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Recent developments in the analysis of actinides, Sr-90 and Ra-226 from difficult matrices

Sherrod L. Maxwell, PhD

Triskem User's Group Meeting 2018

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Critical Needs

- **Rose et al. note that if an Improvised Nuclear Device (IND) detonation occurs, laboratory sample analysis needs to occur in the first 6-24 hours**

  Rose C, Seater R, and Norige A, Analysis of decision making skills for large scale disaster response, 2015 IEEE Global Humanitarian Technology Conference (GHTC), 8-11 Oct. 2015, Seattle Washington, USA

- **Are we ready?**
- **Solid matrices offer significant challenges**
  - analytical methods employed must be able to overcome these difficulties

- **Plus…we will likely have and overwhelming number of samples to process….**

Analysis Needs

- **If an IND detonates, there will be large amounts of:**
  - remaining nuclear material
  - activation products and
  - fission products deposited from the blast, including actinides, ^{89}Sr and ^{90}Sr

- **If a Radiological Dispersive Device (RDD) explosion occurs some of the more common radionuclides that can be expected are alpha emitters such as ^{234}U, ^{235}U, ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{242}Cm, ^{244}Cm and ^{226}Ra and beta/gamma emitters such as ^{57}Co, ^{60}Co, ^{137}Cs, ^{129}I, ^{90}Sr and ^{228}Ra**
  - Radiological Laboratory Sample Analysis Guide for Incident Response –Radionuclides in Soil, EPA 402-R-12-006, September 2012

Challenges

- **Actinides and strontium-89,90 at environmental levels require significant sample preparation/purification**
  - *Cannot simply put sample in gamma spectrometer*
    - *Ex. Cs-137, Co-60*
- **Urban matrices require sample digestion/destructive analysis**
  - *Potential refractory particles*
  - *Need to be fast and very robust*

Recent Advances

- **Urban matrices**
  - Published concrete, brick, asphalt methods that US EPA is utilizing
  - Continued development of assays for limestone, marble, granite, steel, concrete matrices, published in 2016-2018
  - Published
    - *Pu isotopes in steel*
    - *Actinides in granite*
    - *Sr-89/90 in steel*
    - *Ra-226 in steel*
- **Focus today on new work**
  - Ra-226 in fish and beef (Cation exchange resin + DGA Resin + alpha spectrometry)
  - Sr-90 in cheese-DGA Resin (Y-90 with no waiting, gas proportional counting or LSC)
  - Po-210 in urban matrices (alkaline fusion + DGA Resin + alpha spectrometry)

Plutonium Isotopes in Steel Samples

J Radioanal Nucl Chem (2017) 314:1103–1111
DOI 10.1007/s10967-017-5501-x

CrossMark

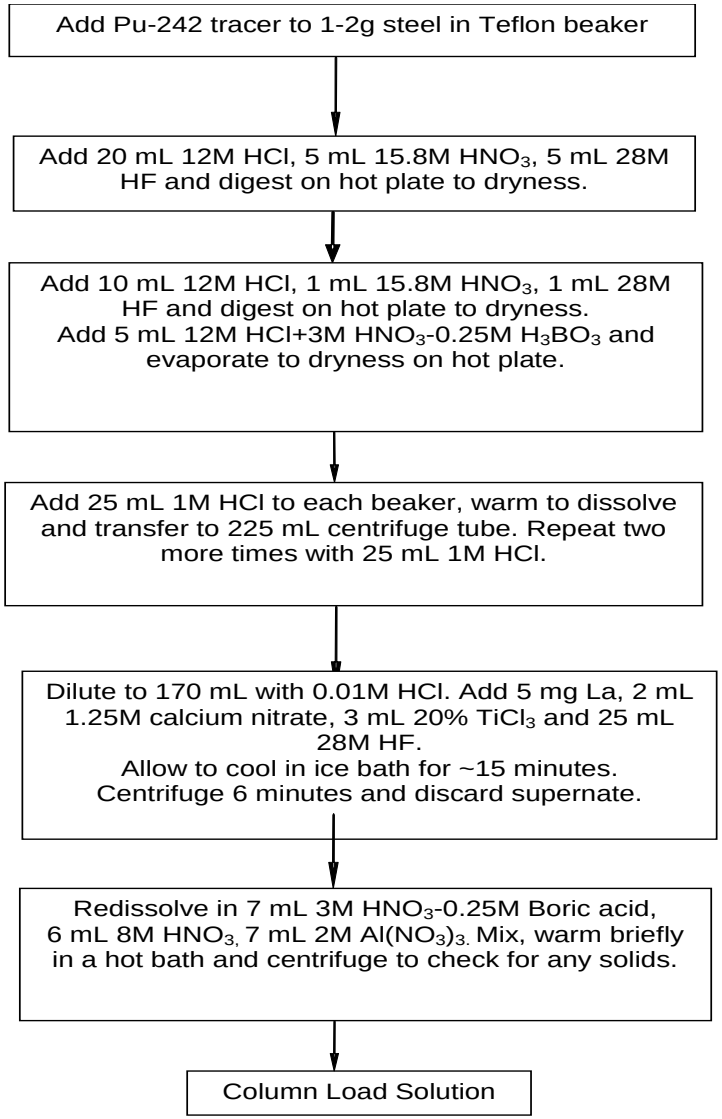
Rapid method to determine plutonium isotopes in steel samples

Sherrod L. Maxwell[1] · Brian Culligan[1] · Jay B. Hutchison[1] · Ralf Sudowe[2] · Daniel R. McAlister[3]

Rapid Method for Plutonium in Steel Samples

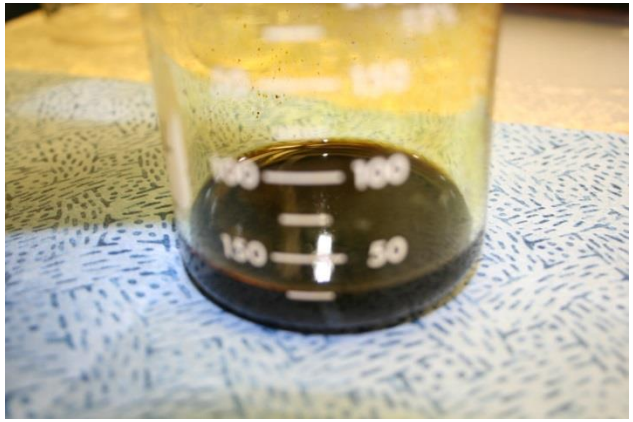
- **Steel- challenges**
  - high iron content, also chromium, nickel, etc
  - Can't fuse directly
- **Explored rapid digestion with aqua regia with or without HF**
  - HF adds ruggedness if refractory particles are present
- **Single precipitation of plutonium with LaF_3/CaF_2**
  - remove much of the Fe from the steel digestion
  - Fe can interfere with some resin separations

Sample Dissolution for Pu Isotopes in Steel



Also tested acid dissolution + fusion option

Rapid Sample Preparation for Plutonium in Steel Samples



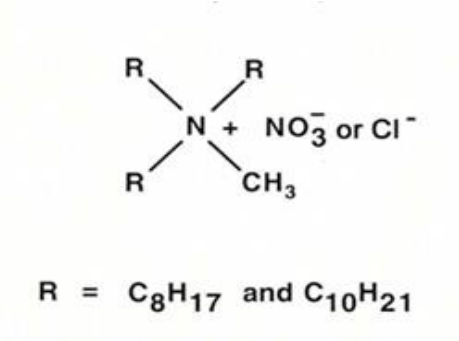
Use Aqua Regia +HF

LaF_3/CaF_2 precipitation

Pu Isotopes
on TEVA Resin

Plutonium Purification for Counting

- **Rapid Column Separations**
  - Pu on TEVA Resin
    - *Anion exchange extractant Aliquat 336*
    - *Valence adjustment to Pu(IV)*
  - Tests with refractory Pu-239/240 show very low recovery without HF
    - *Tested by adding MAPEP 24 soil (refractory Pu)*
    - *Tested acid digestion plus fusion option for steel*



Could also use

TEVA+TRU (Pu and U)
TEVA+DGA (Pu+Am/Cm)

Stainless Steel Samples Spiked with Refractory Pu-239 (with HF)

Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Spiked Value (mBq/sample)	^{239}Pu Measured Value (mBq/sample)	Difference (%)
1	103.1	34.2	24.5	23.16	-5.5
2	98.0	38.6	24.5	23.16	-5.5
3	104.2	48.0	24.5	23.50	-4.1
4	87.7	33.1	24.5	25.12	2.5
5	95.8	37.6	24.5	22.57	-7.9
6	104.8	52.9	24.5	22.64	-7.6
Avg. Spiked Smps	98.9			23.36	-4.7
SD	6.6			0.93	3.8
% RSD	6.6			4.0	
		~2g steel	16 hour count		

Stainless Steel Samples Spiked with Refractory Pu-239 (no HF)

Sample ID	^{242}Pu Yield (%)	Tracer Peak (FWHM)	^{239}Pu Spiked Value (mBq/sample)	^{239}Pu Measured Value (mBq/sample)	Difference (%)
1	93.5	58.6	24.5	0.92	-96.2
2	96.6	63.5	24.5	1.23	-95.0
3	80.0	43.5	24.5	1.56	-93.6
4	87.4	66.2	24.5	0.67	-97.3
Avg. Spiked Smps	89.4			1.094	-95.5
SD	7.3			0.384	1.6
% RSD	8.2				
		~2g steel	16 hour count		

New Work

- **Rapid, rigorous, defensible methods**
  - Ra-226 in fish and beef samples (Cation exchange resin + DGA Resin)
  - Sr-90 in foods such as cheese (Y-90 with no waiting for ingrowth)
  - Po-210 in urban matrices (alkaline fusion + DGA Resin)
    - *Novel collection*
    - *Rugged separation*
    - *Microprecipitation*

Why is Ra-226 a concern?

- Ra-226 ($T_{1/2}$ = 1600 y) - one of the most toxic of the long-lived alpha-emitters present in the environment
- Ingestion or inhalation of ^{226}Ra can lead to a significant committed dose to individuals due to its long half-life and tendency to concentrate in bones
- Ra-226 has been identified by the IAEA as a radionuclide that can harm human health if used in a terrorist attack using a RDD

Need for Reliable Ra-226 Methods

- **Ra-226 has a high specific activity relative to Uranium and many other naturally occurring radionuclides**
  - Ra-226 RDD greater potential dose than Uranium RDD
- **The IAEA AMERA (Analytical Laboratories for the Measurement of Environmental Radioactivity) network administered proficiency testing for the rapid analysis of Ra-226 in water and phosphogypsum in 2008**
  - Most labs used gamma spectrometry, waiting 21 days for ingrowth of progeny to measure $^{214}Pb/^{214}Bi$
  - ***30-40% of the lab results were unacceptable vs IAEA requirements***
- ***Continuing need for fast reliable results for ^{226}Ra in urban matrices***

One more look at steel before we move to foods…

J Radioanal Nucl Chem (2017) 314:1417–1423
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CrossMark

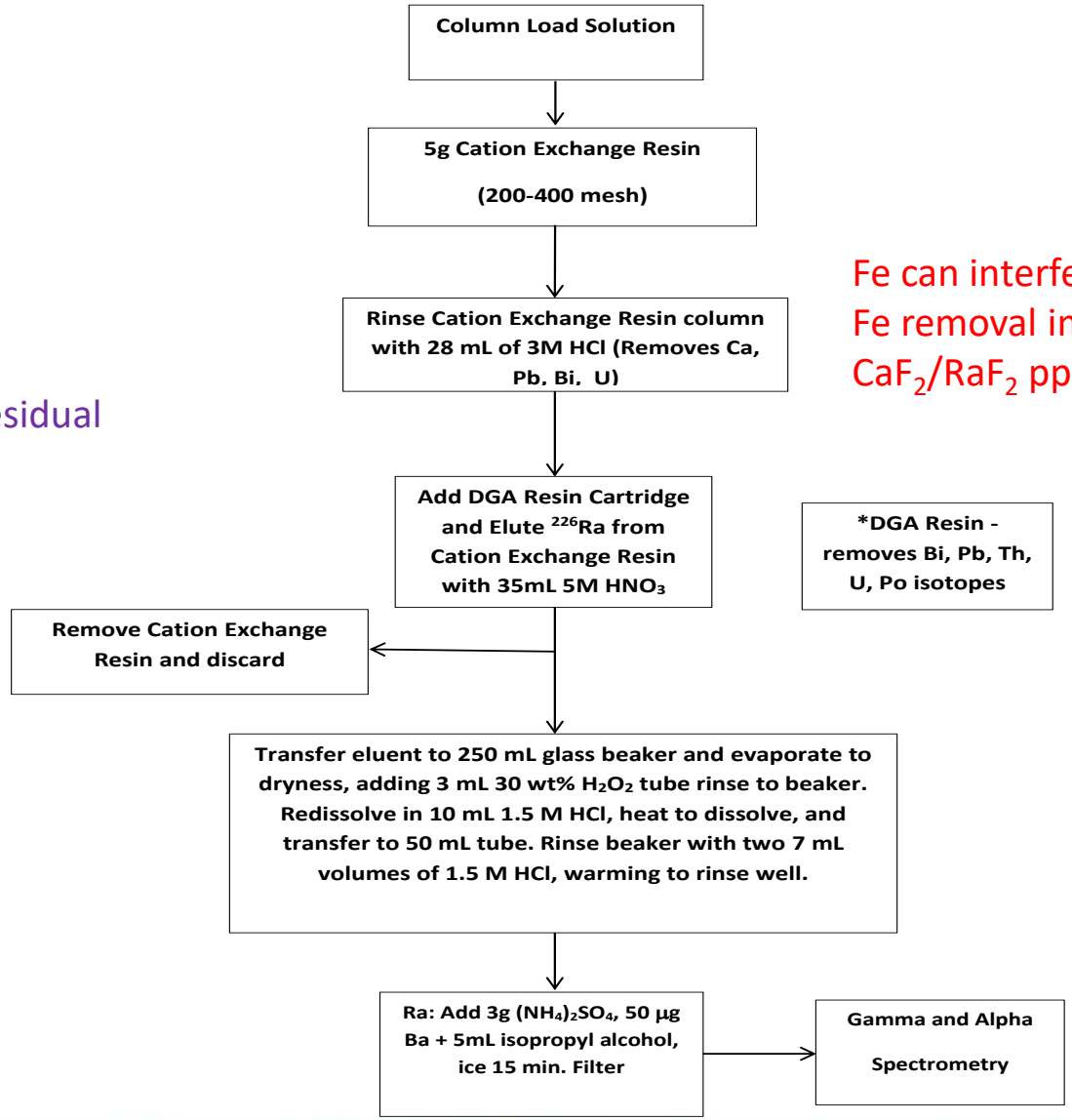
Rapid method to determine ^{226}Ra in steel samples

Sherrod L. Maxwell[1] · Brian Culligan[1] · Jay B. Hutchison[1] · Ralf Sudowe[2] · Daniel R. McAlister[3]

Similar preconcentration to Pu/Sr as fluoride however lower acid needed to effectively ppt RaF_2

Rapid Extraction Method for Ra-226 in Steel

Ascorbic acid added to load solution as well to reduce any residual Fe^{+3} to Fe^{+2}



Fe can interfere so Fe removal important at CaF_2/RaF_2 ppt. step

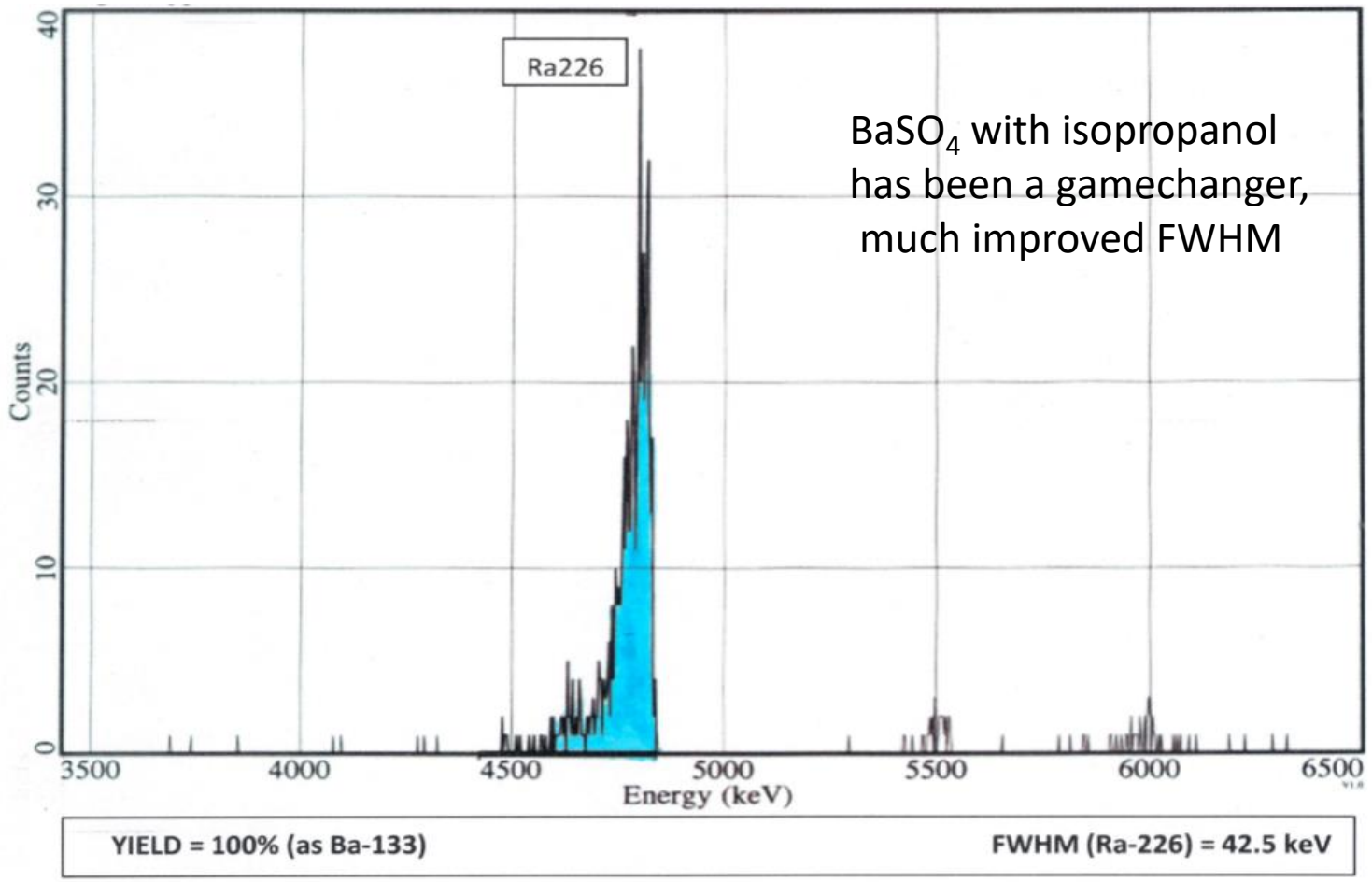
Results for Ra-226 Spiked in Steel Samples

Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	100.0	36.84	35.62	-3.3
2	101.6	36.84	37.67	2.2
3	94.6	36.84	36.23	-1.7
4	86.5	36.84	37.05	0.6
5	94.3	36.84	36.18	-1.8
Avg	95.4		36.5	-0.79
SD	5.9		0.81	
% RSD	6.2		2.2	

Results for Ra-226 Spiked in Steel Samples

Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	101.1	184.2	189.46	2.9
2	89.2	184.2	176.61	-4.1
3	67.6	184.2	184.37	0.1
4	96.2	184.2	182.98	-0.7
5	93.1	184.2	181.26	-1.6
Avg	89.5		182.9	-0.68
SD	13.0		4.7	
% RSD	14.5		2.6	

Ra-226 Spiked in Steel Samples- Alpha Spectra



$BaSO_4$ with isopropanol has been a gamechanger, much improved FWHM

Ra-226 in Fish and Beef

- **Exposure to high levels of internal contamination by ^{226}Ra can lead to *severe, acute or chronic health effects.***
- **Currently no US FDA derived intervention limit (DIL) in place for ^{226}Ra in food,**
  - so decisions about ^{226}Ra would likely be made via a risk analysis after an event occurs
- **For this work it was assumed that intervention levels would be about 10 Bq/kg or 0.27 pCi/g**

Ra-226 in Fish and Beef

- **Approach**
  - 50-100 gram sample aliquot
  - "Reverse" aqua regia digestion, then multiple nitric acid additions and evaporation, then hydrogen peroxide (alternate with HNO_3), furnace overnight, final wet-ash
  - Load to Cation Resin in dilute HCl (removes Ca, etc.)
  - Add DGA Resin to purify Ra-226 during elution from cation exchange resin (from alpha emitters)
  - Count Ra-226 by alpha spectrometry, Ba-133 yield via gamma spectrometry

Sample Preparation Ra-226 in Fish/Beef

Place 50-100 g sample in glass beaker

Add ^{133}Ba as Tracer

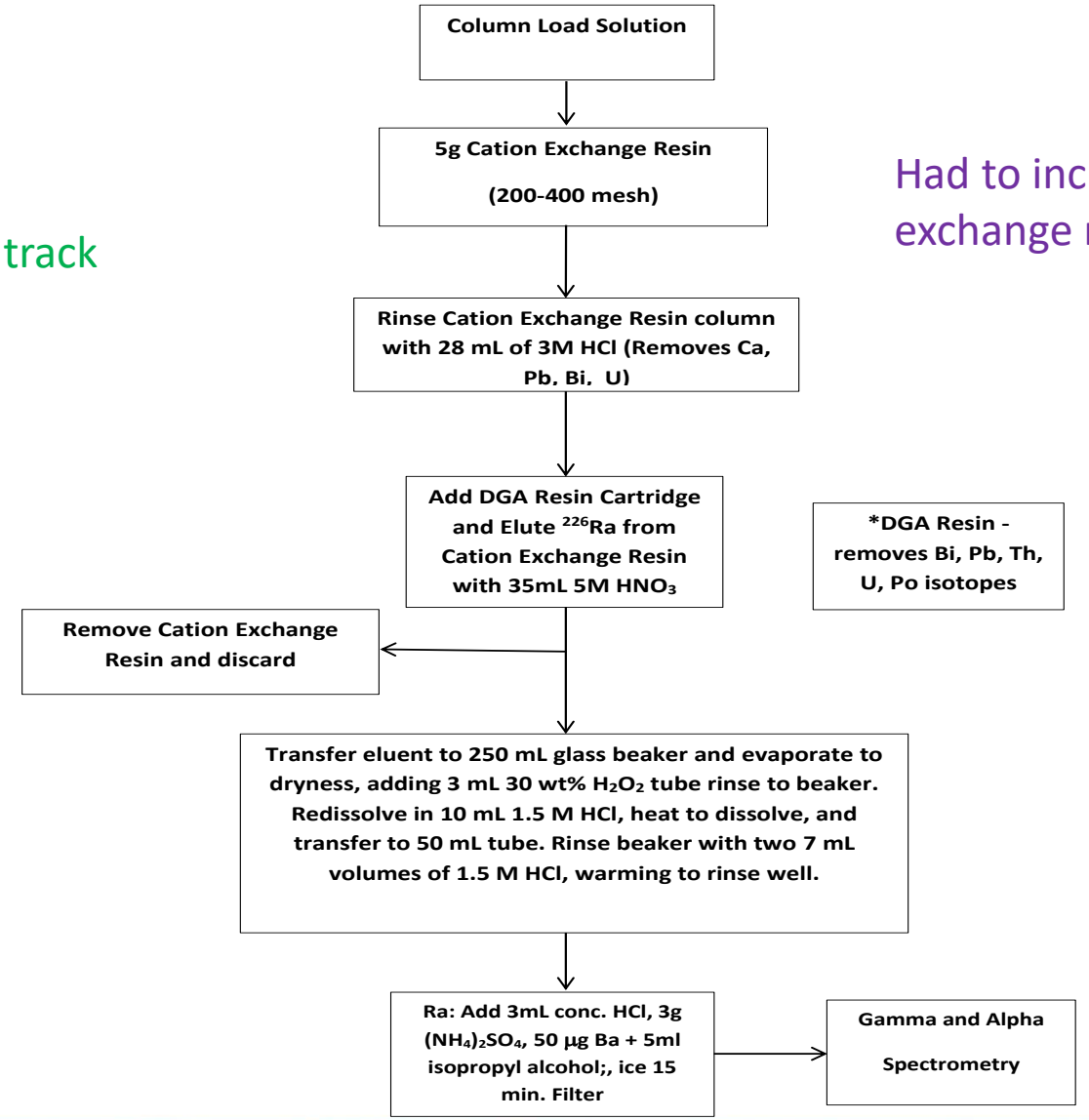
Digest with 'reverse aqua regia' (0.5 mL per gram) on hot plate, evaporate, wet-ash with HNO_3 only several times, alternate wet-ashing with HNO_3 and H_2O_2 several times, and furnace heat at 550C overnight (or less)

Add 15 mL 1.5M HCl, 10 ml 1.5M HCl to dissolve solids, warm and add to tube, Mix well, centrifuge, discard any solids

Column Load Solution

Rapid Ra-226 Separation

Ensure Ba/Ra track well together



Had to increase cation exchange resin to 6g

Ra-226 in Fish and Beef

Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	95.1	36.84	37.23	1.1
2	90.2	36.84	31.86	-13.5
3	95.5	36.84	34.57	-6.2
4	84.6	36.84	39.61	7.5
5	84.8	36.84	37.69	2.3
6	88.5	36.84	36.56	-0.8
Avg	89.8		36.3	-1.6
SD	4.8		2.7	
% RSD	5.3		7.5	
			50 g bass	

Ra-226 in Fish

Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	84.8	36.84	38.15	3.6
2	86.2	36.84	34.87	-5.3
3	74.6	36.84	38.05	3.3
4	88.7	36.84	36.50	-0.9
5	87.9	36.84	35.76	-2.9
6	74.2	36.84	38.56	4.7
Avg	82.7		37.0	0.4
SD	6.6		1.5	
% RSD	8.0		4.0	
			100g bass	

Ra-226 in Beef

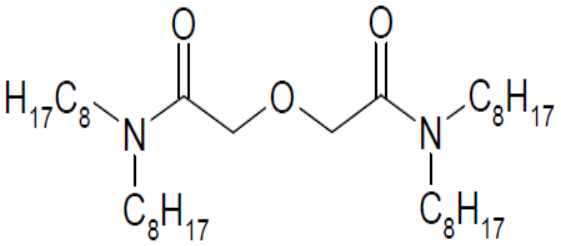
Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	82.7	36.84	35.26	-4.3
2	88.1	36.84	37.55	1.9
3	94.1	36.84	35.86	-2.7
4	78.8	36.84	36.42	-1.1
5	82.1	36.84	33.50	-9.1
6	89.7	36.84	33.67	-8.6
Avg	85.9		35.4	-4.0
SD	5.7		1.6	
% RSD	6.6		4.5	
			50g beef	

Ra-226 in Beef

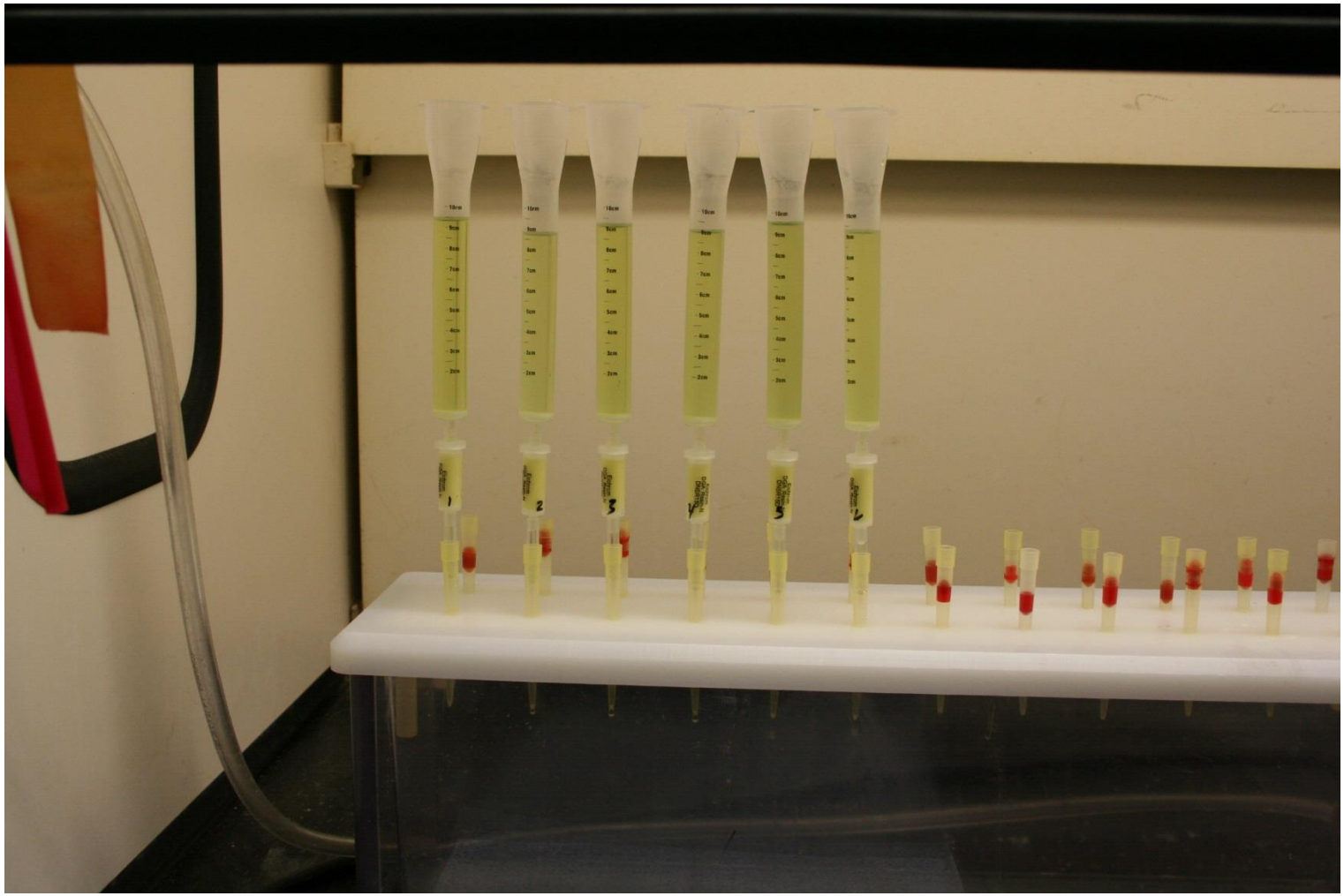
Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	101.4	36.84	33.44	-9.2
2	97.9	36.84	33.40	-9.3
3	105.3	36.84	35.73	-3.0
4	97.6	36.84	36.43	-1.1
Avg	100.6		34.8	-5.7
SD	3.6		1.6	
% RSD	3.6		4.5	
			100g beef	

Sr-90 in Cheese

- **Approach – employ DGA Resin, robust, no waiting for ingrowth**
  - 50 gram sample aliquot
  - 'Reverse' Aqua regia digestion, then multiple nitric acid additions and evaporation, then hydrogen peroxide (alternate with HNO_3), furnace overnight, final wet-ash
  - Load to DGA Resin in 8M HNO_3 plus boric acid/$Al(NO_3)_3$
    - *Very high k' for Y(III)*
  - Purify Y-90, count by gas flow proportional counting, yield via ICP-MS
    - *Option for very high Cs-137, insert YF_3 precipitation step*
    - *With enhanced Cs-137 removal step , adding 37 Bq Cs-137 had no adverse impact on results*
    - *LSC or Cerenkov can be utilized as well*
  - *Y-91 from fresh FP release will interfere, however addition count (s) may allow resolution via simultaneous equations*



Y-90 Purification on DGA Resin



Results for Cheese Spiked with Sr-90

Sample ID	Y carrier Yield (%)	^{90}Sr Reference Value (mBq g^{-1})	^{90}Sr Measured Value (mBq g^{-1})	Difference (%)
1	82.0	5.92	5.54	-6.37
2	84.8	5.92	5.80	-2.04
3	84.3	5.92	5.66	-4.38
4	85.6	5.92	5.67	-4.24
5	83.8	5.92	5.75	-2.92
6	86.9	5.92	5.84	-1.41
Avg. Spiked Smps	84.6			-3.6
SD	1.7			1.8
% RSD	2.0			
		60 minute count		

Results for Cheese Spiked with Sr-90

Sample ID	Y carrier Yield (%)	^{90}Sr Reference Value (mBq g^{-1})	^{90}Sr Measured Value (mBq g^{-1})	Difference (%)
1	86.1	5.64	5.62	-0.38
2	87.2	5.64	5.39	-4.37
3	93.2	5.64	5.29	-6.10
4	95.7	5.64	5.19	-8.03
5	93.5	5.64	5.33	-5.51
6	92.8	5.64	5.96	5.72
Avg. Spiked Smps	91.4			-3.1
SD	3.9			5.0
% RSD	4.2			
		60 minute count	37 Bq Cs-137 added	

Optional CaF_2/YF_3 precipitation step to remove very high interferences such as Cs-137

Summary

- **Significant progress on rapid radioanalytical methods for urban matrices**
  - Limestone and marble
  - Concrete
  - Granite and steel
- **New work**
  - Ra-226 in fish and beef
    - *Cation exchange resin +DGA Resin*
    - *Approach can be applied to other biological samples*
  - Sr-90 in cheese
    - *No waiting for Y-90 ingrowth, robust*
    - *Enhanced removal of beta interferences*
- **Ongoing research for Po-210 in urban matrices**