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Rapid Fusion Method for Plutonium in Large Rice Samples

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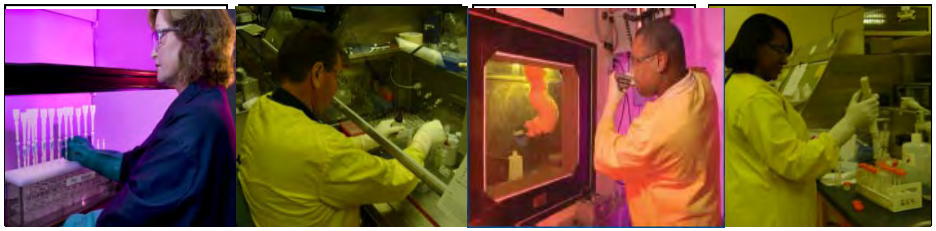
October 31, 2012



Background

- If a radiological dispersive device (RDD), Improvised Nuclear Device (IND) or nuclear accident (Fukushima Daiichi) occurs…
  - there will be a urgent need for rapid analyses of environmental, food and bioassay matrices
- Developed rapid methods for actinides in food (up to 100g)
  - Submitted as US FDA Food Emergency Response Network (FERN) method
    - Maxwell, S., Culligan, B. and Kelsey-Wall, A., G., Rapid determination of actinides in emergency food samples, J. Radioanal. Nucl. Chem, (2012), 292:339–347
- Large aliquots may be needed to assess low level activities/isotope ratios
- *Could we analyze much larger aliquots of rice for Pu isotopes?*

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Rice Sample Furnace Heating

Place 1-1.25 kg Rice Sample in 2L Beaker

↓

Add ^{242}Pu Tracer

↓

Place in furnace and ramp to 350°C for 300 min

↓

Ramp to 525°C and heat for 1000min

↓

Wet ash residue in 2L Beaker

↓

Wet ash residue with 15.8M HNO_3 and 30wt% H_2O_2 on hot plate → Repeat furnace ashing until residue is small

↓

Transfer wet ashed residue (after evaporation to small volume) into 250mL Zr Crucible with 15.8M HNO_3

↓

250mL Zr Crucible Evaporate to dryness on hot plate

↓

Place Zr crucible in furnace at ~450°C and increase heat (if necessary) until solids are white/light colored then wet ash with 15.8M HNO_3 and 30wt% H_2O_2 until purple/light color, heating again in furnace as needed

↓

Rapid Sodium Hydroxide Fusion

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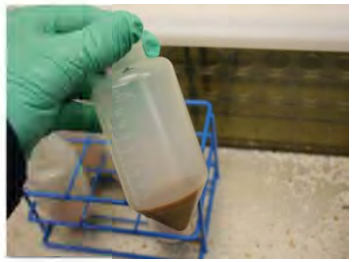
Rapid Rice Sample Fusion

Fuse combined sample and residue in Zr crucible ~15min with 15g NaOH @600°C

Hydroxide precipitation using 10mg La carrier, Fe, Ca, $TiCl_3$

Redissolve in ~100mL 1.5M HCl into 225mL tube



Lanthanum Fluoride Matrix removal. Adjust volume to 170mL with 0.01M HCl, $TiCl_3$ and HF; centrifuge

Redissolve in 5mL 3M HNO_3-0.25M Boric Acid, 6mL 7M HNO_3, 7mL 2M $Al(NO_3)_2$

*Ascorbic acid converts Fe^{3+} to Fe^{2+}

Valence adjust:
0.5mL 1.5M Sulfamic Acid
2mg *Fe (as iron nitrate)
1.25mL 1.5M Ascorbic Acid
1mL 3.5M $NaNO_2$

Column Load

Solution

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Anion Resin such as Dowex 1- HNO_3

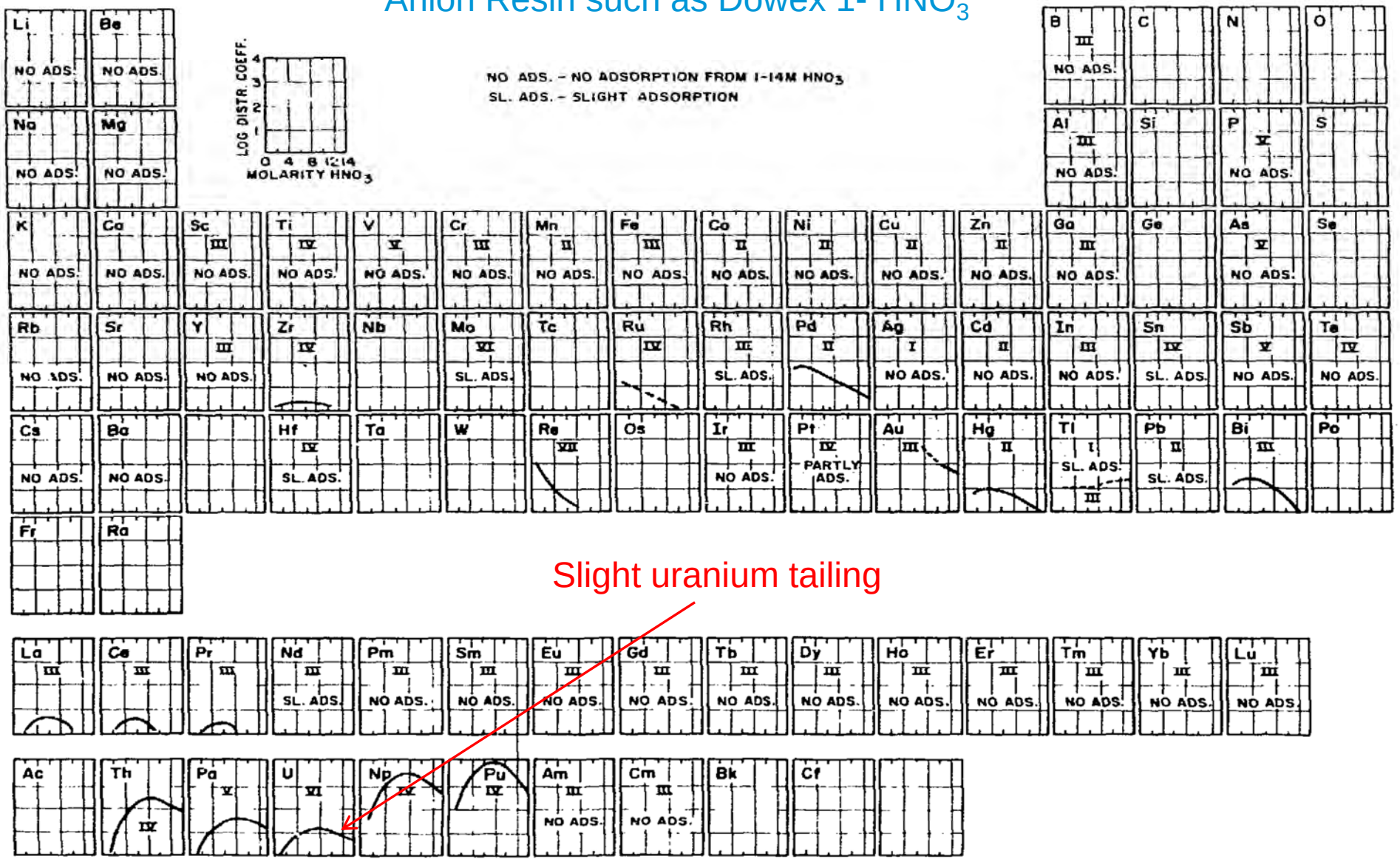


Fig. 1. Removal of Elements from Nitric Acid Solution with Strong-Base Anion Exchange Resin.

Anion Resin such as Dowex 1- HCl

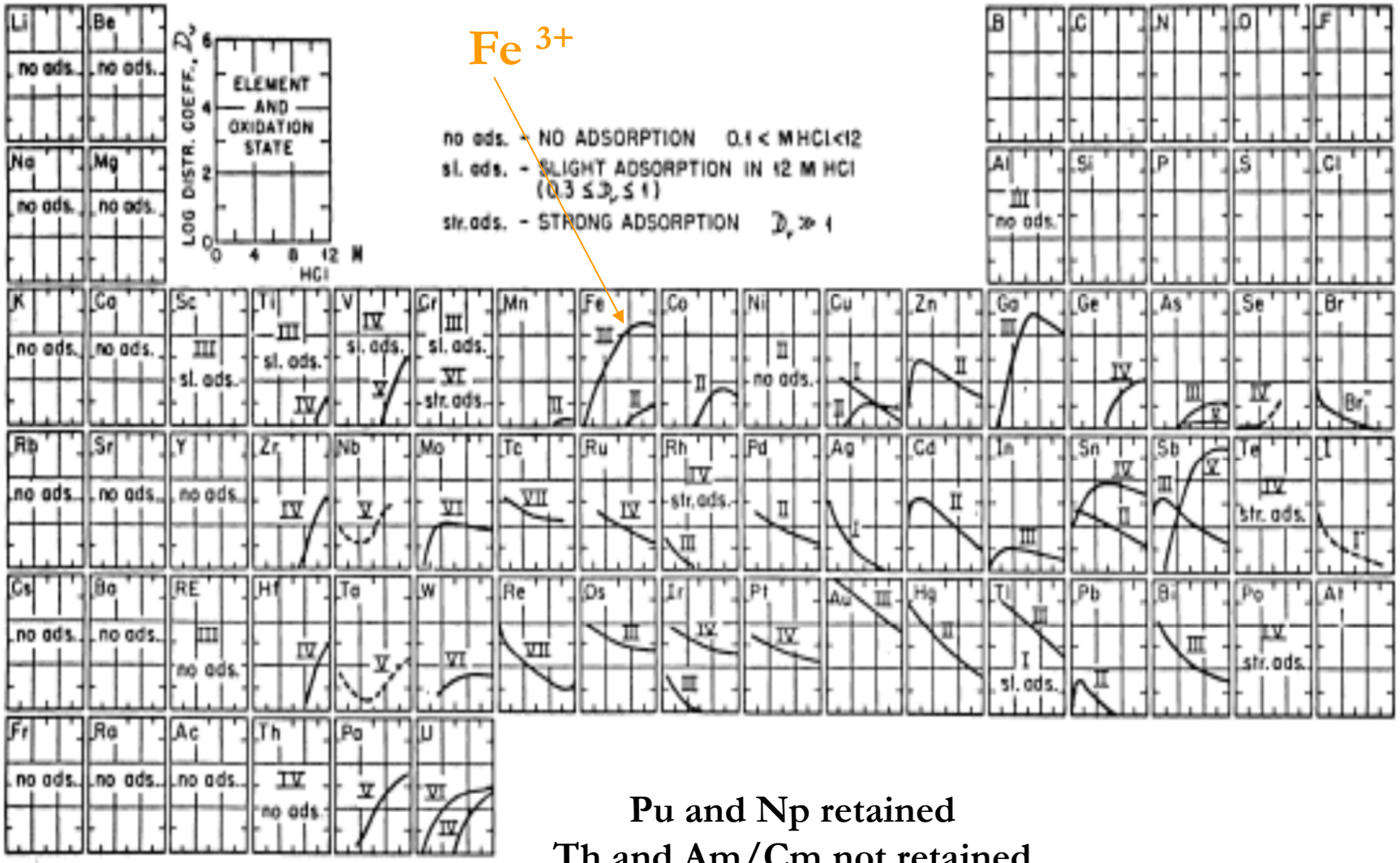
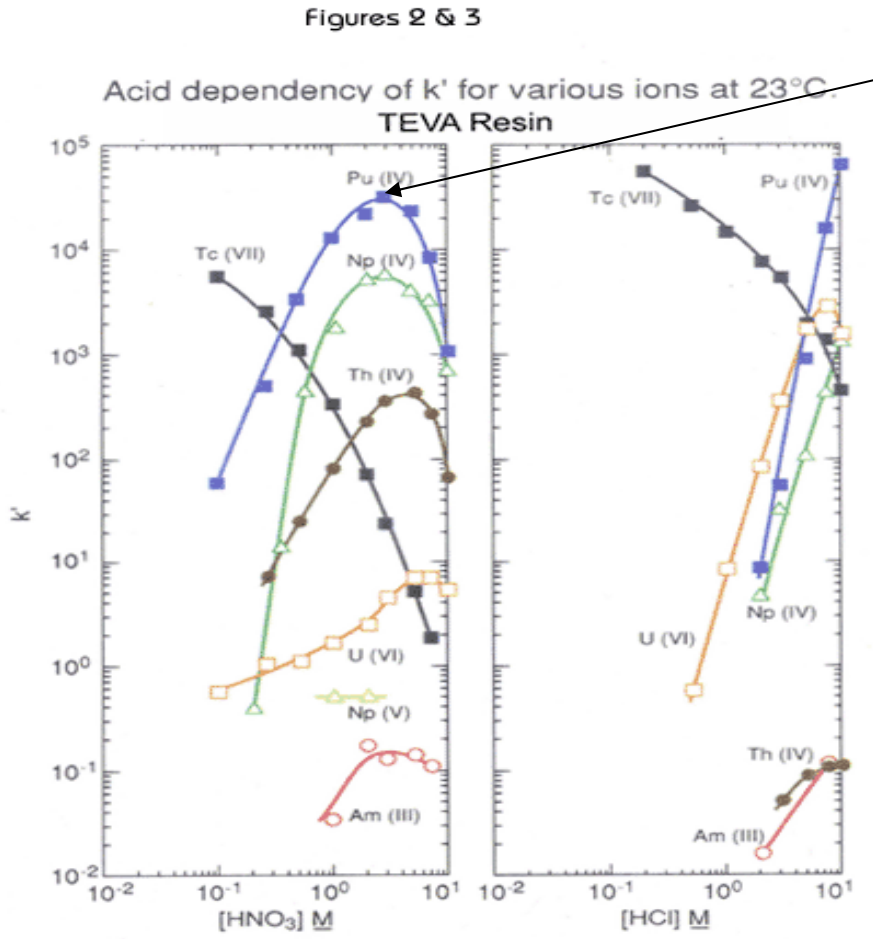


Fig. 6. Anion exchange distribution coefficients in HCl solutions.(Dowex 1-X10) (Ref. 3)

Why TEVA Resin for Pu/Np?



Horwitz, et al. (HP195)

High k' at 3M HNO_3

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

Aliquat 336 extractant

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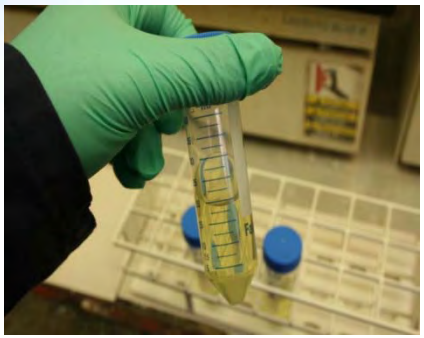
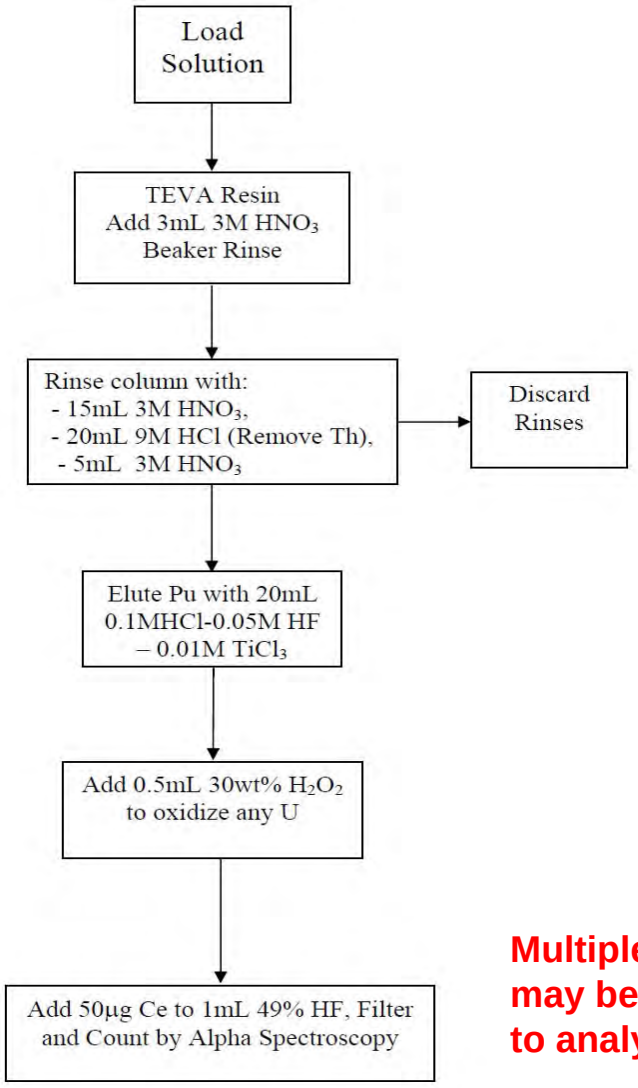
Rapid Pu Column Separation





2mL TEVA cartridge

Rongalite reductant can be used instead of $TiCl_3$ for electrodeposition

Less HF (0.01M) and $TiCl_3$ (0.0001M) if ICP-MS assay

Multiple 1 kg purified sample solutions may be combined as CeF_3 or evaporated to analyze 5 kg samples

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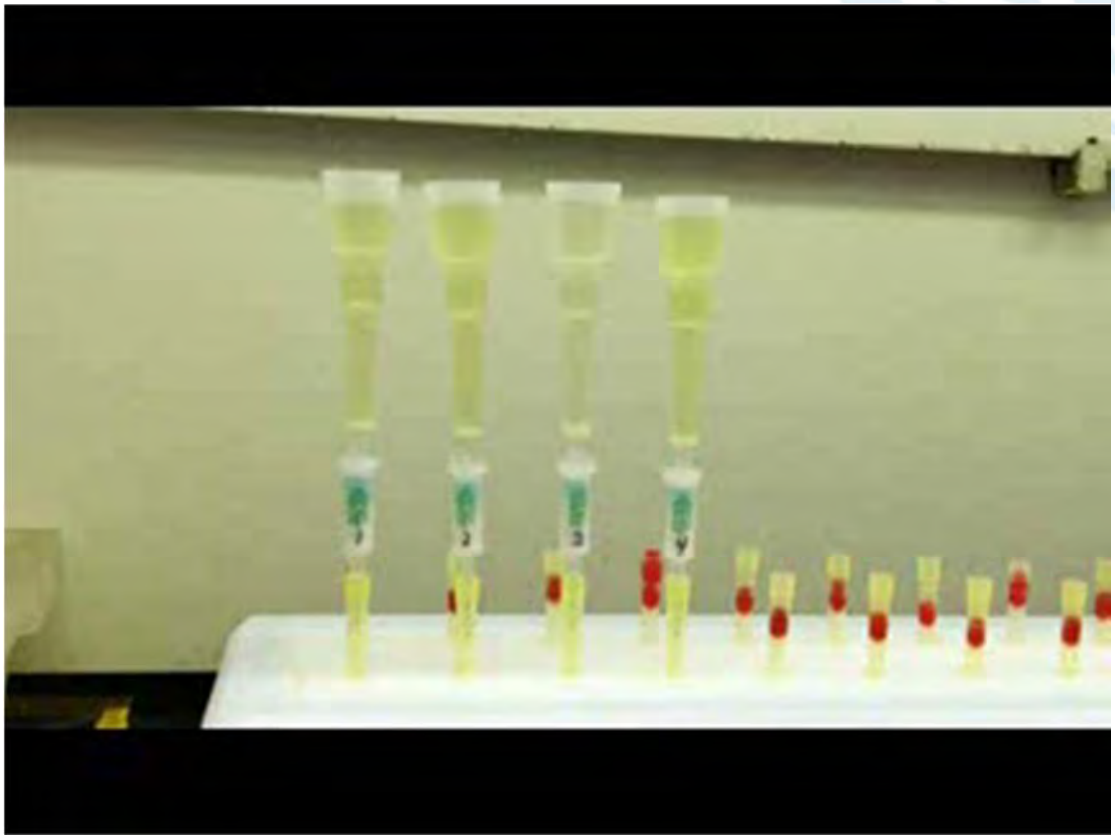
TEVA Separation – Flow rates



Load solution : ~1 drop/second

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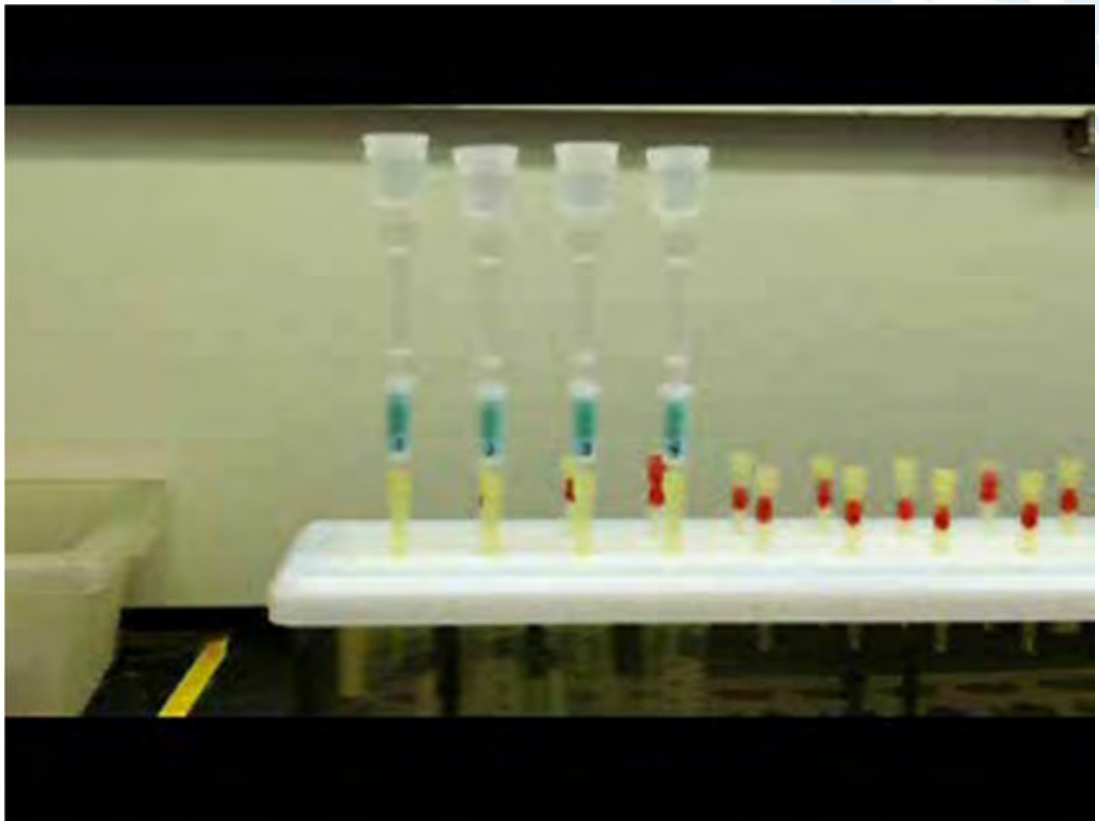
TEVA Separation – Flow rates



Rinse solution : ~2-3 drops/second

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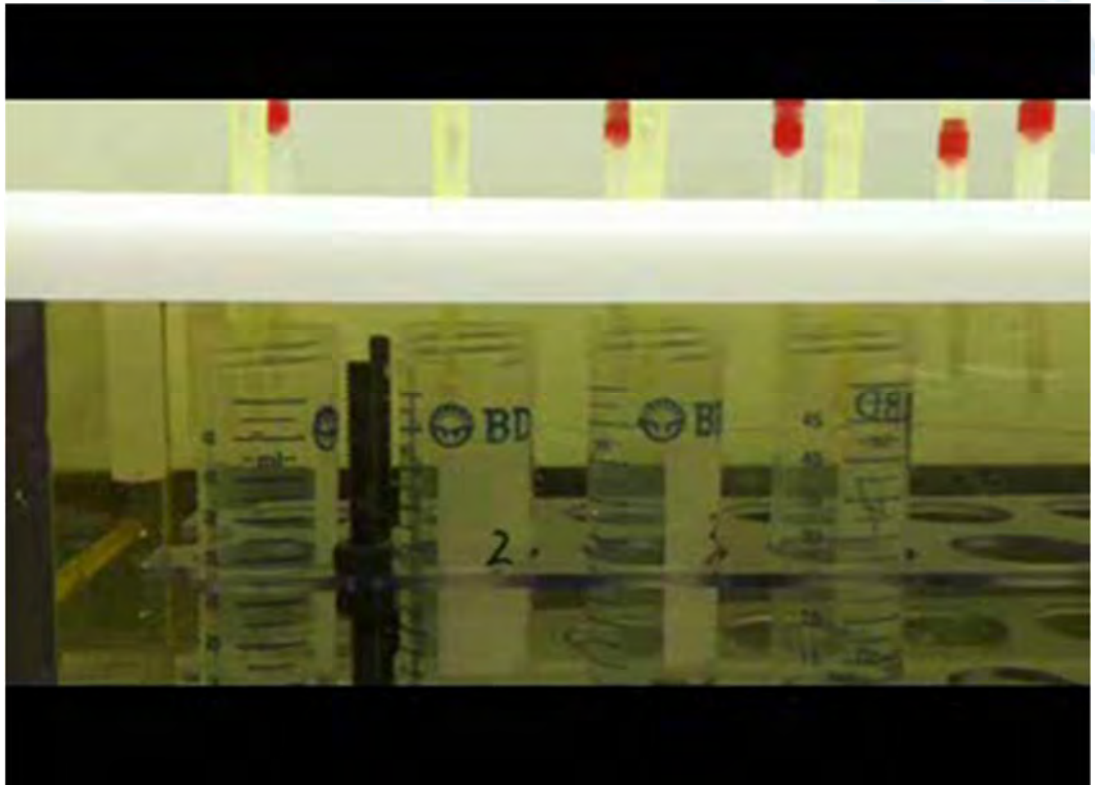
TEVA Separation – Flow rates



Pu Elution : 1 drop/second

Spiked ^{238}Pu in Rice Results - 1 kg samples

Sample ID	^{242}Pu Yield (%)	^{238}Pu Reference Value ($pCi\ kg^{-1}$)	^{238}Pu Reference Value ($mBq\ kg^{-1}$)	Measured Value ($mBq\ kg^{-1}$)	Difference (%)	MDA ($mBq\ g^{-1}$)	Reference
1	88.9	0.287	10.6	11.8	11.0	3.7 E-4	MAPEP 12
2	91.5	0.287	10.6	10.1	-4.3	3.7 E-4	MAPEP 12
3	92.8	0.287	10.6	10.0	-5.2	3.7 E-4	MAPEP 12
4	81.0	0.287	10.6	10.3	-3.1	3.7 E-4	MAPEP 12
5	83.8	0.287	10.6	10.2	-4.0	3.7 E-4	MAPEP 12
6	85.1	0.287	10.6	11.1	5.0	3.7 E-4	MAPEP 12
7	87.1	0.287	10.6	9.9	-7.0	3.7 E-4	MAPEP 12
8	83.7	0.287	10.6	10.8	2.0	3.7 E-4	MAPEP 12
Avg	86.8				-0.7		
% RSD	4.7						

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Spiked ^{239}Pu in Rice Results - 1 kg samples

Sample ID	^{242}Pu Yield (%)	^{239}Pu Reference Value ($pCi\ kg^{-1}$)	^{239}Pu Reference Value ($mBq\ kg^{-1}$)	Measured Value ($mBq\ kg^{-1}$)	Difference (%)	MDA ($mBq\ g^{-1}$)	Reference
1	88.9	0.338	12.5	10.7	-14.4	3.7 E-4	MAPEP 12
2	91.5	0.338	12.5	12.6	0.8	3.7 E-4	MAPEP 12
3	92.8	0.338	12.5	12.4	-0.8	3.7 E-4	MAPEP 12
4	81.0	0.338	12.5	12.2	-2.4	3.7 E-4	MAPEP 12
5	83.8	0.338	12.5	12.8	2.4	3.7 E-4	MAPEP 12
6	85.1	0.338	12.5	12.0	-4.0	3.7 E-4	MAPEP 12
7	87.1	0.338	12.5	11.7	-6.4	3.7 E-4	MAPEP 12
8	83.7	0.338	12.5	10.0	-20.1	3.7 E-4	MAPEP 12
Avg	86.8				-5.6		
% RSD	4.7						

Pu-239 is refractory in MAPEP 12

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Spiked ^{239}Pu in Rice Results - 5 kg samples

Sample	^{242}Pu Yield	^{239}Pu Reference Value	^{239}Pu Reference Value	Measured Value	Difference	MDA	
ID	(%)	(pCi kg^{-1})	(mBq g^{-1})	(mBq g^{-1})	(%)	(mBq g^{-1})	Reference
1	72.6	0.1130	0.00418	0.00396	-5.3	7.40E-05	MAPEP 12
2	70.6	0.0904	0.00334	0.00353	5.6	7.40E-05	MAPEP 12
3	76.9	0.0904	0.00334	0.00366	9.6	7.40E-05	MAPEP 12
Avg	73.4				3.3		
% RSD	4.4						

#1 – 5 x 1.0 kg samples combined
#2– 4 x 1.25 kg samples combined
#3– 4 x 1.25 kg samples combined

Pu-239 is refractory in MAPEP 12

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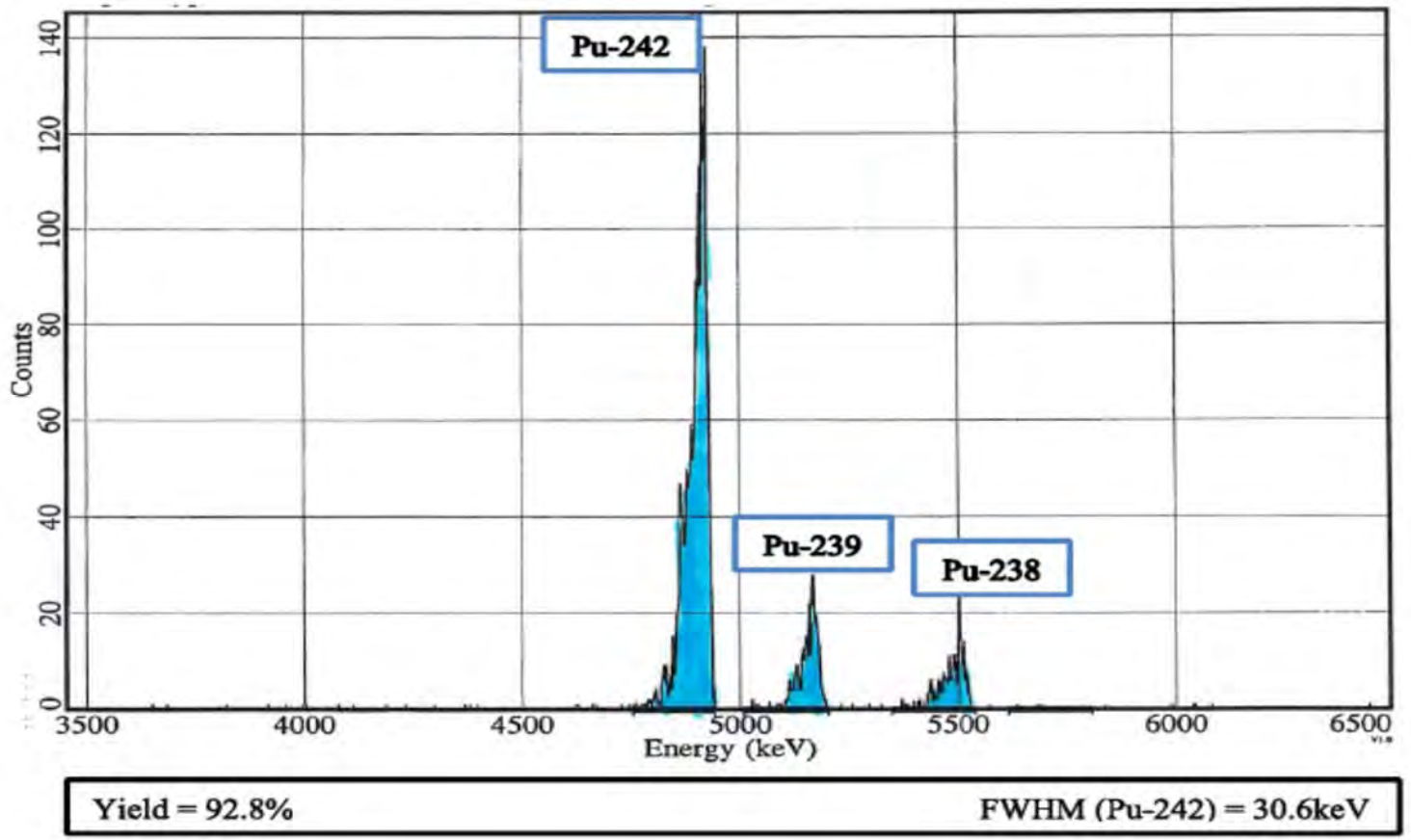
Plutonium Alpha Spectra - Spiked Rice



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^{238}U interference on Pu by 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
  - the ^{238}U level in the purified solutions should be less than 100 pg mL^{-1}
    - to minimize spectral interference in the quantitative analysis of ^{239}Pu and ^{237}Np

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Enhanced U-238 Removal for Pu-239 by ICP-MS

- Typical single column TEVA separation 1000x removal of U
- ICP-MS
  - Option 1
    - for more U removal – redissolve CeF_3 in warm 3M HNO_3-0.25M boric acid and separate again on TEVA Resin with much less Ti in eluent
  - Option 2
    - 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, S L.; Culligan, B K.; Jones, V D.; Nichols, S T.; Noyes, GW.; Bernard, M.* [>10E6 U decontamination of Pu)

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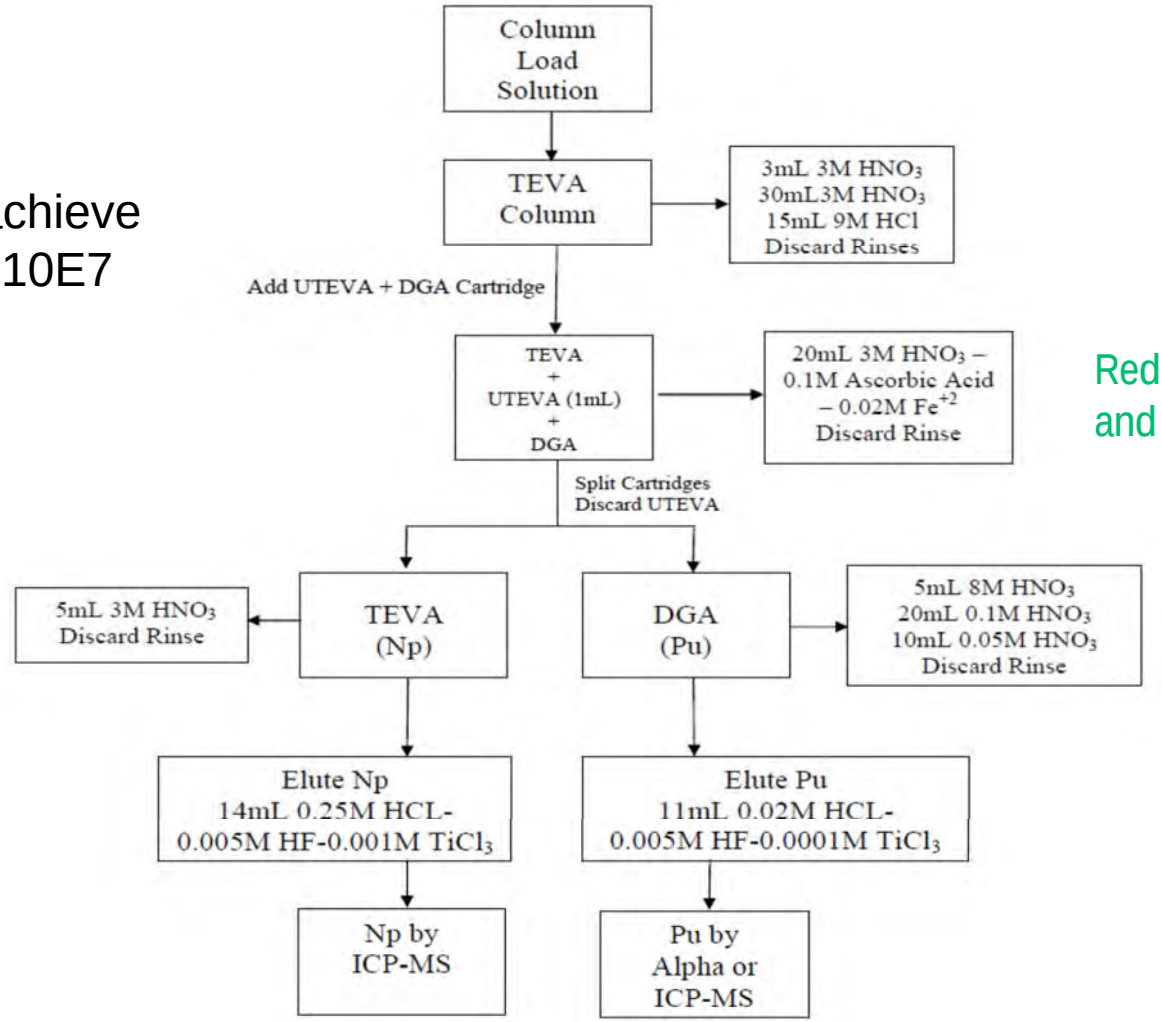
Another Enhanced Uranium Removal Option (ICP-MS)

Option 2 to achieve
U removal > 10E7



Reduce Pu^{4+} to Pu^{3+} and move Pu^{3+} to DGA

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Rapid Actinide Method for Food

Rapid Determination of Actinides in Emergency Food Samples
S. L. Maxwell, B. K. Culligan, A. Kelsey-Wall and P. J. Shaw,
Journal of Radioanalytical and Nuclear Chemistry, (2012) 292:339–347

submitted as a **US FDA FERN Standard Operating Procedure** for the rapid radiochemical analysis of alpha emitting isotopes of americium, curium, plutonium, and uranium.

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Rapid Method Actinides in Food

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

↓

Heat at 700°C for 2 hours in Furnace

↓

Wet Ash with HNO_3 / H_2O_2 on Hot Plate

↓

Heat for ~ 10 min. at 600°C in Furnace

↓

Fuse in Zr Crucible 15 min. (15g NaOH @ 600°C).
Hydroxide precipitation (5 mg La Carrier, Fe, Ca, PO_4,$TiCl_3$)

↓

Lanthanum Fluoride Matrix removal
(1 mg La, Ca, 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 +1mg Fe
1mL 3.5M $NaNO_2$
1.5mL 15.8M HNO_3

↓

Column Load Solution

100g Food
Add Tracers
Ash 12hrs @
550°C

)

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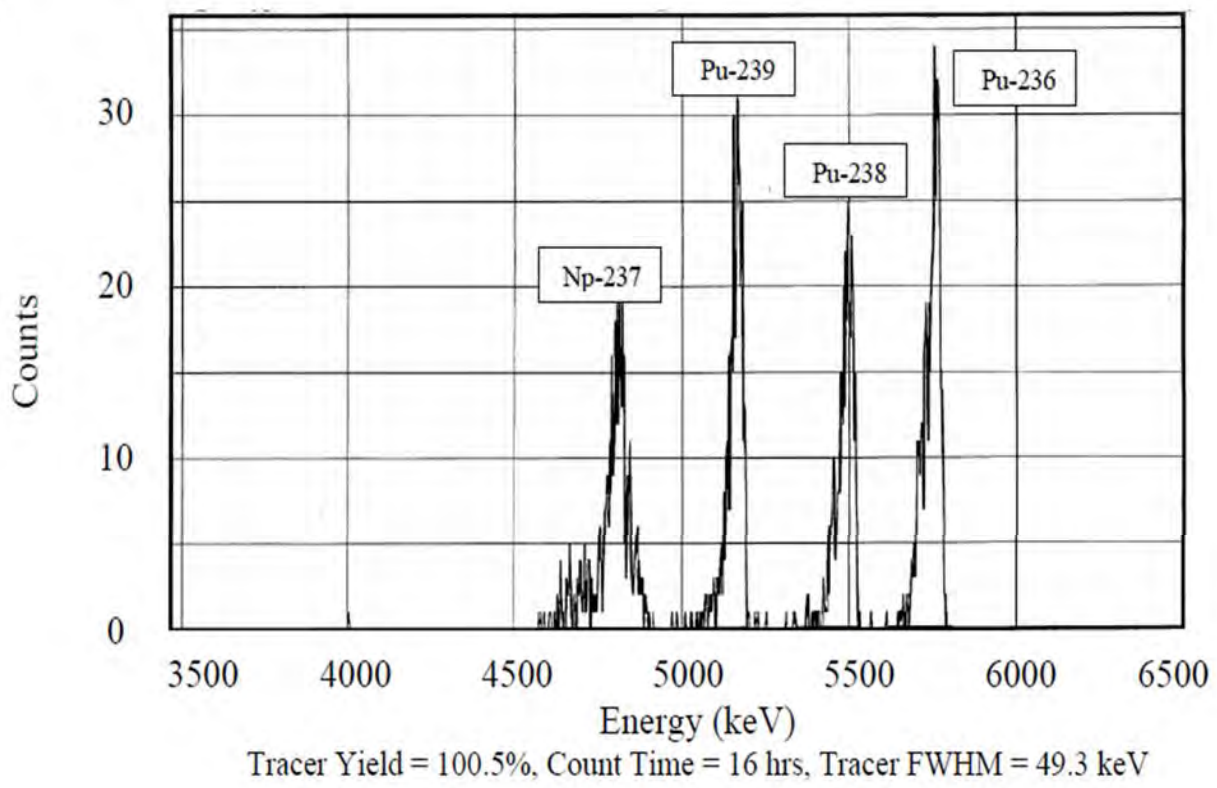
Pu and Np Alpha Spectra Spiked Food Sample



See paper for data on 10g and 100 g food samples:

Rapid Determination of Actinides in Emergency Food Samples
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Journal of Radioanalytical and Nuclear Chemistry, (2012) 292:339–347

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MDA

- U. S. Food and Drug Administration (FDA) provided guidance for accidental contamination of foods to state and local agencies so that protective actions may be taken
  - FDA derived intervention level (DIL) for ^{238}Pu + ^{239}Pu + ^{241}Am is 2 Bq/kg (2 mBq/g or 0.054 pCi/g)
- SRNL method provides a typical MDA of ~0.2 mBq/g for a 10 g food sample and 2 hour count time for each of the actinide isotopes cited in the DIL.
- Method is fast and flexible
  - longer count times can be used to lower MDA levels as needed.
  - For example, for a 16 hour count time and a 10 g sample, an MDA of 0.04 mBq/g can be achieved.
- Typically, the U. S. FDA recommends MDA levels be 1/3 of the DIL
  - These MDAs are readily achievable using this rapid method

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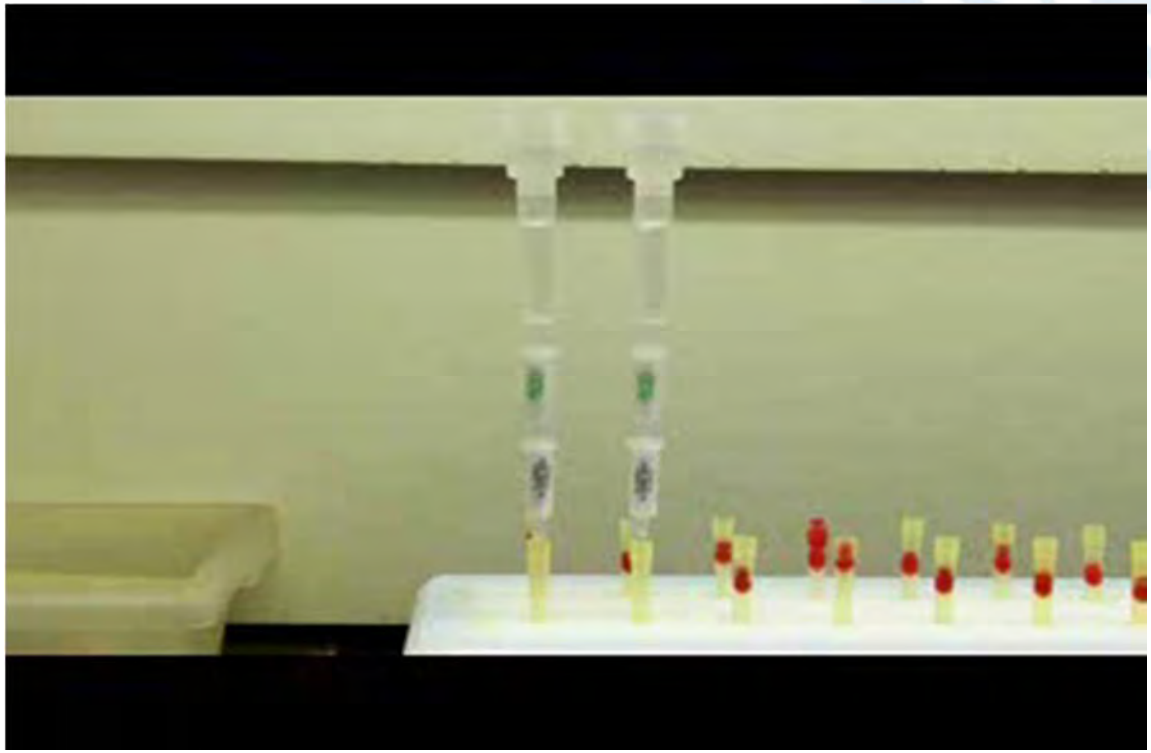
Stacked cartridges



TEVA+ DGA Resin cartridges (Pu and Am)

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Summary

- New method for Pu in rice developed at SRNL Environmental Bioassay lab for up to 5 kg rice
  - MDA for Pu in 5000g rice and 30 hour count = ~7 E-5 mBq/g
- After the initial furnace and wet-ashing….
  - Rapid sodium hydroxide fusion
  - Rapid TEVA cartridge separation
    - Options to use alpha spectrometry or ICP-MS
    - Enhanced uranium removal options
      - *Redissolve CeF_3 and reprocess with TEVA Resin*
      - *Move Pu to DGA Resin and rinse more*
- Good chemical yields
- Rugged for refractory particles

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