Savannah River NUCLEAR SOLUTIONS℠

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Rapid Determination of Ra-226 in Environmental Samples

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Background

- Need for rapid radiochemical methods
  - Emergency response
    - IND, RDD, nuclear accident
    - Rapid turnaround times

- Ra-226
  - EPA and DOE FRMAC radionuclide concern list
  - 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
- Newer, more rapid analytical methods are needed
  - Solid samples
    - Radon emanation/ gamma methods take time (ingrowth)
    - Yield/uncertainty issues?
  - Urine
    - Can be time-consuming

Literature: Water Methods

- Moon DS, Burnett WC, Nour S, Horwitz P, Bond A. 2003. Preconcentration of radium isotopes from natural waters using MnO2 resin. *Applied Radiation and Isotopes* 59:255–62.

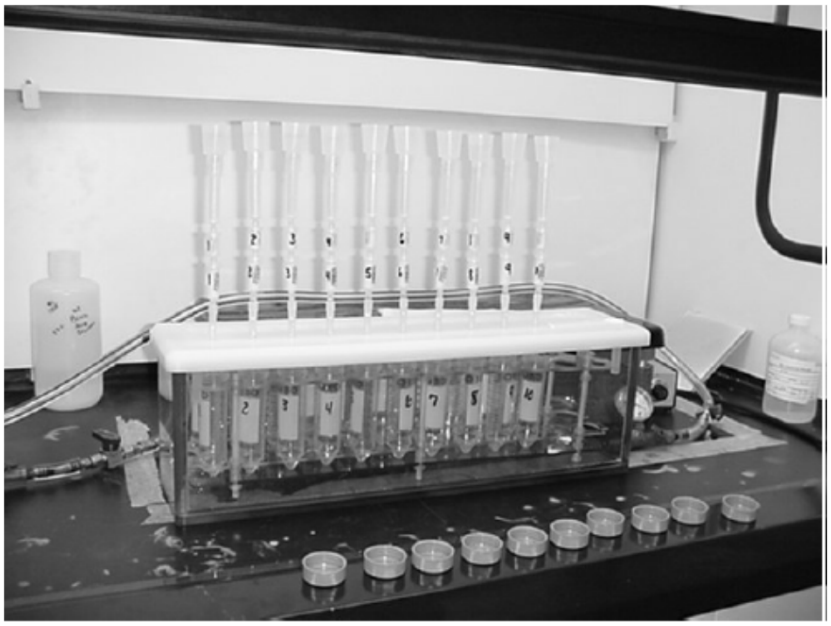
- W.C. Burnett, et al, Radium-228 determination of natural waters via concentration on manganese dioxide and separation using Diphonix ion exchange resin, Appl. Radiation and Isotopes, 2004, Dec 61, 1173

- S.L. Maxwell, Rapid method for 226Ra and 228Ra analysis in water samples Journal of Radioanalytical and Nuclear Chemistry, Vol. 270, No.3 (2006) 651–655

Ra-226 using MnO_2 resin

Ba-133 tracer

Ln Resin and DGA Resin for Ra-226 and Ac-228 separation



Journal of Radioanalytical and Nuclear Chemistry, Vol. 270, No.3 (2006) 651–655
Rapid method for 226Ra and 228Ra analysis in water samples
S. L. Maxwell

Literature: Water Methods

- Galit Sharabia, Boaz Lazarb, Yehoshua Kolodny, Nataliya Teplyakov, Ludwik Halicz, High precision determination of 228Ra and 228Ra/226Ra isotope ratio in natural waters by MC-ICPMS
  - Radium is pre-concentrated from 60 L of Lake Kinneret water (or 2 L of the saline springs water) by co-precipitation with MnO_2.
  - Separation of radium from the matrix elements was by large BioRad® AG50W-X8 and Sr Resin

- Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events, EPA 402-R-10-001 February 2010 (RRMC 2010 presentation. R. Litman, S. Workman
  - MnO_2 resin and Ra-225 tracer

Literature: Solid Samples

- Chabaux, F., Othman, D.B., Birck, J.L., 1994. A new Ra–Ba chromatographic separation and its application to Ra mass-spectrometric measurement in volcanic rocks., Chemical Geology 114, 191–197.
  - Use of multiple, large cation resin columns
  - Sr Resin to separate Ba from Ra

- Larivière, D. K. Brownell, V. N. Epov, R. J. Cornett, and R. D. Evans, Determination of 226Ra in sediments by ICP-MS:A comparative study of three sample preparation approaches
  - Tested various combinations of large cation resin, sulfate precipitation and manganese dioxide
    - Multiple columns
    - 25 ml cation resin (345 ml 6M HCl total rinse volume on 1st column in Chabaux option)

- M.T. Crespo. On the determination of 226Ra in environmental and geological samples by a-spectrometry using 225Ra as yield tracer, Applied Radiation and Isotopes 53 (2000) 109-114
  - Th-229(Ra-225) tracer/At-217

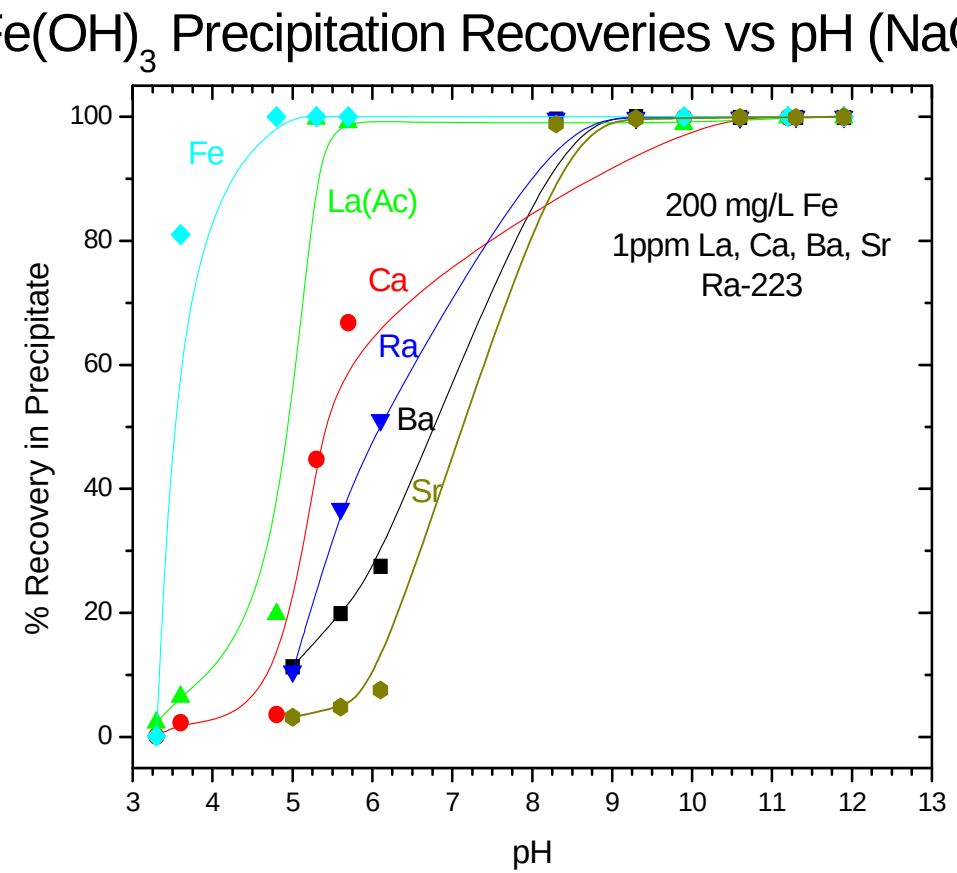
Ra-226 in urine

- 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)

Ra-226 in Emergency Response Samples

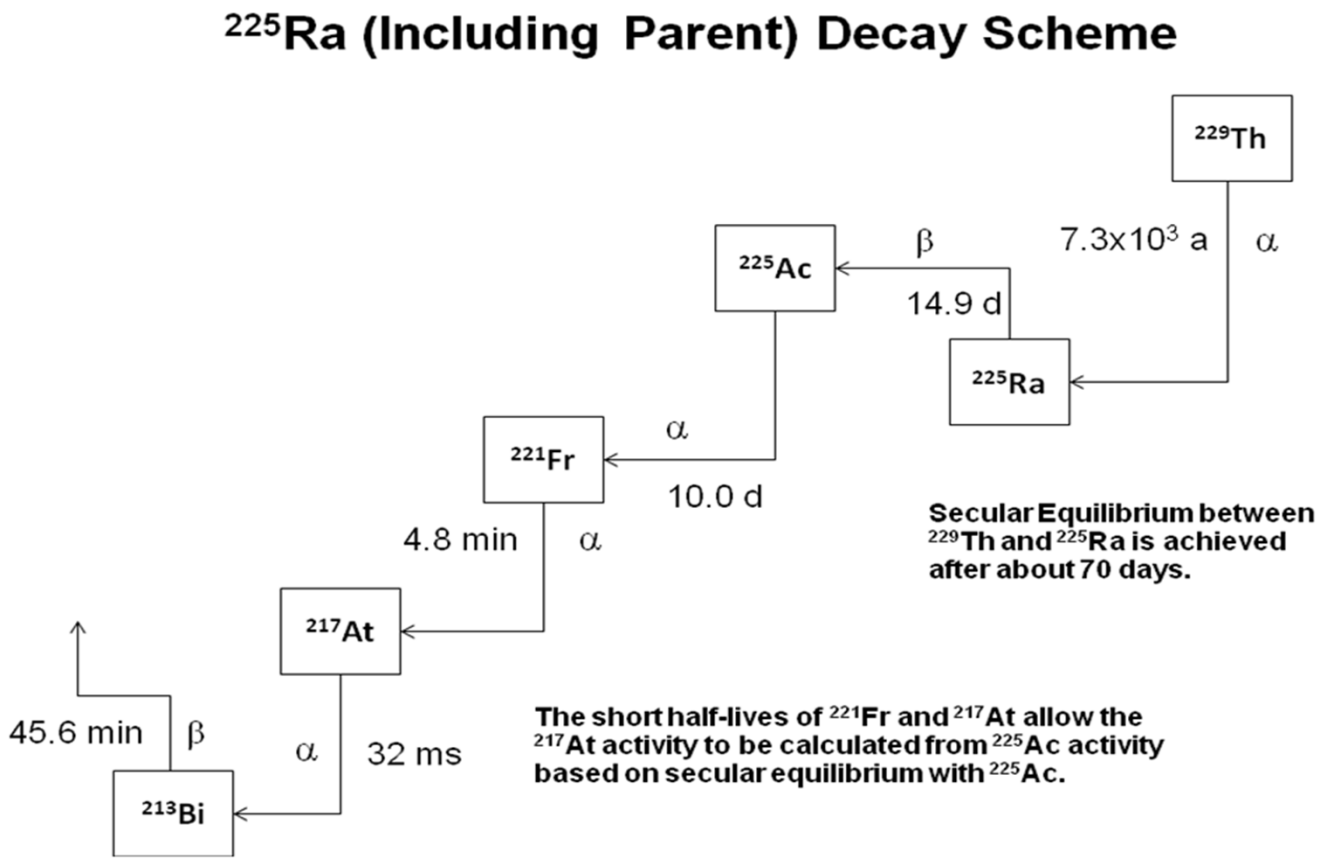
- Ra-226 on emergency response radionuclide list for U.S. EPA and DOE FRMAC
- Challenges
  - Difficulty separating Ca from Ra/Ba
  - Adequate tracer? (Ba-133)
  - Barium interference on alpha spectrometry source preparation
    - Poor alpha resolution
    - Isobaric interferences using ICP-MS (Sr+Ba, Sr + some lanthanides)
  - MnO_2 resin can be used for waters but Ra precipitates with $Fe(OH)_3$ at high pH for solid samples containing Fe
    - MnO_2 separates Ca in water but Ca may ppt when used as a MnO2 ppt from solids
- SRS has developed new methods for alpha or ICP-MS
  - Concrete, brick, vegetation, air filters, urine
  - Ra-225 tracer (At-217 alpha)

Loss of Ra when Fe Is present (High pH)



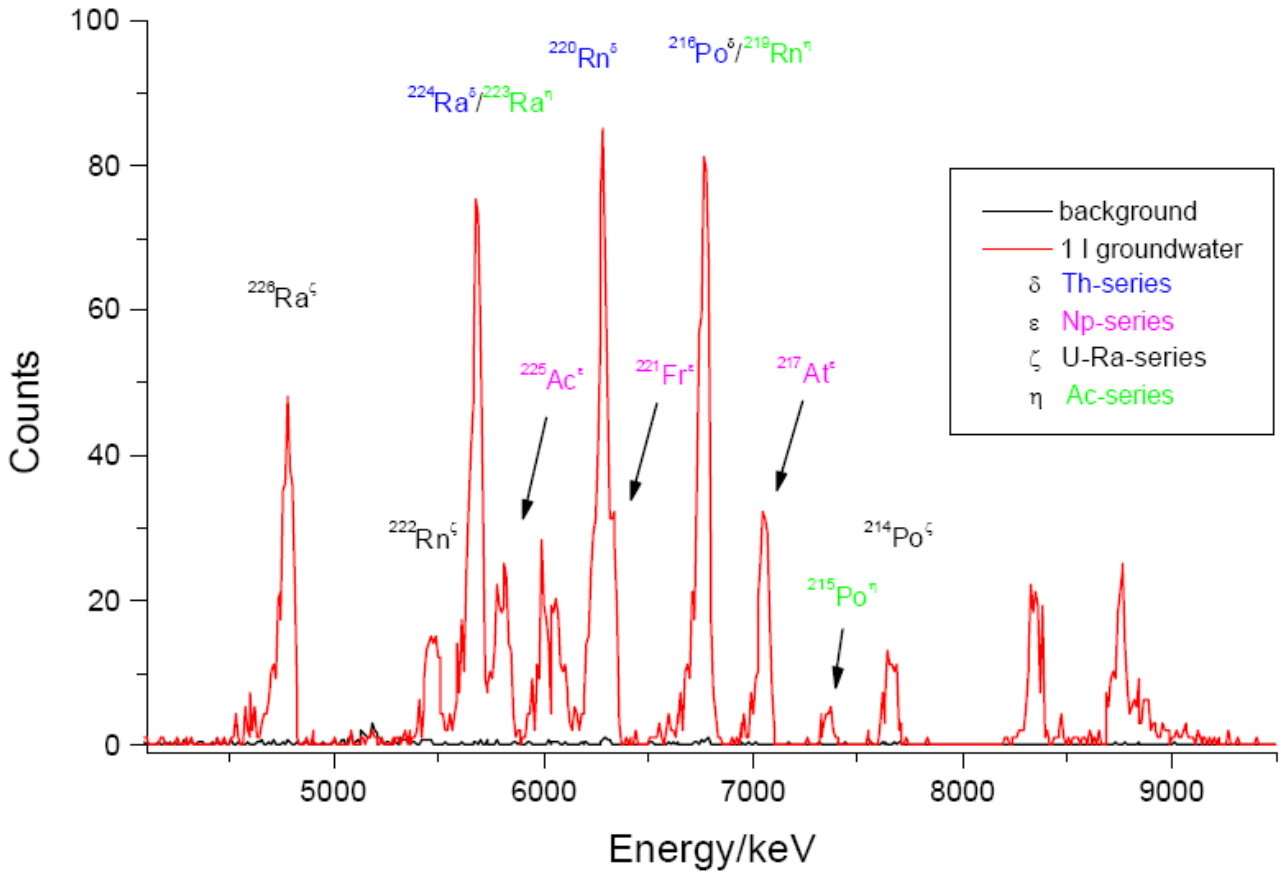
Courtesy Dr. Dan McCalister, P&G Research Foundation

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

Alpha Spectra

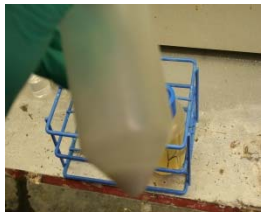


Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events, EPA 402-R-10-001 February 2010

SRS Approach

- Use Ra-225 (At-217)
- Use sodium hydroxide fusion for solid samples
  - refractory particles, fast
- Use calcium carbonate precipitation
  - overcome $Fe(OH)_3$ loss of Ra at high pH and column flow problems using MnO_2 resin at high pH from solid matrices
  - no sulfate to carbonate conversion
  - simplify column procedures
- Remove Ba using Sr Resin
  - to eliminate alpha peak resolution interference
  - to allow large sample aliquots and reduced count times

Rapid Ra-226 Solid Sample Preparation



Air Filter
Add Th-229 (Ra-225) tracer

5g Vegetation
Add Th-229 (Ra-225) tracer

1g Concrete/Brick
Add Th-229 (Ra-225) tracer

Heat at 700°C for 2 hours in Furnace

Wet Ash with HNO_3/H_2O_2 on Hot Plate

Heat for ~10 min. at 600°C in Furnace

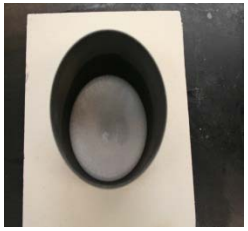
Fuse in Zr Crucible for 15 min. with 10g NaOH at 600°C

Carbonate Precipitation (10mL conc. HCl, Ca*, 25mL 2M Na_2CO_3)

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

Column Load Solution

***Ca addition:**
Air Filter: 125mg
Vegetation: 50mg
Concrete/Brick: 25mg



SRNS
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Rapid Ra-226 Aqueous Sample Preparation

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

↓

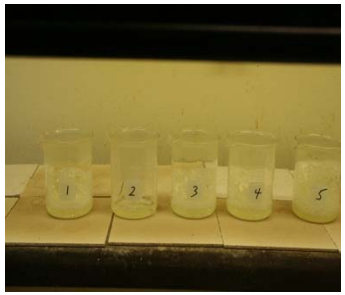
Redissolve in 20mL 1.5M HCl
Add 3mL 1.5M Ascorbic Acid

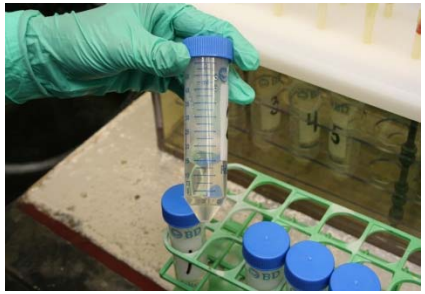
↓

Column Load Solution

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

Wet-ash urine ppt

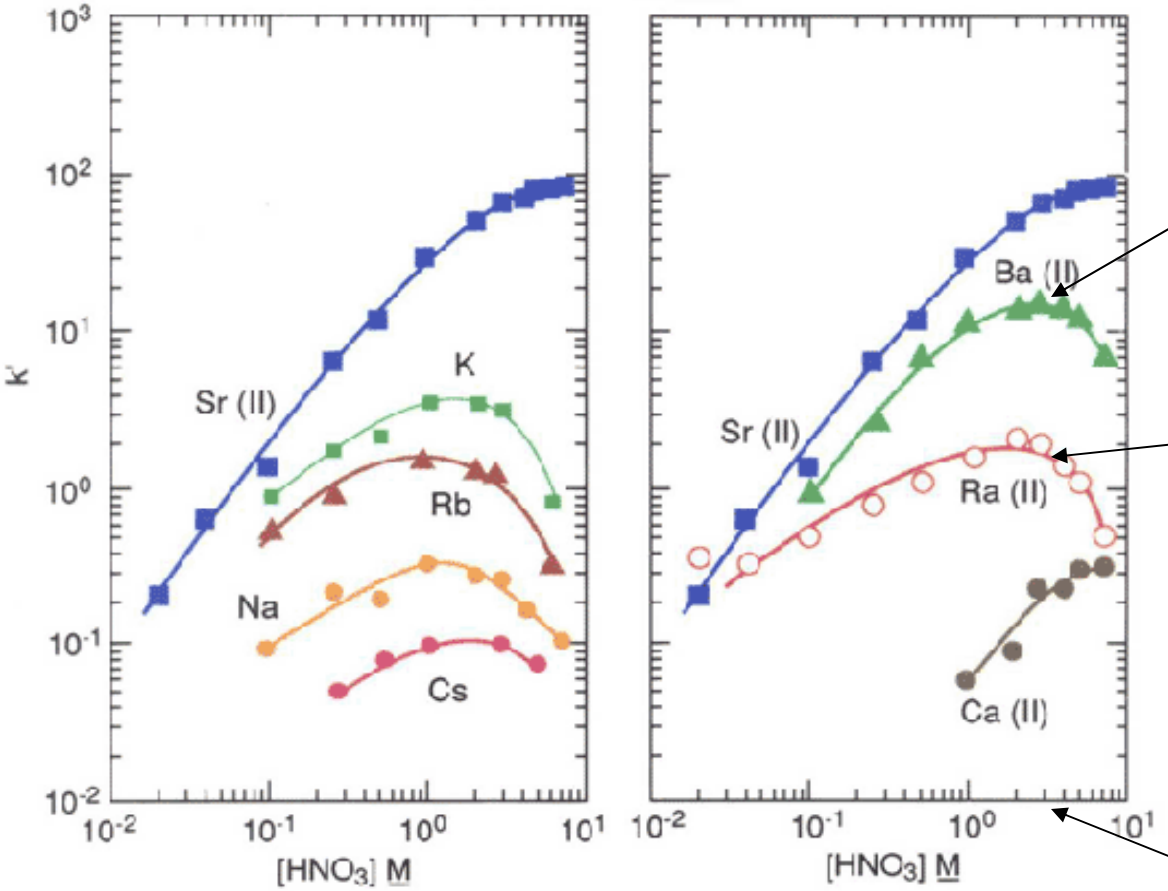




Ba Removal

Figures 2 and 3

Acid dependency of k' for various ions at 23-25°C.
Sr Resin



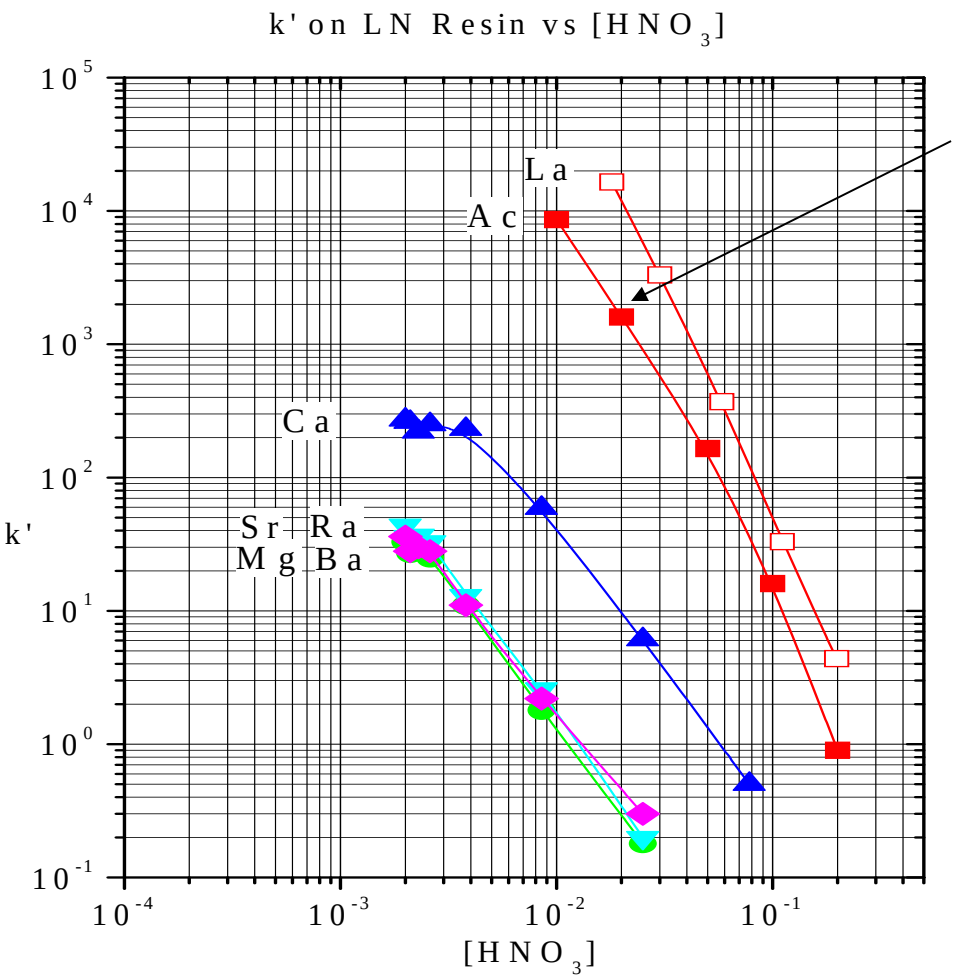
Horwitz, et al., (HP292)

Ba/Sr retained

Ra eluted

3M HNO3 <10 free column volumes

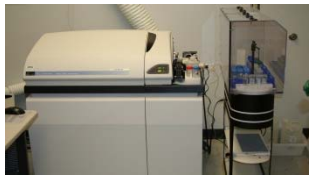
Ln Resin



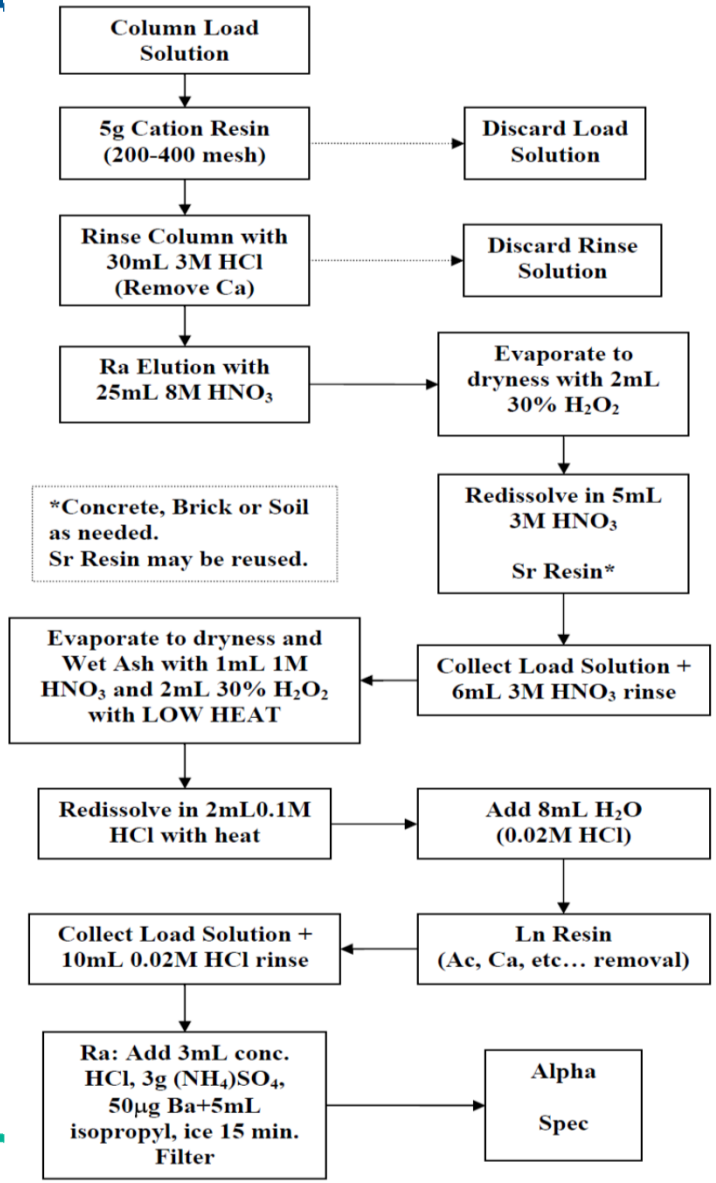
Removal fo Ac-225

Courtesy Dr. Dan McCalister, P&G Research Foundation

Rapid Ra-226 Column Separation

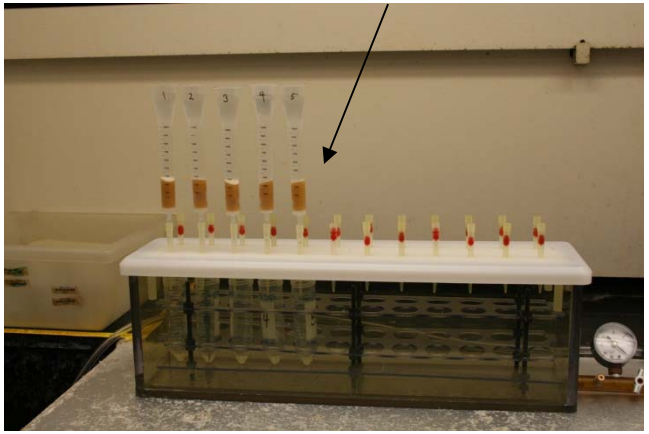


Option: ICP-MS

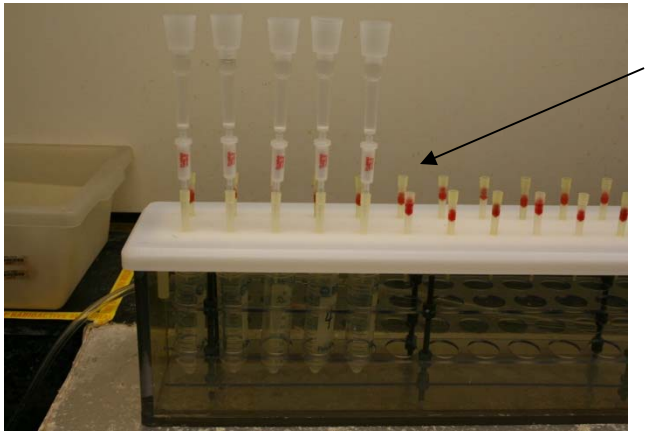


Ra-226 Column Separation

Ca Removal

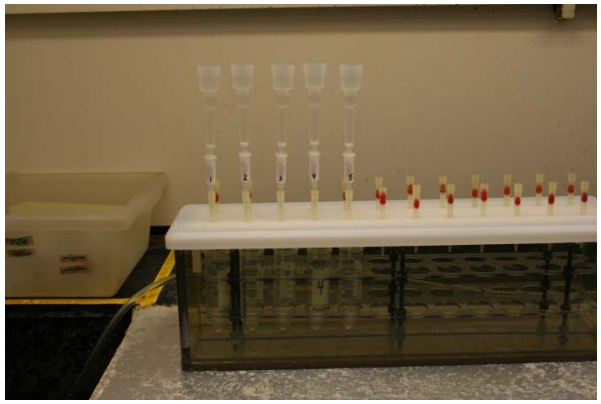


Sr Resin



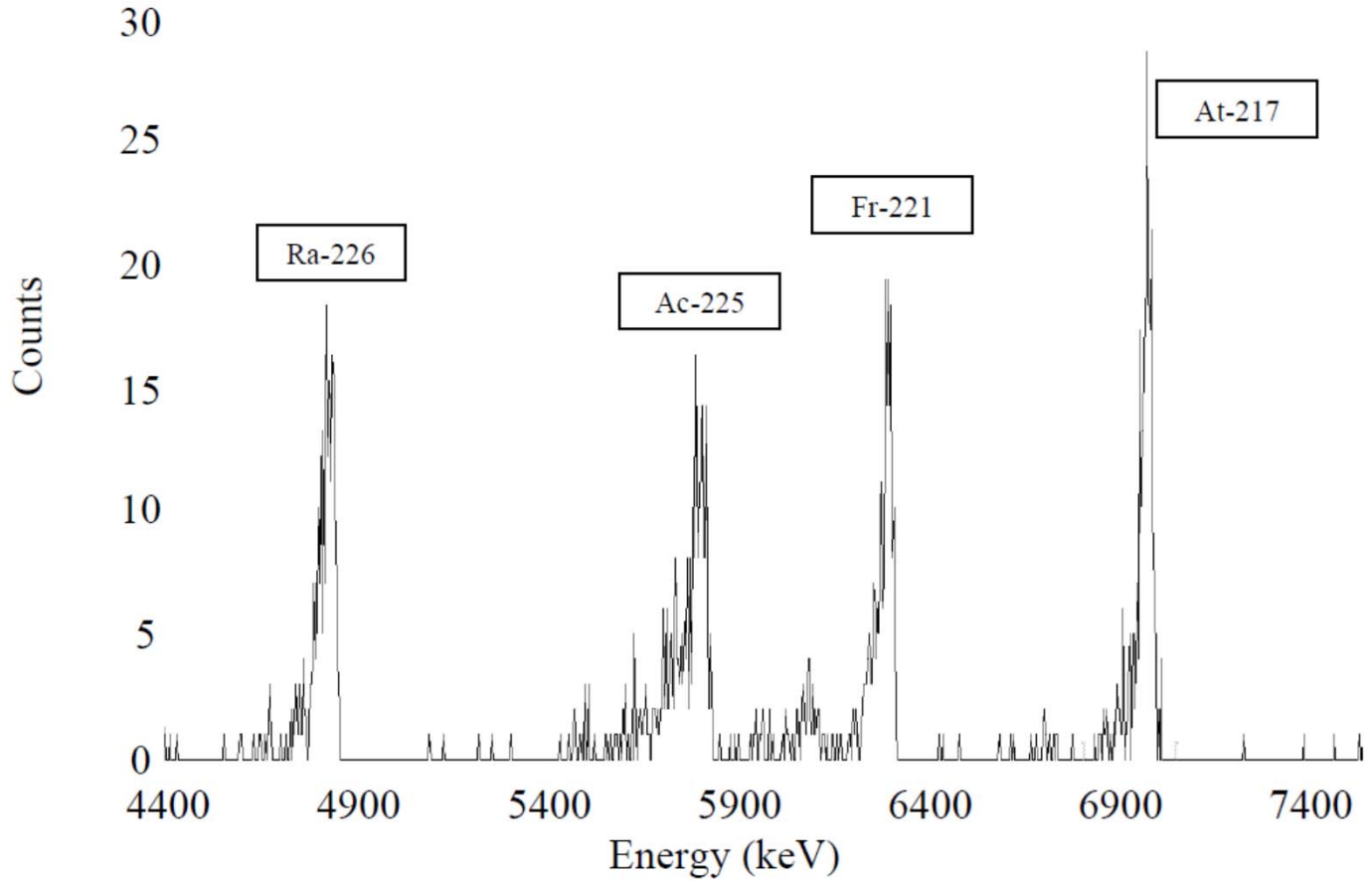
Only if Ba removal needed

Ln Resin



Ready for barium sulfate microprecipitation or ICP-MS

Ra-226 Spectra using At -217 tracer



Ra-226 in Vegetation Samples

Sample ID	^{217}At Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value* (mBq smp^{-1})	Difference (%)
1	91.5	73.8	70.8	-4.0
2	88.3	73.8	73.8	0.0
3	93.1	73.8	69.8	-5.4
4	82.2	73.8	68.5	-7.2
5	80.2	73.8	81.4	10.3
Avg	87.1		72.8	-1.2
SD	5.7		5.1	
% RSD	6.5		7.1	

8hr count time
At -217 ingrowth to mid-point-9.03 hrs.
*corrected for 9.17 mBq Ra-226 native content

Ra-226 in Concrete Samples

Sample ID	^{217}At Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value * (mBq smp^{-1})	Difference (%)
1	88.2	184.5	173.5	-6.0
2	90.8	184.5	188.3	2.1
3	81.2	184.5	172.8	-6.3
4	84.2	184.5	192.4	4.3
5	72.9	184.5	177.6	-3.7
6	90.4	184.5	178.8	-3.1
Avg	84.6		180.6	-2.1
SD	6.8		8.0	
% RSD	8.1		4.4	

4hr count time
At -217 ingrowth to mid-point-11.86 hrs.
*corrected for 26.8 mBq Ra-226 native content

Ra-226 in Brick Samples

Sample ID	^{217}At Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value* (mBq smp^{-1})	Difference (%)
1	77.9	73.8	79.5	7.8
2	88.4	73.8	84.5	14.5
3	86.3	73.8	80.3	8.9
4	90.6	73.8	88.5	19.9
5	79.7	73.8	74.7	1.3
6	91.5	73.8	75.9	3.0
7	94.9	73.8	71.7	-2.8
Avg	87.0		79.3	7.5
SD	6.2		5.8	
% RSD	6.5		6.5	

4hr count time
At -217 ingrowth to mid-point-12.15 hrs.
*corrected for 29.5 mBq Ra-226 native content

Ra-226 in Air Filter Samples

Sample ID	^{217}At Yield (%)	^{226}Ra Reference Value (mBq smp^{-1})	^{226}Ra Measured Value * (mBq smp^{-1})	Difference (%)
1	80.7	73.8	70.5	-4.4
2	79.9	73.8	80.8	9.6
3	78.6	73.8	77.0	4.4
4	73.0	73.8	79.5	7.8
5	71.5	73.8	77.7	5.3
Avg	76.7			
SD	4.2		77.1	4.5
% RSD	1.4			

8hr count time
At -217 ingrowth to mid-point-12.47 hrs.
*corrected for 3.7 mBq Ra-226 in blank air filter

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

Summary

- New method for Ra226 has been developed at SRS
  - for solid samples and urine
- Rapid fusion
  - Ca /Ra carbonate precipitation
  - Ba Removal (if needed)
  - Ra-225 (At-217)
- Cation + (Sr resin) + Ln resin
  - Good yields, column flow
  - Effective removal of Ac-225
  - Alpha spectrometry
  - ICP-MS option