



Savannah River
Nuclear Solutions, LLC
A Fluor Daniel PartnershipSM

Recent Developments in Column Extraction Methods used at SRS

Sherrod L. Maxwell
Savannah River Nuclear Solutions
Aiken, SC
October 28, 2008

54th Radiobioassay and Radiochemical Measurements Conference

Destin, Florida

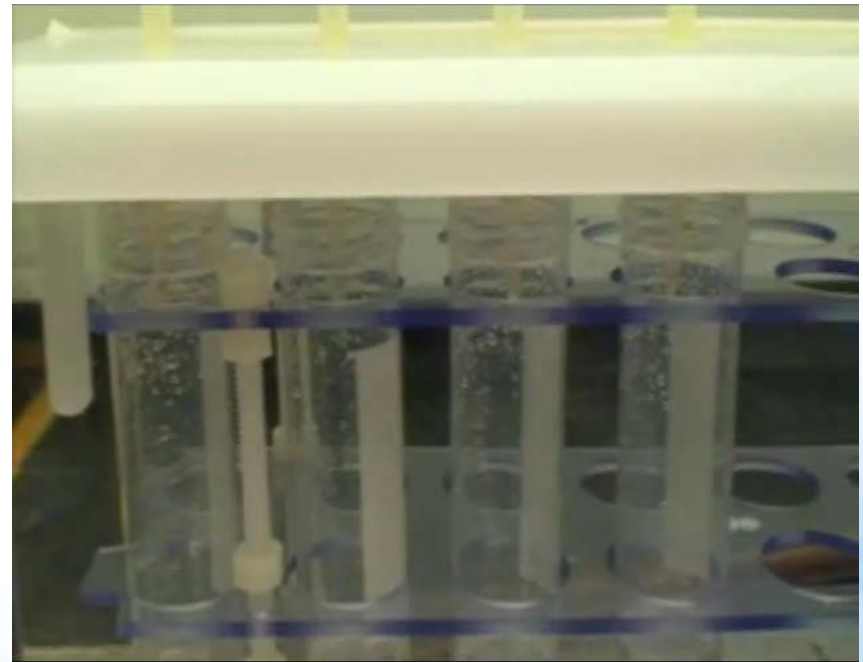


Developments

- **Actinides in urine**
 - NRIP-08 performance (urine/water)
 - Procorad results
 - Actinides by ICP-MS + alpha spectrometry (new hybrid approach)
- **Actinides in fecal samples**
 - New fecal method (CeF₃ matrix removal)
 - Procorad results
- **Actinides in soil samples**
 - Enhanced Po-210 removal

NRIP-08 Performance

- Vacuum essential
- Fastest times ever
- Doubled flow rates





Improvements in NRIP -2008 Urine Samples

	NRIP 2006	NRIP 2007	NRIP 2008
Actinides			
Am-241	7.4 hrs	4.6 hrs	3.1 hrs
Pu-238, 239	7.4 hrs	4.8 hrs	3.3 hrs
U-234, 235, 238	7.4 hrs	5.2 hrs	4.2 hrs
Strontium-90	5.8 hrs	3.9 hrs	2.9 hrs
Gamma isotopes	5.3 hrs	5.0 hrs	N/A

NRIP 2008 Am -241 in Urine in 3 hrs.

Sample ID	NIST Value (Bq/Smp)	SRS Reported Value (Bq/Smp \pm %, k=2)	Difference (\pm %)
724	0.1891	0.203 \pm 31%	+7
727	0.1965	0.221 \pm 29%	+12
735	0.4226	0.456 \pm 26%	+8
736	0.3759	0.366 \pm 27%	-3
742	0.4675	0.499 \pm 25%	+7
		Avg.	+6%

30 minute count



Procorad Results

- Participated in European Procorad Intercomparison program
- Actinides and Sr-90 in low level urine and fecal ash samples
- Urine
 - TEVA + TRU + Sr Resin separation
 - Cerium fluoride microprecipitation
- Fecal
 - Total dissolution (HCL-HF and boric fraction)
 - Cerium fluoride (+ Ca) matrix removal instead of Diphonix Resin
 - TEVA+TRU+DGA resin

Procorad Reference Values

		U-234	U-238	Am-241	Cm-244	Pu-239	Sr-90
		Ref	Ref	Ref	Ref	Ref	Ref
		mBq/smp	mBq/smp	mBq/smp	mBq/smp	mBq/smp	Bq/L
Uranium in urine	A	132	137				
Actinides in urine	B				1.96	1.86	
Sr in Urine	B						5.16
Sr in Urine	C						5.02
Fecal ashes	A	27.0	25.0		10.8	14.4	
Fecal ashes	B	28.3	24.9	22.2	43.1		
Fecal ashes	C	27.2	25.4				
Surprise urine				36.7		70.2	

1 pCi = 37 mBq



Procorad Results

		U-234	U-238	Am-241	Cm-244	Pu-239	Sr-90
		% Bias	% Bias	% Bias	% Bias	% Bias	% Bias
Uranium in urine	A	9.6	4.7				
Actinides in urine	B				6.5	22.5	
Sr in Urine	B						-5.9
Sr in Urine	C						-9.0
Fecal ashes	A	-5.03	-8.24		-6.04	-2.75	
Fecal ashes	B	-6.72	-7.2	0.67	-5.74		
Fecal ashes	C	2.36	-6.04				
Surprise urine				-4.22		-15.0	
	avg	0.05	-4.20	-1.78	-1.76	1.58	-7.45

Actinide Separation for ICP-MS

•Background

- Actinides in urine for emergency response
- Flow injection, automated systems
 - Complexity of instrumentation, reagent limitations
 - Valence control (Np), lower recoveries (~70 %)-Pu stripping

•Vacuum box alternative

- Simpler, less expensive
- Allows complex manipulations, multiple analytes
- Up to 24 samples simultaneously in 2-3 hours (<10 min per sample)
- Multiple vacuum boxes independent of ICP-MS - high throughput
- Flexible, direct aliquot or calcium phosphate precipitation

Advantages of this approach with ICP-MS

- **Effective separations with excellent recoveries**
 - Good Np-237 valence control
 - Effective stripping of Pu from TEVA
 - Rugged/excellent removal of uranium
- **ICP-MS friendly reagents**
- **What about shorter-lived actinides?**
 - Hybrid approach combines ICP-MS with alpha spectrometry for short-lived actinides
 - Pu-238, Am-241, Cm-244, etc.
- **Vernon Jones, SRS (ICP-MS)**

Isotope Mass vs Activity

Isotope	1/2 life	mBq in smp aliquot	pg/ml in 15 ml solution
Cm-244	1.81E+01	5.0	1.11E-04
Am-241	4.32E+02	5.0	2.62E-03
Am-243	7.38E+03	5.0	4.52E-02
Np-237	2.14E+06	5.0	1.28E+01
Pu-238	8.78E+01	5.0	5.26E-04
Pu-240	6.57E+03	5.0	3.97E-02
Pu-239	2.41E+04	5.0	1.45E-01
Pu-242	3.76E+05	5.0	2.29E+00
U-232	7.20E+01	5.0	4.21E-04
U-234	2.44E+05	5.0	1.44E+00
U-235	7.04E+08	5.0	4.17E+03
U-238	4.47E+09	5.0	2.68E+04

5 mBq = 0.135 pCi

Isotope Mass vs Activity

Isotope	1/2 life	m B q in smp aliquot	pg/ml in 15 ml solution
C m -244	1.81E+01	200.0	4.45E-03
A m -241	4.32E+02	200.0	1.05E-01
A m -243	7.38E+03	200.0	1.81E+00
N p -237	2.14E+06	200.0	5.11E+02
P u -238	8.78E+01	200.0	2.10E-02
P u -240	6.57E+03	200.0	1.59E+00
P u -239	2.41E+04	200.0	5.81E+00
P u -242	3.76E+05	200.0	9.17E+01
U -232	7.20E+01	200.0	1.68E-02
U -234	2.44E+05	200.0	5.75E+01
U -235	7.04E+08	200.0	1.67E+05
U -238	4.47E+09	200.0	1.07E+06

200 mBq =5.40 pCi

Actinides Separation for ICP-MS

Calcium phosphate precipitation option*

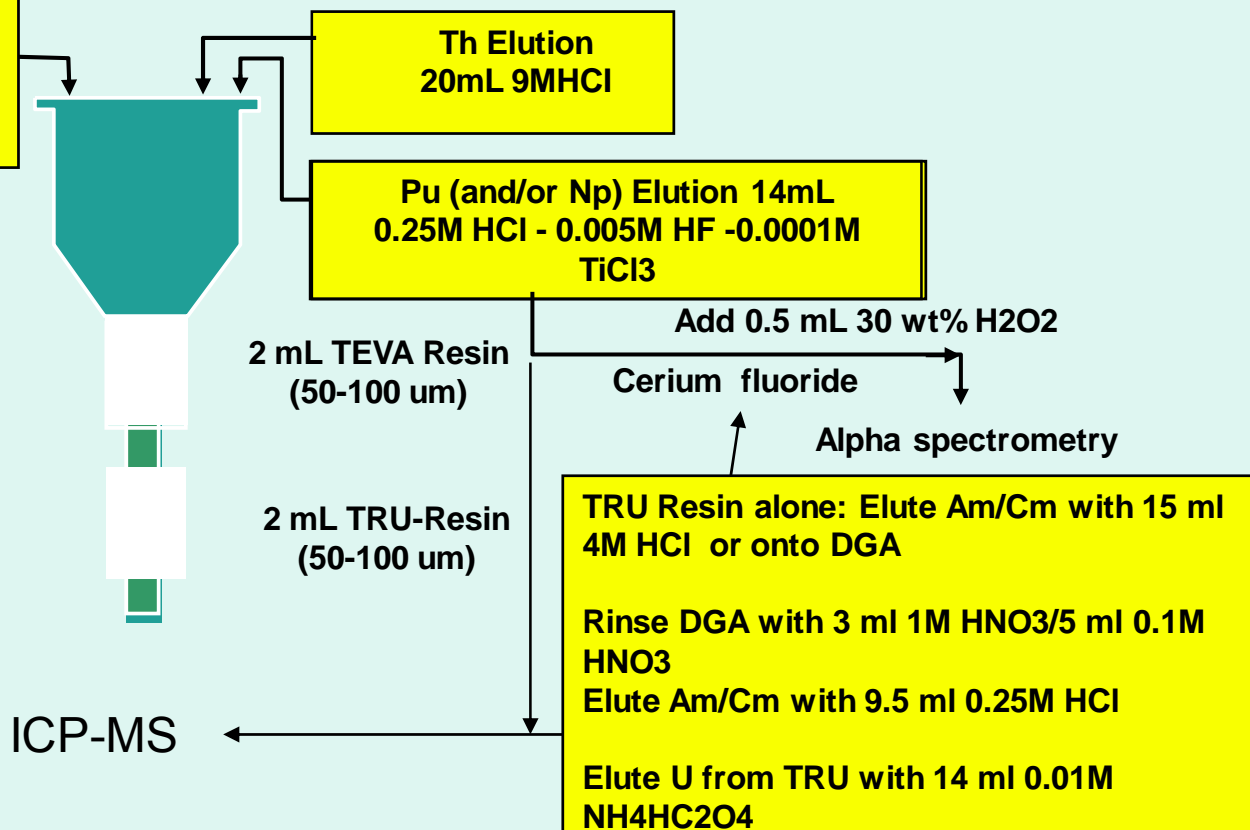
- 1) Redissolve in 8 mL 6M HNO₃ and 8 mL 2M Al(NO₃)₃ OR
- 2) Adjust small sample aliquot with con. HNO₃
- 3) Add 1.5M Sulfamic Acid + 1.5M Ascorbic Acid
- 4) Add 3.5 M Sodium Nitrite

Beaker/tube rinse: 3mL 3MHN03
5mL 3M HN03 to stacked cartridges

Separate cartridges:
TEVA Resin alone: 15 mL 3M HN03

*for larger urine aliquots only

Can use DGA if U not needed



ICP-MS Agilent HP 4500





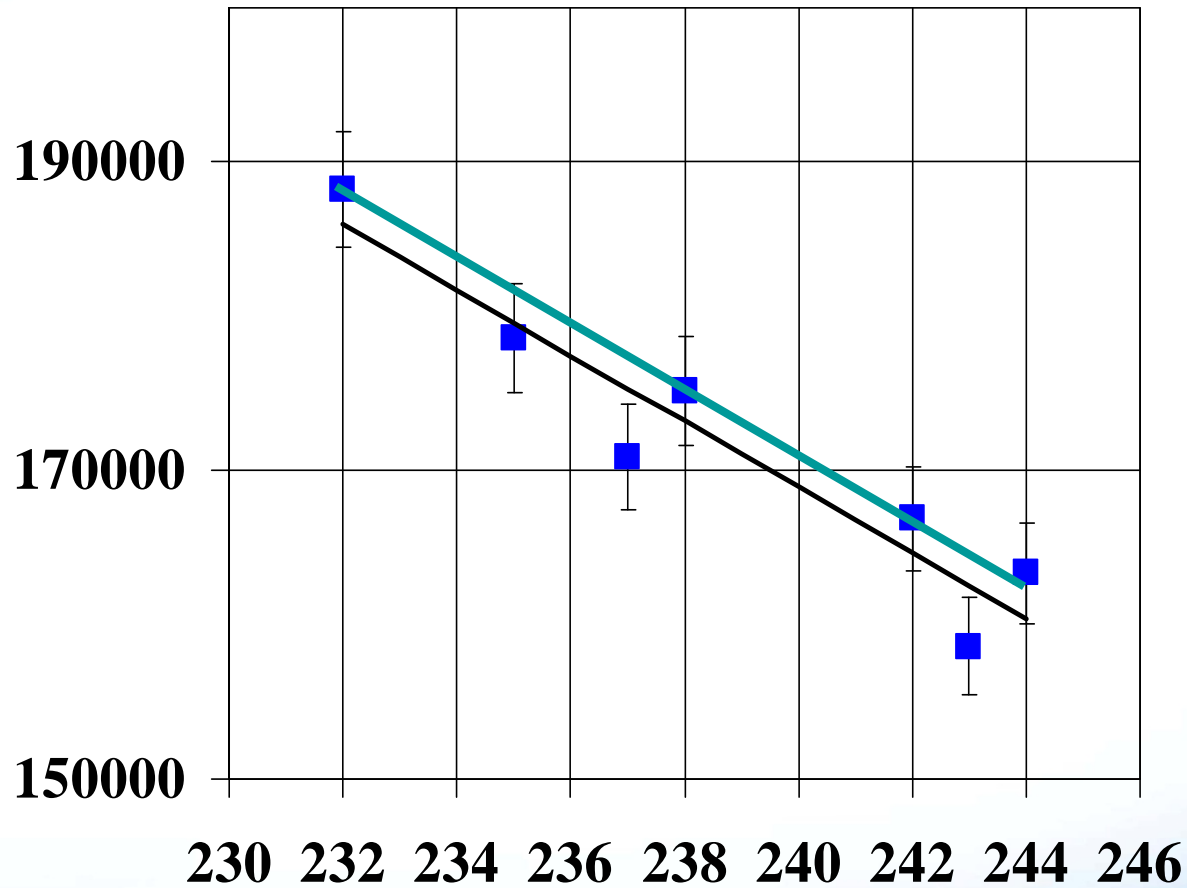
Instrument Parameters

- Agilent 4500 ICP-MS
- Sample Intro:
 - Teflon Microflow nebulizer, 400 uL/min
 - Quartz double pass spray chamber
- Tuning Parameters:
 - RF Power 1400 W
 - Sample Torch Depth 8.5 mm
 - Carrier Gas 0.7-0.8 L/min
- Calibration:
 - ASTM C 1590-04, "Standard Practice for Alternate Actinide Calibration for Inductively Coupled Plasma - Mass Spectrometry"
 - vernon.jones@srs.gov
 - 5 point external calibration from 0 - 150 ug/L (Th-232, U-238)



Actinide Mass / Response Curve* 09/98

*Dependant upon instrument tuning parameters



U-238 in NRIP Urine Sample

U-238 Reference ng/ml	U-238 Measured ng/ml	% Diff
60.99	63.32	3.82
60.99	63.45	4.03
60.99	61.76	1.26
60.99	58.02	-4.87
60.99	60.82	-0.28
60.99	56.73	-6.99
60.99	54.38	-10.84
60.99	56.22	-7.82
Avg.	59.34	-2.71

Reference value in final solution based on 5 ml aliquot diluted to 15 ml

U-234 in NRIP Urine Sample

U-234 Reference ng/ml	U-234 Measured ng/ml	% Diff
0.0032	0.0036	13.92
0.0032	0.0040	26.58
0.0032	0.0033	4.43
0.0032	0.0036	13.92
0.0032	0.0038	20.25
0.0032	0.0035	10.76
0.0032	0.0029	-8.23
0.0032	0.0043	36.08
Avg.	0.0036	14.72

Reference value in final solution based on 5 ml aliquot diluted to 15 ml

U-235 in NRIP Urine Sample

U - 2 3 5 R e f e r e n c e n g / m l	U - 2 3 5 M e a s u r e d n g / m l	% D i f f
0 . 4 3 1 5	0 . 4 5 9 3	6 . 4 5
0 . 4 3 1 5	0 . 4 5 7 6	6 . 0 5
0 . 4 3 1 5	0 . 4 4 4 0	2 . 9 0
0 . 4 3 1 5	0 . 4 1 9 1	- 2 . 8 7
0 . 4 3 1 5	0 . 4 4 6 0	3 . 3 6
0 . 4 3 1 5	0 . 4 0 9 3	- 5 . 1 4
0 . 4 3 1 5	0 . 3 8 7 7	- 1 0 . 1 5
0 . 4 3 1 5	0 . 4 1 3 6	- 4 . 1 5
A v g .	0 . 4 2 9 6	- 0 . 4 4

Reference value in final solution based on 5 ml aliquot diluted to 15 ml

Pu in 100 ml Urine (alpha)

	Pu-236	Pu-239	Pu-239	% Diff	Pu-238	Pu-238	% Diff
	%	pCi added	pCi		pCi added	pCi	
1	111	22.5	19.6	-12.89	0.98	0.97	-1.02
2	104	22.5	22.4	-0.44	0.98	0.93	-5.10
3	108	22.5	22.2	-1.33	0.98	0.964	-1.63
4	107	22.5	22	-2.22	0.98	1.02	4.08
Avg	107.5	22.50	21.55	-4.22	0.98	0.97	-0.92

Am/ Cm in 100 ml Urine (alpha)

	Am-243	Am-241	Am-241	% Diff	Cm-244	Cm-244	% Diff
	%	pCi added	pCi		pCi added	pCi	
1	96.7	1.00	1.05	5	0.93	0.90	-2.9
2	100.1	1.00	0.89	-10.7	0.93	0.79	-15.1
3	98.7	1.00	0.90	-10	0.93	0.91	-2.2
4	95.6	2.00	1.81	-9.5	1.86	1.70	-8.6
5	98.3	2.00	1.81	-9.5	1.86	1.61	-13.4
Avg.	97.9			-6.9			-8.4

Pu/Np in 100 ml Urine (ICP-MS)

	Pu-242	Pu-242	% Diff	Np-237	Np-237	% Diff
	ng/ml	ng/ml added		ng/ml	ng/ml added	
1	0.110	0.1366	-19.5	0.166	0.1825	-9.1
2	0.130	0.1366	-5.0	0.196	0.1825	7.2
3	0.127	0.1366	-6.7	0.211	0.1825	15.6
4	0.130	0.1366	-4.6	0.197	0.1825	7.7
Avg	0.124	0.1366	-9.0	0.192	0.1825	5.3

No tracer correction

Am in 100 ml Urine (ICP-MS)

	Am-243	Am-243	% Diff
	ng/ml	ng/ml added	
1	0.023	0.0253	-10.2
2	0.022	0.0253	-11.1
3	0.023	0.0253	-9.0
4	0.020	0.0253	-20.5
5	0.023	0.0253	-10.5
6	0.023	0.0253	-9.9
Avg	0.022	0.0253	-12.7

No tracer correction/direct std Am-243 measured 0.021 ng/ml (-17%)



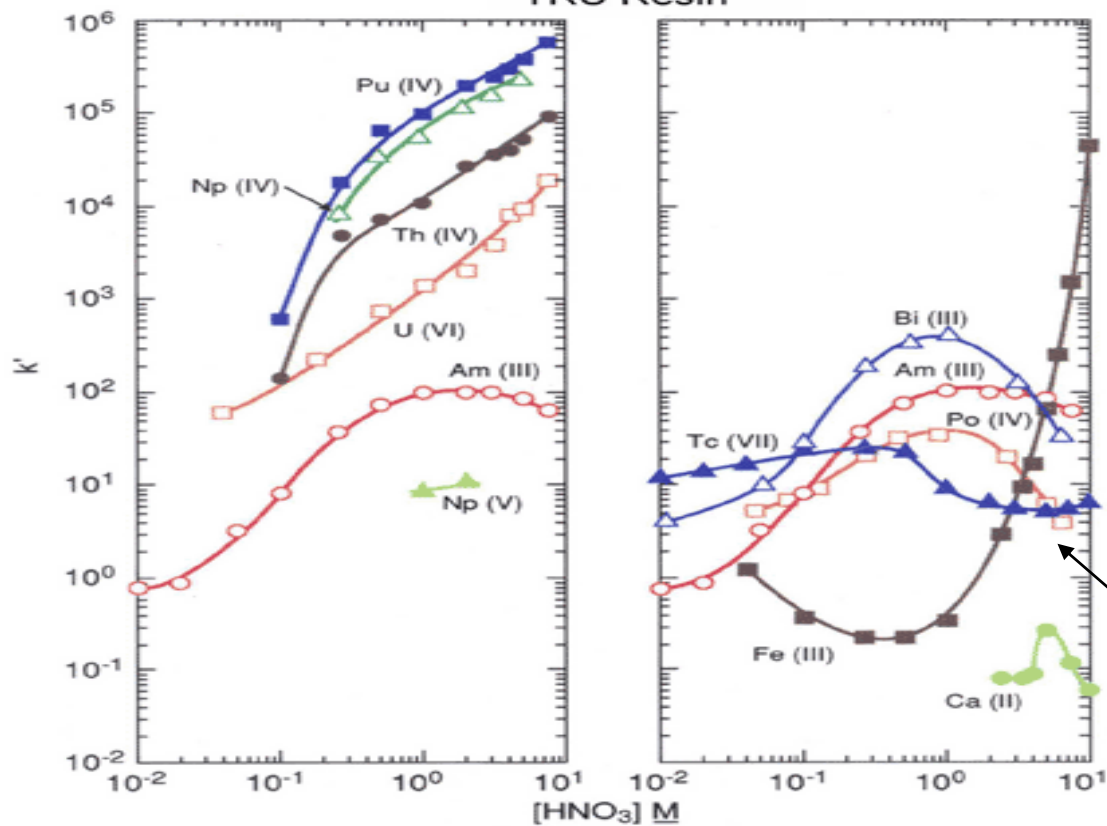
Improved Removal of Po-210 in Soil Samples

- **SRS method**
 - Sodium Hydroxide fusion
 - TEVA+TRU+DGA Resin
- **Po-210 in Soil**
 - Interferes with U-232 tracer correction
- **Po-210 removal**
 - Typically use 7-8M HNO₃ rinse on TRU Resin
 - Some samples require a lot of 8M HNO₃

Po-210 Removal On TRU Resin

Figure 2

Acid dependency of k' for various ions at 23-25°C.
TRU Resin

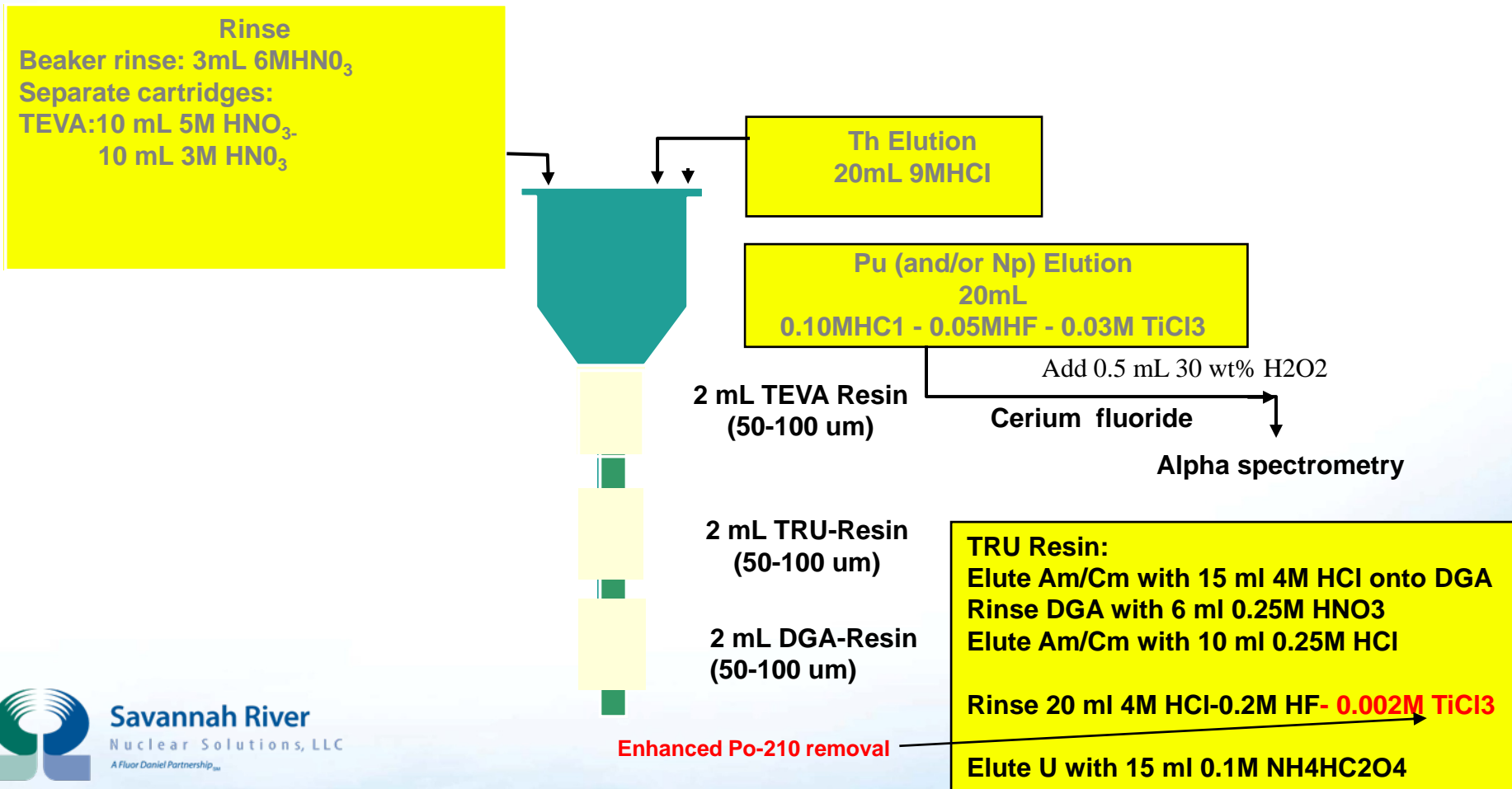


Po-210 Removal

Horwitz, et al. (HP193)

Improved Po-210 Removal-Soil

- 1) Redissolve in 5 mL warm 3M HNO₃ - 0.25M boric acid, add 6mL 7M HNO₃ and 7.5 mL 2M Al(NO₃)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



MAPEP 18 Soil Test: New Po-210 Removal

	U-234	U-238
	Bq/Kg	Bq/Kg
MAPEP 18	143.9	145.0
MAPEP 18	137.6	148.4
MAPEP 18	144.7	140.2
Avg.	142.1	144.5
Rsd	2.72	2.83
Ref	142	148
% Diff.	0.06	-2.33



Summary

- **Improvements in emergency method continuing**
 - Higher flow rates feasible
 - Best times ever NRIP-08
- **Adaptable to routine bioassay**
 - Procorad results
 - Urine and fecal
- **ICP-MS plus alpha spectrometry (hybrid option)**
- **Po-210 removal critical for soil**
 - 4M HCl-0.2M HF-0.002M TiCl_3 effective alternative to 8M HNO_3 on TRU