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Rapid Fusion Method to Determine Sr-89/90 in Large Concrete Samples

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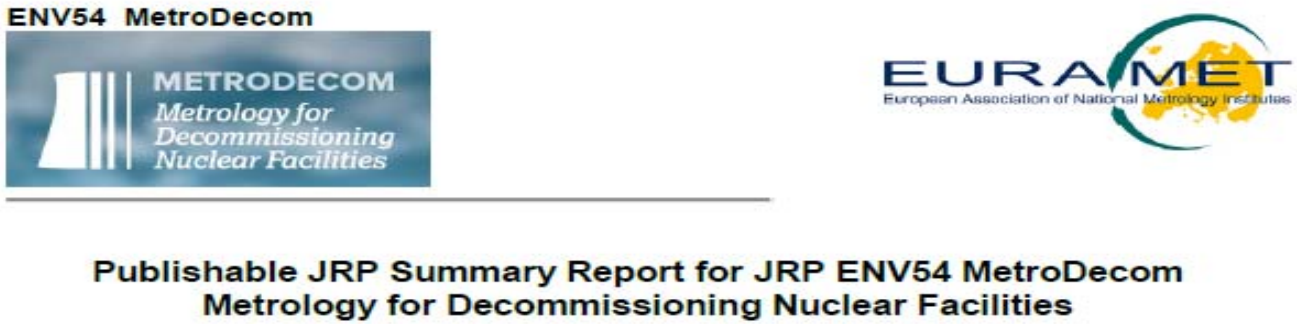
Background

- Need for rapid, reliable radiochemical methods to characterize materials to decommission older nuclear facilities, especially in Europe

- http://www.decommissioning-emrp.eu/?page_id=1300



D&D Analytical Challenges

- "Europe is facing an immediate and major challenge: *the enormous costs of decommissioning many old nuclear facilities*.
- Nuclear decommissioning …. covers all activities from shutdown and removal of fissile material to the environmental restoration of the site.
- *A significant reduction in the enormous decommissioning costs by development and implementation of new measurement techniques is necessary."*

SRNS Approach

- Previous publications on concrete, brick, asphalt and soil
  - Sr-89/90 in soil (large aliquots-acid leach)
    - *Journal of Radioanalytical and Nuclear Chemistry; v. 295(2); Feb 2013; p. 965-971*
  - Fusion of 10-20g soil/concrete for Pu, Np, Am, Cm published (2015)
  - 40g NaOH, large centrifuge tubes, total rapid digestion

J Radioanal Nucl Chem (2015) 305:599–608
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CrossMark

Rapid fusion method for the determination of Pu, Np, and Am in large soil samples

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SRNS Approach

- Could we apply a rapid fusion technique to determine Sr-90 with lower MDA in large concrete samples?
  - 5 to 10g sample aliquots
  - Goals:
    - *Reduced uncertainty for low level Sr-90 measurements*
    - *MDA < 1 mBq/g target*
    - *Germany: Strahlenschutzverordnung vom 20.July 2001 (Radiation Protection Ordinance, 20th July 2001). Limits: 2mBq/g soil; 600 mBq/g concrete…may go to 2mBq/g for concrete as well*

- Approach:
  - 5g : fusion plus Sr Resin to collect and purify Sr-89/90
  - 5g and 10g: fusion plus TRU/DGA Resin to collect and purify Y-90
  - Simultaneous gas flow proportional counting with long counts

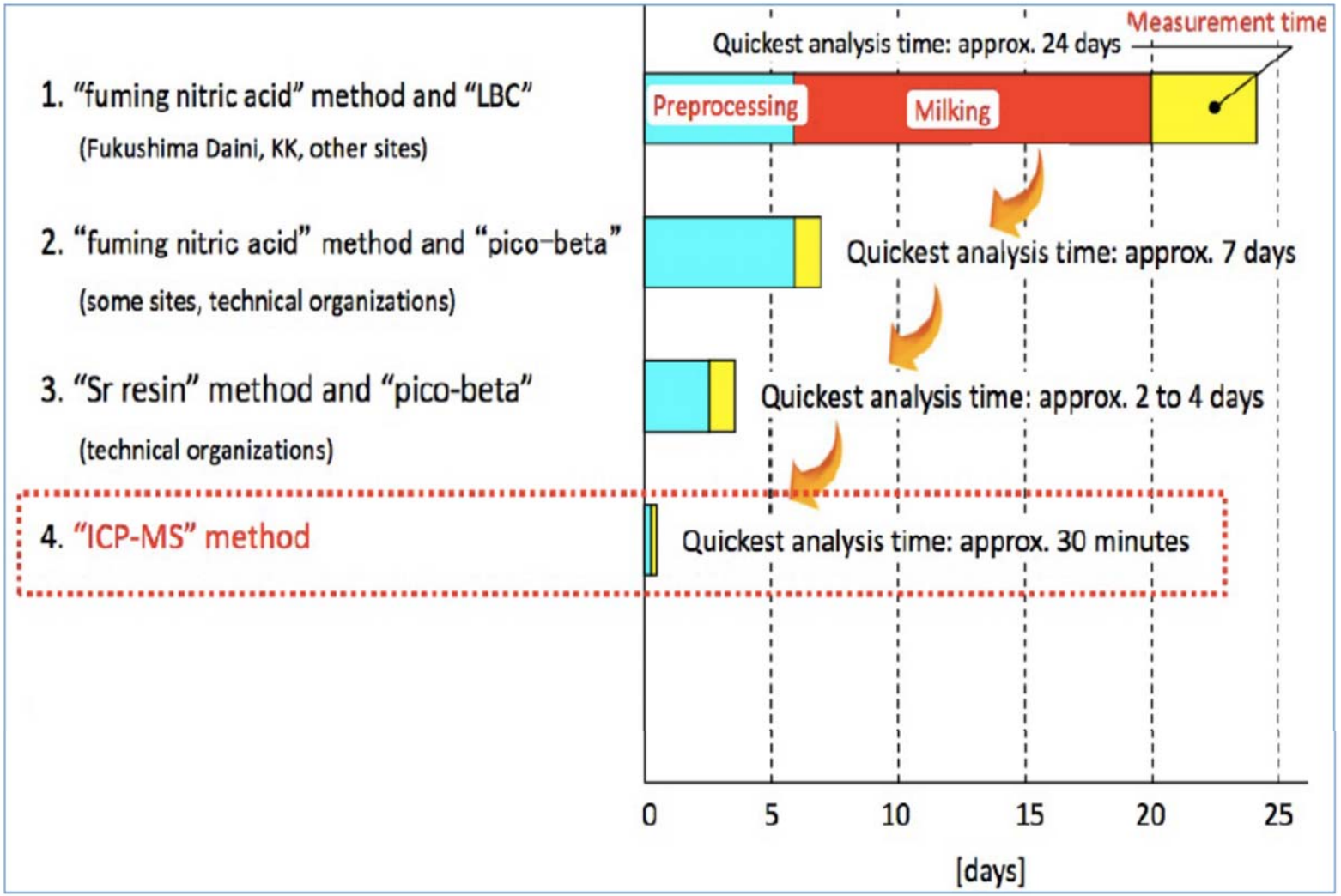
Need for More Rapid Sr-90 Assay: ICP-MS?

But…

Zr-90 interferes

High MDA

1.5 Bq/L -water



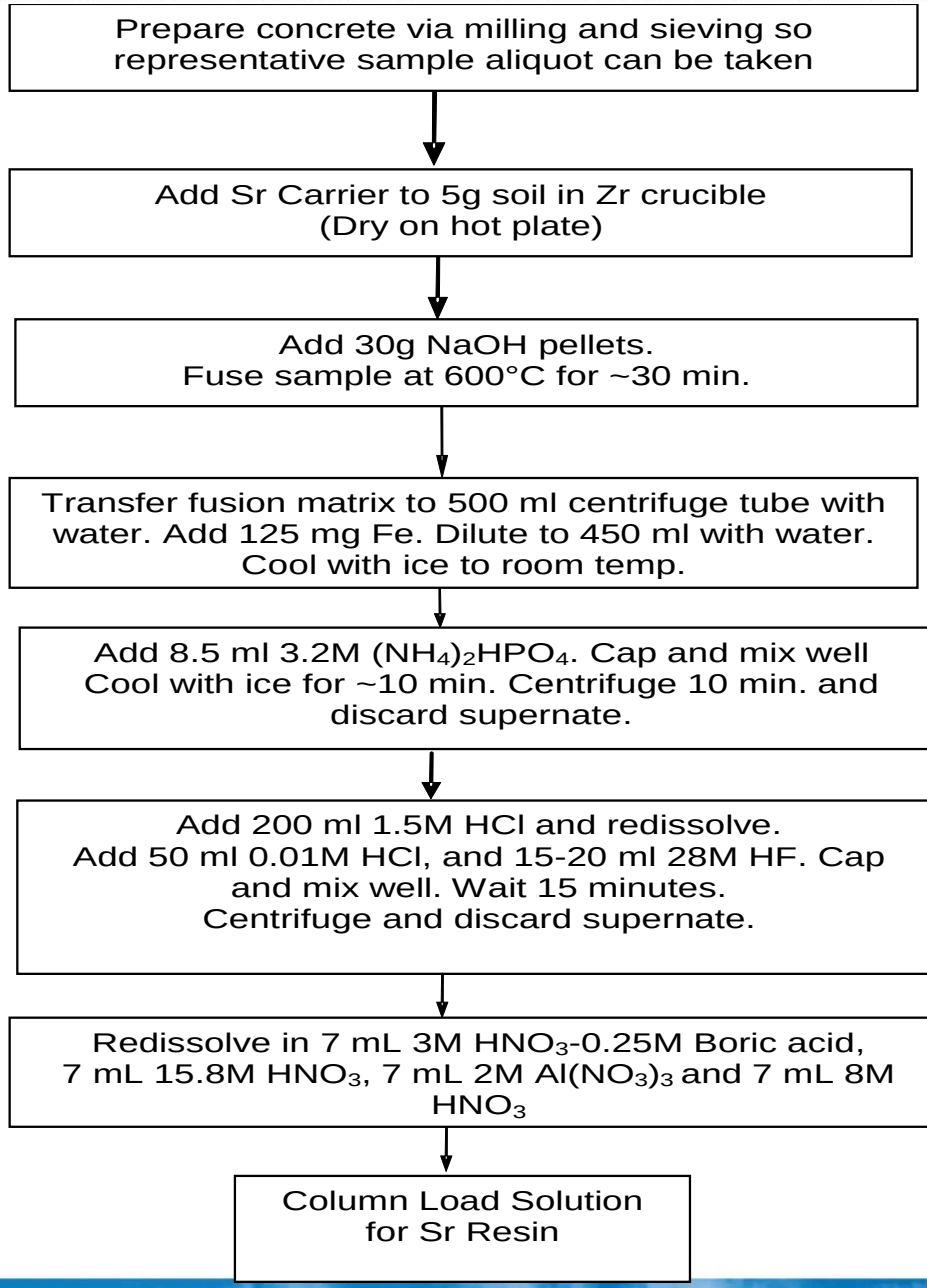
INNOVATIVE TECHNOLOGY TO PROVIDE FASTER RESULTS ON WATER QUALITY AT FUKUSHIMA
http://www.tepco.co.jp/en/press/corp-com/release/2014/1244484_5892.html

Why Sodium Hydroxide Fusion ?

- Easy, rapid and rugged
- 250 mL low form Zr crucibles (reuseable) -$95 each
- Low temperature (600°C), no burner, not one at a time
- Multiple samples processed simultaneously in furnaces
- Unlike lithium metaborate, for example, comes out of crucible easily and allows HF preconcentration steps
- CaF_2 matrix removal step
  - Removes Fe/Si
- *Total digestion of refractory particles faster than HF*

- Why not just acid leach?
  - Undissolved solids raises questions
  - Potential for refractory particles /fusion often faster
  - Ruggedness and quality = public trust

Rapid Sample Preparation – Sr-89/90



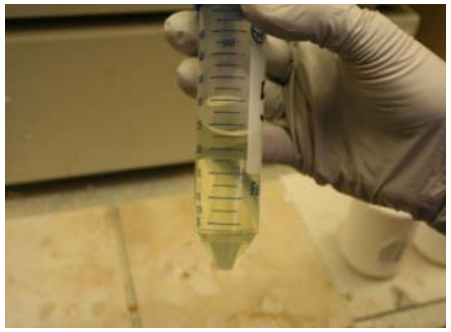
How different from actinides?

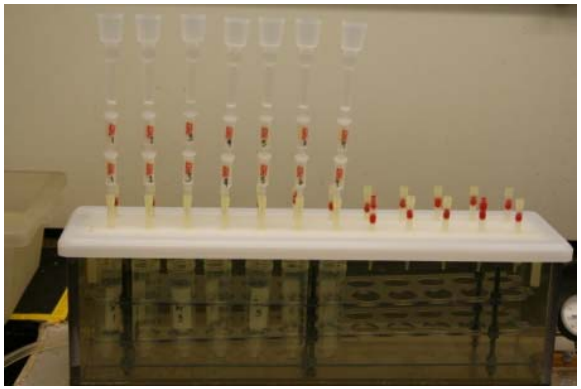
- No Ti^{+3}
- High PO_4^{-3} (to ensure good Sr ppt)
- Higher nitrate in load solution

PO_4^{-3} a limiting reagent

Reduced HF and hard to dissolve ppt eliminated!

Rapid Sr-89,90 Column Separation for Concrete





Column
Load Solution

↓

Sr Resin (2x2mL)
cartridge

↓

Rinse column;
15mL 8M HNO3;
10mL 3M HNO3-0.5M
Oxalic Acid;
10mL 8M HNO3

↓

Elute Sr
18mL 0.5M HNO3

↓

Evaporate on planchet;
weigh for gravimetric
yield

↓

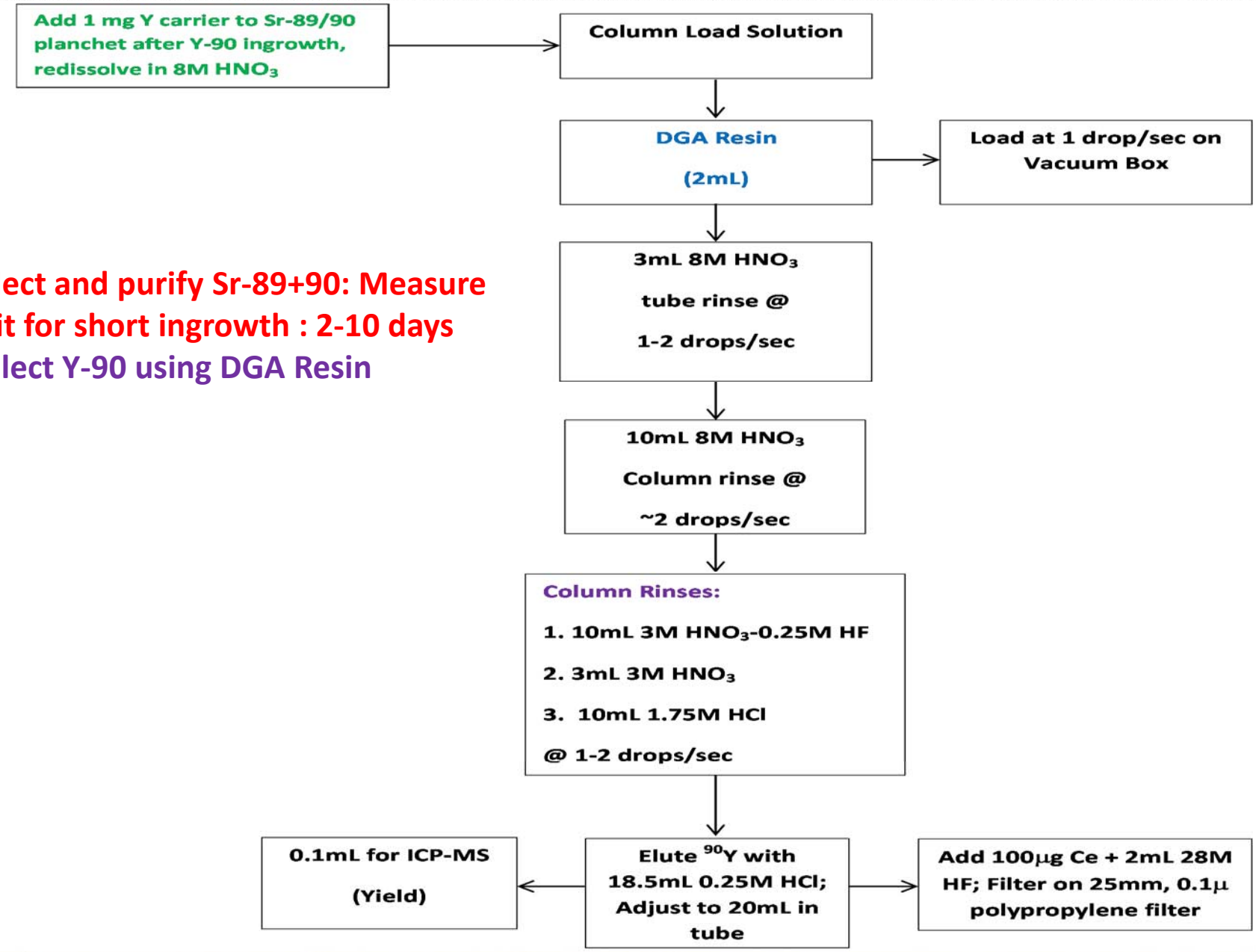
Count by Gas Flow
Proportional Counter

Simultaneous counting

Lower detection limit than LSC

After Sr-Resin…Collect Y-90 Option if High Sr-89/Sr-90 Ratio

1. Collect and purify Sr-89+90: Measure
2. Wait for short ingrowth : 2-10 days
3. Collect Y-90 using DGA Resin



Rapid Total Dissolution

Sr-90 in Concrete: 5 g using Sr Resin; No PO_4^{-3}

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq smp^{-1})	^{90}Sr Measured Value (pCi smp^{-1})	^{90}Sr Measured Value (Bq smp^{-1})	Difference (%)
1	43.2	1.416	43.68	1.616	14.1
2	50.7	1.416	41.66	1.541	8.9
3	47.9	1.416	43.67	1.616	14.1
4	53.4	1.416	41.01	1.517	7.2
Avg. Spiked Smps	48.8		42.5	1.57	11.1
SD	4.4		1.4	0.1	3.6
% RSD	8.9		3.2	3.2	
		60 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 283.2 mBq/g		
		No PO_4^{-3}			

Sr-90 in Concrete: 5 g using Sr Resin

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq smp^{-1})	^{90}Sr Measured Value (pCi smp^{-1})	^{90}Sr Measured Value (Bq smp^{-1})	Difference (%)
1	62.2	0.283	7.814	0.289	2.2
2	66.9	0.283	8.364	0.309	9.4
3	66.3	0.283	7.744	0.287	1.2
4	58.1	0.283	7.869	0.291	2.9
5	64.2	0.283	7.645	0.283	0.0
6	67.0	0.283	7.419	0.275	-3.0
Avg. Spiked Smps	64.1		7.81	0.289	2.1
SD	3.5		0.31	0.012	4.1
% RSD	5.4		4.0	4.0	
		120 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 56.6 mBq/g		
		5 ml 3.2M PO_4^{-3}			
		20 ml 28 M HF			

Yields still a bit low…

Sr-90 in Concrete: 5 g using Sr Resin; More HF

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq smp^{-1})	^{90}Sr Measured Value (pCi smp^{-1})	^{90}Sr Measured Value (Bq smp^{-1})	Difference (%)
1	62.9	1.416	41.53	1.537	8.5
2	68.3	1.416	37.02	1.370	-3.3
3	54.7	1.416	41.42	1.533	8.2
4	65.6	1.416	41.36	1.530	8.1
Avg. Spiked Smps	62.9		40.3	1.5	5.4
SD	5.9		2.2	0.1	5.8
% RSD	9.4		5.5	5.5	
		60 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 283.2 mBq/g		
		5 ml 3.2M PO_4^{-3}			
		50 ml 28 M HF			

Too much HF creates hard fluorosilicate? precipitate solids that are hard to dissolve

Sr-90 in Concrete: 5 g using Sr Resin; More PO_4^{-3}

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq smp^{-1})	^{90}Sr Measured Value (pCi smp^{-1})	^{90}Sr Measured Value (Bq smp^{-1})	Difference (%)
1	71.0	1.416	38.64	1.430	1.0
2	85.9	1.416	39.44	1.459	3.1
3	83.9	1.416	38.22	1.414	-0.1
4	86.6	1.416	38.86	1.438	1.5
5	62.2	1.416	40.73	1.507	6.4
6	58.1	1.416	38.09	1.409	-0.5
Avg. Spiked Smps	74.6		39.0	1.4	1.9
SD	12.6		1.0	0.0	2.6
% RSD	16.9		2.5	2.5	
		60 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 283.2 mBq/g		
		7.5 ml 3.2M PO_4^{-3}			
		30 ml 28 M HF			

Sr-90 in Concrete: 5 g using Sr Resin; More PO_4^{-3}

Sample ID	Sr Carrier Yield (%)	^{90}Sr Reference Value (Bq smp^{-1})	^{90}Sr Measured Value (pCi smp^{-1})	^{90}Sr Measured Value (Bq smp^{-1})	Difference (%)
1	78.5	1.416	40.80	1.510	6.6
2	77.8	1.416	36.50	1.351	-4.6
3	80.5	1.416	38.35	1.419	0.2
4	62.2	1.416	40.27	1.490	5.2
Avg. Spiked Smps	74.8		39.0	1.4	1.9
SD	8.4		2.0	0.1	5.1
% RSD	11.3		5.0	5.0	
		60 minute count			
	yield corrected for native Sr	5 g concrete	spiked at 283.2 mBq/g		
		8.5 ml 3.2M PO_4^{-3}			
		15 ml 28 M HF			

Rapid Sample Preparation – Sr-90 via Y-90

No waiting!

Add 2 mg Y carrier to 5 to 10g concrete in Zr crucible
Dry on hot plate.

↓

Add 30g/40g NaOH pellets.
Fuse sample at 600°C for ~20 min.

↓

Transfer fusion matrix to 500 ml centrifuge tube with water. Add 125 mg Fe.
Dilute to 450 ml with water. Cap and mix well. Cool with ice for ~10 minutes. Centrifuge 6 min. and discard supernate.

↓

Lowers Ca….

Add 150 ml water (pH 8.7-8.9), mix well.
Centrifuge and discard water rinse to remove Ca.
Repeat once more.

↓

Add 200 ml 1.5M HCl and redissolve.
Add 50 ml 0.01M HCl, and 15 ml 28M HF.
Allow to stand for ~10-15 minutes.
Centrifuge 6 minutes and discard supernate.

If YF_3/CaF_2 precipitate is >10 ml, add 100 ml 1.5M HCl, 3ml 28M HF, mix, wait 5 minutes and centrifuge again to reduce precipitate.

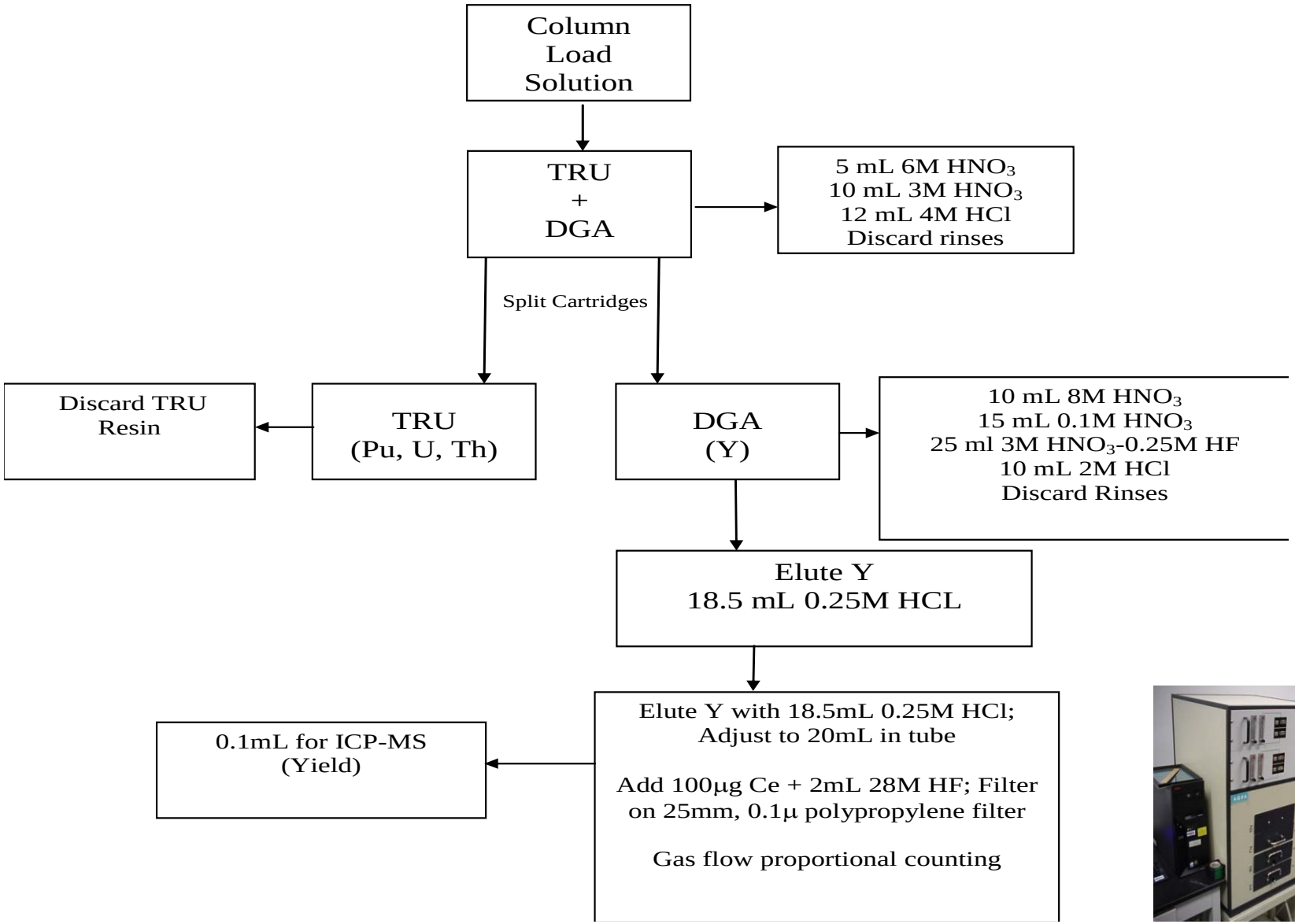
↓

Redissolve in 7 ml 3M HNO_3-0.25M Boric acid,
7 ml 15.8 HNO_3, 7 ml 8M HNO_3, 7 ml 2M $Al(NO_3)_3$.
Mix well. Warm briefly in a hot bath and centrifuge to check for any solids.

↓

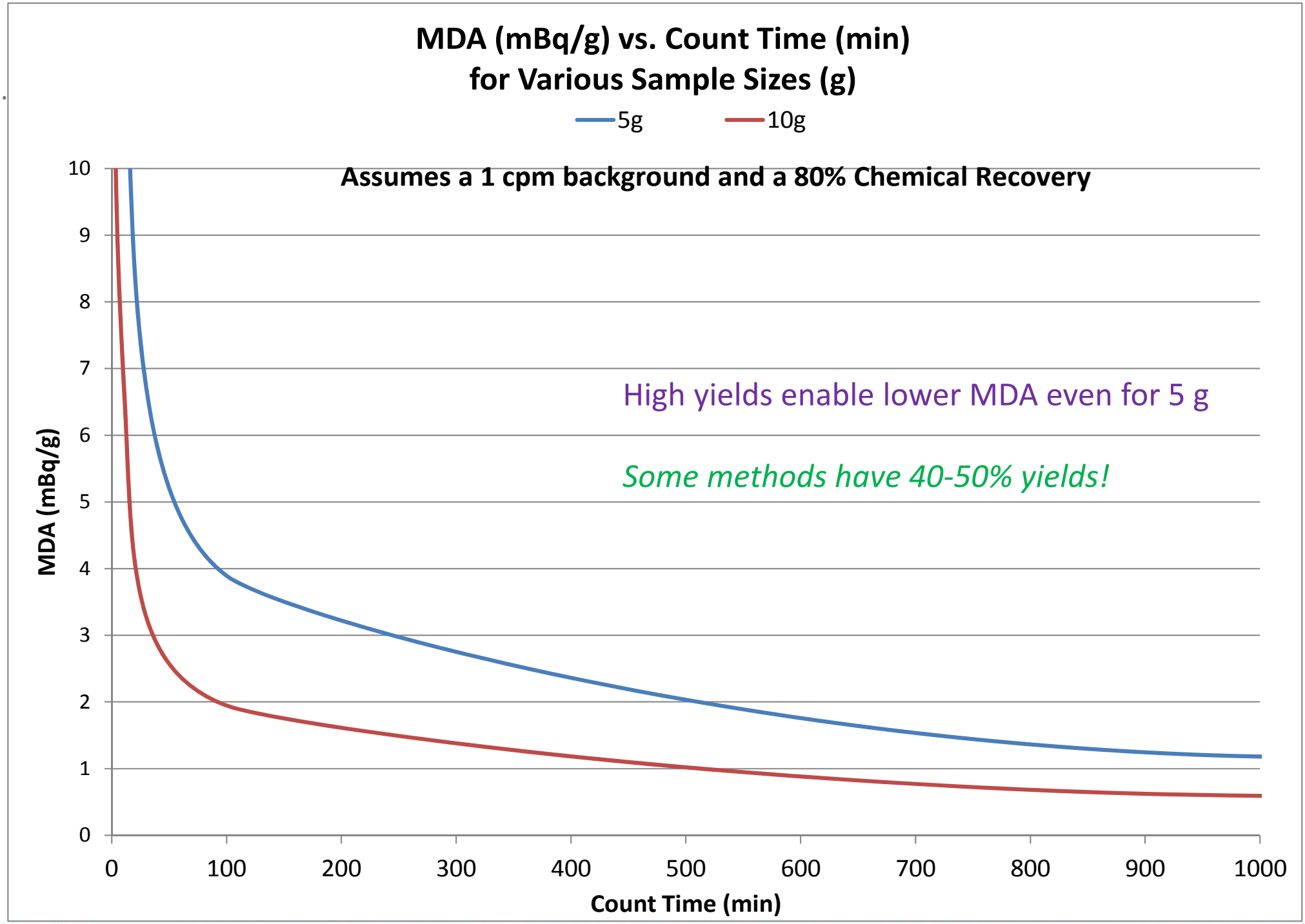
Column Load Solution

TRU+DGA Resin Y-90 Separation Method for Concrete



Sr-90 in Concrete: 10 g using TRU+DGA Resin (Y-90)

Sample ID	Sample Aliquot (g)	Y carrier (%)	^{90}Sr Reference Value (Bq smp^{-1})	^{90}Sr Reference Value (pCi smp^{-1})	^{90}Sr Measured Value (Bq smp^{-1})	Difference (%)
1	10	81.7	0.327	8.36	0.309	-5.4
2	10	83.3	0.327	8.94	0.331	1.2
3	10	83.7	0.327	8.40	0.311	-5.0
4	10	86.3	0.327	8.78	0.325	-0.6
Avg		83.8		Y carrier by ICP-MS		-2.46
SD		1.9				3.2
% RSD		2.3				
				120 minute count	added 0.5 g MAPEP 32	
		yield corrected for native Y		10 g concrete	added 500 pCi Cs-137	
				2 mg Y carrier, no La		


MDA (mBq/g) vs. Count Time (min)
for Various Sample Sizes (g)
5g
10g
Assumes a 1 cpm background and a 80% Chemical Recovery
High yields enable lower MDA even for 5 g
Some methods have 40-50% yields!
MDA (mBq/g)
Count Time (min)
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700
800
900
1000

Acknowledgements

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

Summary

- Need for lower MDA for Sr-90 in concrete samples
  - *high chemical yields and removal of interferences*
  - *robust digestion of solid samples*
  - *Y-90 in 10g ..MDA for 600 min. count <1 mBq/g*

- New Approach could assist with D&D Analytical Needs
  - Creating new measurement capabilities to facilitate standardization of measurements in decommissioning
  - A significant reduction in the enormous decommissioning costs by development and implementation of new measurement techniques

- Future Work
  - Stainless steel
  - Utilize LaF_3 and CaF_2 chemistry to remove Fe