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Rapid Method for ^{226}Ra in Urine Samples

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RRMC

10/29/14

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FLUOR • NEWPORT NEWS NUCLEAR • HONEYWELL

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
  - Rapid assay needed
  - Simple, fast and reliable

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

Passive Radiological Attack

- May 2002, a nuclear expert working in a hospital in China's Guangdong Province tried to kill his colleague by installing an iridium-192 source in the ceiling of his office.
  - The radioactive material sickened the man and 73 other staff members in the hospital, before it was eventually discovered and removed.

- September 1998, a graduate student in Providence, Rhode Island tried to poison his ex-girlfriend by tainting her food with iodine-125 he had stolen from Brown University's molecular pharmacology laboratory.

- 1995, 26 employees of the National Institutes of Health in Bethesda, Maryland, were exposed to radioactive phosphorus, which someone had used to contaminate a water cooler.
  - The FBI and other investigating agencies were never able to identify the culprit.

Need for Rapid Methods

- 1998: Chechen authorities foiled a possible terrorist act when they found and defused a mine attached to a container "full of radioactive substances" near Grozny, (terrorists stole radioactive waste from Russian RADON storage facility)

- *"Mexico Finds Stolen Radioactive Material Amid Dirty Bomb Fears"* http://www.voanews.com/content/nuclear-materia-stolen-in-mexico/1803195.html,12/4/13
  "A dirty bomb detonated in a major city could cause mass panic, as well as serious economic and environmental consequences"

- Are we ready??
  - Environmental and bioassay

Primary Laboratory Target CDG Levels (For Child or Pregnant Female)

		Day 1		Day 2		Day 3		Day 5		Day 7		Day 10		Day 15		Day 20	
Nuclide	Class*	Bq/L	µg/L	Bq/L	µg/L	Bq/L	µg/L	Bq/L	µg/L	Bq/L	µg/L	Bq/L	µg/L	Bq/L	µg/L	Bq/L	µg/L
Ra-226	M	2.44E+01	6.68E-04	4.74E+00	1.30E-04	3.21E+00	8.77E-05	1.68E+00	4.60E-05	8.71E-01	2.38E-05	4.13E-01	1.13E-05	2.14E-01	5.85E-06	1.68E-01	4.60E-06

4.54pCi/L

Calculations by David Saunders, CDC based on NCRP 161

Literature

- K. Kehagia, C. Potiriadis, S. Bratakos, V. Koukouliou and G. Drikos, Determination of 226Ra in Urine Samples by Alpha Spectrometry, Radiation Protection Dosimetry (2007), pp. 1–4
  - Evaporation, wet-ash, overnight in furnace, redissolution, lead sulfate ppt.
  - Anion resin, cation resin, EDTA, electrodeposition
  - 2 days to prep 4 samples, wait 4 days to begin count
  - 7200 minute count time, 50-70% yields, Ra-225 (At-217)

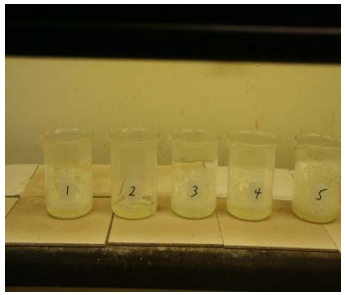
Literature

- Rapid determination of ^{226}Ra in urine samples, X. Dai et al Radiat Prot. Dosimetry 2012 Vol. 151 Issue 1, p30
  - *Radium is separated from urine matrix using cation and anion exchange*
  - *(224)Ra tracer is added, together with its parent (228)Th, for chemical recovery correction*
  - *After separation, hydrous titanium oxide precipitation and BaSO(4) micro-precipitation*
  - *MDA 0.22 Bq /L with 4 h of counting for 20 ml of urine sample.*
  - *Ra-224 has 3.66 day half-life*
    - *Is Ra-224 present in sample?*
    - *What if Ra-224 assay is needed?*

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

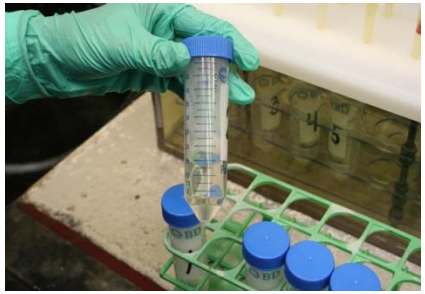
↓

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

↓

Column Load Solution

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



Ra-226 in Urine

Sample ID	^{217}At Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value * (mBq smp^{-1})	Difference (%)
1	91.2	73.8	75.5	2.4
2	88.3	73.8	88.4	19.9
3	84.7	73.8	82.7	12.1
4	85.0	73.8	76.8	4.1
5	94.1	73.8	78.3	6.1
6	87.7	73.8	78.7	6.6
7	99.2	73.8	70.8	-4.0
8	92.3	73.8	64.8	-12.1
Avg	90.3			
SD	4.9		77.0	4.4
% RSD	3.4			

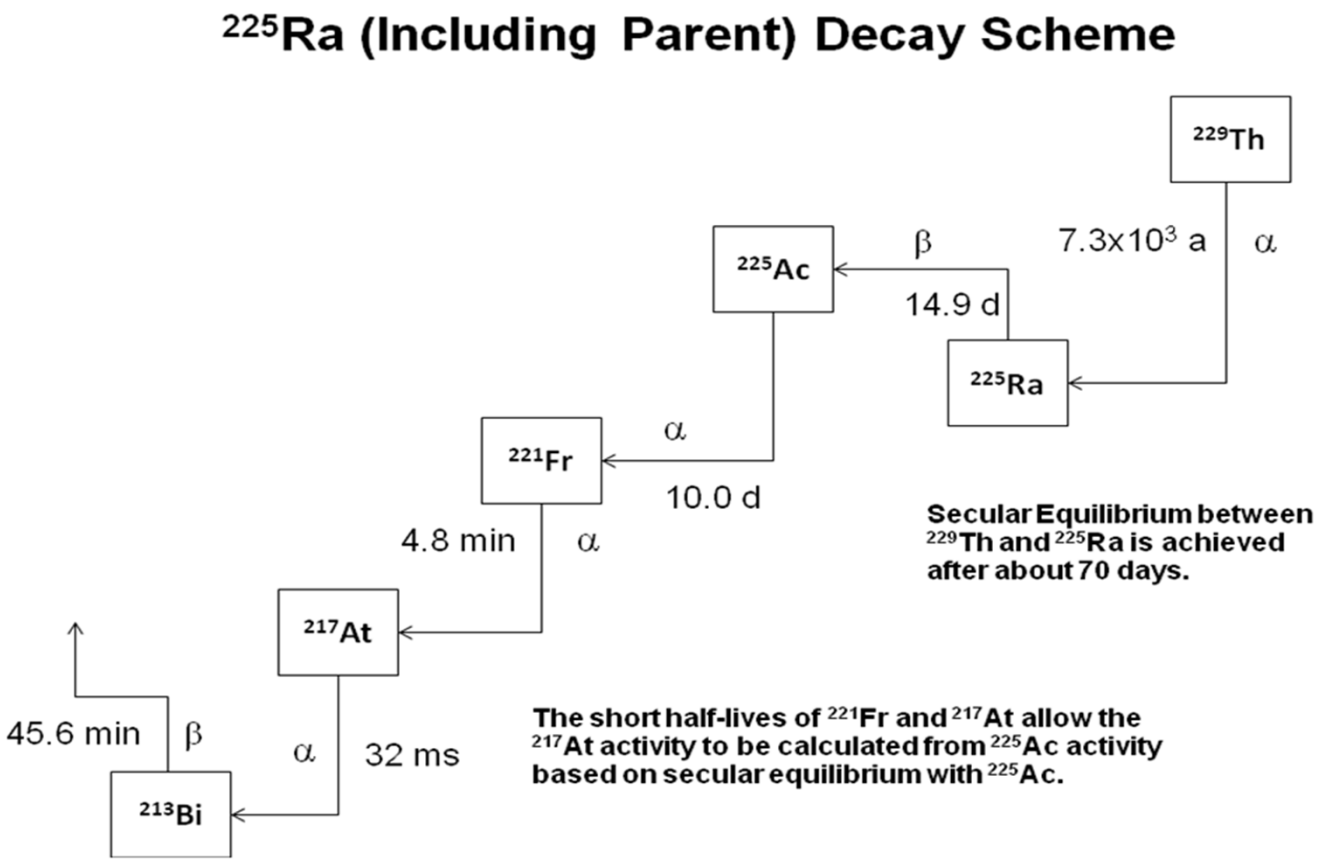
8hr count time
At -217 ingrowth to mid-point-17.75 hrs.
*corrected for 5.0 mBq Ra-226 in blank urine

Cation Resin + Ln Resin

RRMC 2011

S. L. Maxwell and B. K. Culligan, Rapid Determination of Ra-226 in Environmental Samples, Journal of Radioanalytical and Nuclear Chemistry, Volume 293, (2012), No.1, 149-156

Ra-225 Tracer Decay



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

Which tracer option to use?

- It depends…
  - *Ba-133 allows for immediate counting (and Ra-224 assay)*
    - *But for more difficult matrices…. Ba/Ra deviation may be seen*
    - *Ba-133 is counted by gamma spectrometry*
      - *so alpha spectrometry and gamma spectrometry measurement bias must be well-known and accounted for*
    - *For soils: use of Ba-133 means no stable Ba removal (Sr Resin) and small aliquot size*
      - *Ra-225 may have advantage in soil methods*
  - *Ra-225 behaves identically to Ra-226…. but ingrowth time is needed*
    - *Tracking separation times accurately very important*
      - *recounts may have large tracer peaks*
    - *Ra-225 can be added with Th-229 parent or added after "milking"*
      - Ra-225 milking from Th-229 can be done but it requires re-validation time and effort each month or so
      - method has to be able to handle Th-229 effectively if added with Ra-225
    - *Ac-225 interferes with Ra-224*

Emergency urine samples

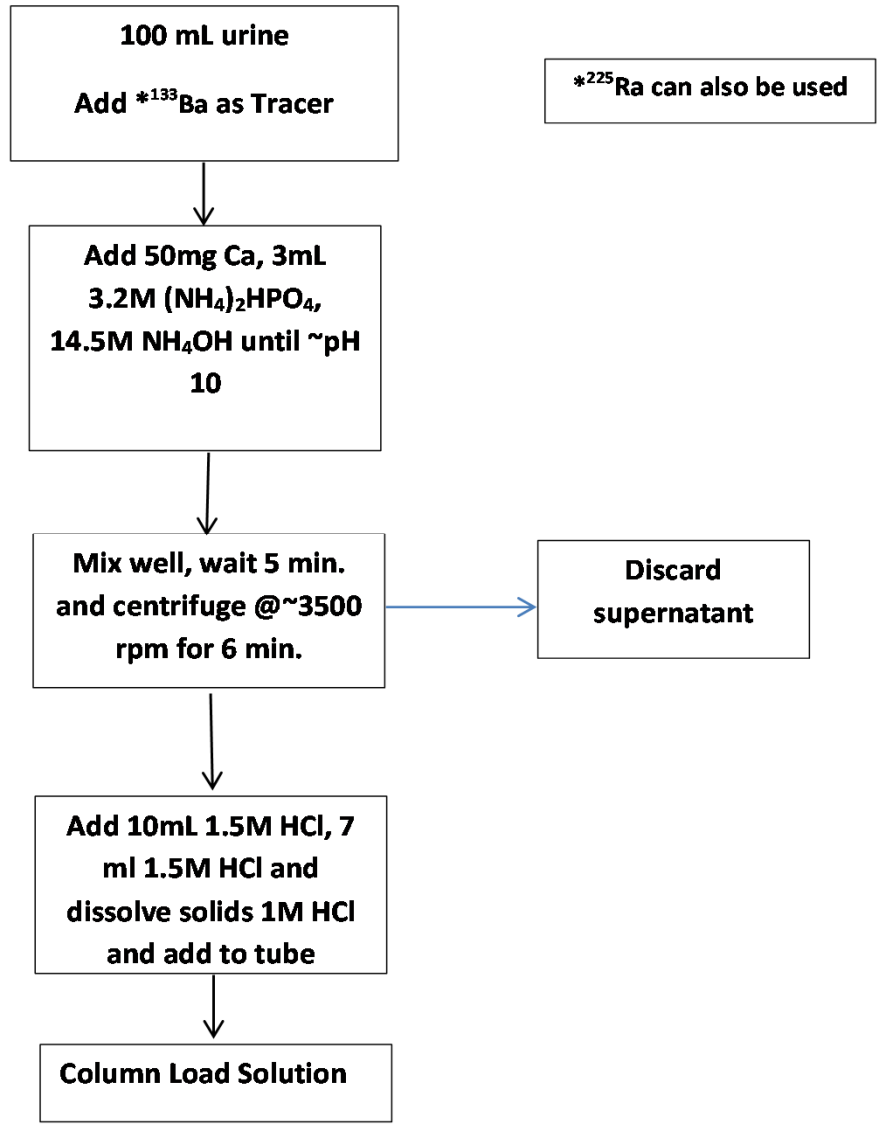
- Ba-133 tracer may be very useful
  - *No waiting for ingrowth*
  - *No need to remove stable Ba (as with soil)*
  - *Allows for Ra-224 assay*
  - *Assurance Ba/Ra are in sync can be managed (no divergence)*
- But
  - 2 counts are needed (gamma count can be very short)
  - Gamma and alpha measurement must not have significant bias vs. each other

SRNL Approach

- Use calcium phosphate instead of calcium carbonate
  - *Slight Ra-226 contamination in sodium carbonate*
  - *Need low urine blanks*
  - *Lower solubility of calcium phosphate – lower Ca needed*
    - *Less Ca* → *less cation resin* → *less volume* → *less time*
- Test DGA Resin vs Ln Resin
  - *Evaporation steps after cation resin just prior to redissolution in 0.02M HCl*
    - *have to be "babied" to avoid lower yields (presumably from oxides) which do not redissolve in the low acid*
  - *Ln Resin sometimes shows inconsistent flow issues at low acid levels*
  - *DGA Resin removes interferences and can be used with much higher acid*

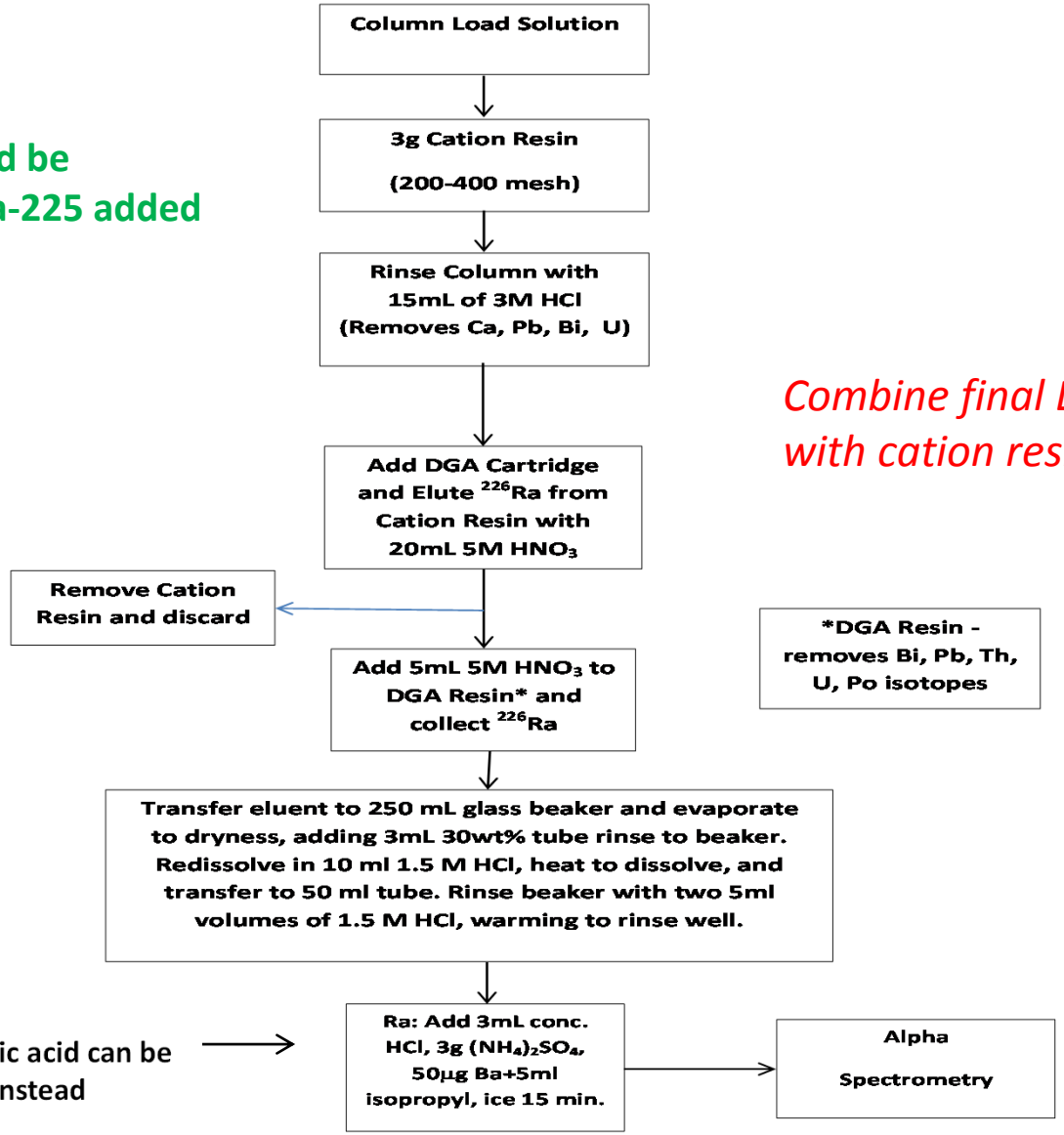
Rapid Sample Preparation for Ra-226 in urine

Less Ca, PO_4 instead of carbonate



Rapid Column Separation for Ra-226 in urine

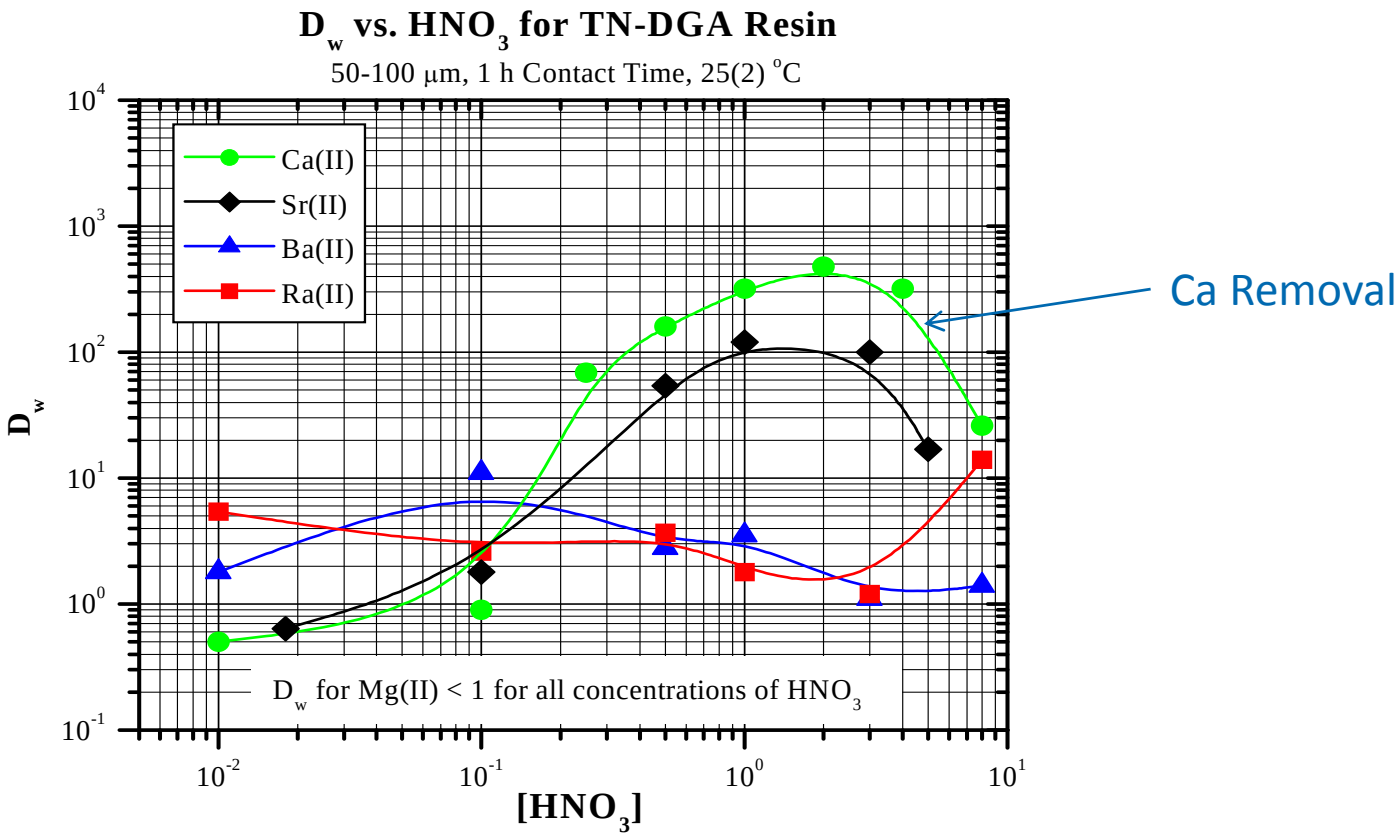
More cation resin would be
Needed with Th-229/Ra-225 added



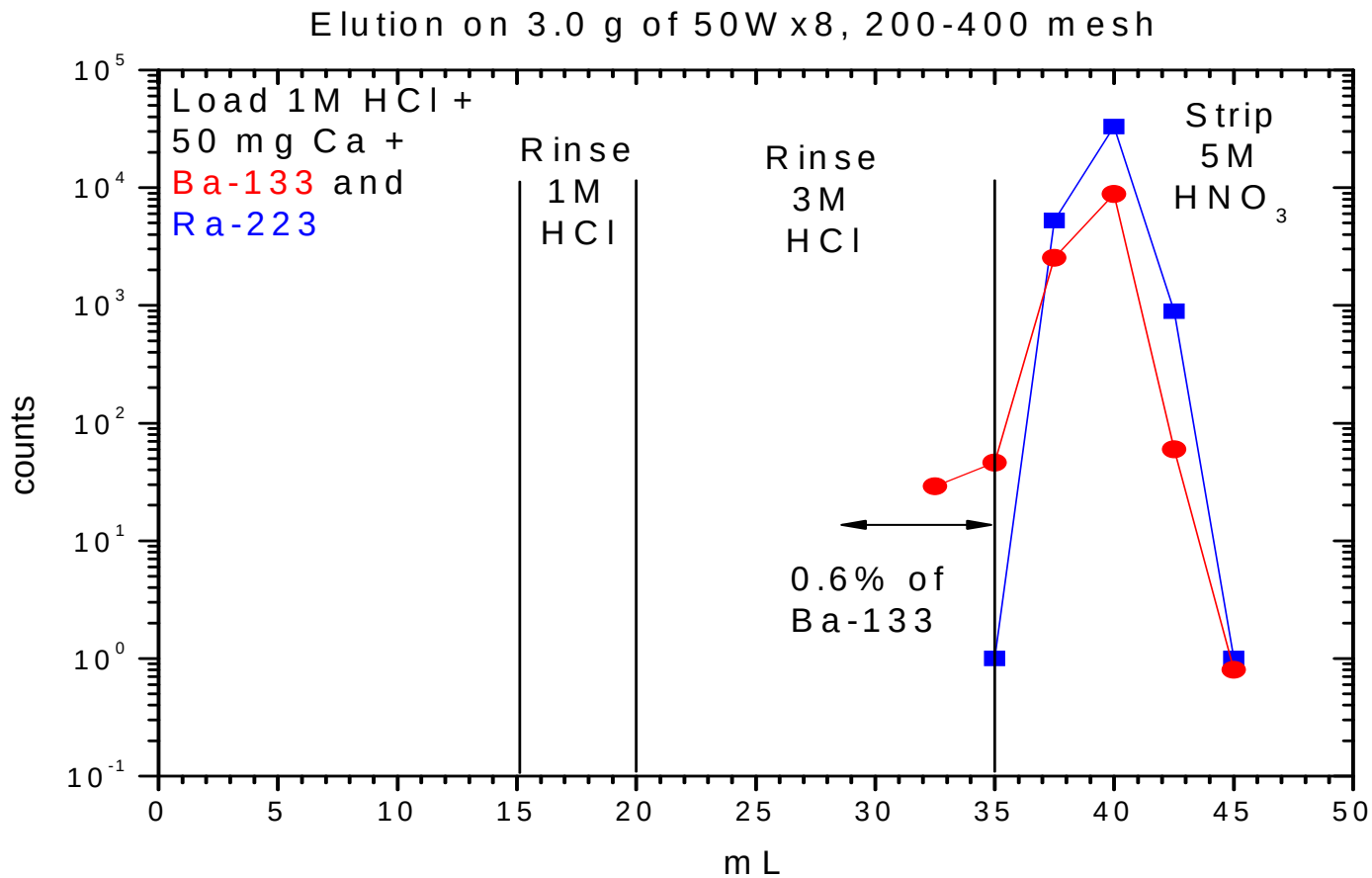
Combine final DGA purification with cation resin elution!

Sulfuric acid can be used instead

Residual Ca Removal using DGA Resin



Ba and Ra Behavior on Cation Resin



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

Rapid Column Separation using Cation + DGA Resin : stacked elution

Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value* (mBq smp^{-1})	Difference (%)
1	95.4	73.67	82.9	12.6
2	96.6	73.67	70.6	-4.2
3	90.1	73.67	79.9	8.5
4	93.1	73.67	78.1	6.0
5	93.0	73.67	72.2	-2.0
6	88.8	73.67	75.3	2.2
Avg	92.8		76.5	3.9
SD	3.0		4.7	
% RSD	3.2		6.1	
	For 100 ml aliquot 73.67 mBq/smp = 736.7 mBq/L			
	16 hour count			

Rapid Column Separation using Cation + DGA Resin : stacked elution

Sample ID	^{133}Ba Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value* (mBq smp^{-1})	Difference (%)
1	100.4	18.42	18.4	-0.2
2	96.0	18.42	18.8	2.2
3	95.1	18.42	17.7	-3.9
4	101.2	18.42	17.9	-3.0
5	99.3	18.42	18.3	-0.8
6	96.1	18.42	16.5	-10.5
Avg	98.0		17.9	-2.7
SD	2.6		0.8	
% RSD	2.6		4.5	
	For 100 ml aliquot 18.42 mBq/smp = 184.2 mBq/L			
	16 hour count			

Blank Test using Cation + DGA Resin : Stacked elution

Sample ID	^{133}Ba Yield (%)	^{226}Ra Blank Value (pCi smp^{-1})	MDC (pCi smp^{-1})	^{226}Ra Blank Value (mBq smp^{-1})	MDC (mBq smp^{-1})
1	95.7	0.0016	0.017	0.058	0.629
2	94.7	0.0036	0.012	0.134	0.444
3	97.0	0.0026	0.014	0.096	0.518
4	84.0	0.0081	0.016	0.301	0.592
5	90.2	0.0077	0.015	0.285	0.555
6	92.7	0.0000	0.017	0.000	0.629
Avg	92.4	0.004	0.015	0.146	0.56
SD	4.7	0.003	0.002	0.122	0.07
% RSD	5.1				
	100 ml sample aliquot				
	blank test with 2 pCi Po-210 and U-238 added				

Summary

- Fast and reliable
  - *Validated and used by US Air Force Radioanalytical Laboratory*
  - *Same method works well with water samples*
- DGA offers improvements over Ln Resin!
- High chemical yields
  - <4-5 hours with simultaneous sample preparation
- Ba-133: No waiting for Ra-225 in-growth
  - but Ra-225 can be used with some adjustments if preferred
  - *allows Ra-224 measurement*
- Can be adapted to smaller or larger urine aliquots as needed
  - *Smaller aliquot if less urine available (spot urine sample)*
  - *Large aliquot if lower MDA needed*
    - *German lab interested in 1.5L aliquot*
    - *Cation resin can be increased to 5g to handle extra Ca*