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Rapid Methods for Ra-226 and Ra-228: An Update

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Outline

- Ra-226 in water
  - Can we apply the approach we used for urine?
  - $PO4^{-3}$ vs. $CO3^{-2}$
  - Ba-133 vs. Ra-225 tracer
  - DGA Resin instead of Ln Resin?
- Ra-226 in vegetation
  - Fusion?
- Ra-228 in water
  - Immediate collection of Ac-228 vs. Ingrowth

Background

- Need for rapid radiochemical methods
  - Emergency response
    - *Radiological event*
    - *Rapid turnaround times*
    - *High capacity*

- Ra-226
  - *in hospitals, laboratories*
  - *alpha emitter, 4.78 MeV (94.5%), 4.61 MeV (5.55%)*
  - *1600 year half-life (alpha spectrometry and ICP-MS)*
  - *radiotoxic, follows calcium in food chain into bones*

- Urine

Maxwell S, Culligan B, Hutchison J, Utsey R and McAlister, D (2014) Rapid determination of ^{226}Ra in emergency urine samples. Journal of Radioanalytical and Nuclear Chemistry, online first, Feb. 2014

Risk from Ra-226

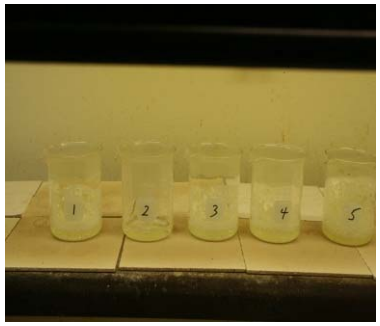
- More dangerous “dirty bomb” than Uranium RDD
  - *Delivers much higher dose*
- Besides RDD…
  - Risk of addition at post-treatment water supply
- Ra-226 has been trafficked repeatedly in different countries
  - *Po-210 has already been used successfully for a criminal act*

- Risk Due to Radiological Terror Attacks With Natural Radionuclides
  - Steinhäusler Friedrich, Rydell Stan, and Zaitseva Lyudmila
  - Citation: AIP Conference Proceedings 1034, 3 (2008); doi: 10.1063/1.2991254

Rapid Ra-226 Aqueous Sample Preparation

RRMC 2011

Wet-ash urine ppt



150mL Water or Urine
Add Th-229 (Ra-225) tracer

↓

Add 10ml conc. NH_4OH

↓

Add Ca*, 25mL 2M Na_2CO_3

↓

Ice for 10 minutes then Centrifuge

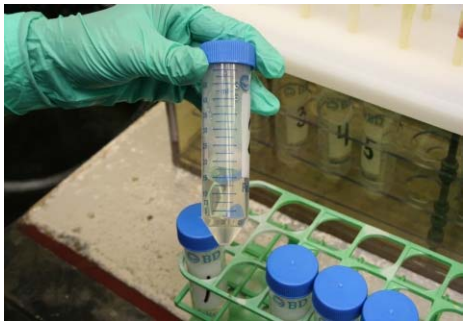
↓

Redissolve in 20mL 1.5M HCl
Add 3mL 1.5M Ascorbic Acid

↓

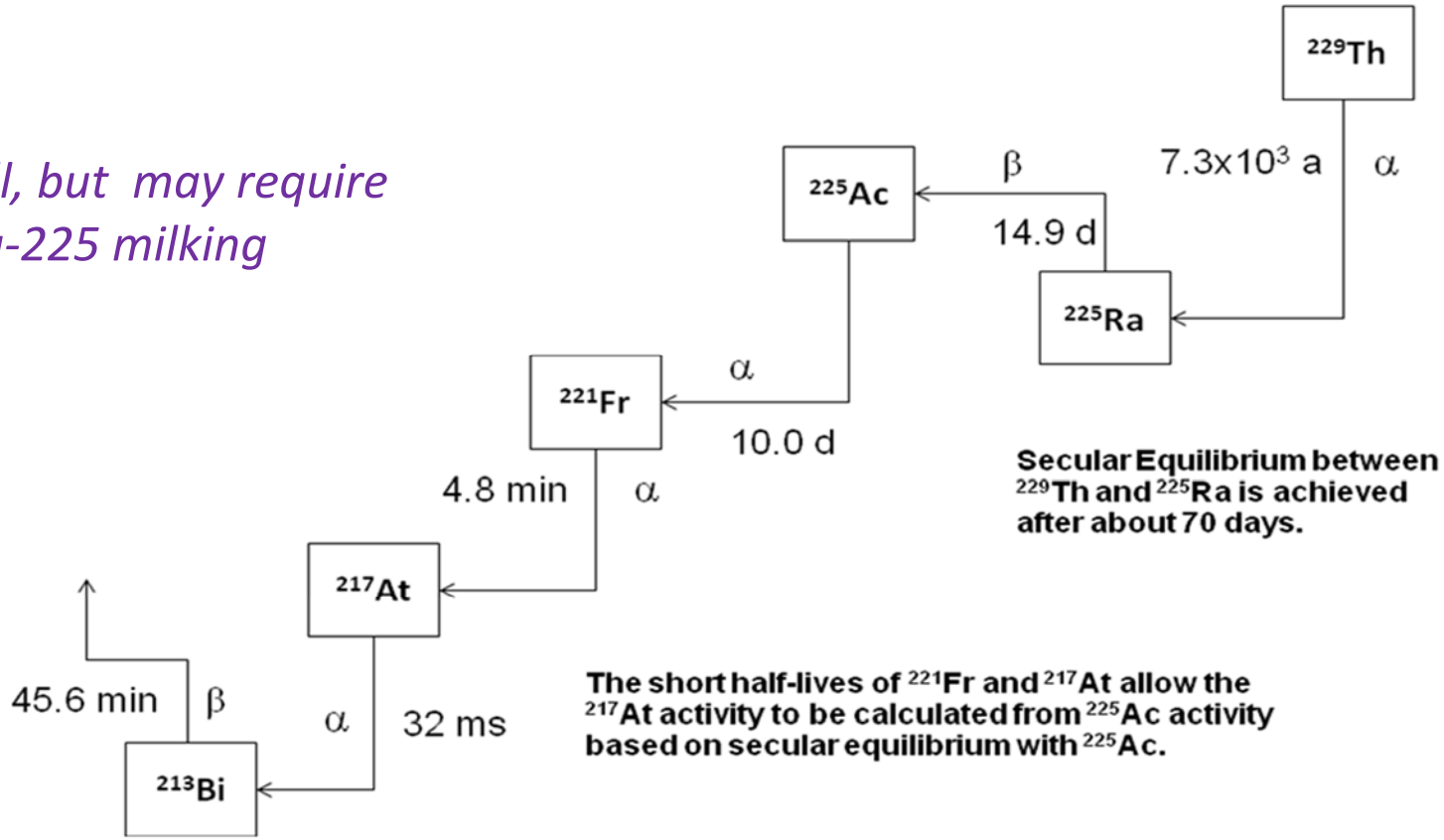
Column Load Solution

***Ca addition:**
Water: 100-150mg
Urine: 100mg



Ra-225 Tracer Decay

Works well, but may require Th-229/Ra-225 milking



Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events, EPA 402-R-10-001 February 2010

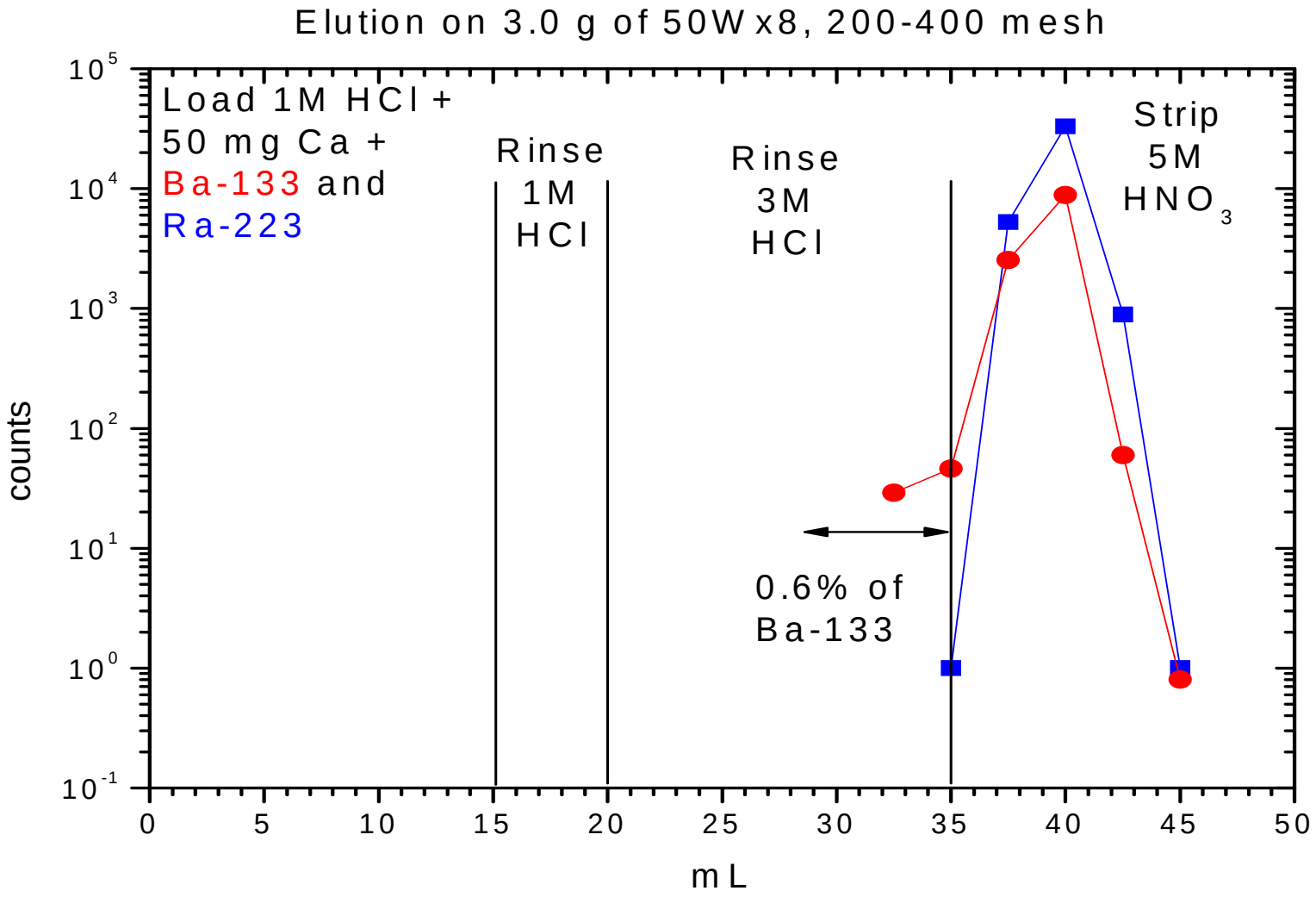
Water Samples

- Ba-133 tracer may be very useful
  - *No waiting for ingrowth*
  - *No need to remove stable Ba (as with soil)*
  - *Allows for Ra-224 assay*
  - *Assurance Ba/Ra are in sync can be managed (no divergence)*
  - *No milking of Th-229/ lower blanks*
  - *Less chance of detector contamination*
- But
  - 2 counts are needed (gamma count can be very short)

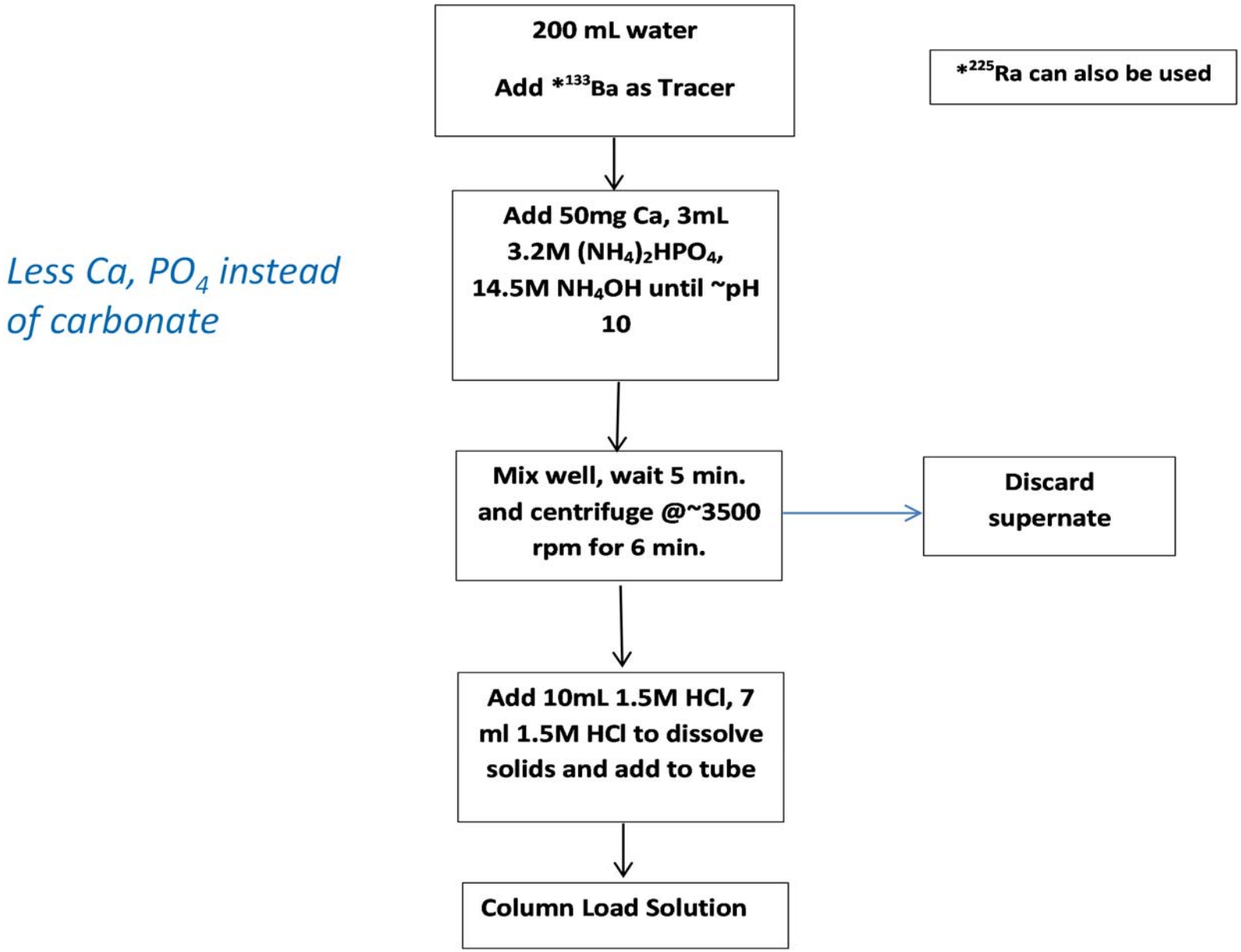
SRNS Approach

- Use calcium phosphate instead of calcium carbonate
  - *Slight Ra-226 contamination in sodium carbonate*
  - *Need low blanks*
  - *Lower solubility of calcium phosphate – lower Ca needed*
    - *Less Ca* → *less cation resin* → *less volume* → *less time*
- Use stacked elution with Cation resin+ DGA Resin to save time

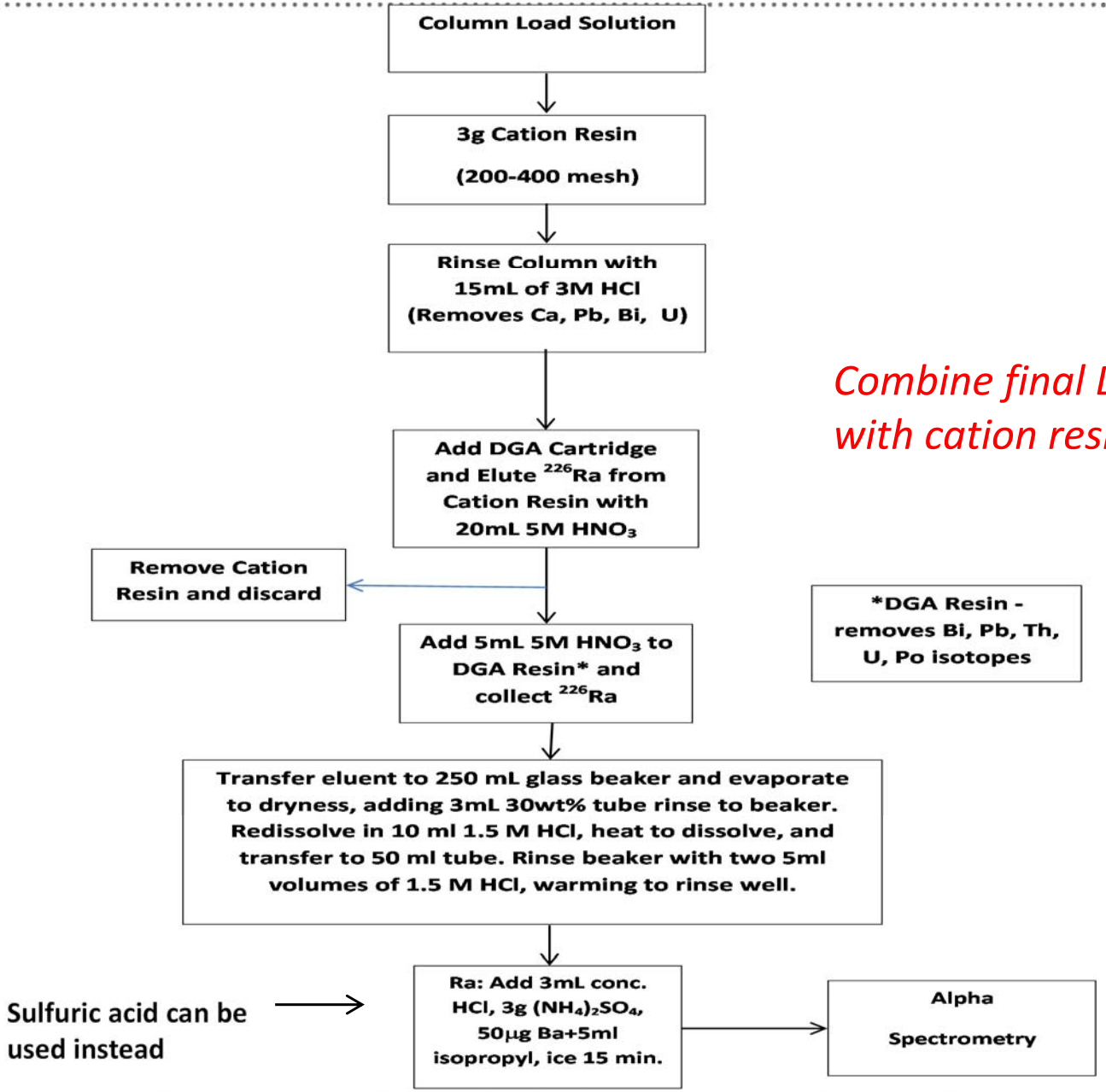
Ba and Ra Behavior on Cation Resin



Rapid Sample Preparation for Ra-226 in Water



Rapid Column Separation for Ra-226 in water



Combine final DGA purification with cation resin elution!

Rapid Separation using Cation + DGA Resin : stacked elution

Sample	Ba-133 pCi	Yield (%)	Ra-226 pCi	Cal factor	Corrected result pCi	Corrected for Ba-133 yield pCi	Bias (%)
1	1319	95.3	2.015	0.955	1.92	2.02	1.40
2	1253	90.5	1.782	0.955	1.70	1.88	-5.60
3	1370	99.0	2.098	0.955	2.00	2.02	1.65
4	1375	99.3	2.168	0.955	2.07	2.08	4.66
5	1288	93.0	1.936	0.955	1.85	1.99	-0.23
6	1340	96.8	1.902	0.955	1.82	1.88	-5.79
7	1338	96.6	2.116	0.955	2.02	2.09	4.97
Avg.	1326.1	94.9				1.98	-0.85
SD	43.8	4.2				0.08	4.12
RSD	3.30	4.5				4.15	

2 pCi in 200 ml aliquot = 10 pCi/L

DI Water

Rapid Separation using Cation + DGA Resin : stacked elution

Sample	Ba-133	Yield	Ra-226	Cal factor	result	Ba-133 yield	Bias
	pCi	(%)	pCi		pCi	pCi	(%)
1	877.2	93.3	0.008	0.955	0.01	0.008	N/A
2	952.5	101.3	4.040	0.955	3.858	3.808	-4.81
3	1024	108.9	4.208	0.955	4.019	3.689	-7.78
4	896.7	95.4	4.350	0.955	4.154	4.355	8.87
5	842.4	89.6	4.234	0.955	4.043	4.512	12.80
6	897.6	95.5	3.693	0.955	3.527	3.693	-7.66
7	945.5	100.6	4.130	0.955	3.944	3.921	-1.97
8	773.9	82.3	3.710	0.955	3.543	4.303	7.59
Avg.	901.2	95.9				4.04	1.01
SD	75.5	8.0				0.34	8.56
RSD	8.38	8.4				8.5	

4 pCi in 200 ml aliquot = 20 pCi/L

ATP water

Rapid Column using Cation + DGA Resin : stacked elution

Sample	Ba-133	Yield	Ra-226	Cal factor	Corrected result	Corrected for Ba-133 yield	Bias
	pCi	(%)	pCi		pCi	pCi	(%)
1	994.8	99.5	0.1007	0.955	0.10	0.097	-3.36
2	968.3	96.9	0.1120	0.955	0.107	0.110	10.42
3	922.1	92.2	0.0854	0.955	0.082	0.088	-11.64
4	901.5	90.2	0.0834	0.955	0.080	0.088	-11.68
5	1057	105.7	0.1210	0.955	0.116	0.109	9.29
6	939.6	94.0	0.1066	0.955	0.102	0.108	8.31
Avg.	963.9	96.4				0.100	0.22
SD	56.3	5.6				0.010	10.5
RSD	5.85	5.8				10.4	

0.1 pCi in 200 ml aliquot = 0.5 pCi/L

DI Water

Blank Test using Cation + DGA Resin : Stacked elution

Sample	Ba-133	Yield	Ra-226	Cal factor	Corrected result	Corrected for Ba-133 yield
	pCi	(%)	pCi		pCi	pCi
1	1347	97.3	0.0007	0.955	0.0006	0.0006
2	1437	103.8	0.0007	0.955	0.0007	0.0006
3	1254	90.6	-0.0014	0.955	-0.0013	-0.0015
4	1319	95.3	0.0051	0.955	0.0049	0.0051
5	1302	94.0	0.0027	0.955	0.0026	0.0028
Avg.	1331.8	96.2				0.0015
SD	67.8	4.90				0.0025
RSD	5.09	5.09				

DI Water

Ra-226 in Vegetation

- Weigh 5g vegetation in 250 ml Zr crucible
- Add Ba-133 tracer
- Ramp from 300C to 600C; remove crucibles
- Wet ash with HNO_3/H_2O_2 briefly on hotplate
- Fuse samples with 10g NaOH at 600C
- Transfer to 225 ml tube…150 ml volume with water

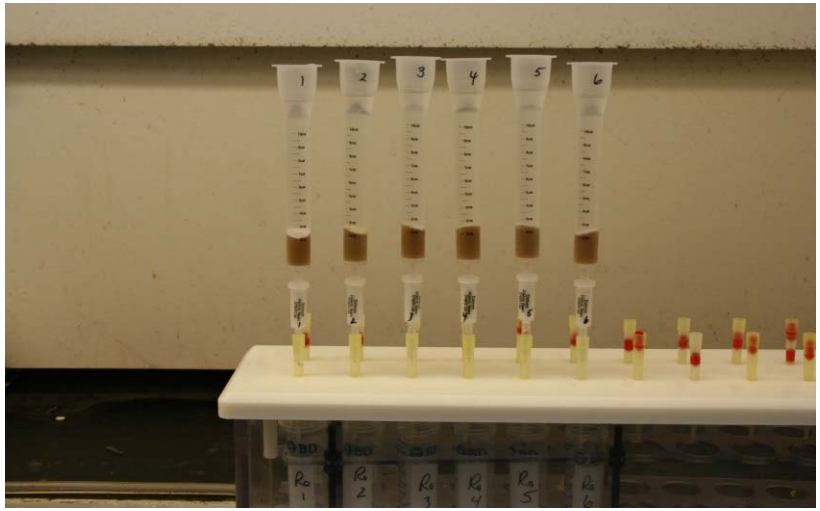
Ra-226 in Vegetation

- Add 10 ml 12M HCl, mix
- Add 100 mg Ca and 10 ml 2M sodium carbonate and mix.
- Wait 10 minutes, centrifuge 5 minutes.
- Dissolve ppt in 1M HCl, some HF (as needed) to dissolve Si solids
- Ready for cation resin

- *Less redissolution problems than with phosphate .....*
  - *but need to minimize carbonate to keep blanks low*

Cation Resin + DGA Resin Rapid Purification

- Load 20 ml 1-1.5M HCl with trace HF to 5g cation resin
- 30 ml 3M HCL rinse (to remove Ca)
- Add DGA Resin
- 20 ml 5M HNO3 elution through DGA
- Convert to HCl, BaSO4 micro-ppt.



- Tested with 5g MAPEP blank vegetation material
- Plan to test with foods….

Ra-226 Results for Spiked Vegetation

Spiked Veg	Ba-133	Yield	Ra-226	Cal factor	Corrected result	Corrected for Ba-133 yield	Corrected for native Ra-226	Bias
	pCi	(%)	pCi		pCi	pCi	pCi	(%)
1	1836	85.1	2.025	0.955	1.934	2.272	2.081	4.03
2	1739	80.6	1.916	0.955	1.830	2.270	2.078	3.91
3	1758	81.5	1.865	0.955	1.781	2.185	1.994	-0.31
4	2033	96.9	2.216	0.955	2.116	2.183	1.992	-0.40
5	2050	97.7	2.208	0.955	2.109	2.157	1.966	-1.70
6	2021	96.4	2.248	0.955	2.147	2.228	2.037	1.83
7	2082	99.3	2.221	0.955	2.121	2.137	1.945	-2.73
Avg.	1931.3	91.1					2.01	0.66
SD	147.9	8.3					0.05	2.66
RSD	7.66	9.07					2.64	

5 g MAPEP blank vegetation, 8 hour count

What about Ra-228 in water?

- Immediate collection of Ac-228
- Some challenges with complete elution of La/Ac from Cation resin and behavior of Ac/La DGA Resin
- Wanted to make more rugged

J Radioanal Nucl Chem (2013) 295:2181–2188
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Rapid method for determination of ^{228}Ra in water samples

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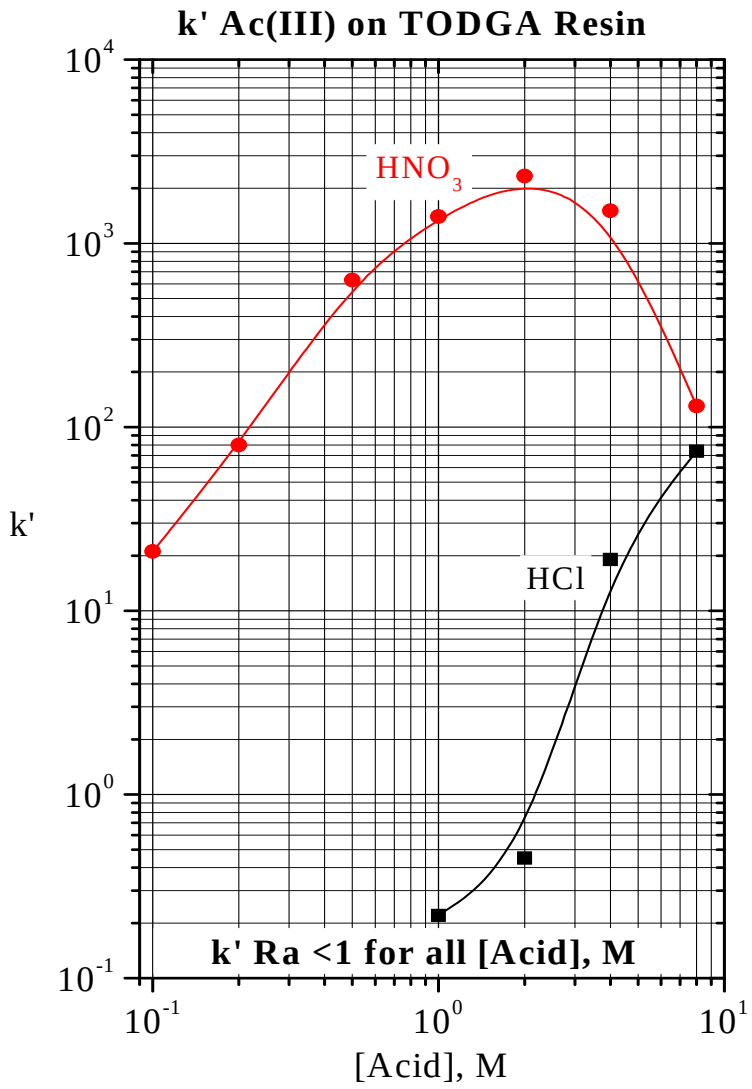
Ra-228 Update

- *Updated our Ra-228 method*
- *La carrier for yield*
- 1L sample aliquot
- CO_3^{-2} ppt enhanced with PO_4^{-3}
- Load to 5g cation resin and remove Ca with 3M HCl
- Elute Ra-228 and La with 8M HNO_3
- *Wait 36 hours for Ac-228 ingrowth*
- Load Ra-228 to DGA Resin from 6M HNO_3. Modified rinses slightly.
- Elute with 2M HCl and measure La yield via ICP-MS
- Count AcF_3 on 25 mm filter by gas flow proportional counting

Enhancements

- Wait on Ac-228 ingrowth
  - Reduces large volume of cation elution (7M HNO_3) passing directly through DGA Resin (stacked)
  - Elute Ra/La from cation resin with 30 ml 8M HNO_3, evaporate, wait 36 hours, redissolve in small load solution (6M HNO_3)



Ra-228 Test Results

Smp	La (Yield)	Ra-228 Reference (pCi/L)	Ra-228 Measured (pCi/L)	Bias (%)
1	96.2	92.6	93.3	0.78
2	97.1	92.6	98.3	6.11
3	95.4	92.6	98.1	5.92
4	92.3	92.6	95.2	2.80
5	97.2	92.6	88.1	-4.90
Avg.	95.6	92.6	94.6	2.1
SD	2.00			4.53
%RSD	2.09			

Ra-228 Test Results

Smp	La (Yield)	Ra-228 Reference (pCi/L)	Ra-228 Measured (pCi/L)	Bias (%)
1	92.5	37	37.1	0.32
2	94.3	37	35.3	-4.51
3	94.2	37	37.9	2.46
4	99.7	37	34.8	-6.05
5	88.7	37	38.2	3.14
6	97.4	37	35.9	-2.95
Avg.	94.5	37.0	36.5	-1.3
SD	3.82			3.80
%RSD	4.05			

Ra-228 Test Results

Smp	La (Yield)	Ra-228 Reference (pCi/L)	Ra-228 Measured (pCi/L)	Bias (%)
1	90.8	9.77	10.52	7.67
2	92.2	9.77	9.90	1.29
3	94.4	9.77	9.53	-2.43
4	97.0	9.77	10.38	6.26
5	97.1	9.77	10.30	5.41
6	95.3	9.77	10.11	3.49
Avg.	94.5	9.77	10.12	3.61
SD	2.55			3.71
%RSD	2.70			

Ra-228 Test Results

Smp	La (Yield)	Ra-228 Reference (pCi/L)	Ra-228 Measured (pCi/L)	Bias (%)
1	92.1	4.81	4.70	-2.25
2	90.8	4.81	4.60	-4.36
3	90.8	4.81	5.17	7.39
4	89.4	4.81	5.14	6.96
5	89.0	4.81	4.74	-1.39
6	95.7	4.81	4.83	0.51
7	91.8	4.81	4.70	-2.30
Avg.	91.4	4.81	4.8	0.65
SD	2.23			4.68
%RSD	2.44			

Ra-228 Test Results

Smp	La (Yield)	Ra-228 Reference (pCi/L)	Ra-228 Measured (pCi/L)	Bias (%)
1	94.8	3.46	3.51	1.45
2	95.3	3.46	3.54	2.31
3	96.8	3.46	3.09	-10.69
Avg.	95.6	3.5	3.4	-2.3
SD	1.06			7.27
%RSD	1.10			

Summary

- Rapid Methods for Ra-226
  - Rapid assessment of radiological impact is critical
  - Mitigate dose and protect the public and environment
  - Maintain public trust
  - *Lowers costs of routine operations*
- Improvements in Ra-226 methods for water and vegetation samples
  - <4-5 hours with simultaneous sample preparation
  - Ba-133: No waiting for Ra-225 in-growth
  - *Allows Ra-224 measurement*
  - Can be adapted to smaller or larger water aliquots as needed
- Improvements in Ra-228
  - Improved ruggedness with Ac-228 ingrowth, then loading to DGA Resin