

Rapid Methods for the Determination of Sr-90 in Steel and Concrete Samples

Sherrod L. Maxwell
Senior Fellow Scientist

LSC 2017

May 2, 2017

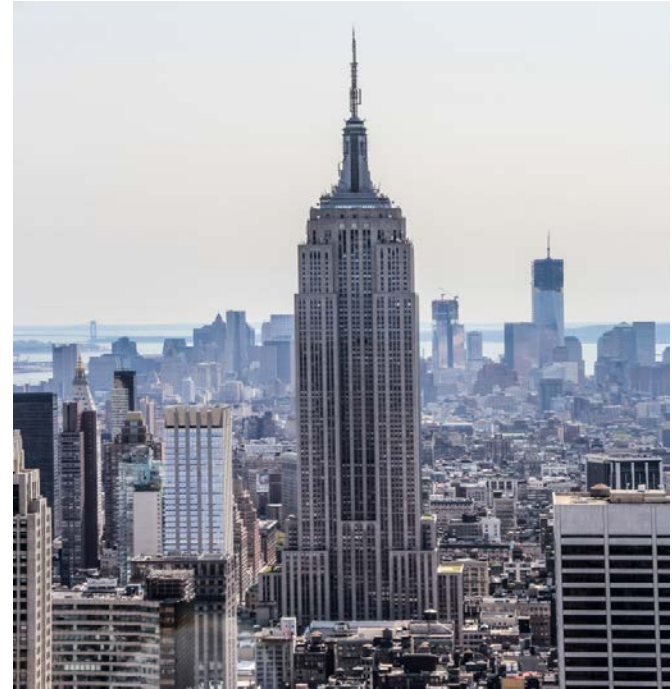
Coauthor: Dr. Ralf Sudowe, Colorado State University

Rapid Radiochemical Methods

- **Savannah River Environmental Laboratory**
 - Published ~ 40 papers in last 12 years on rapid radiochemical methods
 - *Environmental, food and bioassay sample matrices*
 - *Emergency response and more efficient routine laboratory analyses*
- **Validated, reliable analytical methods**
 - US EPA Office of Air and Radiation, National Analytical Radiation Environmental Laboratory, Montgomery, AL
 - US Air Force Radioanalytical Laboratory, Wright Air Force Base, OH
 - ASTM International D19.04 Methods of Radiochemical Analysis
- **Continued Research**
 - *Urban matrices (Actinides and Sr-89/90)*

Rapid Methods for Actinides and Sr-89/90 in Urban Matrices

- Concrete – **yes**
- Brick – **yes**
- Asphalt – **yes**
- Limestone – **yes**
- Marble – **yes**
- Others?
 - *Granite*
 - *Steel*



Maxwell S, et al. Rapid Method to Determine Actinides and Sr-89/90 in Limestone and Marble Samples, *J Radioanal Nucl Chem* October 2016, Volume 310, Issue 1, pp 377–388 [90-100% yields \pm 5% differences from known]

Large Concrete Samples – Lower MDA

J Radioanal Nucl Chem
DOI 10.1007/s10967-016-4787-4



Rapid method to determine $^{89}\text{Sr}/^{90}\text{Sr}$ in large concrete samples

Sherrod L. Maxwell¹ · Brian Culligan¹ · Jay B. Hutchison¹ · Robin C. Utsey¹ ·
Ralf Sudowe² · Daniel R. McAlister³

**Larger aliquots fused for lower MDA
for decommissioning samples**

Received: 26 January 2016
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Sr-90 via Y-90 in 10 gram concrete (TRU+DGA Resins)

Sample	Sample Aliquot	Y carrier	⁹⁰ Sr Reference Value	⁹⁰ Sr Reference Value	⁹⁰ Sr Measured Value	Difference
ID	(g)	(%)	(Bq smp ⁻¹)	(pCi smp ⁻¹)	(Bq smp ⁻¹)	(%)
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		-2.5
SD		1.9				3.2
% RSD		2.3				
				120 minute count	added 500 pCi Cs-137	
		yield corrected for native Y		10 g concrete		
		added 0.5 g MAPEP 32		2 mg Y carrier, no La		

Gas flow proportional counting...but can use LSC

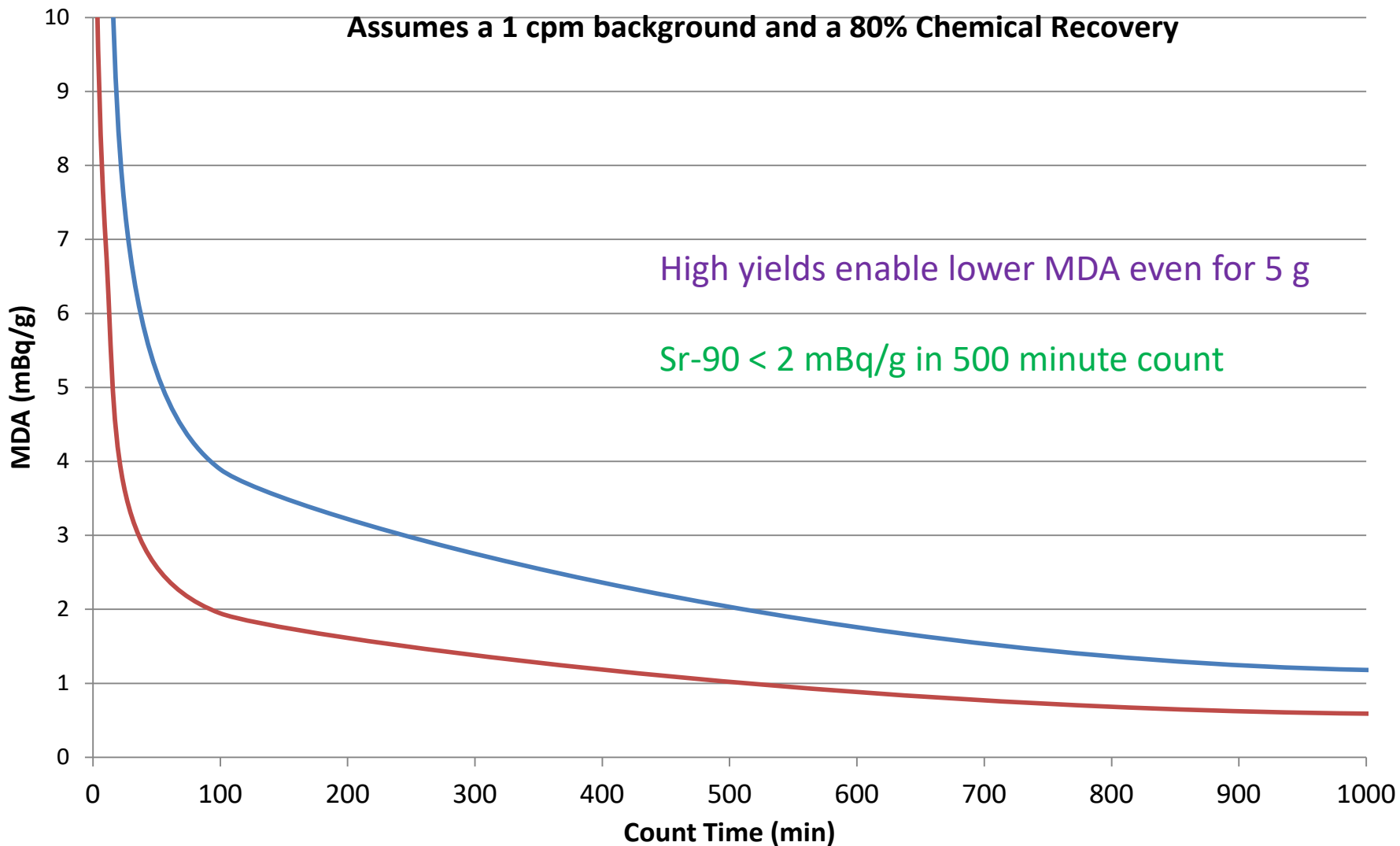
MDA (mBq/g) vs. Count Time (min) for Various Sample Sizes (g)

— 5g — 10g

Assumes a 1 cpm background and a 80% Chemical Recovery

High yields enable lower MDA even for 5 g

Sr-90 < 2 mBq/g in 500 minute count



Literature examples

- Wang - leach NRIP soil, air filters, multiple sequential precipitations, anion resin, TRU resin, Chelex 100 resin, electrodeposition, plutonium (60-76%), americium (40-59%), uranium (57-76%)
 - Sr-90 yields 63-77%
 - Complex and time-consuming
 - Wang, J., Chen, I, and Chiu, J.: Sequential isotopic determination of plutonium, thorium, americium, strontium and uranium in environmental and bioassay samples, Applied Radiation and Isotopes, 61, 299 (2004)

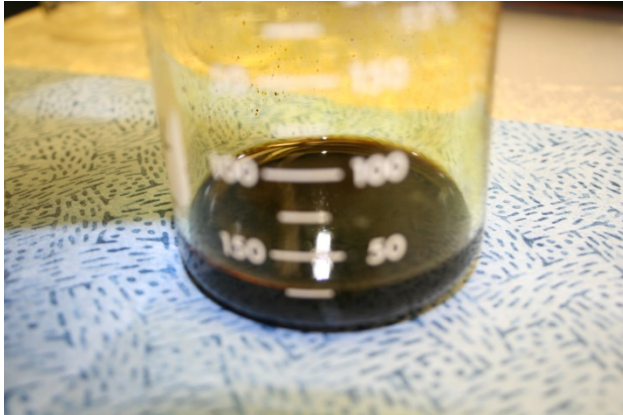
- Grahek et al, J Radioanal Nucl Chem , January 2012, Volume 293, Issue1, pp 815–827
 - Sr-89,90
 - Cerenkov counting options
 - 53-57% yields, $\pm 18\%$ difference from known values

Need for Rapid Radiochemical Method

- Can we rapidly analyze steel samples from debris associated with a radiological event?

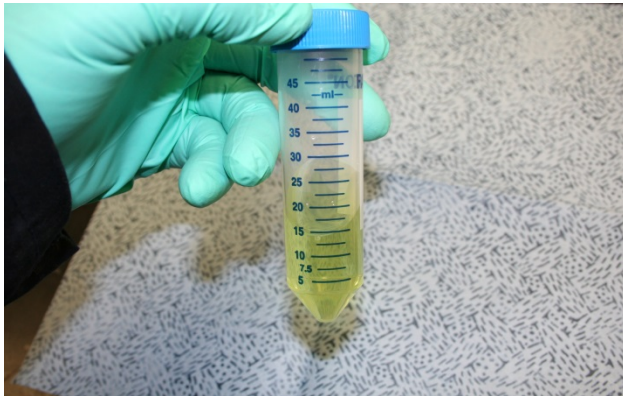
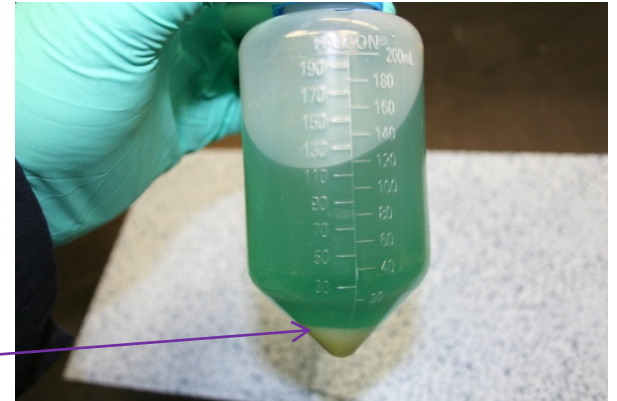


Rapid Sample Preparation for Sr-89,90 in Steel Samples



Acid Digestion
Use Aqua Regia + HF
(with HF use Teflon)

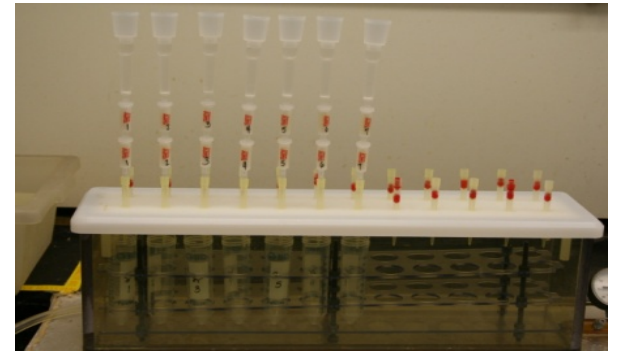
CaF₂ precipitation



Load Solution

Sr-89/90 on Sr Resin
and/or Y-90 on DGA Resin

Used 304 stainless steel disks



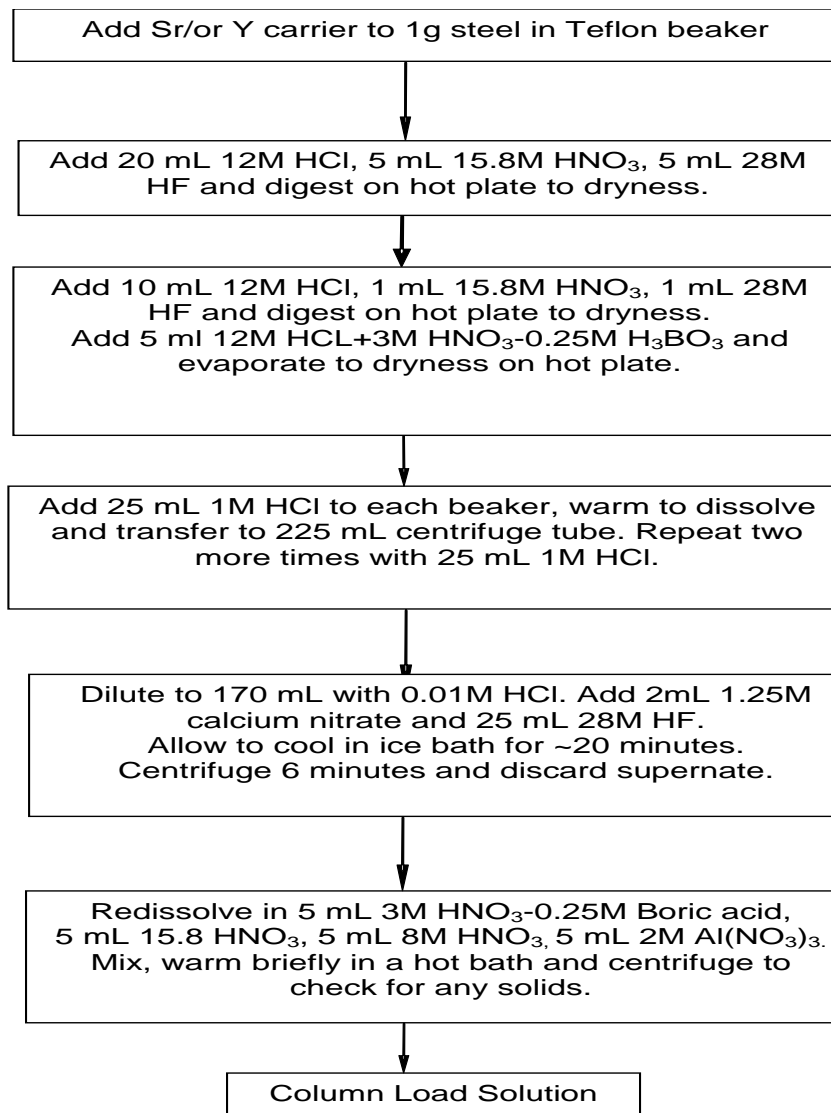
Rapid Method for Sr-89/90 in Steel Samples

- Two Options

- Precipitation of Sr-89,90 with CaF_2
- Precipitation of Y-90 with YF_3/CaF_2 to remove much of the iron
 - *No waiting to rapidly determine Sr-90 with low MDA*
- Remove much of the Fe and radiological interferences such as Cs-137



Steel Dissolution with Sr-89/90 or /Y-90 Preconcentration



Acid Digestion



Single Precipitation

*Can couple with fusion
(steel + concrete)*

Fe, Cs-137 Removal

**Sr-Resin and/or
DGA Resin**

Steel Sample Results: Sr Resin Method for Sr-90

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	87.5	1.415	38.72	1.432	1.2
2	88.5	1.415	39.58	1.464	3.5
3	87.5	1.415	38.94	1.441	1.8
4	91.6	1.415	37.76	1.397	-1.3
5	87.5	1.415	38.91	1.440	1.7
6	88.5	1.415	37.57	1.390	-1.8
7	91.6	1.415	38.05	1.408	-0.5
8	91.6	1.415	36.17	1.338	-5.4
9	92.6	1.415	38.08	1.409	-0.4
10	93.6	1.415	37.22	1.377	-2.7
Avg. Spiked Smps	90.1		38.1	1.41	-0.39
SD	2.4		1.0	0.04	2.6
% RSD	2.6		2.6	2.6	
		60 minute count			

2g steel, acid digestion, CaF₂, Sr Resin, gas flow proportional counting

Sr-90 in Steel Samples (Y-90 Option)

- DGA-Resin

- *Collect Y-90 with no waiting for ingrowth*

- Purify Y-90 using DGA Resin to determine Y-90 (Sr-90)

- Maxwell, S., Culligan, B. , Utsey, R. , Hutchison, J. and McAlister, D. Rapid determination of ^{90}Sr in seawater samples, *J Radioanal Nucl Chem* , January 2015, Volume 303, Issue1, pp 709–717
- Maxwell, S, Culligan, B. , Utsey, R. , Hutchison, J., McAlister, D and Sudowe, R., Rapid method to determine $^{89}\text{Sr}/^{90}\text{Sr}$ in large concrete samples, *J Radioanal Nucl Chem* , October 2016, Volume 310, Issue1, pp 399–411

- Also LSC and Cerenkov options

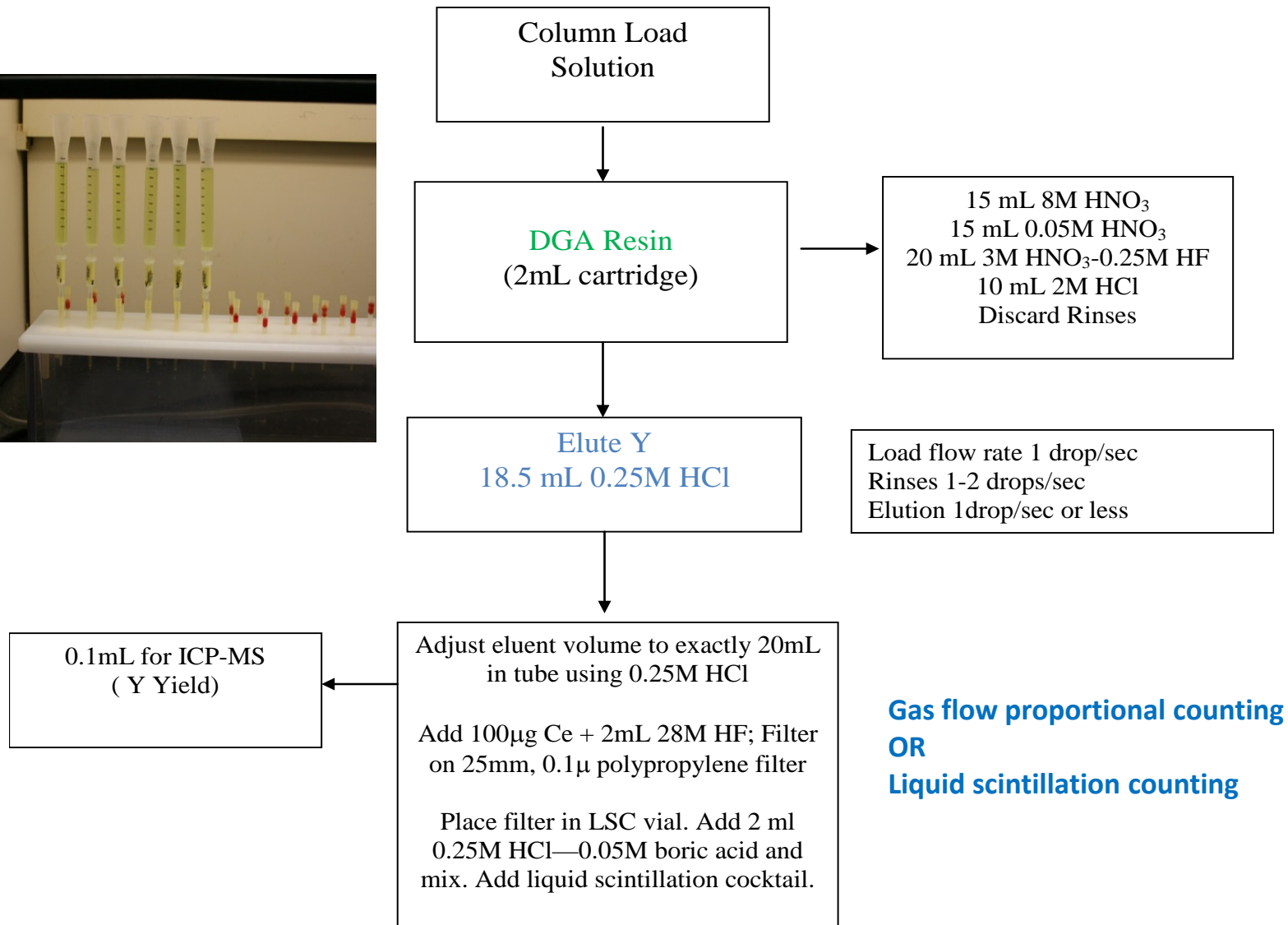
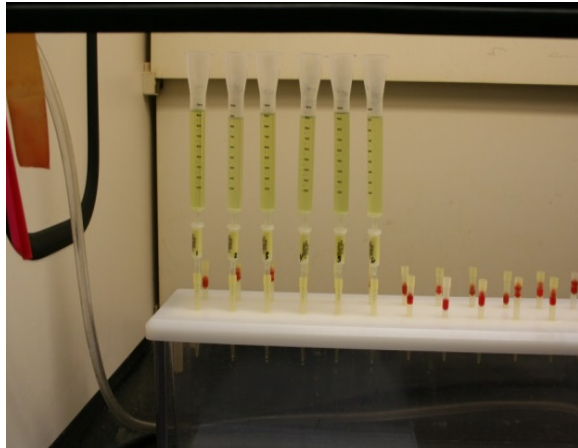
- Amano et al, Method for rapid screening analysis of Sr-90 in edible plant samples collected near Fukushima, Japan, *Applied Radiation and Isotopes*, Vol 112, 2016, pg131 (Cerenkov)

- *Cs-137 decontamination (50 Bq added/no interference!)*

- Illustrates benefits of:

- *Innovative, effective sample digest/preconcentration AND efficient column separation*

DGA Resin Separation for Y-90 in Steel



Steel Sample Results: DGA Resin Method for Sr-90 (Y-90)

Sample ID	Y 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	96.5	1.415	37.74	1.396	-1.3
2	98.5	1.415	37.38	1.383	-2.3
3	95.6	1.415	37.65	1.393	-1.6
4	89.4	1.415	36.30	1.343	-5.1
5	100.0	2.830	76.29	2.822	-0.3
6	101.9	2.830	74.29	2.748	-2.9
7	96.6	2.830	78.50	2.904	2.6
8	97.1	2.830	72.31	2.675	-5.5
Avg. Spiked Smpls	96.9				-2.0
SD	3.7				2.6
% RSD	3.8				
		60 minute count			

1g steel, acid digestion, YF₃/CaF₂, DGA Resin, gas flow proportional counting

Steel Sample Results: DGA Resin Method for Sr-90 (Y-90)

Sample	Y carrier Yield	⁹⁰ Sr Reference Value	⁹⁰ Sr Measured Value	⁹⁰ Sr Measured Value	Difference
ID	(%)	(Bq smp ⁻¹)	(pCi smp ⁻¹)	(Bq smp ⁻¹)	(%)
1	94.8	1.447	37.13	1.374	-5.0
2	92.1	1.447	39.04	1.444	-0.2
3	91.6	1.447	39.10	1.447	0.0
4	93.6	1.447	38.38	1.420	-1.8
5	93.8	1.447	38.62	1.429	-1.2
6	96.1	1.447	38.13	1.411	-2.5
Avg. Spiked Smpls	93.7			1.42	-1.8
SD	1.7			0.03	1.8
% RSD	1.8				
		60 minute count			

1g steel, 50.9 Bq Cs-137 added, acid digestion, YF₃/CaF₂,
 DGA Resin, Liquid Scintillation Counting
 MDC: 60-80 mBq/g steel for 60 minute count LSC

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

Add 1 mg Y carrier to Sr-89/90
planchet after Y-90 ingrowth,
redissolve in 8M HNO₃

Column Load Solution

DGA Resin
(2mL)

Load at 1 drop/sec on
Vacuum Box

3mL 8M HNO₃
tube rinse @
1-2 drops/sec

10mL 8M HNO₃
Column rinse @
~2 drops/sec

Column Rinses:
1. 10mL 3M HNO₃-0.25M HF
2. 3mL 3M HNO₃
3. 10mL 1.75M HCl
@ 1-2 drops/sec

0.1mL for ICP-MS
(Yield)

Elute ⁹⁰Y with
18.5mL 0.25M HCl;
Adjust to 20mL in
tube

Add 100µg Ce + 2mL 28M
HF; Filter on 25mm, 0.1µ
polypropylene filter

FP = Fission Product
High Sr-89/Sr-90 ratio

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

Can adapt to Cerenkov Counting

Amano et al, Applied Radiation and
Isotopes, Vol 112, 2016, pg131

Sr-89 Cerenkov then Y-90 Cerenkov
(or Y-90 with cocktail)

Steel Sample Results: Sr-89+90 Resin Method

Sample ID	Y Carrier Yield (%)	⁸⁹ Sr+ ⁹⁰ Sr Reference Value (Bq smp ⁻¹)	⁸⁹ Sr+ ⁹⁰ Sr Measured Value (Bq smp ⁻¹)	Difference (%)
1	91.41	3.816	4.013	5.2
2	90.72	3.816	4.118	7.9
3	97.59	3.816	3.942	3.3
4	94.16	3.816	3.957	3.7
5	92.10	3.816	3.957	3.7
6	92.78	3.816	3.784	-0.8
7	96.22	3.816	4.013	5.2
8	97.59	3.816	3.998	4.8
Avg. Spiked Smpls	94.1		3.97	4.1
SD	2.8		0.09	
% RSD	2.9			
		60 minute count		

Measure Sr-89+Sr-90, wait a few days, collect Y-90 and purify on DGA Resin
 Sr-89 is determined by difference with appropriate efficiency adjustments.

Steel Sample Results: Sr-90 via Y-90 Assay after short ingrowth

Sample ID	Y Carrier Yield (%)	⁹⁰ Sr Reference Value (Bq smp ⁻¹)	⁹⁰ Sr Measured Value (Bq smp ⁻¹)	Difference (%)
1	99.80	0.566	0.523	-7.6
2	98.90	0.566	0.618	9.2
3	99.80	0.566	0.476	-16.0
4	91.82	0.566	0.618	9.2
5	96.21	0.566	0.581	2.7
6	95.41	0.566	0.562	-0.7
7	100.00	0.566	0.511	-9.7
8	98.40	0.566	0.557	-1.5
Avg. Spiked Smps	97.5		0.556	-1.8
SD	2.9		0.051	
% RSD	2.9			
60 minute count				

MDC: gas flow proportional counting (25 mBq g⁻¹ steel for 60 min/ 12 mBq g⁻¹ steel for 240 min)
 Similar principle can be applied using Cerenkov

Steel Sample Results: Sr-89 by Difference

Sample	Sr Carrier Yield	⁸⁹ Sr Reference Value	⁸⁹ Sr Measured Value	Difference
ID	(%)	(Bq smp ⁻¹)	(Bq smp ⁻¹)	(%)
1	91.41	3.270	3.51	7.2
2	90.72	3.270	3.50	7.0
3	97.59	3.270	3.47	6.1
4	94.16	3.270	3.35	2.3
5	92.10	3.270	3.38	3.5
6	92.78	3.270	3.23	-1.3
7	96.22	3.270	3.51	7.4
8	97.59	3.270	3.45	5.5
Avg. Spiked Smpls	94.1		3.425	4.7
SD	2.8		0.099	
% RSD	2.9			

- Continued to make progress regarding Sr-89/90 in urban matrices
 - *Limestone, marble, concrete published...now steel*
 - *Robust digestion of solid samples with potential refractory particles*
- Developed new steel method for Sr-89/90 (also mixed with concrete)
 - *Rapid digestion plus only one step preconcentration*
 - *Effective removal of matrix interferences (Ex. Cs-137 in HF supernate)*
- Flexible options
 - *Sr-90 (Sr Resin and one count if no Sr-89 present)*
 - *Sr-90 via Y-90 with no waiting for ingrowth (DGA Resin)*
 - *Sr-89+Sr-90 (Sr-Resin, then DGA Resin for Sr-90 and Sr-89)*
 - *Cerenkov, LSC can be applied*