Savannah River
Nuclear Solutions, LLC
A Fluor Daniel Partnership

Rapid Method for Actinides and Sr-89/90 in Soil

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Recent Advances– SRS Environmental Bioassay Lab

- Actinides in NRIP 2009 air filters and soil (3-4 hrs)
- Adapted rapid methods to ICP-MS
  - ICP-MS compatible resin strip solutions
  - hybrid approach
- Implement rapid bioassay method for routine work
  - Plus 24 hour screening using NRIP urine method
- Added Sr-89/90 to actinides in soil method
  - Future potential applications
    - vegetation/foodstuffs
    - fecal samples

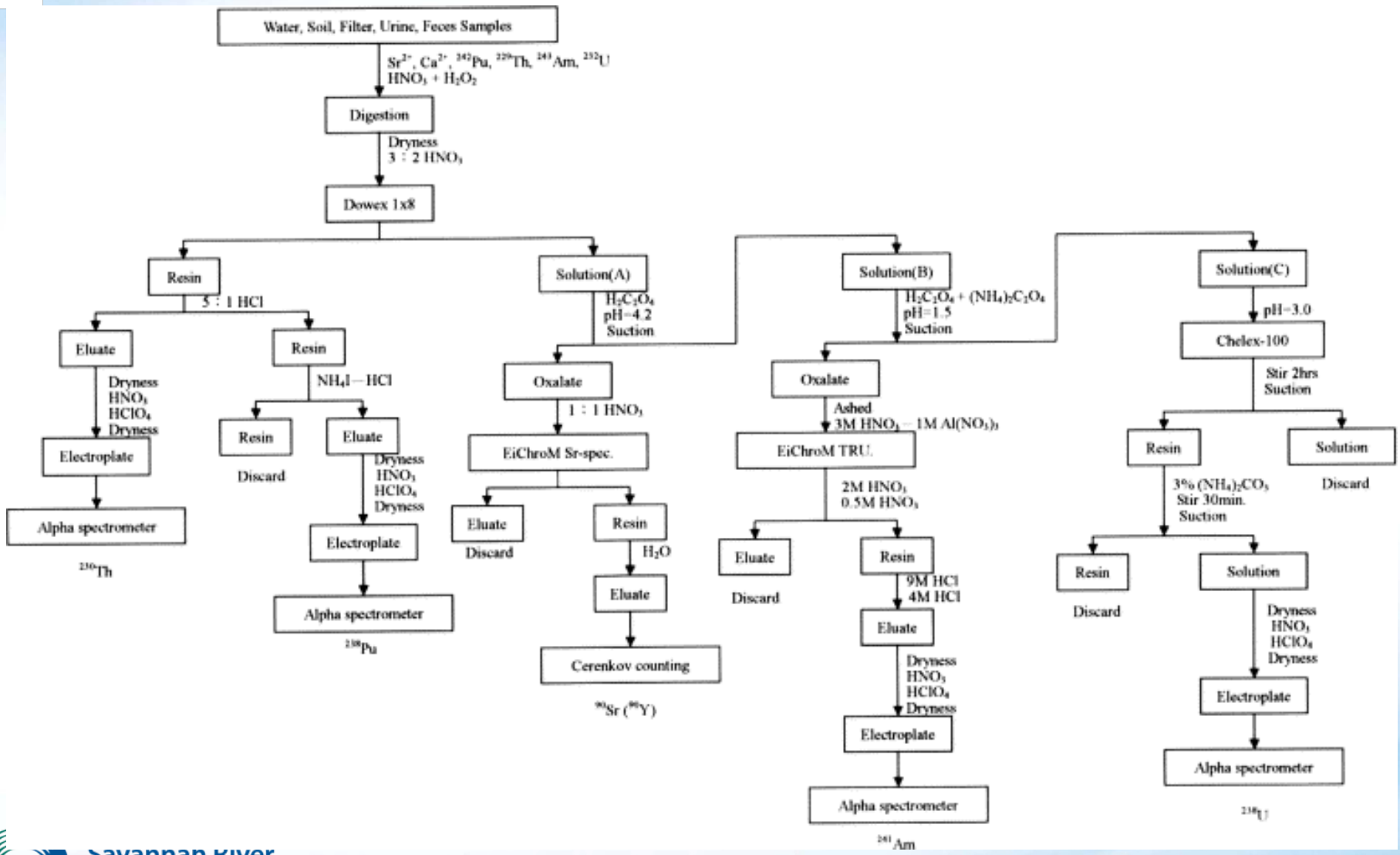
Background

- Need for faster methods for Homeland Security
  - NRIP 2008 actinides and Sr-90 in water/urine samples in 3-4 hours
  - Actinides in NRIP soil samples reported in 4-5 hours
- Benefits
  - More efficient routine analytical methods with cost savings
    - Soil
    - Water, urine
- Literature
  - Usually don't find rapid methods for actinides-maybe 24 hours
  - Often complex with 40-80% actinide yields

Recent Literature: Actinides and Sr in Soil

- Wang, J., Chen, I, and Chiu, J.: Sequential isotopic determination of plutonium, thorium, americium, strontium and uranium in environmental and bioassay samples, Applied Radiation and Isotopes, 61, 299 (2004)
  - Leached NRIP soil, air filters, etc
  - Multiple sequential precipitations
  - Anion resin, TRU resin, Chelex 100 resin
  - Evaporation, wet-ashing and electrodeposition
  - Yields: plutonium (60-76%), americium (40-59%), uranium (57-76%), strontium (63-77%)
  - Sr: oxalate precipitation was performed at pH 4.2 on the anion resin rinse solution followed by a Sr Resin separation.

Wang, et al Flow Chart



Why not Sr-89/90 with actinides in soil?

- Sr-89/90 with actinides in many of our SRS methods
  - Water, urine
  - Air filters
  - Vegetation, fruit
  - Animal tissue
- Can we add Sr-89/90 to the rapid actinide soil method?
  - LaF_3 precipitation-soil matrix removal
  - How can we get Sr to follow the actinides?

Rapid Soil Methods used at SRS

- Actinides in Soil-improvements
  - 1-2 gram routine/emergency method
  - 5-10 gram routine method
    - Use *lanthanum fluoride* instead of cerium fluoride
      - *La k' < Ce k' on DGA*
    - Remove La more quickly on DGA (1-2 gram samples)
      - *instead of TEVA-SCN*
    - Still need TEVA-SCN for 5-10 gram samples

The Magic of DGA

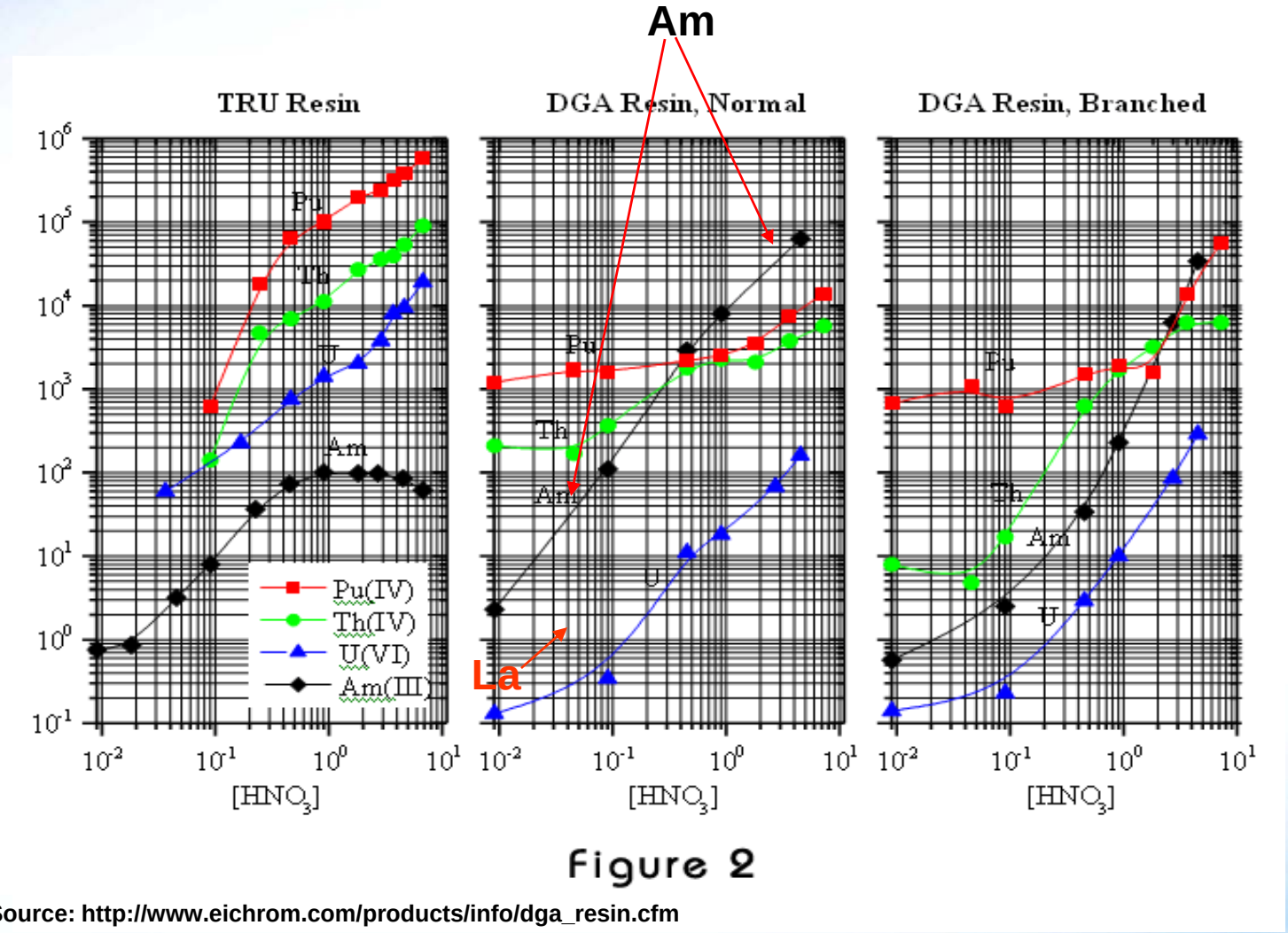


Figure 2

Source: http://www.eichrom.com/products/info/dga_resin.cfm

NRIP -2009 Soil Turnaround Times

Nuclide	Turnaround Time (Hrs.)
^{238}Pu*	5.4
^{240}Pu*	5.4
^{241}Am	4.4
^{238}U	4.1
^{234}U	4.1

*includes TEVA reprocessing

Can we add Sr-89/90 to this rapid soil method?

- Approach
  - Rapid sodium hydroxide fusion
  - LaF_3 soil matrix removal
  - But……also add Ca and PO_4
    - to enhance Sr recovery across the iron hydroxide precipitation after rapid NaOH fusion
  - Add Ca to enhance Sr recovery during LaF_3 precipitation
  - Increase nitrate ions in load solution/beaker rinse
    - increase Am/Cm retention on DGA
    - selects against Ca
    - increases U retention on TRU

Increase Total Nitrate – DGA Resin

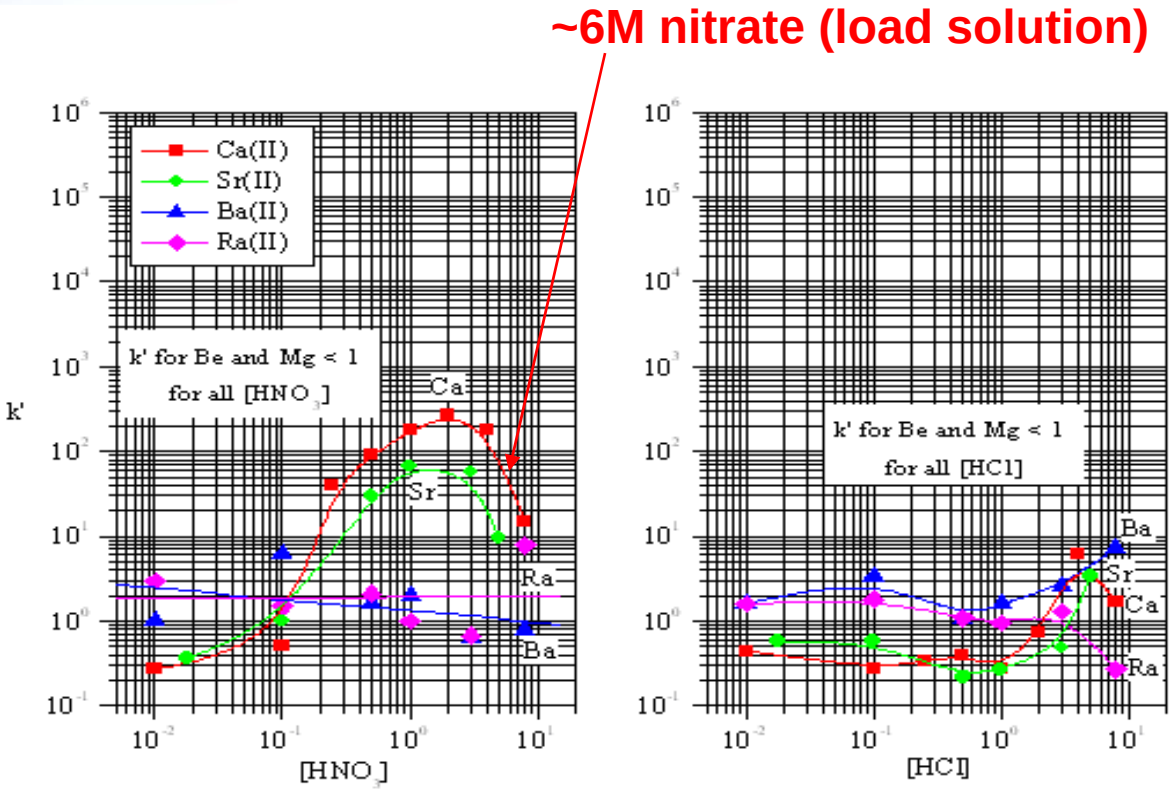


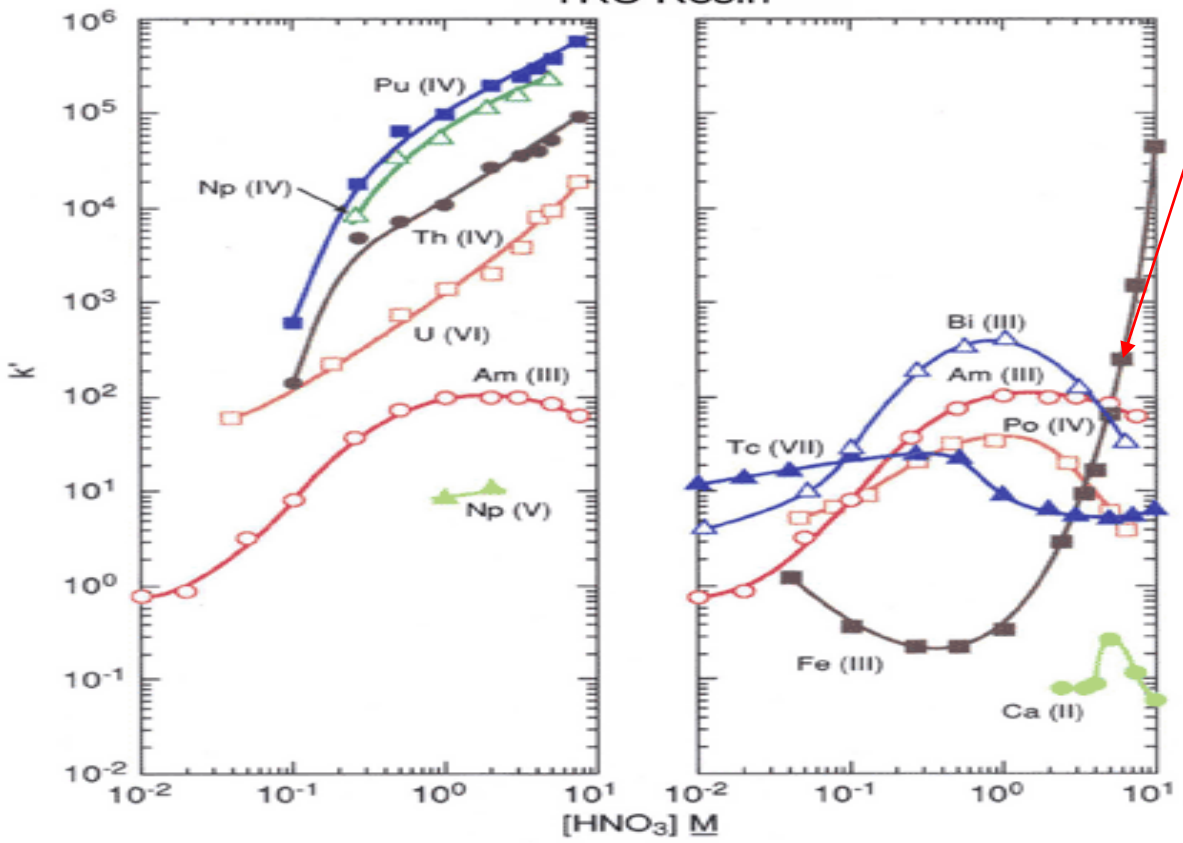
Figure 5

Horwitz, P., McAlister, D. Bond, A., and Barrans Jr, A. B.: Novel extraction chromatographic resins based on tetraalkyldiglycolamides: characterization and potential applications, Solvent Extr. Ion Exch. 23, (3), 319, **(2005)**

Increase Total Nitrate Some…but not too much

Figure 2

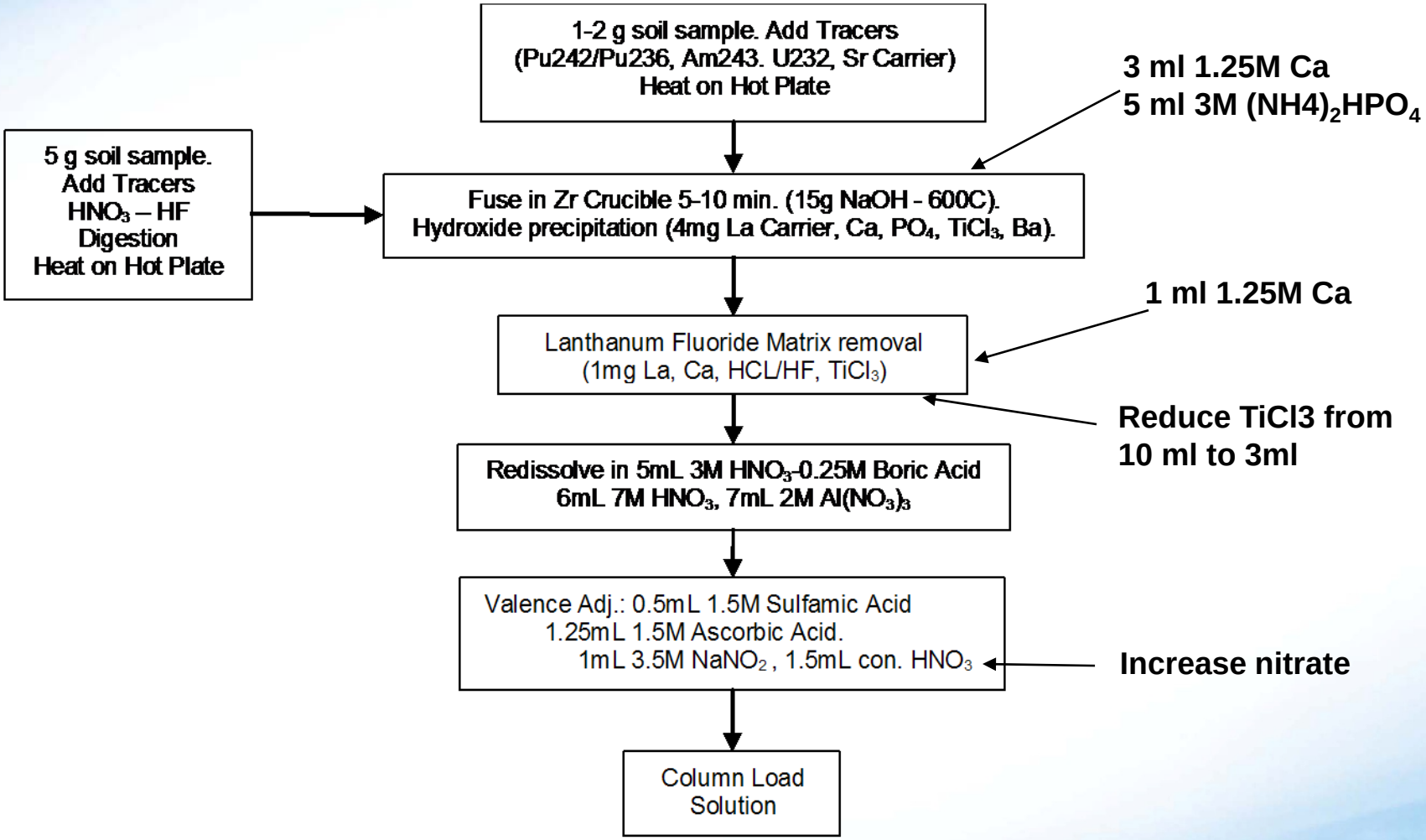
Acid dependency of k' for various ions at 23-25°C.
TRU Resin



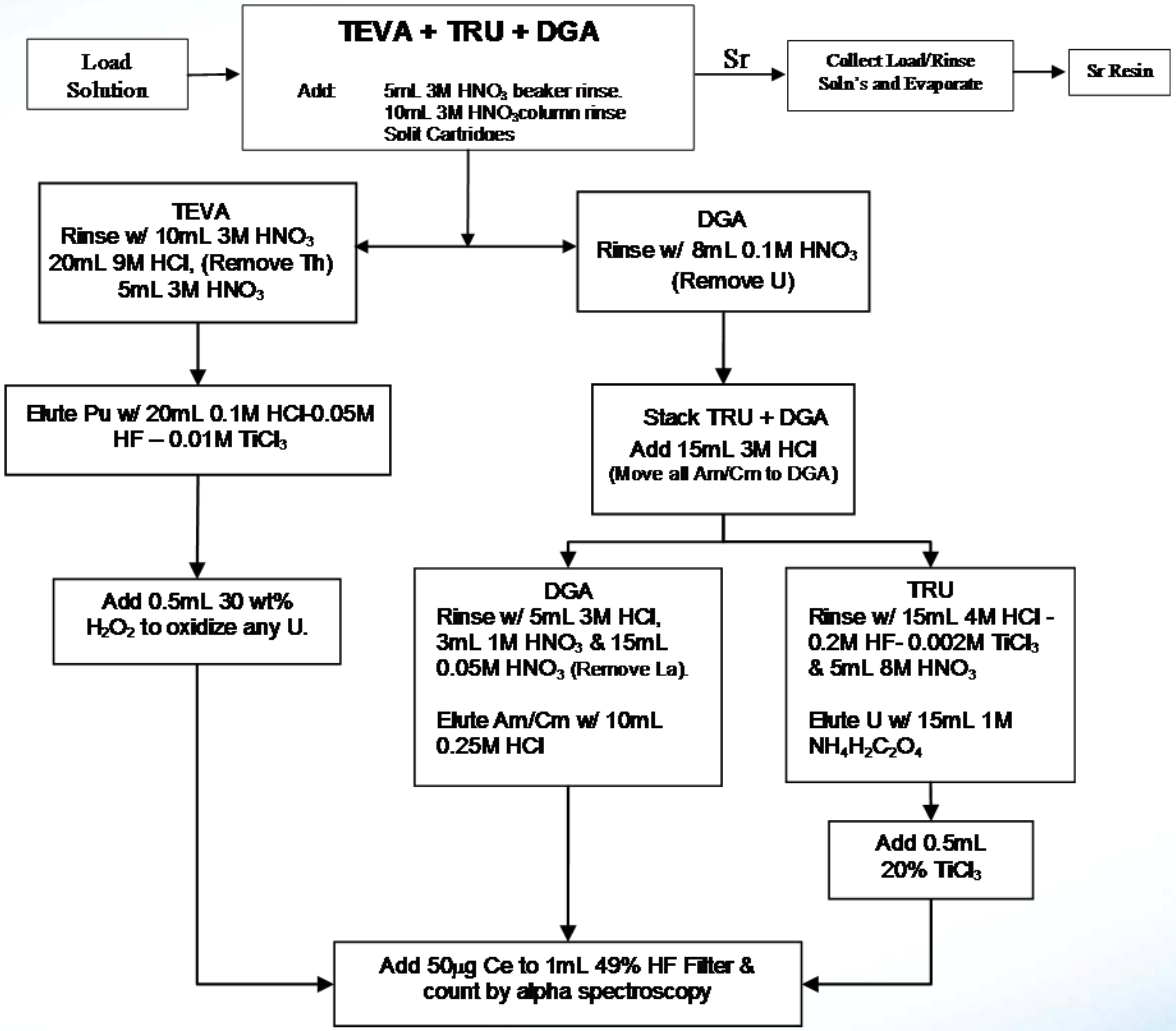
Fe $^{+3}$ impact on U

Horwitz, et al. (HP193)

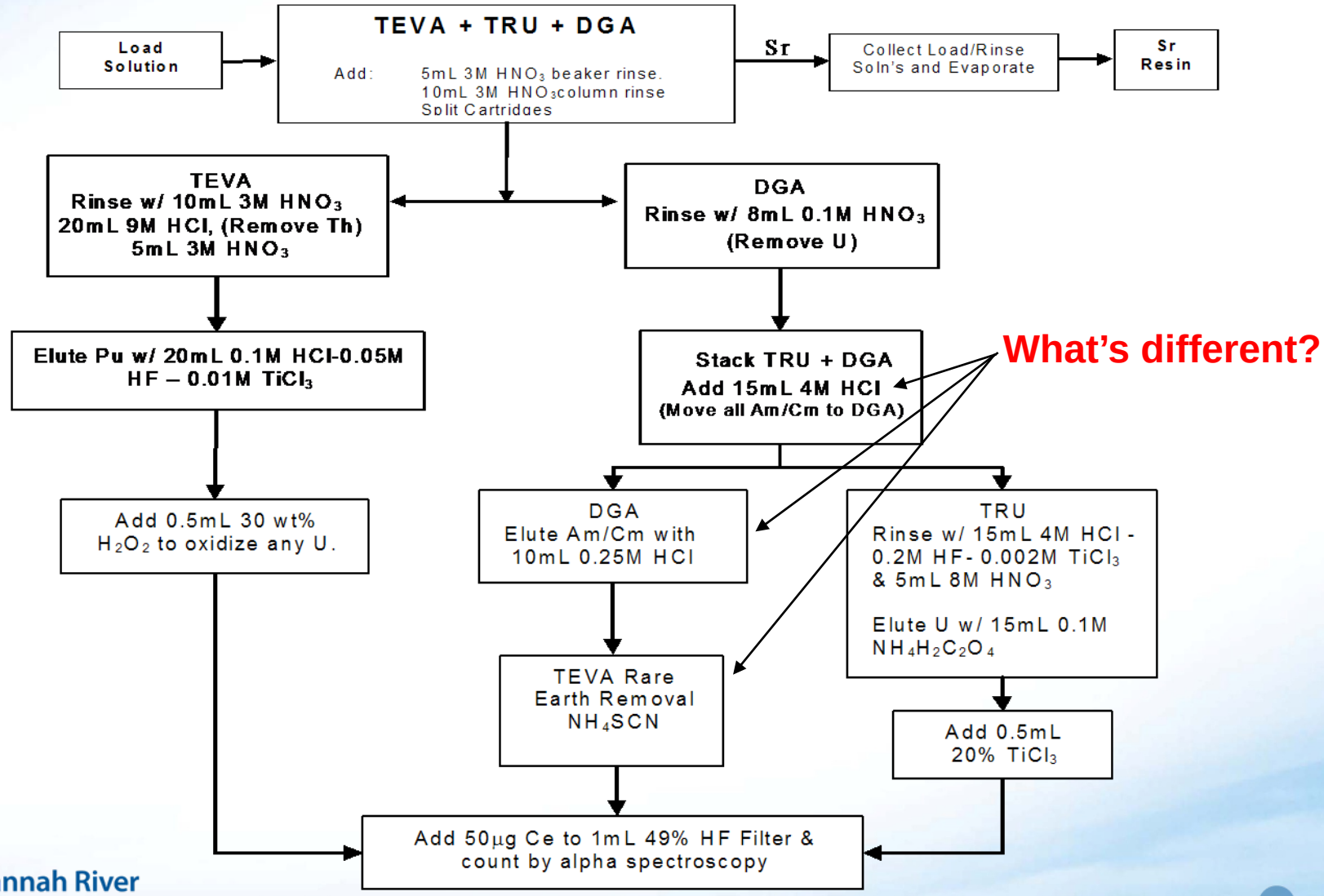
SRS Soil Sample Preparation



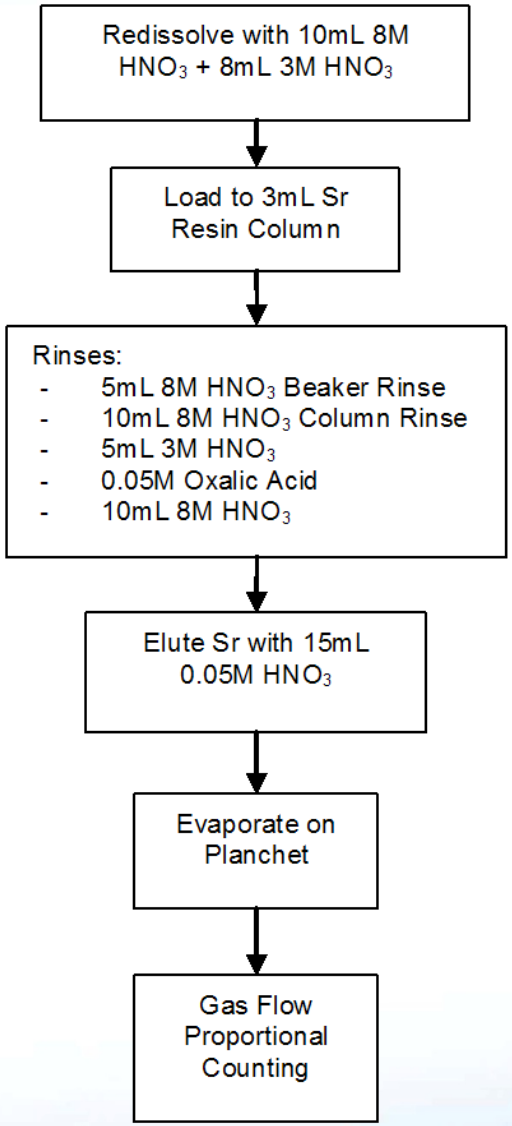
Soil Column Separation (1 – 2 g)



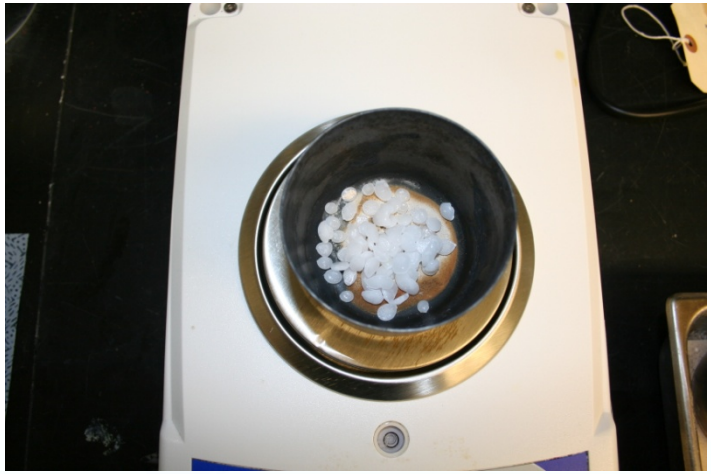
Soil Column Separation (5 g)

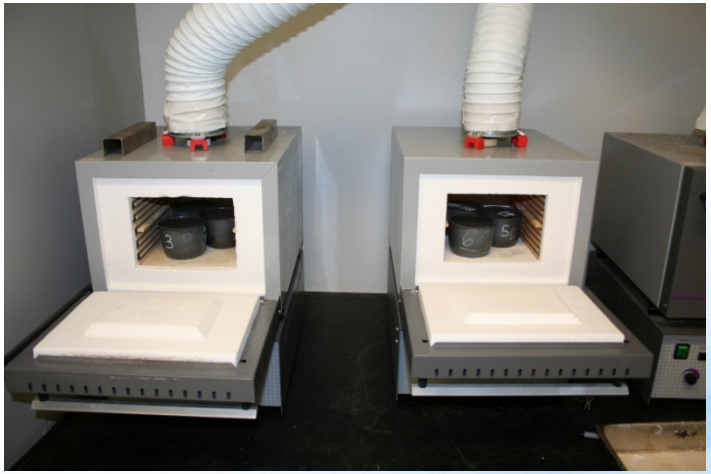


Sr Resin Separation

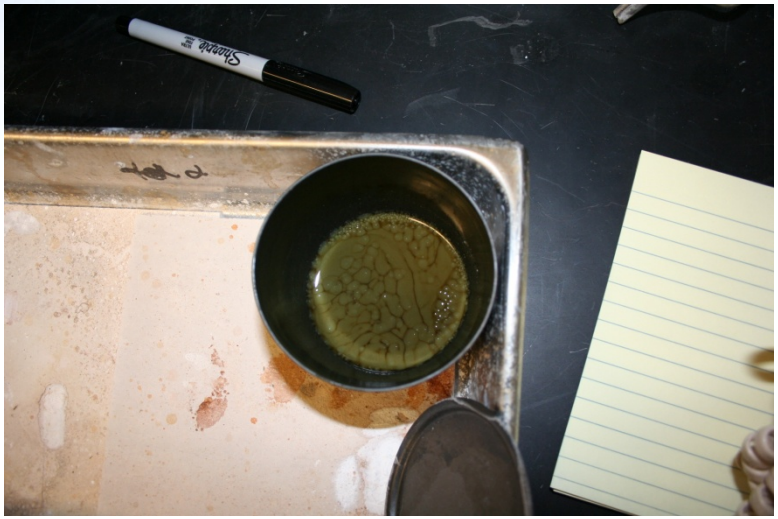


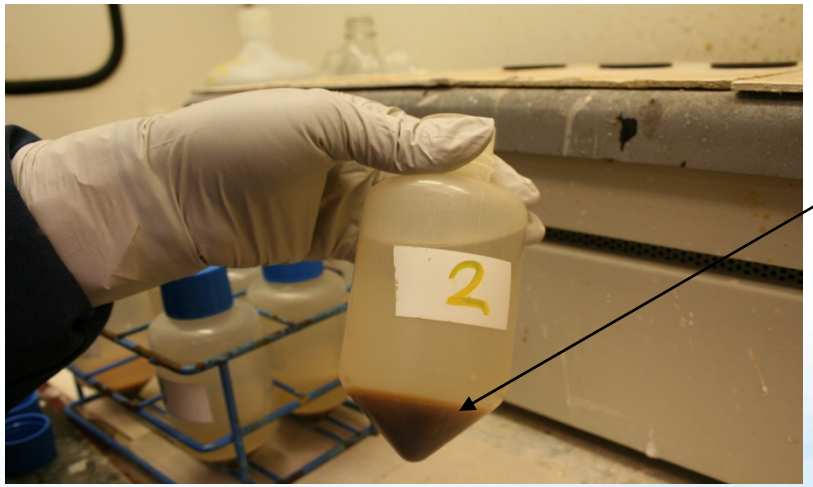
MAPEP 18 Soil- Rapid Fusion





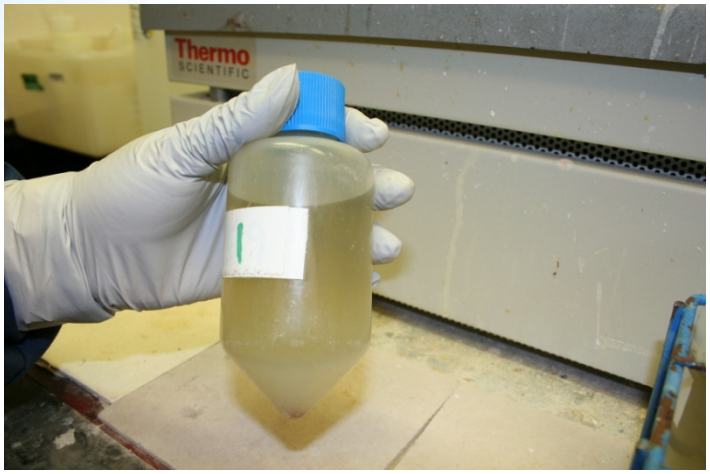
Precipitation after Fusion





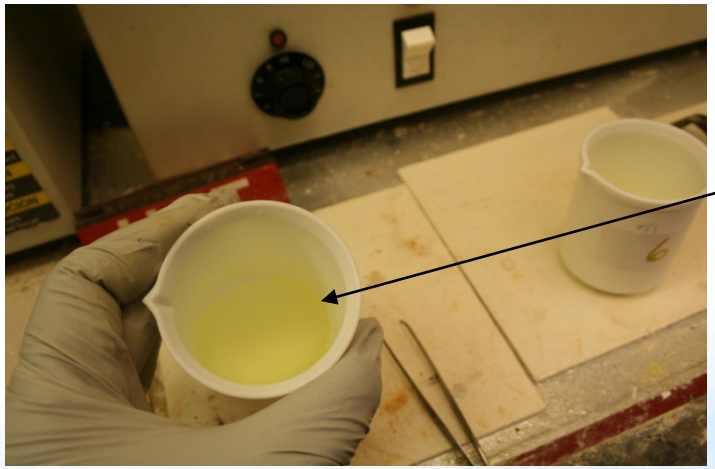
$Fe(OH)_2$ ppt

Lanthanum/Calcium Fluoride Matrix Removal



Ca + La in HCL-HF + $TiCl_3$

LaF_3 /CaF_2 ppt

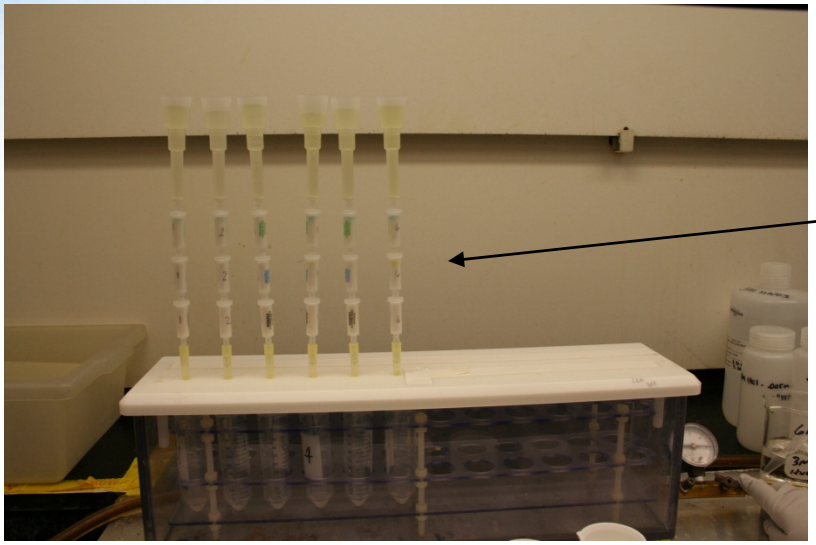


Load Solution

Soil work is fun!

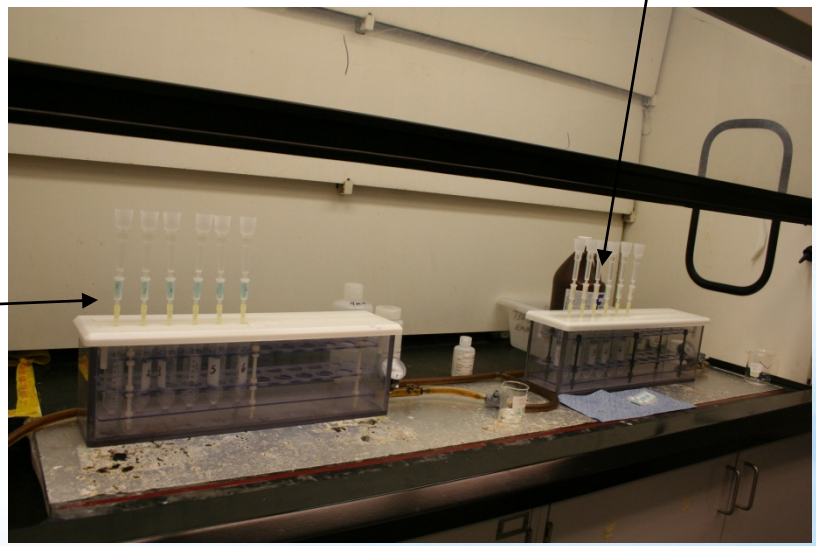
Gravity Flow

Column Separation



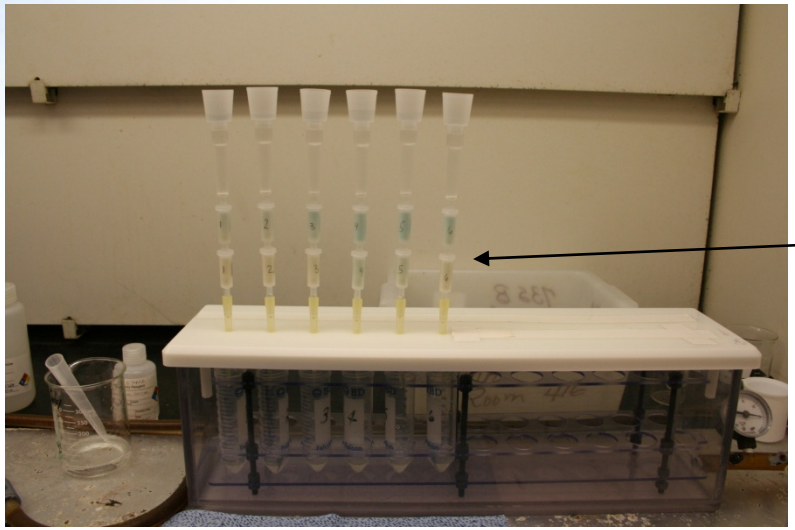
TEVA+TRU+DGA

DGA



TEVA

Column Separation



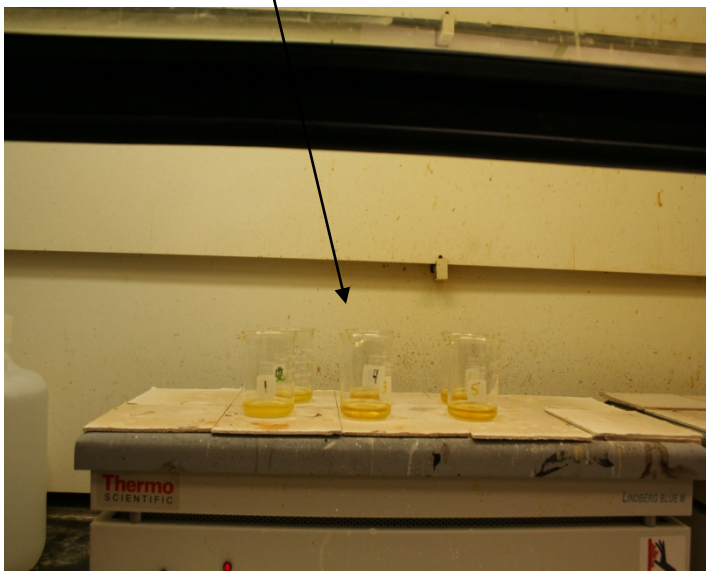
TRU+DGA
(Move Am/Cm to DGA)

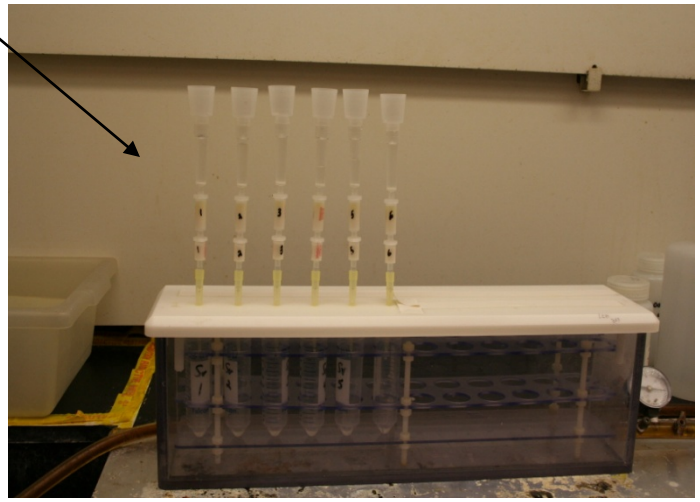
DGA
(Remove La)

Sr Separation

3ml Sr Resin

Load + Rinses

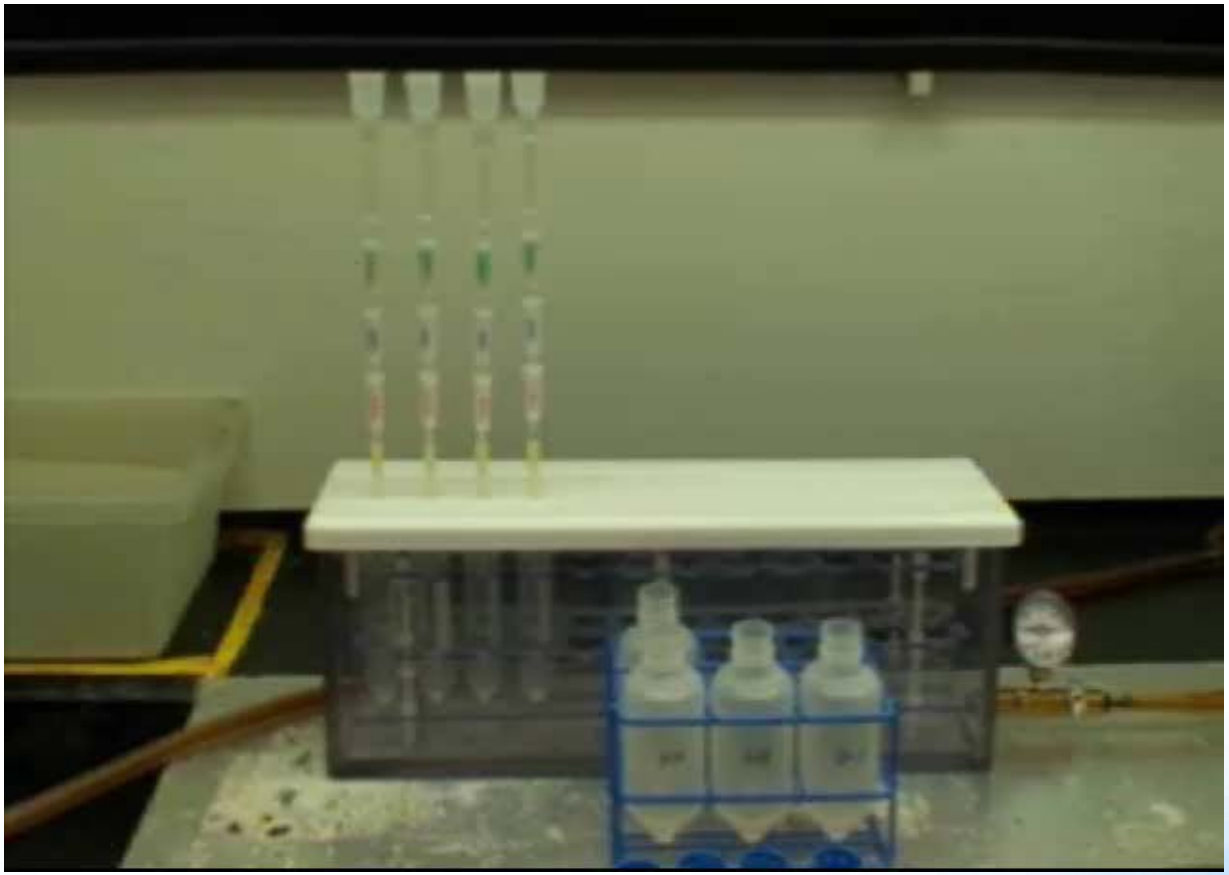




Sr mount with Sr carrier

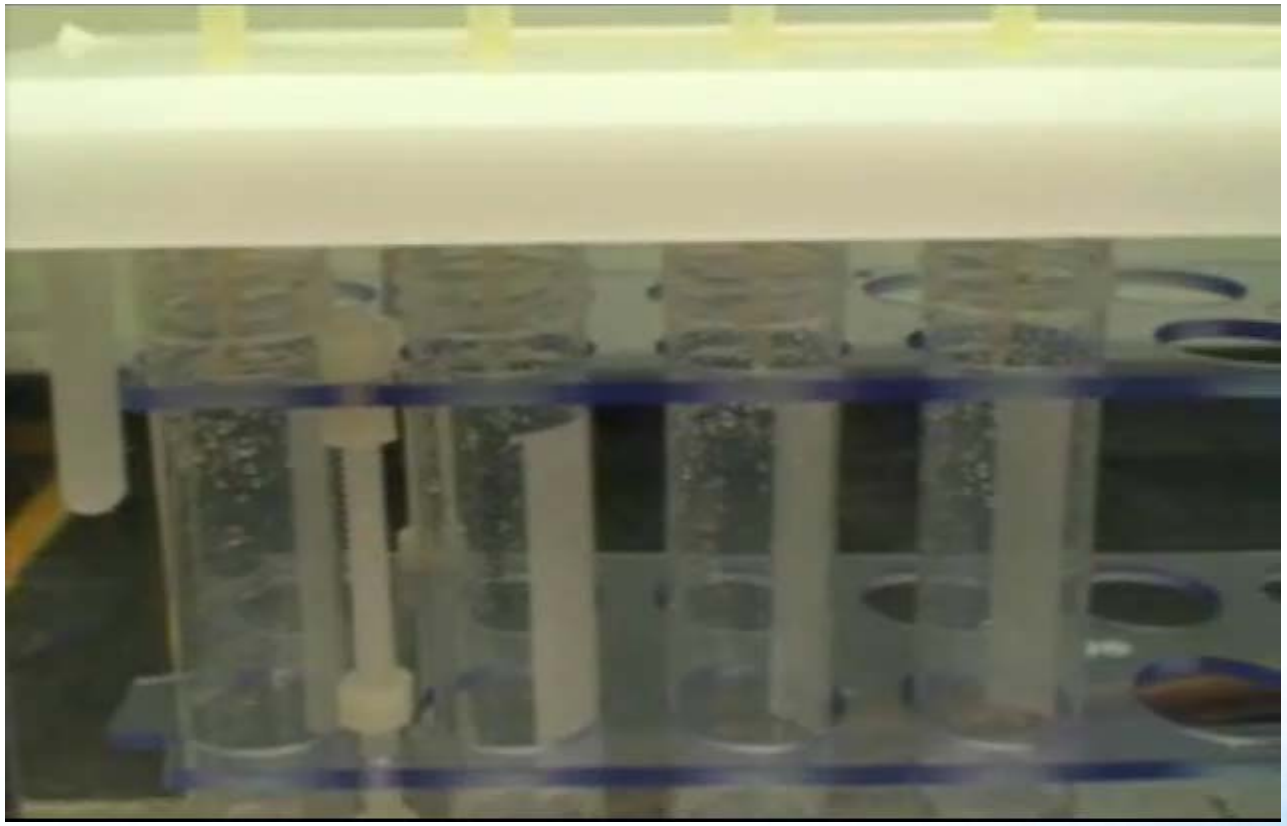
Routine Flow Rates

Load solution ~ 1 drop per second



Routine Flow Rates

Rinse ~ 2 drops per second



MAPEP 18 Soil Results

Refractory

MAPEP 18	Pu-242	Pu-238	Pu-239
	% Rec	Bq/kg	Bq/kg
1	102.1	75.6	88.5
2	107.3	79.8	76.1
3	117.5	75.7	81.3
4	106.9	72.3	103.2
5	90.7	82.9	99.9
6	83.7	82.1	95.5
7	108.7	79.9	94.7
8	100.3	74.3	95.7
avg	102.2	77.8	91.9
RSD	10.48	4.96	10.05
	Reference	72.80	90.1
	% diff	6.93	1.97

MAPEP 18 Soil Results

MAPEP 18	Am-243	Am-241	Cm-244
	% Rec	Bq/kg	Bq/kg
1	97.3	114.1	32.9
2	91.2	125.4	30.0
3	93.7	133.1	33.6
4	96.0	117.9	33.5
5	96.3	124.5	37.4
6	86.7	124.1	32.4
7	102.9	118.4	36.0
8	105.8	119.1	31.1
avg	96.2	122.1	33.4
RSD	6.33	4.85	7.20
	Reference	127.20	32.0
	% diff	-4.02	4.25

MAPEP 18 Soil Results

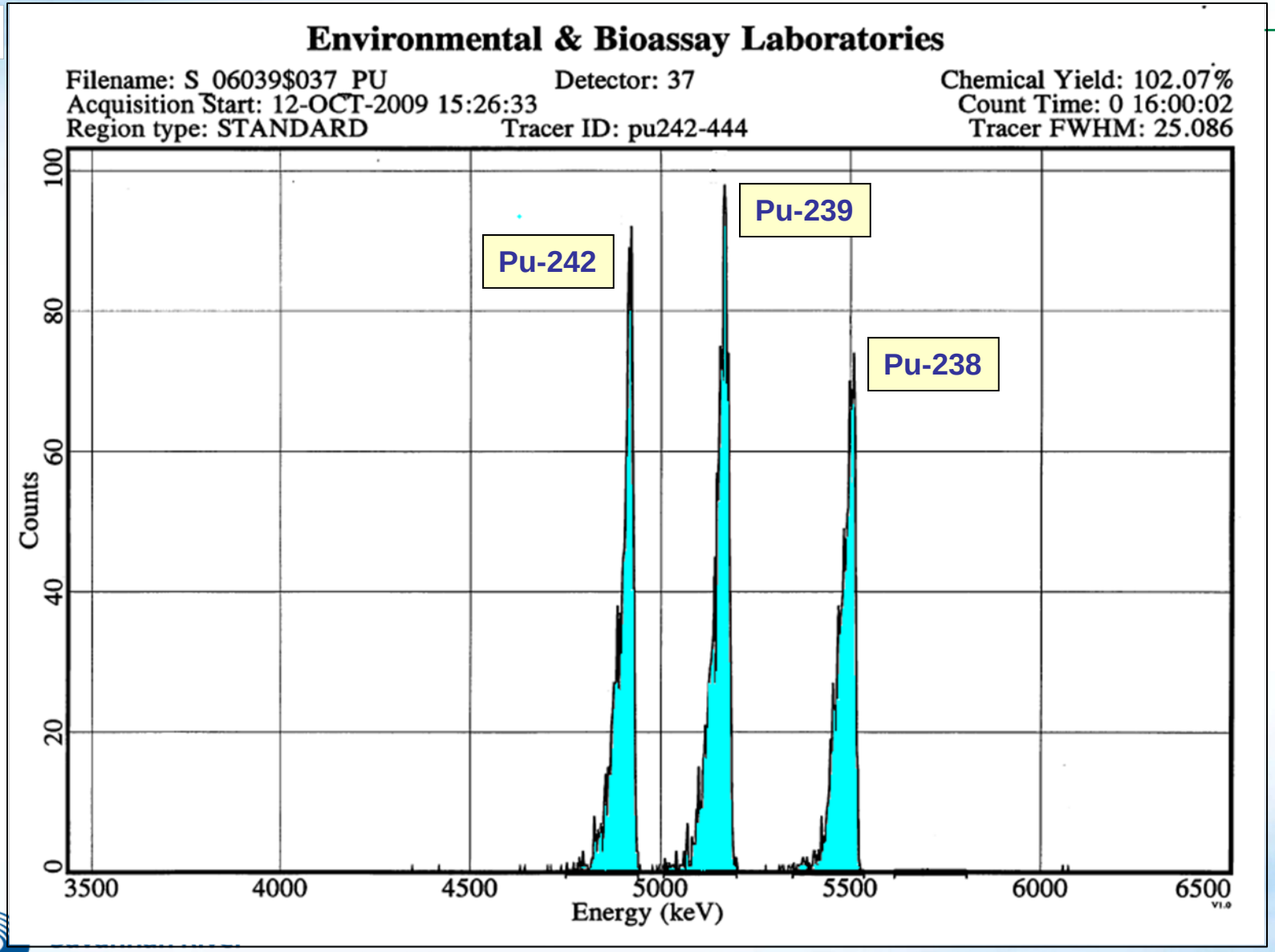
MAPEP 18		U-232	U-234	U-238
		% Rec	Bq/kg	Bq/kg
1		81.4	138.4	146.2
2		81.3	139.9	152.0
3		85.8	136.8	146.2
4		80.8	139.1	148.4
5		85.9	137.3	152.8
6		76.6	141.7	149.5
7		89.9	139.5	146.8
8		90.0	132.5	138.0
	avg	84.0	138.1	147.5
	RSD	5.64	2.00	3.11
		Reference	142	148
		% diff	-2.72	-0.34

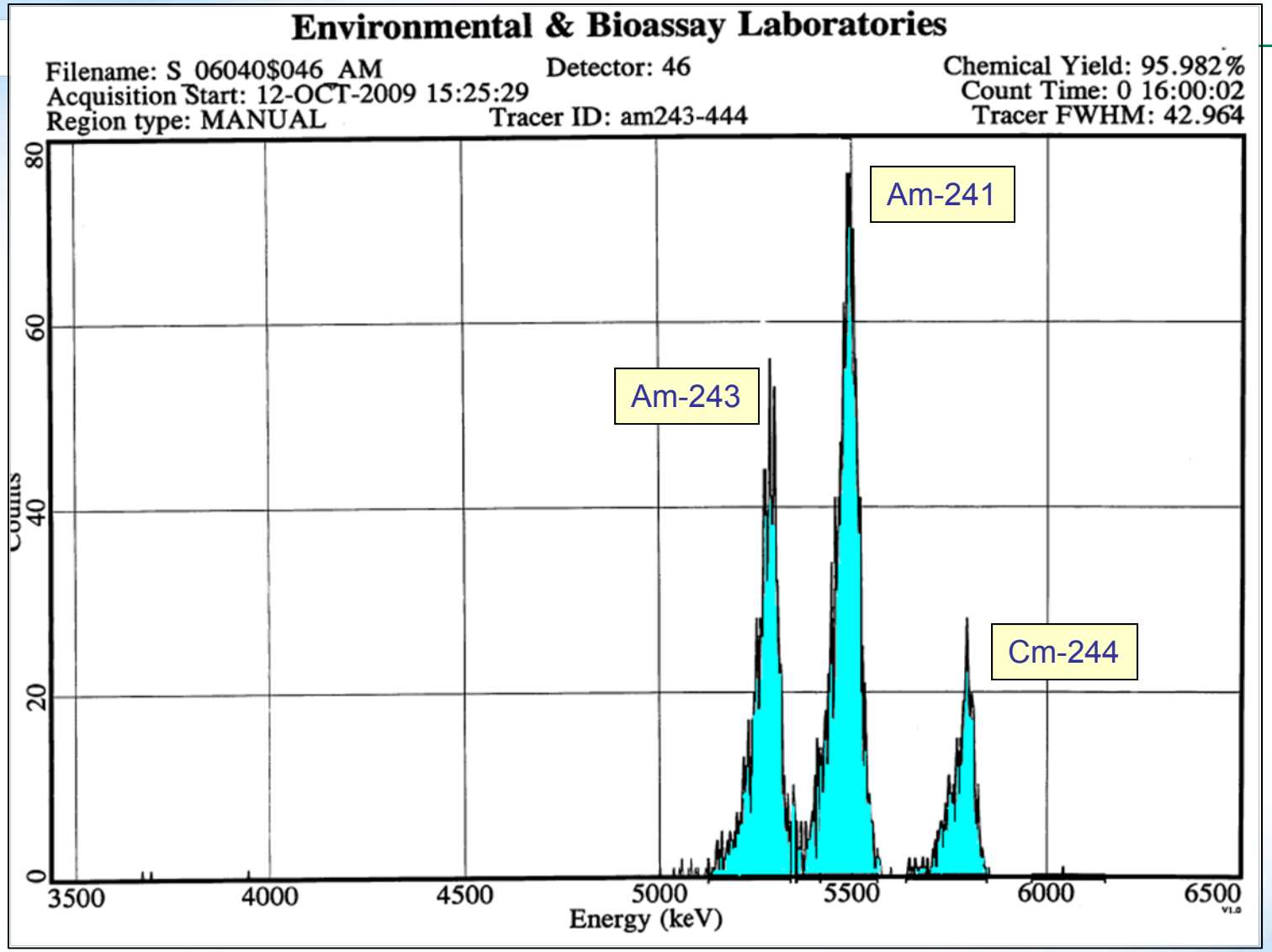
MAPEP 18 Sr-90 Results

MAPEP 18	Sr carrier	Sr-90
	% Rec	Bq/kg
1	61.0	484.0
2	61.0	479.0
4	56.6	536.0
5	59.7	480.0
6	60.4	438.0
7	59.1	447.0
avg	60	477.3
RSD	2.8	7.23
	Reference	493.0
	% diff	-3.18

MAPEP 20 Sr-90 Results

MAPEP 20	Sr carrier	Sr-90
	% Rec	Bq/kg
1	70.8	281.9
2	65.7	267.1
3	65.7	270.7
4	70.1	306.7
5	63.8	269.1
6	60.1	265.6
avg	66.0	276.9
RSD	6.0	5.68
	Reference	257.0
	% diff	7.72


Environmental & Bioassay Laboratories
Filename: S_06039$037_PU
Detector: 37
Chemical Yield: 102.07%
Acquisition Start: 12-OCT-2009 15:26:33
Count Time: 0 16:00:02
Region type: STANDARD
Tracer ID: pu242-444
Tracer FWHM: 25.086
Pu-242
Pu-239
Pu-238
Counts
0
20
40
60
80
100
3500
4000
4500
5000
5500
6000
6500
Energy (keV)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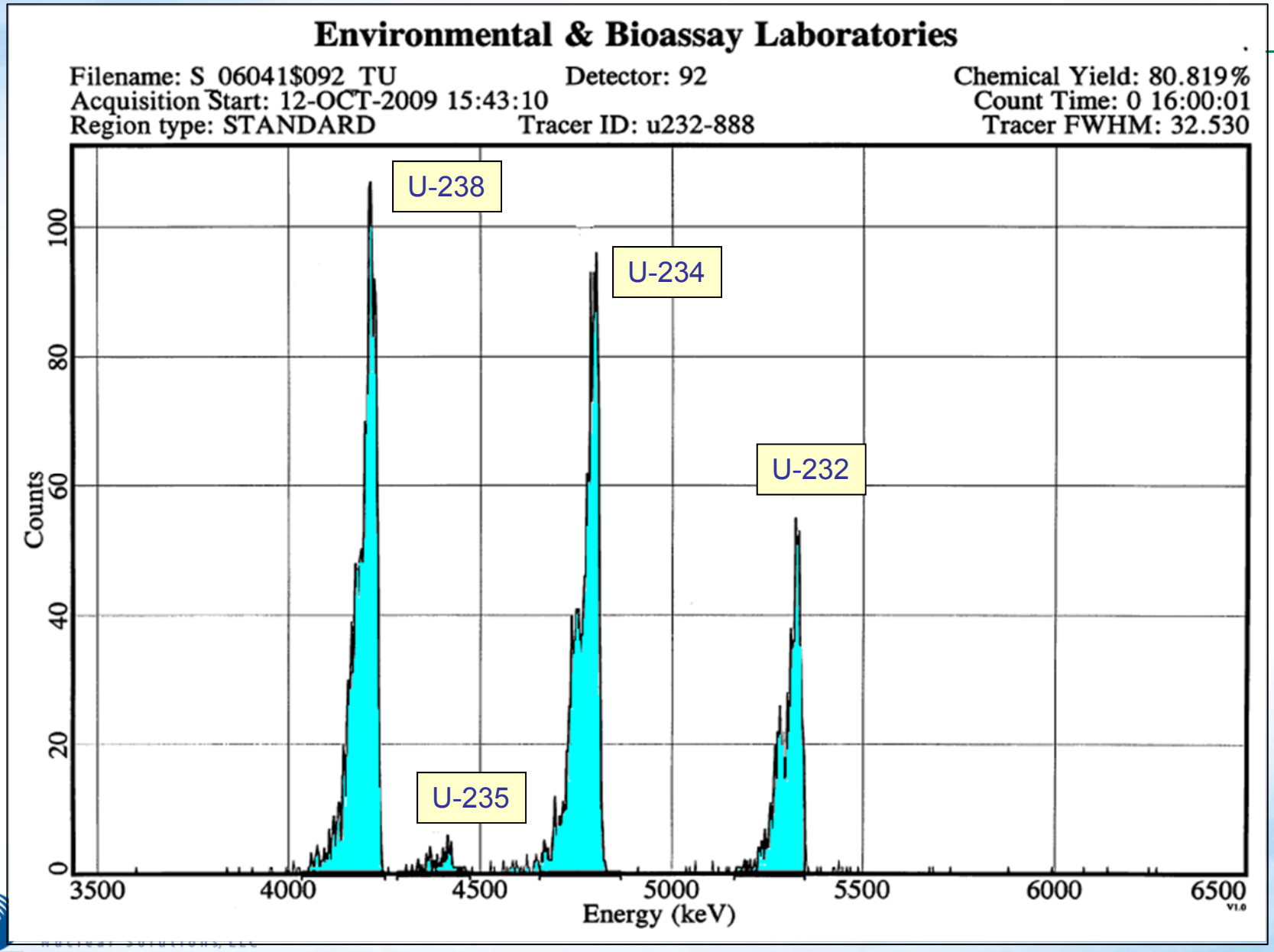
Region type: MANUAL
Detector: 46
Tracer ID: am243-444
Chemical Yield: 95.982%
Count Time: 0 16:00:02
Tracer FWHM: 42.964
Am-241
Am-243
Cm-244
Counts
0
20
40
60
80
3500
4000
4500
5000
5500
6000
6500
Energy (keV)


Environmental & Bioassay Laboratories
Filename: S_06041$092_TU
Acquisition Start: 12-OCT-2009 15:43:10
Region type: STANDARD
Detector: 92
Tracer ID: u232-888
Chemical Yield: 80.819%
Count Time: 0 16:00:01
Tracer FWHM: 32.530
U-238
U-234
U-232
U-235
Counts
0
20
40
60
80
100
3500
4000
4500
5000
5500
6000
6500
Energy (keV)
V1.0

Summary

- Rapid soil method
  - Actinides in soil in ~4 hours (emergency)
- New rapid method with actinides and Sr-89/90 together
- Cost savings
  - Estimate-$60,000 year in labor cost savings for soil samples
  - Eliminates separate Sr-89/90 sample preparation
- Adaptable to ICP-MS
  - Hybrid approach
    - *Maxwell III, S.L. and Jones, V.D. , Rapid determination of actinides in urine by inductively coupled plasma mass spectrometry and alpha spectrometry: A hybrid approach:* Volume 80, Issue 1, 15 November 2009, Pages 143-150
- Adaptable to other difficult matrices

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  - Shermette Upson, Beth Calhoun, Becky Chavous, Jack Herrington
- Chemists
  - Brian Culligan, Gary Noyes