Savannah River National Laboratory™

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Rapid Method for Actinides in Asphalt and Soil Samples

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RRMC

10/28/14

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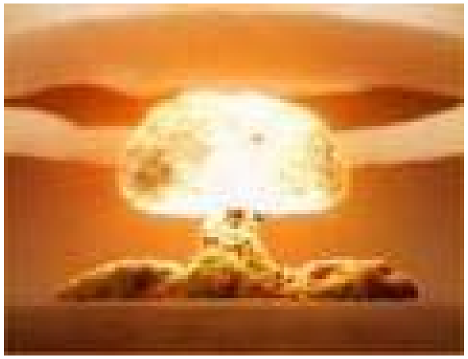
FLUOR • NEWPORT NEWS NUCLEAR • HONEYWELL

Background

- Need for rapid radiochemical methods
  - Emergency response
    - *IND, RDD, nuclear accident*
    - *Rapid turnaround times*
- Actinides
  - Environmental
  - Bioassay
  - Food
  - Concrete/brick/building materials….
- What about asphalt?
  - Need rapid analysis capability
  - High throughput
  - Rugged

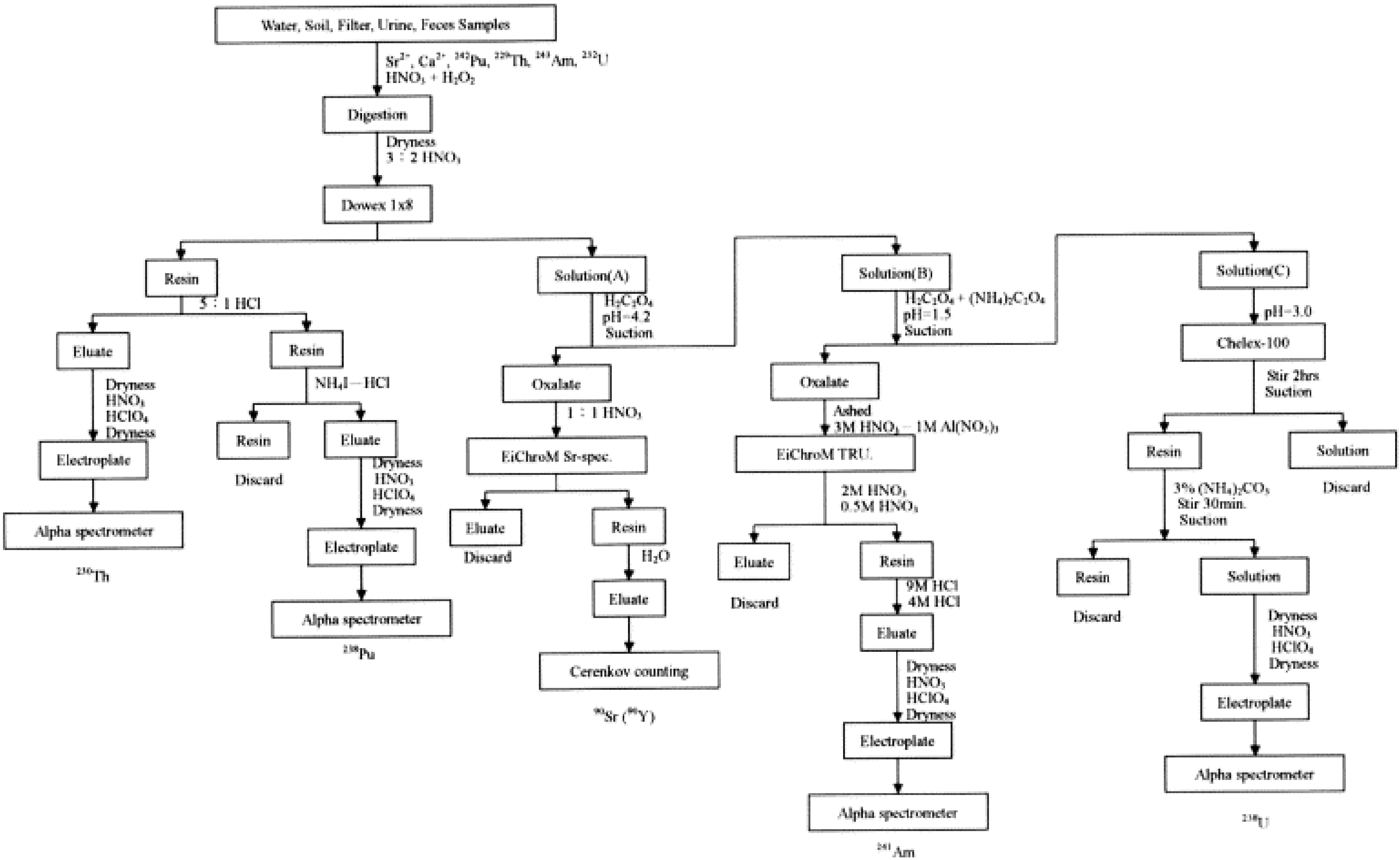


Literature

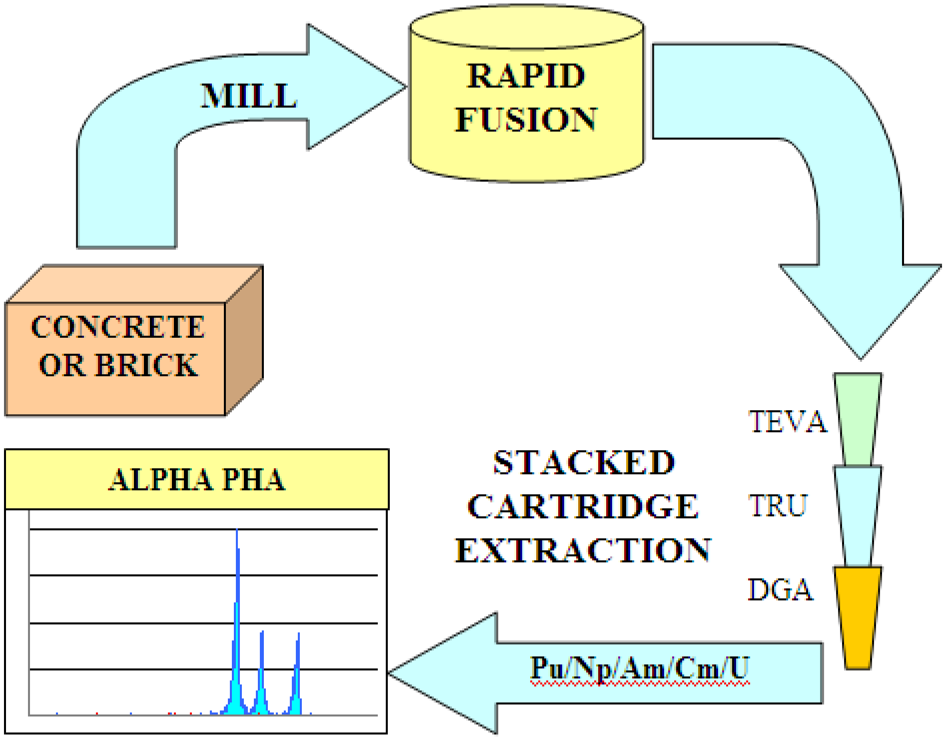
- R. Weinreich, S. Bajo, J. Eikenberg, and F. Atchison., Determination of uranium and plutonium in shielding concrete, Journal of Radioanal. Nucl.Chem, Vol 261 (2004) No 2, p 319-32
  - Multiple HF digestion, BioRAD anion resin + UTEVA resin
  - Variable yields for Pu attributed to valence adjustment problems
    - *Trace Th in Pu fraction*

- Wang - leach NRIP soil, air filters, multiple sequential precipitations, anion resin, TRU resin, Chelex 100 resin, electrodeposition, plutonium (60-76%), americium (40-59%), uranium (57-76%)
  - 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)

Wang et al Flow chart



Rapid Fusion Application for Concrete and Brick

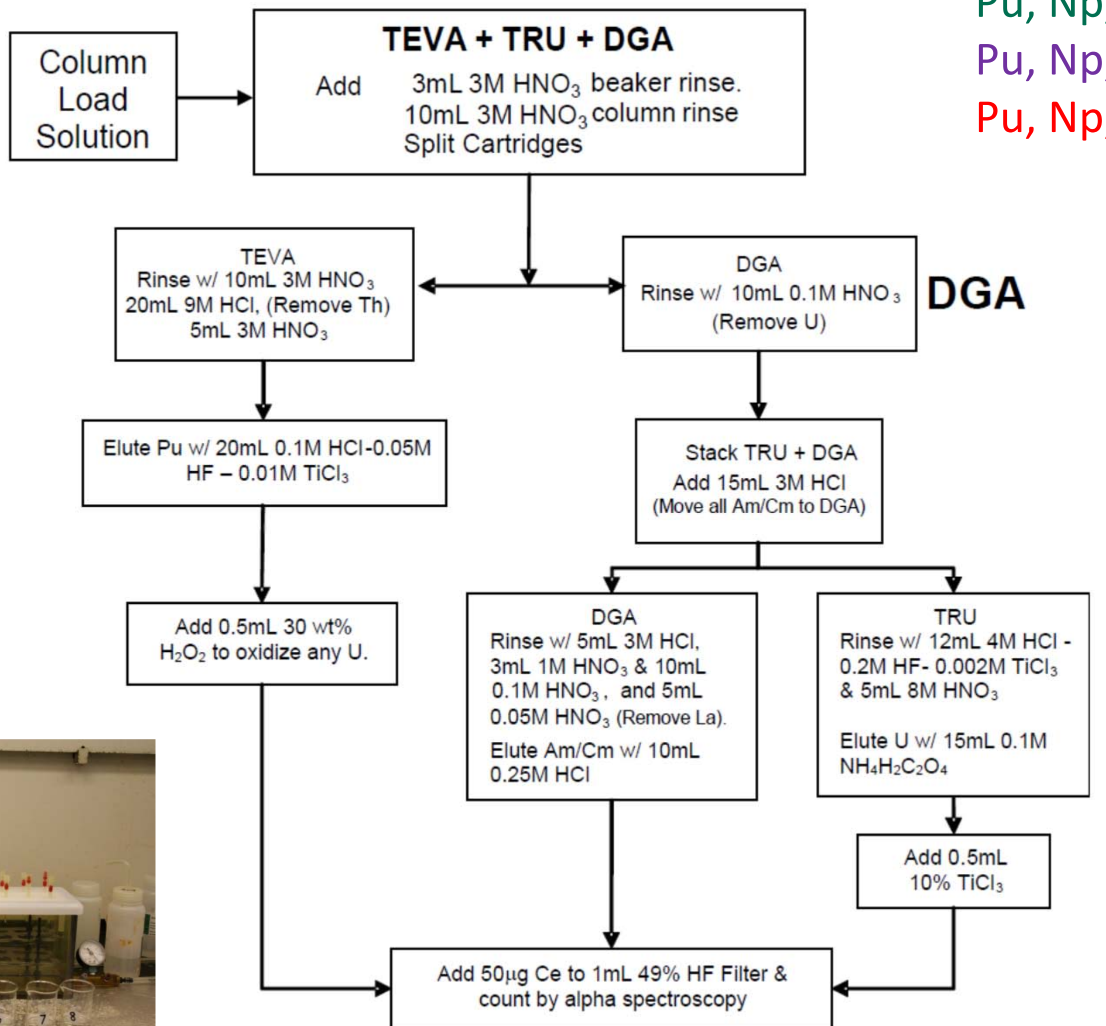


Anal Chim Acta. 2011 Sep 2;701(1):112-8. Epub 2011 Jun 15.
Rapid radiochemical method for determination of actinides in emergency concrete and brick samples.
Maxwell SL, Culligan BK, Kelsey-Wall A, Shaw PJ.

Rapid Column Separation

Pu, Np, Th: TEVA
Pu, Np, U, Th :TEVA+TRU
Pu, Np, Am, Cm :TEVA+DGA

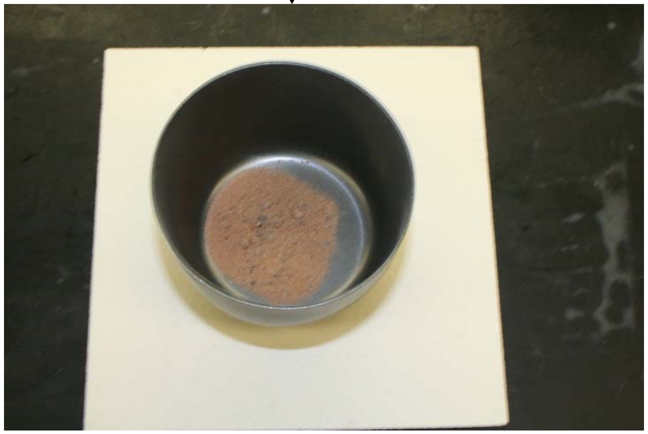
Flexibility!



What about Asphalt?

- Literature ??
  - Not much…
- SRNL approach for asphalt
  - Crush, pulverize, mill to get representative sample
  - *Crushing releases powder/ dries organics*
  - Add tracers to 1g aliquot
  - Furnace to remove bitumen/organics
    - *Similar to how we handle food or vegetation*
  - Process remaining inorganic residue
  - Rapid hydroxide fusion like soil or concrete
  - Rapid column separation
    - *A new option?*

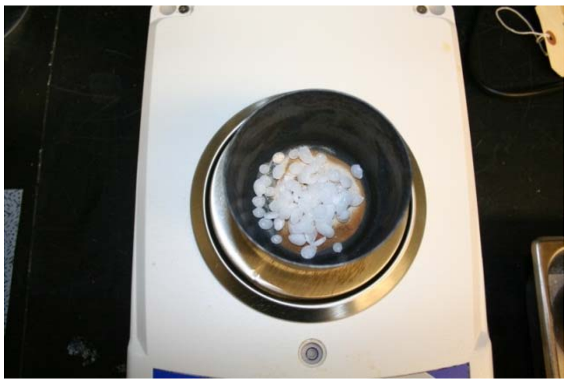
Furnace Heating for Asphalt

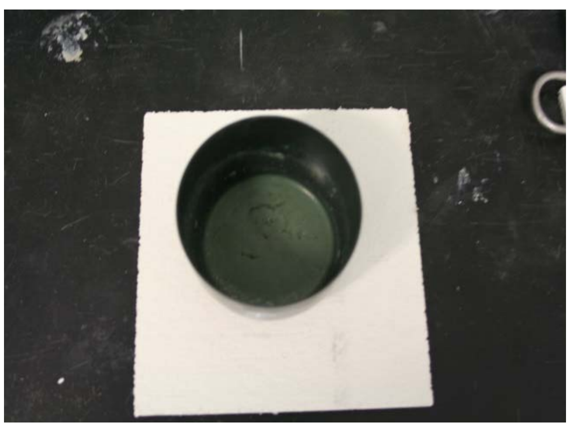


Place crucibles in furnace at about 200°C and ramp immediately to 600°C for 60 min

Rapid Sodium Hydroxide Fusion

- Great to digest solid matrices high in silicates
- ~15-20 minutes





LaF_3/CaF_2 ppt

Why Sodium Hydroxide Fusion ?

- Easy, rapid and rugged
- 250 mL low form Zr crucibles (reuseable) -$95 each
- Low temperature (600°C), no burner
- Multiple samples processed simultaneously in furnaces
- Unlike lithium metaborate, for example, comes out of crucible easily and allows HF preconcentration steps
- LaF_3 matrix removal steps
  - Removes Fe/Ti
  - Eliminates flow problems due to silicates (gel)
- *Total digestion of refractory particles faster than HF*

- Why not just acid leach?
  - Potential for refractory particles in explosion
  - U (and Ra) native content variable with leach

Rapid Asphalt Sample Fusion Method

1g Asphalt Sample
Add Tracers
(^{242}Pu / ^{236}Pu, ^{243}Am, ^{232}U)

↓

Heat at 600^{o}C for 1 hour in Furnace

↓

Wet Ash with HNO_3 / H_2O_2 on Hot Plate ← *May not need to wet-ash..*

↓

Fuse sample in Zr Crucible
15g NaOH 600^{o}C 10-15 minutes ← *Soil samples start here*

↓

Fe/Ti hydroxide precipitation (125 mg Fe, 5 mg La, 100 mg Ca, 5 mL 3.2M $(NH_4)_2HPO_4$, 10 mL 10 wt%$TiCl_3$), Centrifuge

↓

Lanthanum Fluoride Matrix Removal
(1 mg La, HCl/HF, $TiCl_3$)

↓

Only traces of Fe/Ti in load → Redissolve in 5 mL 3M HNO_3-0.25M Boric acid, 6 mL 7M HNO_3, 7 mL 2M $Al(NO_3)_3$

↓

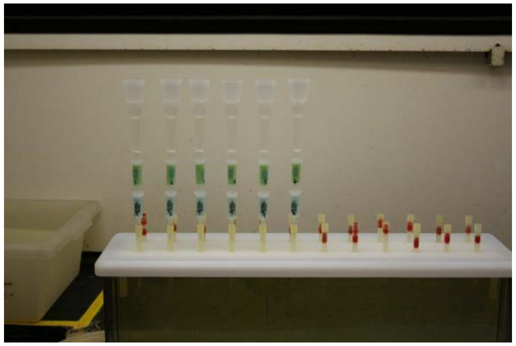
Valence Adjust:
1 mL 1.5M ascorbic acid
1 mL 3.5M $NaNO_2$
4 mL 15.8M HNO_3

↓

Column Load Solution
(~7.5M total nitrate)

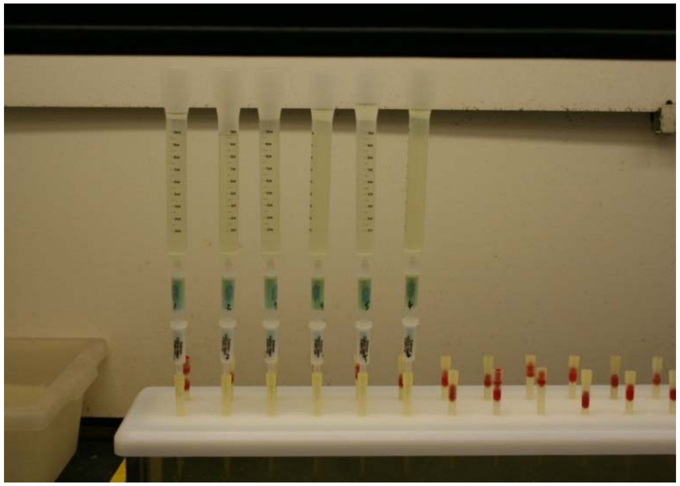
<2.5 hours – ready for column separation !

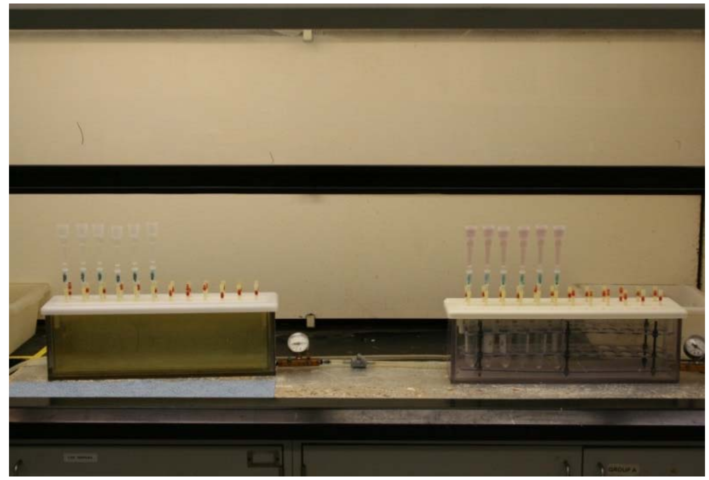
Rapid Two Cartridge Method : TRU+DGA

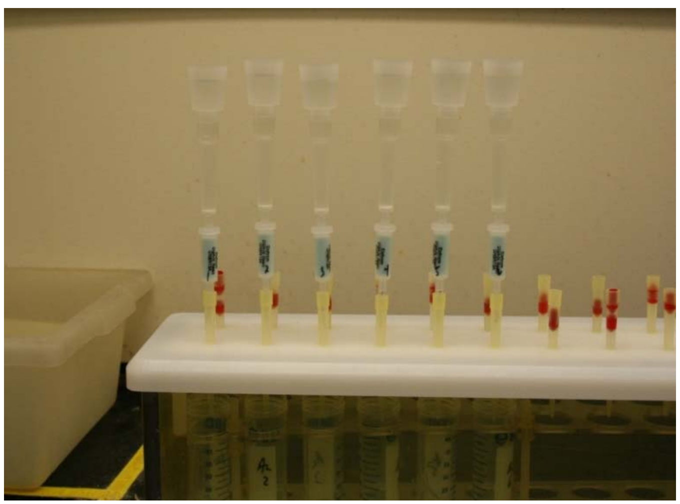


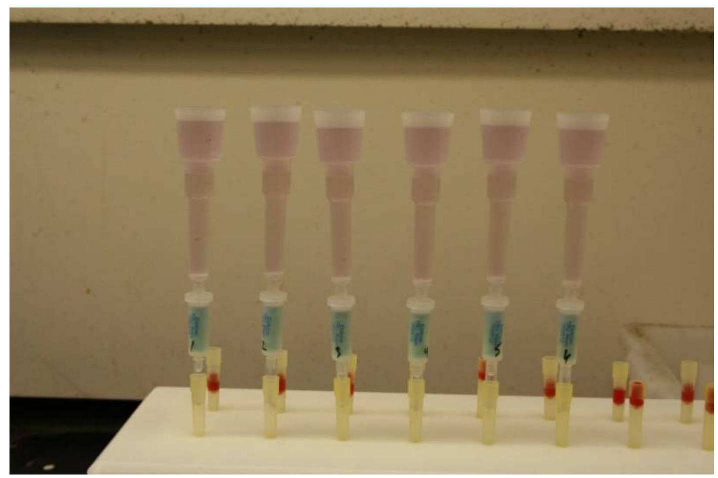
Column Load Solution
TRU + DGA
5 mL 8M HNO_3
10 ml 10M HNO_3
15 mL 4M HCl (Am)
Discard Rinses
Split Cartridges
15 mL 3M HCl-0.025M $TiCl_3$
Elute Pu
TRU (Pu, U)
DGA (Am, Cm)
12 mL 3M HCl
3 ml 1M HNO_3
20 ml 0.05M HNO_3
(Remove U, La)
12 mL 3M HNO_3-0.25M HF
(remove Th)
5 mL 3M HCl
Discard Rinses
5 mL 8M HNO_3 -0.03% H_2O_2 (any U^{+4} to U^{+6})
*10 mL 4M HCl -0.2M HF (remove Np, Th)
7.5 mL 4M HCl -0.2M HF-.002M Ti (Np, Th, Po)
3 mL 8M HNO_3
Discard rinses
Elute U
15mL 0.1M $NH_4HC_2O_4$
Add 0.5mL 10% TiCl3
Add 100 µg Ce, 1 mL 28 M HF, wait 15 minutes and filter
Elute Am, Cm
Collect 12 mL 0.25M HCl
Add 200 µL 30 wt% H_2O_2
Add 30-50 µg Ce, 1mL 28 M HF and filter
Pu:
Add 10 ml water
Add 0.5mL 30 wt% H_2O_2
Add 50 µg Ce, 2 mL 28 M HF and filter
*(increase 4M HCl -0.2M HF if very high Th)

Rapid Two Cartridge Method : TRU+DGA









Comparison: TRU+DGA vs TEVA+TRU [+DGA]

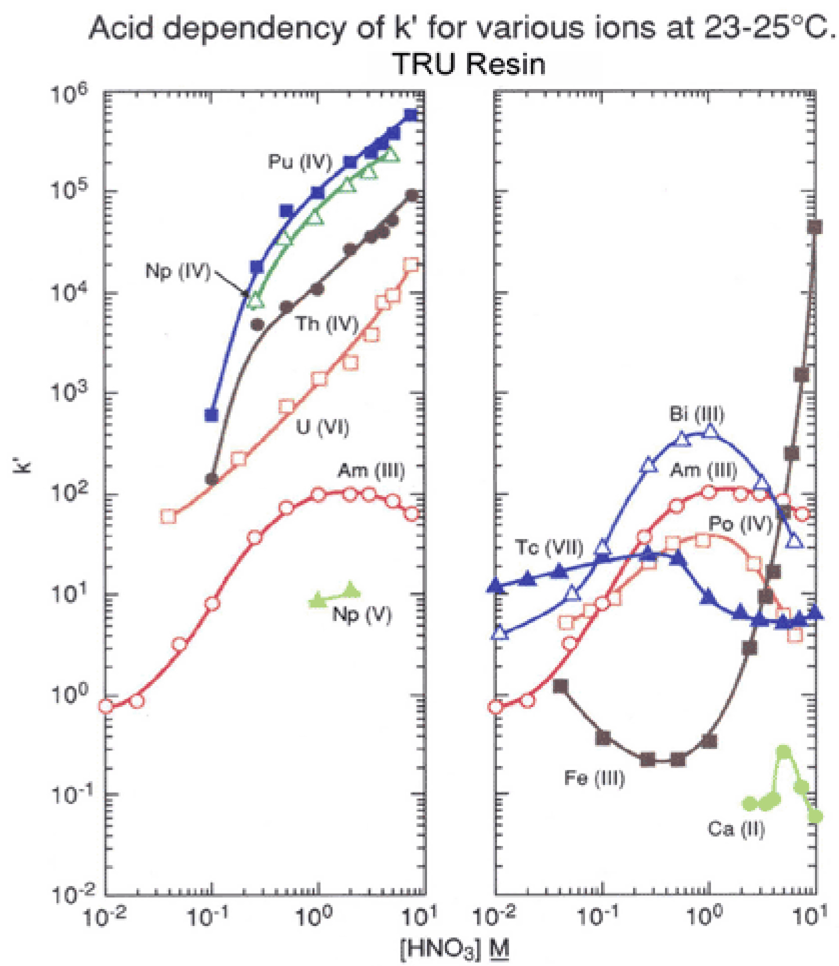
- Both rapid methods
  - are effective with the rapid fusion
  - DGA Resin needed for La carrier (5-6 mg) and good Am/Cm yields
  - Am k' ~50,000 in 3M HNO_3 (no impact from Fe^{+3})
- TRU (Pu,U) +DGA (Am,Cm)
  - *Less resin expense*
    - *Pu k' (loaded as Pu^{+4}) extremely high in high HNO_3*
    - *Slightly more risk of Th interference without TEVA*
    - *Np-237and Th isotopes removed, but not recovered*
- TEVA(Pu, Np,Th) +TRU(U)+ [DGA (Am,Cm)]:
  - *Can do more*
    - *Can collect Pu and Np on TEVA (together using Pu-236 tracer)*
    - *Pu k' ~30,000 in 3M HNO_3 -minimal interferences with Aliquat 336*
    - *Allows for Th purification /assay using TEVA*
  - Pu elution with HCL+HF+Hydroxylamine (HH) option for TEVA (ICP-MS)
    - *can move Pu from TEVA to DGA cartridge, remove more U and elute Pu with 0.02 HCl-0.005M HF-0.02M HH (ICP-MS friendly)*
    - *or count Pu-238 by alpha spectrometry, then go to TEVA and ICP-MS for Pu-239/240*

TRU Resin

Pu^{+4} k' ~ 300,000
In 7M NO_3

U^{+6} k' >10,000
on UTEVA is ~250

Figure 2



Horwitz, et al. (HP193)

LaF$_3$ step removes most of the Fe, allowing use of TRU

Po removal: 10 M HNO_3, plus HCl-HF+ Ti^{+3}

Pu-239 Results for Asphalt Spiked with MAPEP 24 soil

Sample ID	^{242}Pu Yield (%)	^{239}Pu Reference Value (mBq Smp^{-1})	^{239}Pu Measured Value (pCi Smp^{-1})	Measured Value (mBq Smp^{-1})	Difference (%)
1	90.0	N/A	0.005	0.19	N/A
2	77.3	N/A	0.020	0.74	N/A
3	89.4	39.2	1.04	38.3	-2.2
4	86.9	39.2	1.14	42.2	7.6
5	85.9	39.2	1.13	41.8	6.7
6	94.1	39.2	1.03	38.1	-2.8
7	96.2	39.2	1.08	40.0	1.9
8	95.1	39.2	1.05	38.9	-0.9
Avg. Spiked Smps	91.3		1.1	39.9	1.7
SD	6.2		0.0	1.8	
% RSD	6.7		4.4	4.4	

1g asphalt spiked with 0.4g MAPEP 24 soil

Am-241 Results for Asphalt Spiked with MAPEP 24 soil

Sample ID	^{243}Am Yield (%)	^{241}Am Reference Value (mBq Smp^{-1})	^{241}Am Measured Value (pCi Smp^{-1})	^{241}Am Measured Value (mBq Smp^{-1})	Difference (%)
1	104.3	N/A	0.004	0.13	N/A
2	74.0	N/A	0.047	1.74	N/A
3	94.5	24.4	0.67	24.8	1.6
4	92.7	24.4	0.61	22.6	-7.5
5	92.8	24.4	0.63	23.3	-4.5
6	93.4	24.4	0.61	22.6	-7.5
7	67.0	24.4	0.64	23.8	-2.3
8	85.5	24.4	0.56	20.7	-15.1
Avg. Spiked Smps	87.6		0.6	23.0	-5.9
SD	12.1		0.0	1.4	
% RSD	13.8		6.0	6.0	
	1,2= unspiked asphalt		10 hour count		

1g asphalt spiked with 0.4g MAPEP 24 soil

Cm-244 Results for Spiked Asphalt

Sample ID	^{243}Am Yield (%)	^{244}Cm Reference Value (mBq g^{-1})	^{244}Cm Measured Value (pCi g^{-1})	^{244}Cm Measured Value (mBq g^{-1})	Difference (%)
1	105.1	N/A	-0.001	-0.04	N/A
2	79.6	N/A	0.042	1.55	N/A
3	86.2	35.5	0.95	35.2	-1.0
4	95.6	35.5	0.85	31.5	-11.4
5	94.6	35.5	0.91	33.7	-5.2
6	81.7	35.5	0.98	36.3	2.1
7	63.5	35.5	1.21	44.8	26.1
8	83.3	35.5	1.02	37.7	6.3
Avg. Spiked Smps	84.1		1.0	36.5	2.8
SD	12.6		0.1	4.6	
% RSD	14.9		12.6	12.6	

1g asphalt spiked with 0.4g MAPEP 24 soil

U-238 Results for Asphalt Spiked with MAPEP 24 soil

Sample ID	^{232}U Yield (%)	^{238}U Reference Value (mBq Smp^{-1})	^{238}U Measured Value (pCi Smp^{-1})	Corrected Value (pCi Smp^{-1})	^{238}U Measured Value (mBq Smp^{-1})	Difference (%)
1	97.2	N/A	0.880	N/A	32.6	N/A
2	81.8	N/A	1.270	N/A	47.0	N/A
3	88.8	73.6	2.93	1.86	68.6	-6.7
4	90.6	73.6	3.03	1.96	72.3	-1.7
5	82.7	73.6	3.28	2.21	81.6	10.8
6	74.6	73.6	3.30	2.23	82.3	11.9
7	89.7	73.6	2.82	1.75	64.6	-12.3
8	91.4	73.6	2.77	1.70	62.7	-14.8
Avg. Spiked Smps	86.3		3.0		72.0	-2.1
SD	7.0		0.2		8.4	
% RSD	8.2		7.5		11.6	
		spiked results corrected for 1.075 pCi ^{238}U				

1g asphalt spiked with 0.4g MAPEP 24 soil

U-234 Results for Asphalt Spiked with MAPEP 24 soil

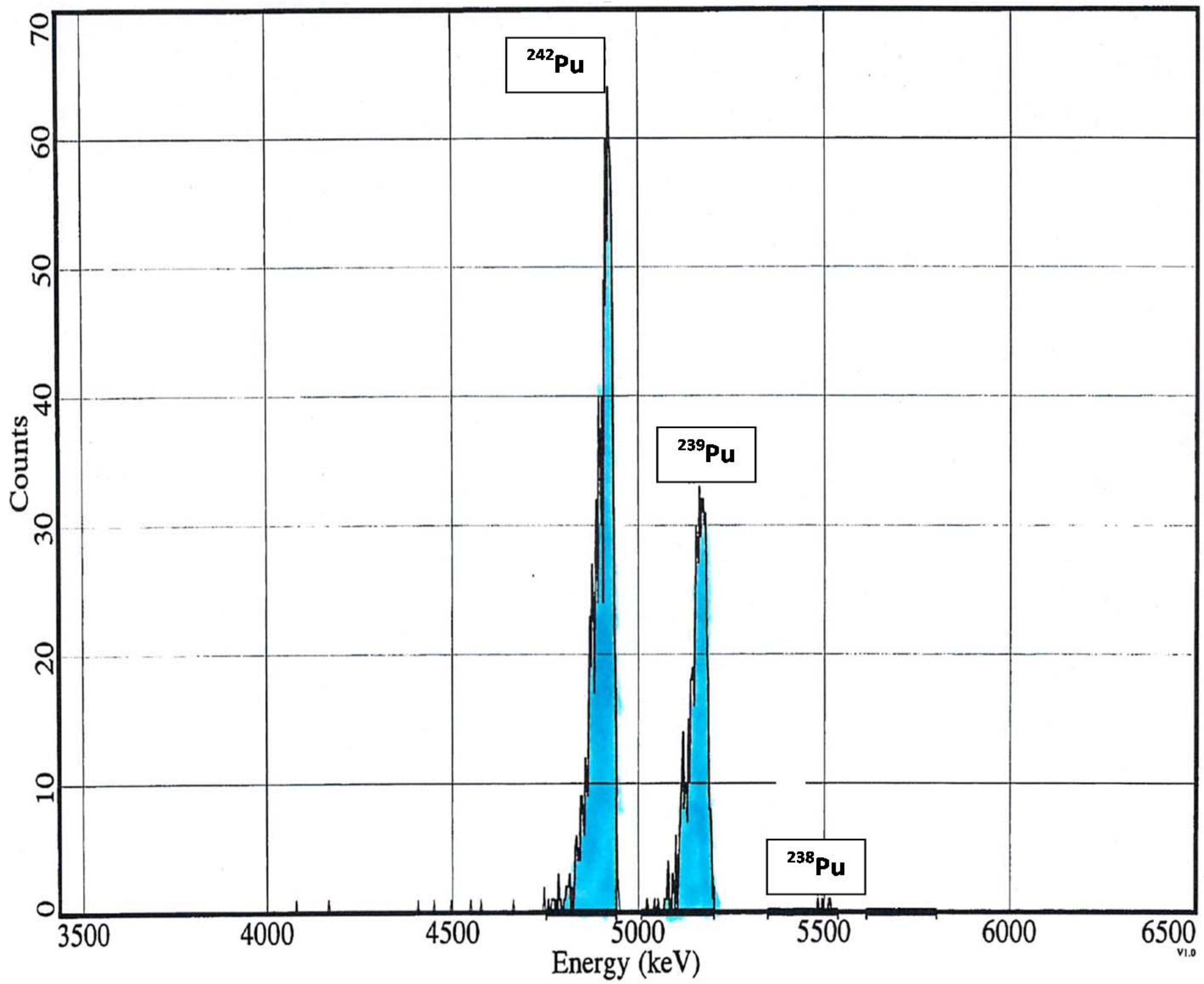
Sample ID	^{232}U Yield (%)	^{234}U Reference Value (mBq Smp^{-1})	^{234}U Measured Value (pCi Smp^{-1})	Corrected Value (pCi Smp^{-1})	^{234}U Measured Value (mBq Smp^{-1})	Difference (%)
1	97.2	N/A	0.860	N/A	31.82	N/A
2	81.8	N/A	1.290	N/A	47.73	N/A
3	88.8	73.6	3.02	1.95	72.0	-2.2
4	90.6	73.6	2.95	1.88	69.4	-5.7
5	82.7	73.6	3.34	2.27	83.8	13.9
6	74.6	73.6	3.22	2.15	79.4	7.8
7	89.7	73.6	2.77	1.70	62.7	-14.8
8	91.4	73.6	2.75	1.68	62.0	-15.8
Avg. Spiked Smps	86.3		3.0		71.5	-2.8
SD	7.0		0.2		8.8	
% RSD	8.2		7.9		12.3	
		spiked results corrected for 1.075 pCi ^{234}U				

1g asphalt spiked with 0.4g MAPEP 24 soil

Blank Asphalt Native U-238 Variability

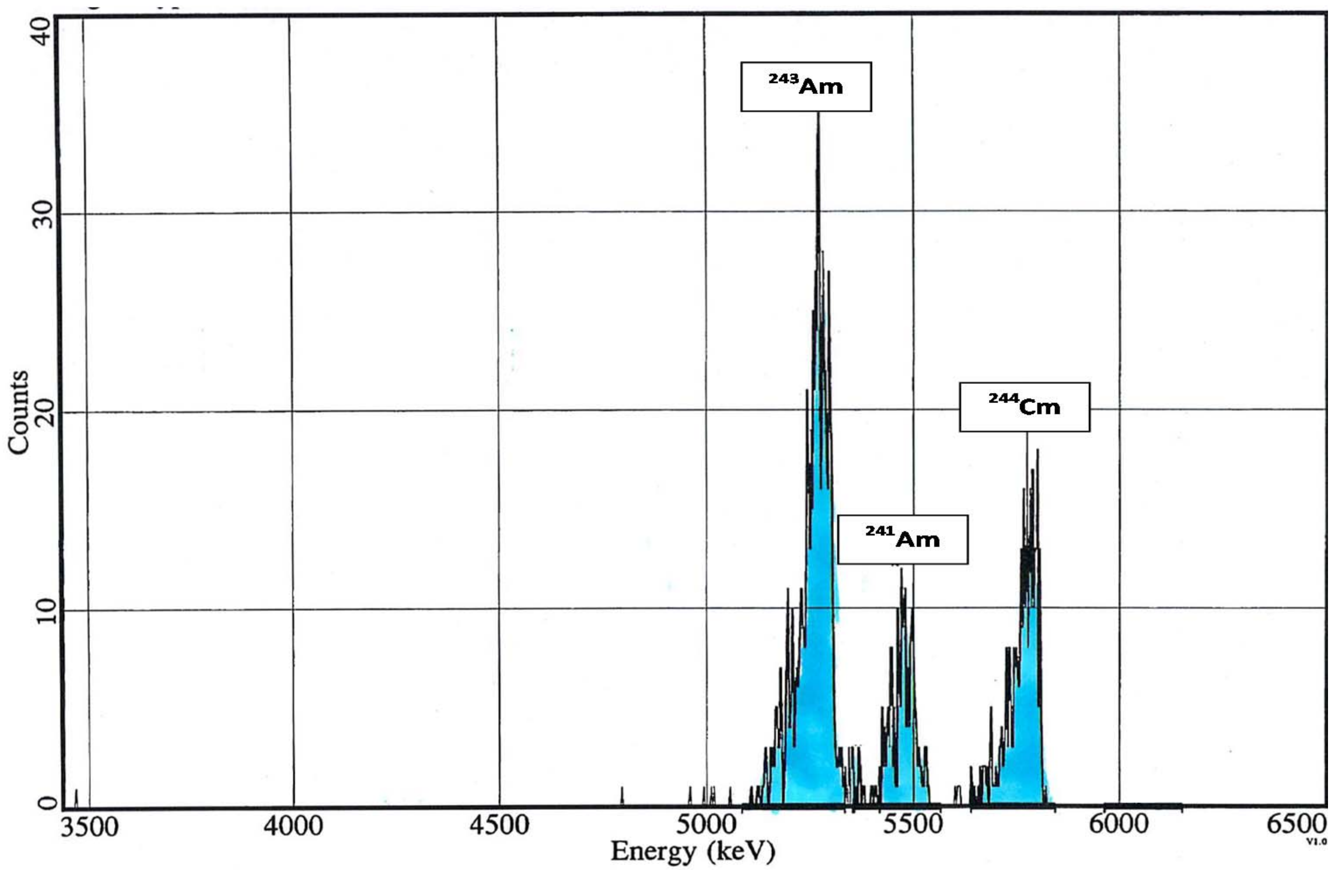
Sample ID	^{232}U Yield (%)	^{238}U Measured Value ($pCi\ g^{-1}$)	^{238}U Measured Value ($mBq\ g^{-1}$)
1	99.6	1.86	68.9
2	95.8	1.77	65.4
3	87.4	2.30	85.0
4	91.3	1.60	59.3
5	86.5	2.07	76.7
Avg	92.1	1.92	71.1
SD	5.6	0.27	10.0
% RSD	6.0	14.1	14.1

Pu Isotopes– Asphalt Sample



Tracer Yield = 97.3%	**Tracer FWHM = 44.1keV**

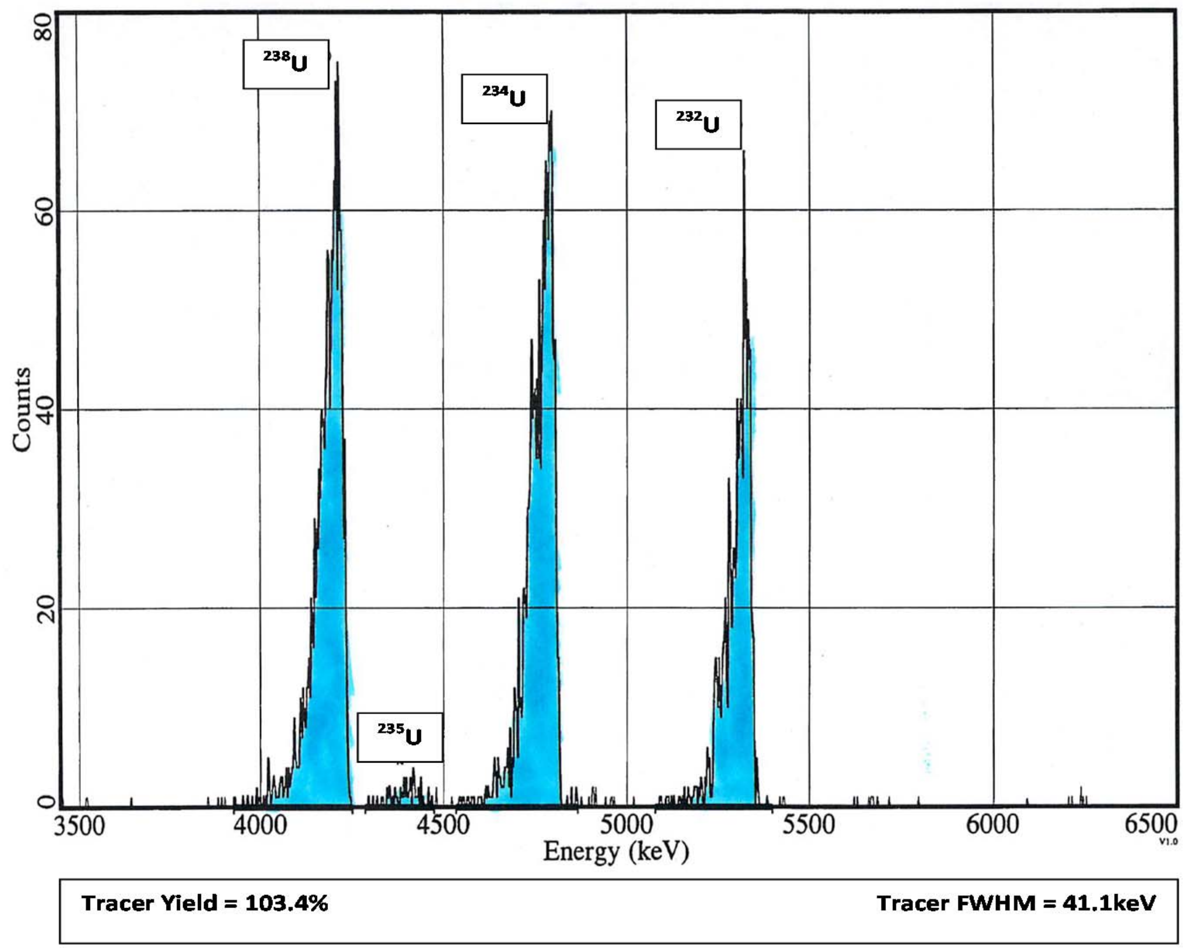
Am/Cm Isotopes– Asphalt Sample



Tracer Yield = 103.1%

Tracer FWHM = 63.5keV

Uranium Isotopes– Asphalt Sample



Pu-239 Results for MAPEP 24 soil

TRU + DGA Resin (loaded as Pu^{+4})

Sample ID	^{242}Pu Yield (%)	^{239}Pu Reference Value (mBq Smp^{-1})	^{239}Pu Measured Value (pCi Smp^{-1})	Measured Value (mBq Smp^{-1})	Difference (%)
1	94.5	98.0	2.71	100.3	2.3
2	87.7	98.0	2.54	94.0	-4.1
3	93.5	98.0	2.56	94.7	-3.3
4	101.2	98.0	2.50	92.5	-5.6
5	115.6	98.0	2.53	93.6	-4.5
6	97.0	98.0	2.45	90.7	-7.5
7	88.8	98.0	2.63	97.3	-0.7
Avg	96.9		2.6	94.7	-3.3
SD	9.4		0.1	3.2	3.2
% RSD	9.7		3.4	3.4	
	16 hour count				

1g MAPEP 24 soil

Need for Rugged Sample Digestion

- Recently ~80% of MAPEP labs failed Uranium in soil PT tests in Series 30
  - US and international labs
  - Even with HF added

MAPEP website:

- The soil used for MAPEP Series 30 contained a much higher concentration of this naturally occurring and more insoluble form of uranium.
- The laboratories using chemical procedures capable of dissolving the entire soil sample reported accurate results; while the laboratories using dissolution techniques that were unable to dissolve the insoluble form of the uranium reported results that were approximately 60% low.

- Example

Uranium-234/233	32.9	81	N	-59.4
Uranium-238	30.9	83	N	-62.8

Uranium in MAPEP 30 soil

-SRNL Environmental Lab passed because of rapid fusion method

Sample ID	^{232}U Yield (%)	^{238}U Reference Value ($mBq\ g^{-1}$)	^{238}U Measured Value ($pCi\ g^{-1}$)	^{238}U Measured Value ($mBq\ g^{-1}$)	Difference (%)
1	89.9	83.0	2.32	85.7	3.3
2	75.7	83.0	2.36	87.3	5.1
3	84.7	83.0	2.27	84.1	1.4
4	72.3	83.0	2.25	83.3	0.4
5	88.0	83.0	2.27	84.1	1.4
6	85.7	83.0	2.22	82.3	-0.8
7	82.9	83.0	2.33	86.1	3.7
8	80.8	83.0	2.42	89.6	8.0
9	98.9	83.0	2.30	84.9	2.3
10	89.5	83.0	2.42	89.6	8.0
11	92.1	83.0	2.36	87.3	5.1
12	98.8	83.0	2.30	84.9	2.3
Avg	86.6		2.32	85.78	3.35
SD	8.1		0.06	2.32	2.79
% RSD	9.4		2.7	2.7	

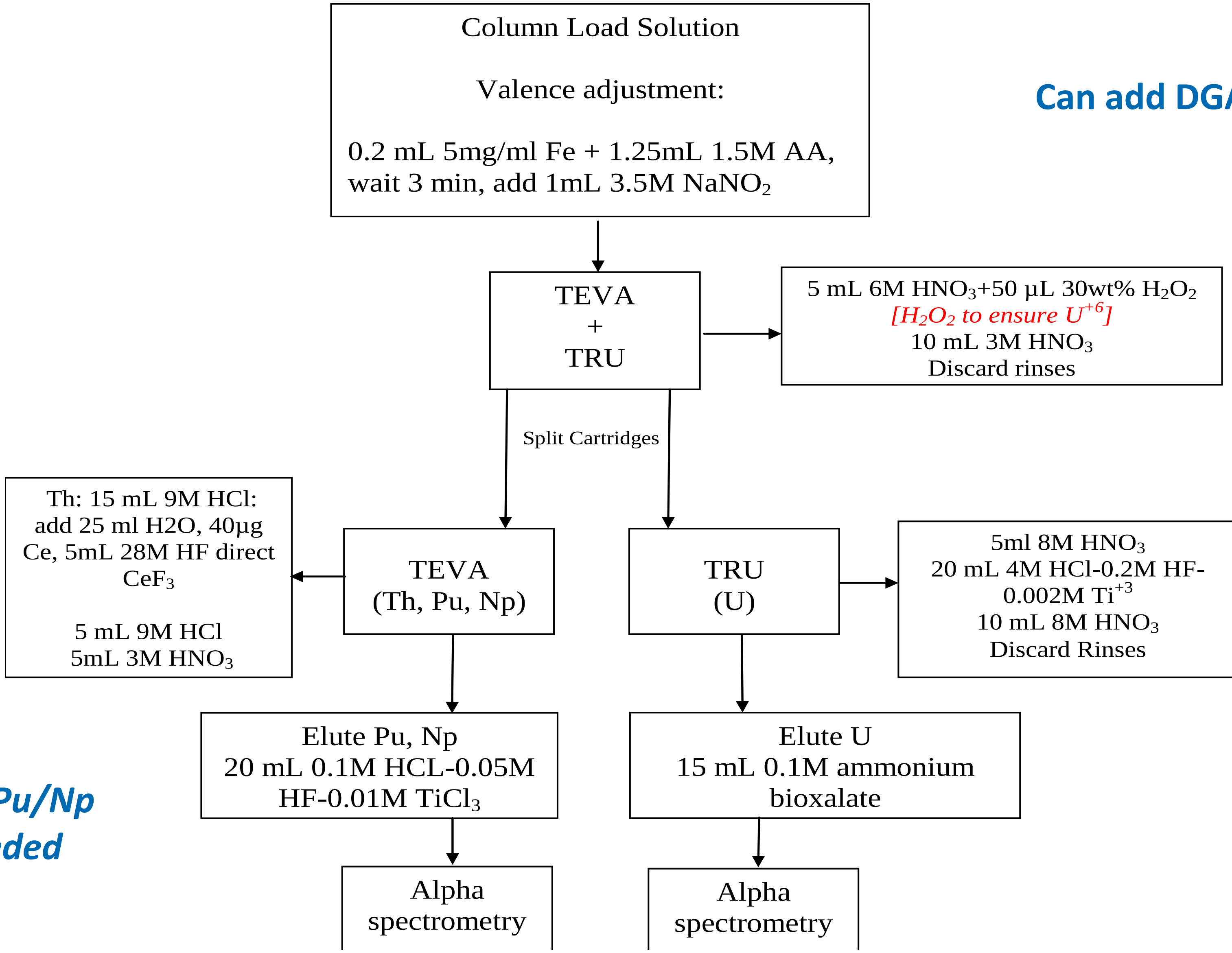
1g MAPEP 30 soil; generated with TEVA+TRU option

Thorium isotopes in soil

- Would rapid fusion plus TEVA+TRU be a good approach for U/Th in soil?
  - TEVA (Th) + TRU (U)
  - *1g soil enough due to relatively high levels of U/Th in soil*
- Test on MAPEP 30 refractory soil?
  - Th retention can be sensitive to PO_4 or F^- on TEVA Resin
  - *Steve Bohrer at RESL analyzed MAPEP 30 soil*
    - *Unofficial values for Th-228, Th-230, and Th-232*
- Optimized rapid fusion steps for U/Th
  - Additional boric acid and Al^{+3} ions
  - Ca levels
  - *Assurance no U^{+4} retention on TEVA*

MAPEP 30 Soil Approach for U, Th

Can add DGA for Am



Also Pu/Np if needed

Th-228 in MAPEP 30 Soil

Sample ID	^{229}Th Yield (%)	^{228}Th Reference Value (mBq g^{-1})	^{228}Th Measured Value (pCi Smp^{-1})	^{228}Th Measured Value (mBq g^{-1})	Difference (%)
1	88.4	51.1	1.44	53.1	4.0
2	87.8	51.1	1.37	50.6	-0.9
3	95.3	51.1	1.31	48.6	-4.8
4	88.1	51.1	1.33	49.2	-3.6
5	82.0	51.1	1.32	48.8	-4.3
6	102.1	51.1	1.27	47.0	-8.0
7	96.4	51.1	1.37	50.7	-0.7
8	93.3	51.1	1.34	49.6	-2.9
9	92.5	51.1	1.39	51.4	0.7
10	93.5	51.1	1.34	49.6	-2.9
11	92.5	51.1	1.46	54.0	5.8
12	80.1	51.1	1.34	49.6	-2.9
Avg	91.0		1.36	50.19	-1.71
SD	6.1		0.05	1.95	3.81
% RSD	6.7		3.9	3.9	

Unofficial Th values - Steve Bohrer DOE-RESL

Th-230 in MAPEP 30 Soil

Sample ID	^{229}Th Yield (%)	^{230}Th Reference Value (mBq g^{-1})	^{230}Th Measured Value (pCi Smp^{-1})	^{230}Th Measured Value (mBq g^{-1})	Difference (%)
1	88.4	96.2	2.58	95.5	-0.8
2	87.8	96.2	2.49	92.1	-4.2
3	95.3	96.2	2.49	92.1	-4.2
4	88.1	96.2	2.36	87.3	-9.2
5	82.0	96.2	2.81	104.0	8.1
6	102.1	96.2	2.59	95.8	-0.4
7	96.4	96.2	2.71	100.3	4.2
8	93.3	96.2	2.69	99.5	3.5
9	92.5	96.2	2.77	102.5	6.5
10	93.5	96.2	2.81	104.0	8.1
11	92.5	96.2	2.73	101.0	5.0
12	80.1	96.2	2.89	106.9	11.2
Avg	91.0		2.66	98.42	2.31
SD	6.1		0.16	5.88	6.11
% RSD	6.7		6.0	6.0	

Unofficial Th values - Steve Bohrer DOE-RESL

Th-232 in MAPEP 30 Soil

Sample ID	^{229}Th Yield (%)	^{232}Th Reference Value ($mBq\ g^{-1}$)	^{232}Th Measured Value ($pCi\ Smp^{-1}$)	^{232}Th Measured Value ($mBq\ g^{-1}$)	Difference (%)
1	88.4	48.8	1.42	52.5	7.7
2	87.8	48.8	1.32	48.8	0.1
3	95.3	48.8	1.22	45.1	-7.5
4	88.1	48.8	1.29	47.7	-2.2
5	82.0	48.8	1.47	54.4	11.5
6	102.1	48.8	1.25	46.3	-5.2
7	96.4	48.8	1.24	45.9	-6.0
8	93.3	48.8	1.40	51.8	6.1
9	92.5	48.8	1.34	49.6	1.6
10	93.5	48.8	1.40	51.8	6.1
11	92.5	48.8	1.49	55.1	13.0
12	80.1	48.8	1.34	49.6	1.6
Avg	91.0		1.35	49.89	2.23
SD	6.1		0.09	3.30	6.76
% RSD	6.7		6.6	6.6	

Unofficial Th values - Steve Bohrer DOE-RESL

Pu-238,239 in MAPEP 30 Soil

Sample ID	^{242}Pu Yield (%)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	92.6	76.8	2.14	79.3	3.2
2	87.8	76.8	2.23	82.5	7.5
3	95.3	76.8	2.06	76.3	-0.7
Avg	91.9		2.14	79.3	3.3
SD	3.8		0.08	3.1	4.1
% RSD	4.1		4.0	4.0	

Sample ID	^{242}Pu Yield (%)	^{238}Pu Reference Value (mBq g^{-1})	^{238}Pu Measured Value (pCi g^{-1})	^{238}Pu Measured Value (mBq g^{-1})	Difference (%)
1	92.6	96.0	2.63	97.1	1.2
2	87.8	96.0	2.81	103.9	8.2
3	95.3	96.0	2.53	93.6	-2.5
Avg	91.9		2.65	98.20	2.29
SD	3.8		0.14	5.24	5.46
% RSD	4.1		5.3	5.3	

Am-241 in MAPEP 30 Soil (DGA Resin)

Sample ID	^{243}Am Yield (%)	^{241}Am Reference Value (mBq g^{-1})	^{241}Am Measured Value (pCi g^{-1})	^{241}Am Measured Value (mBq g^{-1})	Difference (%)
1	94.3	68.0	1.83	67.8	-0.3
2	82.9	68.0	1.96	72.5	6.7
3	90.4	68.0	1.82	67.4	-0.8
Avg	89.2		1.87	69.25	1.83
SD	5.8		0.08	2.86	4.20
% RSD	6.5		4.1	4.1	

Summary

- SRNL has developed a new rapid fusion method for asphalt
  - Furnace heating then rapid sodium hydroxide fusion
  - *New option : TRU+DGA :* requires only 2 stacked cartridges (Pu, U, Am, Cm)
  - Can also be applied to soil, brick, concrete, etc.
- Flexible options with rapid fusion method:
  - *TRU (Pu, U) +DGA (Am)*
  - *TEVA (Pu, Th, Np)+TRU (U) [+DGA (Am)]*
  - *TEVA only (Pu, Np) or TEVA+DGA (Pu, Am)*
- TEVA+TRU tested on MAPEP 30 soil (U/Th)
  - Rugged, good interference removal
- *New version of soil fusion adapted for 10g soil samples for Pu, Np, Am, Cm (TEVA+DGA)*
  - *Tested on asphalt and concrete*