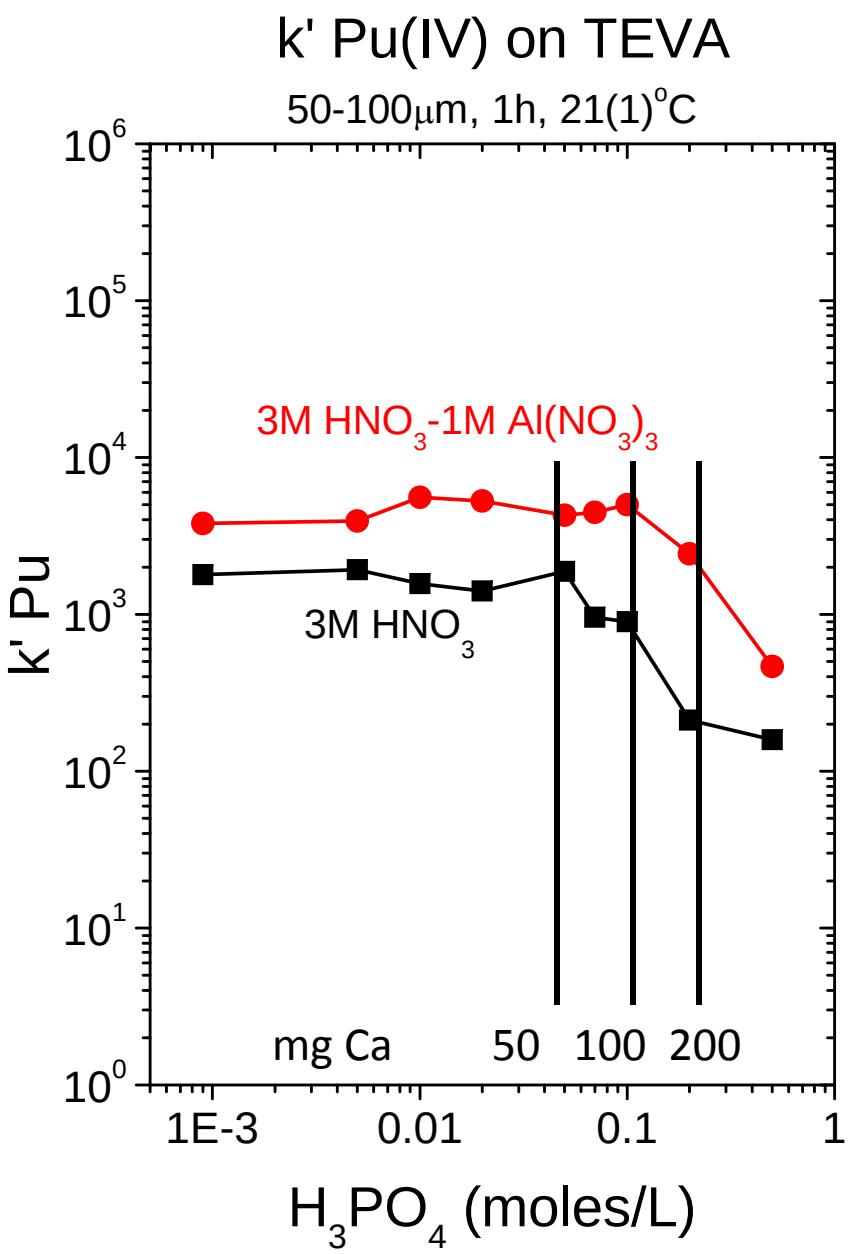
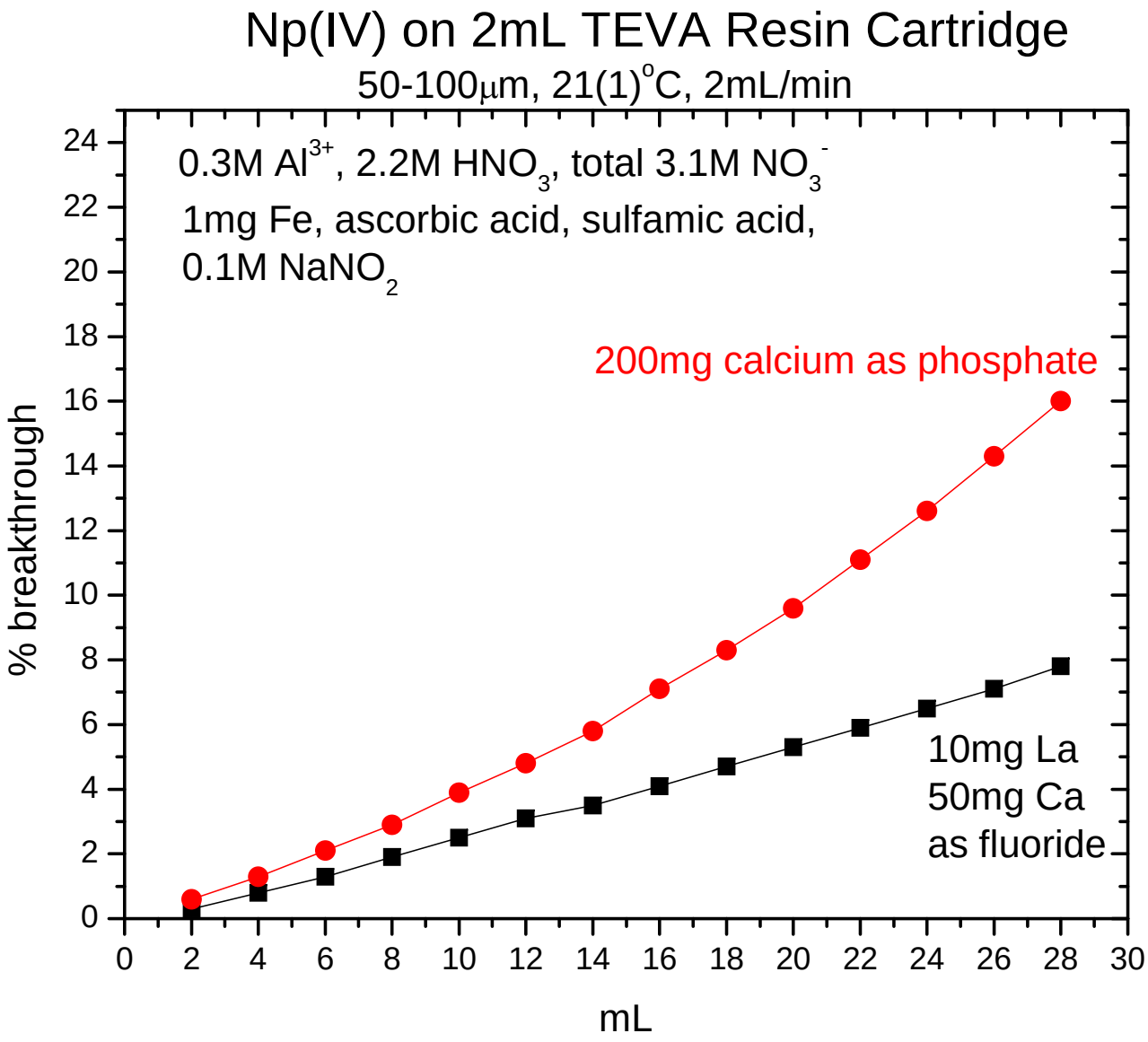
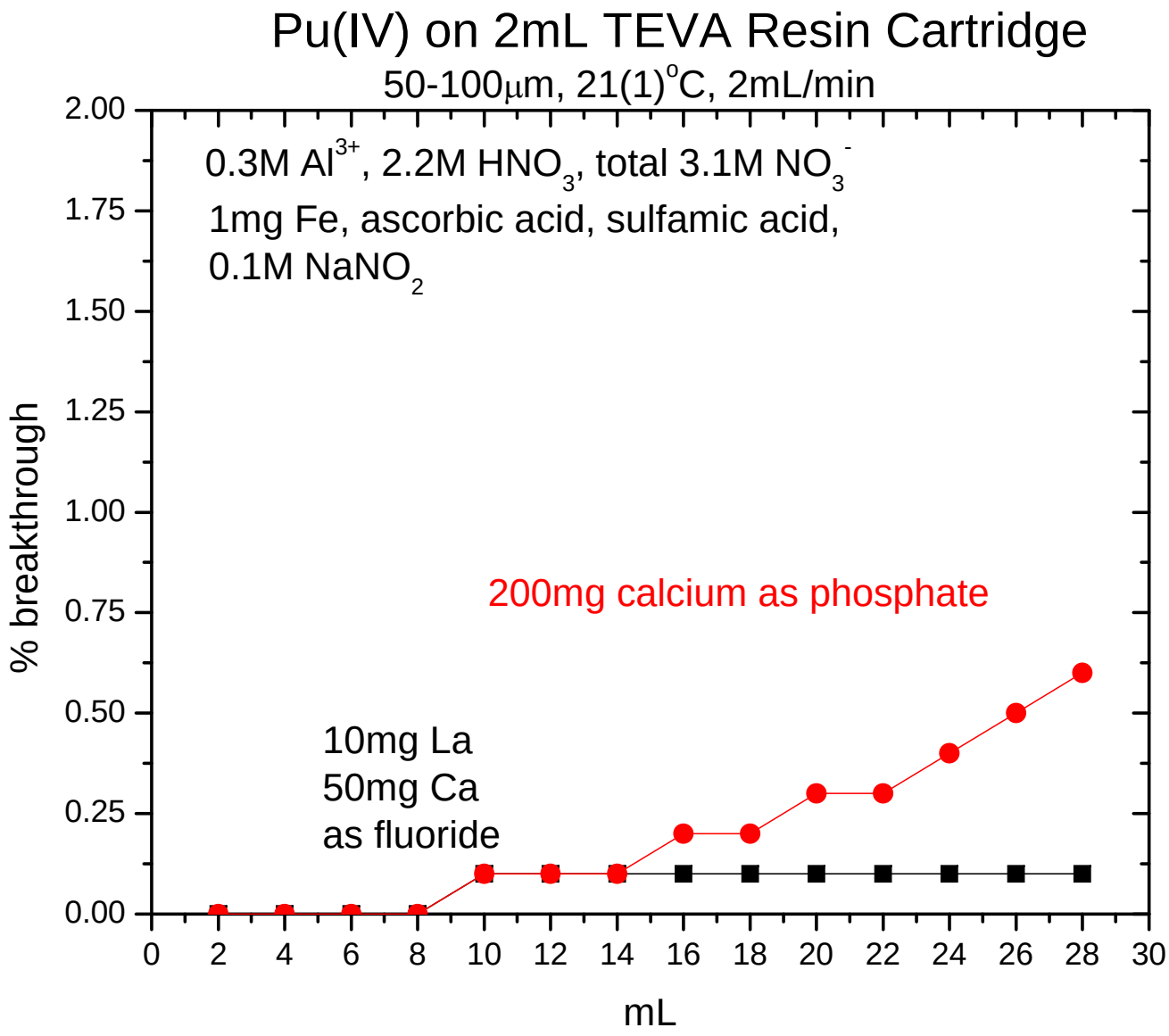

k' Np(IV) on TEVA
50-100μm, 1h, 21(1)°C
3M HNO3-1M Al(NO3)3-0.1M H3BO3
3M HNO3-1M Al(NO3)3
3M HNO3
mg Ca 50 100 200
k' Np
F- (moles/L)

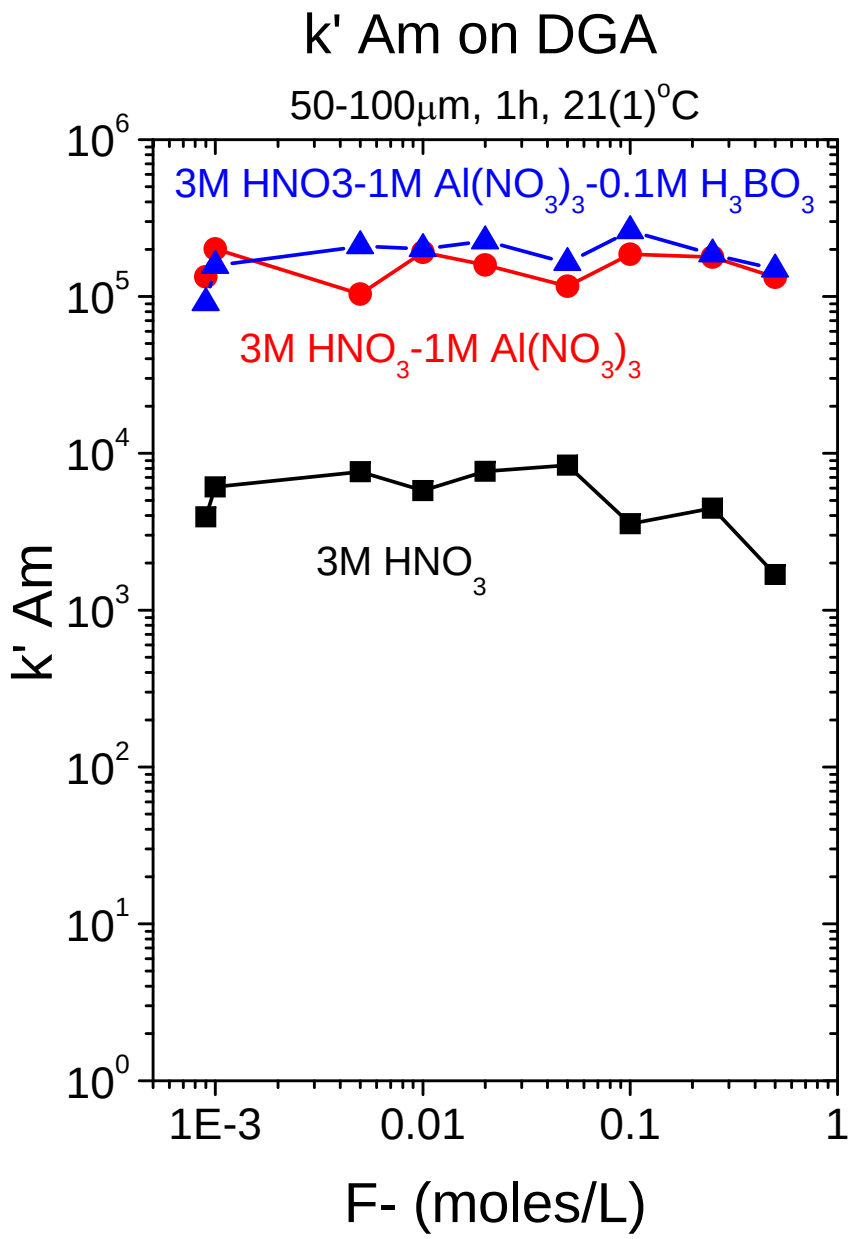

k' Np(IV) on TEVA
50-100μm, 1h, 21(1)°C
3M HNO3-1M Al(NO3)3
3M HNO3
mg Ca 50 100 200
k' Np
H3PO4 (moles/L)

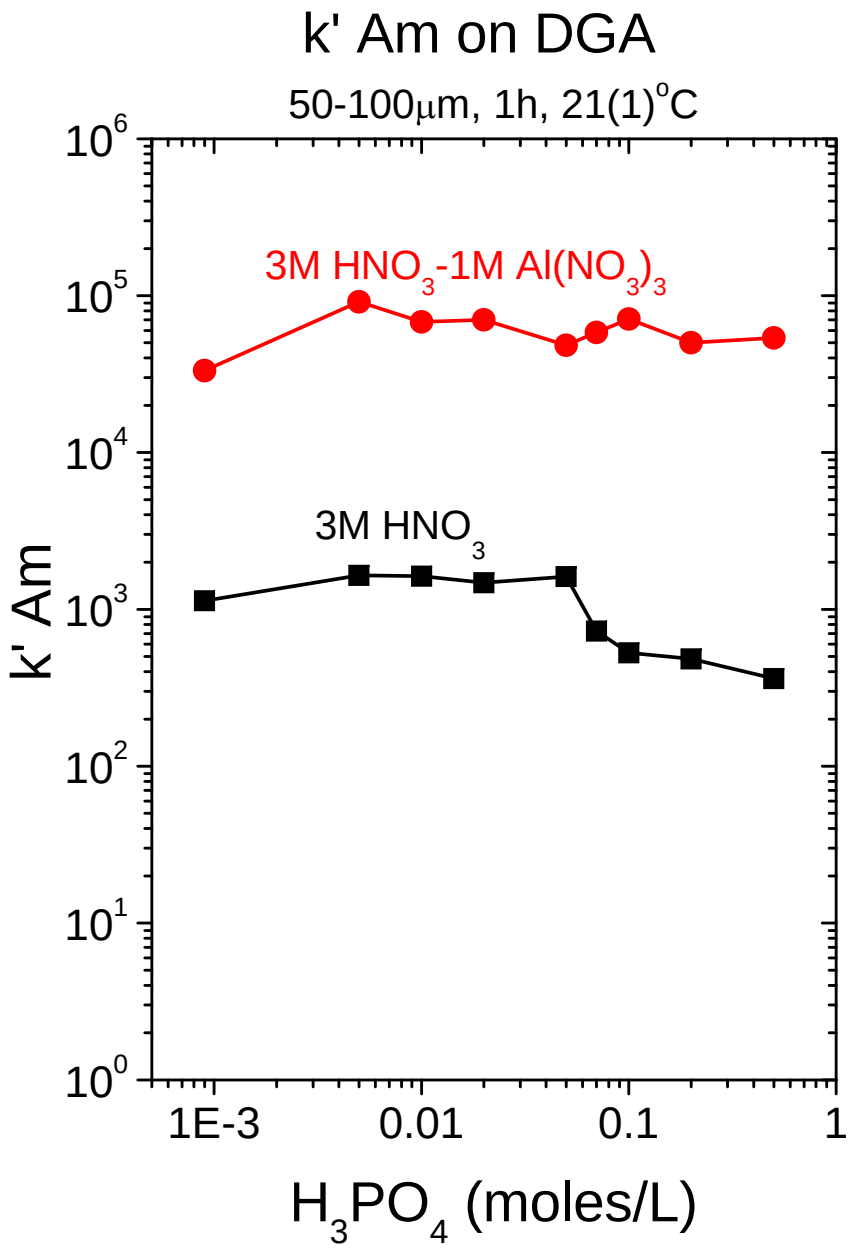

k' Pu(IV) on TEVA
50-100μm, 1h, 21(1)°C
3M HNO3-1M Al(NO3)3-0.1M H3BO3
3M HNO3-1M Al(NO3)3
3M HNO3
mg Ca 50 100 200
k' Pu
F- (moles/L)

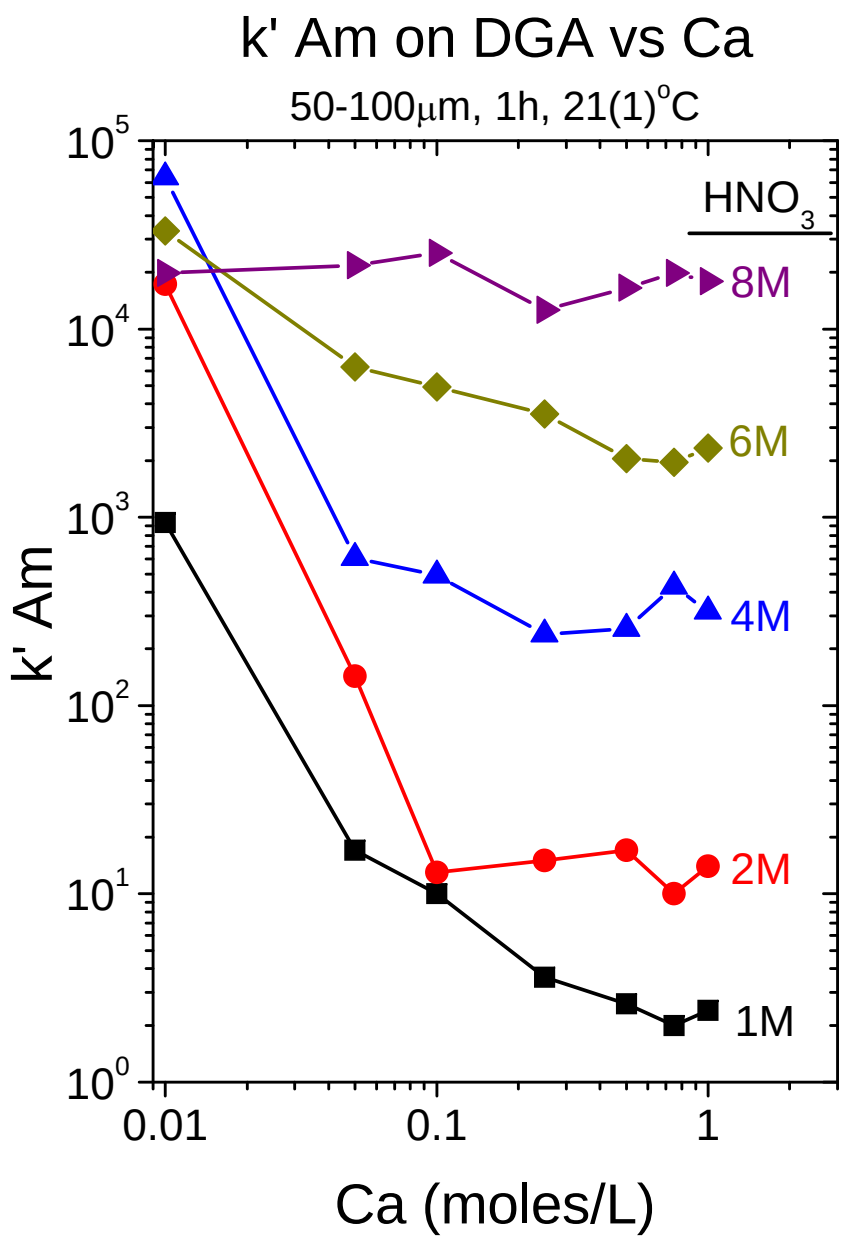

k' Pu(IV) on TEVA
50-100μm, 1h, 21(1)°C
3M HNO3-1M Al(NO3)3
3M HNO3
mg Ca 50 100 200
k' Pu
H3PO4 (moles/L)

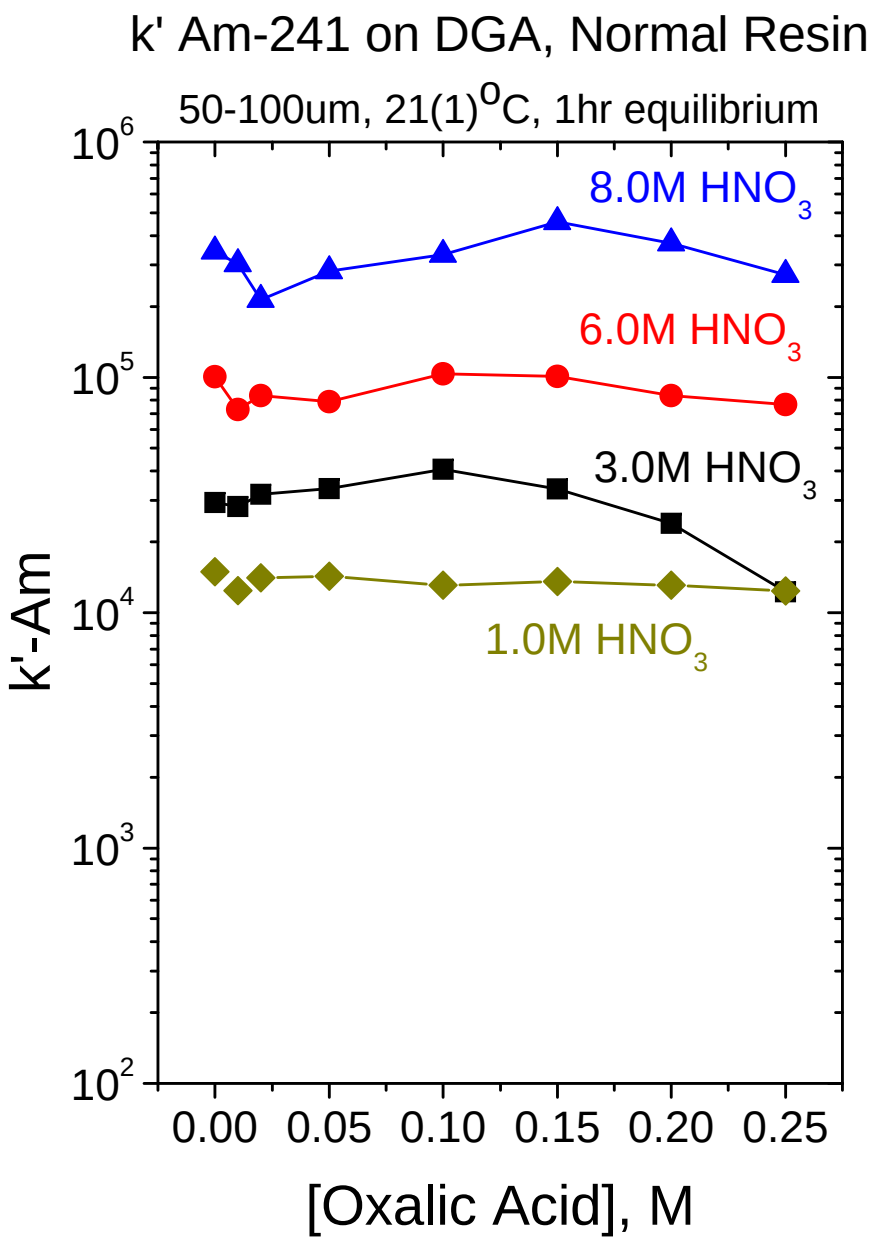

Np(IV) on 2mL TEVA Resin Cartridge
50-100μm, 21(1)°C, 2mL/min
0.3M Al3+, 2.2M HNO3, total 3.1M NO3-
1mg Fe, ascorbic acid, sulfamic acid,
0.1M NaNO2
200mg calcium as phosphate
10mg La
50mg Ca
as fluoride
% breakthrough
mL
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

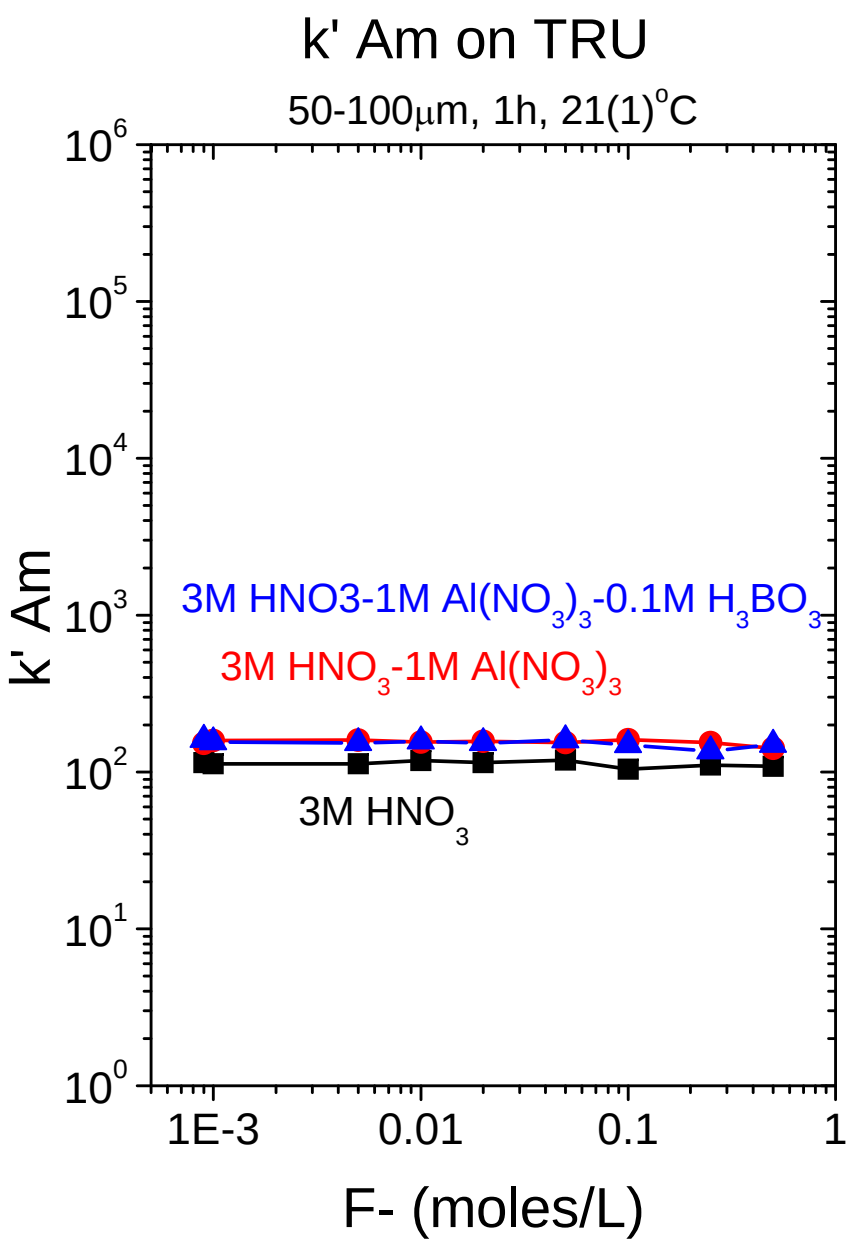

Pu(IV) on 2mL TEVA Resin Cartridge
50-100μm, 21(1)°C, 2mL/min
0.3M Al3+, 2.2M HNO3, total 3.1M NO3-
1mg Fe, ascorbic acid, sulfamic acid,
0.1M NaNO2
200mg calcium as phosphate
10mg La
50mg Ca
as fluoride
% breakthrough
mL
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

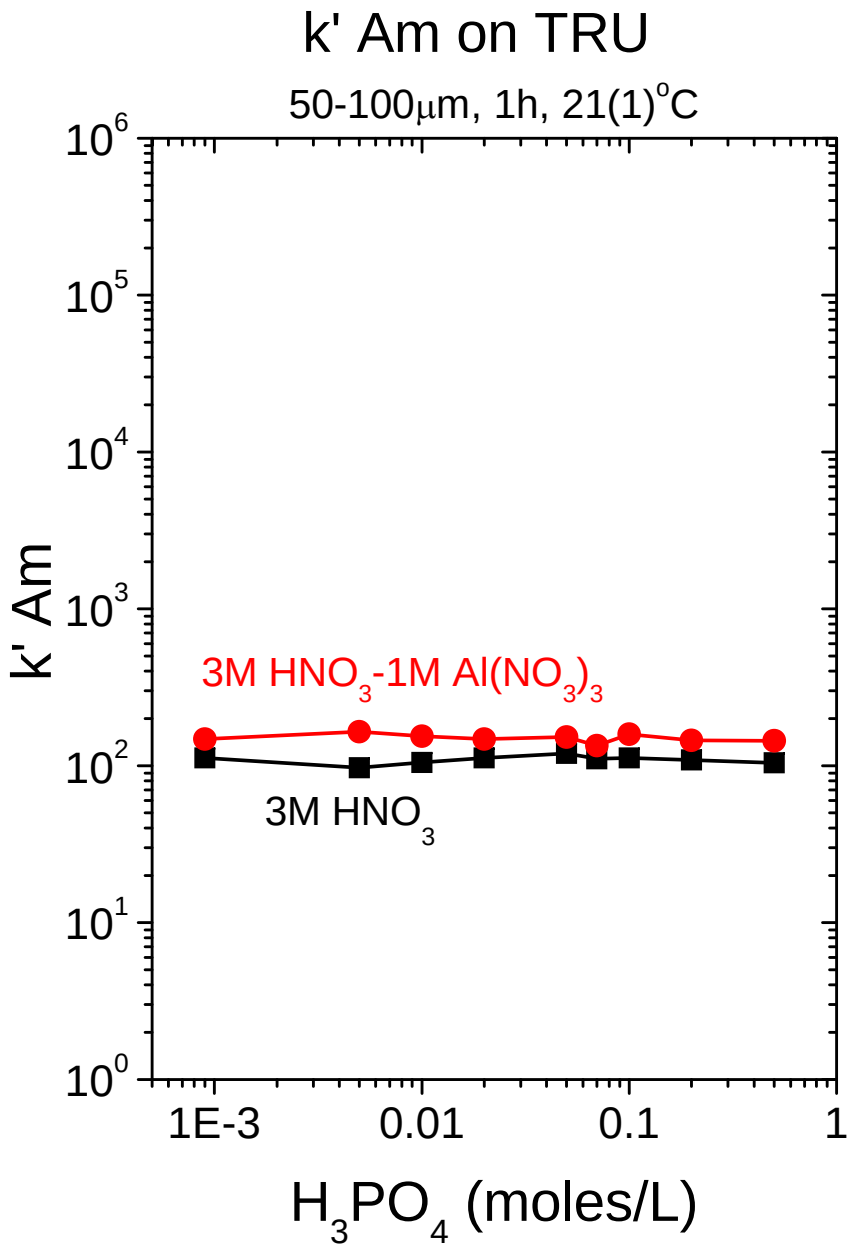

k' Am on DGA
50-100μm, 1h, 21(1)°C
3M HNO3-1M Al(NO3)3-0.1M H3BO3
3M HNO3-1M Al(NO3)3
3M HNO3
k' Am
F- (moles/L)
1E-3
0.01
0.1
1

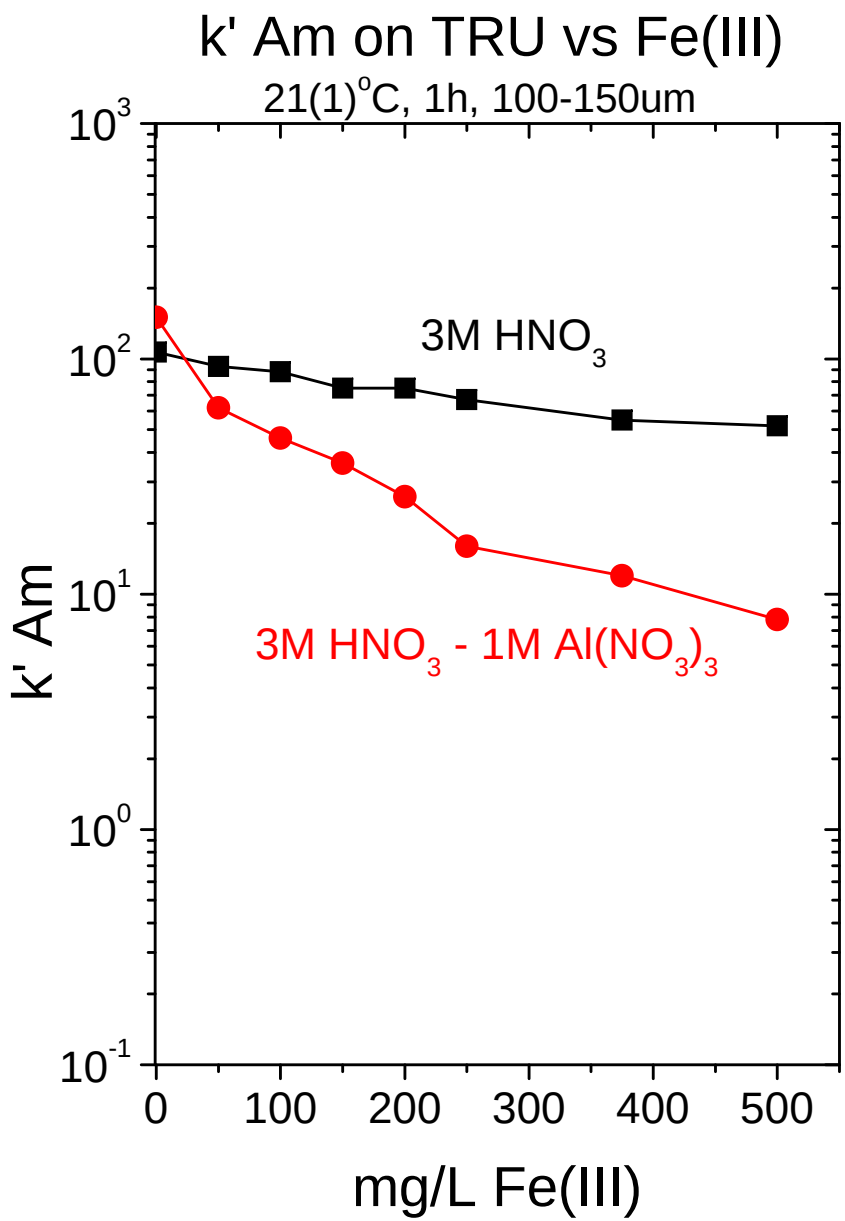

k' Am on DGA
50-100μm, 1h, 21(1)°C
3M HNO3-1M Al(NO3)3
3M HNO3
k' Am
H3PO4 (moles/L)
1E-3
0.01
0.1
1

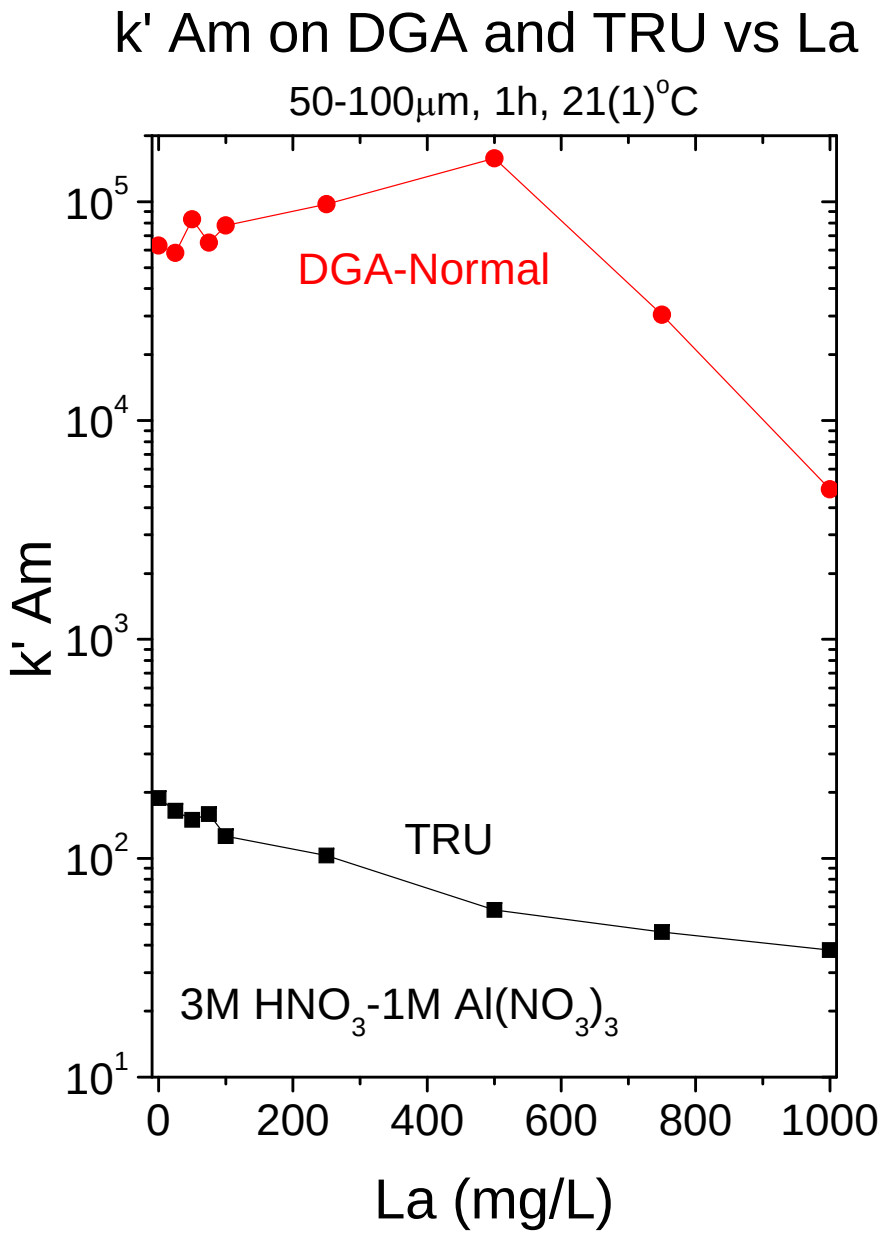

k' Am on DGA vs Ca
50-100μm, 1h, 21(1)°C
HNO3
8M
6M
4M
2M
1M
k' Am
Ca (moles/L)

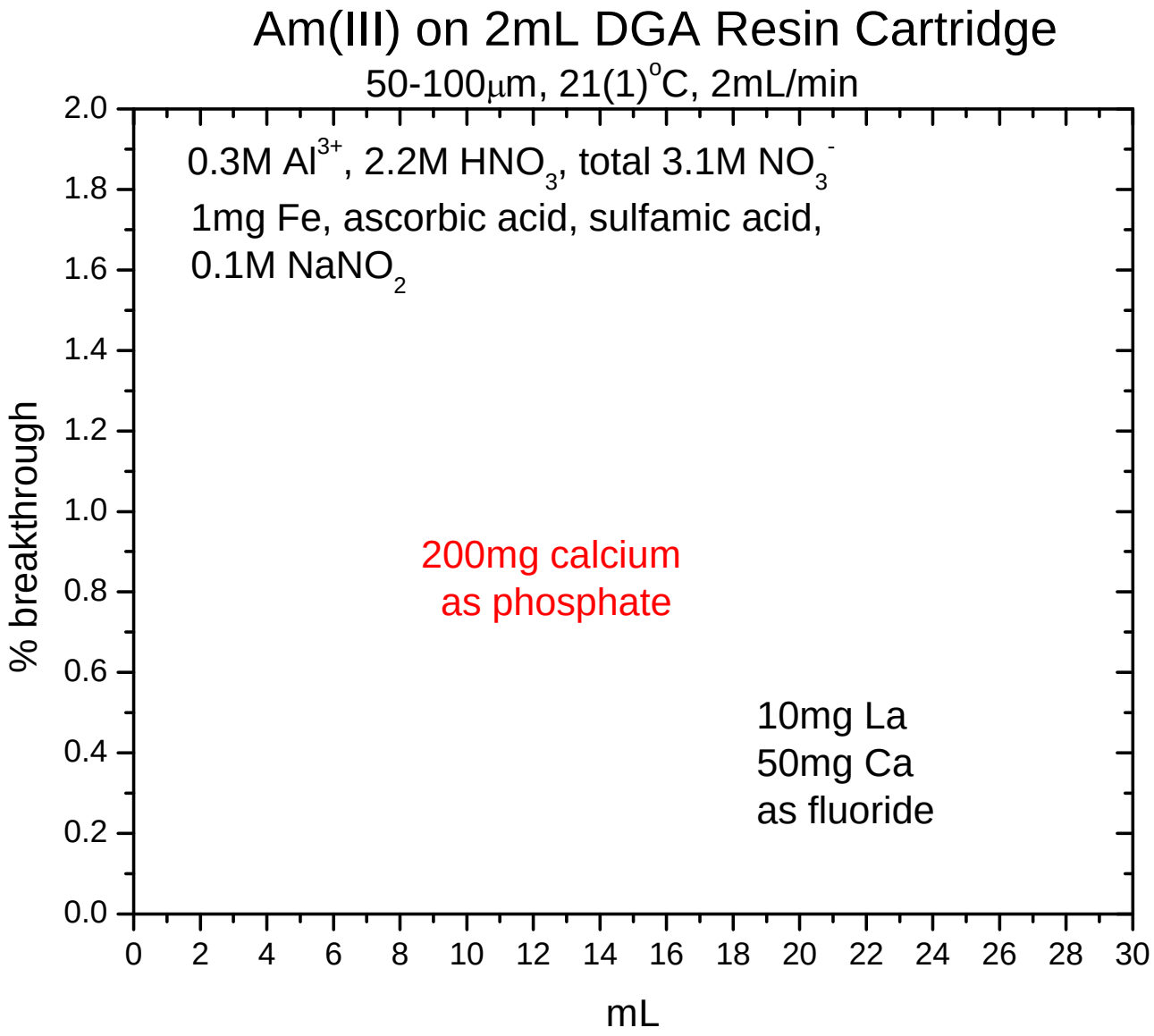

k' Am-241 on DGA, Normal Resin
50-100um, 21(1)°C, 1hr equilibrium
8.0M HNO3
6.0M HNO3
3.0M HNO3
1.0M HNO3
k'-Am
[Oxalic Acid], M

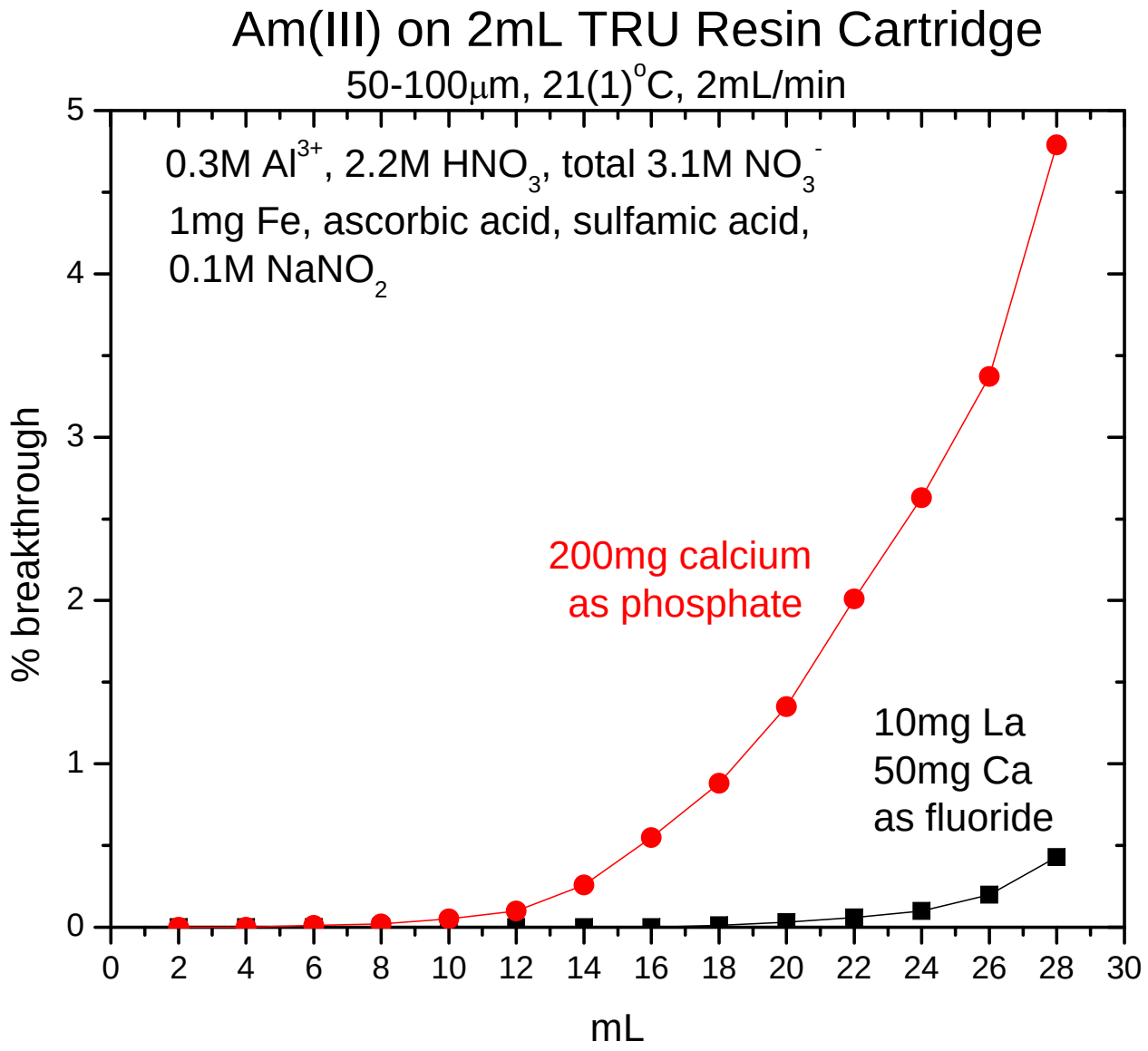

k' Am on TRU
50-100μm, 1h, 21(1)°C
k' Am
F- (moles/L)
3M HNO3-1M Al(NO3)3-0.1M H3BO3
3M HNO3-1M Al(NO3)3
3M HNO3


k' Am on TRU
50-100μm, 1h, 21(1)°C
k' Am
H3PO4 (moles/L)
3M HNO3-1M Al(NO3)3
3M HNO3


k' Am on TRU vs Fe(III)
21(1)°C, 1h, 100-150um
k' Am
mg/L Fe(III)
3M HNO3
3M HNO3 - 1M Al(NO3)3
10^3
10^2
10^1
10^0
10^-1
0
100
200
300
400
500


k' Am on DGA and TRU vs La
50-100μm, 1h, 21(1)°C
DGA-Normal
TRU
3M HNO3-1M Al(NO3)3
k' Am
La (mg/L)
10^5
10^4
10^3
10^2
10^1
0
200
400
600
800
1000


Am(III) on 2mL DGA Resin Cartridge
50-100μm, 21(1)°C, 2mL/min
0.3M Al3+, 2.2M HNO3, total 3.1M NO3-
1mg Fe, ascorbic acid, sulfamic acid,
0.1M NaNO2
200mg calcium
as phosphate
10mg La
50mg Ca
as fluoride
% breakthrough
mL
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30


Am(III) on 2mL TRU Resin Cartridge
50-100μm, 21(1)°C, 2mL/min
0.3M Al3+, 2.2M HNO3, total 3.1M NO3-
1mg Fe, ascorbic acid, sulfamic acid,
0.1M NaNO2
200mg calcium
as phosphate
10mg La
50mg Ca
as fluoride
% breakthrough
mL
0
1
2
3
4
5
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

Conclusion

Precipitation:

- Th, Pu, Am carried well on LaF3, CaF2, Fe(OH)3, Ca-phosphate
- U(VI) can be carried on Ca-phosphate
- U(IV) carried on LaF3, CaF2, Ca-phosphate

Th recovery on TEVA impacted less by F^- than PO_4^{3-}

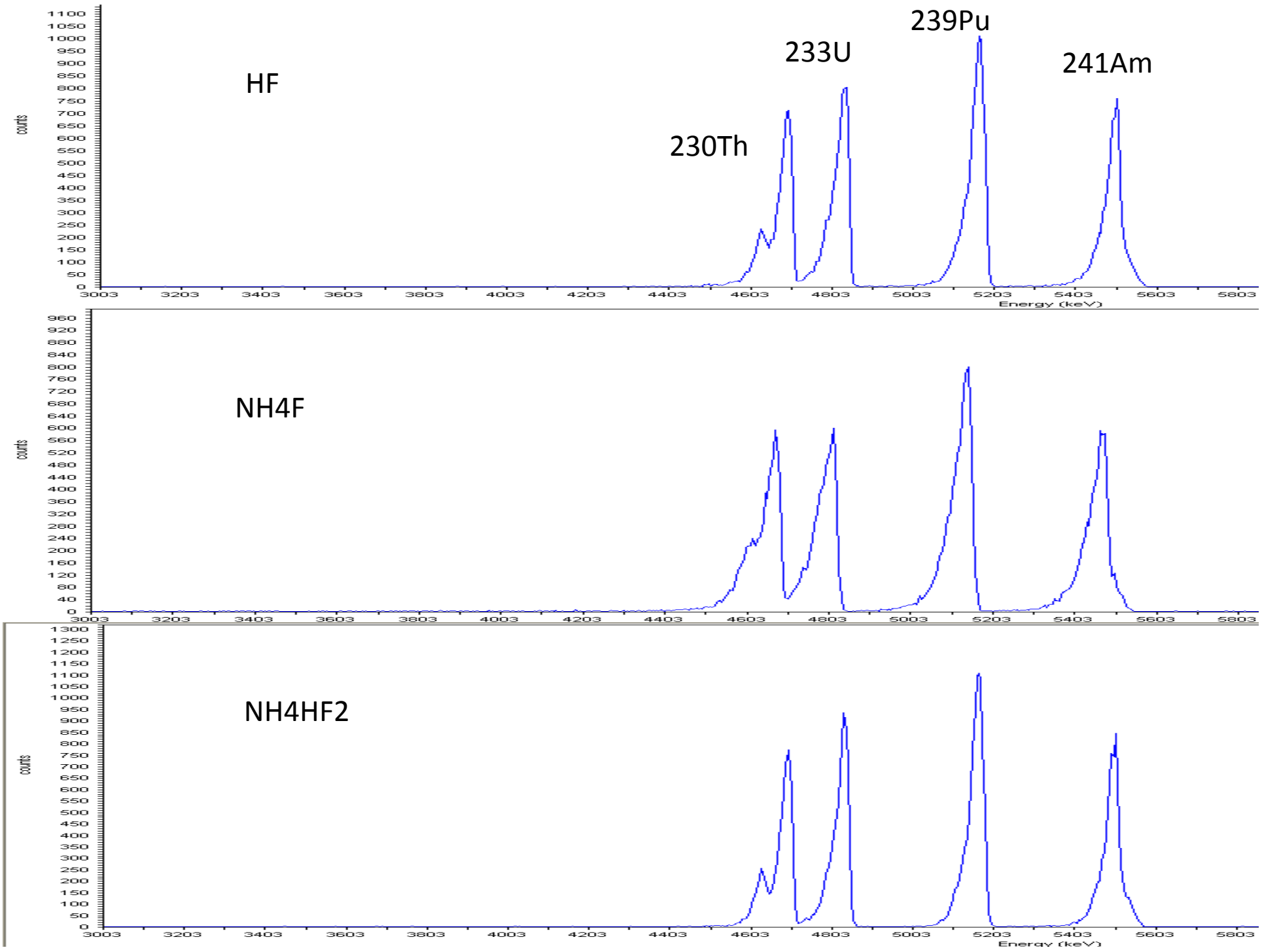
Np/Pu recovery on TEVA impacted less by F^- than PO_4^{3-}

If phosphate must be used (Sr):

- Limit Ca to 50-100mg
- Maximize HNO_3/Al^{3+}

$HF/NH_4F/NH_4HF_2$

Source	Solubility (mol/L)	Practicle Solubility	[F-] (mol/L)
HF	28.9	28.9 M	28.9
NH_4F	12	10 M	10
NH_4HF_2	11	8 M	16


HF
230Th
233U
239Pu
241Am
counts
Energy (keV)
NH4F
counts
NH4HF2
counts
Energy (keV)

		dpm			
Test	**Replicate**	**Th-230**	**U-233**	**Pu-239**	**Am-241**
HF	AVG	570	583	722	571
	SD	15	20	23	11
NH4F	AVG	576	534	715	572
	SD	18	9	17	19
NH4HF	AVG	568	596	747	598
	SD	22	34	25	26
20mL 1M HCl					
50ug Ce					
0.5mL 10% TiCl3					
equivalent of 1mL conc. HF					

	FWHM			
Test	**Th-230**	**U-233**	**Pu-239**	**Am-241**
HF	22	32	35	42
	9	7	6	2
NH4F	24	44	46	54
	5	16	11	1
NH4HF	24	32	36	41
	8	7	6	1