Savannah River NUCLEAR SOLUTIONS℠

FLUOR DANIEL • NORTHROP GRUMMAN • HONEYWELL

Rapid Radiochemical Methods

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Richland, WA

Approach

- Rapid Radiochemical Methods
  - Environmental and bioassay sample matrices
  - Emergency response and routine analyses
- How?
  - Combine innovative sample preparation methods with rapid column extraction techniques
  - Stacked cartridge technology
    - Sequential separation (5X faster than gravity flow)
    - Rapid flow rates
- Time is money

Gravity Flow vs. Vacuum

Needs

- Rapid methods
  - Rugged, easy to use
- Minimize costs
  - Rapid separations to minimize labor costs
- Meet customer TAT and MDA requirements
  - High chemical yields
  - Optimize sample aliquot sizes as needed
  - Minimal rework
- Eliminate interferences
  - Alpha spectrometry
  - Beta counting
    - Gas proportional counting
    - Liquid scintillation counting

Extraction Chromatography

- Large move toward extraction chromatography in literature in last 10-15 yrs from US to Europe to Japan
- Solvent extraction
  - Mixed waste, less efficient
  - 1995-SRS process lab switch to TEVA, UTEVA from TTA, TIOA -xylene and hexone
  - Maxwell III, S.L. , Rapid actinide-separation methods, Radioactivity and Radiochemisty, 1998, vol. 8, No 4, 36-44
- Ion exchange
  - Less selective
  - Larger resin beds/more acid volume
  - Anion Resin +low energy gamma (I-129)
  - SRS Bioassay lab-switch to TEVA and TRU Resin -1998
    - Higher chemical yields/better alpha peak resolution

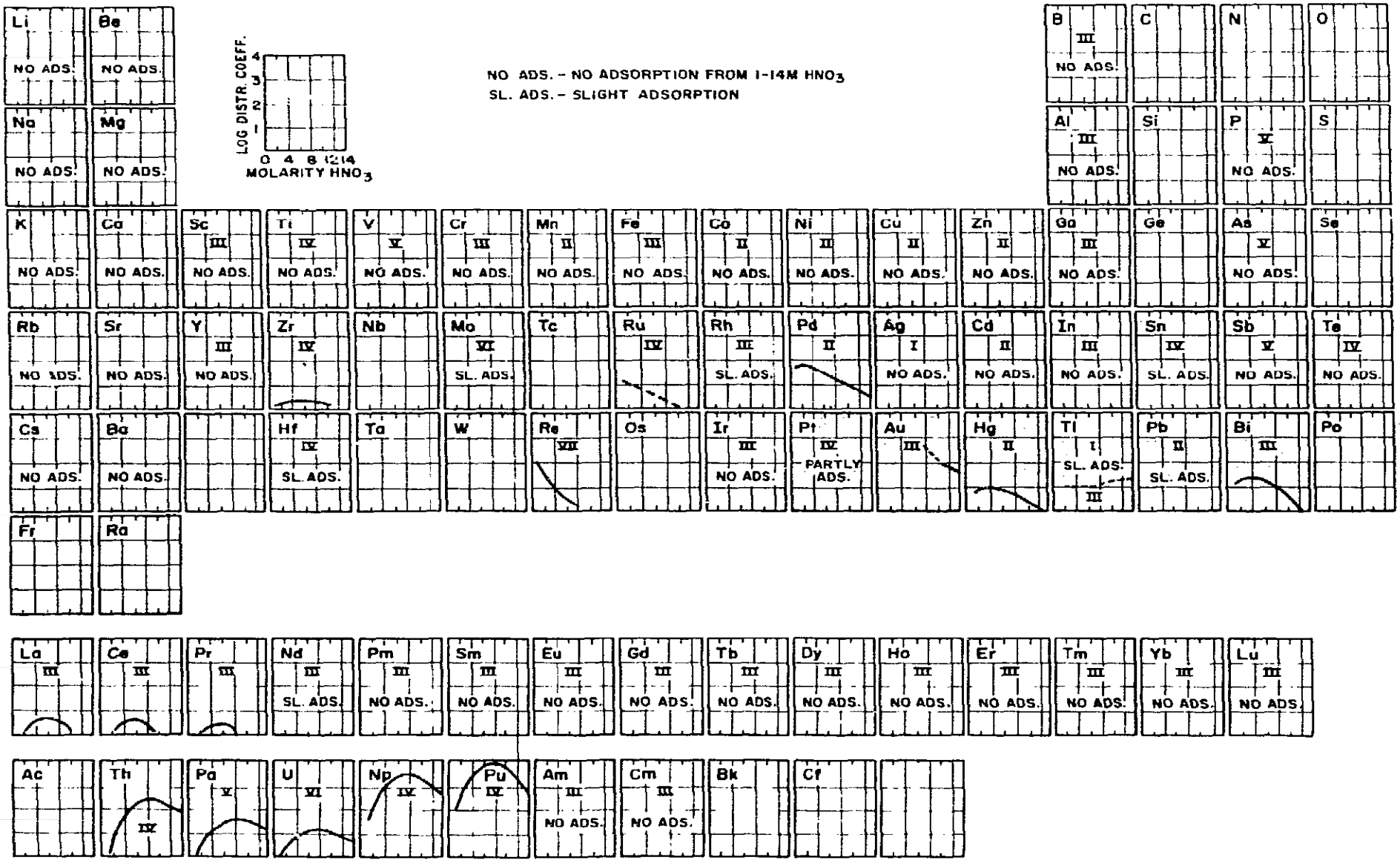


Fig. 1. Removal of Elements from Nitric Acid Solution with Strong-Base Anion Exchange Resin.

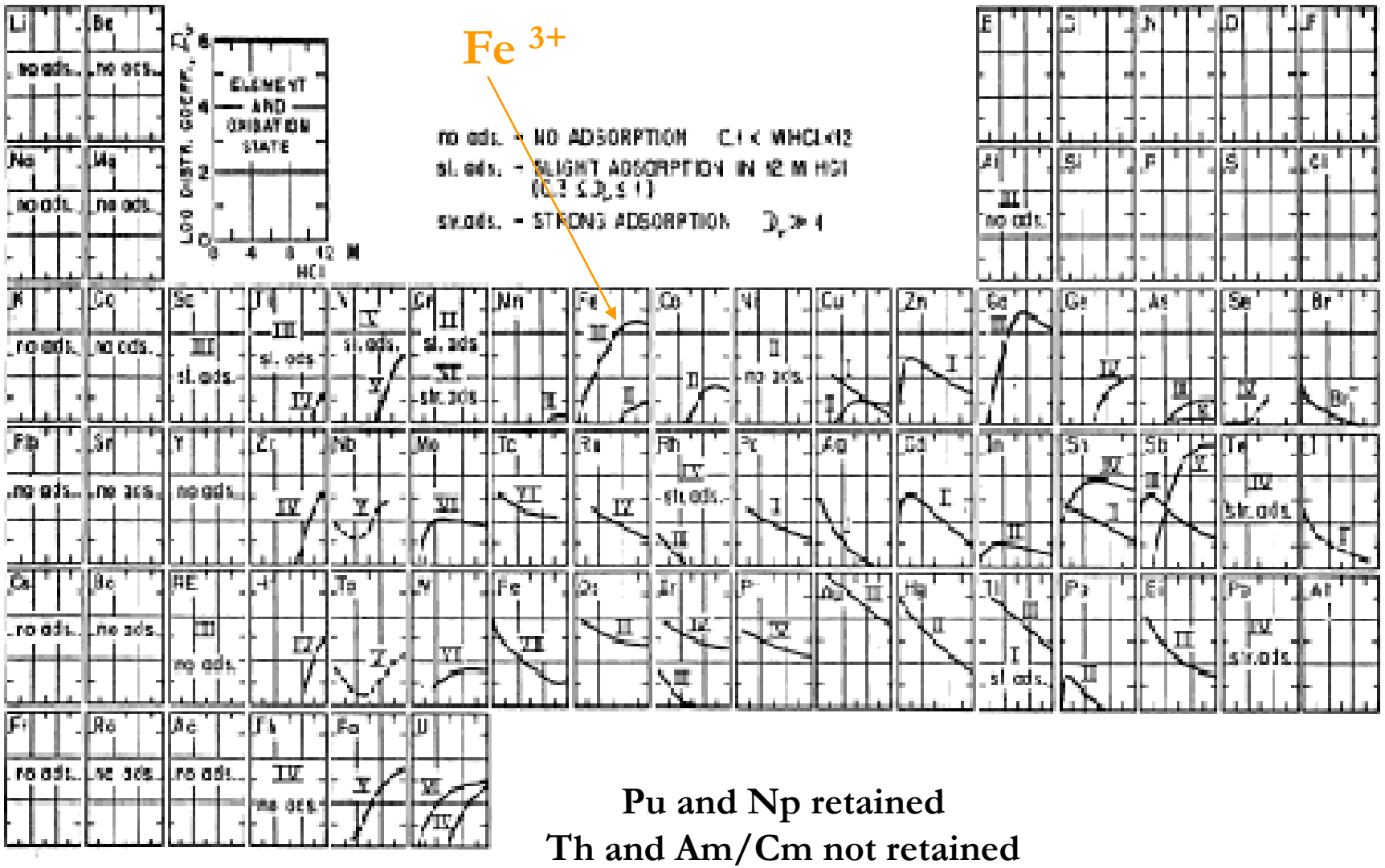
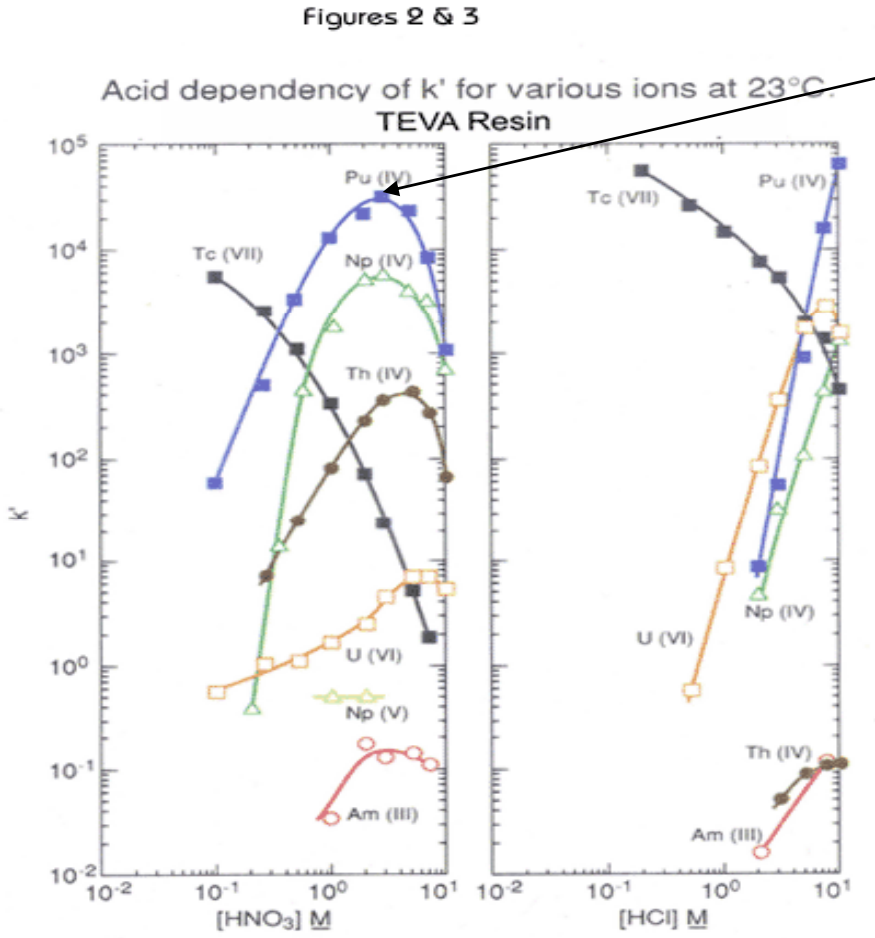


Fig. 6. Anion exchange distribution coefficients in HCl solutions. (Dowex 1-X10) (Ref. 3)

Why TEVA for Pu/Np?



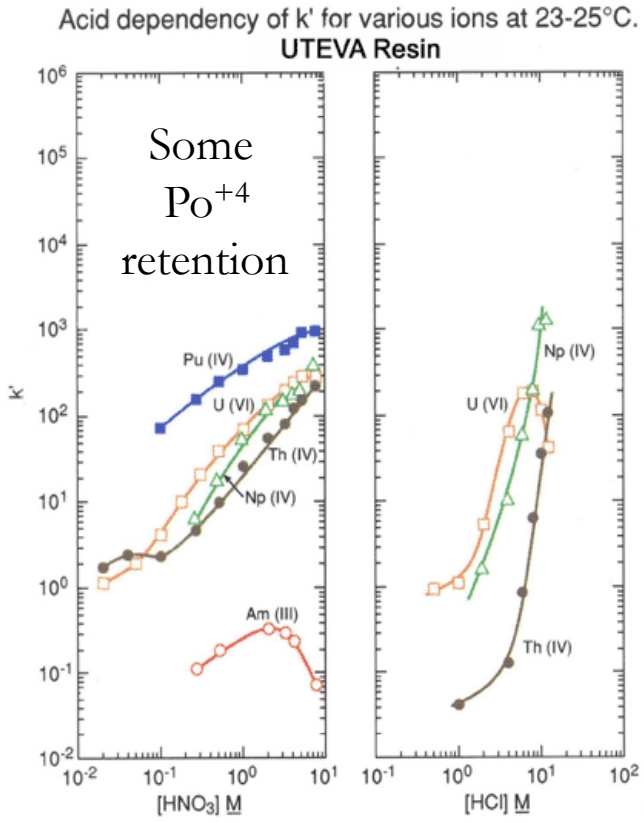
Horwitz, et al. (HP195)

High k' at 3M HNO_3

- Minimal U tailing
- Lower HNO_3
- Good alpha resolution
- Stack cartridges
- Vacuum flow rates
- 2 ml resin
- Acid volumes small

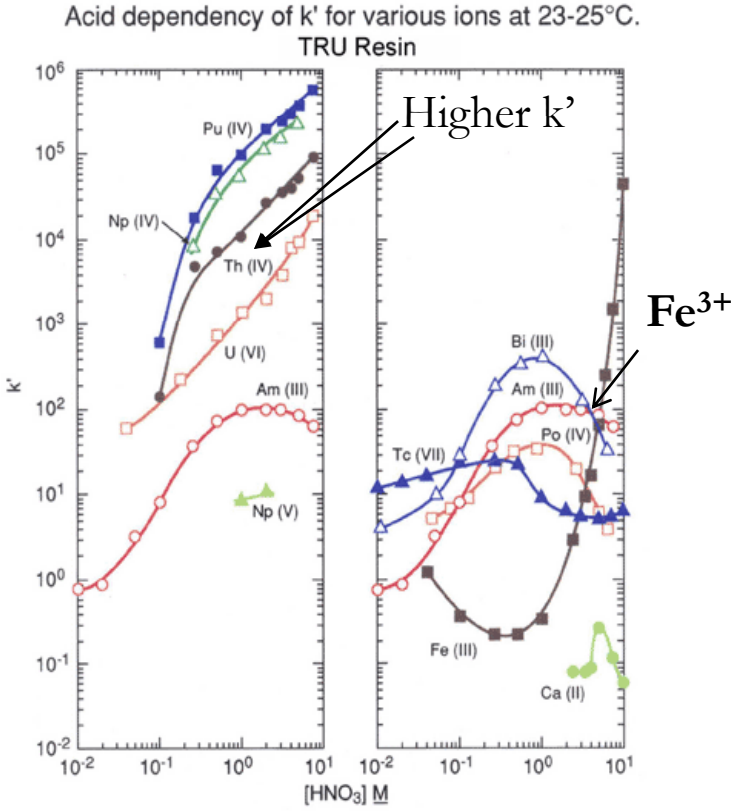
UTEVA vs. TRU

Figures 2 and 3



Horwitz, et al. (HP392)

Figure 2



Horwitz, et al. (HP193)

TRU vs DGA in HNO_3

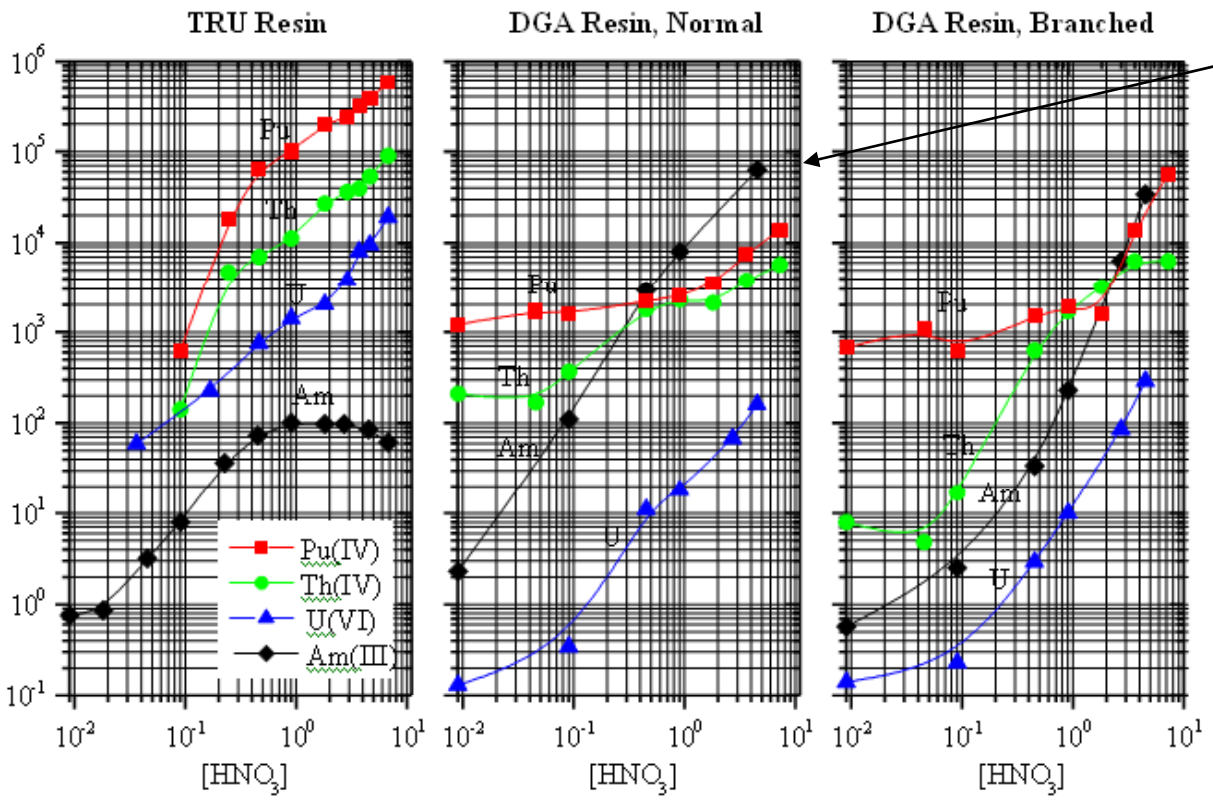


Figure 2

Am k' 30,000

- Great for difficult samples
- Minimal U retention
- Fe^{3+} does NOT interfere

TRU vs DGA in HCl

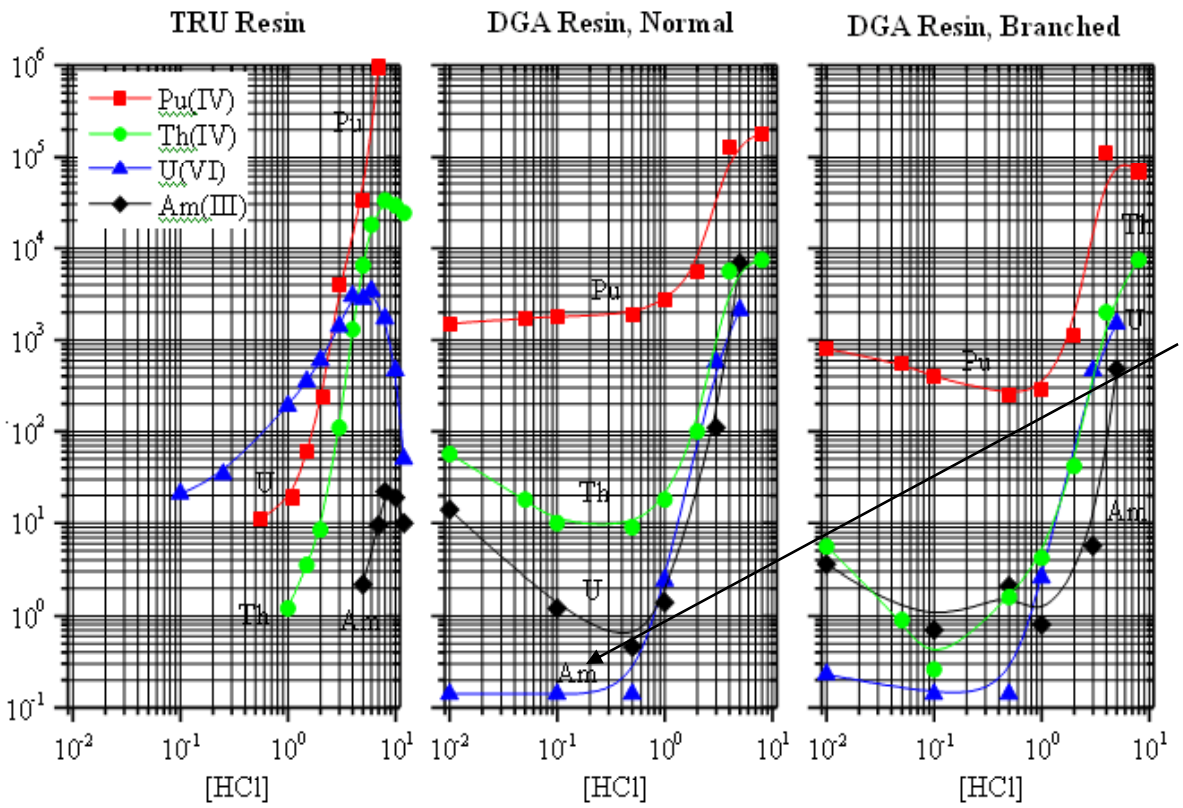


Figure 3

Why do we stack cartridges?

- Cut costs/save time
- Actinide separations on a single resin risk fraction contamination
  - TRU (Pu, Np, Am, U, Th)
  - UTEVA (U, Th, Np) +TRU (Pu, Am)
    - Pu-238 and Am-241; Np-237 and U-234
    - Th isotope interference
    - Po-210 removal
- Stacked cartridges
  - TEVA (Pu, Np) + TRU (Am, U) [+DGA]
  - Faster than collect load + rinses and reload to next resin

Publications

- **Milk**
  Maxwell, S. and Culligan, B., (2009), Rapid method for determination of radiostrontium in emergency milk samples, J. Radioanal. Nucl. Chem, Vol. 279, No.3, 757–760

- **Air Filters**
  Maxwell, S., Culligan, B. and Noyes, G. (2010), Rapid separation method for actinides in emergency air filter samples, Appl. Radiation and isotopes, in press

- **Vegetation**
  Maxwell, S., Culligan, B. and Noyes, G., Rapid Separation of Actinides and Radiostrontium in Vegetation Samples, J. Radioanal. Nucl. Chem, (2010), 286:273–282, DOI 10.1007/s10967-010-0653-y

- **Animal Tissue**
  Maxwell, S. and Culligan, B. (2008) Rapid column extraction method for actinides and strontium in fish and other animal tissue samples, J. Radioanal. Nucl. Chem, 275 (No.3), 605

Publications

- ## Urine and Water

Maxwell, S. and Culligan, B., (2009), Rapid separation method for emergency water and urine samples, J. Radioanal. Nucl. Chem, 279 (No.3), 901

Maxwell, S. L and Jones, V. D., (2009), Rapid determination of actinides in urine by inductively coupled plasma mass spectrometry and alpha spectrometry: A hybrid approach, Talanta, 80 (No.1), 143

Maxwell, S. (2006), Rapid method for 226Ra and 228Ra analysis in water samples J. Radioanal. Nucl. Chem, 270 (No.3), 651

Maxwell, S. and Culligan, B., (2009), New column separation method for emergency urine samples, J. Radioanal. Nucl. Chem, Vol. 279, No.1, 105

Maxwell, S. (2006), Rapid column extraction method for actinides and 89/90Sr in water samples, J. Radioanal. Nucl. Chem, 267 (No.3), 537

S. L. Maxwell, B.K. Culligan, V.D. Jones, S.T. Nichols, G.W. Noyes, (2010) Rapid determination of 237Np and Pu isotopes in water by inductively-coupled plasma mass spectrometry and alpha spectrometry, J Radioanal Nucl Chem, DOI 10.1007/s10967-010-0825-9

S. L. Maxwell, B.K. Culligan, V.D. Jones, S.T. Nichols, G.W. Noyes, M.Bernard (2010) Rapid determination of 237Np and Pu isotopes in urine by inductively-coupled plasma mass spectrometry and alpha spectrometry, Health Physics Journal, in press

Publications

- Soil

Maxwell, S. and Culligan, B. (2006), Rapid column extraction method for actinides in soil, J. Radioanal. Nucl. Chem, 270 (No.3), 699

Maxwell, S. (2008) Rapid method for determination of plutonium, americium and curium in large soil samples, J. Radioanal. Nucl. Chem, 275 (No.2), 395,– U.S. Patent 7,507,583

Maxwell, S., Culligan, B. and Noyes, G. (2010), Rapid method for actinides in emergency soil samples, Radiochmica Acta, in press

S. L. Maxwell, B.K. Culligan, V.D. Jones, S.T. Nichols, G.W. Noyes, M. Bernard (2010) Rapid determination of 237Np and Pu isotopes in large soil samples by inductively-coupled plasma mass spectrometry and alpha spectrometry, Analytica Acta, in press

Maxwell, S., Culligan, B. and Noyes, G. (2010), Rapid Separation Method for 237Np and Pu isotopes in Large Soil Samples, Applied radiation and isotopes, in press

Actinides and Sr-89/90 in Water

- TEVA/TRU/Sr Resin –stacked cartridges
  - One sample preparation
  - Vacuum box flow rates
- Calcium phosphate ppt. (also Sr)
  - Sample aliquot directly in centrifuge tube
  - No water rinse of ppt.
  - No heat*
    - larger samples need heat to aggregate precipitate
- What about alternate preconcentration methods?

Maxwell III, SL, “Rapid Column Separation for Actinides and Sr-89/90 in Water Samples”, Journal of Radioanalytical and Nuclear Chemistry, Vol. 267, No. 3, p 537”

Maxwell, S.L, "Rapid Analysis of Emergency Urine and Water Samples", J. Radioanal. Nucl.Chem., 275 (3), (2008)

Alternate Preconcentration: water,urine

- Evaporation
  - Time-consuming
- Iron hydroxide ppt.
  - Fe^{3+} interferes with TEVA+TRU when Fe in column load solution is oxidized to Fe^{3+} with Pu^{4+} on TEVA
  - Feasible with:
    - TEVA (Pu/Np)
    - TEVA+DGA (Pu/Am)
    - TEVA+UTEVA (Th/U)
    - TEVA+TRU (Th/U) with reduction to Fe^{2+}

Actinides and Sr-90 in Water

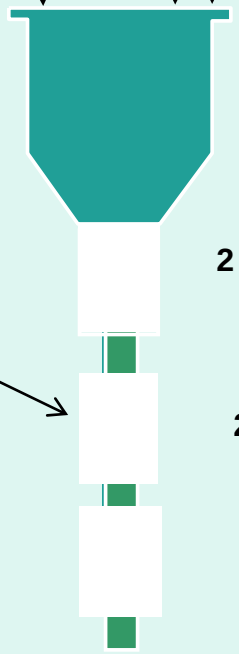
Calcium phosphate precipitation

1) Redissolve in 8 mL 6M HNO3 and 8 mL 2M Al(N03) 3
2) Add 0.5 mL 1.5M Sulfamic Acid + 1.25 mL 1.5M Ascorbic Acid
3) Add 1 mL 3.5 M Sodium Nitrite

Vacuum box procedure

Beaker rinse: 3mL 3MHN03
10 mL 3M HN03 to stacked cartridges

Separate cartridges:
TEVA Resin alone: 10 mL 3M HN03



Th Elution
20mL 9MHCl

Pu (and/or Np) Elution
20mL
0.10M HCl - 0.05M HF - 0.01M TiCl3

Add 0.5 mL 30 wt% H2O2

2 mL TEVA Resin
(50-100 um)

Cerium fluoride

Alpha spectrometry

Too much Fe^{3+} interferes
Not a problem for water

2 mL TRU-Resin
(50-100 um)

Cerium fluoride

Sr Resin alone:
15 mL 8MHN03
10 mL 0.05M strip Sr

2 mL Sr-Resin
(50-100 um)

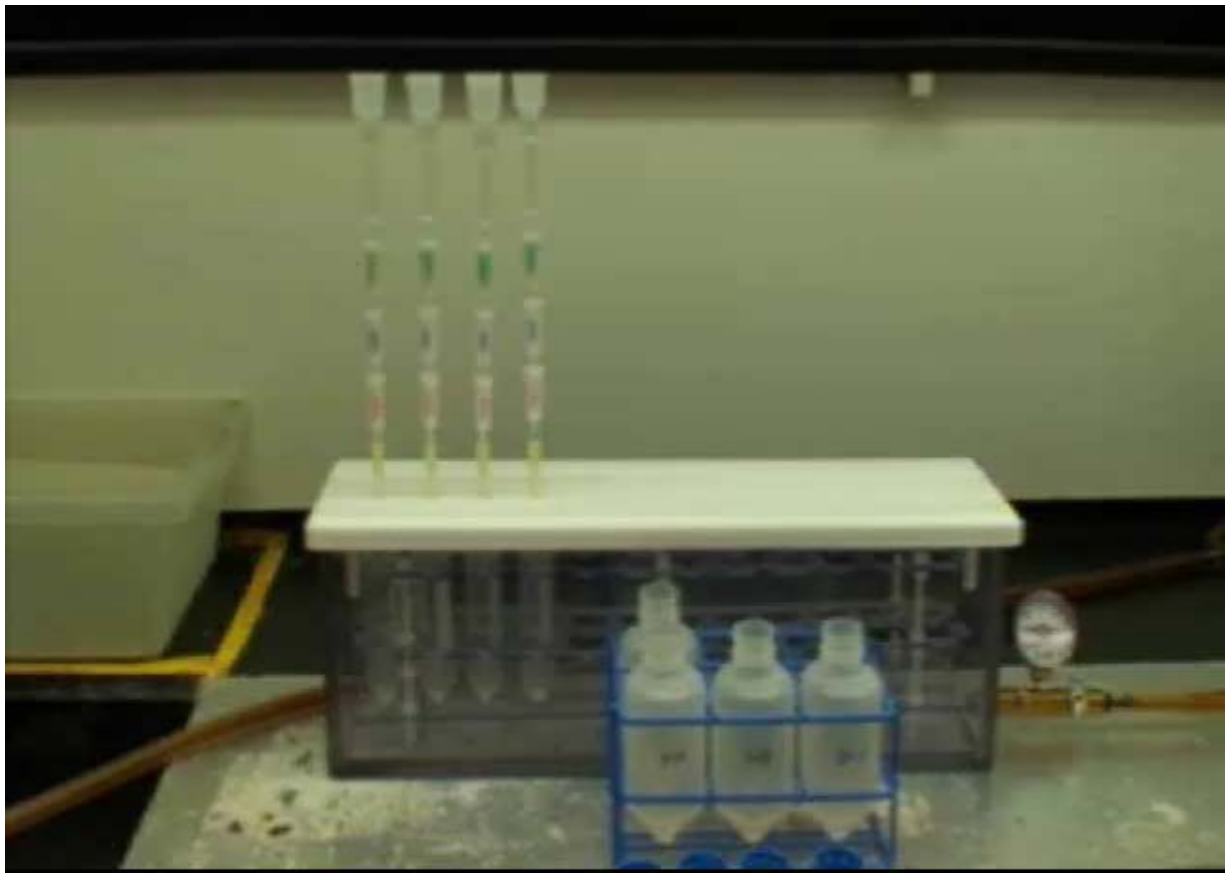
TRU Resin alone:
Elute Am/Cm with 15 ml 4M HCL/add
15 ml H20 + 50 ug Ce+ 3 ml HF
12 ml 4M HCl-0.2M *HF -0.002M TiCl3*
Elute U with 15 ml 0.1M NH4HC2O4

Evaporate/ beta counting

Enhanced Po-210 removal

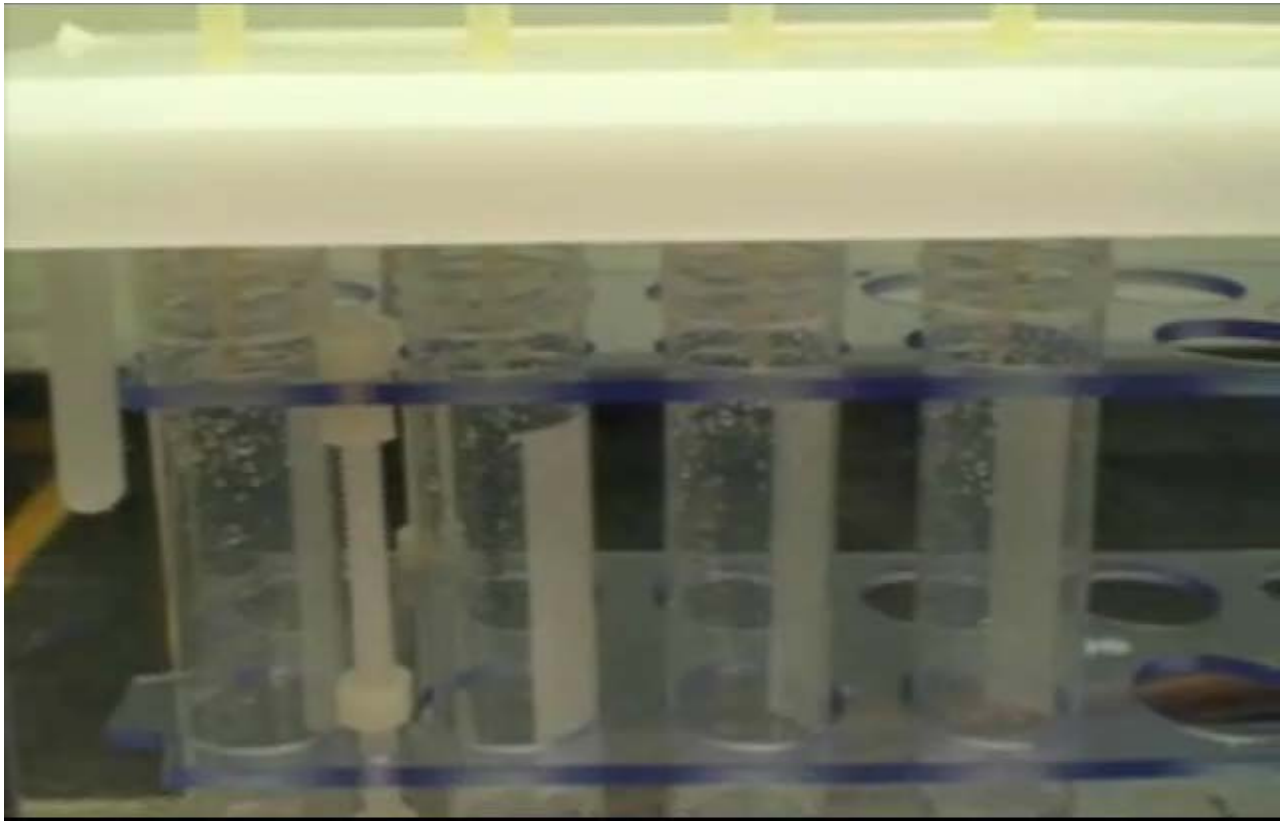
Routine Flow Rates

Load solution ~ 1 drop per second



Rinse Solution Flow Rates

~ 1-2 drops per second



SRNS

* Load flow rate emergency response

Approach

- Pu/Np in water/urine
  - Calcium phosphate or direct urine aliquot
  - TEVA
  - TEVA then Pu on DGA
- Main session
  - ICP-MS and alpha spectrometry
  - Enhanced ^{238}U removal

S. L. Maxwell, B.K. Culligan, V.D. Jones, S.T. Nichols, G.W. Noyes, (2010) Rapid determination of 237Np and Pu isotopes in water by inductively-coupled plasma mass spectrometry and alpha spectrometry, J Radioanal Nucl Chem, DOI 10.1007/s10967-010-0825-9

S. L. Maxwell, B.K. Culligan, V.D. Jones, S.T. Nichols, G.W. Noyes, M.Bernard (2010) Rapid determination of 237Np and Pu isotopes in urine by inductively-coupled plasma mass spectrometry and alpha spectrometry, Health Physics Journal, in press

Rapid urine method: Dose mitigation

- Puncture wound
  - Sample received 6/16/10
  - Results in 6 hrs
  - 8 results in first 10 days following incident
  - Mitigate dose/guide medical treatment

- TEVA
  - Calcium phosphate option (prior to chelation)
  - Evaporation/wet-ashing to destroy DTPA chelation agent

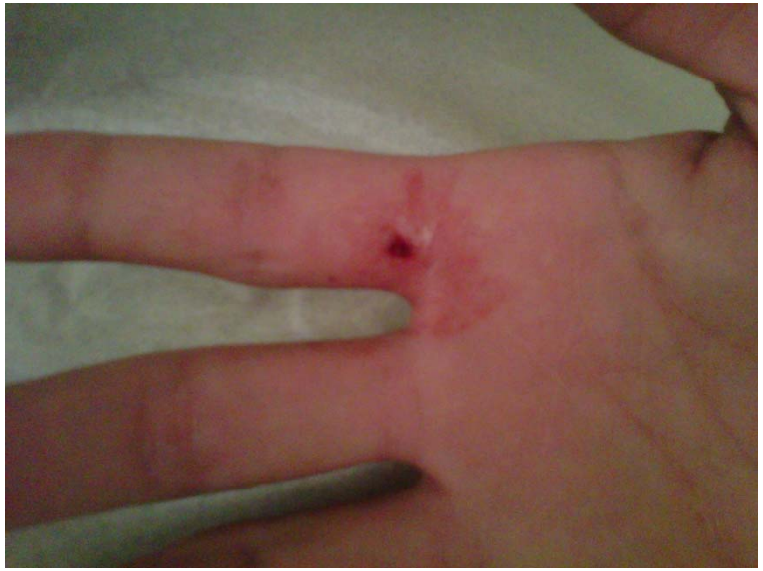
Puncture Wound Incident Lab Support

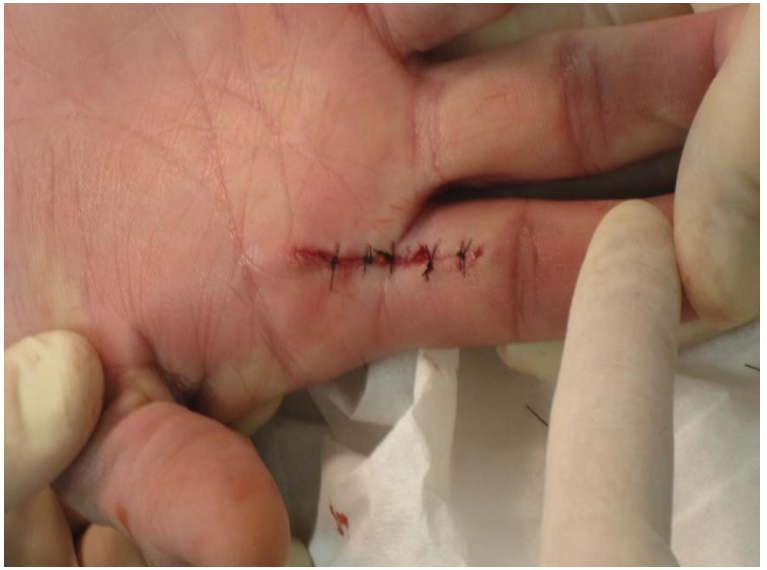
- Sample receipt puncture wound — 6/16/10
- NRIP emergency method [1] results (EM lab) — 6 hrs.
- Rapid Bio Lab results (initial) — 4 days
- Rapid Bio Lab [2] results (final) — 7 days

[1] NRIP method provided HPT 8 data points in first 10 days into event to support dose mitigation (tissue excision and chelation therapy)

[2] DOELAP accredited method official results 7 days earlier than 14 day TAT requirement for Incident samples
Method: Wet-ashing with HNO_3 and H_2O_2 to destroy chelation agent + TEVA Resin (vacuum box)

Post Core Punch Tissue Excision





Initial core punch 13,976 dpm ^{238}Pu

(3.5 hrs post injury)

Effect of Chelation Agent

Aliquot ml	Sample Prep	^{242}Pu Tracer Yield %	^{238}Pu (pCi/ml)	Uncert (pCi/ml)
25	evap/wet-ash	103.5	123	20
25	evap/wet-ash	99.8	126	20
25	calcium phosphate/wet-ash ppt.	55.7	84	16
25	calcium phosphate/wet-ash ppt.	49.7	84	16
25	calcium phosphate/ no wet-ash ppt.	21.9	86	22
25	calcium phosphate/ no wet-ash ppt.	27.0	102	22

Approach

- Actinides (Pu,Np, Am, Cm, U)
  - Soil (0.5-2g)
    - Rapid sodium hydroxide fusion (10 minutes)
      - eliminates refractory particles
      - more rugged; may be faster than acid attack
    - Iron/titanium hydroxide ppt. preconcentration
    - Lanthanum fluoride ppt. matrix removal
      - La removed on DGA
      - Reduces Fe levels
    - TEVA Resin (Pu, Np) +TRU Resin (U) + DGA (Am, Cm) Resin
      - Pu, Np only-TEVA
      - If U not needed, TEVA (Pu, Np)+DGA (Am, Cm) only
    - Alpha spectrometry
  - Adapted to 50 ml tubes

The Magic of DGA

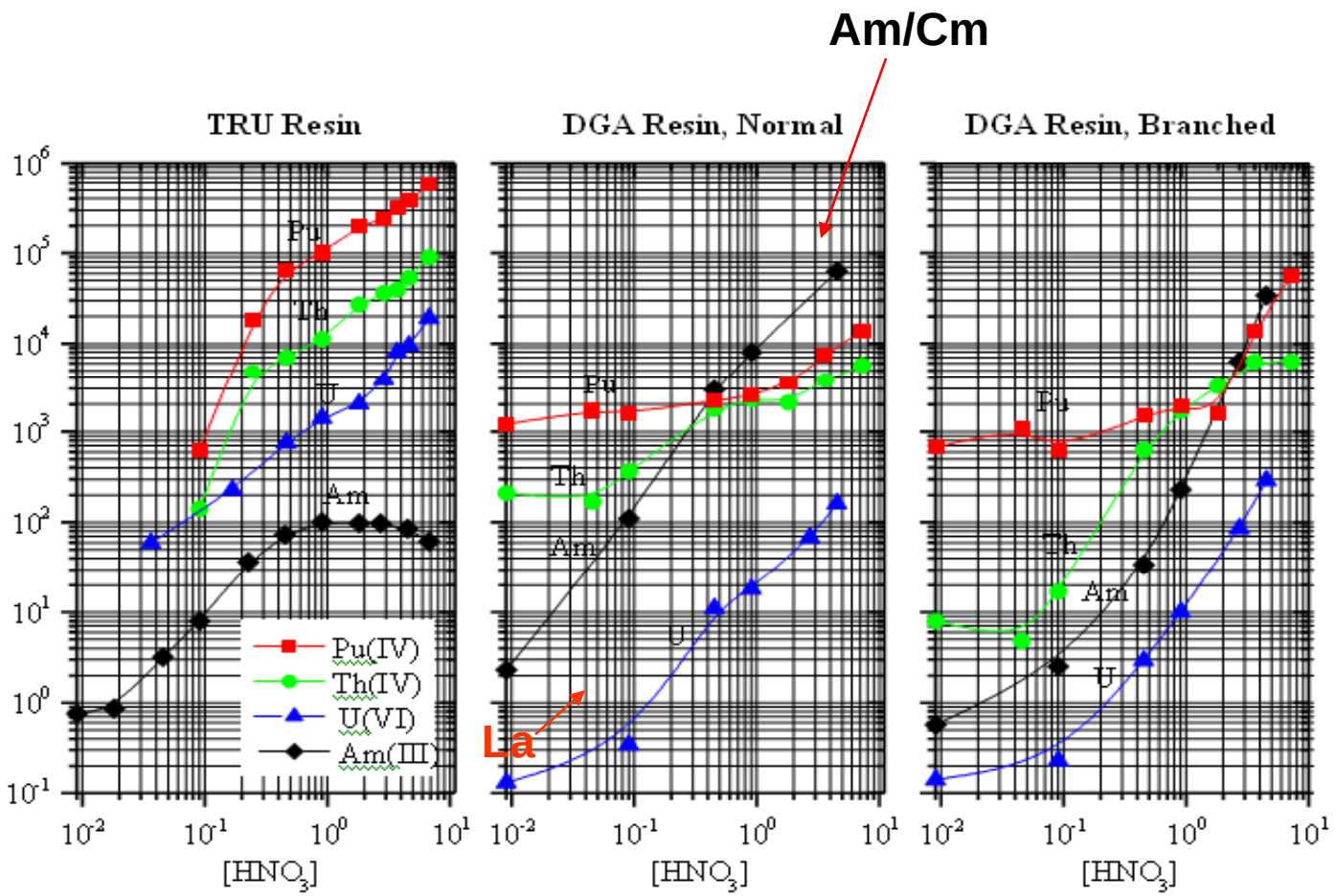
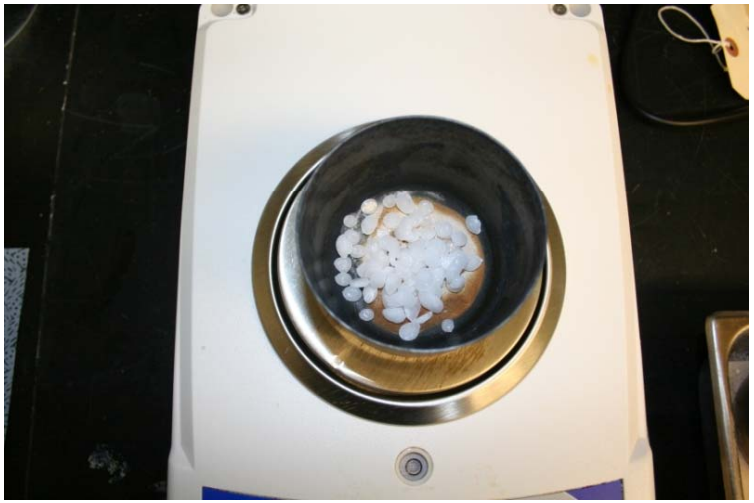
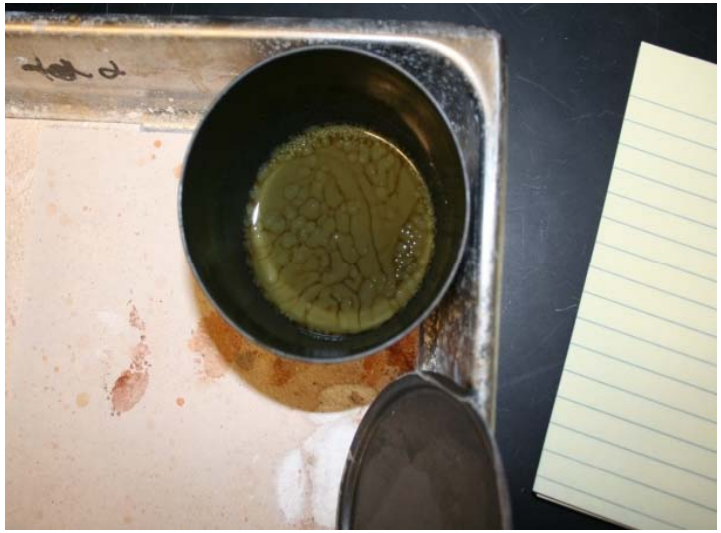


Figure 2

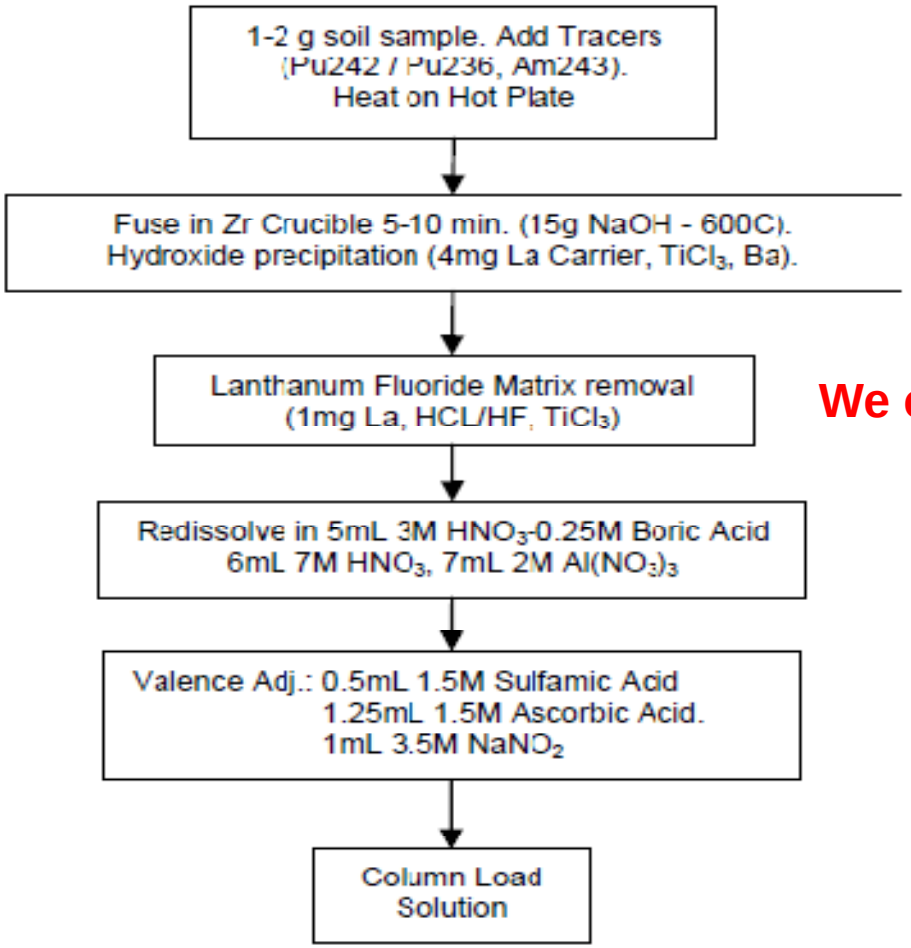
Source: http://www.eichrom.com/products/info/dga_resin.cfm

Rapid Fusion



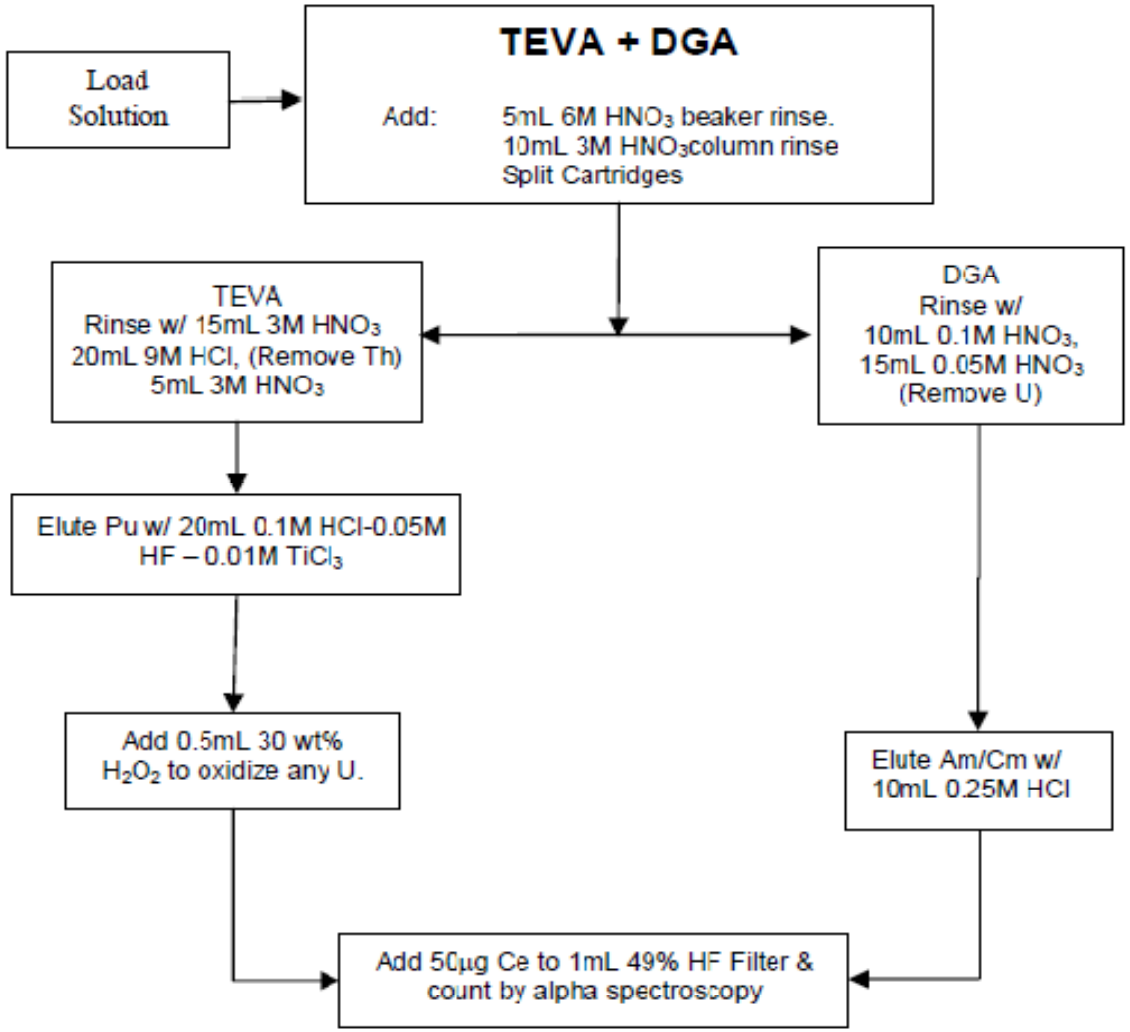


Rapid Pu/Am in soil



We can adapt to 50 ml tubes

Rapid Pu/Am in soil (TEVA+DGA)



Rapid Fusion TEVA+DGA (50 ml tubes)

Sample ID	^{242}Pu Yield (%)	^{239}Pu Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	91.9	82.6	85.6	3.6	MAPEP 18
2	89.5	82.6	87.6	6.0	MAPEP 18
3	86.7	82.6	89.9	8.8	MAPEP 18
4	92.2	82.6	83.5	1.1	MAPEP 18
5	87.6	82.6	94.5	14.4	MAPEP 18
6	95.8	82.6	84.9	2.8	MAPEP 18
Avg	90.6			6.1	
% RSD	3.7				

Rapid Fusion TEVA+DGA (50 ml tubes)

Sample ID	^{242}Pu Yield (%)	^{238}Pu Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	91.9	72.8	72.4	-0.6	MAPEP 18
2	89.5	72.8	77.1	5.9	MAPEP 18
3	86.7	72.8	69.6	-4.5	MAPEP 18
4	92.2	72.8	68.6	-5.8	MAPEP 18
5	87.6	72.8	77.7	6.7	MAPEP 18
6	95.8	72.8	72.4	-0.6	MAPEP 18
Avg	90.6			0.2	
% RSD	3.7				

Rapid Fusion TEVA+DGA (50 ml tubes)

Sample ID	^{243}Am Yield (%)	^{241}Am Reference Value (Bq Smp^{-1})	Measured Value (Bq Smp^{-1})	Difference (%)	Reference
1	85.7	127.2	131.7	3.6	MAPEP 18
2	84.6	127.2	135.1	6.2	MAPEP 18
3	89.0	127.2	134.7	5.9	MAPEP 18
4	96.9	127.2	142.5	12.0	MAPEP 18
5	94.4	127.2	135.3	6.3	MAPEP 18
6	91.8	127.2	141.7	11.4	MAPEP 18
Avg	90.4			7.6	
% RSD	5.4				

Approach

- Pu, Np in Soil (10g-100g)
  - Large soil aliquot needed to reach low MDA
  - Need effective soil matrix removal
  - Chemical yields can be a problem
- Main session
  - ICP-MS and alpha spectrometry

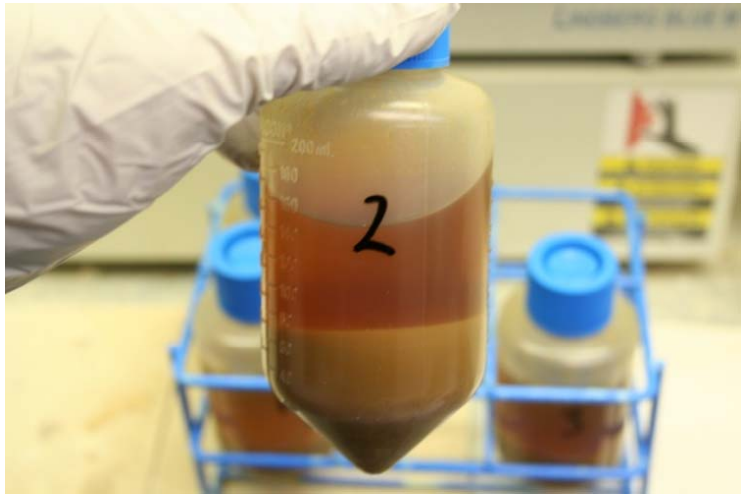
S. L. Maxwell, B. K. Culligan, and G. W. Noyes, Rapid Separation Method for 237Np and Pu isotopes in Large Soil Samples, Applied Radiation and Isotopes, 2010, in press

S. L. Maxwell, B. K. Culligan, V.D. Jones, S. T. Nichols, M. A. Bernard, G. W. Noyes, Determination of 237Np and Pu isotopes in Large Soil Samples by Inductively-Coupled Plasma Mass Spectrometry, Analytica Chimica Acta, 2010 in press

Am in Large Soil

- 100-250g
  - Leach, Fe/Ti OH, LaF3
  - TRU+DGA
  - TEVA-SCN

250g soil samples



LaF_3 ppt

^{241}Am Results on 100g Samples

Sample ID	^{243}Am Yield (%)	^{241}Am Reference Value (mBq smp^{-1})	Measured Value (mBq smp^{-1})	Difference (%)	Reference
1	81.4	89.8	90.7	0.9	MAPEP 21
2	92.8	89.8	77.0	-14.3	MAPEP 21
3	104.4	89.8	77.3	-13.9	MAPEP 21
4	97.5	89.8	82.5	-8.1	MAPEP 21
5	89.2	89.8	82.1	-8.5	MAPEP 21
6	87.1	89.8	90.3	0.5	MAPEP 21
Avg	92.1			-7.2	
% RSD	8.8				

^{244}Cm Results on 100g Samples

Sample ID	^{243}Am Yield (%)	^{244}Cm Reference Value (mBq smp^{-1})	Measured Value (mBq smp^{-1})	Difference (%)	Reference
1	81.4	36.1	45.1	24.9	MAPEP 21
2	92.8	36.1	37.0	2.4	MAPEP 21
3	104.4	36.1	34.3	-4.9	MAPEP 21
4	97.5	36.1	39.4	9.2	MAPEP 21
5	89.2	36.1	32.8	-9.1	MAPEP 21
6	87.1	36.1	40.7	12.7	MAPEP 21
Avg	92.1			5.9	
% RSD	8.8				

Summary

- Rapid radiochemical methods
  - Needed for emergency response
    - RDD, nuclear accident or occupational uptake
  - Needed for routine analyses to cut costs
- Stacked cartridges saves us time and money
- Actinides
  - TEVA+TRU (water, urine, air filters: Pu, Np, Am, Cm, U)
  - TEVA+TRU+DGA (soil, animal tissue, vegetation: Pu, Np, Am, Cm, U)
  - Add Sr Resin for Sr-89/90
- Other options
  - Pu, Np TEVA (extra U removal from Pu-DGA for ICP-MS)
  - Pu, Am TEVA+ DGA
  - Th/U TEVA+ UTEVA or TEVA+TRU