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Rapid Methods for Actinides and Sr-89/90 in Environmental Samples

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9-16-14

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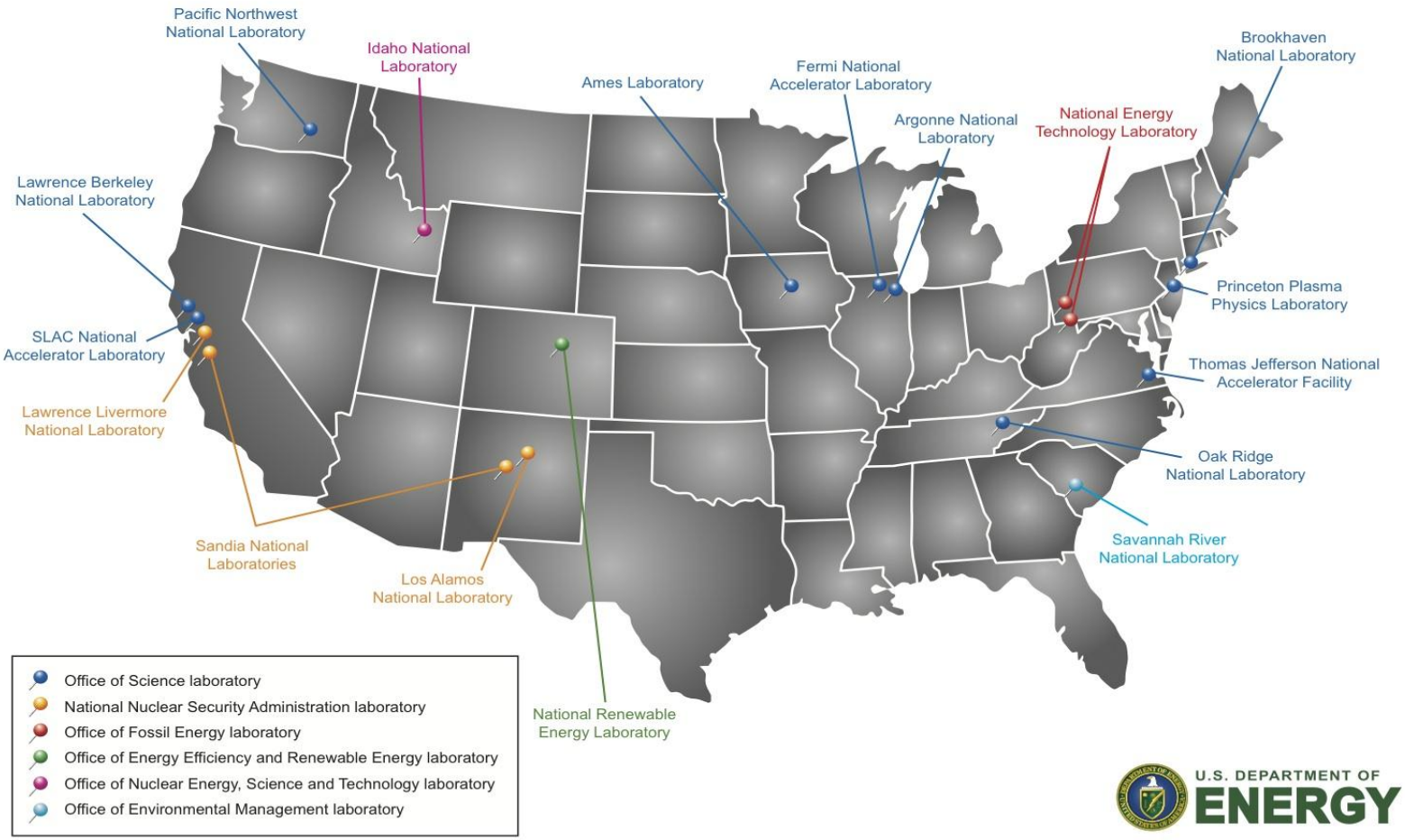
Department of Energy National Laboratories



Rapid Radiochemical Methods

- **Savannah River National Laboratory (SRNL)**
  - US Department of Energy National Laboratory
  - Published ~ 30 papers in last 10 years on rapid radiochemical methods
    - ***Environmental, food and bioassay sample matrices***
    - ***Emergency response and more efficient routine analyses***
- **Validated, reliable analytical methods**
  - US EPA Office of Air and Radiation, National Analytical Radiation Environmental Laboratory, Montgomery, AL
  - Centers for Disease Control, Atlanta, GA
  - US Air Force Radioanalytical Laboratory, Wright Air Force Base, OH
  - ASTM International D19.04 Methods of Radiochemical Analysis and C26 Nuclear Fuel Cycle

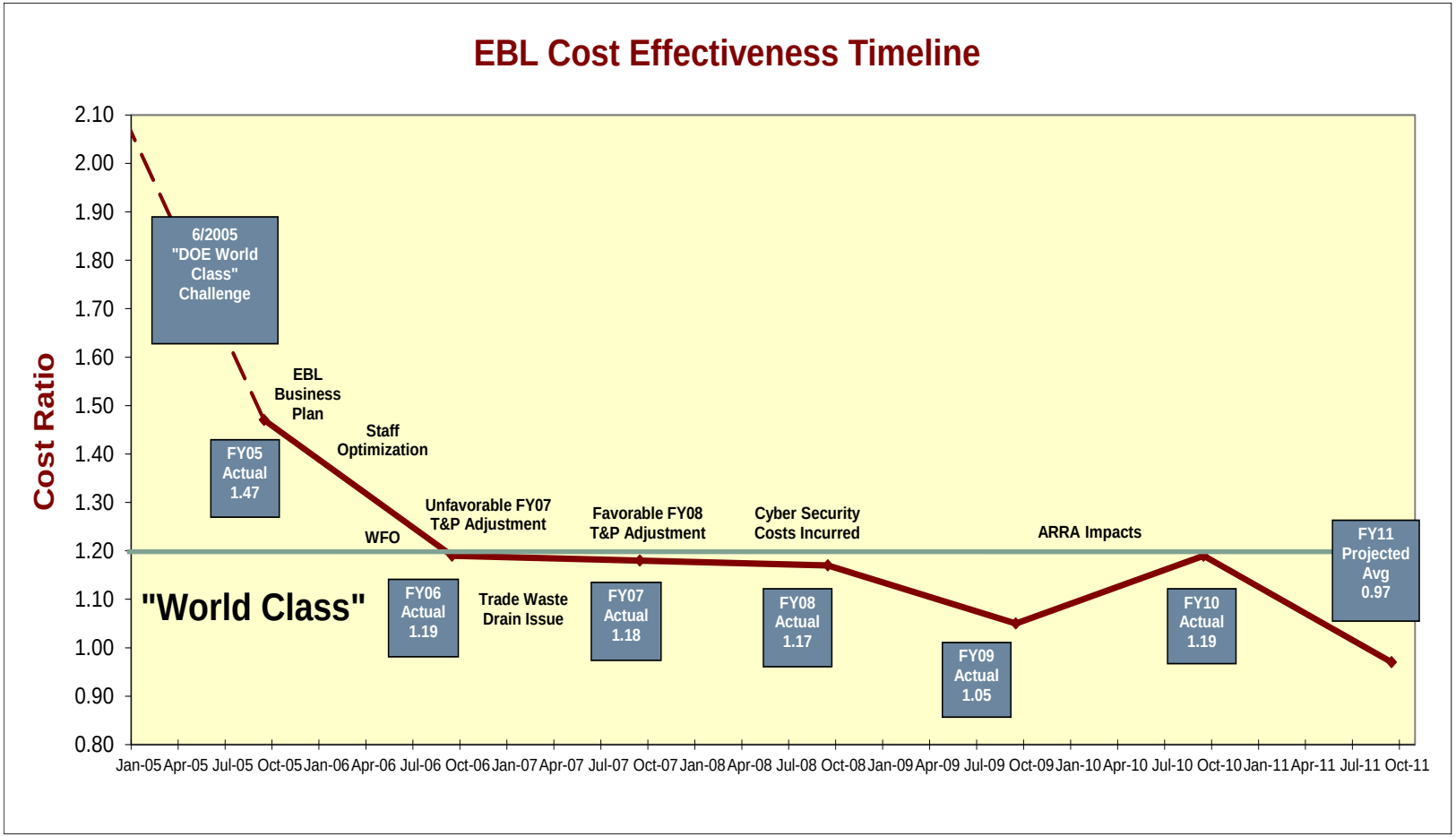
SRNL Approach

- **Combine innovative sample preparation with rapid column extraction**
  - ***Water, air filters, soil, concrete, brick, vegetation, food, milk, fish, urine, feces, etc.***
- **Stacked cartridge technology**
  - ***Sequential separation (5X faster than gravity flow)***
  - ***Time is money***
  - ***Solves waste issues***
- **Reliable, rapid methods are essential**
  - **Validated methods**
  - **Rapid assessment of radiological impact**
  - **Mitigate dose and protect the public and ecosystems**
  - **Maintain public trust**

Actinides and Sr-89/90 in Environmental Samples

- **SRNL- many new methods over last 15 years**
- **Focus today on**
  - Actinides and Sr-89/90 in environmental samples
    - *Water, air filters, soil, concrete, brick, vegetation, food*
  - Actinides in Seawater
  - 80L, <8 hours sample preparation (will be presented at ERA-12)
  - Sr-90 in seawater
    - *Y-90 in seawater (40L), <8 hours sample preparation*
- **Also new but not enough time to discuss:**
  - New Ra-226/Ra-228 methods with cation resin + DGA Resin for water, solid matrices
  - Po-210 in water (*DGA Resin* and *new $BiPO_4$ microprecipitation*)

Cost Reduction vs Private Commercial Labs



Sample Preparation for Environmental Samples

- **Rapid preconcentration and sample matrix removal**
  - Fresh water (calcium phosphate)
    - *Milk (calcium phosphate/acidify ppt. to coagulate fat/protein)*
  - Seawater
    - *Actinides ($FeOH_2$+Ti)/LaF_3*
    - *Sr-89/90 (calcium phosphate +$FeOH_3$)*
    - *Sr-90 via Y-90 ($FeOH_3$)/LaF_3*
  - Air filters - digestion with HNO_3/HF
    - *Swipes –furnace + acid digestion*
  - Soil, brick, concrete, asphalt- furnace + sodium hydroxide fusion
    - *Large soil- acid leach*
  - Vegetation/food –furnace ash + rapid fusion
    - *Animal tissue- fish, deer, shellfish, acid digestion/furnace*

Actinides and Sr-89/90 in Water

- TEVA/TRU/Sr Resin –stacked cartridges as needed
  - One sample preparation
  - Vacuum box flow rates
- Calcium phosphate ppt.
  - Sample aliquot directly in centrifuge tube
  - *No water rinse of ppt.*
  - No heat*

    ** larger samples may need heat briefly to aggregate ppt.*

    **for 1 liter samples, use large beakers, heat, allow, settle, add to tubes*

Maxwell III, SL, "Rapid Column Separation for Actinides and Sr-89/90 in Water Samples", Journal of Radioanalytical and Nuclear Chemistry, 2006, Vol. 267, No. 3, p 537"

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

Actinides and Sr-90 in Water

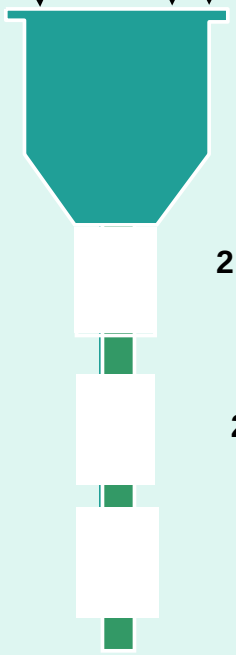
Calcium phosphate precipitation

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

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)

* Enhanced Po-210 removal if needed for high Po smps

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

NIST Radiological Preparedness Exercise (NRIP)

- Emergency analysis samples -1 day notice
  - **Dr. Ken Inn, NIST, spoke at RRMC-2004 of the "need to improve efficiency and effectiveness of radioanalytical capabilities"**
- Need for faster methods-Homeland Security
  - **SRNL has developed rapid methods for actinides and Sr-90 analysis**
  - **participated IN NIST emergency testing for water, urine soil, air filter, fecal samples**
  - ***fastest times***
- Improvements in emergency methods <u>also benefit routine methods</u>
  - *Efficiency, capacity, cost reduction*

SRNL Improvements in NRIP Report Times

Water samples	NRIP 2006	NRIP 2007	NRIP 2008
Actinides			
Am-241	7.2 hrs	4.9 hrs	3.5 hrs
Pu-238, 239	7.2 hrs	5.5 hrs	3.9 hrs
U-234, 235, 238	7.2 hrs	5.6 hrs	4.1 hrs
Strontium-90	4.6 hrs	4.25 hrs	3.2 hrs

Rapid Method-Air Filters

- **Actinides (Pu, Np, Am, Cm, U) and Sr-89/90**
  - HNO_3+ HF +H_2O_2 digestion
  - Rapid and quantitative
  - TEVA Resin +TRU Resin + Sr Resin (same as water method)
  - CeF_3 microprecipitation-alpha spectrometry
    - *Use 50 µg Ce (100 µg Ce for U > 370 mBq)*
  - Sr-89/90- gas proportional counting
    - *Gravimetric recovery-Sr carrier (4-5 mg)*
    - *LSC is an option*
  - *NRIP emergency PT report times <4 hrs*

Maxwell, S., Culligan, B. and Noyes, G. (2010), Rapid separation method for actinides in emergency air filter samples, Appl. Radiation and isotopes, December 2010, Pages 2125-2131

Routine Performance Test Results (air filters)

MAPEP 25

Radiological							Units: (Bq/sample)	
Analyte	Result	Ref Value	Flag	Notes	Bias (%)	Acceptance Range	Unc Value	Unc Flag
Americium-241	0.141	0.147	A		-4.1	0.103 - 0.191	0.011	
Cesium-134	-0.12		A			False Positive Test	0.07	
Cesium-137	2.48	2.60	A		-4.6	1.82 - 3.38	0.16	
Cobalt-57	4.72	5.09	A		-7.3	3.56 - 6.62	0.17	
Cobalt-60	3.11	3.20	A		-2.8	2.24 - 4.16	0.13	
Manganese-54	-0.020		A			False Positive Test	0.07	
Plutonium-238	0.120	0.1183	A		1.4	0.0828 - 0.1538	0.0096	
Plutonium-239/240	0.136	0.135	A		0.7	0.095 - 0.176	0.011	
Strontium-90	1.61	1.67	A		-3.6	1.17 - 2.17	0.23	
Uranium-234/233	0.153	0.162	A		-5.6	0.113 - 0.211	0.012	
Uranium-238	0.158	0.168	A		-6.0	0.118 - 0.218	0.013	
Zinc-65	4.07	4.11	A		-1.0	2.88 - 5.34	0.36	

± 20% acceptance limits

Fukushima Daiichi Air Filters

- **Cellulose filters**
  - HNO_3, H_2O_2, HF digestion
    - *Repeat HNO_3/H_2O_2 to dryness several times, then with 3ml 3M HNO_3 -boric acid*
- **Separate using 2 ml Sr Resin cartridige**
  - twice for very high total beta samples (>37 Bq/filter)
- **High, consistent Sr gravimetric yields (85-95%)**
- **Gas flow proportional counting**
  - Simultaneous drawer counting system
- **Results within hours!**
- **Soil**
  - *SRNL was also selected to analyze Sr-89/90 in Japanese soil to assist Japan*

Sample Preparation Options for Actinides and Sr-89/90 -Soil

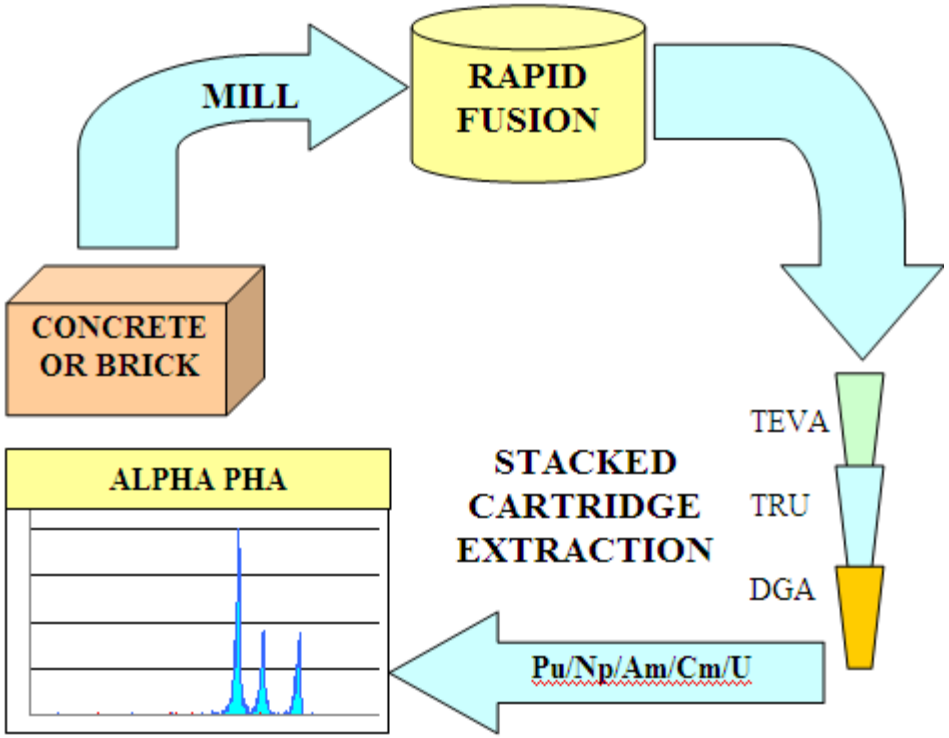
• Actinides	Digestion	Preconcentration	
• 1-10g soil	rapid fusion	Fe/Ti OH	LaF_3
• 10-100g	acid leach	Fe/Ti OH	LaF_3
• Sr-89/90			
• 1-5g soil	rapid fusion	$Fe(OH)_3 + PO_4$	CaF_2
• 5-50g	acid leach	$Fe(OH)_3 + PO_4$	CaF_2

- Removes Fe and silicates
- High yields, removal of interferences, fast

Approach for soil aliquots 10g or less

- **Actinides (Pu, Np, Am, Cm, U)**
  - **Soil (1-10g)**
    - ***Rapid sodium hydroxide fusion (15-20 minutes)***
      - **eliminates refractory particles**
      - **low temperature, multiple samples at same time, inexpensive Zr crucibles**
      - **faster than several hours on hot plate with HNO3-HF**
    - ***Rapid matrix removal***
      - **Iron/titanium hydroxide ppt. preconcentration**
      - **Lanthanum fluoride ppt. matrix removal (no Si flow issues, Fe, Ti removal)**
    - ***TEVA Resin (Pu, Np) +TRU Resin (U) + DGA (Am, Cm) Resin***
      - **Pu, Np only-TEVA Resin**
      - **If U not needed, TEVA (Pu, Np) +DGA (Am, Cm) only**
      - **New TRU+DGA option**
    - ***Alpha spectrometry and/or ICP-MS***

Rapid Fusion Application for Concrete and Brick (soil)



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 Fusion Method for Concrete, Brick, Soil Validated by US EPA

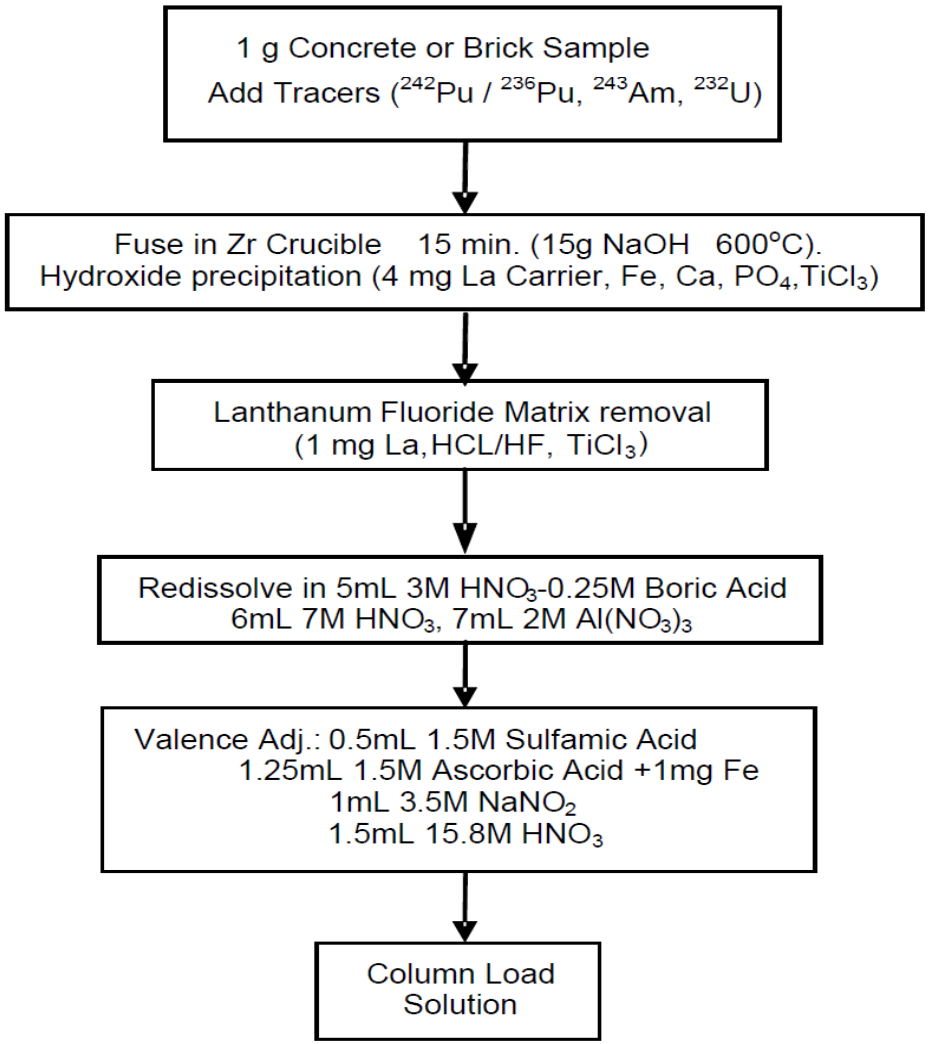
Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses for Environmental Remediation Following Radiological Incidents

U.S. Environmental Protection Agency

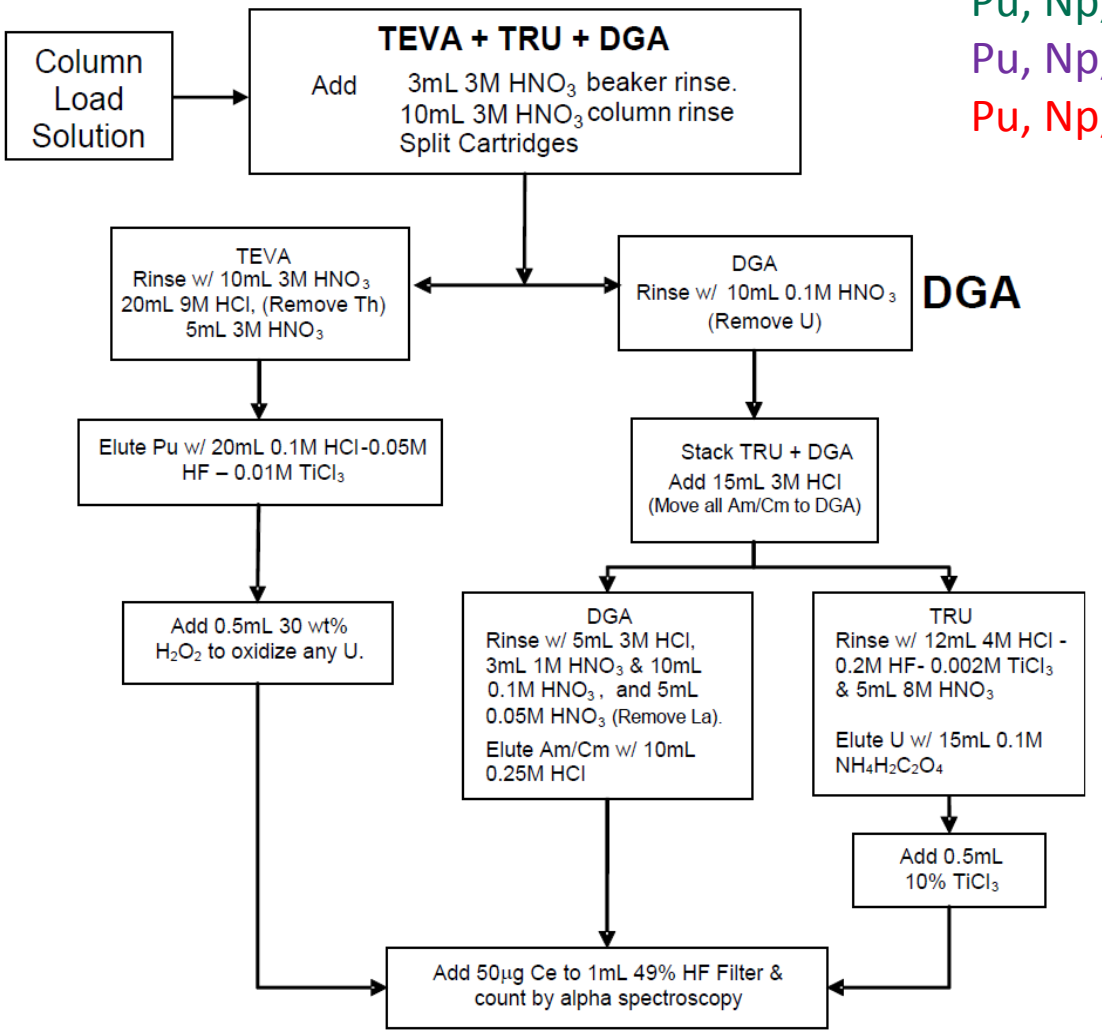
Office of Air and Radiation
Office of Radiation and Indoor Air
National Analytical Radiation Environmental Laboratory
Montgomery, AL 36115

Office of Research and Development
National Homeland Security Research Center
Cincinnati, OH 45268

Rapid Concrete and Brick Sample Preparation



Rapid Column Separation



Pu, Np, Th: TEVA

Pu, Np, U, Th :TEVA+TRU

Pu, Np, Am, Cm :TEVA+DGA

Flexibility!

The Magic of DGA

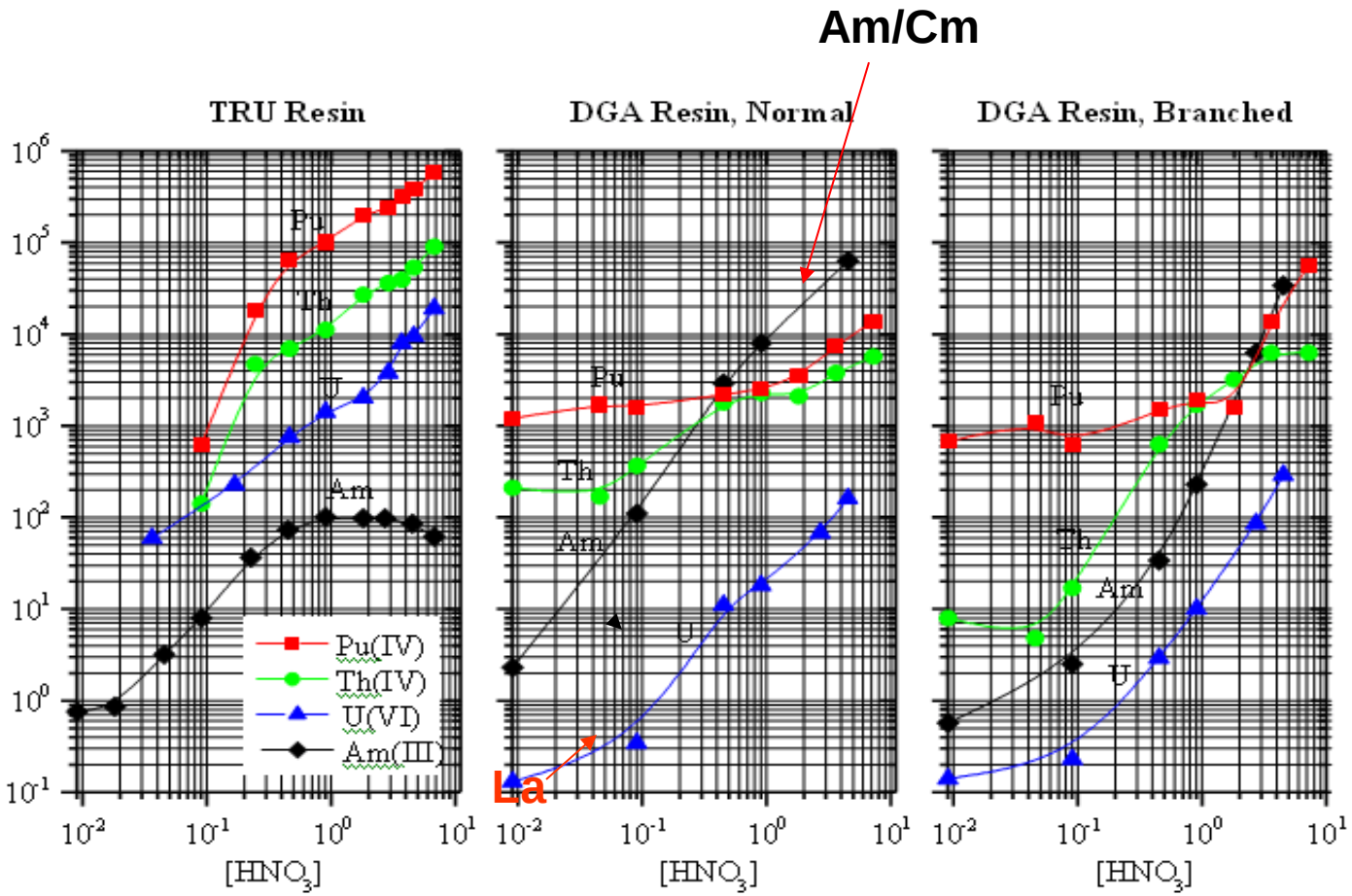


Figure 2

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

Pu-239 Results for 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	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 containing refractory Pu-239

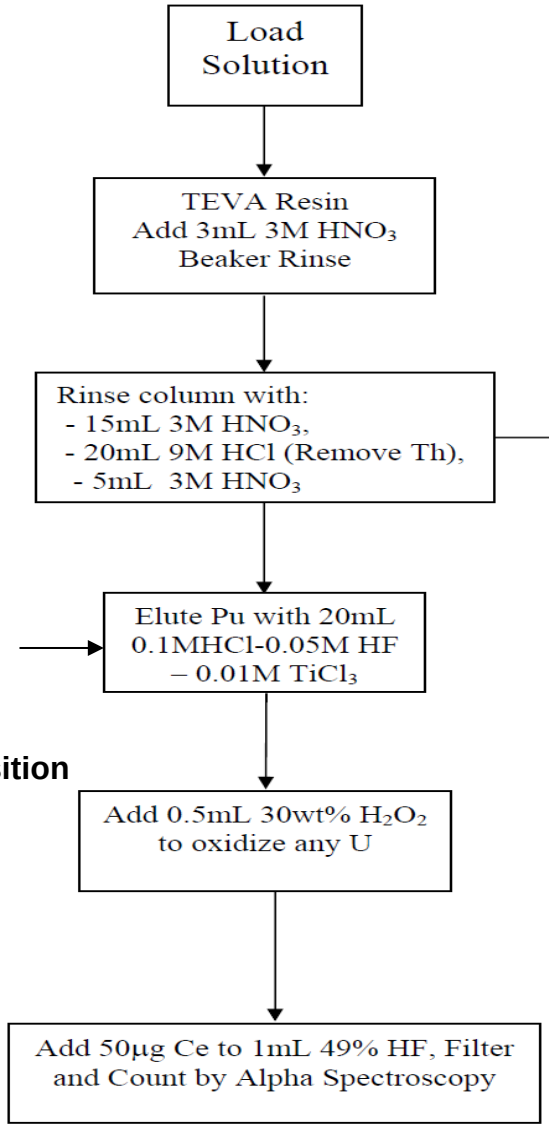
Challenges

- **Pu, Np in Soil (10g-100g+)**
  - Need effective soil matrix removal and good chemical yields
  - Need good valence control of Np
  - Acid leaching
    - *Acid leaching is not appropriate for soil samples containing refractory PuO_2, but has been shown to be acceptable for fallout-derived radionuclides not associated with refractory components in the sample*
  - Alpha spectrometry (and/or ICP-MS)

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, July 2011, Pages 917-923

S. L. Maxwell, B. Culligan, G. Noyes, V. Jones, ST Nichols and M. Bernard (2010), Rapid determination of 237Np and Pu isotopes in large soil samples by inductively-coupled plasma mass spectrometry, Anal Chim Acta. 2010 Dec 3;682(1-2):130-6. Epub 2010 Oct 8.

Rapid Column Separation for Pu/Np Isotopes



^{237}Np eluted with Pu

HH can be used for ICP-MS

Rongalite used for electrodeposition

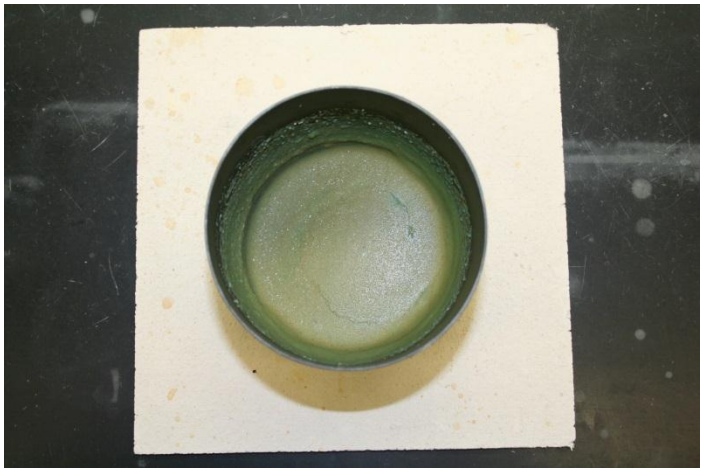
Pu and Np results for 20g samples spiked with MAPEP 21 standard

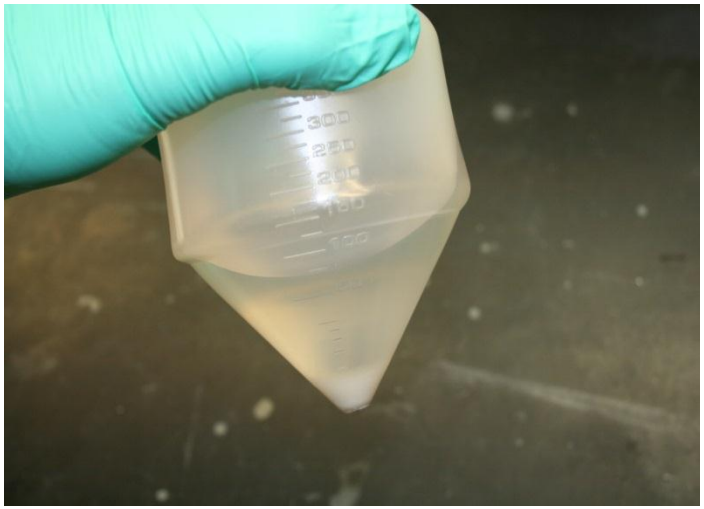
Sample ID	^{236}Pu Yield (%)	^{238}Pu Measured mBq	^{239}Pu Measured mBq	^{237}Np Measured mBq
1	91.3	0.25	1.68	35.5
2	82.0	0.28	1.69	45.9
3	100.8	60.3	112.1	34.5
4	89.0	68.8	125.4	38.5
5	85.8	71.8	126.9	38.9
6	93.8	65.9	120.6	36.6
7	85.4	71.0	124.0	41.4
8	87.1	66.6	111.7	41.1
Avg.	89.4	67.4	120.1	39.0
[A]Corr. Avg.		67.1	118.4	39.0
1SD	5.9	4.2	6.7	3.7
%RSD	6.6	6.2	5.6	9.5
Reference		63.2	116.3	37.0
% Difference		6.2	1.8	5.5

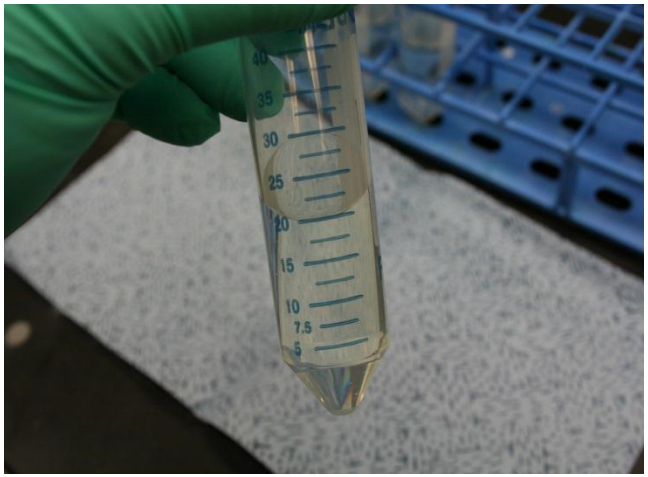
avg ^{238}Pu in unspiked 20g sample = 0.265 mBq
avg ^{239}Pu in unspiked sample = 1.685 mBq

[A] average spiked sample result corrected for unspiked content

New Rapid Fusion method for 10g soil – Total Digestion

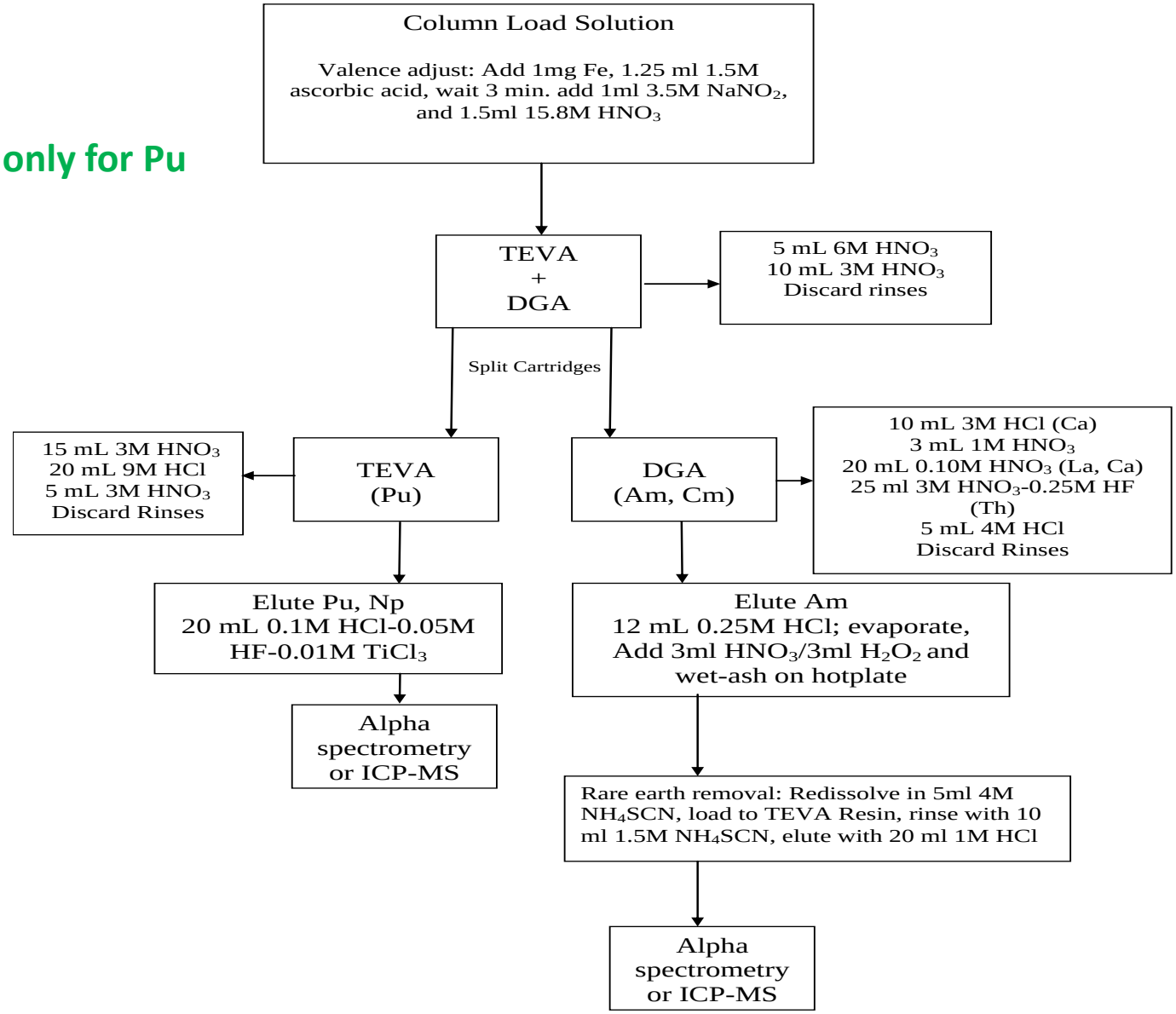




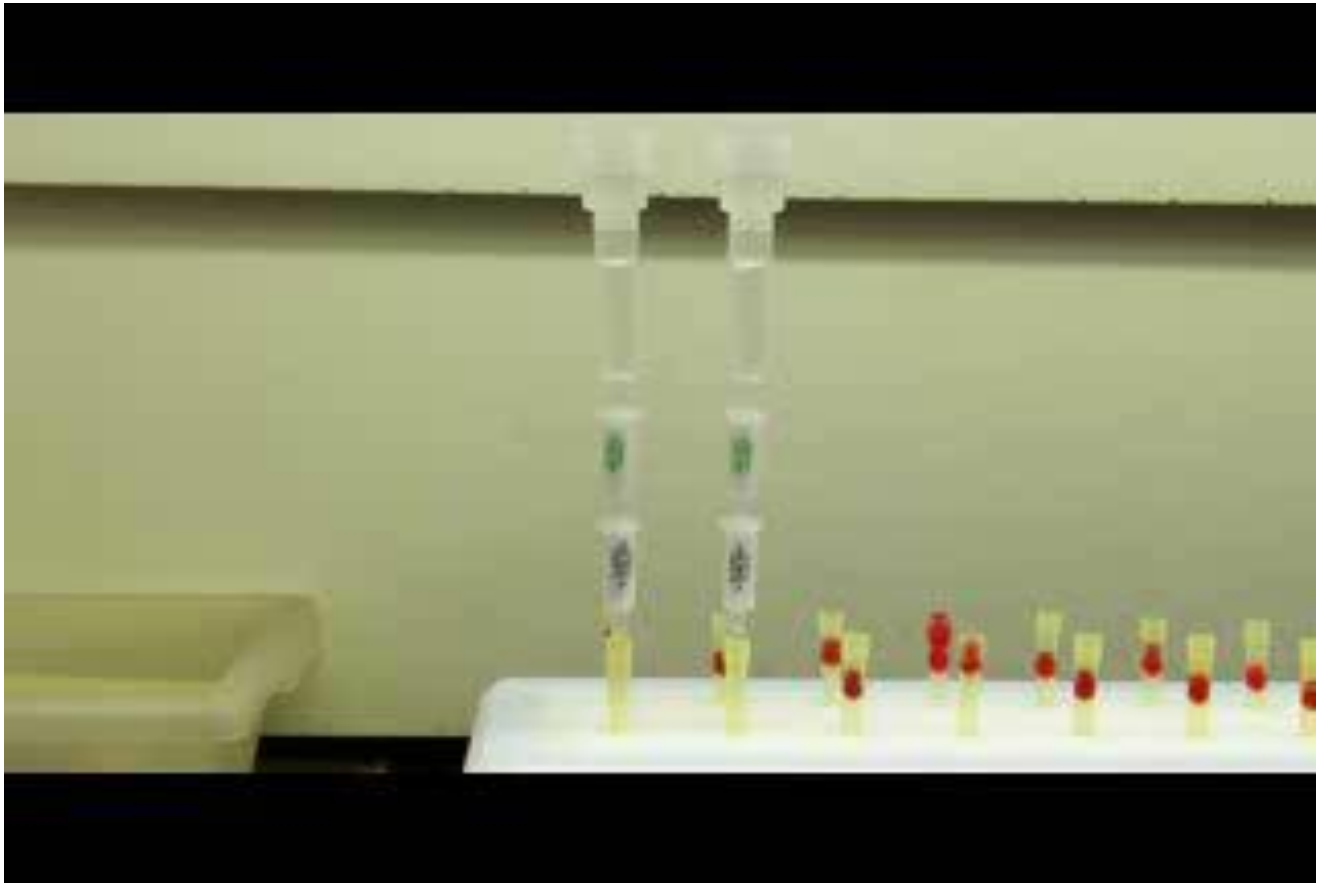


Rapid Separation of Pu and Am

TEVA only for Pu



TEVA+DGA Resin



Pu-239 Results for 10g Soil aliquots Using Fusion

Sample ID	^{236}Pu /^{242}Pu Yield (%)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	^{239}Pu Corrected Value (mBq g^{-1})	Difference (%)
1	91.1	3.43	0.094	3.46	3.39	-1.2
2	80.9	3.43	0.087	3.23	3.16	-8.0
3	89.8	3.43	0.093	3.44	3.37	-1.7
4	76.6	3.43	0.085	3.15	3.07	-10.4
5	83.9	3.43	0.093	3.43	3.36	-2.2
6	84.0	3.43	0.099	3.64	3.64	6.3
7	99.3	3.43	0.091	3.35	3.35	-2.3
8	84.7	3.43	0.097	3.57	3.57	4.2
9	71.8	3.43	0.103	3.80	3.80	10.7
10	82.5	3.43	0.091	3.36	3.36	-2.1
Avg. Spiked Smps	84.5				3.4	-0.7
SD	7.7				0.2	6.3
% RSD	9.1				6.3	
			24 hour count			
			1-6 corrected for blank assay Pu-239/240 (0.074 mBq g^{-1})			

Spiked with 0.35 g MAPEP 24 soil - refractory Pu-239

Am-241 Results for 10g Soil aliquots Using Fusion

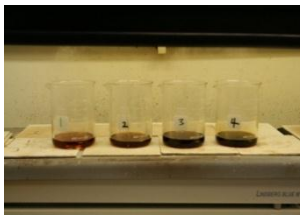
Sample ID	^{243}Am Yield (%)	^{241}Am Reference Value (mBq g^{-1})	^{241}Am Measured Value (pCi g^{-1})	^{241}Am Measured Value (mBq g^{-1})	Difference (%)
1	83.5	N/A	0.0012	0.04	N/A
2	81.0	2.14	0.0581	2.15	0.5
3	92.2	2.14	0.0601	2.22	3.9
4	83.5	2.14	0.0521	1.93	-9.9
5	82.3	2.14	0.0586	2.17	1.3
6	87.9	2.14	0.0591	2.19	2.2
7	91.3	2.14	0.0504	1.86	-12.9
8	96.4	2.14	0.0598	2.21	3.4
9	97.7	2.14	0.0537	1.99	-7.2
10	86.6	2.14	0.0588	2.18	1.7
11	99.1	2.14	0.0490	1.81	-15.3
Avg. Spiked Smps	89.2			2.07	-1.6
SD	6.5			0.16	6.8
% RSD	7.3			7.55	
			24 hour count		

Spiked with 0.35 g MAPEP 24 soil

Rapid Sr-89,90 Acid Leach Method for Larger Soil Aliquots

50 g samples

Add Sr carrier to large soil sample



Acid leach with 15.8M HNO_3; centrifuge, decant and evaporate leachate

Redissolve with 15-20mL 1M HCl

Transfer to 225mL tube and dilute to 180mL with water

Fe hydroxide matrix removal (25mL con. NH_4OH, 50mg Ca, PO_4) Mix and centrifuge

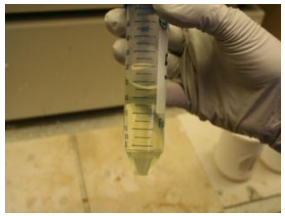
Discard Supernatant

Add 40mL 1.5M HCl. Dilute to 170mL with 0.01M HCl

Ca Fluoride matrix removal Add 25mL 28M HF. Mix and centrifuge

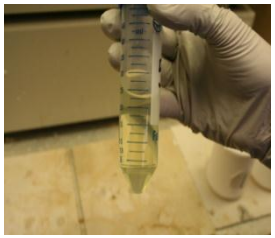
Discard supernatant

Redissolve in 7mL 15.8M HNO3+7mL 3MHNO_3-0.25M H_3BO_3, 7mL $Al(NO_3)_3$



Column Load Solution

Rapid Sr-89,90 Column Separation Method for Soil



Column
Load Solution

↓

Sr Resin* (3mL)
cartridge

↓

Rinse column;
15mL 8M HNO_3;
*5mL 3M HNO_3-
0.05M Oxalic Acid;
15mL 8M HNO_3

← Sample matrix and ^{90}Y removal; start time for ^{90}Y ingrowth after final 8M HNO_3 rinse

↓

Elute Sr
*15mL 0.05M HNO_3

↓

Evaporate on planchet; weigh for gravimetric yield

↓

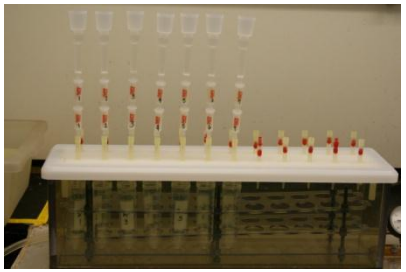
Count $^{89,90}Sr$ by Gas Flow Proportional Counter

↓

Recount after ^{90}Y ingrowth 10 days later to determine ^{89}Sr and ^{90}Sr

50-100g

Can combine 50g eluents



For large soil aliquots:

*4 ml Sr Resin

*10mL 3M HNO_3-0.05M Oxalic Acid

*18 mL 0.05M HNO_3

Sr-90 Soil Method (50 gram)

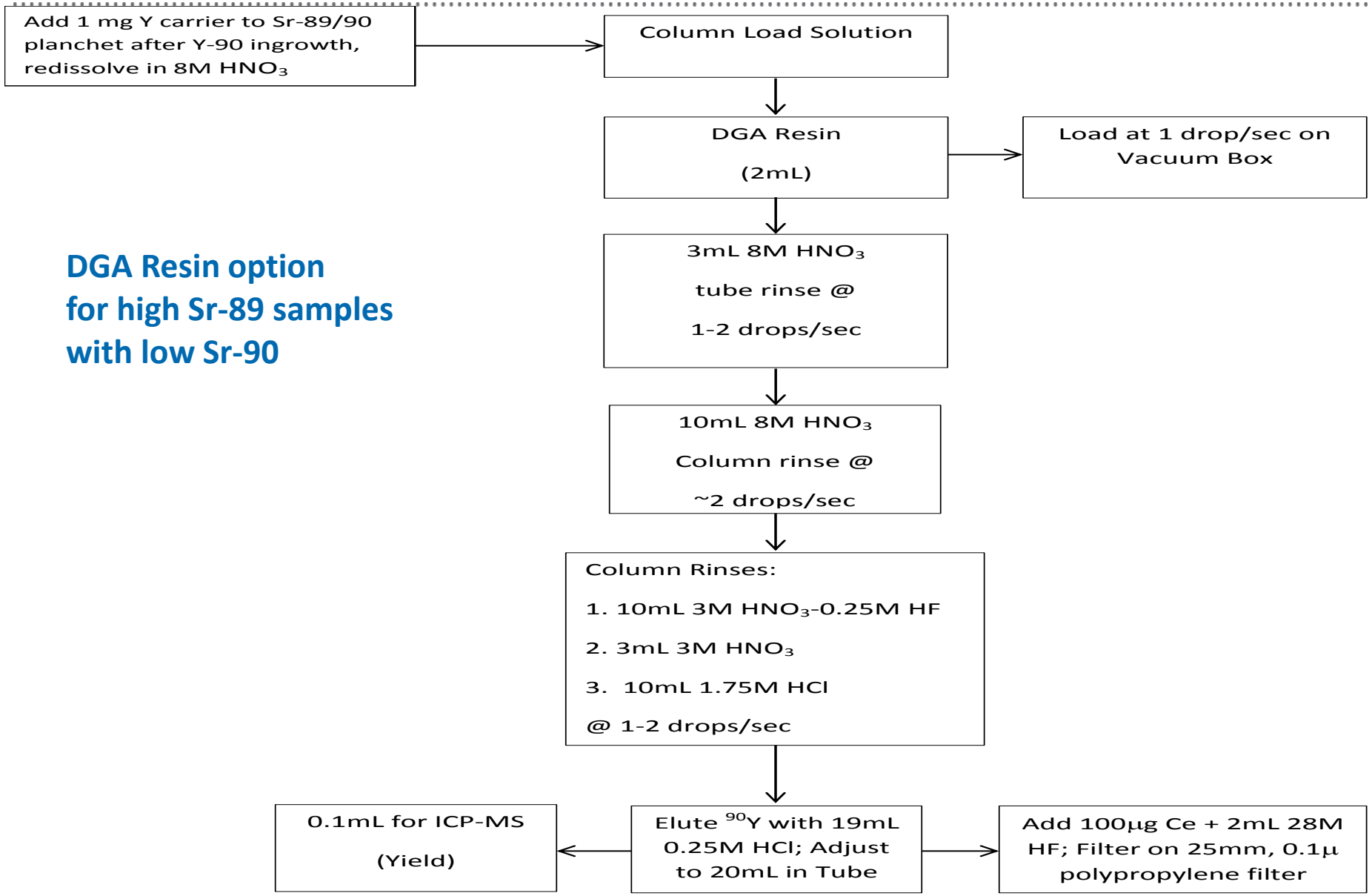
Sample ID	Sr carrier (%)	^{90}Sr Reference Value (pCi g^{-1})	^{90}Sr Reference Value (mBq g^{-1})	^{90}Sr Measured Value (mBq g^{-1})	Difference (%)
1	95.9	0.160	5.92	6.05	2.20
2	98.6	0.160	5.92	6.02	1.69
3	94.6	0.160	5.92	5.82	-1.69
4	91.8	0.160	5.92	6.32	6.76
5	93.2	0.160	5.92	5.96	0.68
6	92.5	0.160	5.92	5.60	-5.41
7	91.2	0.160	5.92	5.85	-1.18
Avg	94.0			5.95	0.43
SD	2.6			0.22	
% RSD	2.8			3.77	
	Measured values corrected for 1.35 mBq ^{90}Sr/g found in unspiked soil				

MDC = 0.011 pCi/g (0.41 mBq/g)
90 minute count

MDC = 0.0032 pCi/g (0.12 mBq/g)
1000 minute count

Rapid Sr-89, Sr-90 Option to Collect Y-90

DGA Resin option for high Sr-89 samples with low Sr-90

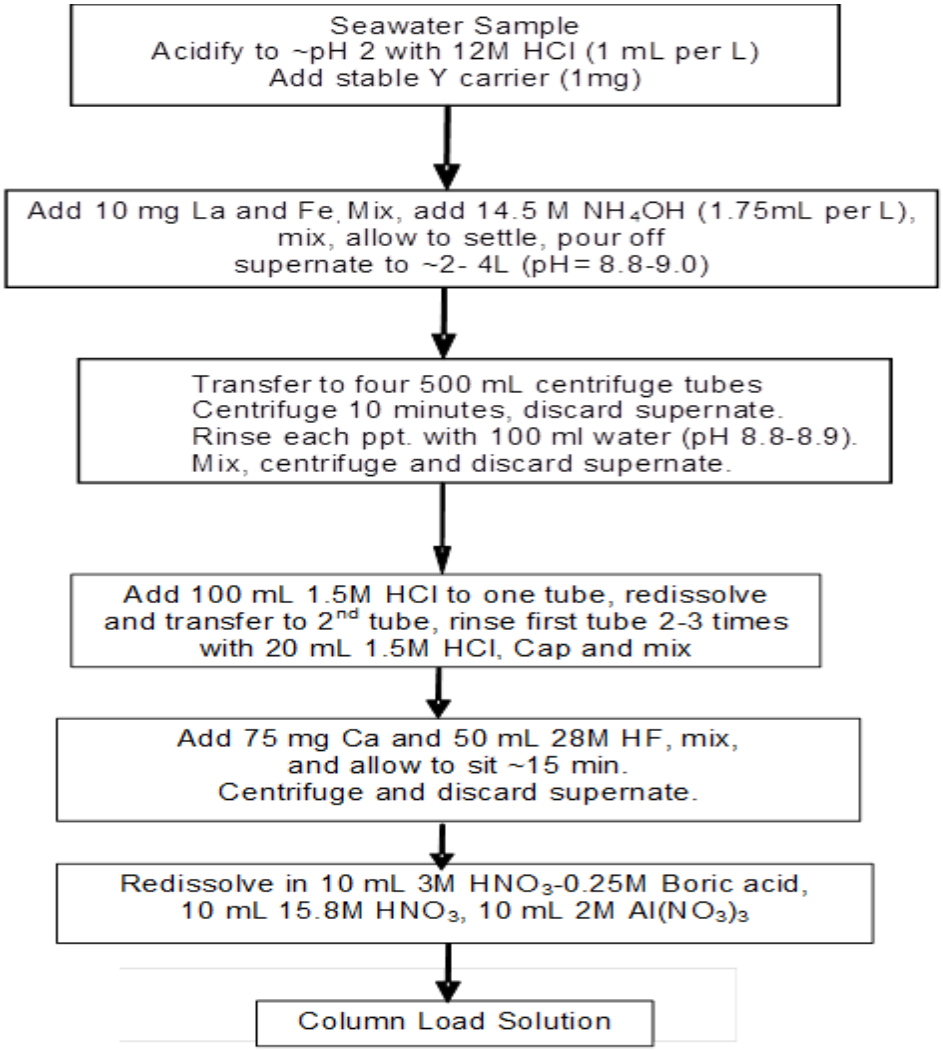


Sr-89/90 in Seawater

- **Maxwell, S., Culligan, B. and Utsey, R. Rapid determination of radiostrontium in seawater samples, J Radioanal Nucl Chem (2013) 298:867–875**
  - Calcium phosphate enhanced with $Fe(OH)_3$ + Sr-Resin
  - Limited by stable Sr (8mg/L) in seawater
  - 1mBq/L MDA with 6L aliquot and long count time using gas flow proportional counting

- **Maxwell, S., Culligan, B. , Utsey, R. , Hutchison, J. and McAlister, D. Rapid determination of ^{90}Sr in seawater samples, J Radioanal Nucl Chem (Aug. 2014) DOI 10.1007/s10967-014-3391-8**
  - Rapid collection and purification of Y-90 in <8 hours from 40L
  - MDA for ^{90}Sr of < 150 µBq/L using a 40 L aliquot and a 1000 minute count with gas flow proportional counting

Rapid Sample Preparation Method for ^{90}Sr in Seawater



Rapid separation of Y-90 using DGA

Rapid Sr-90 (Y-90) in Seawater Method (40L)

Sample ID	Sample Aliquot (L)	Y carrier (%)	^{90}Sr Reference Value ($pCi\ L^{-1}$)	^{90}Sr Reference Value ($mBq\ L^{-1}$)	^{90}Sr Measured Value ($mBq\ L^{-1}$)	Difference (%)
1	10	85.5	8.00	296	310	4.7
2	20	89.2	0.762	28.2	28.1	-0.4
3	30	72.3	0.508	18.8	18.5	-1.6
4	40	87.6	0.381	14.1	13.7	-2.8
5	40	86.5	0.381	14.1	13.9	-1.4
Avg		84.2		Y carrier by ICP-MS		-0.30
SD		6.8				2.9
% RSD		8.1		2 hour count time		

Need to verify decay profile to ensure Y-91 not present or solve decay curve consisting of two independent components

2 ml DGA Resin only

Rapid Actinide Method for Food

approved as a **US Food and Drug Administration (FDA) FERN Standard Operating Procedure** for Pu, Am, Cm, U in food

For use by state labs in Food Emergency Response Network (FERN)

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

Maxwell, SL, Culligan, BK, and Hutchison, J. Rapid Determination of Plutonium Isotopes in Large Rice Samples, (2013), J. Radioanal. Nucl. Chem, J Radioanal Nucl Chem (2013) 298:1367–1374 ***[up to 5kg rice aliquots]***

Summary

- **Savannah River National Laboratory**
  - *many new rapid methods for radionuclides in environmental samples*
  - *high chemical yields and good removal interferences*
  - *robust digestion for solid samples*
  - *sequential methods with reduced labor and time can reduce costs*

- **Validated, reliable analytical methods for environmental samples**
  - *US EPA Office of Air and Radiation, National Analytical Radiation Environmental Laboratory, Montgomery, AL*
  - *ASTM International D19.04 Water and C26 Nuclear Fuel Cycle*

- **Reliable, rapid methods are essential**
  - **Rapid assessment of radiological impact**
  - **Mitigate dose and protect the public and ecosystems**
  - **Maintain public trust**