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Recent developments in the analysis of Actinides, Sr and Ra from difficult matrices

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Difficult Matrices

- **UNLV dissertation: Rapid methods for actinide and Sr-89,90 determination in urban matrices**
  - Previous publications on soil, milk, bioassay samples, animal tissue, vegetation, food, concrete, brick and asphalt
  - Dissertation covers new methods for limestone, marble, large concrete samples, granite and steel
- **Actinides in Granite**
  - Wednesday 10:10 AM
- **Sr-89,90 in Steel**
  - Thursday 8:50 AM
- **Today**
  - Recent work on Pu, Ra in steel, Ra-226 in fish, beef , Sr-90 in cheese

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

- ***Critical that radiochemical assays be completed in just a few hours***
- **Solid matrices offer significant challenges**
  - analytical methods employed must be able to overcome these difficulties
  - dissolution and matrix issues
  - refractory particles

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 an 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

Difficulties

- **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***
    - ***Actinides: separation from other alpha emitters***
    - ***Sr-89,90: separation from other beta interferences***
  - **Urban matrices require sample digestion/destructive analysis**
    - ***Potential refractory particles***
    - ***Need to be fast and robust***

Literature Survey Examples

- **Tavčar et al. reported a method to determine actinides in soil using acid leaching where Pu and Np isotopes were separated using a traditional ion exchange process**
  - The chemical yields for Pu were ~60% and the Np yields were ~40%
  - Acid leaching may not dissolve refractory particles
    - *Tavčar P, Jakopič R, and Benedik L (2005) Sequential Determination of ^{241}Am, ^{237}Np, Pu Radioisotopes and ^{90}Sr in Soil and Sediment Samples, Acta. Chim.Slov. 52: 60-66*

Literature Survey Examples

- **Wang et al. - 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, lower chemical yields*
  - 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
  - 53-57% chemical yields, ±18% difference from known values

Literature Survey - Conclusions

- **Often use acid leaching *without total digestion***
- **Lower chemical yields**
- **Complex methods**
- **Time-consuming**
- **Need fast, reliable methods for urban matrices such as**
  - Limestone
  - Marble
  - Granite
  - Steel

Urban Matrices- Challenges

In addition to refractory particles and the need for *immediate* results…

Sample Matrix	Challenges
– Limestone	high calcium content
– Marble	high calcium content
– Concrete	high calcium, silicates, different aggregates
– Steel	high iron content, other components
– Granite	hardness, lack of homogeneity, silicates

Approach

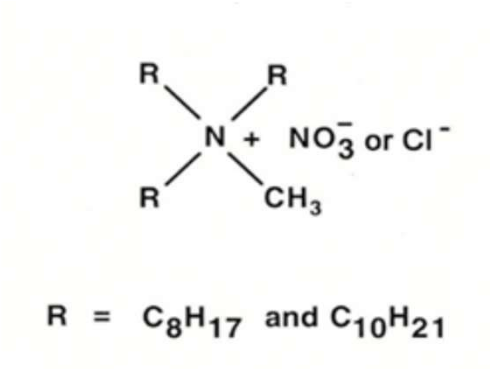
- **Steel**
  - Pu isotopes
  - Ra-226
  - *How to digest? preconcentrate?*
  - Separation/measurement
- **Fish/beef**
  - Ra-226
- **Cheese**
  - Sr-90

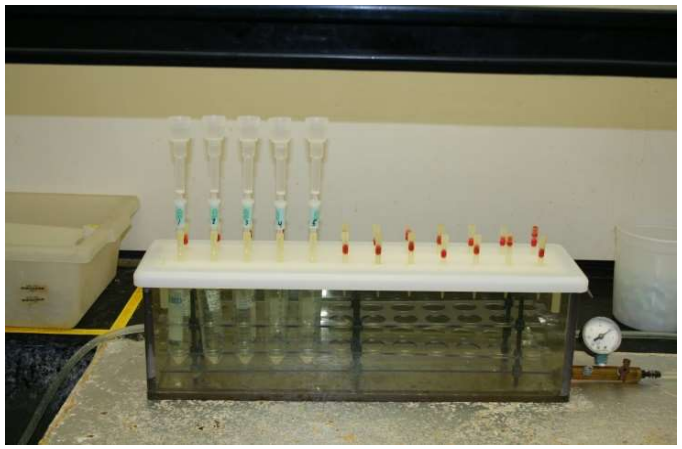
Rapid Method for Plutonium in Steel Samples

- **Steel- high iron content, also chromium, nickel, etc**
- **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 cause larger column load solutions and interfere with some resin separations
    - *TRU Resin, DGA Resin in HCl*

Plutonium Purification for Counting

- **Rapid Column Separations**
  - Pu on TEVA Resin
    - *Anion exchange extractant Aliquat 336 (trialkyl, methylammonium nitrate or chloride)*
    - *Valence adjustment to Pu(IV)*
  - Tests with refractory Pu-239/240 show very low recovery <u>without HF</u>
    - *Tested by adding MAPEP 24 soil (refractory Pu)*
    - *Tested acid digestion plus fusion option*





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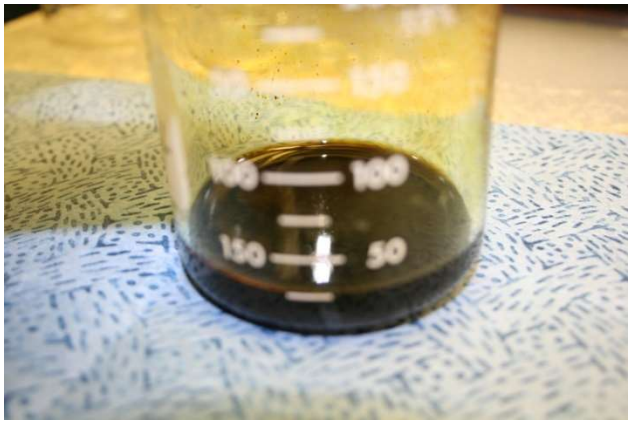
DOI 10.1007/s10967-017-5501-x

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]

One Step Preconcentration



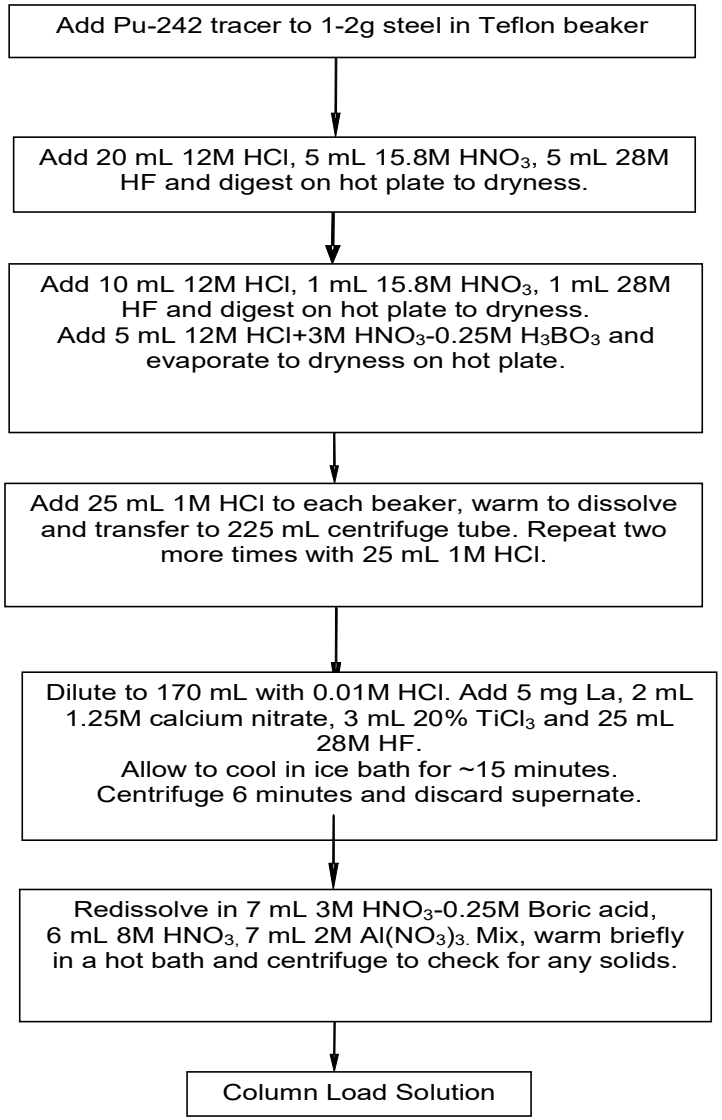
Use Aqua Regia +HF

(If HF use Teflon)

LaF_3/CaF_2 precipitation

Pu Isotopes on TEVA Resin

Sample Dissolution for Pu Isotopes in Steel



Also tested acid dissolution
+ fusion option
- for concrete plus steel

Results for Stainless Steel Samples Spiked with Pu-238

Sample	^{242}Pu Yield	Tracer Peak	^{238}Pu Reference Value	^{238}Pu Measured Value	^{238}Pu Measured Value	Difference
ID	(%)	(FWHM)	(mBq g^{-1})	(pCi g^{-1})	(mBq g^{-1})	(%)
1	90.8	37.1	37.0	0.988	36.56	-1.2
2	85.4	49.8	37.0	0.968	35.83	-3.2
3	89.6	43.0	37.0	1.014	37.53	1.4
4	90.7	42.4	37.0	1.059	39.19	5.9
5	90.2	46.9	37.0	1.064	39.37	6.4
Avg. Spiked Smps	89.3			1.0	37.7	1.9
SD	2.3			0.0	1.6	4.2
% RSD	2.5			4.2	4.2	
		~2 g stainless steel	16 hour count			

TEVA Resin + alpha spectrometry

Tests with refractory Pu – low without HF

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		

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		

Why is Ra-226 a concern?

- ^{226}Ra ($T_{1/2}$ = 1600 y) is 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
- ^{226}Ra 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**
  - the potential is higher for a radiological event leading to a significant committed dose from ^{226}Ra
- **The IAEA AMERA (Analytical Laboratories for the Measurement of Environmental Radioactivity) network administered proficiency testing for the rapid analysis of ^{226}Ra 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***
- ***Need for fast reliable results for ^{226}Ra in urban matrices***

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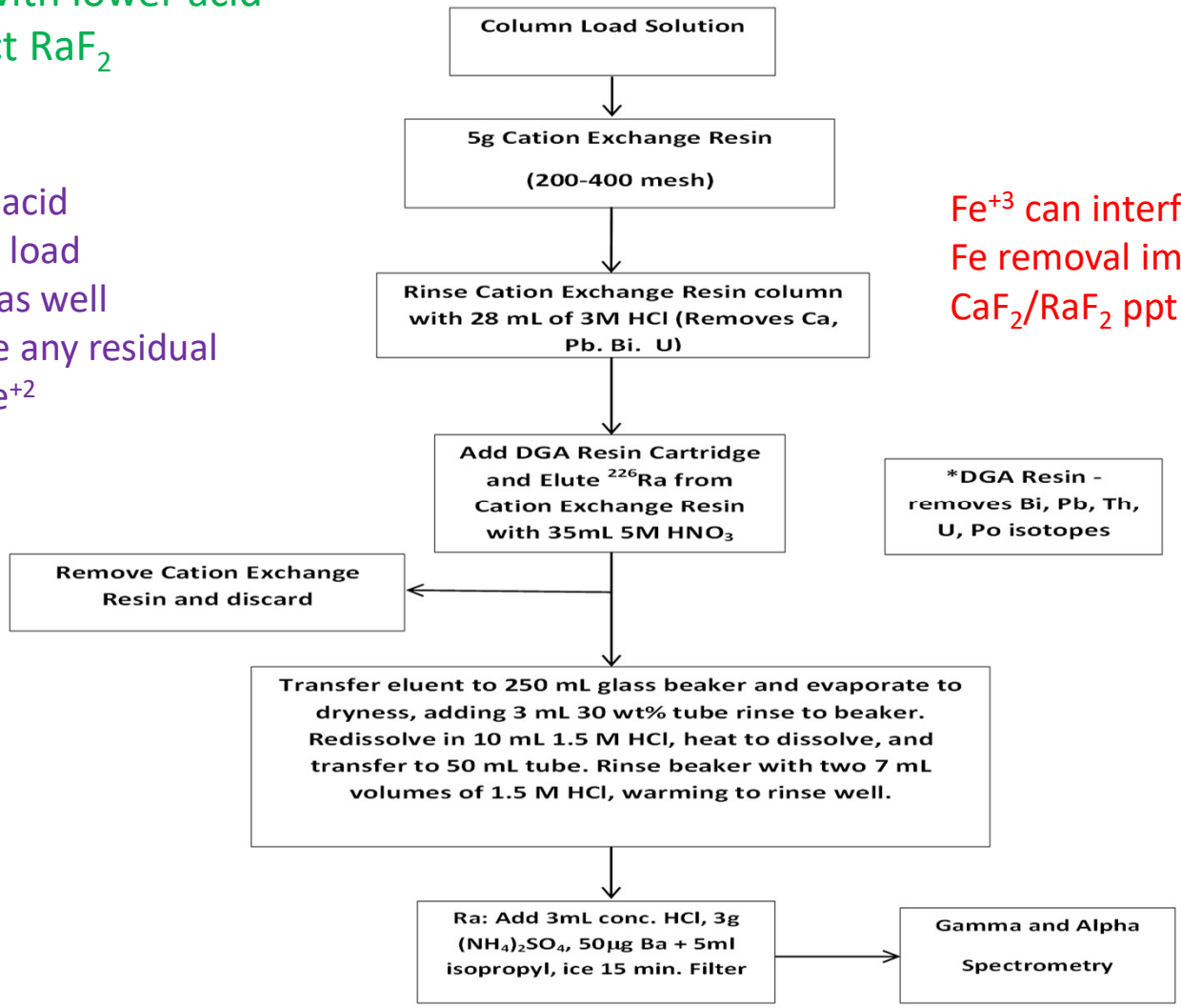
Rapid method to determine ^{226}Ra in steel samples

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

Rapid Extraction Method for Ra-226 in Steel

Ra ppt with lower acid to collect RaF_2

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



Fe^{+3} can interfere so Fe removal important at CaF_2/RaF_2 ppt. step

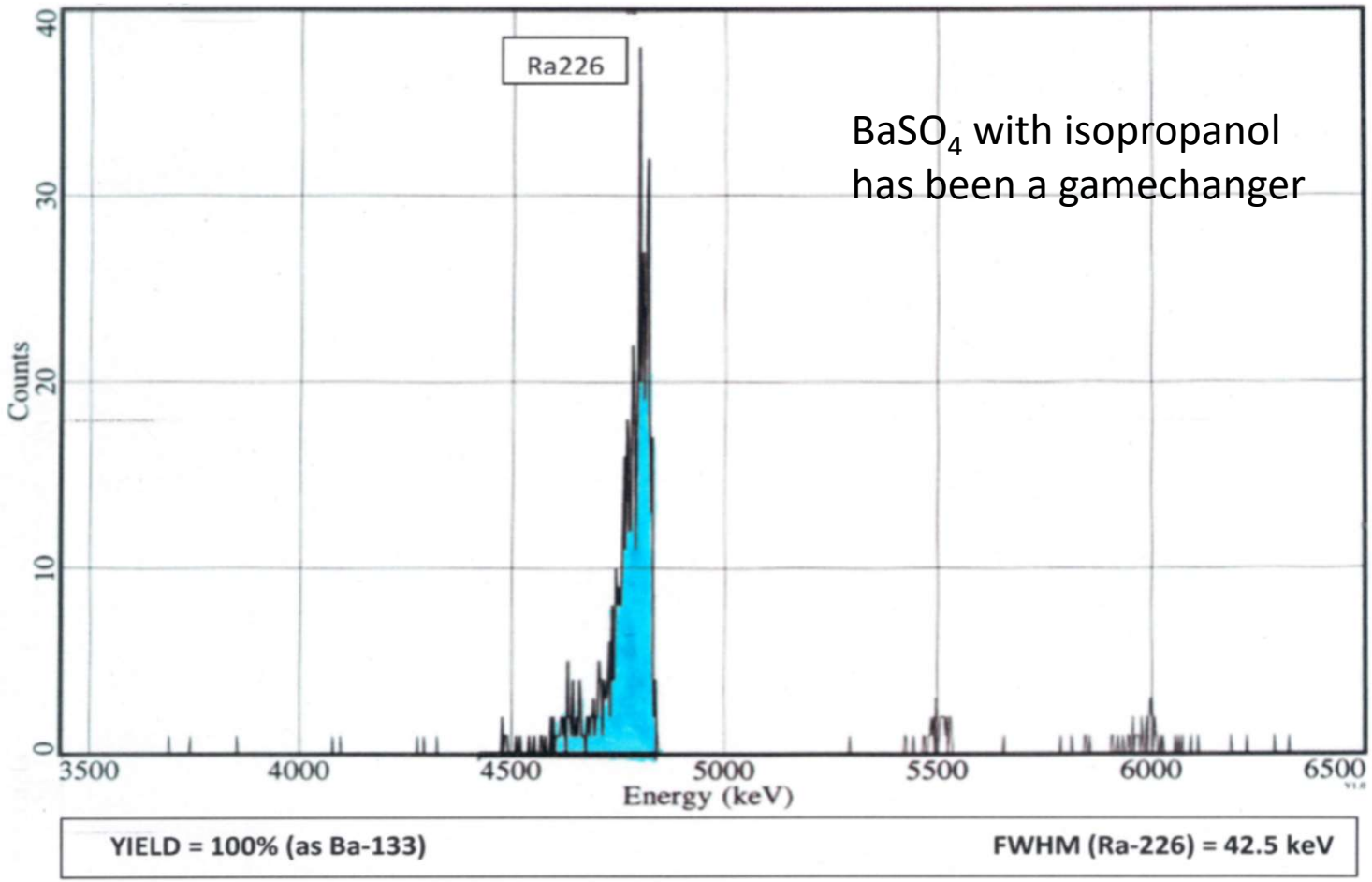
Results for Ra-226 Spiked in Steel

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

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- Alpha Spectra



$BaSO_4$ with isopropanol has been a gamechanger

Ongoing Work

- **Rapid, rigorous, defensible methods**
  - Sr-90 in foods such as cheese for emergency response
  - Ra-226 in fish and beef samples
  - Po-210 in air filters and soil
    - *microprecipitation-faster more rugged than autodeposition sample test source preparation*
    - *Eliminates risk of poor alpha spectra*

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 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
  - Similar to Ra-226 in steel method
  - Count Ra-226 on filter by alpha spectrometry, Ba-133 yield via gamma spectrometry

Sample Preparation Ra-226 in Fish/Beef

Place 50-100 g sample in glass beaker

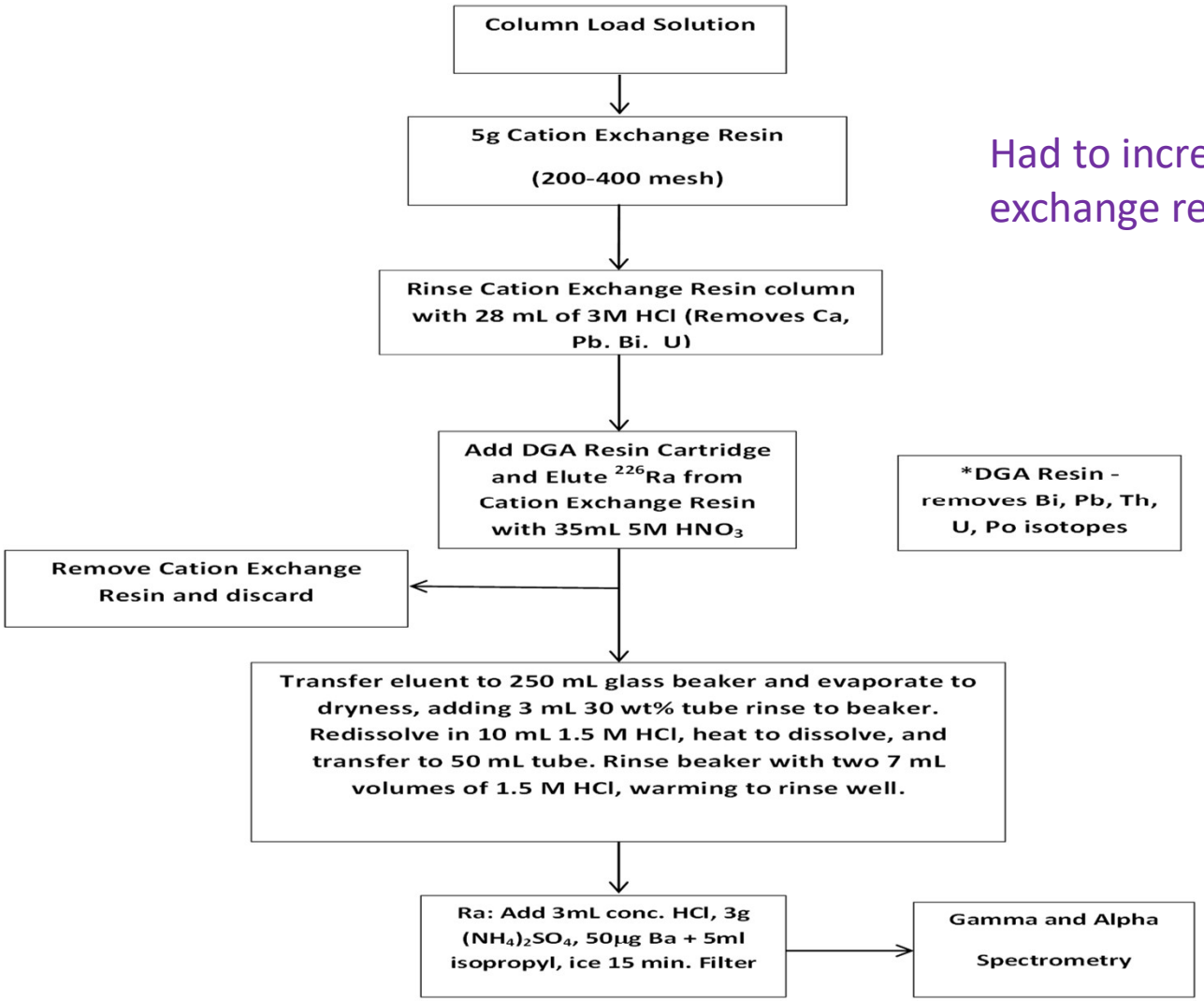
Add ^{133}Ba as Tracer

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



Had to increase cation exchange resin to 6g

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	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	

For 50g aliquot 36.84 mBq/smp = 0.737 mBq/g

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	0.38
SD	6.6		1.5	
% RSD	8.0		4.0	
			100g bass	

For 100g aliquot 36.84 mBq/smp = 0.0.368 mBq/g

Ra-226 in Beef

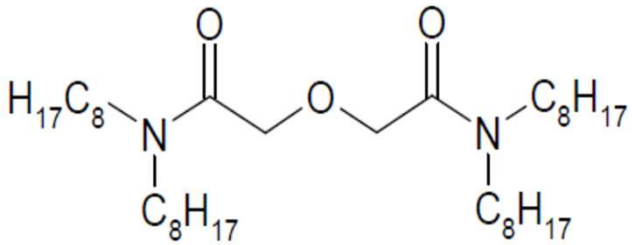
Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	82.7	36.84	35.26	-4.3
2	88.1	36.84	37.55	1.9
3	94.1	36.84	35.86	-2.7
4	78.8	36.84	36.42	-1.1
5	82.1	36.84	33.50	-9.1
6	89.7	36.84	33.67	-8.6
Avg	85.9		35.4	-4.0
SD	5.7		1.6	
%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

Ra-226 in Beef

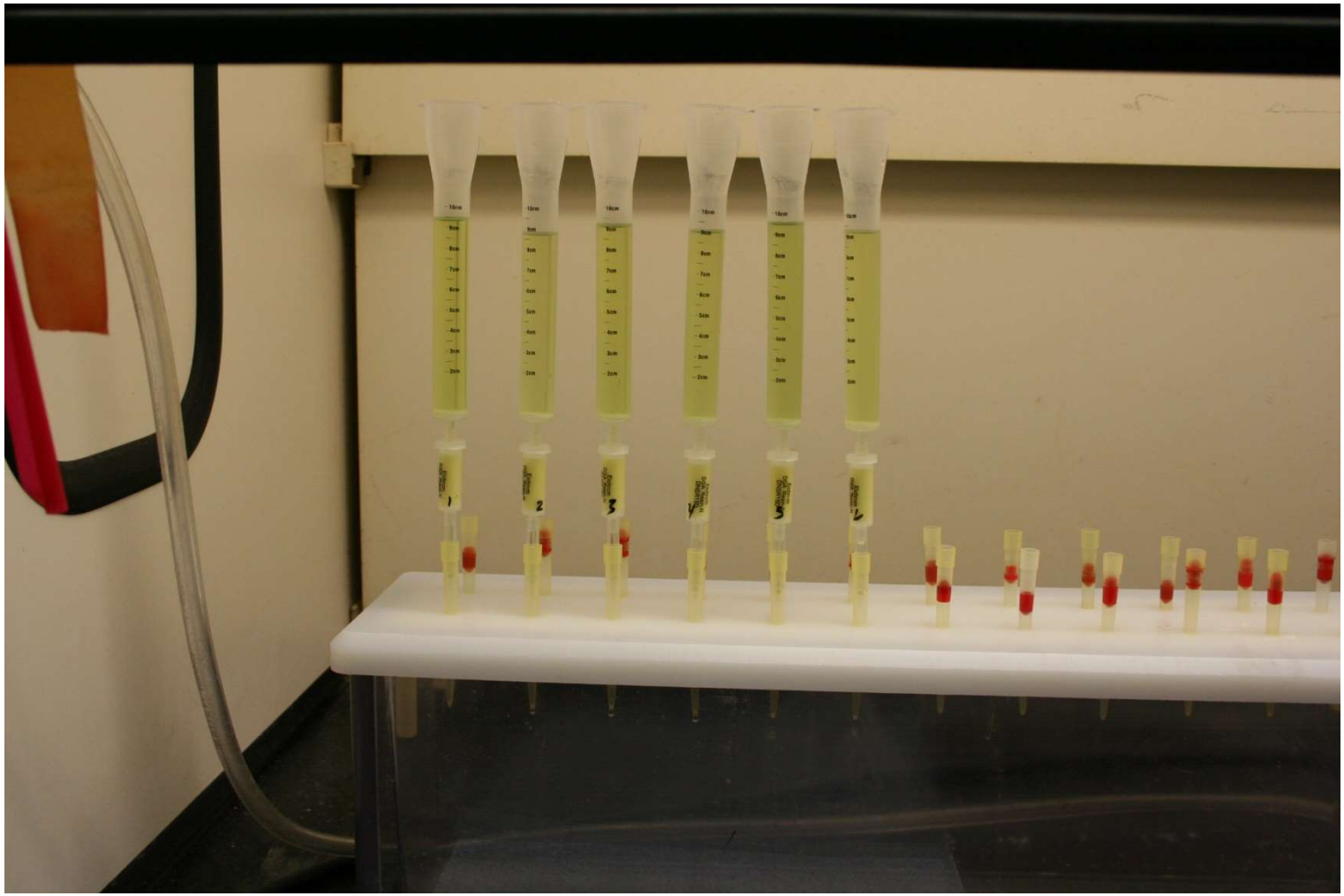
Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value (mBq smp^{-1})	Difference (%)
1	101.4	36.84	33.44	-9.2
2	97.9	36.84	33.40	-9.3
3	105.3	36.84	35.73	-3.0
4	97.6	36.84	36.43	-1.1
Avg	100.6		34.8	-5.7
SD	3.6		1.6	
% RSD	3.6		4.5	
			100g beef	

Sr-90 in Cheese

- **Approach**
  - 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/$Al(NO_3)_3$
  - Purify Y-90, count by gas flow proportional counting, yield via ICP-MS
    - *Option for very high Cs-137, insert YF_3 step*
    - *With enhanced Cs-137 removal step , adding 1000 pCi Cs-137 had no adverse impact on results*
    - *LSC or Cerenkov can be utilized as well*



Y-90 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	

Summary

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