Rapid Preconcentration of Ra-226 in Hydraulic Fracturing Wastewater Samples for Gamma Spectrometry Assay

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Background

- Need for rapid method to preconcentrate Ra-226 in hydraulic fracturing samples
  - Lower MDA
  - Rapid processing

- Challenges
  - Hard to collect Ra-226
  - High levels of dissolved solids: Ca, Ba, Sr, Mg, Na, K, etc.
  - Interference of U-235 on Ra-226 186 keV gamma ray
  - Waiting on Ra-226 progeny hurts turnaround times

- Wanted to use modification of SRNS methods for seawater to help solve the analytical issues

Literature

- A. Nelson et al, Matrix Complications in the Determination of Radium Levels in Hydraulic Fracturing Flowback Water from Marcellus Shale *Environ. Sci. Technol. Lett.*, 2014, *1* (3), pp 204–208
  - very low chemical yields using a wide array of analytical approaches
  - sample processing problems associated with high levels of dissolved solids
  - 20g/L Ca, 10 g/L Ba, 10 g/L Sr
    - *"alkaline earth nightmare"*
  - Direct gamma spectrometry (*precipitation problems)*
    - *using agar/heating to prevent precipitation of ultrafine particulate matter*
    - *~80 pCi/L MDA*
    - *reliance on assumption U-235 is not present*

Literature

- T. Zhang et al, Analysis of Radium-226 in High Salinity Wastewater from Unconventional Gas Extraction by Inductively Coupled Plasma-Mass Spectrometry *Environ. Sci. Technol.*, 2015, *49* (5), pp 2969–2976
  - Need to remove isobaric interferences Ba + Sr using small amount of Sr Resin
  - Sr Resin ability to remove Ba can be easily exceeded with these samples
  - Some residual Ba noted in high Ba samples
  - Goal: 100 pCi/L MDA
  - *No tracer noted!*

	MSW composition (mg/L)				
sample	Na	Ca	Ba	Sr	TDS
S1	11,500	3,440	1,060	808	28,500
S2	23,000	6,880	2,120	1,620	57,000
S3	46,000	13,760	4,230	3,230	114,000
S4	69,000	20,640	6,360	4,850	171,000
S5	11,500	3,440	1,060	808	28,500
S6	46,000	13,760	4,240	3,230	114,000
S7	69,000	20,640	6,360	4,850	171,000

What did not work for Ra-226…

- Calcium phosphate precipitation
  - 100 ml simulant might results in 80 ml ppt
- Direct barium sulfate precipitation
  - Nelson et al called “intractable”
- MnO_2 ppt (high Ba…)
- Iron hydroxide

- Nelson et al covered all this and more….

Got an idea….

- *High Ca level is a major component in the "nightmare"*
- Difficult to separate large amounts of alkaline earth metals
- Tried everything but there was one option left…

- Contacted Dan McAlister, PG Research, and told him what I was thinking…..

Breakthrough!

- *Calcium fluoride* CaF_2 5.3×10^{-9}
- Strontium fluoride SrF_2 2.5×10^{-9}
- Magnesium fluoride MgF_2 3.7×10^{-8}
- *Barium fluoride* BaF_2 1.0×10^{-6}

- Let's acidify to 1.5M HCl, add HF to try to remove Ca and test…
- Then precipitate Ra/Ba sulfate with ammonium sulfate/ 10% ethanol

- *Ca/some of Sr/Mg removed and 80-90% Ba/Ra chemical yield*

Final Geometry

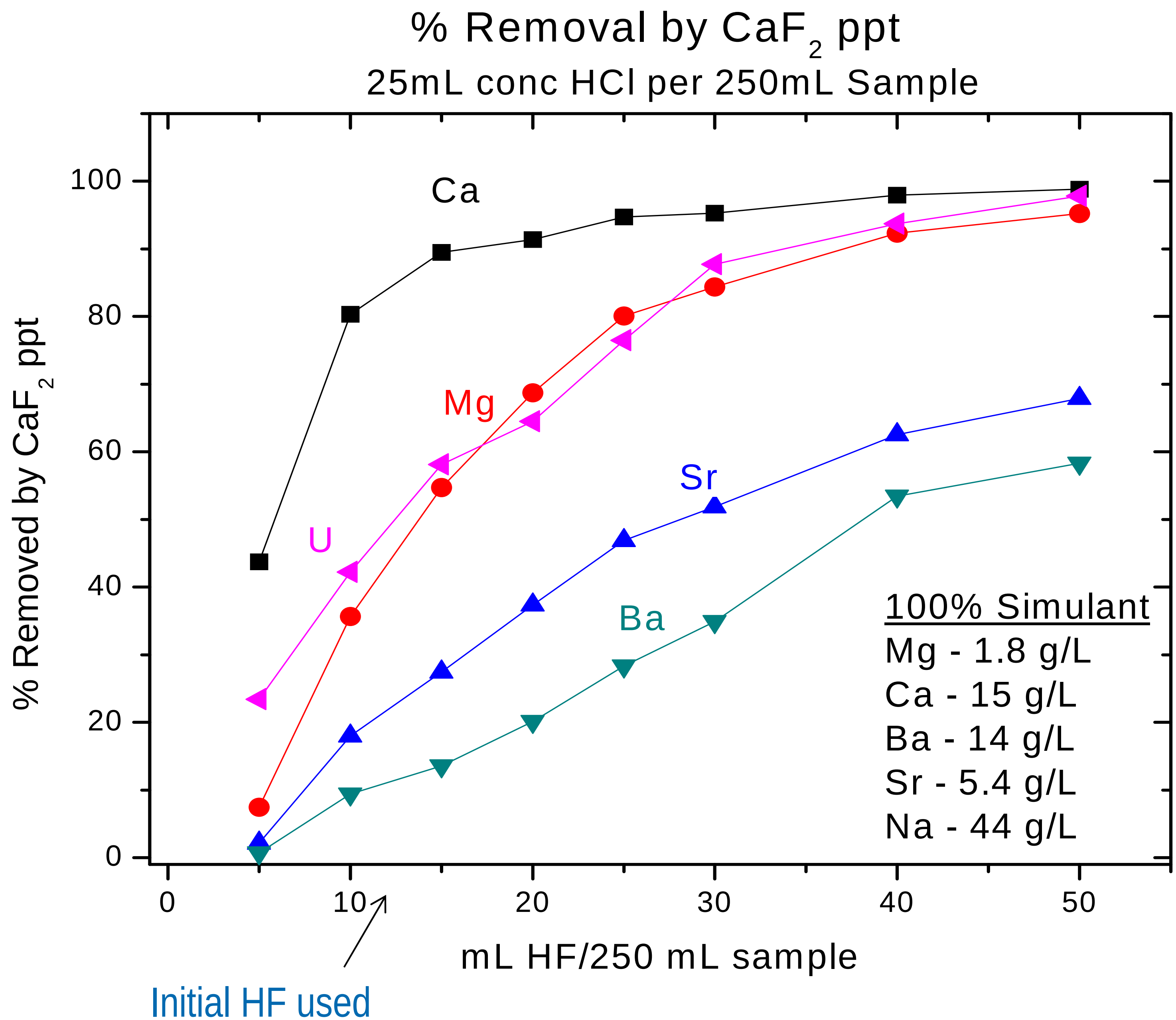
- Initially 500 ml polythylene bottle, $BaSO_4$ suspension
  - Hard to control/settled
- 250 ml Nalgene bottle with centrifuging (Dan McAlister)
  - Reproducible, even layer with varying thicknesses
- Used 356 keV gamma ray for Ba-133 tracer recovery
- *Used Ba-133 81 keV gamma ray correlation with 186 keV Ra-226 gamma ray to correct for geometry/mass attenuation*
  - Plot of 81keV efficiency vs. 186 keV gamma ray efficiency
  - Minor correction also in 356 keV Ba-133 from 81 keV as well (if needed)
    - *low abundance gamma rays (~0.2%) Ra-226, Ra-224, Ra-223 near 81 keV so we use enough Ba-133 to minimize any impact*
- *What about U-235??*

U-235 Gone…

- U removed with CaF_2 (at high levels) regardless for U^{+4} and U^{+6}
- H_2O_2 added initially and all water rinses to ensure U^{+6}
  - Additional U removal as U^{+6}

- U removed 99.9%++
  - 185.715 keV 57.0 % *abundance*

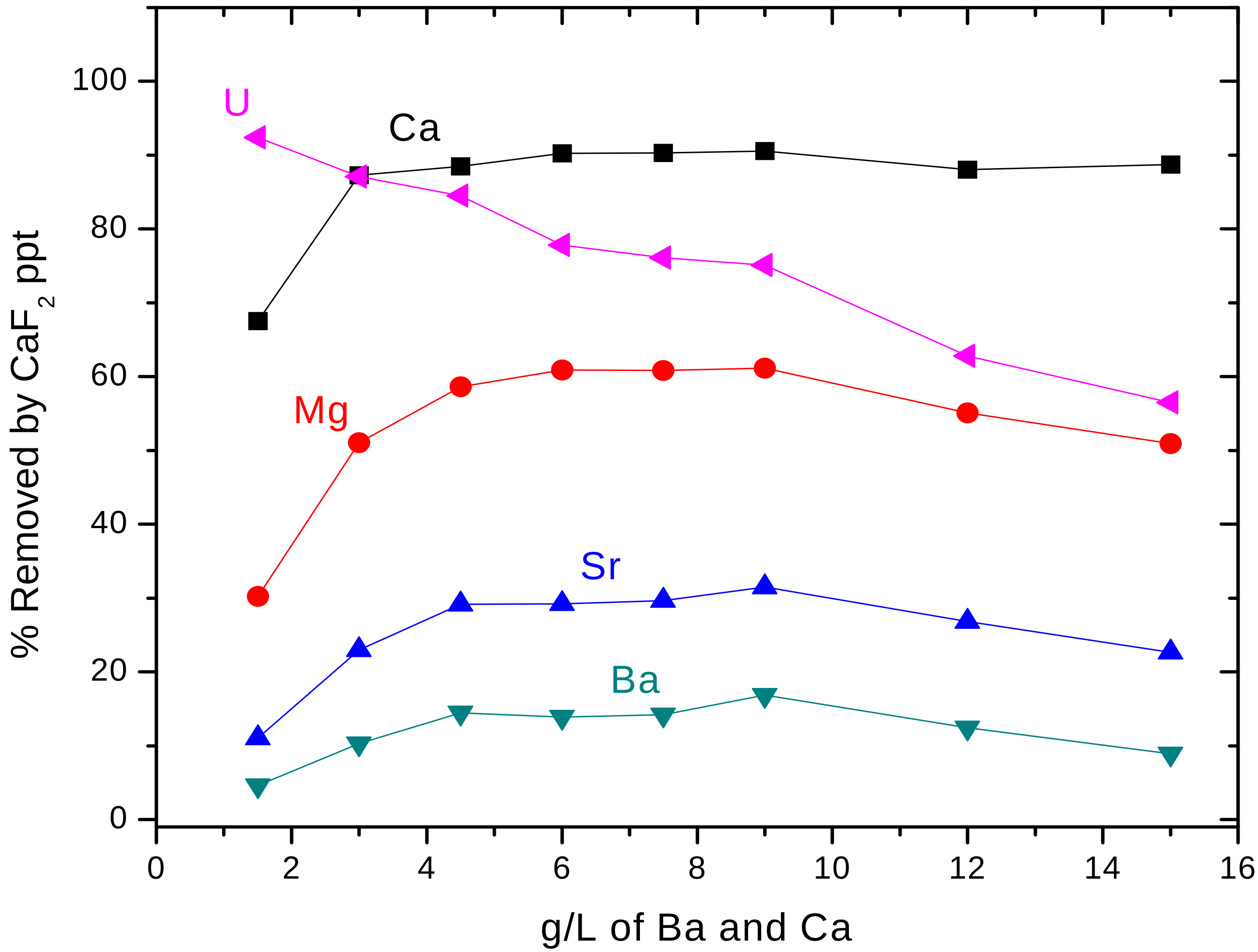
- Ra-226
  - 186.211 keV 3.64 % *abundance*
- *Ba-133*
  - 80.9979 keV 32.9 % *abundance*
  - 356.013 keV 62.05 % *abundance*



Higher Ca/Ba ratio results in greater initial U removal

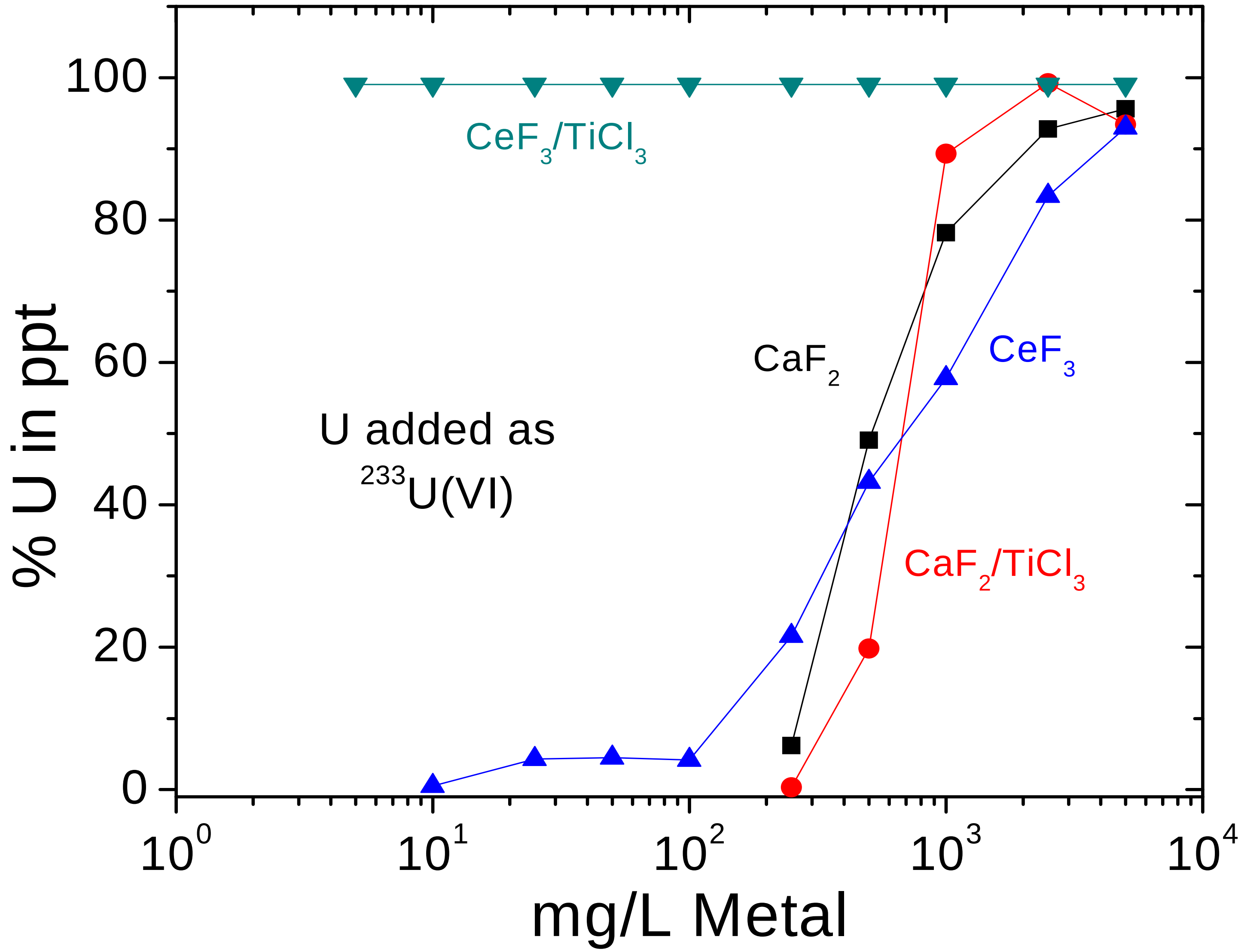
% Removal by CaF_2 ppt

25mL conc HCl, 15mL conc. HF per 250mL Sample



Ca/Ba ratio = ~2

% U in CaF_2 and CeF_3 ppt



Not in simulant; Ce or Ca only

Rapid Preconcentration Method for Ra-226

Add Ba-133 tracer and 1ml 30 wt% H_2O_2 to sample aliquot in 250 ml or 500 ml tubes*. Add 50 ml 12M HCl per 400 ml sample aliquot. Mix well.

↓

Add 20 ml 28M HF per 400 ml aliquot to each tube. Cap and mix well. Centrifuge 10-20 minutes at 3000 rpm or more as needed until supernate is clear.

↓

Transfer supernate to 250 ml or 500 ml centrifuge tube. Add 0.5 ml 30 wt% H_2O_2 and mix well. Add 20 g ammonium sulfate to each tube. Add ~40 ml ethanol to each tube per 400 ml aliquot. Mix well and wait 10 to 15 minutes. Centrifuge 5 to 10 minutes. **

↓

Discard supernate. Add 50-100 ml water, 0.2 ml 30 wt% H_2O_2, mix well and centrifuge 5 minutes.

↓

Transfer precipitate to 50 ml tube (or 250 ml tube if large) using 10-20 ml aliquots of water. Add 0.05 ml 30 wt% H_2O_2, mix well and centrifuge 5 minutes.

↓

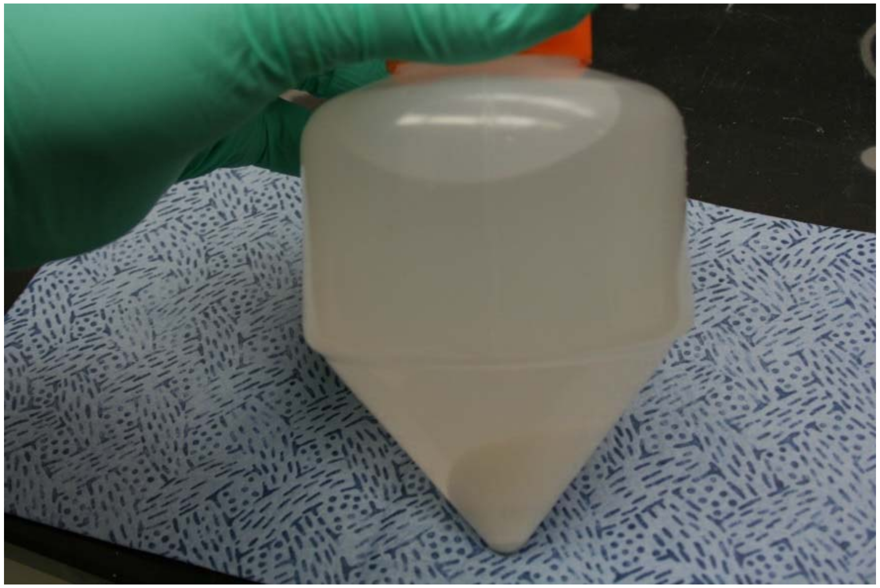
Transfer to 250 ml wide mouth plastic bottle using 10-20 ml aliquots of water. Centrifuge at 1600-2000 rpm in flat bottom centrifuge bucket. → Count by gamma spectrometry

*** Some sample may need to be diluted with water 50% or more if silicates that cause cloudiness are high. Aliquots and tracer may be split between multiple tubes to increase total sample aliquot.***

***** If samples were split between tubes, combine the respective barium sulfate precipitates in a single tube then rinse the combined precipitate with water and proceed.***

<2 hours!

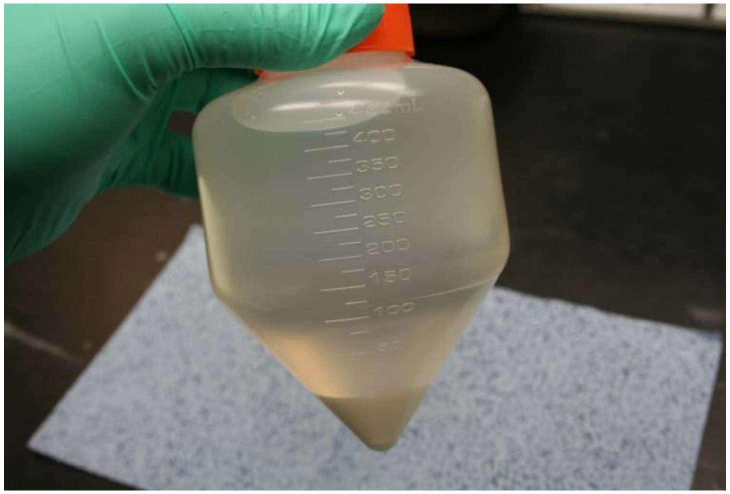
Calcium + U/Th Removal

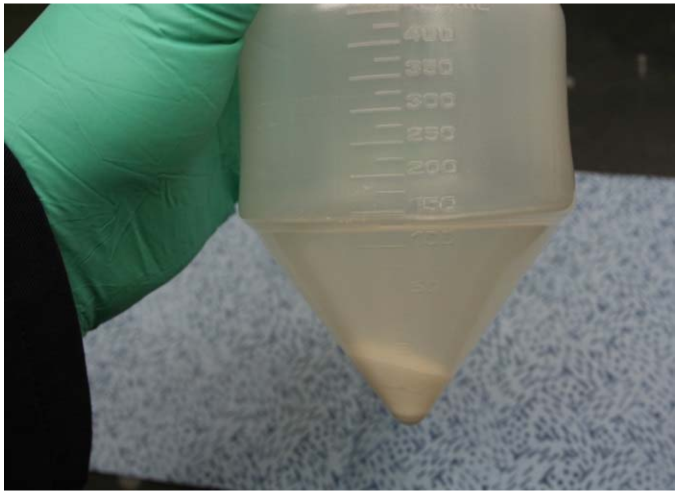


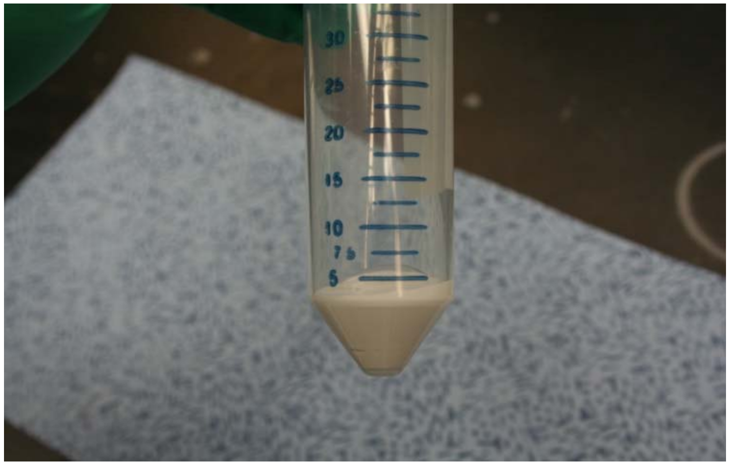
Discard CaF_2

Transfer supernate (Ra/Ba) to new tube

Precipitate Ra/Ba



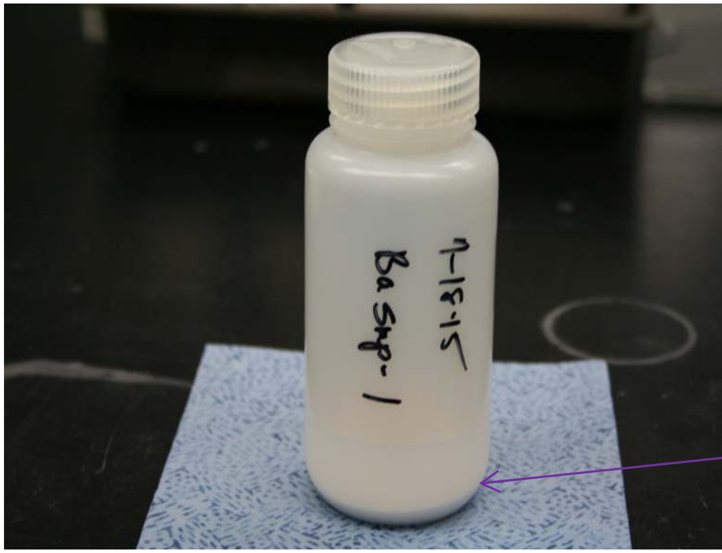




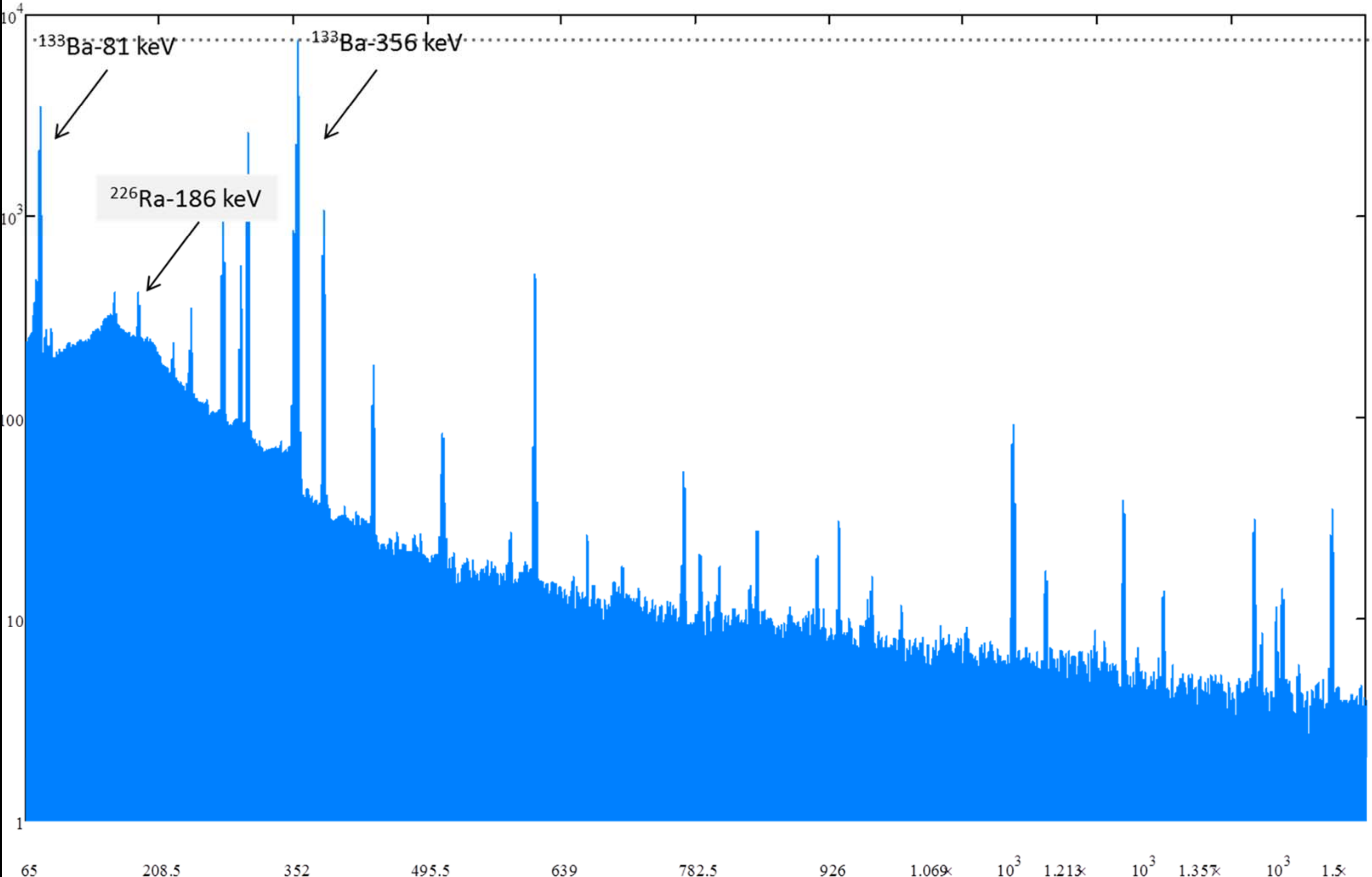
Ammonium sulfate + ~10% ethanol

H_2O_2 and water rinses –ensure no U-235

Transfer to 250 ml Bottle and Centrifuge



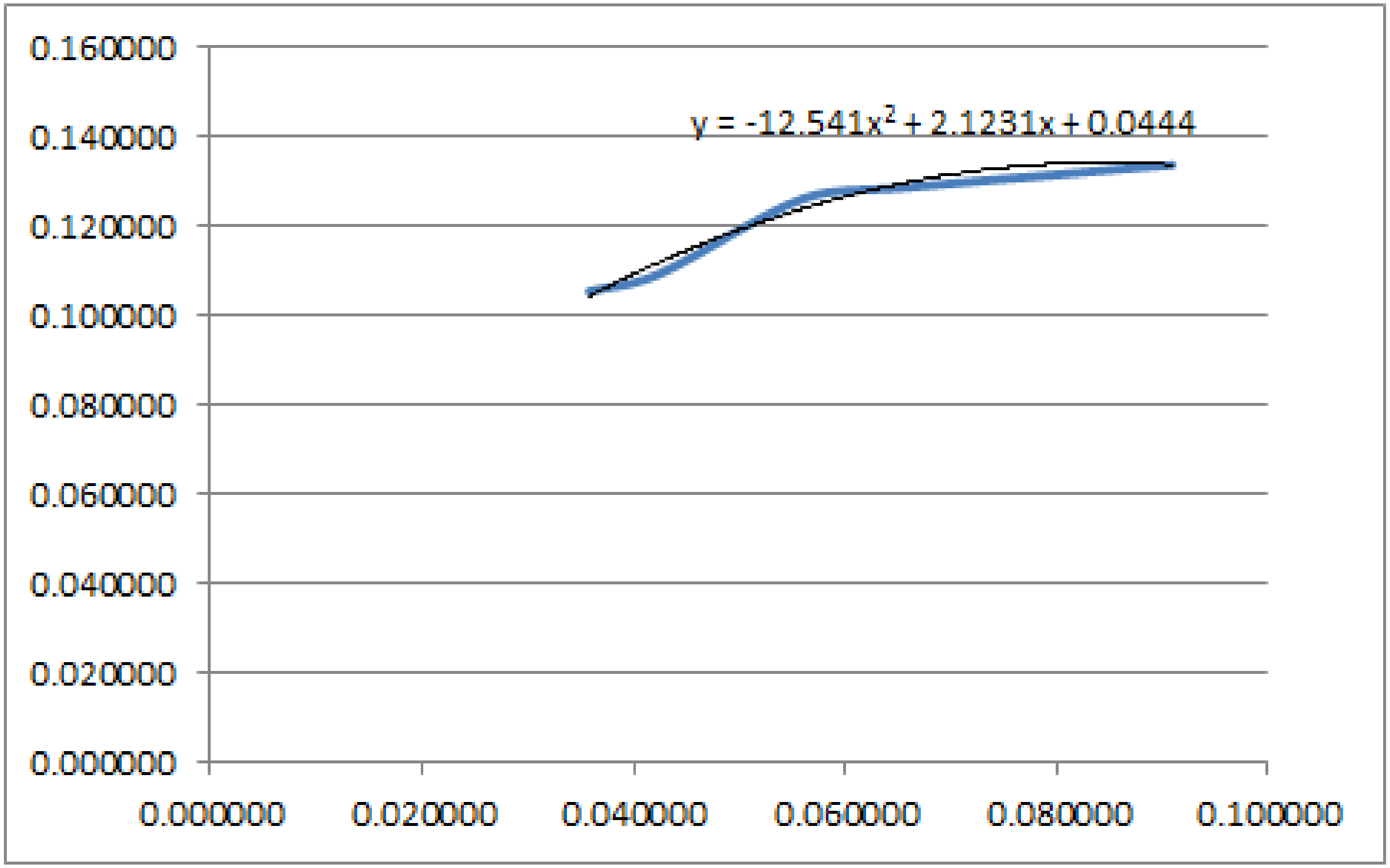
Flat $BaSO_4$ layer from 450 ml simulant



^{133}Ba-81 keV
^{133}Ba-356 keV
^{226}Ra-186 keV
10^4
10^3
100
10
1
65
208.5
352
495.5
639
782.5
926
1.069× 10^3
1.213× 10^3
1.357× 10^3
1.5×

Efficiency Plot of Ra-226 vs Ba-133 (81 keV)

Ra-226 Eff.



Ba-133 Eff. (81 keV)

Also plotted as $y = 0.0327\ln(x) + 0.2156$

Ra-226 in Simulant Measurements

	Simulant Aliquot (ml)	U-235 Added (1388 pCi)	Count Time (min)	Ba-133 Yield (%)	Ra-226 Added (pCi)	Ra-226 Measured (pCi)	Ra-226 Measured (pCi/L)	Bias (%)
1	200	Yes	960	83.5	25.4	25.8	129.0	1.6
2	400	No	720	90.3	634.5	622.0	1555.0	-2.0
3	450	No	720	89.1	634.5	620.2	1378.2	-2.3
4	450	No	720	87.3	31.7	42.5	94.4	34.1
5	450	No	720	86.3	20.0	20.4	45.3	2.0
6	200	No	960	83.9	25.4	27.9	139.5	9.8
8	450	No	960	80.6	126.9	117.9	262.0	-7.1
9	900	No	960	82.0	126.9	118.2	131.3	-6.9
10	1800	Yes	960	71.2	126.9	138.8	77.1	9.4
			Avg.	83.8				4.3
			SD	5.71				12.7

Germanium Detector, 40% Relative Efficiency

SRNS Approach

- *Remove Ca*
- *Remove U-235*
- *Precipitate Ra/Ba to preconcentrate Ra-226 (50-100x)*
- *Utilize Ba-133 tracer (81 keV and 356 keV)*
- *Eliminate need for mass attenuation curve*
  - *Variable Ba content drives size of precipitate*
- *No drying of samples*
- *No column work (Ra-226)*
- *Look at options to collect U/Th for assay*

U/Th Processing Options

- *U/Th by gamma spectrometry*
  - *Th-229 tracer for both? (U-232 has low gamma ray abundance)*
  - *Fe/Ti hydroxide, water rinse, add 1 ml 12M HCl, dissolves in small volume*
  - *Th-229 183.93 keV (0.14%) vs. U-235 185.72 keV (57%)*
  - *If any resolution problems…we can separate U/Th using LaF_3*
  - *U^{+6} in supernate, Th^{+4} in ppt . (HNO_3-H_3BO_3)*
  - *Homogeneous liquid geometry: 200 ml simulant to 10 ml*
- *U/Th by alpha spectrometry*
  - *U-232/Th-229 tracers*
  - *Fe/Ti hydroxide, water rinse, add HCl, LaF_3 (removes Fe/Ti)*
  - *Redissolve LaF_3 in HNO_3-H_3BO_3 for separation*
  - *Separate using TEVA +TRU Resin*

Rapid Preconcentration Method for U/Th

Add Th-229 tracer to sample aliquot in 250 ml tubes. Add 50 mg Fe and 1ml 20% TiCl per 200 ml sample aliquot. Mix well.

↓

Adjust pH to ~8.5 with NH_4OH. Cap and mix well. Centrifuge 5 minutes at 3000 rpm or more as needed until supernate is clear. Discard supernate.

↓

Add 100 ml water (pH 8.7-8.9), mix well. Centrifuge and discard water rinse to remove Ca. Repeat once more with 50 ml water rinse.

↓

U/Th together

Discard water rinse. Add 1ml 12 HCl to dissolve small Fe/Ti ppt and transfer to 50 ml tube. Rinse tube with 5 ml 1M HCl and transfer rinse to 50 ml tube.

↓

Add 5 mg La, 0.5 ml 30 wt% H_2O_2, 2 ml 28M HF and mix well. Centrifuge 5 minutes to collect LaF_3 precipitate. Th^{+4} precipitates and U^{+6} stays in solution. Pour off supernate and collect for U-235 by gamma spectrometry.

↓

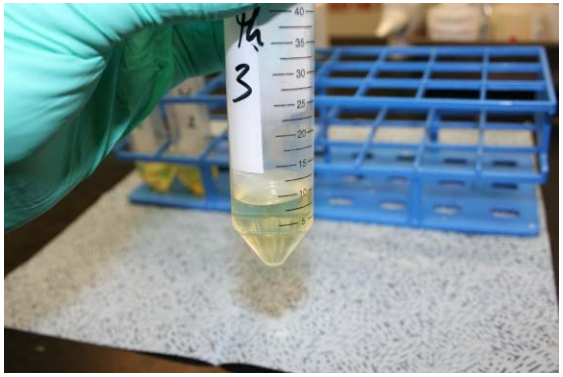
Add 2 ml 1M HCl to La/Th precipitate, 0.2 ml 30 wt% H_2O_2,.5 ml 28M HF. Mix well.

↓

U/Th separate or together

Redissolve LaF_3 precipitate with 4 ml 6M HNO_3, 1ml 3M HNO_3-0.25M H_3BO_3 and 4 ml 2M $Al(NO_3)_3$. Mix well. Sample may be counted by gamma spectrometry or column extraction applied for assay by alpha spectrometry.

Can process U/Th together for alpha spectrometry or separate during LaF_3 step for gamma assay.



Thorium Tracer Yield

	Sample Aliquot	Th-229 Yield	Matrix	U-238
	(ml)	(%)	Ca/Ba/Sr (g/L)	% Removal
1	200	98.8	12.5/6.25/6.25	>99.5%
2	200	100.6	12.5/6.25/6.25	>99.5%
3	200	99.2	12.5/6.25/6.25	>99.5%
4	200	90.8	12.5/6.25/6.25	>99.5%
5	200	97.7	12.5/6.25/6.25	>99.5%
6	200	88.5	12.5/6.25/6.25	>99.5%
	Avg.	95.9		
	SD	5.0		

TRU Resin, 16 hour count, U-238 added to test U Removal

Summary

- Rapid method to preconcentrate Ra-226 developed
  - Removal of Ca is key
  - Up to 1.8L simulant tested
  - U-235 removed
  - 2 hours or less to prepare

- Geometry attenuation correction applied using Ba-133 (81 keV)
  - To Ra-226 based on plot of Ba-133 efficiency (81 keV) vs Ra-226 efficiency (186 keV)
  - And minor yield adjustment to Ba (356 keV) via 81 keV/356 keV efficiency plot

- Difficult matrix
  - 50-100 x preconcentration
  - MDA <20 pCi/L achieved

- U/Th may be preconcentrated for alpha or gamma spectrometry