Savannah River
Nuclear Solutions, LLC
A Fluor Daniel Partnership SM

Rapid Analysis of Emergency Water and Urine Samples

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Aiken, SC
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Background

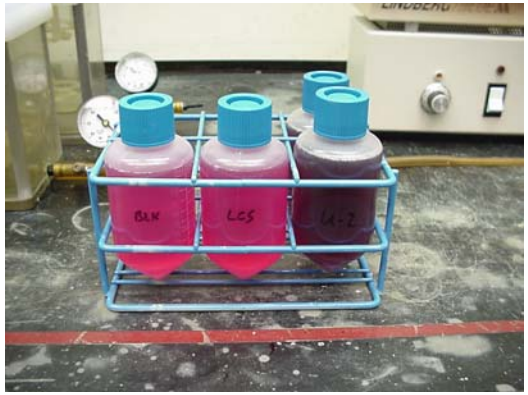
- Radiological Preparedness Exercise (NRIP) administered by NIST
  - emergency analysis samples with 1 day notice
  - Dr. Ken Inn, NIST, spoke at RRMC-2004 of the “need to improve efficiency and effectiveness of radioanalytical capabilities”
- Need for faster methods for Homeland Security
  - SRS Lab has developed rapid methods for actinides and Sr-90 analysis
  - participated in NRIP-06, NRIP-07 and NRIP-08 for water and urine samples

SRS Lab Performance-NRIP-08

- Per NIST, SRS lab had the fastest times reported actinides and Sr-90 for water and urine samples in NRIP-2008
- Quality of results was good
- Improvements in NRIP-2008
  - Larger sample aliquots
    - Urine-5X
    - Water-3X
  - Shorter count time
    - 1/2
  - Faster flow rates
    - 2x

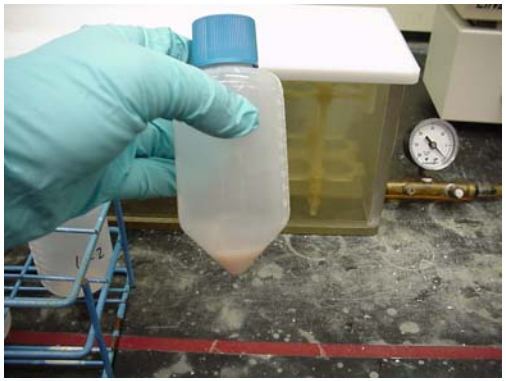
Calcium Phosphate Precipitation

225 ml tubes



500 ml tubes

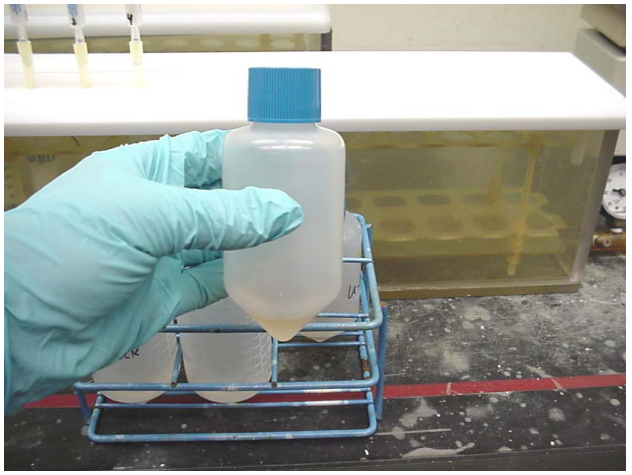
100 ml urine aliquot

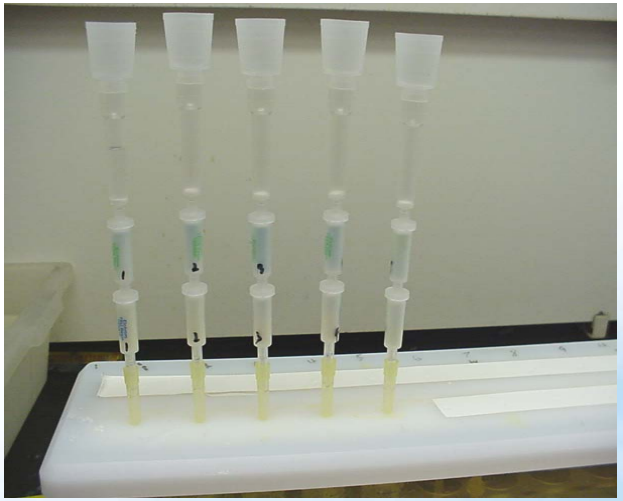


400 ml water aliquot

Faster Flow Rates

- Load directly from centrifuge tubes
- Load at ~2 drops per second
- Rinses at ~3-4 drops per second
- Strip at ~2 drops per second
  - Ce and HF already in collection tubes
  - 10 minute wait time





Actinides and Sr-90 in Urine-NRIP 2008

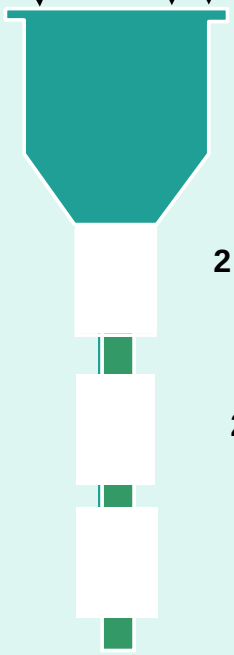
Calcium phosphate precipitation

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 2 mL 3.5 M Sodium Nitrite

Vacuum box procedure

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

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



Th Elution
20-25 mL
9MHCl

Pu (and/or Np) Elution
20mL
0.10M HCl - 0.05M HF - 0.03M TiCl3

2 mL TEVA Resin
(50-100 um)

Add 0.5 mL 30 wt% H2O2

Cerium fluoride

Alpha spectrometry

2 mL TRU-Resin
(50-100 um)

Cerium fluoride

2 mL Sr-Resin
(50-100 um)

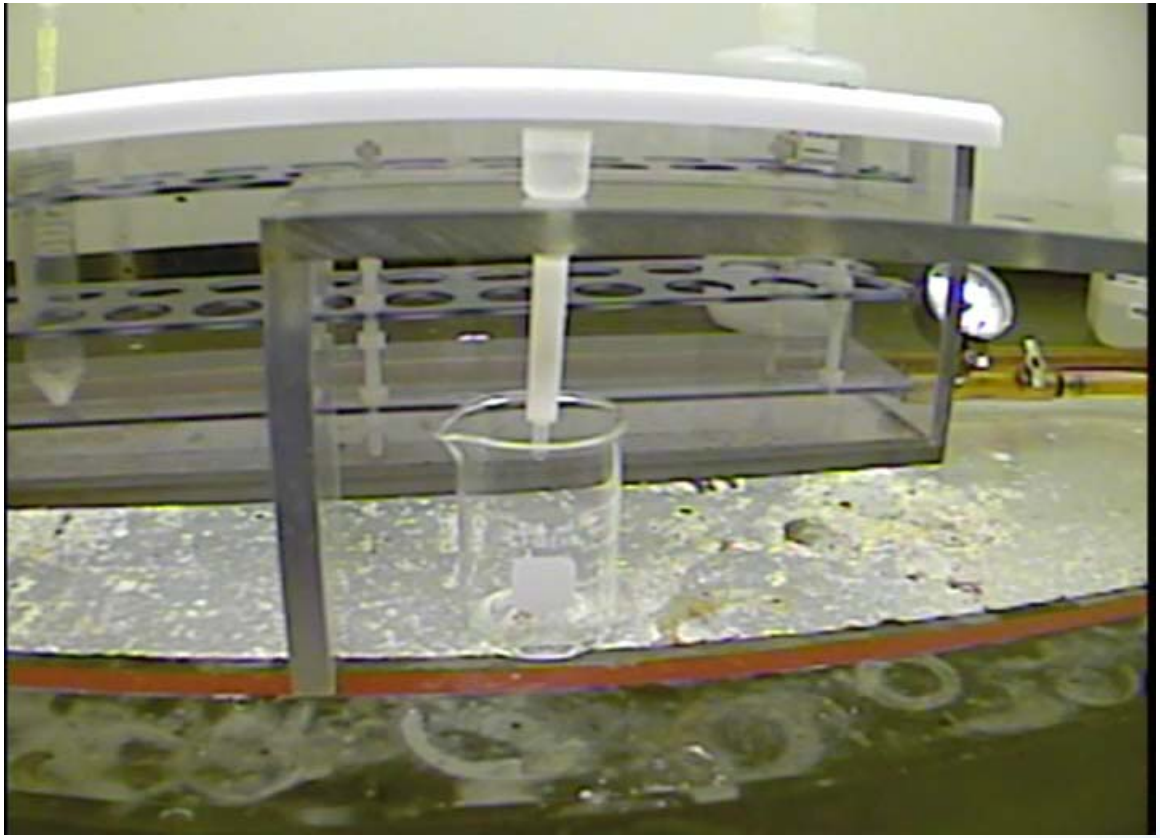
Sr Resin alone:
15 mL 8MHN03
10 mL 0.05M strip Sr

Evaporate/ beta counting

TRU Resin alone:
Elute Am/Cm with 15 ml 4M HCL/add
15 ml H20 + 50 ug Ce+ 3 ml HF

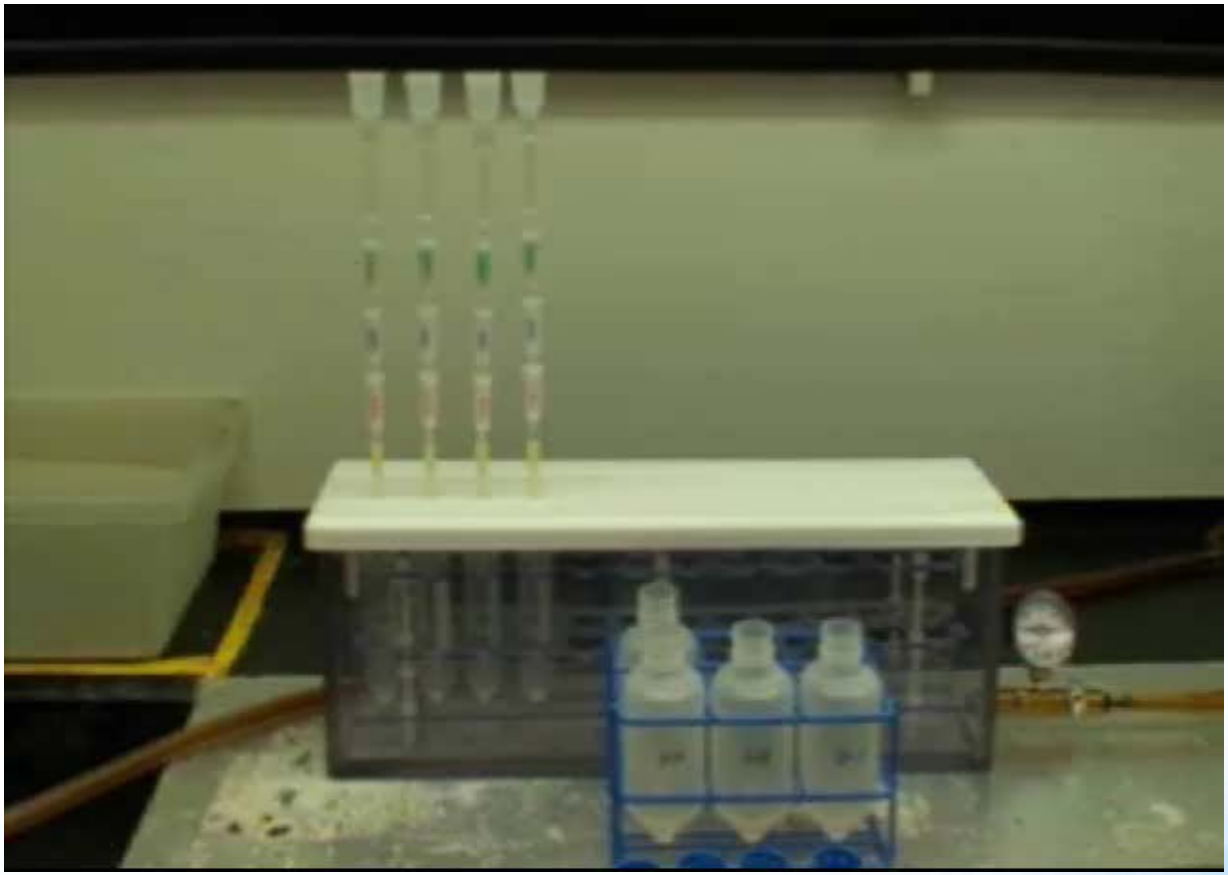
Rinse 12 ml 4M HCl-0.2M HF
Elute U with 15 ml 0.1M NH4HC2O4

Gravity Flow



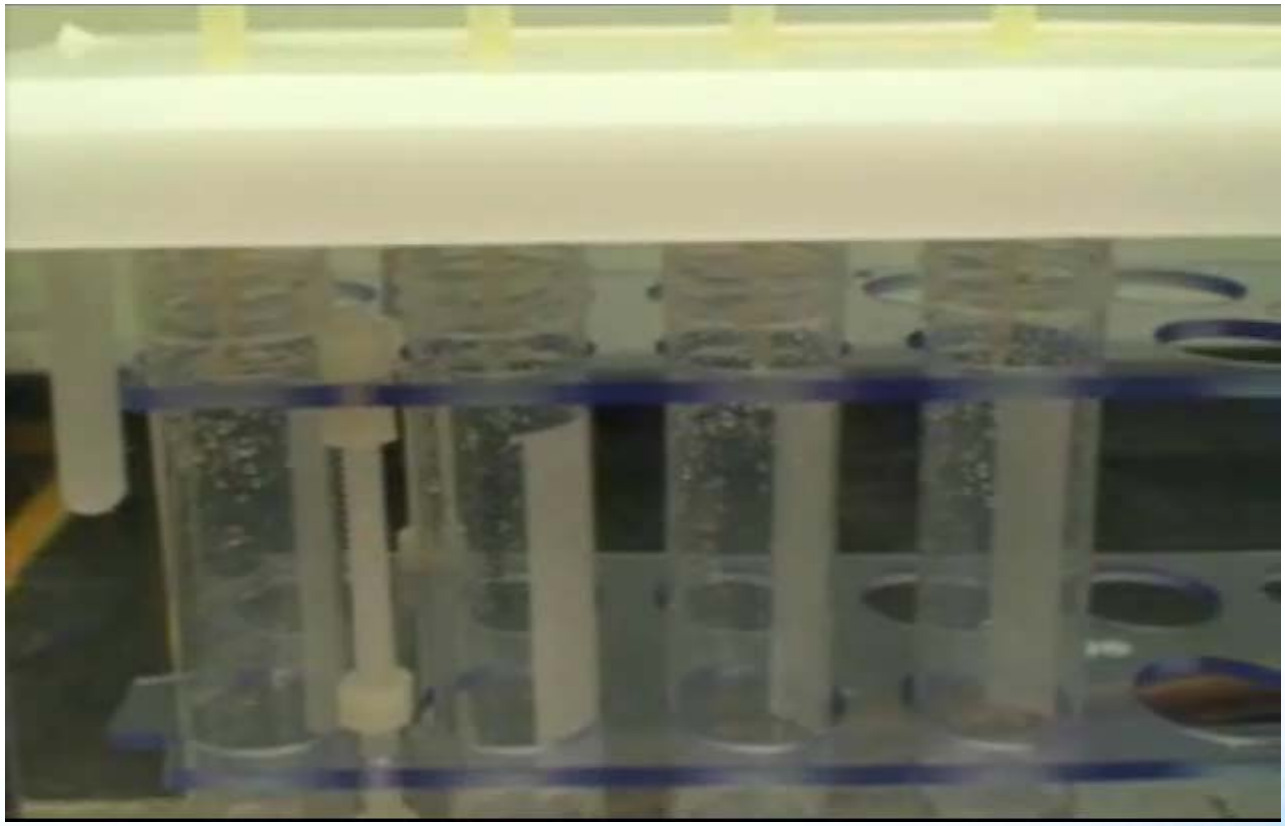
NRIP-07 Flow rates

Load solution ~ 1 drop per second



NRIP-08 Flow rates

Load solution ~ 2 drops per second

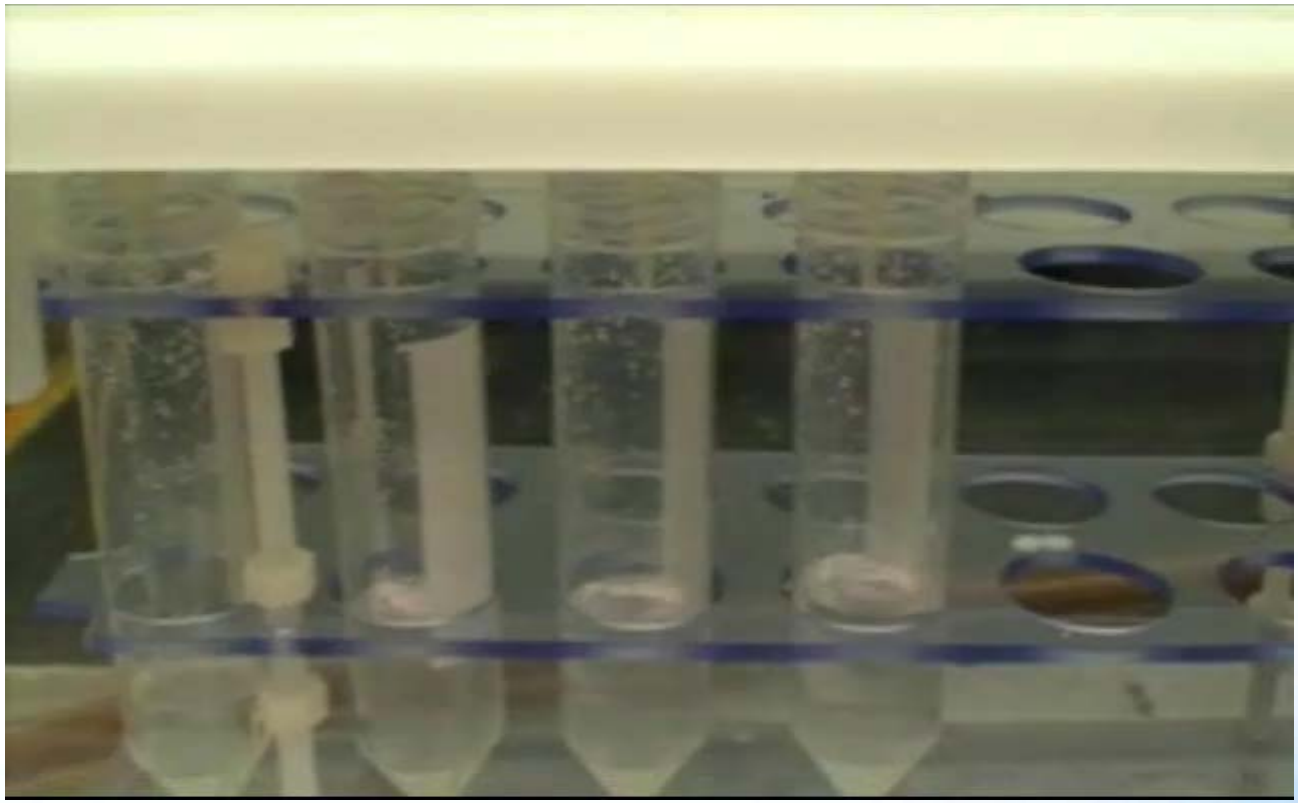


NRIP-07 Flow rates

Rinse solution ~ 1-2 drops per second
Strip solution ~ 1 drop per second

NRIP-08 Flow rates

Rinse solution ~ 3-4 drops per second
Strip solution ~ 2 drops per second



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

Improvements in NRIP -2008 Water Samples

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
Gamma isotopes	6.2 hrs	2.5 hrs	3.9 hrs

NRIP-2008 Water Analysis Results

Nuclide	Avg. Difference Reported vs NIST	Avg. Difference Longer Recounts
Pu-238	13 %	6.3%
Pu-240	- 2.3%	-4.5%
Am-241	9.6%	1%
U-238	-0.5%	-5.4%
U-234	9.0%	-6.7%
Sr-90	-14 %	N/A

Actinides: 45 minute count time / Recounts: 2 hour count time

NRIP-2008 Urine Analysis Results

Nuclide	Avg. Difference Reported vs NIST	Avg. Difference Longer Recounts
Pu-238	24%	24%
Pu-239	16%	18%
Am-241	6 %	1%
U-238	-41%	-1.6%*
U-234	-46%	-3.1%*
Sr-90	1.7%	N/A

Actinides: 30 minute count time / Recounts: 2 hour count time

*With additional purification

NRIP 2008 Am -241 in Urine in 3 hrs.

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

30 minute count

NRIP 2008 Am -241 in Water in 3.5 hrs

Sample ID	NIST Value (Bq/Smp)	SRS Reported Value (Bq/Smp ± %, k=2)	Difference (±%)
9	0.765	0.871 ±21%	+14
13	0.649	0.587 ±21%	-9
16	0.445	0.491 ±23%	+10
27	0.445	0.530 ±22%	+19
42	0.175	0.199 ±30%	+14
		Avg.	+9.6%

45 minute count

NRIP 2008 U-238 in Urine

Sample ID	NIST Value (Bq/Smp)	SRS Reported Value (Bq/Smp ± %, k=2)	Difference (±%)
724	0.2137	0.160 ±32%	-25
727	0.2220	0.193 ±32%	-13
735	0.4776	0.178 ±29%	-63
736	0.4248	0.218 ±32%	-49
742	0.5284	0.236 ±33%	-55

What happened?

- QC was good
- NRIP-07 Uranium urine results excellent
- NRIP-08 Uranium water results very good

NRIP 2008 U-238 in Water

Sample ID	NIST Value (Bq/Smp)	SRS Reported Value (Bq/Smp ± %, k=2)		Difference (±%)
9	0.8635	0.981 ±26%		+13
13	0.7327	0.731 ±24%		-0.2
16	0.5020	0.478 ±26%		-4.8
27	0.4835	0.481 ±25%		-0.5
42	0.1975	0.177 ±35%		-10
			Avg.	-0.5

What happened?

- 100 % of 100 ml urine sample (20% in NRIP-07)
- 40% of 1 L water sample (15% in NRIP-07)
- Same chemistry for water/urine with faster flow rates
- Po-210 has 5.30 meV alpha energy
- U-232 tracer has 5.26 and 5.32 MeV alpha energies
- Po-210 in NRIP samples much higher than routine samples
- Po-210/U-232 ratio

Po-210 to U-232 Tracer Ratio (NRIP Urine)

Sample ID	Po-210 added (dpm)	Po-210/U-232 Ratio	Bias (%)
724	23.08	1.05	-25
727	23.98	1.09	-13
735	51.58	2.35	-63
736	45.87	2.09	-49
742	57.06	2.60	-55

Po-210 to U-232 Tracer Ratio (NRIP Water)

Sample ID	Po-210 added (dpm)	Po-210/U-232 ratio	Bias (%)
9	37.30	1.70	13.6
13	31.65	1.44	-0.23
16	21.69	0.99	-4.78
27	21.69	0.99	-0.80
42	8.53	0.39	-10.4

U-238 in Urine After Enhanced Po-210 Removal

Sample ID	NIST Value (Bq/Smp)	SRS Reported Value (Bq/Smp)		Difference (±%)
724	0.2137	0.223		+4.4
727	0.2220	0.209		-5.9
735	0.4776	0.487		+2.0
736	0.4248	0.412		-3.0
742	0.5284	0.501		-5.2
			Avg	-1.6
729 *	0.228	0.217		-4.8
730 **	0.181	0.181		0

- Analysis of additional NRIP samples using enhanced Po-210 removal options
  - * 15 ml 8M HNO3 rinse-TRU Resin
  - ** Added reductant (15-20 ml 4M HCL-0.2M HF-*0.001M* $TiCl_3$)-TRU Resin (no 8M HNO3)

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

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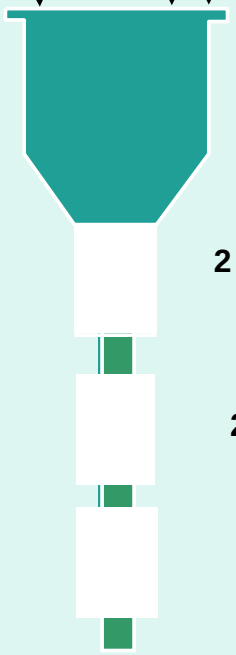

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2 mL TRU-Resin
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Sr Resin alone:
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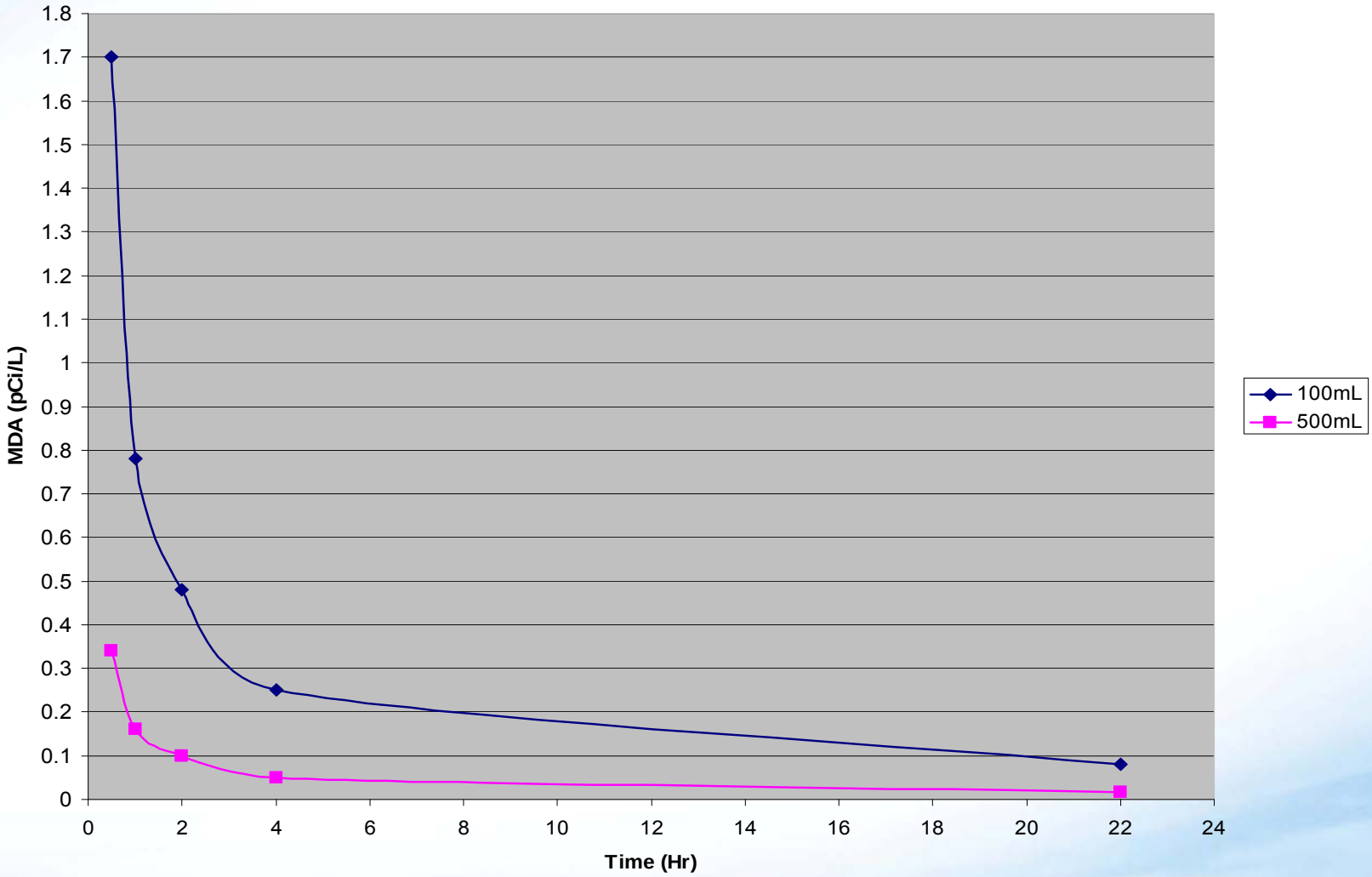
2 mL Sr-Resin
(50-100 um)

TRU Resin alone:
Elute Am/Cm with 15 ml 4M HCL/add
15 ml H20 + 50 ug Ce+ 3 ml HF
15 ml 4M HCl-0.2M *HF-0.001M TiCl3*
Or 15 ml 8M HNO3
Elute U with 15 ml 0.1M NH4HC2O4

Evaporate/ beta counting

Enhanced Po-210 removal

MDA (alpha) vs Time by Aliquot



Summary

- NRIP emergency exercise program
  - Valuable performance measurement and improvement tool
- SRS Environmental Bioassay Lab
  - Continual improvement NRIP-06 to NRIP-08
  - Actinides in 3 to 4 hours/ Sr-90 in ~ 3 hours
  - Need rugged methods/benefits routine methods
- Rapid emergency methods essential
  - Draft procedure ASTM D19.04 subcommittee/ rapid methods-water
  - Same column chemistry used at SRS for vegetation, fruit and air filters
  - Simultaneous separation of actinides can be adapted to ICP-MS
    - Flexible alternative to flow injection
    - ICP-MS friendly reagents developed
    - Hybrid approach (ICP-MS+ alpha)

Acknowledgements

- Chemists in SRS Environmental Bioassay Lab
  - Bioassay - Brian Culligan
  - Environmental-Don Faison, Jessie Melton
  - Vern Jones-ICP-MS
- Lab Technicians
  - Ken Mishoe, Dale Duke, Gene Cooke, Tony Melton, Becky Chavous, Jack Herrington, Dan Stewart, Christy Posey, Kim Larson