



National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

Radiochemistry Webinars

Radium Chemistry



*In Cooperation with our
University Partners*



Meet the Presenter... *Bahman Parsa*



Dr. Parsa is the Environmental and Chemical Laboratory Services Director with the New Jersey Department of Health, with a secondary

appointment as the Department's Radioanalytical Services Manager. He earned a PhD in Nuclear Chemistry at the Massachusetts Institute of Technology. After serving as a Professor and the Director of the Tehran University Nuclear Center for 16 years, Dr. Parsa joined the New Jersey Department of Environmental Protection in 1984, first as a Research Scientist. He became the Radioanalytical Services Manager in 1997 at the New Jersey Department of Health, and was appointed as Environmental and Chemical Laboratory Services Director in 2011. As Radioanalytical Services Manager, his primary focus has been supervising method development and performing routine laboratory activities related to the measurement of radionuclides.



Dr. Parsa has developed a number of radiochemical procedures for the analysis of environmental samples, including emergency response radiological testing capabilities. Many of these methods have been approved by the U.S. EPA as alternate test procedures for Safe Drinking Water Act compliance monitoring. As Environmental and Chemical Laboratory Services Director, Dr. Parsa manages the provision of chemical testing services in Inorganic Chemistry, Organic Chemistry, Chemical Terrorism/Biomonitoring and Radioanalytical Services, as well as managing the Information Technology unit. He is charged with monitoring and assuring the accuracy of laboratory data and the transmission of data to clients. Dr. Parsa's primary fields of interest are radionuclide assay in drinking water, activation analysis, and decay scheme studies.

Contact information:

Phone: (609)530-2820

Email: Bahman.Parsa@doh.state.nj.us



Radium Chemistry

Bahman Parsa, PhD
New Jersey Department of Health



National Analytical Management Program (NAMP)
U.S. Department of Energy Carlsbad Field Office

TRAINING AND EDUCATION SUBCOMMITTEE



Acknowledgements

- **Prof. Bill Burnett**
Florida State University
- **James Henitz and Kirk Nemeth**
New Jersey Department of Health, Radioanalytical Services
Laboratory
- **Jennifer Goodman**
New Jersey Department of Environmental Protection,
Radiation Protection Program
- **Berta Oates**
Carlsbad Field Office Technical Assistance Contractor
(Portage, Inc.)
- **Dr. Patricia Paviet-Hartmann**
Idaho National Laboratory

Topics

- **Background Information**
- **Chemical Properties**
- **Methods of Detection**
- **Occurrence**
- **Impact on Drinking Water**
- **Impact on Energy Industry**
- **Health Effects**

Date of Radium Discovery: 1898

Discoverers: Pierre and Marie Curie

Nobel Prizes: 1903 and 1911

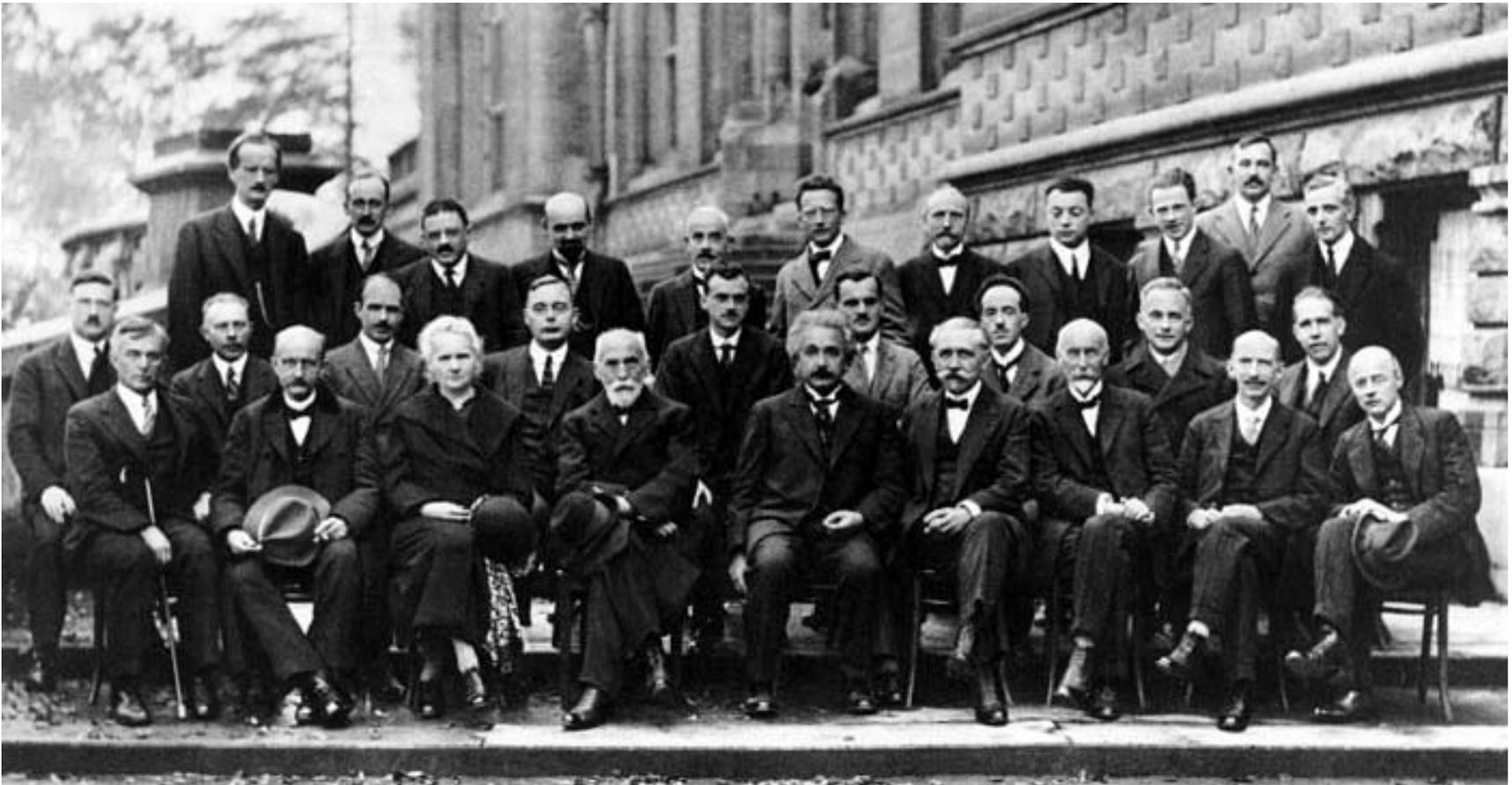


Historic photograph taken at the 5th Solvay Congress, Brussels, October 1927

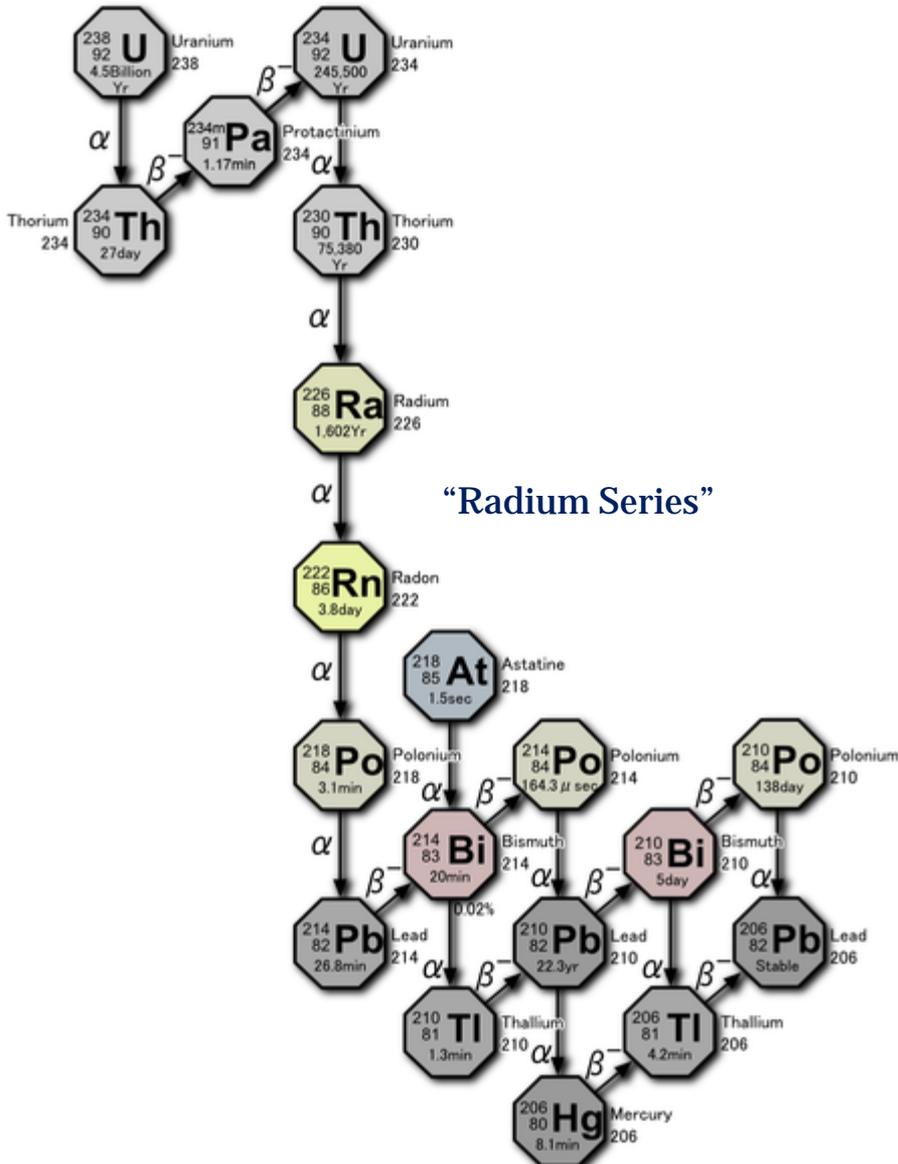
Front Row (from left): I. Langmuir (1932), M. Plank (1918), M. Curie (1903 & 1911), H. Lorentz (1902), A. Einstein (1921), L. Langevin, C.E. Guye, C.T.R. Wilson (1927), and O.W. Richardson (1928)

2nd Row (from left): P. Debye (1936), M. Knudsen, W.L. Bragg (1915), H.A. Kramers, P.A.M. Dirac (1933), A.H. Compton (1927), L.V. de Broglie (1929), M. Born (1954), and N. Bohr (1922)

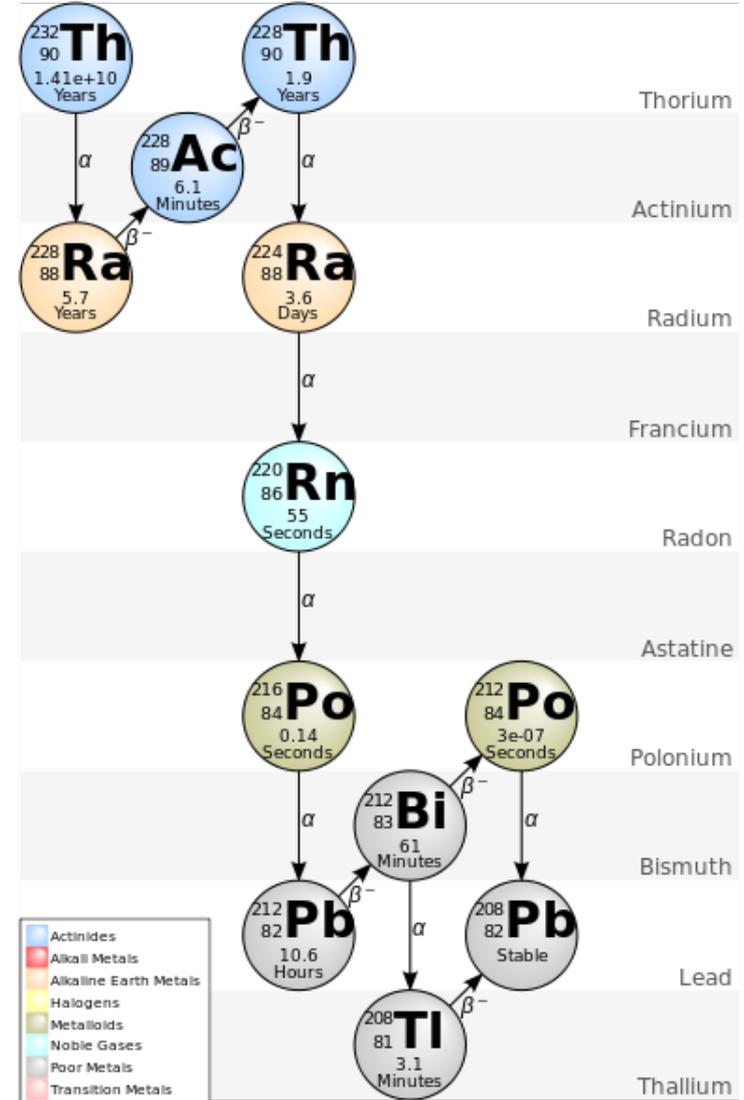
3rd Row (from left): A. Picard, E. Henriot, P. Ehrenfest, E. Herzen, T. De Donder, E. Schrodinger (1933), E. Verschaffelt, W. Pauli (1945), W. Heisenberg (1932), R.H. Fowler, and L. Brillouin.



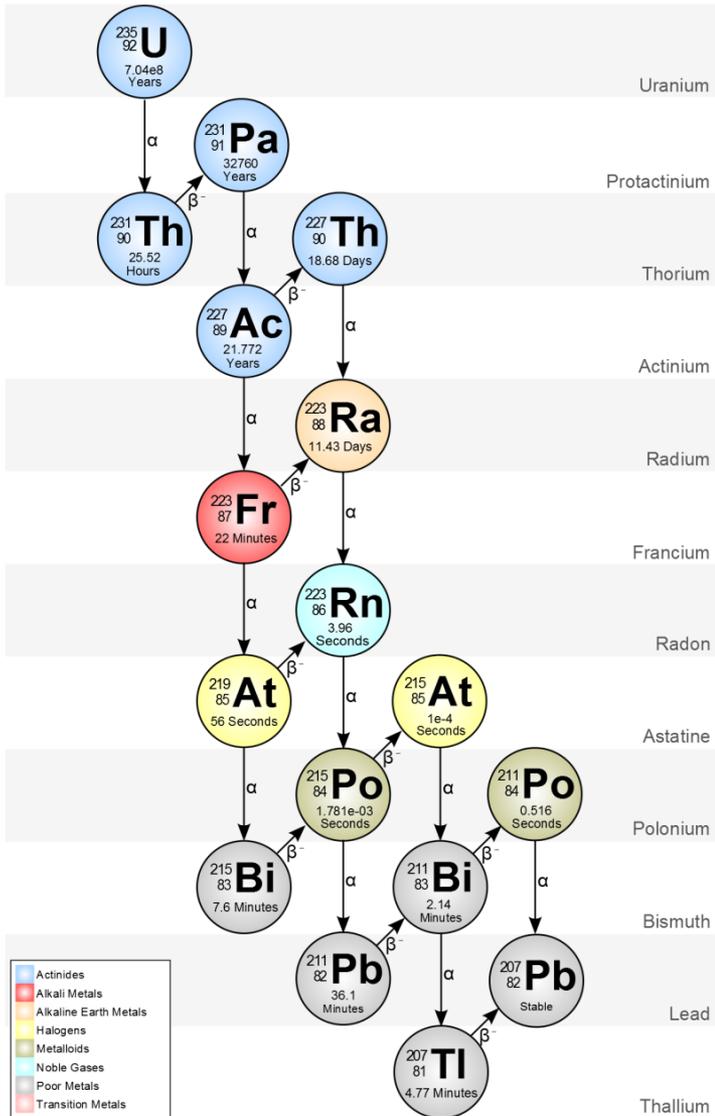
Uranium Series



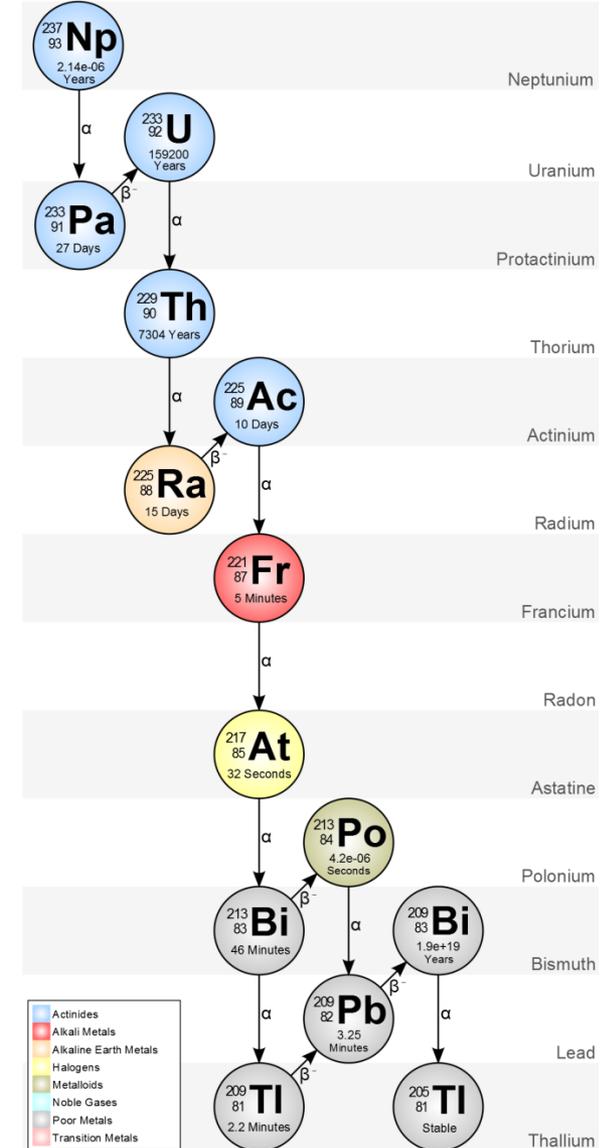
Thorium Series



Actinium Series



Neptunium Series



Naturally Occurring Radium Isotopes

Isotope	Decay Chain	Half-life	Decay Mode	Energy MeV
^{223}Ra	^{235}U	11.4 d	α	5.61 5.72
^{224}Ra	^{232}Th	3.66 d	α	5.69
^{226}Ra	^{238}U	1600 y	α	4.78
^{228}Ra	^{232}Th	5.75 y	β	0.046

Units of Radioactivity

- **Becquerel (Bq)**
1 Bq = one disintegration per second
- **Curie (Ci)**
1 Ci = the decay rate of one gram of Ra-226
- **1 pico (10^{-12}) Ci = 0.037 Bq**

Periodic Table of Elements

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The Alkaline Earth Metals

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																			
↓ Period																																					
1	1 H		<div style="border: 2px solid black; padding: 5px; text-align: center;"> <p>2A</p> <p>4 Be</p> <p>12 Mg</p> <p>20 Ca</p> <p>38 Sr</p> <p>56 Ba</p> <p>Ra</p> </div>																																		2 He
2	3 Li	4 Be																											5 B	6 C	7 N	8 O	9 F	10 Ne			
3	11 Na	12 Mg																											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar			
4	19 K	20 Ca																			23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr			
5	37 Rb	38 Sr																			41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe			
6	55 Cs	56 Ba																			73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn			
7	87 Fr	88 Ra																			105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo			
					58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu																			
					90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr																			

Chemical Properties

- Radium in its pure form is a silvery-white heavy metal that oxidizes immediately upon exposure to air.
- Radium is an alkaline earth element with chemical properties very similar to those of barium.
- It exhibits only one oxidation state (+2) in solution.
- Because of its highly basic character, the divalent ion is not easily complexed and, in comparison, radium has the least tendency of all alkaline earth metals to form complex ions.
- Radium compounds are simple ionic salts, which are white when freshly prepared, turning yellow and ultimately dark with age owing to self-decomposition from the alpha radiation.
- Chloride, bromide, and nitrate of radium are soluble in water.

Chemical Properties (Cont.)

- Radium hydroxide is the most soluble of the alkaline earth hydroxides.
- Radium yields the same insoluble compounds as does barium, with even higher insolubility.
- Only radium carbonate is more soluble than barium carbonate. This property is used in fractionation of radium from barium in radium-barium mixtures.
- Radium sulfate is the most insoluble of the alkaline earth sulfates. Its solubility is 2.1×10^{-4} gram per 100 mL of water. Precipitation as the sulfate is a common practice for the recovery of radium, particularly with the addition of radium or lead as a carrier.

Chemical Properties (Cont.)

- Radium compounds have very low solubilities in organic solvents. The insolubility of radium compounds in organic solvents is frequently the basis for the separation of radium from other elements.
- Radium can sometimes be leached from a solid sample without complete dissolution of matrix, but complete recovery can't be assured.
- Radium mixed with copper-doped zinc sulfide produces a paint that will glow in the dark. The radiation from decaying radium excites the electrons in the doped zinc sulfide to a higher energy level. When electrons return to the lower energy level, a visible photon is emitted.



Radium was widely used to make luminous clock and watch dials. Many watch factory workers died from it.

<http://periodictable.com/Elements/088/index.html>

Methods of Detection

- Chemical techniques in radium assay range from a minimum of steps to various procedures to isolate and purify radium by utilizing classical coprecipitation, complexing, or ion exchange, which are dependent on the measurement technique to be employed and the sample media being processed.
- Measurement techniques employed vary from measurement by scintillation chamber, to mathematical procedures related to alpha or beta counting of the coprecipitated final sample forms, gamma spectrometry, alpha spectrometry, coincidence counting, and liquid scintillation techniques.
- A large portion of these methods are focused on the determination of radium isotopes in water because of the enforcement of federal drinking water or discharge regulations. Some of these methods are EPA-approved either through the rule-making process or ATP (alternate testing procedure) route.

TABLE I-8.—ANALYTICAL METHODS APPROVED BY EPA FOR RADIONUCLIDE MONITORING (§ 141.25)

Contaminant	Methodology	Reference (method or page number)								
		EPA ¹	EPA ²	EPA ³	EPA ⁴	SM ⁵	ASTM ⁶	USGS ⁷	DOE ⁸	Other
Naturally occurring:										
Gross alpha ¹¹ and beta ...	Evaporation	900.0	p 1	00-01	p 1	302, 7110 B		R-1120-76		
Gross alpha ¹¹	Co-precipitation			00-02		7110 C				
Radium 226	Radon emanation	903.1	p 16	Ra-04	p 19	7500-Ra C	D 3454-91	R-1141-76	Ra-05	N.Y. ⁹
	Radiochemical	903.0	p 13	Ra-03		304, 305, 7500-Ra B	D 2460-90	R-1140-76		
Radium 228	Radiochemical	904.0	p 24	Ra-05	p 19	304, 7500-Ra D		R-1142-76		N.Y. ⁹ N.J. ¹⁰
Uranium ¹²	Radiochemical	908.0				7500-U B				
	Fluorometric	908.1				7500-U C (17th Ed.)	D 2907-91	R-1180-76	U-04	
	Alpha spectrometry			00-07	p 33	7500-U C (18th or 19th Ed.)	D 3972-90	R-1181-76 R-1182-76	U-02	
	Laser phosphorimetry						D 5174-91			
Man-made:										
Radioactive cesium	Radiochemical	901.0	p 4			7500-Cs B	D 2459-72	R-1111-76		
	Gamma ray spectrometry	901.1			p 92	7120	D 3649-91	R-1110-76	4.5.2.3	
Radioactive iodine	Radiochemical	902.0	p 6 p 9			7500-1 B 7500-1 C 7500-1 D	D 3649-91			
	Gamma ray spectrometry	901.1			p 92	7120 (19th Ed.)	D 4785-88		4.5.2.3	
Radioactive Strontium 89, 90.	Radiochemical	905.0	p 29	Sr-4	p. 65	303, 7500-Sr B		R-1160-76	Sr-01 Sr-02	
Tritium	Liquid scintillation	906.0	p 34	H-2	p. 87	306,7500-3H B	D 4107-91	R-1171-76		
Gamma emitters	Gamma ray spectrometry	901.1			p 92	7120 (19th Ed.)	D 3649-91	R-1110-76	4.5.2.3	
		902.0				7500-Cs B	D 4785-88			
		901.0				7500-I B				

¹ "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," EPA 600/4-80-032, August 1980. Available at U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161 (Telephone 800-553-6847), PB 80-224744.

² "Interim Radiochemical Methodology for Drinking Water," EPA 600/4-75-008 (revised), March 1976. Available at NTIS, *ibid.* PB 253258.

³ "Radiochemistry Procedures Manual," EPA 520/5-84-006, December 1987. Available at NTIS, *ibid.* PB 84-215581.

⁴ "Radiochemical Analytical Procedures for Analysis of Environmental Samples," U.S. Department of Energy, March 1979. Available at NTIS, *ibid.* EMSL LV 053917.

⁵ Standard Methods for the Examination of Water and Wastewater, 13th, 17th, 18th, 19th Editions, 1971, 1989, 1992, 1995. Available at American Public Health Association, 1015 Fifteenth Street N.W., Washington, D.C. 20005. Methods 302, 303, 304, 305 and 306 are only in the 13th edition. Methods 7110B, 7110 C, 7500-Ra B, 7500-Ra C, 7500-Ra D, 7500-U B, 7500-Cs B, 7500-I B, 7500-91 C, 7500-D, 7500-Sr B, 7500-3H B are in the 17th, 18th and 19th editions. Method 7500-U C Fluorometric Uranium is only in the 17th Edition, and 7500-U C Alpha spectrometry is only in the 18th and 19th editions. Method 7120 is only in the 19th edition. Methods 302, 303, 304, 305 and 306 are only in the 13th edition.

⁶ Annual Book of ASTM Standards, Vol. 11.02, 1994; American Society for Testing and Materials; any year containing the cited version of the method may be used. Copies may be obtained from the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

⁷ "Methods for Determination of Radioactive Substances in Water and Fluvial Sediments," Chapter A5 in Book 5 of Techniques of Water-Resources Investigations of the United States Geological Survey, 1977. Available at U.S. Geological Survey Information Services, Box 25286, Federal Center, Denver, CO 80225-0425.

⁸ "EML Procedures Manual", 27th Edition, Volume 1, 1990. Available at the Environmental Measurements Laboratory, U.S. Department of Energy (DOE), 376 Hudson Street, New York, NY 10014-3621.

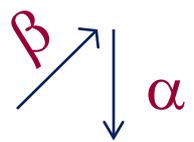
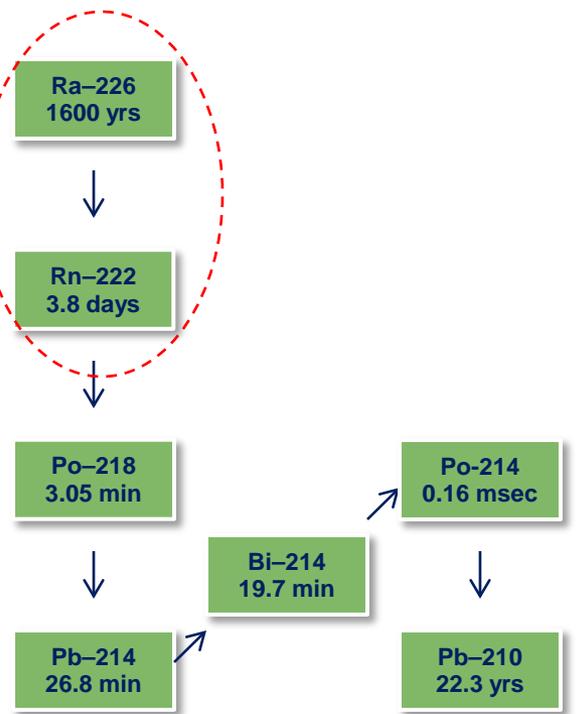
⁹ "Determination of Ra-226 and Ra-228 (Ra-02)," January 1980; Revised June 1982. Available at Radiological Sciences Institute Center for Laboratories and Research, New York State Department of Health, Empire State Plaza, Albany, NY 12201.

¹⁰ "Determination of Radium 228 in Drinking Water," August 1980. Available at State of New Jersey, Department of Environmental Protection, Division of Environmental Quality, Bureau of Radiation and Inorganic Analytical Services, 9 Ewing Street, Trenton, NJ 08625.

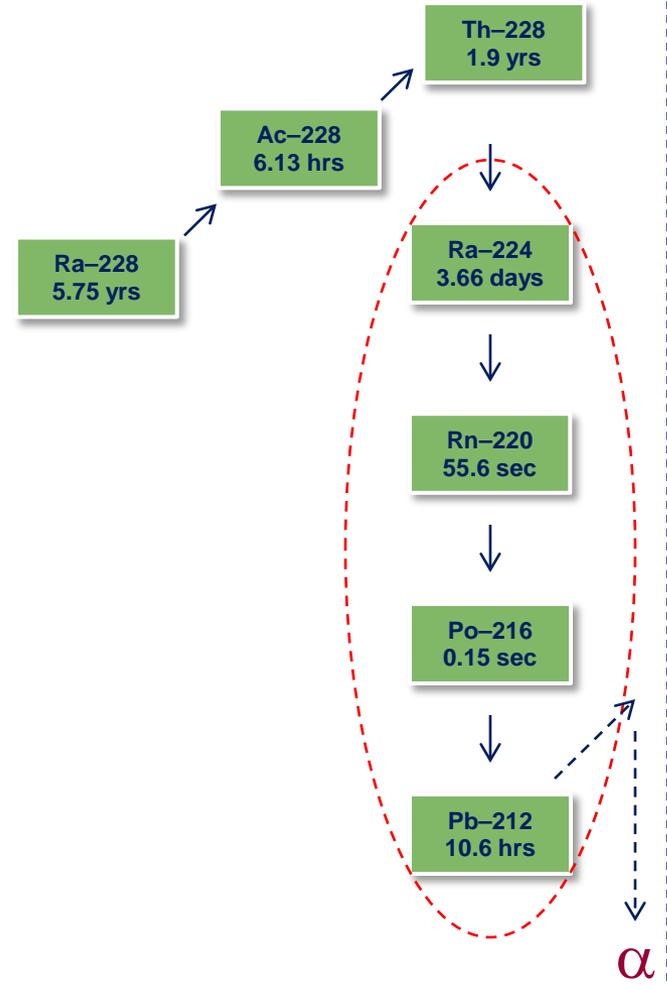
¹¹ Natural uranium and thorium-230 are approved as gross alpha-particle activity calibration standards for the gross alpha co-precipitation and evaporation methods; and cesium-241 is approved for use with the gross alpha co-precipitation methods.

¹² If uranium (U) is determined by mass-type methods (*i.e.*, fluorometric or laser phosphorimetry), a 0.67 pCi/μg uranium conversion factor must be used. This conversion factor is conservative and is based on the 1:1 activity ratio of U-234 to U-238 that is characteristic of naturally-occurring uranium in rock.

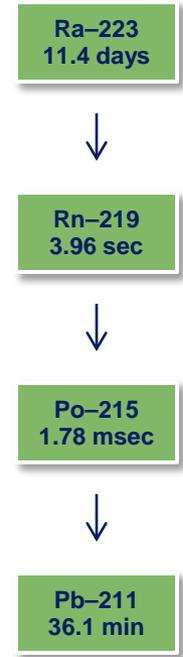
U-238 series



Th-232 series



U-235 series



Methods of Detection (Cont.)

Emanation Method (SM 7500-Ra C; EPA 903.1; ASTM D 3454-91)

- Take 1-L aliquot.
- Separate the radium by coprecipitation with barium as sulfate.
- Dissolve in ethylenediamine-tetraacetate solution (EDTA), pour the solution into a radon emanation storage tube, and allow for Rn-222 ingrowth.
- In the presence of refractive material, treat with HF to remove silicates as SiF_4 or decompose insoluble radium compounds.
- Heat and fume with phosphoric acid to remove sulfites.
- Dissolve in 3M HCl reagent and allow the crystals to dissolve.
- Pour solution into a sealed bubbler and store for ingrowth of ^{222}Rn .
- After ingrowth, purge the gas into a scintillation cell.
- When the short-lived Rn-222 progenies are in equilibrium with the parent (about 4 hours), count the scintillation cell for alpha activity.

Methods of Detection (Cont.)

Precipitation Method (SM 7500-Ra B, EPA 903.0, ASTM D 2460-90)

- This method applies to the measurement of alpha-emitting radium isotopes.
- Lead and barium carriers are added to the sample containing alkaline citrate.
- Sulfuric acid is added to precipitate Ra, Ba, and lead sulfates.
- The precipitate is dissolved in alkaline EDTA and re-precipitated as Ba(Ra)SO_4 , after pH adjustment to 4.5.
- The slightly acidic EDTA keeps other naturally occurring alpha emitters and the lead carrier in solution.
- The final barium sulfate precipitate, which includes Ra-224, Ra-226, and Ra-223, is alpha-counted in a low-background gas-flow proportional counting system or an alpha scintillation counter to determine the total disintegration rate of alpha-emitting radium isotopes.
- The alpha counts are corrected for barium recovery.

Methods of Detection (Cont.)

Precipitation Method (SM 7500-Ra B, EPA 903.0, ASTM D 2460-90)

- The measured total alpha-particle activity in this method is due the sum of the activities of Ra-224, Ra-226, Ra-223, and their respective alpha-emitting progenies. Because of the difference in half-lives of the radium isotopes and their respective daughter products, these isotopes can be identified by the rate of ingrowth and decay of their daughters in the barium sulfate precipitate, leading to a rather complicated ingrowth and decay curve.

Methods of Detection (Cont.)

Precipitation Method Ra-224 and Progeny Decay/Growth Using Bateman Equations

$$A_1 = A_1^0 e^{-\lambda_1 t} \quad (1)$$

$$A_2 = A_1^0 e^{-\lambda_1 t} \quad (2)$$

$$A_3 = A_1^0 e^{-\lambda_1 t} \quad (3)$$

$$A_4 = 1.14 A_1^0 (e^{-\lambda_1 t} - e^{-\lambda_4 t}) \quad (4)$$

$$A_5 = 1.14 A_1^0 e^{-\lambda_1 t} - 1.26 A_1^0 e^{-\lambda_4 t} + 0.104 A_1^0 e^{-\lambda_5 t} \quad (5)$$

where:

A_1^0 = Initial Ra-224 activity,

A_1 = Activity of Ra-224 at any time t ,

A_2 = Activity of Rn-220 at any time t ,

A_3 = Activity of Po-216 at any time t ,

A_4 = Activity of Pb-212 at any time t ,

A_5 = Activity of Bi-212 at any time t , and

λ_1 , λ_4 , and λ_5 are decay constants for Ra-224, Pb-212 and Bi-212, respectively.

Methods of Detection (Cont.)

Precipitation Method Ra-226 and Progeny Decay/Growth

- The alpha-particle ingrowth factor for Ra-226 is given by:

$$1 + 3 (1 - e^{-\lambda_{\text{Rn-222}} t})$$

Where:

$\lambda_{\text{Rn-222}}$ = the decay constant of Rn-222, and

t = the time between sample preparation and counting time.

Factor 3 is due to ingrowth of three alpha-particle-emitting Ra-226 daughter products, Rn-222, Po-218, and Po-214.

- At the time of secular equilibrium, four alpha particle emissions occur for each Ra-226 disintegration.

Alpha Energy & Mass Effects in Alpha Counting

Isotope	T_{1/2}	E_α (MeV)	Isotope	T_{1/2}	E_α (MeV)
Ra-224	3.66 D	5.69	Ra-226	1600 Y	4.78
Rn-220	55.6 S	6.29	Rn-222	3.82 D	5.49
Po-216	0.15 S	6.78	Po-218	3.11 M	6.00
Bi-212	60.6 S	6.05	Po-214	164 μS	7.69
Po-212	0.8 μS	8.78			

Factors to be considered (Arndt and West 2008):

- Variation of alpha activity as a function of residue mass, sample geometry, time between sample collection and counting, time between sample preparation and counting.
- Variation in detection efficiencies between high- and low-energy radium isotopes and their progenies, compared to the detector calibration standard.

Methods of Detection (Cont.)

Precipitation Method (Percival & Martin 1974; NJ Method, Parsa & Hoffman 1992, SM 7500-Ra D)

- One-liter aliquot of sample is initially coprecipitated with PbSO_4 .
- Pb(Ra)SO_4 is dissolved in sodium diethylenetriamine pentaacetate (DTPA).
- Ra-228 from this solution is coprecipitated with BaSO_4 , while the DTPA supernate, which contains the preexisting Ac-228, is discarded.
- Ba(Ra)SO_4 precipitate is allowed to ingrow, generating Ac-228.
- The precipitate is then dissolved in DTPA, isolating the Ac-228.
- The DTPA supernate, which contains Ac-228, is partitioned with di-(2-ethylhexyl phosphoric acid), HDEHP, in n-heptane.
- Ac-228 is stripped from the organic phase with 1 M HNO_3 and coprecipitated with cerium oxalate.
- The precipitate is collected on a filter paper and beta counted.

Methods of Detection (Cont.)

Precipitation Method (NJ Method, Parsa & Hoffman 1992)

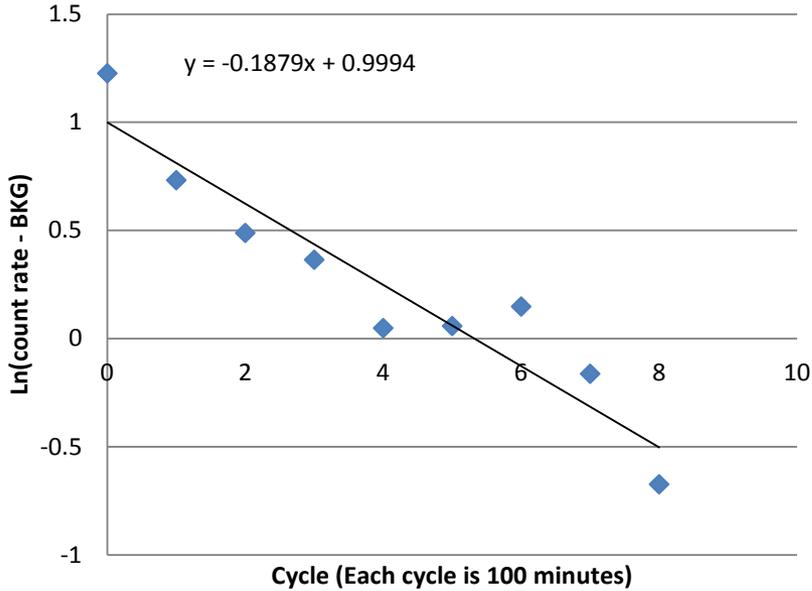
- In the New Jersey Method, the Ac-228 activity is followed during several consecutive 100-minute count times. The change of the net Ac-228 count rate with time is plotted.
- Using a computer-generated least square fitting, a linear curve is constructed. An acceptable slope should be within the 10% of the Ac-228 half-life, 6.13 hours. This way, one can check the radiochemical purity of the sample source, as well as detect any potential variation in background and/or counting efficiency, and attain a more accurate Ra-228 measurement.
- The minimum detectable concentration (MDC) for Ra-228 in water with this procedure is about 0.40 pCi/L, based on a one-liter aliquot of sample, 100-minute count time, and a 3-hour decay interval between the end of Ac-228 ingrowth and start of counting.

Ra-228 New Jersey Method

Plotted Regression Analysis

Final Sample Report

Ac-228 Decay



◆ Ac-228 Decay
 — Linear (Ac-228 Decay)

Determination of Ra228 Activity

LC#	B100031-01 ✓	Analyst:	NR ✓
T1	30-Mar-10 13:45 ✓	Collection Date:	8-Mar-10
T2	01-Apr-10 8:05 ✓	Conversion Factor(cpm/pCi)	1.29245 ✓
Start Date/Time:	01-Apr-10 12:00 ✓	Decay Factor:	0.64622
Count time per cycle(min):	100 ✓	Collection Decay:	0.99195
Sample Volume (L):	1 ✓	Detector:	B4 ✓

Background Determination for Sample		Half life Acceptance and Regression Analysis		
Cycle	Count rate(cpm)	Cycle	Count rate (cpm)	Plotted Data (Ln)
21	0.84 ✓	0	4.18 ✓	1.22671
22	0.89 ✓	1	2.85 ✓	0.73237
23	0.75 ✓	2	2.4 ✓	0.48858
24	0.78 ✓	3	2.21 ✓	0.36464
25	0.9 ✓	4	1.82 ✓	0.04879
26	0.77 ✓	5	1.83 ✓	0.05827
27	0.73 ✓	6	1.93 ✓	0.14842
28	0.68 ✓	7	1.62 ✓	-0.16252
29	0.79 ✓	8	1.28 ✓	-0.67334
30	0.57 ✓	9		
Average Background	0.77 ✓	10		
		11		
		12		
		13		

Regression Results:		Slope:	-0.1879
Y intercept:	0.9994	Calculated Half Life (in Minutes):	368.8923
Initial Count Rate(minus BKG):	2.7167 cpm	HALF LIFE WITHIN ACCEPTED RANGE	

Ra228 Activity: 3.5932 +/- 0.3716 pCi/L
 Minimum Detectable Concentration: 0.5763 pCi/L

UNCERTAINTIES ARE AT 90% LEVEL OF CONFIDENCE

Methods of Detection (Cont.)

Precipitation Method Ra-228 Measurements (NJ Method)

$$D = \frac{C}{CF * V} \left(\frac{1}{1 - e^{-\lambda t_1}} \right) \left(\frac{1}{e^{-\lambda t}} \right) \left(\frac{\lambda T}{1 - e^{-\lambda T}} \right) \left(\frac{1}{e^{-\lambda_1 t_2}} \right)$$

- D = Ra-228 activity concentration, in pCi/L.
- C = Corrected sample net count rate (in cpm) for the first counting cycle.
- T = Counting interval, which is 100 minutes in this procedure.
- t = Ac-228 decay period, measured from the actinium separation step to the beginning of counting.
- t₁ = Ac-228 period of ingrowth from Ra-228.
- t₂ = Ra-228 decay period, measured from sample collection date to actinium separation date.
- CF = Conversion factor, in cpm/pCi, as obtained from a DI water fortified with Ra-228 standard and carrying through the entire sample preparation process.
- V = Volume of sample, in liters.
- λ = Ac-228 decay constant, which is 0.693/T_{1/2}, T_{1/2} is 6.13 hours.
- λ₁ = Ra-228 decay constant, which is 0.693/ T_{1/2}, ²²⁸Ra T_{1/2} is 5.75 years.

Methods of Detection (Cont.)

Sequential Precipitation Method (SM 7500-Ra D, EPA 904.0)

- Ra-226 and Ra-228 are concentrated and separated by coprecipitation with Ba and Pb as sulfates, and purified by EDTA chelation.
- After 36-hour ingrowth of Ac-228 from Ra-228, Ac-228 is coprecipitated onto yttrium oxalate and beta-counted.
- The yttrium oxalate is weighed for chemical recovery determination.
- Ra-226 in the supernate is precipitated as sulfate, purified, and alpha-counted using the precipitation procedure discussed earlier, or it is transferred to a radon bubbler and determined by the emanation method.
- The Percival and Martin method also has sequential measurement capability to assay Ra-226 and Ra-228.

Methods of Detection (Cont.)

Gamma-Ray Spectrometry Method (SM 7500-Ra E)

The New Jersey Method

- To a 3-L water aliquot, add sodium sulfate and concentrated H_2SO_4 .
- Bring the solution to boiling and add lead nitrate carrier solution.
- Cool and filter using a pre-weighed membrane filter.
- Retain the filter for chemical recovery determination.
- Radium isotopes Ra-224, Ra-226, and Ra-228 are measured through their respective gamma-ray-emitting progenies, Pb-212, Pb-214 (and/or Bi-214), and Ac-228, by means of a high-resolution intrinsic Ge detector. The detector is calibrated with custom-made NIST-traceable, mixed radionuclide gamma-ray standard source of similar geometry as the prepared sample.
- Ra-224 and Ra-228 can be measured 2-3 days after sample preparation.
- For Ra-226 assay, repeat counting after about 21 days to ensure that Ra-226 progenies are in equilibrium with their parent.

Methods of Detection (Cont.)

Gamma-Ray Spectrometry Method (^{224}Ra Assay) (SM 7500-Ra E)

$$A^{\circ}_{224} = \frac{C_s - C_b}{1.14 * E * A * V * 2.22 * Y} \left(\frac{1}{e^{-\lambda_{224}t} - e^{-\lambda_{212}t}} \right) \left(\frac{\lambda_{224}t_s}{1 - e^{-\lambda_{224}t_s}} \right)$$

Where,

A°_{224} = ^{224}Ra activity concentration at sample collection time (pCi/L).

λ_{212} = ^{212}Pb decay constant (1.086×10^{-3} /min).

λ_{224} = ^{224}Ra decay constant (1.31×10^{-4} /min).

C_s = Sample net count rate under 238.6-keV photopeak region, cpm.

C_b = Background net count rate for 238.6-keV photopeak region, cpm.

E = Detection efficiency for 238.6-keV gamma ray, (counts/gamma).

A = Fractional gamma-ray abundance for 238.6-keV ^{212}Pb , 0.436 gamma/disintegration.

V = Volume of sample, L.

2.22 = Conversion factor from dpm to pCi/L.

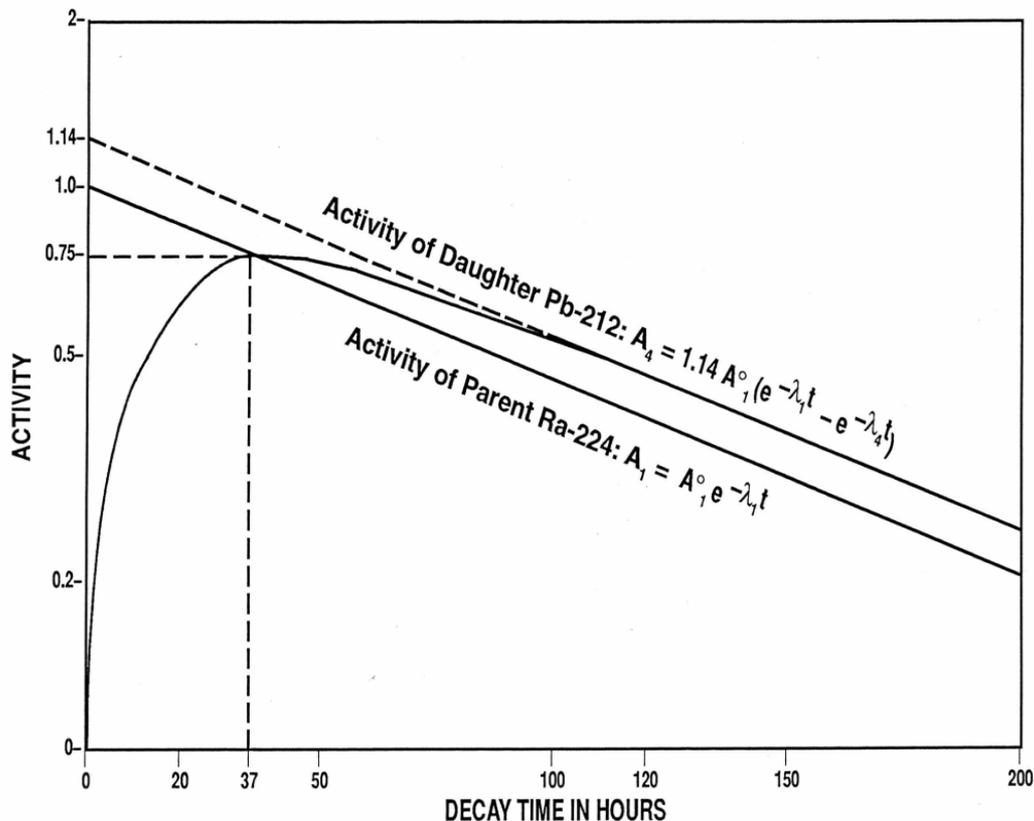
Y = Chemical yield.

t = Time from sample collection to the start of counting.

T_s = Sample count time, min.

Decay of Ra-224 Parent and Ingrowth/ Decay of Pb-212 Progeny

Where at $t = 0$ the activity of Ra-224 = 1
and the activity of Pb-212 = 0



$$A_4 = 1.14 A_1^0 (e^{-\lambda_1 t} - e^{-\lambda_4 t})$$

Where $A_1^0 = {}^{224}\text{Ra}$ activity at $t = 0$
and $A_4 = {}^{212}\text{Pb}$ activity at t .

λ_1 and λ_4 are decay constants for
 ${}^{224}\text{Ra}$ & ${}^{212}\text{Pb}$, respectively.

The time for maximum ${}^{212}\text{Pb}$ -
activity can be calculated by
differentiation of its activity and
setting it equal to zero.

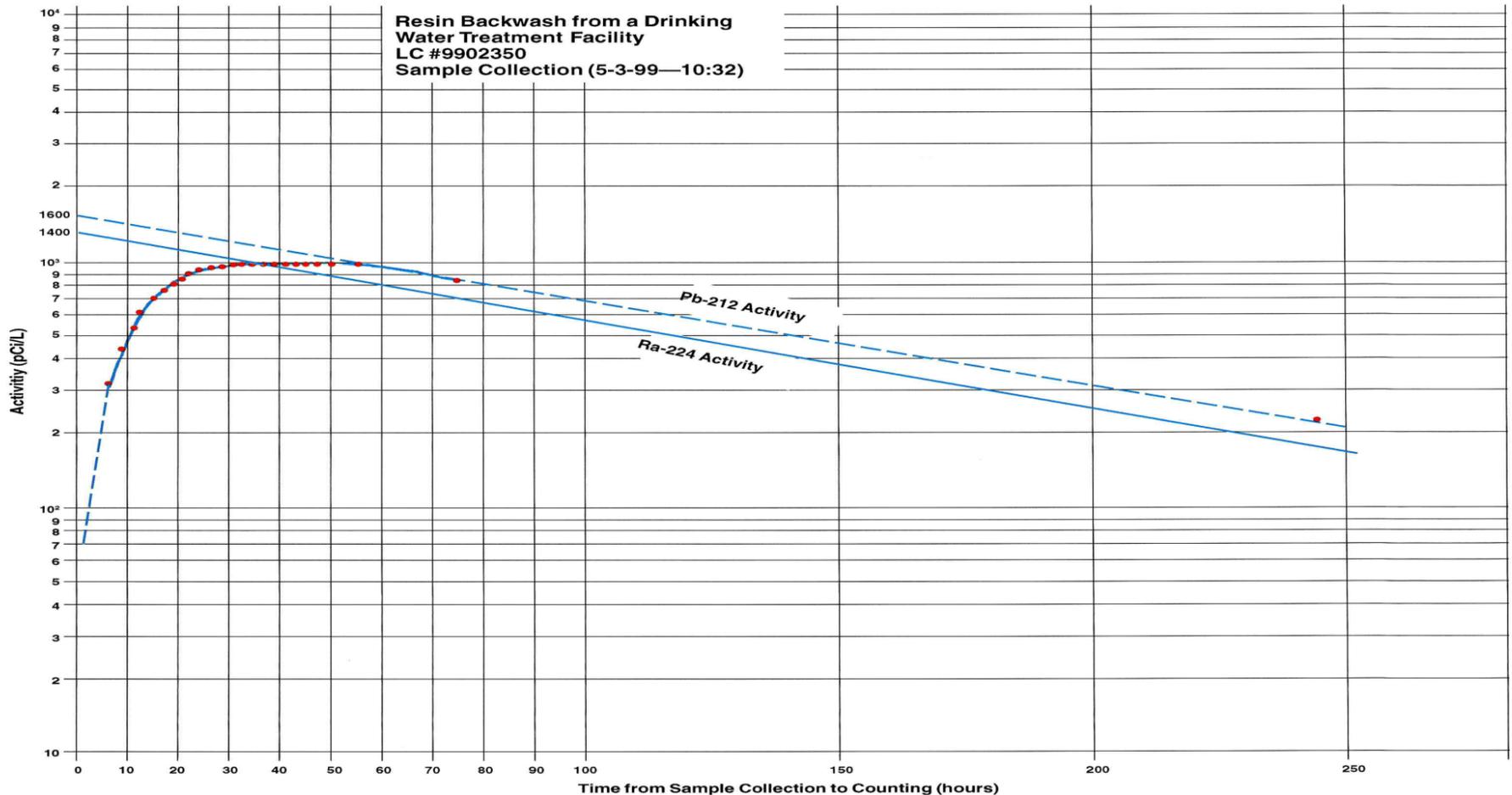
$$\lambda_1 e^{-\lambda_1 t_{\text{max}}} + \lambda_4 e^{-\lambda_4 t_{\text{max}}} = 0$$

where t_{max} is the time for
maximum Pb-212 activity.

$$t_{\text{max}} = \frac{\ln(\lambda_4 / \lambda_1)}{\lambda_4 - \lambda_1}$$

$$= 36.9 \text{ hours}$$

Ra-224 Measurement of a Backwash Sample Through its Pb-212 Progeny at Different Counting Intervals



Methods of Detection (Cont.)

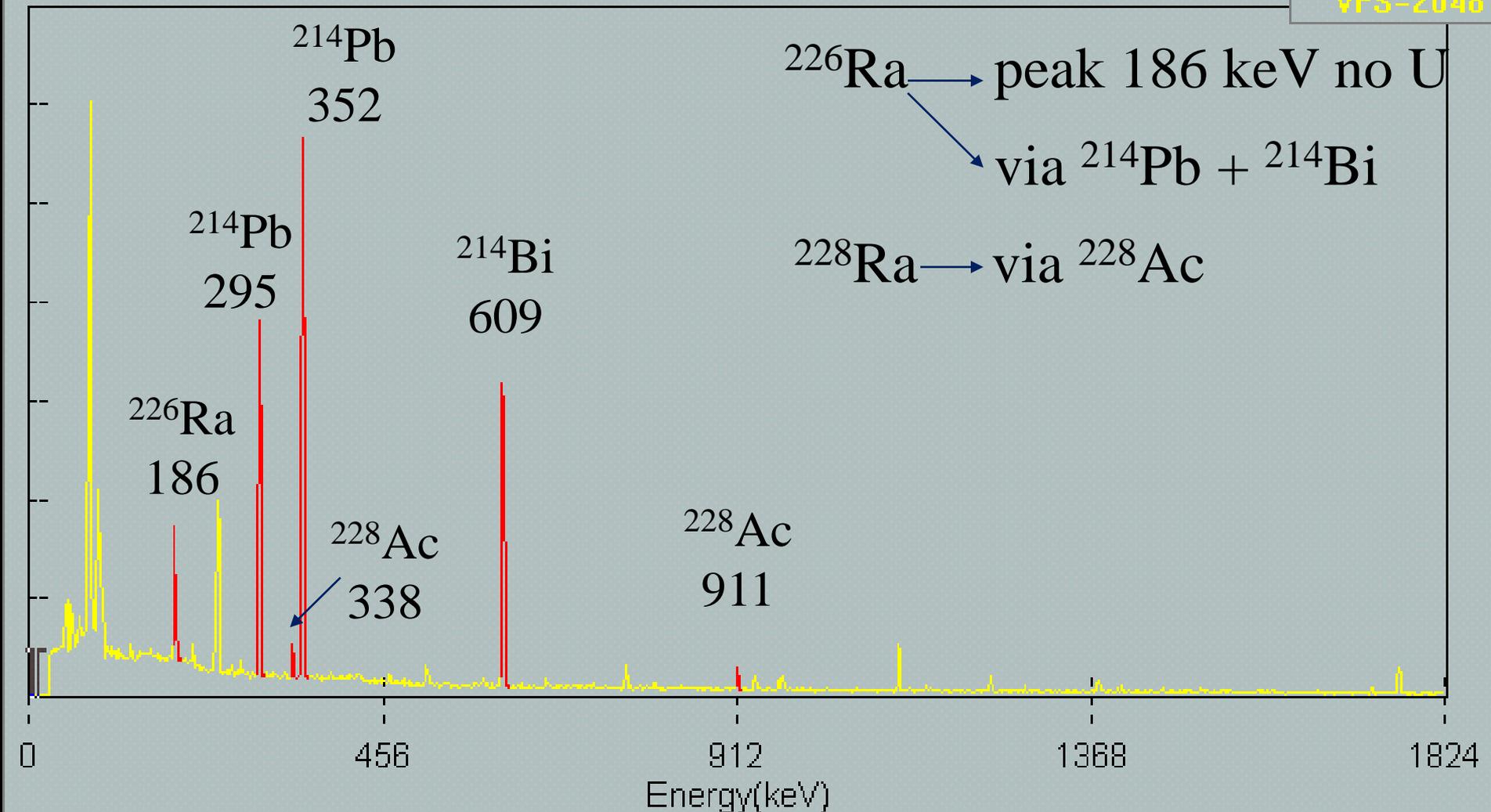
Gamma-Ray Spectrometry Method (SM 7500-Ra E)

The Georgia Tech Method

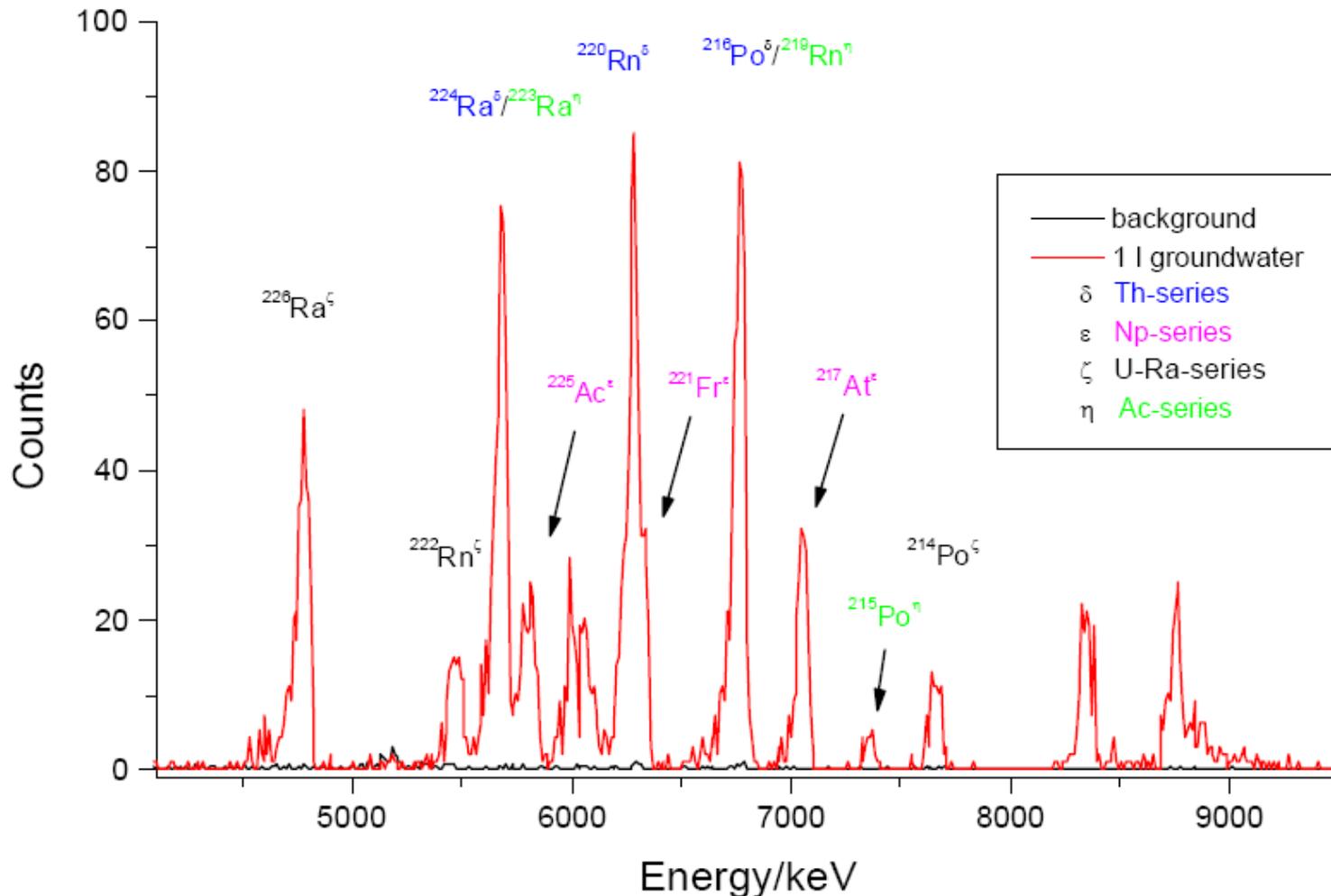
- Take 3-L aliquot and add concentrated HCl and barium carrier.
- Bring to boil and add concentrated H_2SO_4 to form $\text{Ba}(\text{Ra})\text{SO}_4$ precipitate.
- After cooling, filter using a pre-weighed filter.
- Retain filter for chemical recovery determination.
- Detector is calibrated specifically for gamma rays associated with Ra progenies detection. This is done by using DI water fortified with Ra-226 and Ra-228 standards, and carried through the entire sample preparation process.

Gamma-Ray Spectrometry

VFS=2048



Example Alpha Spectrum from a Processed Sample (S. Purkl, 2003)



Methods of Detection (Cont.)

Alpha Spectrometry (USEPA 2010)

- 200 mL of sample is initially spiked with Ra-225 standard (extracted from Th-229 standard), digested using concentrated HNO₃, followed by volume reduction and conversion to the chloride salt using concentrated HCl.
- The solution is pH neutralized and equilibrated with MnO₂ resin to separate radium from interfering radionuclides and matrix constituents.
- Further selectivity is achieved using a column that contains Diphonix resin.
- The radium radionuclide, including Ra-226, is eluted from the column and prepared for counting by microcoprecipitation with BaSO₄.
- Low-level measurements are performed by alpha spectrometry.
- Ra-226 region of interest is corrected for chemical recovery based on the observed activity of At-217, the third progeny of Ra-225.

Methods of Detection (Cont.)

Coincidence Procedure (NY Method 1980)

- In this method, radium in the sample is coprecipitated with BaSO_4 and the precipitate is re-dissolved in EDTA.
- The solution is purged and transferred to a sealed radon bubbler.
- After Rn-222 has grown back into solution, the gas is transferred into a ZnS-coated scintillation cell.
- The activity of Rn-222 in equilibrium with its daughters is measured at 2-day intervals in order to follow the Rn-222 growth.
- The Rn-222 activity is determined by using a least-squares method to fit counting data to the theoretical growth curve for Rn-222.
- Ra-226 concentration is calculated from Rn-222 activity.
- To determine Ra-228, the BaSO_4 is re-precipitated from the EDTA solution and chemical recovery is measured by gamma counting of Ba-133 tracer.
- After ingrowth, Ac-228 is measured by beta-gamma coincidence counting.
- The counting system consists of 0.25-mm thick x 2.4 cm diameter plastic scintillator, and a 10 x 10 NaI(Tl) gamma detector.

Methods of Detection (Cont.)

Coincidence Procedure (Cont.) (McCurdy and Mellor 1981)

- This method measures Ra-224, Ra-226, and Ra-228, first by a radiochemical separation and then by alpha/gamma and beta/gamma coincidence counting.
- Radium isotopes are coprecipitated with BaSO_4 , dissolved in alkaline EDTA, and re-coprecipitated with BaSO_4 doped with ZnS.
- Then alpha/gamma coincidence emissions of Ra-224 and Ra-226 and the beta/gamma coincidence emissions of Ac-228 are used for the analysis.
- A delayed coincidence technique is used to differentiate between alpha/gamma and beta/gamma coincidence events.
- Minimum detectable concentrations (MDC) of 0.2, 0.3, and 0.5 pCi/L can be attained for Ra-224, Ra-226, and Ra-228, respectively, based on 1-L sample aliquot and 200-minute count.

Methods of Detection (Cont.)

Radon-in-Air Technique (FSU Method, Guebuem et al. 2001)

- This method measures low levels of radium isotopes in natural waters, during on-site sampling and determinations. 20-200 L of sample are collected.
- The radium present is first preconcentrated on MnO_2 -coated acrylic fiber.
- The radon gas produced from the adsorbed radium, ^{220}Rn and ^{222}Rn , is then circulated through a closed air-loop connected to a commercial radon-in-air monitor, RAD7.
- The monitor counts alpha decays of radon progenies (polonium isotopes), which are electrostatically collected onto a silicon semiconductor detector.
- Count data are collected in energy-specific windows, which eliminate interference and maintain very low background.
- ^{224}Ra is measured immediately after sampling via ^{216}Po , and ^{226}Ra is measured via ^{218}Po after a few days of Rn-222 ingrowth.



$^{220}\text{Rn} =$
0.5-790
pCi/L

Ra Collection
on Mn-fiber

Rinse & Moisture
Adjustment

Short-lived
radium → Delayed Coincidence Counting
 ^{223}Ra & ^{224}Ra

Ashing/Leaching + Sealing

20-day hold for ^{222}Rn ingrowth

Long-lived
radium →

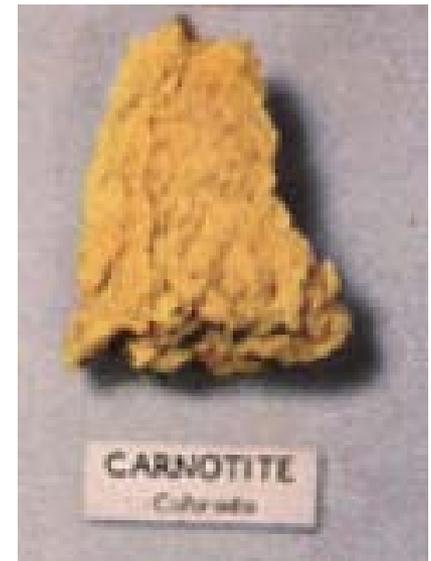
Gamma-spectrometry
 ^{226}Ra & ^{228}Ra

Occurrence

- Radium is present in soil, minerals, foodstuffs, groundwater, and many common materials.
- As U-238 and Th-232 progenies, radium isotopes are widely distributed in small amounts throughout the earth's crust.
- Originally, radium was obtained from the rich pitchblende ores found in Bohemia.
- The carnotite sands of Colorado furnish some radium, but richer ores are found in Republic of Zaire and the Great Lakes Region of Canada.
- Ra-226 and Ra-228 activities should be about the same, considering their parents' abundance ratio of $^{232}\text{Th}/^{238}\text{U}$ to be about 3 in the earth's crust and their specific radioactivity being 1/3 (U-238 $T_{1/2} = 4.47 \times 10^9$ years and Th-232 $T_{1/2} = 1.41 \times 10^{10}$ years).
- As pH decreases, all isotopes of radium become more mobile, because hydrogen ions compete effectively with radium for available sorption or exchange sites.
- Because the sorption and exchange capacity of sediments that make up certain aquifer systems are extremely low, even a small increase in free hydrogen-ion content can result in a substantially diminished sorption and exchange capacity and enhanced radium mobilization.



Pitchblende ores, Příbram-Haje,
Central Bohemia, Czech Republic



Occurrence (Cont.)

- The source of the radium in groundwater is naturally occurring radium in soils and rocks, but geochemical and physical factors will influence radium mobilization.
- Zoltan Szabo and his colleagues at the USGS have conducted a number of studies on the occurrence of radium isotopes in U.S.
- Concentration of radium isotopes in water samples has shown statistically significant differences with predominant land use.
- Radium concentrations generally are higher in samples from agriculture-dominated areas than in samples from other areas.
- Examination of effects of agricultural activities on radium mobility and distribution of radium concentrations with depth in water in the aquifer systems have found that the concentrations of radium were highest in acidic water from shallow to medium depth.
- Concentration of species that are related to agriculture, such as nitrate and divalent cations Ca, Mg, Ba, and Sr, are significantly higher in the outcrop area.
- The divalent cations compete with radium for sorption sites, thereby providing a second chemical mechanism of radium mobilization that enhances the mobilization effects of acidic water.

Occurrence-Water Treatment Effects

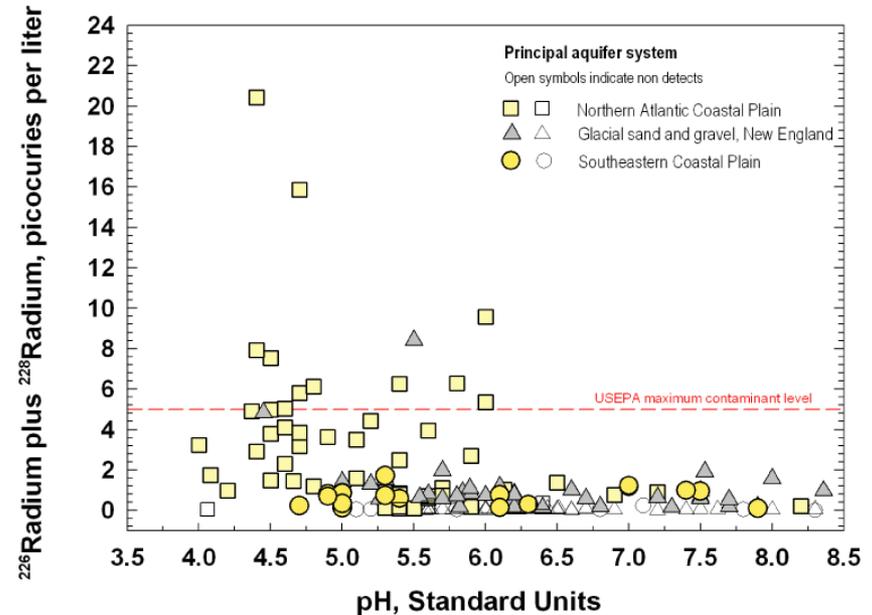
- Water softeners (cation-exchange units) efficiently remove Ra (about 90%) along with constituents that cause water hardness, such as calcium, magnesium, and iron.
- In some areas, elevated radium concentrations in drinking water has led to the increased use of water softeners for the purpose of radium removal, and not just water softening.
- Proper maintenance of water softeners includes regular regeneration of the capacity of the cation-exchange media with Cl^- brine solution.
- The waste (regeneration) brine bearing large concentrations of Ra (max detect at 2,200 pCi/L) is commonly flushed to septic systems.
- Once in the septic system, the waste is diluted and flushed to the environment.
- There is likelihood of continued Ra mobility, or an increase in Ra mobilization, in water effluent mixtures in the leachfield and at the water table for the unconfined aquifer receiving the cation-exchange regeneration brine waste through the discharge of effluent from septic systems.

Occurrence-Water Treatment Effects (Cont.)

- Rapid development of densely populated residential areas reliant on septic systems for waste disposal, especially in areas with private wells that produce water that is treated with softeners, has been shown to be associated with increased salinity (Cl^- concentration) and nitrogen and phosphorous concentrations in the waters of the underlying sandy aquifers.
- USGS's Zoltan Szabo, et al. (2008), have studied the fate of Ra in the septic-tank effluent water at the water table downgradient of the leachfields in unconfined aquifers in the New Jersey Coastal Plain. The combined Ra-226 and Ra-228 concentrations were commonly low at the water table. The combined Ra concentrations in the discharged septic-tank effluents ranged from 0.7 pCi/L to 6.6 pCi/L. The effluents were about neutral in pH.
- In moderately acidic conditions ($\text{pH} < 5.3$) at the water table, Ra was readily detectable, and in some sites, combined Ra concentrations were greater than in the discharging septic-tank effluents, despite dilution. Maximum combined Ra concentration at the water table was about 27 pCi/L where pH was the lowest (4.8).
- The combined Ra concentrations of sludge from the septic tanks ranged from less than 1 to about 10 pCi/g (dried weight), about a 10-fold increase from the concentration in the sandy aquifer sediment, in which combined Ra concentrations ranged from 0.2 to 1.1 pCi/g. These results indicate that long-term land application of the sludge as fertilizer might result in an increase in Ra in soil.

Radium Occurrence Summary

- Ra in rivers and groundwater is mostly attached to particles, some dissolved.
- Ra desorbs when particles reach salinity – high ionic strength, common ions out-compete Ra from the surface.
- Ra desorbs from surfaces in groundwater aquifer due to saltwater recharge.
- Radium mobility increases as pH decreases.
- Enhanced radium mobility is due to the alpha-recoil process within rock/water interface in the aquifer.

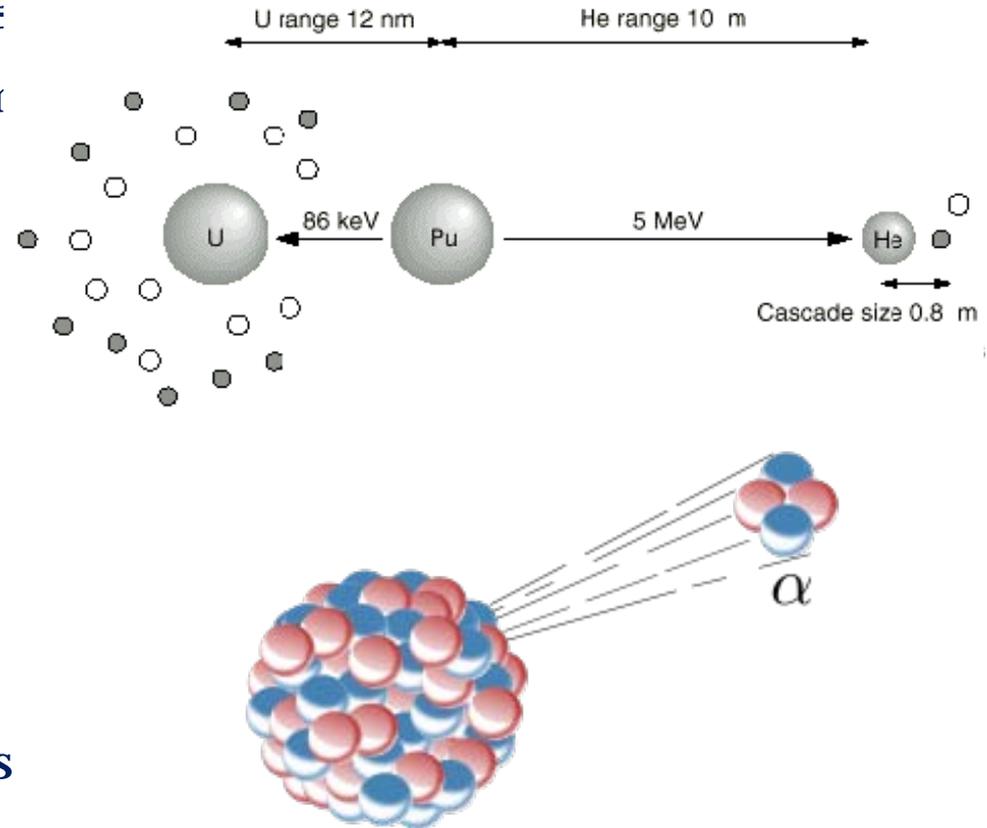


Acidic groundwater contains elevated concentrations of combined radium (Ra-226 plus Ra-228) compared to groundwater with higher pH. Low-pH conditions decrease the likelihood of adsorption of radium to aquifer materials enhancing the mobility of radium into groundwater. In this study, low-pH conditions were most commonly found in the North Atlantic Coastal Plain, but low-pH conditions were also found in the Southeastern Coastal Plain, and in parts of the Glacial aquifer system in the New England States. A pH less than about 6 increases the likelihood that combined radium will exceed the combined radium drinking water standard. <http://water.usgs.gov/nawqa/trace/radium/maps/fig3.html>

Alpha Recoil Process

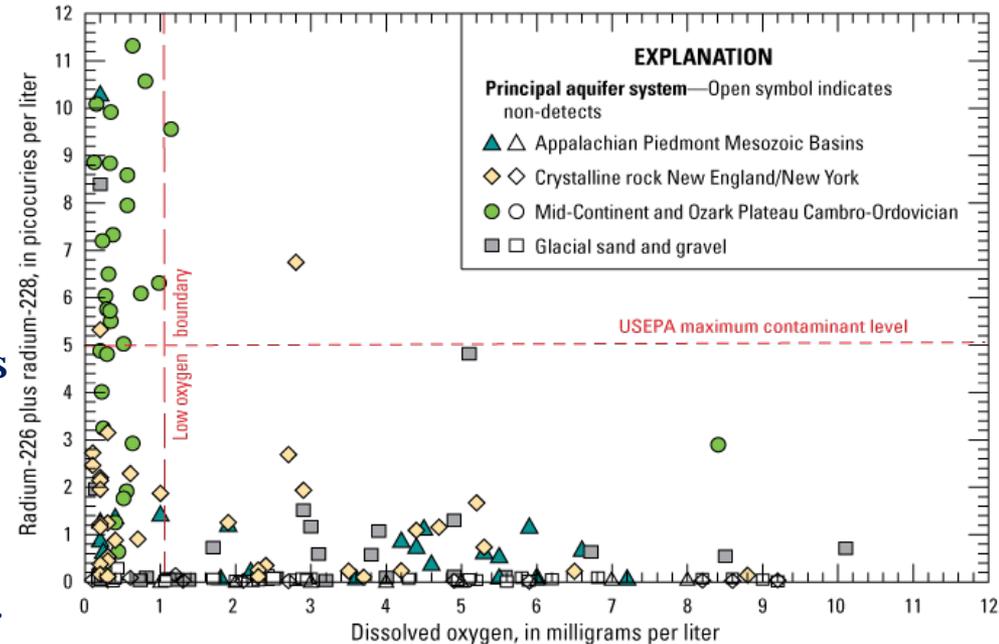
- During decay of radionuclide by α emission, the alpha particle is ejected from the nucleus, carrying off most of the excess energy, much like a bullet being shot from a gun.
- Alpha recoil is a process whereby the balance kinetic energy is imparted to the product radionuclide. The newly created progeny radionuclide actually recoils in the opposite direction, much like the recoil kick of the gun, with energies that are over 10^4 times larger than typical chemical bond energies.
- As such, the decay product breaks free from the surrounding structure, damaging the crystal lattice, and recoils directly in the water in a pore space.

Plutonium Alpha Decay Recoil Process



Impact on Drinking Water

- The concentration of radium in drinking water is generally low (less than 2 pCi/L for combined ^{226}Ra and ^{228}Ra), but there are specific geographic regions in the U.S. where higher concentrations of radium occur in water due to geologic sources.
- In the absence of uranium, the major gross alpha activity in drinking water is attributed to the radium isotopes. In this regard, in the past, the focus for the elevated gross alpha activity was centered on the presence of Ra-226 and its progeny.
- In recent years, studies have shown that a significant source of elevated gross alpha activity in drinking water is due to the presence of unsupported Ra-224. This discovery has raised the concern that moderate to high levels of alpha-particle activity may exist in many drinking water supplies, but have gone undetected because of the time delays typical between sampling and analysis.



Oxygen-poor groundwater contains elevated concentrations of combined radium (radium 226 plus radium 228) compared to groundwater with higher dissolved oxygen concentrations. Low-oxygen conditions decrease the likelihood of adsorption of radium to aquifer materials enhancing the mobility of radium into groundwater. In this study low-oxygen conditions were generally found in parts of the Appalachian Piedmont Mesozoic Basins, New England-New York crystalline rock, Mid-Continent and Ozark Plateau Cambro-Ordovician, and parts of the Glacial aquifer systems in the eastern United States. Oxygen concentrations less than 1 milligram per liter increase the likelihood that combined radium will exceed the combined radium drinking water standard. <http://water.usgs.gov/nawqa/trace/radium/maps/fig2.html>

Impact on Drinking Water (Cont.)

Federal Regulations

- The Final Rule for radionuclides came out December 7, 2000 (Federal Register Vol. 65, No. 236, pp 76708-76753), and became effective on December 8, 2003.
- Combined ^{226}Ra and ^{228}Ra Maximum Contaminant Level (MCL) is retained at 5 pCi/L.
- From the available data, there are two specific geological regions in the U.S. where more than 75% of the known Ra violations occur: (1) the Piedmont and Coastal Plain provinces in New Jersey, North Carolina, South Carolina, and Georgia; and (2) a north-central region, consisting of parts of Minnesota, Iowa, Illinois, Missouri, and Wisconsin. The rest of the violations are generally scattered clusters, notably along the Arizona-New Mexico border, Texas, Mississippi, Florida, and Massachusetts. (Hess et al., 1985)

Impact on Drinking Water (Cont.)

Federal Regulations (Cont.)

- EPA believes that ^{224}Ra is a health concern and is a greater risk factor than previously thought. It is considered to be a local issue and additional national occurrence data are needed.
- Based on EPA recommendations in 2000, the states suspecting Ra-224 contributions in their public water supplies are to perform gross alpha testing within 48-72 hours from sample collection to capture alpha-particle emissions due to the presence of Ra-224.
- The Federal Safe Drinking Water Act oversees only community public water systems and only applies to communities with systems that have service connection to 15 or more households or are larger than 25 residents. The Act does not apply to private wells or non-community systems (such as schools, factories, or office complexes served by water systems categorized as non-transient systems) or non-community transient systems which serve some hotels and gas stations.

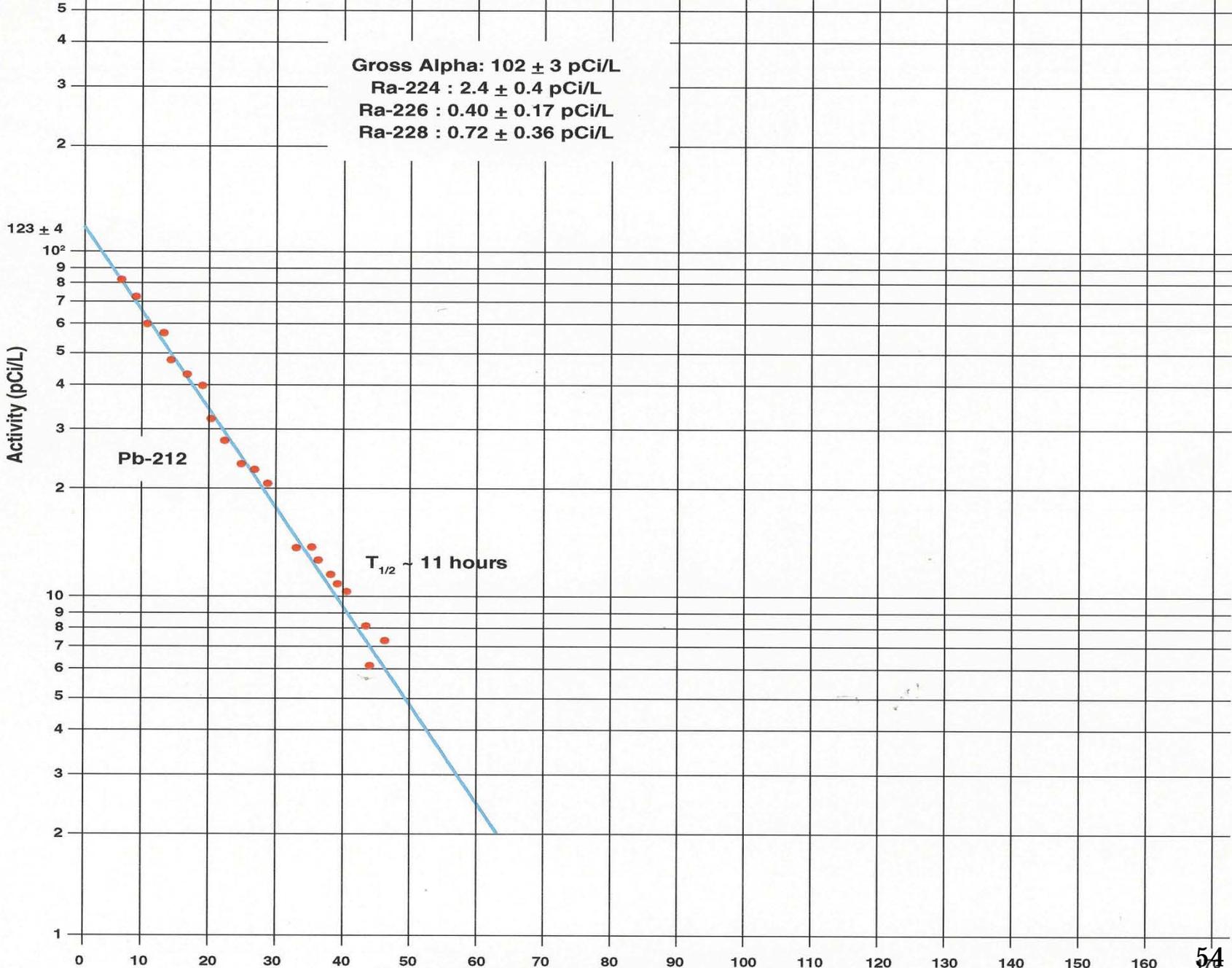
Impact on Drinking Water (Cont.)

Current New Jersey Regulations

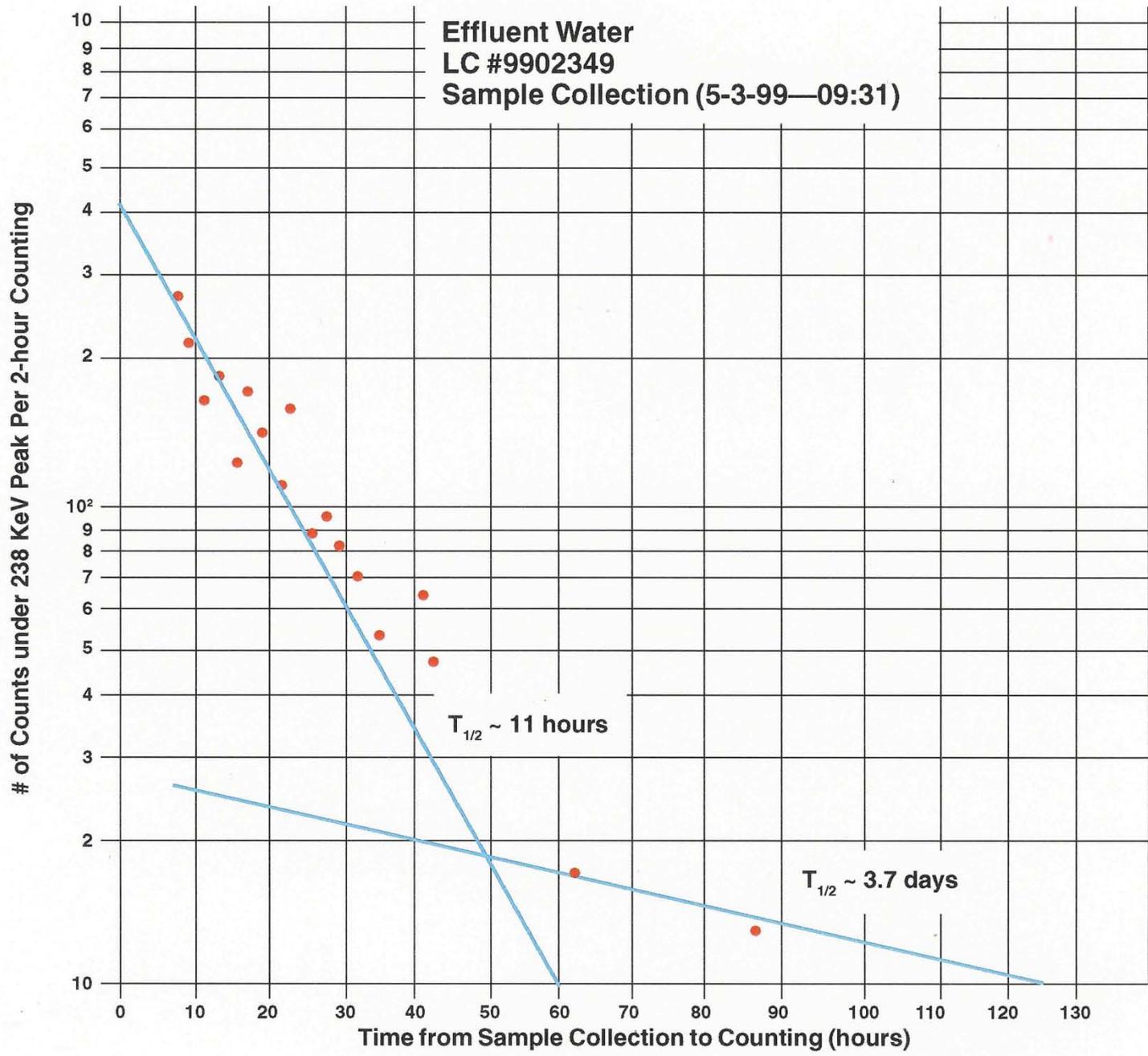
- Follow the current federal regulations, plus:
 - Requires gross alpha testing within 48 hours from sample collection, to include α -particle emissions due to the presence of ^{224}Ra ; per EPA's recommendations to states and utilities, January 27, 1999 memorandum and Notice of Data Availability (NODA), FR April 21, 2000.
 - Recounts samples with gross α over 5 pCi/L 24 hours later to minimize ^{222}Rn and ^{220}Rn progeny contributions to the gross α assay.
 - Considers that all the federal maximum contaminant levels and action levels and state testing regulations apply to all New Jersey public and nonpublic water systems and they shall be subject to the state monitoring requirements.
- In this effect, about a decade ago, the state initiated a study measuring the radioactive content of some of the communities not addressed in the federal regulations. The state also regularly monitors the radioactive quality of private wells, through the New Jersey Private Well Testing Act (NJAC 2002).

Gross Alpha: 102 ± 3 pCi/L
Ra-224 : 2.4 ± 0.4 pCi/L
Ra-226 : 0.40 ± 0.17 pCi/L
Ra-228 : 0.72 ± 0.36 pCi/L

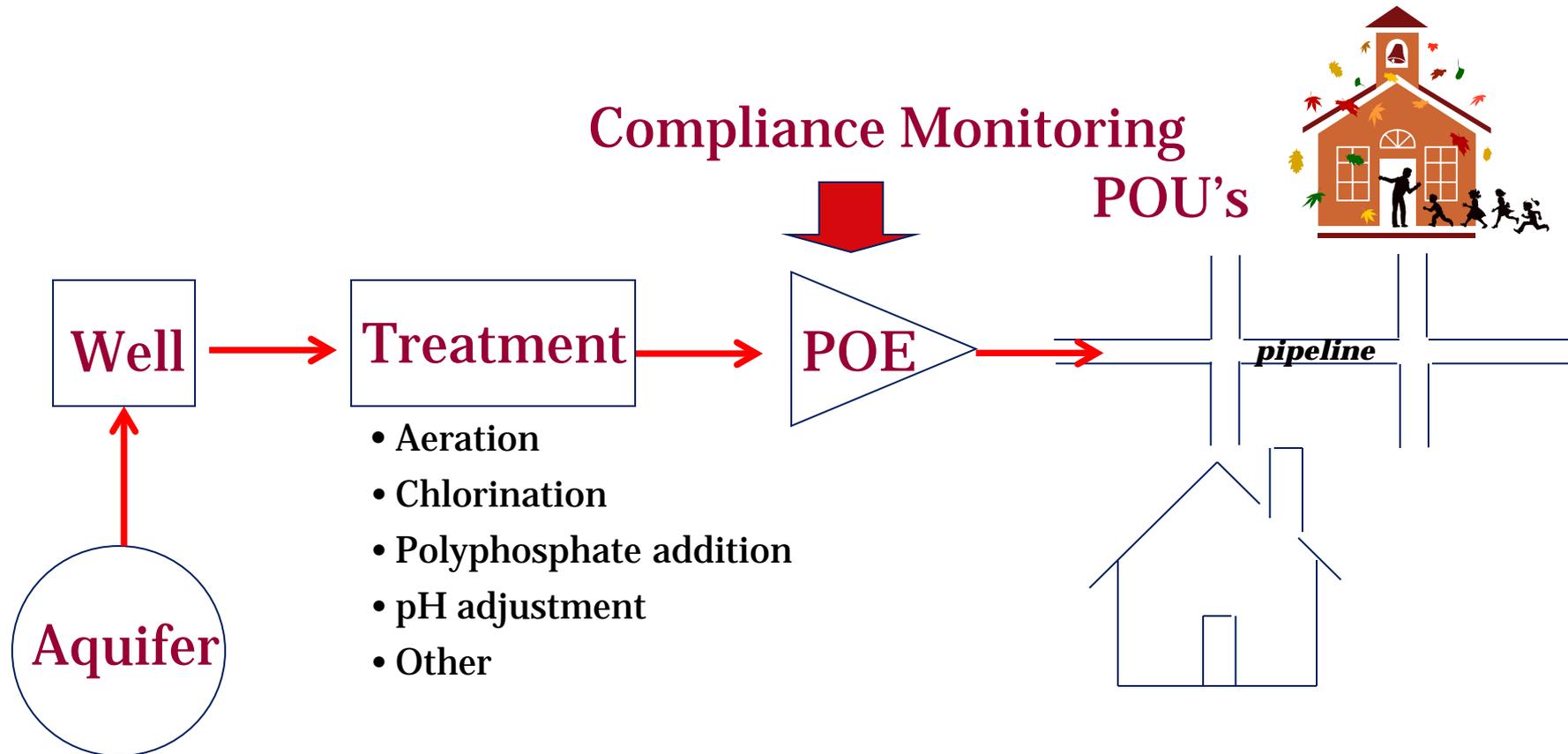
Activity (pCi/L)



Time from Sample Collection to Counting (hours)



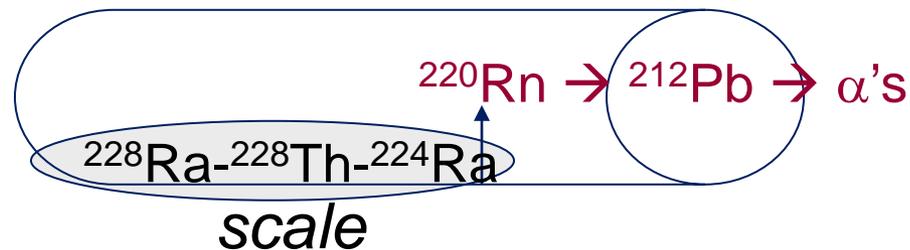
Water Distribution Systems



POE = point of entry
POU = point of use

New Jersey Anomalies

- High “gross alphas” (>EPA MCL 15 pCi/L)
- Unsupported ^{212}Pb (Pennsgrove: ~2-60 pCi/L; Florence: ~8-110 pCi/L)



Section of a 60-Year-Old, 10-Inch Main Water Pipe



Gamma-ray Spectroscopy of Pipe Scaling

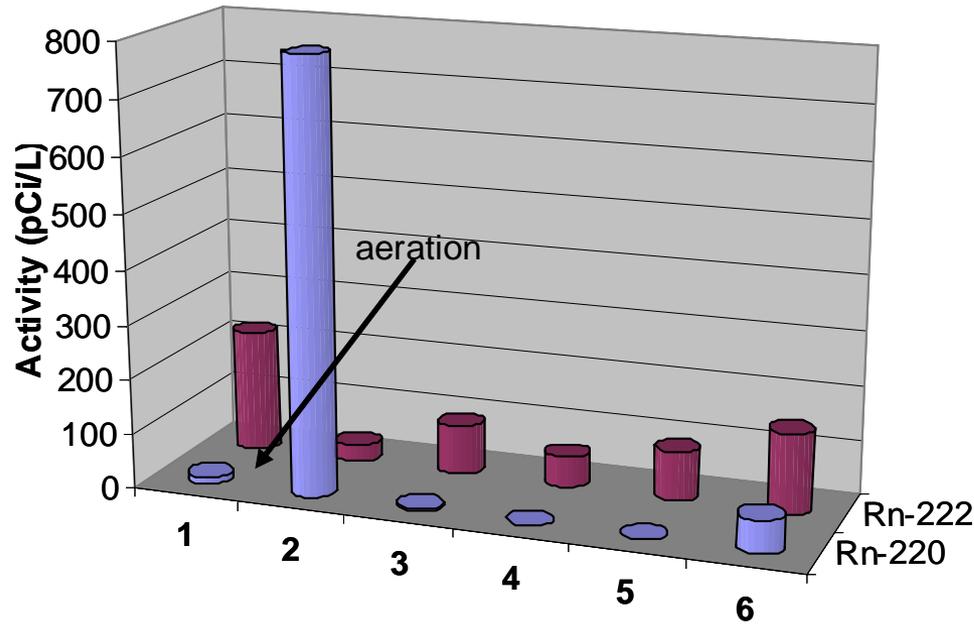
- Revealed Ra-224 and Ra-228 to be in equilibrium with the activity of 6.7 ± 0.2 pCi/g each.
- Ra-226 activity was 2.1 ± 0.1 pCi/g.
- Assuming uniform scale build-up throughout the pipe, the Ra-228 activity alone is estimated to be 1 nCi/in or 60 mCi/mile of pipeline.

New Jersey Sampling





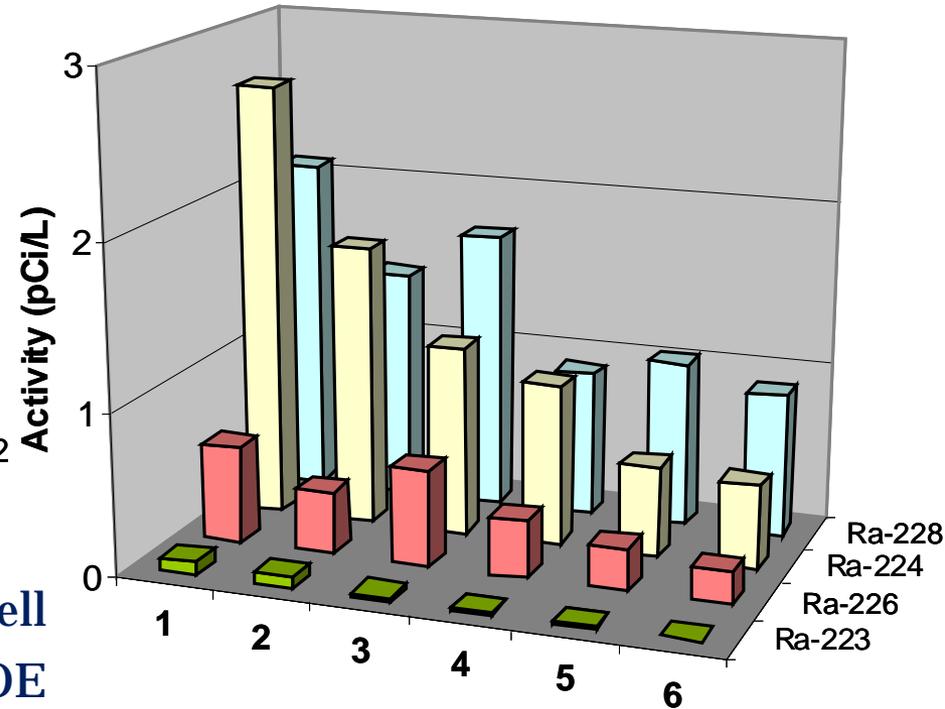
Radon isotopes



Aeration performed to remove Fe – hydrous Fe oxides sorbing Ra?

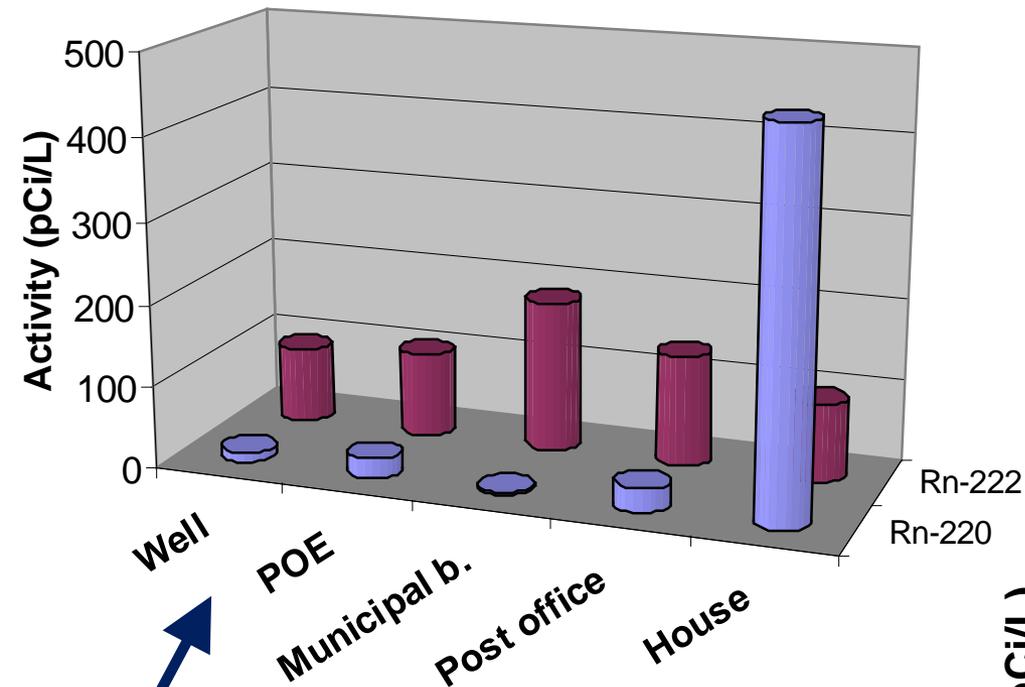
Florence, NJ

Radium isotopes



1. Well
2. POE
3. Hydrant
4. High school
5. Muncipal building
6. House

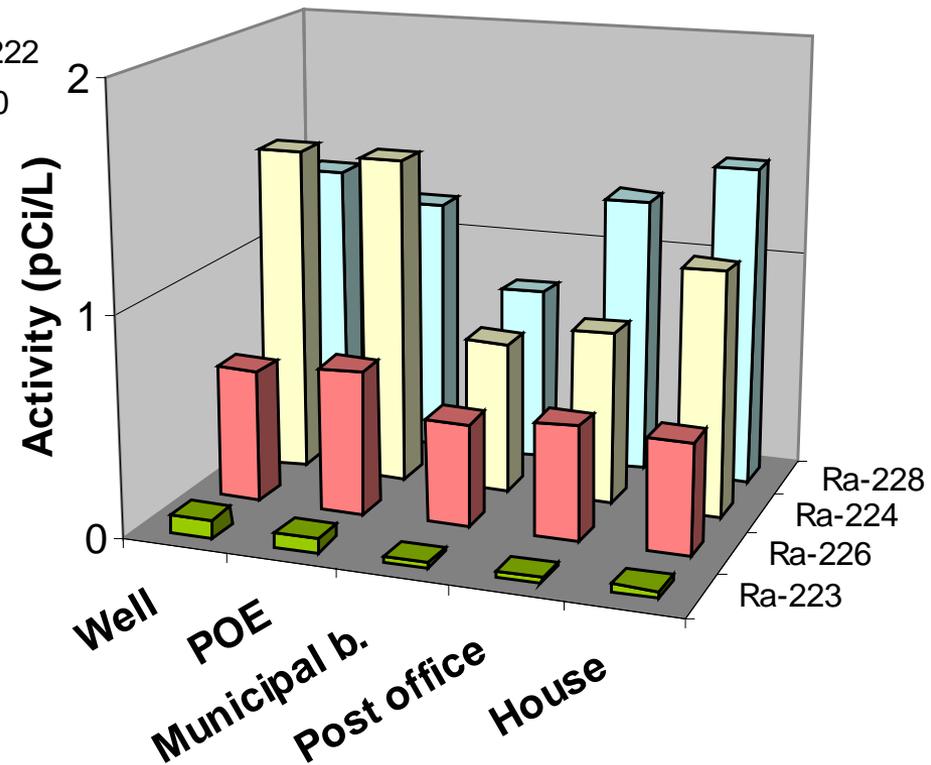
Radon isotopes



Water Tower

Pennsgrove, NJ

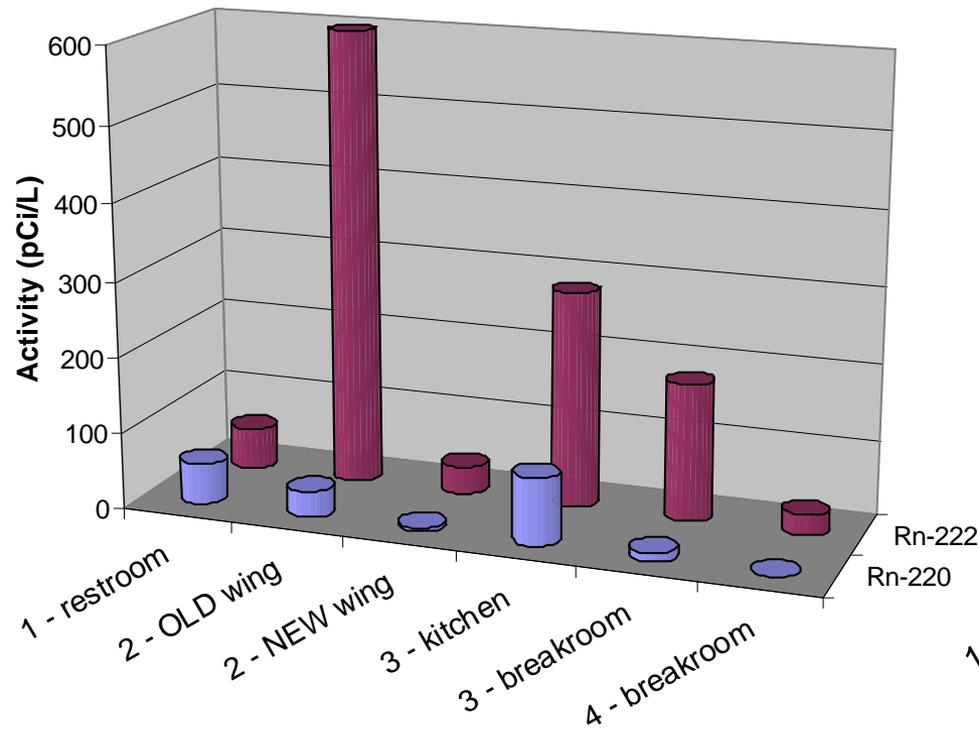
Radium isotopes



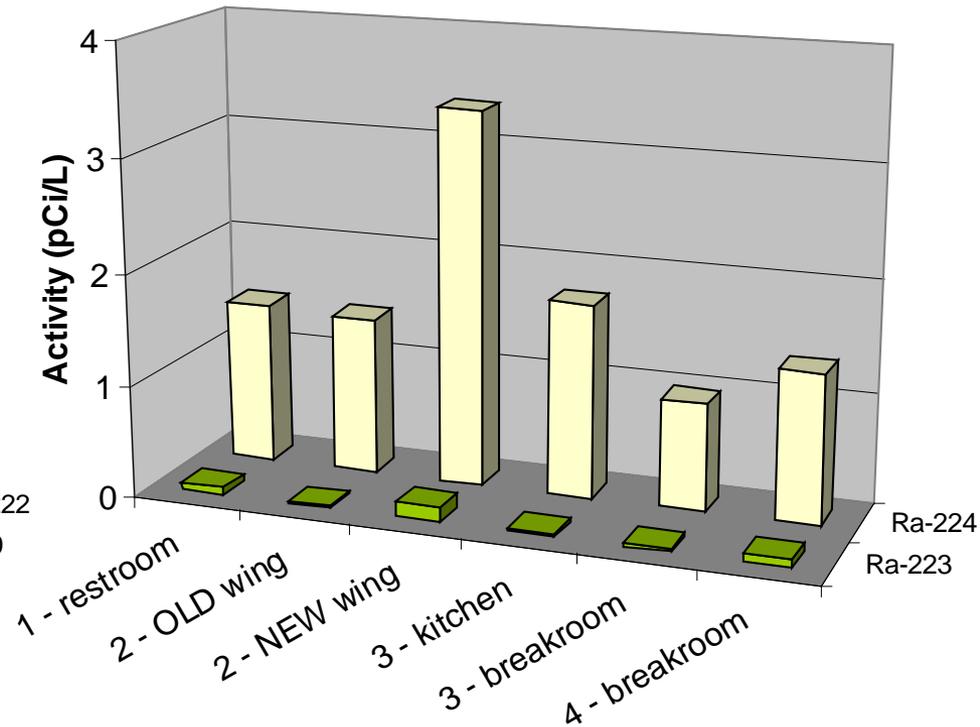
Pensacola, FL

We visited four schools

Radon isotopes



Radium isotopes



Sampling in Pensacola



$^{220}\text{Rn} =$
0-90
pCi/L

Summary of the Study

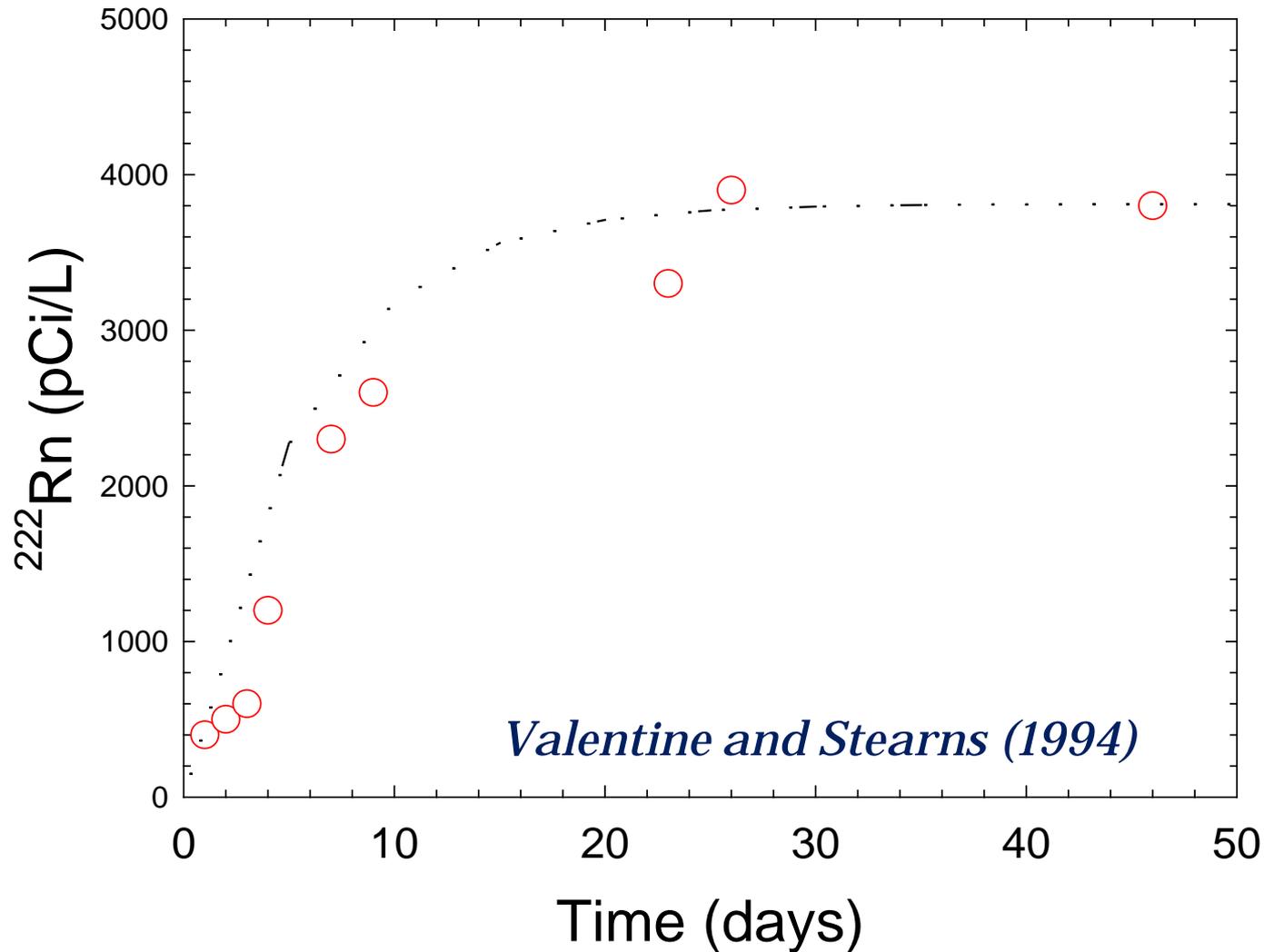
- Scavenging of Ra by hydrous Fe/Mn oxides results in a “source.”
- The “thoron prospecting” tool should be able to locate areas of Ra-228-bearing scale.
- Results shown for New Jersey and Florida – the problem is surely more widespread.

Impact on Drinking Water

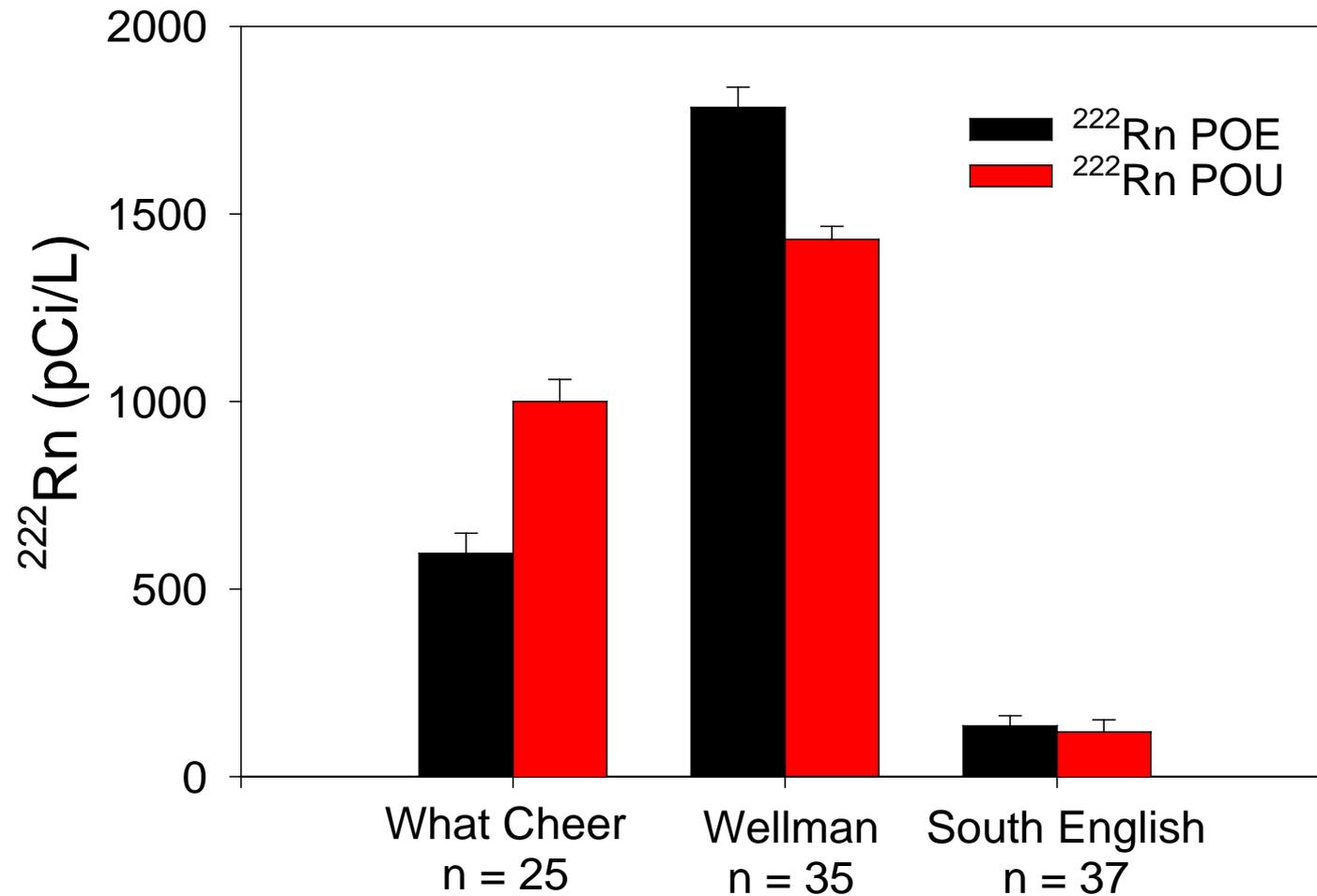
University of Iowa Studies (Valentine & Stearns 1994, Fisher et al. 1998, 2000)

- Studies have shown that buildup of radium-bearing scale or adsorption of radium onto corrosion products inside water distribution pipelines can act as a source of Rn-222 generation.
- This can result in the unusual circumstance of having more radon appear at points along a water distribution pipeline than actually entered the system from a natural source.
- Further inspection on the old pipelines showed that there were some Fe-based scale deposits that contained significant concentrations (about 270 pCi/g) of Ra-226.

Rn Release from Pipe Scale

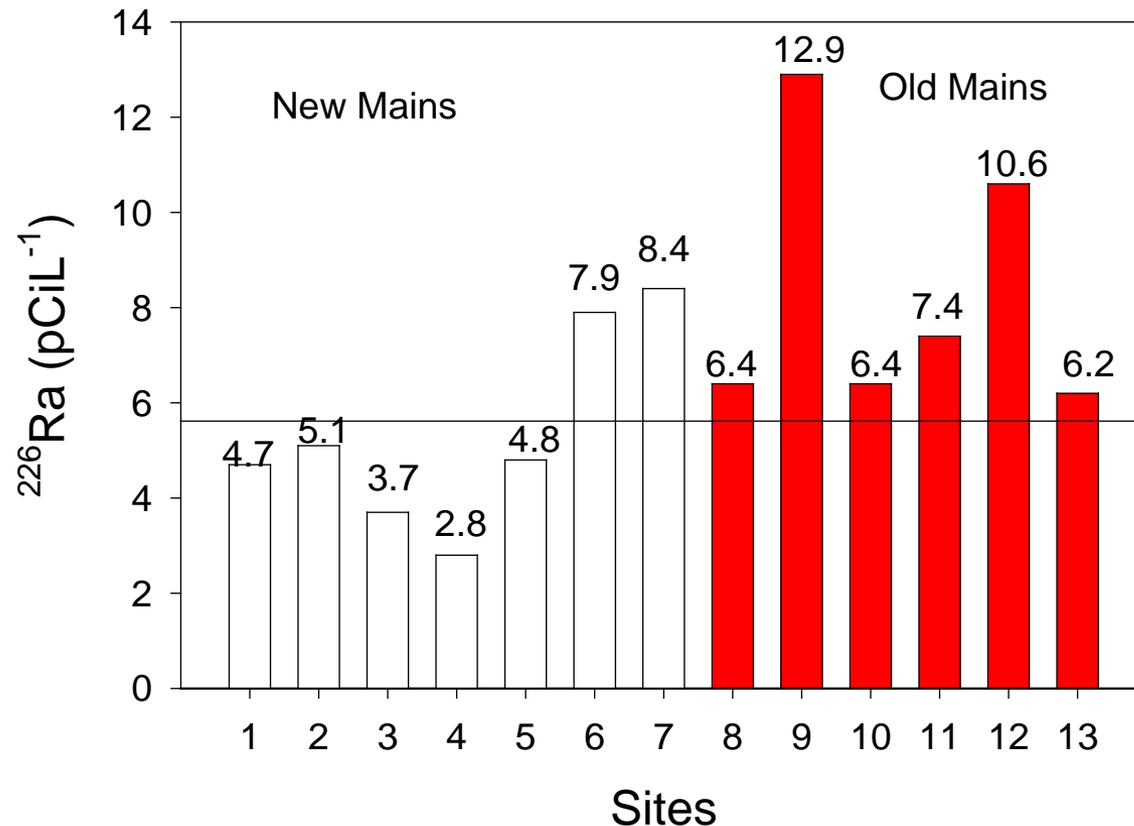


^{222}Rn in Iowa



Fisher et al. (1998)

Ra in Drinking Water



^{226}Ra concentrations from residences connected to new and old water mains, What Cheer, Iowa (pop. 762). The average POE ^{226}Ra concentration = 3.8 pCi/L.

Impact on Energy Industry (USGS 1999)

- Groundwater containing naturally occurring radioactive materials (NORM) coexists with deposits of oil and can have unusually high concentrations of dissolved constituents that build up during prolonged periods of water/rock contact.
- Many oil-field waters are particularly rich in chloride, and this enhances the solubility of other elements such as radium.
- Some of this saline, radium-bearing water, called “produced water,” is unavoidably brought to the earth’s surface with oil and must be separated from the coexisting crude oil and then disposed.
- The concentration of Ra-226 in the “produced water” has been measured to be about several thousand pCi/L, but concentrations above 10,000 pCi/L have been reported in the U.S.
- “Produced water” also contains dissolved Ra-228, which is typically one half to twice the concentration of Ra-226.
- Pipes and tanks that handle large volumes of “produced water” can become coated with scale, typically a mixture of carbonate and sulfate minerals. One of these sulfates minerals is barite (barium sulfate), which is known to incorporate Ra-226 in its structure.

Impact on Energy Industry (Cont.)

- Radium accumulation in oil-field equipment in the U.S. first became apparent in the 1980's when scrap metal dealers began to routinely detect unacceptable levels of radioactivity in shipments of oil-field pipes.
- Pipes, casings, fittings, and tanks that have an extended history of contact with "produced water" are more likely to contain radioactive deposits.
- Results of a 1989 American Petroleum Institute study indicated that gamma-ray radiation levels at the exterior surfaces of oil-field equipment exceeded natural background radiation levels at 42% of the sites.
- The maximum radium concentration in most reported oil-field scale from the U.S. is several thousand, although very small quantities of scale have been reported with as much as 400,000 pCi/g of radium. For comparison, most natural soils and rocks contain approximately 0.5-5 pCi/g of total radium.

Radioactive Scale Deposits inside an Oil-field Pipe

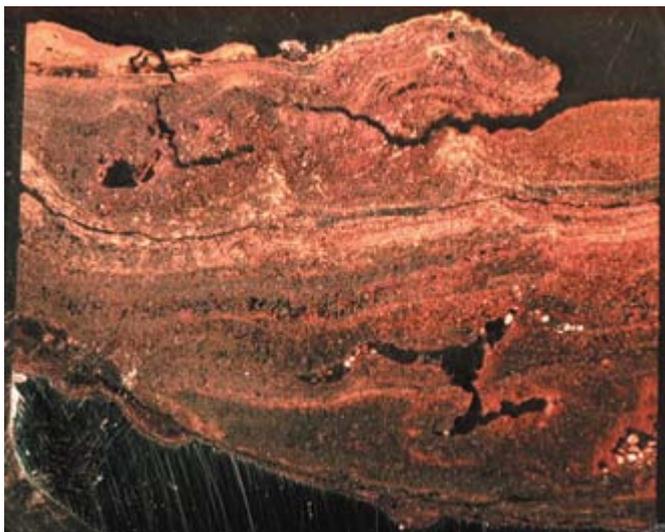


Figure A

Figure A shows radioactive scale deposits inside an oil-field pipe. Figure B shows the distribution of alpha-particle-emitting radium and radium decay products in the same sample. Brighter regions on the alpha emission image indicate areas of scale with higher concentrations of radioactive elements (USGS 1999).

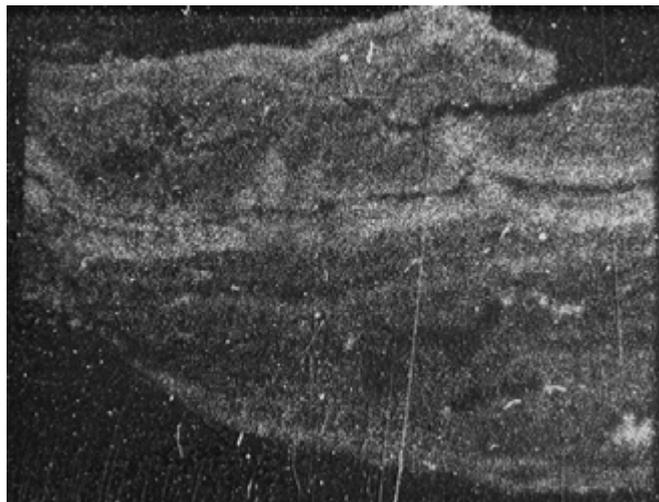


Figure B

Impact on Energy Industry (Cont.)

- No Federal regulations currently exist that specifically address the handling and disposal of oil-field NORM wastes. Only a few states, such as Texas, Louisiana, New Mexico, and Mississippi, have enacted specific NORM regulations.
- Standards for cleanup of radium-contaminated soils that typically appear in enacted or proposed NORM regulations call for an average concentration of less than 5 pCi/g in the upper 15 cm of soil and an average of less than 15 pCi/g in deeper increments of 15 cm. Some states allow an average of as much as 30 pCi/g of radium in the upper 15 cm of soil.

Health Effects

- Because Ra is present at low levels in the natural environment, everyone has some minor exposure to it.
- Individuals may be exposed to higher levels of radium if they live in areas where there is an elevated level of Ra in surrounding rock and soil. Private well water in such areas can also be a source of radium.
- People can be exposed to Ra if it is released into the air from the burning of coal or other fuels.
- Certain occupations can also lead to high exposures to radium, such as working in a uranium mine or a plant that processes ores.
- Phosphate rocks typically contain relatively high levels of U and Ra and can be a potential source of exposure where phosphate is mined.



Coal factory, Qinghai, China



Open-pit phosphate mine

Health Effects (Cont.)

- In some parts of the U.S., former Ra processing plants exist that were highly contaminated with Ra. However, most of these have been cleaned up and no longer pose a serious health threat.
- Radium is a radiation source in some industrial radiography devices to inspect for flaws in metal parts.
- Alpha radiation is only a concern if radium is taken into the body through inhalation or ingestion. Gamma radiation can expose individuals at a distance.



EPA removes radium-contaminated soil from a neighborhood in Essex County, NJ

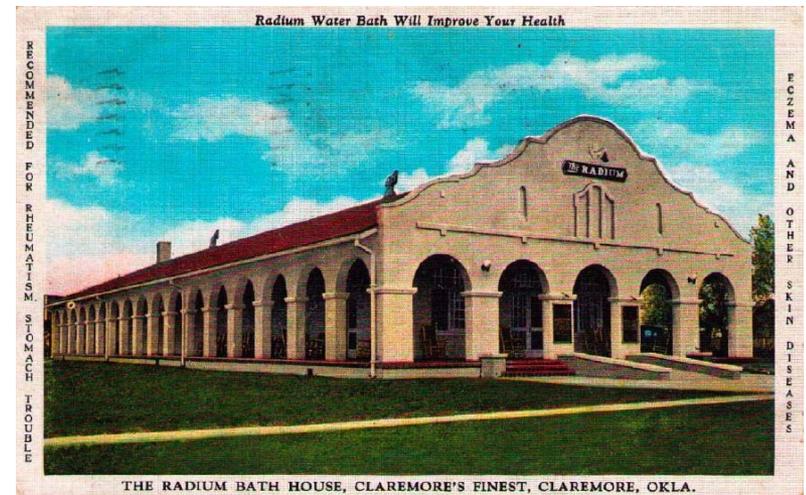
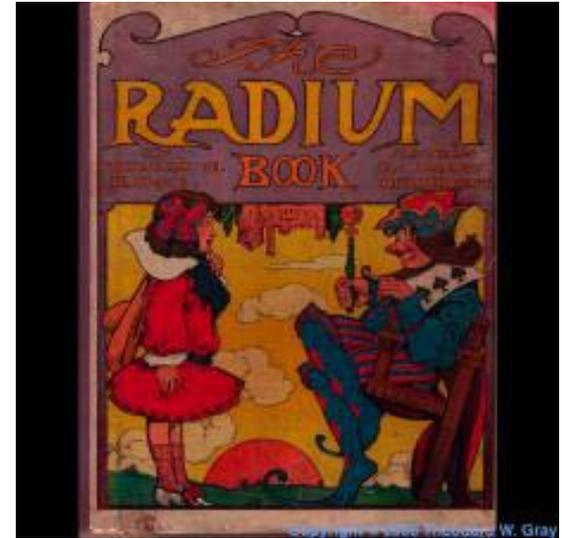
In 2002, \$3 million was allocated for cleanup operations. To date, funding for the cleanup has totaled \$103 million.

More than 240 properties have been identified so far as having radium-contaminated soil due to operations at the former radium-processing facility; more than 123,000 tons of contaminated soil have been removed to date, and property investigations are ongoing.

<http://www.epa.gov/superfund/accomp/success/usradium.htm>

Health Effects (Cont.)

- In the early 1900's, when it was newly discovered, no one knew the dangers of radium.
- People were fascinated with its mysterious properties, especially the luminescence produced when mixed with phosphorous compounds.
- Industries sprang up to manufacture hundreds of consumer products containing radium.
- Advertisements proclaimed that radium had special powers and unique curing effects in such products such as hair tonic, toothpaste, chocolates, and ointments.



Radium bathhouse postcard

T. W. Gray,

<http://periodictable.com/Items/088.24/index.html>

The Bungalow Hotel and Bath House was located in Claremore, OK, well known as the home of Will Rogers and just as well known for its radioactive waters. The water was promoted as being radioactive and a cure for a wide variety of ailments. The water jug was an advertising gimmick that was probably sold in the hotel gift shop. The hotel kept one of these jugs in each of the guest rooms and refilled them daily. Today the bath houses are all closed and the area has fallen into disrepair.



Bungalow Hotel and Bath House, Claremore, Okla.



Health Effects (Cont.)

- Glow-in-the-dark watch and clock faces were immensely popular.
- Factory workers manufacturing these types of commodities were directly affected. Some worked for the United States Radium Corporation applying radium-containing fluorescent paint to the numbers and hands on watch faces and military instrument panels.
- Because the work required great detail, workers were instructed to “point” the small brush tip with their lips, tongues, and teeth, thus ingesting a small amount of radium every time. Each person would repeat this hundreds of times a day and as a result, consumed large amounts of Ra-226 and Ra-228.

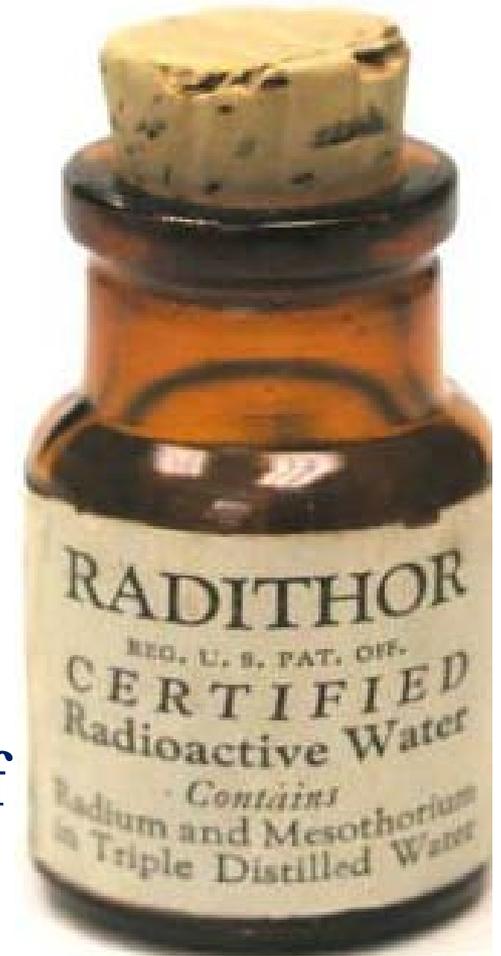


Produced by the Radium Ore Revigator Co., San Francisco, CA. 9-inch diameter base and 12 inches high. Hundreds of thousands were sold between 1922 and the mid-1930s.

Radithor

“Perpetual Sunshine”
“A Cure for the Living Dead”

- Bailey Radium Laboratories, East Orange, NJ
- Every ½-oz. bottle guaranteed to contain at least 1 microcurie each of Radium-226 and Radium-228



Eben M. Byers (1880-1932)

- Chairman of A. M. Byers Co.
- National Amateur Golf Champion – 1906



- Was “prescribed” Radithor for an arm injury, continued drinking 3 bottles a day for 2 years
- Following his death, the *Wall Street Journal* ran the headline: “The Radium Water Worked Fine Until His Jaw Came Off”

Health Effects (Cont.)

- About 80% of the radium taken in by ingestion promptly leaves the body in feces. The remaining 20% enters the bloodstream and is carried to all parts of the body.
- Inhaled radium can remain in the lungs for several months, then gradually enters the bloodstream and is carried throughout the body.
- The metabolic behavior of Ra in the body is similar to that of Ca; therefore, an appreciable fraction is preferentially deposited in bones and teeth. The bones are then exposed to tissue-damaging α and β radiation.
- Tissue damage from continuous exposure may cause malignancies. Risk increases with increased exposure.
- The cancer risk from Ra-224 is less than that from Ra-226 and Ra-228 because of its short half-life, limiting its radiation dose to the bone. However, much of the Ra-224 decays on the bone surface, where it may have enhanced effectiveness.
- The amount of radium in bone decreases with time from the exposure, but its release from bone is slow, so a portion of inhaled and ingested radium will remain in the bones throughout a person's lifetime.

Health Effects (Cont.)

- The majority of epidemiological data on the health effects of Ra-226 and Ra-228 in humans comes from the studies of radium dial painters, radium chemists, the technicians exposed through medical procedures or other luminized objects.
- These studies, as well as experimental studies on animals, indicate that chronic exposure to inhaled or digested radium can induce diseases such as lymphoma, bone sarcomas, and the diseases that affect the formation of blood, such as leukemia and aplastic anemia.
- These effects usually take years to develop. The minimum latency period is 7 years after the first exposure, but tumors can continue to appear throughout an exposed individual's lifetime.
- External exposure to radium's gamma radiation increases the risk of cancer to varying degrees in all tissues and organs. However, the greatest health risk from radium is from exposure to its radioactive decay product, Rn-222. It is common in many soils and can collect in homes and other buildings.

Health Effects (Cont.)

- In estimating the health effects from radionuclides, federal and state regulatory agencies use the linear, non-threshold model, which assumes that any exposure to ionization radiation has a potential to produce deleterious effects on human health, and the magnitude of the effects are directly proportional to the exposure levels.
- As such, the extent of such harm can be estimated by extrapolating effects on human health that have been observed at higher doses to those likely to be encountered from environmental sources of radiation.
- Regulatory agencies recognize the inherent uncertainties that exist in estimating the health impact at low levels of exposure and exposure rates expected to be present in the environment.
- They also recognize that, at these levels, the actual health impact from ingested radionuclides will be difficult, if not impossible, to distinguish from natural disease incidences, even using very large epidemiological studies employing sophisticated statistical analyses.

Morbidity (Cancer Incidence) Risks Associated with Radium in Drinking Water (Using Federal Guidance Report #13) (NJDEP 2001)

- $\text{Risk} = \text{AC} \times \text{RC} \times \text{TWI}$

Where:

Risk = Lifetime cancer risk corresponding to AC (unitless)

AC = Activity Concentration (pCi/L)

RC = Risk coefficient from Federal Guidance Report No. 13

TWI = Total water intake (2 liter/day x 365 d/y x 70 y)

Radium Isotope	Activity Concentration (pCi/L)	Risk
^{224}Ra	1	8.51×10^{-6}
^{226}Ra	1	1.96×10^{-5}
^{228}Ra	1	5.31×10^{-5}

The USEPA has established a range of 1×10^{-4} to 1×10^{-6} as an acceptable cancer incidence risk.

Estimates of Total Dietary Intake (pCi/Day) of ^{226}Ra , ^{228}Ra Contributions from Different Foodstuff Categories (NCRP, 1987)

	Radium-226			Radium-228	
	New York	San Francisco	San Juan	New York	San Francisco
Cereal and grain products	0.57	0.38	0.13	0.43	0.38
Meat, fish, eggs	0.46	0.081	0.011	0.13	0.081
Milk and dairy products	0.13	0.054	0.019	0.054	0.11
Green vegetables, fruits	0.54	0.24	0.54	0.43	0.38
Root vegetables	0.054	0.027	---	0.11	0.081
Water ^{a,b}	0.032	0.046	0.019	---	---
Daily Total	1.8	0.78	0.72	1.2	1.0

^a Assuming 2 liters per day daily intake.

^b If the median concentration of ^{226}Ra + ^{228}Ra in the Kirkwood-Cohansey aquifer of 3.85 pCi/L is used, the intake of radium in water would be 7.7 pCi/day.

References

- Annual Book of ASTM, American Society for Testing and Materials, Conshohocken, PA, USA.
- M.F. Arndt and L. E. West, “An Experimental Analysis of the Contribution of Ra-224 and Ra-226 and Progeny to the Gross Alpha-Particle Activity of Water Samples,” *Health Physics* 94(5), 459 (2008).
- W. C. Burnett, G. Kim, and D. Lane-Smith, *Jour. Radioanal. Nucl. Chem.*, 249, 167 (2001).
- W. C. Burnett and H. Dulaiova, *Jour. Environ. Radioact.*, 69, 21 (2003).
- W. C. Burnett, N. Dimova, H. Dulaiova, D. Lane-Smith, B. Parsa, and Z. Szabo, “Measuring Thoron (^{220}Rn) in Natural Waters,” chapter in “Environmental Radiochemical Analysis III,” (ed. P. Warwick) Royal Society of Chemistry, RSC Publication, Cambridge, 24-37, 2007.
- H. Dulaiova, R. Peterson, W.C. Burnett, and D. Lane-Smith, *Jour. Radioanal. Nucl. Chem.*, 263(2), 361 (2005).
- R. W. Field, E. L. Fisher, and R. L. Valentine, “Radium-Bearing Pipe Scale Deposits: Implications for National Waterborne Radon Sampling Methods,” *Ameri. Jour. Public Health*, 85(4), 567 (1995).
- E. L. Fisher, L. J. Laurence, J. Ledolter, D. J. Steck, and R. W. Field, “Temporal and Spatial Variation of Waterborne Point-of-Use Rn-222 in Three Water Distribution Systems,” *Health Physics* 74(2) 242 (1998).
- E. L. Fisher, L.J. Fuortes, R.L. Valentine, M. Mehrhoff, R.W. Field, *Environ. Internat.*, 26, 69 (2000).
- K. Guebuem, W. C. Burnett, H. Dulaiova, P. W. Swarzenski, and W. S. Moore, Measurement of Ra-224 and Ra-226 Activities in Natural Waters Using a Radon-in-Air Monitor, *Environ. Sci. Technol.* 35, 4680 (2001).
- C. T. Hess, J. Michel, T. R. Horton, H. M. Prichard, and W. A. Coniglio, “The Occurrence of Radioactivity in Public water Supplies in the United States,” *Health Physics* 48:553-586 (1985).
- B. Kahn, B. Rosson, and J. Cantrell, “Analysis of Ra-228 and Ra-226 in Public Water Supplies by Gamma-Ray Spectrometer,” *Health Physics* 59:125-131 (1990).
- D. McCurdy and R. Mellor, “Determination of Ra-224, Ra-226, and Ra-228 by Coincidence Spectrometry,” *Anal. Chem.* 53, 2212 (1981).
- W. Moore and R. Arnold, “Measurement of Ra-223 and Ra-224 in Coastal Waters Using a Delayed Coincidence Counter,” *Jour. Geophys. Res.* 101, 1321 (1996).
- National Council on Radiation Protection and Measurements, “Exposure of the Population in the United States and Canada from Natural Background Radiation,” Bethesda, MD, NCRP Report No. 94 (1987).
- NJAC. The New Jersey Private Well Testing Act Regulations, Trenton: New Jersey Register; NJR 3236-3255 (2002).
- New Jersey Department of Environmental Protection, “Report on Ra-224,” New Jersey Drinking Water Quality Institute, Health Effects Subcommittee, November (2001).

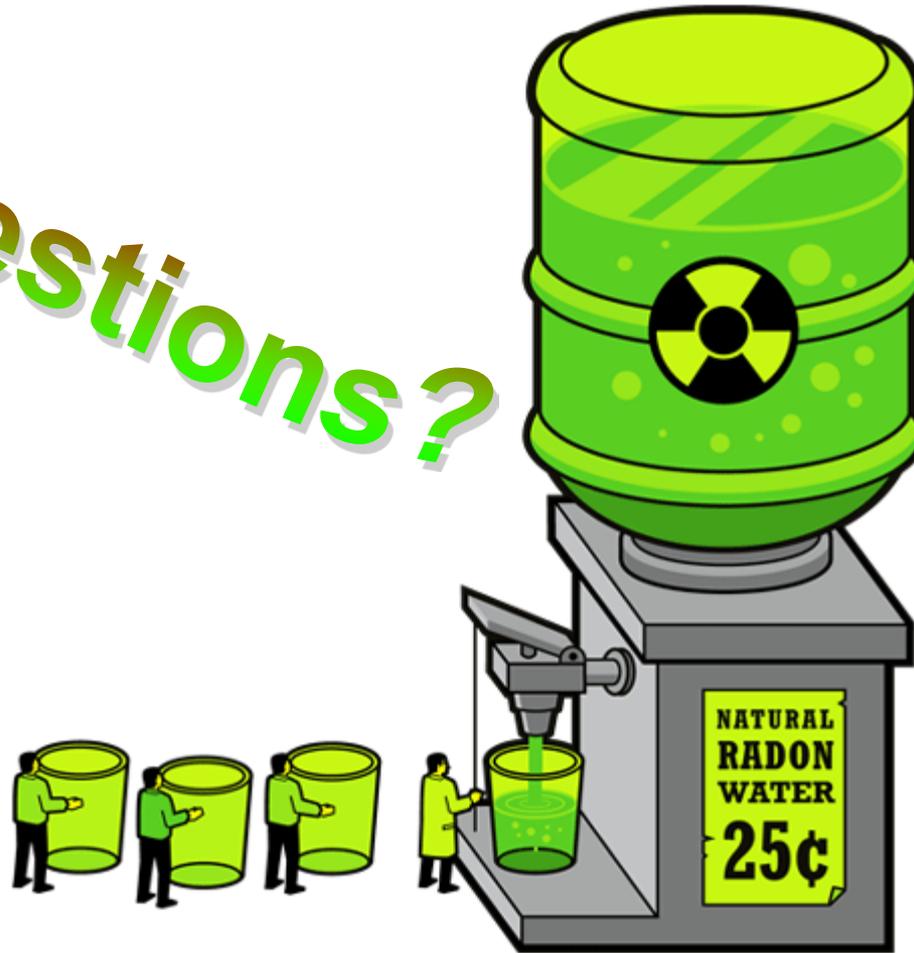
References (cont.)

- New York State Department of Health, "Determination of Ra-226 and Ra-228," Empire State Plaza, Albany, NY (Jan 1980, revised June 1982).
- B. Parsa and A. Hoffman, "Determination of Ra-228 in Drinking Water," *Journal of Radioanal. and Nucl. Chem.*, 158, 53 (1992).
- B. Parsa, "Contribution of Short-Lived Radionuclides to Alpha-Particle Radioactivity in Drinking Water and Their Impact on the Safe Drinking Water Act Regulations," *Journal of Radioactivity and Radiochemistry*, Vol. 9, No. 4, 41 (1998).
- B. Parsa, W.K. Nemeth, and R.N. Obed, "The Role of Radon Progenies in Influencing Gross Alpha-Particle Determination in Drinking Water," *Journal of Radioactivity and Radiochemistry*, Volume 11, No. 2, 11 (2000).
- B. Parsa, W.K. Nemeth, R.N. Obed, Z. Szabo, V.T. dePaul, and N. Stanley, "Investigation of Factors Contributing to the Presence of Unsupported Lead-212 in Acidic Drinking Water Supplies, Southern New Jersey," Presented at the 46th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry, Seattle, WA, November 12-17 (2000).
- B. Parsa, R. N. Obed, W. K. Nemeth, and G. P. Suozzo, "Concurrent Determination of Ra-224, Ra-226, Ra-228, and Unsupported Pb-212 in a Single Analysis for Drinking Water and Wastewater: Dissolved and Suspended Fractions," *Health Physics*, Vol. 86, No. 2, 145-149 (2004).
- B. Parsa, R. N. Obed, W. K. Nemeth, and G. Suozzo, "Determination of Gross Alpha, 224Ra, 226Ra, and 228Ra Activities in Drinking Water Using A Single Sample Preparation Procedure," *Health Physics*, Vol. 89, No. 6, 660-666 (2005).
- B. Parsa, J. B. Henitz, and J. A. Carter, "Rapid Screening and Analysis of Alpha- and Gamma-Emitting Radionuclides in Liquids Using a Single Sample Preparation Procedure," *Journal of Health Physics* Vol. 100, No. 2, 152-159 (2011).
- D. Percival and D. B. Martin, "Sequential Determination of Radium-226, Radium-228, Actinium-227, and Thorium Isotopes in Environmental and Process Waste Samples," *Anal. Chem.* 46(12), 1742 (1974).
- Purkl, Stefan, Dissertation: Entwicklung und Anwendung neuer analytischer Methoden zurschnellen Bestimmung von kurzlebigen Radiumisotopen und Radon im Grundwasserbeeinflussten Milieu der Ostsee; Chapter 2, Figure 3; Christian-Albrechts Universitaet, Kiel, Germany, 2003.
- C. W. Sill, K. W. Puphal, and F. D. Hindman, "Simultaneous Determination of Alpha-Emitting Nuclides of Radium Through Californium in Soil," *Anal. Chem.*, 46, 1725 (1974).
- Z. Szabo, V. T. DePaul, T. Kraemer, and B. Parsa, "Occurrence of Radium-224, Ra-226, and Radium-228 in Water of the Unconfined Kirkwood-Cohansey Aquifer System, Southern New Jersey," U. S. Geological Survey Scientific Investigations Report 2004-5224, 92 p (2005).

References (cont.)

- Z. Szabo, E. Jacobsen, T.F. Kraemer, and B. Parsa, “Environmental Fate of Radium in Ion-Exchange Backwash Waste Stream and Septic-tank Sludge and Liquids, Southern New Jersey,” 18th World Soil Science Congress, Philadelphia, PA, July 2006.
- Z. Szabo, E. Jacobson, T.F. Kraemer, and B. Parsa, “Concentrations and Environmental Fate of Ra in Cation-Exchange Regeneration Brine Waste Disposed to Septic Tanks and Accumulation in Sludge, New Jersey Coastal Plain, U.S.A.,” *Journal of Environmental Radioactivity*, Vol. 99, 947-965 (2008).
- Z. Szabo, E. Jacobsen, T. F. Kraemer, and B. Parsa, “Environmental Fate of Ra in Cation-Exchange Regeneration Brine Waste Disposed to Septic Tanks, New Jersey Coastal Plain, USA: Migration to the Water Table,” *Journal of Environmental Radioactivity* , Vol. 101, Issue 1, 33-44 (2010).
- *Standard Methods for Analysis of Water and Wastewater: American Public Health Association, Washington, D.C., 22nd edition, Method 7500-Ra (2012).*
- United States Geological Survey, ”Naturally Occurring Radioactive Materials (NORM) in Produced Water and Oil-Field Equipment – An Issue for the Energy Industry,” USGS Fact Sheet FS-142-99 (September 1999).
- United States Environmental Protection Agency, *Radiochemistry Procedures Manual*. Cincinnati, OH: EPA Office of Radiation Programs, EPA 520/5-84-006 (December 1987).
- United States Environmental Protection Agency, *Prescribed Procedures for Measurements of Radioactivity in Drinking Water*. Cincinnati, OH: EPA Environmental Monitoring and Support Laboratory; EPA 600/4-80-032 (1980).
- United States Environmental Protection Agency, *Cancer Risk Coefficients for Environmental Exposure to Radionuclides (Federal Guidance Report No.13)*; EPA 402-R-99-001 (1999).
- United States Environmental Protection Agency. *National Primary Drinking Water Regulations: Radionuclides; Final Rule*. Federal Register 65:76708-76753 (2000).
- United States Environmental Protection Agency, *National Primary Drinking Water Regulations: Radionuclides; Notice of Data Availability; Proposed Rule*. Federal Register 65:21576-21627 (2000).
- United States Environmental Protection Agency, *Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events*, Cincinnati, OH: National Air and Radiation Environmental Laboratory; EPA 402-R-10-001 (Feb 2010).

Questions?



Upcoming Environmental/Bioassay Radiochemistry Series

Data Validation and Verification – May 23, 2013

Traceability and Uncertainty – July 25, 2013

EPA Incident Response Guide and Rapid Methods Overview – TBD

Radiobioassay – TBD

Subsampling – TBD

For more information and to access recorded webinars, visit the NAMP website at
www.inl.gov/namp