



THE LEADER IN ENVIRONMENTAL TESTING

Radium Isotopes by Alpha Spectrometry

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October 28, 2014

- **Determination of radium isotopes by alpha spectrometry:**
 - ~ Specifically for ^{226}Ra
 - ~ ^{224}Ra is possible
- **Applicable to liquid or other media where complete dissolution and carrier exchange are readily achievable in the laboratory.**

Radium/Radon Isotopes

Ra 220 23.0 ms E 7.60	Ra 221 ⁵⁺ 28.0 s E 6.29	Ra 222 38.0 s α E 6.68	Ra 223 ³⁺ 11.4 d α E 5.96	Ra 224 87.8 h α E 5.79	Ra 225 ¹⁺ 14.8 d E 3.57	Ra 226 1.6E3 a α E 4.87	Ra 227 ³⁺ 42.2 m E 1.33	Ra 228 5.75 a E 0.46
Fr 219 ⁵⁺ 20.0 ms E 7.45	Fr 220 ¹⁺ 27.5 s E 6.80	Fr 221 ⁵⁺ 4.80 m E 6.46	Fr 222 ²⁺ 14.8 m E 2.03	Fr 223 ³⁺ 21.8 m E 1.15	Fr 224 ¹⁺ 160 s E 2.82	Fr 225 ³⁺ 3.90 m E 1.87	Fr 226 ¹⁺ 48.0 s E 3.63	Fr 227 ¹⁺ 144 s E 2.49
Rn 218 35.0 ms E 7.25	Rn 219 ⁵⁺ 3.96 s E 6.95	Rn 220 55.8 s α E 6.41	Rn 221 ⁷⁽⁺⁾ 25.0 m E 1.22	Rn 222 91.8 h α E 5.59	Rn 223 ⁷⁺ 43.0 m E 2.82	Rn 224 107 m E 1.87	Rn 225 ⁷⁺ 4.50 m E 3.63	Rn 226 6.00 m E 2.49
At 217 ⁵⁺ 32.0 ms E 7.20	At 218 ⁽²⁺⁾ 2.00 s E 6.87	At 219 54.0 s E 6.39						
Po 216 150 ms E 6.91	Po 217 10.0 s E 6.95	Po 218 183 s E 6.12						

- ^{226}Ra is most common radium isotope
- Member of Uranium (^{238}U) decay chain, 1600 yr half-life
- Primarily an alpha-emitting isotope:
 - ~ 94.45% @ 4784 keV
 - ~ 5.55% @ 4601 keV
- One gamma-ray of note:
 - ~ 3.5% @ 186 keV

- ^{224}Ra is first progeny of ^{228}Th , part of Thorium (^{232}Th) decay chain
- Short-lived at 87.8 hours
- Primarily an alpha-emitting isotope:
 - ~ 95.1% @ 5686 keV
 - ~ 4.9% @ 5449 keV
- One gamma-ray of note:
 - ~ 3.95% @ 241 keV

- **Several methods have been employed:**
 - ~ EPA 903.0 (SW846 9315, SM 7500 Ra-B, ASTM D2460-90, EPA Ra-03)
 - ~ EPA 903.1 (SM 7500 Ra-C, EPA Ra-04, ASTM D3454-91, DOE Ra-05)
 - ~ MnO₂ preconcentration
 - ~ 3M Empore RAD radium disks
 - ~ Ion exchange/extraction chromatographic approaches
 - ~ Gamma Spectrometry

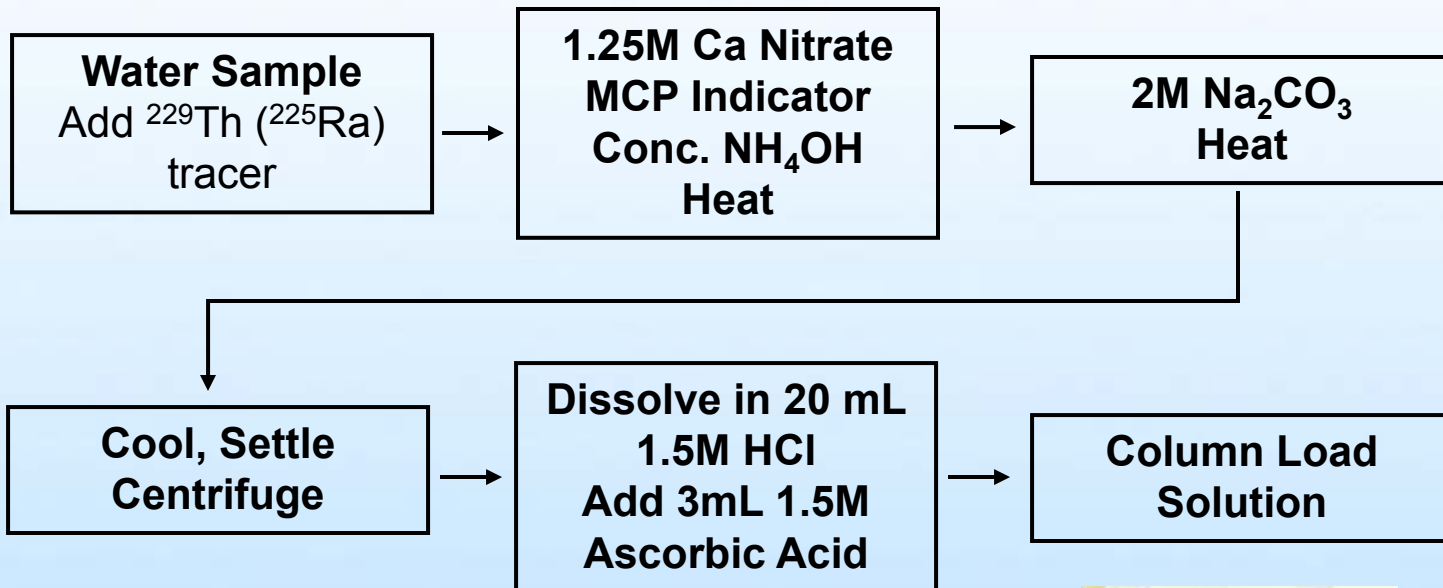
New Approach

- Co-precipitation with calcium carbonate
- Radium further purified with cation-exchange and extraction chromatography
- Final barium sulfate precipitate; mounted
- Short wait (1-2 days) for ingrowth of ^{225}Ra daughters through ^{217}At
- Count by alpha spectrometry
- ^{226}Ra specific (also ^{224}Ra)



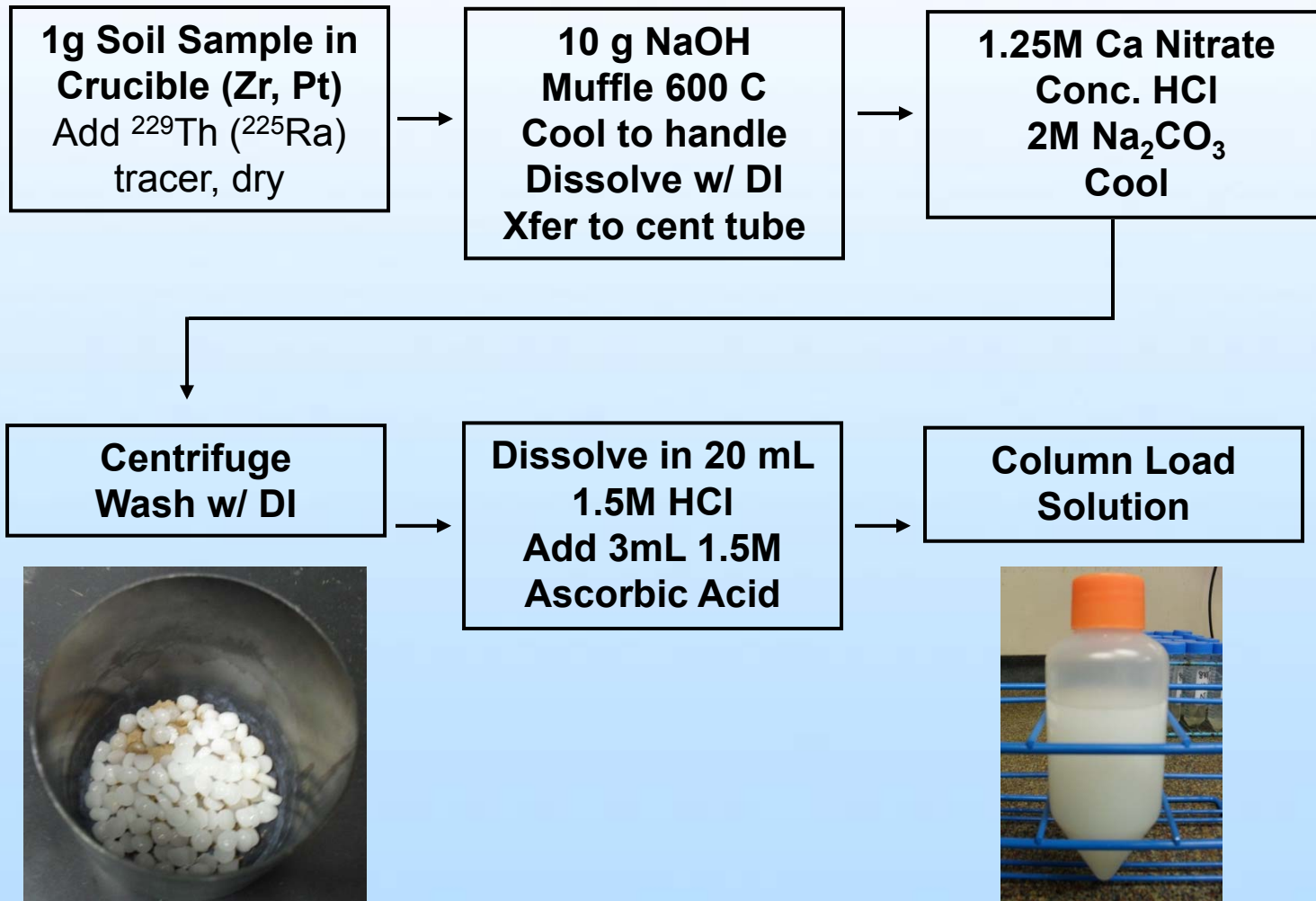
- Aliquot of nitric preserved sample
 - ~ Trace: $^{229}\text{Th}/^{225}\text{Ra}$
 - ~ Add MCP indicator
 - ~ 1.25M Calcium Nitrate (~5 mL or less)
 - ~ Ammonium hydroxide to MCP end point
 - ~ Heat to near boiling
 - ~ 2M sodium carbonate (~25 mL), Heat
 - ~ Allow to cool, settle, collect in cent. tube
 - ~ Dissolve with 1.5M HCl (~20 mL total)
 - ~ 1.5M ascorbic acid (~3 mL)

Initial Water Prep



- 1g of dry/disaggregated soil
 - ~ Place soil in Crucible (Zr, Pt)
 - ~ Trace: $^{229}\text{Th}/^{225}\text{Ra}$
 - ~ Briefly dry on hotplate
 - ~ 10 grams NaOH
 - ~ Muffle at 600 degrees C (30+ minutes), cool
 - ~ Dissolve with DI on hotplate, transfer to 225 mL centrifuge tube, cool to room temp
 - ~ 1.25M Calcium Nitrate (1 mL)
 - ~ Conc. HCl to reduce alkalinity
 - ~ 2M sodium carbonate (~25 mL)
 - ~ Allow to cool, centrifuge, wash w/ DI
 - ~ Dissolve with 1.5M HCl (~20 mL total)
 - ~ 1.5M ascorbic acid (~3 mL)

Initial Soil Prep



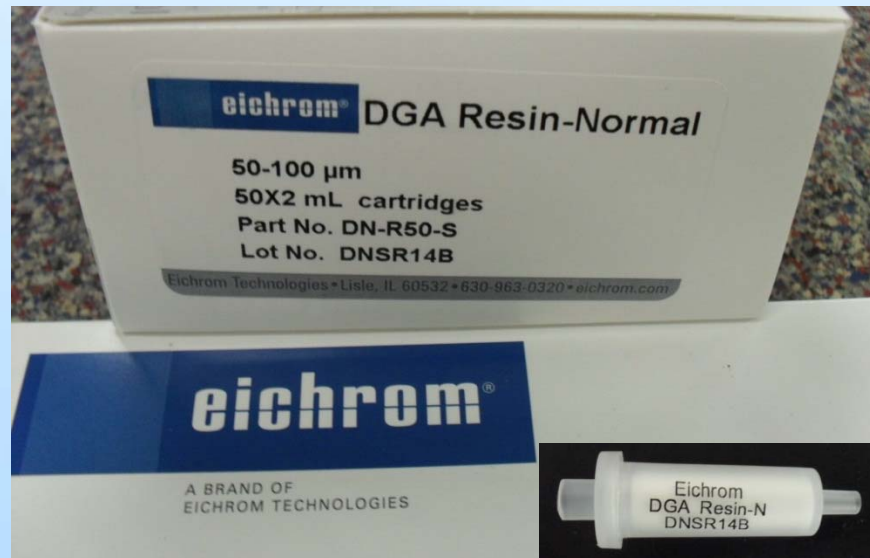
Separation (Cation)

- Cation Column (AG 50W-X8)
 - ~ Condition/Rinse column w/ 1.5M HCl
 - ~ Load sample solution, gravity feed
 - ~ Rinse w/ 30mL 3M HCl
 - ~ Record date/time of end of rinse



Separation (DGA Stack)

- Stack DGA under Cation Column
 - ~ Condition/Rinse DGA cartridge w/ 8M HNO₃
 - ~ Discard waste, replace with collection tube
 - ~ Stack DGA cartridge under Cation column
 - ~ Elute Ba/Ra with 15 mL 8M HNO₃, 1-2 mL/min
 - ~ 2 mL H₂O₂, Evaporate to incipient dryness



Separation (Ba removal)

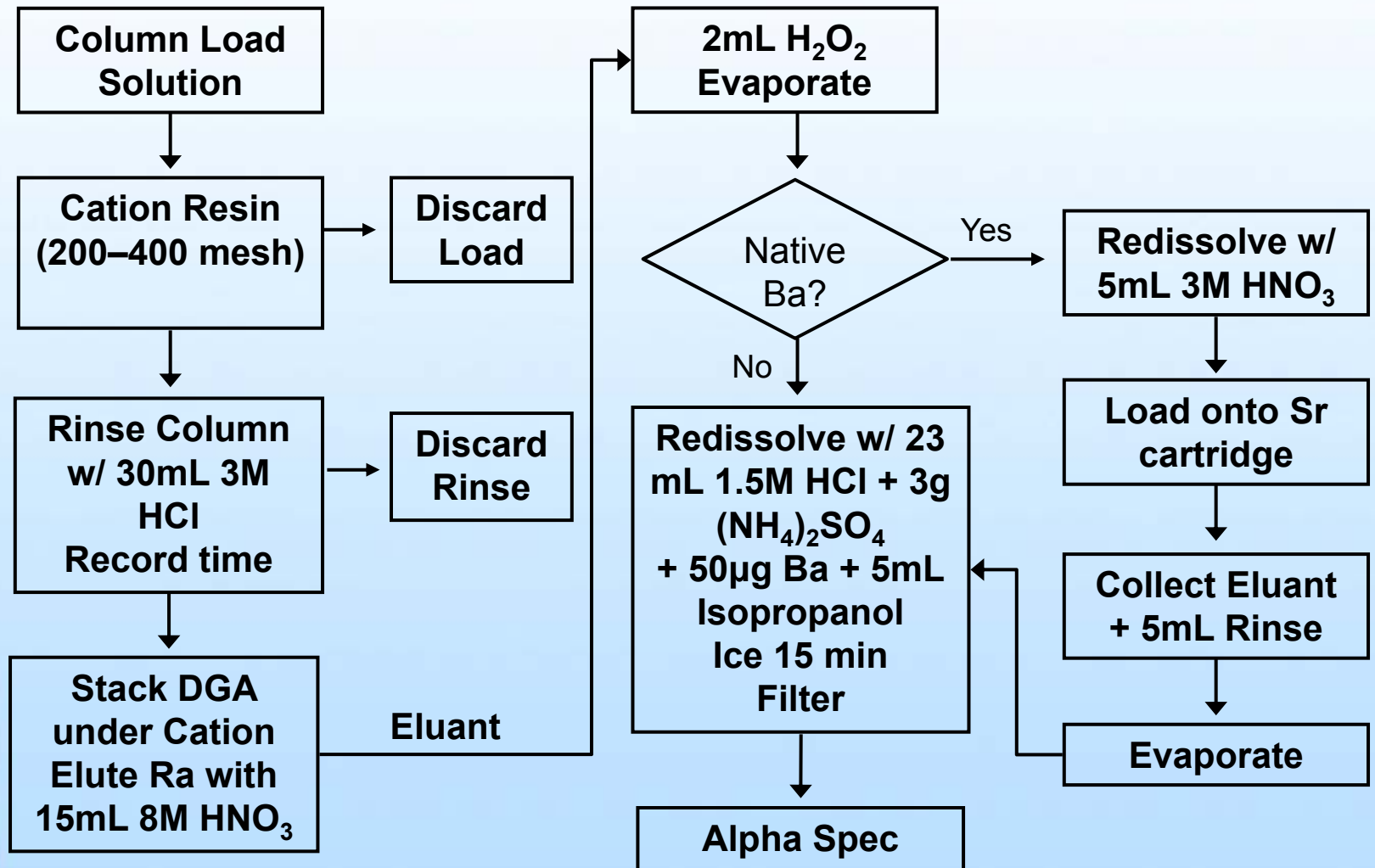
- Sr Cartridge (if Ba expected)
 - ~ Condition cartridge w/ 3M HNO₃
 - ~ Redissolve sample in 5mL 3M HNO₃
 - ~ Load on column, Rinse with 5mL 3M HNO₃
 - ~ Evaporate combined eluant to incipient dryness



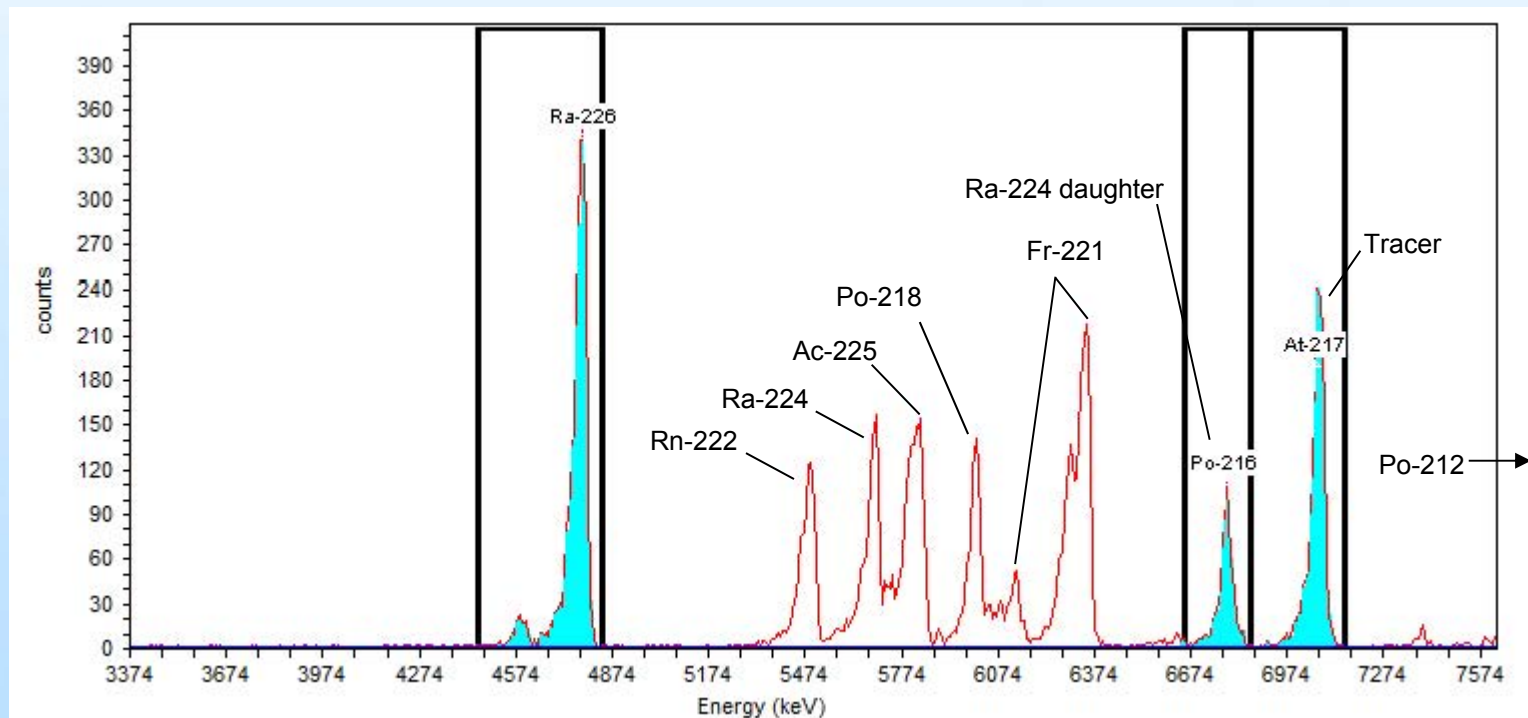
- Coprecipitation with BaSO_4
 - ~ Redissolve in 1.5M HCl (23 mL)
 - ~ Transfer to tube with 3g $(\text{NH}_4)_2\text{SO}_4$
 - ~ Add 50 μg Ba, Mix
 - ~ Add 5mL Isopropanol, Mix, Cool/Ice
 - ~ Mount on Resolve® filter



Separation



- MDC achievable below 0.1 pCi/g, 0.1 pCi/L
- Rapid TAT (as little as ~3 days)
- Spectral confirmation



$$A_2 = \left(A_2^0 * e^{-\lambda_2 \Delta t} \right) + A_1^0 \left(\frac{\lambda_2}{\lambda_2 - \lambda_1} \right) \left(e^{-\lambda_1 \Delta t} - e^{-\lambda_2 \Delta t} \right)$$

Where:

- A_2 = activity of the tracer at the midpoint of the count
- A_1^0 = activity of ^{225}Ra at the separation time
- A_2^0 = activity of ^{217}At at the separation time (is zero at the separation time, and thus this whole term goes to zero)
- λ_1 = decay constant for ^{225}Ra (0.04652)
- λ_2 = decay constant for ^{217}At (0.06931)
- Δt = time between the separation and the midpoint of the count

Rocky Flats Soil

^{226}Ra Results

Sample	Known (pCi/g)		Result (pCi/g)		Recov	Yield
	Activity	TPU (1 σ)	*Activity	TPU (1 σ)	%	%
160-6278-36	1.162	0.052	1.165	0.074	100.2%	75.4%
160-6278-37	1.162	0.052	1.143	0.071	98.4%	69.4%
160-6278-38	1.162	0.052	0.986	0.064	84.8%	99.4%
160-6278-39	1.162	0.052	1.084	0.080	93.3%	79.6%
160-6278-40	1.162	0.052	0.957	0.073	82.3%	93.2%
160-6278-41	1.162	0.052	1.159	0.072	99.7%	82.6%
160-6278-42	1.162	0.052	1.106	0.068	95.1%	78.5%
				Average:	93.4%	82.6%
				StDev:	7.2%	10.4%

*Results corrected for 0.075 pCi/g seen in 7 reps of method blank

²²⁶Ra Results

Sample	Known (pCi/g)		Result (pCi/g)		Recov	Yield
	Activity	TPU (1 σ)	*Activity	TPU (1 σ)	%	%
160-6278-22	3.66	0.165	3.824	0.168	104.5%	84.1%
160-6278-23	3.66	0.165	3.597	0.183	98.3%	81.1%
160-6278-24	3.66	0.165	3.858	0.169	105.4%	79.1%
160-6278-25	3.66	0.165	4.142	0.204	113.2%	79.9%
160-6278-26	3.66	0.165	3.510	0.172	95.9%	80.8%
160-6278-27	3.66	0.165	3.609	0.185	98.6%	81.2%
160-6278-28	3.66	0.165	3.669	0.182	100.3%	78.9%
				Average:	102.3%	80.7%
				StDev:	5.9%	1.8%

*Results corrected for 0.075 pCi/g seen in 7 reps of method blank

²²⁶Ra Results

Sample	Known (pCi/g)		Result (pCi/g)		Recov	Yield
	Activity	TPU (1 σ)	*Activity	TPU (1 σ)	%	%
160-6278-8	12.2	0.549	12.312	0.625	100.9%	74.2%
160-6278-9	12.2	0.549	11.815	0.575	96.8%	76.1%
160-6278-10	12.2	0.549	12.482	0.565	102.3%	71.1%
160-6278-11	12.2	0.549	11.692	0.585	95.8%	77.2%
160-6278-12	12.2	0.549	12.347	0.575	101.2%	74.4%
160-6278-13	12.2	0.549	12.365	0.575	101.3%	74.9%
160-6278-14	12.2	0.549	12.215	0.580	100.1%	73.9%
				Average:	99.8%	74.6%
				StDev:	2.5%	1.9%

*Results corrected for 0.075 pCi/g seen in 7 reps of method blank

Tap Water Samples

²²⁶Ra Results

	0.451 pCi/L		0.901 pCi/L		4.51 pCi/L	
	Recov	Yield	Recov	Yield	Recov	Yield
Repetition	%	%	%	%	%	%
1	84.5%	89.1%	102.2%	76.1%	86.3%	87.9%
2	97.2%	83.8%	96.4%	93.1%	93.6%	83.5%
3	101.5%	84.7%	97.7%	86.4%	97.4%	83.7%
4	90.3%	79.8%	93.7%	80.6%	88.3%	91.0%
5	99.1%	78.5%	99.4%	86.9%	90.2%	82.3%
6	115.4%	77.7%	99.6%	86.2%	100.8%	82.6%
7	96.9%	78.1%	93.9%	74.6%	96.6%	83.9%
Average:	97.8%	81.7%	97.6%	83.4%	93.3%	85.0%
StDev:	9.7%	4.3%	3.1%	6.6%	5.3%	3.2%

*Results corrected for 0.114 pCi/L seen in 7 reps of tap water blank

- New method for ^{226}Ra by Alpha Spec
- Tested for Water, Soil - rugged
- Demonstrated to be selective for radium
- Should perform well for other matrices (filters, biota, vegetation, brick, etc)
- Respectable spike recoveries
- Good chemical yields
- ^{225}Ra (^{217}At) tracer offers advantage over ^{133}Ba (single AS measurement)
- Ba/Ra sulfate microprecipitation in isopropanol results in excellent peak resolution

Special thanks to:

- Sherrod Maxwell, Savannah River National Laboratory
- Terry O'Brien, Eichrom Technologies

Both have been more than generous with their time and knowledge!!

Questions?

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