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Rapid Method for Actinides and Sr-89/90 in Limestone and Marble Samples

Sherrod L. Maxwell
Senior Fellow Scientist

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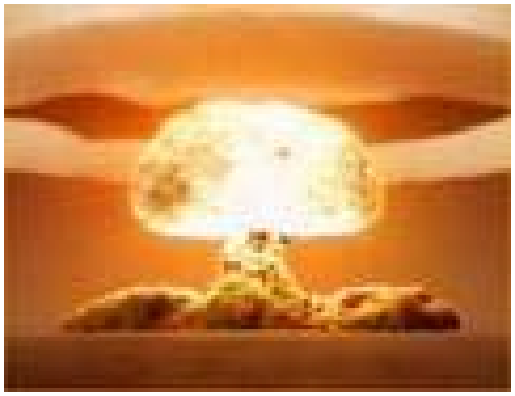
Background

- Need for rapid radiochemical methods
  - Emergency response
    - *IND, RDD, nuclear accident*
    - *Rapid turnaround times*
- Actinides and Sr-89/90
  - Environmental
  - Bioassay
  - Food
  - *Urban matrices….*



Urban Matrices

- Concrete – yes
- Brick - yes
- Asphalt - yes
- Others?
  - Limestone, marble, sandstone ….

RDD Samples…

- Limestone and marble?
  - have been used in many important buildings and monuments in the U.S, including the Pentagon, the Lincoln Memorial, the Washington Monument and the Empire State Building.

SRNS 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
  - Rapid assessment of radiological impact
  - Mitigate dose and protect the public and ecosystems
  - Maintain public trust

2009 NRIP Soil Samples

Nuclide	Turnaround Times
^{241}Am	4.42 hrs
$^{238, 239}Pu$	5.40 hrs
$^{234, 235, 238}U$	4.15 hrs

Maxwell, S., Culligan, B. and Noyes, G. (2010), Rapid method for actinides in emergency soil samples, Radiochimica Acta, Vol. 98, No. 12, pp. 793-800.

Need for Rugged Sample Digestion

- Recently ~80% of MAPEP labs failed Uranium in soil PT tests in Series 30
  - US and international labs
  - Even with HF added

MAPEP website:

- The soil used for MAPEP Series 30 contained a much higher concentration of this naturally occurring and more insoluble form of uranium.
- The laboratories using chemical procedures capable of dissolving the entire soil sample reported accurate results; while the laboratories using dissolution techniques that were unable to dissolve the insoluble form of the uranium reported results that were approximately 60% low.

- Example

Uranium-234/233	32.9	81	N	-59.4
Uranium-238	30.9	83	N	-62.8

Rapid Sample Preparation - Actinides

Add tracers to 1-2g limestone/marble in Zr crucible
Dry on hot plate

↓

Add 15g NaOH pellets.
Fuse sample at 600°C for ~15-20 min.

↓

Transfer fusion matrix to 225 ml centrifuge tube with water. Add 125 mg Fe, 5 mg La.
Dilute to 160 ml with water. Add 20 ml 12M HCl. Mix.
Cool with ice to room temp.
(U) Add 5ml 3.2 M $(NH_4)_2HPO_4$. Mix.

↓

Add 4 ml 20% $TiCl_3$. Cap and mix well
Cool with ice for ~10 min. Centrifuge 6 min. and discard supernate.

↓

Dilute to 80 ml with1.5M HCl and redissolve.
Dilute to 170 ml with 0.01M HCl, add 1mg La, 2 ml 20% $TiCl_3$ and 15 ml 28M HF.
Allow to stand for ~10 minutes.
Centrifuge 6 minutes and discard supernate.

↓

Redissolve in 7 ml 3M HNO_3-0.25M Boric acid, 6 ml 7M HNO_3, 7 ml 2M $Al(NO_3)_3$ and 3 ml 3M HNO_3.
Mix, warm briefly in a hot bath and centrifuge to check for any solids.

↓

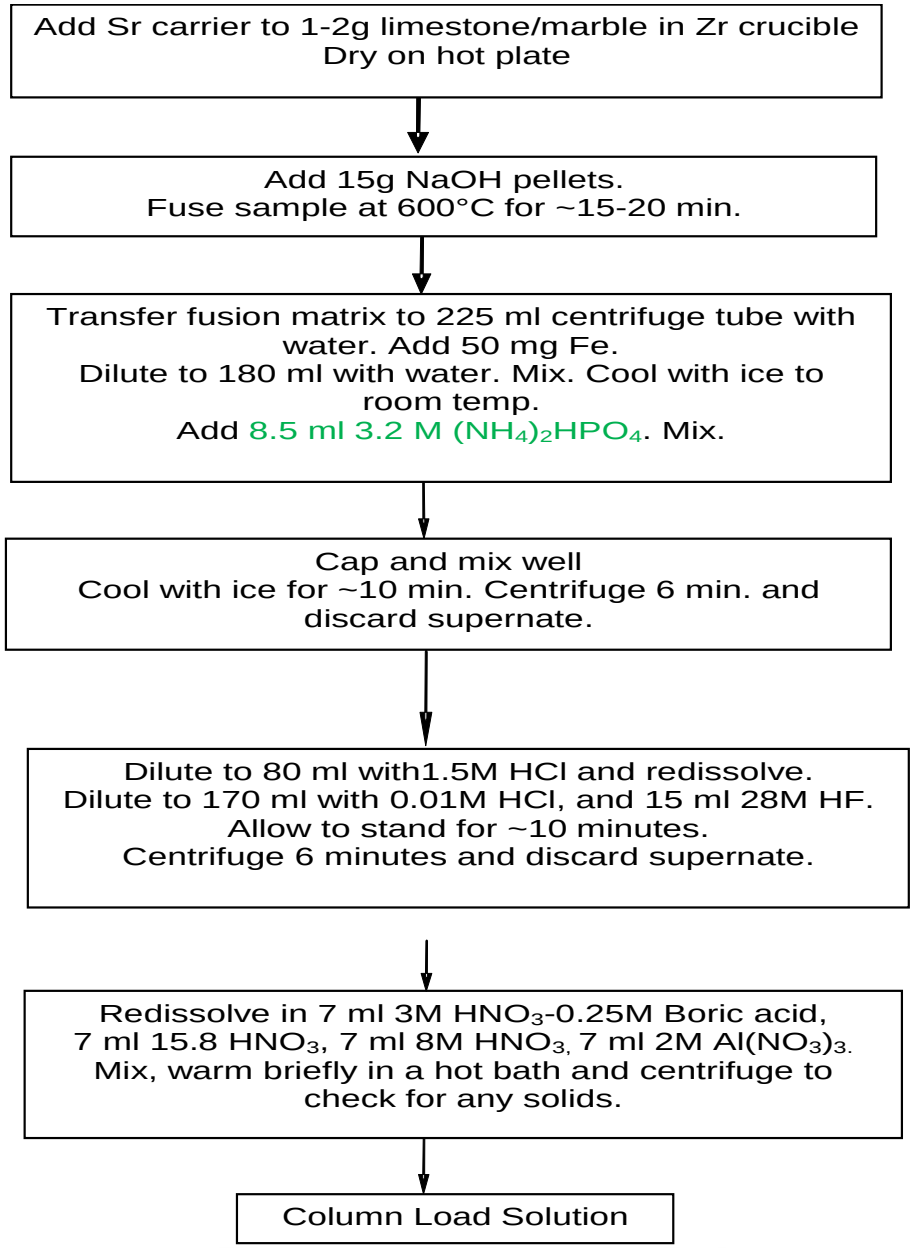
Column Load Solution

Add con HCl to reduce Ca ppt..
And neutralize some CO_3^{3-}

No additional Ca!

PO_4^{3-} seems to enhance tracer equilibration with U

Rapid Sample Preparation – Sr-89/90

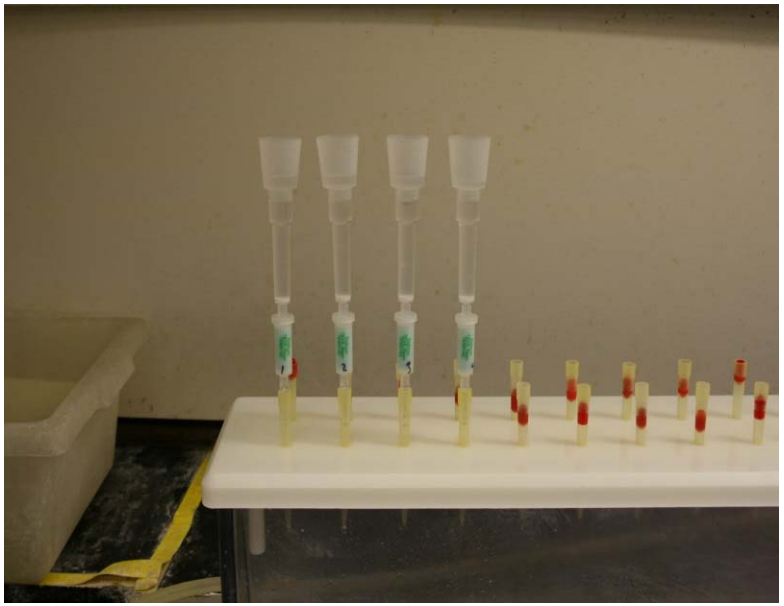


How different from actinides?

- No con. HCl
- Less Fe
- No Ti^{+3}
- High PO_4^{-3} (to ensure good Sr ppt)
- Higher nitrate in load solution

Column Separation Options

- Pu, Np – TEVA Resin
- Am, Cm- TEVA Resin + DGA Resin
- U - TEVA Resin + TRU Resin
- Sr- Sr Resin (and DGA Resin)



J Radioanal Nucl Chem (2015) 305:631–641
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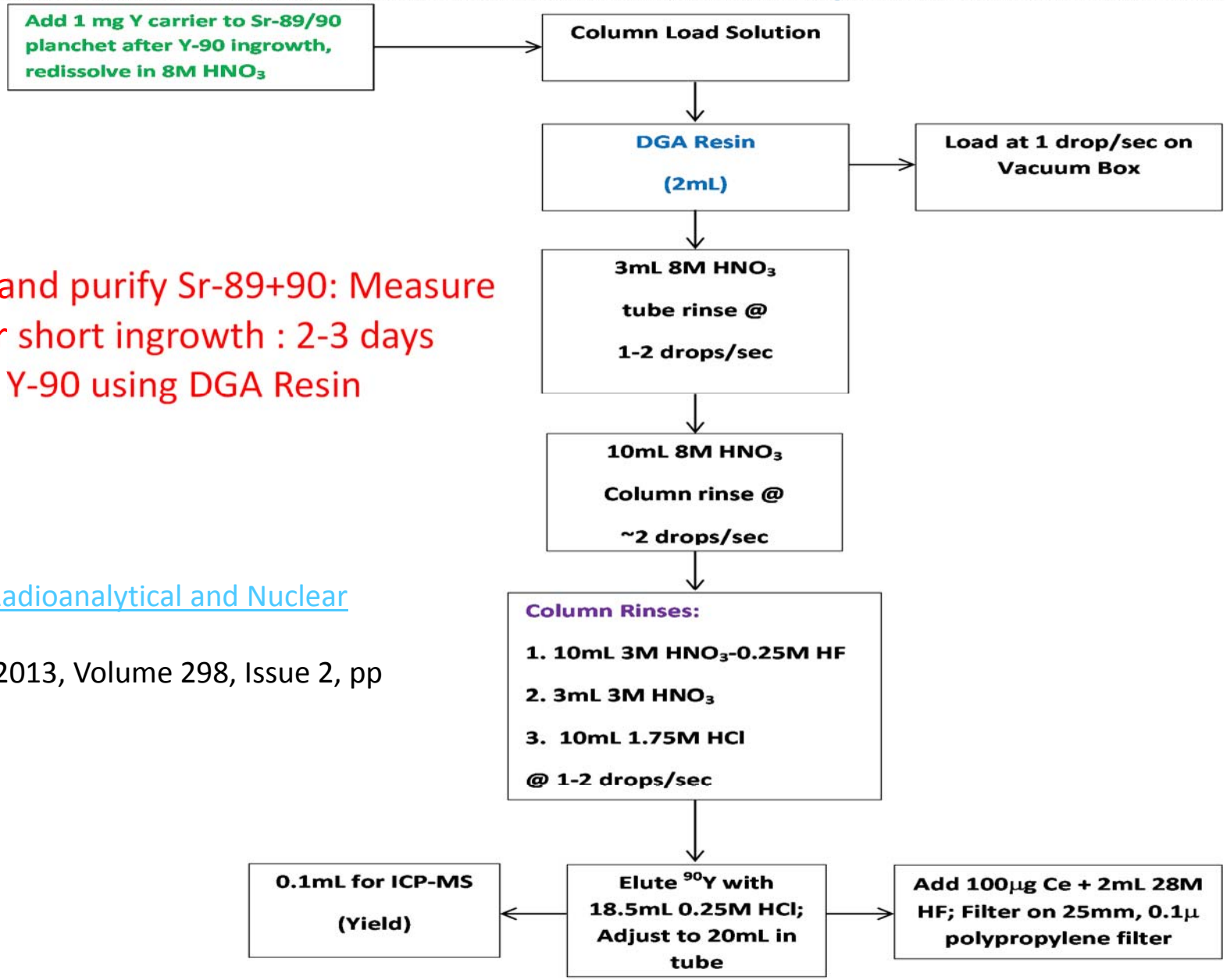
CrossMark

Rapid fusion method for the determination of refractory thorium and uranium isotopes in soil samples

Sherrod L. Maxwell · Jay B. Hutchison · Daniel R. McAlister

High Sr-89/Low Sr-90 following FP Incident

1. Collect and purify Sr-89+90: Measure
2. Wait for short ingrowth : 2-3 days
3. Collect Y-90 using DGA Resin



Journal of Radioanalytical and Nuclear Chemistry
November 2013, Volume 298, Issue 2, pp 867-875

Pu-239/240 Results for Limestone Spiked with MAPEP 24 Soil

Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	104.6	40.5	29.4	0.747	27.64	-6.0
2	98.9	50.1	29.4	0.803	29.71	1.1
3	104.5	27.1	29.4	0.819	30.30	3.1
4	92.1	34.4	29.4	0.731	27.05	-8.0
5	97.4	46.9	29.4	0.796	29.45	0.2
6	102.7	58.3	29.4	0.900	33.30	13.3
Avg. Spiked Smps	100.0			0.80	29.6	0.6
SD	4.9			0.06	2.2	7.5
% RSD	4.9			7.5	7.5	
			16 hour count	MAPEP 24 contains refractory Pu		

Shorter count times adequate with higher tracer activity for emergency

Pu-239/240 Results for Limestone Spiked with MAPEP 30 Soil

Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	91.3	32.5	23.0	0.682	25.23	9.5
2	87.8	70.8	23.0	0.604	22.35	-3.0
3	101.2	60.8	23.0	0.683	25.27	9.7
4	98.9	59.9	23.0	0.651	24.09	4.5
5	93.9	49.9	23.0	0.611	22.61	-1.9
6	85.7	82.7	23.0	0.618	22.87	-0.8
Avg. Spiked Smps	93.1			0.64	23.7	3.0
SD	6.1			0.04	1.3	5.7
% RSD	6.5			5.6	5.6	
			16 hour count			

Pu-238 Results for Limestone Spiked with MAPEP 30 Soil

Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{238}Pu Reference Value (mBq g^{-1})	^{238}Pu Measured Value (pCi g^{-1})	^{238}Pu Measured Value (mBq g^{-1})	Difference (%)
1	91.3	32.5	28.8	0.852	31.53	9.5
2	87.8	70.8	28.8	0.750	27.75	-3.7
3	101.2	60.8	28.8	0.808	29.90	3.8
4	98.9	59.9	28.8	0.809	29.93	3.9
5	93.9	49.9	28.8	0.711	26.29	-8.7
6	85.7	82.7	28.8	0.786	29.07	0.9
Avg. Spiked Smps	93.1			0.79	29.1	1.0
SD	6.1			0.05	1.8	6.4
% RSD	6.5			6.3	6.3	
			16 hour count			

Np-237 Results for Limestone Spiked with MAPEP 30 Soil

Sample ID	^{236}Pu Yield (%)	Tracer Peak (FWHM)	^{237}Np Reference Value (mBq g^{-1})	^{237}Np Measured Value (pCi g^{-1})	^{237}Np Measured Value (mBq g^{-1})	Difference (%)
1	91.3	40.5	37.0	1.06	39.22	6.0
2	87.8	50.1	37.0	1.15	42.55	15.0
3	101.2	27.1	37.0	1.10	40.52	9.5
4	98.9	34.4	37.0	0.98	36.26	-2.0
5	93.9	46.9	37.0	1.06	39.04	5.5
6	85.7	58.3	37.0	0.96	35.34	-4.5
Avg. Spiked Smps	93.1			1.05	38.8	4.9
SD	6.1			0.07	2.7	7.2
% RSD	6.5			6.9	6.9	
			16 hour count			

Pu-239/240 Results for Marble Spiked with MAPEP 24 Soil

Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Reference Value (mBq g^{-1})	^{239}Pu Measured Value (pCi g^{-1})	^{239}Pu Measured Value (mBq g^{-1})	Difference (%)
1	93.4	61.2	29.4	0.728	26.9	-8.4
2	93.6	50.9	29.4	0.860	31.8	8.2
3	98.7	46.9	29.4	0.814	30.1	2.4
4	98.5	39.2	29.4	0.839	31.0	5.6
Avg. Spiked Smps	96.0			0.81	30.0	2.0
SD	2.9			0.06	2.1	7.3
% RSD	3.0			7.2	7.2	
			16 hour count	MAPEP 24 contains refractory Pu		

Am-241 Results for Marble Spiked with MAPEP 32 Soil

Sample ID	^{243}Am Yield (%)	Tracer Peak (FWHM)	^{241}Am Reference Value (mBq g^{-1})	^{241}Am Measured Value (pCi g^{-1})	^{241}Am Measured Value (mBq g^{-1})	Difference (%)
1	89.7	39.4	29.1	0.742	28.8	-0.9
2	92.3	35.8	29.1	0.742	28.8	-0.9
3	89.7	43.3	29.1	0.770	29.9	2.8
4	83.7	49.5	29.1	0.703	27.3	-6.1
Avg. Spiked Smps	88.8			0.74	28.7	-1.3
SD	3.7			0.03	1.1	3.7
% RSD	4.1			3.7	3.7	
			16 hour count			

Cm-244 Results for Marble Spiked with MAPEP 32 Soil

Sample ID	^{243}Am Yield (%)	Tracer Peak (FWHM)	^{244}Cm Reference Value (mBq g^{-1})	^{244}Cm Measured Value (pCi g^{-1})	^{244}Cm Measured Value (mBq g^{-1})	Difference (%)
1	89.7	39.4	34.8	0.908	33.6	-3.5
2	92.0	35.8	34.8	0.912	33.7	-3.0
3	89.7	43.3	34.8	1.032	38.2	9.7
4	82.4	49.5	34.8	0.882	32.6	-6.2
Avg. Spiked Smps	88.4			0.93	34.5	-0.7
SD	4.2			0.07	2.5	7.1
% RSD	4.7			7.2	7.2	
			16 hour count			

U-238 Results for Limestone Spiked with MAPEP 32 Soil

Sample ID	^{232}U Yield (%)	Tracer Peak (FWHM)	^{238}U Reference Value (mBq g^{-1})	^{238}U Measured Value (pCi g^{-1})	^{238}U Measured Value (mBq g^{-1})	Corrected for Native U (mBq g^{-1})	Difference (%)
1	86.9	67.6	50.2	1.58	58.5	50.0	-0.5
2	91.8	61.9	50.2	1.59	58.8	50.3	0.3
3	88.7	83.1	50.2	1.50	55.5	47.0	-6.4
4	100.5	32.7	50.2	1.54	57.0	48.5	-3.4
6	87.6	38.0	50.2	1.48	54.8	46.3	-7.8
7	101.5	40.0	50.2	1.54	57.0	48.5	-3.4
8	92.3	58.9	50.2	1.53	56.6	48.1	-4.2
Avg. Spiked Smps	92.8					48.4	-3.6
SD	6.0					1.5	2.9
% RSD	6.5					3.0	
			16 hour count		Native ^{238}U = 0.23 pCi/g (8.5 mBq/g)		

Added PO_4^{-3} to Fe/Ti precipitation

Increased nitrite plus wait time load solution to ensure U^{+6}

Sr-90 Results for Spiked Limestone - Initial

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq g^{-1})	^{90}Sr Measured Value (pCi g^{-1})	^{90}Sr Measured Value (Bq g^{-1})	Difference (%)
1	78.0	1.415	38.1	1.41	-0.5
2	69.2	1.415	38.3	1.42	0.1
3	71.9	1.415	37.4	1.38	-2.3
4	74.6	1.415	37.3	1.38	-2.5
5	76.7	1.415	36.8	1.36	-3.8
6	71.9	1.415	37.3	1.38	-2.5
7	74.0	1.415	40.2	1.49	5.1
Avg. Spiked Smps	73.8		37.9	1.40	-0.89
SD	3.0		1.13	0.04	2.95
% RSD	4.1		2.98	2.98	
		60 minute count			
		7 ml 3.2M PO4, 10 ml 28 M HF			

Can we increase chemical yields?

Sr-90 Results for Spiked Limestone – Increase PO_4^{-3}

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value ($Bq\,g^{-1}$)	^{90}Sr Measured Value ($pCi\,g^{-1}$)	^{90}Sr Measured Value ($Bq\,g^{-1}$)	Difference (%)
1	77.3	1.415	37.6	1.39	-1.6
2	76.0	1.415	38.6	1.43	1.0
3	74.6	1.415	38.3	1.42	0.2
Avg. Spiked Smps	76.0		38.20	1.41	-0.12
SD	1.4		0.50	0.02	1.32
% RSD	1.8		1.32	1.32	
		60 minute count			
		8.5 ml 3.2M PO4, 10 ml 28 M HF			

What else can we try?

Sr-90 Results for Spiked Limestone- Increase F^-

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value ($Bq\,g^{-1}$)	^{90}Sr Measured Value ($pCi\,g^{-1}$)	^{90}Sr Measured Value ($Bq\,g^{-1}$)	Difference (%)
1	84.1	1.415	38.2	1.41	-0.2
2	84.8	1.415	38.4	1.42	0.3
3	84.8	1.415	37.2	1.38	-2.7
Avg. Spiked Smps	84.6		37.92	1.40	-0.85
SD	0.4		0.61	0.02	1.60
% RSD	0.5		1.61	1.61	
		60 minute count			
		8.5 ml 3.2M PO4, 15 ml 28 M HF			

High levels of Ca in limestone/marble need more PO_4^{-3} and F^-

Acknowledgments

- Co-authors:
  - *Dr. Ralf Sudowe, UNLV*
  - *Brian Culligan, SRNS*

Summary

- Need for rapid methods for actinides and Sr-89/90 in urban matrices
  - *high chemical yields and removal of interferences*
  - *robust digestion of solid samples with potential refractory particles*

- Limestone and marble matrices have been tested with refractory particles added
  - With MAPEP 24 - refractory Pu
  - With MAPEP 30 - refractory U

- Additional urban matrices to investigate
  - *Granite*
  - *Sandstone*
  - *Steel*