Comparative Use of Two Radiometric Techniques for Determining Radium Activity in Simulated Surface Waters to Assess Method Suitability

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Abstract

Although rapid and routine radiochemical methods are readily available for most radionuclides, methods for low-level ^{226}Ra analysis remain limited, time-consuming, and primarily designed for assessing drinking water quality. Monitoring radium levels in environmental waters with diverse matrices and varying mineral compositions requires further understanding of the matrix effect on the analytical method. This study aims to explore these effects to ensure robust analytical methods capable of accurate measurements are achieved despite potential interferences from elevated mineral water components.

This study presents a fast radio-analytical method for determining ^{226}Ra activity concentration in natural surface water sources, utilizing two radiometric techniques, alpha spectrometry and liquid scintillation counting. The aim is to evaluate the suitability of each technique given the variations in natural water matrices resulting from industrial effluent releases. This study was specifically aimed to identify effects on sample dissolution and the quality of the source required to obtain high-resolution alpha spectrum at high chemical recovery for accurate concentration determination. In addition, another radiometric technique was implemented for measurement to compare the results obtained from alpha spectrometry. Simulated natural water samples with different mineral contents and concentrations were analyzed using both radiometric techniques to assess their suitability with regards to matrix effect.

The study concludes that both alpha spectrometry and liquid scintillation counting (LSC) can be effective for determining ^{226}Ra concentrations in environmental surface water samples, with some exceptions where high amounts of certain minerals are present in the sample. Both techniques exhibit high tolerance for magnesium, sodium, and calcium levels in the sample, but lower tolerance for barium and iron. This research provides guidance for accurately determining ^{226}Ra concentrations in various environmental surface water or effluent samples. It also highlights the importance of evaluating mineral water content, resin capacity, and being aware of self-adsorption effects to achieve accurate measurements of ^{226}Ra for samples with complex matrix. Although alpha spectrometry is generally the preferred technique for the determination of alpha emitters due to its lower detection limit, the LSC technique, particularly after radiochemical separation, can be advantageous for samples with higher mineral content, such as calcium, since it does not suffer from poor source quality due to self-adsorption effects.

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List of Abbreviations

Bq	Becquerels
CPM	Counts per minute
HPGe	High Purity Germanium
IAEA	International Atomic Energy Agency
LSC	Liquid Scintillation Counting
MAC	Maximum Acceptable Concentration
MARB	Maximum Acceptable Relative Bias
MCA	Multichannel analyzer
MDC	Minimum Detectable Concentration
MMER	Metal Mining Effluent Regulations
NIST	National Institute of Standards and Technology
NORM	Naturally Occuring Radioactive Material
PIPS	Passivated Implanted Planar Silicon
PLI	Pulse Length Index
PMT	Photomultiplier Tubes
PSA	Pulse Shape Analysis
ROI	Region of Interest
TDCR	Triple to Double Coincidence
TMF	Tailings Management Facility

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Chapter 1 Introduction

1.1 Discovery of Radium

Radium is an alkaline earth metal that was first discovered as radium chloride by Marie and Pierre Curie in 1898 in the residue of uranium ore. The term radioactivity was coined by Marie Curie and the historical unit for radioactivity, the Curie, is based on one gram of radium. Initially, radium was not considered a possible hazard and was used for diagnostic and therapeutic medical purposes. Perhaps the most well-known case of radium was its use in self-luminous paints for watches, where factory workers painting the dials with radium-containing paint were using their mouths to shape the brushes, ingesting toxic amounts of radium. In the mid-1900s, the use of radium in commercial and medical applications ceased due to its high radiotoxicity and was identified as a pollutant mainly due to uranium mining and milling. Later, other industries, such as oil and gas, phosphate fertilizer production, and mining of raw materials have also been identified as sources of radium release in the environment[1].

1.2 Chemistry of Radium

Radium is a naturally occurring radioactive material (NORM) that is ubiquitous in the earth's crust. There are 34 known isotopes of radium of which four (^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra) are naturally occurring in the environment as part of decay series of primordial radionuclides. Of the four naturally occurring radium isotopes, ^{226}Ra is the most stable with a half-life of 1600 years and is the most abundant in nature. The estimated average ^{238}U concentration in the continental crust is 32.9 becquerels per kilogram and assuming radioactive equilibrium, the crustal ^{226}Ra activity is expected to be of the same order. It is also one of the most radiotoxic radionuclides and is a main contributor to the natural radiation dose received by all living organisms.[1,2] Given the radiotoxicity of various radionuclides, radium isotopes hold significance as they can readily integrate into bones, resembling elements from Group II (e.g., calcium). This property allows them to generate short-lived radionuclides with high specific activity. In everyday scenarios, the ingestion of radium through food and water can result in the accumulation of these isotopes in the body, thereby contributing to the radiological dose experienced by individuals in the general population.[3] Therefore, the ability to accurately assess the dose received by the population through ingestion of food or drinking water is heavily dependent on the robust measurement of its activity at natural levels.

1.3 Radium Release Regulations

National and international regulators have shown growing interest in regulating levels of radium across various industries and consumer products. Regulations related to the release of radium into the environment vary depending on the jurisdiction but generally falls under environmental laws and regulations governing radioactive substances. In Canada, the release of radium is regulated by both federal and provincial authorities. For example, the Metal Mining Effluent Regulations (MMER) in Canada set specific limits of for the release of radium from uranium mining of a maximum authorized monthly mean concentration of 0.37Bq/L[4]. For drinking water, Canada has a maximum acceptable concentration (MAC) for ^{226}Ra of 0.5Bq/L[5], while the US Environmental Protection Agency has set a limit of 0.185 Bq/L for the combined sum of ^{226}Ra and ^{228}Ra.[6] The MAC of 0.5Bq/L in Canada is determined based on one tenth of the annual public dose limit of 1mSv/year. For reference, the average dose received from natural background radiation in Canada is about 2mSv/year. Millisievert (MSc) is a unit of radiation dose that measures the biological effects of ionizing radiation to the body and accounts for both the amount of radiation absorbed and the type of radiation; while Becquerels (Bq) measures the quantity of radioactive decay. The release levels of radium to the environment are aimed to minimize risks to human health and the environment while allowing for responsible resource development.

1.4 Uranium mining in Canada

Uranium is used to power nuclear power plants all over the world and in order to meet the demand for energy and to decrease the worlds reliance on coal, large amounts of uranium are mined every year. Canada is a leading producer of uranium since the mid 1950s and has the worlds largest deposits of high-grade uranium of up to 20% in ores, shown in Figure 1.1. In 2018, Canada was the world's second-largest producer of uranium with 13% of global production. [7,8] While mining is governed by provincial regulations, uranium mining is under federal jurisdiction. The Canadian Nuclear Safety Commission (CNSC), which is Canada's nuclear regulator, regulates uranium mines and mills and all subsequent stages of the nuclear-fuel cycle from refining to fuel fabrication, to protect the health, safety, security, and the environment.[9] One major issue with uranium mining is the mill tailings produced that can contain high levels of contaminants including radium that threaten the environment and human health[10]. Tailings are the waste products generated after uranium is removed from the ore in the milling process and this waste consists of leach residue solids, solutions and chemical precipitates that requires proper long-term management .[11]

Figure 1.1 Uranium facilities in Canada.[10] Used with permission from World Nuclear Association.

1.4.1 Uranium Tailings

The mining and processing of uranium ores can expose the surface of the earth to quantities of uranium, thorium and their decay series, which initiate mobilization of radionuclides into the surrounding environment. During the mining process, large amounts of radon are also released into the air. The residues are stockpiled and waste waters, containing different amounts of isotopes such as radium, can be released either accidently or in a controlled manner into the nearby water bodies. Through the mining and processing of uranium ore, the natural environment including the natural bodies of water can be altered. This is due to existence of residues or tailings, resulting from uranium mining and processing activities. These tailings contain radium and consequently the entire short-lived radionuclide inventory of the ore, in addition to leaching chemicals such as, acids, NaOH, ammonia, etc. that could also affect the total dissolved solids in the surface water. The safe storage of such tailings is of particular importance, and best practices are documented in a guideline by the International Atomic Energy Agency.[12] Most importantly, the release of radon to the atmosphere and the drainage of contaminated tailing seepage must be kept as low as possible[10].

The chemistry of uranium tailings is complex and varies depending on many factors such as the original composition of the ore, the extraction and processing methods, and specific storage conditions. The conventional U milling process usually starts with the crushing of the U ores to optimize the exposure of U minerals in the leaching process. The ore is then fed to a leaching process as a slurry to dissolve U minerals. In Canada, usually a strong acid such as sulfuric acid is used in combination with O_2, $HClO_4$, or H_2O_2 to convert insoluble U(IV) to soluble U(VI). As a result, Fe(II) is generated by the dissolution of Fe-containing minerals and from oxidation of elemental Fe from the mechanical abrasion of equipment in the grinding circuits.[13] In some case, Ferric sulphate is also added to ensure U(IV) is oxidized to maximize U recovery. The uranium is now in solution form which is then separated from other minerals that remain as solids. After which, a purification step is done to separate the U from other dissolved metals and metalloid through solvent extraction. The resulting aqueous solution, called raffinate (Table 1.1), is acidic and a primary carrier of ^{226}Ra exceeds the recommended limits by several orders of magnitude (>100Bq/L). The raffinate is neutralized to increase pH and treated by barium chloride to remove radium from the aqueous phase via precipitation reactions. After which, the precipitates are separated from the aqueous solution using thickeners and after further site-specific treatment process, the neutralized aqueous solution is analyzed. If the concentrations of the radium and other elements meet regulatory requirements, it is discharged to the environment. The thickened precipitates are pumped as slurry to tailing management facilities for final disposal. As an example, the chemical composition of a raffinate sample from Key Lake Mill analyzed in a study in 2009 is shown below in Table 1.1, which contains elevated levels of iron, calcium, magnesium and radium.

Table 1.1. Chemical composition of a raffinate sample from Key Lake mill, Saskatchewan in 2009[14]

Element	mg/L	Element	(mg/L)
Fe	2555	Ca	576
Ra	150 (Bq/L)	Mg	3020
Na	102.1		

1.4.2 Uranium Tailings Management

Currently, management of tailing waste in Canada is managed by both federal and provincial authorities that involves a comprehensive approach to minimize environmental impacts, protecting human health, and sustainable mining practices. Current management of tailings involve long term storage of tailings in specific designed facilities that isolate the tailings from surrounding environment. These tailing management facilities or TMFs are located within mined-out open pits or in surface impoundments that utilizes geographical features and man-made barriers such as dams to ensure groundwater and surface water is diverted from tailing to prevent any contamination.[15,16]

In Canada, tailings are deposited in TMFs at Cameco Corporation's Key Lake and Rabbit Lake operations, and Orano's McClean Lake operation, all of which are in-pit TMFs as show in Figure 1.2.

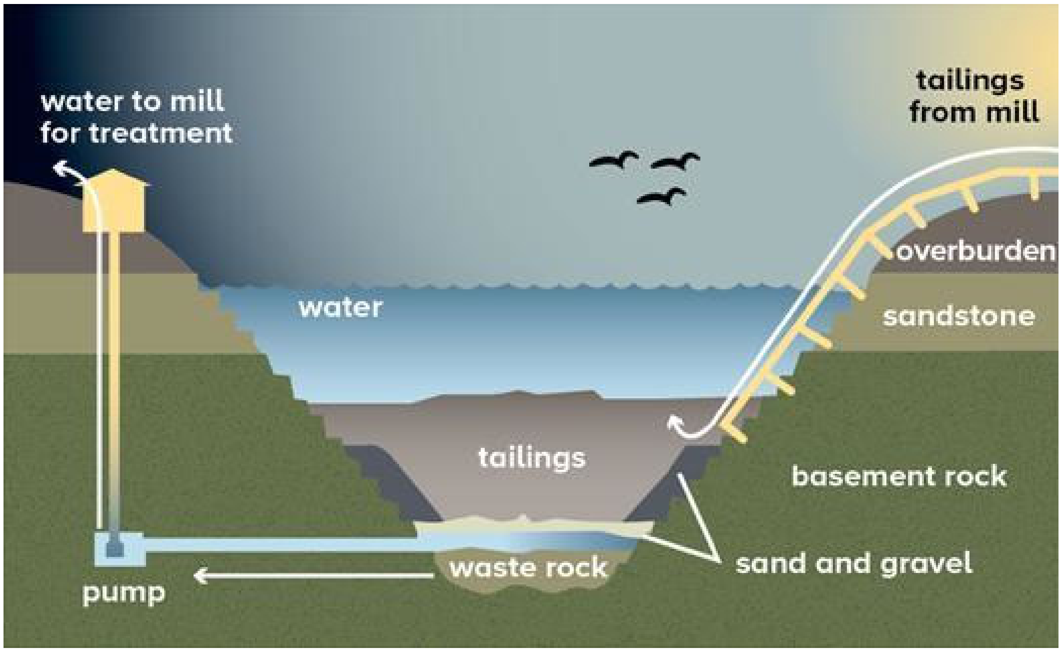

Figure 1.2. Uranium tailing facility[15] . Used with permission from Canadian Nuclear Safety Commission.

Tailings are deposited in the TMF as a slurry and while the solid settles, the liquid is collected and processed through a water treatment plant to remove contaminants, and the resulting effluent is discharged into the environment after meeting the regulatory quality requirements. During the milling and water treatment process, radium levels are reduced through neutralization of the leached solution and chemical treatment such as barium chloride and ferric sulphate. [12,17,18]

1.4.3 Tailings Legacy

Although current practices of tailing management in Canada is comprehensive and under stringent environmental regulations, in the early years of uranium mining worldwide, the safe and environmentally acceptable storage of the produced tailings was not adequately considered and resulted in contamination of nearby environmental compartments. Many of these mines operated without any environmental safeguards and led to the improper disposal of legacy tailings and contamination of the surrounding environment. Until 1965, effluents were released into streams without prior treatment, and it was not known at that time that radium (^{226}Ra) would be present in large concentrations in the surface water of tailings ponds. This led to a decrease in water quality of several water basins in around the mines, where the ^{226}Ra levels increased to ten times above the Canadian drinking water guideline of 0.5Bq/L in spite of the fact that the testing area is more than 20km from the nearest tailing pond.[17,19] Since 1965, the effluents have been treated with barium chloride and ferric sulphate to precipitate ^{226}Ra and radium concentration followed a gradual downturn reaching 0.01Bq/L in the early 2000s.[19]

In recent years, progress has been made in remediation efforts and environmental monitoring that aims to mitigate the environmental risks and protect human health. Therefore, continued monitoring and management of legacy sites are essential to safeguard the environment and public health for future generations. Furthermore, robust analytical methods to monitor radium levels in not only drinking water sources but also in contaminated water systems in various stages of the fuel fabrication and waste management are of critical importance. At the CNSC, water samples for compliance verification activities are collected around the mines and mills and at effluent release points are analyzed for various analytes (Table 1.2). These samples have been shown to be high in hardness (>1000mg/L), which is calculated from the concentration of calcium and magnesium as follows:

$$2.497\,[Ca] + 4.118\,[Mg] = Hardness\,(mg/L)$$

The amount of hardness is expressed in milligrams per litre (mg/L) as calcium carbonate. And conversion factors, 2.497 and 4.118 are used to account for the molar mass of calcium and magnesium and their charge.

For reference, the guideline for Canadian drinking water quality considers the level of hardness over 500mg/L to be unacceptable[5]. As a result, this study aims to assess the suitability of the analytical method employed for quantification of ^{226}Ra in environmental water samples, including effluent samples collected near mining and milling facilities.

Table 1.2. Concentrations of analytes in a typical water effluent sample for compliance activities.[a]

	Concentration	
	mg/l	Bq/l
Ca	372 ± 24	
Mg	116 ± 5	
Na	94 ± 6	
Fe	1.16 ± 0.05	
Ra-226		1.11± 0.09

[a] Based on results from our laboratory.

1.5 Objective

This study evaluates the efficacy and reliability of a fast analytical approach for determining radium activity concentration in simulated surface water sources with varying concentrations of different minerals, employing two radiometric techniques: high resolution alpha spectrometry and liquid scintillation counting. The objective is two-fold, to assess the chemical separation of radium in simulated surface water samples with varying mineral content and the measurement technique’s resilience and limitations, given the sample’s varying matrix effect.

A range of radium standard concentrations in tap water samples are first measured for ^{226}Ra using both measurement techniques, alpha spectrometry and liquid scintillation counting following the chemical separation method using MnO_2 resin and barium sulfate co-precipitation. Both radiometric techniques are used for comparison to determine pros and cons of each.

To validate the method's robustness, a series of experiments were conducted to evaluate the matrix effect of various minerals on the analysis. Tap water samples containing increasing concentrations of calcium, magnesium, barium, sodium, and iron were analyzed for ^{226}Ra using the same techniques. The samples were spiked with known amounts of ^{226}Ra with ^{133}Ba as tracer to determine recovery rates.

Chapter 2 Radiometric Techniques to Measure ^{226}Ra

2.1 Radioactivity

Henri Becquerel first discovered radioactivity in 1896 by placing uranium salts that blackened a photographic plate placed in the dark. It was later discovered that this process is the emission of radiation originating as a result of the spontaneous decay of unstable atomic nuclei, or a nuclear reaction. Three of the most common types of decay modes are alpha, beta and gamma decay.

Alpha decay is the nuclear decay process by which the parent nucleus emits an alpha particle. The alpha particle is equivalent to the nucleus of a helium atom and consist of two protons and two neutrons. It is emitted as a decay product of many heavy radionuclides predominantly of those at atomic number greater than 82. Alpha particle is relatively large and heavy but has low penetrating power and can be stopped by a few centimeters of air or a piece of paper. Beta decay consists of fast-moving electrons ejected from the nucleus of an atom. Beta particles have greater penetrating power than alpha particles but can be stopped by a few millimeters of aluminum. Gamma radiation is high-energy photons and are highly penetrating.[20]

Radioactivity, A, is the number of decays per unit time, usually disintegrations per second and the SI unit is the Becquerel.

$$A = -\frac{dN}{dt} = \lambda N \qquad （2.1）$$

Where N is the total number of atoms and λ is the decay constant.

For reference, a Curie of activity, which is based on 1 gram of radium is equal to 3.7 x 10^{10} disintegrations per second or Becquerels (Bq). The activity determined in samples are normally expressed as activity concentration, which is the activity per unit mass or volume (Bq/g, or Bq/L).

Radionuclide decay at a characteristic rate that remains constant and is a logarithmic relation and the number of atoms at anytime, N(t) is given by

$$N(t) = N(0)e^{-\lambda t} \qquad (2.2)$$

Where N(0) is the initial amount of active substance. If half of the nuclides decay, $N(t) = \frac{N(0)}{2}$, the amount of time it takes is the half-life.

$$T_{1/2} = \frac{ln2}{\lambda} \qquad (2.3)$$

The half-life differs for each radioisotope, ranging from fractions of a second to billions of years.

2.1.1 Radium Decay Chain

The nuclei of radioactive atoms are unstable and undergo decay to form stable elements by emission of radiation in the form of alpha particles, beta particles, neutrons, and gamma ray photons. Most often, the progenies of decay are also radioactive and undergo nuclear decay until a stable isotope is produced forming a nuclear decay chain. There exist three main decay series of natural radionuclides starting from ^{238}U, ^{232}Th and ^{235}U, which were formed at the birth of the Universe some 13.7 billion years ago and they have survived in the earth since its birth. These three primordial radionuclides each initiates a decay chain leading to a stable lead isotope. Of these chains, ^{226}Ra is a radionuclide in the decay chain of ^{238}U shown in Figure 2.1. ^{238}U accounts for more than 99% of uranium in uranium ore and has a half life of 4.5 billion years. [3,21,22]

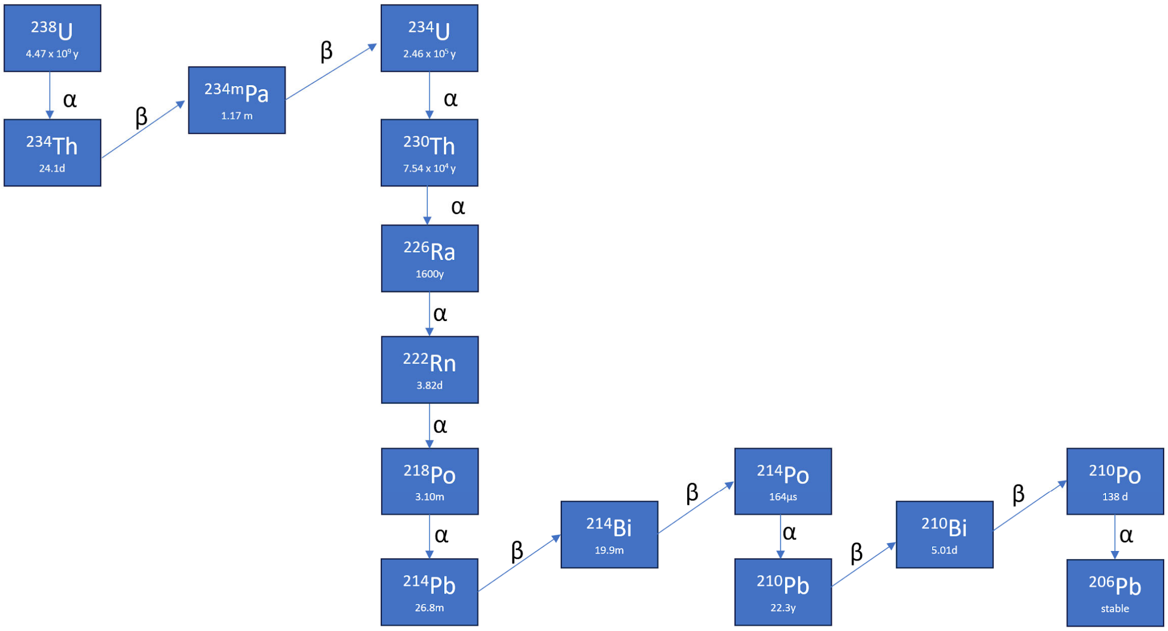

Figure 2.1 ^{238}U Decay chain with half lives.

2.1.2 Radium Decay Scheme

The two major alpha particle emissions in the decay of Ra-226 to ^{222}Rn shown in Figure *2.2* occur at 4.78 and 4.61MeV with relative intensities at 94.5% and 5.55%, respectively. Gamma radiation often accompanies radionuclide decay that occurs by alpha emission and in this case, a 186.2keV gamma ray is emitted at 3.3%. It is important to note that after decay, the progenies of ^{226}Ra as shown in Figure 2.1 continuously decay in a very short time and several alpha particles, beta particles and gamma ray emissions are emitted as well.

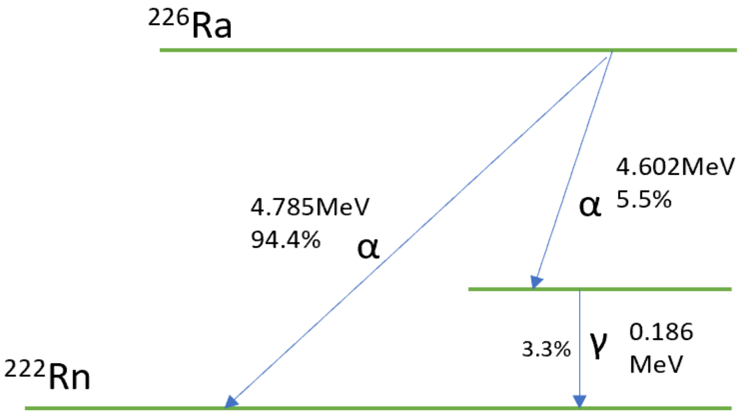

Figure 2.2. ^{226}Ra Decay Scheme

2.2 Radiometric Measurements

There are many methods for the determination of ^{226}Ra in water. The two main measurement categories are radiometric measurements (decay counting) and mass spectrometric measurements (atom counting)[19]. For the purpose of this study, only radiometric methods are discussed. Radiometric methods for ^{226}Ra include direct detection of ^{226}Ra by its alpha particles or gamma ray emission and indirect method of detecting the progenies of ^{226}Ra where radioactive equilibrium is reached. The most common methods are based on alpha spectrometry, gamma spectrometry and liquid scintillation counting (LSC) techniques[23,24]. In this work, two alpha radiation detection systems, LSC and alpha spectrometry will be used for comparison.

2.2.1 Alpha Spectrometry

Alpha spectrometry is based on the detection of different kinetic energies of the alpha particles in the range of 4-9 MeV using nuclear detectors. Common detectors are gas ionization, semiconductors, and scintillation detectors. When an alpha particle enters the detector, it produces charge carriers such as electron-cation pairs, electron-hole pairs, or electrons. Under the influence of an electric field, the charge carriers move to the electrodes and produce a voltage pulse. Therefore, the interactions of the alpha particles with the material of the detector are used to produce a pulse height that is proportional to the energy of the alpha source and the pulse frequency or count rate is proportional to the activity of the alpha source. [20,24] After collection of the spectrum, the activity concentration is calculated by the following equation:

$$A\ (Bq) = \frac{(C - B)}{\mathcal{E}Rt} \qquad （2.4）$$

Where A is the activity (Bq), C is the counts from Region of Interest, B is the background count within the same energy interval, Ɛ is the detector efficiency (%); R is the fraction of the tracer analyte recovered; t, the live counting time (s).

Although several types of detectors such as ionization chambers, proportional counters, and scintillation detectors can be used, semiconductors are the most frequently used detectors for alpha particles. The term alpha spectrometry is most commonly referred to semiconductor detector systems. In this case, the alpha particles are stopped in the depletion region of the semi-conductors, forming electron-hole pairs by interacting with the electrons of the detector material through excitation and ionization. The number of electron-hole pairs created is detected and registered as pulses with heights that are proportional to the energy of the alpha particle. Due to the short range of alpha particles, alpha spectrometry with solid detectors requires the measurement to be done in a vacuum to avoid energy losses in the air. Furthermore, the sample is required to be purified from the matrix by radiochemical separation and deposited in a thin and homogeneous layer in a process termed source preparation. This is important due to the limited range of the alpha particle as it is relatively large particle and is easily blocked by the source itself if the source is too thick. [20]

Figure 2.3. 12 Chambers Canberra/Mirion Alpha Analyst

High-resolution alpha spectrometry is the most sensitive radiometric technique due to its low background, high sensitivity, and good energy resolution with a very low detection limit. For this reason, alpha spectrometry is the most widely used technique for environmental and geological studies. [20] In addition, the high energy resolution allows for the separation of alpha peaks of ^{226}Ra ($E\alpha$ = 4784 keV) and that of its daughters, ^{218}Po ($E\alpha$ = 6002.6 keV), ^{222}Rn ($E\alpha$ = 5449 keV), and ^{214}Po ($E\alpha$ = 7686.9 keV). For example, a typical alpha spectrometer with a semiconductor detector has a peak resolution with full width half maximum (FWHM) of 20-30 keV. The main disadvantages of alpha spectrometry are the need to do radionuclide specific chemical separations that can be time consuming and to achieve low detection limits for environmental samples, long counting times may be needed. The semiconductor alpha detectors employed in this work were the passivated implanted planar silicon (PIPS) detectors. The PIPS detectors with its low reverse leakage current have high peak stability with minimal peak shift with temperature variation and low noise contribution.

The assigning of channels in the multi channel analyzer is performed using a conversion gain of 1024. Furthermore, the useful region of the analogue-to-digital converter can be shifted by a constant value using the so-called Analogue to Digital Converter offset to a measurement region between 3.5– 6.4 MeV. In this measurement region, all of the alpha emitters relevant to this work could be measured.

2.2.1.1 Source preparation for alpha spectrometry

Source preparation is an essential step in the radiochemical analysis for alpha spectrometry. After radium is chemically separated or preconcentrated from the sample, it needs to be prepared to a thin, flat, and uniformed surface or source that is suitable for the detector. Polished disks or planchets of stainless steel and other materials have been used as substrates. The most frequent used method for source preparation for ^{226}Ra is electrodeposition and micro co-precipitation. [2,20,21]

2.2.1.2 Micro co-precipitation

The most used source preparation for radium is $BaSO_4$ as described by Sill[25]. In this method, stable barium is used as a carrier for co-precipitation with radium. The $Ba(Ra)SO_4$ precipitate is collected on a smooth surface membrane filter of small pore size (0.2µm) and mounted on a substrate for alpha spectrometry. Micro-precipitation is much faster method of source preparation and thus chosen for this method.

2.2.1.3 Electrodeposition

Electrodeposition is the process where radionuclides are electrochemically plated from an electrolyte solution onto a metal cathode surface, usually a polished stainless steel planchet. For radium electrodeposition, an aqueous/alcohol electrolyte solution can be used or an aqueous solution of ammonium acetate and nitric acid have been done to achieve a good recovery and resolution of the alpha spectra. Electrodeposition is often performed at a constant current and low voltage (>14V) for up to 4 hours. [20,26,27]

2.2.1.4 Tracers for alpha spectrometry

Since chemical separations are performed, losses of analytes can occur in different parts of the process. For example, losses of the analytes may occur due to sample splashing, or absorption on the walls of the beakers or surfaces of undissolved residues. Therefore, chemical recovery based on tracers are used to accurately quantify the analyte. Tracers are chosen so that they are not in the sample or the amount present in the sample is negligible and is assumed to behave in the same way as the analyte nuclide.[20] Since no stable isotope exist for ^{226}Ra, a non-isotopic tracer with similar chemical properties like ^{133}Ba is commonly used in ^{226}Ra analysis to determine the chemical recovery. ^{133}Ba decays by electron capture followed by gamma emissions mainly to two excited levels. The activity concentration of ^{133}Ba in the sample can easily be determined by gamma-ray spectrometry using its key gamma line at 356 keV with a high-purity germanium detector. [3]

The relative measurements based on the gamma peak areas of the added tracer ^{133}Ba (P_{Ba}) and a ^{133}Ba standard source ($P_{Ba\text{-}Std}$) that was prepared by direct spiking on a filter is used to determine the chemical yield (R_{chem}) as the following formula:

$$R_{chem} = \frac{\frac{P_{Ba}}{t_{Ba}}}{\left(\frac{A_{Ba}}{A_{Ba-Std}}\right)\left(\frac{P_{Ba-Std}}{t_{Ba-Std}}\right)} \qquad （2.5）$$

Where A_{Ba} is the activity of the ^{113}Ba added, $A_{Ba\text{-}Std}$ is the activity of the ^{133}Ba standard, t_{Ba} and $t_{Ba\text{-}Std}$ are the counting times of the sample and standard.

With a half life of 10.5 years, a small quantity of diluted sub-sample of ^{133}Ba is prepared from a NIST（National Institute of Standards and Technology） traceable stock standard and decay correction for ^{133}Ba is applied to the date of sample preparation.

2.2.1.5 Calibration

The detectors can be calibrated for energy against channel number and for detection efficiency with a NIST traceable mixed reference source containing alpha emitters (^{238}U, ^{234}U, ^{239}Pu,^{241}Am), as shown in Figure 2.4. This calibration source covers the entire energy spectrum of the detection system and is in similar geometry as that of the sample. The detection efficiency is the ratio of the number of alpha particles detected by the system to the number of particles actually emitted by the radioactive source. A calibration curve for energy and detection efficiency is obtained for the entire measurement range, see Figure 2.5. The mean efficiency is calculated from the full energy peaks of each certified radionuclide and is used as the alpha efficiency for a given specific detector.

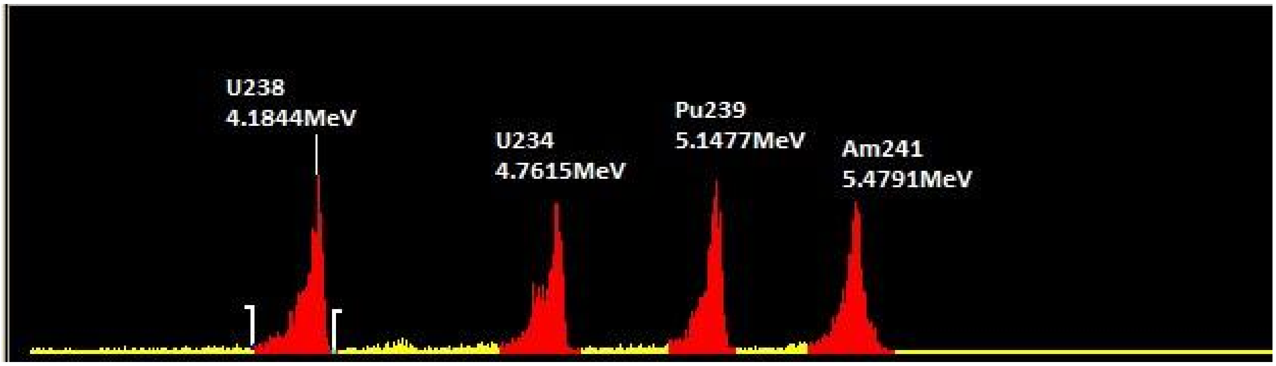

Figure 2.4. Alpha spectrum for mixed reference source (^{235}U, ^{238}U, ^{239}Pu, ^{241}Am)

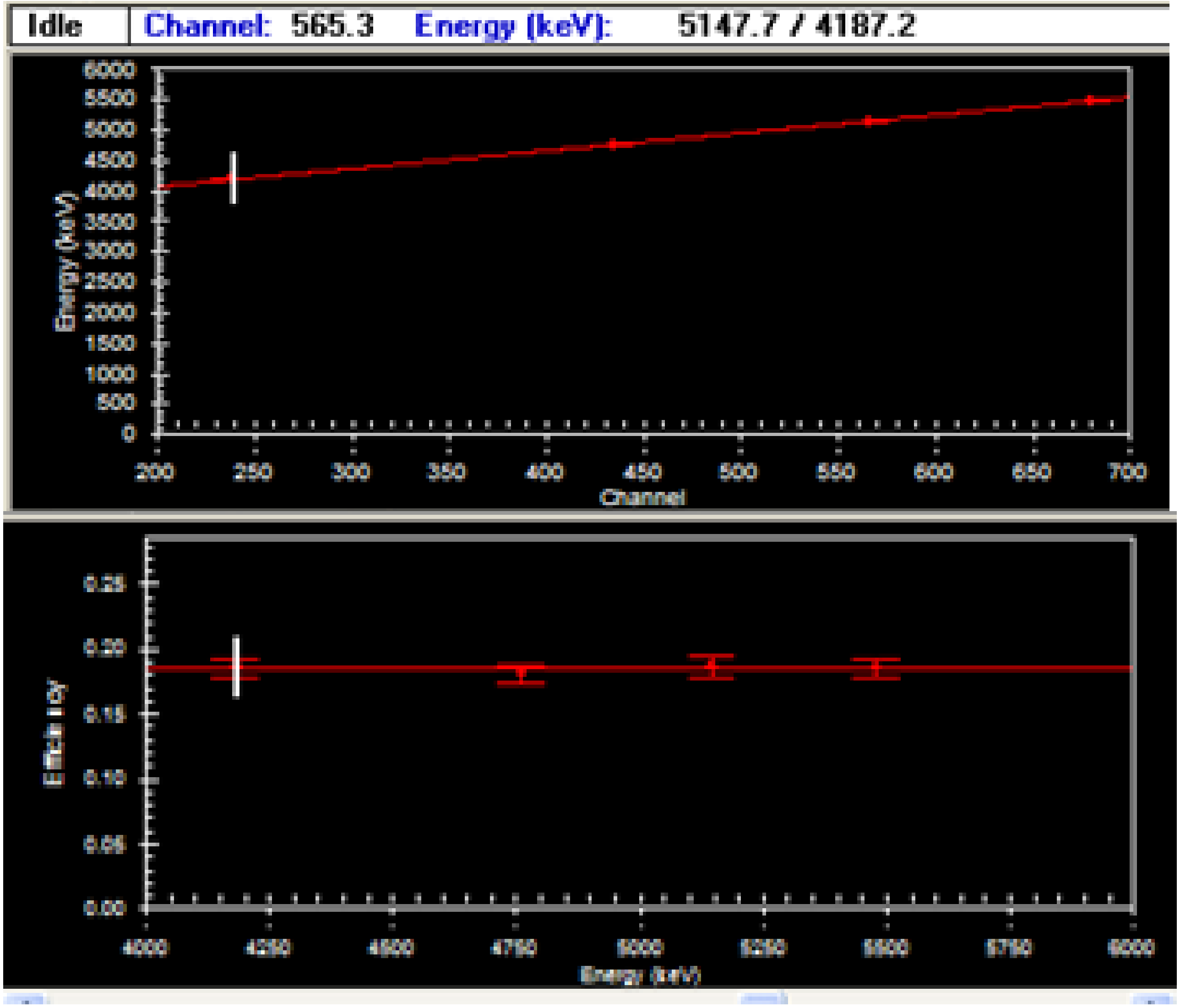

Figure 2.5. Calibration curve for energy (upper) and efficiency (lower).

2.2.2 Gamma Spectrometry

Gamma spectrometry utilizes a high-purity germanium semiconductor as a detector that can be used to measure radionuclides that emit gamma and X-rays. Gamma spectrometry is a non-destructive measurement technique and requires minimal sample processing where samples can be measured directly. The high resolution of modern gamma detector enables most measurements with no prior chemical separations needed. In the case of ^{226}Ra, a relatively high level of concentration is required in environmental and biological samples, owing to its low gamma emission probability. While ^{226}Ra can be quantified directly using its gamma peak at 186.2keV, the low gamma emission probability of 3.3% at this peak energy and the high Compton background at this energy range, makes gamma spectrometry less suitable for low activity samples. Another issue with gamma spectrometry is the presence of another potential overlapping peak at 185.9keV emitted by ^{235}U, also a naturally occurring isotope, which can't be resolved easily contributing to an overestimation of ^{226}Ra. In addition, the MDC using the key gamma peak of ^{226}Ra is 4 Bq/L at present, which is much higher than the radium levels found in environmental water samples. Another approach to measure ^{226}Ra by gamma spectrometry is to seal the sample and wait until the secular equilibrium is reached after 21 days has elapsed. The sample can then be measured through analysis of gamma peaks of its daughters, ^{214}Pb, and ^{214}Bi, with higher gamma emission probabilities of 37.2% and 46.3%, respectively, than that of ^{226}Ra. The less interference at higher energies and emission probability of its daughters lead to a more sensitive and accurate quantification with a lower MDC of approximately 1Bq/L. It should be noted however, that the long waiting period to achieve secular equilibrium is undesirable for compliance and time sensitive samples requiring rapid analysis to make regulatory decisions. In addition, the prevention of radon escapes and a tightly sealed sample container is crucial to ensure accurate measurement[2,19 2,20,21]. Although gamma spectrometry is not used to measure radium in this study, it is used to measure ^{133}Ba used as tracer for chemical recovery determination.

2.2.3 Liquid Scintillation Counting

Liquid scintillation counting (LSC) is an important and versatile radiometric technique for many radionuclides. It is conventionally used for pure beta emitting radionuclides but with the application of alpha-beta discrimination, alpha emitting radionuclides can also be measured. Alpha-beta discrimination refers to the ability to differentiate between alpha particles and beta particles based on their distinct properties. Due to its high counting efficiencies, relatively simple sample preparation process, and high availability in radioanalytical laboratories, LSC is a key technique for the measurement of naturally occurring radionuclides. [20,28]

Liquid scintillation counting is based on the process in which radioactive decay energy is converted to visible light and measured in an organic liquid environment. Specifically, it works by the transfer of decay energy to an organic solvent molecule, which activates the solvent molecules and in turn they transfer their energy to the organic scintillator which reemits as photons. The light is then detected by photomultiplier tubes (PMT) and the number of photons or light produced is proportional to the original nuclear decay energy. In other words, the pulse height at the output of the PMT is proportional to the specific energy of the beta or alpha particles. [20]

A conventional LSC uses two PMTs for detection, allowing coincidence light detection and coincidence pulse summation to be able to detect low-energy radionuclides (e.g. tritium, 18.6 keV) and distinguish instrument background from true nuclear events. This is coincidence counting which is based on the fact that light produced in a scintillation vial due to a nuclear decay event is emitted equally in all directions or isotropic. Also, with a single PMT, the background due to the large amplification factor of the PMT and background thermal and electronic noise would be too high, 10,000 counts per minute (CPM) for a 0-2000 keV counting region. Therefore, with two PMTs, the background can be reduced to 30 CPM. Given ^{226}Ra is an alpha emitter, the LSC can be calibrated to discriminate alpha events from beta events. This is done by doing a pulse shape analysis (PSA) using a pure alpha emitter and pure beta emitter standard solution, in which alpha and beta counts are stored in separate storage bins of a multichannel analyzer (MCA) due to the differences in their pulse shape. Once a PSA analysis is completed, an optimum PSA value is selected, where the misclassification of β-pulses from α-pulses are at the lowest percentage. In a conventional LSC with 2 PMTs, the sample's chemical and physical properties may affect the scintillation process resulting in variable light production, called quenching. Thus, quench correction must be applied to determine the activity. Thereby, different degrees of quenching and other sample/cocktail changes will affect the optimal PSA value and in turn affect the detection efficiency and the separation effect of α/β pulses. In this case, the chemical composition of the standard solutions should be as similar to that of the samples to minimize the adverse effects on optimal PSA value. [20]

2.2.3.1 Triple to Double Coincidence Ratio (TDCR) Technique

In recent years[29], a new technique in the LSC measurements has been the development of the triple to double coincidence ratio method, where three photomultiplier tubes as a triple detector is configured to screen for alpha and beta activity in one measurement scan without prior knowledge of pulse shape. In recently designed LSCs with three PMTs, good α/β-discrimination can be achieved, where the pulses are not affected neither by the scintillation cocktail, nor by quenching effects. In this type of LSC, pulses are analyzed both by pulse duration and by pulse height and an enhanced counting geometry with three PMTs (120° angle to each other), automated quench correction by triple to double coincidence ratio (TDCR), and luminescence free counting is achieved. [30]

In the HIDEX LSC system, pulses are classified based on their energy and pulse length index (PLI) to achieve optimal alpha and beta particle separation. The PLI setting, which accounts for the electronic pulse rise and decay time, is typically longer for alpha particles due to their extended deexcitation and light emission processes in scintillation materials. This difference is illustrated in Figure 2.6, where the x-axis represents channel number (or energy) and the y-axis represents PLI values, clearly showing distinct PLI and energy regions for alpha and beta emitting isotopes. In this case, the count rate for alphas is in the area above the PLI horizontal line around 4 in Figure 2.6 and the count rate for betas is in the area below PLI 4.

The alpha region of interest is generally set between channels 500 and 900, whereas the beta region is usually defined more broadly from channels 5 to 1000 to cover all possible beta energies. To establish the optimal PLI threshold, pure alpha and beta standards are employed. Pulses with PLI values above this threshold are classified as alpha, while those below are classified as beta.

The resulting 2-dimensional graph, shown in Figure 2.6 simplifies the interpretation of the spectrum and facilitates real-time adjustments to the PLI, thereby enhancing the separation of alpha and beta pulses.[31,32]

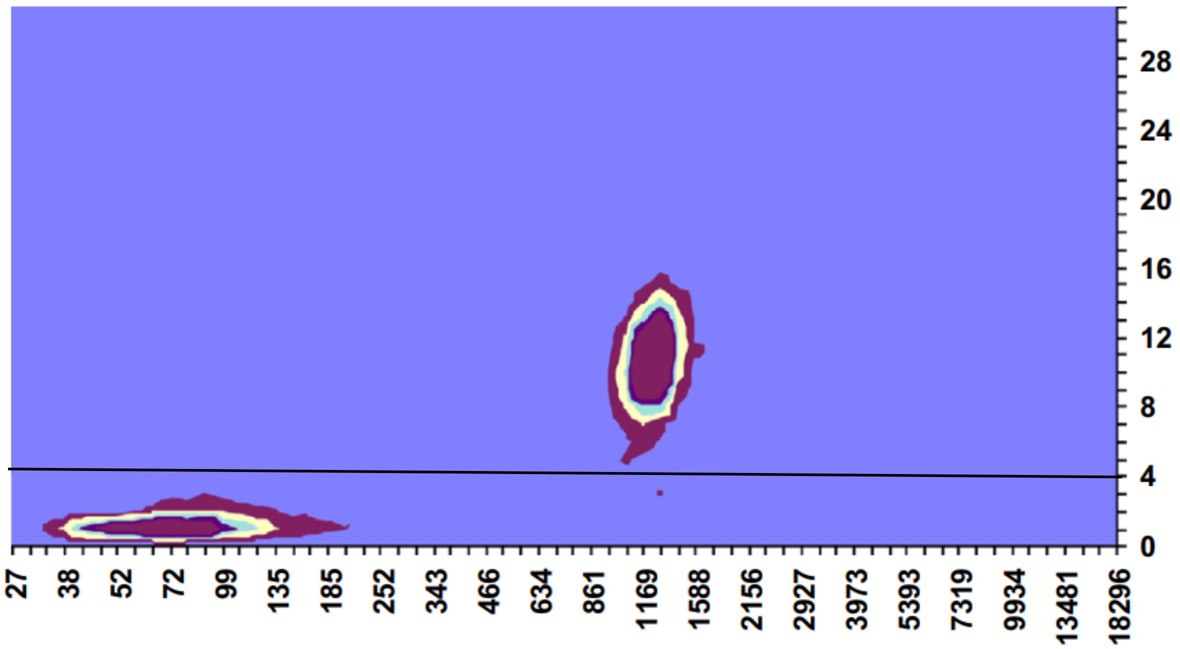

Figure 2.6. Pulse length index (PLI) values (y-axis) for alpha and beta emitters in a two-dimensional graph with channel number on the x-axis.[33] Used with permission from Elsevier: Applied Radiation and Isotopes.

The counting efficiency or how efficiently the nuclear decay is detected for almost all alpha decays is approximately 100% using a liquid scintillation cocktail. This is due to the unique pulse height spectral characteristics of alpha detection in a liquid scintillation counter and their slow pulse decay times. As the work by Jost Eikenberg[33] in Figure 2.7 below shows, the Hidex LSC doesn’t require to be specifically calibrated for efficiency determination to quantify ^{226}Ra, as the TDCR value obtained for the counter is equivalent to the efficiency for ^{226}Ra determination.

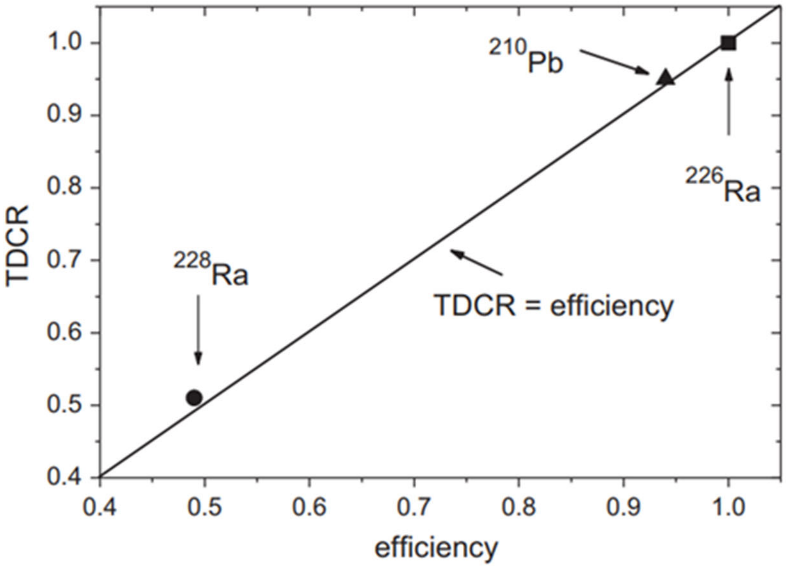

Figure 2.7 Measured TDCR values vs. efficiency for three isotopes.[33] Used with permission from Elsevier: Applied Radiation and Isotopes.

The activity of total alpha and beta can thus be determined by the following formula:

$$Activity(Bq) = \frac{C_s - C_B}{(t * TDCR \ * \ R)} \qquad （2.6）$$

Where, C_s is the count rate of the sample, C_b is the count rate of the blank, t is the time, TDCR is the triple to double coincidence ratio or efficiency, and R is the chemical recovery.

^{226}Ra can be measured directly or indirectly by liquid scintillation technique. The indirect method, or emanation method, permits the determination of ^{226}Ra activity from the pre-concentrated sample after setting the sample aside for approximately 3 weeks and allowing its daughters to ingrown from ^{226}Ra until secular equilibrium is reached. Secular equilibrium is a steady state condition of equal activities between a long-lived parent radionuclide and its short-lived daughters as illustrated in Figure 2.8. This is due to the fact that half-lives of the daughters (^{222}Rn, ^{218}Po, ^{214}Po) are much shorter than the half life of the parent radionuclide, ^{226}Ra of 1600 years. Once equilibrium is reached, the total radioactive of the isotopes remains constant because their production rates of the progeny is equal to the decay rates of the parent. In this case, the counting efficiency will be high as ^{226}Ra has 3 alpha emitting daughters. However, the long waiting period is disadvantageous and is not suitable for emergency situations where fast turnaround time is important.[28,34]

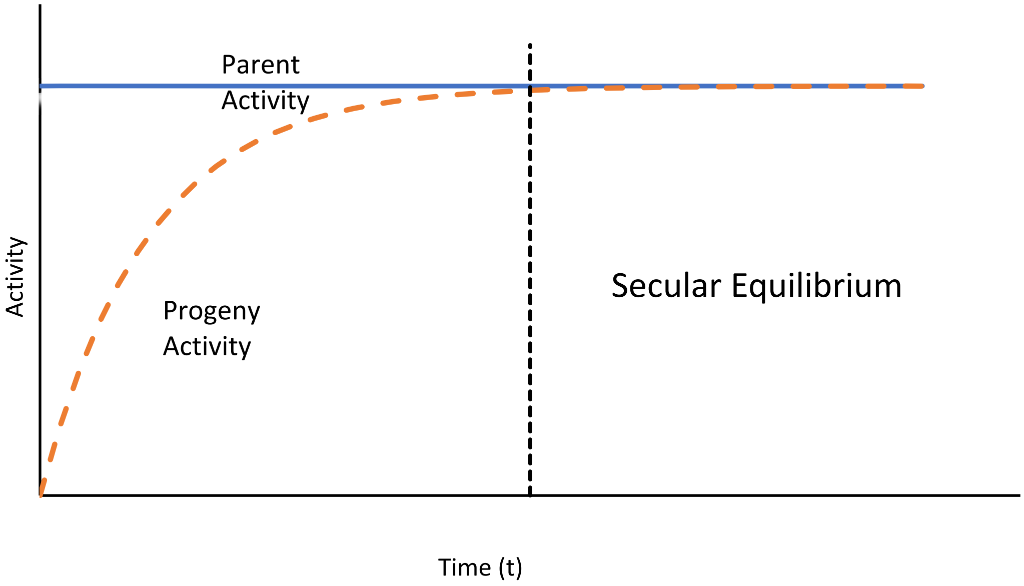

Figure 2.8 Secular equilibrium.

Another method for directly measuring ^{226}Ra with LSC involves accounting for its growing progenies. Unlike alpha spectrometry with semiconductor detectors, LSC has lower resolution and the alpha progenies of ^{226}Ra have similar emission energies, making it challenging to quantify ^{226}Ra independently within the counting window. Therefore, the measurement must account for the combined decay of ^{226}Ra and its progenies using general decay equation 2.7 and the following assumptions:

1) The long-lived parent isotope (^{226}Ra) experiences negligible decay during the counting period.
2) The short-lived progenies are increasing in activity during the separation and counting process.
3) There is complete separation between the parent and daughter isotopes during chemical processing.

The activity A of daughter Y with time is dependent on the production rate from the parent X and its own decay rate as the following equation.

$$A_y(t) = \frac{dN_y(t)}{dt} = \lambda_x N_x - \lambda_y N_y \qquad (2.7)$$

This differential equation can be solved analytically by setting the initial conditions of $A_x = A_x(0)$ and $A_y = A_y(0)$ to obtain the following equation:

$$A_y(t) = A_x(0)\frac{\lambda_y}{\lambda_y - \lambda_x}\left(e^{-\lambda_x t} - e^{-\lambda_y t}\right) + A_y(0)e^{-\lambda_y t} \qquad (2.8)$$

Since the half-life of the parent is considerably large (decay constant λ_x considerably small) compared to its growing daughters, such that:

$$\lambda_x \ll \lambda_y \rightarrow \frac{\lambda_y}{\lambda_y - \lambda_x} \rightarrow 1 \qquad (2.9)$$

And the decay of the parent isotope is meaningless during the counting acquisition time, $e^{-\lambda_x t} \rightarrow 1$, the activity of the daughter can be calculated by the following equation:

$$A_y(t) = A_x(0)\left(1 - e^{-\lambda_y t}\right) \qquad (2.10)$$

In this case, the total alpha activity is the sum of the parent and progenies such that

$$A_{total}^{\alpha} = A_{Ra226}^{\alpha} + A_{Rn222}^{\alpha} + A_{Po218}^{\alpha} + A_{Po214}^{\alpha} \qquad (2.11)$$

With the efficiency or TDCR value for alpha decay at 1, the net measured total count rate of an alpha emitting isotopes equals the sum of activity of ^{226}Ra and the activity of its progenies and can thus be calculated by equation (2.11). The following equation can be obtained to calculate ^{226}Ra activity from the total measured alpha count rate.

$$A_{Ra226} = \frac{A_{tot}}{(1+3f)} \qquad (2.12)$$

$$f = (1 - e^{-\lambda t})$$

Where f is the ingrowth factor, A_{tot} is the total activity measured in the alpha spectrum, t is time from separation and measurement, and λ is the decay constant for ^{222}Rn. The progenies ^{218}Po and ^{214}Po have very short half-lives of minutes such that it can be assumed it is in secular equilibrium with ^{222}Rn and that it is growing in at the same rate. This equation is used to determine the ^{226}Ra activity using the total alpha activity measured by the LSC.[33]

2.2.4 Radiation Safety Protocols

Radiation safety protocols are critical to minimize exposure to harmful radiation and ensure the protection of workers, the public, and the environment. The use of nuclear substances is highly regulated to ensure their safe handling, transport, and disposal, and to minimize the risks of radiation exposure. These regulations vary depending on the country and are enforced through national regulatory bodies. In Canada, the CNSC regulates the use of nuclear substances and facilities according to the Nuclear Safety and Control Act. [35]

In this work, the laboratory has a consolidated license on the use of nuclear substances that was granted by the CNSC, allowing the facility to manage nuclear materials within prescribed safety guidelines. To ensure adherence to radiation safety protocols, the laboratory follows a comprehensive radiation safety program. This program is managed by a Radiation Safety Officer who ensures compliance with regulations, implements safety protocols, conducts training and leads emergency response efforts.

Chapter 3 Radiochemical Separation and Pre-concentration

In environmental samples, radium is present at very low concentrations, therefore for all detection methods, radiochemical separations and or pre-concentration are unavoidable and is a critical step for accurate measurement. A clear differentiation between pre-concentration and separation is not always given in practice. Traditional pre-concentration and separation techniques based on evaporation, co-precipitation, adsorption, ion exchange, and solvent extraction have been successfully applied to ^{226}Ra. In recent years, extraction chromatography using resins or solid phase extraction has become popular for the separation of radionuclides including ^{226}Ra to achieve higher separation efficiency and reduce the amount of hazardous wastes produced. [26,36–38] This technique separates analytes from a liquid sample by passing it through a solid absorbent material, which selectively retains the target compounds while allowing impurities to pass through. Current popular resins used to pre-concentrate radium include manganese dioxide (MnO_2) resins, Sr-resins, lanthanide (Ln) resin, RAD disks, and a variety of other extractants sorbed on inert polymeric supports[39–43]. The use of multiple resins including ion exchange is often necessary to further purify radium for final analysis. The use of vacuum boxes and small-sized column is also advantageous for time saving and necessary for emergency response requirements. [20]

Figure 3.1 Vacuum box and columns for separation

3.1 Manganese Dioxide (MnO_2) resin

Manganese dioxide (MnO_2) resin is an inorganic resin that consists of MnO_2 precipitated on an inert microporous substrate and it was intended to pre-concentrate radium from natural waters.[44,45] It was first applied for radium pre-concentration by adsorption in 1972.[46] The resin is stable under an optimal pH range of 4-8, and recoveries of >90% have been achieved in water and low salinity water with Barium as a proxy.[44] At low pH, the slow dissolution of MnO_2, increases the positive surface charge of the resin and prevents the sorption of radium and other positively charged alkaline earth species. At higher pH, complexation of Ra lowers sorption to the resin.

Based on previous experience with this method and considering the simplicity of the method (only one column with limited number of reagents), MnO_2 resin was chosen for this study. Th use of MnO_2 based methods for separation and preconcentration of ^{226}Ra is widely used in literature.[44,47,48] As demonstrated by Eikenberg et al[45], MnO_2 coated polyamide discs can be used directly for low-level alpha spectrometry without the need of further separation and preparation methods and thus is suitable for radium isotopes at environmental levels. Similarly, Dulanska et al[49] verified a rapid method for ^{226}Ra in natural mineral waters using MnO_2-PAN (polyacrylonitrile) composite ion absorber with ^{133}Ba as tracer, that had high recovery yield (90-100%). Furthermore, the same group[50] tested MnO_2-SiO_2 composite resin with good results using natural waters.

The effect of pH on ^{133}Ba(^{226}Ra) sorption on the MnO_2 based resins have been studied previously by many researchers and have all show good recovery within pH 4-9. [44,45,51]

Bojanowski et al [48] further investigated the influence of high salt concentrations on MnO_2 co-precipitation efficiency using barium as proxy for ^{226}Ra and concluded that sodium chloride concentrations up to 100g/L do not affect the recovery of barium and radium. However, the effect of calcium and magnesium ions was much stronger with limits of 0.2g/l to 1g/l, respectively and required a second or third precipitation step to obtain high recovery.

Given the previous studies done for pH, flow rate and salt content, ^{133}Ba have shown to be a suitable tracer for pre-concentrating ^{226}Ra using MnO_2 resin with recoveries above 80%. However, a loss in recovery of greater than 50% was observed when the chemical recoveries of Ba and Ra start to differ from each other, ^{133}Ba, can no longer be considered as chemical analogue, making its use as a tracer undesirable. In such cases, the ^{226}Ra content can be overestimated when the ^{133}Ba recovery is below 60%. [52]

Chapter 4 Material and Methods

4.1 Radium source

In this work, the radium standard source was obtained from Eckert & Ziegler Analytics. Specific details about the ^{226}Ra source are given below.

Producer: Eckert&Ziegler Isotope Products

Reference Date: 11-Sept-2020

Source Number: 117132

Radionuclide: ^{226}Ra

Total Activity: $(5.019 \pm 0.236) \times 10^4$ Bq

Volume: 5ml

Chemical Form: Liquid

4.2 Reagents and Materials

$NaCl$, $MgCl_2$, $CaCl_2$, $BaCl_2$, HCl, $(NH_4)_2SO_4$, isopropanol used are analytical grade and were obtained from Fisher Scientific and SCP Scientific. Fe standard element solution at 1000µg/ml was purchased from SCP science. MnO_2 resins (100-200µm) and polypropylene filters were purchased from Eichrom Technologies, part number MN-B100-A. Standards and acids were diluted with ultrapure water (18 MΩ, <5µg/L TOC) from Millipore IQ70005 water purification system. Ultima Gold AB LSC cocktail is obtained from Revvity. Proficiency testing sample provided by the International Atomic Energy Agency (IAEA) exercise (IAEA-TERC-2023-01).

4.3 Sample Preparation of ^{226}Ra

For comparison of ^{226}Ra analysis, standard solutions were prepared with an activity of 0.1, 0.5, 1, 1.5, and 2 Bq/L. The selected radium concentration range is typical of what is found in environmental and effluent type samples. To simulate natural waters and assess the effect of matrix variability on the method, a stock of 2L bottle of tap water was spiked with ^{226}Ra standard source of 20Bq/L activity and the sample was shaken by hand for homogeneity. Aliquots of 50ml of the sample were then spiked with different concentrations of various minerals, Ca^{2+}, Mg^{2+}, Na^{2+}, Ba^{2+} and Fe^{2+} likely present in surface water systems near nuclear and mining facilities, where effluents may be released.

Table 4.1 Concentrations of elements tested.

Element	Source	Concentration range
Na	NaCl	1 – 100 g/L
Mg	$MgCl_2$	0.5 – 20 g/L
Ca	$CaCl_2$	0.5 – 80g/L
Ba	$BaCl_2$	0.1 – 10mg/L
Fe	1000ug/ml	1 – 60mg/L

4.4 Sample Pre-concentration

^{133}Ba certified standard solution from Eckert & Ziegler was added to each sample prior to preconcentration as a chemical yield tracer for radium determination. The MnO_2 resin columns are first rinsed with 25ml of deionized water to remove any loose MnO_2 prior to loading the samples. Samples are loaded at a flow rate of 10ml/s minimum. After sample loading, the sample beakers are rinsed with 5ml of deionized water and was also loaded onto the column. The MnO_2 and radium and barium are then dissolved and stripped from the resin with 20ml of 5M HCl -1.5% H_2O_2 into a 50ml centrifuge tube. The H_2O_2 reduces Mn(IV) to Mn (II), which dissolves easily in HCl.

Polycarbonate vacuum boxes purchased from Eichrom with a rack to hold 20ml centrifuge tubes were used. An inner liner was used to collect the sample during preconcentration after passing through the MnO_2 Resin columns.

4.5 Source Preparation – Barium Sulfate Micro-precipitation [25,53]

50µl of 1mg/mL of barium carrier, 3g of ammonium sulfate and 6ml of isopropanol was added to each sample and mixed. Samples were then placed on ice for 30 minutes to allow a complete precipitation before filtering onto a pre-conditioned 0.1micron 25mm polypropylene filters and rinsed with 20% isopropanol. Iso propanol is used to reduce the amount of Ba and Ra lost to the filtrate as it reduces the barium sulphate solubility in the wash solution[48]. The filters are then dried naturally and glued on a plastic substrate to be counted on alpha spectrometer for ^{226}Ra quantification and gamma detector for ^{133}Ba quantification. The filters were then carefully removed from the plastic substrate and placed in a glass 20ml vial with 18ml of Ultima Gold A/B scintillation cocktail and were analyzed by LSC. Figure 4.1 illustrates the steps involved in sample pre-concentration and source preparation.

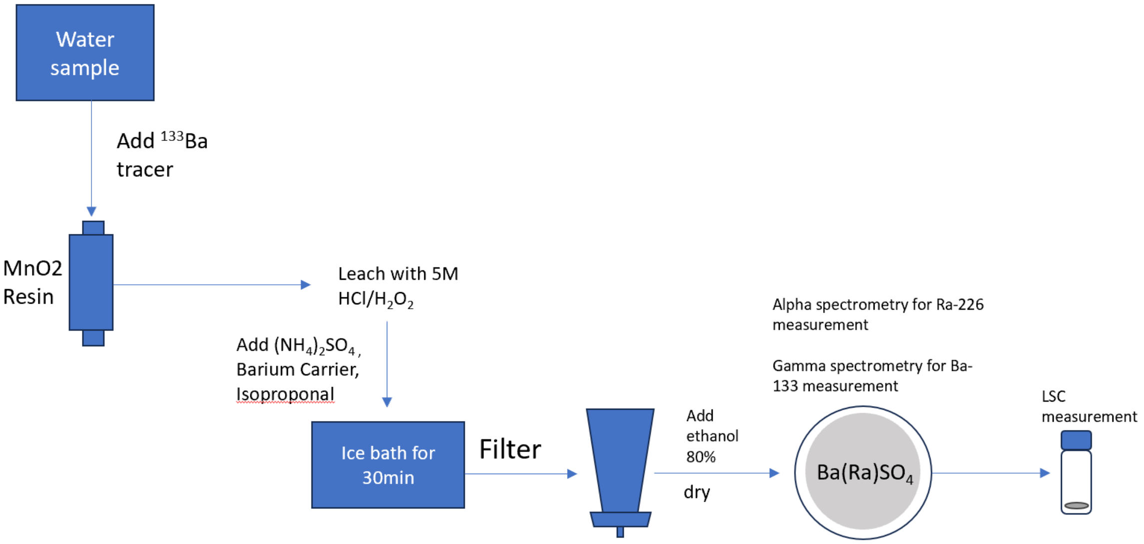

Figure 4.1. Schematic of sample pre concentration and source preparation.

4.6 Determination of ^{226}Ra using Alpha Spectrometry

Alpha spectrometry was performed by an alpha-particle pulse height measurement using Passivated Implanted Planar Silicon (PIPS) detectors provided by Canberra Industries Inc with alpha analysis software Genie2000. The PIPS detectors have an active surface area of 450mm^2. The alpha spectrometer was calibrated with a standard reference source containing traceable activity of radionuclides, ^{238}U, ^{234}U, ^{239}Pu, and ^{241}Am (Eckert& Ziegler, reference date 2012-12-14). Using the standard source, an energy calibration and a counting efficiency calibration at the counting geometry can be determined. The counting efficiency was determined to be approximately 19%. The distance between the sample and the detector surface was 2mm. The chambers were operated at 60V and pressure below 20 Torrs. The number of counts under the peak is divided by the counting time and corrected for efficiency of the detectors at the specific energy level using equation 2.4.

4.7 Determination of ^{226}Ra using Liquid Scintillation Counting

The LSC apparatus used for ^{226}Ra determination was a Hidex 300 SL (Hidex, Finland). The triple to double coincidence ratio, which is the same as efficiency, was used and found to be 100% for the alpha region. To set the region of interest (ROI) window for evaluation of ^{226}Ra, a diluted standard source of ^{226}Ra with activity of 1Bq was prepared in the laboratory. The total area under the ROI window from 550 to 900 was selected to account for the total alpha emissions and used to calculate the total number of counts.

4.8 Determination of ^{133}Ba Tracer using High Purity Germanium (HPGe) Gamma Analysis

The gamma-ray spectrometry system used for ^{133}Ba determination was an HPGe detector (Mirion), coupled with a digital multichannel analyzer. The gamma detector is housed in a low-background lead shield. The system was calibrated using multi energy mixed standard source supplied by Eckert& Ziegler. Data analysis was performed using software Genie2000. The ^{133}Ba content was determined by taking the ratio of the peak area of key gamma line of ^{133}Ba at 356 keV in the sample to that of the traceable Ba-133 standard.

Chapter 5 Results and Discussion

5.1 Evaluation of ^{226}Ra Concentrations in Simulated Water Samples using Alpha Spectrometry

In this experiment, tap water/well water were used as simulated natural environmental samples. To analyze ^{226}Ra using the selected techniques, each water sample required chemical separation to isolate ^{226}Ra before counting and a co-precipitation procedure was used for the preparation of the radium sources using $BaSO_4$ as a carrier. Due to their similar chemical properties, ^{133}Ba was used as a tracer for ^{226}Ra, to determine the chemical yield of the separation step. ^{133}Ba emits strong gamma rays following its electron capture decay, and its activity concentration in the sample was easily determined by the non-destructive technique of gamma spectrometry using a HPGe detector.

The separation of ^{266}Ra in water samples were done by chromatographic column separation using the MnO_2 resin, which is known to have a great affinity for radium and barium, making it a highly effective separation method. The total time for the radiochemical separation including separation step and micro-precipitation step to prepare the source takes approximately 5 hours for a 300ml sample. However, it is possible to process multiple samples simultaneously using a vacuum box with multiple slots and filters, to achieve efficiency.

For the purpose of evaluating the effect to ^{226}Ra recovery by the mineral content (see detailed discussion in Section 5.6 - 5.11), the mineral content of the tap water/well water was determined using an Agilent 8900 ICP-MS and the results are shown in table below.

Table 5.1 Mineral contents of tap (well) water used.

Element	Concentration
Ca	200 µg/L
Mg	120 µg/L
Fe	10 µg/L
Ba	0.7 µg/L
Na	130 mg/L

To assess the accuracy and precision of the method at low radium concentrations using Alpha spectrometry, varying concentrations of radium were first prepared by spiking the tap water samples with the radium NIST traceable standard were first prepared and measured. The range of activity concentration used was at lower levels to be similar to environmental samples and typical compliance samples collected following effluent releases at around 1Bq/L (Table *1.2*).

Other radionuclides besides radium may be present in the sample matrix and can disrupt the alpha spectrometric determination of radium nuclides if they are not completely separated out. Potential interferences with the alpha energy of ^{226}Ra can be caused by nuclides such as ^{230}Th, ^{229}Th, ^{231}Pa, and ^{234}U. However, due to prior chemical separations, the number of interfering radionuclides likely to appear during measurement is drastically minimized[1]. Counts from a well-defined peak are integrated over a region of interest (ROI), providing an accurate quantification of the area under the peak.

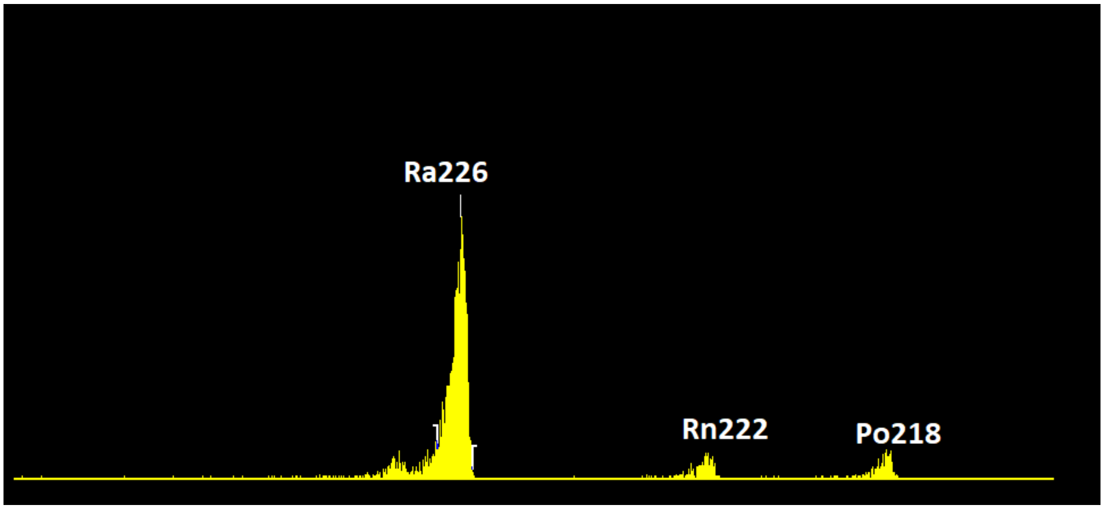

Figure 5.1. Alpha spectrum of ^{226}Ra standard in tap water.

The individual analytical results are listed in the following table along with expected values of ^{226}Ra. The uncertainty values at 1σ are also tabulated below and derived from major uncertainty components associated with the counting statistics, chemical recovery, and the standards used as described in further details in section 5.11.

The results in Table *5.2* show that from 0.1 – 2 Bq of ^{226}Ra activity in simulated water samples, the method can analyze the Ra accurately at a recovery from 99% to 105%. The relative standard deviation shows a slight increase from 7.0% to 8.4% with the decrease of the ^{228}Ra activity from 2 to 0.1Bq/L.

Table 5.2. Alpha spectrometry results for ^{226}Ra standards in tap water samples.

Spiked ^{226}Ra activity (Bq)	Measured ^{226}Ra (Bq)	Measured ^{226}Ra uncertainties	RSD (%)	^{226}Ra recovery (%)
0.10	0.10	0.008	8.4	101
0.49	0.49	0.037	7.5	99.3
0.50	0.53	0.039	7.5	105
0.50	0.50	0.037	7.5	100
1.08	1.10	0.078	7.1	102
1.46	1.51	0.106	7.0	104
1.97	1.98	0.139	7.0	101

5.2 Evaluation of ^{226}Ra Concentration in Simulated Natural Water Samples using Liquid Scintillation Counting

5.2.1 Liquid scintillation counting results over time

Unlike alpha spectrometry, where radium can be measured directly using its alpha particle emission after source preparation, ^{226}Ra cannot be measured directly with LSC due to its poor peak resolution and the similar alpha particle emission energies of its progenies (^{222}Rn, ^{218}Po, ^{214}Po). Instead, the total alpha emission, which includes the alpha emission from ^{226}Ra and its three alpha emitting daughters is measured to derive ^{226}Ra activity. In this case, the total alpha emission will depend greatly on the time difference between the separation and measurement. This can be seen clearly through the 2-dimentional graphs of the counts provided by the Hidex software as shown in Figure 5.2, as the time increases, the number of alpha counts increases as well due to its daughters growing in. Figure 5.2 also illustrates that after 22 days from separation, the alpha daughters have reached secular equilibrium, and total alpha activities will stay constant.

The progenies of ^{226}Ra also include beta-emitting radionuclide (^{214}Pb, ^{214}Bi, ^{210}Pb, and ^{210}Bi) and in this case, the added ^{133}Ba tracer. Due to the high background count rate in the beta window, alpha/beta discriminated counting was required to exclude certain counts to achieve accurate results. The pulse length index (PLI) used for alpha/beta discrimination can be clearly seen in Figure 5.2. The pulse length of alpha particles is longer than that of beta particles, as alpha particles react with the scintillation cocktail, resulting in delayed phosphorescence. Therefore, the spectra in the high-PLI region above 12 corresponds to the alpha particles, whereas those in the low PLI region (below 12) corresponds to beta particles. To accurately discriminate the alpha/beta pulses, the PLI can be adjusted easily depending on the spectra. In this case, the PLI was adjusted slightly with the growing daughters from 12 at one day after separation to 16 at 20 days after separation.

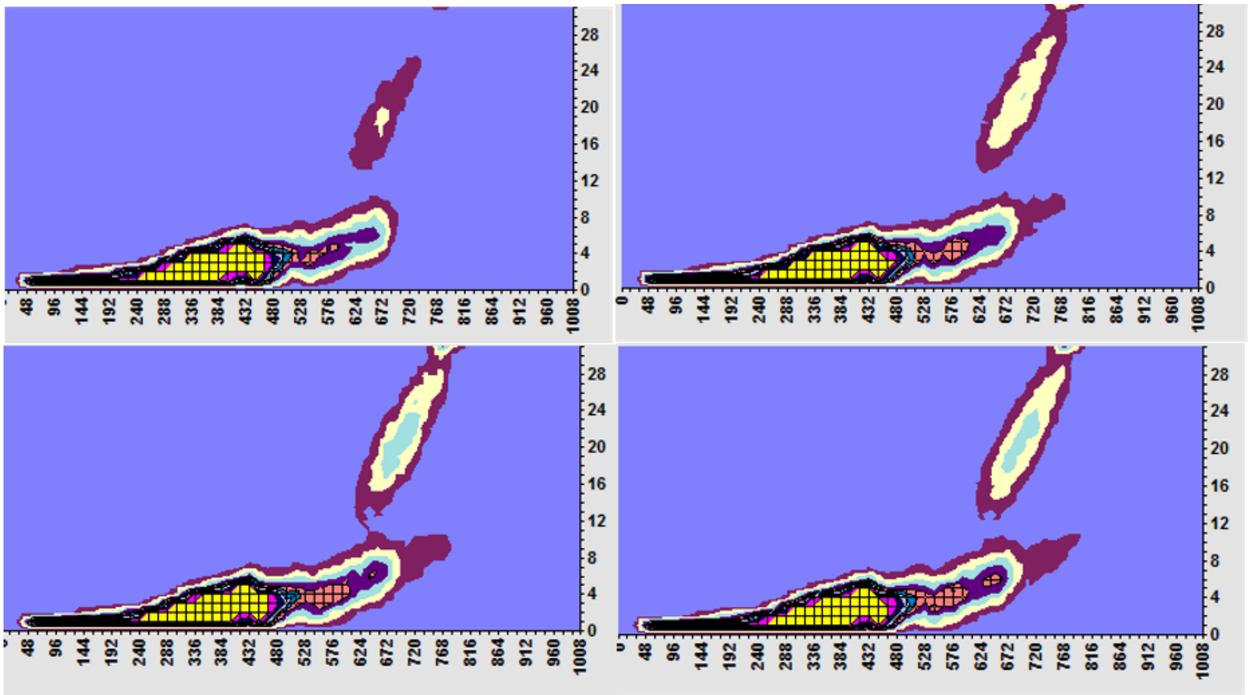

Figure 5.2. 2-Dimensional graphs with PLI values on y-axis with channel number on the x-axis for a radium standard measured on LSC after 3 (top left), 9 (top right), 22 (bottom left), and 30 days (bottom right).

^{226}Ra concentration measured using LSC can be determined any time after separation provided that alpha/beta separation parameters (PLI and ROIs) have been selected correctly and that progenies are accounted for properly by using Equation 2.12 in Chapter 2 of this work. Figure 5.3 below shows the total alpha counts measured using LSC and its derived calculated ^{226}Ra activity over time after separation along with the expected values of the ^{226}Ra standard. As can be seen in the figure, there is a strong correlation between the expected values and the measured data. Therefore, the decay equations and assumptions described in Chapter 2 of this work are suitable to apply for this approach. This is an advantage over conventional LSC methods where measurements will only take place after sector equilibrium is reached, usually 21 days after separation to measure the progenies.

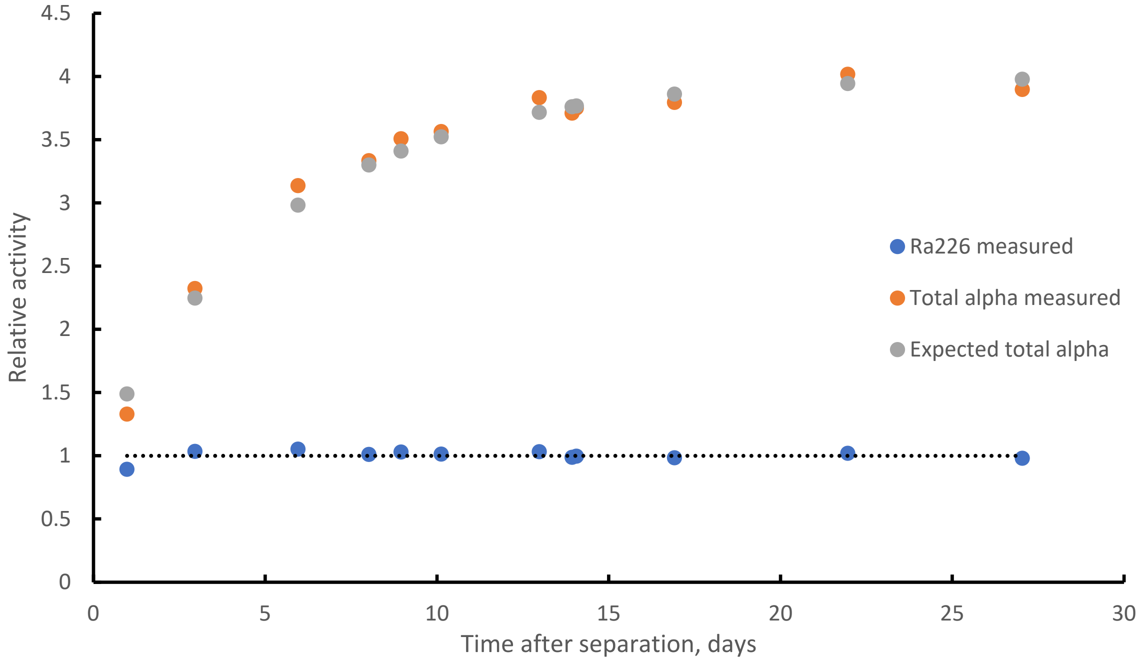

Figure 5.3. Measurement results for ^{226}Ra activity in spiked water samples using LSC over time.

Table 5.3 lists the same set of ^{226}Ra standards used for alpha spectrometry with its expected values and its measured value using LSC. The uncertainty values at 1σ are also tabulated below and derived from uncertainties associated with the counting, chemical recovery, and the standard used. The results show that from 0.1 to 2 Bq of ^{226}Ra activity in simulated water samples, the method can analyze ^{226}Ra activity accurately from 97% to 104%.

Table 5.3. LSC results for ^{226}Ra standards in tap water samples.

Spiked Ra226 activity (Bq)	Measured Ra226 (Bq)	Measured Ra226 uncertainties	RSD (%)	Ra226 Recovery (%)
0.10	0.10	0.007	6.8	103
0.49	0.51	0.035	6.9	103
0.50	0.49	0.033	6.7	97.3
0.50	0.50	0.033	6.7	100
0.99	1.11	0.074	6.7	103
1.46	1.44	0.095	6.6	98.5
1.97	2.05	0.134	6.5	104

5.3 Comparison of LSC and Alpha spectrometry results

The correlation between ^{226}Ra results of the two radiometric methods, alpha spectrometry and LSC is determined and shown in Figure 5.4. In this figure, the results of each standard solutions using LSC and alpha spectrometry is plotted against the expected value to allow for a meaningful comparison. This figure shows the results are in strong agreement in the range between 0.1 - 2 Bq/L with correlation coefficients exceeding 0.99. Therefore, both techniques are suitable for accurate determination of ^{226}Ra concentration in natural surface water samples with typical mineral content similar to that of tap water.

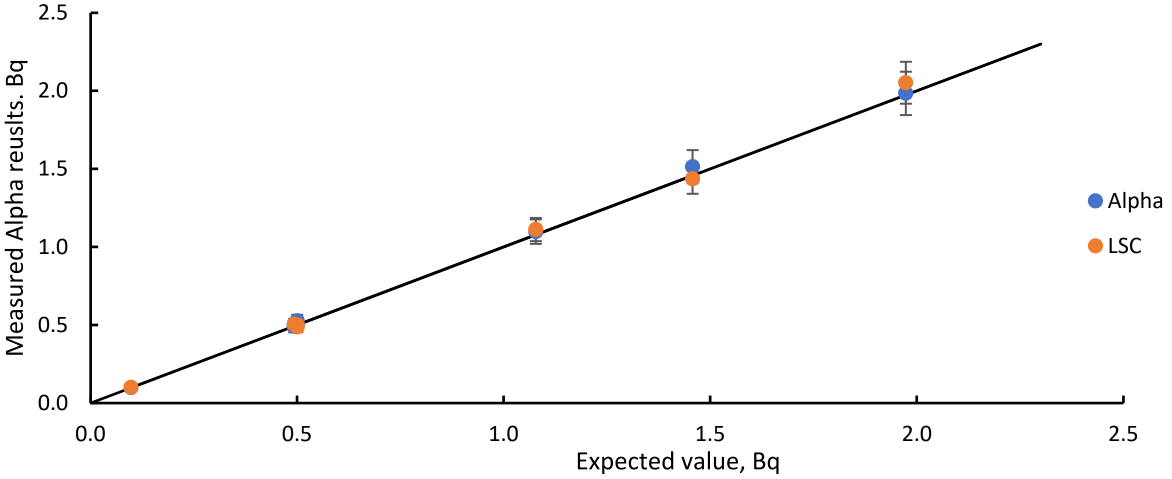

Figure 5.4. Relationship between results of LSC and Alpha spectrometry

5.4 Minimum Detection Activity

The minimum detectable activity or MDA is mainly affected by the blank activity according to the Currie[54] formula:

$$MDA = \frac{2.71 + 4.66\sqrt{B}}{EVt} \qquad (5.1)$$

Where, B is the background counts; t, counting time; E, counting efficiency; Y, chemical Yield; V, the sample volume. The MDA is the smallest activity concentration that yields a net count above background with a 95% confidence.

The MDA for ^{226}Ra was evaluated to be 0.007 Bq/L for alpha spectrometry and 0.05 Bq/L for LSC using the same counting time of 200 minutes for a 300ml sample. Although MDA evaluated for the two methods are well below Canada's drinking water guideline of 0.5Bq/L, the MDA achieved with alpha spectrometry is about an order of magnitude lower than that of LSC technique. This is due to the fact that LSC technique has a much higher background as compared to alpha spectrometry technique; therefore, with identical measurement time, alpha spectrometry yields the lowest MDA.

5.5 Proficiency Testing Results

To further validate and compare these two methods, one proficiency testing sample provided by the International Atomic Energy Agency (IAEA) exercise (IAEA-TERC-2023-01)[55] were also measured. The results are listed in Table *5.4*. The relative bias for IAEA-TERC-2023-01 sample was determined to be -4.53% and -0.19% for alpha spectrometry and LSC results, respectively for IAEA-TERC-2023-01. Both results are well below the Maximum Acceptable Relative Bias (MARB) of± 30% for this exercise. Results from the PT exercise demonstrate that alpha spectrometry and LSC's precision and accuracy are in excellent agreement with assigned values, yielding acceptable passing results.

Table 5.4. IAEA Proficiency Testing results for ^{226}Ra (IAEA-TERC-2023-01)

Parameter	Target Value	Measured Value by Alpha Spectrometry	Measured Value by LSC
Activity Conc. (Bq/kg)	6.32	6.03	6.31
Uncertainty 1s (Bq/Kg)	0.32	0.36	0.39

In the following sections, results of ^{226}Ra spiked tap water samples with varying mineral content are presented. These simulated water samples are prepared to mimic natural surface water systems potentially affected by migration of effluent releases likely to be found in environments prone to industrial releases containing ^{226}Ra as presented in Table 1.1. These types of samples are analyzed using both LSC and alpha spectrometry as shown below to assess the effect of matrix on suitability of each technique.

5.6 Influence of Ca content on ^{226}Ra Recovery

The influence of calcium concentration on radium determination is shown in

Figure 5.5. The chemical recovery was found unaffected by increasing calcium concentration up to 80 g/L and recovery was in the expected range of 80-100%. This concludes that the added Ca did not affect the adsorption of Ba and Ra, or in other words, it did not compete with the adsorption sites of the MnO_2 resin for Ba and Ra. However, ^{226}Ra recovery by alpha spectrometry decreased significantly when added calcium concentration increased from 20g/L to 50g/L. At 80g/L of added calcium concentration, no radium was detectable alpha spectrometry. This difference could be explained by the absorption and self-adsorption of the alpha particles within the thick source when alpha spectrometry is utilized. In alpha spectrometry, the alpha particle emitted by the radionuclides embedded in the source material must be able to travel through the air space present in the vacuum chamber as well as the source itself to the detector. Both processes will contribute to the total absorption and cause reduction of the total energy deposited to the detector. They heavily depend on the composition, density, homogeneity and surface roughness of the absorber and the source. Ideally, in alpha spectrometry the sources should be infinitely thin to avoid self-absorption. However, in this case, it is suspected that as the

calcium concentration increased, the thickness of the source also increases, thereby diluting the Ra, and reducing its concentration at the surface where alpha particle sampling occurs. This assumption is further proved by the radium results obtained by LSC, which showed better recovery than alpha spectrometry where adsorption and self-adsorption don't pose an issue, since the scintillator is mixed directly with the sample and alpha particles are not trapped in the filter.

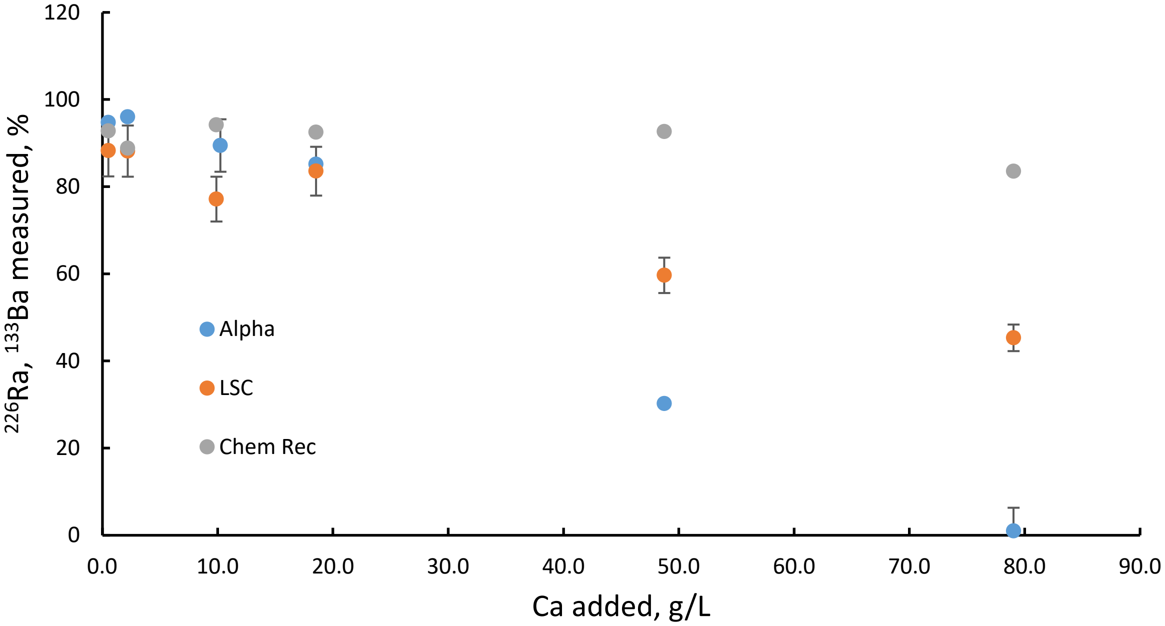

Figure 5.5. Influence of Ca content on ^{226}Ra recovery.

Furthermore, it was noted that increasing calcium concentrations led to poorer resolution in the alpha spectrum as seen in Figure 5.6, which affected the ability to accurately quantify ^{226}Ra activity. This degradation of the spectrum is likely caused by the buildup of calcium sulphate crystals on the filter surface, compromising its thin and uniform structure. As a result, alpha particle attenuation occurs, leading to a loss of counts and broadening of the peak shape as shown in Figure 5.6 for a sample containing 50g/L of added calcium spiked with ^{226}Ra.

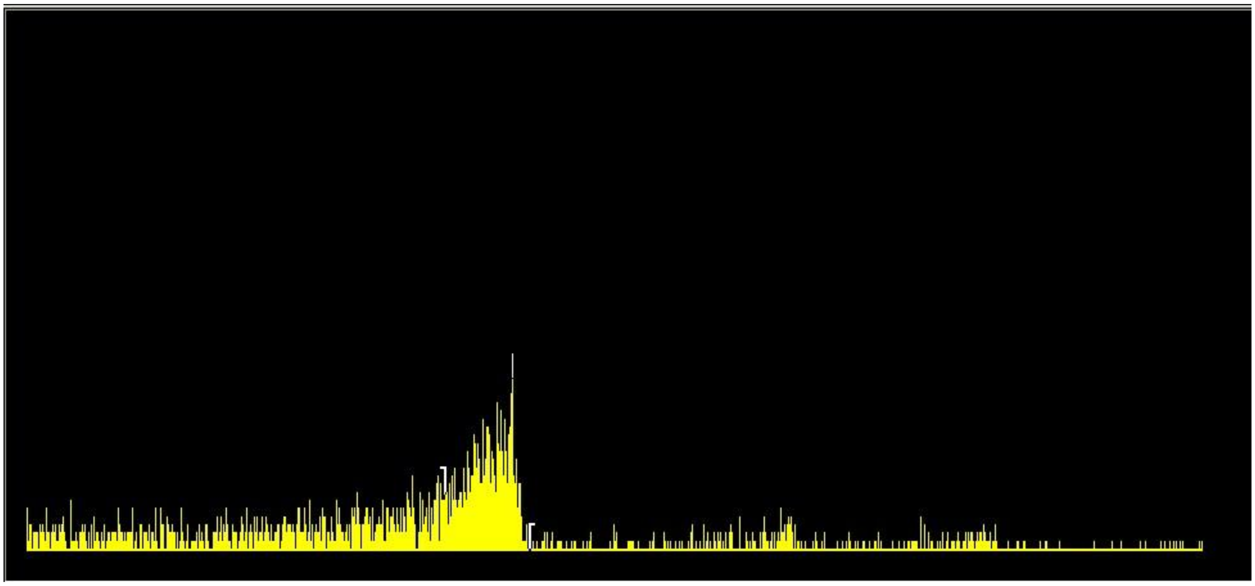

Figure 5.6 Alpha spectrum of a spiked ^{226}Ra sample with 50g/L Ca added with channel numbers on the x axis and counts on the y axis.

To examine the thickness of the source contributing to self-adsorption effect in alpha spectrometry, two samples, one with no added calcium and one with added calcium was prepared and analyzed using a Scanning Electron Microscope with an energy dispersive X-ray spectroscopy (SEM-EDS) to examine the surface of the prepared source/ filter (Figure 5.7). Although no quantitative results were available for this analysis, it can be seen clearly that calcium is present on the surface of the filter/source in the sample with added calcium, while the sample with no added calcium had no observed calcium. This demonstrates that some calcium is absorbed onto the resin and is also co-precipitated along with radium and barium as sulphate such that the micro size pores of the filter is filled with calcium sulphate.

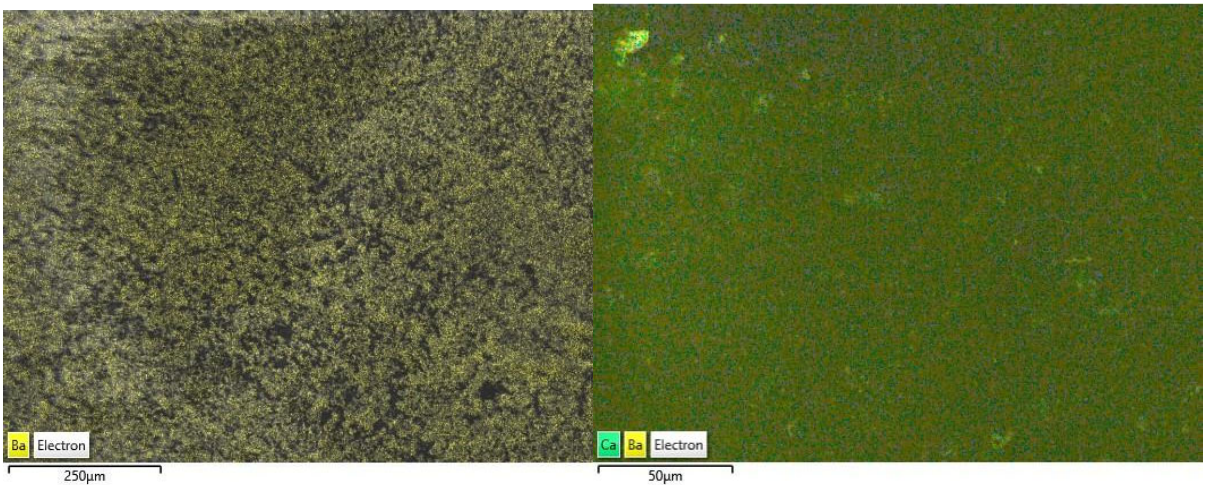

Figure 5.7. SEM EDS (Zeiss EVO MA10 and Oxford EDS detector) for sample with no calcium added on the left and sample with added calcium on the right.

While the LSC method for quantifying ^{226}Ra performed better than alpha spectrometry at higher calcium concentrations, a 20% decrease in recovery was observed starting at a calcium concentration of 50 g/L. Initially, this decline was attributed to potential quenching effects from calcium salts interfering with the energy transfer to scintillator molecules. However, adding $CaCl_2$ salts directly to a ^{226}Ra standard solution did not result in decreased recovery, suggesting that quenching effects were not the cause.

Instead, it was hypothesized that the decrease in recovery was due to the formation of precipitates on the filter that were not adequately dissolved in the LSC cocktail, affecting the energy transfer to the scintillator. To test this, a ^{226}Ra sample spiked with calcium at 50 g/L was prepared without micro-precipitation. The eluent was evaporated to dryness at 100°C and then reconstituted in 1 ml of dilute acid and 17 ml of LSC cocktail, since the original eluent was too acidic for direct mixing with the LSC cocktail. The result showed a 103% chemical recovery of

^{226}Ra, indicating that the observed decrease in recovery was indeed due to dissolution effects of undissolved precipitates in the LSC cocktail.

5.7 Influence of Na content on ^{226}Ra Recovery

Contrary to the results of calcium effect, sodium concentration of up to 80g/L did not show an adverse effect on radium detection/recovery in either technique. ^{226}Ra concentration measured using both LSC and alpha spectrometry resulted in higher than 90% recovery. This observation was expected and can be explained by sodium's different chemical properties compared to calcium in both MnO_2 resin column separation and micro-coprecipitation source preparation steps. Firstly, MnO_2 resin does not retain sodium, an alkaline metal, so the majority of the sodium had been removed by the MnO_2 column prior to the source preparation by micro-coprecipitation. Secondly, for a similar reason, any sodium residue with barium and radium in the solution, did not form precipitate with sulphate, therefore it would not contribute to source thickness. On the other side, as an alkaline earth element in the same group as barium and radium, smaller amount of calcium as residue with barium and radium in the solution was co-precipitated and contributed to the thickness of the source adversely affecting alpha spectrometry. The chemical yields for this set of data were in the expected range of greater than 85% up to a sodium concentration of 80g/L. This result is in agreement with the study from Burns et al [48] which reported that concentrations of sodium chloride up to 100g/L have no effect on sorption for both radium and barium.

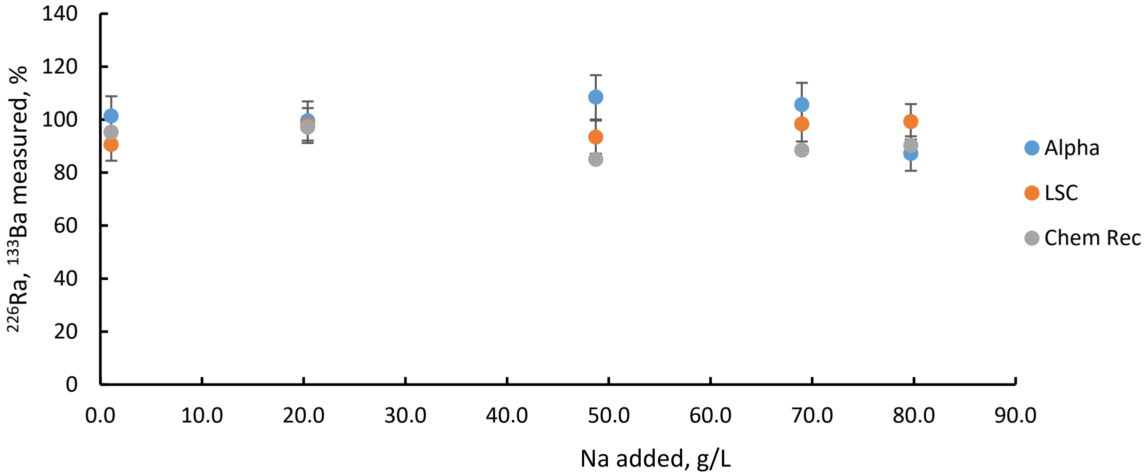

Figure 5.8. Influence of Na content on Ra recovery

5.8 Influence of Mg content on ^{226}Ra Recovery

The effect of magnesium content, which is another component contributing to hardness, did not show an adverse effect on ^{226}Ra recovery measured by alpha spectrometry and LSC when magnesium levels increased of up to 20g/l, Figure *5.9*. Both radiometric techniques showed good radium recovery of above 80% when Mg was less than 20 g/L. Firstly, also a member of the alkaline metal group, Mg was found to behave similarly as Ca within the concentration range of less than 20 g/L that not affecting the MnO_2 resin column separation and both alpha spectrometry and LSC determination of ^{226}Ra. Strictly speaking, this comparison should be done by molarity concentration than the mass concentration where 20 g/L of Mg, or 0.82 M of Mg is equivalent to 0.82 M Ca or 32.9g/L.

It is worthwhile to discuss more the influence of Ca and Mg concentration to Ra recovery by their chemical properties. Ca, Mg, Ba and Ra are elements belonging to the alkaline earth group in the periodic table together with Be and Sr. Although they behave similarly in chemical reactions, however, they do show differences in chemical behavior gradually in the order from Be, Mg, Ca, Sr, Ba, and Ra. Ba is the closest in chemical properties to Ra, and the difference increase as the elements' atomic number becomes smaller. Experiment carried out by Eichrom Environment[52] has shown that MnO_2 resin had similar and higher adsorption for Ra and Ba ($D_w = 1\times10^3$ under pH 7). Its adsorption for Sr and Ca was lower (D_w = 0.1 to 0.15 under pH 7) compared to that for Ba and Ra. MnO_2 resin showed lowest adsorption for Mg (Dw = 0.05 under pH 7) of these five alkaline earth elements. This implies that when loading the sample solution onto the MnO_2 column, Ba and Ra were quantitatively adsorbed by the resin while only a small fraction of Ca, Mg (and Sr) could be adsorbed.

In micro co-precipitation step, examining the solubility product constants (K_{sp}) of alkaline metal sulfates can provide insights into how the concentrations of Ca and Mg affect the recovery of Ra. The K_{sp} values for $MgSO_4$, $CaSO_4$, $SrSO_4$, $BaSO_4$, and $RaSO_4$ are 5.9×10^{-3}, 4.9×10^{-5}, 7.6×10^{-7}, 1.1×10^{-10}, and 3.7×10^{-11}, respectively. [56] These values indicate that, at equal concentrations, magnesium will be less likely to co-precipitate compared to calcium due to its higher solubility. Consequently, magnesium contributes less to the thickness of the precipitate layer in the source.

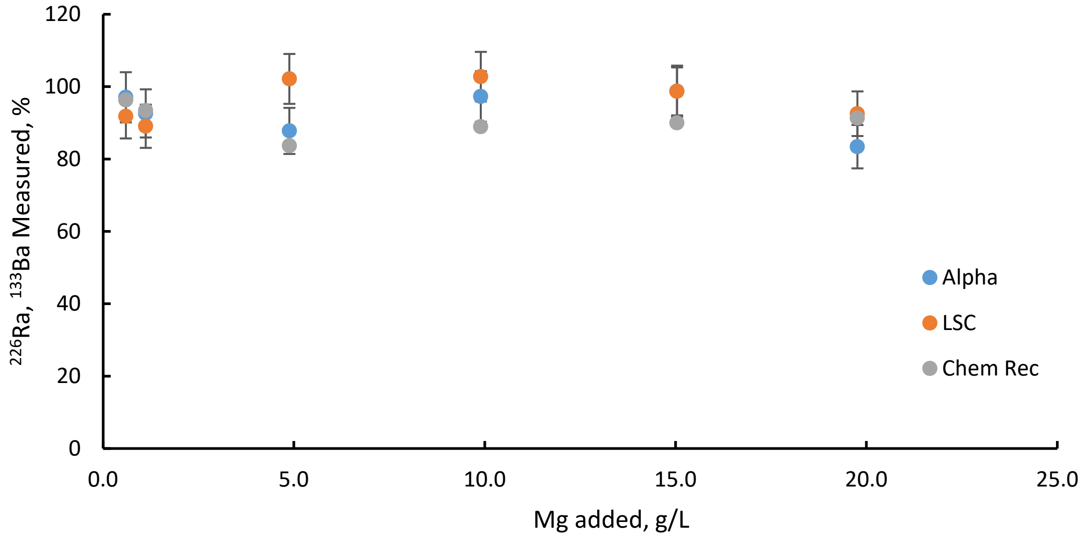

Figure 5.9. Influence of Mg on ^{226}Ra recovery.

5.9 Influence of Fe content on ^{226}Ra recovery

The maximum Fe content chosen to test its influence on the method was higher than the average drinking water Fe levels (>1mg/L) which have been observed in effluent samples. Ferric sulphate is also used as a common chemical treatment additive for tailing management to control radium levels. Fe had a noticeable effect on radium recovery/detection using both counting techniques starting at around 10mg/l, where the radium recovery was determined to be over 125% as illustrated in Figure *5.10*. It is important to note that the barium chemical recovery in this case showed a decreasing trend with an increasing amount of Fe. This is different from the effect of other ions (Ca, Mg, Na) that showed good chemical yields (>80%) even when high concentrations of these ions were used. In this case, it is speculated that the Fe interferes or competes with the barium absorption sites of the MnO2 resin resulting in a lower-than-expected chemical yield, which in turn results in an overestimation of measured ^{226}Ra concentration.

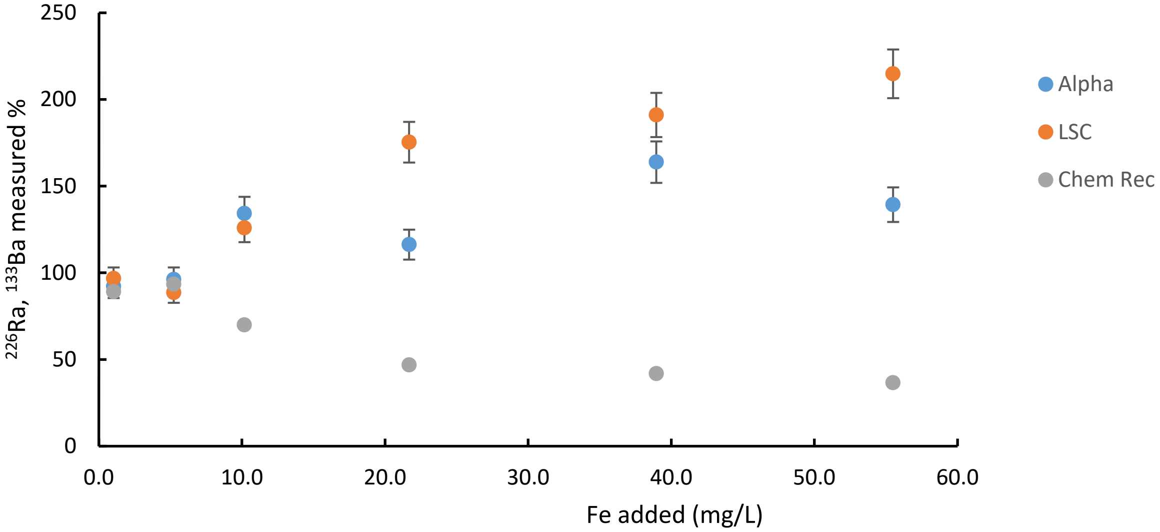

Figure 5.10. Influence of Fe on ^{226}Ra recovery.

To further investigate this effect, a separate sample was prepared with 20mg/L of Fe added into the sample after the sample was preconcentrated on the MnO_2 resin. The calculated chemical recovery from this sample was found to be over 90%, which is within the expected range. This supports the hypothesis that Fe is affecting the barium adsorption sites of the MnO_2 resin and is not affecting the microprecipitation step with barium sulphate. This result demonstrates that ^{133}Ba is not a suitable tracer for radium analysis using MnO2 resin when Fe levels exceed 5mg/L.

Table 5.5. Chemical yield for Fe before and after resin.

	Chemical yield, %
20mg/L Fe added before MnO_2 resin	47
20mg/L Fe added after MnO_2 resin	92

Assuming the chemical recovery is within the acceptable/expected range of 80-100%, it was interesting to see that the ^{226}Ra measurement results using LSC produced more accurate results with radium recovery in the range of 85% as illustrated in Figure 5.11. Therefore, it is concluded in such cases a different tracer, such as ^{225}Ra, should be selected for this method where concentration of Fe is greater than 5mg/l.

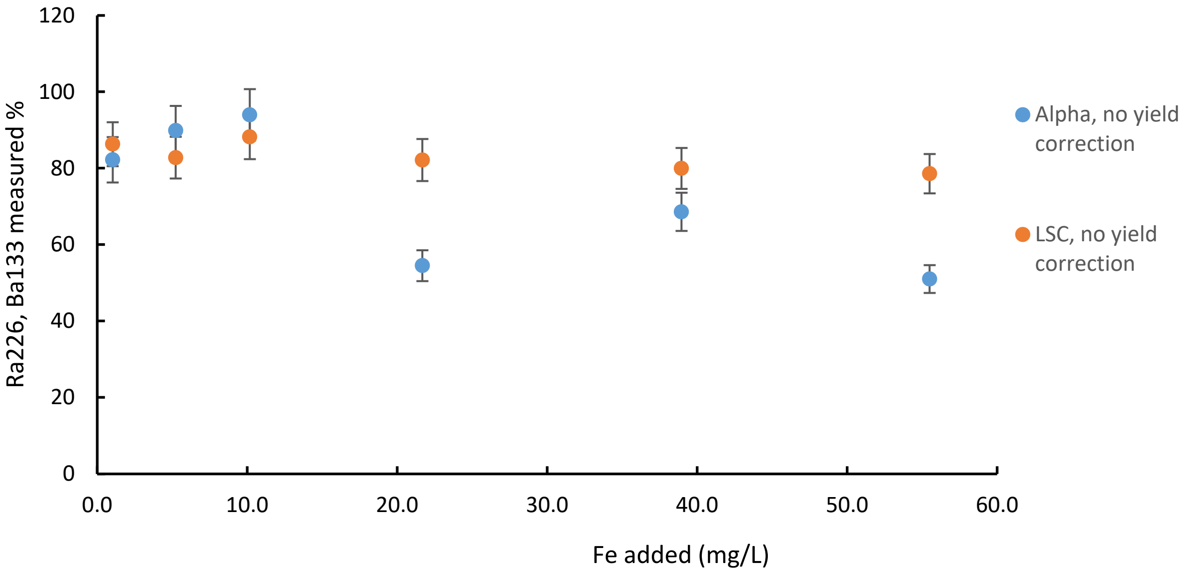

Figure 5.11 Influence on Fe on ^{226}Ra recovery without yield correction.

5.10 Influence of Ba content on ^{226}Ra recovery

Barium is known to affect the method as ^{133}Ba is used as the tracer based on its similar properties as a chemical analogue. High barium concentration will compete with the adsorption site on the resin as a proxy for radium as well as causing self-adsorption effect on the source. Likely, the lower radium recovery results by alpha spectrometry are an indication of self-adsorption while the decreasing LSC results shows the loss of adsorption sites on the MnO2 resin. Another contributing factor could be that the precipitates are not well dissolved in LSC cocktail, as was discussed in section 5.6 for high calcium content on radium recovery.

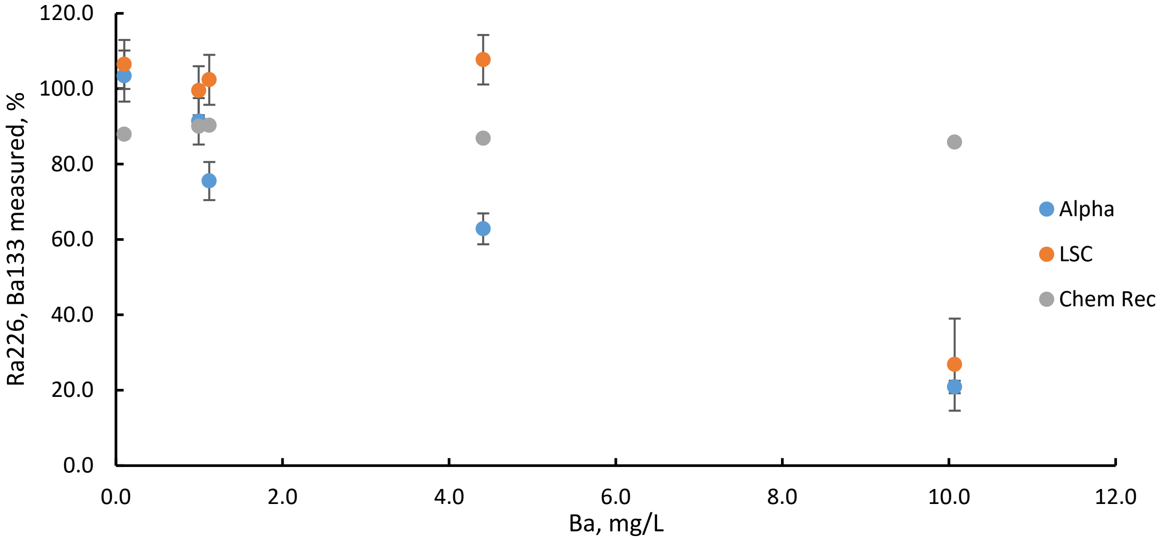

Figure 5.12 Influence of Ba on ^{226}Ra recovery

5.11 Uncertainty

The main factors that contribute to the major uncertainty components for this method are sample preparation step, the chemical recovery or yield ratio determination, efficiency factor, and counting statistics[57]. Since radioactive emission follows the Poisson statistics, counting uncertainty and efficiency uncertainty is calculated by the square root of the total counts. The uncertainty associated with the mass of the sample is estimated using the data from uncertainty estimation of the balance calibration. Based on literature, a deviation of up to 8% have been reported for chemical yield to account for differences in the chemical behavior of radium and barium. [58,59] The authors suggest that this value gives an estimation of the error due to the different chemical behavior of radium and barium and should be considered as a systematic uncertainty (or bias) when applied to real samples. To confirm, this study looked at the yield uncertainties for a series of samples with varying amount of radium concentrations. The results are listed in the following table.

Table 5.6 Chemical and radium recovery for various radium concentrations.

^{226}Ra (Bq)	Yield$_{Ra226}$, %	Yield$_{Ba133}$, %	Y_{Ba133}/Y_{Ra226}
0.10	93.01 ± 5.52	91.84 ± 2.24	1.013 ± 0.064
0.49	87.28 ± 3.98	87.89 ± 2.17	0.993 ± 0.052
0.99	96.93 ± 3.76	87.37 ± 2.16	1.109 ± 0.046
1.46	97.35 ± 3.57	93.68 ± 2.27	1.039 ± 0.044
0.50	93.52 ± 4.19	93.68 ± 2.27	0.998 ± 0.051
0.50	96.13 ± 4.27	91.32 ± 2.23	1.053 ± 0.051
1.97	85.46 ± 3.09	85.00 ± 2.11	1.005 ± 0.044

The average value for the ratio obtained was 1.03 with a standard deviation of 0.04. A two tailed t-test was performed on the obtained value with unity to verify there were no significant differences, thus confirming ^{133}Ba as a suitable tracer for ^{226}Ra determination in tap water samples. The highest standard uncertainty observed for this set of data is 6% which is used as uncertainty factor for yield in this work. This value is slightly lower than the reported value of 8% by Lozano. [59] This difference may be due to the different pre-concentration step, where co-precipitation method was used instead of an MnO_2 resin chromatography

The uncertainties due to system dead time correction, counting time and decay correction are considered to be negligible compared to the other uncertainty components and are not included in the uncertainty budget. The combined uncertainty budget equation is as follow:

$$u(A) = A * \sqrt{\left(\frac{u(C)}{C}\right)^2 + \left(\frac{u(\mathcal{E})}{\mathcal{E}}\right)^2 + \left(\frac{u(R)}{R}\right)^2 + \left(\frac{u(m)}{m}\right)^2} \qquad (5.2)$$

Where, A = Activity, C = counts, $\mathcal{E}$ is the efficiency, R is the recovery , m = mass of the standard.

Chapter 6 Discussion Summary, Conclusions and Future Directions

6.1 Discussion Summary

The determination of ^{226}Ra in simulated natural water samples was conducted using two radiometric techniques for comparative analysis. One method involved measuring the alpha peak of ^{226}Ra and its progenies via LSC following radiochemical separation and barium sulfate precipitation, achieving a high counting efficiency of 100%. The LSC samples were prepared by adding 18 ml of scintillation cocktail to the filter containing the precipitate, and measurements were performed using a Hidex300SL counter with an optimized pulse length to minimize alpha and beta pulse misclassification. The overall chemical yield for ^{226}Ra was determined using ^{133}Ba tracer, achieving yields > 80% for most analyzed samples.

Maintaining low background levels is crucial for achieving low detectable activities of ^{226}Ra. Alpha spectrometry offers exceptionally low detection limits due to minimal background interference. For ^{226}Ra, the minimum detectable activity was as low as 0.01 Bq L–1, surpassing requirements for ^{226}Ra determination of environmental water samples according to drinking water guidelines. The method proved effective across aqueous samples with ^{226}Ra activities spanning from a few mBq per L up to >100 Bq per L.

Additionally, both method's validity was confirmed through analysis of a proficiency testing samples in an IAEA exercises (IAEA-TERC-2023-01), where precision and accuracy were found to be in excellent agreement with assigned IAEA values, yielding acceptable results.

The reliability of the method was tested with simulated natural water samples with high ionic strength as well as higher levels of calcium, magnesium, iron, barium, and sodium affecting the water hardness level. Sodium and magnesium of up to 80g/L and 20g/l respectively did not show an adverse effect on radium recovery, showing good recovery using both radiometric methods. Calcium concentration greater than 20g/L significantly decreased radium recovery and at 80g/L, no radium was detected by alpha spectrometry. LSC measurements performed better than alpha spectrometry although still suffered a noticeable loss of radium recovery starting at 50g/L calcium. This result suggest that some calcium was absorbed on the resin and precipitated onto the filter, which hindered the alpha particles from escaping the source itself due to self adsorption effects. A closer look on the SEM image of the source showed calcium to be present on the source that supporting this justification. Fe had a noticeable effect on the radium recovery at 10mg/L in both methods. Specifically, it had a decreasing effect on the chemical recovery of ^{133}Ba. This is different from the effect of other ions (Ca, Mg, Na and Ba) that showed good chemical yields (>80%) even when high concentrations of these ions were used. In this case, it is speculated that the Fe competes with the barium absorption sites of the MnO2 resin resulting in a lower-than-expected chemical yield, which in turn results to an overestimation of measured ^{226}Ra concentration. Further investigation indicates that Fe is affecting the barium adsorption sites of the MnO_2 resin.

6.2 Conclusions

In this study, it is concluded that two radiometric techniques, alpha spectrometry and LSC are suitable techniques to determine ^{226}Ra concentrations in environmental surface water samples. Novel observations include that while both techniques had a high tolerance for magnesium, sodium, and calcium and lower tolerance for barium and iron. This study further guides the Laboratory in determination of ^{226}Ra concentrations in various environmental surface water or effluent samples. We also concluded that for samples with complex matrices, it is important to test for resin capacity and self-adsorption effects on the source for achieving accurate measurements. Although alpha spectrometry is the preferred method of choice for detecting alpha emitters in environmental water samples due to its low detection limit, it was observed that LSC, following selective radiochemical separation could offer an advantage over alpha spectrometry for water samples with higher amounts of mineral content such as calcium to avoid self adsorption effects.

6.3 Future Considerations

Since it is observed that Fe can affect the absorption rate of the barium such that it doesn't get scavenged with the same efficiency as Ra, it is preferable to use another isotope of Ra itself as tracer for samples with high Fe content rather than a chemical analogue. ^{224}Ra, ^{223}Ra and ^{225}Ra have been used as radiochemical yield tracers that would avoid this issue. [21] Of these three isotopes, ^{225}Ra with a half life of 12.82 days is likely to be the most suitable tracer for the determination of low-level natural Ra as this doesn't occur naturally and therefore not present in the environment. Its alpha emitting daughters ^{217}Ac is also detectable in the alpha spectrum without interference from ^{226}Ra and its progenies.

It is also worthwhile to extend the study to other environmental matrices, for example sediment, soils, and even tailing samples from the mining sites. The adaptation of the proposed method would require additional investigation of the different sample preparation/digestion methods and exploring different chemical/sequential separation approaches to minimize matrix and interfering effects. However, this work could offer a promising possibility to investigate the mobility of ^{226}Ra in the environment, particularly to evaluate transport rates and transfer factors.

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