



Optimization of Radioanalytical Methods for the Determination of Radium in Process Water Samples from the Oil & Gas Industry

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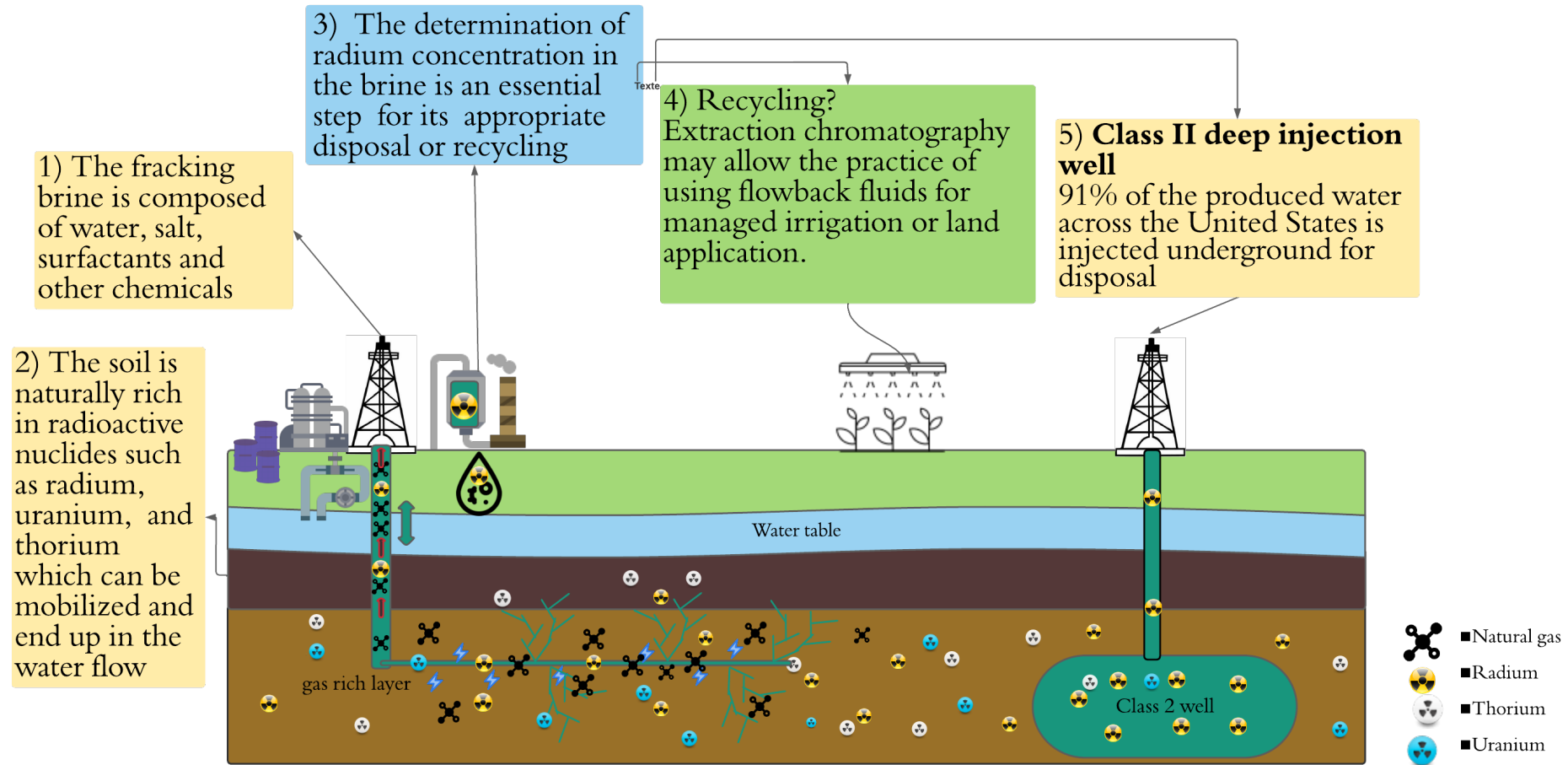
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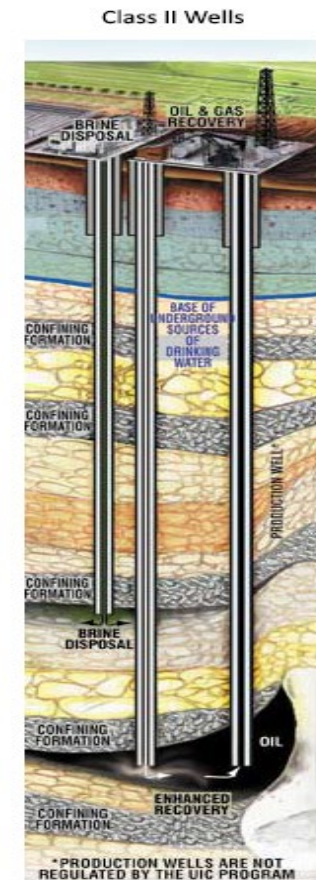
Triskem Workshop
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Hydraulic Fracturing



Hydraulic Fracturing

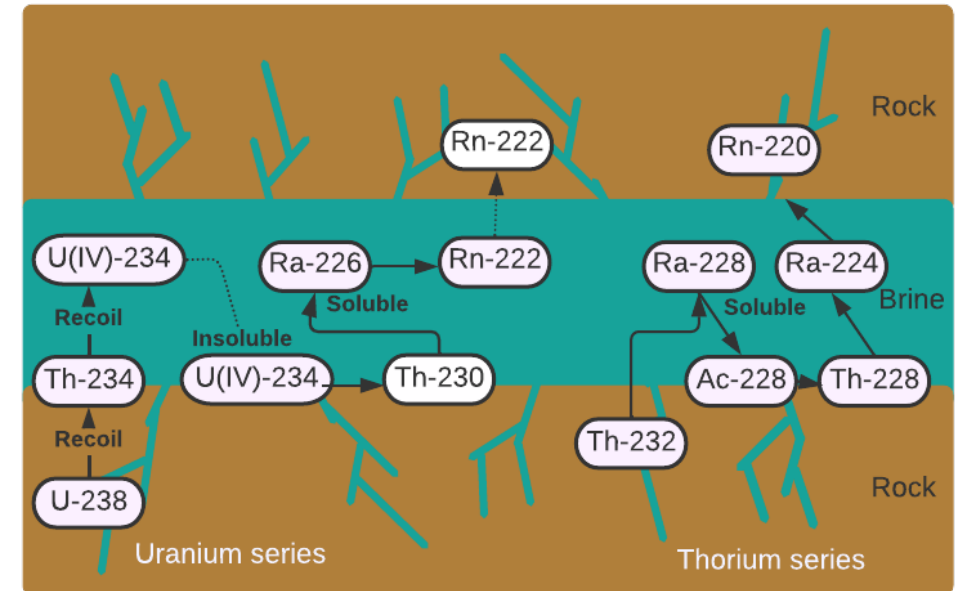
- More than 18 billion barrels of fracking wastewater containing NORM are generated annually.
- The radium concentration in these process fluids must be analyzed to provide appropriate wastewater management plans, complying with the state's laws.
- The radioactivity of the waste in enclosed systems is expected to increase in 100 years by a factor >8 .



Source: EPA, <https://www.epa.gov/uic/class-ii-oil-and-gas-related-injection-wells>,
Accessed May 5, 2022

What is the Issue with Radium?

- Selectively extracted into the brine during the extraction.
- Under geologic conditions, the insoluble alpha-emitting daughters are not preferentially extracted.
- Radium in the body follows a similar accumulation pathway as Ca^{2+} and is a primary concern due to its radiotoxicity.



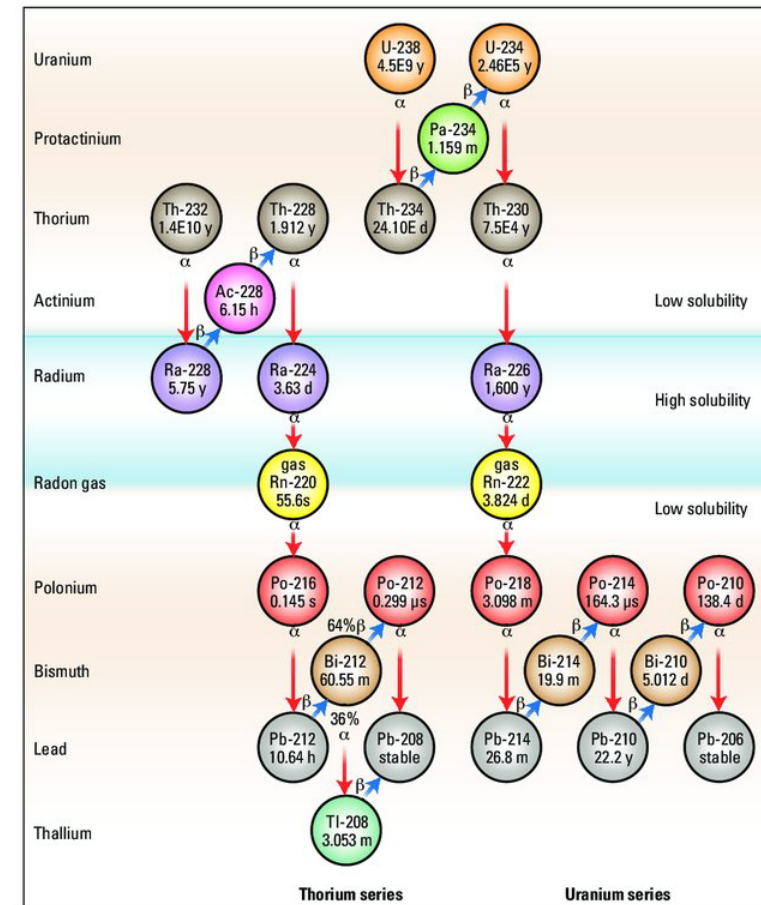
Environmental Stakes

- Inappropriate management of flowback and produced fluids before release can lead to Ra contamination.
- Continuous discharge of pre-treated water with a low radium concentration (0.2-1 Bq/L) lead to contamination of a stream in Pennsylvania.
- The accumulation of radium in the sediments lead to elevated ^{226}Ra and ^{228}Ra activities as high as 25,000 Bq/kg.



Radium

	Ra-226	Ra-228
Decay series	U-238	Th-232
Half-life (y)	1600	5.75
Alpha (MeV)	4.78 (93.84%) 4.60 (6.16%)	-
Beta (keV) mean energy	-	29.93
Gamma emitter	Yes (186.2)	No

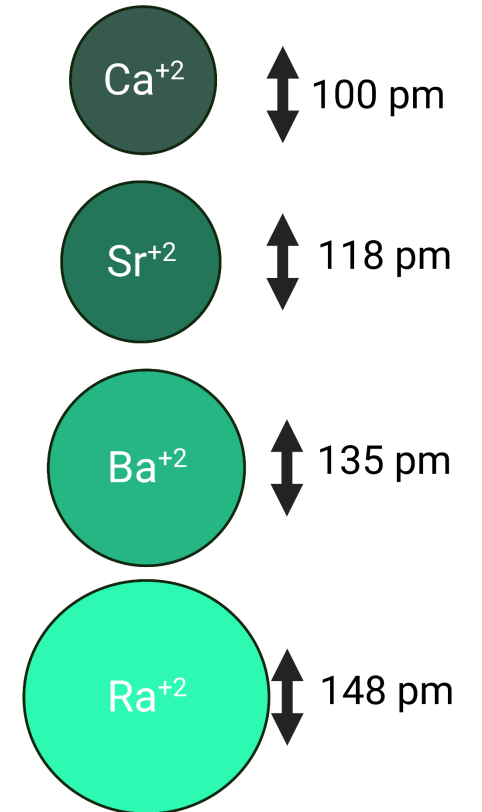


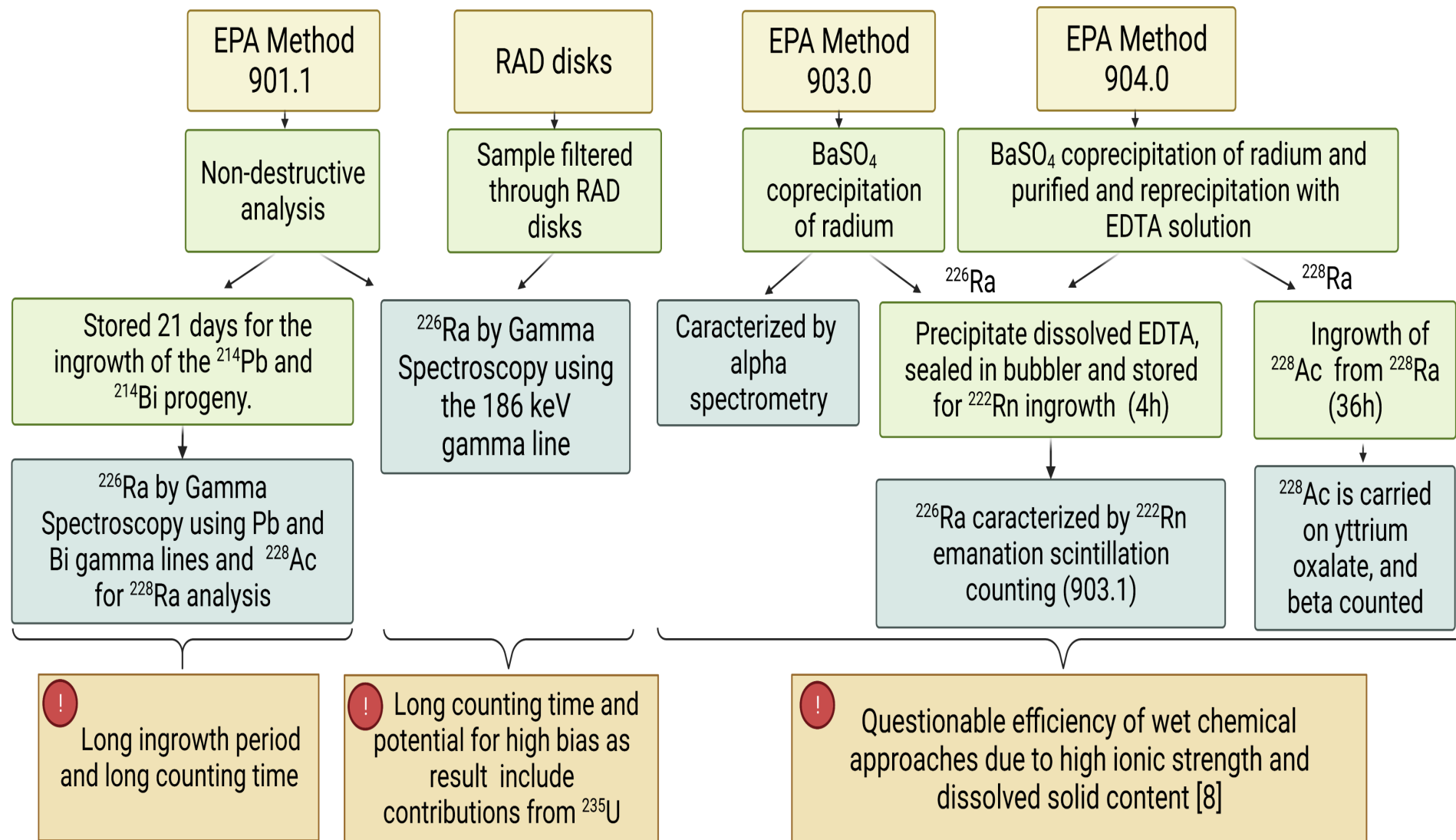
Source: Andrew W. et al. Understanding the radioactive ingrowth and decay of naturally occurring radioactive materials in the environment: An analysis of produced fluids from the Marcellus Shale, Environmental Health Perspectives, 2015, Vol. 123.



Alkaline Earth Metals

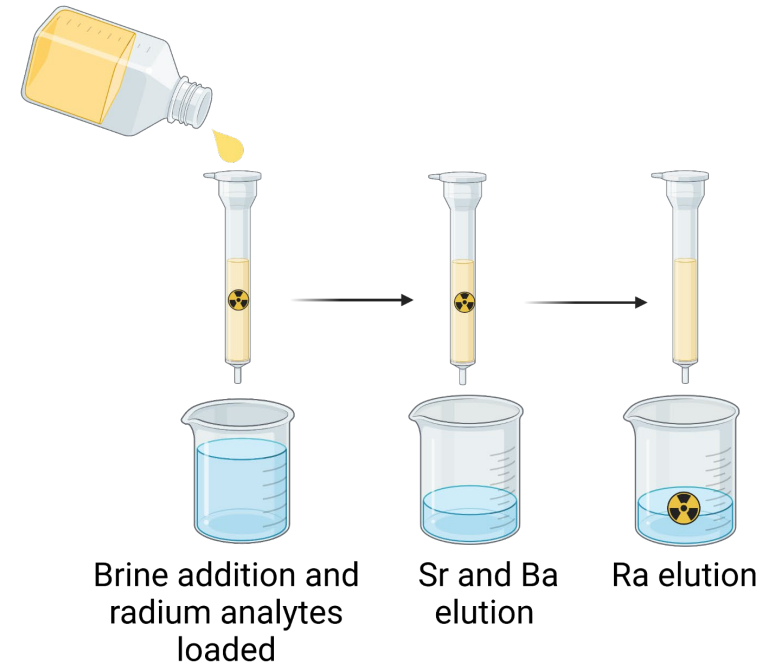
- Belong to the second group of the periodic table and have 2s orbital electrons in their outer shell.
- Occur as M^{2+} ions in aqueous solutions.
- No vacancy occurs in their outer shell, so they rarely form covalent bonds with organic compounds.
- Soluble in neutral and alkaline environments.
- Readily precipitate as chromate, carbonate, phosphate, or sulfate salts.



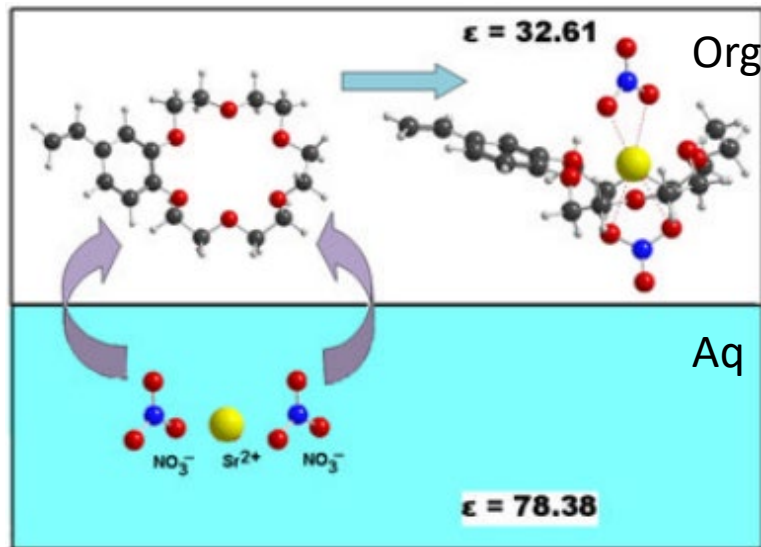


Exploring Alternate Resins for Ra Analysis

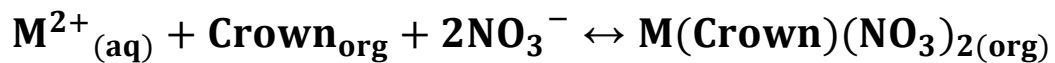
- Challenge:
Separating Ra from chemical homologs Sr and Ba.
- Goal:
Study uptake of all three elements on different extraction chromatographic resins at various nitric acid concentrations.



Why Crown Ethers Extractants?



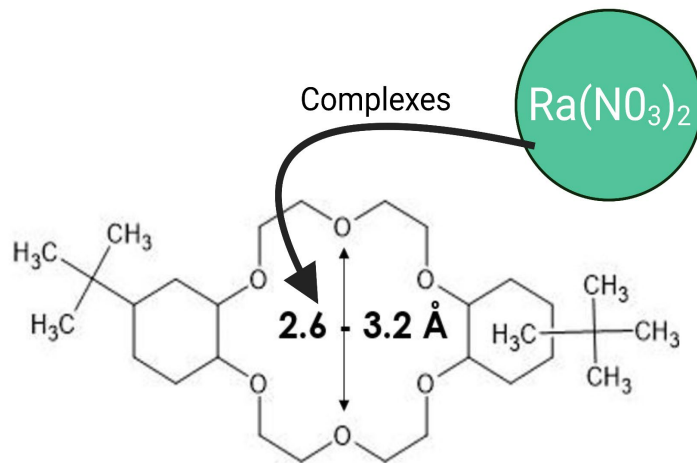
Source: Saprizal, H. Extraction of strontium (II) by crownether: Insights from density functional calculations, 2012, Indo. J. Chem., 12 (3), 207 – 216



- Crown ethers readily complex with alkaline earth metals.
- Successful separation shown in solvent extraction and extraction chromatography.
- Current separation factor for extraction chromatography is ~ 2
- Selectivity based primarily on the ionic radius-cavity size.

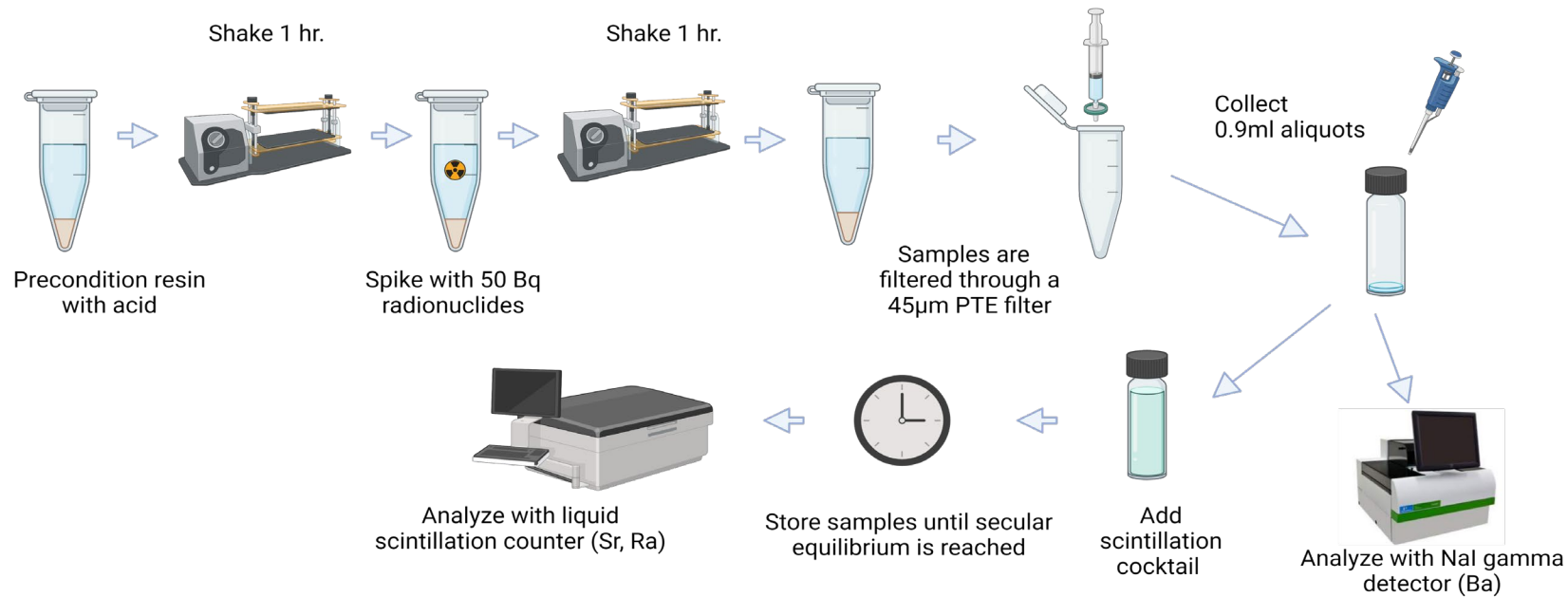
Crown Ether Based Extractants

- Five crown ether-based resins were studied.
- The effects of diluents and synergistic extractant systems were explored.



RESIN	EXTRACTANT	DILLUENT
Pb	Crown ether	Isodecanol
Sr	Crown ether	n-octanol
TK100	Crown ether/ HDEHP	-
TK101	Crown ether/ IL	-
TK		-

Batch Contact Technique



Weight distribution ratio for each sample was calculated with the following equation:

$$D_w = \frac{A_0 - A_s}{A_s} \cdot \frac{V_s}{M_r}$$

A_0 = Activity of the initial solution

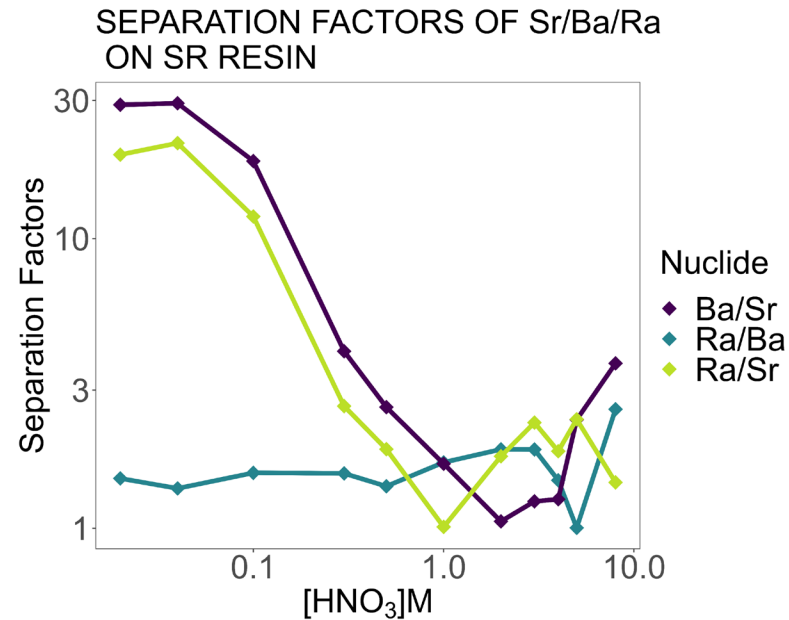
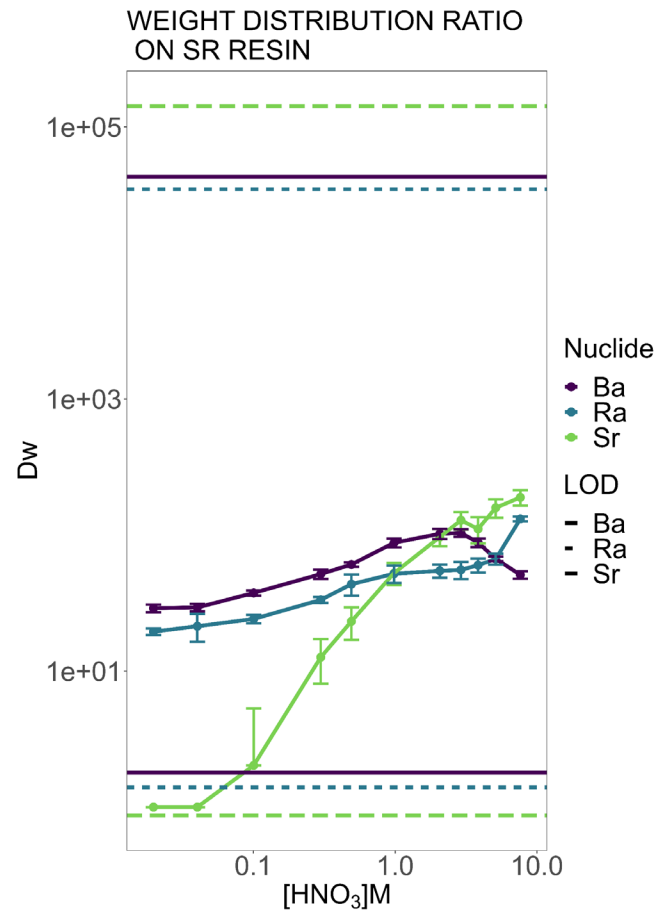
A_s = Activity of the aqueous solution

$A_0 - A_s$ = Activity adsorbed onto the resin

M_r = Weight of the resin (g)

V_s = Volume of aqueous solution (mL)

Results: SR Resin

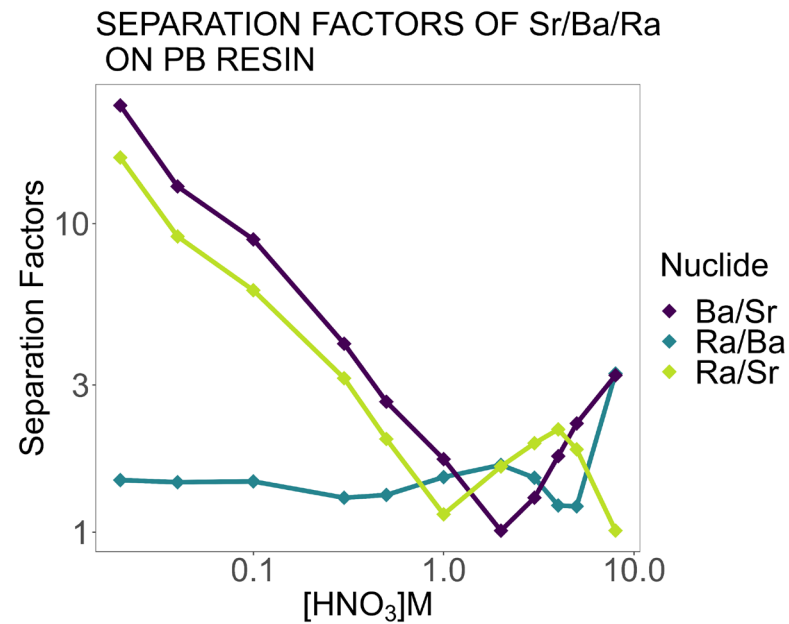
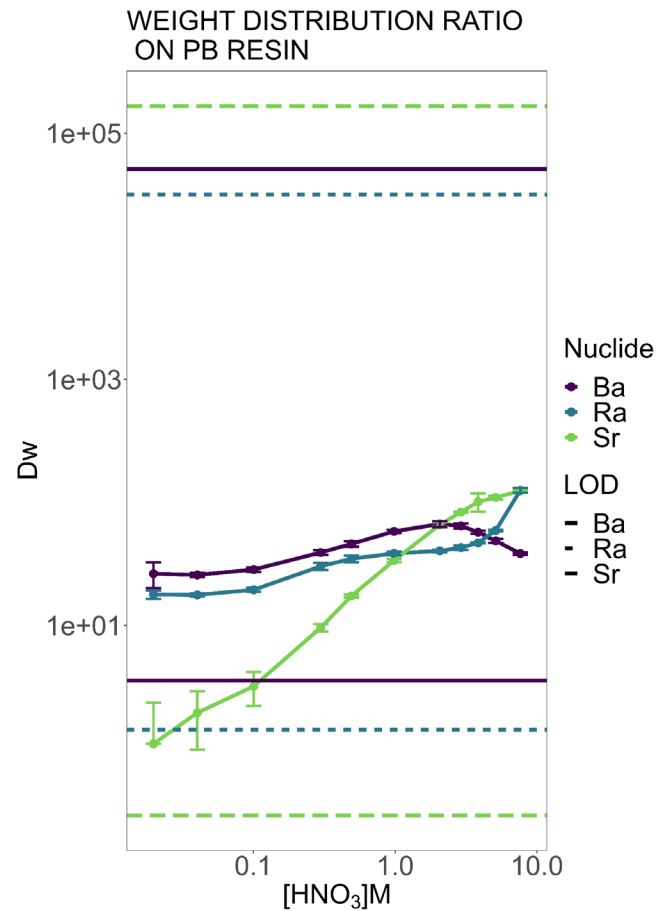


- Nearly identical Ra and Ba behavior
- Sr less retained at lower acid concentrations
- Sr is easily separated from Ra and Ba (SF > 19 at 0.02M HNO₃).

Source: Coupanec, M. Optimization and comparison of radioanalytical methods for the determination of radium and other alpha-emitting radionuclides in process water samples from the oil & gas industry, M.S. Thesis, Department of Environmental and Radiological Health Sciences, Colorado State University, 2022.



Results: PB Resin

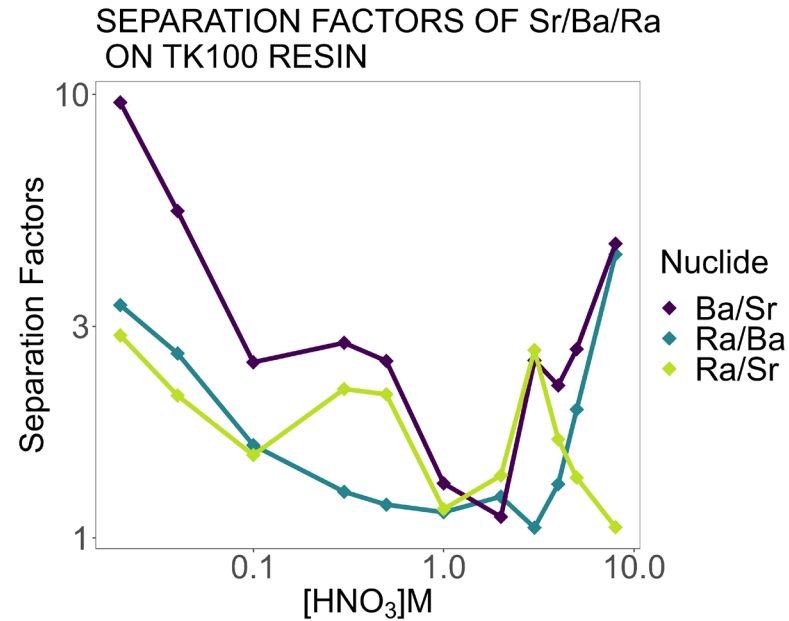
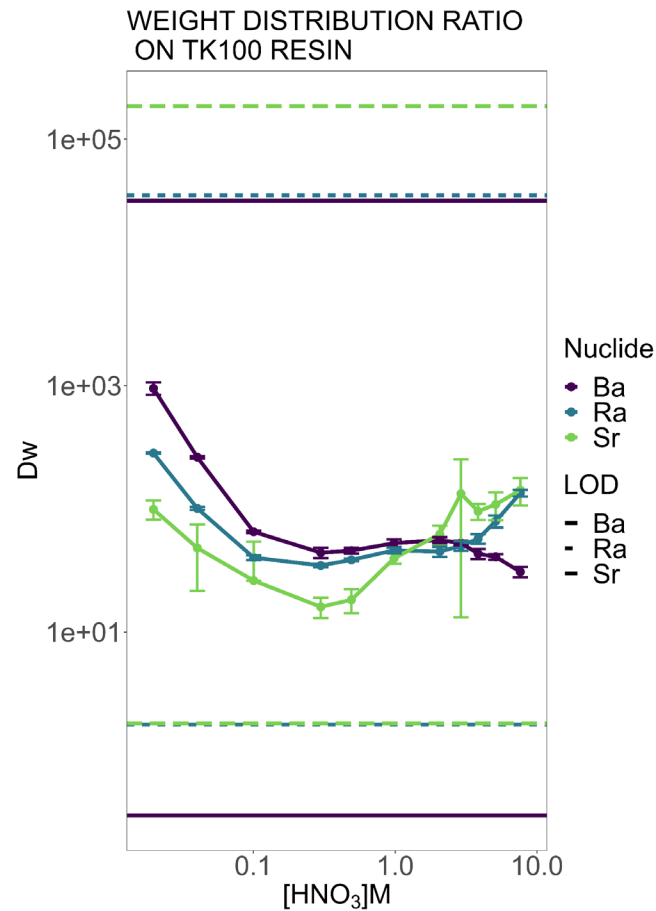


- Nearly identical Ra and Ba behavior
- Sr less retained at lower acid concentrations
- Sr is easily separated from Ra and Ba (SF > 24 at 0.02M HNO₃).

Source: Coupanec, M. Optimization and comparison of radioanalytical methods for the determination of radium and other alpha-emitting radionuclides in process water samples from the oil & gas industry, M.S. Thesis, Department of Environmental and Radiological Health Sciences, Colorado State University, 2022.



Results: TK100 Resin

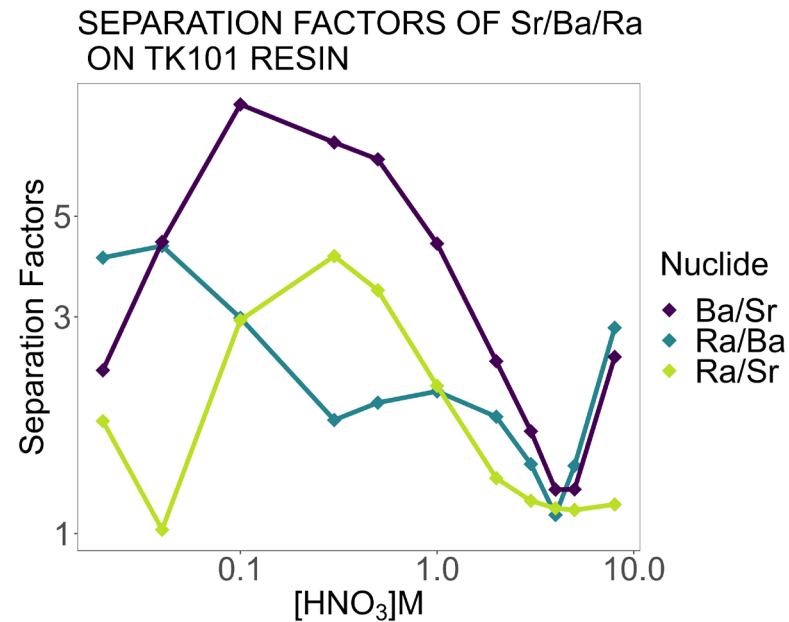
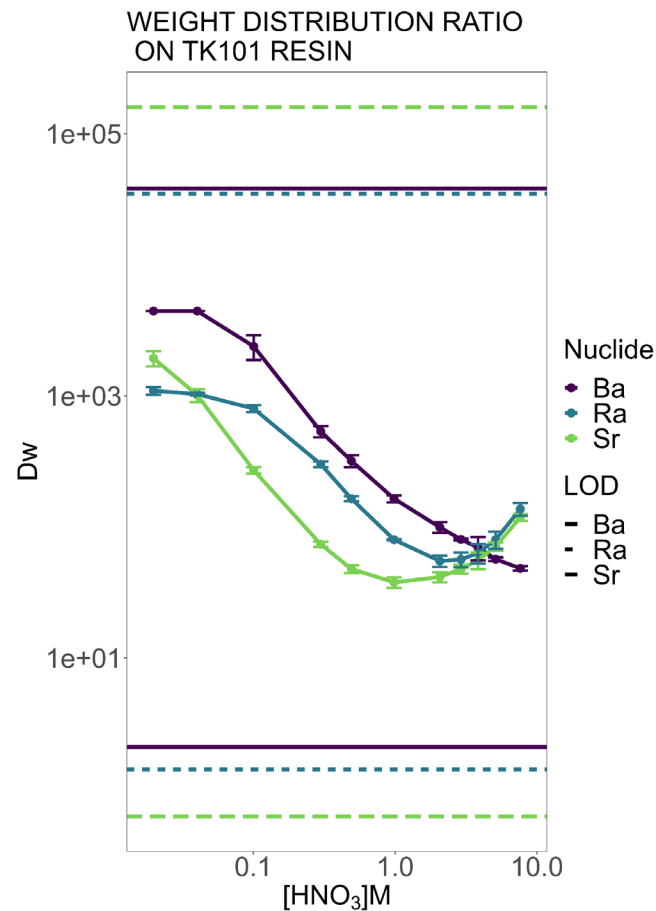


- Similar retention trend Ba>Ra>Sr at most acid concentrations
- Promising Ra/Ba separation potential (SF=4.3 at 8M HNO₃)

Source: Coupanec, M. Optimization and comparison of radioanalytical methods for the determination of radium and other alpha-emitting radionuclides in process water samples from the oil & gas industry, M.S. Thesis, Department of Environmental and Radiological Health Sciences, Colorado State University, 2022.



Results: TK101 Resin

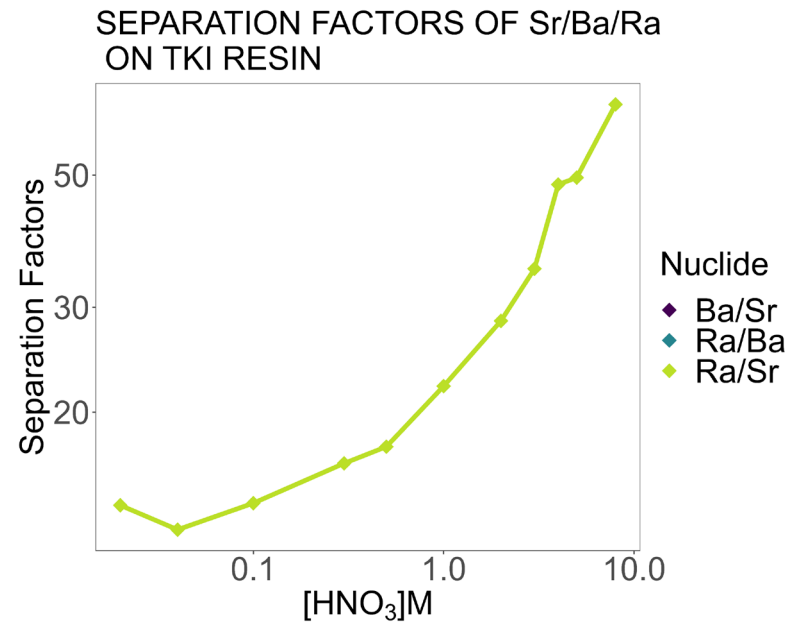
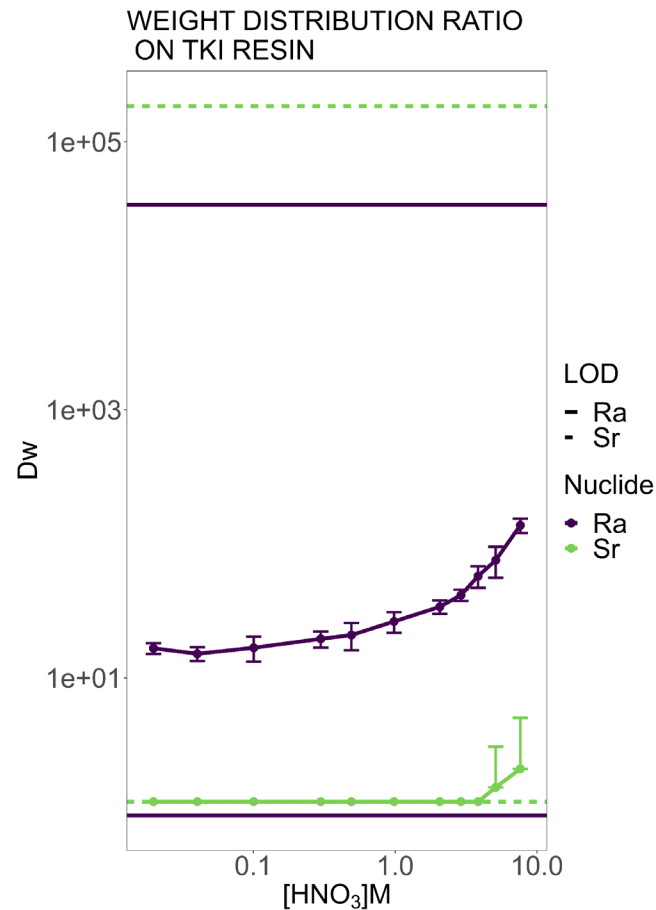


- Similar retention trend Ba>Ra>Sr at most acid concentrations
- Promising Ra/Ba separation potential (SF=4.3 at 0.04 M HNO₃)
- Twice the SF for Ra/Ba compared to SR resin

Source: Coupanec, M. Optimization and comparison of radioanalytical methods for the determination of radium and other alpha-emitting radionuclides in process water samples from the oil & gas industry, M.S. Thesis, Department of Environmental and Radiological Health Sciences, Colorado State University, 2022.



Results: TKI Resin



- No Sr retention until 5M HNO₃
- Best Ra/Sr separation (SF=73.4 at 3 M HNO₃)
- Further studies with Ba will indicate if the resin provides a better Ra/Ba separation.

Source: Coupanec, M. Optimization and comparison of radioanalytical methods for the determination of radium and other alpha-emitting radionuclides in process water samples from the oil & gas industry, M.S. Thesis, Department of Environmental and Radiological Health Sciences, Colorado State University, 2022.



Future Work

- Study preconditioning time, contact time, and temperature dependency.
- Perform dynamic column studies with simulated processed waters.
- Batch contact studies with additional resins developed by TrisKem International, LLC.

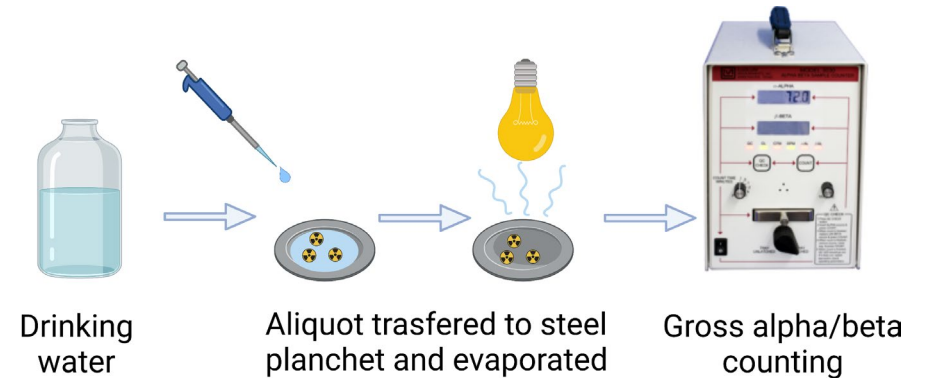


EPA Method 900

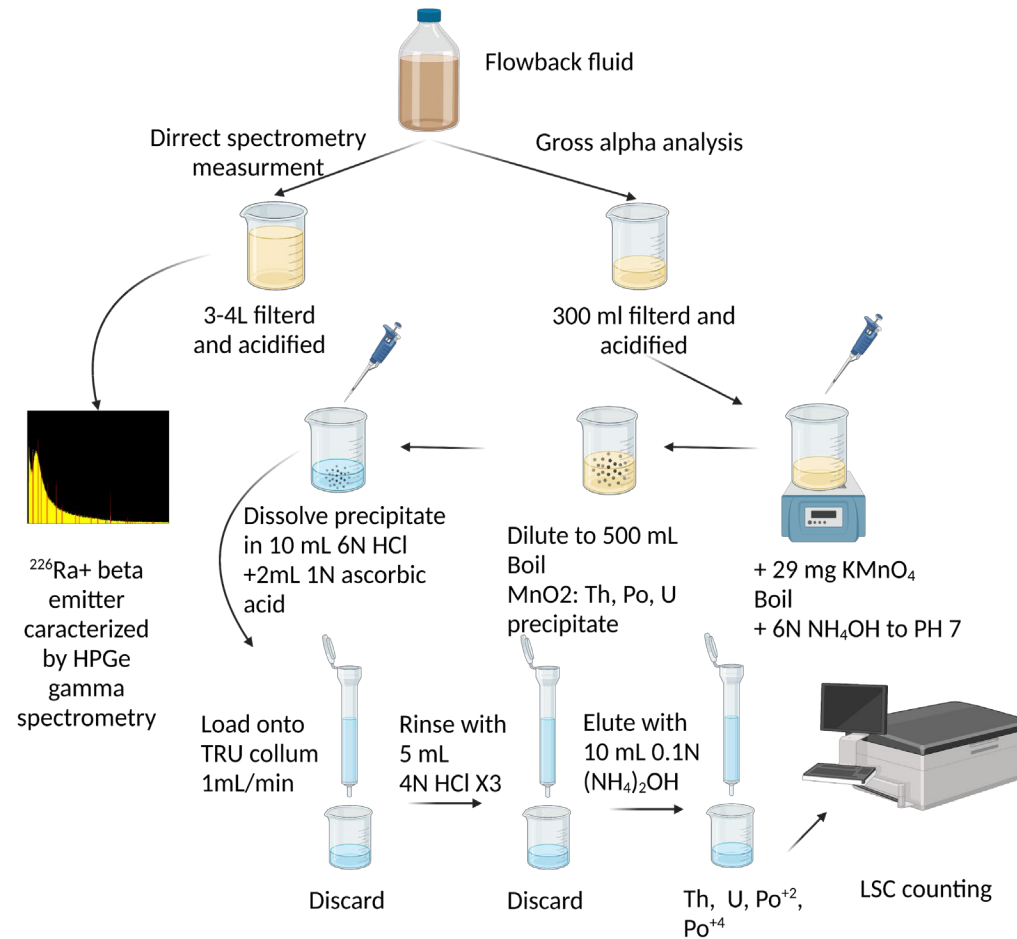
➤ Evaporation of the fluid followed by gas proportional counting.

➤ High dissolved solid content in flowback fluid interferes with the preparation of an ideal counting source.

➤ Self-absorption within the sample decreased the counting efficiency to less than 10% when 100 mg of solid remains on the planchet.



EPA Method for Flowback Water

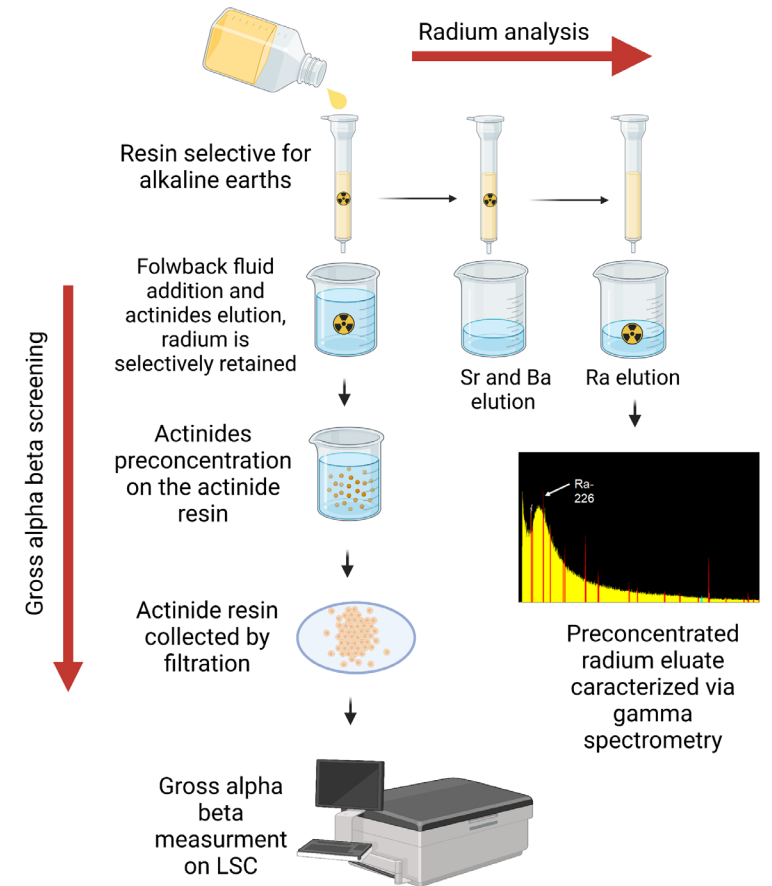


Source: EPA, Development of rapid radiochemical method for gross alpha and gross beta activity in flowback and produced water from hydraulic fracturing operations, July 2014, EPA/600/R-14/107



Just an Idea...

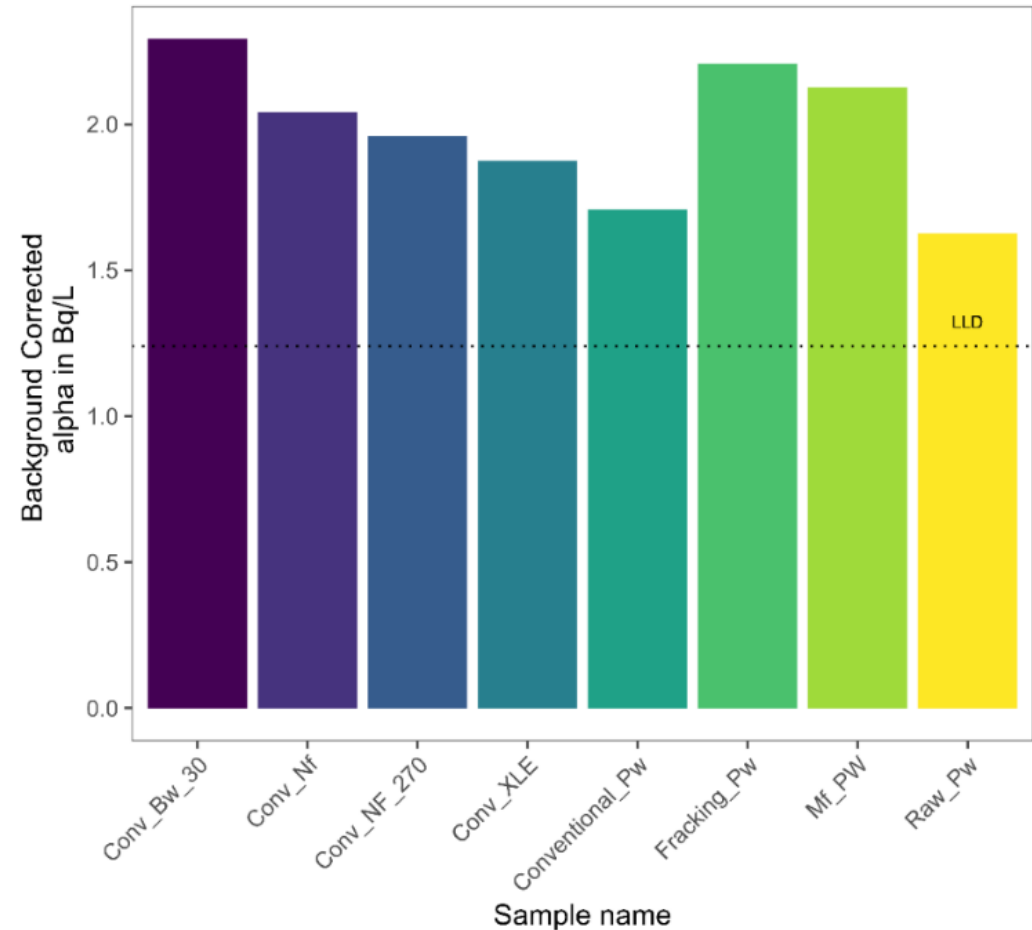
1. Preconcentrate Th and U onto Actinide[®] resin.
 - Collect actinides on resin and count via LSC.
 2. Measure the eluted Ra using HPGe.
 - Ra only weakly retained on Actinide[®] resin
- Provides route for complete Ra, Th, and U screening.



Results: Gross Alpha Activity

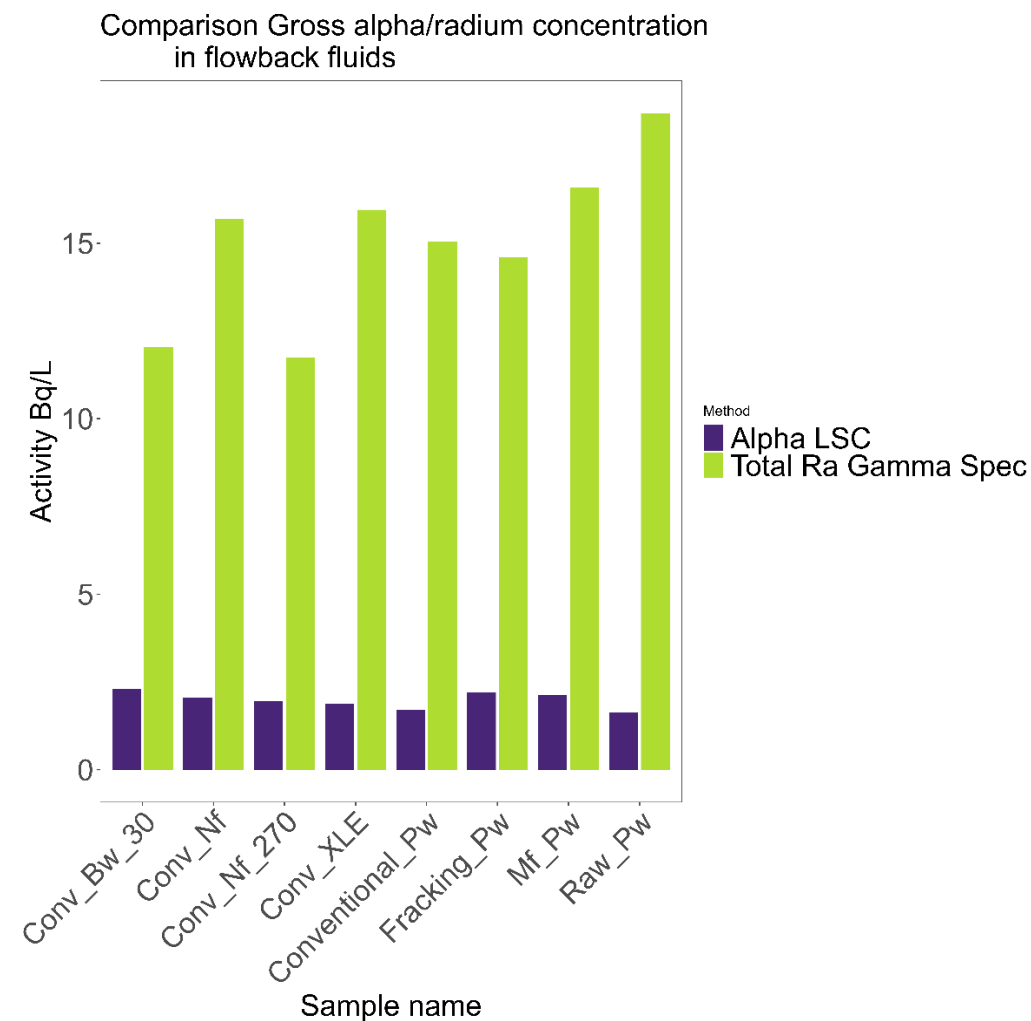
- Activity ranged from 1.6 to 2.3 Bq/L.
- The lower limit of detection achieved after 1 hour of counting.
- Liquid scintillation counting is an adequate means of detection for alpha screening in processed water.

Gross Alpha Measurement in Processed fluid
Using Extraction Chromatography



Results: Gross Alpha/Ra Comparison

- Samples analyzed via HPGe and gross alpha methods were compared.
- Significantly less activity was measured in the gross alpha method.
 - Gross alpha/Total Ra: 8.7-16.7%
- Low selectivity of resin for Ra evident.



Future Work

- Determine retention of Ra, Th, U, and Po on Actinide resin
 - Prepare simulated flowback water with known composition and activities of radionuclides.
 - Conduct batch contact studies with varying acid concentration.
- Investigation possible Ca and Fe interference that may decrease actinide retention on the resin.
 - Perform batch contact studies with varying concentrations of Ca and Fe.



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Program



Acknowledgements

