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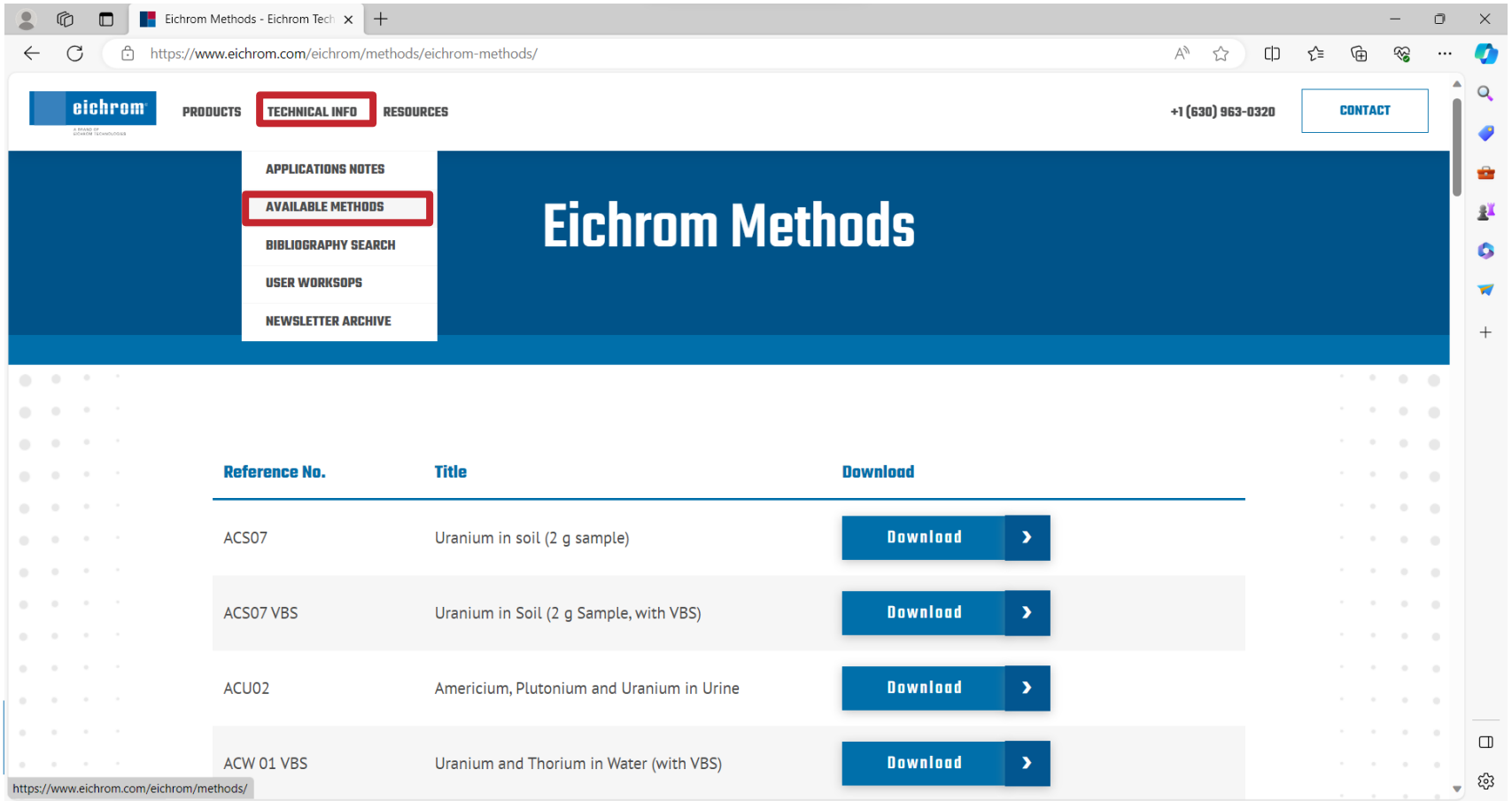
EICHROM TECHNOLOGIES

Eichrom Method ACU02-VBS
Am, Pu, and U in urine

https://www.eichrom.com/eichrom/methods/eichrom-methods



Outline

- Steps
  - Tracer Equilibration/Mild Digestion
  - Calcium Phosphate Precipitation
  - Precipitate Digestion to remove organics
  - Load Solution and Red/Ox Adjustments
    - Reducing Conditions: Am(III), Pu(III)/Np(IV), U(VI), Fe(II)
  - UTEVA/TRU Separation
  - Alpha Source Preparation (CeF3)

Acidification and Tracer Equilibration

Urine Sample in glass beaker. HNO_3 digest.

1) Aliquot up to 1200mL of water into glass beaker. (Filter if necessary)

2) Add yield tracers.
$^{243}Am(^{239}Np)$, ^{232}U*, ^{236}Pu or ^{242}Pu

*Self-cleaning (Eichrom Method TPO1)

3) Add 1mL of 1.25M $Ca(NO_3)_2$. (50 mg Ca)

Add 2-3 drops of 1-octanol. (minimize foam)

4) Add 25 mL of conc. HNO_3.

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

6) Remove samples from heat.

Calcium Phosphate Precipitation

6) Add 2.5mL 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. Mix 30 minutes at low heat.

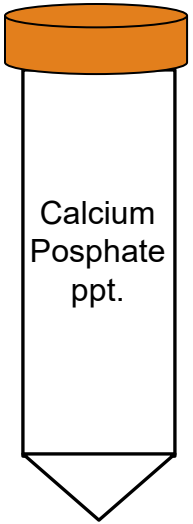
8) Cool to room temperature.
Allow precipitate to settle or centrifuge.

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.

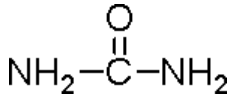


Centrifuge.
Decant Supernate.
Wash ppt with H_2O.
Centrifuge. Decant.

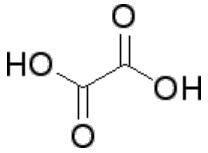
What is in Urine? (Varies based on person, diet, hydration)

1) Volume: 600- 2500 ml/24 hrs. Average: 1,200 ml.
2) Specific gravity: 1.003 - 1.030
3) (pH: 4.7 - 7.5) Average pH: 6.0
4) Total solids: 30 - 70 g/liter.

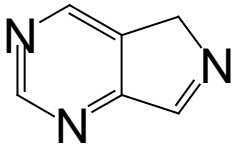
Na^+ (3-6g)
K^+ (1-3g)
Ca^{2+} (0.1-0.3g)
PO_4^{3-} (1-2g)
SO_4^{2-} (1-4g)
Mg (40-200mg)
NH_4^+ (0.3-1g)
I (50-250mg)
Cl^- (9-16g)



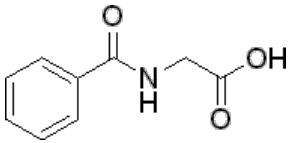
Urea (25-30g)



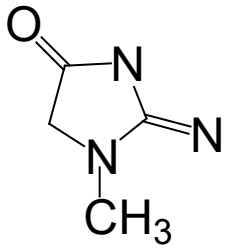
Oxalic acid (15-20mg)



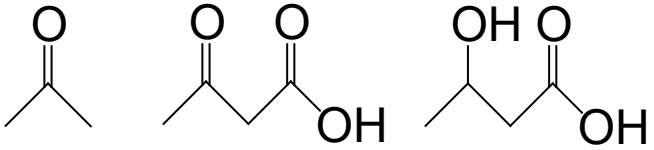
Purine Bases (7-10mg)



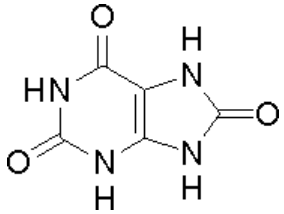
Hippuric acid (0.1-1g)



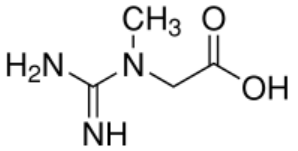
Creatinine (0.5-2g)



Ketone Bodies (3-15mg)

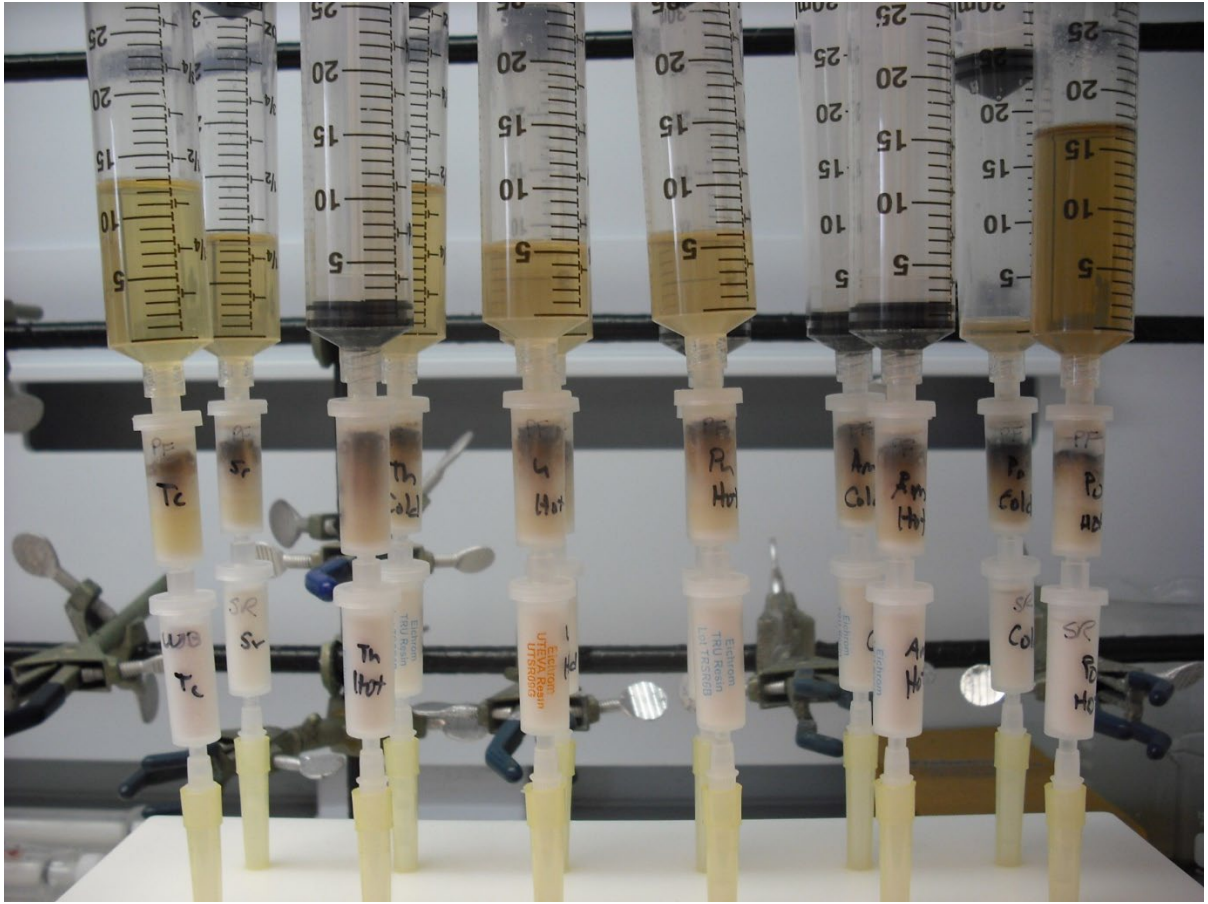


Uric acid (0.3-1g)



Creatine (0.5-2g)

Need to destroy organic material



Can clog columns or cartridges.

Interferes with separations.

Decreases yields.

Digest Precipitate

13) Rinse original beaker with 5 mL conc. HNO_3.
Transfer to centrifuge tube containing precipitate.
Dissolve precipitate and transfer to 200 mL glass beaker.

14) Rinse centrifuge tube with 2x 5 mL conc. HNO3.
Transfer rinses to the 200 mL beaker.

15) Add 1 mL 30% H_2O_2 and evaporate samples to dryness.
Watch samples and remove from heat as they dry.
Heating too long can make them difficult to re-dissolve, especially Pu and Th.

16) While samples are still hot, carefully add 2-3 drops of 30% H_2O_2 to digest remaining organics.

Add 5 mL of conc. HNO_3 and 5 mL 30% H_2O_2.
Evaporate to dryness. Repeat until precipitate is white.

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

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

Add Ammonium thiocyanate indicator (turns red with Fe(III))

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

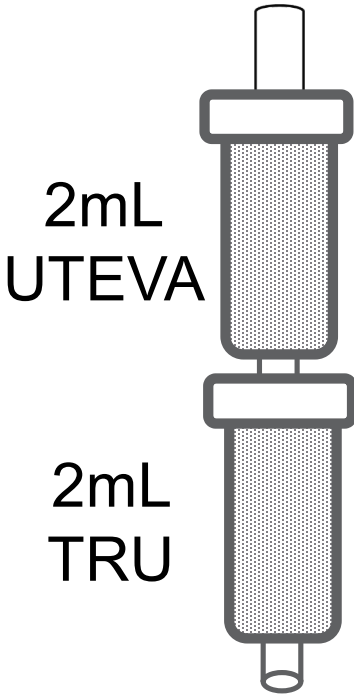
0.5 mL of 5 mg/ mL Fe, (will act as reducing agent)

1-2 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)

Solution should be clear: Fe(II), U(VI), Pu(III), Np(IV), and Am(III)

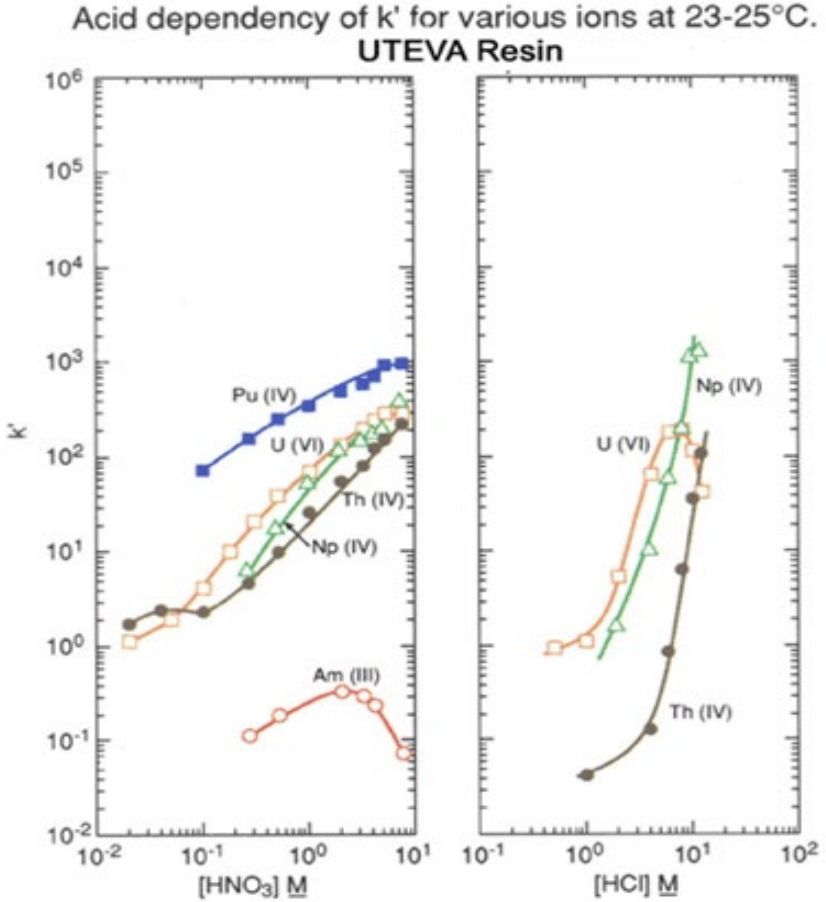
Cartridge Separations

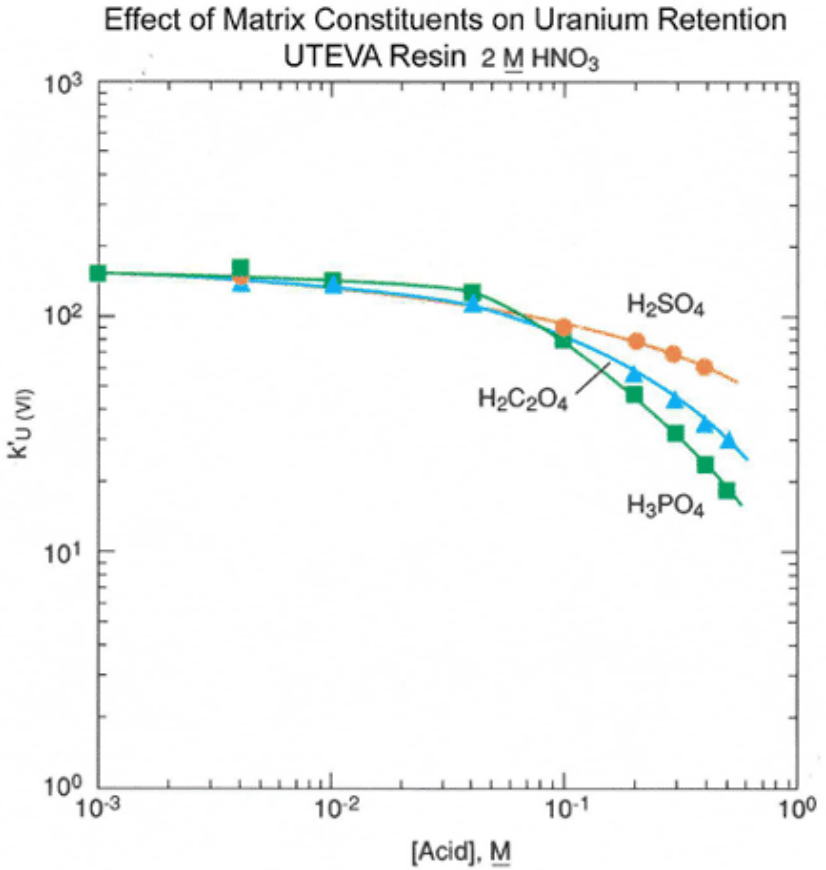


Retains (IV) and (VI) actinides from HNO_3.
Sensitive to phosphate.

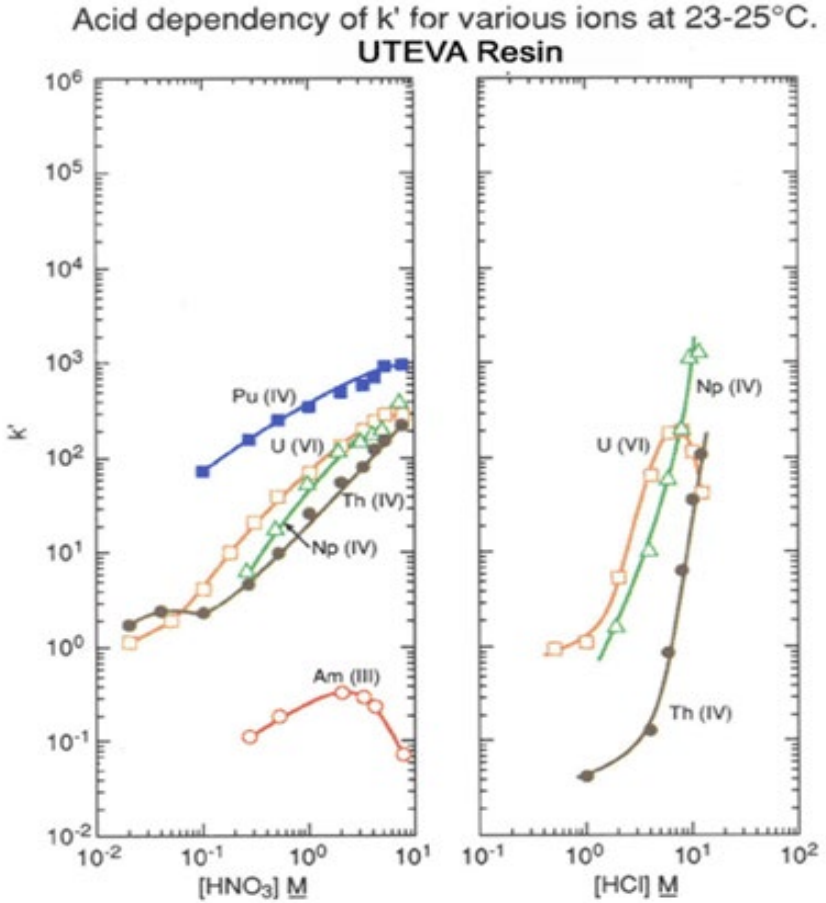
Retains (III), (IV), (VI) actinides from HNO_3.
Pu/Am/Cm(III) Sensitive to Fe(III).

UTEVA Resin


Acid dependency of k' for various ions at 23-25°C.
UTEVA Resin
k'
Pu (IV)
U (VI)
Th (IV)
Np (IV)
Am (III)
[HNO3] M
Np (IV)
U (VI)
Th (IV)
[HCl] M


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

UTEVA Resin



18) Precondition UTEVA-TRU with 5mL 3M HNO_3.

19) Load sample onto UTEVA-TRU at 1-2 mL/min.
UTEVA retains U(VI). TRU retains Pu(III) and Am(III).

20) Rinse sample tube with 5mL 3M HNO_3.
Add rinse to UTEVA-TRU. Allow liquid to drain.

21) Rinse UTEVA-TRU with 5mL 3M HNO_3.
Allow liquid to drain.

22) Separate UTEVA and TRU cartridges.

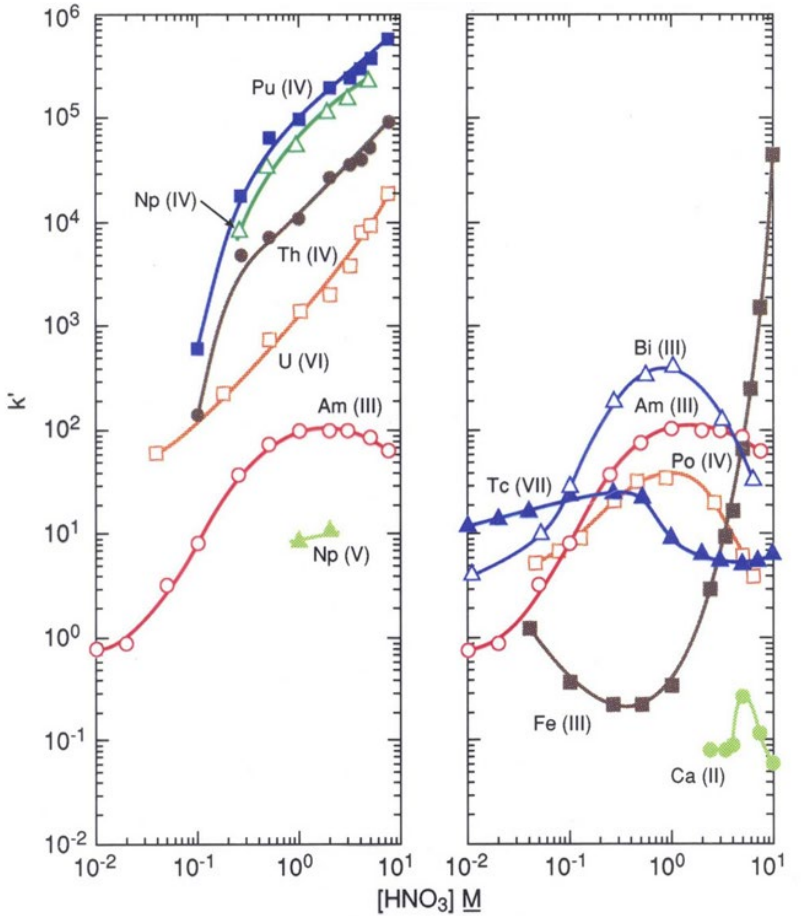
23) Rinse UTEVA with 15mL 8M HNO_3. (Po removal)

24) Rinse UTEVA 15mL 9M HCl. (convert to HCl).

25) Rinse UTEVA with 20 mL 5M HCl-0.05M oxalic acid.
Removes Th(IV) and any traces of Pu(IV)/Np(IV).

26) Place a clean 50 mL centrifuge tube below each UTEVA cartridge. Elute U with 15 mL 1M HCl.
(set aside for CeF_3).

TRU Resin



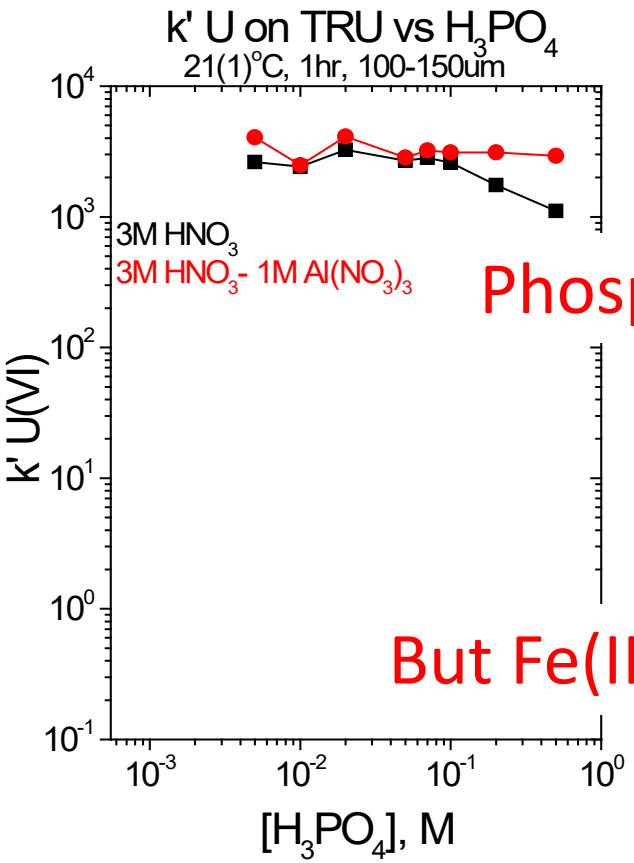
27) Rinse TRU with 5 mL 2M HNO_3 – 0.1M $NaNO_2$.
Converts Pu(III) to Pu(IV). Cartridge may turn pale blue.

28) Place clean 50 mL centrifuge tube below each TRU cartridge.
Strip Am(III) with 15 mL of 4M HCl. (Set aside for CeF_3).

29) Rinse each TRU cartridge with 25 mL 4M HCl-0.1M HF.
(Removes any traces of Th(IV) that may have broken through UTEVA).

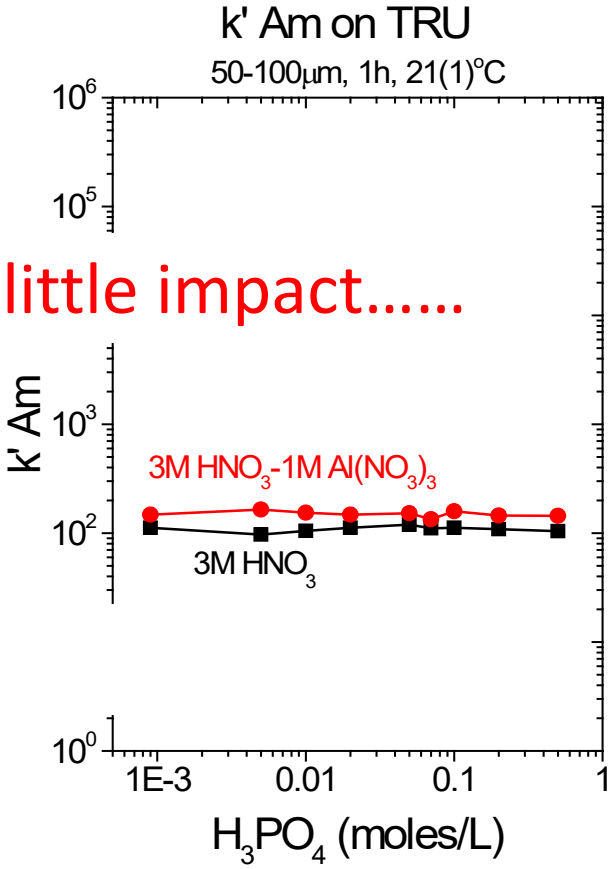
30) Place a clean 50 mL centrifuge tube below each TRU cartridge.
Strip Pu with 10 mL of 0.1M ammonium bioxalate.
(set aside for CeF_3).

TRU Resin

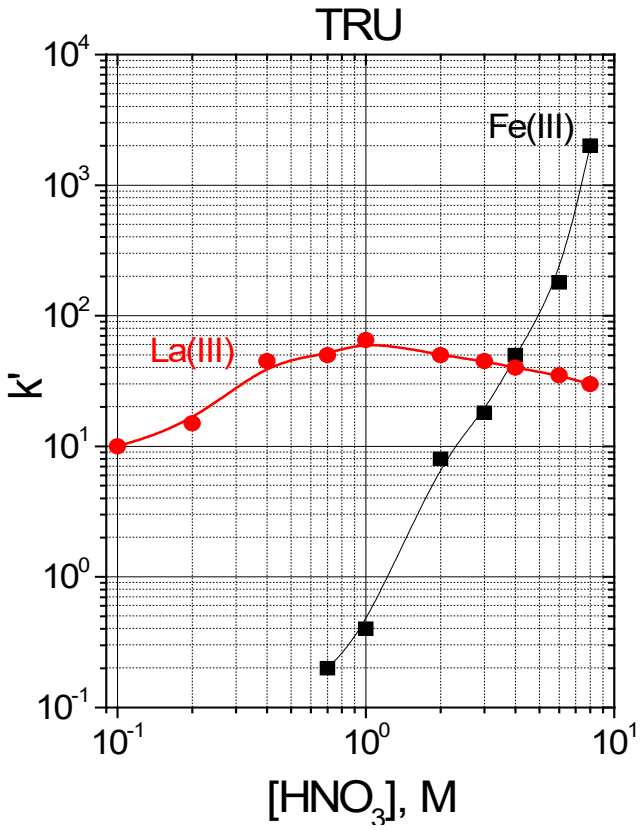


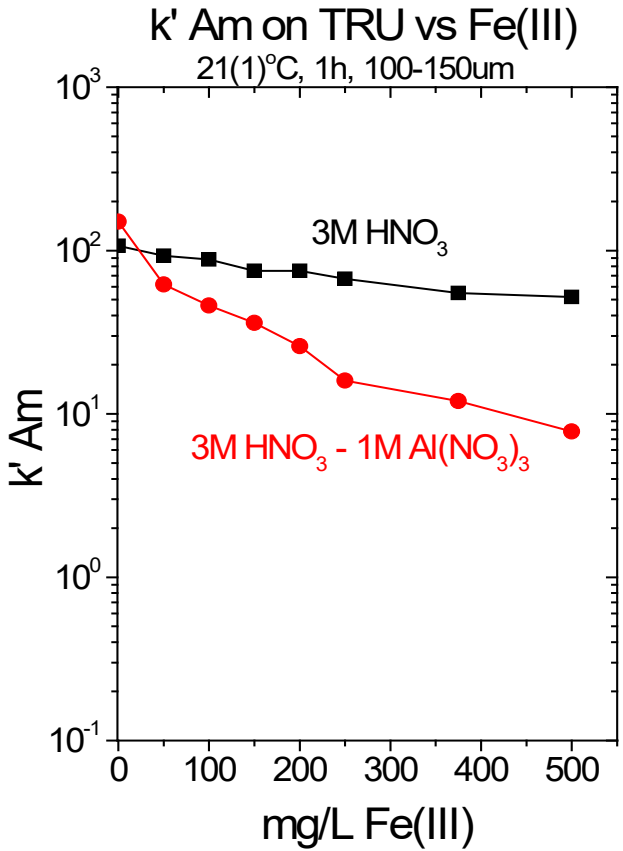
Phosphate has little impact……

But Fe(III)…….



TRU Resin


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


k' Am on TRU vs Fe(III)
21(1)°C, 1h, 100-150um
3M HNO3
3M HNO3 - 1M Al(NO3)3
k' Am
mg/L Fe(III)

Rare earths will elute from TRU with Am(III)

(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.

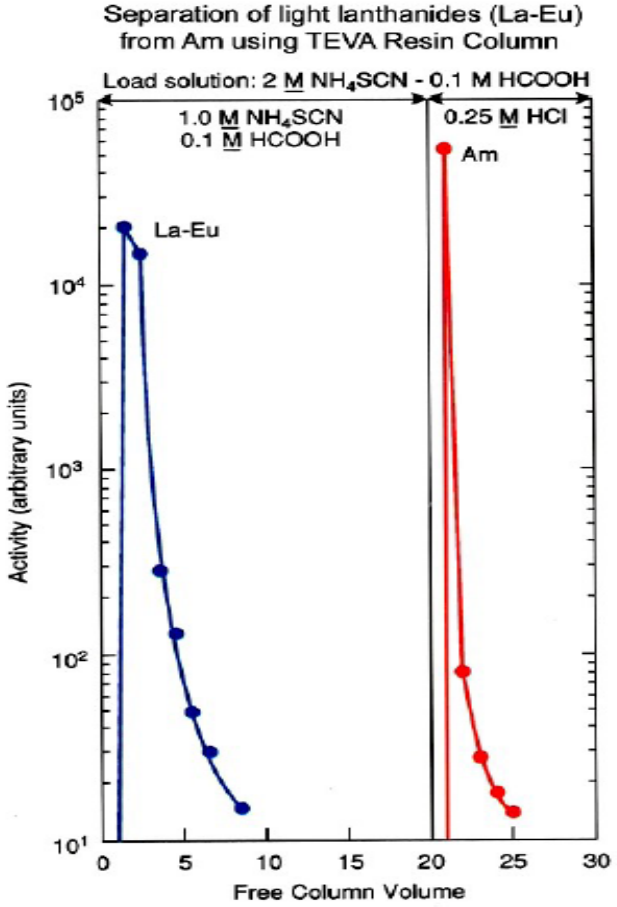
(5) Load Am/Cm from step (3) on TEVA.

(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.

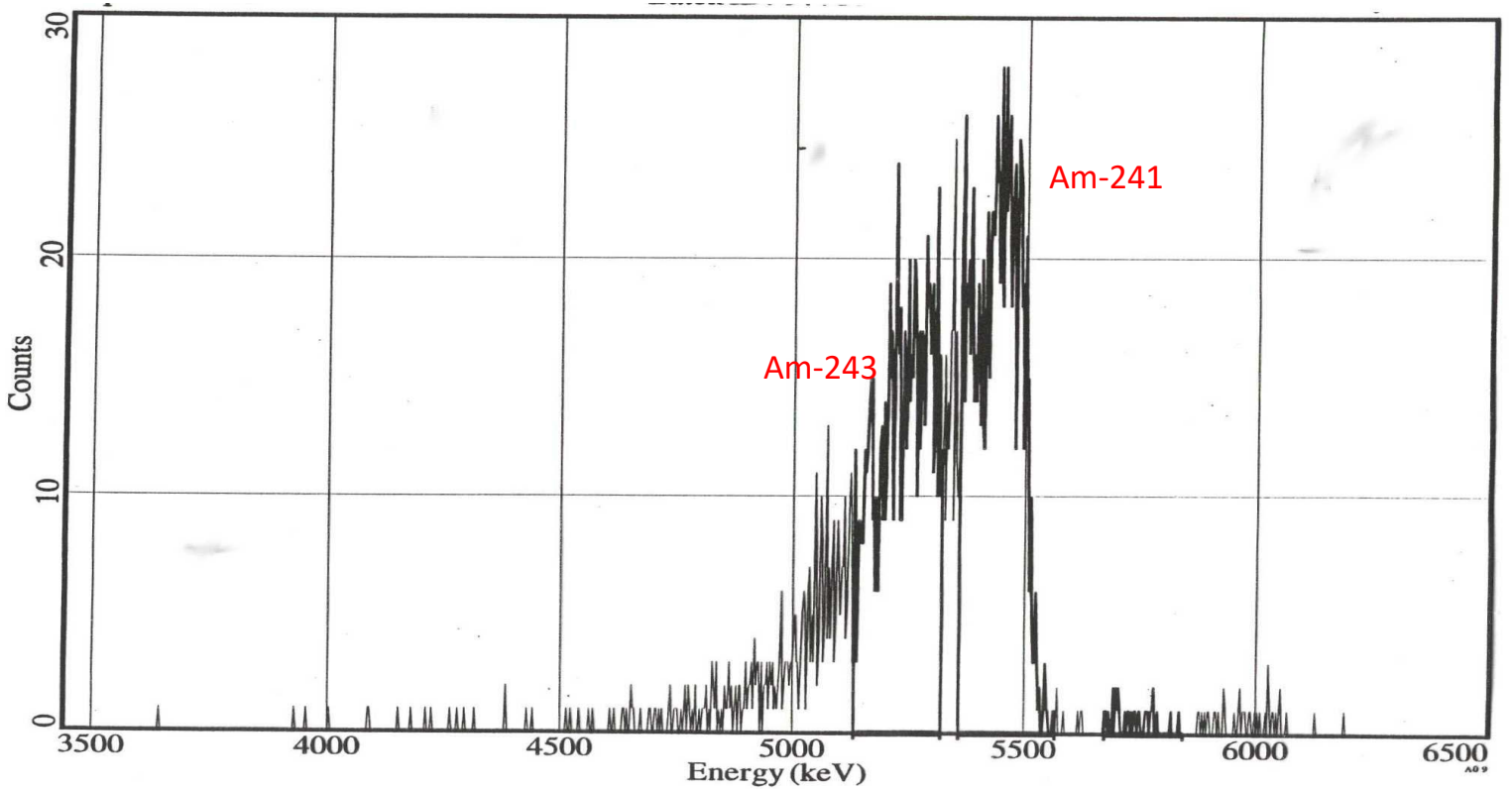
(8) Strip Am/Cm from TEVA with 20 mL 1M HCl.

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



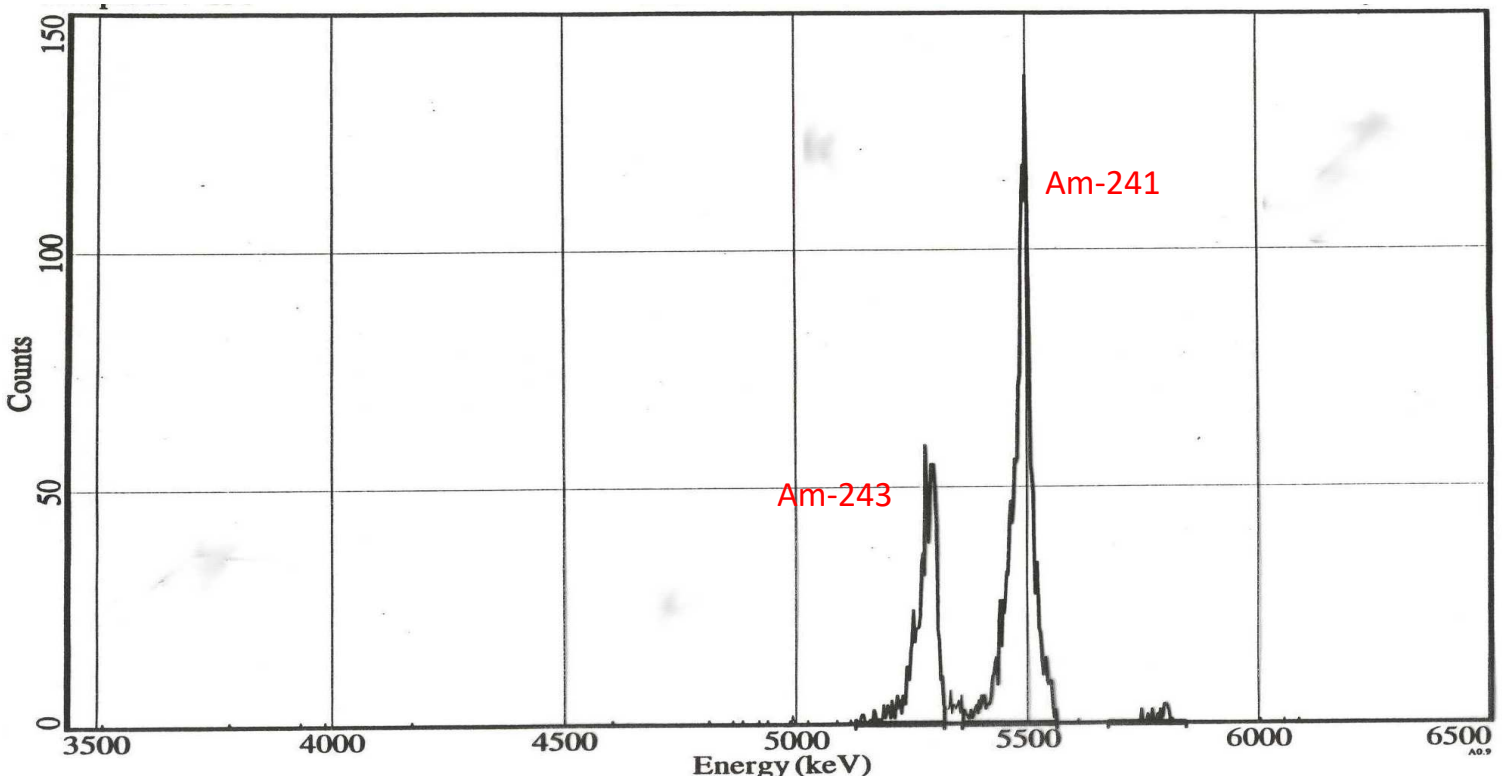
Americium Spectrum after TRU Resin Separation

presence of rare earths degrades spectrum- self absorption issues



Am Spectrum after TEVA Resin Separation

Lanthanide elements removed - cleaner spectrum



Alpha Source Preparation (CeF_3)

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

Alpha Source Preparation (CeF3)

Typical Performance of CeF_3 Microprecipitation onto Eichrom Resolve Filters

Nuclide	µg Ce	Matrix	Yield	Resolution (FWHM)
^{230}Th	50	30 mL 4.5M HCl	>95%	20-30 keV
$^{238/234}U$	100	20 mL 1M HCl	>95%	30-40 keV
^{239}Pu	50	20 mL 0.1M HCl-0.05MHF-0.01M$TiCl_3$	>95%	30-40 keV
^{241}Am	50	15 mL 4M HCl	>95%	22-28 keV

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

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

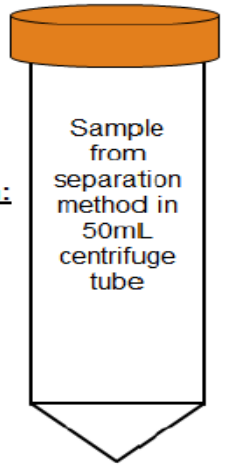
3) **Th, Np, Pu, Am/Cm samples requiring additional U decontamination:** Add 50mL 30% H_2O_2.

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.

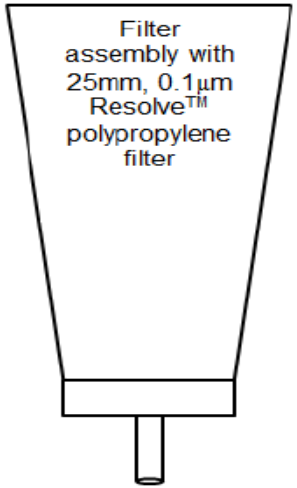
13) Rinse tube with 5mL DI water and add to filter assembly.

14) Allow all fluid to pass through filter.

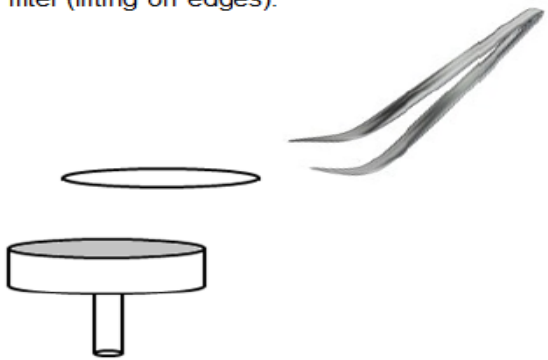
15) Rinse filter funnel with 3-5mL DI Water.

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

17) Filter until dry.



18) Remove filter (lifting on edges).

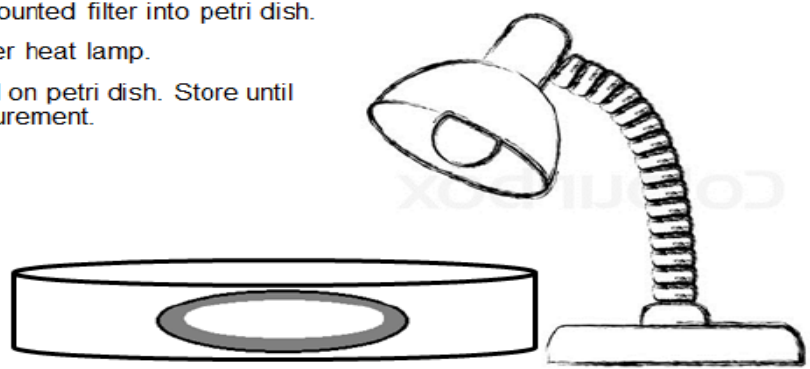


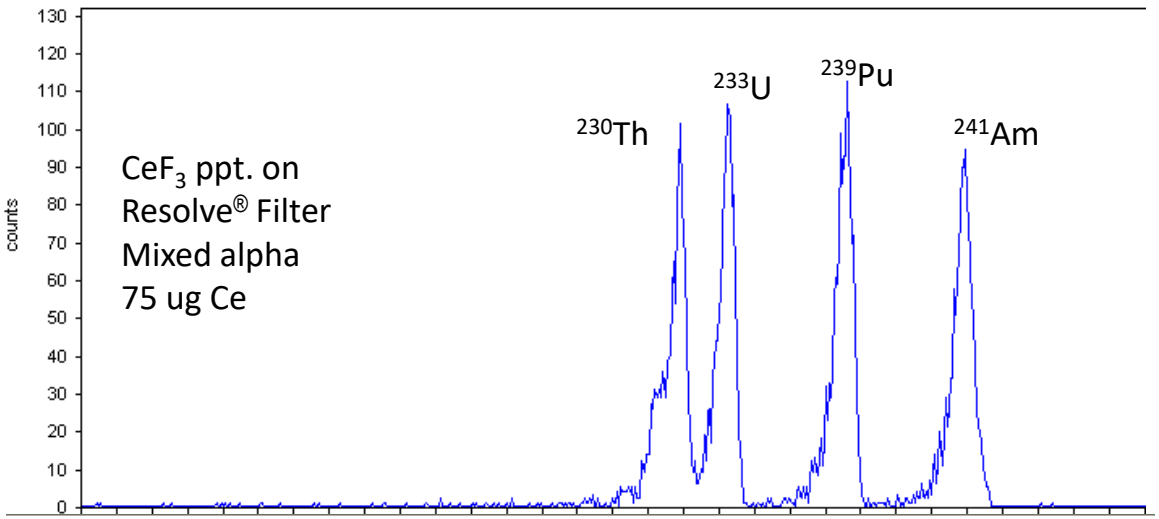
19) Mount filter to stainless steel planchet.

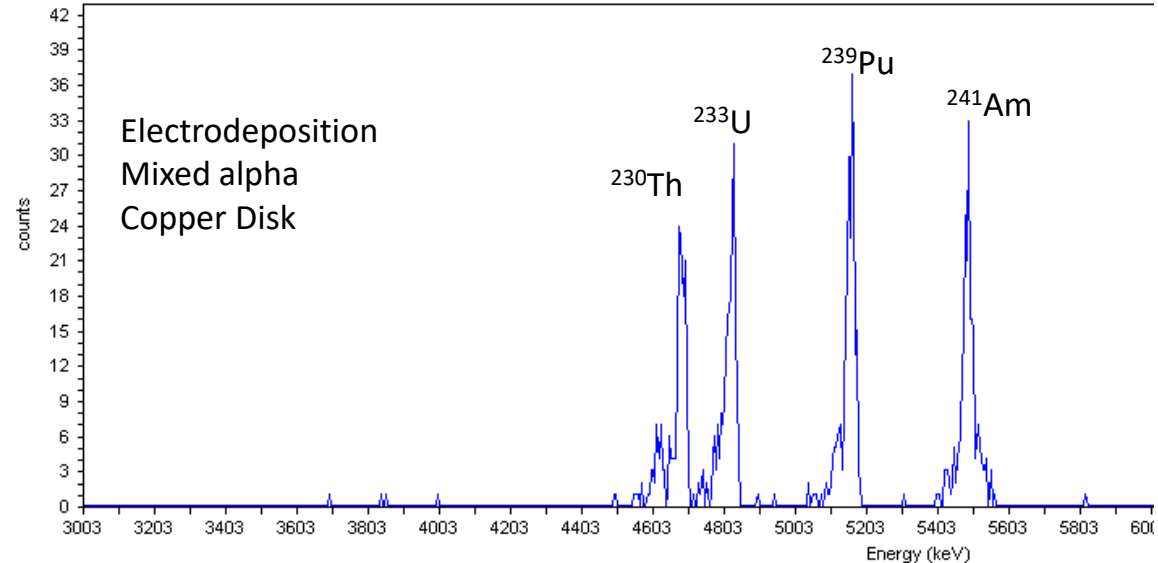
20) Place mounted filter into petri dish.

21) Dry under heat lamp.

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

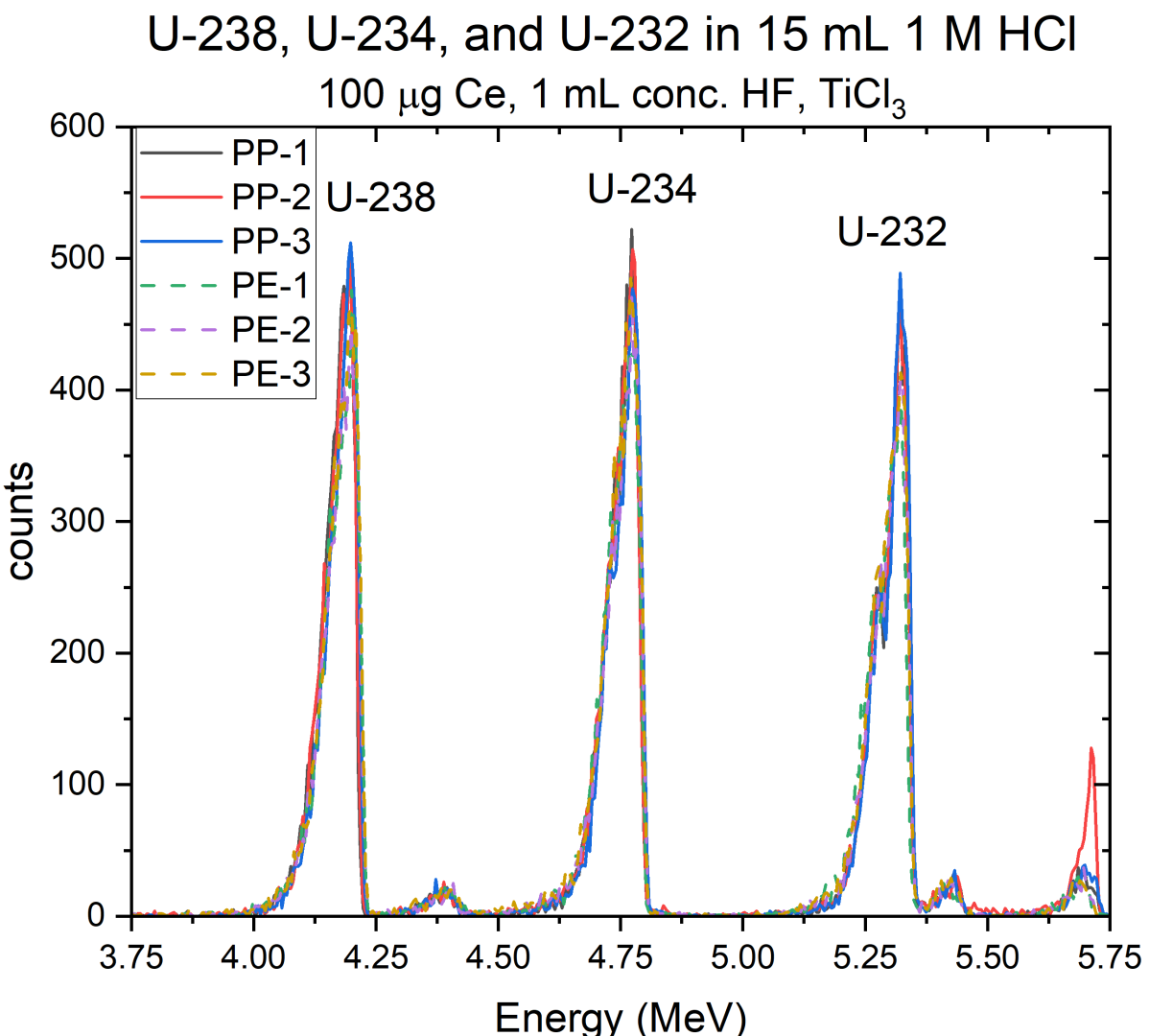


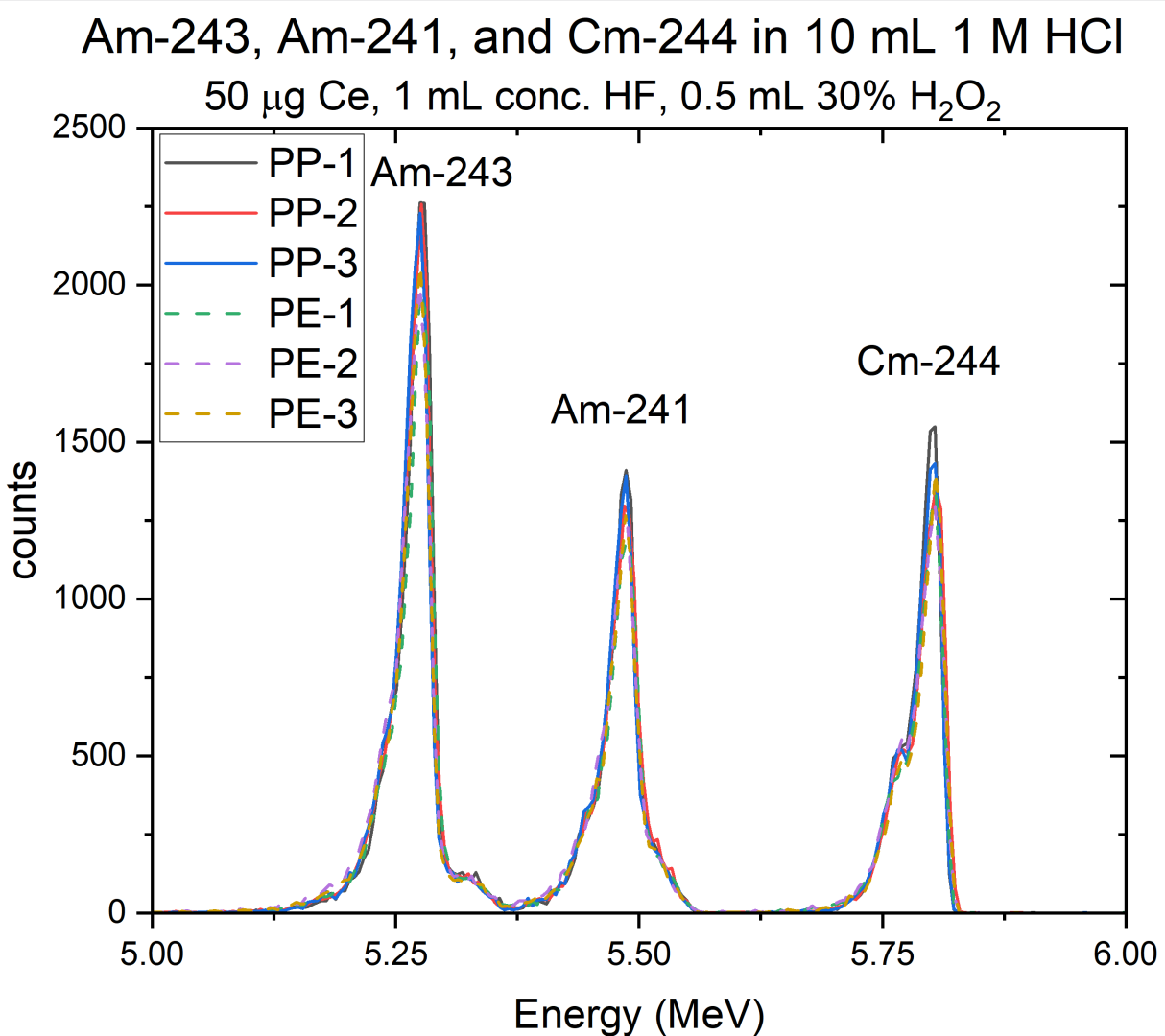




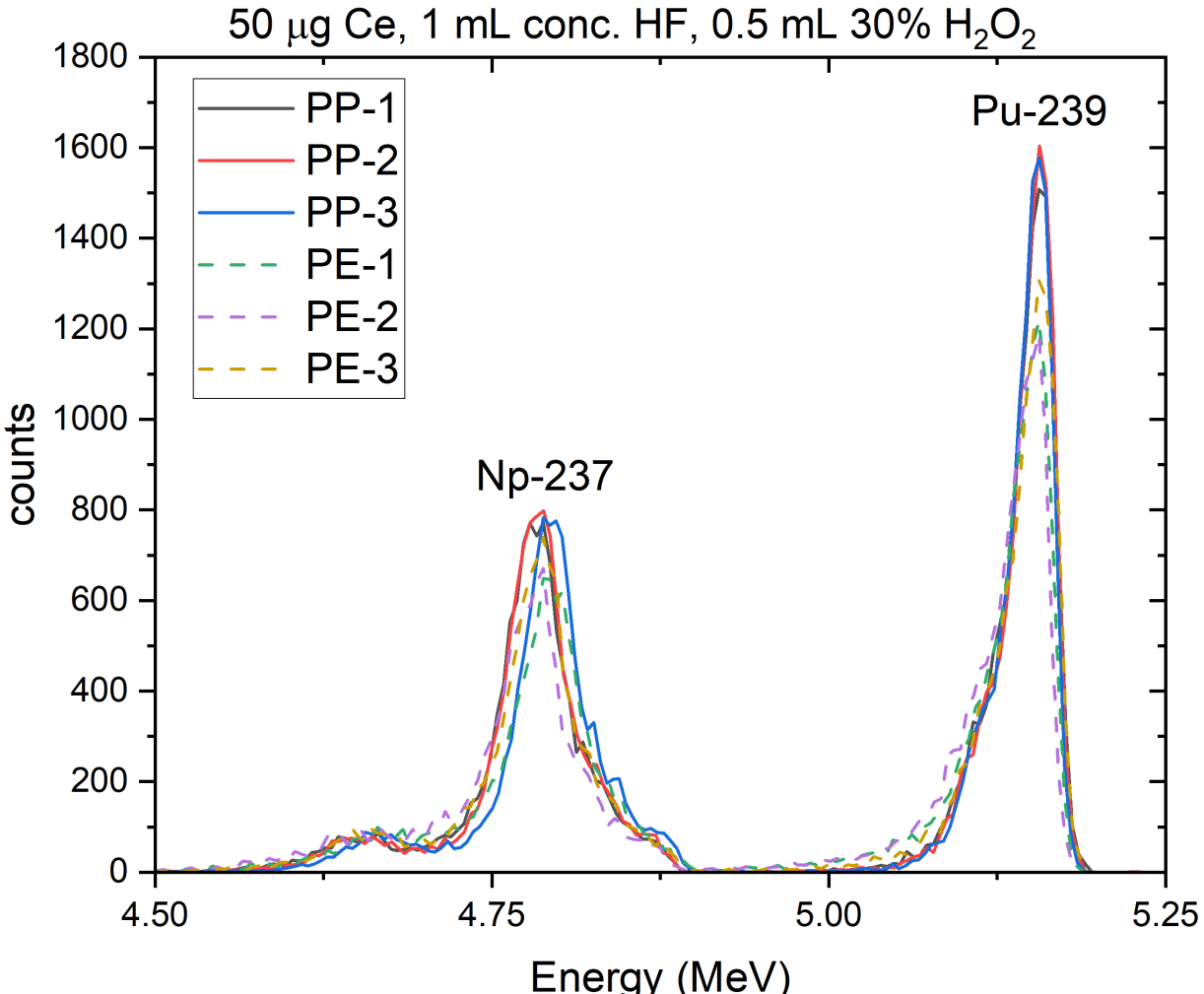
CeF3 filter
- Faster
- Simpler
- Adequate resolution
- Less durable (contamination)
- Additional U purification

Electrodeposition
- Slower
- More complex
- Superior resolution
- More durable


U-238, U-234, and U-232 in 15 mL 1 M HCl
100 μg Ce, 1 mL conc. HF, TiCl3
PP-1
PP-2
PP-3
PE-1
PE-2
PE-3
U-238
U-234
U-232
counts
Energy (MeV)
0
100
200
300
400
500
600
3.75
4.00
4.25
4.50
4.75
5.00
5.25
5.50
5.75


Am-243, Am-241, and Cm-244 in 10 mL 1 M HCl
50 μg Ce, 1 mL conc. HF, 0.5 mL 30% H2O2
PP-1
PP-2
PP-3
PE-1
PE-2
PE-3
Am-243
Am-241
Cm-244
counts
Energy (MeV)
2500
2000
1500
1000
500
0
5.00
5.25
5.50
5.75
6.00

Np-237 and Pu-239 in 20 mL 0.1 M HCl + 0.05 M HF + 0.01 M $TiCl_3$



Questions????