Savannah River NUCLEAR SOLUTIONS℠

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Rapid Radiochemical Method for Actinides in Emergency Concrete and Brick Samples

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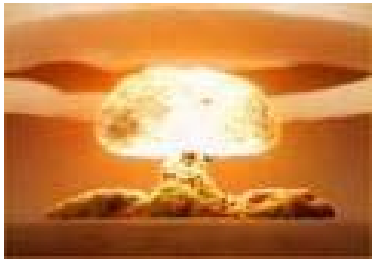
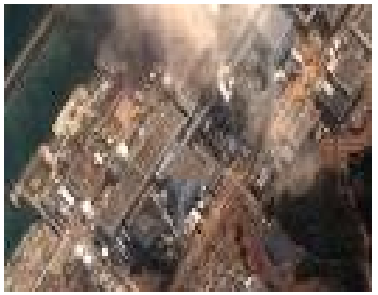
Background

- Need for rapid radiochemical methods
  - Emergency response
    - IND, RDD, nuclear accident
    - Large numbers of samples
      - environmental and bioassay analyses
    - Rapid turnaround times
  - Routine sample analyses
    - Lowers costs
    - Increases lab throughput capacity
    - Allows more with less





Fukushima Decontamination

- Fukushima City plans to remove radioactive materials from private houses, parks and meeting venues in the city.
- The plan includes decontamination of all 110,000 residences in the city over two years, with emphasis on households with children.
- Cleaners will scrub roofs, remove *concrete* and decontaminate ditches.

http://safetyfirst.nei.org/japan/fukushima-city-to-decontaminate-110000-residences/

What about concrete and brick?

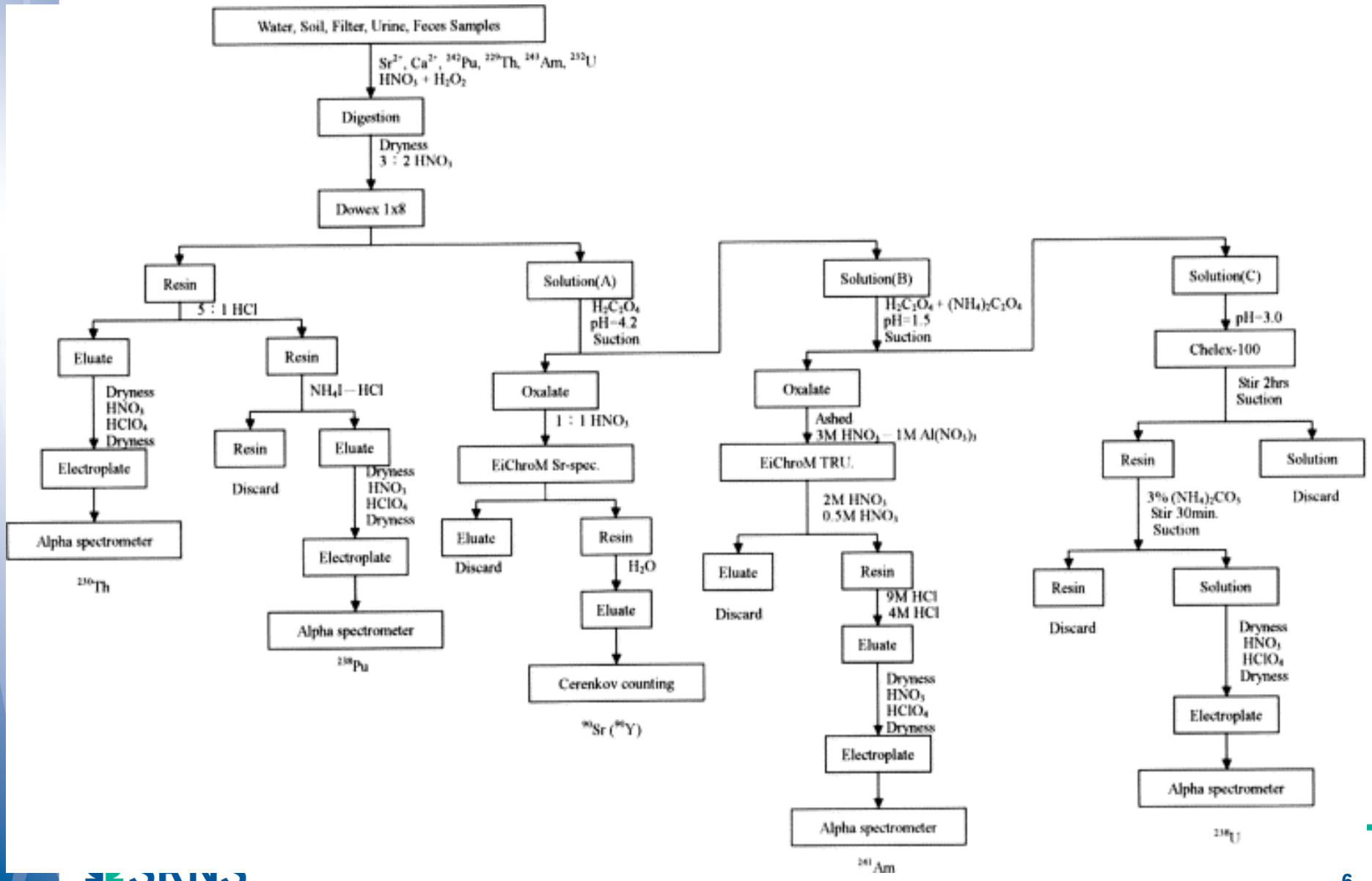
- Concrete, brick and asphalt analyses may be needed if an IND, RDD or nuclear event occurs
- Refractory particles may be present
- Could we develop a rapid method for actinides in concrete and brick?
  - rugged and reliable

Literature

- R. Weinreich, S. Bajo, J. Eikenberg, and F. Atchison., Determination of uranium and plutonium in shielding concrete, Journal of J. 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, 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)
  - 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, et al Flow Chart



Rapid Soil Sample Preparation

NRIP soil results - 4hrs

1-2 g soil sample. Add Tracers (^{242}Pu / ^{236}Pu, ^{243}Am, ^{232}U). Heat on Hot Plate

↓

Fuse in Zr Crucible 5-10 min. (15g NaOH - 600°C). Hydroxide precipitation (6mg La Carrier, $TiCl_3$, Ba). ← **We now add some Ca and PO4 also, no Ba**

↓

Lanthanum Fluoride Matrix removal (2mg La, HCL/HF, $TiCl_3$)

↓

Redissolve in 5mL 3M HNO_3-0.25M Boric Acid 6mL 7M HNO_3, 7mL 2M $Al(NO_3)_3$

↓

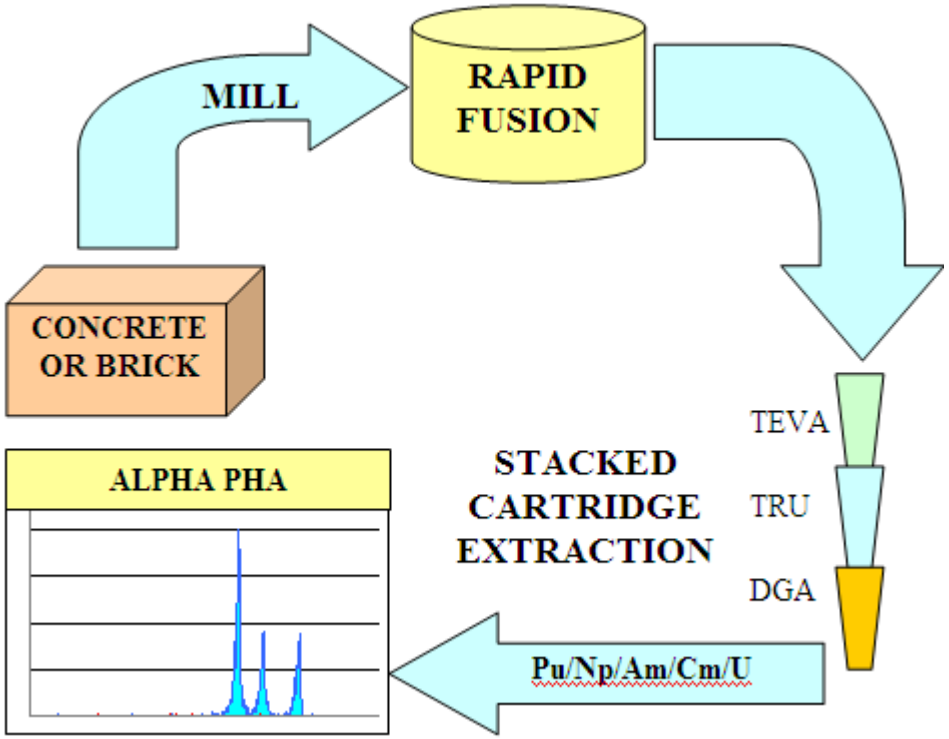
Valence Adj.: 0.5mL 1.5M Sulfamic Acid
1.25mL 1.5M Ascorbic Acid.
1mL 3.5M $NaNO_2$ + 1.5mL 15.8M HNO_3

↓

Column Load Solution

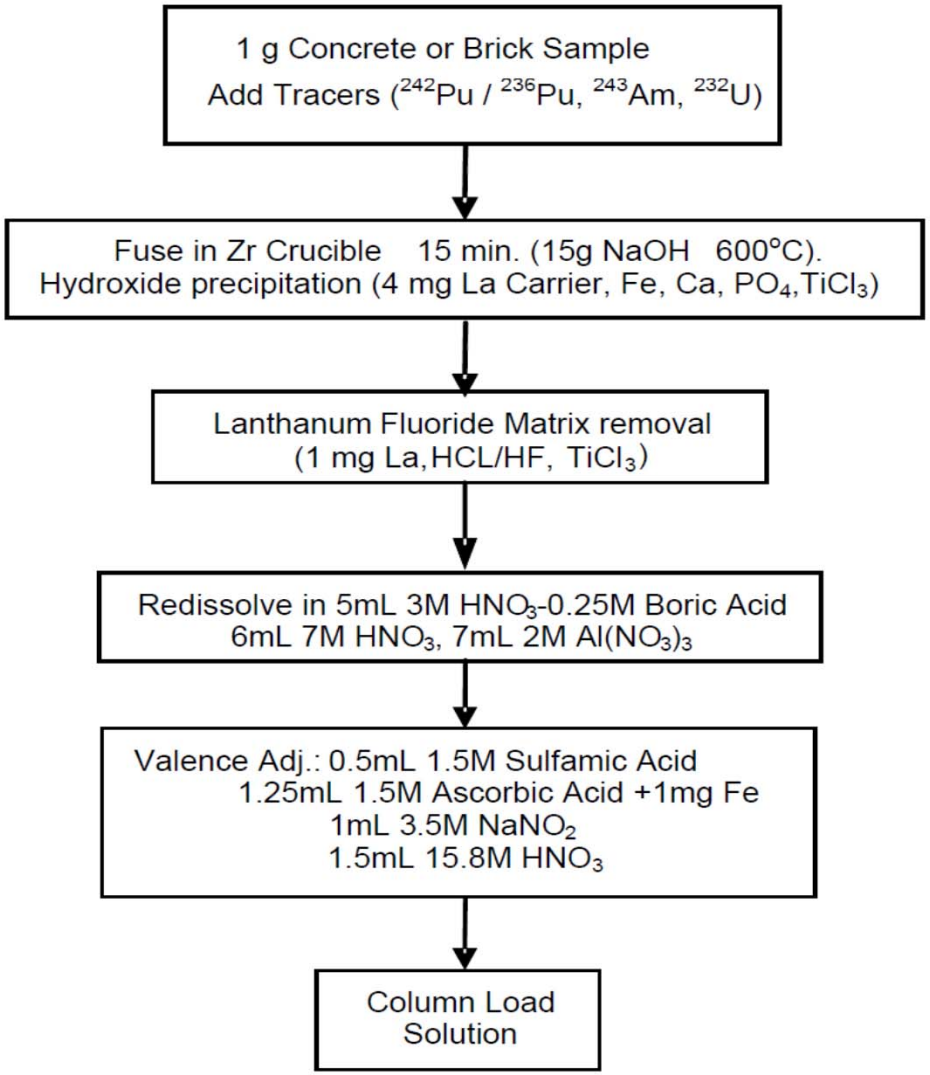
Maxwell, S., Culligan, B. and Noyes, G. (2010), Rapid method for actinides in emergency soil samples, Radiochimica Acta, Vol. 98, No. 12, pp. 793-800.

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.

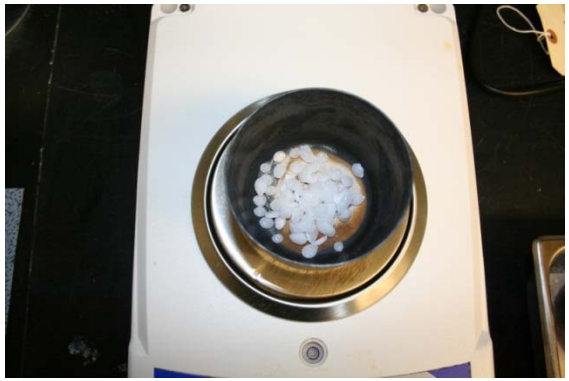
Rapid Concrete and Brick Sample Preparation

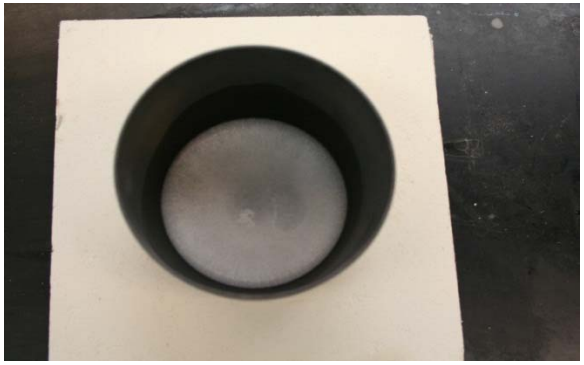


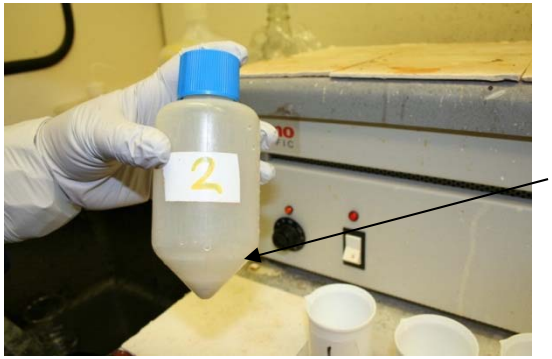
We now add Ca and PO4 for soil, concrete and brick

Rapid Sodium Hydroxide Fusion

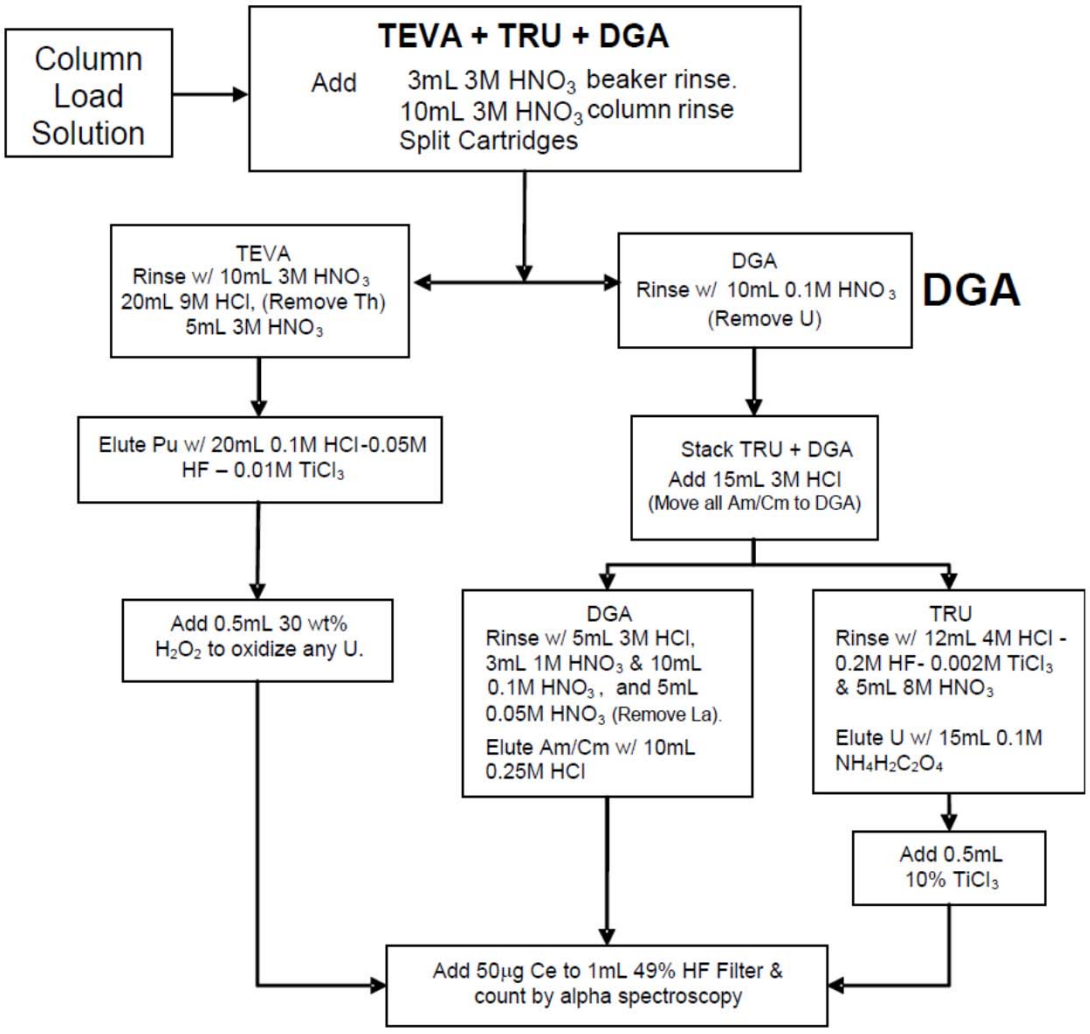
- Great for silicates
- ~10 minutes







Rapid Column Separation



The Magic of DGA

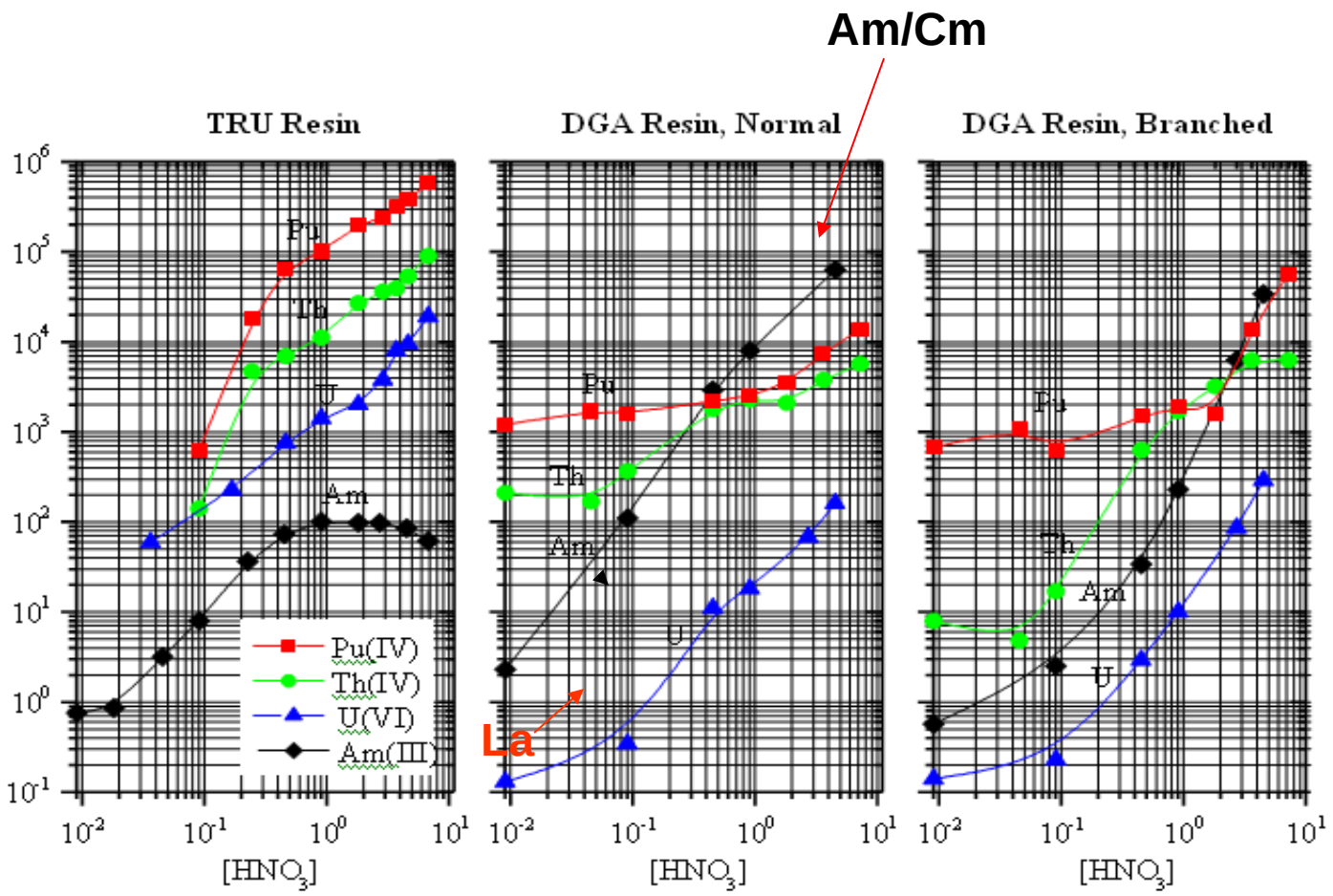


Figure 2

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

Pu and Np results for brick samples (with MAPEP 18 standard)

Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq g^{-1}	^{239}Pu Measured mBq g^{-1}	^{237}Np Measured mBq g^{-1}
1	95.9	15.4	20.6	34.3
2	89.5	16.6	16.5	35.2
3	107.6	13.7	18.0	32.2
4	85.0	14.0	14.8	33.4
5	95.7	15.6	16.2	40.3
Avg.	94.7	15.1	17.2	35.1
1SD	8.5	1.2	2.2	3.1
%RSD	9.0	7.9	12.8	8.9
Reference		14.8	18	37
% Difference		1.8	-4.3	-5.2

Pu-239 is refractory in MAPEP 18 soil standard

Am and Cm results for brick samples (with MAPEP 18 standard)

Sample ID	^{243}Am Yield (%)	^{241}Am Measured mBq g^{-1}	^{244}Cm Measured mBq g^{-1}
1	91.5	22.6	38.1
2	92.0	24.5	35.8
3	94.8	24.3	34.6
4	92.4	26.2	34.9
5	98.0	23.3	34.4
Avg.	93.7	24.2	35.6
1SD	2.7	1.4	1.5
%RSD	2.9	5.7	4.3
Reference		25.4	35
% Difference		-4.8	1.6

U results for brick samples (with MAPEP 18 standard)

Sample ID	^{232}U Yield (%)	^{234}U Measured mBq g^{-1}	^{238}U Measured mBq g^{-1}
1	81.1	31.5	26.9
2	85.7	27.8	31.4
3	89.3	27.8	29.9
4	91.4	21.5	28.8
5	92.8	25.2	27.7
Avg.	88.1	26.7	28.9
Corr. Avg.		25.7	28.0
1SD	4.7	3.7	1.8
%RSD	5.4	13.8	6.1
Reference		28.4	29.6
% Difference		-5.9	-2.3

avg ^{238}U in unspiked 1g sample = 0.94 mBq
avg ^{234}U in unspiked 1g sample = 1.02 mBq

[A] average spiked sample result corrected for unspiked content

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Pu and Np results for concrete samples (with MAPEP 18 standard)

Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq g^{-1}	^{239}Pu Measured mBq g^{-1}	^{237}Np Measured mBq g^{-1}
1	88.5	14.8	19.2	34.9
2	90.7	16.2	19.5	32.2
3	92.5	12.4	15.8	32.9
4	97.7	14.7	14.8	31.3
5	78.5	16.5	18.7	32.3
Avg.	89.6	14.9	17.6	32.7
1SD	7.1	1.6	2.1	1.4
%RSD	7.9	11.0	12.1	4.1
Reference		14.8	18	37
% Difference		0.8	-2.2	-11.5

Am and Cm results for concrete samples (with MAPEP 18 standard)

Sample ID	^{243}Am Yield (%)	^{241}Am Measured mBq g^{-1}	^{244}Cm Measured mBq g^{-1}
1	82.6	23.3	34.1
2	90.1	23.6	37.7
3	90.3	22.9	32.7
4	86.5	26.2	34.9
5	77.1	23.3	34.4
Avg.	85.3	23.9	34.8
1SD	5.6	1.4	1.9
%RSD	6.5	5.7	5.3
Reference		25.4	35
% Difference		-6.0	-0.7

U results for concrete samples (with MAPEP 18 standard)

Sample ID	^{232}U Yield (%)	^{234}U Measured mBq g^{-1}	^{238}U Measured mBq g^{-1}
1	78.4	33.5	36.4
2	77.6	26.5	30.9
3	76.3	24.3	30.5
4	80.5	21.7	28.6
5	71.5	26.1	29.4
Avg.	76.9	26.4	31.2
[A] Corr. Avg.		25.8	30.5
1SD	3.4	4.4	3.1
%RSD	4.4	16.7	9.8
Reference		28.4	29.6
% Difference		-7.0	5.2

avg ^{238}U in unspiked 1g sample = 0.596 mBq
avg ^{234}U in unspiked 1g sample = 0.674 mBq

[A] average spiked sample result corrected for unspiked content

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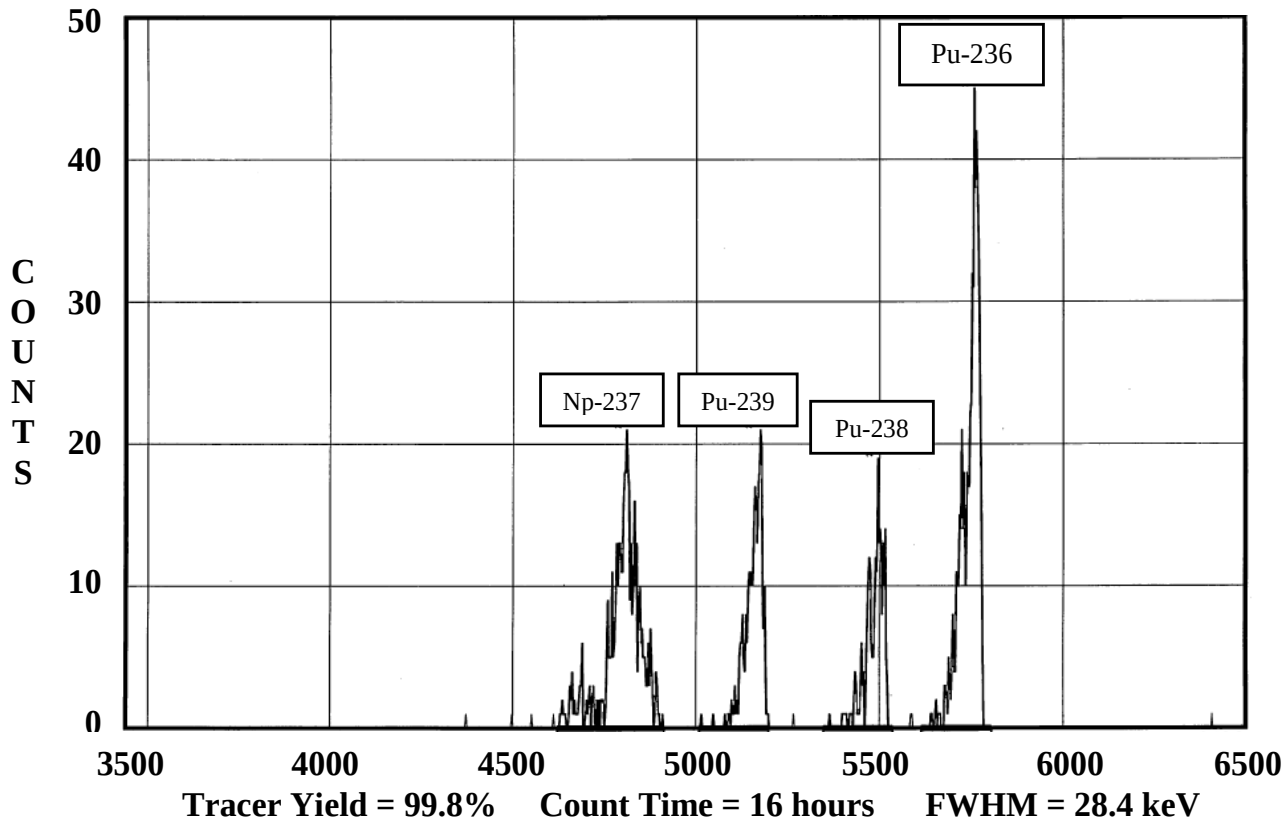
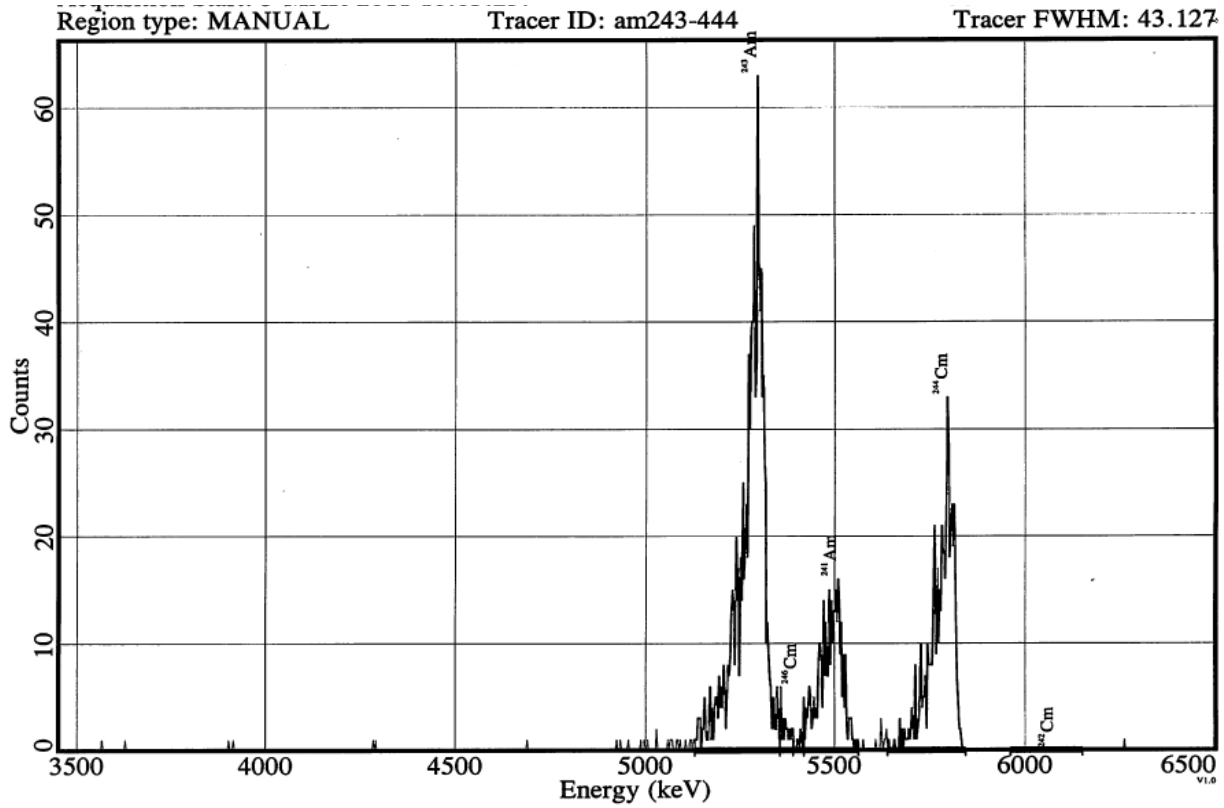
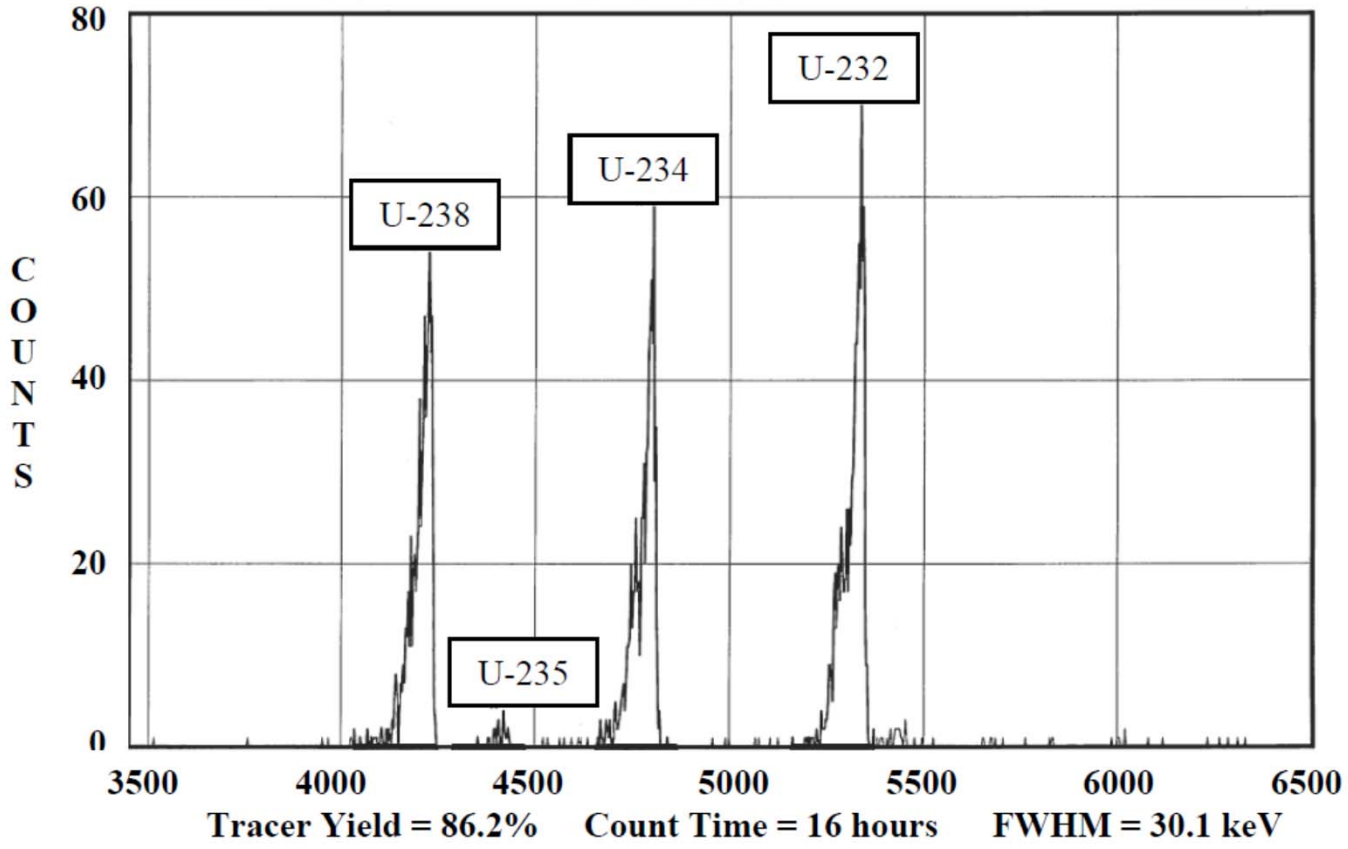
Pu and Np spectra for concrete sample



Am and Cm spectra for concrete sample



U isotope spectra for concrete sample



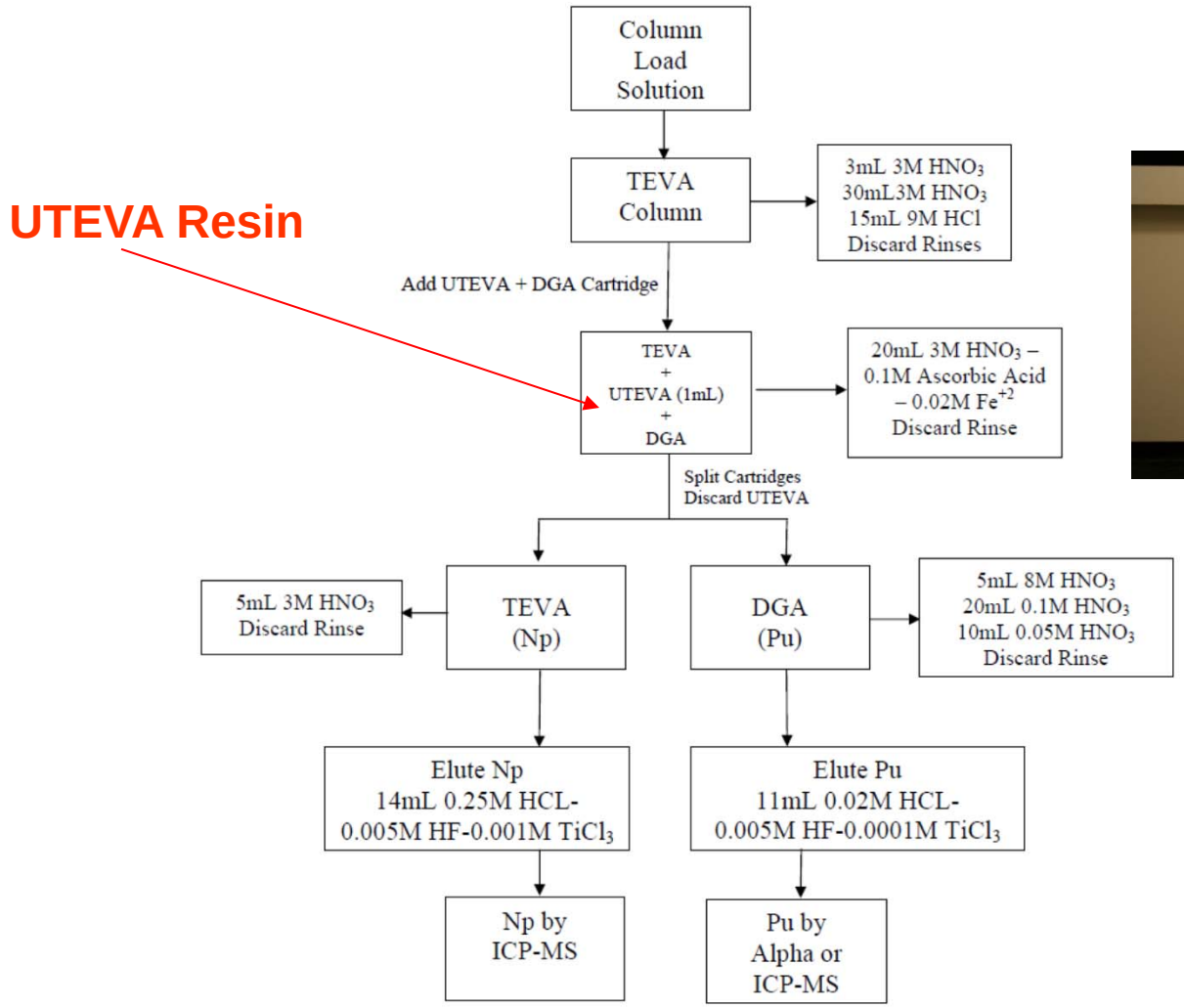
What about ICP-MS?

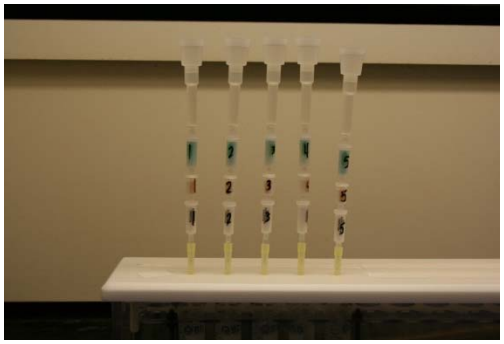
Kim, C.S., Kim, C.K., and Lee, K.J., (2004), *J. Anal. At. Spectrom*., 19, 743 concluded that uranium separation is needed even with DRC the 238U level in the purified solutions should be less than 100 pg mL-1 to minimize spectral interference in the quantitative analysis of 239Pu


Inductively Coupled Plasma (ICP) Mass Spectrometer

Health Physics: August 2011 - Volume 101 - Issue 2 - pp 180-186, Rapid Determination of 237Np and Plutonium Isotopes in Urine By Inductively-Coupled Plasma Mass Spectrometry and Alpha Spectrometry, Maxwell, Sherrod L.; Culligan, Brian K.; Jones, Vernon D.; Nichols, Sheldon T.; Noyes, Gary W.; Bernard, Maureen A.*

Move Pu from TEVA to DGA (ICP-MS)





Summary

- Rapid fusion method is effective for concrete and brick
  - Stack cartridges with vacuum flow
  - TEVA (Pu,Np) +TRU (U) +DGA (Am,Cm)
  - TEVA (Pu, Np)
  - TEVA+DGA (Pu+Am,Cm)
  - TEVA+TRU (Pu, U)
- Alpha spectrometry or ICP-MS