A BRAND OF
EICHROM TECHNOLOGIES

Eichrom Method ACW17-VBS
Am/Cm, Pu/Np, Th, U, Sr in water

Outline

- Steps
  - Tracer Equilibration
  - Calcium Phosphate Precipitation
  - Load Solution and Red/Ox Adjustments
    - Oxidizing: Pu(IV)/Np(IV)
  - TEVA/TRU vs TEVA/TRU/DGA
  - Alpha Source Preparation (CeF_3)

Acidification and Tracer Equilibration

Water Sample in glass beaker. Acidify pH 2.

1) Aliquot up to 1000mL of water into glass beaker. (Filter if necessary)

2) Add 5mL concentrated HNO_3 and yield tracers.

^{229}Th, ^{243}Am, ^{232}U*, ^{236}Pu or ^{242}Pu, Stable Sr

*Self-cleaning (Eichrom Method TPO1)

3) Add 2mL of 1.25M $Ca(NO_3)_2$. (100 mg Ca)

4) Heat samples at medium setting for 30-60 minutes.

5) Remove samples from heat.

Calcium Phosphate Precipitation

6) Add 0.75mL of phenolphthalein and 5mL of 3.2M $(NH_4)_2HPO_4$. (excess PO_4^{3-})

7) While stirring sample, slowly add conc. NH_4OH until reaching pH 8-9.

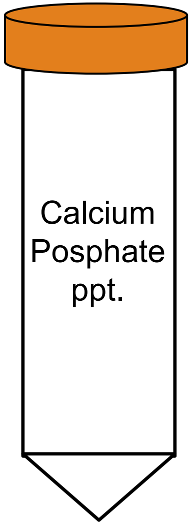
8) Cool to room temperature. Allow precipitate to settle or centrifuge.

9) Decant supernate and discard as waste.

10) Transfer precipitate to centrifuge tube with DI water.

11) Centrifuge ~10minutes at 2000rpm. Decant supernate.

12) Add 10mL DI water to ppt. Mix well. Centrifuge. Decant supernate.



Centrifuge.
Decant Supernate.
Wash ppt with H_2O.
Centrifuge. Decant.

Calcium Phosphate Precipitation

Calcium phosphate - carrier for actinides in all oxidation states, Fe(III) and Sr.

Requires pH adjustment to 8-9. (Higher pH can carry more matrix)

Easy to dissolve in acid for further processing.

Phosphate will strongly affect separation of Th(IV), Pu(IV) and Np(IV) on TEVA and UTEVA.

Addition of $Al(NO_3)_3$ reduces impact by complexing phosphate.

Load Solution and Red/Ox Adjustments

14) Dissolve residue in 16mL 3M HNO_3-1M $Al(NO_3)_3$. (Al complexes PO_4^{3-})

Add 0.5 mL 1.5M Sulfamic Acid, (scavenges NO_2^-)

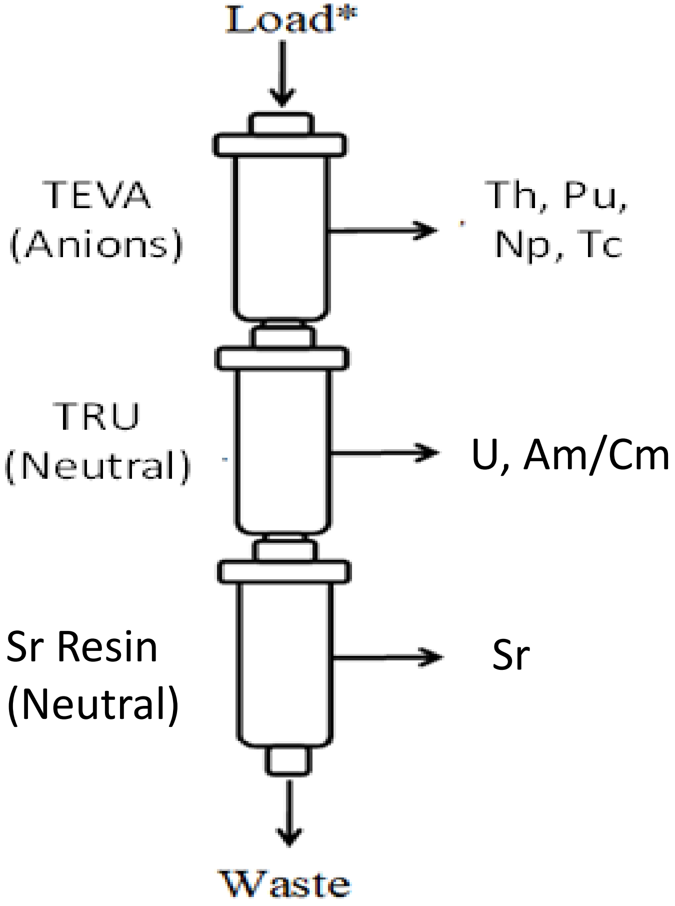
0.2 mL of 5 mg/ mL Fe, (will act as reducing agent)

1.5 mL 1M Ascorbic Acid (reduces to Fe(II) => Pu(III)/Np(IV))

Swirl to mix. Wait 3-5 minutes. (Np(V) to Np(IV) slower, may need more time)

15) Add 1mL 3.5M $NaNO_2$. Swirl to mix. (Pu(III) to Pu(IV), Fe(II) to Fe(III))

Cartridge Separations



Retains (IV) actinides from HNO_3.

Sensitive to phosphate.

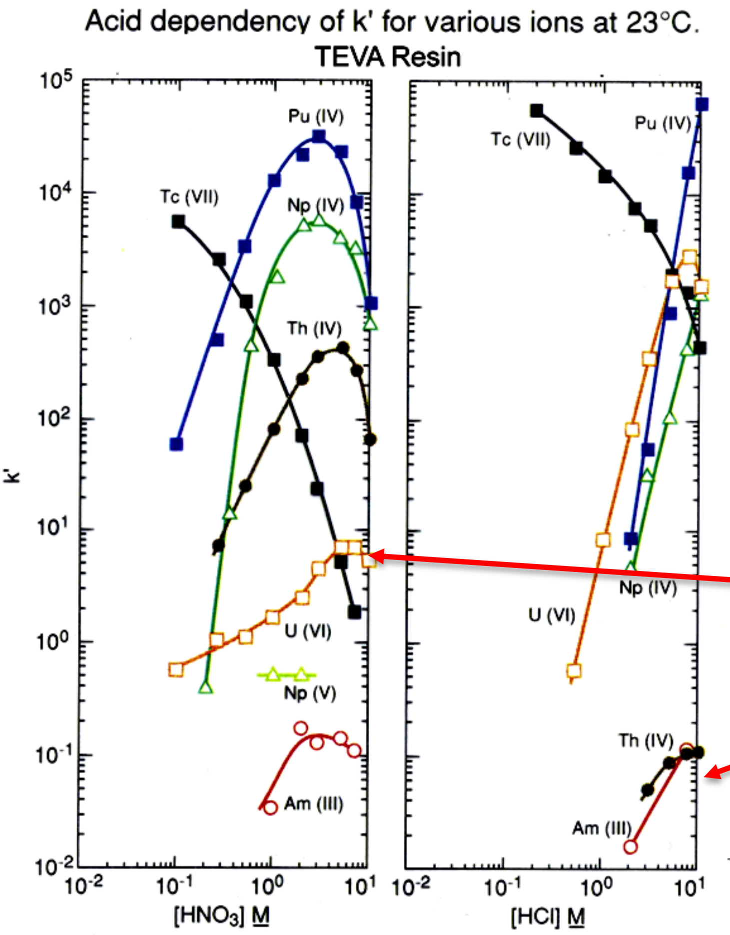
Retains (III), (IV), (VI) actinides from HNO_3.

Am/Cm(III) Sensitive to Fe(III).

Retains Sr(II)

Sensitive to Ba(II), K(I), very large excess of Ca(II).

TEVA Resin



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16) Precondition TEVA-TRU-Sr with 5mL 3M HNO_3.

17) Load sample onto TEVA-TRU-Sr. Allow liquid to drain. TEVA retains Th, Np, Pu. TRU retains Am, Cm, U. SR resin retains Sr.

18) Rinse sample tube with 5mL 3M HNO_3.
Add rinse to TEVA-TRU-Sr. Allow liquid to drain.

19) Rinse TEVA-TRU-Sr with 5mL 3M HNO_3. Allow liquid to drain.

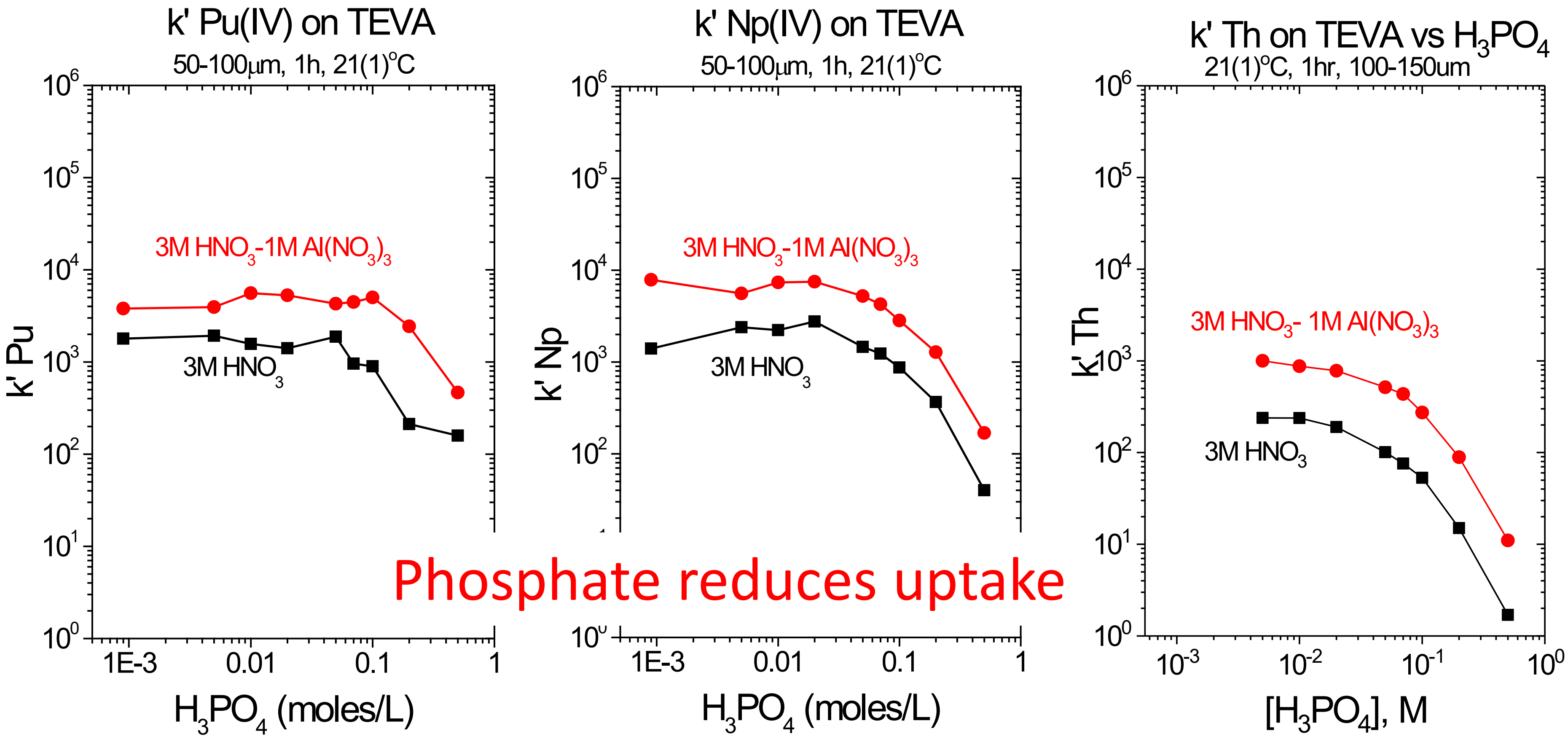
20) Separate TEVA,TRU,Sr cartridges.

21) Rinse TEVA column with 20mL 3M HNO_3.
Remove last traces of U(VI)

22) Place clean centrifuge tube below TEVA.
Strip Th with 15mL 9M HCl.

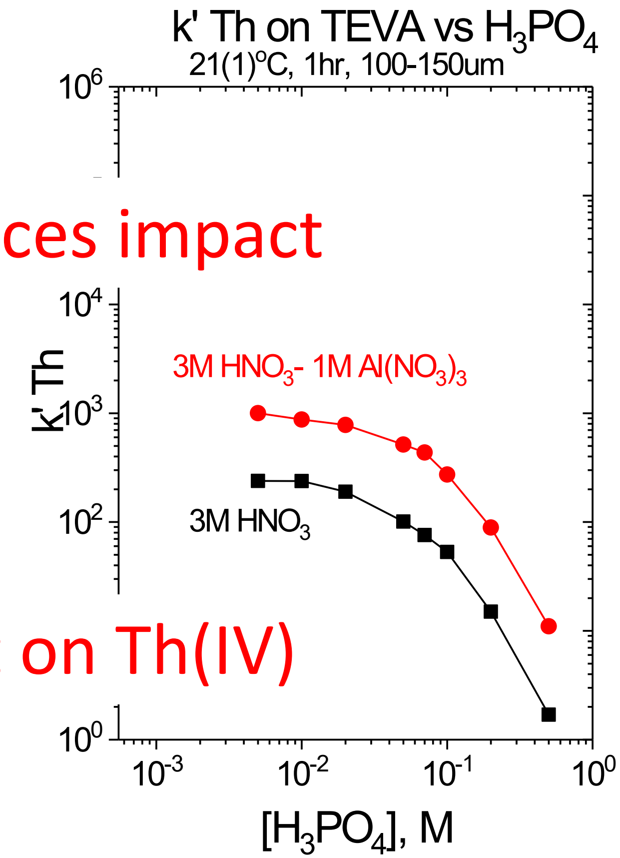
23) Place clean centrifuge tube below each TEVA. Strip Pu-Np with 20mL 0.1M HCl-0.05M HF-0.03M $TiCl_3$.

TEVA Resin (Impact of phosphate)



Phosphate reduces uptake

TEVA Resin (Impact of phosphate)



$Al(NO_3)_3$ reduces impact

High Ca samples may require
20-30 mL 3M HNO_3-$Al(NO_3)_3$

Largest Impact on Th(IV)

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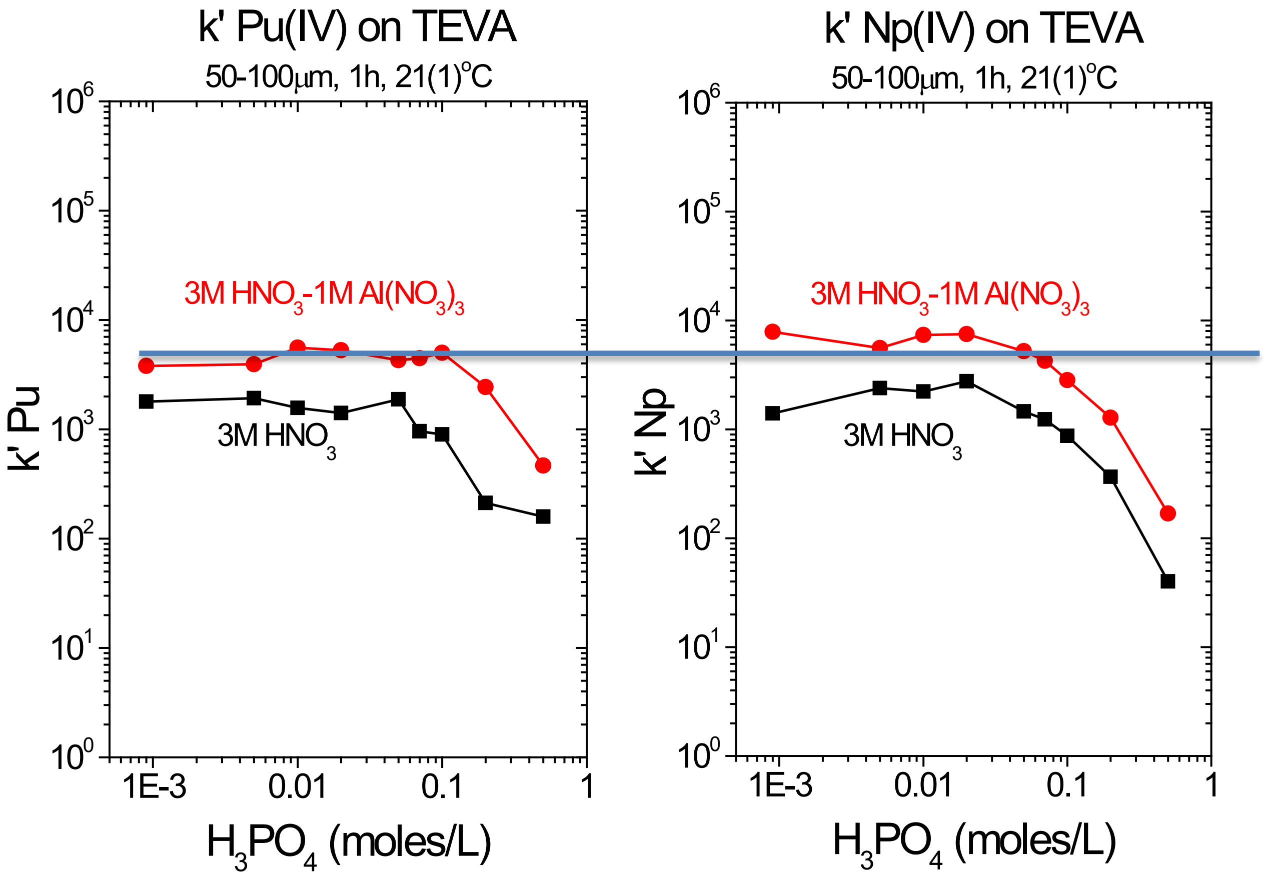
TEVA Resin

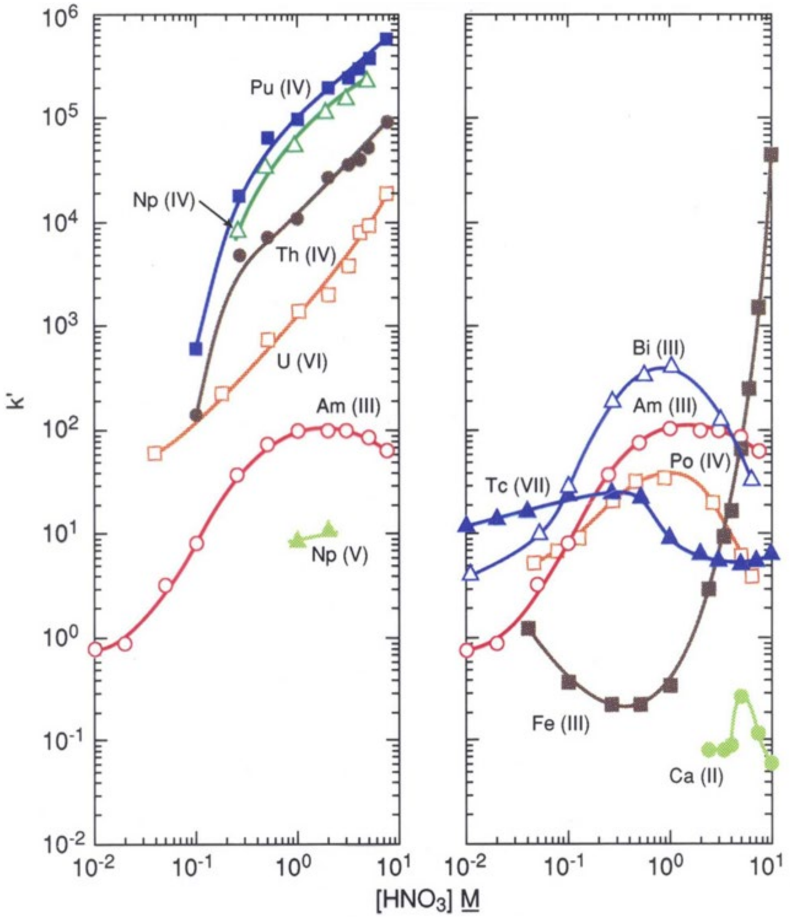
Recovery of Th-230 on 2 mL TEVA Cartridge (200 mg Ca)				
volume (mL)				
3M HNO3	**mL**	**% Th-230**		
1M Al(NO3)3	**Load Volume**	**Load**	**Rinse**	**Strip**
10	18	24.2	6.0	69.8
20	28	3.2	3.1	93.7
30	38	1.5	1.0	97.5
40	48	0.5	0.5	99.0
50	58	0.5	0.1	99.4

TEVA Resin (Impact of phosphate)



$Al(NO_3)_3$ important to ensure similar recoveries Np(IV)/Pu(IV) when using ^{236}Pu tracer for both.

TRU Resin

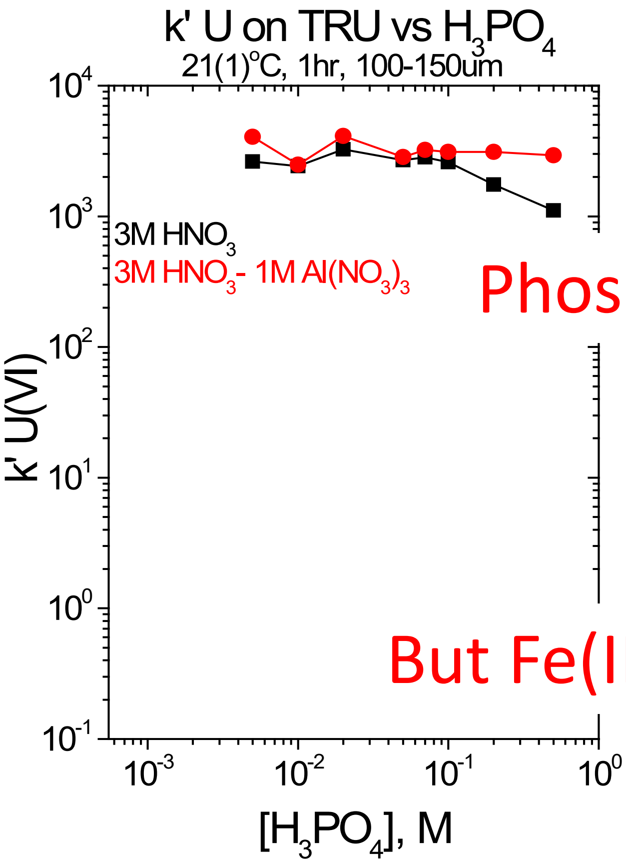


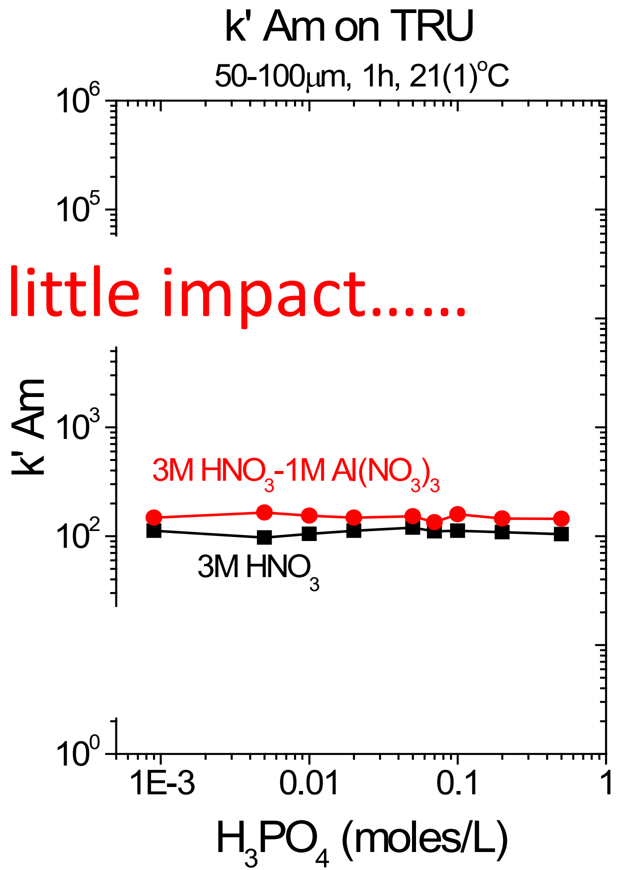
24) Place clean centrifuge tubes below TRU.
Strip Am with 15mL of 4M HCl. (DGA)

25) Rinse TRU with 12mL 4M HCl-0.1M HF. Discard as waste.

26) Place a clean centrifuge tube below each cartridge. Strip U with 15mL 0.1M ammonium bioxalate.

TRU Resin

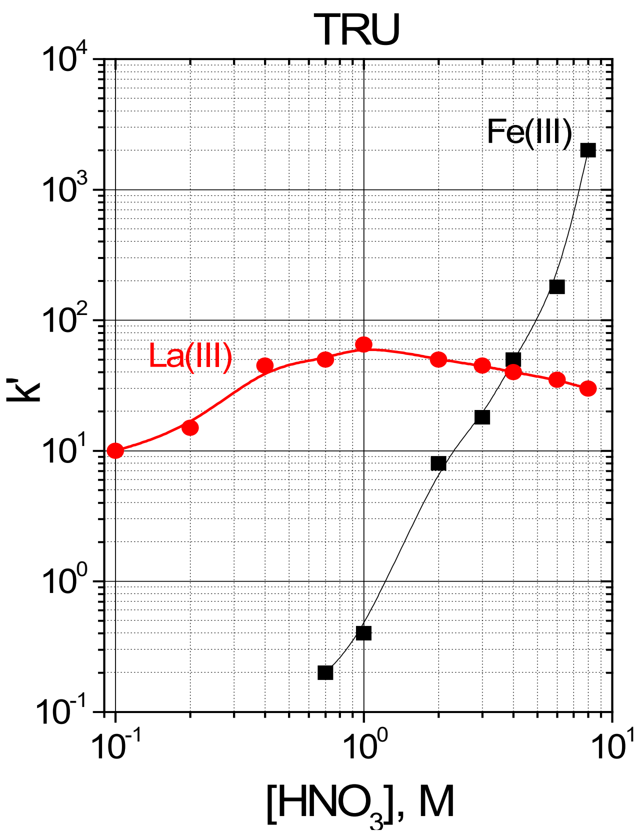




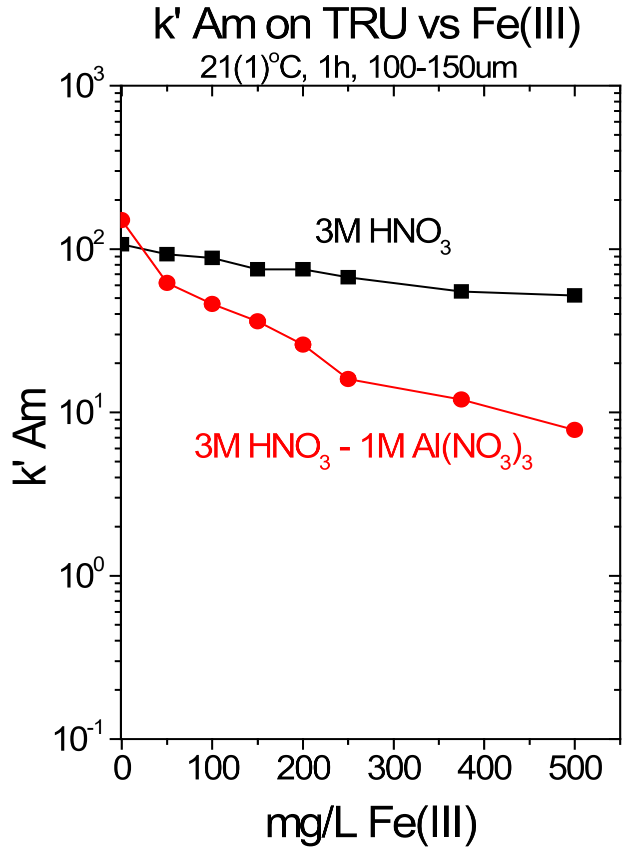
Phosphate has little impact......

But Fe(III).......

TRU Resin

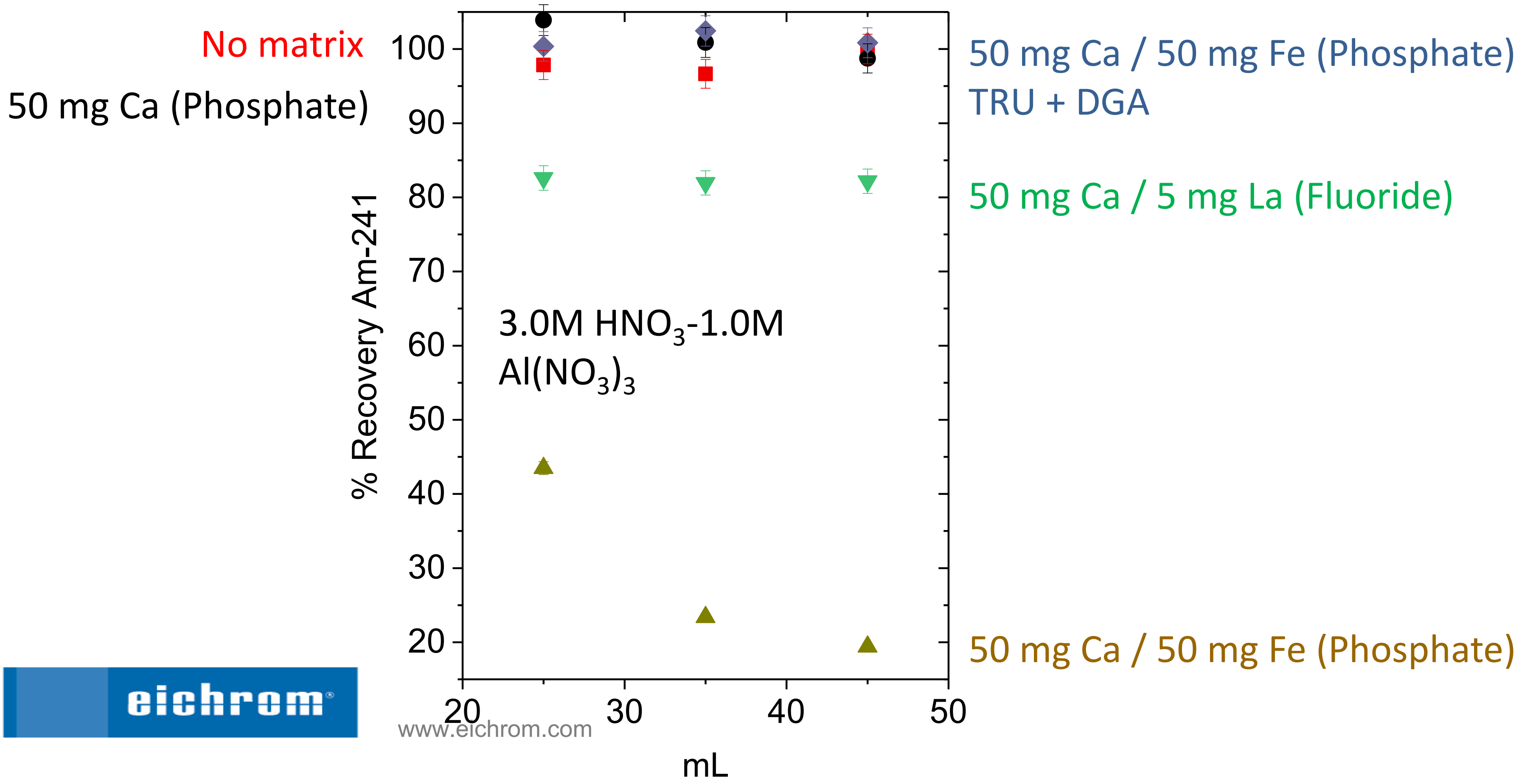


TRU
10^4
10^3
10^2
10^1
10^0
10^-1
k'
Fe(III)
La(III)
10^-1
10^0
10^1
[HNO3], M



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

Recovery of Am-241 on 2 mL TRU Resin Cartridge vs volume of load solution



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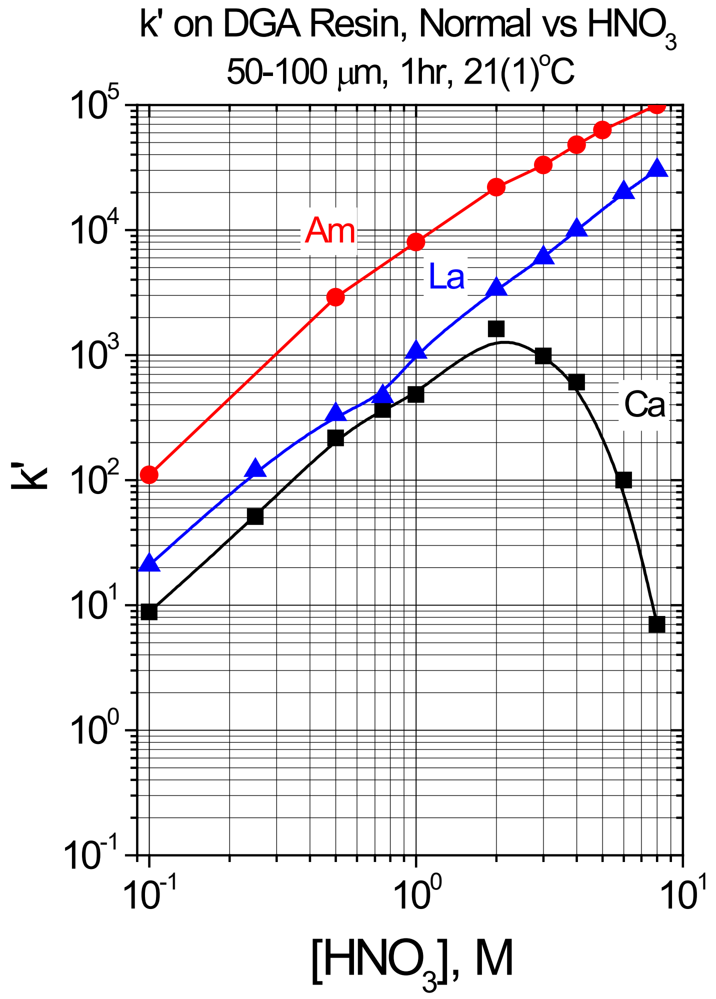
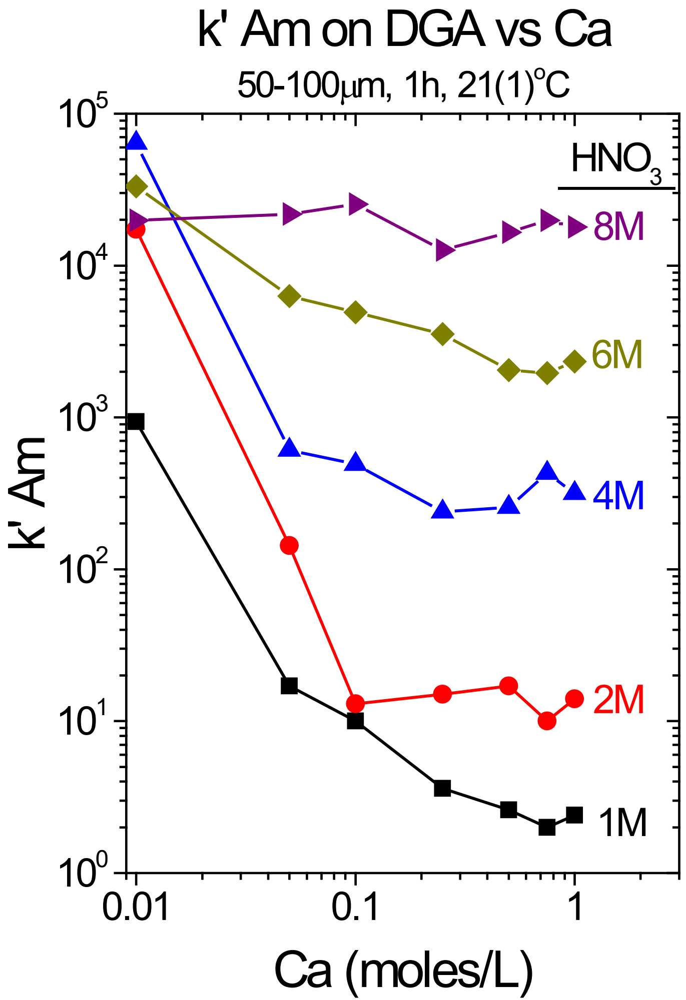
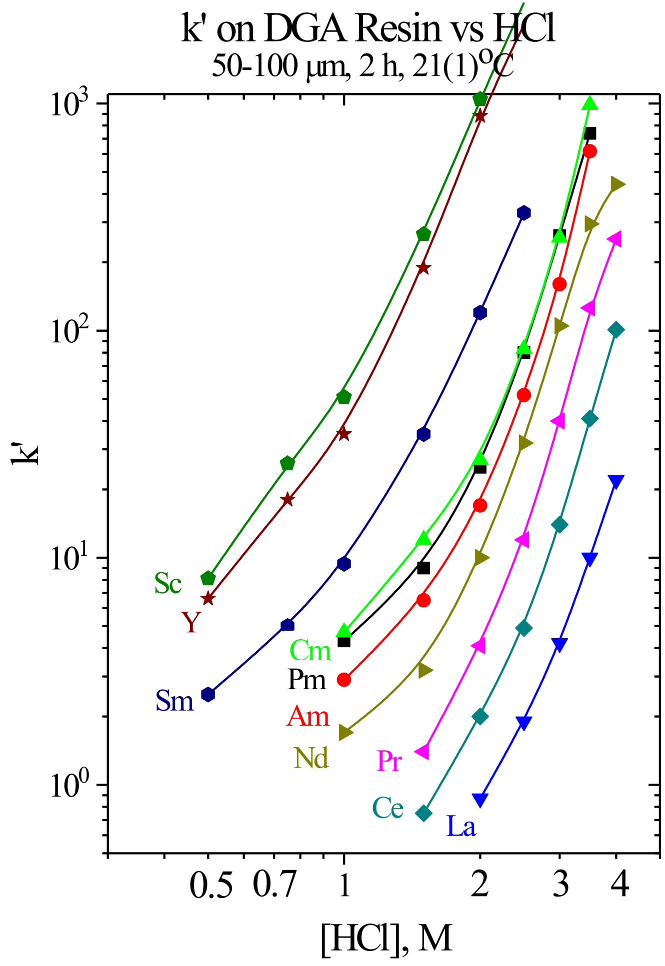

k' on DGA Resin, Normal vs HNO3
50-100 μm, 1hr, 21(1)°C
Am
La
Ca
k'
[HNO3], M


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



DGA also allows separation of light REE (La, Ce) from Am/Cm using a 2-3M HCl rinse.

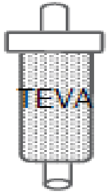
Separation of heavier REE (soils, rocks, etc.) requires TEVA-SCN.

(1) Add 2 mL 70% HNO_3 + 50 uL 10% H_2SO_4 to Am/Cm eluate from TRU or DGA Resin separation. Evaporate to dryness.

(2) Ash to dryness with 3 mL 70% HNO_3 + 2 mL 30% H_2O_2.

(3) Dissolve Am/Cm in 5 mL 4M NH_4SCN -0.1M Formic acid.

(4) Precondition 2 mL TEVA cartridge with 5 mL 4M NH_4SCN -0.1M Formic acid.



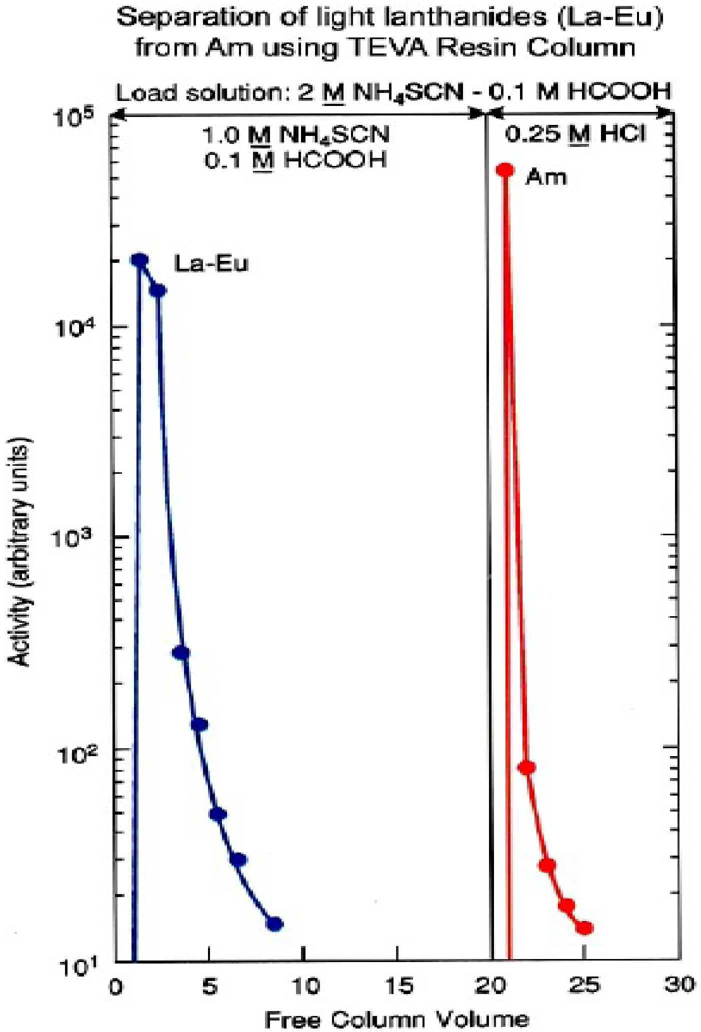
(5) Load Am/Cm from step (3) on TEVA.

(6) Rinse Am/Cm beaker with 5 mL 4M NH_4SCN-0.1M Formic acid. Add to TEVA.

(7) Rinse TEVA w/ 10 mL 1.5M NH_4SCN-0.1M Formic acid.

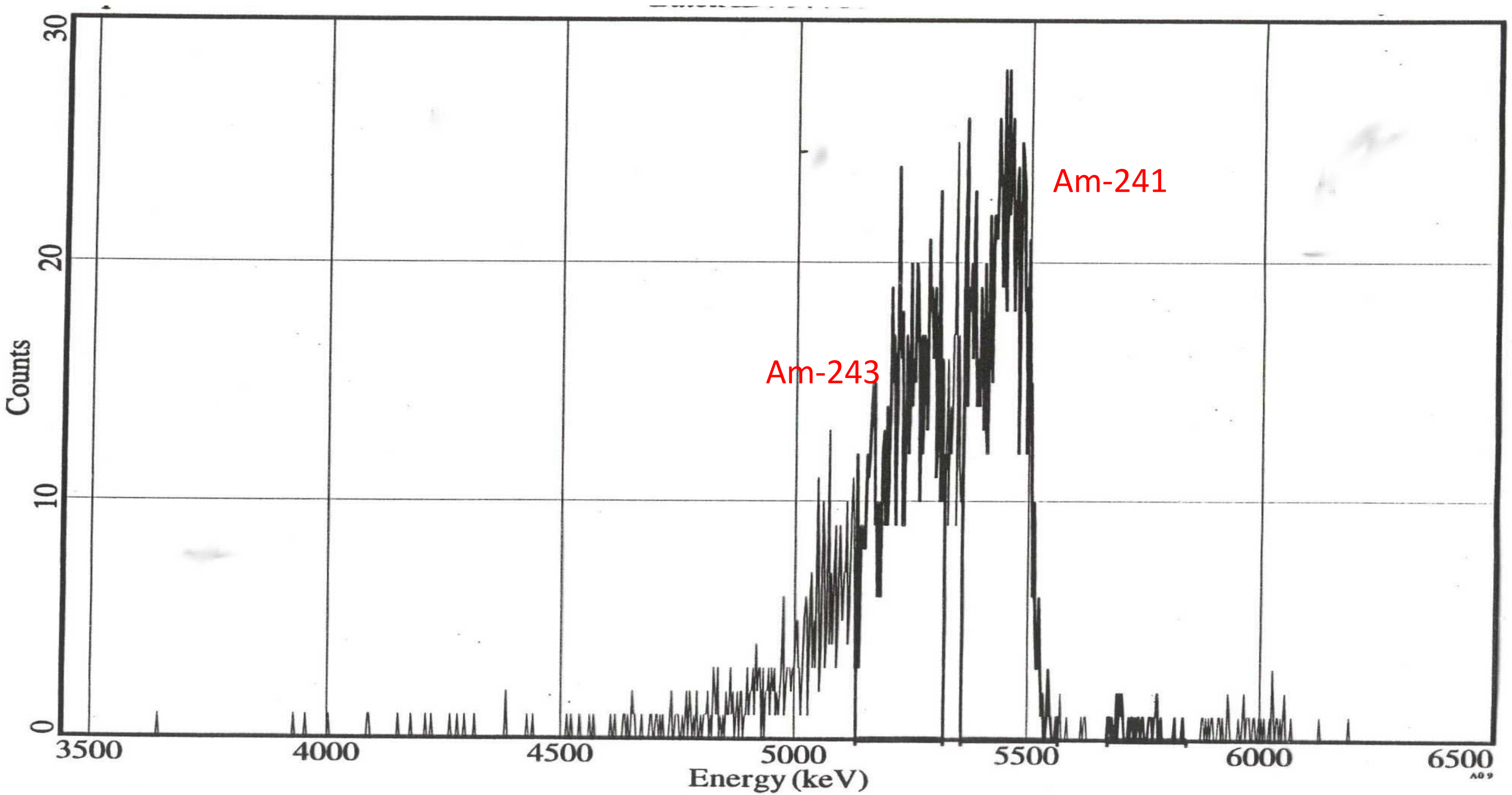
(8) Strip Am/Cm from TEVA with 20 mL 1M HCl.

(9) Prepare alpha spectrometry source using rare earth fluoride microprecipitation (AN-1805).



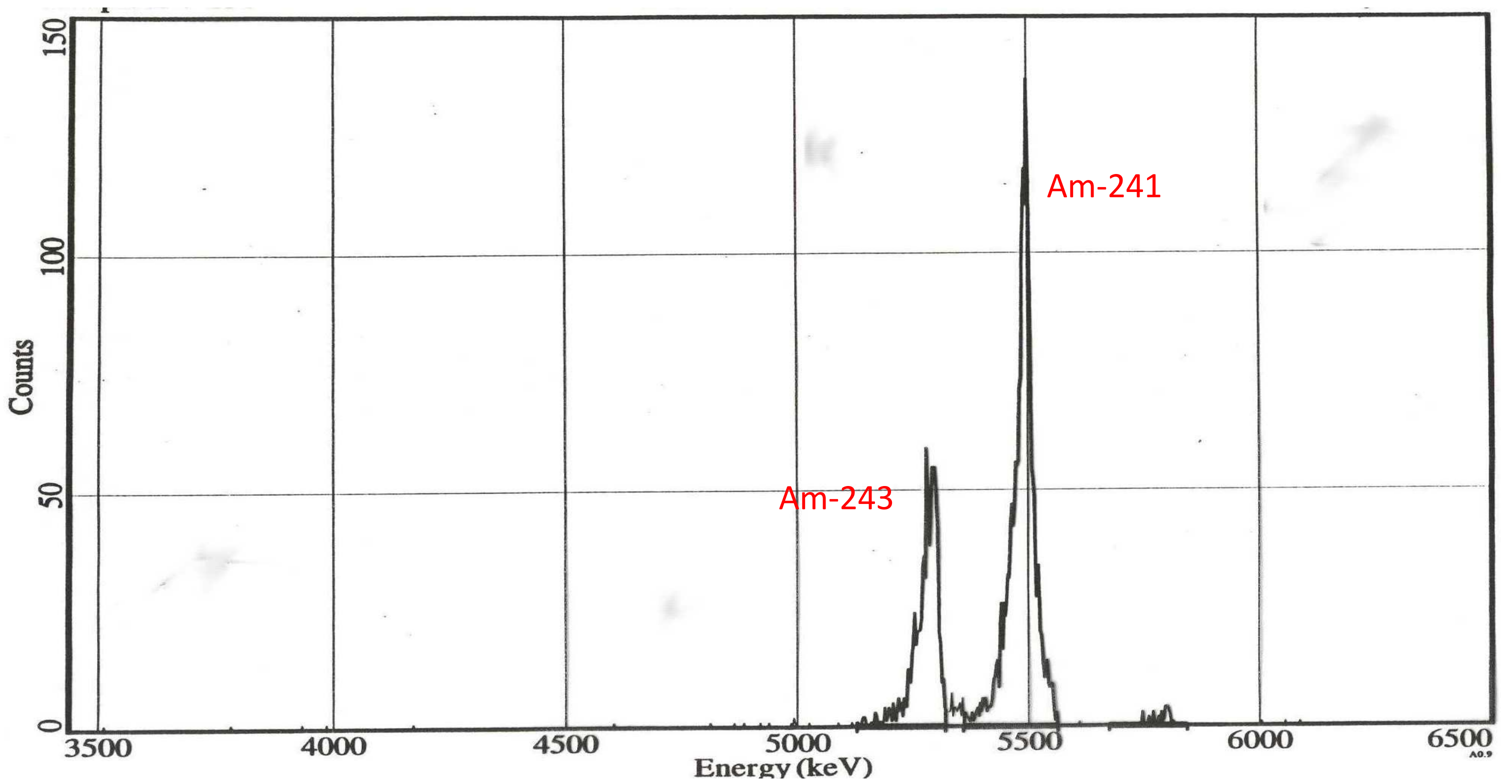
Americium Spectrum after TRU Resin Separation

presence of rare earths degrades spectrum- self absorption issues

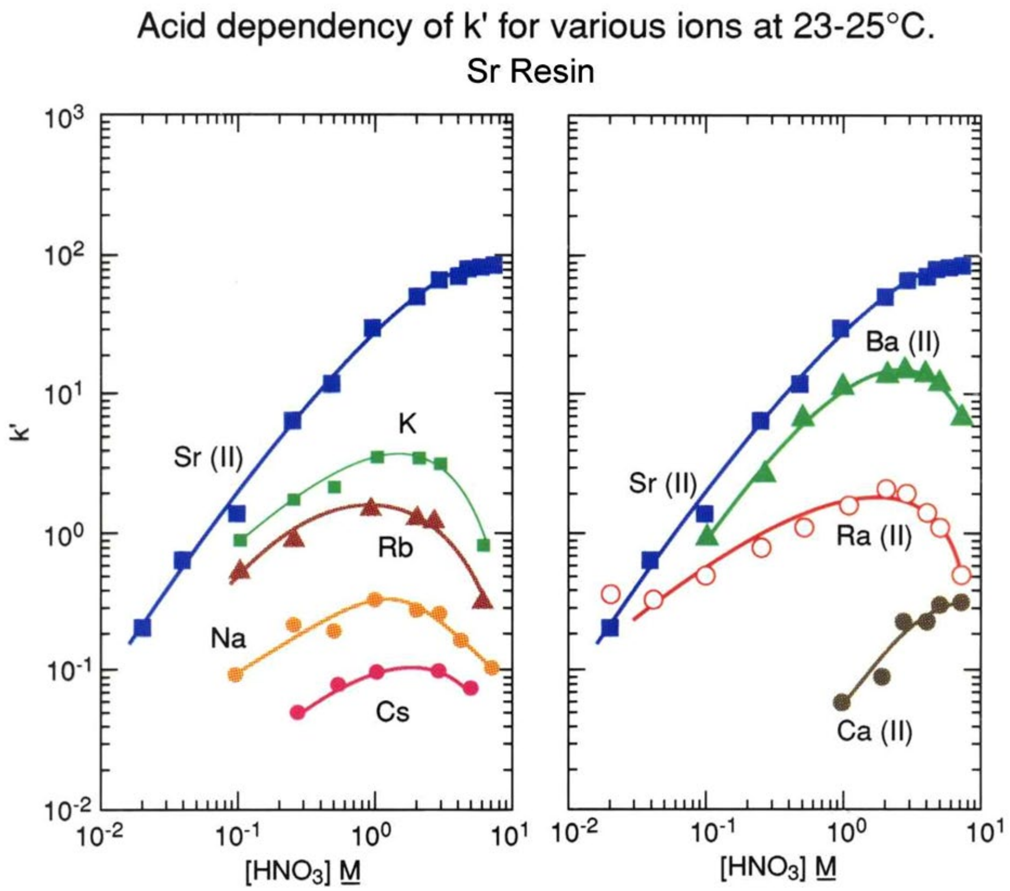


Am Spectrum after TEVA Resin Separation

Lanthanide elements removed - cleaner spectrum



Sr Resin



27) Rinse Sr Resin with 5mL 3M HNO_3-oxalic acid.

28) Rinse Sr Resin with 5mL 8M HNO_3.

29) Rinse Sr Resin with 15mL 0.05M HNO_3.

Sr fraction will contain all radio-strontium and stable Sr carrier.

Determine Sr yield from stable Sr via ICP-AES, ICP-MS or gravimetrically.

Count Sr via gas flow proportional counter or LSC for total radiostrontium or follow method for discrimination of 90Sr/89Sr.

Properties of Selected Nuclides								
		Decay		Detector Suitable for Measurement				
Nuclide	**Half-Life**	**Mode**	**Energy**	**GFPC**	**LSC**	**Cerenkov**	**MS/AES**	**Gamma**
^{82}Sr	25.35 days	ε						
^{82}Rb	1.25 min	β^+	β^+mean = 1479 keV γ = 511 keV (190.4%)					
^{85}Sr	64.849 days	ε/γ	γ = 514 keV (96%)	No	Yes	No	No	Yes
^{88}Sr	Stable			No	No	No	Yes	No
^{89}Sr	50.563 days	β^-	β_{max} = 1500 keV β_{mean} = 587 keV	Yes	Yes	Yes	No	No
^{90}Sr	28.79 years	β^-	β_{max} = 546 keV β_{mean} = 196 keV	Yes	Yes	No	Yes	No
^{90}Y	64 hours	β^-	β_{max} = 2280 keV β_{mean} = 934 keV	Yes	Yes	Yes	No	No

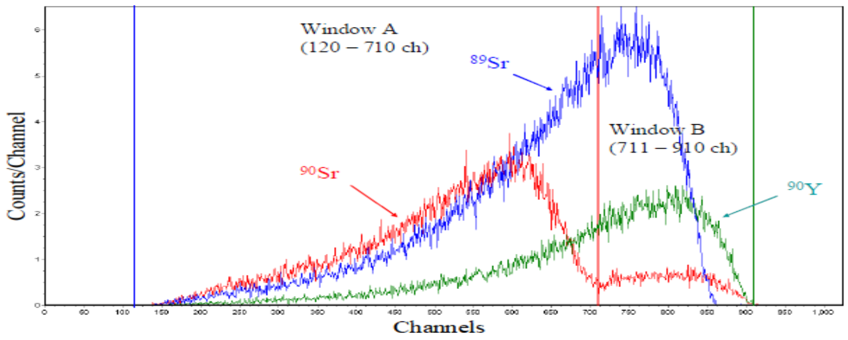
Yield tracers

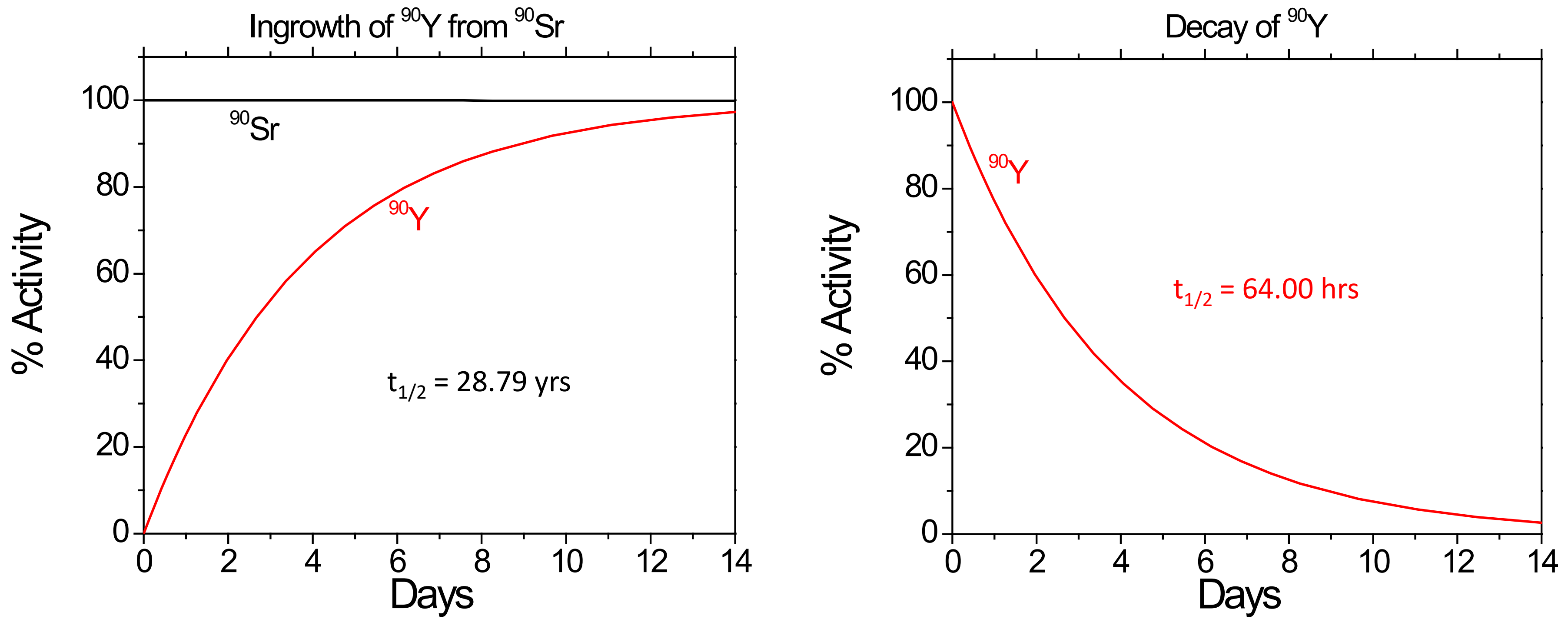
analytes

Why is $^{89}Sr/^{90}Sr$ Challenging?

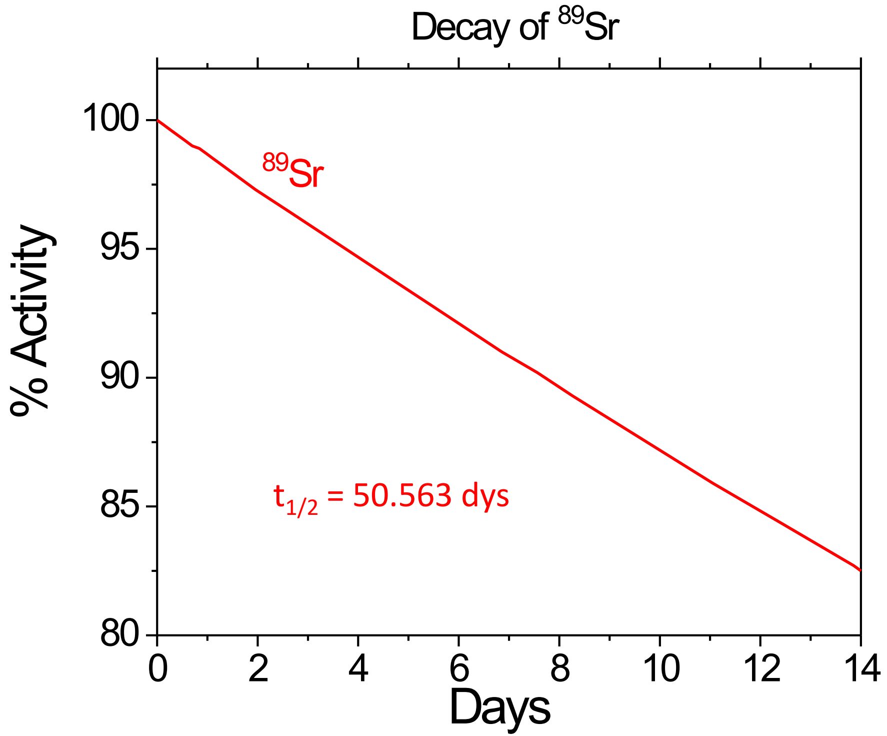
Decay of $^{89}Sr/^{90}Sr$ + Ingrowth ^{90}Y

Pure Beta emitters



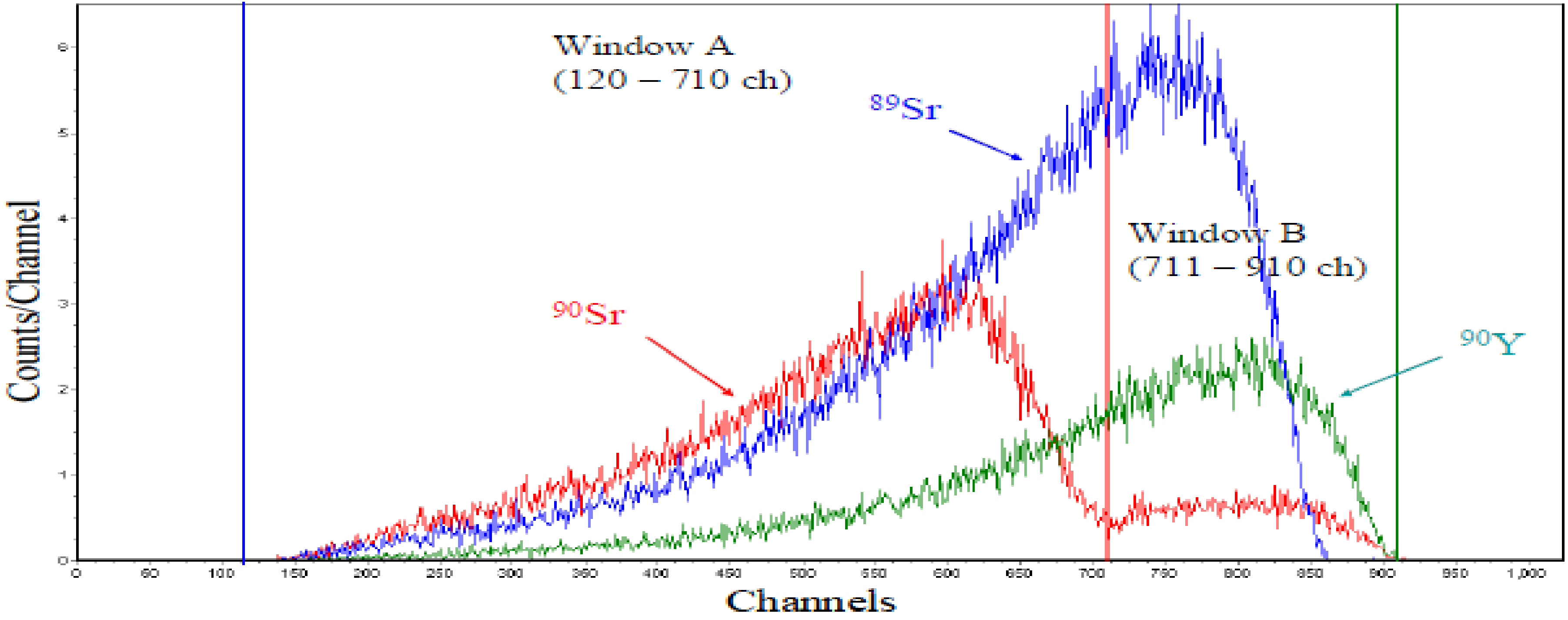


^{90}Y decays into stable ^{90}Zr



^{89}Sr decays into stable ^{89}Y

LSC Spectra



IAEA/AQ/27, “Rapid Simultaneous Determination of 89Sr and 90Sr in Milk: a Procedure Using Cherenkov and Scintillation Counting,” IAEA Analytical Quality in Nuclear Applications Series No. 27.

Cherenkov Spectra

Pros:

No cocktail = No Quench

No luminescence

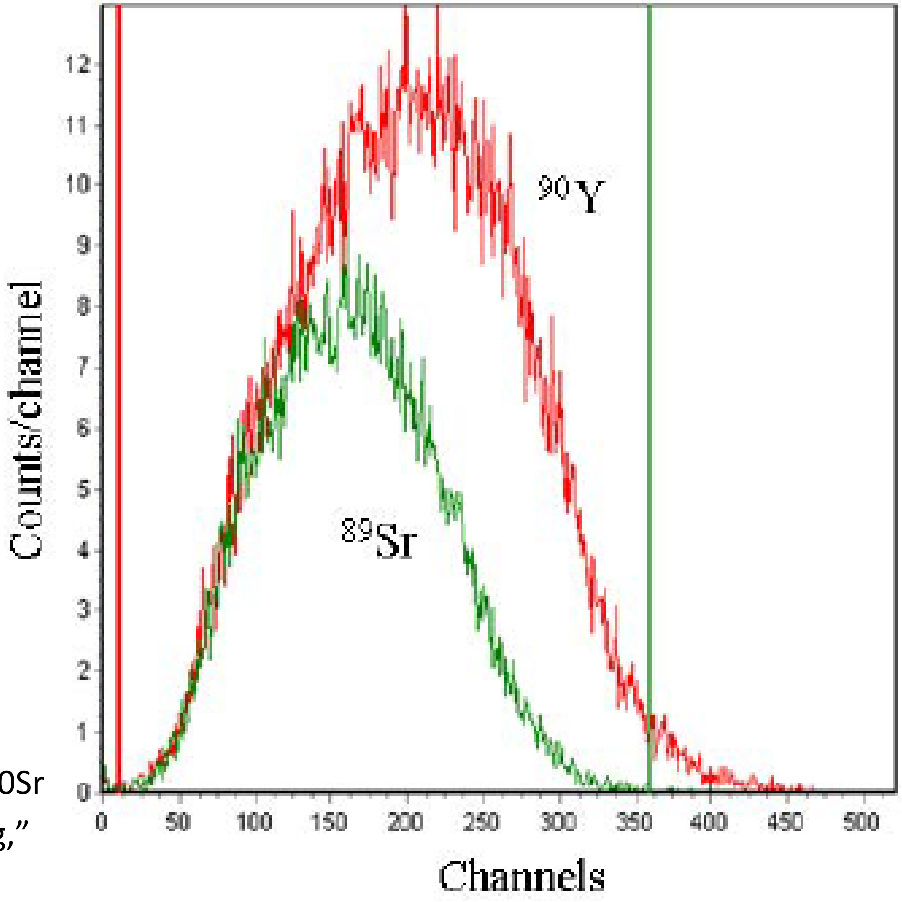
Non-destructive

Selective for high energy β-/β+.

(Measure ^{89}Sr/^{90}Y, reject ^{90}Sr)

Cons:

Lower Efficiency than LSC



IAEA/AQ/27, "Rapid Simultaneous Determination of 89Sr and 90Sr in Milk: a Procedure Using Cherenkov and Scintillation Counting," IAEA Analytical Quality in Nuclear Applications Series No. 27.

Method Options

Following Matrix Removal/Sr Resin Isolation of Sr:

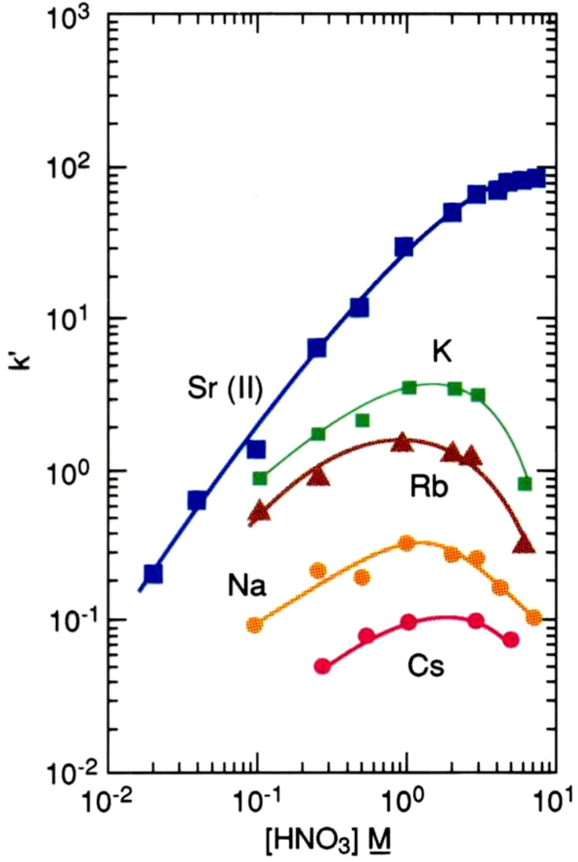
1) MS (^{90}Sr Only)

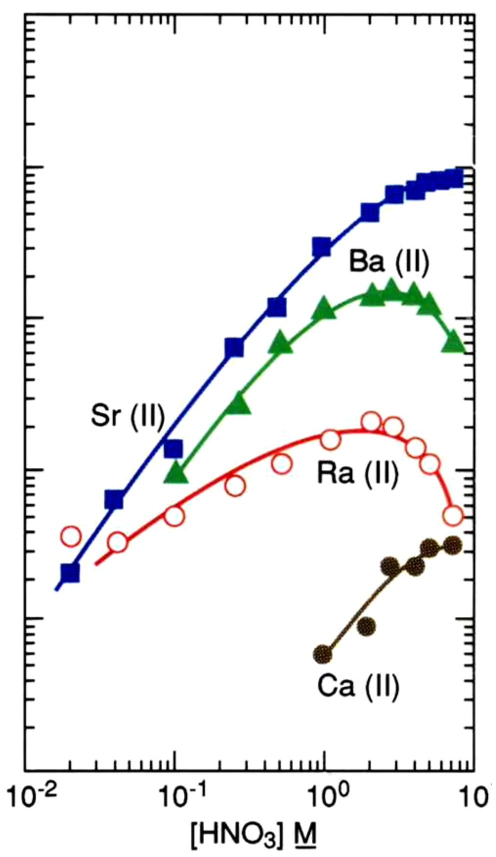
2) Two count methods
   - Different counting techniques
   - Same technique with period of ingrowth (^{90}Y)

3) Count, ingrowth, Separate ^{90}Y

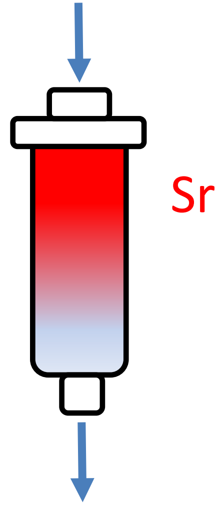
Described in detail in AN-1624 and Eichrom RRMC workshop 2018

Uptake on Sr Resin



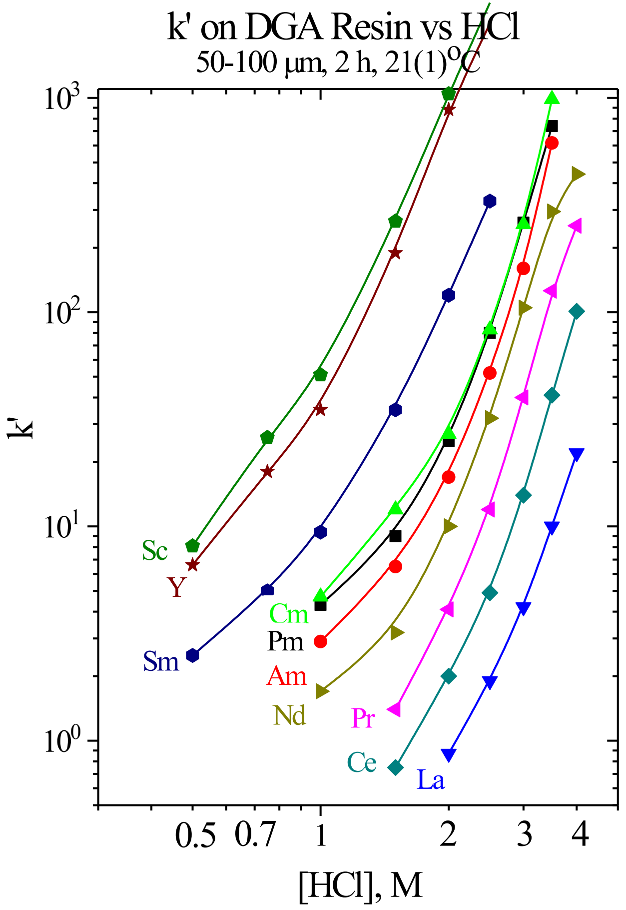


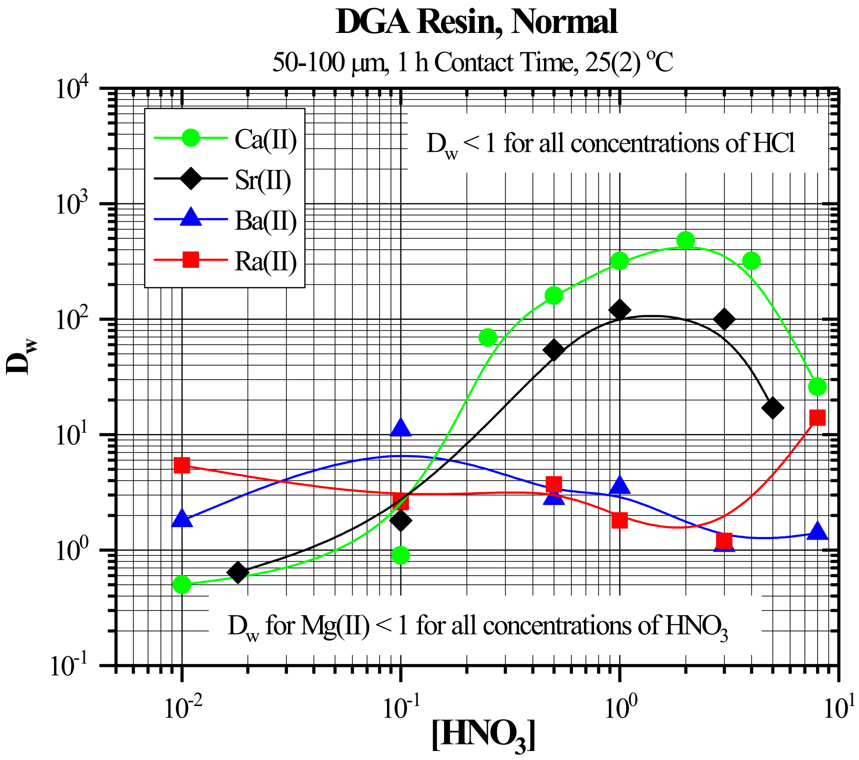
3-8M HNO_3
5 mg Stable Sr
$^{89/90}Sr + ^{90}Y$



^{90}Y

Uptake on DGA Resin, Normal

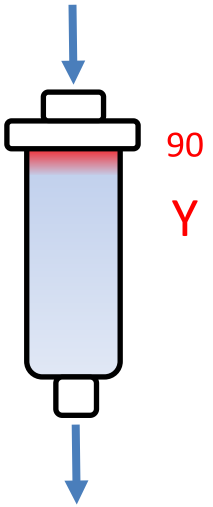




$3\text{-}8M\ HNO_3$

5 mg Stable Sr

$^{89/90}Sr + {}^{90}Y$



Sr

Rinse, Rinse, Rinse!

Alpha Source Preparation (CeF3)

Rapid method with adequate resolution for most analyses.

- No evaporations
- Additional removal of U(VI)

Add 50-100 ug of Ce

Add $TiCl_3$ to U samples, U(IV) will carry on CeF_3

Add H_2O_2 to non-U samples, U(VI) will not carry on CeF_3

Add HF (or NH_4HF) to all samples

1) Dilute samples as necessary and add Ce Carrier (See Table I).

2) **U Samples**, Add 0.5mL 10% $TiCl_3$

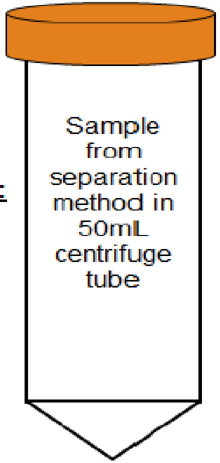
3) **Th, Np, Pu, Am/Cm samples requiring additional U decontamination:** Add 50mL 30% H_2O_2.

4) Swirl to mix.

5) Add 1-3.5mL conc. HF (see Table I).

6) Swirl to mix.

7) Wait 20-30 minutes before filtration.



8) Ensure tight fit of filter assembly.

9) Engage vacuum.

10) Wet filter with 3-5mL 80% ethanol.

11) Wet filter with 3-5mL DI water.

12) Add sample.

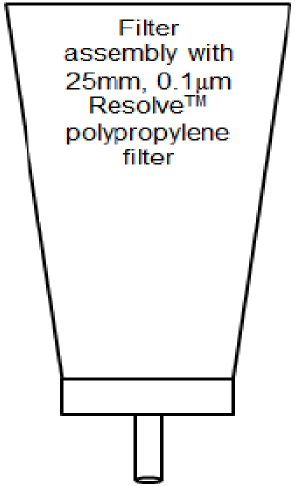
13) Rinse tube with 5mL DI water and add to filter assembly.

14) Allow all fluid to pass through filter.

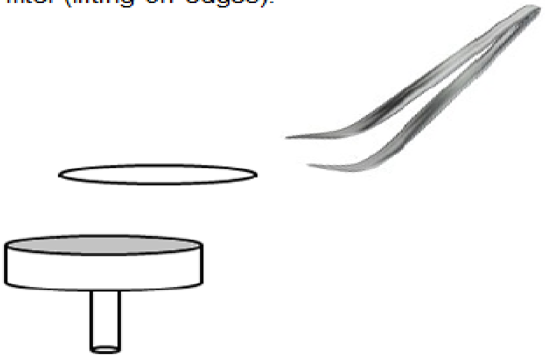
15) Rinse filter funnel with 3-5mL DI Water.

16) Rinse filter funnel with 2-3mL ethanol.

17) Filter until dry.



18) Remove filter (lifting on edges).

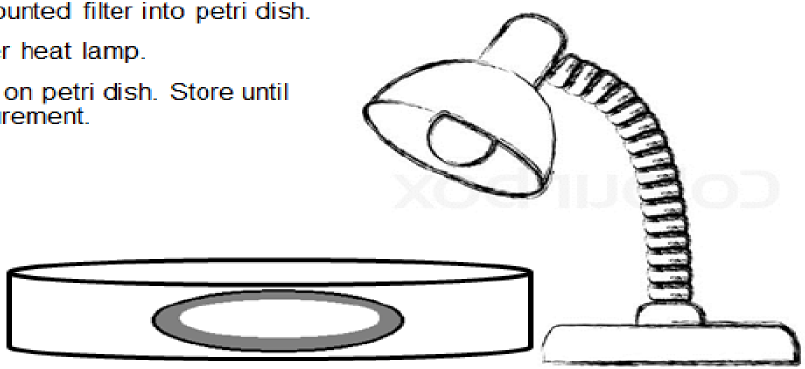


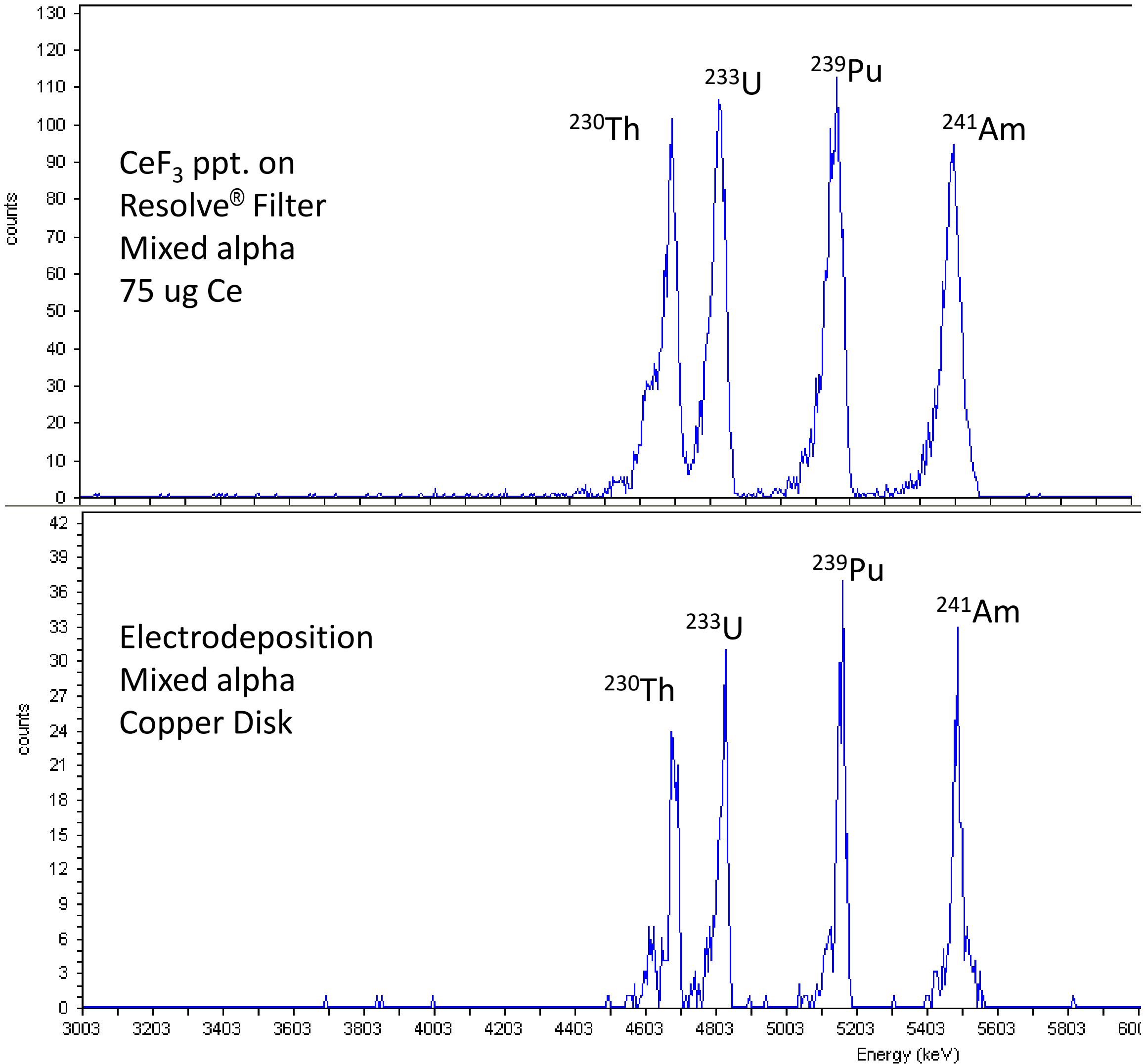
19) Mount filter to stainless steel planchet.

20) Place mounted filter into petri dish.

21) Dry under heat lamp.

22) Place lid on petri dish. Store until alpha measurement.





CeF3 filter

- Faster
- Simpler
- Adequate resolution
- Less durable (contamination)
- Additional U purification

Electrodeposition

- Slower
- More complex
- Superior resolution
- More durable

Questions????