THESIS

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

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ABSTRACT

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

A major concern arising from hydraulic fracturing is the generation of a large volume of flowback water potentially containing various amounts of dissolved Naturally Occurring Radioactive Material (NORM). Up to four million gallons of water-based fluid is injected per well, of which 10–70% is subsequently recovered as flowback. Improving the separation and measurement of “Technologically Enhanced Naturally-Occurring Radioactive Material” (TENORM) is a priority in efficiently determining the amount of radionuclides present. An accurate assessment of radium concentration in flowback water is needed to understand potential environmental contamination from hydraulic fracturing sites and bodies of water affected by the mining industry. A significant scientific challenge in radium determination in flowback water is the presence of chemical analogues, calcium, barium, and strontium, in the flowback and produce water. Thus, the development of an accurate radium measurement and separation process is an essential step for appropriate disposal of the flowback water as regulated or non-regulated NORM-containing wastes. Non-destructive analysis of radium using direct gamma spectrometry measurements was performed on flowback water and provided accurate quantities. However, the long counting time necessary to achieve the detection limits renders the analysis impractical.

Several approaches to improving radium separation and measurement methods are explored in this work. Pre-conconcentration of radium with barium sulfates was investigated to provide a more rapid gamma screening. The use of Actinide resin instead of TRU resin for column separations was studied as a means to preconcentrate Th, U, and Po in flowback and produced water from the oil and gas industry. The use of an actinide resin is expected to improve the recently developed EPA method for alpha and beta dual analysis for a complete Ra, Th, U, and Po screening or flowback water. Complete separation of radium from the wastewater matrix is ideal and will provide faster radium analysis, reducing the costs associated with handling, treatment, and disposal of wastewater. Multiple proprietary extraction chromatographic resins developed by TrisKem Int. (Bruz, France) were investigated as a function of nitric acid concentration to quantify and enhance the separation of radium from its chemical analogues. Separation of strontium from the resin matrix could easily be achieved using TKI, Sr, or Pb resin as large separation factors were obtained. The TK101 resin is promising for achieving the more difficult separation of barium from radium as the separation factor was found to be 4.3 at 0.04 M HNO_3.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

The use of hydraulic fracturing has unlocked new resources of natural gas and oil that traditional drilling could not access. Hydraulic fracturing has provided financial stability to the energy industry leading to a drop in natural gas prices. The Energy Information Administration estimated in 2020 that the U.S. has more than 2,926 trillion cubic feet (tcf) of technically recoverable natural gas, including 464 tcf of proved reserves. (1) Offering more energy independence, fracking has allowed the country to not rely as much on other countries to supply fossil fuels. However, as hydraulic fracturing drilling expands, concerns about undesirable environmental impacts are rising. Among those concerns is the presence of various radionuclides extracted in the resulting fluid or flowback water.

The brine used for hydraulic fracturing is composed of a mixture of water, salt, and additive chemicals for the extraction of the shale-bound natural gas. As part of the extraction process, the brine is driven into the deep geological formation at a high pressure to fracture rocks and expand existing cracks in and below the Earth's surface. Hydraulic fracturing also extracts dissolved naturally occurring radioactive material present in the rock formation. The solubility of naturally occuring radionuclides depends on the salinity, pH, temperature, and pressure of the brine. (3) Radium tends to concentrate into the brine, making it a naturally occurring radionuclide of environmental concern. The average concentration of radium in oil and gas wastes is approximately 4.44 Bq g^{-1}, but may exceed several hundreds Bq per gram. (4) (5) The average radium concentration in the flowback, and processed water varies from well to well depending on the chemistry of the geological formation and the characteristics of the production process. The main locations of fracking operations in the United States are shown in Figure 1. While location plays a significant role in the quantity of radium present in the brine, radium concentrations have also been observed to increase with the salinity of the water and the age of the well. (6)

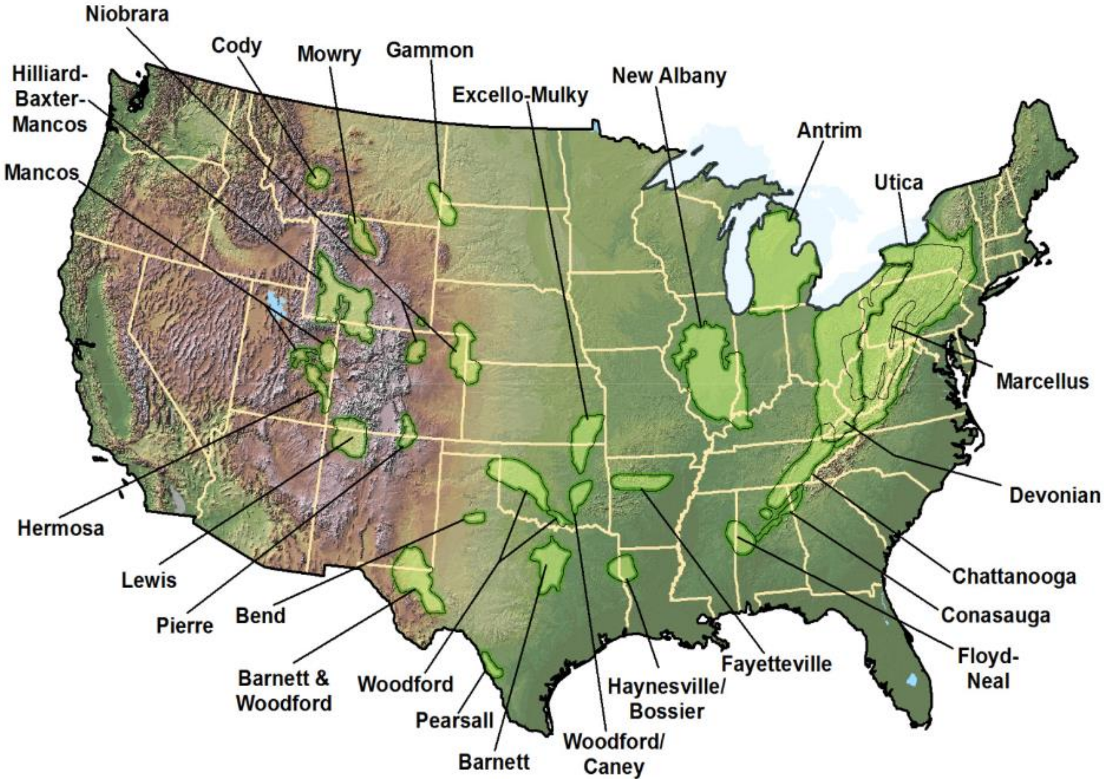


Figure 1: United States shale basin Locations **(2)**

Oil and gas industry waste effluent characterization should be a priority to avoid unintended environmental consequences. The unintentional release of radium isotopes from the Appalachian oil and gas wastewaters (OGW), in Pennsylvania, lead to contamination of local stream sediments near the CWT facility disposal sites. Even though the pre-treated discharged water contained radium concentrations in the range of 0.2-1 Bq/L, accumulation of radium on sediments elevated ^{226}Ra and ^{228}Ra activities and sediments were determined to be as high as 25,000 Bq/kg. The abnormally high concentration of radium in the sediment in contrast to upstream sediments near the facility suggests that the release of low low-activity radium effluents can potentially result in high radium accumulation in sediments at disposal sites. (7) Far from being an isolated case, brine spills are also a major source of contamination. Since the beginning of unconventional oil extraction and hydraulic fracturing in 2007, there have been approximately 3900 brine spills reported to the North Dakota Department of Health by well operators. The Blacktail Creek Spill, also resulting from a pipeline leak, occurred in January 2015, and released nearly 70,000 barrels of brine near Blacktail Creek, which flows into the Little Muddy River, a tributary of the Missouri River. Analysis showed that soil and sediment at spill sites had elevated total radium activities relative to the background, indicating an accumulation of radium in impacted soil and sediments. (8) Therefore, monitoring the radioactivity concentration and developing efficient treatments for the oil and gas industry wastewater is crucial to propose effective waste management strategies.

1.2 NATURALLY OCCURRING RADIOACTIVE MATERIAL

Naturally Occurring Radioactive Materials (NORM) are radionuclides of natural origin. Primordial radioisotopes, which can be divided into non-series and natural decay series radionuclides, are one of the two categories of NORM. The other category of NORM is cosmogenic radioisotopes. Primordial radioisotopes were created in nova or supernova events that occurred billions of years ago. Primordial radioisotopes have been present since the formation of the earth approximately 4.5 billion years ago but have half-lives longer than the age of the Earth and are still detectable today. Generally found in low concentrations, primordial radionuclides are everywhere in the environment including soil, rocks, water, and vegetation. Three commonly naturally occurring radioactive nuclides are ^{232}Th, ^{238}U, and ^{235}U. These elements are the unstable parents of decay chains and undergo radioactive decay one after another, starting a long decay chain until to a stable element. Since radium is the progeny of the ^{238}U and ^{232}Th decay series, it is considered a NORM element. Earth's surface contains an estimated 1.8×10^{13} grams (2×10^{7} tons) of radium. (9)

NORM is distributed unequally, and concentrations varies with geological formation. The NORM background values promulgated by the state of Colorado for some common radionuclides are: (6)

- Ra-226: 1.4 pCi/g
- Ra-228: 1.3 pCi/g
- Pb-210: 1.4 pCi/g
- Po-210: 1.4 pCi/g

Those values serve as a standard for the rules and regulations in Colorado but are subject to change radically from one place to another. They have been derived from a mean concentration across the state.

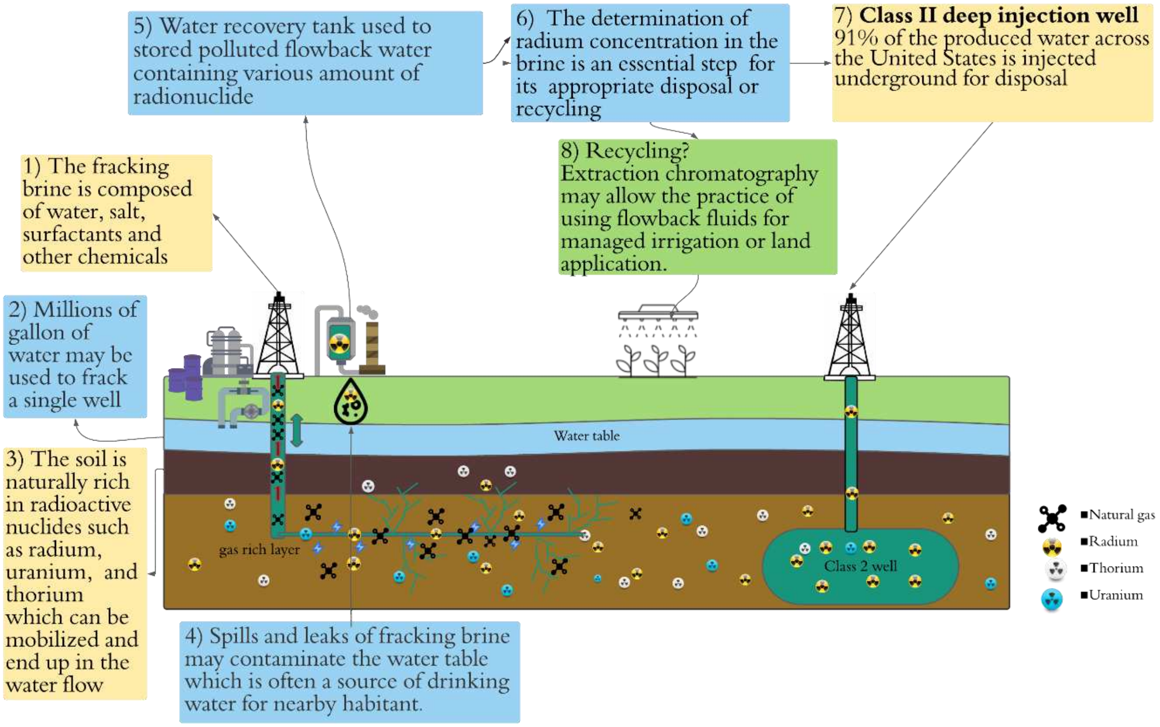
1.3 TECHNOLOGICALLY ENHANCED NATURALLY OCCURRING RADIOACTIVE MATERIAL

Technologically Enhanced Naturally Occurring Radioactive Material are defined by ANSI/HPS N13.53-2009 standard *Control and Release of Technologically Enhanced Naturally Occurring Radioactive Material (TENORM)* as: *"*naturally occurring radioactive material disturbed or altered from natural settings or present in a technologically enhanced state due to past or present human activities and practices, which may result in a relative increase in radionuclide concentrations, radiation exposures and risks to the public, and threat to the accessible environment above background radiation levels." (10)

The TENORM definition varies between states and especially between agreement states and non-agreement states. Some states have adopted the Environmental Protection Agency (EPA) definition which includes NORM that has been made more accessible, as well as materials that have been altered by human activities to increase NORM concentrations while some other states have adopted the CRCPD (Conference of Radiation Control Program Directors) definition which includes only materials that have been altered to increase NORM concentrations. (6) The oil and gas industry produces TENORM waste, making naturally occurring radioactive material more accessible and sometimes concentrates it.

1.4 REGULATIONS AND WASTE MANAGEMENT

Hydraulic fracturing is a water-demanding process (Figure 2). As much as four million gallons of water-based fluids are injected per well of which 10-70% is recovered as flowback water. The ratio of produced water to oil in conventional wells is approximately 10 barrels of produced water per barrel of oil. According to The American Petroleum Institute (API), more than 18 billion barrels of waste fluids containing Naturally Occurring Radioactive Material (NORM) from oil and gas production are generated annually in the United States. (11) The produced wastewaters are generally reinjected into deep class II wells or recycled. The EPA estimates that 180,000 class II wells (Figure 3) are in operation in the US. Of those, 80% are used for enhanced recovery where the brine, freshwater, steam, polymers, or carbon dioxide are injected into oil-bearing formations to recover residual oil and natural gas and 20% are disposal wells. About 91% of the produced water across the United States is injected underground. (6) However, deep class II wells require monitoring and testing of the content. Injections of processed fluids may be prohibited if the proposed operations could result in leaks contaminating an underground source of drinking water that may cause a violation of the U.S. EPA Drinking Water Regulations (40 C.F.R. § 141). Under section 1422 or 1425 of the EPA's Safe Drinking Water Act, the EPA has set the drinking water standard to 5 pCi/L or 0.185 Bq/L for ^{226}Ra and ^{228}Ra combined. EPA standards are in place to protect the underground source of drinking water by prohibiting the disposal of TENORM in a way that could jeopardize the drinking water quality.



5) Water recovery tank used to stored polluted flowback water containing various amount of radionuclide

6) The determination of radium concentration in the brine is an essential step for its appropriate disposal or recycling

7) **Class II deep injection well** 91% of the produced water across the United States is injected underground for disposal

1) The fracking brine is composed of water, salt, surfactants and other chemicals

8) Recycling? Extraction chromatography may allow the practice of using flowback fluids for managed irrigation or land application.

2) Millions of gallon of water may be used to frack a single well

3) The soil is naturally rich in radioactive nuclides such as radium, uranium, and thorium which can be mobilized and end up in the water flow

4) Spills and leaks of fracking brine may contaminate the water table which is often a source of drinking water for nearby habitant.

Figure 2: Fracking and TENORM environmental stakes created with Lucidchart.Com

Neither the Nuclear Regulatory Commission (NRC), nor the EPA have established federal regulations for the disposal of NORM containing waste from the oil and gas industry. The Suggested State Regulations (SSR) for control of radiation for TENORM sets standards and proposes state regulations for the disposal of those wastes. (12) It states that "TENORM waste shall not be diluted for the sole purpose of making the waste exempt from the disposal requirements without prior Agency approval." The disposal of the brine in an injection well is allowed if the TENORM content is in accordance with the state laws or for disposal at an out-of-state injection well if approved by the applicable governmental authority.

Since no federal agencies set rules for the disposal of TENORM, state laws are largely inconsistent across states. In Colorado, the responsibility for regulating wastes such as flowback fluid lies with the Colorado Oil and Gas Conservation Commission (COGCC). Part N of the Conference of Radiation Control Program Directors (CRCPD) SSR specifies that "waste with a TENORM concentration of fewer than 185 becquerels per kilogram (Bq/kg) or 5 picocuries per gram (pCi/g) of Ra^{226} and Ra^{228} combined, excluding natural background are exempted from regulations." Above this threshold, waste producers and handlers are required to acquire a license. A State of Colorado Specific Radioactive Materials Licence entitles oil and gas companies to possess produced fluids that contain or are contaminated at concentrations, excluding natural background, greater than 5 pCi/g but not in excess of 250 pCi/g each in dry weight of Radium-226, Radium-228, Lead-210, and Polonium-210. However, if the produced fluids contain concentrations, excluding natural background, in dry weight in excess of 50 pCi/g of any TENORM radionuclide and contain greater than 10% solids, it shall be confined in an enclosed tank and it shall only be transferred for disposal. Options for disposal of produced water in Colorado are (13):

- Injection into a Class II UIC Well, permitted pursuant to the 2 CCR 404-1,800 Series Rules or class I well if permitted by the EPA.
- Disposal at a commercial solid waste disposal facility.
- Discharge into state waters but must be in accordance with the Water Quality Control Act, and follow regulations under 2 CCR 404-1, Rule 905.
- Evaporation in a properly lined pit at a centralized E&P waste management facility if in accordance with rule 907 of 2 CCR 404-1.
- Disposal at a facility authorized to receive such material under terms of a specific radioactive materials license.

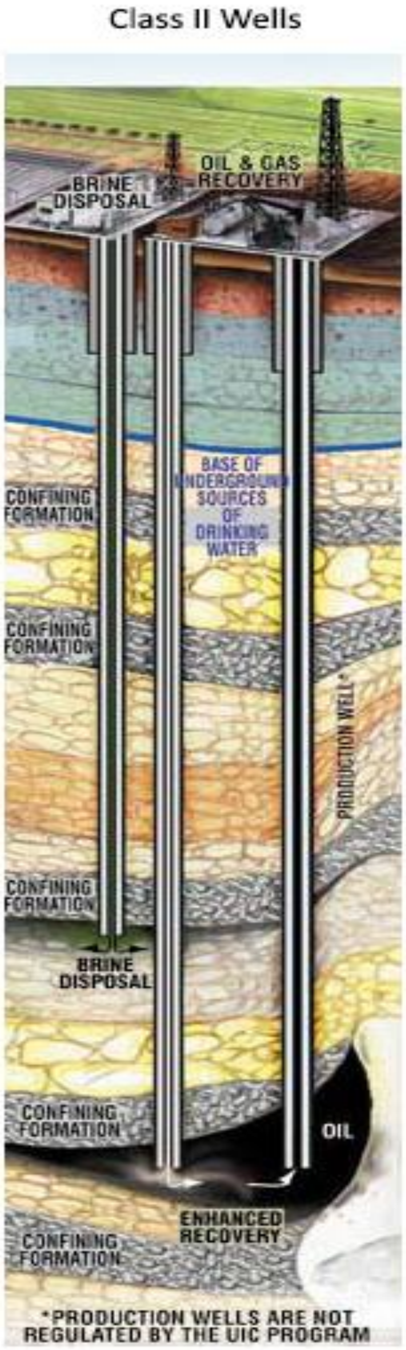


FIGURE 3: CLASS II WELL **(14)**

Advances in flowback fluid treatment technology like filtration, reverse osmosis, decomposition in constructed wetlands, ion exchange, and other technologies may allow the practice of using flowback fluids for managed irrigation or land application. (6) According to 6 CCR 1007-1, Part 20 produced water may be reused and recycled for enhanced recovery, drilling, completion, and other approved uses but no set rules are in place. Therefore, each waste management plan for every well must be examined and must comply with water quality standards and classifications established by the Water Quality Control Commission in order to be implemented. (13)

Illinois has more specific regulations concerning the recycling of flowback water and products from the oil and gas industry. Illinois state laws stipulate that "the materials containing ^{226}Ra and ^{228}Ra less than or equal to 100 pCi/g may be used for soil conditioning on agricultural cropland provided that the cumulative increase of the combined ^{226}Ra and ^{228}Ra concentration in the soil does not exceed 1.0 pCi/g and that the final soil concentration does not exceed 3pCi/g, the level which is accepted as background". (6)

Disposal of the flowback fluid is managed on a site-to-site basis. When developing a wastewater management plan, oil and gas producers must comply with state laws, and consider the availability of facilities and the limiting capacities of wastewater treatment plants. Examples of flowback fluids disposal plans for different shale gas basins are stated in Table 1.

Table 1: Examples of produced water management by shale gas basin **(2)**

Shale Gas Basin Water	**Water Management Technology**	**Technology Availability**	**Comments**
Barnett Shale	Class II injection wells	Commercial and non-commercial	Disposal into the Barnett and underlying Ellenberger Group
	Recycling	On-site treatment and recycling	For reuse in subsequent fracturing jobs
Fayetteville Shale	Class II injection wells	Non-commercial	Water is transported to two injection wells
	Recycling	On-site-recycling	For reuse in subsequent fracturing jobs

Haynesville Shale	Class II injection wells	Commercial and non-commercial	
Marcellus Shale	Class II injection wells	Commercial	Limited use of Class II injection wells
	Treatment and discharge		Primarily in Pennsylvania
	Recycling	On-site-recycling	For reuse in subsequent fracturing jobs
Woodford Shale	Class II injection wells	Commercial	Disposal into multiple confining formation
	Land application		Permit required through the Oklahoma Corporation Commission
	Recycling	Non-commercial	Water recycling and storage facilities at a central location
Antrim Shale	Class II injection wells	Commercial and non-commercial	
New Albany Shale	Class II injection wells	Commercial and non-commercial	

1.6 RADIUM

In 1898, Marie Curie discovered radium as a component in pitchblende. She received the Nobel prize in Chemistry in 1911 for its separation and characterization. Radium was named after the Latin word “radius” which means “ray” and has the atomic symbol Ra. (15) Under the supervision of Henry Becquerel, she studied uranium radiation, as denoted at the time, for her doctoral research. She discovered that thorium compounds featured the same propriety as uranium in its radiation. The property, atomic by nature and never altered by the element’s chemical form, was later named “radioactivity” by the Curies. At that time, Marie contributed to many advancements in understanding radioactivity, but she did not graduate with her Ph.D. until 1903, as she could not find time to write her thesis because of her experimental work leading to the discovery of polonium and radium.

Her first research task was to develop an accurate method for measuring radioactivity. Pierre Curie and his brother, Jacques, developed the Curie piezo electrometer before they met Marie, as they were interested in the curious proprieties of the crystal. Marie then used the Curie piezo electrometer to develop an instrument capable of measuring the current caused by radioactive elements in the ionization chamber. The early prototype of an ionization chamber radiation detector consisted of a quadrant electrometer, piezoelectric quartz, and a flat condenser as an ionization chamber. "The objective of the measurement was to determine the amount of electricity coming from the ionization of the air by a radioactive material, which developed inside a condenser (ionization chamber) […]. The instrument was made of a piece of a monocrystal of quartz, the shape, and orientation of which is specific to produce a piezoelectric effect. The crystal is suspended vertically in the brass cylinder at the bottom of which is a plateau. By dropping a weight on the plateau, a precise amount of electrical charge appeared on both sides of the slice of quartz. The charge is compared to that developed in the ionization chamber using the electrometer as a comparator. If the two charges are equal the spot of light stayed in the middle of the plate." (16) By measuring the deviation of the spot of light, Marie Curie could back-calculate the current relative to the amount of radioactivity flowing in the flat condenser. The measurement approach was unique and gave quantitative results unlike the photometric plate methods used until then.

As Marie investigated different uranium ores, pitchblende, and the mineral chalcocite, she soon realized that some compounds were more active than metallic uranium. Since she thought that uranium was the only source of activity, Marie designed an experiment comparing synthetic chalcocite made using pure compound, to the natural chalcocite. She soon realized that the natural chalcocite had higher activity than the artificial one. Based on her experimental results, she concluded that some other element must be responsible for the increased radioactivity.

Pierre and Marie then decided to use pitchblende and electromagnetic methods to identify the activity of various minerals. The activity of each compound separated from the pitchblende was assayed and compared to the whole activity to assess if it came from one compound or was divided among products. They first identified polonium, which was akin to bismuth in its chemical properties. Further similar research led them to the discovery of radium, an element behaving like barium. (17) Henry Becquerel presented their research and shared the discovery of radium at the French Academy of Science in December 1898. “The various reasons we have just enumerated lead us to believe that the new radioactive substance contains a new element to which we propose to give the name radium. The new radioactive substance certainly contains a very strong proportion of barium; in spite of that its radioactivity is considerable. The radioactivity of radium must therefore be enormous.” (18) Bunsen flame spectrometry later confirmed that a new element was discovered as line 3814.8 A.U. (absorbance units) characteristic of radium was present. Without spectroscopic proof, the paper would have been refused by the Academy. Later on, they determined radium’s molar mass and activity. As one gram of ^{226}Ra undergoes 3.7×10^{10} disintegrations per second, a level of activity was defined: the curie (Ci), an early unit of radioactivity.

Radium is the heaviest of the alkaline earth metals and has similar chemical properties to those calcium, strontium, and barium, all with a prevalent oxidation state of +2. The physical proprieties of ^{226}Ra and ^{228}Ra are displayed in table 2.

Table 2**:** Radium physical proprieties (19)

	Ra-226	**Ra-228**
Atomic number	88	88
Decay series	U-238	Th-232

Progeny	Rn-222	Ac-228
Half-life (y)	1600 (most stable of the radium isotopes)	5.75
Alpha (MeV)	4.78 (93.84%) 4.60 (6.16%)	-
Beta (keV) **mean energy**	-	29.93
Gamma emitter	Yes (186.2)	Not directly but Ac-228 is

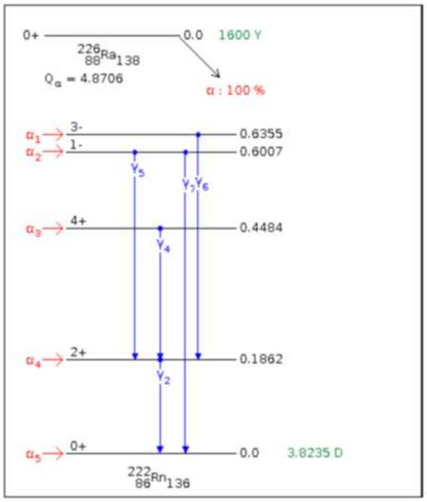


Figure 4: Decay scheme of ^{226}Ra **(20)**

1.7 RADIOTOXICITY OF RADIUM

Radium can enter the body through inhalation or ingestion. Twenty percent of radium taken into the body via inhalation or swallowing (in water or with food) will enter the bloodstream while the rest is excreted, mostly in feces. (21) Radium follows a similar accumulation pathway as Ca^{2+}, explicitly to the mineral bone tissues where most dose is delivered (Figure 5).

Many deaths have been associated with radium exposure. An early report details the death of a 36-year-old chemist who had worked with radium for 14 years. He died of bronchopneumonia a month after developing acute leukopenia. Post-mortem analysis showed an elevated radium concentration in his skeleton. (22) Throughout the early 20th century, radium was believed harmless at best, or even healthy. Hundreds of thousands of people drank radium-infused tonic water, brushed their teeth with radium toothpaste, and wore radium cosmetics. The infamous story of the "radium girls" is another example of exposure to radium. Female radium dial painters in the 1920's were exposed by tipping their paint brushes with their lips or tongues, and ingested elevated quantities of the water-based paint containing ^{226}Ra and ^{228}Ra in the process. The workers were assured by their supervisors that practices were safe. The dial painters were fascinated by the glowing paint, and often painted their nails and teeth with the radium containing paint. Medical reports from 1925–1926 detail short-term health effects such as "radium jaw", aplastic anaemia, and cancer. The medical reports raised concerns regarding the toxicity of radium and lead, resulting in several lawsuits against companies. (23) Over 30 radium related deaths have been reported among the radium dial painters.

Radium and many of its decay progenies are alpha emitters. Alpha particles have a high linear transfer energy (LET) and deposit energy locally in the body, close to the area of radium deposition (range ~ 10^{-4} cm). Alpha radiation is particularly efficient at damaging DNA, which can potentially lead to cancer. The decay products of radium, except radon, are particulate atoms. Radon is a noble gas and can diffuse rapidly from the site of production and potentially leave the body before decaying. Since ^{222}Rn has a longer half-life than ^{220}Rn, the likelihood of ^{222}Rn leaving the body before decaying is greater. Diffusion of ^{222}Rn results in a major reduction of the radiation dose to tissues. Therefore, ^{228}Ra is about 2.5 times as effective, per μCi, inducing bone sarcomas as ^{226}Ra. (24) Ra-226 delivers 2.8×10^{-7} Sv per becquerel ingested while ^{228}Ra delivers 6.7×10^{-7} Sv per becquerel ingested. (21)

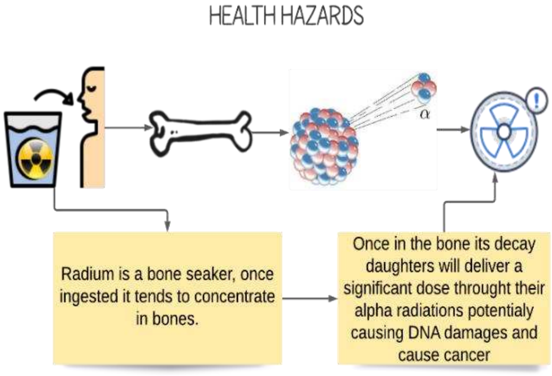


Figure 5: Health hazard associated with radium ingestion; figure created with LucidChart.com

1.8 BARIUM

Barium (Ba) is the fifth element of the alkaline earth metal group and has an oxidation state of +2. The atomic number of barium is 56. Barium is found in the Earth's crust as a mixture of seven primordial nuclides, mainly stable. The most abundant isotope of barium in nature (71.7%) is the stable ^{138}Ba isotope. Two of the natural barium isotopes are unstable: ^{133}Ba and ^{130}Ba.

Since all barium isotopes have the same chemical properties, ^{133}Ba is used in this study as a radioanalytical tracer. Barium can be easily quantified by gamma spectrometry and was used to assess the weight distribution ratio of various extraction chromatographic resins. Ba-133 disintegrates by electron capture followed by gamma emissions mainly to two excited levels of ^{133}Cs at 437 keV (85.4%) and 383 keV (14.5%) with three very minor branches to the 160 keV, 81 keV excited levels, and the ground state (Figure 6). (25). Ba-133 has a half-life of 10.51 years. Ba-133 is not found in nature, and created by thermal neutron capture (0.0253eV) of enriched Ba-132 in a High Flux Isotope Reactor. (26) Ba-133 is used for a variety of purposes, such as instruments calibration, and as a gamma source in multiphase flow meters used for example, in the oil and gas industry.

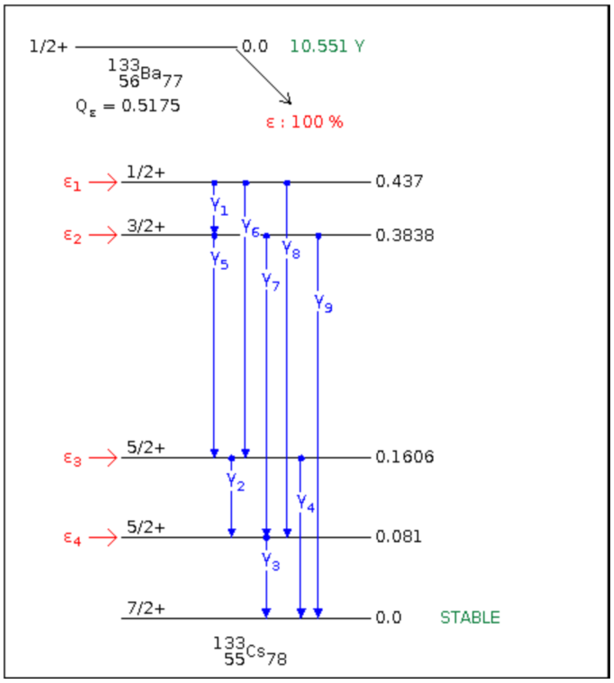


Figure 6: ^{133}Ba decay scheme **(20)**

1.9 STRONTIUM

Strontium (Sr) has an atomic number of 38 and is the fourth element in the alkaline earth metal group. Like radium and barium, its exclusive oxidation state is +2. Thirty-five isotopes of strontium are known to exist; only 4 are stable: ^{84}Sr (0.56 %), ^{86}Sr (9.86 %), ^{87}Sr (7.0 %), and ^{88}Sr (82.58 %). Strontium comprises about 0.025% of the earth's crust. (27) These four isotopes represent the majority of the strontium on earth. Radioactive ^{90}Sr (half-life of 28.78 years) is produced by nuclear fission, and was deposited in the environment in small quantities following atmospheric nuclear weapons testing, and the Chernobyl and Fukushima disasters. Strontium-90 is a calcium analogue, and is considered the most dangerous constituent of fallout, accumulating in bones and teeth. (28) Sr-90 is the longest-lived radioactive isotope of strontium. (28) Strontium-90 decays into unstable ^{90}Y that later decays into stable ^{90}Zr (Figure 7). The two successive decays result in almost 100% beta emissions with a maximum energy of 545.9 keV (average 196 keV) and 2278.7 keV. (29) The yttrium-90 lifetime is a much shorter half-life than ^{90}Sr. Yttrium-90 (half-life of 64 hours) and strontium-90 reach secular equilibrium after approximately 21 days. After this ingrowth period, the activities of ^{90}Sr and ^{90}Y in a sample are equal.

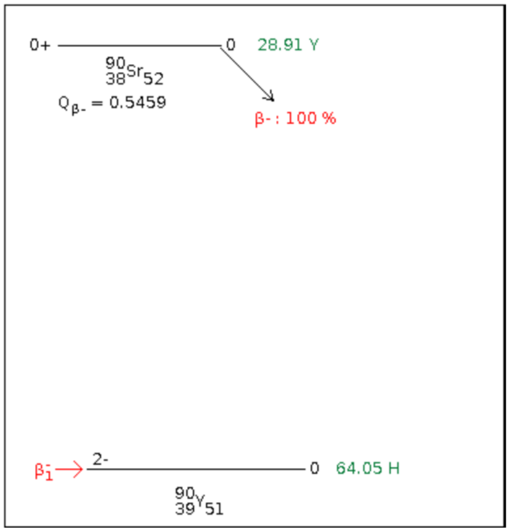


Figure 7: ^{90}Sr decay scheme **(20)**

CHAPTER 2: RADIOANALYTICAL CHEMISTRY OF ALKALINE EARTH METALS AND FLOWBACK WATER

2.1 CHEMISTRY OF THE ALKALINE EARTH METALS

The alkaline earth metals belong to the second group of the periodic table and have 2 s-orbital electrons in their outer shell. They appear as M^{2+} ions in aqueous solutions. The electropositivity of the alkaline earth metal increases with atomic number (Sr < Ba < Ra). Because of their electropositivity, alkaline earths mostly form ionic bonds and are highly soluble. As no vacancy occurs in their outer electron shells, alkaline earths rarely form covalent bonds with organic compounds. Hence, solvent extraction is not commonly used for alkaline earth partitioning apart from the use of crown ethers which readily form strong complexes with strontium and radium. The ionic size of alkaline earth metals increases with the atomic number, but the hydrated ionic size increases in reverse order (Table 3). (30)

Table 3: Electronegativities and ionic radii of alkaline earth metals **(31) (30) (32)**

	Electronegativity (Pauling)	**Crystal Ionic Radius (pm)**	**hydrated ionic radius**
Strontium	1.0	118	412
Barium	0.9	135	404
Radium	0.9	148	<404

Separation and preconcentration of radium is typically done by precipitation of Ra, Ba, or Pb as hydroxide, chromate, carbonate, or phosphate salts. Barium and radium can be readily separated from calcium and strontium by chromate precipitation (pH 4) or by sulfate precipitation in strong sulfuric acid, as radium and barium chromate and sulfate are far less soluble than those of calcium and strontium. Since the solubilities of radium and barium sulfate compounds in water at 20 °C are

0.0031 and 0.021 g/L, respectively, sulfate coprecipitation is the more widely used technique (Table 4).

Table 4: Solubility product of common compounds of alkaline earth metals **(30) (33)**

	Calcium	**Strontium**	**Barium**	**Radium**
Hydroxide-M(OH)$_2$	5.5×10^{-6}	soluble	Soluble	Soluble
Chromate-MCrO$_4$	7.1×10^{-4}	2.2×10^{-4}	2.2×10^{-10}	$< 2.2 \times 10^{-10}$
Carbonate MCO$_3$	3.8×10^{-9}	1.1×10^{-10}	5.1×10^{-9}	$< 5.1 \times 10^{-9}$
Sulfate-MSO$_4$	9.1×10^{-6}	3.2×10^{-7}	1.1×10^{-10}	4.25×10^{-11}

Ion exchange chromatography is another common method for isolating radium (see Chapter 7.1). Although the selectivity among alkaline earth metals is generally poor, the sequential elution of individual ions can be achieved to an extent by employing solutions containing complexants such as ammonium citrate or EDTA. Other techniques such as radium adsorption on manganese oxide or hydrous titanium oxide have also been used to separate and analyze radium. (34) Lastly, the use of Na-4-mica ($Na_4Al_4Si_4Mg_6O_{20}F_4 \bullet H_20$) radium adsorbent clay has been investigated as a way to immobilize the radium in a matrix for water treatment. (35) These techniques could be used for the removal of Ra^{2+} ions from an aqueous solution, but they suffer from poor selectivity.

2.2 CHEMISTRY OF THE PROCESSED AND FLOWBACK FLUID FROM THE OIL AND GAS INDUSTRY

Processed fluids have a high salinity as well as a high Total Dissolved Solids (TDS) content varying from below 5,000 ppm to 100,000 ppm TDS or higher. The dissolved constituents may vary from one shale to the next or even by area within a shale. (2) Elevated concentrations of calcium barium, strontium, bromides, chlorides, sulfates, sodium, TDS, and benzene are typically found within the flowback fluids. To optimize the gas extraction process, drilling and fracking additives are added to the brine and are often found in the flowback fluids but can be removed through treatment. Typical treatments of flowback fluid use Na_2SO_4 to promote the precipitation of metals, as well as Ra, before the treated brine is discharged or reused for further fracking operations. Commonly used chemicals and additives used in hydraulic fracturing processed are listed in Table 5. The total amount of chemical additives constitutes only up to 0.5–1% of the process fluid.

Table 5: Categories of chemicals used in hydraulic fracturing, their purposes, and example(s) of commonly used chemicals (29)

Functional category	**Purpose**	**Example of chemical(s)**
Diluted acid	Improve the injection and penetration, minimize clogging by dissolving minerals and clay, aid gas flow, and open pores.	Hydrochloric acid
Biocide	Minimize the bacterial contamination of the hydrocarbons and reduces bacterial production of corrosive by-products to maintain wellbore integrity and prevent the breakdown of gellant.	Glutaraldehyde
Breaker	Assist flowback of the brine from wellbore, breaks down gel polymers.	Ammonium persulfate
Clay stabilizer	Establishes fluid barrier to prevent clays from swelling, keeps pores open, creates a brine carrier fluid.	Potassium chloride
Corrosion inhibitor	Maintains integrity of steel casing, prevents corrosion of pipes and casing.	N,N-Dimethylformamide
Crosslinker	Thicken the fluid.	Borate salts

Defoamer	Lowers surface tension and allows gas to escape.	Polyglycol
Foamer	Reduces fluid volume and improves proppant carrying capacity.	Acetic acid (with NH_4 and $NaNO_2$).
Friction reducer	Improves fluid flow efficiency, reduces friction caused by high-pressure conditions	Polyacrylamide
Gel/gellant	Thickens fluid	Guar gum
Iron control	Prevents materials from hardening and clogging the wellbore, prevents metal oxide precipitation	Citric acid
Oxygen scavenger	Protects casing and pipes from corrosion by removing oxygen from the fluids.	Ammonium bisulfate
pH adjusting agent/ buffer	Controls pH of solution, protects pH-dependent effectiveness of other chemicals	Sodium carbonate, potassium carbonate
Proppant	Hold fractures open to allow gas to escape from the shale.	Silica, sometimes glass beads
Scale control	Prevents clogging from minerals formation and block fluid or gas flow	Ethylene glycol
Solvents	Improve fluid wettability or ability to maintain contact between the fluid and the pipe	Stoddard solvent
Surfactant	Improves fluid by reducing surface tension	Isopropanol

Radium is the major source of radioactive contaminants in processed fluid. A report on the gross alpha level in fluid from the Marcellus Shale noted Ra activity concentrations were similar to the gross alpha level in the brine (Figure 8). (36) This implies that radium is selectively extracted into the brine during the extraction process, while the other alpha-emitting progenies in secular equilibrium remained insoluble under the geochemical conditions. (5)

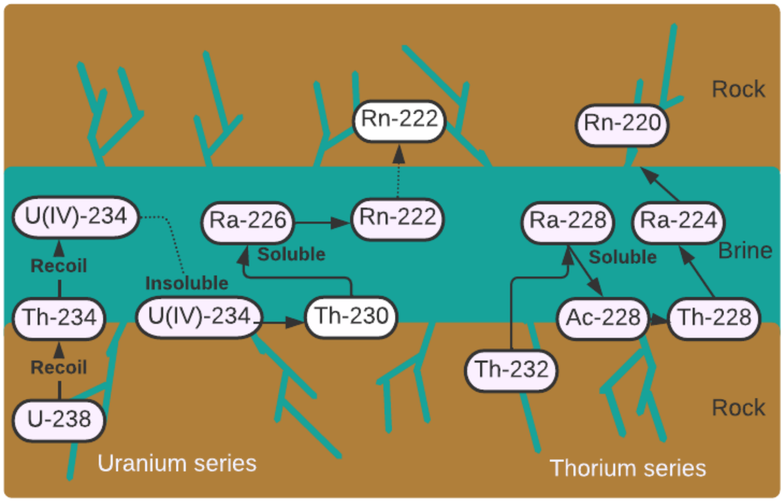


Figure 8: Theoretical model of NORM in Marcellus Shale based on HPGe and alpha spectrometry of produced fluids. A solids arrow indicates radioactive decays. A dashed arrow indicates a physical or chemical partitioning process. Created with Lucidchart.Com (31)

As ^{226}Ra and ^{228}Ra belong to two extended decay series, projections have shown that for flowback fluids stored in an enclosed system which prevents radon gas from escaping, total activity would be increased by a factor > 5 within 15 days following the extraction due to progenies ingrowth. (5) Because of ^{226}Ra's long half-life (1,600 y), the radioactivity level of waste in enclosed systems, such as the class II well, is expected to reach its maximum approximately 100 years after the extraction. The long-lived ^{210}Pb and its decay products will reach equilibrium with ^{226}Ra at approximately 100 years, leading to a total radioactivity increase by a factor >8. But as part of the oil and gas water treatment, most of the radium may be stripped from the brine using Na_2SO_4 to promote the precipitation of metals before the treated brine is discharged. Such radium removal practices are typical, but are not always utilized, as each fracking site has its individual wastewater management plans.

2.3 METHOD REVIEW FOR RADIUM ANALYSIS IN ENVIRONMENTAL FLUIDS

A major challenge for the appropriate disposal of flowback waters is the difficulty in radium concentration assessment. Many states have opted for the EPA's methods for the determination of radium in drinking water procedure (Figure 9). Although EPA methods are efficient for drinking water, a major concern develops when flowback water is considered because of the high dissolved solid content. Monitoring radium in a water matrix requires accurate determination close to the detection limit. Commonly used methods for ^{226}Ra screening rely on direct alpha spectrometry, direct gamma spectrometry (186 keV), or indirect measurements when the secular equilibrium has been established either by alpha measurement (^{222}Rn, ^{218}Po, ^{214}Po), beta measurement ^{214}Pb and ^{214}Bi), or gamma spectrometry (^{214}Pb and ^{214}Bi). (37)

EPA Method 903 measures the total soluble alpha-emitting radioisotopes of radium, namely ^{223}Ra, ^{224}Ra, and ^{226}Ra, in drinking water. The radium is collected by coprecipitation with barium and lead sulfate and purified by re-precipitation from an EDTA solution. Citric acid (5 mL of 1N) is used to acidify the 1 L sample before lead and barium carriers (both 15 mg/ml) are added. Then 18N H_2SO_4 is added with vigorous mixing and the precipitate is allowed to settle overnight. The $BaSO_4$ precipitate is centrifuged, washed with 0.1N H_2SO_4, and separated from the supernatant multiple times. The $BaSO_4$ precipitate is redissolved in 15 mL of 0.25N EDTA and CH_3COOH is added to reform a purified precipitate. The final precipitate is centrifuged and counted on a pre-calibrated gas-flow internal proportional counter or alpha scintillation counter to determine the alpha activity. (38) Since the EPA method was designed for low-solid samples such as drinking water, the very high dissolved solid content in flowback fluid biases the alpha spectrometry analysis. The excessive precipitate formation requires that only a small aliquot <10 mL could be analyzed at a time, which would inevitably decrease the radium content and therefore limit the sensitivity. Moreover, the alpha counting efficiency must be questioned due to self absorption of alpha particles in the precipitate. (39)

EPA Method 903.1 measures exclusively ^{226}Ra and is based on the emanation and scintillation counting of its progeny ^{222}Rn. The chemical processing is relatively similar to Method 903, but the precipitate dissolved in EDTA is placed in a sealed bubbler and stored for ingrowth of radon-222. After ingrowth, the gas is purged into a scintillation cell. When the short-lived radon-222 progenies are in equilibrium with the parent (4 h), the scintillation cell is counted for alpha activity. Measurement of ^{226}Ra in flowback water via ^{222}Rn emanation is advantageous relative to Method 903 because the radon gas may be stripped from the large precipitate allowing for larger sample volumes and lower detection limits. (40) Similarly, the radon de-emanation method (Rad 7 radon detector) is reasonably successful, but concerns are often raised due to samples foaming and extended turnaround time (7-21 days). (41)

If the level of ^{226}Ra is above 3 pCi/L, the sample must also be measured for ^{228}Ra. When a ^{228}Ra analysis is required, EPA Method 904 is usually performed simultaneously with Method 903.1. The radium is coprecipitated with barium sulfate and purified by reprecipitation of the EDTA solution. One mL of a 10 mg/mL and 18 mg/mL strontium-yttrium mixed carrier solution, 1 mL of 9 mg/mL yttrium carrier solution, and 1 mL of a 1.5 mg/mL lead carrier solution are added, and the solution is kept sealed for 36 hours. $(NH_4)_2S$ and NaOH are added to form a lead sulfite precipitate which is discarded. The yttrium hydroxide carrying ^{228}Ac is then precipitated with NaOH, purified, and reprecipitated with $(NH_4)_2C_2O_4 \cdot H_2O$. The final precipitate is transferred to a tared stainless steel planchet and ^{228}Ac is beta counted. This method is often used as it allows the characterization of ^{226}Ra and ^{228}Ra conjointly, but even if the wet chemical methods (903.1 and 904) are robust for drinking water, their reliability is questionable with a recovery that may be as low as 1% due to the remarkably high ionic strength of flowback fluids. (39)

Empore Radium RAD Disks are thin, filter-like (47 mm) membranes, consisting of an inert matrix of polytetrafluoroethylene fibrils impregnated with a chromatographic extractant. (42) Empore Radium RAD disks are used to selectively remove Ra from aqueous samples as a substitution for the barium sulfate precipitation and are often analyzed via gamma spectrometry. Empore Radium RAD Disks are a viable approach for drinking water but the concentration of strontium, barium, and calcium in flowback fluids interferes with the separation of radium. (43) (41) Empore Radium RAD Disks are an appealing approach that is rapid, with fewer wet chemical steps than methods 903.1 and 904 but the radium recovery is questionable (13 ± 1%) due to the flowback fluid's high-ionic strength. (39)

A widely used radium analysis method is gamma spectrometry. Gamma spectroscopy allows the simultaneous measurement of various gamma-emitting radionuclides without separating them from the sample matrix. Two types of gamma detectors are currently widely used, the thallium activated sodium iodide crystal, NaI(T1), and the high-purity germanium detector, HPGe. (44) NaI(Tl) detectors can be obtained with large sensitive volumes, but generally have poor resolution compared to HPGe detectors. HPGe detectors have a much better energy resolution than NaI(Tl) detectors, but generally have a significantly smaller sensitive volume. An HPGe is recommended in EPA method 901 to measure gamma-emitting radionuclides in water samples. Ra-226 non-destructive analysis can be done by direct measurement using the 186.2 keV gamma emission or by the analysis of the ^{214}Pb and ^{214}Bi gamma-emitting progeny, assuming secular equilibrium (minimum ingrowth of 21 days). As one of ^{235}U photopeak overlaps with the 186.2 keV gamma line of ^{226}Ra, results may be biased. However, since uranium is unlikely extracted by the fracturing process, the bias is usually irrelevant. Analysis of ^{228}Ra concentration may be performed simultaneously with ^{226}Ra by examining the adjacent progeny, ^{228}Ac, after reaching secular equilibrium in the sample (2 days). Measurement of Ac-228 can be performed on a well-calibrated HPGe, but low radium concentrations in a sample hinders achievement of detection limits which depend primarily on sample size, detector efficiency, and available counting time. Despite being more precise, the Ac-228 measurement method requires a long counting time, therefore the preconcentration of radium was investigated to provide a good and faster analysis.

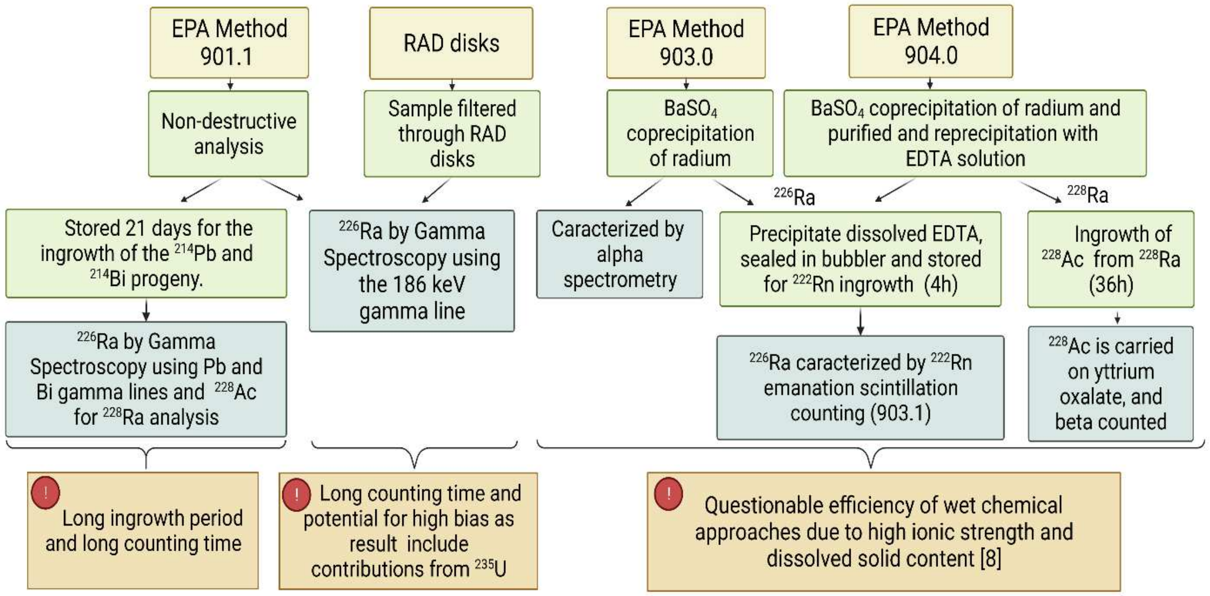


Figure 9: Methods review for the measurement of radium in flowback fluids created with Lucidchart.Com

2.4 METHOD REVIEW FOR GROSS ALPHA AND GROSS BETA ANALYSIS IN ENVIRONMENTAL FLUIDS

Gross α and β activity screening procedures have been developed to determine if further specific radionuclide analysis is required. Gross α and β activity is a good first indicator of the presence of radium , and certain wastewater facilities require gross α and β screening to accept flowback fluid for treatment. Gross α and β measurements give indications of the total radionuclide concentration in a sample with ^{238}U, ^{232}Th, their progeny, and ^{40}K being accountable for 95% of the naturally occurring radioactivity.

The EPA Method 900 is the most commonly used method for the measurement of gross alpha and gross beta particle activities in drinking water. An aliquot of the water sample is evaporated to a small volume and then transferred to a tared 50 mm diameter stainless steel counting planchet. The sample residue is dried to constant weight, reweighed to determine dry residue weight, then counted for alpha and/or beta radioactivity using gas flow proportional counting, alpha spectrometry, or beta counting. Volatile radionuclides, such as radon, will not be measured with the process. (45) The advantage of this method is that it is rapid and cheap, but it presents several limitations:

- Under-response to low energy beta emitters like ^{210}Pb and ^{228}Ra
- Dependent on the time of the measurement, as the activity will increase with time due to ingrowth
- Design for low-solid samples, the density of the solid thickness must be below 5 mg/cm^2

The counting efficiency for alpha-particles declines to less than 10% when 100 mg of solids remain on the planchet due to alpha particle self-absorption.

As flowback fluids have a very high dissolved solid content, and the upper threshold of 100 mg of solid on the planchet will restrict the sample size to a fraction of a milliliter, the sensitivity will be drastically reduced. Since the sensitivity of the measurement is inversely proportional to the size of the sample, the capacity of the method could be reduced by one thousand. Therefore, the reliability of the method is questionable for flowback fluid analysis.

The EPA tried to improve Method 900 for flowback fluid, investigating liquid scintillation counting with an alpha/beta discriminator for the gross α and β measurements as it tolerates a larger amount of solid, up to 50 mg per sample, and is less impacted by self-absorption. However, the direct addition of the sample to the liquid scintillation cocktail resulted in precipitation which made the method unsuitable. (41)

In their attempt to create a rapid and economically viable method to characterize the gross α and β activity in flowback fluids, the EPA investigated an approach for isolating and analyzing Ra, Th, U, and Po in a single test source (Figure 10). However, due to the complex matrix and the overwhelming amount of group II elements, they did not achieve a group separation of Ra, Th, U, and Po.

As a result, EPA proposed stripping Th, U, and Po from the sample using extraction chromatography. The sample is pre-treated with potassium permanganate and ammonia to coprecipitate the radionuclides which are then separated using a TRU resin. The eluate activity is characterized by LSC counting. Subsequently, an aliquot of the sample would be counted on an HPGe detector to obtain the ^{226}Ra activity using the 186 keV peak and to obtain the gross beta activity by summing the gamma emitter's activity plus beta only emitters that are parents with gamma emitters. (41)

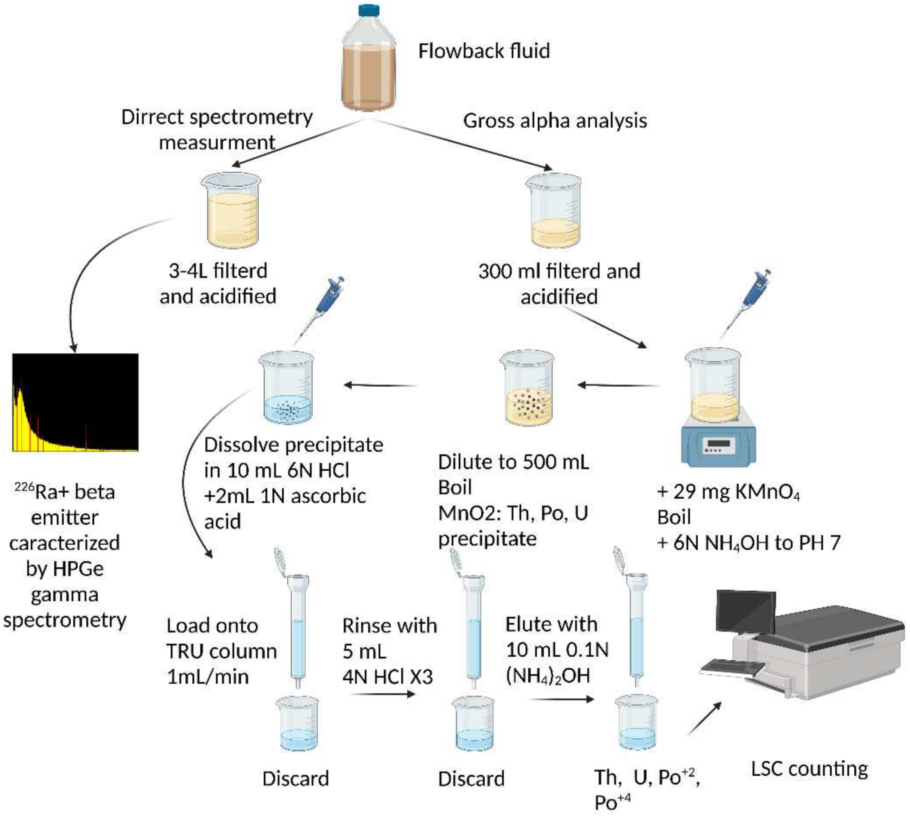


Figure 10: EPA alpha/beta screening in flowback and produce waters Created with BioRender.com

The new EPA approach was an improvement compared to Method 900 but requires two measurements making it time-intensive. Uranium and polonium recoveries were consistently found above 90% while thorium recovery was fluctuating from 57% to 104%, averaging at 74%. Additional exploration of the chemical separation of Th, U, and Po should be done to improve individual recovery and consistency throughout different flowback water matrixes. Investigation of the chemical separation of radium from the sample, especially its chemical analogues, could result in a faster single-step separation and analysis. (41)

2.5 SCOPE OF THIS WORK

The goal of this study is to provide a faster way to determine the total radium activity in flowback water from hydraulic fracturing activities. The chemical preconcentration of radium is investigated to allow for faster HPGe measurements (Figure 11).

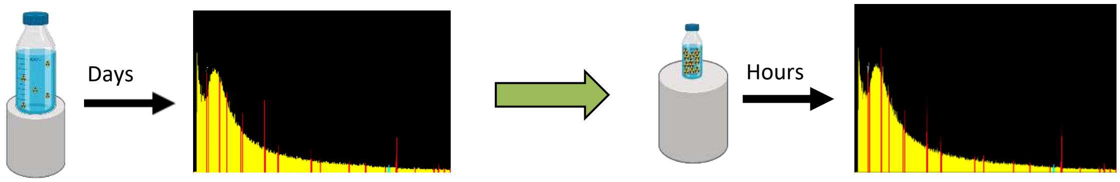


Figure 11: Preconcentration of radium for faster measurements created with BioRender.com

Additionally, the separation of radium from its closest chemical analogues is studied to support the following specific aims:

- Provide faster Radium HPGe measurements
- Provide a faster and improved gross alpha beta screening method
- Provide a way to treat flowback water with elevated radium content to be recycled

CHAPTER 3: INSTRUMENTATION

3.1 GAMMA SPECTROSCOPY

3.1.1 SODIUM IODIDE

Sodium iodine detectors are commonly used for gamma spectrometry. The NaI(Tl) crystal is a scintillator with a good light yield and linearity. When an incident gamma photon enters the detector, there are three ways it could interact with the crystal. If the gamma-ray interacts via the photoelectric effect, then the height of the pulse recorded is directly proportional to the energy of the gamma-ray. It gives rise to a well-defined peak in the gamma spectrum. In this case, the photon will interact with a tightly bound electron from the K or L shell of the iodine in the crystal. The photon will be absorbed and disappear, all its energy is given the electron. The electron emits an energy of $E_{e-} = E_{photon} - E_{binding\ energy}$ (Equation 1). Since the K shell electrons in the iodine have a binding energy of 33 eV, most of the gamma-ray energy will be transferred to the electron as kinetic energy. Therefore, the photoelectron will express all of the incident photon energy as kinetic energy (less the binding energy of the electron). The photoelectron travels through the crystal, losing energy by exciting and ionizing atoms in the NaI crystal. The photoelectron transfers energy to the NaI crystal atoms, and a fraction of the electron energy is converted into UV light that is collected at the photomultiplier tube photocathode (PMT). A voltage divider resistor is attached to the photocathode and dynode to provide a positive voltage on the dynode that will attract electrons ejected from the photocathode due to the incident UV light. Then, secondary electrons emitted by the first dynode will be attracted to the second dynode and more electrons will be generated, amplifying the signal. Eventually, all electrons from the electron cascade will be collected at the anode and an electric pulse will be produced (Figure 12). The electronic pulse is directly proportional to the energy of the incident gamma-ray. The pulse signal will be amplified and then fed into the multichannel analyzer (MCA) for analysis.

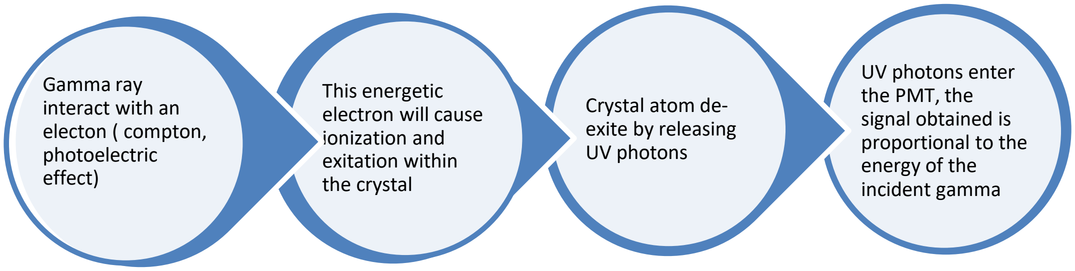


Figure 12: Chain process in the NaI detector

The photopeak can be broadened because of statistical fluctuation, and due to the energy of ionization of NaI(Tl). Those fluctuations in the expected value of the pulse height may come from:

- The actual amount of energy from the gamma-ray that is converted to light in the photoelectric interaction
- The amount of light collected on the photocathode of the PMT
- The efficiency of the photocathode surface for producing electrons
- The gain of the PMT

Gamma-rays not only interact via the photoelectric effect. Gamma rays may undergo Compton interactions, pair production, or even interact in the shielding. Therefore, backscattered photons and lead characteristic X-rays can be detected. Figure 13 shows a diagram of the NaI detector and possible gamma interactions before the subsequent photon interactions in the detector.

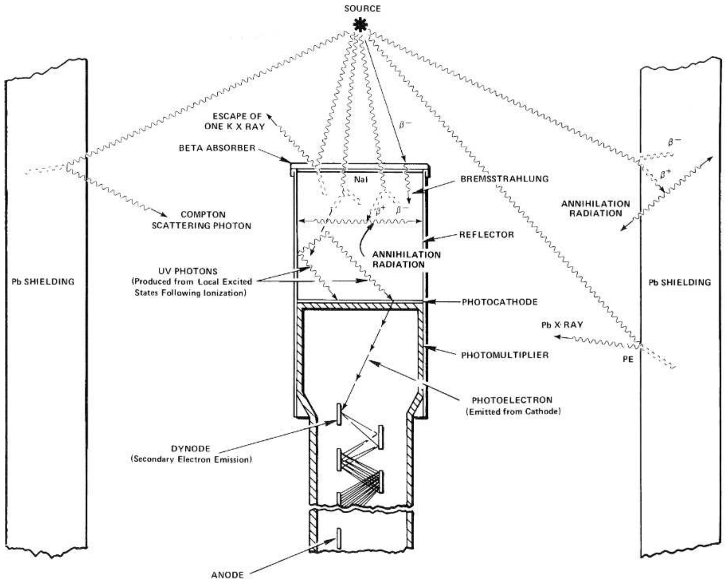


Figure 13: Diagram of the NaI crystal detector, gamma source, photomultiplier, and lead shielding, showing the various type of interactions **(46)**

Gamma-rays can interact in different ways within the detector (Figure 14). Those different interactions will cause result in multiple peaks or edges even for a monoenergetic gamma-ray emitter.

If the gamma-ray interacts by Compton scattering, only a portion of the incident gamma-ray energy will be deposited into the crystal. Compton interactions in the NaI crystal form a broad distribution of pulse energies from the Compton edge down to the electronic cut-off. If the gamma-ray undergoes Compton scattering, then the incident photon will collide with a loosely bound electron or a free electron. Only part of the photon energy will be transferred to the electron and the photon will be scattered at an angle from its original path and may escape the NaI detector. The energy deposited in the NaI depends on the scattering angle of the photon. Because the recoiling electron does not absorb all of the photon's energy, the resulting pulse will occur at a lower energy (channel) than the photopeak.

Pair production is another type of interaction that is likely to occur in the NaI(Tl) crystal if the incident gamma has an energy greater than 5 MeV, energy above which its cross sections becomes higher than the other interactions. If the photon undergoes pair production in the vicinity of one of the iodine nuclei, then the photon will disappear, and an electron and a positron will be created. The energy must be greater than twice the rest mass of an electron, 1022 keV. If the photon has more energy than 1022 keV, then the electron and positron pair will have some kinetic energy. Both electron and positron lose energy through ionization in the crystal. Within a few nanoseconds, the positron will annihilate with an orbital electron in the detector. The annihilation interaction causes the disappearance of the positron and electron, resulting in two gamma rays of 0.511 MeV which are emitted in opposite directions resulting in a peak at the corresponding channel.

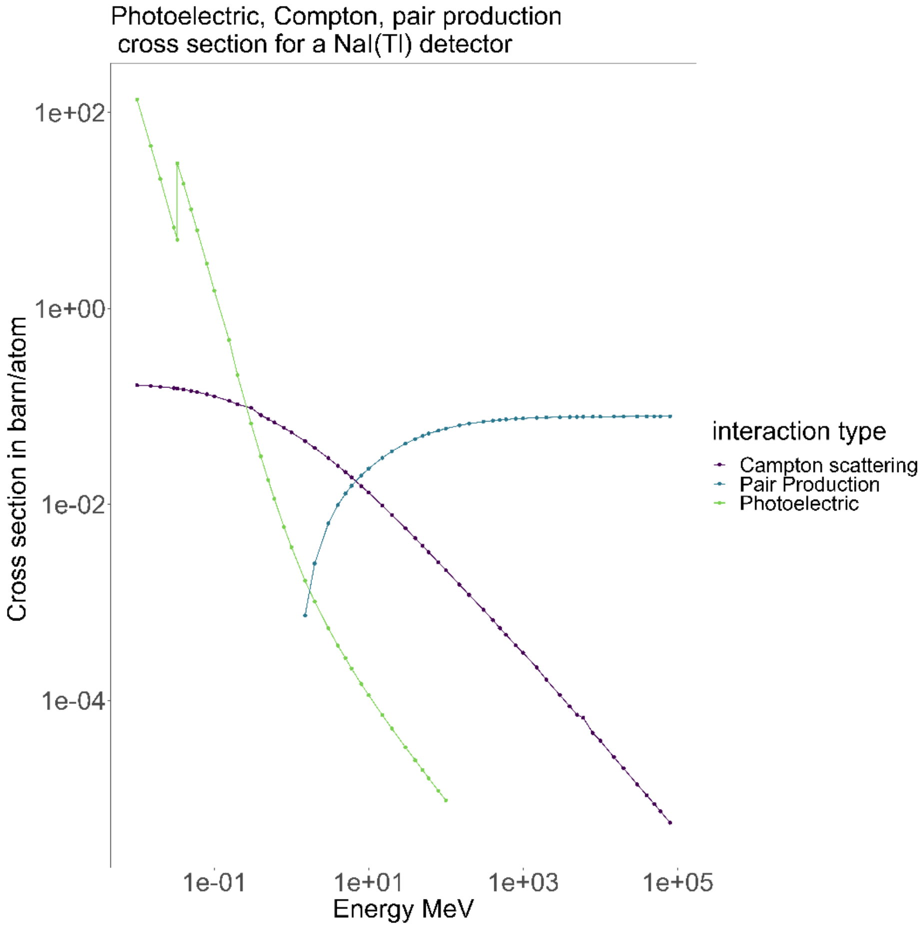


Figure 14: Photoelectric, Compton, pair production and total cross section for a NaI(Tl) detector versus photon energy **(47)**

The main advantage of using a NaI detector is that it offers better efficiencies than a high purity germanium (HPGe) detector due to the higher atomic number (Z) of iodine compared to germanium. As the Z increases, the probability of gamma-ray interaction within the crystal also increases, leading to a better efficiency. The main drawback of NaI(Tl) detectors is the poor energy resolution due to the energy to excite and ionize electrons, and conversion and amplification of the incoming energy in several steps, each introducing random variation.

3.1.2 HIGH PURITY GERMANIUM DETECTOR

High purity germanium detectors (HPGe) are often used for the characterization of environmental samples because of their greater energy resolution. Historically, semiconductor detectors were considered solid-state ionization chambers. The sensitive volume of an HPGe detector is a germanium crystal which is characterized as a semi-conductor. HPGe detectors must operate at the very low temperature of liquid nitrogen (-196°C), because at room temperatures the noise caused by thermal excitation is very high. (48) When a gamma-ray enters the sensitive volume, it will interact with the germanium by one of the three-photon interactions processes described above. The energy lost by ionizing radiation in semiconductor detectors ultimately results in the creation of electron-hole pairs. The number of electron-hole pairs produced in the semiconductor is proportional to the energy of the radiation. The average energy, ε, necessary to create an electron-hole pair in germanium detector is 2.95 eV at 80 K, resulting in excellent resolution. (49) Electrons are transferred from the valence band to the conduction band, and an equal number of holes are created in the valence band. An electric field allows electrons and holes to drift towards the electrodes. The resulting current is fed to a charge-sensitive (integrating) preamplifier with a high dynamic input capacitance. The charge-sensitive preamplifier integrates on its feedback capacitance the current signal delivered by the detector and produces a voltage pulse signal to the filter amplifier (main amplifier). This pulse is then interpreted by the electronics and will result in a count at the corresponding gamma-ray energy. The activity per gram of sample can be calculated using the following equation:

$$\frac{A}{m} = \frac{N}{\varepsilon \times f \times t \times m} \qquad \text{(Equation 2)}$$

Where A is the activity (Bq),

m is the mass of the sample,

N is the number of counts under the peak area,

ε is the efficiency of the detector at that energy,

f if the branching ratio,

t is the counting time,

The low value of ε compared with the average energy necessary to create an electron-ion pair in a gas (typically 15 to 30 eV) results in the better efficiency and energy resolution of semi-conductor detectors (49). By convention, HPGe detectors are characterized by “relative efficiency”. Relative efficiency is defined as the efficiency of measuring a cobalt-60 point source at 25 cm from the face of the HPGe compared to the efficiency of a standard 3-inch × 3-inch right circular cylinder NaI(Tl) detector under the same measurement conditions.

3.2 LIQUID SCINTILLATION COUNTING

Liquid scintillation counting (LSC) is a common and easy technique used to determine the activity content of samples containing beta or alpha emitters. An aliquot of the sample is placed in a scintillation vial and dissolved in an organic scintillation cocktail that contains an aromatic organic solvent, such as xylene or toluene, and small amounts of other additives known as ‘fluors’, or scintillators, and surfactants. Radionuclides decaying within the sample emit alpha or beta radiation, and the particle’s energy is transferred to the organic solvent molecules triggering an electron transition within the energy levels of individual organic molecules. This excitation energy is transferred from one organic solvent molecule to another until it reaches a scintillation molecule, where the de-excitation occurs. Those electrons relax to their original ground energy state, and by doing so, they will emit (typically) UV photons isotropically. Since relaxation is not instantaneous, this phenomenon is called scintillation. In addition to the solvent and scintillator, a wave shifter is added to the cocktail. This wave shifter absorbs the scintillation photons from the primary scintillator and re-emits photons at a longer average wavelength (~425 nm) where photomultiplier tubes (PMTs) are more sensitive. When the photons, which are proportional to the number of alpha or beta particles emitted, interact with both PMTs within six nanoseconds, the light is converted into a current which is then interpreted by the electronics as a decay count. (50)

The typical fluorescent yield for the scintillators is approximately 10,000 scintillation photons per MeV absorbed in the cocktail. The fluorescent yield corresponds to a conversion of about 3%, meaning that on average, 3% of the energy absorbed by the cocktail is converted into scintillation photon energy. The conversion factor is accounted for and corrected when the liquid scintillation counter is calibrated using calibration standards (^{3}H, ^{14}C, Background). Two PMT's on each side of the sample provide a 4π geometry (as well as coincidence counting to electronically eliminate some background) and, contrary to other radiation detection equipment, the sample is immersed in the active scintillation medium. Those two characteristics are responsible for the large counting efficiency of the LSC.

During calibration, the voltage applied to each of the PMTs is adjusted until the two tubes have been synchronized in their response to meet factory-supplied quench and performance requirements. This process is designed to assure that the instrument accurately quantifies the energy from all particle emissions.

Quenching is defined as any chemical process that would reduce the photon output. Two types of quenching must be accounted for and corrected while calibrating the instrument. Chemical quench refers to the absorption of the excitation energy by another chemical other than the scintillator present in the solvent (Figure 15). This impurity emits photons at a wavelength incompatible with the PMTs leading to a loss of signal. Chemical quench also refers to a competing excitation state of the scintillator which leads to the emission of a photon at a wavelength other than the prompt fluorescence. Finally, optical quench happens when part of the light output of the scintillators is absorbed by coloring in the sample.

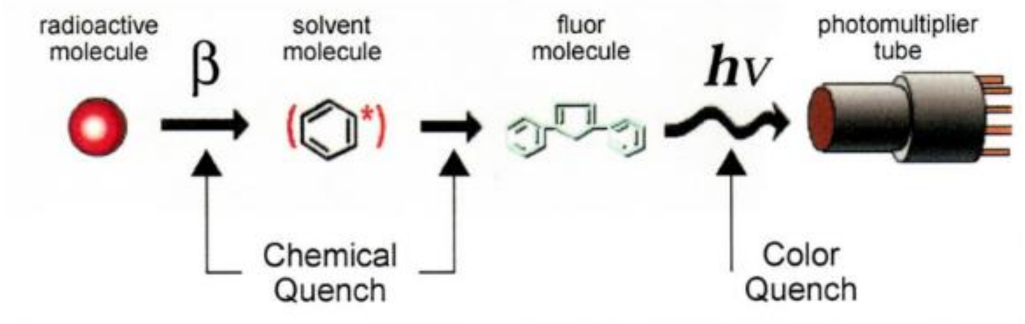
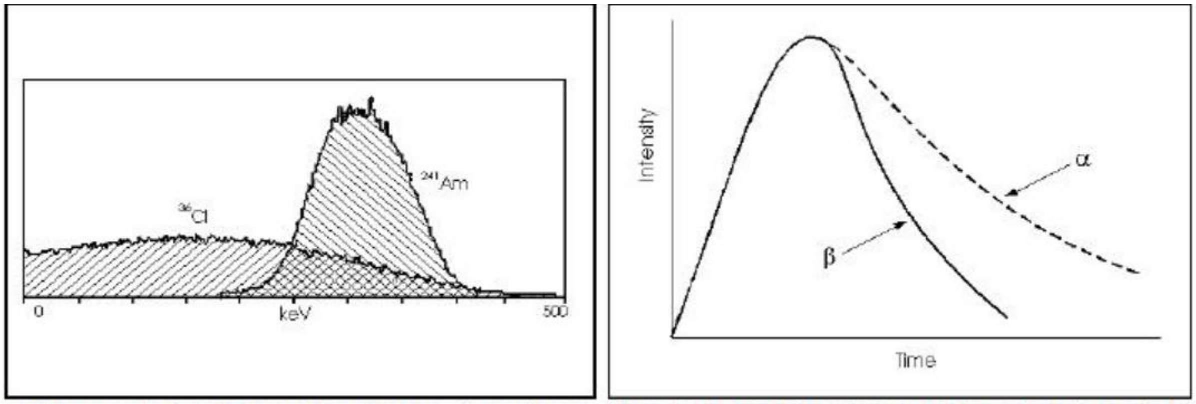


Figure 15: Quenching in the energy transfer process **(50)**

3.2.1 ALPHA/BETA DISCRIMINATOR

Liquid scintillation counting with alpha/beta discrimination capability is an effective method for the determination of gross alpha/gross beta activity. A Pulse Decay Analysis (PDA) may be employed to discriminate alpha events from beta events in samples based on the pulse shape and the duration of the light pulse (Figure 16). The pulse duration for alpha particles is typically longer than for betas. During counting, alpha and beta events are recorded in two different multichannel windows. (51)



Multichannel Analyzer Display Alpha/Beta LSC - ^{241}Am and ^{36}Cl Characteristic Light Pulse Shapes of Alpha and Beta Pulses in LSC

Figure 16: Example of alpha/beta discrimination for ^{36}Cl and ^{241}Am **(51)**

CHAPTER 4: DIRECT MEASUREMENT OF RADIUM IN PROCESSED FLUIDS USING HPGE GAMMA SPECTROMETRY

4.1 RADIUM AND HPGe MEASUREMENTS

Gamma-ray spectrometry is widely used for measuring the radioactivity in water because the sample can be preserved for further tests and does not require chemical alteration. The DOE method, Ga-0 1-R/901.1, "Gamma-emitting radionuclides in drinking water", is well-established for the determination of the levels of ^{228}Ra and ^{226}Ra, in environmental samples. (52) For ^{226}Ra gamma spectrometry (3- to 5-day measurement), a direct count can be determined at the 186.1 keV peak. Due to the proximity of the 185.7 keV ^{235}U gamma emission, the discrimination between the two energies is inaccurate or impossible. Results will be biased high when ^{235}U is present, because the ^{235}U activity is counted as ^{226}Ra. Counting without accounting for ^{235}U is generally accepted in most states as the activity is biased high. The bias is irrelevant when the high bias result is below the regulatory standard. Additionally, only a small amount of natural U is extracted during the hydraulic fracturing process due to the insolubility of U under the reducing conditions in the shale. (53)

Ra-226 gamma spectrometric analysis may also quantify ^{214}Pb and ^{214}Bi progeny by assuming secular equilibrium, and reporting the average of the ^{214}Pb and ^{214}Bi activities as ^{226}Ra (54). Assuming secular equilibrium is generally considered more accurate because of the higher gamma emission yield of the progeny.

Measurements of ^{228}Ra radium activities may be performed simultaneously with ^{226}Ra by measuring its closest progeny, ^{228}Ac, after reaching secular equilibrium in the sample (2 days). Table 5 summarizes the main gamma lines and yields used for the determination of ^{226}Ra/^{228}Ra in environmental samples.

Table 6: Main gamma lines used for the determination of radium isotopes **(55)**, **(56)**

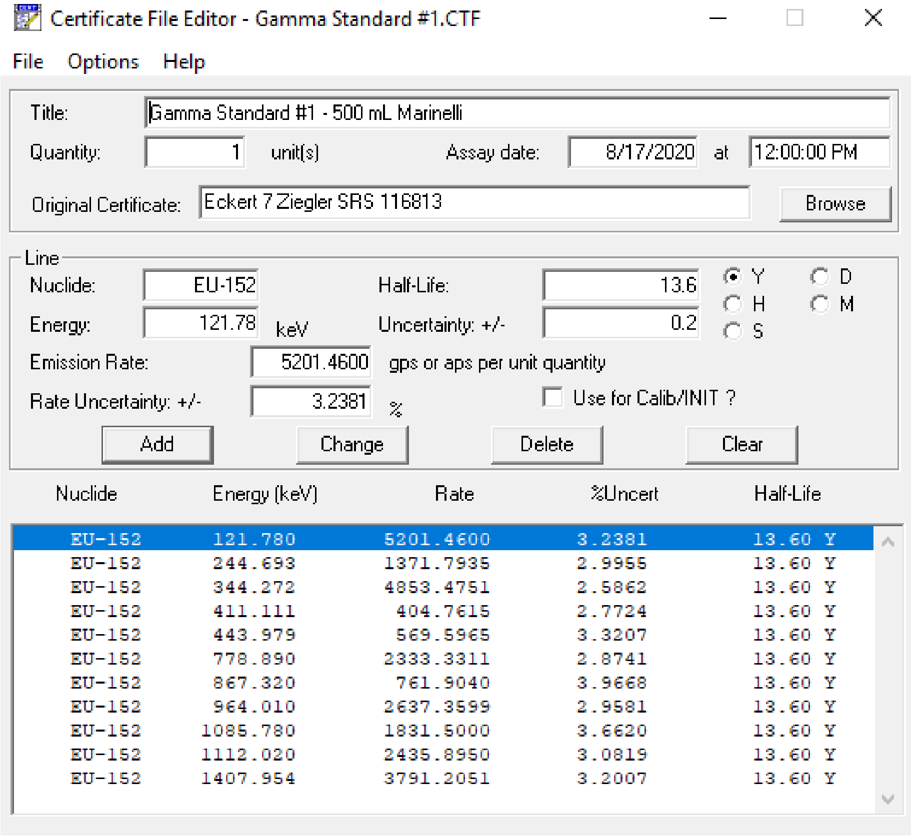
Radionuclide	Progeny	Energy (keV)	Gamma emissions probability (%)
^{226}Ra	^{226}Ra	186.1	3.57
	^{212}Pb	295.2	18.5
		351.92	38.5
	^{214}Bi	609.3	44.8
		1,120.4	14.8
^{228}Ra	^{228}Ac	338.3	11.3
		911.2	26.6
		969	16.2

4.2 METHODS

Eight different process fluids of unknown compositions were analyzed for their radium concentrations. A 500 mL aliquot of each sample was transferred into a Marinelli beaker. The lid was sealed with parafilm to prevent radon from escaping the sample. A blank sample was prepared with 500 mL of deionized water and a standard sample of 18,315 ± 385Bq of ^{152}Eu, was made in the same geometry.

Each sample, including the blank, was counted for 24 hours and again for 5 days on a coaxial HPGe (ORTEC Model: GEM-35190-S, Tennessee, Oak Ridge) of 35% relative efficiency.

The efficiency and energy calibration curves were generated using a standard ^{152}Eu solution prepared with a known activity. The standard sample was counted for 24 h on the HPGe. A certificate file was generated using the GENIE-2000 certificate file editor and applied to the standard spectrum (Figure 17). The resulting energy and efficiency calibration was applied to each spectrum (Figures 18 & 19).



Title: Gamma Standard #1 - 500 mL Marinelli

Quantity: 1 unit(s)   Assay date: 8/17/2020 at 12:00:00 PM

Original Certificate: Eckert 7 Ziegler SRS 116813

Nuclide: EU-152   Half-Life: 13.6   ● Y ○ D ○ H ○ M ○ S

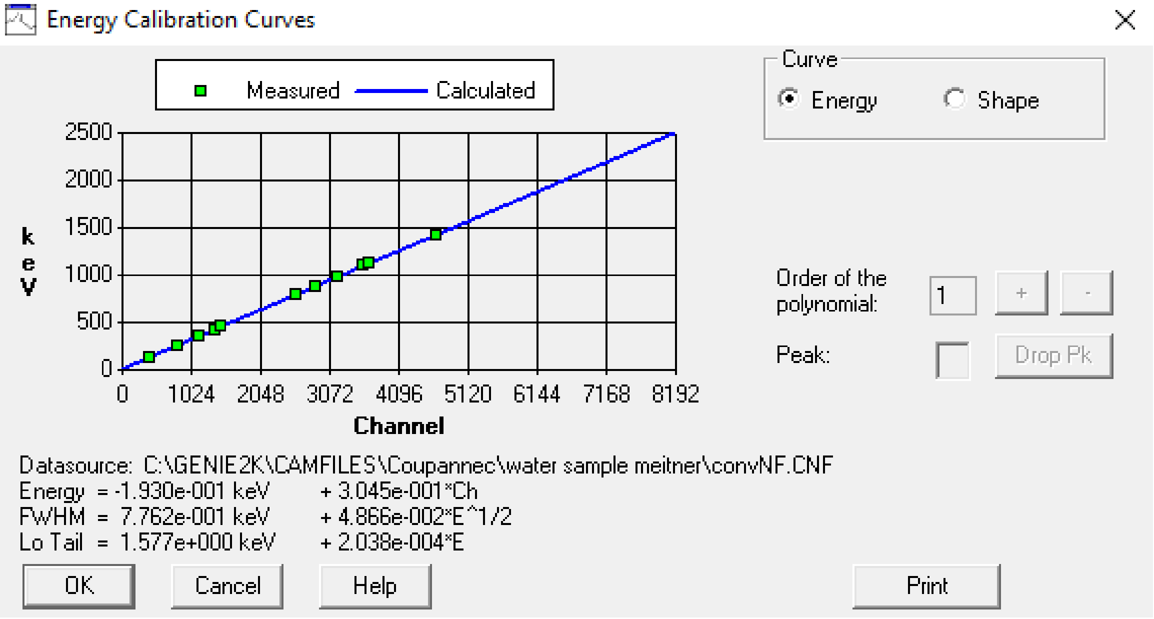
Energy: 121.78 keV   Uncertainty: +/- 0.2

Emission Rate: 5201.4600 gps or aps per unit quantity

Rate Uncertainty: +/- 3.2381 %   ☐ Use for Calib/INIT ?

Nuclide	Energy (keV)	Rate	%Uncert	Half-Life
EU-152	121.780	5201.4600	3.2381	13.60 Y
EU-152	244.693	1371.7935	2.9955	13.60 Y
EU-152	344.272	4853.4751	2.5862	13.60 Y
EU-152	411.111	404.7615	2.7724	13.60 Y
EU-152	443.979	569.5965	3.3207	13.60 Y
EU-152	778.890	2333.3311	2.8741	13.60 Y
EU-152	867.320	761.9040	3.9668	13.60 Y
EU-152	964.010	2637.3599	2.9581	13.60 Y
EU-152	1085.780	1831.5000	3.6620	13.60 Y
EU-152	1112.020	2435.8950	3.0819	13.60 Y
EU-152	1407.954	3791.2051	3.2007	13.60 Y

Figure 17: 500 mL ^{152}Eu standard certificate file



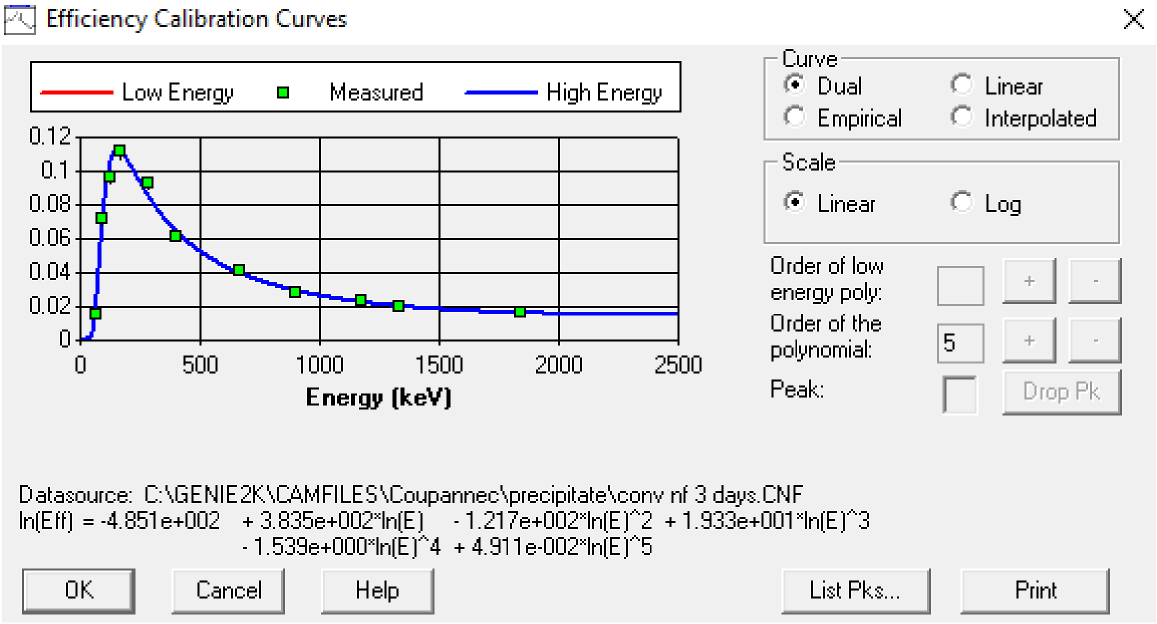
Curve: ● Energy ○ Shape

Order of the polynomial: 1

Peak: ☐

Datasource: C:\GENIE2K\CAMFILES\Coupannec\water sample meitner\convNF.CNF
Energy = -1.930e-001 keV + 3.045e-001*Ch
FWHM = 7.762e-001 keV + 4.866e-002*E^1/2
Lo Tail = 1.577e+000 keV + 2.038e-004*E

Figure 18: 500 mL Eu-152 standard energy calibration



Curve
● Dual ○ Linear
○ Empirical ○ Interpolated

Scale
● Linear ○ Log

Order of the polynomial: 5

```
Datasource:  C:\GENIE2K\CAMFILES\Coupannec\precipitate\conv nf 3 days.CNF
ln(Eff) = -4.851e+002   + 3.835e+002*ln(E)    - 1.217e+002*ln(E)^2  + 1.933e+001*ln(E)^3
                        - 1.539e+000*ln(E)^4  + 4.911e-002*ln(E)^5
```

Figure 19: 500 mL ^{152}Eu standard efficiency calibration

The detection efficiency at given energy was internally calculated by the software using the following equation:

$$\varepsilon(E) = \frac{S}{T_{1\times} y \times A \times K \times U_f} \qquad \text{(Equation 3)}$$

where S is the net peak area of the calibration peak,

A is the activity

T_1 is the counting time,

y is the branching ratio of the gamma energy under consideration

K is the correction factor for the nuclide decay

U_f is the sample activity unit conversion factor

The spectra were background corrected using the blank spectrum and analyzed using the GENIE-2000 software and the STDL standard library. The mass of the water sample was entered in the sample information field to obtain an accurate and precise activity per gram. The standard library was modified to obtain the minimum detectable activity (MDA) for all isotopes of interest, namely ^{226}Ra, ^{228}Ac, ^{214}Bi, and ^{214}Pb. The MDA automated calculation was enabled by authorizing it in the "more..." setting for each isotope in the library. The physical properties such as gamma yield and half-life were left unmodified.

Each spectrum was analyzed by following the steps:

- Unidentified second differential peak analysis, with the peak discriminator set to 2.00
- Sum/Non-linear LSQ fit peak area analysis
- Peak area correction and background subtraction
- Dual efficiency correction
- Nuclide Identification (NID) (To obtain the 186 keV activity of ^{226}Ra)
- NID with correlation interference to obtain the ^{228}Ac, ^{214}Bi, ^{214}Pb respective activities in the sample
- Currie MDA to obtain the minimum detectable activity of each isotope in the sample with a confidence factor set to 5%.

The Currie MDA was chosen as it is widely accepted and used. The Currie method is based on two statistically important quantities: a critical level, L_c, and a detection limit, L_d. The former is the quantity below which a net signal cannot be reliably detected and is considered a detection sensitivity with a Type I error of 5%. The latter is the smallest net signal that can reliably be quantified or the lower limit of detection with both Type I and II error of 5% (57).

Mathematically, the critical level is defined as:

$$L_C = k\sqrt{B + \left(\frac{T_s}{T_b}\right) I_b + \left(\frac{N}{2n}\right)^2 (B_1 + B_2) + \left(\frac{T_s}{T_b}\right)^2 \sigma_{ib}^2} \qquad \text{(Equation 4)}$$

And the detection limit is defined as:

$$L_D = k^2 + 2L_C \qquad \text{(Equation 5)}$$

Where B is the value of the continuum peak subtracted, k is the confidence level factor, I_b is the net peak area of the background measurement, σ_{ib} is the uncertainty on the net peak area of the background measurement, T_s and T_b are the counting time of the sample and the background measurements, N is the number of channels in the peak region, n is the number of channels on each side of the peak region, and B_1 and B_2 are the number of counts to the right and left of the centroid in the peak area.

In gamma spectrometry, the MDA per unit of sample mass is defined and calculated with the following equation:

$$\text{MDA} = \frac{L_D}{T_s \times \varepsilon' \times y \times V \times K_c \times C_f \times U_f} \qquad \text{(equation 6)}$$

Where ε' is the attenuation corrected efficiency

y is the branching ratio of the gamma energy under consideration

V is the mass or volume of the sample

K_C is the correction factor for the nuclide decay during counting

C_f is the sample mass unit conversion factor

U_f is the sample activity unit conversion factor

4.3 RESULTS

Ra-226 analysis was performed by examining the 186.2 keV gamma line with a yield of 3.51%. Results from the analysis are reported in Figure 20. The 500 mL aliquots of processed fluids were first counted for 24 hours. The mean ^{226}Ra activity measured ranged from 0 Bq/L to 5.7 Bq/L. The uncertainty of the activity was larger than the measurement, suggesting poor accuracy of the results. Additionally, the MDA analysis revealed that the mean ^{226}Ra activities were all below the detection limits. Therefore, the 24 hour measurements were not adequate to obtain statistically satisfactory results. The samples were recounted for 5 days to improve the measurement accuracy. The mean ^{226}Ra activity measured dramatically increased and ranged from 10.07 Bq/L to 17 Bq/L. The uncertainty on the activity varied between 8.38% and 11.6% of the measurements. All activities were found above the MDAs.

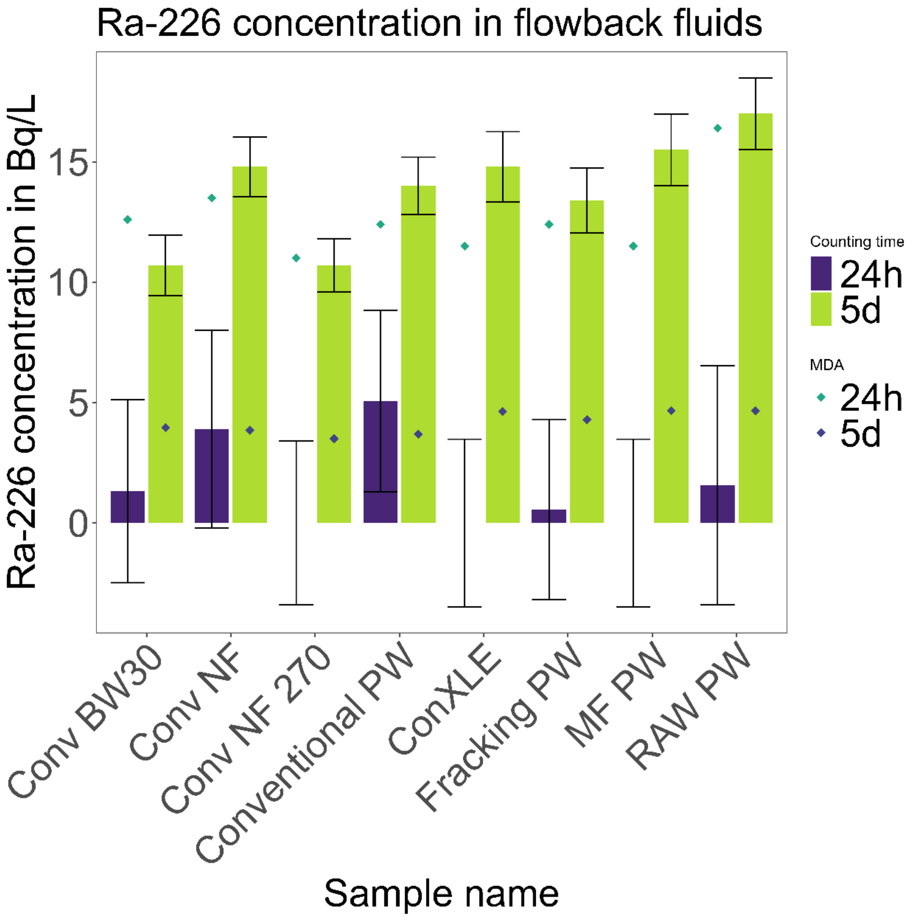


Figure 20: ^{226}Ra HPGe measurements at the 186.2 keV gamma line in process fluids for 24 hours and 5 days

To achieve better accuracy ^{226}Ra analyses were performed by measuring the progeny's activities in secular equilibrium (Figure 21). Similar to the ^{226}Ra direct measurement, the spectra obtained after a 24 hour counting time did not provide adequate results as the uncertainties were large and most activities were found below the MDA. The analyses were performed again after a five-day count time and the resulting ^{214}Pb and ^{214}Bi activities were more accurate. For most samples, the mean ^{214}Bi activity decreased compared to the 24 hours count time suggesting that radon escaped the sample with increasing time. All activities were above the MDA and uncertainties generally improved compared to the ^{226}Ra 186 keV evaluation, except for the Con BW30 sample.

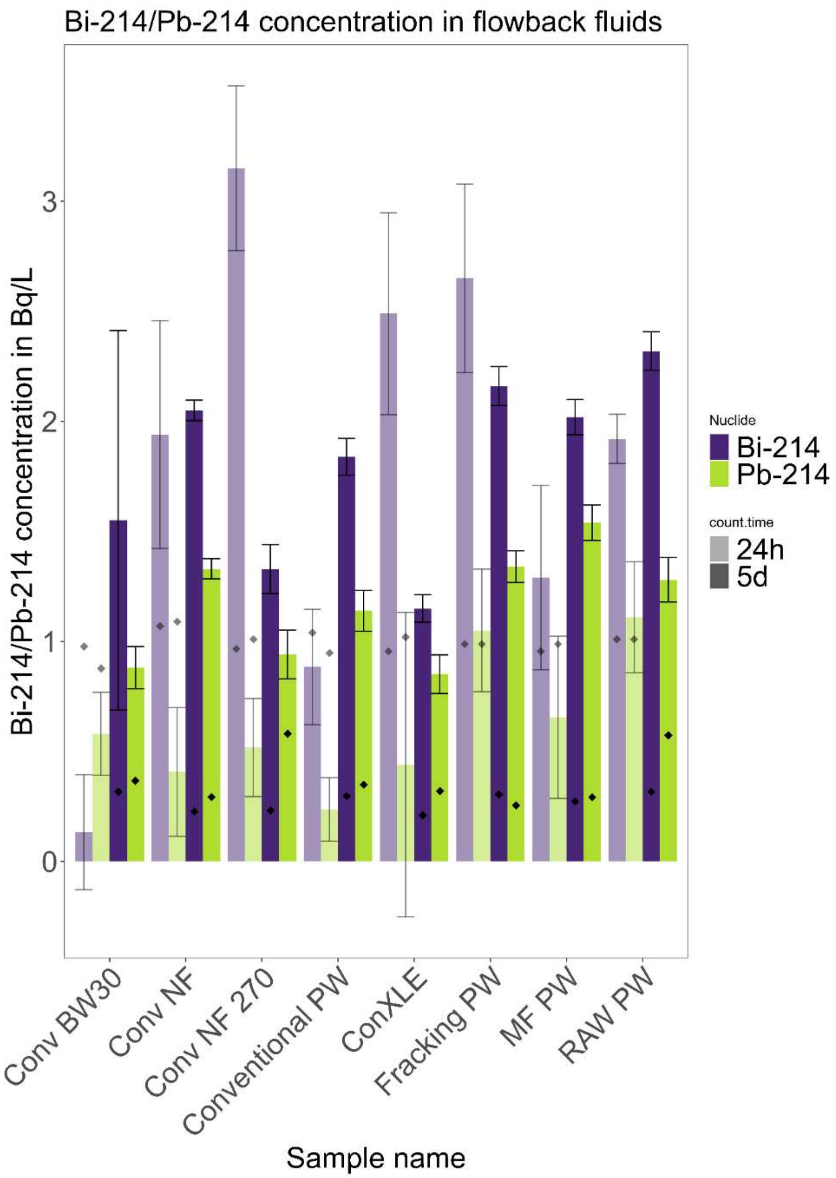


Figure 21: ^{214}Bi and ^{214}Pb HPGe measurements in processed fluids counted for 24 hours and 5 days

The results of the ^{214}Pb and ^{214}Bi activities in the samples disagree with the assumption that the ^{226}Ra was in equilibrium with its closest progeny. Pb-214 and ^{214}Bi activities are found to be incoherent throughout all samples instead of being within the margin of uncertainties of one another. Additionally, Figure 22 reinforces this assumption as it demonstrates that the ^{226}Ra activities found by using the 186.2 keV signal are an order of magnitude above the ^{214}Pb and ^{214}Bi activities. The unequal activities suggest that the samples were improperly sealed allowing radon to escape and therefore reducing the ^{214}Pb and ^{214}Bi signals. The 186.2 keV signal may also be biased high because of the 185.7 keV peak overlap of ^{235}U present in the waste fluids. As the HPGe is incapable of distinguishing the two peaks, the ^{226}Ra magnitude of the peak may be higher than due to the ^{235}U photons, introducing a greater imbalance between the ^{226}Ra, ^{214}Pb, and ^{214}Bi activities.

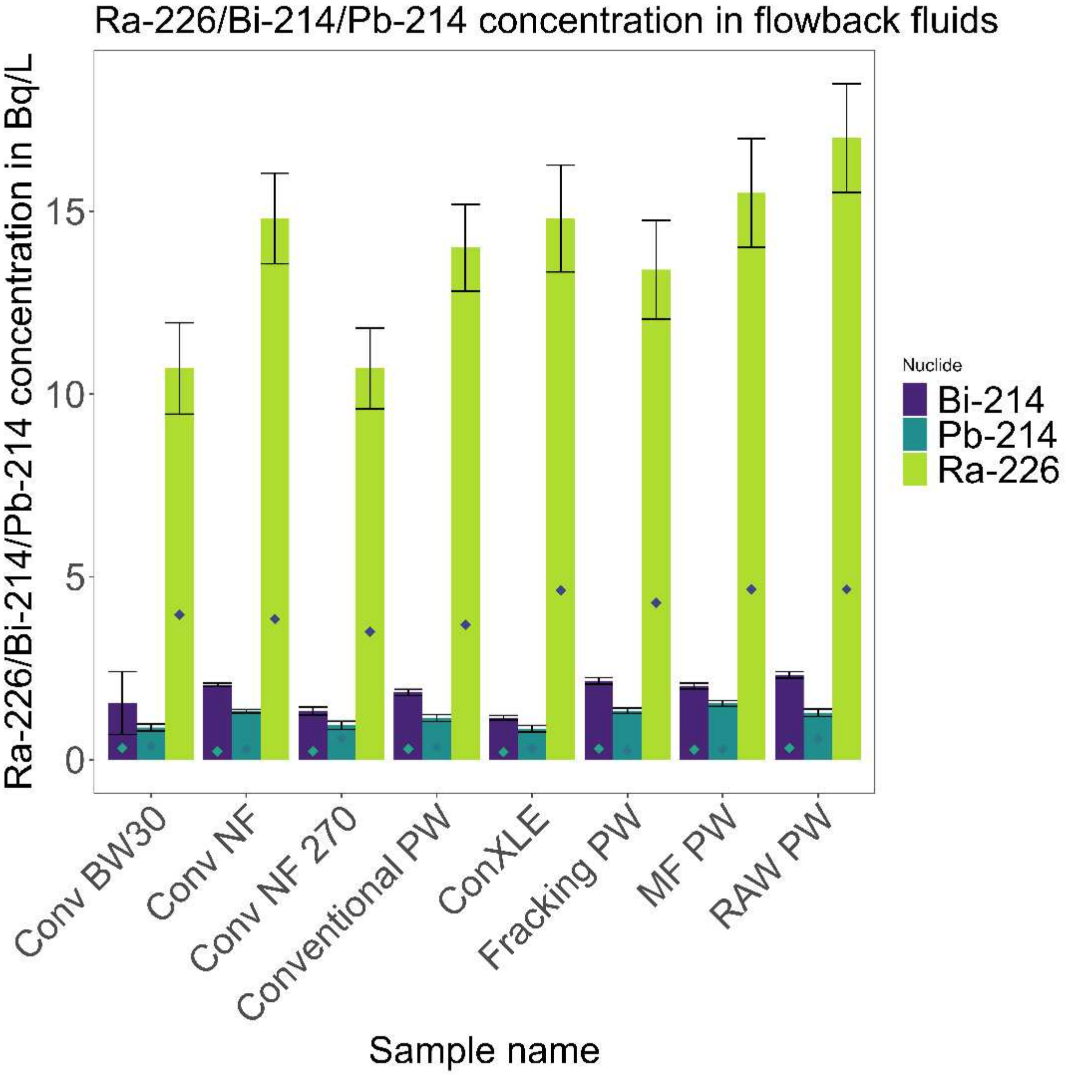


Figure 22: ^{226}Ra, ^{214}Bi, and ^{214}Pb HPGe measurements in processed fluids counted for 5 days

Figure 23 shows the ^{228}Ra activity in the sample and Figure 24 summarizes the difference between ^{226}Ra and ^{228}Ra concentration. Once more, the 24-hour counting time spectra showed little reliability as most activity values were below the MDA and the uncertainties in the measurements were large. The samples counted for five days were more accurate. The ^{228}Ra activity concentrations were between 0.88 Bq/L to 1.7 Bq/L. The ^{228}Ra/^{226}Ra ratios ranged from 7.9% to 17.4%. All samples were one order of magnitude below the above pCi/L (0.185 Bq/L) drinking water standard for Ra^{226} and Ra^{228} combined, so the processed fluids are exempted from radium regulations according to the CRCPD.

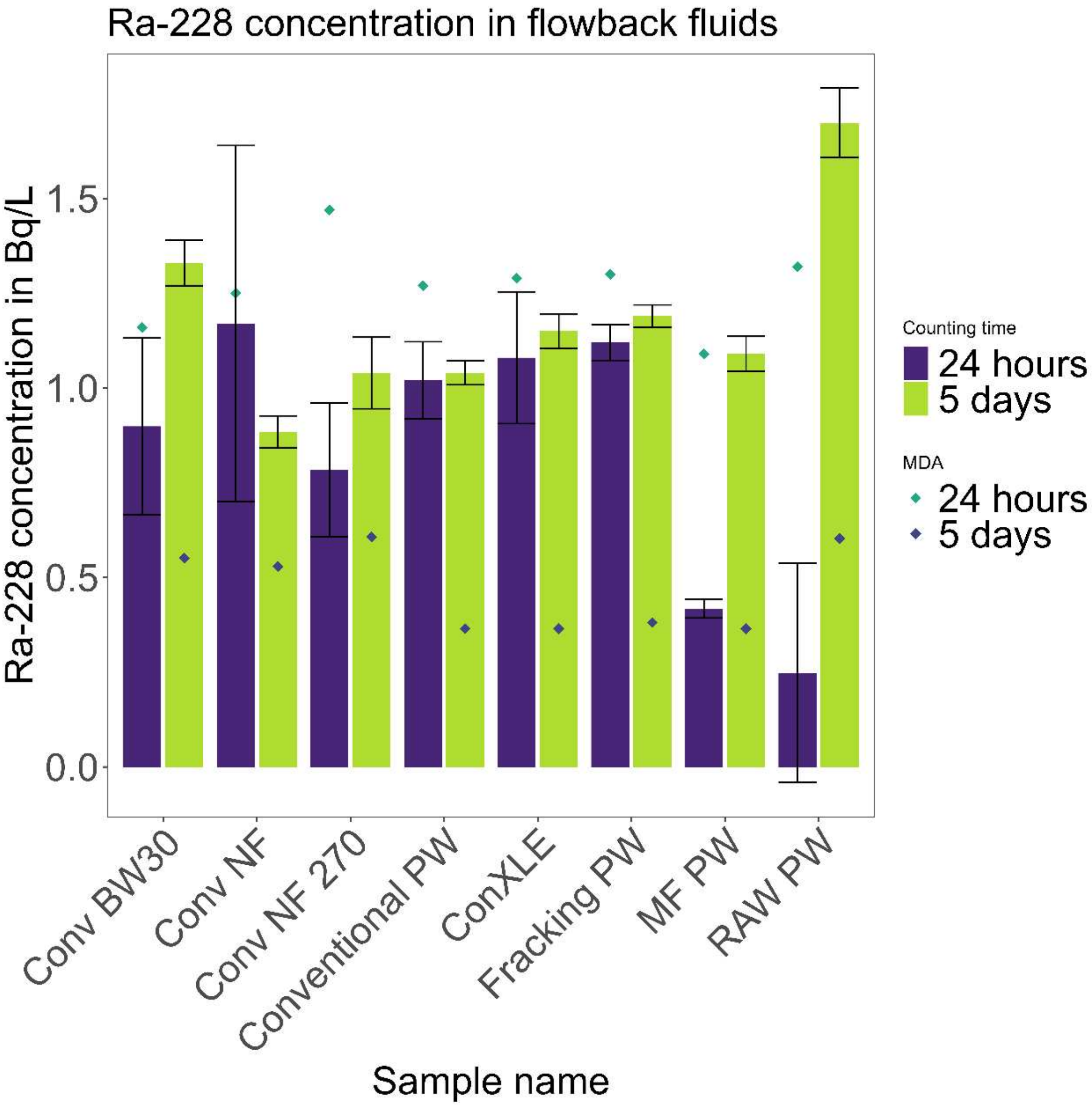


Figure 23: ^{228}Ra HPGe measurements in processed fluids counted for 24 hours and 5 days

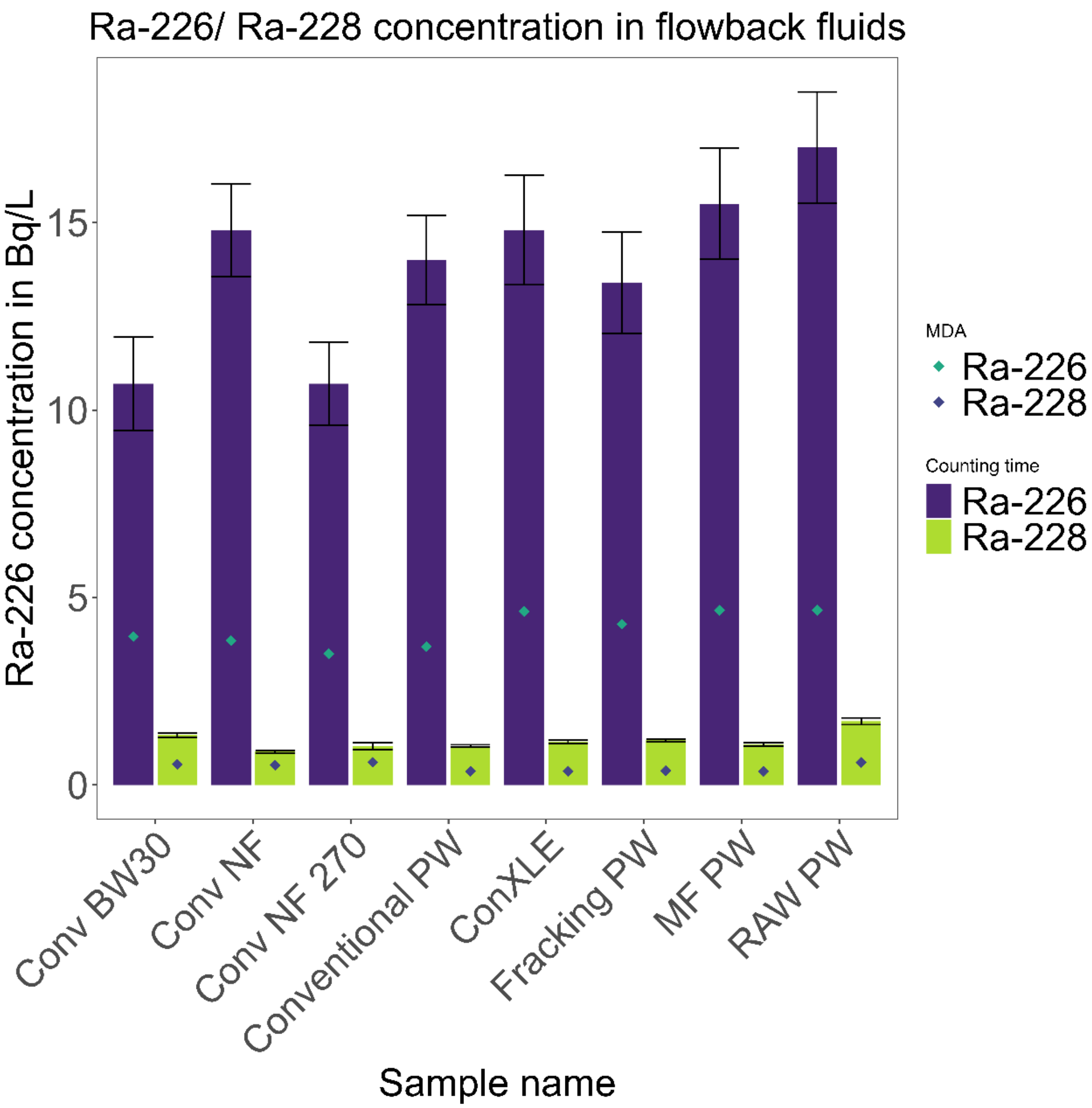


Figure 24: ^{228}Ra and ^{226}Ra HPGe measurements in processed fluids counted for five days

4.4 DISCUSSION

The HPGe gamma spectra revealed that a counting time of five days was necessary for each isotope analysis in order to obtain satisfactory results on the raw processed fluids. All samples counted for 24 hours did not reach the MDA activities and therefore were unacceptable. Since the industry desires results faster than 5 days, increasing the sample size or concentrating the radium is necessary before reliable analysis can be achieved. Radium determination through the analysis of the ^{214}Pb and ^{214}Bi peak areas is even more time-consuming as the samples need to be stored over 22 days to reach equilibrium. Moreover, ^{214}Pb and ^{214}Bi were not in equilibrium with ^{226}Ra suggesting the samples were not properly sealed or the 186.2 keV signal was overly biased because of the ^{235}U present in the fluids. Parafilm may not be an appropriate sealant to achieve equilibrium for radium analysis in environmental samples, and teflon tape, electrical tape, or steel can containers may be more suitable. (54)

CHAPTER 5: PRECONCENTRATION AND CHARACTERIZATION OF RADIUM IN FLOWBACK WATER USING HPGe GAMMA SPECTROMETRY

5.1 INTRODUCTION

In 1980, the Georgia Tech approach for the determination of radium by gamma spectroscopy was developed to quantify and determine the combined ^{226}Ra and ^{228}Ra concentration in drinking water (Figure 25). In 2004, the method was approved by the EPA. (58) The Georgia Tech approach fulfilled the need for a new screening procedure where a larger water sample (1 gallon) could be analyzed with a detection limit of 1 pCi/L at the 95% confidence level. (58) The protocol is similar to the EPA Methods 903 and 903.1 as it involves the precipitation of radium together with barium sulfate. The 3.78 L sample is first acidified with concentrated (12 N) hydrochloric acid. A 5 ml barium carrier (88 mg $BaCl_2.2H_20$) is used because radium is only present in very small quantities in the environment and cannot be precipitated alone. Thus, the addition of a carrier in solution before the precipitation is required. Radium does not have any stable isotopes so barium, its nearest chemical analogue, is therefore preferred as a carrier. To start the precipitation process, 20 mL of 18 N sulfuric acid is added and the solution is heated to a boil. The precipitate is allowed to settle overnight and is collected on a tared glass fiber filter (Gelman type A/E, 47 mm diameter) using vacuum filtration. The filter is washed with 10 mL of ethanol and 10 mL of diethyl ether and is dried under a heat lamp. Unlike methods 903 and 903.1, gamma-ray spectral analysis was chosen as it is not affected by self-attenuation, and it permits simultaneous measurement of ^{226}Ra and ^{228}Ra. The natural radiation background is stripped from the sample spectrum obtained in a 10 minutes counting time. To align with the other EPA methods the samples must be counted long enough to obtain a 0.004 Bq/L MDA for ^{226}Ra (^{214}Pb + ^{214}Bi) and 0.04 Bq/L for ^{228}Ra.

In 2020, Nguyen et. al. showed that longer counting times were often required to obtain the 0.04 Bq/L MDA for ^{228}Ra depending on the efficiency of the gamma detector. Additionally, a loss of ^{222}Rn during the progeny ingrowth period could reduce the yield of ^{226}Ra during quantification using the lead and bismuth gamma peaks. Nguyen et. al. modified the original Georgia Tech gamma method by sealing the precipitate inside a petri dish enclosed in a Marinelli beaker and in an attempt to decrease the loss of ^{226}Ra progenies due to radon escape. (59)

The Georgia Tech approach is investigated in this work to determine the validity of the method to quantify ^{226}Ra and ^{228}Ra in flowback fluids. Successfully concentrating radium could allow the HPGe detection limit to be reached faster and therefore, provide an improved screening method. The impact of the sealing of the precipitate on the method

was meant to be explored but was abandoned due to time constraints.

5.2 METHOD

A 200 mL aliquot of the brine was transferred into a 400 mL borosilicate glass beaker (VWR). A 405 µL (1.5 Bq) aliquot of a ^{133}Ba radiotracer solution with an activity of 3.705 kBq/L was added to assess the radium recovery. To determine the yield of the separation, the gamma-emitting ^{133}Ba radiotracer was used since no suitable radium radiotracer is available. (60) The solutions were acidified with 12 N HCl to pH 2. The acid was added gradually in 10 µL increments and the pH was measured simultaneously on a calibrated Five Easy FE20 pH meter (Mettler Toledo). Five mL of a 9 mg/mL barium carrier $BaCl_2.2H_2O$ solution was added to each sample. The solutions were stirred using a Fisher Scientific magnetic stirring plate and brought to a boil. The samples were cooled to room temperature, 10 mL of 18N H_2SO_4 was added in small portions, and the solutions were stirred for 30 minutes. After settling overnight, the precipitates were collected on a pre-weighed 47 mm 45µm pore size membrane filter (Pal Corporation) using a vacuum filtration setup and rinsed with 20 mL of DI water. The precipitates were dried in a Thermolyne F600 oven at 105-110°C. The precipitates were massed and mounted into a petri dish. The petri dishes were sealed with parafilm and stored in a cool, dry environment for 22 days.

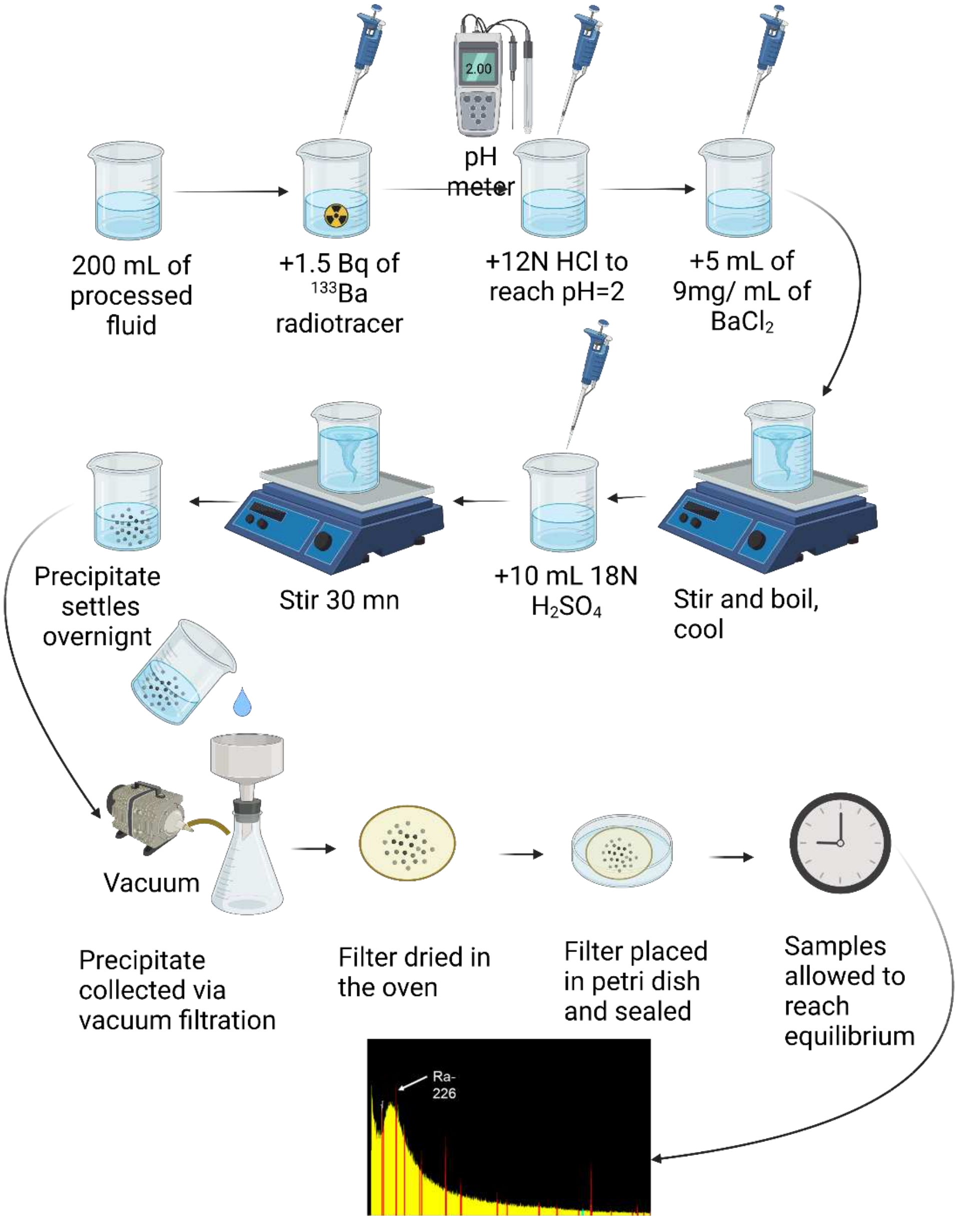
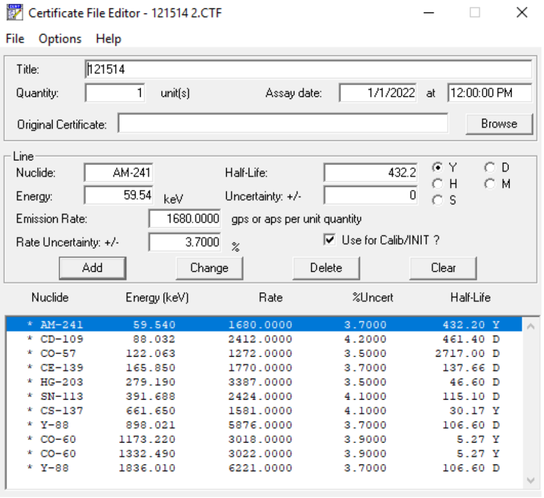


Figure 25: Protocol of the improved Georgia Tech method created with BioRender.com

Each sample was counted for 3 days on a coaxial HPGe (ORTEC Model: GEM-35190-S) with a 35% relative efficiency. The energy and efficiency calibrations were obtained using a certified Eckert & Ziegler mixed gamma filter (Figures 26 & 27) counted in the same geometry as the samples. The background was obtained by counting a blank filter sealed in a Petri dish for three days. Each spectrum was analyzed following the protocol stated in Chapter 4.

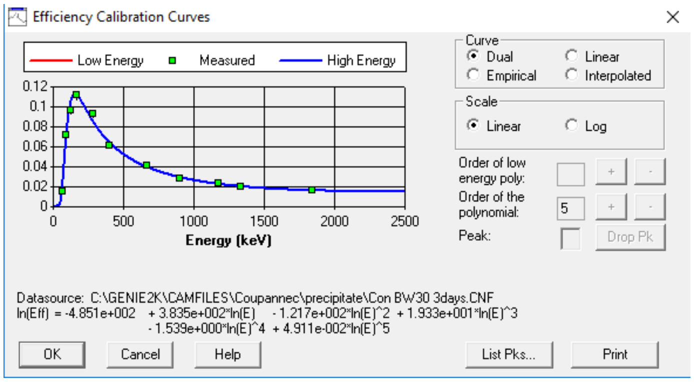


Title: 121514
Quantity: 1 unit(s)
Assay date: 1/1/2022 at 12:00:00 PM
Original Certificate:

Nuclide: AM-241
Energy: 59.54 keV
Half-Life: 432.2 ● Y ○ H ○ S ○ D ○ M
Uncertainty: +/- 0
Emission Rate: 1680.0000 gps or aps per unit quantity
Rate Uncertainty: +/- 3.7000 %
☑ Use for Calib/INIT ?

	Nuclide	Energy (keV)	Rate	%Uncert	Half-Life
*	AM-241	59.540	1680.0000	3.7000	432.20 Y
*	CD-109	88.032	2412.0000	4.2000	461.40 D
*	CO-57	122.063	1272.0000	3.5000	2717.00 D
*	CE-139	165.850	1770.0000	3.7000	137.66 D
*	HG-203	279.190	3387.0000	3.5000	46.60 D
*	SN-113	391.688	2424.0000	4.1000	115.10 D
*	CS-137	661.650	1581.0000	4.1000	30.17 Y
*	Y-88	898.021	5876.0000	3.7000	106.60 D
*	CO-60	1173.220	3018.0000	3.9000	5.27 Y
*	CO-60	1332.490	3022.0000	3.9000	5.27 Y
*	Y-88	1836.010	6221.0000	3.7000	106.60 D

Figure 26: Certificate file mixed gamma standard filter



Curve: ● Dual ○ Linear ○ Empirical ○ Interpolated
Scale: ● Linear ○ Log
Order of low energy poly:
Order of the polynomial: 5
Peak: ☐

Datasource: C:\GENIE2K\CAMFILES\Coupannec\precipitate\Con BW30 3days.CNF
ln(Eff) = -4.851e+002 + 3.835e+002*ln(E) - 1.217e+002*ln(E)^2 + 1.933e+001*ln(E)^3 - 1.539e+000*ln(E)^4 + 4.911e-002*ln(E)^5

Figure 27: Efficiency calibration curve of the mixed gamma standard filter

5.3 RESULTS

The ^{133}Ba radiotracer peaks were easily identified in the spectrum and were dominant. The recovery of the radiotracer ranged from 79 to 90% which indicated that the radium coprecipitation with barium sulfate had a good yield across all the samples (Figure 28).

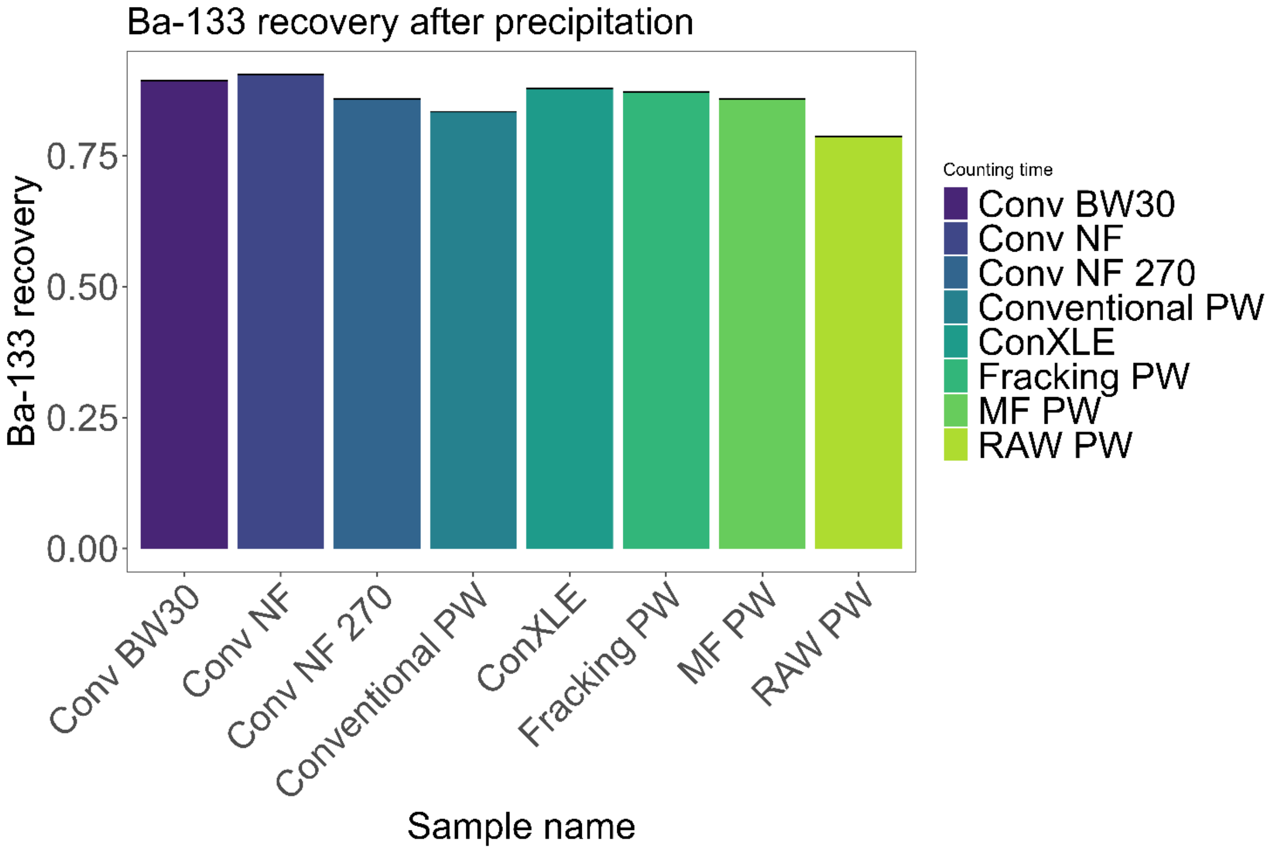


Figure 28: Recovery of the ^{133}Ba radiotracer

The analysis of ^{226}Ra at the 186.1 keV gamma line and ^{228}Ac shown in Figure 29 revealed that, after a three-day count, the activities in the sample did not reach the detection limits. The activity precipitated from the raw water did not correlate with the activity measured by gamma analysis of the raw water samples. Since the activities found are below the MDA, no statistical conclusion can be made. The MDAs were significantly higher than the required 0.004 Bq/L and 0.04 Bq/L and ranged from 6 to 8 Bq/L for the ^{226}Ra peak and 0.68 to 1.1 Bq/L for ^{228}Ac. The elevated MDAs suggest that a longer counting time, increased volume samples, method adjustments, or a lower background are required.

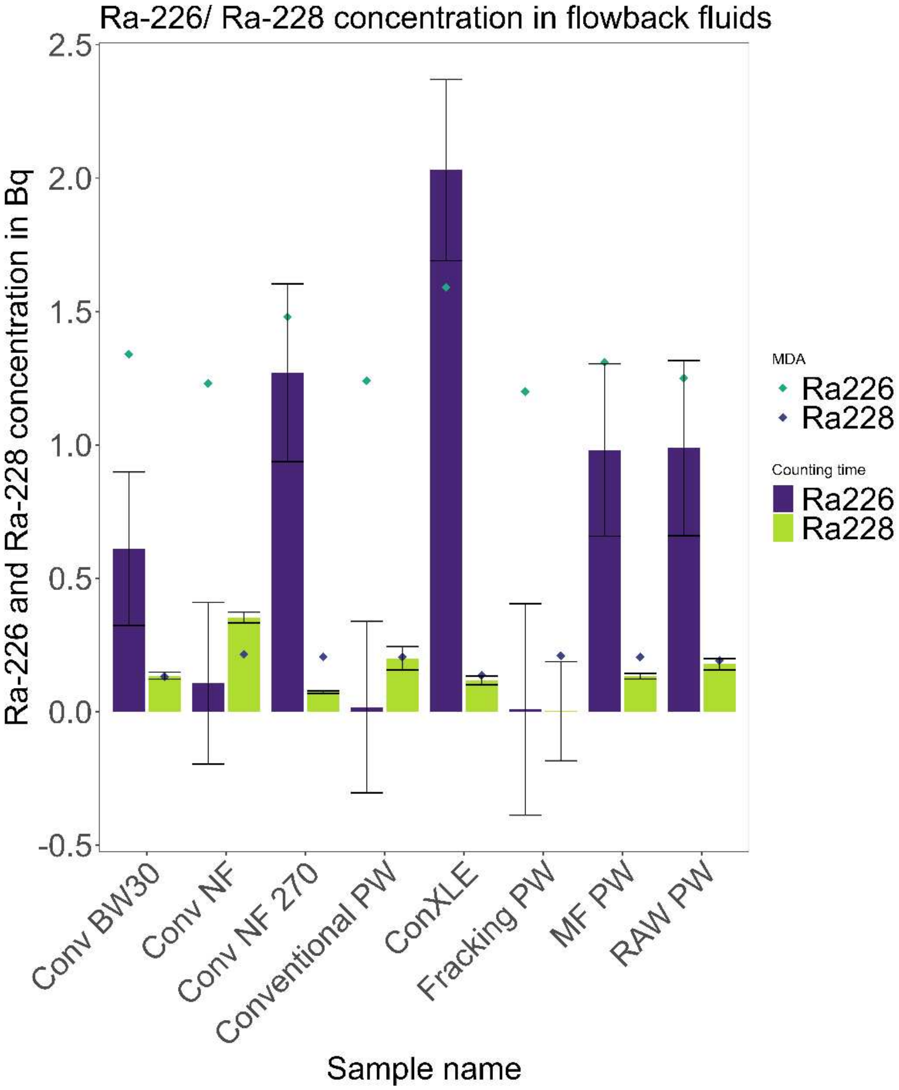


Figure 29: ^{226}Ra and ^{228}Ra activities of the precipitate analyzed by HPGe gamma spectrometry

Figure 30 shows the ^{214}Pb and ^{214}Bi activities compared to the ^{226}Ra activities. Most ^{214}Pb signals did not exceed the MDA, so no statistical conclusions could be reached. The results of the ^{214}Pb and ^{214}Bi activities in the precipitates are inconsistent with the assumption that the ^{226}Ra was in equilibrium with its closest progeny. ^{214}Pb and ^{214}Bi activities are found to be inconsistent and smaller than the activities at the ^{226}Ra peak. The Raw PW sample seems to show equilibrium of ^{214}Bi and ^{226}Ra to a better degree, but the

^{214}Pb activity disagrees with this assumption. The unequal activities suggest that the radon escaped during the ingrowth period, reducing the ^{214}Pb and ^{214}Bi signals due to the incomplete sealing of the samples. Again, the ^{214}Pb and ^{214}Bi MDAs of roughly 0.6 Bq/L were found above the prescribed detection limits.

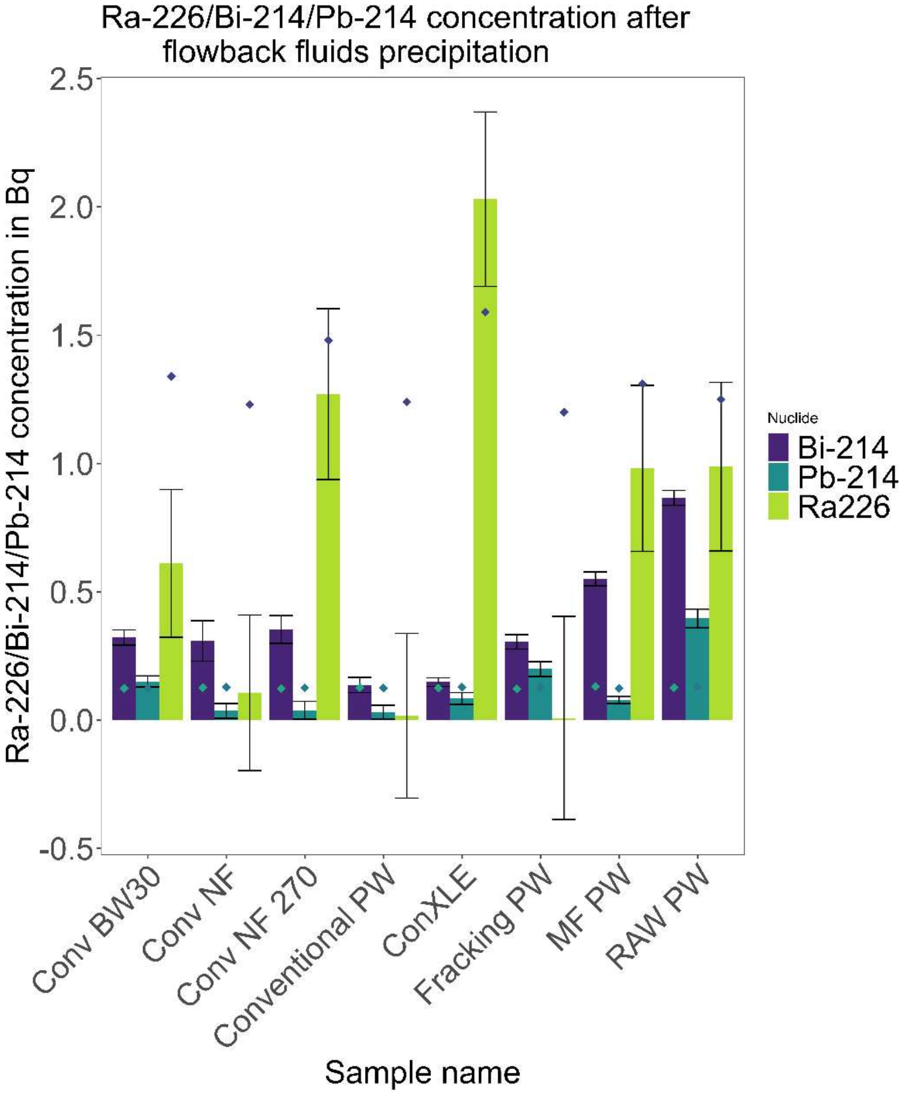
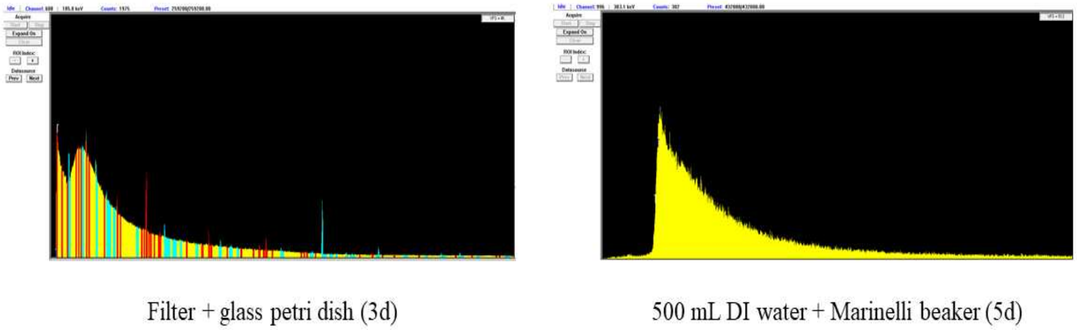


Figure 30: ^{226}Ra, ^{214}Pb, and ^{214}Bi activities in the precipitate analyzed by HPGe gamma spectrometry

The source of the elevated MDAs was further investigated to improve the protocol. Peak analysis of the background spectrum revealed an elevated background activity of the blank at all peaks of interest.

Results showed that the filter or the glass petri dish is responsible for the high radium background. Thus, the blank is very likely responsible for the higher MDAs. Different blanks were prepared to ensure that the high background was not due to accidental contamination, but the results were consistent across all trials. In contrast, the peak analysis of the 500 mL sample of deionized water used for the background subtraction in Chapter 4, did not have identifiable radium background (Figure 31).



Filter + glass petri dish (3d)

500 mL DI water + Marinelli beaker (5d)

Figure 31: Background spectrum comparison

Since the recovery of this method was satisfactory, the high radium concentration of the precipitate blank is assumed to be the cause of the bias of the precipitation gamma analysis. The activities found in the filter blank and the 500 mL of deionized water in a Marinelli beaker are reported in Table 6.

Table 6: Activities found in the blank for the radionuclides of interest

Blank	Nuclide	Activity in Bq	Activity uncertainty in Bq
filter	^{226}Ra	2.29	2.72E-02
filter	^{214}Pb	0.281	2.22E-03
filter	^{214}Bi	1.17	3.59E-03
filter	^{228}Ac	0.426	1.26E-03
filter	^{235}U	0.164	6.51E-04
Marinelli beaker +DI 500 mL	no peak identified		

5.4 FUTURE WORK

The coprecipitation of radium with barium sulfates is a promising approach to preconcentrate radium since the ^{133}Ba recoveries were high across all samples. Additional investigation is required to decrease the background radioactivity of the blank in an attempt to lower the MDAs. Different filters and plastic Petri dishes should be tested as they are suspected to be the major source of bias. The impact of the sample volume on the yield, MDA, and counting time should be investigated as increasing the sample size is expected to lower the MDAs and provide a faster measurement. An alternative sealing method should be adopted to restrict radon from escaping the sample. As proposed by Nguyen et. al., the precipitate shall be placed in a plastic petri dish sealed with epoxy sealant and enclosed in a BL container to decrease the loss of ^{226}Ra progenies.

CHAPTER 6: GROSS ALPHA DETERMINATION IN FRACKING WATER USING ACTINIDE RESIN AND LSC COUNTING

6.1 EXTRACTION CHROMATOGRAPHY

Extraction chromatography is a solid-liquid separation method used as an alternative to conventional liquid-liquid extraction as it produces less hazardous waste while maintaining selectivity. The chromatographic method was created more than 70 years ago after Siekierski and Winchester independently wrote about their results obtained with chromatographic columns after successfully separating inorganic substances in the process of reprocessing spent fuel. (62) Extraction chromatography is a separation technique where analytes in solution may be separated by allowing the sample analyte to be transported through a packed bed of the stationary phase. As the individual components of the mixture are transported through the packed bed, the separation occurs through differences in selectivity of the analytes for the solid phase. The analytes may adsorb onto the stationary phase impregnated with the extracting agent. Once the analyte is extracted onto the solid phase, desorption is required to transfer the bound analyte to an aqueous buffer or organic solvent. This step is called elution. Breakthrough of an analyte from the column is a function of its k', particle size, flow rate, and temperature.

Most extraction chromatographic resins have similar construction. They consist of an inert backbone made from inorganic material like silica gel or organic matrices such as microporous styrene-divinylbenzene copolymers (XAD resin). The extracting agent, which provides an interface for partitioning, is coated onto the backbone support. This stationary phase provides the chemical surface to which the analytes are selectively attracted. (63)

The weight distribution ratio, D_w, is a value that quantifies the affinity of an analyte for a specific resin. It can be obtained by measuring the amount of a given analyte taken up by a measured weight of resin from a given volume of an aqueous solution. The weight distribution ratio can be calculated with the following equation:

$$D_w = \frac{A_0 - A_S}{A_S} \times \frac{V_S}{M_r} \qquad \text{(Equation 7)}$$

- A_0 is the initial activity of the aqueous solution.
- A_0-A_s is the activity that was adsorbed onto the resin.
- M_r is the weight (g) of the resin.
- A_s is the activity of the aqueous solution
- V_s is the known volume (mL) of an aqueous solution.

However, for well characterized resins, the affinity of an analyte for a resin is usually expressed in terms of capacity factors, or k'. This factor includes the conversion of the weight distribution ratios to a retention factor by dividing the weight distribution ratio by the free column volume (FCV). This parameter corresponds to the amount of mobile phase that has to pass through the column before reaching the maximum elution peak of the analyte.

$$F = \frac{free\ collum\ volum}{mass\ resin} \qquad k' = \frac{D_W}{F} \qquad \text{(Equation 8 \& 9)}$$

6.2 ACTINIDE RESIN

Eichrom's Actinide Resin® is based on the DIPEX® Extractant shown in Figure 32 dissolved in isopropanol and adsorbed onto a styrene-based polymer matrix. The resin has a high affinity for the actinide elements in an acidic medium of less than 1M. The resin forms metal complexes of high stability by chelating actinides through either ionized or neutral diphosphonic acid ligands. The retention of actinides is superior on Actinide Resin than on TRU Resin, but this high affinity can be the pitfall of the resin since it is difficult to strip the actinides from the resin with aqueous solutions. Hence, the resin may be batch contacted with a water sample and counted directly by liquid scintillation for a rapid alpha and beta screening.

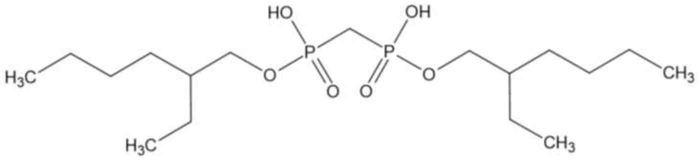


Figure 32: P,P' -di(2-ethylhexyl) methanediphosphonic acid, DIPEX extractant realised with ChemSketch (61 & 66)

This resin has been shown to be useful for the preconcentration of actinides from large aqueous samples and for the monitoring of actinides in aqueous discharges. This analysis is routinely used for gross alpha activity determination in drinking and nuclear wastewater samples in the Netherlands. (64) Since the actinide resin has a stronger affinity for the tri-, tetra-, and hexavalent oxidation states, alkaline earth metals are not as selectively retained as actinides (Figure 33). Alkaline earth capacity factors are at least 3 orders of magnitude below those of the actinides. Very little selectivity is exhibited among the alkaline earth metals. Their selectivity for phosphoric acids is assumed to decrease in the order $Ca^{2+} >> Sr^{2+} > Ba^{2+} > Ra^{2+}$.(34) Thus, competing ions such as Ca and Fe (for actinides) may have a negative influence on the preconcentration. (61 & 65)

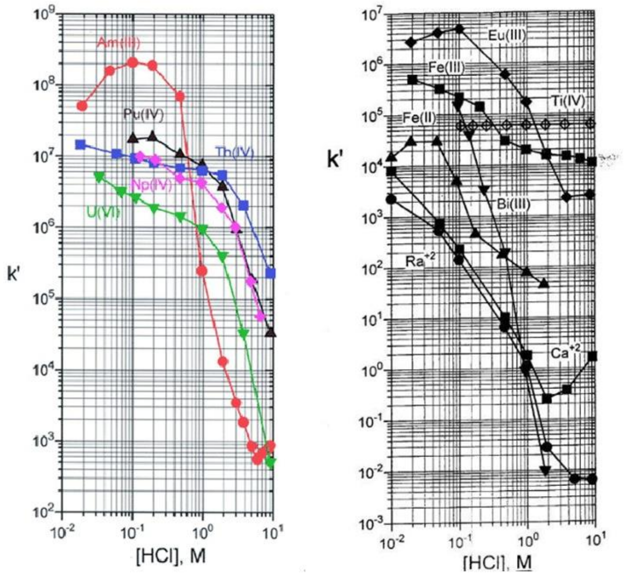


Figure 33: Uptake of several nuclides by the actinide resin (61)

6.3 OBJECTIVES

In an effort to simplify the rapid radiochemical method for gross alpha and beta activity concentration in flowback and produced water recently developed by the EPA (see Chapter 2), Actinide resin was investigated as a means to preconcentrate the Th, U, and Po in flowback and produced water from the oil and gas industry. This method would be faster and more cost effective as the preconcentration could occur by contacting the resin directly with an acidified sample. (66) Since radium is retained on the resin, to a lesser extent, a separation of radium from the sample might be investigated in the future to fulfil the need for a complete Ra, Th, U, and Po screening.

6.4 METHOD

A 250 mL aliquot of the processed fluids was collected into a 1 L VWR borosilicate glass beaker. The samples were acidified with concentrated HCl to pH 2. The acid was added gradually in 10 μL increments. The pH was measured simultaneously on a calibrated pH meter (Mettler Toledo, Five easy FE20). An aliquot of 0.5 g of actinide resin (Eichrom, 100-150 mesh) was added to each acidified sample.

The samples were then stirred on a magnetic stirring plate (Fisher Scientific) for a contact time of 18 hours (overnight). The resin was collected on a 0.45 µm Gelman cellulose nitrate membrane filter with a diameter of 47 mm using a vacuum filtration setup. The filters were then transferred to a watch glass and placed under a heat lamp (75 cm above) for approximately 15 minutes to dry the resin. The dry resin and filters were carefully transferred into scintillation vials and 18 mL of Ultima Gold cocktail (PerkinElmer) was added to each vial. The samples were counted for 60 minutes in the alpha region of 90 and 500 keV on a PerkinElmer Tricarb 5110TR LSC (Waltham, MA).

The lower limit of detection was determined using the Curie method:

$$LLD = 4.66\sqrt{\sigma_b} + 3 \ (67) \qquad \text{(Equation 10)}$$

where σ_b is the standard deviation of the background.

6.4 RESULTS

Figure 34 shows the gross alpha count in each processed fluid sample. The activity was relatively low and ranged from 1.6 to 2.3 Bq/L. Despite the low counts, every sample reached the lower limit of detection in an hour counting time, proving that liquid scintillation counting is an adequate means of detection for alpha screening in processed water.

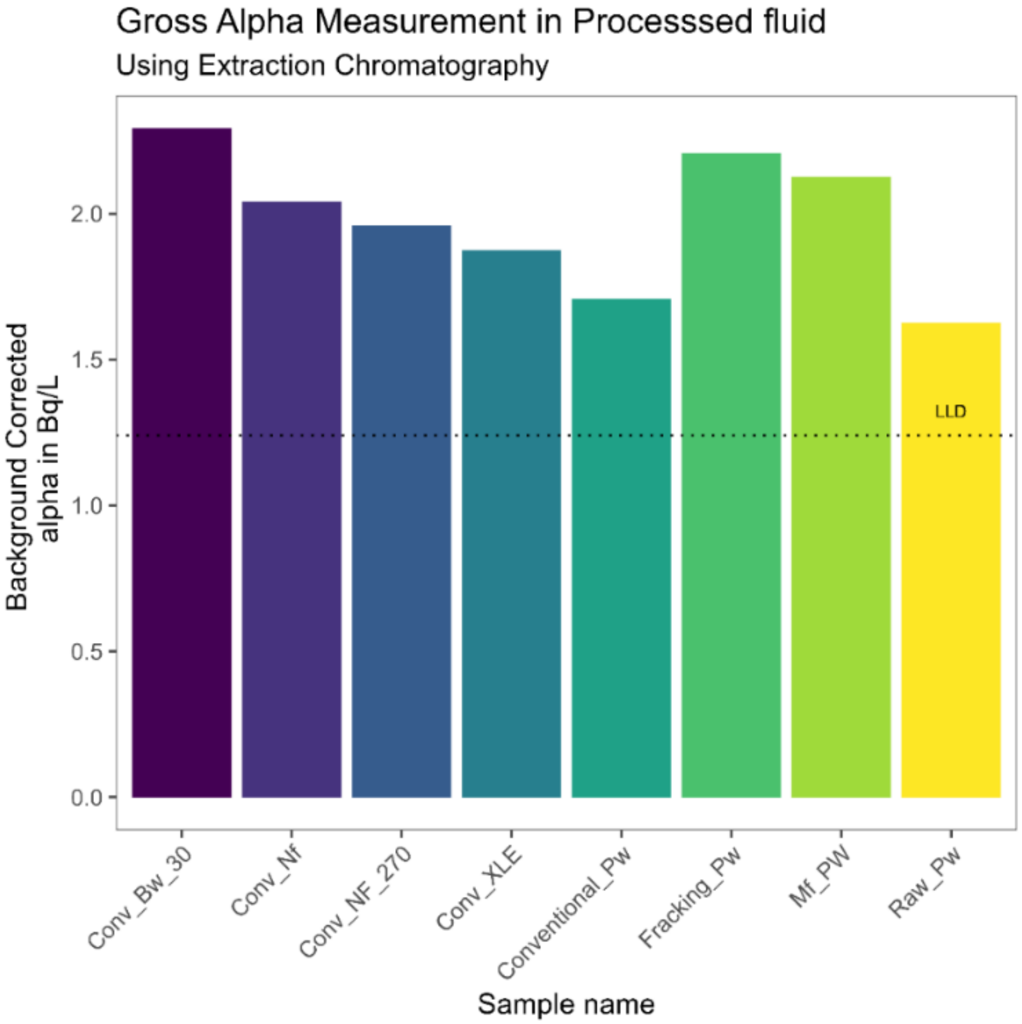


Figure 34: Gross alpha activity, actinide resin counted via LSC

The gross alpha count was compared with the cumulative ^{226}Ra and ^{228}Ra activities measured via direct gamma spectrometry (see Chapter 4) and are represented in Figure 35. The gross alpha count was well below the ^{226}Ra and ^{228}Ra activities. The low selectivity of the resin for radium appears clearly as the gross alpha/radium activity only ranged from 8.7 to 16.7%. This ratio may suggest that the actinide concentration in the processed fluid is indeed not as significant as the radium concentration.

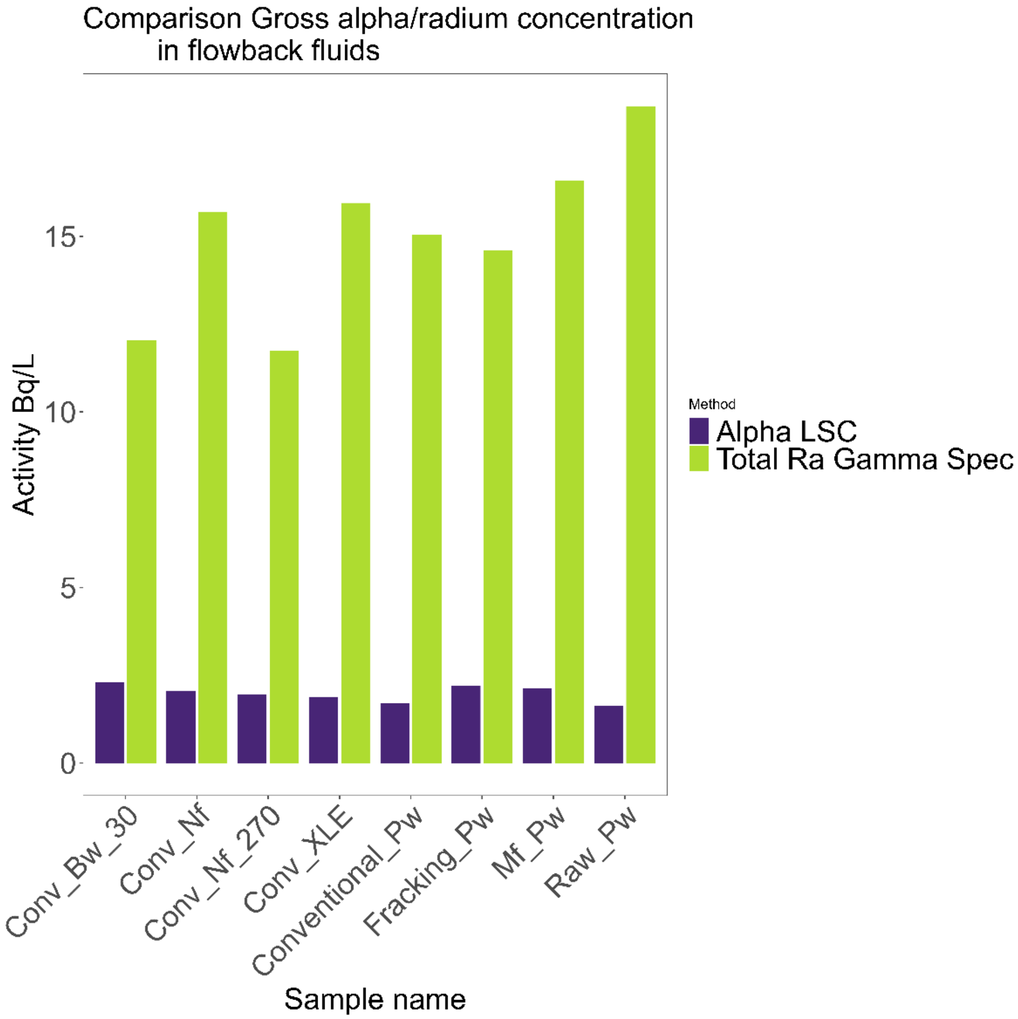


Figure 35: Gross alpha counts activity to total radium activity

6.5 FUTURE WORK

The individual recovery yield of Ra, Th, U, and Po must be investigated to ensure an appropriate interpretation of the result. A future experiment will entail the reproduction of the analysis with a synthetized process fluid of known composition spiked with varying amounts of either Ra, Th, U, or Po. This experiment will quantify the affinity of the radionuclides for the resin in a complex wastewater matrix because the solution used in the experiment did not have a known quantity of the radionuclides. The preparation of a simulated fracking water solution containing known amounts of the analytes of interest will allow for a more accurate determination of retention or recovery.

The method must be designed to accommodate a high level of dissolved solids, including group II elements because the presence of other cationic species can result in competition for binding sites on the resin, decreasing the retention of the radionuclides. Therefore, it would be beneficial to complete batch studies that explore how the concentration of Ca, Sr, and Fe in the matrix affects the retention of the analytes.

Additionally, the radioactive decay and ingrowth of the uranium and thorium retained on the resin will cause the alpha measurements to change over time. As a result, the extent of the radionuclide ingrowth impacts the results based on the time between sampling and analysis must be investigated by computational analysis.

To more efficiently achieve the dual analysis of radium and the actinides, a potential alternative route would be to use a resin that is selective for radium over the actinides, Ca, Ba, and Sr. To concentrate the actinides, the eluate containing the actinides will be contacted with the actinide resin and analyzed via liquid scintillation counting for gross alpha beta analysis. The radium retained on the initial resin would be stripped, preconcentrated, and analyzed via HPGe. This proposed method, shown in Figure 36, would represent an improvement to the EPA method since it would:

- Limit the number of chemical separations steps
- Decrease the detection limits of the radium analysis
- Decrease the counting time for the radium measurement

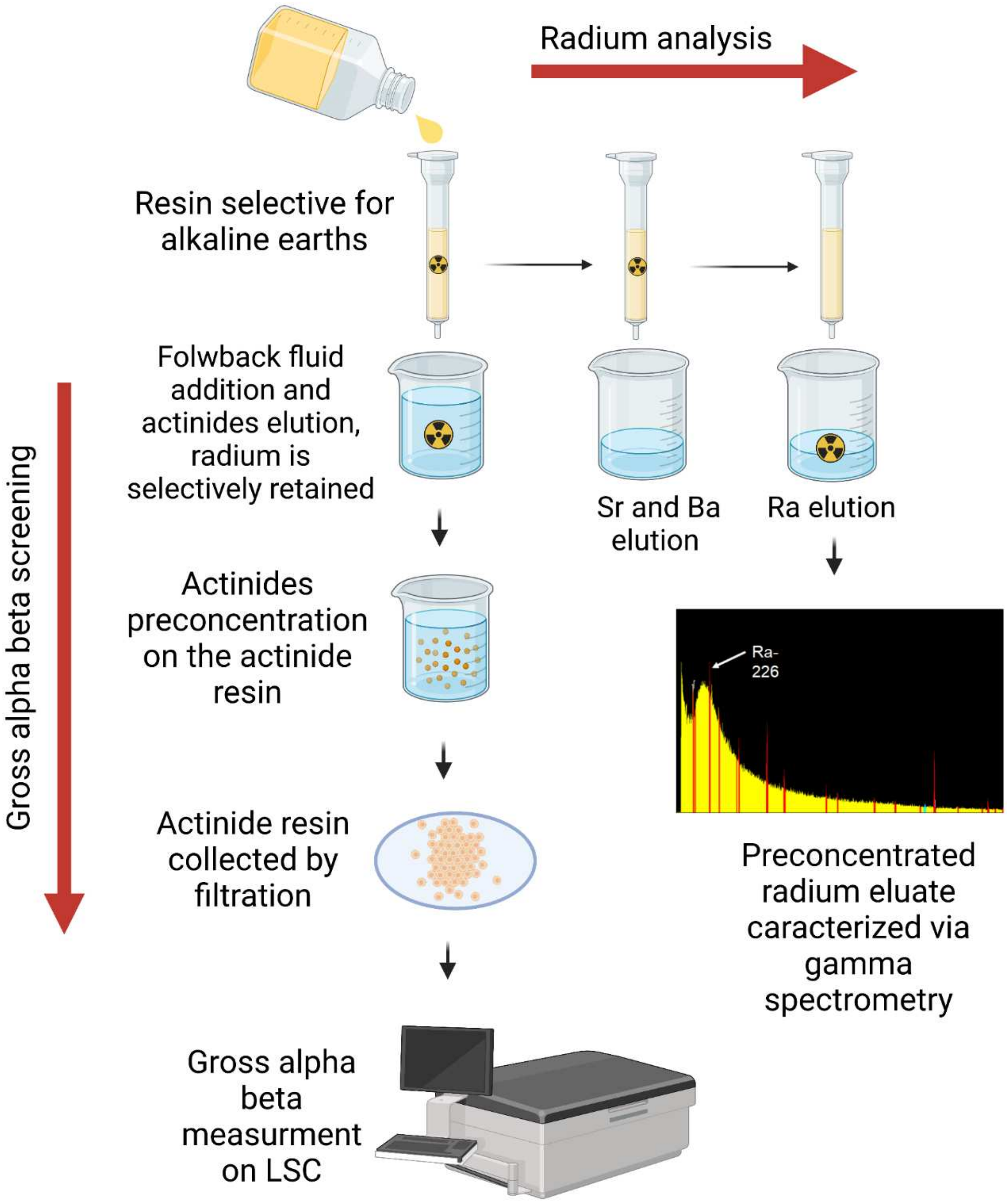


Figure 36: A proposed dual method for radium and gross alpha beta screening

CHAPTER 7: INVESTIGATION OF VARIOUS EXTRACTION CHROMATOGRAPHIC RESIN FOR THE SELECTIVE EXTRACTION AND ANALYSIS OF RADIUM IN PROCESSED AND FLOWBACK FLUIDS.

In this chapter, the selective separation of radium cation from solutions containing an excess of salt compared to the amount of extractant will be discussed.

7.1 SEPARATION OF RADIUM USING ION-EXCHANGE

The cation exchange behaviour of radium resembles that of barium; thus, these analogues are always adsorbed together from the aqueous media. To achieve separation of the adsorbed Ba and Ra, an eluent containing organic complexing agent must be used. Those eluents have been demonstrated to be more efficient than those obtained with a non-complexing mineral acid such as HCl. (33) Ammonium citrate, citric acid, EDTA, and ammonium formate may be used to sequentially elute barium and radium.

Using ammonium citrate at pH 5.6, the elution of barium and then radium from a Dowex 50 (50-100 mesh size, Na4$^{+)}$, gives a recovery of radium at 99% with only 0.01% barium concentration. However, the radium to barium concentration ratio, [Ra]/[Ba], was drastically inferior to processed fluids; (68) therefore, the reliability of the method seems questionable for that application.

Similarly, radium has been successfully separated from barium using a Dowex 50 (50-100 mesh size, Na^{4+}), with di-ammonium salt and 0.01M ethylenediaminetetraacetic acid (EDTA). Barium may be eluted with EDTA at pH 8.8 while radium is retained and subsequently eluted with the same solution at pH 10.5. The method showed an efficient separation of the two analogues but the [Ra]/[Ba] ratio was roughly one.

Using the same ion exchange column, and 1.5 mL of ammonium lactate at pH 7 and 78°C, radium separation from the analogues is quantitative within a few hours. Figure 37 shows the typical elution curve. (33)

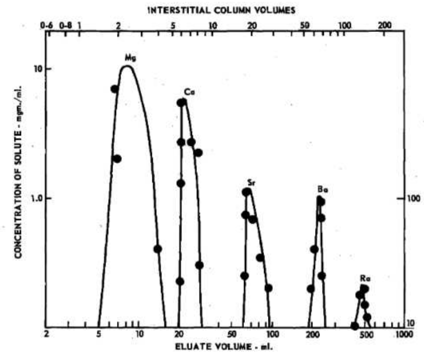


Figure 37: The separation of magnesium, calcium, strontium, barium, and radium with ammonium lactate eluant 1.5 M at 7.1. 1X8 cm. column, flow rate 1.0 ml./min. T = 78 °C **(33)**

Although those methods showed great separation of radium from the other alkaline earth metals, their reliability in a complex matrix such as flowback fluids is questionable. The large excess of Ba, Sr, Ca, and other competing ions may render the separation difficult when only trace amounts of radium are present.

7.2 CARACTERISITIC OF RADIUM ORGANIC EXTRACTANT

More recently, the possibility of using radium selective organic ligands has been explored. To successfully recover radium over the other analogues, the extractant must exhibit a preferential complexation tendency towards Ra over Ca, Sr, and Ba. This is a challenge since radium has the lowest tendency of all alkaline earth metals to form complexes. However, the size of the extractant plays a critical role in the complexation behavior among the analogues. (69) The extractant must be large enough to incorporate Radium ions (1.48-1.70 Å) and should possess oxygen donor atoms because Ra is a hard Lewis acid.

Crown ethers are selective ligands that form stable complexes with metal ions based primarily on the ionic radius-cavity size. Thus, there has been considerable interest in the use of crown ether ligands to achieve ion-selective separations, either for liquid-liquid extraction or as an extractant adsorbed onto a silica or polymer support (extraction chromatography). (70)

Previous literature demonstrated the synergistic effect of crown ether dissolved in the aqueous phase on sulfonic and di-sulfonic acid-based cation exchange resin. The use of crown ether enhanced the sorption and selectivity of the resin among the alkaline earth metals. The synergistic effect on the selectivity of the excess of 18-crown-6 and 21-crown-7 for the heaviest alkaline earth metal was demonstrated. This enforces the theories that radium forms a strong complex with crown ether with the right hole size. The use of larger crowns (24 to 30) showed to provide better Ra/Ba separation but the complexing power of radium with larger ring size crown ether was shown to drop.

Additionally, crown ethers with a carboxylic acid group have been used to separate radium from alkaline media via solvent extraction. Results showed that 22-crown-7 gave a higher distribution coefficient over other crown ethers studied. The study showed that radium could successfully be stripped from the organic phase with acid. (70) Crown ether appears to be a strong ligand for the separation of radium. The size of the crown and hydrocarbon substituents appears to play an important role in the selectivity for radium. Those parameters will therefore be studied in subsequent research.

7.3 CROWN ETHER AND EXTRACTION CHROMATOGRAPHY

In an attempt to provide a faster radiostrontium screening method in environmental samples, the use of crown ether gained popularity as a way to isolate strontium from solutions containing potentially interfering radionuclides or large amounts of calcium. Horwitz et al. showed that extraction chromatography using 4,4’(5’)-bis-(ter-butylcyclohexano)-18-crown-6 as an extractant dissolved in 1-

octanol was an efficient method for the preconcentration and separation of strontium from nitric acid media. The separation and recovery of strontium and calcium were greater that 99%. (71)

This free-flowing separation medium using di-t-butylcyclohexono-18-Crown-6 (Figure 38) is found in a patent that discloses the separation of the alkaline earth cations, such as barium cations from radium cations, and particularly strontium cations from other alkaline earth cations, present in an acidic aqueous solution (72). This resin is, to this day, the reference chromatographic method for the separation of radium from barium in environmental samples. However, the separation efficiency is often poor and must be repeated to obtain a measurable radium fraction.

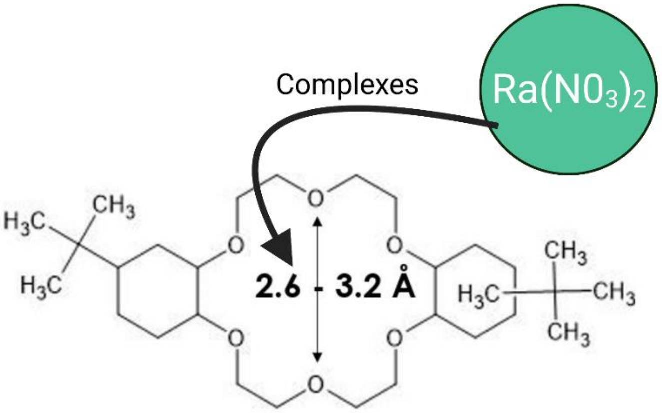


Figure 38: 4,4'(5')-di-t-butylcyclohexano-18-crown-6^A and radium complexation

Multiple proprietary extraction chromatographic resins developed by TrisKem International all using the crown ether extractant discussed above were investigated at different nitric acid concentrations to quantify their selectivity towards radium nitrate. The respective affinities of each chemical analogue for the resins are to be exploited to separate and preconcentrate radium from processed fluid solutions. Different chromatographic systems are investigated (Table 7). The influence of the diluent, such as isodecanol or octanol, on the selectivity is explored with the Pb and Sr resins (73) (74). The TK100 and TK101 resins explore the possibility of a dual extractant system. The electrostatic effect provided by Di(2-ethyl-hexyl) phosphoric acid (HDEHP) or another ionic liquid is studied with those resins (75). The extraction equilibrium for all systems is assumed to be:

$$M^{2+}{}_{(aq)} + Crown_{org} + 2NO_3{}^{-} \leftrightarrow M(Crown)(NO_3)_{2(org)}$$

Table 7: Extraction systems of the various resins studied

RESIN	EXTRACTANT	DILUENT
Pb	Crown-ether^{A}	Isodecanol
Sr	Crown-ether^{A}	octanol
TK100	Crown-ether^{A}/ HDEHP	-
TK101	Crown-ether^{A}/ Ionic Liquid	-

7.4 METHOD

All batch studies were completed with four replicates. Polypropylene microcentrifuge tubes (VWR, Denver, CO) were filled with 50 ± 0.5 mg of the chosen extraction chromatographic resin. The resin was preconditioned with 0.5 mL of the desired nitric acid concentration solution and agitated for one hour using a Labquake rotisserie-shaking table. The acid concentrations were verified via titration with standardized NaOH. The samples were then spiked with a suitable spike activity of either ^{90}Sr, ^{133}Ba, or ^{226}Ra. A 0.9 mL of the desired acid concentration was added to each sample. The microcentrifuge tubes were agitated for an additional hour using the Labquake rotisserie-shaking table. The solutions were subsequently filtered through a 0.45 μm PTFE syringe filter (VWR). A 0.9 mL aliquot of the filtrate was used for analysis. The

Ba samples were analysed directly via a 10 minute count time using NaI gamma spectrometry using a PerkinElmer 2470 WIZARD^2 (Waltham, MA) automated gamma counter.

The Sr and Ra aliquots were transferred into a 20 mL high-density polyethylene (HDPE) vial. Eighteen mL of Ultima Gold AB cocktail was added. Prior to liquid scintillation analysis, the Sr and Ra samples were allowed to reach equilibrium in a cool and dark environment for 21 days and 27 days, respectively. Sr and Ra samples were counted for 60 minutes. Figure 39 illustrates the protocol employed. Radium aliquots were counted on a PerkinElmer Tricarb 5110TR LSC (Waltham, MA), using the alpha window. Strontium aliquots were counted on a Packard TriCarb 1900 LSC (Waltham, MA)

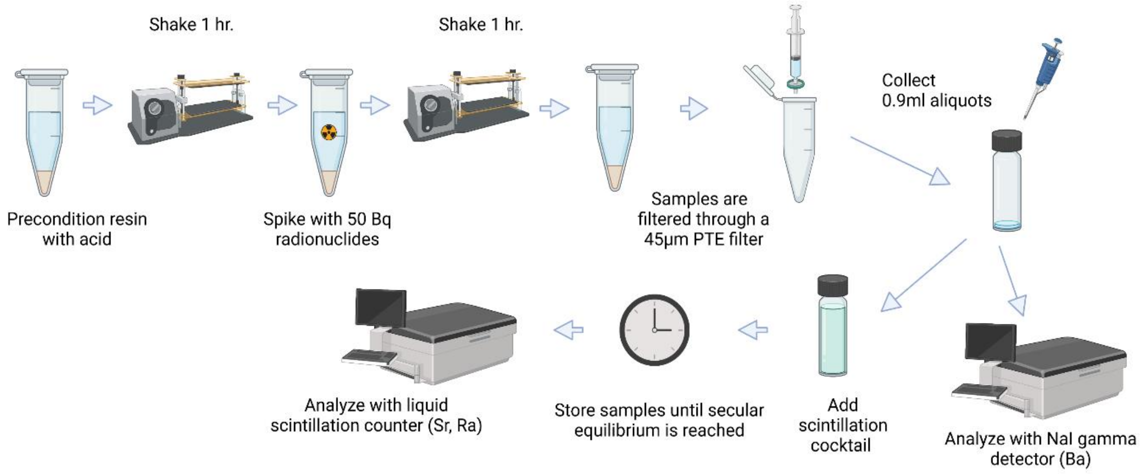


Figure 39: Method for batch study, figure created with BioRender.com

The automated gamma counter 2470 WIZARD^2 was normalized for barium before the analysis. 20,505 Bq of ^{133}Ba was used for the multi-peak normalization procedure. The peak deviancy was found to be 29% and the efficiency was internally set to 16%.

The weight distribution ratio, D_w, was calculated for each sample using Equation 7 (see Chapter 6). The maximum and minimum D_w values were calculated for each batch using a 95% confidence interval. The maximum D_w was derived using the Currie LLD (equation 10), and the minimum D_w was calculated using $-1.96\sigma_{spike}$ of the spike activity. Uncertainties are displayed at 2σ.

7.5 RESULTS

The weight distribution ratio of each batch study is reported in Figure 40. On the Sr and Pb resin, the radium and barium behaviours are almost identical across all acid concentrations. Strontium, at low acid concentrations, has a lower affinity than its analogues for the crown extractant. Therefore, separation of strontium from radium and barium using Sr or Pb resin is likely possible by eluting strontium with a low acid concentration while the others are retained.

On the TK100 and TK101 resins, the analogues mostly followed the same retention trend with Ba>Ra>Sr, at most acid concentrations. Those resins seem to be the most promising for Ra/Ba separations as their behaviors are more distinctive. These results show that the macrocyclic effect of the crown ether combined with the electrostatic effect provided by the HDEHP or the ionic liquid is desirable for the separation of the alkaline earth metals.

On all four resins discussed above, barium is the more strongly retained of the analogues except at high acid concentrations where its retention drops. This suggests that the ring size is more favorable for barium complexation over radium. A larger crown ring might be preferential for the complexation of radium over barium and therefore, increase its D_w.

The TKI resin showed promising results for radium/strontium separation. Strontium did not show any selectivity for the resin until a 5 M concentration of nitric acid was reached. Radium, on the other hand, was retained to a degree. Radium retention increased with nitric acid concentration. Further study with barium will indicate if the resin provides a better Ra/Ba separation.

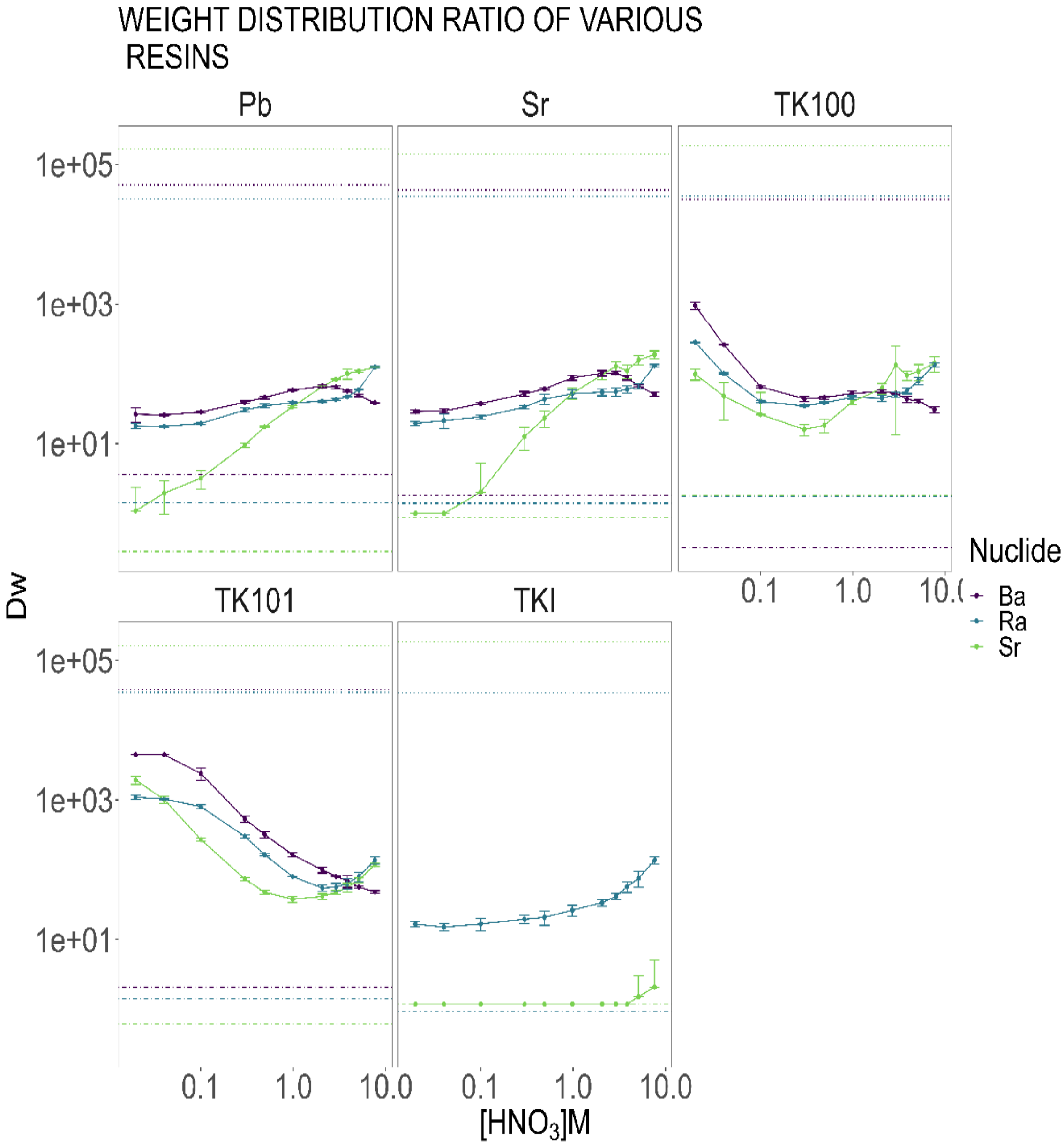


Figure 40: Weight distribution ratio of radium, strontium, and barium on various extraction chromatographic resin

Results suggest that a separation of the chemical analogues is possible using these resins. Figure 41 shows the separation factors obtained for the separation of the alkaline earth metals. Strontium can easily be separated from radium using the TKI, Sr, and Pb resin as the separation factors are 73.4, 19.1, and

16.3 at 3 M, 0.02 M, and 0.02 M, respectively. Ba could be separated from radium using the TK101 resin as the separation factor is 4.3 at 0.04 M.

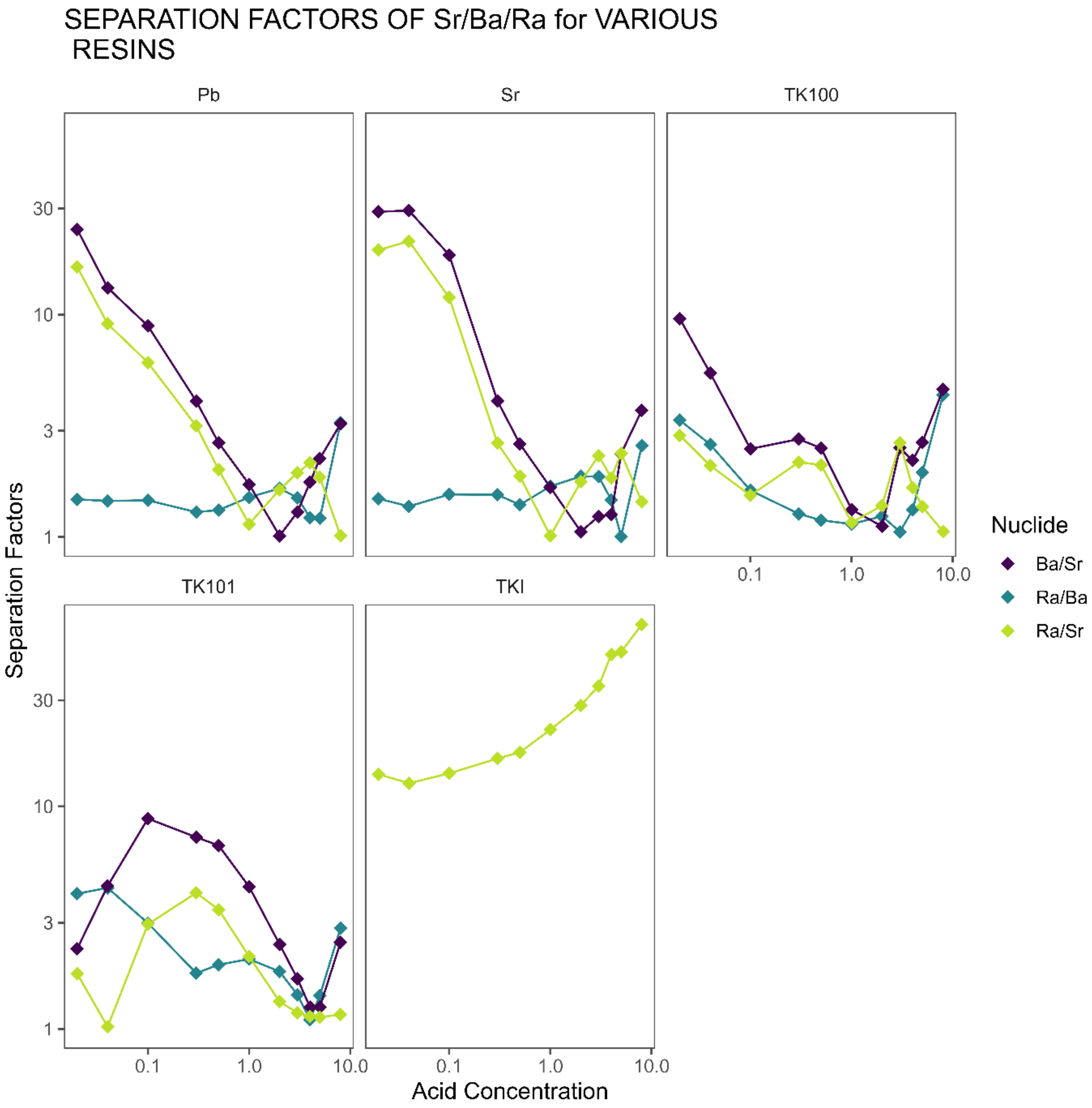


Figure 41: Separation factors of radium, strontium, and barium provided by various extraction chromatographic resin

7.6 FUTURE WORK

Further batch contact studies with additional resins developed by Triskem International, LLC will be completed in an effort to improve the separation of radium from the analogues. Although resins showed that separation is possible, the high concentration of barium and strontium in flowback fluids over the traces amount of radium might render the separation difficult.

Previous literature has shown successful stripping of Ba from Sr resin columns using chelating agents (76). It would be beneficial to explore how various chelating agents such as EDTA, NTA, CDTA, HDEHP, and DTPA may strip these radionuclides from the proprietary resins provided by TrisKem to improve the separation factors of Ra and Ba. Batch studies using aqueous phases containing various concentrations of the chelating agents would provide a preliminary assessment of retention differences. If the results prove promising, using these solutions could strip Ba or Ra selectively from a column packed with these resins to achieve separation.

Increasing the ring size of the crown ether (22 or 21 crowns) may provide a more appropriate ring size for radium complexations. The investigation of a lower pH range must be considered as radium seems to be extracted to a greater extent from basic media. (70) In addition, to optimize the selectivity of radium for a given extractant, a combination of the macrocyclic effect and electrostatic effect is desirable. The use of crown ether functionalized with pendent acid groups such as amino carboxylic, alkyl phosphoric, sulfonic, and alkyl carboxylic acids (78) must be investigated in an extraction chromatographic system as it has shown promising results in liquid-liquid extraction. As an example, a mixture of cyclohexanol-21-crown-7 and 2-heptyl-2 methyl nonanoic acid gave a Radium distribution coefficient (Ra_{org}/Ra_{aq}) larger than 200. (77)

Finally, promising work using liquid-liquid extraction methods for gas-field produced water has shown that thiacalix[4]crowns and a system of guanines and (iso)guanines are capable of selectively extracting radium from the complex matrix. Those two organic ligands showed great recoveries (83% and 62%) of radium from the aqueous phase under extremely high concentrations of chemical analogues. Moreover, it was shown that radium could be quantitatively stripped from the organic media with a pH 2

HCl aqueous solution. (34) The investigation of immobilization of the extractant discussed above onto inert support shall be investigated. The creation of an extraction chromatographic resin may provide greater separation of radium from the analogues as its selectivity has been tested in produced fluids. Moreover, extraction chromatography is usually preferred by the industry as it generates less hazardous waste.

Kinetics studies will be done to assess the effect of contact time and temperature on retention for promising extraction of chromatographic resins. Finally, the radium recovery and separation on dynamic columns with simulated processed waters will be studied.

CONCLUSION

In the United States, 18 billion barrels of waste fluids containing Naturally Occurring Radioactive Material (NORM) from oil and gas production are generated annually. Accurate and fast measurement of the major radioactive contaminant, radium, is an essential step for the waste water's adequate disposal, or possibly its recycling.

Direct measurement of the processed fluids via gamma spectrometry is an accurate and easy way to determine the radium concentration. However, long counting times and/or long waiting periods for the ingrowth of ^{214}Bi and ^{214}Pb are required to achieve the detection limits. A counting time of 24 hours was shown to be insufficient so longer counting periods of 5 days were necessary. In an attempt to decrease the counting time, the radium was coprecipitated with barium sulfates. This approach seems promising since the ^{133}Ba recoveries were large across all samples. However, the detection limits were not achieved even with a 3-day counting period due to the background radioactivity of the blank. For both radium screening methods, the ^{214}Bi and ^{214}Pb analyses were revealed to be inconclusive. Parafilm did not provide a complete sealing, allowing radon to escape the sample volume.

To simplify the rapid radiochemical method for gross alpha and beta activity concentration in flowback and produced water, the use of Actinide resin instead of TRU column separation was investigated as a means to preconcentrate Th, U, and Po in flowback and produced water from the oil and gas industry. The gross alpha count was found well below the ^{226}Ra and ^{228}Ra activities determined by direct gamma spectrometry. The low selectivity of the resin for radium was evident as the gross alpha radium activity only ranged from 8.7 to 16.7%. Since radium shows a poor affinity for the resin, a separation of radium from the sample might be investigated to perform a dual analysis and fulfil the need for a complete Ra, Th, U, and Po screening.

The oil and gas industry produces water with high dissolved solid material content leading to a significant scientific challenge in achieving separations of radium due to the high concentration of chemical analogues such as barium, strontium, and calcium. Multiple extraction chromatographic resins developed by TrisKem International were investigated at different nitric acid concentrations to quantify and enhance the separation of radium from the chemical analogues. Results showed that Sr could easily be separated from radium using the TKI, Sr, and Pb resin as large separation factors were obtained. The separation of barium from radium seems more difficult since their affinity for each resin was more similar. However, results showed that a Ba/Ra separation is possible with the TK101 resin as the separation factor was found to be 4.3 at 0.04 M. Further studies on different extracting systems, with larger crown ether, potentially functionalized with pendent acid groups, or stronger complexing extractants should be done to improve the selectivity of the resin for radium.

Investigations were made to provide a faster radium screening method in processed and flowback fluids by preconcentrating radium. Results suggest that the various approaches investigated are promising. Further studies will confirm if the hypotheses that the preconcentration of radium by precipitation or by chromatographic extraction are viable methods for radium analysis. As the separation of radium from its chemical analogues appears possible, extraction chromatography could be a way to treat processed and flowback water with elevated radium content to be recycled.

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APPENDICES

APPENDIX A: RESULTS OF HPGE GAMMA ANALYSIS OF FLOWBACK FLUIDS COUNTED FOR 24 HOURS

SAMPLE NAME	NUCLIDE	COUNT TIME (h)	ACTIVITY (Bq/L)	UNCERTAITY (Bq/L)	MDA (Bq/L)
Conv BW30	Ra-226	24	1.32	3.81	12.6
Conventional PW	Ra-226	24	5.07	3.77	12.4
Conv NF	Ra-226	24	3.89	4.11	13.5
ConXLE	Ra-226	24	0.00	3.48	11.5
Fracking PW	Ra-226	24	0.57	3.74	12.4
MF PW	Ra-226	24	0.00	3.48	11.5
RAW PW	Ra-226	24	1.57	4.96	16.4
Conv NF 270	Ra-226	24	0.00	3.40	11
Conv BW30	Ra-228	24	0.89	0.23	1.16
Conventional PW	Ra-228	24	1.02	0.10	1.27E
Conv NF	Ra-228	24	1.17	0.47	1.25
ConXLE	Ra-228	24	1.08	0.17	1.29
Fracking PW	Ra-228	24	1.12	0.05	1.30
MF PW	Ra-228	24	0.42	0.03	1.09
RAW PW	Ra-228	24	0.25	0.29	1.32
Conv NF 270	Ra-228	24	0.78	0.18	1.47
Conv BW30	Pb-214	24	0.58	0.19	0.88
Conventional PW	Pb-214	24	0.24	0.14	0.95
Conv NF	Pb-214	24	0.41	0.23	1.09
ConXLE	Pb-214	24	0.44	0.69	1.02
Fracking PW	Pb-214	24	1.05	0.28	0.99
MF PW	Pb-214	24	0.66	0.37	0.99
RAW PW	Pb-214	24	1.11	0.25	1.01
Conv NF 270	Pb-214	24	0.52	0.22	1.01
Conv BW30	Bi-214	24	0.13	0.26	0.98
Conventional PW	Bi-214	24	0.88	0.26	1.04
Conv NF	Bi-214	24	1.94	0.52	1.07
ConXLE	Bi-214	24	2.49	0.46	0.96
Fracking PW	Bi-214	24	2.65	0.43	0.98

MF PW	Bi-214	24	1.29	0.42	0.96
RAW PW	Bi-214	24	1.92	0.11	1.01
Conv NF 270	Bi-214	24	3.15	0.37	0.97

APPENDIX B: RESULTS OF HPGE GAMMA ANALYSIS OF FLOWBACK FLUIDS COUNTED FOR 5 DAYS

SAMPLE NAME	NUCLIDE	COUNT TIME (d)	ACTIVITY (Bq/L)	UNCERTAITY (Bq/L)	MDA (Bq/L)
Conv BW30	Pb-214	5	0.88	0.1	0.37
Conventional PW	Pb-214	5	1.14	0.9	0.35
Conv NF	Pb-214	5	1.33	0.05	0.29
ConXLE	Pb-214	5	0.85	0.09	0.32
Fracking PW	Pb-214	5	1.34	0.07	0.25
MF PW	Pb-214	5	1.54	0.08	0.29
RAW PW	Pb-214	5	1.28	0.10	0.57
Conv NF 270	Pb-214	5	0.94	0.11	0.58
Conv BW30	Bi-214	5	1.55	0.09	0.32
Conventional PW	Bi-214	5	1.84	0.08	0.31
Conv NF	Bi-214	5	2.05	0.05	0.23
ConXLE	Bi-214	5	1.15	0.06	0.21
Fracking PW	Bi-214	5	2.16	0.09	0.21
MF PW	Bi-214	5	2.02	0.08	0.27
RAW PW	Bi-214	5	2.32	0.09	0.32
Conv NF 270	Bi-214	5	1.33	0.10	0.23
Conv BW30	Ra-226	5	10.70	1.25	3.96
Conventional PW	Ra-226	5	14.00	1.19	3.69
Conv NF	Ra-226	5	14.80	1.24	3.85
ConXLE	Ra-226	5	14.80	1.46	4.63
Fracking PW	Ra-226	5	13.4	1.35	4.29
MF PW	Ra-226	5	15.5	1.48	4.66
RAW PW	Ra-226	5	17.0	1.49	4.66
Conv NF 270	Ra-226	5	10.7	1.11	3.50
Conv BW30	Ra-228	5	1.33	0.06	0.55
Conventional PW	Ra-228	5	1.04	0.03	0.37
Conv NF	Ra-228	5	0.88	0.04	0.53
ConXLE	Ra-228	5	1.15	0.05	0.37
Fracking PW	Ra-228	5	1.19	0.03	0.38
MF PW	Ra-228	5	1.09	0.05	0.36

RAW PW	Ra-228	5	1.70	0.09	0.60
Conv NF 270	Ra-228	5	1.04	0.09	0.61

APPENDIX C: ^{133}Ba RADIOTRACER RECOVERY AFTER COPRECIPITATION OF RADIUM WITH BARIUM SULFATE

SAMPLE NAME	COUNT TIME (d)	NUCLIDE	ACTIVITY (Bq)	RECOVERY
Conv BW30	5	Ba-133	1.34	0.89
Conventional PW	5	Ba-133	1.25	0.83
Conv NF	5	Ba-133	1.36	0.91
ConXLE	5	Ba-133	1.32	0.88
Fracking PW	5	Ba-133	1.31	0.87
MF PW	5	Ba-133	1.29	0.86
RAW PW	5	Ba-133	1.18	0.78
Conv NF 270	5	Ba-133	1.29	0.86

APPENDIX D: RESULTS OF THE HPGE GAMMA ANALYSIS OF THE BA(SO4) PRECIPITATED COUNTED FOR 3 DAYS

SAMPLE NAME	COUNT TIME (d)	NUCLIDE	TOTAL ACTIVITY (Bq)	UNCERTAITY (Bq)	MDA (Bq)
Conv BW30	3	Ra-226	0.61	0.28	1.34
Conventional PW	3	Ra-226	0.02	0.32	1.24
Conv NF	3	Ra-226	0.02	0.30	1.23
ConXLE	3	Ra-226	2.03	0.34	1.59
Fracking PW	3	Ra-226	0.01	0.40	1.20
MF PW	3	Ra-226	0.98	0.32	1.31
RAW PW	3	Ra-226	0.99	0.33	1.25
Conv NF 270	3	Ra-226	1.27	0.33	1.48
Conv BW30	3	Ra-228	0.13	0.01	0.13
Conventional PW	3	Ra-228	0.2	0.04	0.01
Conv NF	3	Ra-228	0.35	0.02	0.22
ConXLE	3	Ra-228	0.12	0.02	0.14
Fracking PW	3	Ra-228	0.003	0.19	0.21

MF PW	3	Ra-228	0.13	0.01	0.21
RAW PW	3	Ra-228	0.08	0.02	0.19
Conv NF 270	3	Ra-228	0.07	0.003	0.21
Conv BW30	3	Pb-214	0.15	0.02	0.12
Conventional PW	3	Pb-214	0.003	0.03	0.13
Conv NF	3	Pb-214	0.004	0.03	0.13
ConXLE	3	Pb-214	0.085	0.02	0.13
Fracking PW	3	Pb-214	0.2	0.03	0.13
MF PW	3	Pb-214	0.08	0.01	0.12
RAW PW	3	Pb-214	0.4	0.04	0.13
Conv NF 270	3	Pb-214	0.04	0.04	0.13
Conv BW30	3	Bi-214	0.31	0.03	0.12
Conventional PW	3	Bi-214	0.14	0.03	0.13
Conv NF	3	Bi-214	0.30	0.08	0.13
ConXLE	3	Bi-214	0.15	0.02	0.13
Fracking PW	3	Bi-214	0.31	0.03	0.12
MF PW	3	Bi-214	0.51	0.03	0.13
RAW PW	3	Bi-214	0.86	0.03	0.13
Conv NF 270	3	Bi-214	0.35	0.05	0.12

APPENDIX E: RESULTS OF GROSS ALPHA DETERMINATION IN FRACKING WATER USING ACTINIDE RESIN AND LSC COUNTING

SAMPLE NAME	CPM	BACKGROUND CORRECTED CPM	ACTIVITY (Bq/L)
Mf PW	32	25.5	2.1
Conventional Pw	27	20.5	1.7
Raw Pw	26	19.5	1.6
Conv Bw 30	34	27.5	2.3
Conv Nf	31	24.5	2.0
Conv XLE	29	22.5	1.9
Conv NF 270	30	23.5	2.0
Fracking Pw	33	26.5	2.2
Blank averaged	6.5	-	0.5

APPENDIX F: RESULTS OF THE WEIGHT DISTRIBUTION RATIO OF RADIUM, STRONTIUM, AND BARIUM ON VARIOUS EXTRACTION CHROMATOGRAPHIC RESIN

ACID CONCENTRATION	RESIN	NUCLIDE	Dw	UNCERTAITY

0.02	Sr	Sr	LOD*	0
0.04	Sr	Sr	LOD*	0
0.10	Sr	Sr	2.0	3.3
0.30	Sr	Sr	12.6	4.6
0.49	Sr	Sr	23.2	6.3
0.98	Sr	Sr	52.6	9.7
2.07	Sr	Sr	96.7	13.9
2.9	Sr	Sr	128.5	18.8
3.85	Sr	Sr	110.9	24.2
5.12	Sr	Sr	158.7	24.6
7.64	Sr	Sr	189.2	24.7
0.02	TK101	Sr	1938.9	261.2
0.04	TK101	Sr	1011.4	116.4
0.10	TK101	Sr	270.9	14.9
0.30	TK101	Sr	73.7	3.6
0.49	TK101	Sr	47.8	3.4
0.98	TK101	Sr	37.8	3.6
2.07	TK101	Sr	41.5	3.7
2.9	TK101	Sr	47.8	3.7
3.85	TK101	Sr	55.7	8.1
5.12	TK101	Sr	71.0	5.0
7.64	TK101	Sr	118.2	7.2
0.02	Pb	Sr	1.1	1.3
0.04	Pb	Sr	1.9	1.0
0.10	Pb	Sr	3.2	1.0
0.30	Pb	Sr	9.6	0.7
0.49	Pb	Sr	17.4	0.5
0.98	Pb	Sr	33.7	1.0
2.07	Pb	Sr	66.0	2.7
2.9	Pb	Sr	83.4	1.0
3.85	Pb	Sr	101.1	17.0
5.12	Pb	Sr	109.7	3.7
7.64	Pb	Sr	123.9	1.8
0.02	TK100	Sr	99.0	17.4
0.04	TK100	Sr	48.1	26.5
0.10	TK100	Sr	26.1	27.9
0.30	TK100	Sr	16.0	3.0
0.49	TK100	Sr	18.3	4.0
0.98	TK100	Sr	39.6	3.8
2.07	TK100	Sr	62.2	11.0
2.9	TK100	Sr	132.6	119.4
3.85	TK100	Sr	95.4	14.2
5.12	TK100	Sr	108.6	27.7

7.64	TK100	Sr	141.8	35.6
0.02	TKI	Sr	LOD*	0
0.04	TKI	Sr	LOD*	0
0.10	TKI	Sr	LOD*	0
0.30	TKI	Sr	LOD*	0
0.49	TKI	Sr	LOD*	0
0.98	TKI	Sr	LOD*	0
2.07	TKI	Sr	LOD*	0
2.9	TKI	Sr	LOD*	0
3.85	TKI	Sr	LOD*	0
5.12	TKI	Sr	1.5	1.5
7.64	TKI	Sr	2.1	2.9
0.02	Pb	Ba	26.4	6.2
0.04	Pb	Ba	25.7	1.0
0.10	Pb	Ba	28.5	1.2
0.30	Pb	Ba	39.2	1.7
0.49	Pb	Ba	46.0	2.3
0.98	Pb	Ba	58.1	1.7
2.07	Pb	Ba	66.8	3.7
2.9	Pb	Ba	64.5	3.1
3.85	Pb	Ba	57.3	1.7
5.12	Pb	Ba	48.7	1.8
7.64	Pb	Ba	38.4	0.9
0.02	TK101	Ba	LOD*	0
0.04	TK101	Ba	LOD*	0
0.10	TK101	Ba	2388.3	508.0
0.30	TK101	Ba	535.8	53.3
0.49	TK101	Ba	319.0	33.8
0.98	TK101	Ba	164.4	9.9
2.07	TK101	Ba	99.5	9.5
2.9	TK101	Ba	80.3	1.5
3.85	TK101	Ba	69.6	14.1
5.12	TK101	Ba	56.7	1.9
7.64	TK101	Ba	48.3	1.8
0.02	Sr	Ba	29.0	1.8
0.04	Sr	Ba	29.3	1.9
0.10	Sr	Ba	37.6	1.6
0.30	Sr	Ba	51.7	4.1
0.49	Sr	Ba	60.8	2.2
0.98	Sr	Ba	87.8	6.5
2.07	Sr	Ba	102.2	8.9
2.9	Sr	Ba	103.8	6.6
3.85	Sr	Ba	88.0	6.3

5.12	Sr	Ba	66.9	2.6
7.64	Sr	Ba	51.0	3.2
0.02	TK100	Ba	949.9	110.7
0.04	TK100	Ba	262.6	5.8
0.10	TK100	Ba	65.1	1.5
0.30	TK100	Ba	44.1	4.3
0.49	TK100	Ba	45.8	2.5
0.98	TK100	Ba	52.6	3.8
2.07	TK100	Ba	55.8	3.0
2.9	TK100	Ba	52.8	2.2
3.85	TK100	Ba	43.2	4.0
5.12	TK100	Ba	40.8	2.0
7.64	TK100	Ba	30.8	3.0
0.02	Pb	Ra	17.9	1.4
0.04	Pb	Ra	17.7	0.6
0.10	Pb	Ra	19.5	0.7
0.30	Pb	Ra	30.3	2.0
0.49	Pb	Ra	34.8	2.2
0.98	Pb	Ra	38.6	1.4
2.07	Pb	Ra	40.4	1.0
2.9	Pb	Ra	42.9	1.8
3.85	Pb	Ra	46.9	0.4
5.12	Pb	Ra	59.1	1.0
7.64	Pb	Ra	125.5	5.4
0.02	Sr	Ra	19.5	1.1
0.04	Sr	Ra	21.4	5.0
0.10	Sr	Ra	24.2	1.8
0.30	Sr	Ra	33.4	1.6
0.49	Sr	Ra	43.5	7.7
0.98	Sr	Ra	52.0	7.5
2.07	Sr	Ra	54.6	6.1
2.9	Sr	Ra	55.5	8.0
3.85	Sr	Ra	60.1	7.1
5.12	Sr	Ra	66.7	6.1
7.64	Sr	Ra	131.4	5.4
0.02	TK100	Ra	283.5	3.4
0.04	TK100	Ra	100.7	2.8
0.10	TK100	Ra	40.2	1.8
0.30	TK100	Ra	34.7	1.1
0.49	TK100	Ra	38.5	1.0
0.98	TK100	Ra	46.1	2.6
2.07	TK100	Ra	45.0	4.3
2.9	TK100	Ra	50.0	4.4

3.85	TK100	Ra	57.2	5.1
5.12	TK100	Ra	79.4	8.8
7.64	TK100	Ra	134.2	8.6
0.02	TKI	Ra	16.6	1.5
0.04	TKI	Ra	15.1	1.8
0.10	TKI	Ra	16.7	3.6
0.30	TKI	Ra	19.6	2.7
0.49	TKI	Ra	20.8	4.8
0.98	TKI	Ra	26.3	4.6
2.07	TKI	Ra	33.8	3.9
2.9	TKI	Ra	41.4	3.9
3.85	TKI	Ra	57.4	10.5
5.12	TKI	Ra	75.4	19.6
7.64	TKI	Ra	137.5	16.9
0.02	TK101	Ra	1095.5	75.4
0.04	TK101	Ra	1031.9	26.2
0.10	TK101	Ra	799.8	48.4
0.30	TK101	Ra	301.2	15.7
0.49	TK101	Ra	164.2	7.4
0.98	TK101	Ra	79.9	0.9
2.07	TK101	Ra	55.0	5.6
2.9	TK101	Ra	56.4	7.3
3.85	TK101	Ra	63.3	10.7
5.12	TK101	Ra	80.0	12.0
7.64	TK101	Ra	137.0	15.5

* Limit of detection, calculated using a 95% confidence interval.

GLOSSARY

Process fluid: Water found in shale formations that is naturally occurring and flows to the surface throughout the entire lifespan of the gas well**.**

flowback water: Water based solution injected in the well that flows back to the surface during and after the completion of hydraulic fracturing.

Fracking brine: Water based Saline liquid, including all hydraulic fracturing additives, used to perform hydraulic fracturing operations.

Peak deviancy: Measured drift of the peak centroid compared to the reference channel.