Application of modern analytical techniques for quantification of selected radioactive metals in environmental samples

By

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A dissertation submitted to the Department of Chemistry, Faculty of Sciences,
Engineering and Agriculture, University of the Venda in fulfilment of the
requirements for the degree of
Masters of Science in **Chemistry**

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June, 2022

Declaration

I, **Nkhumeleni Murendeni Royell** (15005424), hereby declare that this dissertation "Application of modern analytical techniques for quantification of selected radioactive metals in environmental samples" submitted for the Master of Sciences in Chemistry, Faculty of Sciences, Engineering and Agriculture at the University of Venda by me is my own work, that it has not been submitted for any examination or degree at this or any other institution, and that all the sources used or quoted have been indicated and duly acknowledged by complete references.

Signature: …… ....Date: 25/02/2022

List of publications

This dissertation is based on the following papers:

1. **Modern developments for efficient applications of dispersive liquid-liquid micro-extraction technique during analysis of radioactive metals in environmental samples: A review**
   Murendeni Royell Nkhumeleni and Nikita Tawanda Tavengwa
   (To be submitted to Journal of Radioanalytical and Nuclear Chemistry).

2. **Recent developments for efficient analytical separation techniques during analysis of radionuclides in the environmental samples: A review**
   Murendeni Royell Nkhumeleni and Nikita Tawanda Tavengwa
   (To be submitted to Journal of Nuclear and Radiochemical Sciences).

3. **Application of vortex assisted liquid-liquid micro-extraction for pre-concentration of cobalt prior to determination by FAAS**
   Murendeni Royell Nkhumeleni and Nikita Tawanda Tavengwa
   (To be submitted to Journal of Radioanalytical and Nuclear Chemistry).

4. **Preconcentration of palladium from the environmental samples using DLLME**
   Murendeni Royell Nkhumeleni and Nikita Tawanda Tavengwa
   (To be submitted to Journal of Radioanalytical and Nuclear Chemistry).

5. **The applications of membrane assisted solvent extraction for the analysis of cobalt in environmental samples**
   Murendeni Royell Nkhumeleni and Nikita Tawanda Tavengwa
   (To be submitted to Journal of Nuclear and Radiochemical Sciences).

Commitment of the authors

In the written review papers (**paper I and II**), the primary author reviwed the literature and critically analyse, and write the context of the paper. Whereas the co-author reviewed the written draft papers and made recommendations, and suggested corrections for improvement. In the written manucripts (**paper III**, **IV and V**) the primary author, engaged in designing, carrying out the experiments, optimization, sampling, analyzing, and evaluation of the results, and writing of the context of the paper. Whereas the co-author reviewed the drafts of the written papers and make suggestions for improvement.

Abstract

In this study, the recent micro-extraction and pre-concentration techniques, namely vortex-assisted liquid-liquid micro-extraction (VA-LLME), dispersive liquid-liquid micro-extraction (DLLME) and membrane assisted solvent extraction (MASE) were used for the extraction of radioactive metals from the environmental samples. The VA-LLME and MASE were used for the extraction of cobalt, while DLLME was used for the extraction of palladium. The work is divided into five papers.

The first paper of this work reviewed the modern developments for efficient applications of DLLME technique during analysis of radioactive metals in environmental samples (**paper I**). This study discussed various modifications of the DLLME technique used for improving the technique during the analysis of radioactive metals, as well as the challenges it present. The major advantage, among others, of DLLME is miniaturisation in which the volumes of the extraction and dispenser solvent are reduced tremendously. This was in attempt to solve challenging factors during the analysis of radioactive metals such as their existance in trace level that is normally lower than the limits of detection of most analytical instruments. Recent developments for efficient analytical separation techniques during analysis of radionuclides in environmental samples were reviewed (**paper II**). This part outlined the efficient analytical extraction and separation techniques during analysis of radionuclides with focus on the review of non-consecutive extraction of analytes, non-toxic solvents, less-hazardous waste generation, and high selective and green analytical separation methods. Furthermore, possible simultaneous selective extraction of metals of interest in a complex matrix such as water, soil and minerals were dicussed. This offers tremendous advantages for extraction and separation techniques of radionuclides.

Cobalt concentration in environmental water samples was pre-concentrated using VA-LLME and detected using flame atomic absorption spectrometry (FAAS) (**paper III**). Based on the results, 2 min vortex time, 3 mL sample volume, 6.0 sample pH level, 600 mL volume of complexing angent give, and 300 μL extraction solvent give the highest enrichment factors. Trace amount of cobalt in real samples, were 102.5 ± 1.0 μg L^{-1} (n = 3, RSD) which is below the maximum acceptable limit for cobalt, according to Water Quality Guidelines for cobalt by British Columbia Report. The pre-concentration of palladium in the environmental samples by DLLME was studied (**paper IV**). The important parameters that have an impact on the effectiveness of DLLME technique were also optimized using the univariate approach. The methanol and chloroform was used as dispenser solvent and extraction solvent, respectively. The volumes of 500 µL for dispenser solvent and, 400 µL for extraction solvent showed the maximum enrichment factors. Dithozone was used as a chelating agent in this study, and acetone was used as a diluent to dissolve the sedimented phase in the DLLME method. The volume of 600 µL was an adequate amount of acetone used to ensure that sufficent palladium species in the samples are converted to form a complex.

Cobalt extraction by MASE was also investigated (**paper V**). The key parameters that have an impact on the effectiveness of MASE technique were also optimized using the univariate approach. The maximum enrichment factors were obtained at the pH of 3.5; 60 min extaction time and 2.0 rpm stirring rate. Under the optimized conditions, the developed method was used for the analysis of real samples. The samples obtained from the area suspected to the exposure of cobalt were pre-concentrated using MASE prior to analysis with graphite furnace atomic absorption spectrometry (GFAAS). Hexane and dithizone were used as extraction solvent and chelating agent, respectively. The pH of the samples was adjusted using nitric acid or sodium hydroxide solution. The ammonium chloride buffer solution was used to precisely maintain constant sample pH at nearly optimal value during the MASE technique.

Keywords: Pre-concentration, environmental samples, modern analytical techniques, quantification, radioactive metals, miniaturization.

Dedications

This dissertation is dedicated:

- To my brother, Mr W Nkhumeleni for the motivation to work harder.
- To my father, Mr NT Nkhumeleni for his continuous support, and for teaching and encouraging me to work hard for the things I aspire to achieve.
- To my sisters, Ms L Nkhumeleni, Mrs C Bilankulu, Ms E Nkhumeleni and Ms VA Nkhumeleni, I would like to thank their unconditional love, support and words of encouragment.

Acknowledgements

I would like to express my heartfelt gratitude to the following:

- I would like to express my gratitude to the Almighty God for providing me with life, strength, and protection throughout my studies. I give all glory and honor to him.
- For his important guidance, support, encouragement, and advise during this project, I am grateful to my supervisor, Dr. N.T Tavengwa. Furthermore, I am appreciative for his willingness to go above and beyond to ensure the success of this project.
- The National Energy Regulator of South Africa (NERSA) for its financial support.
- I am also grateful to lecturers, technical staff and colleagues of the Department of Chemistry for their precious support.

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List of abbreviations

AAS	Atomic absorption spectrometry
BWR	Boiling water reactor
DLLME	Dispersive Liquid-Liquid Micro-extraction
DoE	Department of energy
DOT	Department of Transportation
FAAS	Flame atomic absorption spectrometry
FBR	Fast breeder reactors
GCR	Gas-Cooled Reactor
GFAAS	Graphite furnace atomic sbsorption spectrometry
GO	Graphene oxide
GY	Gray
IAEA	International Atomic Energy Agency
ICP-OES	Inductively coupled plasma optical emission spectrometry
LLE	Liquid–liquid extraction
LLME	Liquid–liquid micro-extraction
LOD	Limit of detection
LOQ	Limit of quantification
LWGR	Light water (cooled) graphite (moderated) reactor
MASE	Membrane Assisted Solvent Extraction
MLIS	Molecular Laser Isotope Separation

Necsa	South African Nuclear Energy Corporation
NEMA	National Environmental Management Act
NORM	Naturally Occurring Radioactive Materials
PHWR	Pressurized heavy water reactor
PWR	Pressurized water reactor
R&D	Research and development
SAFARI-1	South African Fundamental Atomic Research Installation
SI	System International
SMR	Small modular reactors
SPME	Solid phase micro-extraction
TENORM	Technologically Enhanced Naturally Occurring Radioactive Materials
US	United States
USGS	United States Geological Survey
USSR	Union of Soviet Socialist Republic
UV-vis	Ultraviolet and visible
VA-LLME	Vortex-Assisted Liquid-Liquid Micro-extraction

Chapter 1: Introduction and background

This contains the introduction and the background of the study as well as the aim, problem statement and objectives. It further gives an outline on how the work is presented in this dissertation.

Chapter 1: Introduction

1.1. Background of the study

Countries such as South Africa that depends on coal as the main energy source should be able to remedy the potential environmental impacts of the chosen energy source. Nuclear energy has been discussed as the potential replacement of the coal energy generation in South Africa. However, this may come with the problem of radioactive waste, which could create an environmental burden for thousands of years. Apart from that, human activities have produced and discharged a large number of radionuclides into the environment. Industrialization and mining are among human cause that influences the distribution of radioactive metals into the environment. The negative effect associated with radioactive substances include severe damage to the natural environment and human health.

Palladium and cobalt are amongst hazardous elements containing radioactive nuclides species that occur in natural environment (Mu et al., 2019; Laprise-Pelletier et al., 2017; Weller et al., 2021; Thakare et al., 2021; Iryna, 2017; Saleh et al., 2020; Oh et al., 2019). Palladium at sufficiently high concentrations has toxic and allergic effects on biological systems. Recent evidence has shown that palladium can cause allergic reactions in those who are exposed to it through jewelry or dental restorations, which could be mediated by the production of palladium ions, that behave as effective sensitizers (Muris et al., 2015; Iavicoli et al., 2015). In addition, the exposure to palladium have been shown to significantly affect the respiratory and blood circulatory systems, and further lead to the production and release of different cytokines that result in tumor necrosis factor in human peripheral blood mononuclear cells (Iavicoli et al., 2015; Naqvi et al., 2021; Gurunathan et al., 2019; Fontana et al., 2015). Previous studies showed that the highest accumulation of palladium was in the kidney, liver, spleen, lungs, bone and heart in animal models (Wataha and Hanks, 1996; Hosseini, 2015). Consequently, high palladium cause sensitization, asthma and dermatological disorders such as rhinitis, conjunctivitis, contact urticarial and death (Hosseini, 2015; Ahmed et al., 2021a; Li et al., 2019; Rinkovec et al., 2018).

Cobalt on the other hand cause radiation and biochemical damages including adverse health effects such as vomiting, diarrhea, renal edema, skin dermatitis, pulmonary fibrosis, high blood pressure, nausea central nervous system, cancer, liver damage and kidney failure (Khan et al., 2016a; Khan et al., 2016b; Bulska and Ruszczyńska, 2017; Deniz et al., 2019; Mohammadi et al, 2015; Shah et al., 2016; Ding et al., 2015).

These elements are constituented of many minerals and ores that form part of raw materials during energy production (Yildiz et al., 2019; Langevelde et al., 1999; Payolla et al., 2019; Can et al., 2013). However, the challenge is that they further form part of toxic waste that pollutes the environment. For instance, some palladium isotopes such as ^{107}Pd, and ^{105}Pd are present in spent nuclear wastewater produced by fission of uranium (Mu at al., 2019). Radioactive nuclide, ^{60}Co, is released in nuclear wastes from nuclear energy industries together with other radionuclides such as ^{154}Eu, ^{232}Th, ^{235}U, ^{235}Np, ^{239}Pu, ^{241}Am, and ^{247}Cm (Zhu et al., 2020; Payolla et al., 2019; Larramendy and Soloneski, 2016). Therefore, there is a need for developing and tightening radiation protection standards and to ensure proper licensing of industrial operations.

The remediation technologies of radioactive metals do not produce 100% results. Some trace amounts of pollutants are found in the environment even after application of decontamination process (Adella et al., 2017). Radioactive metals pollutants can affect the ecosystem, including human health even at trace level. Furthermore, these radioactive metals tend to chemically and biologically react with organic matter and other biological features such as clays, and the results of these are more radioactive than the other rocks minerals (Yasmin et al., 2018). It is therefore of importance that effective techniques should be used to pre-concentrate and monitor the trace occurrence of radioactive metals in the environment.

Many techniques have been used for the pre-concentration of radioactive metals in environmental samples. These methods of pre-concentration include dispersive liquid-liquid micro-extraction (DLLME) (Sadeghi and Davami, 2019; Gouda et al., 2018; de Almeida et al., 2018; Sá et al., 2021; Niazi et al., 2015), solid phase micro-extraction (SPME) (Duff et al., 2008; Shyam Sunder et al., 2020; Rohanifar et al., 2018; Rahmi et al., 2010), and vortex assisted liquid-liquid micro-extraction (VA-LLME) (Tarhan et al., 2019; Zolfonoun and Salahinejad, 2013).

The pre-concentration techniques can be divided into modes of pre-concentration methods such solvent-based pre-concentration techniques and membrane-based extraction techniques.

The solvent-based techniques include methods such as VA-LLME and DLLME, whereas membrane-based techniques include methods such as membrane assisted solvent extraction (MASE). These methods are unique in design, but they all have same purposes: namely, aiming to reduce amount of solvents into micro volumes, short extraction time, use of green solvents, high extraction efficiencies, reduce cost, and follow the requirements of green analytical chemistry (Obotey et al., 2020; Veyseh and Niazi, 2017; Pérez-Outeiral et al., 2014; Gadlula et al., 2019; Jiang, 2017; Ncube et al., 2018; Mañana-López et al., 2021; Salgueiro-Gonzálezet al., 2015; Lemos et al., 2020; Sousa at al., 2020; Chaiyamate et al., 2018; Bahadir et al., 2016; Jiao et al., 2017; Chen et al., 2019; Psillakis, 2019; Bosch, 2018; Rassou et al., 2020). Consequently, in recent years, priority of use has been focused towards the modern techniques which comprised these methods, which miniaturised the volumes of solvents used.

1.2. Problem statement

There are several types of radiation produced by radioactive materials that are present in nature and by manmade sources. Besides the naturally occurring radionuclides, huge amount of radioactive metals are released by industries (i.e., mining, agriculture and power plants) to the environment (Kumar and Kundu, 2020; Larramendy and Soloneski, 2016; Saha et al., 2017; García-Tenorio et al., 2015; Zeng et al., 2020). The further increase in level of radioactive materials in the environment is primarily due to the indiscriminate waste disposal and poor waste management (Ifeoluwa, 2019; Nwachukwu et al., 2013; Kgosiesele and Zhaohui, 2010; Nandan et al., 2017; Larramendy and Soloneski, 2016). Furthermore, the increase in world growth energy demand further lead to the extensive exploration of radioactive metals as energy sources (Oladeji, 2015; Bose, 2010; Church and Crawford, 2020; Arutyunov and Lisichkin, 2017). Therefore, regulation standard need to be tighten during these operations. However, the potential danger radioactive metals pose to the environmental is a problem that calls for concern (Caridi et al., 2016; Pehoiu et al., 2016; Burger and Lichtscheidl, 2018; Ali et al., 2020). They are toxic towards living organisms including human, thereby cause very serious health problems (Madhav et al., 2020; Li et al., 2018; Tasker et al., 2018). In addition to the toxicity, one of the most challenging factors is the occurrence of radioactive metals in trace level which makes it difficult to detect them (Pandey, 2017; Rosenblum et al., 2017; Al-Khawlany et al., 2018; Habib et al., 2019).

1.3. Aim and objectives of the study

1.3.1. Aim

The aim of this study is to use spectroanalytical techniques after application of modern analytical extraction methods to quantify selected radioactive metals in liquid samples.

1.3.2. Objectives

- To provide overview of the radioactive waste management.
- To perform VA-LLME for the extraction of cobalt.
- To perform DLLME for the extraction of palladium.
- To perform MASE for the extraction of cobalt.

1.4. Outline of the dissertation

The dissertation's outline (which consists of five chapters) is as follows:

Chapter 1: A general introduction and background to environmental pollution and contamination by radioactive metals, as well as the modern pre-concentration techniques are briefly discussed. Furthermore, in this chapter the problem statement and objectives are given and hence, setting up the context, relevance and aim of this research.

Chapter 2A: A comprehensive overview of radioactive metals as environmental pollutants and contaminants, as well as the importance of radioactive metals in the economic sectors is given.

Chapter 2B: A critical reviews of the recent pre-concentration techniques for the analysis of radioactive metals is given in this chapter (papers I - II).

Chapter 3: The materials and methods are laid out in this chapter.

Chapter 4: This chapter contains manuscripts (papers III, IV, and V) prepared for the MSc examination. Each paper includes the study conducted, results and discussion.

Chapter 5:	This chapter gives the general conclusions and future research based on experimental findings.
References:	At the end of the dissertation, there is a list of references cited in the introduction and literature reviews (Chapters 1 and 2A).
Appendix:	This section contains information that is not included in the main text of all written manucripts.

References

This section gives the references used in chapter 1

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Chapter 2: Literature review

This chapter outlines the literature survey and overview of radioactive metals including their importance, application, distribution in the environment, toxicity as environmental pollutants as well as environmental contaminants. The application of modern analytical extraction and pre-concentration methods for the extraction, remediation, treatment, and removal of these radioactive metals was fully unpacked.

2.1. Radioactive metals

Nuclides (also know as elements) are defined as any kind of atom with a specific number of protons and neutrons (Harmon, 2018). The elements will be stable only if certain number(s) of neutrons are present corresponding to the given number of protons (Al-Othman et al., 2019). Two atoms of the same element with different number of neutrons are referred to as isotopes. Some isotopes are radioactive, some are not (Holden et al., 2019; Davies, 2020). Radioactive isotopes undergoe an energy state transition by releasing a photon, without altering the elemental composition, which resulting in the stable form of that element, which does not decay spontaneously to emit any kind of radioactivite product (Długosz-Lisiecka and Perka, 2020). Radioactivity is the emission of radiation or particles by radioactive metals through the spontaneous nuclear decay transformation or disintegration of the atomic nuclei of radioactive molecules (Abubakar, 2019). Radioactive metals occurs naturally at different concentrations in the earth's crust (minerals, soil, rocks), however they can be manmade (Islam, 2018; Jiang, 2017). Isotopes of radioactive metals are emitters of radionuclides (Mikolajczak et al., 2021; Strumińska-Parulska and Falandysz, 2020; Ferrier et al., 2019). In the de-excitation stage of radionuclides, there are numerous forms of processes, i.e. γ-ray emission, electron capture, internal conversion, α decay, β decay and spontaneous fission (Larramendy and Soloneski, 2016; Bai et al., 2017; Hamideen and Sharaf J, 2012). During the decay process, these radionuclides produce α, β and γ-particles, depending on the type of radionuclide (Długosz-Lisiecka and Perka, 2020). The excited nucleus that is formed as a result of α or β decay of radionuclide can futher undego de-excitation by emitting γ-rays with specific energy (Jiang, 2017). Most radioactive metals de-excite into other atoms that are also radioactive and they are called decay products (Hamilton, 2020; Hotokezaka et al., 2016; Nelson et al., 2015).

The detail in radioactive elements and their decay products is available from the United States Geological Survey (USGS). This information can be obtained on the World Wide Web at: http://energy.er.usgs.gov/products/databases/CoalQual/intro.htm. The radioactive metals cause harmful impact on the environment and human (Bai et al., 2017; Corcho et al., 2014). Some isotopes of radioactive metals are needed for living species; however, they emit strong radiation that causes various health hazards (Yasmin et al., 2018).

2.2. Common radioactive labels

Some of the markings on a radioactive material substances include the following: DOT package labels, DOT radioactive (class 7) placard and radiation symbol that are shown in Figure 1, Figure 2 and Figure 3, respectively. These symbols indicate potential hazards of radioactive materials, and are commonly used during packaging and transport of radioactive materials

Figure 1: DOT Package Labels

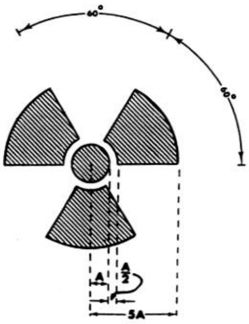


Figure 2: DOT Radioactive (Class 7) Placard

Figure 3: Radiation symbol

2.3. Distribution and sources of radionuclides

There are many factors that enhance environmental radioactivity levels in the surrounding environment and in the vicinity where people lives. Common known sources that enhanced naturally occurring radioactive materials, humans are exposed to is coal-fired power plants, mining, nuclear fuel and power plants, fuel reprocessing, nuclear industries and accidents, mineral extractions, pharmaceuticals, and fertilizers that are used in agriculture (Veyseh, 2017; Janković et al., 2016; Dhawan and Sharma, 2019; Mohammadi, 2015; Oliveira et al., 2015).

Exploitation of energy is a key source of radioactive material distribution (Larramendy and Soloneski, 2016). Coal, the world's most dominant energy source, is widely used in the generation of power in many countries among the traditional combustion energy sources (Owusu et al., 2016; Munawer, 2018; Sharma and Sumbali, 2019). The contribution of coal in the energy mix as of 2019 was 38 % of total electricity generation in the world (Purevsuren and Kim, 2021). The burning of coal in coal-fired power plants plays a major influence in the distribution of radioactive materials to the natural environment. Energy sources based on coal power plants emits dusts and gases containing volatile radioactive elements in different amounts or concentrations (Długosz-Lisiecka and Perka, 2020; Purevsuren and Kim, 2021; Özden and Filizok, 2011; Al-Masri et al., 2014). This is due to the presence of naturally occurring radioactive materials and their daughter products in coal (Purevsuren and Kim, 2021). According to the 2005 report of the International Atomic Energy Agency (IAEA) (Ahmed et al., 2020), average concentration of the main radionuclides in coal ranges from 1-785 Bq kg^{-1}.

Nuclear power is a reliable source of electricity and a carbon-free source of energy. It is also one of the most promising alternatives to traditional combustion energy sources for addressing current energy and environmental challenges. However, exploitation of the nuclear energy is also a key source of radionuclides (Trojanowicz et al., 2018; Takahashi et al., 2021). Radiation as a result of exploitation of the nuclear energy can enter the environment at any stage of the nuclear fuel cycle, from the mining and processing of uranium ore to the manufacturing and recycling of nuclear fuels, as well as the processing and disposal of radioactive wastes.

Nuclear weapons testing, which began in the United States (US) in 1945, is another key source of radionuclides (Hughes et al., 2019; Ohtsuru et al., 2015). Nuclear weapon testing has contaminated a vast number of sites across the world with radioactivite materials (Ruff, 2015). Nuclear weapons testing involve the direct discharge of large quantities of radioactive metals into the environment at at different concentrations (Prăvălie, 2014). Depending on the half-life of the radionuclide, residual radiation from nuclear testing can last from days to years, decades, centuries, and beyond (Hughes et al., 2019; Hain et al., 2020). The first nuclear explosions of the hydrogen bomb were conducted in 1954 by the US in the Marshall Islands, on the Bikini atoll (the Castle Bravo test); and then in 1961, by the Union of Soviet Socialist Republic (USSR), in the Novaia Zemlia archipelago, north of the Ural mountains (the Tsar test) (Simon and Bouville, 2015). Nuclear tests are carried out in a variety of locations, including the atmosphere, the land, and the sea. About a quarter of the experiments (530) were conducted in the atmosphere, and another part (75%) were conducted underground (1517 tests) (Prăvălie, 2014). There were only few cases of nuclear test conducted beneath water. Each nuclear explosion creates hundreds of radionuclides (Simon and Bouville, 2015; Hain et al., 2020).

Around 90% of all nuclear tests were carried out in the northern hemisphere, mostly by the U. S, the USSR/Russia, and China, with just 10% (about 208 tests) carried out in the southern hemisphere by countries like as France and the United Kingdom. Due to the existence of enormous quantities of radioactive isotopes (particularly ^{14}C, ^{137}Cs, and ^{90}Sr) discharged into the atmosphere during nuclear weapons tests, the northern hemisphere is more contaminated than the southern (Prăvălie, 2014).

On the other hand, the rock minerals contain naturally occurring radioactive materials (NORM), which have a long half-lives (Yasmin et al., 2018; Harlow, 2017). These radioactive materials are deposited on land by volcanic actions, and exist in a variety of rock types, ranging from sedimentary to volcanic (Yasmin et al., 2018). Studies have shown that basement complex materials, such as igneous and metamorphic rocks, have been linked to high radioactive radiation, whereas sedimentary rocks have been linked to low radiation (Wejood et al., 2016; Qureshi et al., 2014; Joel et al., 2019). Natural phenomena such as wind, water action, rain, weathering and geologic processes breaks these rocks, and makes radioactive components of the rocks to form a part of the soil (Yasmin et al., 2018). In addition, studies on radionuclides in soils and rocks has been on the rise across the world in the past decades due to the health risk that it might pose on the individual or populace (Usikalu et al., 2016; Omeje et al., 2018; Joel et al., 2019; Joel et al., 2018).

Natural radioactivity is widely distributed across the earth's environment, and naturally occurring radionuclides can be found at different concentrations in a variety of geological formations, including soils, rocks, plants, water, and air, as well as in building materials. (Shoeib and Thabayneh, 2014; Kasumović et al., 2018). The activity concentrations of ^{40}K, ^{137}Cs, ^{232}Th, ^{226}Ra and ^{238}U in natural raw materials for concrete, cement, mortar, bricks, and other building materials vary considerably depending on the source and nature of that compound (Bai et al., 2017; Hamideen and Sharaf, 2012). Natural building materials, in general, reflect the geology of their origin, with average activity concentrations of ^{40}K, ^{232}Th and ^{226}Ra in the Earth's crust measuring abount 400, 40 and 40 Bq kg^{-1}, respectively (Kasumović et al., 2018).

Other sources of radioactive contamination are less common such as incidents during use of radioisotopes in agriculture, industry, or medicine (He and Cai, 2019; D'Auria, 2019). Nuclear accidents, including the Chernobyl (Ukraine, 1986) and Fukushima events (Japan, 2011), resulted in significant impacts on people, environment, and facilities. These incidences contaminated the environment on a lager scale, including living organisms, soil, water and air (IAEA, 2015; Andersson et al., 2018). Water level as high as 15 meters inundated the Fukushima Daiichi nuclear power station after the earthquake and tsunami in Japan's east coast on March 11, 2011, resulting in one of the most significant discharges of artificial radionuclides into the environment (Yu et al., 2015). The severity of the Chernoby incident disaster was measured by the fact that in 1993, the maximum radioactive contamination in the soil was found to be 3500 times higher than before the Chernobyl incident (Larramendy and Soloneski, 2016). During the transportation, treatment, characterization, segregation and disposal of radioactive waste, an accidental release of radionuclides may also occur (Smičiklas and Šljivić-Ivanović, 2016).

Many of radioactive elements did not exist prior to discovery of nuclear fission (D'Auria, 2019). Huge amount of energy is generated during nuclear fission as heavy atomic nuclei split apart to form lighter atomic nuclei. These atomic nuclei are distinguished by their atomic numbers, mass numbers, and the number of emitted neutrons, as well as the γ-rays associated with the excitation main nuclei (Al-Othman et al., 2019). Some of the radionuclides produced by fission of elements are given in Table 1. Fission isotopes are produced by controlled reactions that produce nuclear power and by nuclear explosions that have mostly been eliminated (Knapp and Pevec, 2018). The radionuclides such as ^{90}Sr, ^{97}Zr, ^{103}Ru, ^{105}Rh, and ^{132}Te are released at the reactor stage; ^{137}Cs, ^{129}Te, ^{131}I and ^{134}Cs are produced during fuel element transport; and ^{106}Ru, ^{137}Cs, and ^{144}Ce are released during fission product solidification (Larramendy and Soloneski, 2016).

Table 1: Radionuclides produced by nuclear fission (Payolla et al., 2019).

^{213}bismuth	^{59}iron	^{153}samarium
^{131}caesium	^{212}lead	^{75}selenium
^{137}caesium	^{177}lutetium	^{24}sodium
^{51}chromium	^{99}molybdenum	^{89}strontium
^{60}cobalt-60	^{103}palladium	^{99}mtechnetium
^{165}dysprosium	^{32}phosphorus	^{227}thorium
^{169}erbium	^{42}potassium	^{133}xenon
^{166}holmium	^{223}radium	^{169}ytterbium
^{131}iodine	^{186}rhenium	^{177}ytterbium
^{192}iridium	^{188}rhenium	^{90}yttrium

Apart from natural weathering events, there are industrial activities which produce technologically enhanced naturally occurring radioactive materials (TENORM). This include the following: mining, the oil and gas production, metal smelting, production of rare earth minerals, titanium and zirconium as mineral sands, and phosphate fertilizer industry (Devi and Sumbali, 2021; Kasumović et al., 2018; Larramendy Soloneski, 2016; Shoeib and Thabayneh, 2014). Depending on the area where the natural minerals and ores (phosphate rock, bauxite, uranium ore, monazite, coal, etc.) are mined, they may contain different amount of radioactive elements (Ahmed et al., 2020). Some rocks that are mined from underground mines contain more concentration of radioactive metals (Yasmin et al., 2018). These radioactive elements include thorium, uranium, and their numerous decay products including radon and radium which are widely spread into the environment (Singh et al., 2015; Purevsuren and Kim, 2021).

High content of these radionuclides are normally determined in their by-products, transport of minerals and wastes such as phosphogypsum, fly ash and red mud (Larramendy Soloneski, 2016). As a result, non-nuclear industries are also regarded as a constant source of natural radioactive materials pollution due to the emissions and spread of dust and waste dumps, as well as waste water overflow from treatment ponds (Larramendy Soloneski, 2016). It is confirmed that reprocessing plant discharges contribute to high radioactive material discribution (Hain et al., 2020). In addition, the continuos usage of phosphate fertilizers rich with TENORM could result in the spread of radioactive materials. Depending on the level of contamination, land use restrictions or remediation methods may be necessary to avoid the distribution of radioactive material in to the environment. Table 2 shows some of the sources and production reactions of radionuclides in environmental, biological, and waste samples.

Table 2: The sources and production reactions of radionuclides in the biological, environmental, and waste samples (Hou, 2008).

Nuclides	Sources	Nuclear reactions for the production of radionuclide
^{3}H	NWT, ONF, RP	^{2}H(n, ϒ) ^{3}H; ^{3}He(n, p)^{3}H; ^{6}Li(n, α) ^{3}H
^{14}C	CRR, NWT, ONF, RP	^{14}N(n, p)^{14}C; ^{13}C(n, ϒ) ^{14}C; ^{17}O(n, α) ^{14}C
^{36}Cl	CRR, NWT, ONF, RP	^{35}Cl(n, ϒ) ^{36}Cl; ^{40}Ar(p, nα) ^{36}Cl; ^{36}Ar(n, p)^{36}Cl; ^{39}K(n, 2n2p)^{36}Cl; ^{40}Ca(n, 2n3p)^{36}Cl; ^{40}Ca(μ-, α) ^{36}Cl; ^{39}K(n, α) ^{36}Cl
^{41}Ca	NWT, ONF	^{40}Ca(n, ϒ) ^{41}Ca
^{59}Ni	NET, ONF	^{58}Ni(n, ϒ) ^{59}Ni
^{63}Ni	NET, ONF	^{62}Ni(n, ϒ) ^{63}Ni; ^{63}Cu(n, p)^{63}Ni
^{79}Se	ONF, RP	^{78}Se(n, ϒ) ^{79}Se; ^{235}U(n, f)^{79}Se
^{89}Sr	NWT, ONF, RP	^{235}U(n, f)^{89}Sr; ^{88}Sr(n, ϒ) ^{89}Sr
^{90}Sr	NWT, ONF, RP	^{235}U(n, f)^{90}Sr
^{99}Tc	ONF, RP, NOR	^{235}U(n, f)^{99}Tc; ^{98}Mo(n, ϒ) ^{99}Mo(β) ^{99}Tc
^{129}I	NWT, ONF, RP	^{129}Xe(n, p)^{129}I; ^{235}U(n, f)^{129}I; ^{127}I(2n, ϒ) ^{129}I
^{135}Cs	NWT, ONF, RP	^{235}U(n, f)^{135}Cs
^{137}Cs	NWT, ONF, RP	^{235}U(n, f)^{137}Cs
^{237}Np	ONF, RP	^{238}U(n, 2n)^{237}U→^{237}Np; ^{235}U(n, ϒ) ^{236}U(n, ϒ) ^{237}U→^{237}Np
^{238}Pu	ONF, RP	^{235}U(n, ϒ) ^{236}U(n, ϒ) ^{237}U(β-) ^{237}Np(n, ϒ) ^{238}Np(β-) ^{238}Pu, ^{238}U(n, 2n)^{237}U(β^{-}) ^{237}Np(n, ϒ) ^{238}Np(β^{-}) ^{238}Pu
^{239}Pu	ONF, RP	^{238}U(n, ϒ) ^{239}U(β^{-}) ^{239}Np(β^{-}) ^{239}Pu
^{240}Pu	ONF, RP	^{238}U(n, ϒ) ^{239}U(β^{-}) ^{239}Np(β^{-}) ^{239}Pu(n, ϒ) ^{240}Pu
^{241}Pu	ONF, RP	^{238}U(n, ϒ) ^{239}U(β^{-}) ^{239}Np(β^{-}) ^{239}Pu(n, ϒ) ^{240}Pu(n, ϒ) ^{241}Pu
^{242}Pu	ONF	^{238}U(n, ϒ) ^{239}U(β^{-}) ^{239}Np(β^{-}) ^{239}Pu(n, ϒ) ^{240}Pu(n, ϒ) ^{241}Pu(n, ϒ) ^{242}Pu

^{241}Am	ONF, RP	$^{238}\text{U}(n, \Upsilon)\ ^{239}\text{U}(\beta^{-})\ ^{239}\text{Np}(\beta^{-})\ ^{239}\text{Pu}(n, \Upsilon)\ ^{240}\text{Pu}(n, \Upsilon)\ ^{241}\text{Pu}$

NB: NWT- nuclear weapons testing; ONF- operation of nuclear facilities; CRR- Cosmic ray reaction; NOR- normal occurring radionuclide; RP- reprocessing plants.

2.4. Units of measurements of radioactivity

There are traditional units and also System International (SI) units, see Table 3, for measurements of radioactivity. The gigabecquerel (GBq), Curie (Ci), gray (GY), Sievert (Sv), Coulombs per kilogram (C kg^{-1}), Rad, Rem and roentgen (R) are mostly used units to measure radiation (D'Auria, 2019). The GBq is a unit of radioactivity that is defined as1.37 x 10^{-12} atomic decays per second and quantifies the number of gamma rays emitted from a source of radiation. The material comprising a GBq varies in weight. The units varies depending on the type of medium; for air is in Bq m^{-3}, water and milk in Bq L^{-1}, deposition in Bq m^{-2}, soil in Bq kg^{-1} dry mass and Bq m^{-2} , grass in Bq kg^{-1} dry mass and Bq m^{-2} and foods in Bq kg^{-1} fresh mass. Smaller units, such as the millicurie, microcurie, and picocurie, which are 10^{-3}, 10^{-6} and 10^{-12} respectively, are commonly used when dealing with biological systems (Odum, 1971; Guidebook, 1989). The GY is another unit used to measure radiation. The absorption of 1 joule of radiation energy per kg of tissue is referred to as the absorbed dose of 1 GY. The roentgen which is basically similar to the GY is used to measure gamma and x-ray exposure. All these units are related to the total amount of radiation received per unit time.

Table 3: Traditional unit, the comparable SI unit, and conversion factors for measurement radioactivity.

Traditional unit	SI unit	Conversion Factor (smaller unit to the larger unit)
Curie (Ci)	Becquerel (Bq)	1 Ci = 37 billion Bq
Rad	Gray (Gy)	Be1 Gy = 100 rad
Rem	Sievert (Sv)	1 Sv = 100
Roentgen (R)	Coulombs per kilogram (C kg^{-1})	1 c kg^{-1} = 3876 R

2.5. Uses of radioactive metals in the energy sector

2.5.1. Nuclear energy

The sustainability of energy supply has been a major worry for many countries. This sparked a number of research projects aiming to find alternative energy sources that are inexpensive, reliable, and environmentally friendly (Al-Othman et al., 2019). Nuclear energy, in particular, has received a lot of attention. The possibility for lower nuclear fuel costs was the driving force behind nuclear power plant installation between 1970s and 1980s, particularly after the oil crisis of the 1970s (World Energy Council, 2016). Nuclear power facilities are now available in many countries across the world. Country such as Japan, Kazakhstan, and the Middle East are just a few examples (Al-Othman et al., 2019). In 2016, 441 nuclear reactors with a total capacity of 382.9 GW(e) (giga-watt electricity) were operating in more than 30 counties (IAEA, 2016).

In China, the growth and demand for radioactive minerals like uranium resources is increasing due to the development of nuclear power industries (Bai et al., 2016; Bai et al., 2017), as well as the rising price of uranium internationally (Miao et al., 2013). The desire to meet required energy supply, expand fuel sources, and reduce reliance on non-renewable energy sources including fossil fuels has influenced the quick rise in the development of nuclear energy sectors (Qvist and Brook, 2015). These factors coexist with a number of environmental concerns caused by the excessive use of fossil fuels as a main energy source, including climate change, greenhouse gas emissions, and air pollution (Al-Othman et al., 2019).

According to a 2012 report by the IAEA, worldwide energy demand will increase by one-third by year 2035 (Kavvadias and Khamis, 2014). In a studies done by the World Energy Council in 2016, it was discovered that uranium resources have expanded by around 70% in recent years, and would provide sufficient energy supply for more than 100 years based on current consumption rates (World Energy Council, 2016). Nuclear energy has expanded rapidly over the last three decades, accounting for about 14% of total electricity generation in 2009 and over 18.9% in 2016 (IAEA, 2016; Al-Othman et al., 2019). Nuclear-generated electricity is recognized as the most cost-effective electricity supply alternative in many markets due to low fuel costs (ASSAf, 2014; Qvist and Brook, 2015). Apparently, nuclear power has emerged as a potential alternative for the generation of clean energy (Al-Othman et al., 2019). However, the most significant challenge in nuclear energy research is the work to be done on nuclear safety (both in terms of reactor operation and the safe disposal of nuclear waste products) and nuclear policy (Qvist and Brook, 2015; Perera, 2018; World Energy Council, 2016).

In the year 2018, IAEA projected that nuclear energy can now generates as much electricity as all other sources combined did in the early 1960s. With reactors in thirty-two countries, civil nuclear power plants serve around 11% of global electricity needs. Commercial nuclear power reactors have a total installed electrical generating capacity of more than 392 GW(e) worldwide. Fifty-five nuclear power reactors are currently under development, accounting for roughly 16% of total nuclear capacity (IAEA, 2018).

2.5.2. Nuclear energy development in South Africa

Many views were shared on the state nuclear energy in South Africa have been discussed severally. In August 2014, Academy of Science of South Africa (ASSAf) conducted a research in relation to the state of energy research in South Africa. Sameer (2014) reported findings from his studies on the state nuclear energy in South Africa. These studies are share the similar views including the fact that the South Africa's Department of Energy (DoE) in its 2010 Integrated Resource Plan, mentioned that the nuclear power would contribute 9.6 GW of the planned 42 GW of additional electricity generation capacity to be built by 2030.

These studies futher showed that South Africa has the world's greatest natural uranium resource, as well as other minerals that are essential for nuclear power. Uranium is a radioactive element. When its decay composed of radionuclides daughters progeny such as thorium and radium, in its decay process it produced vast amount of energy as heat. As a result, it plans to implement, or at least generate interest in, the entire nuclear fuel cycle, which includes uranium mining and milling, conversion, enrichment, and fuel manufacturing. It would also mean that the country could benefit from its own natural resources rather than relying on others to do so at a large additional cost. Uranium enrichment and fuel manufacture are the most technologically complex of the many fuel cycle processes, but they also represent the highest value items in the entire value chain.

South Africa's nuclear industry began in 1959 when the Cabinet decided to build a domestic nuclear sector. The development of nuclear energy in South Africa has been marked by a number of significant milestones, which have been facilitated by the research and development (R&D) programme.

The 2014 ASSAf report showed that the Y pilot uranium enrichment facility, based on the innovative Helikon aerodynamic vortex tube technique developed in South Africa, was built between 1971 and 1975. As part of its economic sanctions on South Africa, the US halted the export of highly enriched uranium fuel for the South African Fundamental Atomic Research Installation (SAFARI-1) reactor. The Y-Plant began generating 45% enriched uranium in 1979, and the first SAFARI-1 fuel assemblies from Valindaba were produced in 1981. The Y- Plant operations were terminated in 1990, and the plant was decommissioned under IAEA supervision. Intensive nuclear fuel manufacturing and uranium enrichment initiatives were supported from 1984 - 1997. The Z-Plant was commissioned in 1984 and came into full production in 1988 with a capacity of 300 000 SWU/yr. The Koeberg Nuclear Power Station received fuel elements which gives about 3.25% enrichment. A Molecular Laser Isotope Separation (MLIS) initiative began in 1983, with French involvement in 1995. Due to lack of finance and technical difficulties, the MLIS initiative was discontinued in 1997. During this time, a centrifuge-based R&D project was funded.

In 1984–1985, two 900 MWe French-built nuclear power plants were commissioned at Koeberg. In 2007, the draft nuclear energy policy was released. This included an ambitious programme to develop all aspects of the nuclear fuel cycle, including: conversion, enrichment, fuel fabrication and also reprocessing of used fuel. The Pebble Bed Modular Reactor Project, which was shut down in 2010, was funded by the Westinghouse, Eskom, South African government, and the Industrial Development Corporation between 1999 and 2009. The initiative, in which South Africa was regarded as a world leader, was shut down due to a number of circumstances. The economic climate, public opinion, the PBMR placement under the Department of Public Enterprises, unrealistic cost contrains, and a transition in technical focus, including licensing constrains, were all found to be the fundamental causes.

The Nuclear Energy Corporation of South Africa (Necsa) was formed in 1999. The R&D division of Necsa was incorporated on April 1, 2007, to strengthen the corporation's research and technology development activities and to consolidate the corporation's ability to deliver on the following mandate of Necsa, as derived from the Nuclear Energy Act (Act 46 of 1999): first, to undertake and promote research on nuclear energy, radiation sciences and technology; second, to process source, special, and restricted nuclear material, including uranium enrichment. The Act also provides for the delegation of specific responsibilities to the corporation, including the operation of the SAFARI-1 reactor; applying radiation technology for medical and scientific purposes; decontamination and decommissioning of nuclear facilities from historic strategic programmes; and implementing and executing national safeguards and other international obligations. The Necsa will also be responsible for operating the SAFARI-1 reactor, applying radiation technology for medical and scientific purposes, decontaminating and decommissioning nuclear facilities from historic strategic programmes, and implementing and enforcing national safeguards and other international obligations, according to the derived Act. The Nuclear Energy Policy, which was adopted in June 2008, reaffirmed Necsa's mandate and established it as the country's main platform for nuclear energy research, development, and innovation. The policy also emphasized the importance of the corporation developing viable nuclear fuel cycle options to assist South Africa's desired nuclear energy expansion. In addition to the nuclear fuel cycle, Necsa has adopted the short-term approach focus in support of isotope production.

2.5.3. Nuclear power reactors

As of 2016, all operating nuclear power plants use the nuclear fission technique to generate electricity (Knapp and Pevec, 2018). The splitting of heavy atomic nuclei in order to generate lighter atomic nuclei releases a lot of energy during nuclear fission. These atomic nuclei are distinguished by their mass numbers, atomic numbers, and the quantity of emitted neutrons, as well as the γ-rays associated with the main nuclei's excitation (Al-Othman et al., 2019).

Nuclear reactors are responsible for converting the thermal energy produced into electricity (Knapp and Pevec, 2018; Matarranz e al., 2013). Around the world, various nuclear reactor configurations are currently in use. They are divided into generations based on their historical development. The main types are liquid metal cooled fast reactors (LMFRs), gas-cooled reactors (GCRs), pressurized heavy water reactors (PHWRs), boiling water reactors (BWRs), advanced gas-cooled reactors, fast breeder reactors (FBRs), high temperature gas-cooled reactors (HTGRs), pressurized water reactors (PWRs) and light water (cooled) graphite (moderated) reactors (LWGRs) (Alemberti et al., 2014).

There are currently approximately 441 nuclear reactors in operation in the world. PWR reactors account for around 68%, BWR reactors for about 20%, PHWR reactors for about 6%, and the remaining are said to be the GCR, LWGR, and FBR reactors (Al-Othman et al., 2019). Due to the considerable population expansion, other new reactor technologies and configurations are continually being made. Small modular reactors (SMRs) and fast neutron reactors (FNRs) are the most promising technologies for the coming years (Khan et al., 2017). SMRs are advanced nuclear reactors capable of producing up to 300 MW(e) of electric power (Khan et al., 2017). These reactors are regarded as the most feasible because they can be built and carried into the facility. They are distinguished by the ease and speed with which they may be moved and fitted to meet the energy requirements of the facility. Many countries throughout the world, including the Japan, Argentina, Russia, Italy, France, South Korea, China, U.S and India, have recently made significant contributions to the construction and design of SMRs (NEA, 2021; NEA, 2016; WNA, 2015).

2.5.2. Role of radioactive metals in other economic sectors

Radionuclides have a wide range of uses in numerous fields that use nuclear technology. Inspite of wide arrays application of radioactive metals in energy industries, they also play important role in other economic sectors such as material engineering , medicine, indicators of atmospheric dynamic processes, and tracing airborne pollutants (Guerrero et al., 2020; Długosz-Lisiecka at al., 2020; Jiang, 2017; Długosz-Lisiecka, 2019). The use of radionuclides are becoming increasingly important in medicine for diagnosis and therapy all around the world. Radioisotopes with shorter half-lives are applied in medicine because they decay rapidly and can be used for diagnosis and therapy (Rahman et al., 2018).

Radiopharmaceuticals are applied in diagnostic imaging and radiotherapy in nuclear medicine, and they are crucial for medicine in general to aid in organ diagnosis and treatment of pathological disorders, including cancer (Jiang, 2017; Rahman et al., 2018). In the imaging modality, radiopharmaceuticals are taken orally, intravenously, or inhaled to allow viewing of numerous organs, such as kidneys, lungs, thyroid and heart functions, bone metabolism, and blood circulation, using radioactive tracers. A high dosage of radiation is applied using particular radiopharmaceuticals targeting the diseased organ in a therapeutic modality aimed at treating cancer or an over functioning thyroid gland (WHO, 2010).

Nuclear medicine diagnostic procedures rely on radioactive tracers that emit gamma radiation from inside the body (Payolla et al., 2019). For example, a photon emission computerized tomography, is used to diagnose blood deprived areas of the brain (ischemic), spinal stress fractures (spondylolysis), and malignancies by visualizing blood flow through veins and arteries, perform pre-surgical evaluation of seizures (Wells, 2016). Radiation and radionuclides are being used in medicine for diagnosis and therapy around the world. According to the World Nuclear Association, one out of every 50 people in developed countries (1/4 of the world's population) is exposed to nuclear medicine, with radionuclide therapy accounting for around 10% of that number (WNA, 2018). Nuclear medicine uses radiation to collect information about a person's organs in order to treat a disease. Information is frequently utilized to make a rapid diagnosis. The thyroid, bones, heart, liver, kidney, and a variety of other organs can all be seen in the generated image, as well as any anomalies in their functions. Radionuclides are used in around 10,000 hospitals around the world, and about 90% of the processes are for diagnosis. Technetium-99 m (99 mTc) is the most commonly utilized radionuclide in diagnostics. It is utilized in around 40 million exams each year, accounting for approximately 80% of all nuclear medicine exams performed worldwide (Payolla et al., 2019). Radionuclides are used in around 20 million medicinal applications in the U.S each year, and about 10 million in Europe (Payolla et al., 2019) (Table 4). According to the Nuclear and Energy Research Institute of Brazil, there were three hundred and sixty diagnostic clinics and nuclear medicine hospitals in 2017. The 70% of them located in the South and Southeast of Brazil, 72 PETs installed, with more to be licensed, thirty-three hospitals with therapy rooms, and approximately 1.8 million patients per year (Grupen, 2010).

Table 4: Radionuclides used in medicinal application (Payolla et al., 2019).

sodium iodide (^{123}I)	sodium phosphate (^{32}P)
sodium iodide (^{131}I)	^{111}indium (^{111}In)
gallium citrate (^{67}Ga)	dotatate (^{177}Lu)
thallium chloride (^{201}Tl)	Barium-133 (^{133}Ba)
sodium chromate (^{51}Cr)	Cobalt-57 (^{57}Co)
generator ^{99}Mo – ^{99m}Tc	Caesium-137 ^{137}Cs
sodium sulfate (^{35}S)	Iridium-192(^{192}Ir)
phosphoric acid (^{32}P)	Iodine-125 (^{125}I)

Radioisotopes are widely applied in agriculture, and their application is enabling people to solve numerous agricultural problems in a short space and with more precision (Rohr et al., 2019). As a result, radioisotopes have become a critical resource for scientists working to solve agricultural challenges. Radioisotopes are being used as an experimental tool to develop new strains of farming goods that are drought and disease resistant, have higher quality, take less time to grow, and yield more (Diwan et al., 2019).

In agricultural industry studies, radioactive isotopes are used in the same way as stable isotopes. Radioisotope technologies not only provide a clear image of how parasites and diseases affect hosts, but they also show how management and genotypes (breeds and species) can be changed to reduce the disease or parasite's impact on final production (Diwan et al., 2019). Ionizing radiation was successfully utilized to create an attenuated vaccine against lungworm in sheep and cattle, and this information is being passed on to nations like Ethiopia, India, and Brazil, where control of this parasitic infection is critical (Pourjafar, 2017).

Radioisotopes are commonly utilized as tracers in the agriculture industry (Rahman et al., 2018). Insects can be exterminated with radiation, and the sterile insect technique (SIT) is used to lower the population of insects by inhibiting their ability to reproduce (Urquidi et al., 2015). Although ^{15}N is the most common stable isotope used in agriculture, a diverse range of other stable isotopes are produced and are becoming more widely used (Pourjafar, 2017). Radiation like gamma rays can be utilized to measure and assess the human population's exposure to terrestrial radiation and to identify regions where natural radiation hazards may occur (Inoue et al., 2020; Hanfi et al., 2021). Moreover, radioactive metals have also put to usage for the benefit of human being in material engineering (Jiang, 2017).

Finally, radionuclides are also used as effective indicators of atmospheric dynamic processes like removal or washout ratios, residence time (Długosz-Lisiecka, 2019; Długosz-Lisiecka et al., 2020), and tracing airborne pollutants (Guerrero et al., 2020; Długosz-Lisiecka et al., 2020). Meanwhile, environmental tracers can be made from radionuclides generated by reprocessing plants (Du Bois et al., 2020; Hanfi et al., 2021; Wefing et al., 2019) for the investigation of transport of atmospheric circulation (^{129}I)and water mass (^{134,137}Cs, ^{99}Tc, ^{129}I). The South African Fundamental Atomic Research Installation reactor (SAFARI-1) uses radioactive metals in research (Gama et al., 2018).

2.6. Radioactive material waste management

Radioactive waste is defined as any material that is radioactive or has been polluted by radioactivity at levels higher than those established by the regulatory authorities and cannot be used again (Adella et al., 2017). This type of waste comes mostly from nuclear power production, but also from a range of industries, medicine, agriculture, research, and education, as well as other activities that utilise radioisotopes (Larramendy and Soloneski, 2016; Veyseh and Niazi, 2017; Zhu et al., 2020). Radioactive materials when not handled properly, may become an issue and problematic in ecosystems (Adella et al., 2017). It is concerning that large quantities of radioactive waste are released into the environment through various ecomonic activities, posing a long-term danger to the surface and subsurface environments (Yu et al., 2015). Radioactive nuclides such as ^{60}Co, ^{154}Eu, ^{232}Th, ^{235}U, ^{235}Np, ^{239}Pu, ^{241}Am, and ^{247}Cm, in nuclear wastes from industries directly pollute the environment including surface water and groundwater resources (Zhu et al., 2020). Although concerns have been raised, handling of radioactive waste remains a global challenge, and the level at which these challeges are universally considered contrains the exploration and expansion of use radioactive materials (Sun et al., 2019; Larramendy and Soloneski, 2016; Zhu et al., 2017).

Once created, radioactive waste may undergo treatment depending on the type of waste and the strategy for its management. The treatment may involve decontamination, chemical adjustment, segregation, and collection or may all be part of the process, as well as duration of interim storage (Nath, 2018; Larramendy and Soloneski, 2016). Basically, this is about to separate waste into channels that will be managed in the same way, and to segregate non-radioactive wastes and recyclable materials. Treatment involves altering the waste's characteristics by reducing its volume, removing radionuclides, or changing its composition. The compaction of dry solid waste or cremation of solid or organic aqueous wastes (volume reduction); filtering or ion exchange of aqueous waste (radionuclide removal); and precipitation or flocculation of chemical species are examples of common treatment processes (change of composition). Thus, the application of waste hierarchy, as demonstrated by Ferrari et al. (2016), which encourages the adoption of options for managing waste in the order of priority: (1) prevention, (2) preparing for reuse, (3) recycling, (4) disposal.

There are many common challenges that are linked to radioactive waste. Firtly, the creation of waste cannot be avoided; secondly, possibility of formation of highly radioactive waste and lastly, radioactive waste cannot be easily stored safely and permanently (Abu-Dalo et al., 2020; Prăvălie, 2018; Horvath and Rachlew, 2016; Prăvălie, 2014). In order to increase the safety of radioactive waste management, instead of treating, radioactive wastes are buried deeply in the underground repositories or deep in the ocean (Natarajan et al., 2020; Stefanovsky et al., 2016). Many studies including Blue Ribbon Commission on America’s Nuclear Future (2012), Fuks et al. (2018) and Wigeland et al. (2014) have described temporary storage in dry casks and permanent disposal in drilled tunnels or deep boreholes in geological reserves as other solution to radioactive waste management and disposal of spent fuel. The sludge component of the radioactive is immobilized in a borosilicate glass which is then stored on-site on an interim basis (Stefanovsky et al., 2016). However, highly radioactive waste are dangerous, as it persists in the environment for many years (Horvath and Rachlew, 2016; Prăvălie, 2014), which makes safe storage almost unattainable. In terms of disposal, these metals are not degradable by biological or physical processes; hence remain in the soil for a long time, posing a long-term environmental threat (Yan et al., 2020; Suman et al., 2018).

Nowadays, in order to increase the safety of radioactive waste management, one of the most important approach it is to convert them into solid chemically and radiation stable forms prior disposal in deep underground (Stefanovsky et al., 2016). As a result, a variety of methods including physical, chemical methods and biological technologies have been investigated as potential means used in the disposal of radioactive waste (Abu-Dalo et al., 2020; Zare et al., 2021; Natarajan et al., 2020; Yu et al., 2015; Shao et al., 2016; Li et al., 2018; Liu et al., 2017; Chang, 2016).

2.7. Remediation and/or removal of radiometals

2.7.1. Physical methods

The physical methods include incineration, distillation, dumping, evaporation and sorption.

2.7.1.1. Incineration

This waste treatment method entails the high-temperature combustion of solid radioactive waste, resulting in the release of CO_2, H_2O, S, and hydrochloric acid as by-product (Saffarzadeh et al., 2014). To regulate radioactive discharges, this technique needs gas-filtering equipment. Pre-treatment is required for thickening and water removal. (Prado et al., 2020; Oshita et al., 2015; Jing et al., 2016).

2.7.1.2. Distillation

The waste treatment approach entails reducing the volume of radioactive waste in solid form (Chen et al., 2019). This is a pretreatment technique of incineration (Shao and Li, 2019). The disadvantage of this technique is that it consumes a lot of energy and gives a slow output (Natarajan et al., 2020).

2.7.1.3. Evaporation

This is a unit process that involves removing heavy metals, salts, and other hazardous waste components from effluent wastes, such as radioactive waste (Sorokin, 2019; Deng et al., 2021). Evaporation results in the decrease of radioactive waste and other harmful materials in low and intermediate-level wastes (Natarajan et al., 2020). The method has the disadvantage of being highly expensive due to its high energy consumption (Thimmaraju et al., 2018). More also, the presence of a large volume of inactive salts slows the evaporation process with some organic salts, potentially resulting in an evaporation explosion (Xu et al., 2019).

2.7.1.4. Dumping

In this method, the solid or mixed radioactive waste is buried or disposed deep in the ocean. To avoid contamination, radioactive waste is processed in the following order: incineration, evaporation, and compaction before being dumped into the ocean (Stefanovsky et al., 2016). Previously, most of the radioactive waste was managed by direct deposition (Natarajan, 2020). The radioactive material will remain underground entirely (Fuks et al., 2018; Wigeland et al., 2014). The drawback of this technique is that there is a high risk of radioactive waste leakage and contamination into groundwater or the ocean.

2.7.1.5. Sorption

Sorption technique have been widely applied for the removal of radioactive metals from radioactive because it is simple to undertake, cost-effective, and may be used on a wide scale for practical applications. Radioactive metals are sorbed onto the environmentally stable structure of adsorbents that is assessed as a remediation agent for radioactive waste sites (Imam et al., 2019). A variety of adsorbents, such as metal hydroxides (Gu et al., 2018; Chen et al., 2016), clay minerals (Yu et al., 2015; Chagneau et al., 2015), metal–organic framework material (Li et al., 2018; Liu et al., 2017), nanoparticles (Zhu et al., 2020), and carbon nanotubes (Zare et al., 2021), has been developed for the removal of radionuclides.

One of most widely studied sorbent studied, for an example, is graphene oxide (GO) for the removal of radioactive materials from the environmental samples (Wang et al., 2015; Zhu et al., 2020). It has the advantages of large specific surface area, high acid and alkali resistance, and excellent irradiation resistance (Yu et al., 2015; Zhu et al., 2020). The GOs is a kind of one or several atomic layers of graphite that have a unique two-dimensional (2D) structures and special physicochemical properties, and have attracted intense multidisciplinary research areas in recent years (Yu et al., 2015). It is known for higher sorption capacity than other natural or manmade materials (Chen et al., 2017a; Yang et al., 2015; Wang et al., 2017). Not only that graphene oxides demonstrated the maximum adsorption capacities for cobalt, it is also highly active for other metal ions (Chen et al., 2016). Zhu et al. (2020) prepared and used graphene oxide GO composites for the removal of highly toxic U(VI) with other metal ions (Cs^+, Sr^{2+}, Co^{2+}) from aqueous solution. Adsorption capacity of 87.8 mg g^{-1} at low pH (pH = 3.6 ± 0.03) was achieved along with a manifested excellent selective adsorption. This is because of a large number of reactive oxygen-containing functional groups (hydroxyl, carboxyl); leading to efficient capture of organic and inorganic pollutants through π-π or electrostatic interactions and hydrogen bonding (Chen et al., 21017a; Shao et al., 2014). In comparison to other methods, the adsorption technology is often used to eliminate radionuclides due to its high efficiency, low cost, and ease of operation (Hu et al., 2014).

2.7.2. Chemical methods

There are many chemical methods that can be used for the successful treatment of radioactive waste material. This include chemical precipitation, acid digestion, wet oxidation, ion exchange, etc. (Santander-Muñoz et al., 2021).

2.7.2.1. Chemical precipitation

The radioactive materials are eliminated from waste through a process of precipitation and the sorption of particles. Chemical precipitation has been used to treat liquid radioactive waste. The use of this method, limits the transportation quantity to only reduced volume of the radioactive bottom sludge. The volume of the sludge is extremely smaller than the total liquid amount (Santander-Muñoz et al., 2021). This is because, most of the radioactivity is precipitated by chemical agents to the bottom sludge, and a large amount of liquid waste could be reused or safely discharged to the environment (Osmanlioglu, 2018). This technique can be used to manage and eliminate radioactive materials from low- and intermediate-level radioactive waste from nuclear power plants and research laboratories (Natarajan, 2020). Removal of radioactive materials from the environmental water samples by the use of copper ferro(II)cyanide and sodium tetraphenylborate is another application of this method (Osmanlioglu, 2018). This method was successfully used by Osmanlioglu (2018) to precipitate ^{137}Cs, ^{134}Cs, and ^{60}Co from radioactive waste water at the volume of 35 m^3 using potassium ferrocyanide, nickel nitrate and ferrum nitrate.

2.7.2.2. Wet oxidation

This approach involves the of dissolved and suspended components of waste materials. The thechnique is used to treat organic aqueous radioactive wastes. Hazardous liquids, foam, resins, ion exchange, and cellulosic waste are among the wastes found in organic aqueous radioactive wastes (Walling et al., 2021; IAEA, 2018). The oxidation process transforms/degrades the waste by using oxygen as an oxidant (Bokare and Choi, 2014; De Araujo and Marumo, 2018). Ozone peroxide, hydrogen peroxide, and other oxidizing agents are used in wet oxidation. When carbon-based waste is decomposed by chemical oxidizers, carbon dioxide, water, and non-toxic elements are produced (Natarajan, 2020; Stegenta-Dąbrowska et al., 2019).

2.7.2.3. Acid digestion

It is an oxidative destruction method that may be used to treat organic liquid wastes like polyethylene cellulose, oils, plastic, latex rubber, and other organic compounds (Turek et al. 2019; Yang et al., 2013). Strong acids, such as phosphoric acid and nitric acid, are used to decompose radioactive waste in this technique (Yang et al., 2013; Kobayashi et al., 2012; Liu et al., 2020). In order to breakdown of bonds of the waste components, the processes are undertaken at a high temperature and with appropriate atmospheric pressure (Mohammed et al., 2017; Turek et al. 2019). The inorganic liquids and gases including O_2 and CO_2 are the products of this process (Valdovinos et al., 2014).

2.7.2.4. Recent methods

According to recent investigations, cement can be utilized to immobilize hazardous material and operate as a radiation shielding system (Faiz et al., 2017; Szajerski et al., 2019), by lowering the solubility and permeability of the matrix. This method is designed to prevent waste pollutants such as liquids and sludge from moving near deposition site (Goo et al., 2021). Silicates, Portland cement, lime, pozzolanic materials, and polymers are the most commonly utilized stabilization materials (Rahman et al., 2014; Garg and Pundir, 2014). The immobilize radioactive waste produced in power plant is crucial. This is because BWRs generate a large amount of the waste (Goo et al., 2021; Rahman et al., 2014), which include radioisotopes of ^{60}Co, ^{134}Cs, and ^{137}Cs. There are physical constraint in the use of Portland cement to immobilize radioactive waste; hence it might be made more efficient to use nanoparticles of polymers and a constructed matrix. In addition, this matrix could be improved by combining recycled polymers with cementitious materials. Expanded polystyrene, polyethylene terephthalate, and expanded polypropylene are other forms of polymers that can be used. From this, the composite formula of Portland cement and post-consumer expanded polystyrene is identified as it is a low-cost binder material and assists in the immobilization of radioactive waste (Ozbakkaloglu et al., 2017; Sayadi et al., 2016; Mercader-Moyano et al., 2016). Another form of chemical method is ion exchange used by Adella et al. (2017). In this method, solid polymeric or materialistic ion exchangers, ions exchange between an electrolyte solution and a complex or between two electrolytes are used. The method was applied for the removal of ^{137}Cs and ^{60}Co from hazardous and toxic radioactive liquid waste which are discharged from nuclear research laboratory (Adella et al., 2017).

2.7.3. Biological methods

Recent advances in bioscience have resulted in significant changes in research outcomes, in not just biology, but also in interdisciplinary fields such as biotechnology, electrochemistry, and bioinformatics. Biological techniques are environmentally friendly and play an important part in the efficient and environmentally friendly treatment of radioactive waste (Upadhyay et al., 2020). In the case of biological techniques, the conversion of radioactive waste into a non-radioactive form is a possibility, afterwards the radionuclides, in this case, are used for their growth. Plant remediation, microbial remediation, phytoremediation, and other biological processes are examples of biological methods.

2.7.3.1. Microbial bioremediation

Bioremediation is the technique of removing or disposing of radioactive waste from the environment using microorganisms. The removal and conversion of radioactive substances to less radioactive/non-radioactive forms is facilitated by the metabolic activity of microorganisms (Chandrakant and Shwetha, 2011; Vandana et al., 2021). The physical, chemical, and biological characteristics of the microbe determine the ability of the microbial remediation process. This method includes reduction, oxidation, dissolution, leaching, precipitation, and sorption processes, all of which have a significant impact on the radioactive waste's toxicity reduction (Vandana et al., 2021; Roh et al., 2015).

Major isotopes radioactive elements like $^{238}U/^{235}U$, ^{137}Cs, ^{237}Np, ^{239}Pu, ^{241}Am, ^{99}Tc, and ^{90}Sr are soluble in nature, and are deposited underneath the sea, polluting the underground water. These reduced forms of these chemicals are insoluble, immobilized, and precipitated (Saleh et al., 2017). Each microorganism has its unique manner of interacting with different heavy metals and radioactive elements based on the redox characteristics of the radioactive element (Tkavc et al., 2018; Igiri et al., 2018; Ali et al., 2019). Furthermore, bioremediation can be used to dispose of radioactive waste and convert it to electricity, based on technological advancements and knowledge of microbes (Chang, 2016).

2.7.3.2. Plant bioremediation

Scientists use the capacity of plants to gather radioactive materials/nuclei in a process known as phytoremediation. Phytoremediation is the process of using plants to remove pollutants from soil and water. It is an eco-friendly and cost-effective extraction method (Yan et al., 2020). It takes advantage of its uniqueness, selectivity and naturally occurring ability to absorb pollutants through the root system of plants (Jacob et al., 2018; Yan et al., 2020). The ability of the entire plant to store pollutionts and translocate the uptaken components is strengthened by bioaccumulation (Jacob et al., 2018). For the past years, researchers have been working to develop phytoremediation with the use of modern technologies (Burges et al., 2018; Gerhardt et al., 2017).

Phytoremediation is a cost-effective and environmentally friendly approach. Phytoremediation may be the most essential method for managing pollution and ensuring the safety of the environment in the future (Jacob et al., 2018; Yan et al., 2020). According to Yan et al. (2020), phytoremediation is classified into a variety of processes based on the degradation of radioactive nuclides and heavy metals: Phytoextraction, phytovolatilization, phytostabilization, rhizofiltration, and phytodegradation. Waste water treatment, toxic pollutant removal, organic pollutant removal, soil contamination, and radionuclide-contaminated water are some of the applications of phytoremediation (DalCorso et al., 2019).

2.7.3.3. Macrophytes in phytoremediation

Many aquatic and terrestrial macrophytes have been proven to be effective at absorbing and removing toxic contaminants such as zinc, cadmium, lead, and chromium (Akhtar et al., 2017). Ludwigia stolonifera, water hyacinth, water ferns, hydrilla are some examples of these macrophytes (Saleh et al., 2019b). These plants can absorb metals in their root without affecting the ecosystem. However, if the concentration of uptaken radioactive metarials is high, this will harm the environment (Saleh et al., 2019a). As technology advances, it will be possible to remove toxic waste without harming the environment or ecosystem by enhancing our knowledge of plant absorption mechanisms and functions. Nearly 400 plant species have been identified as capable of remediation of toxic pollutants in soil and water (Natarajan et al., 2020).

2.8. Environmental and health effects of radioactive metals

2.8.1. Pollution

Radioactive metals continue to bring challenges because they are one of the major causes of environmental pollution, and this is known to be a very serious issue of health concern (Ahmed et al., 2020). Industrialization and urbanization are the major point sources of radioactive pollutants (Ruff, 2015; Veyseh and Niazi, 2017; Zhu et al., 2020).

The level of radionuclides air pollution is significantly influenced by point source emissions from fossil fuel power plants (Kılıç et al., 2019; Filizok et al., 2014). Spent nuclear fuels generally contain actinides series metals like uranium, thorium and various fission products (Mohammadi et al., 2015). When radioactive metals are emitted at a high temperature, they typically produce volatile compounds, which quickly condensates into fine dust, and simply go into the atmosphere (Dugosz-Lisiecka and Perka, 2020). Suhana and Rashid (2016a,b) found that isotopes formed on the surface of dust or ash can spread easily over long distances, increasing the radioactive background (Dugosz-Lisiecka, 2016; Dugosz-Lisiecka and Perka, 2020).

Another source of air pollution and toxic elements including radioactive gases and dusts to the environment is coal-fired power plants (Długosz-Lisiecka and Perka, 2020; Du et al., 2020).

Coal power plants release high concentrations of radioactive materials/metals in released aerosols (Długosz-Lisiecka and Perka, 2020). This is due to the presence of naturally occurring radioactive elements including uranium and thorium, as well as their decay products, in coal (Purevsuren and Kim, 2021). Health and environmental problems linked with the use of coal is due to the inorganic matter and trace elements in coal–minerals (Munawer, 2018; Ahmed et al., 2020). The concentration of most radioactive elements in solid combustion byproducts like fly ash and bottom ash will be higher than that of the original coal (Ozden et al., 2018). In the U.S, for example, the concentration of most radioactive elements in solid combustion wastes is around 10 times that of the original coal (where the average ash content of coal burned is estimated to be around 10%) (Ahmed et al., 2020). As a result, the radionuclides in enriched coal were in the combustion products (Suhana and Rashid, 2016a,b).

Nuclear power is a reliable source of electricity and a carbon-free source of energy. It's also one of the most promising alternatives to traditional combustion energy sources for addressing energy and environmental issues. However, during normal operation, the nuclear power plant releases trace amounts of radioactive materials into the environment in the form of gas and liquid (Purevsuren and Kim, 2021). Nuclear energy development is a major source of radionuclides pollution (Larramendy and Soloneski, 2016).

Nuclear weapons production and testing result in the environmental pollution. Form every phase, from development, deployment and use result in contamination of the environment. Nuclear tests have been carried out in the atmosphere, on the surface of the Earth, underground, underwater, and in space. They emit radioactive materials/radionuclides directly into the ground, air and water (Ruff, 2015). The largest amounts of ^{137}Cs radioactive debris are accumulated in oceans and seas. Among the radionuclides discharged in large quantity during nuclear testing were ^{14}C, ^{3}H, ^{241}Am, $^{239/240}$Pu, and ^{90}Sr (Prăvălie, 2014). The Northeastern Atlantic Ocean (the Irish and North Seas), Barents Sea, Baltic Sea, and Black Sea had the highest mean ^{137}Cs seawater concentration values which their mean concentrations exceeded the 10 Bq m^{-3} threshold in year 2000 (Prăvălie, 2014). These marine regions' radioactivity resulted from the converging outcomes of additional sources. It was also discovered that wet deposition accounts for 90% of overall ^{90}Sr and ^{137}Cs deposition during rainfall (Hughes et al., 2019).

Mining activities contaminate the environment with concentrations of toxic metals, which can accumulate and have an impact on the diversity and quantity of biological communities (Devi and Sumbali, 2021). There are reports on contamination of the environment by radioactive metals around mines (Wang et al., 2013). There are few studies related to radionuclides and heavy metals assessment from mining areas (Bai et al., 2017), including around prospective mining areas. A pre-mining assessment of radiation levels and heavy metals in mining sites could provide baseline information on environmental radiation levels and serve as a valuable future reference tool (Bai et al., 2017; Karunakara et al., 2014).

The incidents at Chernobyl (1986) and Fukushima Daiichi (2011), which resulted in the release of huge amounts (among these, ^{131}I, ^{134}Cs, and ^{137}Cs were the most dominant nuclides in Fukushima Daiichi, the emitted amount of each nuclide estimated was around 160, 18, and 15 PBq, respectively) of radionuclides into the atmosphere, are the most prominent examples of unprecedented pollution (Prăvălie, 2014). Nuclear accident in Chernobyl, had resulted about 96% deposition rate of radionuclide ^{90}Sr, ^{137}Cs, and ^{131}I from the atmosphere to the ground level (WHO, 2010).

2.8.2. Impacts on environment

All living organisms in the ecosystem are impacted by radioactive waste. They have a genetic effect on an organism, and this is passed down through the generations. It has a significant direct and indirect impact on the environment and humans.

Contaminating ecosystem with traces radioactive metals may have an impact on biological diversity and communities. This is due to the fact that a variety of microorganisms, including filamentous fungus, yeasts, and bacteria, have been found to digest any substance that may contain radioactive metals including coal, by enzymatic action, and use it as their sole source of carbon. Furthermore, the surroundings where mining occurs have bioaerosols, which may contain living or dead peptidoglycans, allergens, pathogenic or non-pathogenic bacteria, viruses, fungi, mycotoxins, bacterial endotoxins and other substances that can cause skin, respiratory, and other health issues (Devi and Sumbali, 2021).

When radioactive waste is deposited in the soil or on land, it contaminates the soil and releases hazardous radioactive materials into developing plants. Because the radioactive substances reach plants, they cause mutation, which leads to retarding growth and potentially the plant's death (Natarajan et al., 2020). Plant's products, like fruits, are polluted with dangerous radioactive material, which poisonous to the organism that ingests it. The food chain will be adversely affected by radioactive contamination from plants.

Radioactive chemicals will pollute the water if stored under the deep ocean or in deeper wells. Living organism that consumes such water will suffer serious health consequences. Both terrestrial and marine environments are unsuitable for the disposal of radioactive waste; contamination will pose a serious threat to both humans and the environment.

Due to its dissolved chemical form, radioactive materials are not removed from water by sedimentation, but transported and mixed together with the corresponding water masses, which have a strong influence on the climate (Hain et al., 2020). High-yield thermonuclear explosions cause enormous radioactive contamination to the environment. These hydrogen bombs, when tested on small islands in the ocean, produce radionuclides that settle in the ocean sediment. Even decades later, significant contamination may remain in the sediment surface and deep into the sediment layers (Hughes et al., 2019).

2.8.3. Impact on human beings

The toxicity of these radionuclides containing metals cannot be over emphasised and their excess release poses potential environmental risks and may affect human health (Veyseh and Niazi, 2017). The burning of radioactive containing materials leads to the release of toxic gases, which has a negative impact on both human health and the environment (Owusu et al., 2016).

Exposure to these gases has been linked to a variety of health issues, including skin, cardiovascular, blood, brain, and lung disorders, leukaemia and different cancers (Munawer, 2018; Paraschiv and Mohamad, 2020; Sharma and Sumbali, 2019). People who have been exposed to ionising radiation in childhood mostly develop a thyroid cancer (Simon and Bouville, 2015). Even though exposure to ionising radiation radioactive materials may have occurred some years ago, a the danger of excess radiation-related cancers can last for decades after exposure. Organ like thyroid is more sensitive to radiation, and can accumulate an internal dose of radioactive metals after consuming contaminated foods, such as fresh milk and other dairy products that acquire radioactive iodine when dairy animals graze in polluted area (Simon and Bouville, 2015).

Radiation emitted by radiometals is capable of damaging the genes in humans (Dhawan and Sharma, 2019; Larramendy and Soloneski, 2016). It is possible for cancer to develop if the genes are damaged. A mutation may occur if genes in reproductive organs are damaged. A mutation like this might be passed down to future generations (Khan, 2017). It was reported that radionuclides cause progressive or irreversible renal injury (Mohammad, 2015), and on white blood cells (Mohammad, 2015; Dhawan and Sharma, 2019; Sharma and Giri, 2016).

Few hours after exposure to radiation result into development of radiation sickness or radiation syndrome (UNSCEAR., 2000). This is a massive cell damage and cell death, also known as a deterministic phenomenon. The symptoms of this syndrome develop in bone marrow and related organs like intestines, lungs, and eyes (Hatch et al., 2005). The radiation source in such cases is usually gamma or X-rays (Simon and Bouville, 2015; Ahmed et al., 2020). Ionisation radiation causes extreme degrading effects on living tissues (Larramendy Soloneski, 2016). Table 5 gives some of the maximum allowable limits of radioactive nuclides for human consumption in different sunstances.

Table 5: Maximum allowable limits of radioactive nuclides for human consumption.

Radioactive element	Matrice(s)	Maximum allowance limit (MAL)	Reference
U	Drinking water	0.015 mg L^{-1}	Veyseh and Niazi, 2017
Ni	Fruits and vegetables	10 mg kg^{-1}	WHO, 1996
Ra	Drinking water	0.18 Bq L^{-1}	Olatunji et al., 2018
Cd	Fruits and vegetables	0.02 mg kg^{-1}	WHO, 1996
Th	Drinking water	0.59 Bq L^{-1}	Official Gazette, 2011
Cd	Drinking water	3.0 µg L^{-1}	Fırat et al., 2018
Pb	Drinking water	0.1 Bq L^{-1}	Sadi, 2016

2.9. Exposure

The word "radioactive contamination" refers to the presence of radioactive chemicals on surfaces or within biota, solids, liquids, or gases that is unplanned or undesired (Larramendy and Soloneski, 2016). The redistribution of radioactive metal in soil and rocks, as well as in water is spreading throughout the environment by wind, rain and geological processes. Therefore, it is dissolve in the water to be consumed by any organism (Yasmin et al., 2018). Humans are exposed to dust particles by eating and inhalation via mouth and nose, as well as skin contact (Lu et al., 2014; Bai et al., 2017).

In the aquatic biota, accumulation and transfer of radionuclides to human is through food chain cycle (Hughes et al., 2019). Once they reach an aquatic ecosystem, even trace amounts of these pollutants can trigger consequences for the environment and the living organisms that thrive in it (Janković et al., 2016). High-mobility radionuclides in contaminated water would spread into soils and plants, eventually becoming a part of animals and humans (Yu et al., 2015).

Soil is the largest receiving pool of emitted radionuclides in terrestrial ecosystems. Because the abiotic and biotic components of the ecosystem are related to the nutrient cycles and energy flow, soils contaminated with radionuclides lose their capacity to produce high-quality agricultural products and are therefore categorized as degraded (Larramendy and Soloneski, 2016). The challenges surrounding the degradation of radioactively contaminated soils are being treated as a unique sort of chemical contamination, with extra, distinct characteristics associated to ionizing radiation.

Over exposure to radiation may cause external irradiation to penetrate through clothes and ultimately reaching the body, and this may result in high dose of radiation in the body (Hatch et al., 2005; Hughes et al., 2019; Veyseh and Niazi, 2017). External radiation exposure occurs at trace levels from different sources, including soils and air (Janković et al., 2016; Gama et al., 2018).

Radioactive metals bonds to organic matter and other biological features such as clays, and the results of this are more radioactive than the other rocks minerals (Yasmin et al., 2018). Human accumulate radioactive dose through inhalation of radionuclides aerosols (Długosz-Lisiecka and Perka, 2020). The mobility and biological uptake of these radionuclides are affected by their various physico-chemical properties.

2.10. Health risk assessment

The assessment of the concentration of radionuclides in the environment is important for the assessment of exposure doses for people living directly in the region of emission (Długosz-Lisiecka and Perka, 2020). Health risk assessment model established by the US Environmental Protection Agency is used to calculate the doses as follows (Lu et al., 2014; Bai et al., 2017):

$$D_{ing} = \frac{C \times IngR \times EF \times ED}{BW \times AT} \text{ x } 10^{-6}$$

$$D_{inh} = \frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT}$$

$$D_{dermal} = \frac{C \times SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6}$$

where D_{ing}, D_{inh}, D_{dermal} are the average daily intake by ingestion, inhalation, and dermal absorption in mg $(kg{\cdot}day)^{-1}$, C is the concentration of metal in the soil (mg kg^{-1}), IngR and InhR are the ingestion and inhalation rate of soil, respectively (mg per day, m^3 per day), EF is the exposure frequency (day per year), and ED is the exposure duration (year). SA is the exposed skin area (cm^2), SL is the skin adherence factor, ABS is the dimensionless dermal absorption factor, PEF is the particle emission factor in m^3 kg^{-1}, BW is the average body weight (kg), and AT is the average time (day).

The doses calculated for each element and exposure pathway are then divided by the corresponding reference dose (mg $(kg\ day)^{-1}$) to produce a hazard quotient or non-cancer risk, whereas the dose for carcinogens is multiplied by the corresponding slope factor (mg $(kg\ day)^{-1})^{-1}$ to produce a level of cancer risk. The hazard index is then calculated by adding the hazard quotient and the non-cancer risk (Xu et al., 2013).

The dosage level from radioactive elements has increased in recent years (Pan, 2014; IAEA, 2014). The natural radiation exposure's annual effective dose to the population around the world is 2.4 mSv (Bai et al., 2017), while in China, it is 3.1 mSv, up from 2.3 mSv in the 1990s (Luevano-Gurrola et al., 2015; Korkulu and Özkan, 2013).

2.11. South African regulation on waste and pollution

Activities and hydrometallurgy processes for exploiting radioactive sources were heavily strengthened due to an increase in environmental contamination by radioactive metals (Wang et al., 2013). In 1999, the South African government released a National Waste Management Strategy, which included a long-term strategy for addressing important waste management challenges, needs, and difficulties. The National Radioactive Waste Disposal Institute Act of 2008 establishes a National Radioactive Waste Disposal Institute to oversee the disposal of radioactive waste in South Africa. Few years after the establishement of that Act, Necsa has took over responsibility for nuclear waste disposal. Necsa is a state-owned corporation in charge of most nuclear-related issues, including waste management and safeguards. The South

African Bureau of Standards, also have pollution regulating standards in specific environmental compartments.

The National Environmental Management Act, 1998 (Act 107 of 1998) (NEMA), which replaced the Environmental Conservation Act, 1989 (Act 73 of 1989), is the primary law in South Africa that governs and regulates environmental management. NEMA, on the other hand, is applied in combination with other Acts. Examples of these are; the White Paper on Integrated Pollution and Waste Management (2000), the National Water Act, 1998 (Act 36 of 1998) and Air Quality Act, 2004 (Act 39 of 2004). Everyone has the right to an environment that is not damaging to their health and well-being, according to the South African constitution (1996). The Consumer Protection Act, which took effect on April 1, 2011, regulates goods and services that have real or prospective environmental and/or health consequences.

2.12. Sample pre-concentration techniques for radioactive metals

The IAEA report (1983), suggested key step for monitoring radioactive metals is through their identification in order to transform them into stable and solid forms suitable for storage, transport and disposal. However, the removal of analytes from large complex matrix into a smaller quantity of analytes is important before instrumental analysis. This is because in some instances, due to poor sensitivity or matrix interferences, it is difficult to detect small concentrations of metals in environmental samples (Gonçalves et al., 2017). Moreover, the direct determination of metals by these techniques is often challenging due to the trace occurrence of metals below the detection limits of the instrument (Khan et al., 2016a; Nomngongo and Ngila, 2015). Hence there is a need to pre-concentrate the analytes. Therefore, to pre-concentrate radionuclides from environmental samples, efficient and environment-friendly techniques are needed (Zhu et al., 2020). The VA-LLME, DLLME and MASE are emerging technologies for pre-concentration of radioactive metals (Deniz et al., 2019; Sadeghi and Davami, 2019; Bosch et al., 2014; Zolfonoun and Salahinejad, 2013; Sajid et al., 2020). In these methods, higher pre-concentration factors can be obtained with micro-extraction while using little amounts of extraction solvents, and are rapid and easy methods when compared with regular liquid–liquid extraction (LLE), and they employ small amounts of organic solvents resulting in high pre-concentration factors (Gonçalves et al., 2017).

2.12.1. Vortex assisted-liquid-liquid micro-extraction (VA-LLME)

The VA-LLME (Figure 4) is a new and rapid equilibrium-based solvent micro-extraction method that was developed in 2010 by Yiantzi et al. The technique was designed to boost the convetional liquid-liquid micro-extraction (LLME) through the introduction of mechanical stirring by a vortex agitator which further favors the dispersion of the organic phase in the aqueous phase (Ojeda and Rojas, 2018). Similarly, the analytes are extracted in the small droplets form, resulting in a higher extraction efficiency. The mixture is then centrifuged to separate the two phases and decanted (Chen et al., 2017b). The separation is carried out by means of a microsyringe (Jiao et al., 2017; Ojeda and Rojas, 2014). This has the inherent advantage of greater efficiency, rapidity and simplicity. VA-LLME has proven to be reliable in removing trace contaminants with high enrichment factors and low detection limits (Ojeda and Rojas, 2018; Psillakis, 2019, Jiao et al., 2017).

Tarhan et al. used VA-LLME for the pre-concentration of uranyl ion in water samples prior spectrophotometric detection (Tarhan et al., 2019). The accuracy studies were achieved by spiking of 1 and 5 µg L^{-1} U(VI) into water samples and the percentage recovery obtained was between 99-111%, and enrichment factor was 91.

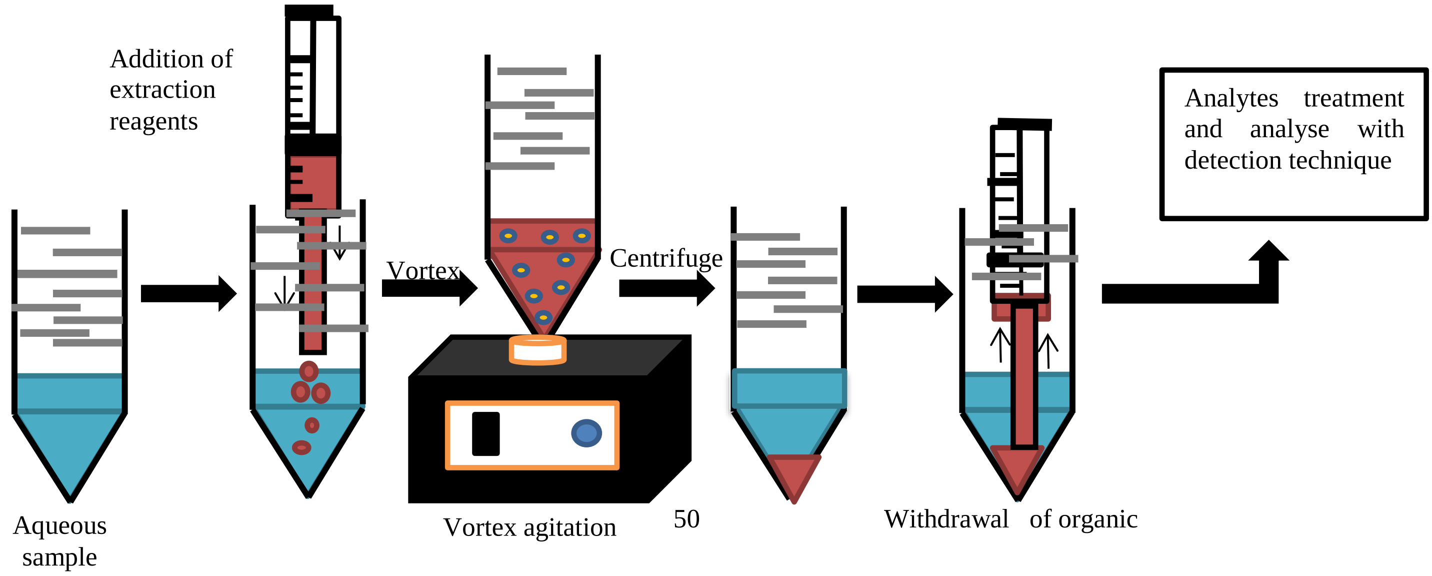
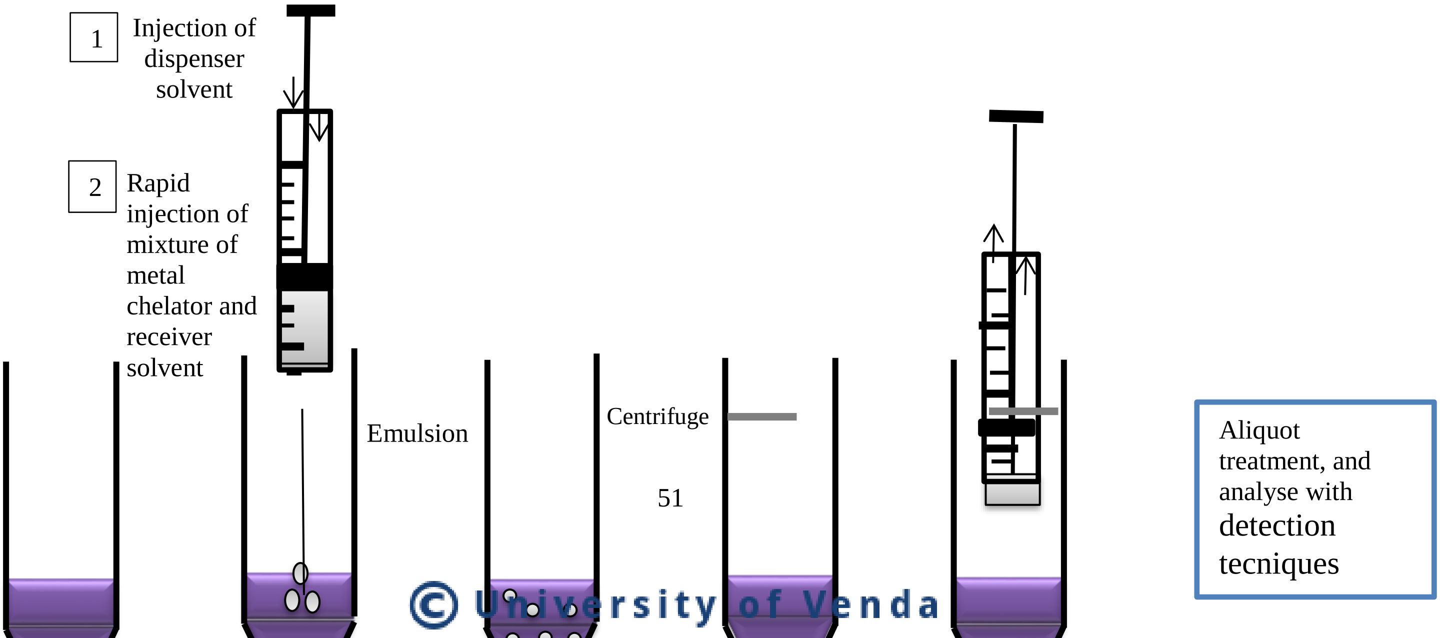


Figure 4: The general flow of the VA-LLME approach during the analysis of environmental samples.

2.12.2. Dispersive liquid-liquid micro-extraction

The DLLME (Figure 5) is one of the most commonly used micro-extraction method that was developed for the removal and pre-concentration of metal analytes from different environmental samples (Khan et al., 2016b). This technique is known for easy process and low cost (Tarhan et al., 2019). In DLLME, an aqueous sample is rapidly injected with a mixture of extraction and dispersion solvents, with the dispersion of the extraction solvent increasing the surface area to enhance extraction efficiency. Centrifugation separates the aqueous phase from the solvent, and a microsyringe is used to collect the extraction solvent containing the analytes for analysis (Gonçalves et al., 2017).

This method showed multiple advantages over the other methods for palladium determination. This includes: (1) use of low-toxic solvents; (2) small volumes of reagents and solvents reduce chemical waste; (3) palladium extraction is accomplished using a single micro-extraction procedure, which is quick; (4) there is no need for heating the sample for activation (Bazel' et al., 2021; Tupys, 2015). Bazel' et al. (2021) used DLLME for pre-concentration of palladium from various real samples. The method has been successfully tested and used for the extraction of palladium in real-world objects.



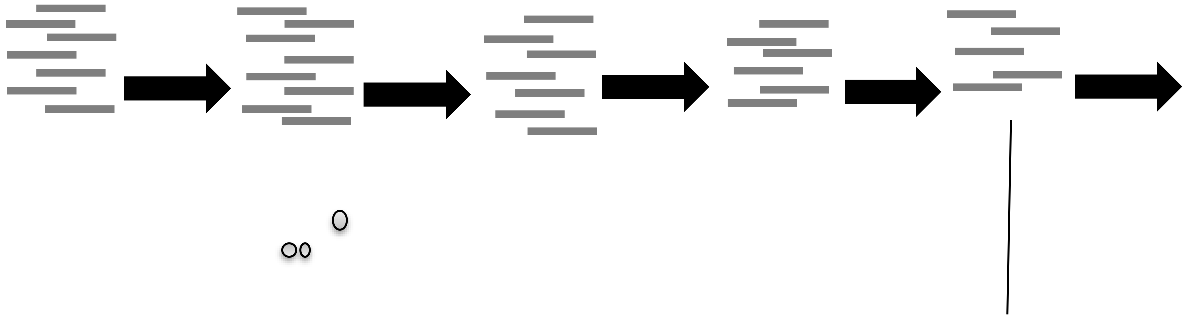


Figure 5: General flow steps for DLLME approach for the analysis of environmental samples.

2.12.3. Membrane assisted solvent extraction

The MASE technique (Figure 6) was proposed by Salgueiro-González et al. (2013) for the analysis of water samples. This method is based on the movement of organic compounds dissolved in an aqueous sample through membrane bag into a small amount of solvents.The advantages miniaturized MASE include simplicity, sensitivity, ease of handling, and low cost.

MASE is a simple but unique pre-concentration technique is characterised by packing of the liquid extractant or samples inside a porous membrane bag (Ncube et al., 2017; Iparraguirre et al., 2014). In MASE, a non-porous membrane serves as the interface between the sample (donor phase) and the organic solvent (acceptor phase). The organic phase in the mixture penetrate the membrane material and dissolve into the acceptor phase (Ncube et al., 2018). The membrane do not only act as a barrier for particles and macromolecules, but it also gives selectivity in terms of penetration and transport through the membrane. Therefore choosing the most appropriate membrane and accepter phase is imperative in MASE (Khulu et al., 2022; Salgueiro-González et al., 2013). The use of membranes is becoming promising solvent free pre-concentration methods. MASE can be coupled to various detection techniques to improve the efficiency (Jiang, 2017). The extraction of radioactive metals have not been reported widely. However, this technique have been mainly reported for the analysis of polycyclic aromatic hydrocarbons (PAHs) (Mañana-López et al., 2021; Ncube et al., 2018; Khulu et al., 2022).

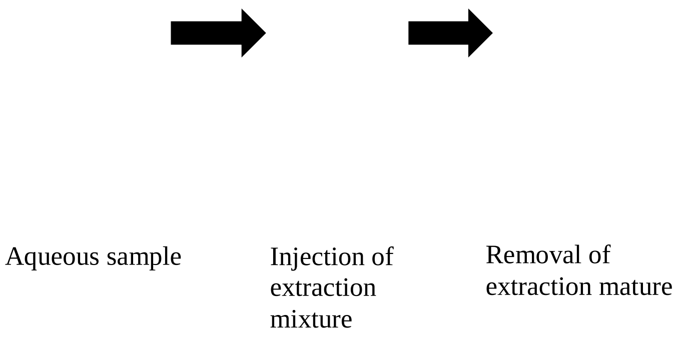


Figure 6: General flow steps for MASE approach for the analysis of environmental samples.

2.13. Detection analytical instruments for radioactive metals

Instrumental detection devices have advanced recently, allowing for the sensitive measurement of numerous elements.

2.13.1. Atomic absorption spectroscopy

Atomic absorption spectrometry (AAS) is one of the most commonly used methods for quantitative trace elements determination in various environmental and industrial samples (Karpiuk et al., 2016; Bulska at al., 2017). This analytical technique is remarkable for its selectivity, speed and fairly low operational cost (Tavallali and Asvad, 2011). Atomic absorption spectrometry based on hydride generation (HGAAS), photochemical vapor generation (PVGAAS), flame furnace (FFAAS), and graphite furnace (GFAAS) are very sensitive instruments for trace metals analysis (Kasa et al., 2017). Flame atomic absorption spectrometry (FAAS) is the most widely used technique for the quantification of trace elements that are present in parts per million concentration range (Bulska and Ruszczyńska, 2017; Saxena and Singh, 2012). The FAAS is reliable, specific and sensitive technique with significant precision and accuracy for the quantification of metals in the environmental samples (Sulthoniyah et al., 2018; Hill and Fisher, 2017). Different forms of extraction/pre-concentration procedures have been developed and applied for a range of elements in various matrices in order to improve FAAS detection power system (Gonçalves et al., 2017).

Gonçalves et al. determined cobalt by FAAS (Gonçalves et al., 2017). Jiang et al. coupled DLLME with FAAS and achieved a detection limit of 0.97 µg L^{-1} for cobalt, and futhter applied this method for tap and waste water samples. Rezaee et al. (2015) determined the trace amounts of palladium in water and spiked synthetic samples by GFAAS. Under the optimum conditions, the detection limit of 0.3 µg L^{-1} was reported.

2.13.2. Ultraviolent visible spectroscopy

Ultraviolet and visible (UV-Vis) absorption spectroscopy is a type of spectroscopy in which the attenuation (strength/intensity weakening) of a light beam after it passes through a sample or reflects from a sample surface is measured. The UV-Vis principle is based on the manner in which chemical compounds absorb ultraviolet or visible light, which results in the formation of different spectra (Azmi, et al., 2016; Watanabe et al., 2018).

UV-Vis is a vibrational spectroctroscopy method. It is the pattern of junctional vibration that lead to the spectrum of a compound or matter. This occurs after exposure to UV-Vis wavelength of radiation. The interaction of light and matter is the foundation of spectroscopy. Excitation and de-excitation occur as matter absorbs light, resulting in the formation of a spectrum (Liang et al., 2019). UV-Vis spectroscopy has been widely used, especially during the quantitative analysis of a specific analytes. Tarhan et al. coupled vortex liquid–liquid micro-extraction of U(VI) from aqueous solutions (Tarhan et al., 2019) with UV-vis for analysis. This approach was used for quantification uranyl ion, and the limit of detection of 0.06 µg L^{-1} was obtained under optimum conditions. Bazel' et al. (2021) analysed palladium using UV-vis spectrometry for detection. The limit of detection, based on the signal-to-noise (S/N) ratio of 3, was 0.093 µg mL^{-1}. In this manner, UV-Vis spectrophotometric methods are used due to their easy, inexpensive and sensitive features (Akl, 2016; Tarhan et al., 2019).

2.14. Occurrence and toxicity of selected radioactive metals

2.14.1. Cobalt

The primary characteristic of transition metals is the ability to occur in various oxidation states.The oxidation states of cobalt are mostly +2 and +3. In an acidic medium Co exist as the Co^{2+} ion, which is pink in color, and acts as a reductive agent, whereas the cobaltous hydroxide ($Co(OH)_2$) has a blue color (Sotiles et al., 2019).

In radiotoxicology all radionuclides consolidated in four groups of radiation danger (group of radiotoxicity) (Iryna, 2017). Group A (radionuclides with a particularly high level of radiotoxicity), group B (radionuclides with a high level of radiotoxicity), group C (radionuclides with an average level of radiotoxicity), and group D (radionuclides with a low or minimal level of radiotoxicity). Cobalt is one of the toxic radionuclides grouped into four radioactive danger groups, and it is found in group C (Thakare et al., 2021; Iryna, 2017). These radionuclides are released through natural and anthropogenic activities and enter the environment through wastewater, soil and sediment. The National Atomic Law (November 29, 2000, Journal of Law 2018, item 792) discribed and characterise levels of activity of radioactive sources (Długosz-Lisiecka and Perka, 2020). Seawater spray, wind-blown dust, volcanoes, forest fires, continental and marine biogenic emissions are natural sources, while sludge, fossil fuel combustion, phosphate fertilizers, mining and smelting of cobalt ores, processing of cobalt alloys, and industries that use cobalt compounds are anthropogenic sources of cobalt materals (Deniz et al., 2019).

There are numerous nuclear installations sites in the country, including 40 000 Ci cobalt sterilization facilities (El-Zakla et al., 2011). Relatively short-lived radionuclides, ^{60}Co ($t_{1/2}$ = 5.3 y) and ^{134}Cs ($t_{1/2}$ = 2.1 y) are found in low-level liquid waste released by nuclear power plants. Radioactive nuclide, ^{60}Co, is released in nuclear wastes from nuclear energy industries together with other radionuclides such as ^{154}Eu, ^{232}Th, ^{235}U, ^{235}Np, ^{239}Pu, ^{241}Am, and ^{247}Cm, that directly pollute surface water and groundwater resources (Zhu et al., 2020). Cobalt-60 radionuclides are also produced by nuclear fission and cyclotrons (Payolla et al., 2019). After the reactor has been stopped, the most numerous radionuclides in contaminated residues are usually ^{60}Co, fission and corrosion products (Larramendyand Soloneski, 2016). Several corrosion products produced during fission could become significant soil contaminants. Furthermore, most metallic surfaces corrode and form a corrosion coating rich in structural element oxides during nuclear reactor operation. This layer is subjected to extreme pressures and temperatures, and radionuclides are produced as a result of neutron activation (Larramendy and Soloneski, 2016). The corrosion products and their relative quantities vary depending on the composition of the reactor materials and trace elements, reactor type and design, thermal power, years of irradiation, and shutdown period. The products of steel corrosion contain cobalt-60, which becomes the most prominent for the first 10 years. Reinforced concrete's corrosion products contain cobalt-60, among other radioactive isotopes (Bai et al., 2017).

One of the empirical concerns is that a lot of these elements occur in different matrices at low levels (Bulska and Ruszczyńska, 2017). Cobalt toxic trace metal is one of the major causes of pollution of the environment (Shah et al., 2016; Khan et al., 2016a). Even at low concentration they accumulate within organs and tissues, causing negative health effects. (Deniz et al., 2019; Mohammed, 2017). Cobalt has the potential to accumulate through food chains such as plants, living organisms, soil and water and air and cause radiation and biochemical damages to human organs due to their long-term radioactivity (Ding et al., 2015; Deniz et al., 2019). Moreover, their trace occurrence to toxic levels in various tissues, particularly in aquatic animals and humans, causes serious health problems such as renal edema, liver damage, cancer, nausea, central nervous system, kidney failure, high blood pressure, skin dermatitis, diarrhea, pulmonary fibrosis, and vomiting, among others (Khan et al., 2016a; Khan et al., 2016b). (Khan et al., 2016a; Khan et al., 2016b). Workers exposed to cobalt-contaminated air at concentrations of roughly 0.038 mg m^{-3} for 6 hours were found to have respiratory problems such as asthma and pneumonia (Deniz et al., 2019). As a result, determining cobalt at trace levels utilizing sensitive and reliable analytical methodologies is critical.

2.14.2. Palladium

Palladium is a radioactive element with radioisotopes such as ^{103}Pd, ^{107}Pd, ^{105}Pd (Mu et al., 2019; Laprise-Pelletier et al., 2017). Palladium is a platinum group metal (PGM) that is in high demand in industry. It is one of the most commonly used elements in the platinum group (Thormann et al., 2017). Palladium can be found in a wide range of ores. It can be found in all platinum ores to some extent, as well as a number of copper, nickel, and gold ore minerals (Yildiz et al., 2019). Palladium radionuclides possess the nuclear- physical characteristics (Can et al., 2013). Palladium is interesting not only as a source of energy radiation, but also as a generator of a radionuclide rhodium-103m (Langevelde et al., 1999).

The use of palladium has increased in recent years as a result of growing demand from the automotive, jewellery, electronics, and dental industries (Bazel et al., 2021). Palladium is widely used in a variety of fields of science and technology, including metallurgy, and as a catalyst, particularly in the hydrogenation and dehydrogenation of some of the most significant organic molecules (Oh et al., 2019; Anjum et al., 2020; Merve et al., 2021). Palladium is widely used in the electronic sector for multi-layer ceramic (chip) capacitors, conductive tracks in hybrid integrated circuits, plating connectors and lead frames, and jewellery due to its electrical conductivity and durability, respectively (Faghih et al., 2017; Sabermahani et al., 2015). The manufacturing of catalytic converters for automobile engines is one of palladium's most known applications (Yousif, 2019). Palladium is also a component of the catalytic system for the manufacturing of nitric acid and petroleum in the chemical industry. It is used to make a variety of synthetic polymers, including rubber and nylon. Palladium alloys are utilized in the manufacture of fuel cells (Tymoshuk et al., 2020; Azmi et al., 2016).

The rise in usage of palladium increased palladium emissions into the environment (Tymoshuk et al., 2020; Azmi et al., 2016); these emissions are mainly linked with the operation of transport catalysts, as well as the production and processing of catalytic converters (Yashnik and Ismagilov, 2019). Palladium is one of the metals among the fission products in waste from nuclear fuel (Ochs et al., 2016). It is also contained in high-level radioactive nuclear liquid wastes that are generated in the reprocessing of spent nuclear fuels or in the decommissioning of nuclear reactors (Watanabe et al., 2018). There are some palladium isotopes such as ^{107}Pd, ^{105}Pd present in spent nuclear wastewater produced by fission of uranium (Mu at al., 2019). The most prevailing oxidation state of palladium in water is +II (Ochs et al., 2016). Aquatic species have been reported to be more mobile and bioaccumulate anthropogenic palladium, than other platinum group elements (Han et al., 2021). The transport of these particles through storm water may cause further pollution of aquatic systems. Palladium is believed to undergo methylation processes in the aquatic environment at the optimum pH and redox potential conditions and could be accumulated along the food chain (Azmi et al., 2016). Furthermore, metallic palladium has the potential to cause allergic reactions in humans (Kawano et al., 2014). Palladium monitoring in environmental samples is critical for estimating future risks to human health and the environment. Certain palladium compounds have previously been proven to be potentially harmful to people, causing conjunctivitis, allergies, asthma, and a variety of other diseases (Li et al., 2019; Rinkovec et al., 2018). Due to these reasons, environmental monitoring of palladium content appears to be a critical issue that requires the development of efficient analytical techniques.

Palladium analysis requires effective analytical techniques with excellent sensitivity, selectivity, and limited interference. Following pre-concentration step, identification of palladium have been widely studied using different quantification techniques, such as atomic fluorescence spectroscopy (de Almeida et al. 2018), inductively coupled plasma with optical emission spectroscopy (ICP-OES) (Biata et al., 2021; Somerset et al., 2015; Nguyen et al., 2021), inductively coupled plasma mass spectrometry (ICP-MS) (van der Horst et al., 2018) and total reflection X-ray (Marguí et al., 2019). These detection techniques have been employed considering quite number of factors such as ease of operation, sample volume requirements, and sensitivity. However, the most widely used methods for the quantification of palladium in environmental samples include GFAAS (Rezaee et al., 2015).

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Chapter 3: Critical analysis of literature

This chapter gives a critical analysis of literature on the application of pre-concentration technique of during the analysis of radioactive metals in environmental samples. This section consists of two review papers.

3.1. Paper I

This review “Modern developments for efficient applications of dispersive liquid-liquid micro-extraction technique during analysis of radioactive metals in environmental samples” briefly discussed the general principles of dispersive liquid-liquid micro-extraction, and its costomized approaches during analysis of radioactive metals in environmental matrix. The extensive use of these customized techniques in the extraction and pre-concentration of radioactive metals in environmental samples was also highlighted.

Modern developments for efficient applications of dispersive liquid-liquid micro-extraction technique during analysis of radioactive metals in environmental samples: A review

Abstract

The growth and increase in industrialisation and urbanisation to boost the economic growth, and exploration of energy sources to meet energy demands of the world, has resulted in the exposure of the population to environment with a high content of radioactivity from radioactive metal sources.
In this review, the ever-increasing use of dispersive liquid-liquid micro-extraction (DLLME) as a micro-extraction techniques is discussed, focusing on the extended reasons needed to replace the traditional DLLME technique with modern, and efficient approaches that follow the objectives of green analytical chemistry during the analysis of radioactive metals in environmental samples. The properties of recent customised DLLME with different approaches such as the use of modern methods of dispersion extraction solvents, ionic liquids (ILs), deep eutectic solvents (DESs) and centrifuge free techniques are reviewed, highlighting their outstanding performance and analytical properties, and explaining their current high level of scientific interest in the family of DLLME modes. Emerging developments on the pre-concentration of radioactive metals in environmental matrix have several advantages including high extraction efficiency and enrichment factors, micro-drop of extractants, environmental and eco-friendly and cost and time effective.

Keywords: DLLME, radioactive metals, environmental samples, micro-extraction, ionic liquids, deep eutectic solvents, green analytical chemistry.

3.1.1. Introduction

Radioactive metals at trace levels are difficult to extract completely from environmental matrices due to their existence in complex components and interfering substances. Any interference in the sample treatment process may result in some degree of uncertainty in the determination of radioactive metals in the environmental matrix matrices (Trojanowicz et al., 2018). Therefore, sample treatment is a critical step in the process of a comprehensive radioactive metals analysis, and is often the most work-intensive part of chemical analysis in order to precisely quantify the target analytes in environmental samples (Talan, 2021; Qiao, 2020; Rodríguez, 2016; Kim, 2015).

The solvent micro-extraction technique such as dispersive liquid-liquid micro-extraction (DLLME) (Rezaee et al., 2015) is one of the pre-concentration technique which can be used during trace analysis of radioactive metals in environmental matrix. This method have several merits including the reduction of the amount of the organic solvents that is used during the extraction process (Rezaee et al., 2019; Chaiyamate et al., 2018; Çelik et al., 2015; Teshale and Taye, 2019). DLLME it is one of the solvent-based pre-concentration methods that has generated enormous attention and interest among researchers. Rezaee et al. (2006) presented a novel micro-extraction technique based on a bi-component solvent system in which a water-immiscible extraction solvent that is heavier than water is dispersed in fine drops into the aqueous sample with the help of a dispersive solvent that facilitate the dispersion process during the target analytes extraction. Extraction solvents mostly applied in DLLME are chlorobenzene, chloroform, dichloromethane and carbon tetrachloride with higher density than water, and all of which are potentially toxic to human and the environment. Typically, most DLLME method needs a centrifugation step in order to sediment extraction solvent. It is noted that organic solvents lighter than water are not used compared to heavier solvents. DLLME technique has been recently applied on a pre-concentration step during trace analysis of radioactive metals in aqueous and solid samples (Hassan et al., 2016; Sadeghi et al., 2019; Shukla et al., 2020; Tarhan at al., 2019; Sá et al., 2021). Hence, DLLME is one of the commonly used technique preferably for pre-concentration in environmental (Qiao, 2020; Rassou et al., 2020; Wang, 2015).

The growth and increase in industrialisation and urbanisation to boost the economic growth, and exploration of energy sources to meet energy demands of the world, has resulted in the exposure of the population to environment with a high content of radioactivity from radionuclides. This has also prompted the rapid proliferation of researches that involve the use of DLLME technique during trace analysis of radioactive metals in environmental matrix. However, there are very few review papers on the application of the DLLME pre-concentration technique during analysis of radioactive metals in the environmental samples, because most of them has focused on the extraction pesticides. Furthermore, during DLLME procedure, solvents are required, and there are some limitations on the kind of solvents that can be used. Otherwise, additional steps such as freezing, centrifugation, and auxiliary solvent demulsifiers are performed, eliminating the scale reduction benefits. This review seeks to close that research gap. In this paper, the recent developments for efficient applications of various DLLME models to pre-concentrate radioactive metals in environmental samples were reviewed as well as the challenges of DLLME configurations.

3.1.2. Emergence of DLLME over other extraction techniques

Many sample pre-concentration techniques have been reported during the trace analysis of radioactive metals in environmental matrix. These include sorbent-based techniques such as solid phase extraction (SPE) (Rodríguez et al., 2016; Fuks et al., 2018; Rodríguez et al., 2015), solid-phase micro-extraction (SPME) (Gao et al., 2017) and micro-solid phase extraction (µ-SPE) (Zolfonoun and Yousefi, 2020; Kocot et al., 2015). Solvent-based pre-concentration techniques have also found widespread application during analysis of radioactive metals in environmental matrix. Such solvent-based techniques include hollow-fibre liquid-liquid micro-extraction (HF-LPME) (Plastiras, 2020), liquid-liquid micro-extraction (LLME) (Veyseh and Niazi, 2017); and single drop micro-extraction (SDME) (Šrámková et al., 2018). These methods vary in layout, but they all have one thing in common: they all employ small quantities of organic solvent and so meet the green analytical chemistry requirements (Spietelun et al., 2014). They are cost-effective, fast, and easy to use because no additional equipment is required, and they can be used with a variety of quantification techniques. However, methods such as SPE column needs pre-treatment and requires toxic organic solvent for the elution step. Therefore, SPME has been used for pre-treatment of radioactive metals as an alternative (Gao et al., 2017).

The reason for this is because it is portable, quick, simple to operate and require no organic solvent. However, SPME has significant disadvantages: its fiber is fragile and has a limited lifespan, and sample carry-over is also a challenge (Rezaee et al., 2019). On the other hand, methods such as SDME that have been used, but the drop is unstable, implying a lower level of precision and accuracy; also, the volume and surface of the drops are limited, excluding reactions with slow kinetics (Rassou et al., 2020). Therefore, DLLME technique is an alternative technique used to overcome these challenges (Quigley et al., 2016; Sá et al., 2021).

3.1.3. Principles of the conventional DLLME during analysis of radioactive metals

The conventional DLLME technique (Figure 7) for analysis of radioactive metals in environmental samples, is based on having multiple parts system including an aqueous environmental sample, a water miscible solvent (dispersion solvent) and a water immiscible solvent (receiver solvent) (Sadi, 2016; Bağda, 2015). The mixture of dispersive solvent and receiver solvent is injected rapidly into aqueous environmental sample. Then, a stable emulsion is formed with cloudy droplets of extraction solvent dispersed in an aqueous environmental sample solution resulting in a large increase in contact area between the two phases (Quigley et al., 2016; Teshale and Taye, 2019). As a result, the radioactive metals are easily transferred into the receiver phase. After extraction, the emulsion is separated into two phases by centrifugation, which causes the receiver phase, containing radioactive metal species, to sediment at the bottom of centrifugation tube (Liao et al., 2020; Tarhan et al., 2019; Barros et al., 2016). If the receiver solvent is not compatible with the detection instrument, the withdrawn sedimented phase is dried followed by reconstitution before analysis (Bahadir et al. 2016; Psillakis, 2019; Gouda et al. 2018; Rykowska et al., 2018).

High recovery, high enrichment factor and purification efficiency, short extraction time and easy performance are the main advantages of the DLLME method (Rezaee et al., 2019). However, there are still some drawbacks to conventional DLLME. Firstly, conventional DLLME requires a component that is miscible in both water and the receiver solvent known as the dispersive solvent (Quigley et al., 2016). Organic solvents, such as acetonitrile and acetone, methanol are often used as dispersion solvents (Chaiyamate et al., 2018). Secondly, the receiver solvent must have low solubility in water, a density higher than that of the aqueous phase, and suitable chromatographic behaviour. Receiver solvents mostly used in DLLME are chloroform, carbon tetrachloride and chlorobenzene, all of which are potentially harmful to human and are not eco-friendly (Rezaee et al., 2015a,b). Lastly, to facilitate the separation of the phases, a centrifugation step is necessary for conventional DLLME, and the extraction phase, which sediments at the bottom is removed with a micro-syringe before instrumental analysis (Chatzimitakos et al., 2021; Alahyari et al., 2018).

Centrifugation, however, prolong the process (Chaiyamate et al., 2018). Therefore, modelling of the conventional DLLME mode, for instance, by introducing efficient process, substituting toxic organic extraction solvents with eco-friendly solvents, eliminating or reducing the use of a dispersion solvent, and separating the phases rapidly without using the time-consuming centrifugation step, will promote a versatile, fast, simple, inexpensive, effective rugged, safe extraction and efficient pre-concentration step.

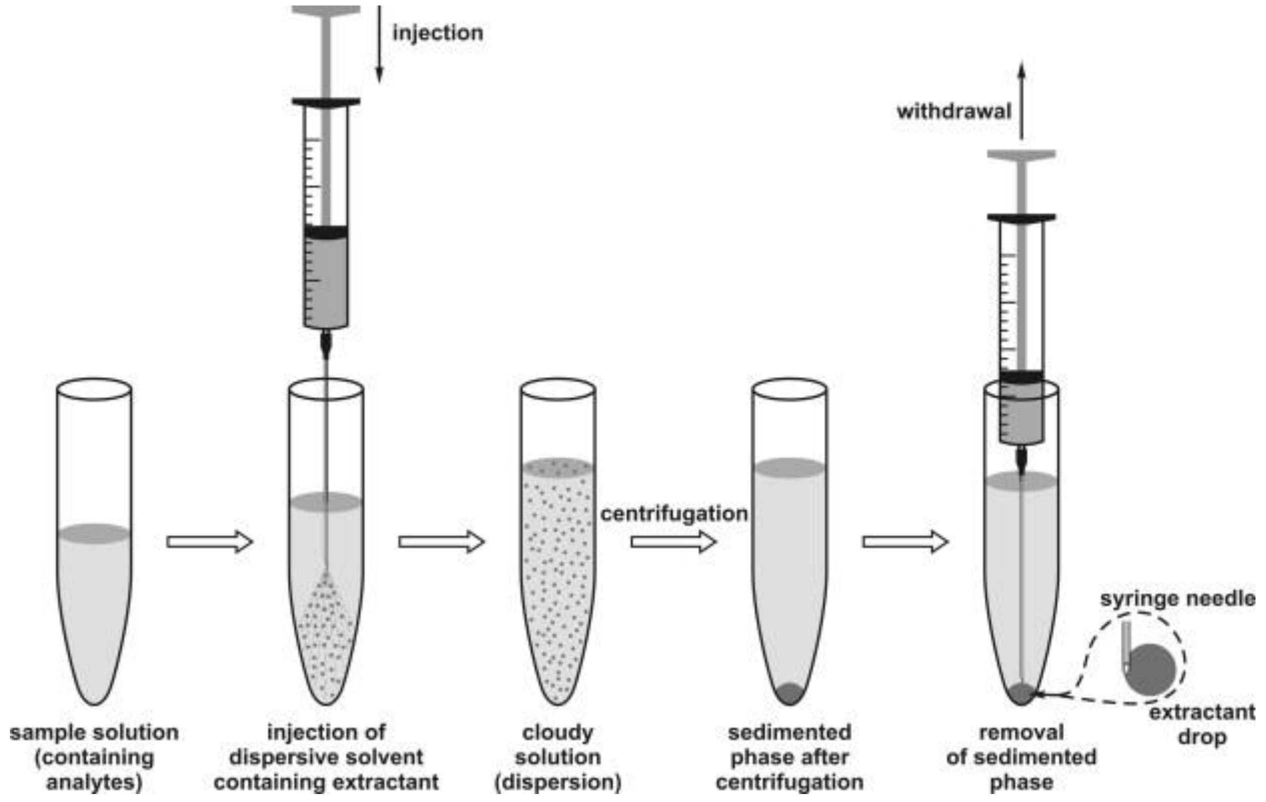

Figure 7: The DLLME procedure (Quigley et al., 2016).

3.1.3.1. Customizing of the conventional DLLME procedure

3.1.3.1.1. Customized conventional DLLME using deep eutectic solvents

In recent years, there has been a growing focus on replacing traditional extraction methods with so-called "efficient" extraction methods. The extraction techniques include analytical procedures that has reduced the volume and toxicity of solvents and reagents used in the measurement step, particularly with automation and miniaturization (Armenta et al., 2015). A new group of solvents called deep eutectic solvents (DESs) has been identified in this field as a new and very promising tool (Plastiras et al., 2020, Smith et al., 2014). DESs have attracted considerable attention as green alternative solvents to conventional solvents used in DLLME during pre-concentration of radioactive metals in environmental samples because they are not only environmentally safe, non-toxic, and biodegradable organic substances, but they are also inexpensive and simple to make (Plastiras et al., 2020). DESs are drawing attention for the novel generation of sustainable extractants in DLLME (Pena-Pereira et al., 2014).

When these DESs are employed for separation processes as extraction agents for DLLME, their dissolution capability, i.e., their ability to donate and accept protons and electrons, facilitates the formation of hydrogen bonds between molecules (Li and Row, 2019; Smith et al, 2014). The adjustable physicochemical properties of DESs, such as their polarities, are also important in the DLLME process. For example, the polarity of DESs can be adjusted to make them either polar or non-polar, making them efficient solvents for the extraction of a wide range of natural compounds (Zainal-Abidin et al., 2017, Smith et al, 2014). Thus, DES consisting of water-soluble and water-insoluble compounds can be used as both extractant and dispersant during DLLME (El-Deen and Shimizu, 2019; Shishov et al., 2020a,b); Shishov et al., 2018; Smith et al, 2014). The DESs, whose non-polar precursor is soluble in organic liquid samples (for example, edible oil), can also be used in reversed-phase DLLME, resulting in the dispersion of the polar precursor and the extraction of polar analytes. DESs have also been used in DLLME conjugation with various methods of modification, including air-assisted modification (Li et al., 2018b), ultrasound-assisted (Guo et al., 2020) and effervescence-assisted (Shishov et al., 2020b). DESs were introduced in 2001 as sustainable solvents for the adaptation of green extraction techniques. Since then, many scientists around the globe pursued the utilization of DESs as effective extractants during the pre-concentration of radioactive metals in environmental samples (Zeid et al., 2020; Kabeer et al., 2020; Li and Row, 2019; Plastiras et al., 2020).

In addition to asymmetrical ions with a low lattice energy and low a melting points, DESs are less expensive and easier to prepare (Wang et al., 2017). Compound such as choline chloride (ChCl) and phenols, which are most often used in the synthesis of DESs are less expensive (Aydin et al., 2017). In many reports, DESs are typically prepared by simply mixing ChCl with hydrogen bond donors, such as urea, carboxylic acids or polyols, without the need for solvents or complex purification steps (Li and Row, 2019). DESs showed a stronger eco-friendly profile, with simple and less cost of production, while having similar properties to conventional extractants used in DLLME (Kissoudi and Samanidou, 2018) wich makes them the most considerable for use. They are regarded as sustainable solvents that can be used for the elimination of problems such as the biodegradability, toxicity, stability, and the costs associated with the extraction processes (Pena-Pereira and Namie´snik, 2014). The DESs are perfect solvents for use because of the characteristics they possess (Plastiras et al., 2020). That means, DES-DLLME procedure has the advantages of simple operation, non-volatility, non-flammability, low vapor pressure, good thermal stability, low toxicity, wide liquid range, good biodegradability, and ability to be reutilized during the extraction of radioactive metals in the environmental samples (Li and Row, 2019; Aydin et al., 2017).

The utilization of DESs on the DLLME procedure has attracted increasing attention for the extraction and pre-concentration of radioactive metals in the environmental samples. Numerous works have shown effective extraction of DESs. For instance, Zeid et al. (2020) successfully applied DES in DLLME procedure for enrichment, separation and determination of palladium at ultra-trace levels in environmental samples. Zounr et al. (2018) used DES-DLLME based air assisted liquid for separation and pre-concentration of lead in environmental samples. Panhwar et al. (2017) used DES-DLLME based ultrasonic assisted (AU) for speciation and pre-concentration of selenium in environmental samples. In addition to the use for environmental samples, researchers such as Werner (2020) used a DES-based UA-DLLME, combined with solidification of the aqueous phase, prior to HPLC-UV for pre-concentration and determination of cobalt and lead in water samples. The proposed methodology used a new class of DES, prepared through mixing trihexyl(tetradecyl)phosphonium chloride : thiosalicylic acid ([P14,6,6,6] Cl and TSA) at 1:2 molar ratio, with addition of salt (NaCl) in the micro-extraction step, to expedite the separation. The limits of detection were 0.05 µg L^{-1} and 0.06 µg L^{-1}, for lead and cobalt, respectively. Additionally, the method was evaluated by testing spiked certified reference materials, where the recoveries were in the range 91.4–101.6% (Werner, 2020).

3.1.3.1.2. Customized conventional DLLME using ionic liquids

Some organic solvents are volatile, unstable, and toxic, while ionic liquids (ILs) are non-organic solvents that do not emit harmful vapours into the environment (Yulianti et al., 2020). They fulfil the requirements of green chemistry (Khandelwal et al, 2016). Ionic liquids have emerged as very a high-tech material with several unique properties, which make them more preferred than conventional types of solvents that have ever existed in the past, and usually employed as extraction solvents in the DLLME procedure during pre-concentration of radioactive metals in environmental matrix. This is due to (1) solvating ability: because ionic liquids contain just ions, the reaction occurs under completely different conditions than when mixing water or conventional organic solvents, which contain neutral molecules; (2) none or low vapor pressure: because ionic liquid vapour pressure can be ignored, it is critical to reduce exposure to harmful volatile vapours, such as those found in organic solvent; (3) non-flammable; (4) a high degree thermal, chemical, and electrochemical stability; (5) easy to recover; (6) wide fluid range: wide temperature range between liquid and gas; (7) have a strong polarity; (8) a lack of coordination; (9) water and other organic solvents are incompatible; (10) Stereoselectivity can be controlled using chiral ionic liquids; (11) has conductivity; (12) has a longer time (not decomposed easily) (Rout et al., 2015; Rykowska et al., 2018; Yulianti et al., 2020; Irge et al., 2016; Mori et al., 2015; Verma et al., 2021). Ionic liquids are materials made entirely of anions and cations, whereas neutral solvents like benzene, chloroform, methanol, water, and others are made up of neutral species (Irge et al., 2016). Ionic liquids also have the following advantages: they are thermally stable up to 300°C soluble in a variety of organic-inorganic and organometallic compounds, polarity, hydrophilic or lipophilic qualities may be modified, and some physical and chemical properties can be adjusted (Hough-Troutman et al., 2009). The DLLME equipped with ionic liquids as extraction solvents is referred to as ionic liquid dispersive liquid- liquid micro-extraction (IL-DLLME).

The traditional IL-DLLME approach relies on a simple mixture of an aqueous sample containing analytes and IL as the extractant and dispersive solvent. The transfer analytes in the IL micro-droplet can be separated by centrifugation after the mixture has been manually agitated. Because it does not require any further steps, this is the simplest procedure for the IL-DLLME. As dispersive solvents, organic solvents (mostly methanol) have been widely used. This IL-DLLME operational mode is most closely similar to the traditional DLLME method, with the exception that an IL is used as the extractant solvent instead of a traditional organic solvent. The procedure was described by Trujillo-Rodríguez et al. (2013).

Liu et al. (2009) were the first to describe the IL-DLLME method for determining heterocyclic pesticides in water and since then, it has been widely applied for the pre-concentration of radioactive metals in environmental matrix (Filik and Avan, 2017; Jalbani and Soylak, 2014; Tarhan et al., 2019; Trujillo-Rodríguez et al., 2013; Sadeghi et al., 2018). The first review of recent IL-DLLME method applications and improvements was published in 2013 (Trujillo-Rodríguez et al., 2013). The authors compiled a list of the most recent analytical advances in the use of ionic liquids (ILs) in dispersive liquid-liquid micro-extraction (DLLME). Conventional IL-DLLME, temperature-controlled IL-DLLME, ultrasound-assisted, microwave-assisted, or vortex-assisted IL-DLLME, and in-situ IL-DLLME were the basic operation modes reported (Rykowska et al., 2018). The dispersive solvent in these modes included organic solvents, surfactants, or hydrophilic IL. However, a dispersive solvent may not be required in some instances. The paper also gave an outline of how ILs were used in DLLME to determine radioactive metals in a variety of environmental samples (Trujillo-Rodríguez et al., 2013).

The analytical applications of traditional IL-DLLME have been performed on both liquid and solid samples. When using solid samples with IL-DLLME, a dissolution sample step, or sample extraction, followed by a reconstitution of the sample with water is required (Rykowska et al., 2018).

IL-DLLME carries similarities to a traditional DLLME during the analysis of radioactive elements in environmental samples, but the receiver solvent is an IL. The most prominant charactaristics of DLLME are the choice of extraction conditions and selection of extraction solvents that are compactable for analytes. For a suitable receiver, the solvent has to be immiscible with aqueous phases for the formation of the cloudy solution that enhance the interaction between the two phases, which result in high extraction efficiency (Herrera-Herrera et al., 2010; Rykowska et al., 2018). Ionic liquids have generated attention in a variety of fields of research and engineering in recent years; they can be effectively isolated and reused to lower the cost of their applications significantly. Another big advantage of ionic liquids is that you can mix and match ions to get an IL with the required physical and chemical properties like, density, viscosity, melting point, water and solvent miscibility. As a result, ILs are commonly referred to as modeling solvents (Rykowska et al., 2018). Therefore, ILs are, however, more costly than the organic solvents used in DLLME during pre-concentration of radioactive elements in environmental matrix samples. Moreover, they can also be used as either receiver or disperser solvent because they are miscible with water and other solvents (Yulianti et al., 2020).

Other researchers pre-concentrated radioactive metals in environmental employing some of the four main IL conjugate DLLME operation modes aforementioned. For example, Escudero et al. (2012) successfully used traditional IL-DLLME for the pre-concentration of thallium species in environmental samples. For lead quantification, Bai et al. (2010) designed a method named temperature-controlled IL-DLLME. The lead was extracted as dithizone complex into the continuous IL drops at 80°C in this method. The IL was properly dissolved and combined with the sample. On the other hand, Nyaba et al. (2017) used ultrasound-assisted IL-DLLME to determine tellurium in environmental samples.

3.1.3.1.3. Customized conventional DLLME by centrifugation free approach

When using DLLME, centrifugation plays an important role in the enrichment of analytes during analysis of radioactive metals in environmental matrix. The process of centrifugation is important to facilitate phase separation of emulsion that has formed after the injection of the mixture of the extraction and dispersive solvent into the sample solution during the DLLME. Not only that longer centrifugation dissociate the sedimented phase, it is also a time-consuming and tedious step during the DLLME procedure (Chaiyamate et al., 2018; Li et al., 2014(b); Seebunrueng et al., 2015; Li et al., 2018c). However, it can be avoided by using centrifugation free approach. This approach is reported to be more efficient, simple, effective and convenient modern analytical method for trace level analysis with high extraction and enrichment factors (Li et al., 2018; Chaiyamate et al., 2018). Moreover, to overcome DLLME drawbacks such as the need for extra time for the centrifugation step, different DLLME-based approaches have been proposed, which eliminates the centrifugation step to save time (Seebunrueng et al., 2015; Guo et al., 2016). Researchers like Chaiyamate et al. (2018), described the developed vortex-assisted low density solvent and surfactant-based dispersive liquid–liquid micro-extraction (VALS-DLLME) prior to spectrophotometric detection of cobalt. The process involved complexing Co(II) with pyrocatechol violet (PV) and then utilizing VALS-DLLME to pre-concentrate the Co-PV complex. VALS-DLLME was performed with 300 μL of 1-dodecanol as the extraction solvent, and 300 μL of acetonitrile as the dispersive solvent in a vortex for 20 seconds with the addition of 0.02 mmol L^{-1} CTAB as cationic surfactant. The linearity was in the range of 0.1–10 mg L^{-1}, the enrichment factor (EF) was 13.5, and the limit of detection (LOD) was low, 0.04 mg L^{-1} under optimum conditions. The approach was used to evaluate cobalt concentrations in water and plant samples. The method yielded good recovery rates ranging from 86 to 104%, and more importantly, it omitted the centrifugation step to reduce time consumption (Chaiyamate et al., 2018).

Rezaee and Khalilian (2015b) adopted this approach during the extraction of trace metal containing radioactive isotopes in environmental water samples. In the study, an aqueous sample was injected with a mixture of extraction and homogenous solvents. A homogenous solution was formed in the initial step of injection, and then an emulsion comprised of fine droplets of the extraction solvent was formed as the injection continued. The solubility of extraction solvent in water increases due to homogeneous solvent. The two phases were separated by the addition of salt.

The method requires air flotation to facilitate the collection of the low-density organic extraction solvent at the upper phase, without need for centrifugation procedure. However, due to high toxicity and the constraints in extracting different analytes using a single extraction solvent, two different aspects must be considered, which are the introduction of new solvents, like ionic liquids, and the broadening of the application scope using polar and low-density organic solvents, such as long-chained alcohols or hydrocarbons (Hassan et al., 2016).

Shirani et al. (2019) proposed the novel DES-AADLLME method for the simultaneous pre-concentration of some metals containing radioactive isotopes. In this method, the extraction solvent consisted of DES-based magnetic multiwall carbon nanotubes that are separated easily from the environmental matrix with no need for centrifugation (Shirani et al., 2019). The suitable closeness of the enrichment factors in the range of 635-644.5 to the pre-concentration factor (640) confirmed the quantitative accuracy of the proposed extraction method with the RSDs of 2.5-3.1 ($n = 7$). On the other hand, Li et al. (2018) by-passed the centrifugation step by means of air-assisted based deep eutectic solvent for the determination of multiple trace components. From study of this method, simple operation, short time of analysis, efficient enrichment, excellent linearity, precision, low LODs and satisfying recoveries have been reported. In addition to the centrifugation free DLLME approach during the analysis of radioactive metal in environmental matrix, disperser solvent can also act as a demulsifier, breaking up the oil–water (O/W) emulsion and completing the extraction process without centrifugation (Chen et al., 2010 a,b). That is, after a given amount of time has passed since the injection of the disperser solvent-containing extraction mixture, another amount of disperser solvent is injected into the top surface of the aqueous bulk to rapidly break up the emulsion. It should be emphasized that the solvent terminated dispersive liquid–liquid micro-extraction (ST-DLLME) approach was only used with low density extraction solvents such acetonitrile, methanol, acetone, ethanol, and tetrahydrofuran (Al-Saidi and Emara, 2014).

3.1.3.1.4. Customize conventional DLLME by reducing dispersive solvent solvents

DLLME has some drawbacks, including as (i) the use of toxic chlorinated solvents with densities higher than water, and (ii) the use of huge quantities of dispersive solvents, which causes analyte partition coefficients to decrease (Seebunrueng et al., 2015). To address these limitations and accomplish efficient extraction, several DLLME-based approaches have been proposed, such as using more ecologically acceptable extraction solvent groups than the ones used in the conventional DLLME, and using external forces in the dispersion process (Ragheb et al., 2015). External forces commonly applied in the dispersion process include techniques such as VA-DLLME, UA-DLLME, microwave-assisted-DLLME (MA-DLLME) and AA-DLLME (Chaiyamate et al., 2018; Acar and Kara, 2014; Abdolahi-Baraei and Afzali, 2015; Yang et al., 2015; Lu et al., 2016).

VA-DLLME is a mode of DLLME that uses vortex agitation to extract analytes from large sample volumes (aqueous donor phase) to the small amount of organic receiver solvent (intermediate phase). This process has the same general benefits as DLLME, but it does not require a dispersive solvent (Li and Row, 2019; Li et al., 2019b; Zhang et al., 2019; Faraji, 2019; Li et al., 2020d; Safavi et al., 2018). Another technique which does not require use dispersive solvent is UA-DLLME, where the ultrasound is applied to enhance efficiency and the rate of mass transfer between two immiscible phases; hence, dispersive solvent is not necessary during the analysis of environmental samples. Thus ultrasound used as a dispersing agent during preparation of environmental samples such as water samples (Plastiras et al., 2020; Wang et al., 2017b); Altunay et al., 2019; Werner, 2020; Abdolahi-Baraei and Afzali, 2015). The centrifugation is used to break up the emulsion, and the organic phase settles to the bottom of the conical tube, and is withdrawn using a syringe (Leong et al., 2014).

Altunay et al. (2020) used UA-DLLME method to determine traces of inorganic metals in in environmental samples by flame atomic absorption spectrometry (FAAS). Before any application, several conditions, such as the volume of the natural deep eutectic solvents, the type and volume of aprotic solvent used to achieve a cloudy state, ultrasound time and temperature, sample volume, and so on had to be optimized (Plastiras et al., 2020). The limits of detection and quantification were in the range of 0.23–2.94 µg kg^{-1} for the analytes, respectively, and a range of 90.3–98.4% for the recovery. Abdolahi-Baraei and Afzali (2015) on the other hand used same the method, but when determining thallium in environmental soil sample. In the study, supersonic-waves created by ultrasound were utilized to facilitate mass transfer between matter in two separate phases, and supersonic-waves caused by ultrasound replaced the dispersive solvent that was omitted. Under the optimal condition, the LODs of 0.0003 µg L^{-1} for thallium was achieved, revealing the high value in practical applications. Researchers such as Werner (2020) successfully avoided the used of dispersive solvent during the pre-concentration of lead and cobalt in the environmental water samples by utilizing the same technique. The purpose of the study was to use of ultrasound as an effective dispersing agent which makes the method environmentally friendly (Werner, 2020). As a result, additional cost and pollution was avoided. However, prolonged ultrasound-assisted emulsification may result in analyte disintegration (Leong et al., 2014).

A number of studies have found that using manual shaking enhances extraction efficiency and reduces ultrasonic extraction time, and also reducing analyte disintegration (Shu et al., 2012; Chung et al., 2012). Lin and Fuh (2010) formed a cloudy suspension by ultrasound and manual agitation and had good results.

Microwave assisted DLLME was also reported as another efficient mode of DLLME which does not require the use of dispersive solvent, with recoveries up to 102% (Torbati et al., 2019), where the sample and extraction solvent are placed in a glass vial under microwave to facilitate the dispersion.

Farajzadeh et al. (2012) proposed an alternative green approach in which air is introduced during the dispersion procedure instead of a dispersion solvent called Air assisted DLLME, which avoids some disadvantages such as higher solubility and allows for better extraction performance during the analysis of environmental samples such as river water, and wastewater samples with advantages of high enrichment factors and extraction efficiency (Farajzadeh and Mogaddam, 2012; Plastiras et al., 2020; Ge et al., 2018; Jouyban et al., 2020). Fine organic droplets are generated in this method by aspirating and expelling the mixture of aqueous sample solution and extraction solvent repeatedly in a conical test tube using a syringe.

Once the extraction is complete, a centrifuge is used to separate the phases, and the enriched analytes in the organic phase are determined by the detection technique. This method use small volume of organic solvent, and does not require the use of a disperser solvent (Asghari et al., 2017; Li and Row, 2019). The extraction solvent is dispersed by aspiration and expulsion of the sample mixture by syringe instead of using disperser solvent. It is simple, and applicable for extraction of various components in aqueous samples.

Overall, the use of reduced dispersive solvent-base methods constitute a major modification in DLLME, because they are considered cost-effective and eco-friendly. Continuous advancements are often presented, including the use of one solvent (DESs) that act as both extraction and dispersive solvent for the pre-concentration of environmental samples (Plastiras et al., 2020; Shishov et al., 2020 (c)). DESs are separated from aqueous solution using aprotic solvents such as tetrahydrofuran (THF), 1,4-dioxane, or acetone in most of this form of extraction procedure (Khezeli et al., 2015; Karadaş and Kara, 2019).

So far, a few studies have looked into the use of DESs to facilitate extraction and dispersive solvent function in the pre-concentration process. For instance, Arain et al. (2016) adopted this procedure for pre-concentration of cobalt. In this method, 1-nitroso-2-naphthol was used as ligand. Under optimum conditions, LOD, LOQ, pre-concentration factor (PF) and % RSD were determined as 1.10 μg L^{-1}, 3.60 μg L^{-1}, 15 and 7.1% respectively. Karadaş and Kara, (2019) successfully used choline chloride/2-chlorophenol (at a 1:2 molar ratio) as a water-miscible extraction solvent and tetrahydrofuran as an emulsifier solvent for the pre-concentration of radioactive isotopes containing metals. The limit of detection method was 5.93 μg L^{-1}. The method showed the results that were statistically in good agreement at 95% confidence level.

Other researchers (Aydin et al., 2017; Yilmaz and Soylak, 2016; Panhwar et al., 2017; Zounr et al., 2017) also reported similar approach for the pre-concentration of inorganic metals containing radioactive isotopes in environmental samples. Tavakoli et al. (2021) used ultrasound-assisted deep eutectic solvent-based dispersive liquid-liquid micro-extraction (UA-DES-DLLME-SFO) to pre-concentrate and determine cobalt in environmental samples by FAAS. In this method, 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol (5-Br-PADAP) was employed as the chelating agent, while decanoic acid and dl-menthol (dextro,laevo-menthol) were employed as deep eutectic solvents. In this case, the ultra-sonication was used to increase on the micro-extraction efficiency (Tavakoli et al. 2021). The optimal condition resulted in detection limits of and 0.4 μg L^{-1}, quantification limits of 1.3 μg L^{-1}, and pre-concentration factors of 50.

3.1.3.2. Application of DLLME to various environmental samples

DLLME has been introduced to separate inorganic analytes from variety of liquid matrices (Hassan et al., 2016; Tolcha and Megersa, 2018). DLLME is cost-effective, quick, simple, and requires small volumes of sample and produce high enrichment factors.

It has been widely applied during the analysis of radioactive metals as part of the inorganic analytes (Sadi et al., 2016; Hassan et al., 2016; Villar et al., 2015; Veyseh and Niazi, 2017b); Tarhan et al., 2019). DLLME techniques have been used in the pre-concentration of various samples such water samples, sediment, soil, and plants. DLLME is a commonly used sample pre-concentration step in procedures for analysing radioactive metals in environmental matrix (Hassan et al., 2016).

DLLME have been applied for the extraction and concentration determination of a wide variety of radioactive metal ions (Villar et al., 2015; Hassan et al., 2016; Rodríguez et al., 2016; Sadi et al., 2016), mainly from water samples (Leong et al., 2014; Tolcha and Megersa, 2018). Metals are the second (Leong et al., 2014), and most common analytes that are extracted by DLLME (Tolcha and Megersa, 2018). DLLME has been extensively used in the past few years for the extraction and pre-concentration of radioactive metals from the water samples followed by quantification with various detection techniques. The method generally resulted in efficient extraction, high enrichment factors and low detection limits (Table 6). To extract the metal ions, a chelating agent is introduced to the sample. Ions from the liquid phase are then extracted as a complex into the extracting solvent. One of the first approaches widely used, is for the extraction of Pd and Au using DLLME in the environmental water sample (Hassan et al., 2016).

Using general procedure, the DLLME methods have also been used for the analyses of various radionuclides metal ions in different environmental matrix (Table 7). Ions were analysed through appropriate techniques.

Table 6: Application of the DLLME technique to water samples

Metals with radioactive isotopes	Matrix	Analytical technique	Extraction solvent	Dispersive solvent	Detection technique	LOD	EF	LOQ	Ref
Uranium	Synthetic and waste water	MA-DLLME	chloroform	Ethanol	UV–Vis	6.7 ng mL^{-1}	165	ng	Niazi et al., 2015
Gold	Tap, lake, and mining water	Conventional DLLME	1-Octanol	Acetonitrile	ICP-OES	0.09 ng mL^{-1}	150	ng	Hassan et al., 2016
Erbium	Water from uranium mine	Conventional DLLME	Mixture of carbon tetrachloride and trichlorethylene	Ethanol	EDXRF	1.3 µg L^{-1}	20	4.3 µg L^{-1}	Sá et al., 2021
Gadolinium, cerium, ytterbium and praseodymium	Water	LL-DLLME	Carbon tetrachloride	Acetone	ICP-MS	0.68 - 26.6 ng L^{-1}	16	ng	Çelik et al., 2015

Lead	River water, lake water, and well water.	UA-DLLME	DES5 ($[P_{14,6,6,6}]Cl$: TSA, 1:2)	nu	HPLC-UV	$0.05\ \mu g\ L^{-1}$	154	ng	Werner, 2020
Thorium	Water from uranium mine	Conventional DLLME	Mixture of carbon tetrachloride and trichlorethylene	Ethanol	EDXRF	$2.0\ \mu g\ L^{-1}$	6	$6.6\ \mu g\ L^{-1}$	Sá et al., 2021
Cobalt	Water	UA-DES-DLLME-SFO	Decanoic acid and dl-menthol	Decanoic acid and dl-menthol	FAAS	$0.4\ \mu g\ L^{-1}$	ng	$1.3\ \mu g\ L^{-1}$	Tavakoli et al., 2021
Samarium	Lake surface water	D-SPE-DLLME	Carbon tetrachloride	Ethanol	ETV-ICP-MS	$0.006\ ng\ L^{-1}$	341	ng	Guo et al., 2014
Cobalt	River water, lakewater, and well water.	UA-DLLME	$[P_{14,6,6,6}]Cl$:TSA, 1:2	nu	HPLC-UV	$0.06\ \mu g\ L^{-1}$	162	ng	Werner, 2020

Thulium	Lake surface water	D-SPE-DLLME	Carbon tetrachloride	Ethanol	ETV-ICP-MS	0.004 ng L^{-1}	557	ng	Guo et al., 2014
Thallium, strontium and cobalt	Groundwater	Conventional DLLME	Chloroform	Methanol	ICP-QMS	0.05–0.55 ng L^{-1}	94–102	ng	Chandrasekaran et al, 2012
Ytterbium	Water from uranium mine	Conventional DLLME	Mixture of carbon tetrachloride and trichlorethylene	Ethanol	EDXRF	2.1 µg L^{-1}	43	7.0 µg L^{-1}	Sá et al., 2021
Cobalt	Water	VALS-DLLME	1-dodecanol	Acetonitrile	FAAS	0.04 mg L^{-1}	13.5	0.13 mg L^{-1}	Chaiyamate et al., 2018
Molybdenum	Shallow groundwater	Conventional DLLME	Carbon tetrachloride	Acetonitrile	ETAAS	0.017 µg L^{-1}	165	0.062 µg L^{-1}	Tissot et al., 2017
Uranium	Water from uranium mine	Conventional DLLME	Mixture of carbon tetrachloride and trichlorethylene	Ethanol	EDXRF	0.3 µg L^{-1}	ng	1.1 µg L^{-1}	Sá et al., 2021

Cobalt	High-salinity produced water	VA-DLLME	Carbon tetrachloride	Methanol	ICP-OES	0.003 µg L^{-1}	19.8	0.01 µg L^{-1}	Guedes et al., 2020

Note: ng – not given; nu- not used; SA- sonication assisted; BS- binary extraction solvents; IMS- Ion-mobility spectroscopy; ([$P_{14,6,6,6}$]Cl : TSA, 1:2)- trihexyl(tetradecyl)phosphonium chloride:thiosalicylic acid at a molar ratio of 1:2; EDXRF- energy dispersive x-ray fluorescence spectrometry ; ETV-ICP-MS- electrothermal vaporization-inductively coupled plasma mass spectrometry; D-SPE-DLLME- dispersive solid phase extraction-dispersive liquid–liquid microextraction; ICPQ-MS- inductively coupled plasma quadrupole mass spectrometry; LL-DLLME- ligandless-dispersive liquid–liquid microextraction; ETAAS- electrothermal atomic absorption spectrometry.

Table 7: Application of the DLLME technique to other environmental samples

Metals containing radioactive isotopes	Matrix	Detection technique	Extraction technique	Extraction solvent	Dispersive solvent	LOQ	Enrichment factor	LOD	Ref
Thallium	Soil	GFAAS	US-DLLME	1-undecanol	ng	ng	ng	0.0003 µg L^{-1}	Abdolahi-Baraei and Afzali, 2015
Cobalt	Plants	UV–vis	IL-DLLME	[Hmim][Tf2N]	Ethanol	ng	ng	0.065 ng m L^{-1}	Khani and Shemirani. 2013

Cobalt	Plants	FAAS	UA-IPSE-DLLME	1- dodecanol	nu	7.9 µg L^{-1}	48	2.4 µg L^{-1}	Arpa and Aridaşir, 2019
Cerium	Lake and river sediments	ETV-ICP-MS	D-SPE-DLLME	Carbon tetrachloride	Ethanol	ng	321	0.048 ng L^{-1}	Guo et al., 2014
Neodymium	Lake and river sediments	ETV-ICP-MS	D-SPE-DLLME	Carbon tetrachloride	Ethanol	ng	341	0.073 ng L^{-1}	Guo et al., 2014
Samarium, europium gadolinium, and dysprosium	Powdered uranium dioxide	ICP OES	Conventional DLLME	1-hexyl-3-methylimidazolium hexafluorophosphate	Methanol	ng	19–86	0.02-0.23 ng L^{-1}	Mallah et al., 2009
Thorium	Rock	UV-vis	DESs-DLLME	[HMIM]-SA	nu	ng	59	2.1 ng m L^{-1}	Sadeghi and Davami, 2019
Thorium	Soil	UV-vis	SsDLLME	1-decanol	THF	ng	40	0.4 µg L^{-1}	Gouda et al., 2018

Cobalt	Soil	EDXRF	Conventional DLLME	trichloroethylene	Methanol		58	0.2 μg Kg^{-1}	de Almeida et al., 2018
Palladium	Anode slime, catalytic converter, ore, and road sediment	FAAS	Conventional DLLME	Chloroform	Acetone	ng	113	0.6 μg L^{-1}	Özdemir et al., 2014

Note: ng – not given; nu- not used; SA- sonication assisted; BS- binary extraction solvents; IMS- Ion-mobility spectroscopy; UA- ultrasound assisted; GFAAS- graphite-furnace atomic- absorption spectrometry; [Hmim][Tf2N]- 1-hexyl-3-methylimmidazolium bis (trifluormethylsulfonyl)imid); UA-IPSE-DLLME- ultrasound assisted-dispersive ionic liquid-suspension solid phase micro-extraction; ([HMIM]-SA- mixture of 1-hexyl-3-methylimidazolium and salicylic acid; UV–vis- Ultra-violent Visible spectrophotometry.

3.1.3.3. Important parameters that affect enrichment factors in DLLME during the of radioactive metals in environmental samples

There are many forms DLLME that have been used for the analysis of environmental samples, this include ultra-sound/ultrasonic assisted (UA-DLLME), microwave assisted (MA-DLLME), vortex assisted (VA-DLLME), and air assisted (AA-DLLME), which are all listed as liquid–liquid micro-extraction (LLME) techniques (Leong et al., 2014; Fernández and Vidal, 2014). In every case of analysis where these methods are used, there are varieties of parameters that can affect their extraction efficiency. For example, the sample pH, type and volume of extracting and dispersive solvents, electrolyte addition, extraction time, centrifugation rate and centrifugation time, and sample volume can affect the extraction efficiency (Werner, 2020; Tolcha and Megersa, 2018; Plastiras et al., 2020; Abdolahi-Baraei and Afzali, 2015), and many other factors depending on the technique of DLLME used for the analysis of radioactive metals in the environmental samples. These factors should be carefully optimized during analysis of radioactive metals in environmental matrix in order to obtain high enrichment factors.

The ability of the DLLME technique to remove radioactive metals in the environmental samples, depends on the proper selection of extraction solvents. For a successful DLLME, a syringe is used to inject an appropriate mixture of extraction and disperser solvents into aqueous samples containing analytes, and a cloudy solution forms. The hazy appearance is caused by the production of small droplets of extraction solvent distributed throughout the sample solution (Plastiras et al., 2020). Therefore, the appropriate extraction solvent must be able to well extract the radioactive metals in the aqueous solution, and must have low solubility in aqueous medium. High-density extraction solvents, are mostly halogenated and generally toxic, therefore, alcohols and other extraction solvents with lower densities than aqueous solutions and less volatile are recommended for the extraction of radioactive metals in environmental sample by DLLME (Hassan et al., 2016).

The cloudy solution formed as a result of injection of the extraction solvent is centrifuged and the fine droplets are sedimented at the bottom of centrifuge tube (Tolcha and Megersa, 2018). The small droplets of extraction solvent settles from the aqueous bulk, usually by centrifuging the emulsion. The quantification of analytes in the sedimented phase is then carried out after centrifugation (Hassan et al., 2016). Therefore, centrifugation step plays a huge role in the extraction efficiency of radioactive metals in environmental matrix, and should be optimised during analysis of radioactive metals in environmental samples when DLLME technique is to be used.

The optimised parameters can be centrifugation speed and time (Tolcha and Megersa, 2018). Although the process of centrifugation is important to settle down the micro droplets of extraction solvent from the aqueous layer, it is a time-consuming stage during the DLLME procedure (Li et al., 2018; Li et al., 2014b). A long centrifugation time causes the sedimented phase to dissolve thereby having a negative impact on the enrichment factors during micro-extraction of radioactive metals in the environmental samples.

In addition, one of the initial condition of selecting dispenser solvent is that both water and the extraction solvent must be highly miscible with the disperser solvent (Tolcha and Megersa, 2018). The disperser solvent has a significant impact on reducing the interfacial tension between water and the extraction solvent, resulting in smaller droplet sizes (Hassan et al., 2016). Thus, the ratio of volume of receiver solvent to disperser solvent should be optimised. The volume of the sedimented phase is, significantly influenced by disperser type and volume. However, solvents such as ketones, alkanes, ethers, alcohols and acetates that are commonly used in DLLME during environmental analysis of radioactive metals possess lower density than water (Al-Saidi and Emara, 2014; Yan and Wang, 2013).

Because of the polarity of these disperser solvents, analytes may have good solubility in them, especially when the compounds are more polar, reducing the analytes partition with extractant droplets and reducing extraction efficiency. Therefore, the application of these solvents in dispersion-based micro-extraction methods like DLLME is a challenge (Rezaee et al., 2015). As such, user friendly and efficient dispersive solvents need to be adopted in order to obtain high recoveries and enrichment factors during the analysis of radioactive metals in environmental samples. The volume of disperser solvent has a direct impact on the formation of emulsion, the degree of extraction solvent dispersion in the aqueous phase, and the extraction efficiency. Small volumes of disperser solvent would be unable to sufficiently disperse the extraction solvent, resulting in the poor formation of a emulsion. Inversely, increasing the volume of disperser solvent increases the solubility of analytes in water, resulting in an incomplete extraction process. Moreover, since the variation in volume of dispenser solvent cause a change in emulsion intensity of extracted radioactive metals in environmental samples, it is therefore necessary to optimize the volume of disperser solvent (Hassan et al., 2016).

For metal ion separation, DLLME requires the formation of a complex with sufficient hydrophobicity. With a small volume of the receiver phase, this complex should be able to be attached to the organic solvent.

The pH of the aqueous solution is a primary factor for the extraction of radioactive metal ions in environmental samples; it facilitates the interactions between the analyte and the chelating reagent (Arain et al., 2016) and the hydrogen ion concentration of the matrix during the extraction of radioactive metals (Rezaee et al., 2015). For this reason, curves between extractability and pH at constant reagent concentration have always been of great analytical significance. The pH plays an important role in the establishment of s metal cations' complex and stability in DLLME (Abdolahi-Baraei and Afzali, 2015). Therefore, it is of importance to optimise the level of sample pH during the extraction of radioactive metals in the environmental samples. Using DLLME, many researchers have shown that, during pre-concentration of radioactive metals in environmental matrix, high extraction efficiency is obtained when the pH level is acidic (Abdolahi-Baraei and Afzali, 2015).

The solubility of radioactive metals and extraction solvent in the aqueous phase normally decreases as ionic strength increases because of the salting out effect (Al-Saidi and Emara, 2014). As the salt concentrations increase, the volume of organic phase obtained increases, reducing both the target analyte concentration and the enrichment factor. Electrolyte addition does not appear to have a significant impact on extraction efficiency in several studies. However, using higher salt concentration reduces extraction efficiency of radioactive metals in environmental samples, due to the increase in solution viscosity that lowers dispersion (Rezaee et al., 2015). Therefore, salt concentration must be carefully optimised during the DLLME. In the separation and pre-concentration studies involving DLLME during analysis of radioactive metal ions in environmental matrix, sample volume is an important factor that must be taken into consideration in order to achieve high enrichment factors (Arain et al., 2016). The mass transfer mechanism is accelerated by the large contact surface between the sample and the extractant droplets (Farajzadeh et al., 2019). Therefore, the sample volume must be sufficient.

3.1.4. Important calculations in DLLME during the analysis of radioactive metals in the environmental samples

Generally, the enrichment factor (E_f), extraction recovery (E_r) are the common calculation used to evaluate the extraction efficiency of the parameters optimised in the DLLME during the analysis of radioactive metal in environmental samples, and these can be expressed as following equations (Hassan et al., 2016; Al-Saidi and Emara, 2014; Barfi et al., 2016):

$$E_f = \frac{C_{eq}^{e}}{C_{ini}^{i}} \text{ x } 100\% \qquad (1)$$

$$\mathrm{E_r} = \frac{n_{ex}}{n_{ini}} = \frac{C_{eq}^{ex} V_{ex}}{C_{ini}^{sam} V_{sam}} \qquad (2)$$

where C_{eq}^{e} denotes the analyte's final concentration in the organic phase, $C_{ini}^{sam} C_{ini}^{i}$ is the analyte's initial concentration in the sample phase, n_{ex} is the number of moles of analyte extracted during the extraction process and n_{ini} is the total moles of the analyte, and V_{ex} and V_{sam} are the final (separated) volume of extracting phase and initial volume of sample, respectively.

E_f can be also defined as the slope of the calibration curve related to DLLME procedure to that of DLLME procedure:

$$\mathrm{E_f} = \frac{DLLMEcalibration\ slope}{Aqueous\ calibration\ slope} \times 100\% \qquad (3)$$

3.1.5. Challenges and future aspects

The present review has focused on the developments for efficient application of DLLME and its conjunction with different technical approaches for the pre-concentration and determination of radioactive metals, and metals containing radioactive isotopes in various environmental samples. Although the performance of DLLME in environmental samples is magnificent, it has not yet eliminated the use of organic solvents during analysis of environmental samples. Therefore, it requires further improvements in future. Primary disadvantages of DLLME is the consumption of relatively high energy during dispersion step (i.e. microwave and ultrasound), and disintegration of analytes, which usually occurs when emulsification is extended for a longer time. For the future improvement, and to avoid these challeges from happening, it is suggested to use of manual shaking to improve the extraction efficiency, and lowers the ultrasonic extraction time, which minimizes decomposition of analytes (Shu et al., 2012; Chung et al., 2012; Lin and Fuh, 2010).

In DLLME for pre-concentration of radioactive metal species, hydrophobic metal-complex formation is an important step for the extraction of analytes of interest. The main concern is, most the complexing agents have no/little selectivity toward target radioactive metal species and their radioactive isotopes. However, this competition for the complexing agent from other interference ions with target analytes cannot be neglected.

Although some researchers have effectively reduced some of these interferences by adding salting out agent, this technique is reagents-consuming, hence add another cost. Therefore, further research in this step is still needed to get rid of such interferences in suitable cost efficient and environmental friendly route. Although the performance of DLLME in analysis of environmental samples is marvellous, it still faces counterparts in analysis of radioactive metals and radionuclides isotopes in complex matrixes such as solid samples.

The analysis of solid samples requires strong and complete digestion by strong acids, and high temperatures which compromise the stability of the targets analyst in the system. Therefore, it needs further improvements in future in this area. Another key area in which further research is still necessary is the type of the solvent which are injected into the instrument for quantification of anaytes soon after successful extraction. Some these solvents have very low boiling point, hence they evaporate before quantification signal by the instrument (i.e., FAAS) is established, thereby result to poor precision. Therefore, further look out is necessary in this area.

3.1.6. Conclusion

In this review, the most key features that affect the extraction efficiency of DLLME during the analysis of radioactive metals and metals containing radioactive isotopes in environmental samples were successfully reviewed. DLLME modes have been widely reported in the scientific literature. However, the report for its application for the analysis of radioactive metals in the solid environmental matrix is limited. The combined use of conjunction conventional DLME for pre-concentration in and ideal quantification techniques have versatile and robust wide application in determination of radionuclides. Under the developed customization of DLLME with different approach like DESs and dispersive techniques, have the advantages such as simplicity, speed, cost-effective and high enrichment factors over the traditional DLLME and other pre-concentration techniques. Moreover, DLLME may be utilized as green chemistry since it reduces consumption of hazardous organic solvents.

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Chapter 3.2: Paper II

This review “Recent developments for efficient analytical separation techniques during analysis of radionuclides in the environmental samples” briefly discussed the overview, and the general principles of various recent pre-concentration techniques during analysis of radioactive metals in environmental samples including traditional liquid-liquid micro-extraction, dispersive liquid-liquid micro-extraction, and vortex assisted liquid-liquid micro-extraction. The successful application of these methods during the extraction and pre-concentration of radioactive metals in environmental matrix was also outlined.

Recent developments for efficient analytical separation techniques during analysis of radionuclides in the environmental samples: A review

Abstract

Over the past years, many analytical separation techniques have sparked interest in multiple areas during analysis of radionuclides in the environmental samples. Most of these methods have been reviewed considering number of factors including their modifications with modeling solvents, and ionic liquids (ILs) that can be successfully separated and reused to significantly reduce the cost of their application as great advantage. Although results showed a success, however, these methods still have shortfalls; they require consecutive extraction of analystes, use toxic solvents and generate hazardous toxic wastes. In this paper, the efficient and miniaturized analytical techniques for the analysis of radionuclides in the environmental samples have been reviewed, emphasizing on the efficient extraction procedure, non-toxic extractants, and efficient detection techniques. Their pitfalls were also detailed during the analysis of radioactive metals in the environmental samples.

Keywords: Radionuclides, radioactive metals, environmental samples, efficient, miniaturized analytical techniques.

3.2.1. Introduction

Chemical separation of radionuclides plays a critical role in various sectors including (1) characterisation of nuclear wastes generated during operations and decommissioning; (2) nuclear emergency planning to identify the composition of a radioactive source and assess the impact of a nuclear accident/incident; (3) monitoring of radioactivity in the environment and in the vicinity of nuclear power plants and (4) waste management. In such instances, chemical separation and purification is often necessary for unambiguous and reliable quantification of radionuclides (Talan, 2021; Qiao, 2020; Rodríguez, 2016; Kim et al, 2015). Economically viable extraction processes of radionuclides remain a challenge (Fouquet et al., 2014; McLellan, 2014). However, regardless of their primary or newly identified radionuclides sources, the extraction of radioactive elements has always created environmental concerns. Therefore, for the sake of the environment and public safety, radioactive elements must be treated and purified (Talan, 2021). This process involves concentrating analyte(s) and removal of matrix/interferences. As such it is conducted to typically to improve sensitivity and detection limits during trace analysis of radionuclides by instrumental techniques. Efficient separations processes for the remediation of radioactive metals are regarded as priority in energy sectors and waste treatment plants (Rajasulochana and Preethy, 2016).

During these processes different methodologies are selected for the extraction of radionuclides in unique sample types (Cerdà, 2019; Trojanowicz, 2018; Rodríguez, 2016). Depending on the analytical techniques used, some methods come with challenges that may include toxicity of the solvent used, cost-effective and waste generation that could impose some environmental threat (Hellé et al., 2012; Rodríguez et al., 2015; Quigley et al., 2016). Moreover, most methodologies do not come to terms with the concept of efficient analytical processes. Large volume of samples and organic solvents are known to be a concern for a variety of reasons. Most of these organic solvents are harmful to living organisms and the environment; as a result, particular precautions must be taken when disposing of them to avoid damage they may cause. In addition, the importance of purity cannot be over emphasized, hence they must be of high purity to avoid contamination of extracts in trace analysis, which contributes significantly to the high cost of analysis.

The strategies to attain efficient radionuclides extraction techniques is feasible through development of rapid radionuclides analytical separation techniques that are associated with low cost, low sample consumption, sequential extraction of analytes, use of environmental friendly solvents, non/less-hazardous waste generation, high selective and green analytical separation methods (Qiao, 2020; Kim et al, 2015). In all instances, the objective is to achieve required purity and quality assurance to ensure reliability with maximum efficiency and healthy safe environment.

In the past years, several applicable radionuclides extraction methods have been reported for the analysis of environmental samples. Some separation techniques are based on solid phase extraction (SPE) (Rodríguez et al., 2015), liquid-liquid extraction (LLE) (Martini et al., 2019, Kokosa, 2013) and cloud point extraction (CPE) (Hamed and Aglan, 2019; Bulska and Ruszczyńska, 2017), and extraction chromatography (Hoang, 2016). Although these techniques do the work adequately, they have a lot of drawbacks. For instance, LLE is too cumbersome for use, with large volume of samples and often requires the use of hazardous, flammable, and toxic solvents (Razmara et al., 2011). Moreover, the composition and chemistry of the aqueous phase, as well as the reaction processes that drive the exchange of target metal onto the organic phase, are all factors of the extraction process in this method (Martini et al., 2019), hence large volume of organic solvents is used. Another drawback of this method is that it does not provide sufficiently clean analytes (Gabriella, 2020), and this, do not conform to the concept of efficiency. SPE uses considerably less solvent than LLE, but it can be relatively expensive. SPE is time consuming because mostly it is repeated several times in order to produce satisfactory recoveries (Rodríguez et al., 2015). CPE on the other is time consuming and involves the use of at least some chemical additives as well as specialized equipment (Bulska and Ruszczyńska, 2017). Therefore, efficient methods for radionuclides determination is required (Rodríguez et al., 2015). This pre-supposes that the efficient, selective, and economical method for the separation of radionuclides are largely needed (Smičiklas, 2021; Trojanowicz et al., 2018).

To improve the efficiency, cost-effectiveness and sort falls of the traditional methodologies, modern extraction technologies has been introduced in the recent years for the extraction and pre-concentration of radioactive metals in the environmental samples. This include, liquid liquid micro-extraction (LLME) (Veyseh and Niazi, 2017), hollow fibre liquid-phase micro-extraction (HF-LPME) (Plastiras, 2020) and single drop microextraction (SDME) (Šrámková et al., 2018). These methods vary in design, but they all have one feature in common: they all use small quantities of organic solvent and so meet the green analytical chemistry requirements (Kocúrová, 2013; Spietelun et al., 2014). They are efficient cheap, fast, and easy to use because no additional equipment is required, and they can be used with a variety of analyte quantification techniques, hence they have recently found widespread application in pre-concentration and extraction of radionuclides (Qiao, 2020).

These miniaturized pre-concentration methods are user-friendly, fast and very efficient for trace analysis of environmental samples. The volume of solvent utilized during radioactive pre-concentration is on the microliter scale, thus there is little interaction with the solvent during sample preparation for these micro-extractions methods. In addition, most of these techniques combined separation, pre-concentration, and sample introduction in one step. The most significant merit of these methods is that almost all of the anayte volumes of the organic extraction phase can be either be reconstituted or directly introduced into the quantification device whereas traditional pre-concentration methods only introduce a small amount of the large volume of concentrated solvent into the analytical instrument (Yilmaz and Soylak, 2016). Thus, low cost-effective, low sample consumption, selectivity, and environmental friendliness of these modern radio-analytical extraction methods show profound way to move towards the goal of efficiency, and through miniaturization, these extraction methods has ability to overcome their normal pitfalls.

A number of review papers have been published, focusing either on sample manipulations, method simplicity, flexibility, and cost for analytical extraction and separation techniques in sample preparation steps for radionuclides analysis in various environmental samples. This focast offers tremendous advantages for extraction and separation techniques of radionuclides. However, in sample preparation steps, harmful organic liquid waste are generated, and harmful solvents are used. Besides, they are considered less selective and may require multiple extractions, lengthening the analytical procedure, which also consume energy in economic point of view. This study outline the efficient analytical extraction and separation techniques for analysis of radionuclides with focus on the review of non-consecutive extraction of analytes, non-toxic solvents, non/less-hazardous waste generation, and high selective and green analytical separation methods. Although this discussion is by no means exhaustive, the intent is to provide a general overview of the efficient radionuclides separation approach, underlying the challenges involved and highlight the merits of this these techniques for the use and development of efficient radionuclides extractions suitable for ecofriendly applications.

3.2.2. Ways to model efficient chemical extraction methods during analysis of radionuclides in the environmental samples

In order to free itself from reliance on harmful techniques that generates hazardous liquid waste, uses harmful solvents, and prolong extraction time; the arm of radio-analytical techniques has focused on recent efficient separation domains that promote non-consecutive extraction of analytes, non-toxic solvents, less waste generation and miniaturization of extraction technique during the analysis of radioactive metals in environmental samples (Figure 8).

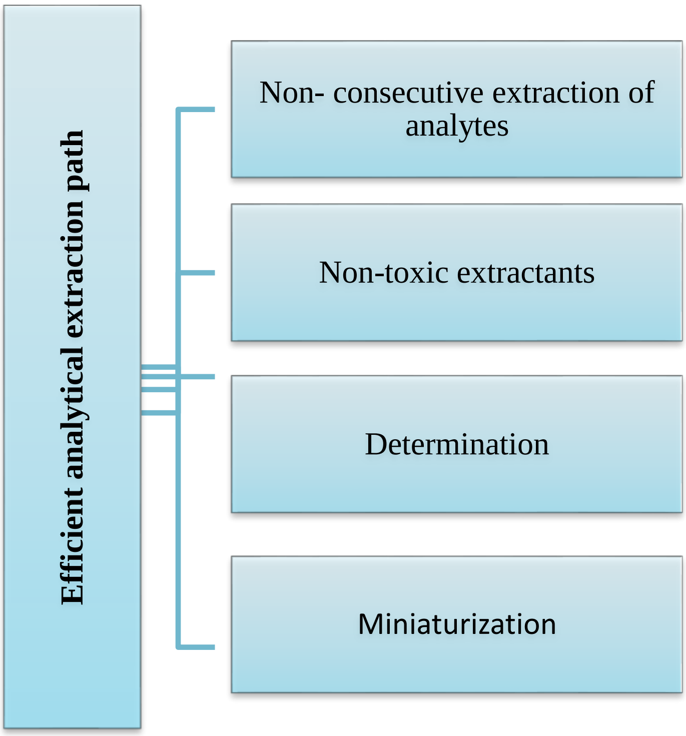


Figure 8: Ways to model efficient chemical extraction methods during analysis of radionuclides in environmental samples.

3.2.2.1. Miniaturization

The analyses of radionuclides in environmental samples are in great demand, and a cost effective technique for the separation of analytes is required. In order to achieve and improve the analytical technique performances while promoting the concept of efficiency, radiochemical methods needs to miniaturize its analytical systems (Hellé et al., 2012). Miniaturization of liquid-based extraction techniques can be achieved by a significant reduction of samples and the extractant phase volumes (Bulska and Ruszczyńska, 2017).

The minimization of the volume of extractant increases the fastness of the analytical operations, and improves radiochemical analyses (Rassou et al., 2020). Therefore, to abide by the operating protocols for efficient analysis of radionuclides in the environmental samples, the volumes of the samples and solvents are reduced to micro-scale (Hellé et al., 2012). The use of analytical micro-scale methods is rapidly growing due to the high potential of the technology to significantly minimize the hazards and constraints related to radionuclides analysis (Rassou et al., 2020). These alternatives miniaturized pre-concentration methods based on their application during radionuclides trace analysis that, uses negligible volumes of extraction solvent, and requires minimum number of steps for sample preparation. Many miniaturized techniques have been applied during radioactive metals analysis in environmental samples including the common class of LLME (i.e., VA-LLME and DLLME).

3.2.2.2. Non-consecutive extraction of analytes

When there are multiple radioactive metals of interest in one sample, the non-consecutive extraction could be a solution. Non-consecutive extraction where several elements can be pre-concentrated simultaneously in one sample is the most desirable dimensions because they are not time consuming and they are of low cost (Naghizadeh et al., 2015; Xu et al., 2013). This also avoid the generation of waste during separation procedure for each radioactive element of interest in the environmental samples. Recently, non-consecutive extraction that can be used as potential alternative of the time consuming procedures during trace analysis of radionuclides in environmental samples has appeared (Ghaedi et al., 2007). The non-consecutive extraction techniques include community bureau of reference (BCR) sequential extraction, flow system and co-precipitation.

BCR is now a well-established extraction a method for separating trace metal content in soils, sediments, and related materials, introduced by the standards, measurements and testing programme (formerly BCR) of the BCR for determination of metal pollutants in sediment and soil (Tong, 2020). In this method samples are treated with a series of reagents chosen on the basis of their capacity to react with various major matrix components and remove trace metals associated with them. BCR extraction method has become one of the user-friendly technique applied in trace analysis of radioactive metals in sediment samples, with negligent errors in the sample treatment, and it is more operationally effective (Ferna´ndeza, 2004). BCR sequential extraction is a three step technique known as the most popular method for trace and sediments sequential extraction of radionuclides (Rosado et al., 2016).

This technique has been exploited for the quantitative extraction of metal ions and radioactive metals in trace level from a variety of environmental sediment samples. It has demonstrated the ability for simultaneous extraction of radionuclides and has been validated for the most significant alpha-emitter natural radionuclides (^{210}Po, ^{234}U, ^{238}U, ^{230}Th, ^{232}Th and ^{226}Ra) (Pérez-Moreno, 2018). For instance, Pérez-Moreno et al. (2018) used the BCR sequential extraction method. The authors showed that in this method, the mobility of radionuclides is associated to the type of radionuclide and speciation under certain environmental conditions such as the case of the pairs ^{234}U^{238}U and ^{230}Th^{232}Th.

Therefore, radium was mostly attached to the reducible fraction (Fe and Mn-oxyhydroxides), uranium to the oxidizable fraction (organic matter and sulphides), while polonium and thorium isotopes had a high affinity for the particulate phase (non-mobile fraction).

Rauret et al. (1999) extracted multi-class radioactive elements in sediment and soil using an improved BCR sequential extraction procedure through intercomparison exercises for small-scale interlaboratory study. The authors further used multiple modified BCR extraction method to determine several groups of radioactive metals in soils and sediments. Arain et al. (2008) also used BCR extraction for mobility and availability determination of radionuclides containing elements in contaminated lake sediment. However, in order to maximize the efficiency of the widespread use of BCR methods, the technique must be accompanied by several modifications, and optimization of the method.

When BCR model is not favourable, co-precipitation is one of the most efficient pre-concentration technique for the separation of trace metals from environmental sample matrix, including radioactive metals (Hikichi et al., 2020; Huang et al., 2019; Fujikawa et al., 2015; Jiao et al., 2021). It is a simple, rapid, green technique (Soylak and Murat, 2014), and hence efficient. Co-precipitation is a strategy for separating and collecting radionuclides in solution that are present at very low concentrations (Hoang, 2016). It takes place when metal ions and other pollutants are moved down in a solution with or in a precipitate. There are many types of co-precipitants in the literature. The most common radionuclide compounds are iron (III) hydroxide ($Fe(OH)_3$) and manganese dioxide (MnO_2) (Hoang, 2016). Co-precipitation has several advantages that make it considerable, such as simplicity and rapidity, hence, several analytes ions can be pre-concentrated and separated from a matrix simultaneously. Two important aspects make co-precipitation interesting route. First, it is inexpensive, efficient in energy consumption and extract various radionuclides at once.
Secondly, several inorganic co-precipitants can be used as efficient collectors of trace radioactive metals. Metal hydroxides are most popular for the co-precipitation of metals at trace levels, due to good trace recoveries and separation of analyte elements (Soylak and Murat, 2014). Furthermore, by-products of hydroxide materials co-precipitants are environmental friendly (Yazid and Joon, 2019).
Recently, it has also been viewed that ferrous hydroxide co-precipitation shows the merit of simultaneous pre-concentration of all target radionuclides (Qiao et al., 2014). It is for this reason that co-precipitation offers a considerable opportunity with prominent values for efficient non-consecutive extraction of radiactive analytes. For instacce, Qiao et al. (2014) successfully used ferric hydroxide co-precipitant for the separation of technetium from the actinides via valence control of

technetium (as Tc(VII)) in a ferric hydroxide co-precipitation. Soylak and Murat (2014) used co-precipitation model that used lutetium hydroxide as a precipitant for Co, Cd, Fe, and Ni in herbal plant and water samples.

An alternative to co-precipitations is flow system introduced in the 1950s by Skeggs (Skeggs, 1957), and this has recently gained attention. This method is considered an efficient and universal analytical technique (Kołacińska and Trojanowicz, 2014). Furthermore, it is a safe approach with limited interventions and a drastic reduction of reagents and sample volumes, hence reducing the generation of waste. Thus, it holds principles of green chemistry and efficient analytical technique (Rodríguez-Maese et al., 2020). Kołacińska et al. (2018) reported that various methods used in chemical isolation and purification such as liquid-liquid extraction (LLE), electrochemically modulated separations (EMS), liquid-liquid micro-extraction (LLME), solid phase extraction chromatography (SPEC), capillary electrophoresis (CE), ion exchange chromatography (IEC) and molecularly imprinted polymer (MIP), can be introduced into flow system. This further allows multiple pre-concentration of metals ions sample in a short time (Fajardo et al., 2008). Flow system is a suitable unique tool for multi-radionuclide and multi-samples simultaneous processing that vitalizes the developed method in obtaining reliable results with reduced analytical cost and time.

Flow system also exhibit features extremely favourable over their batch counterparts which makes it efficient, e.g. high enrichment efficiencies and reproducibility, low reagent and sample consumptions, low risk sample of contamination, simple automated operation and very limited laboratory bench space and glassware are required. This domain have proven to be appropriate platforms for the development of automated radiochemical analyzers, with advantages of quick and low-cost procedures, with little reagent use and no waste generation, as well as low analyte manipulation (Rodríguez et al., 2015).

A multi-sample processing flow system simultaneous pre-concentration has been tremendously used for the separation of radionuclides in the environmental samples. Qiao et al. (2014) reported the use of flow system for simultaneous pre-concentration of ^{236}U, ^{238}U, ^{237}Np, ^{239}Pu, ^{99}Tc, and ^{240}Pu in seawater. On the other hand, Vicente et al. (2018) successfully used flow system for the separation and determination of radiostrontium in industrial aqueous samples using overall analysis time of less than 10 minutes per aqueous sample. The non-consecutive extraction and rapidness of flow system makes it an excellent choice of efficient pre-concentration techniques.

3.2.2.3. Non-toxic extractants

The non-toxic extractants that hold for the definition of efficiency must have characteristics such as biocompatibility, good extraction performance, low solubility in the aqueous phase, density different to that of the aqueous phase, chemical stability, and contribution to the sustainability of the process, as well as economic and performance aspects (Dafoe and Daugulis, 2014; Pandey and Tripath, 2014; Lemos et al., 2017). Many organic solvents of different classes, such as carboxylic acids, alcohols, oils, and esters, have been evaluated in terms of their characteristics (Keasler et al., 2013; Lemos et al., 2017), but have not been mainly evaluated for their efficiency and unfavorable effect during the analysis of radioactive metals from the environmental samples. The choice of suitable solvents during the analysis of radioactive metals in environmental samples can be classified in many ways, one of the most significant classifications is whether they include potentially harmful components or have a safe composition that qualifies them as non-toxic solvents (Pandey and Tripath, 2014; Lemos et al., 2017).

Using the environmental friendly type of solvents can reduce a variety of negative health problems including acute (e.g., upset stomach and dizziness) and chronic (e.g., nerve damage and cancer) diseases. This is an indirectly efficient approach from health and economic point of view, because by making the use of environmental friendly type of solvents industries saves money by helping to avoid the following situations: a) Acute health effects from toxic chemical exposure which might last for days after the source of the exposure has been removed; b) chemical-related injuries in the workplace; c) toxic torts and the tremendous impact they can have on the bottom line employees as people will not be working on toxic chemicals; d) high expenditure the level of PPE required for working with toxic reagents. All these can be made possible through the use of non-toxic extractants such as deep eutectic solvents (DESs) and neutral extractants, but not limited these.

3.2.2.3.1. Deep eutectic solvents

Green chemistry has advanced significantly in every discipline of chemistry during the past years, with an emphasis on the development of green solvents. The concept of deep eutectic solvents (DESs) was first described by Abbot et al. in 2001. The concept of DESs has emerged to overcome constraints, like toxicity, poor biodegradability, and high cost of other extraction solvents that limit the industrial applications (Dugoni et al., 2021), these are characteristics of efficient solvent. DESs also have some recognized properties, such as poor conduction, high viscosity, low vapor pressure, high thermal stability (Mbous et al., 2017) and are non-toxic (Torregrosa-Crespo et al., 2020).

DESs have received a lot of attention in recent years in a variety of applications including extraction of dissolved metal (Gilmore et al., 2018), removal of pollutants from water (Van Osch et al., 2017), and promotion of redox chemistry of uranium ion were reported. DESs are synthesised based on the mostly used procedure reported in the literature (Dugoni et al., 2021). Briefly, choline chloride or acetate (HBA) is mixed with the various HBDs, urea, glycolic acid, diglycolic acid, or imidazole at 80°C for 30 minutes while stirring until a homogenous and transparent solution was formed. Without any purification, the produced the mixture is cooled to 22°C and used for the extraction tests. In general, a DES is a form of solvent made by combining two components that act as hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD) in an appropriate molar ratio (Figure 9). A combinatorial approach of HBD and HBA has resulted in the rapid development of a large number of novel DESs.

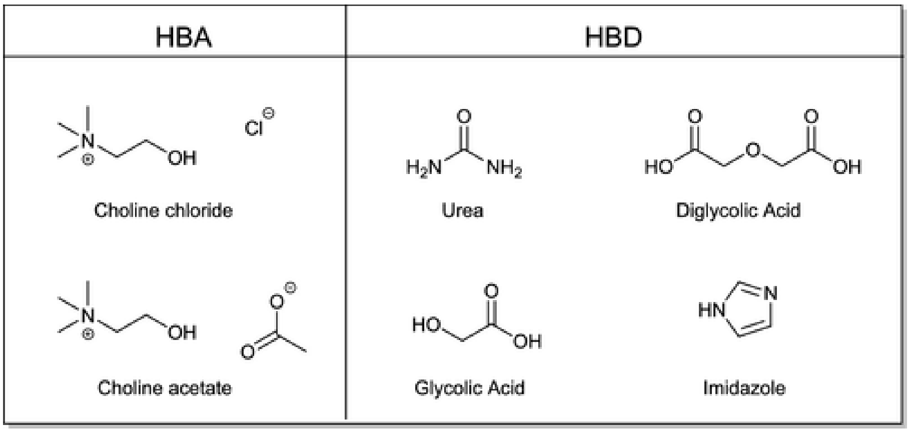


Figure 9: Molecular formulae of the components of DESs used (Dugoni et al., 2021).

The DES components produce a mixture with a significantly deeper melting point depression than would be expected based on ideal mixing, resulting in homogeneous liquids with unique solvent properties at standard temperature (Dugoni et al., 2021). The eutectic mixture of choline chloride (ChCl) and urea in a molar ratio of 1:2 is the most studied DES in the literature (Mokbel et al., 2016). Choline chloride is a vitamin B salt that is a quaternary ammonium salt (vitamin B4). It is a biodegradable and non-toxic salt.

Many of these solvents are made from choline chloride, a vitamin used as a food additive for farm animals in huge numbers (Mudd et al., 2016), and a hydrogen bonding agent like glycerol. Deep eutectic solvents (DES) made from choline chloride are a less harmful and less expensive alternative to ionic liquids that were recently developed (Abbott et al., 2004). This means that DESs can be made from inexpensive and relatively harmless compounds. Dugoni et al. (2021) used acetate-based DESs as co-solvents made from choline chloride and ethylene glycol (ethaline) due to the the chemistry is easier than the choline chloride/lactic acid eutectic for the extraction of radiotoxic metals such as technetium, indium and palladium by liquid liquid extraction. The work of Albler et al. (2017) also showed that elements such cobalt and nickel from the environmental samples can be captured in deep eutectic solvents. However, DESs are now being researched as potential green solvents, particularly in the fields of food, tastes, perfumes, and medicinal plant processing, industries because they are non-toxic (Choi and Verpoorte, 2019).

3.2.2.3.2. Neutral extractants

In industry, the value of a product is determined not only by the cost of production but also by the method of production. Safety of the process, avoiding the use of potentially hazardous chemicals to human health and an environmentally friendly disposal of the waste products are nowadays important aspects that should also be taken into account in calculating real costs of production. Organophosphorous compounds (e.g., Tributyl phosphate (TBP), Dibutyl butylphosphonate (DBBP) and Tri-n-octylphosphine oxide (TOPO)) are neutral organic liquids extractants and have recently been used to remove metals from the liquid phase by the solvating action (Waghmare et al., 2011; Wilson et al., 2014). Table 8 shows some of the structures and common commercial names of some solvating extractants. The technique involves forming an addition complex with the organic extractant and undissociated, electrically neutral molecules. In the organic phase, the addition complex is more soluble than in the aqueous phase. As a result, neutral species are transferred from the aqueous to the organic phase. These neutral extractants are mostly used extractants in hydrometallurgy (Matveev et al., 2020).

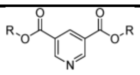
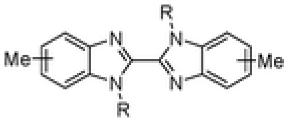
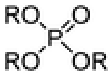
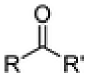
Neutral extractants have no charge, only extract neutral complexes or charged balance ion pairs. The neutral extractants sometimes may dissolve in organic diluent, or they may be the organic diluent itself (e.g., diethylether, methylisobutylketone, tributyl phosphate). The extraction of uryl nitrate into diethyl ether, which was utilized in the Manhanttan project to purify the uranium used in the first reactors, is the most notable example of this (Manhattan Project, 2021).

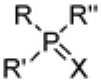
The Redox method was one of the first large-scale procedures to recover uranium and plutonium from irradiated fuel, thethyl isobutyl ketone was used to extract a group of metals as nitrites. The extraction is improved by rendering the complex more lipophilic. This is accomplished by either expanding the coordination sphere, or by replacing water molecules in the first coordination sphrere of the metal ion (Choppin, 1981; Waghmare et al., 2011; Hellé et al., 2012; Matveev et al., 2020). The selectivity of the extraction is achieved by the addition of a salting agent such as NHO_3, $NaNO_3$

and $Ca(NO_3)_2$ (Wilson et al., 2014; Matveev et al., 2018; Matveev et al., 2020), where the extent of extraction recovery is increased by salting out effect. Neutral extractants includes various alcohols, ethers, ketones and sulphides, which has been used extensively. In the view of Burger (1963), the most popular neutral extractats is TBP (Jorjani et al., 2016; Matveev et al., 2018) that most likely reacts with metals elements according to a solvation mechanism as a result of high polarity of the phosphoryl group (Waghmare et al., 2011).

TBP is a group of esters (Burger, 1963), it forms complexes with element like Th, U, Np, and Pu by using the phosphoryl oxygen to form a bond with the central metal atom, and can achieve higher than 100 g L^{-1} organic phase loading (Matveev et al., 2020). It has the advantage of much lower flammability and high separation factors. Most recently, Matveev and Petrov (2020) evaluated neutral extractants such as TBP and di-(2-ethylhexyl)phosphoric acid (HDEHP). In this case, the neutral extractants were investigated in the presence of $Ca(NO_3)_2$ Pr(III) and Nd(III). Because of its high capacity and cation extraction order (Nd > Pr), TBP was found to be the best choice. Ma et al. (2017) published a paper on separation of Fe(III) and Cr(III) from tannery sludge bioleachate using organophosphorus acid extractants, namely, di(2-ethylhexyl) phosphoric acid (D_2EHPA) and TBP. The results showed good that Fe(III) can be completely extracted by adding TBP at above 10 vol%. Although neutral extractants shows ability in the extraction of radioactive materials, they appear to be active only in acidic solutions.

Table 8: The structures and common commercial names of some solvating extractants (Wilson et al., 2014; Tasker et al., 2004; El-Nadi et al., 2007).

Phosphine	Substituents	Molecular formula	Commercial name(s)
	R	$C_{10}H_{21}$	Acorga CLX50
	R	$COOC_{13}H_{27}$	Acorga ZNX50
	R	n-C_4H_9	TBP
	R	Me	MIBK
	R′	i-C_4H_9	
	R = R′	i-C_4H_9	DIBK

	X	S	R = R′ = R″	i-C_4H_9	Cyanex 471
	X	O	R = R′ = R″	$CH_3(CH_2)_7$	Cyanex921, TOPO
	X	O	R = R′ = R″	i-$CH_3(CH2)_7$	Cyanex 925
	X	O	R = R′ = R″	$CH_3(CH_2)_5$ and $CH_3(CH_2)_7$	Cyanex 923

3.2.3. Determination of radionuclides

Determination basically refers to the detection of radionuclides. There are various quantification techniques that may be used in radionuclides analysis in the environmental samples (Zolfonoun and and Salahinejad, 2013; Janković et al., 2016; Pöllänen, 2017). The systems are based on the concepts of matter-radiation interaction. The efficiency of particle detection and discrimination on the instrument is influenced by a number of factors including particle type. Each system has advantages and disadvantages that influence its viability as determination method, such as efficiency and ease of use (Hoang, 2016). Concerns about radionuclides in the environment have led to research and development initiatives that have resulted in better and more efficient technology for radionuclide detection and improved environmental sample analysis (Jorge, 2013). Recently, some detection methods have emerged that can be used as potential substitutes of the traditional techniques. Such detection technique is normally through radiations by radiometric methods, and directly counting of their atoms by mass spectrometric method. Other techniques for analysis of radioactive metals do not require sample preparations (Islam, 2018) and therefore are efficient.

3.2.3.1. Radiometric methods

Recently, radiometric methods have been introduced as analytical detection intruments for quantification of radionuclides. Table 9 shows the comparison of performance for the quantification of radionuclides with radiometric methods. Even though radiometric quantification techniques are recently introduced to radionuclides determination, they are mostly used in environmental monitoring of large number radioactive samples for radioactive metals exploration. For trace level radionuclides determination in the environmental samples, the radiometric measurements are not mainly used; perhaps due to the need for a relatively extended counting period. The radiometric quantification techniques which have been used in determination of radionuclides include liquid scintillation counter (LSC) for alpha emitters, alpha (α) spectrometry for alpha emitters, beta (β) spectrometry for beta emitters and gamma (γ) spectrometry for gamma, alpha and beta emitters (Trojanowicz et al., 2018; Pöllänen, 2017; IAEA, 2017).

The γ-spectrometry can be used to determine the quantitative properties of gamma-emitting radionuclides quickly and precisely (Trojanowicz et al., 2018). The γ-spectrometer show vast ability in sequential determination of radionuclides and at times does not require complex sample preparations (Pöllänen, 2017). This makes the technique relatively efficient for radionuclides determination, since no waste will be generated, and no hazardous solvent will be used on the pre-concentration step. Furthermore, this technique also has the ability for periodically monitoring the short-lived emitters radioactive isotopes of noble gases such as ^{135,138}Xe, ^{87,88}Kr, ^{41}Ar as well as ^{137,138}Cs and ^{88}Rb isotopes. For example, various Xe radioisotopes were monitored when determining the gaseous fission product yield from ^{238}U fission (Cassata et al., 2016). Also the determination of ^{137}Cs was reported by many authors (Liu et al., 2014; Dolniak et al., 2019; Vukašinović et al., 2018). Although the techniques possess the requirements of efficient analytical approach, the pre-concentration should be performed for the trace analysis of radioactive materials for accuracy and precision purpose.

Despite the fact that there are different strategies for measurement of radionuclides, for example, proportional counting and α-spectrometry; these techniques usually apply complex procedures that entails a number of separation and purification steps (Trojanowicz et al., 2018). For more information related to strategies for measurement of radionuclides there are a number reviews published on analytical methods for the determination of Sr radionuclides (Vajda and Kim, 2010) or plutonium isotopes (Qiao et al., 2009).

Having mentioned these techniques, γ-spectrometry is the commonly used technique for quantification of both man-made and naturally occurring radionuclides, due to the following reasons: (a) it enable the determination of several radionuclides in a sample at the same time; (b) relatively simple sample preparation; (c) It can also be used to determine radionuclides that do not release gamma radiation directly, depending on concentration of their gamma-emitter decay products (Pöllänen, 2017). The γ-spectrometry technique can be used for determination of trace concentrations of radionuclides such as ^{228}Ra, ^{226}Ra and ^{224}Ra in environmental samples (Guogang and Jing, 2012), and a MDA of about 2-40 mBq L^{-1} can be achieved (Table 9). The MDA could meet the requirement of national regulation limit of 37 or 40 mBq L^{-1} for Ra isotopes as stipulated by WHO. However, due to very limited and less accessibility of gamma ray spectroscopy, the use of gamma ray spectroscopy in trace analysis of radionuclides is rarely reported.

Table 9: Comparison of performance for the determination of radionuclides with radiometric methods.

Radiometric method	Radionuclides	Sample matrix	Performance	Reference
Alpha-Spectroscopy	^{226}Ra	Human	LOD: 0.01 ng L^{-1}	Pöllänen et al., 2017
	^{238}U	Water	LOD: 0.9 µg L^{-1}	Hassan et al., 2016
	^{228}Ra, ^{226}Ra, ^{224}Ra and ^{223}Ra	Water and sediments	MDA: 0.1 mBq L^{-1}	Guogang and Jing., 2012
	240Pu/239Pu	Nuclear waste	LOD: 0.1 mBq L^{-1}	Raeder et al., 2012
Liquid scintillation counter (LSC)	^{226}Ra	Water and sediments	MDA: 10-40 mBq L^{-1}	Guogang and Jing., 2012
	^{90}Sr	Wastewater	LOD: 2.62 Bq g^{-1}	Kołacińska and Trojanowicz, 2014
	^{89}Sr	Water	MDC: 30 mBq L^{-1}	St-Amant et al., 2011
	^{226}Ra	Water	MDC: 2 mBq L^{-1}	St-Amant et al., 2011
Gamma- spectrometry	^{137}Cs	Soil	LOD: 2 kBq m^{-2}	Cresswell et al., 2013

Radiometric method	Radionuclides	Sample matrix	Performance	Reference
	^{228}Ra, ^{226}Ra and ^{224}Ra	Water and sediments	MDA: 2-40 mBq L^{-1}	Guogang and Jing., 2012
	^{208}Tl	Soil	LOD: 3 Bq kg^{-1}	Cresswell et al., 2013

NB: MDA-Minimum detectable activity; LOD-limit of detection

3.2.3.2. Mass spectrometry (MS)

Mass spectrometry (MS) is one of the analytical techniques that can be used for the quantification of radionuclides with different ionization methods. The emergence of using MS for the quantification of radionuclides is almost by definition equivocal with the establishment of elemental MS in the 1980s, when this method was commercialized. Since that time, numerous review papers have been published on the MS determination of radionuclides (Mohammadi et al., 2015; Veyseh and Niazi, 2017 and Niazi, 2017; Trojanowicz et al., 2018). The detection of long-lived radionuclides using mass spectrometry allows for multi-component analysis as well as the determination of transuranic isotopes with significantly improved detection limits (Trojanowicz et al., 2018).

ICP-MS is the most widely used mass spectrometric technique for determining elements and isotope ratios in trace and ultratrace concentration range, with quantitative measurements ranging from 1-10 ng L^{-1}, high linear dynamic range, high precision and accuracy in measurement, and negligible interferences (Veyseh and Niazi, 2017). This technique performs better than other instruments in terms of sensitivity in the direct quantification of elements. ICP-MS is an effective analytical instrument for the determination of very low concentration analytes because it allows for the analysis of metal ions at very high sensitivity.

Solid-state MS techniques like laser ablation ICP-MS, glow discharge MS or secondary ion MS allow the quantification of radionuclides in the solid phase, and give spatial information on radionuclides of interest as indicated by Russell et al. (2014) and Tiong et al. (2017) during the determination of cesium and plutonium isotopes, respectively. However, extraction chromatography resins are used in all of these methods to improve selectivity.

Other form of efficient mass spectrometry is the multi-collector ICP-MS which was used by Trojanowicz et al. (2018) for the trace determination of Pu in aquatic samples. However, the drawback of this technique is the presence of numerous isobaric interfering species, especially different argides, formed whenever argon was used as a plasma gas (Karasiński et al., 2020). Because analyte ions can be formed in different ways, different means of extracting them from a mixture of multiple ions to processing them in specific MS spectrometers can result in considerable changes in detectability or sensitivity, to isobaric interferences (Trojanowicz et al., 2018). Table 10 shows an example of the limit of detection (LOD) values for various radioactive elements obtained from various matrix. Based on the literature, the most widely used method is ICP-MS, and the differences in the resulting LOD values (depending on the sample processing used) can be quite significant. For example, according to the comparison reported for ICP-MS measurements of uranium isotopes, the measured LOD values can range between 0.01 (Chajduk et al., 2012) and 0.27 ng L^{-1} (Veyseh and Niazi, 2017), depending on the sample processing methods.

Table 10: Comparison of limits of detection (LOD) for the determination of radioactive metals with MS methods.

MS method	Radionuclides	Sample matrix	LOD	Reference
Quadrupole ICP-MS	U and Pu	Sediments	0.09 - 1.55 ng mL^{-1}	Tiong et al., 2017
	Cs	Soil	9.1×10^{-17} g g^{-1}	Zhu et al., 2020
	Sr	Soil	2.3 Bq L^{-1}	Takagai et al., 2014
ICP-MS	U	Waste water	0.27 ng L^{-1}	Veyseh and Niazi, 2017
	Sr	Soil	$3.6x10^{-7}$ pg mL^{-1}	Suzuki et al., 2017
	U	Sediments	$7x10^{-9}$ pg mL^{-1}	Diez-Fernández et al., 2020
	Pu	Standard solutions	$0.04\text{-}0.15x10^{-3}$ pg mL^{-1}	Olufson et al., 2016
Accelerator MS	Np	Urine	0.2–0.4 fg L^{-1}	Dai et al., 2015

MS method	Radionuclides	Sample matrix	LOD	Reference
ICP-sector field MS	Cs	Low level nuclear waste	0.05 ng kg^{-1}	Russell et al., 2014
Thermal ionization MS	Pb	Natural water	1µ L^{-1}	Seeger et al., 2017

3.2.4. Analysis of radionuclides by efficient extraction technologies

In the presence of a relatively high concentration of varied (interference) elements, it is difficult to quantify low concentration of radioactive elements directly. Therefore, isolation and pre-concentration procedures are imperative prior to measurement step (Mohammadi, 2015). Sample preparation has always been considered the major step of the analytical procedure due to lots of bottlenecks associated with numerous factors such as tediousness, a high level of manipulation, the possibility of losses and contamination, the use of huge quantities of samples, solvents, and sorbents, and therefore the formation of large quantities of wastes (Mohammadi, 2015). As a result, considerable efforts have been made in recent years to reduce the negative impact of the analytical technique (Oliveira et al., 2015; Janković et al. et al., 2016).

The efficient emerging axes of development of laboratories radionuclides extraction technologies does not only advance the reduction of the sample quantities needed by the analytical laboratory, it also promote the increase of the fastness of the analytical operations (Rassou et al., 2020). Many efficient separation techniques have been applied during radioactive metals analysis in environmental samples including the common class of LLME (i.e., VALLME and DLLME), in addition to BCR sequential extraction, flow system and co-precipitation. The class of LLME technique is of course considered to be among the fundamental characteristics of the most twelve green and efficient analytical chemistry principles (Gałuszka et al., 2013). These essential techniques and methods are to reduce environmental and health hazards. The efficient aspects of these technique stem from the fact that they reduce turnaround times, inexpensive, lower the cost of analysis, offer better performance, produce desired quality of results, and reduces the formation of secondary mixed waste (Jorge, 2013; Bulska and Ruszczyńska, 2017). Using general procedure, these efficient extraction methods have also been used for the analyses of various radionuclides metal ions in different environmental matrix.

LLME is form of LLE considered a very simple and easy approach which reduces extraction solvent to µL volume for the pre-concentration of different metals in different kinds of environmental samples (Veyseh and Niazi, 2017). Unlike a conventional LLE, miniaturized LLME has been used in modern research due to its simplicity, easily modified and high level of efficiency (Khan et al., 2017). It is simple, rapid, inexpensive, and efficient and has a high degree of manipulation (Mohammadi, 2015; Seeger et al., 2017; Veyseh and Niazi, 2017). Its high degree of manipulation can be an advantage when couples with gamma spectroscopy and other analytical technique for simultaneous/sequential determination of radionuclides. LLME is widely used in the isolation and purification of radionuclides in various environmental samples (Sadi, 2016). Due to these advantages, LLME methods has found broad acceptance in various analytical areas, particularly ultra-trace pre-concentration sequential/simultaneous determination of radioactive metals.

3.2.5. Basic principle of conventional LLME

Like described by (Yan, 2018; Borijihan, 2014; Maese, 2015; Rodríguez et al., 2016), in LLME the analytes are extracted from an aqueous matrix into water immiscible low boiling point solvent. The type of matrix and solvent used are optimised to enable selective extraction of the analytes after which the solvent is evaporated and the analytes reconstituted in the sufficiently small amount of solvent. The solvent used is in microliters (µL). The advantage of LLME is the wide variety of solvents and solvent mixtures available to achieve a selective extraction of the analytes using a small volume of solvents. During LLME, micro-liters of an organic solvent is added to the centre of the stirring vortex of the liquid sample (Padrón, 2014). The analytes in the organic solvent which are concentrated due to the direct interaction between the solvent and the aqueous samples is subsequently removed for further treatment. LLME is advanced by high degree of manipulation of its miniaturization techniques such as DLLME (Martins et al., 2014; Pourreza et al., 2015; Rahmani et al., 2016; Seeger et al., 2017), VA-LLME (Wang et al., 2017) and HLLME (Veyseh and Niazi, 2017). The most commonly used solvents for extraction of radionuclides is xylenol orange (XO) (Zolfonoun and Salahinejad, 2013), tributylphosphate (TBP) (Shukla et al., 2020), cetyltrimethylammonium bromide (CTAB) (Zolfonoun and Salahinejad, 2013) and other salts, because of their abilities to react with many metal ions in different oxidation states.

Most common detection techniques coupled LLME during determination of radionuclides is ICP-OES (Mohammad et al., 2015), UV (Zolfonoun and Salahinejad, 2013), ICP-MS (Veyseh and Niazi, 2017, 2017) and LSC (Villar et al., 2015). In trace determination Pa, Knight et al. (2016) used high-purity germanium (HPGe) gamma-ray spectrometry for the analysis of standard sources immediately after LLME the separation process, but the focus was on the development of a simple technique for the preparation of a Pa tracer from a Np standard source. The method provide acceptable loradiochemical yields that are comparable to the other methods, with virtually 100% radiochemical counting source purity. In this method, the of Pa and Np separated based on the selective extraction of Pa by aliphatic primary alcohols, using chromatographic-resin material, and 1-octanol as the extractant. At radioactivity quantities of Pa tracer (14.5 Bq/sample) in typical environmental samples, excellent separation and radiochemical isolation of Pa, as well as recovery of parent Np, were observed. The purity of the Np was determined to be 99.2% in the regions 300.1, 311.9, and 340.5 keV. The yield of Pa was calculated from the 311.9 keV area and found to be 99.1%. This suggested that the approach need to be modified to support higher amount of Np for various uses.

3.2.6. Modifications of the conventional LLME procedure

3.2.6.1. Modified LLME by dispersive solvent

One of the solvent-based pre-concentration techniques that have gained enormous attention and interest during trace analysis of metal ions from environmental samples is DLLME (Wang, 2015; Pérez-Outeiral, 2014; Sadi, 2016). In 2006, DLLME was proposed for the first time (Rezaee et al., 2006). DLLME works by dispersing the extraction solvent in aqueous bulk samples with the help of a disperser solvent. During the development of the cloudy solution, the analytes are allowed to be extracted into fine droplets of extraction solvent. The separated organic phase will be analysed with the appropriate instrument after centrifugation (Hassan et al., 2016). The advantages of this technique include simplicity of operation, rapid extraction, and high-enrichment factors (Leong et al. 2014). Application of DLLME during the analysis of radioactive metals may reduce the cost of using large volumes of organic solvents in conventional solvent extraction. This approach can also be considered environmentally friendly as it would lower the exposure to many of the organic solvents that are known to be chemically toxic (Musarurwa et al., 2019). Moreover, application of DLLME as an efficient sample preparation technique in radioanalytical chemistry holds great potential with dispersive solvents that are capable of extracting more than one radioactive metals each time (Sadi, 2016).

The DLLME technique has been recently applied during trace analysis of radioactive metals (Shukla et al., 2020; Villar, 2015; Bağda, 2015; Sadi, 2016). For extraction of radionuclides, Sadi et al. (2011) created a method for analysing Ra in water samples with LSC detection by employing a de-emulsifier instead of centrifugation for phase separation. Shukla et al. (2020) used DLLME for ultra-trace levels determination of uranium elements in water samples. In his method, uranium present at ultra-trace levels was selectively removed by 60 µL of the extractant tributylphosphate (TBP) in dodecane. The detection limit of uranium was found to be 0.39 ng mL^{-1}, with XRF detection. The developed methodology was further extended to analyse uranium contamination in different water bodies with a great recovery. Same solvent was used by Hasan and Shukla (2003) for extraction of Ce, Cs, Ru, Zr, U and Pu(IV). Also, Orabi et al. (2013) used same solvent for extraction of uranium from slightly acidic solution. Villar et al. (2015) used the same method and solvents with recoveries of 82-119%, but in this case was for extraction of Tc, and using LSC quantification. Mohammad et al. (2015) also described this method coupled to GFAAS using same solvents for determination of Pd from natural water samples. Thus, the technique was further recommended powerful tool to monitor the entry of radionuclides into the environment.

More recently, potential application of DLLME methods for extraction of radioactive nuclides have been reported (Sadi, 2016; Bağda, 2015). As time goes on, some modifications of the original DLLME were developed to eliminate the need for a dispersion solvent or to reduce the amount of dispersion solvent used. Such modified DLLME procedures include effervescence-assisted dispersive liquid-liquid micro-extraction (EA-DLLME) (Borahan et al., 2021), air-assisted dispersive liquid-liquid micro-extraction (AA-DLLME) (Farajzadeh and Mogaddam, 2012), ultrasound- assisted dispersive liquid-liquid micro-extraction (UA-DLLME) (Pirsaheb et al., 2013). However, modifications DLLME during extraction of radionuclides from the environmental samples are not mainly reported. Although DLLME proved a potential during the analysis of radioactive metals, there are yet a mumber of innate weaknesses of DLLME, which limit the technique's use in other areas, and this have led to different attempts or recommendations to improve this technique (Yana et al., 2013; Rykowska et al., 2018). The following issues are frequently mentioned, among others: limits on the extraction solvent, such as having a density larger than water for simple phase separation and forming a cloudy solution in the presence of the disperser solvent. Similarly, another constraint of DLLME lies in the requirements related to the involve the use of complexing reagents (Hassan et al., 2016).

3.2.6.2. Modified LLME by vortex mixing

Vortex-assisted liquid–liquid micro-extraction (VA-LLME) was introduced by Yiantzi et al. (2010) whereby the organic extraction solvent is dispersed into a liquid samples by vortex mixing, which is a strong but gentle emulsification technique. The fine droplets of organic solvent can rapidly extract target analytes from water because of the shorter diffusion distance and larger interfacial area (Zolfonoun and and Salahinejad, 2013). The approach was created to eliminate the need for a disperser solvent in DLLME (Ghasemi and Zolfonoun, 2012). Therefore, the extraction solvent can dispersed into aqueous samples containing any radioactive metal by vortex mixing. This method has been applied for the determination of trace pollutants metal ions in the environmental samples (Chamsaz, 2013). The vortex agitation has the inherent advantages of low cost, overcoming the need of a disperser solvent, and preventing the problem of possible analyte degradation due to a mild emulsification step (Shalash, 2011). Therefore, VA-LLME has been successfully applied to the analysis of different radioactive compounds from several different samples (Bosch and Sánchez, 2014).

Wang et al. (2017) used vortex-assisted liquid-liquid micro-extraction method for pre-concentration of strontium in aqueous samples. In this method, strontium was complexed with 4′,4″(5″)-di-(*tert*-butylcyclohexano)-18-crown-6 in the presence of tetraphenylborate as the counter anion, which improved the association complex's hydrophobicity. Strontium from the organic phase was removed with nitric acid back to liquid solution and quantified by ion chromatography, and the limit of detection for strontium was 0.005 mg L^{-1} under the optimum conditions. On the other hand, recent green VA-LLME method by Ali et al. (2021) was developed for pre-concentration of selenium in natural water and agricultural solid samples. The most important parameters of VA-LLME are the selection of vortexing rate and time. A suitable vortexing rate and time has to be sufficient in order to effectively increase the interaction between the two phases, resulting in high extraction efficiency (Bosch and Sánchez, 2014). Excessive vortexing rate and time may result formation of bubbles, and hence cause samples degradation during a mild emulsification. However, a manual shaking may also be an alternative. Apart from that, another challenging factor is that the vortexting step is time-consuming, quickly becomes tedious and required additional cost (Chrimes, 2016).

3.2.7. Challenges and future aspects

The class of LLME methods is a miniaturized sample pre-concentration techniques that is used for the separation and extraction of analytes can be liked together with various detection techniques in order to achieve a very versatile technique for sequential analysis of radioactive metals. However, one of the most important requirements related is to this technique involve the use of complexing reagents that must selectively bind with the radioactive metals of interest, which however bring an additional expense. Therefore, it is important that the future work must focus of the alternatives that will eliminate this step. Methods such as BCR sequential extraction give unsatisfactory results if the sequential extraction is applied to a small amount of samples compared to when applied to the large amount of samples (Nemati et al., 2011; Sagagi and Imam, 2017). Therefore future work should look at an alternative validated route to obtain satisfactory results when the amount of sample is miniaturized. The major challenge is that most of the LLME configurations currently being used by researchers, extract single element using extractant solvents or organic solvents. Therefore, in the present study, a DESs and natural extractents for the pre-concentration and spectrophotometric determination of radionuclides in environmental samples is proposed.

Various LLME modes modified with DESs, low sample volumes, and natural extractants are sensitive, efficient, and easy to use for the isolation and pre-concentration of trace metals. The challenge is that single radionuclide of interest is extracted at a time, and different solvents are required, which is time consuming and expensive. Thus, future work should have, as its main premises, multiple extraction of radioactive elements during LLME technique. This goal may be achieved when research efforts are focused on the use single extractants solvents for sequential extraction of analytes, and avoid toxic organic solvents and waste generation. Also, using mass spectrophotometry and radiometric methods as a quantification technique exhibits a low primary and operational cost. The proposed pre-concentration and quantification method gives a low LOD and good R.S.D.

3.2.8. Conclusion

The reviewed analytical techniques show a versatile efficiency characteristics that can be applied to a variety of environmental samples during the analysis of radioactive metals. These methods has been extensively used during the analysis of radionuclides in different environmental matrices. From the reviewed literature, it can be seen that the LLME modes are desirable for the analysis of radioactive metals in environmental matrices due to: (i) its ability to significantly enrich trace radionuclides, (ii) ability to extract multiple radioactive metals at once and (iii) ability to couple with various detection techniques. Similarly, BCR is a well-established extraction procedure for the separation of trace metal content in soils, sediments, and related materials for determination of radioactive metal pollutants in sediment and soil (Tongn et al., 2020). BCR extraction method is user-friendly technique used in trace analysis of radioactive metals sediment samples with negligent errors in the sample treatment and more operationally effective. A is flow system is an efficient. It has limited interventions and a drastic reduction of reagents and sample volumes, hence reducing the formation of waste. Thus, it holds principles of green chemistry and efficient analytical technique. Co-precipitation is the efficient pre-concentration technique for the separation of trace metals from environmental sample matrix. It is a simple, rapid, green technique and hence efficient. Co-precipitation isolates and removes radionuclides present in solution at very low concentration. LLME modes show ability for simultaneous extractions of radioactive substances which reduced time and amount of solvents used. Therefore, the choice of analytical route is of great importance when the method is intended to be applied as a method for determination of radionuclides especially related to the delay time before analysis, sample measurement and sample sealing. Other approaches do not require pre-concentrations, neither other complex sample predations, like gamma spectrometry that is extensively employed in radionuclide determination, and that can also be used even in the quantification of radionuclides that do not emit gamma radiation directly, but based on their gamma-emitter decay products' concentration.

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Chapter 4: Materials and methods

This chapter outlines the general approaches of the methods and materials that have been used for VA-LLME (paper III), DLLME (paper IV), and MASE (paper V).

4.1. General approach of VALLME

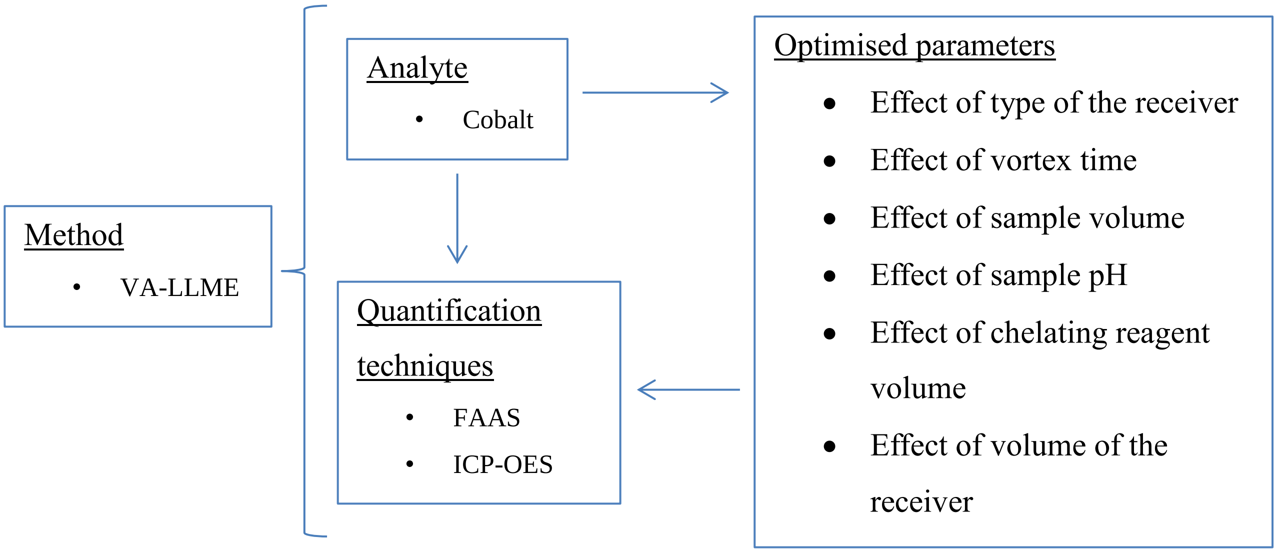

Figure 10: General approach for VALLME during the analysis of cobalt in environmental samples (paper III).

4.2. General approach of DLLME

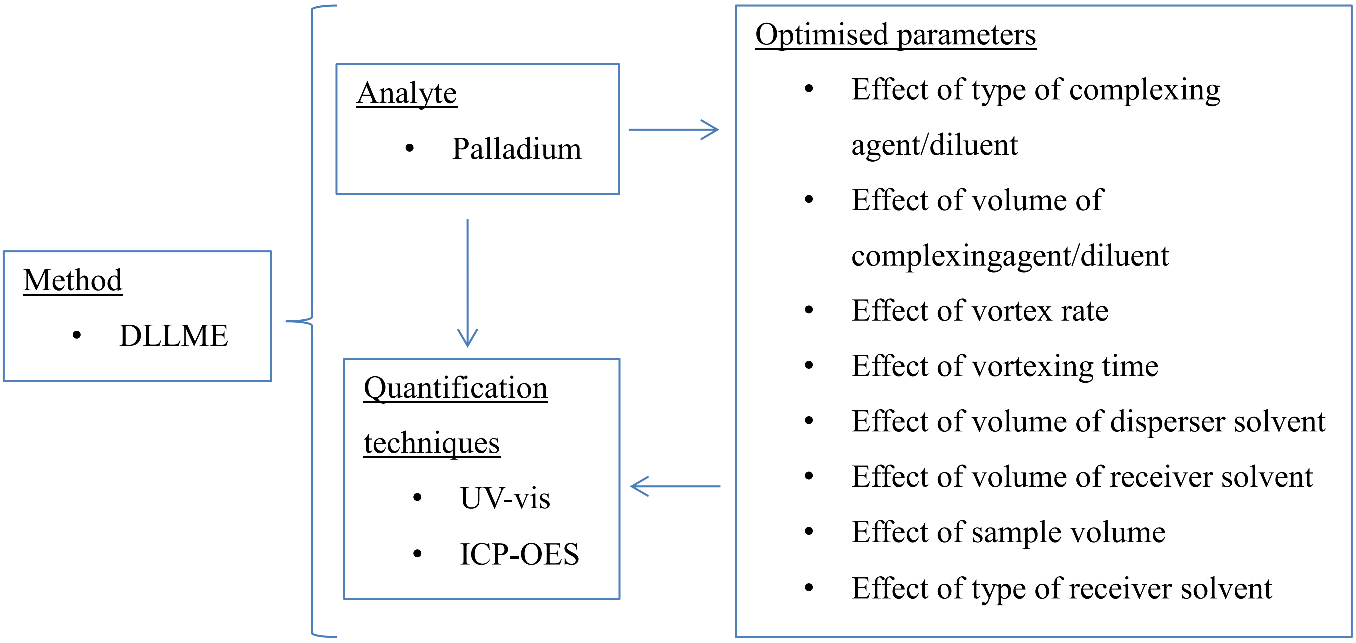

Figure 11: General flow of the DLLME approach during the analysis of cobalt in environmental samples (paper IV).

4.3. General approach of MASE

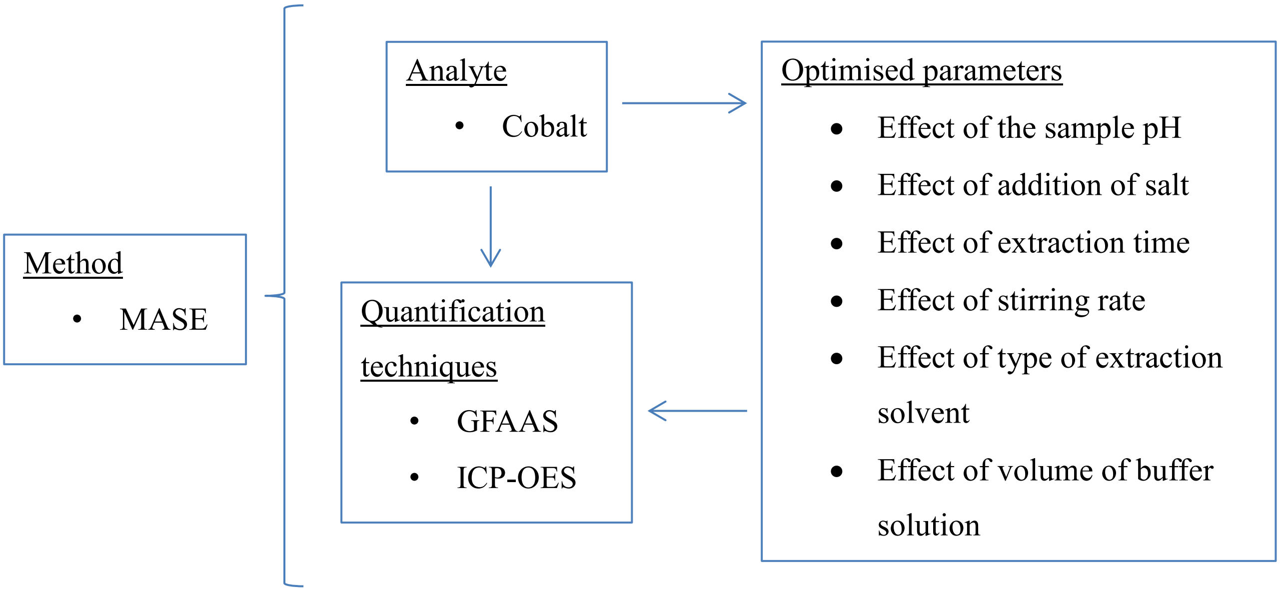

Figure 12: General flow steps for MASE approach for the analysis of cobalt in environmental samples (paper V).

Chapter 5: Prepared manuscripts

This chapter gives the manuscripts that were written during the MSc program.

5.1. Paper III

This paper “Application of vortex assisted liquid-liquid micro-extraction for pre-concentration of cobalt prior to determination by FAAS” detailed the application of vortex assisted liquid-liquid micro-extractionon for pre-concentration cobalt was investigated.

Application of vortex assisted liquid-liquid micro-extraction for pre-concentration of cobalt prior to determination by FAAS

Abstract

The effects of radioactive metals on human health and the natural environment is of concern. Cobalt is one of the element containing radionuclides that are harmful. Vortex-assisted liquid-liquid micro-extraction (VA-LLME) is a recent form of liquid-liquid micro-extraction (LLME) used for the separation and pre-concentration of radioactive analytes. It is combined with multiple detection techniques to create a highly adaptable method for radionuclide chemical analysis. This allows the analysing of a great variety of analytes in very dilute concentrations. Parameters such as pH, type and volume of receiver solvent, and sample volume, were optimized for VA-LLME prior to analysis of cobalt from the environmental samples by flame atomic absorption spectrometry (FAAS). This technique was successfully applied for the removal of cobalt from the waste water treatment plant discharge. The samples were collected randomly in a region suspected to have been exposed to radioactive substances and taken through the pre-treatment steps. The cobalt concentration found in environmetal waste water sample was 102.5 ± 1.0 µg L-1 (n = 3, RSD). The limit of detection (LOD) were 6.1451 µg L^{-1}, while the limit of quantification (LOQ) were 20.4835 µg L^{-1}. The correlation coefficients (R^2) were 0.9943. This method can also be used for the other applications.

Keywords: Cobalt, pre-concentration, VA-LLME, radioactive, radionuclides and toxicity.

5.1.1. Introduction

The presence of harmful elements in various matrices must be determined in order to assess occupational and environmental exposure. The toxicity of radioactive pollutants in the environment has been treated as a major concern in recent years [1, 2]. Although these radioactive metals occur naturally in the environment [3, 4], their significant release into the environment is influenced by human activities [5]. These radionuclides are released through geological and anthropogenic activities such as coal-burning power plants [6, 7], and enter the environment through wastewater, soil and sediment at trace levels [8]. The World Health Organization suggests very little amount of concentration of radioactive elements may be admissible for human consumption [9, 10]. For instance, maximum allowance limit of uranium, radium and thorium drinking water is 0.015 mg L^{-1}, 0.18 Bq L^{-1} and 0.59 Bq L^{-1}, respectively [11-13]. Therefore, due to a small concentration allowed for consumption of radioactive elements, correct precautions should be taken in determining their occurrence in the environment [8].

Cobalt form part of the toxic radionuclides consolidated in different groups of radiation danger [14, 15]. It is commonly found in mafic, ultramafic, sedimentary rocks, fossil fuels, coal, oil and Ni-containing materials [16-18], with its radioactivity proportional to the cobalt content in that certain material [18]. The high uses of cobalt-containing substances in industries inevitably also lead to environmental pollution at all stages of production, recycling and disposal [19]. Furthermore, it poses a potential health risk such as asthma, flushing and allergy; damage the heart, thyroid and liver along with genetic mutations [20]. One of the empirical concerns is that a lot of composite of radioactive elements occur in different matrices at low concentration content [8], and have significance problem in human health and ecosystem [21]. As a result, the need for accurate determination of cobalt at small amount of contents is required and necessary [22].

In various environmental, biological and geological samples, the invention and application of modern, sensitive and precise techniques for pre-concentration, isolation and quantification of cobalt at trace levels is of great importance and interest [20-24]. Various analytical techniques have been used for quantitation of cobalt such as chemiluminescence [25], FAAS [26], inductively coupled plasma mass spectrometry (ICP-MS) [27], inductively coupled plasma optical emission spectrometry (ICP-OES) and neutron activation analysis (NAA) [20]. Among them, FAAS is one of the most promising analytical technique for determination of cobalt due to advantages such as analysis by cost-effective equipment, high efficiency in determining a single element, ability to define the elements in mg g^{-1} concentrations, and the use of electrothermal atomization graphite furnace, which improves detection to ng g^{-1} range [22, 26, 28, 29]. However, the complexity of matrix interferences and trace concentration levels of cobalt in some industrial products and environmental samples make the direct measurement difficult because the analytes are too dilute in such a way that it is very small and cannot be picked or detected by the instrument. Thus, determination of trace elements and contaminants in complex matrices often requires proper sample preparation and/or extraction before the sample is subjected for instrumental analysis.

Various tracditional techniques have also been used for extraction and pre-concentration of cobalt at trace levels including liquid-liquid extraction (LLE) [27]; solid-phase extraction (SPE) [29], and cloud point extraction (CPE) [22, 28]. These techniques have some disadvantages. For example, methods such as liquid-liquid extraction and solid-phase extraction are time-consuming and laboratory intensive [23]. These methods produce low enrichment factors, use a lot of hazardous solvents, and have a lot of sample pre-treatment processes [30-32]. Vortex assisted-liquid-liquid micro-extraction (VA-LLME) is promising for the extraction and pre-concentration of trace elements from environmental samples prior to their quantification due to its simplicity, fastness, accuracy, high enrichment factor, to being a low-cost process, use of less chemical reagents, and it is environmentally friendly [33]. The VA-LLME have been widely used for sequestration of various metal analytes [33-36]. However, its use is rarely reported for the determination of cobalt from the mine discharges. Recent researches focus on minimization of the sample quantities and improve of the fastness of the analytical methods as emerging axes for advanced radiochemical analyses [37]. Therefore, VA-LLME is another form of liquid micro-extraction method which reduces extraction solvent to µL volume.

VA-LLME have been used for the purpose of environmental monitoring; but so far no studies have been reported for the use of this method when coupled with FAAS, using xylenol orange (XO) as chelating ligand and cethyltrimethyl ammonium bromide (CTAB) as cationic surfactants media for the extraction of cobalt from mine discharge. This study aims to actualize the applications of recent VA-LLME procedure with some other manipulations for the rapid and straight forward pre-concentration of cobalt from the environmental samples. Furthermore, it report on the outcome obtained in a study of the VA-LLME and pre-concentration of cobalt, and later analysis by FAAS. The advantage of the method is the sequential extraction of cobalt without the need for any chemometric method. The proposed method is applied to the determination of cobalt from waste water treatment plant discharge.

5.1.2. Materials and methods

5.1.2.1. Chemicals and reagents

All chemicals, including xylenol orange and cethyltrimethyl ammonium bromide, carbon tetrachloride, tributyl phosphate, nitric acid, sodium hydroxide, chloroform, toluene, dichloromethane and ethanol were bought from Sigma-Aldrich (Johannesburg, South Africa). Reagents were of analytical grade. The working solutions of diverse elements were made from the high purity salts of the cations by dissolving appropriate amounts of that reagent in distilled water.

5.1.2.2. Instruments

The quantifications were made using a PerkinElmer PinAAcle 900T atomic absorption spectrometer (PerkinElmer Inc., Shelton, CT, USA), advanced with the intuitive Syngistix™ for AA software for sample analysis, data reporting, and obtaning results. The metal ions analytical instrument was equipped with flame settings operational procedures. The instrument was pre-heated at its maximum allowance temperature, slit of 2 nm and lamp current of 20 mA.

Metrohm model 744 digital pH meter, advanced with a liked glass-calomel electrode, was used for the pH measurements. A Hettich centrifuge model EBA 20 (Oxford, England) was used for phase separation. A GeneMate vortex mixer was used for mixing of solutions during VA-LLME was bought from Sigma-Aldrich (Johannesburg, South Africa).

5.1.2.3. Sampling and sample preparations

Representative water samples were collected from Tswinga wastewater treatment plant (Limpopo, South Africa) for laboratory analysis. The grab samples were collected from discharge stream at different points. The samples collected were placed in laboratory screw cap containers immediately after collection. Samples were acidified with 0.1% (v/v) HNO_3, which was added to sample bottles prior to sampling. The samples was filtered the using a 0.45

µm membrane filter, and adjusted to the optimised pH using HNO_3 or NaOH, and kept for cobalt analysis using VA-LLME for their pre-concentration.

5.1.2.4. VA-LLME procedure

VA-LLME was described by [38] was used with further modifications. Briefly, a 1-9 mL (0.2 mg.L^{-1}) sample or standard solution containing cobalt (pH 2.0-10.0), 3.2 x 10^{-5} mol L^{-1} XO (200-700 µL), and 3.1 x 10^{-5} mol L^{-1} CTAB was transferred into a 15 mL conical-bottom polypropylene centrifuge tube. The volume of 200-800 µL of dichloromethane, toluene, carbon tetrachloride and chloroform were compared as extraction solvents, and the mixture was then vigorously shaken using a vortex agitator for 1-6 min at 3000 rpm. Fine droplets were generated during the vortex process which facilitated mass transfer of Co-XO-CTAB complex from water to the extraction solvent. In order to separate the phases, the solution was centrifuged for 5 min at 4000 rpm, and the aqueous phase was extracted with a transfer pipette. Thereafter, the sedimented phase was dissolved in 500 µL ethanol, and then prepared (Adding 2 mL distilled water, heat in water bath at 65°C with a constant shaking to evaporate organic solvents) for FAAS analysis.

5.1.3. Results and discussion

5.1.3.1. Effect of type of the receiver

The first step in the development of the VA-LLME technique was to select a proper receiver. In VA-LLME, various water-immiscible organic solvents and ionic liquids with densities higher or lower than that of water were investigated [33, 36]. The final solvent was chosen based on a comparison of selectivity, extraction efficiency, water solubility, low toxicity, and the last being in accordance with green analytical chemistry principles [33]. Figure 13 shows different receiver solvents (dichloromethane, toluene, carbontetracloride and chloroform) that were tested to investigate the effect of receiver solvent. The receiver should possess some special properties, such as high extraction capability of the Co-XO-CTAB complex and low solubility in water. From the results, it was observed that chloroform had the highest enrichment factor for the cobalt metal complex. Chloroform has relatively lower solubility in water (10.01 g L^{-1}) as compared to the other organic solvents, like dichloromethane with a solubility of 17.50 g L^{-1}, used during the evaluation of the effect of extraction solvents on enrichment factors.

The complex formed between CTAB-XO and most of metals like cobalt is neutral and non-polar. Thus, it effectively interacts with the non-polar organic solvents such as chloroform through Van der waals forces resulting in high extraction efficiencies [39-40]. Due to its lower solubility in water, chloroform impregnated with Co-XO-CTAB complex, can be easily separated from the aqueous medium during the micro-extraction. Chloroform has a higher density (1.50 g mL^{-1}) than water (1.00 g mL^{-1}) and this facilitates its sedimentation during the centrifugation stage in the VA-LLME method [41]. Furthermore, its density is also higher than that of dichloromethane (1.33 g mL^{-1}), and therefore, chloroform has an edge over dichloromethane during sedimentation on centrifugation. Carbontetrachloride, however, has a higher density (1.59 g mL^{-1}) as well as lower solubility in water (1.20 g L^{-1}) than chloroform, but the enrichment factors obtained when it was used as an extraction solvent were lower than those of chloroform.

The bulky nature of carbontetrachloride probably prevented the close packing of it with the Co-XO-CTAB complex thereby weakening the intermolecular forces between them. This probably hampered the extraction process when carborntetrachloride was used resulting in lower enrichment factors. Toluene on the other hand has a lower density (0.86 g mL^{-1}) as compared to the density of water. That is, it will float on top of the aqueous solution and during the centrifugation step, the Co-XO-CTAB complex will probably be forced to sink back from the toluene to the aqueous solution, hence, no mass transfer will take place between the receiver and the complex formed. Thus, chloroform was selected as the optimum receiver. Many researchers have also used chloroform as the extraction solvent in various pre-concentration methods for the trace analysis of radioactive metals, including cobalt, in different matrices [42-45]. This is because it has been showing high efficiency compared to other extraction solvents.

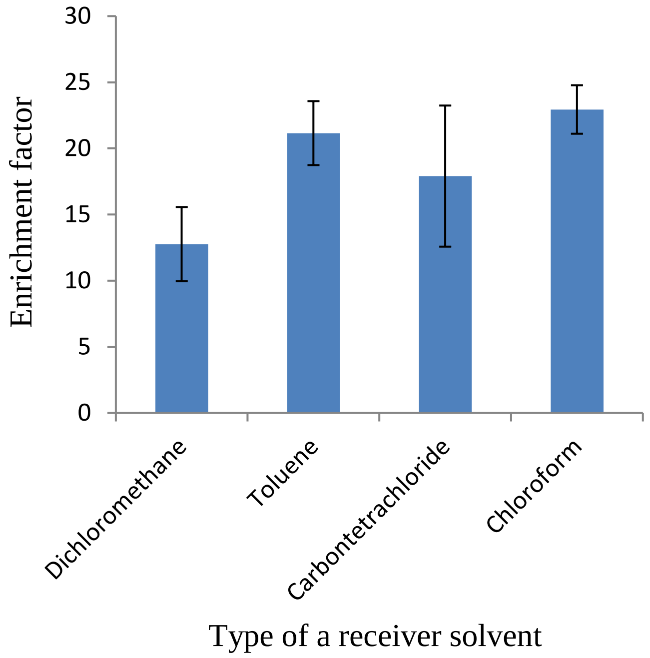

Figure 13: Effect of type of receiver solvent on the enrichment factor of cobalt (n = 3, RSD). Experimental conditions: Sample volume, 5 mL; chelating ligand (XO) volume, 500 µL; receiver volume, 200 µL; sample pH, 4.0; vortex time, 3 min.

5.1.3.2. Effect of vortex time

Contact time is the most important factor and key step that determines whether the VA-LLME is successfully carried out or not. Figure 14 shows the effect of vortex time on the extraction of cobalt that was investigated in the range of 1-6 min, under rotational speed of 3000 rpm. The experimental results showed that the enrichment factors increased from 1 to 2 min, then decreased from 2 to 4 min. From 4 to 6 min there is no significant change in the enrichment factors.

The decrease in the extraction efficiency after 2 min is probably due to formation of bubbles in the mixture as a result of extended agitation time, and thus led to the disintegration/ degradation of the complex formed in the receiver. However, when the vortex time increased from from 4-6 min there was no significant change in the extraction efficiency, the enrichment factors remained nearly constant. This is because in VA-LLME, there is a point where the overall enhancement in extraction rates could reach partition [46, 33], hence there was no change in the extraction efficiency in the interval of 4 to 6 min.

Generally, it is suggested that vortex agitation times that gives high yields of the system should be used, and based on this considerations, 2 min of vortex time was selected as the optimum time, and used for further study. Wang et al. [47] in using VA-LLME, found 4 min as the optimum time; however, their main focus was on disinfectants. On the other hand, Zolfonoun and Salahinejad [38], using similar set up, reported 3 min as the optimum, but their element of pollutant was radioactive thorium. These results are more comparable with 3 min although the reason for this variation could be the difference in the vortex rate.

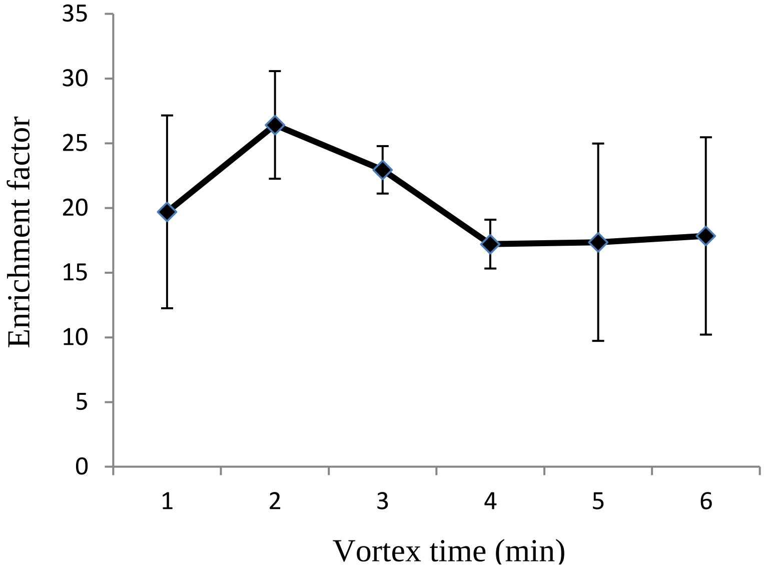

Figure 14: Effect of vortex time on the enrichment factor of cobalt (n = 3, RSD). Experimental conditions: Sample volume, 5 mL; chelating ligand (xylenol orange) volume, 500 µL; receiver volume, 200 µL; sample pH, 4.0; receiver solvent, chloroform.

5.1.3.3. Effect of sample volume

Evaluating the amount of sample required for the method is very important. In this study, the sample volumes were varied between 1 - 9 mL (Figure 15). It was observed that the highest enrichment factors were obtained when an amount of 3 mL was used as the enrichment factors increased from 1-3 min and then decrease above 3 min. The decrease is probably due to the overloading of the XO capacity with the analyte at increasing sample volumes above 3 mL. Furthermore, XO is a complexometric indicator and potentiometric reagent. It can react with many metal ions in different oxidation states, but because XO behaves as a polybasic ligand with two coordinate sites, then when it is overloaded, the characteristics of the resulting chelates are usually complicated [38, 48].

Based on the theoretical considerations, volume of the sample somewhat dependent on the size of the centrifuge vials used. In this way, the necessary turbulent flow conditions easily take place to ensure the generation of tiny sized droplets in samples. From these results, 3 mL of sample was selected as the optimum volume. Similar trend from the volume ranging from 25-250 mL was reported by Soylak and Akkaya [49] for the various elements (Cu, Ni, Cd, Pb, Fe and Co) studied. However, in this case different extraction method was used. Tautkus et al. [50] reported the same trend of decrease of extraction efficiency with increase in volume (ranging between 100 to 200 mL), but their focus was on iron.

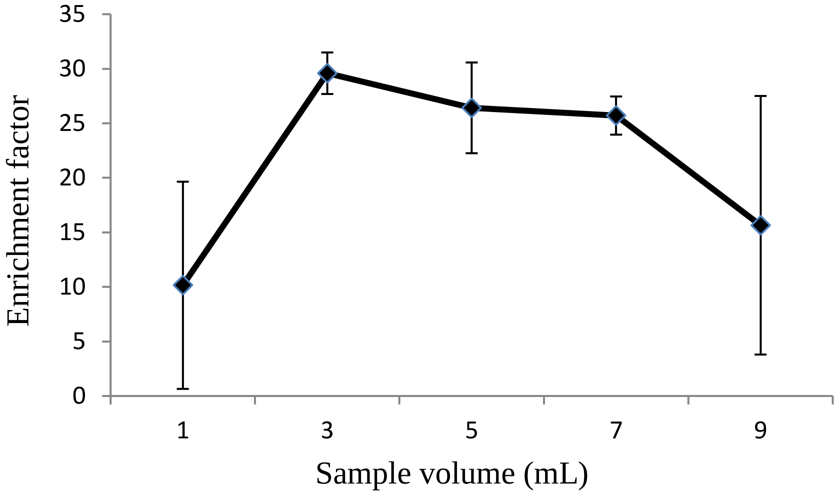

Figure 15: Effect of sample volume on the enrichment factor of cobalt (n = 3, RSD). Experimental conditions: chelating ligand (xylenol orange) volume, 500 µL; receiver volume, 200 µL; sample pH, 4.0; receiver solvent, chloroform; vortex time, 2 min.

5.1.3.4. Effect of sample pH

During the extraction of metal ions with different ionic species, complexing and extraction efficiency are commonly associated with the pH of the extraction system. In many cases, cobalt (II) should be converted into a complex form, using salting agents like xylene orange, to make the extraction process with organic solvents, commonly, chloroform possible. In order to evaluate the favourable complexing and pre-concentration efficiency, the range of pH values from 2.0-10.0 were investigated. From the plot (Figure 16), it was noted that, from pH of 2.0-6.0, the enrichment factors increased with increase in pH, and then decreases as enrichment factors increase from pH 6.0-8.0. This indicate that the Co-XO-CTAB complex is favourable under slightly acidic conditions.

Perhaps this because XO exist as polyprotic complexing agents, which tend to form a complex with metal ions with 2+ ions [51-53]. Moreover, ion with 2+ charges are also regarded as acidic due to the pull of the electrons towards the positive central ion [51]. Therefore, in more acidic or more alkaline solutions, enrichment factors decreased due to the incomplete complex formation and hydrolysis of the complex. Thus, the optimum was at the pH level of 6.0.

Slimani et al. [43] found that cobalt extraction is more active at pH range from 6.5, which is more comparable to the value obtained in this work. The work of Otomo [54] also shows that solutions containing 2+ ions such as Co(II) form complexes with XO at higher pH's - typically around 5.0-6.0, although they can go down to about 3.0. On the other hand, Mustafa and Akkaya [49] work found the optimum pH range for quantitative recovery of cobalt using XO to be 6.0-9.0. Using ethylenediaminetetraacetic acid (EDTA), Narayana et al. [55] reported the optimum Co-EDTA complex solution at pH 5.0-6.0.

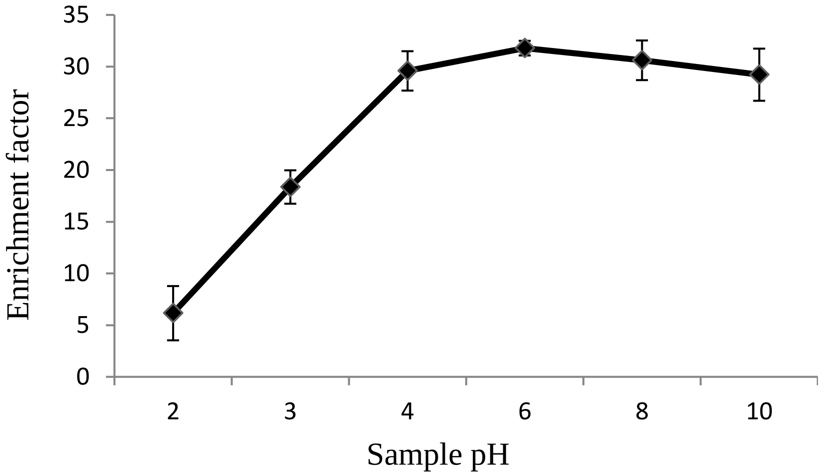

Figure 16: Effect of pH on the enrichment factor of cobalt (n = 3, RSD). Experimental conditions: Chelating ligand (XO) volume, 500 µL; receiver volume, 200 µL; receiver solvent, chloroform; vortex time, 2 min; sample volume, 3 mL.

5.1.3.5. Effect of chelating reagent volume

Chelating agents provide a specific binding site for metals to bind and form a complex. The effect of the volume of the chelating agent was investigated by varying it from 200 to 700 μL while keeping all the other VA-LLME parameters constant. Figure 17 shows the results of the relationship between the enrichment factor and the volume of the chelating agent that were obtained during the investigation. From the results, it was noted that initially, the enrichment factors were increasing with the increase in the volume of the chelating agent (from 200 to 600 μL), thereafter decreased beyond 600 μL.

As volume increased, moles of XO added were increasing and making the stoichiometric amount required for complete reaction corresponds with the moles of cobalt. Thus, the increase in amount of the Co-XO-CTAB complex formed. As a result, increase in enrichment factors was obtained. The decrease in the enrichment factors beyond 600 μL could have been due to the lower amount of CTAB present as an ion pairing agent. This led to the poor interaction of cobalt with XO and CTAB which formed a solid ion-associate which is insoluble in chloroform because chloroform is a non-polar organic solvent that possess a low dielectric constant [40]. Additionally, the reason for this trend is due to the excess of XO since it has a density greater than that of water and is more soluble in chloroform than water. This probably caused the sedimentation of Co-XO-CTAB complex. As a result, reduction in enrichment factors will likely to occur. The volume of 600 μL was taken as the optimum volume to be used in subsequent experiments. Although Jiang et al. [56], Al-Qahtani [57] and Wirosoedarmo et al. [58] used different chelating ligand and volumes; however, they observed similar trends on their experiments.

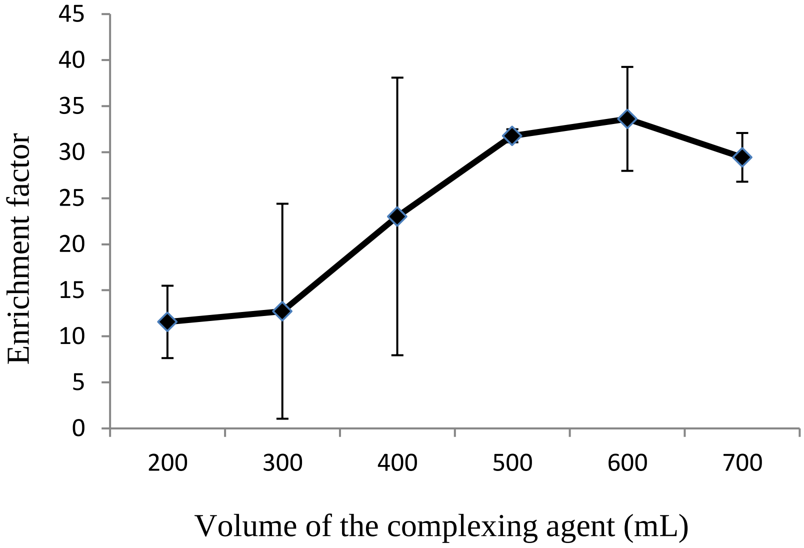

Figure 17: Effect of volume chelating agent on the enrichment factor of cobalt (n = 3, RSD). Experimental conditions: Receiver volume, 200 µL; pH during complex extraction, 4.0; receiver solvent, chloroform; vortex time, 2 min; sample volume, 3 mL; sample pH, 6.0.

5.1.3.6. Effect of volume of the receiver

In this study, different volumes of chloroform from 100 µL to 800 µL were investigated. From the volume of 200 to 300 µL the enrichment of cobalt to the receiver increased whereas from the volume of 300 to 800 µL the enrichment of Co-XO-CTAB complex to chloroform decreased (Figure 18). At smaller volumes of the chloroform lower than 300 µL are not sufficient to properly extract the complex in solution, probably fewer droplets were formed on dispersion causing a reduction in surface area and poor emulsion for the chloroform to get exposed to the Co-XO-CTAB complex, hence gave the lower enrichment factors. When volumes of chloroform higher than 300 µL are used, there is significant dilution of the Co-XO-CTAB complex in the solvent, which decreased the concentration of the complex formed, and consequently reduce the measured enrichment factors. In addition, the decrease of measured enrichment factors is probably due to the overcrowding of the droplets occurred resulting in their overlapping and fusion into larger drops with reduced their surface area.

As a result, the extraction efficiency of chloroform was reduced, and the enrichment factors decreased. This trend tends to follow the fact that at any given sample or material, the concentration is inversely proportional to the volume. Hence higher volumes gave lower enrichment factors. Thus, 300 µL of chloroform was selected as an optimum and used in other experiments. Lemos et al. [21], with their volume ranging from (30 to 70 µL) showed the same trend in their experiments when determining cobalt in vitamin B12 and water samples, but using dispersive liquid-liquid micro-extraction (DLLME) and digital image analysis method. The work of Kozani et al. [59] also investigated the effect of volumes of receiver solvent (ranging from 60 to 140 µL). However, initially, they observed similar trend, but the extraction efficacy remained the same at volumes above the optimum. Although there is a difference in the range of volumes used in variety of studies, the trends of the results are more comparable.

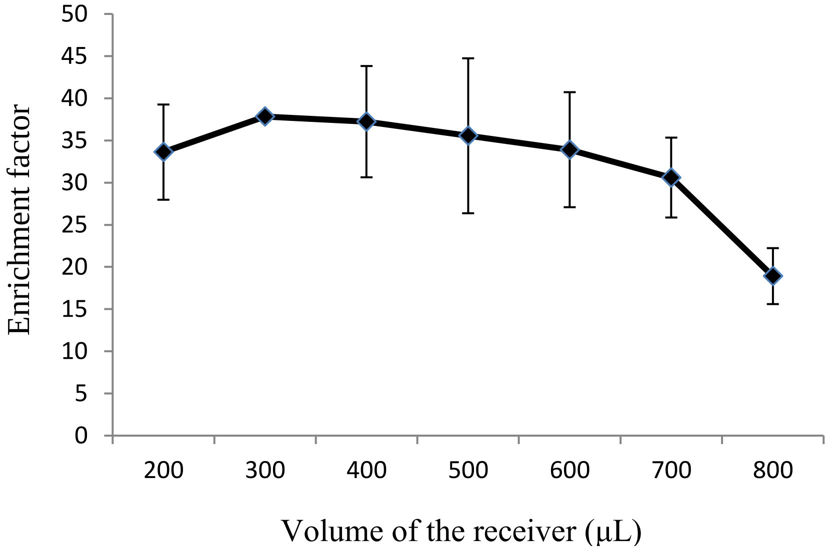

Figure 18: Effect of volume receiver solvent (chloroform) on the enrichment factor of cobalt (n = 3, RSD). Experimental conditions: Receiver solvent, chloroform; vortex time, 2 min; sample volume, 3 mL; sample pH, 6.0; chelating ligand (xylenol orange) volume, 600 µL.

5.1.4. Physico-chemical parameters

The availability and occurrence of metals in environmental waters is strongly dependent on pH. The lower pH levels usually increase the availability and toxicity of most metals. The pH value determined in the Twinga wastewater treatmemt plant (WWTP) was 7.61 and complied with DWAF (1996) and WHO (2011) guidelines for domestic water.

Water quality components such as temperature, electrical conductivity (EC), and total dissolved solids (TDS) are used to describe salinity levels. These components are correlated and generally given by a simple equation: TDS = k EC (in 25℃), where k is the constant

(Taylor et al., 2018). The values measured of these parameters in Twinga WWTP are 471.00 µS cm^{-1}, 24.90 °C and 283.00 mg L^{-1} for EC, Temperature and TDS, respectively.

The temperature is near normal room temperature. The values of electrical conductivity and total dissolved solids measured in Twinga WWTP complied with DWAF [60] and WHO [61] guidelines.

5.1.5. Method validation

The analytical performance of the developed method was investigated before application to real samples in terms of linearity, limit of detection (LOD) and limit of quantification (LOQ). The calibration curve was linear in the range of 0.1–1.0 mg L^{-1} with the regression equation $y = 0.1489C_{Co} + 0.0051$ ($R^2 = 0.9943$), where y is the AAS absorbance and C_{Co} is the cobalt concentration in mg L^{-1} under the optimum conditions of the proposed method. The LOD, defined as $C_L = 3S_B/m$ (where C_L, S_B, and m are the LOD, standard deviation of the blank signal, and slope of the calibration graph, respectively), 6.1451 µg L^{-1}. The LOQ, defined as $C_Q = 10S_B/m$ (where C_Q, S_B, and m are the LOQ, standard deviation of the blank signal, and slope of the calibration graph, respectively), was 20.4835 µg L^{-1}.

To demonstrate the performance and applicability of the developed method, it was also used to extract and quantify cobalt concentration in environmental water samples from the wastewater treatment plant.

The measured cobalt concentration in wastewater treatment plant was 102.5 ± 1.0 µg L^{-1} (n = 3, RSD; results given as the average and relative standard standard deviation). This concentration amount of cobalt maybe attributed largely to agricultural appliances, brick industries and the waste eluted through the drains from hospitals and research laboratories [16-18]. Standard agencies like, WHO or BIS did not recommended any permissible value for cobalt [62]. The maximum and lowest acceptable limit for cobalt is 110 µg L^{-1} according to ambient Water Quality Guidelines for cobalt by a report of British Columbia Report [63].

5.1.6. Conclusion

In this work, VA-LLME have been successfully optimized and used extraction and pre-concentration of cobalt in waste water samples. It is based on the extraction of chelated cobalt from environmental samples using VA-LLME followed by FAAS analysis. It used the vortex agitation to enhance the Co-XO-CTAB complex into organic phase (chloroform). This method solves the issue of analytes volume by re-constitution of the analyte with distilled water prior to determination by FAAS. The developed method proved to be highly effective, efficient, and it gives high enrichment factors. The extraction technique has been validated by pre-concentrating cobalt from waste water discharge. This proves that the method can be further used for other application. The future work of this study will look at the quantification of cobalt analytes using ICP-OES to compare its performance with FAAS during the analysis of cobalt.

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5.2. Paper IV

This paper "Quantification of palladium from the environmental samples using DLLME" outlined the application of DLLME for the pre-concentration of palladium in environmental matrix was investigated.

Pre-concentration of palladium from the environmental samples using DLLME

Abstract

Palladium is part of the platinum group metals (PGMs) that occur naturally at different concentrations in the earth's crust, and it contain a dozen of radioactive isotopes. This element is known to have acute toxicological effects in humans, and its derivatives are potentially carcinogenic in the environment. In this study, the micro-extraction of palladium was studied. The palladium in the environmental samples was pre-concentrated using dispersive liquid-liquid micro-extraction (DLLME) prior to spectroanalytical analysis. Chloroform and acetone were used as receiver solvent and complexing agent/diluent, respectively, for the efficient determination of palladium in aqueous samples. The parameters (sample volume, extraction solvent and volume of complexing agent) that influenced the efficiency of the DLLME technique were optimized using the univariate approach, and the optimum enrichment factors values were 12.7, 14.3, 16.7, 20.0, 20.6, 27.1, and 30.5 for acetone, volume of complexing agent/diluent, vortexing rate, vortexing time, methanol, chloroform and sample volume, respectively.

Keywords: Palladium, radioactive, DLLME, modern analytical techniques, dithizone, pre-concentration.

5.2.1. Introduction

Palladium is a radioactive metal containing long-lived fission products of palladium species that occur in natural environment [1]. Radiation are produced by radioactive metals and despite the fact that they are an unavoidable element of environmental materials (e.g., soil and water), their potential danger to human health has become a serious public concern [2]. Palladium has no known biological role, and all palladium substances are highly toxic and potentially carcinogenic [3, 4]. Thus, due to the increase in use and toxicity of palladium compounds, the removal and the quantification of palladium is of great interest in environmental samples [5, 6]. Radionuclides in environmental samples are often present at very low concentrations [4, 7]. Moreover, the complexity of matrix interferences and small concentration levels of palladium in some industrial by-products and environmental samples make the direct measurement of this metal difficult. Under these challenges, a separation and pre-concentration step is often required prior to the instrumental analysis. Hence, a simple and sensitive extraction method is of primary importance for the successful quantification of palladium traces in environmental samples.

Many extraction methods have been used for the removal of trace elements such as palladium. These includes liquid-phase micro-extraction (LPME) [3, 8, 9], vortex assisted liquid-liquid micro-extraction (VA-LLME) [10], hollow fiber liquid phase micro-extraction (HF-LPME) [11], and single drop micro-extraction (SDME) [11, 12]. Most of these techniques focused on the miniaturization and/or increasing the pre-concentration ability for traditional liquid-liquid micro-extraction (LLME) [13]. These methods are however time consuming, and give unsatisfactory enrichment factors [11]. For example, during the use of SDME, the drop is difficult to control, and also during quick stirring or in the presence of air bubbles, there is possibility of an extractant droplet detaching off the syringe.

On the other hand, HF-LPME also faces several pitfalls. One of them is that, this process mostly work at high stirring rates and applies to samples containing dissolved solids or complicated matrices [14, 15]. Its disadvantage involves potential contamination when holding the fiber and a reliance on hollow fiber manufacturers [14, 15]. In order to avoid these pitfalls, dispersive liquid liquid micro-extraction (DLLME) was developed in 2006 as a simple, fast, and reliant analytical technique that uses small volume of organic solvents [14]. This method has been widely used for various applications [11, 16-18]. However, it has not been used mostly for the removal of palladium from soil sample which is the basic matrix of interest in this study.

As a result of the difficulty in achieving the micro-volume of extraction solvent to the necessary volume needed for the instrument, the coupling of pre-concentration techniques with UV-vis spectrophotometry has been recently used as the alternative [14, 19-21]. This problem has been sometimes solved by evaporation to dryness of the organic phase, dilution or by making use of special instrumentation [18, 21-23]. A lot have been done in determination for identification and quantification of various metal groups which include platinum group metals using UV-vis [24-26], but very little has been done on the identification and quantification of palladium in soil samples.

The use of chelating reagent during extraction of radioactive metal has been recommended for improving the extraction efficiency of organic solvents [27-33]. Chelating reagent has porous crystalline components assembled by the bonding of metal ions with coordination or complex compounds consisting of a large molecule(s) [34, 35]. Chelating reagents have flexible and porous structures that allow incoming molecules to move into the bulk structure, and the shape and size of the pores enhance the selectivity of the incoming substance that may be adsorbed. The selectivity of different chelating reagents is achieved by careful monitoring of the experimental conditions [24, 26], and this has allowed several pre-concentration processes to be carried out. Chelating reagents such as α-furildioxime [3], thiosemicarbazones [36] and nheterocyclic carbenes [37] have been successfully used for the extraction and determination of palladium in different samples. The commonly used chelating reagent is dithizone (H_2Dz, 1,5-diphenylcarbazone) [38]. It has been used for different applications in research including during extraction of cadmium by SDME in environmetal samples [39]. However the utility of dithizone for extraction of palladium is reported rarely. Dithizone can form a stable complex with most metals such as palladium under special conditions, as a result of its –SH and –NH– functional groups [38]. Hence this study actualizes its ability to chelate palladium to enhance good enrichment factors.

The aim of this study is to develop a simple and inexpensive method for analysis of palladium at low level concentration by DLLME. In this way, increase of the cost as a result of the special instrumentation may be avoided. In order to develop the optimum experimental conditions, several experimental parameters were optimised.

5.2.2. Material and methods

5.2.2.1. Chemicals and reagents

All dilute solutions were made using distilled water. All chemicals used for the experiment were analytical grade and were purchased from Sigma-Aldrich (Johannesburg, South Africa). This include palladium standard stock solution, ethanol, hydrochloric acid, sulphuric acid, hydrogen peroxide, nitric acid, acetone, methanol, tributyl phosphate (TBP), hexane, chloroform, dichloromethane and tetrachlorocarbon.

Reagents such as dithizone, urea, sodium hydroxide and weighing balance were bought from Sigma-Aldrich (Johannesburg, South Africa). Working standard solutions were prepared by serial dilutions of the high purity salts of the cations with distilled water prior to analysis. The type of syringe used for all injections was the Hamilton (USA) Gastight fixed needle syringe with 0.22 gauge cone tip with 100 µL capacities.

5.2.2.2. Instruments

A SpectraMax, M3, UV-vis spectrometer with UltraVision 96 FC well material, ultra-clear wall color**,** micro-volume microplate was used for UV-vis spectra acquisition (PerkinElmer Inc., Shelton, CT, USA). Reduction settings: Wavelength combination: !Lm1; spectrum reduction: Lambda at maximum; start = 200, end = 800; min OD = 0, max OD = 4; temperature = 25°C. Metrohm model 744 digital pH meter, advanced with a combined glass-calomel electrode, was used for the pH adjustments. A Hettich centrifuge model EBA 20 (Oxford, England) was used for phase separation. A GeneMate vortex mixer was used for thorough mixing of solutions bought from Sigma-Aldrich (Johannesburg, South Africa).

5.2.2.3. Sampling and sample preparation

Representative soil samples were collected from area suspected to exposure of radioactive metals at the area surrounding Medupi power station (Lephalale). They were immediately put into an air-tight sample bags after collection. Samples were crushed, sieved (homogenized in less than 1-2 mm fine grain size mesh sieve) and then air-dried at room temperature to constant mass in order to remove the moisture. The pH, electrical conductivity (EC) and other physic-chemical propaties of the soil slurry were measured with a pH multi-meter at 1:5 (w/v) ratio soil to water.

5.2.2.4. Acid digestion of the solid samples

Approximately, 0.5 g of samples was transfered in beaker contaning 25 mL aqua regia (5 mL HNO_3 and 15 mL HCI) and heated to dryness on a heating mentle; then 20 mL of 0.1% (v/v) HNO_3 was added into the beaker. The solution was filtered through Whatman No. 42 filter paper into a 250 mL volumetric flask and topped up to the mark using distilled water, and kept for analysis using DLLME.

5.2.2.5. DLLME procedure

All experiments were performed at room temperature using previously published method by Perez-Outeiral et al. [13]. Succinctly, micro-extraction was achieved in a centrifuge tube containing 4.5-10.5 mL of 0.3 mg L^{-1} sample at pH 3.0, and 500-2250 µL of disperser solvent (methanol). A volume of 150 μL of dithizone (34 mg L^{-1}) (chelating reagent) in 150-1000 µL of receiver solvent (tributyl phosphate, hexane, chloroform, dichloromethane and tetrachlorocarbon) was rapidly injected in the solution with Hamilton syringe. The mixture was gently shaken for 0.5-5 min. The hazy solution was centrifuged at 3500 rpm for 1 min in order to speed up phase separation. The organic phase was removed with a hamilton syringe and transferred to a plastic vial. The analytes were treated with complexing agent/diluent and analysed at 290 nm with UV-vis spectrometer.

5.2.3. Results and discussion

5.2.3.1. Optimisation parameters

5.2.3.1.1. Effect of type of complexing agent/diluent

As one of the miniaturized sample pre-treatment method, the volume of the resultant sample was in micro volume. To realize the hyphenation, proper dilution was necessary, which would affect the enhancement factors. Hence, there was a need to optimise the type of diluent used for complexation of palladium from after DLLME procedure. Therefore, attempts were made to find out the suitable complexing agent/diluent among ethanol, urea+HCL, acetone, HCL+ H_2O_2 and HNO_3 (Figure 19).

From the results, it is observed that acetone has maximum enrichment factor, followed by ethanol, HNO_3, urea+HCL, and HCL+H_2O_2 having given the lowest enrichment factor.

Acetone showed higher enrichment factor due to that acetone act as a polar aprotic solvent in various organic reactions. Therefore, during its reaction with metal ions, the lone pairs of the carbonyl group bonded to two hydrocarbon groups' which act as hydrogen bond acceptors accompanied by proton elimination and rearrangement of acetone molecule, leading to the formation of various acetonyl metal (palladium) complexes. Ultimately, this result in formation of possible structures which are UV-active due to the presence of the double bonds, thereby, high enrichment factors were favoured. Moreover, acetone acts as a high-reactive moiety towards palladium carboxylates, and coordination of acetonyl via the carbon atom of the enolate group which favours formation of stable complex [40]. Furthermore, acetone has an obvious sensitization to the spectrophotometric determination, which contributed to the high sensitivity and enrichment factor, as was illustrated by Wen et al. [39].

Diluent such as HNO_3 is monoprotic acid, which completely ionizes into hydronium (H_3O^+) and nitrate (NO_3^-) ions in most reactions, and a powerful oxidizing agent. Its reaction promotes the preferential adsorption of OH^- or H_3O^+ ions at the interface. Therefore, when it react with charged target analytes like palladium species, this may result in electrostatic attraction (or repulsion depending on the charge) between the analyte and the complex interface, thereby affecting enrichment factors [41]. On the other hand, diluent such as ethanol has only two unique forms of bonding between its constituent atoms. The nonpolar covalent bonds are usually formed between hydrogen and carbon atoms. The bonds between hydrogen and oxygen, as well as carbon and oxygen, are polar covalent bonds. Therefore, the reaction between palladium and ethanol is a nonpolar interaction, and electronegativity values of the two atoms are not considerably different in a nonpolar covalent bond, therefore they share electrons equally. When reacts with palladium it gives hydrogen gas and palladium ethoxide as the final product. Hydrogen has an electronegativity of 2.20, while carbon has an electronegativity of 2.55; as a result, the electronegativity difference between hydrogen and carbon is 0.35, which is insufficient to form a polar covalent bond [41]. Therefore, acetone was the optimum complexing agent/diluent that was used in subsequent experiments. Wen et al. [39] also found acetone giving good enrichment factors over other complexing agent/diluent such as methanol, ethanol and acetonitrile that were investigated. However, their focus was on cadmium. Bahadir et al. [11] diluted palladium analytes using nitric acid-methanol solution. Gouda et al. [21] and Kozani et al. [3] successful used ethanol as a diluent for analysis of palladium and thorium, respectively. However, no variations of diluents were optimised.

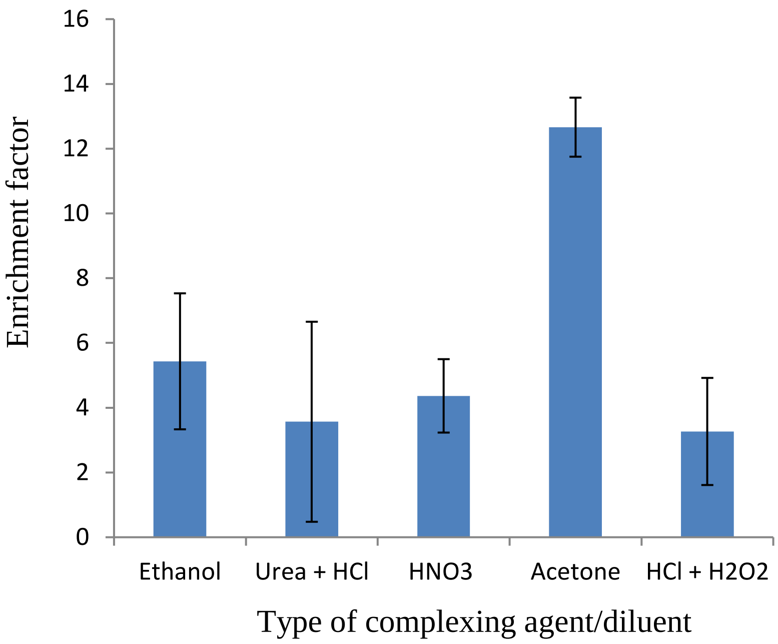

Figure 19: Effect of type of complexing/diluent on the enrichment factor of palladium (n = 3, SD). Experimental conditions: Sample volume, 7.5 mL; type of receiver, chloroform; volume of receiver, 200 µL; vortex time, 3 min; volume of dispenser solvent (methanol), 300 µL; volume of complexing/diluent agent, 1.5 mL; vortex rate, 3500 rpm.

5.2.3.1.2. Effect of volume of complexingagent/diluent

During complexation, an adequate amount of acetone should be added palladium metal to ensure that all the palladium species in the samples are converted to form a complex. The effect of the volume of the complexing agent/diluent was investigated by varying the volumes of acetone between 200-1500 µL while keeping all the other DLLME parameter constant (Figure 20). From the results, it was observed that the maximum enrichment was obtained when the volume of acetone was 600 µL and this was taken as the optimum volume of the complexing/diluent to be used in subsequent experiments. At the optimum volume of 600 µL, the stoichiometric amount of the acetone required for complete complexation with the palladium species (mostly Pd (II)) would have been added, resulting in higher enrichment factors.

At volumes lower than the optimum, the moles of acetone added were less than the stoichiometric amount required for complete the compexation. As a result lower enrichment factors were obtained. When the volume of acetone exceeded the optimum, there was a general decrease in enrichment factor with an increase in the volume of acetone. This is expected to be the case according to Le Chateliar's principle. The increase in volume favours the dissociation of the complex formed thereby causing a decrease in the palladium complex enrichment factors. For analysis of palladium, Ezoddin et al. [42] and Kozani et al. [3] successfully used 100 µL and 200 µL of ethanol, respectively, as complexing agent/diluent. The variation in volumes is probably due to different volume of analytes used. On the other hand, Chamsaz et al. [43] used 500 µL of ethanol to complex/dilute the samples for UV-vis analysis. Also, Bahadir et al. [11] used complexed/diluted palladium analytes with 500 µL using nitric acid-methanol solution. These volumes are comparable to the optimum obtained in this study.

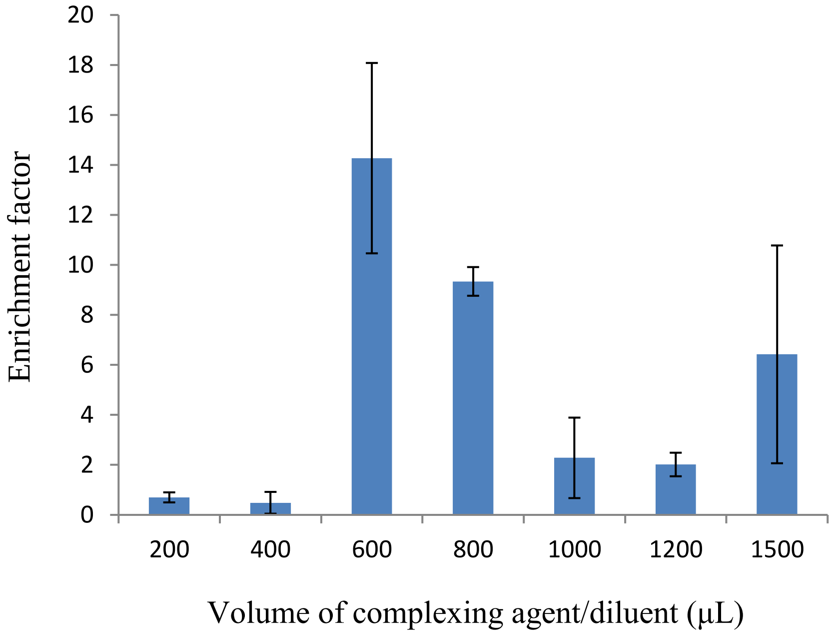

Figure 20: Effect of volume of complexing/diluent (acetone) agent on the enrichment factor of palladium (n = 3, SD). Experimental conditions: Sample volume, 7.5 mL; type of receiver, chloroform; volume of receiver, 200 µL; vortex time, 3 min; volume of dispenser solvent (methanol), 300 µL; vortex rate, 3500 rpm; type of complexing/diluent agent, acetone.

5.2.3.1.3. Effect of vortex rate

In order to realize complete extraction, the effect of vortexing rate on the enrichment factor of palladium was investigated in the range of 1000-3500 rpm. The effect of vortexing rate on enrichment factor of palladium is illustrated in Figure 21. It was noticed that the enrichment factors increased with increasing vortexing rate, reaching plateau values at 2000 rpm. A further increase of the vortaxing time led to a decline of the enrichment factors.

At low vortexing speeds, there was a lower collision rate between the molecules of the atoms, and the sizes of droplets are still big enough, which result to an increase in the interfacial area available for mass transfer, hence increased enrichment factors was obtained. Contrary to that, during emulsion formation, a high vertexing rate will enhance Reynolds number and provide a turbulent flow regime in the extraction vial, size of droplets will be reduced due to high collision speed and bonds breaking due to vibrations. This leads to the small size of droplets and/or small density difference between the two phases that result in low sedimentation rate [44], and consequently result in decrease of enrichment factors. To obtain high exraction efficiency and good factors, a vortex rate of 2000 rpm was selected for subsequent work. The work of Chamsaz et al. [43] successfully pre-concentrated cadmium at 2800 rpm vertex rate.

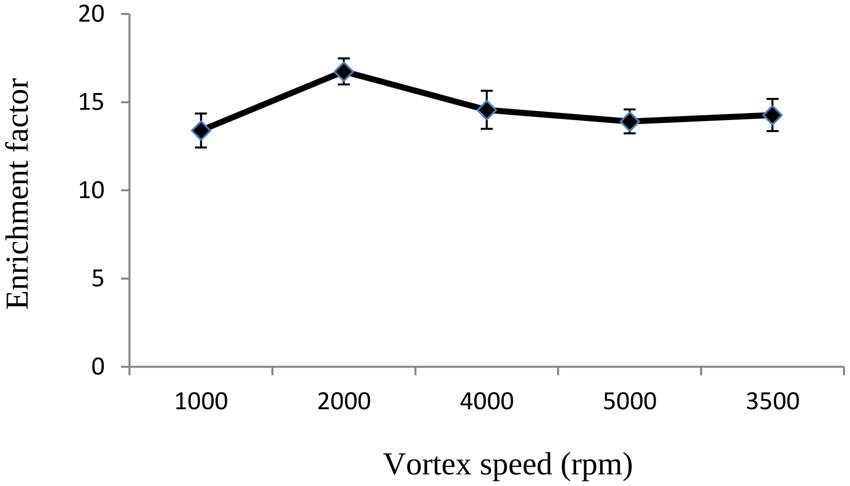

Figure 21: Effect of vortex rate agent on the enrichment factor of palladium (n = 3, SD). Experimental conditions: Sample volume, 7.5 mL; type of receiver, chloroform; volume of receiver, 200 µL; vortex time, 3 min; volume of dispernser solvent (methanol), 300; type of complexing/diluent agent, acetone; volume of complexing/diluent (acetone), 600 µL.

5.2.3.1.4. Effect of vortexing time

Contact time is the most important factor to enhance extraction efficiency in a DLLME by facilitation of the dispersion of the reciever solvent into aqueous solution. Figure 22 shows the effect of vortex time on the extraction of palladium that was investigated in the range of 0.5-5 min, in rotational speed 2 000 rpm. Initially, enrichment factors increased, and then decreased after 2 min. The results showed that maximum enrichment factors were obtained at 2 min. The emulsions created during the vortexing step are thermodynamically unstable, and as time passes [41], the average drop will increase to allow phase separation to occur when the emulsion is left to rest. Short vortex time may enhance enough interactions between droplets and stabilize the emulsion formed, resulting in a slow phase separation in aqueous phase and mass transfer of palladium at the interface. This will ultimatly result in high enrichment factors.

Long vortex times are likely to alter mass transfer processes, as diffusion coefficients may be affected due to the changes in the structural bonds of the molecules, leading the formed molecules to lose energy, as a result the molecule disintegrate. Moreover, long vortex time increases the speed of the mixture leading to the evaporation of the receiver solvent as it get exposed to air, ultimately decease the analysis quantity. Therefore, higher enrichment factors were obtained in 2 min and this was taken as the optimum agitation time to be used in subsequent experiments.

Ezoddin et al. [42] used 1 min to ultrasonically pre-concentrate palladium from dust and water samples. Kasa et al. [45], on the other hand, obtained maximum extraction efficiency after 30 second vortex agitation. Chamsaz et al. [43] reached maximum enrichment factor at 6 min. However, their focus was on cadmium. The reason for this variation is probably due to the volume of chelating ligand used that took time to disperse in the solution.

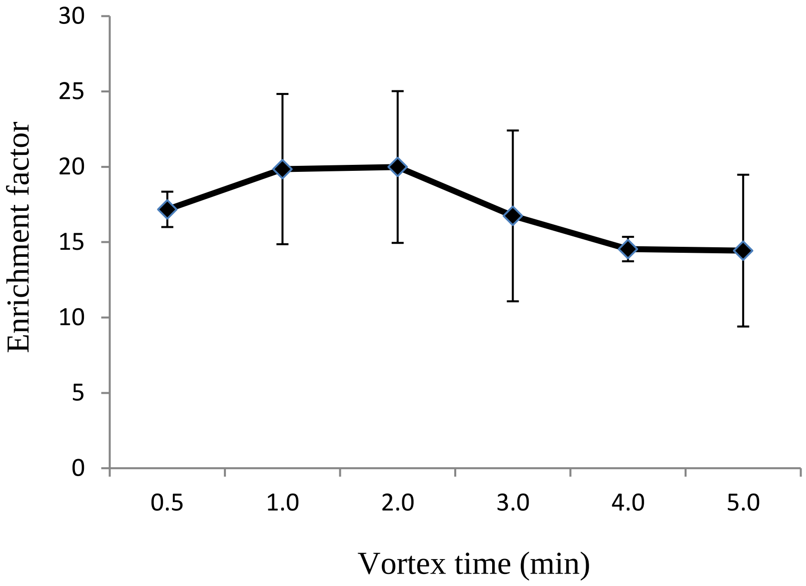

Figure 22: Effect of vortex time on the enrichment factor of palladium (n = 3, SD). Experimental conditions: Sample volume, 7.5 mL; type of receiver, chloroform; volume of receiver, 200 µL; vortex rate, 3500 rpm; volume of dispenser solvent (methanol), 300; type of complexing/diluent agent, acetone; volume of complexing/diluent (acetone), 600 µL.

5.2.3.1.5. Effect of volume of disperser solvent

The influence of the methanol volume on the extraction efficiency was also evaluated. The optimal volume of methanol was investigated by making a series of extractant mixtures by changing the quantity of methanol volume between 500-2250 µL. Figure 23 show the results of the effect of methanol volumes that were investigated. The results showed that 500 µL volume of methanol gives the highest enrichment factor.

The enrichment factors initially decreased with increasing volume. A general decrease in enrichment factors could be associated with the fact that methanol forms stronger interactions (hydrogen bonds) with water than with the receiver solvent. Large volumes of methanol, therefore, made the aqueous medium to be less polar and more soluble to the dithizone-palladium complex. As a result, extraction of the complex from the aqueous medium became more difficult at higher methanol volumes and the enrichment factors are reduced. Therefore, 500 µL was taken as the optimum volume of methanol, and was used in subsequent experiments.

Kozani et al. [3] reported 750 µL of dispenser solvent using almost similar setups investigated in the range of 250-2000 µL. Saçmacl et al. [46] used volume of 400 µL methanol for the extraction of palladium which is also comparable to our optimum. Soylak et al. [47] also reported maximum extraction efficiency at 500 µL of methanol using similar set up. However, their focus was on copper. Between the range of 200-1000 µL investigated, Lemos et al. [16] obtained the highest absorbance at the volume of 600 µL of dispersive solvent in DLLME. Despite the different dispersive solvent and anaylte used (ethanol and cobalt), the volume is comparable to optimum determined in this work.

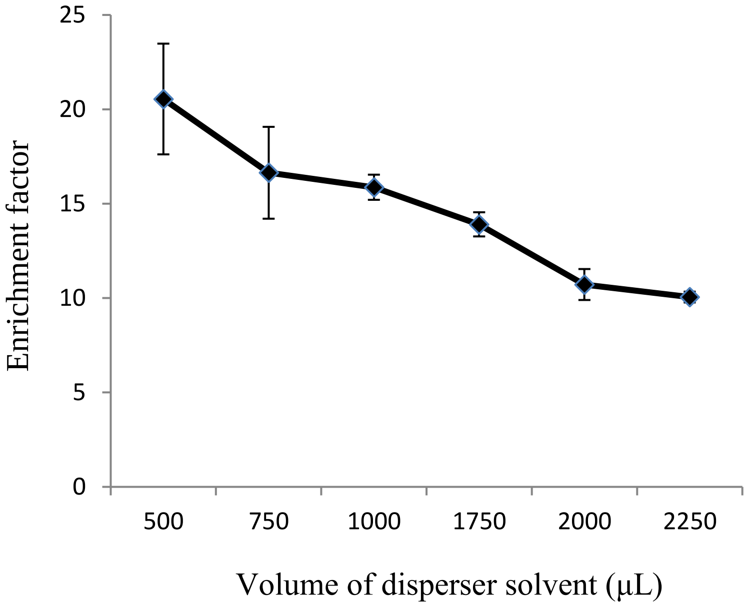

Figure 23: Effect of volume of dispenser solvent (methanol) on the enrichment factor of palladium (n = 3, SD). Experimental conditions: Sample volume, 7.5 mL; type of receiver, chloroform; volume of receiver, 200 µL; vortex time, 3 min; type of complexing/diluent agent, acetone; volume of complexing/diluent (acetone), 600 µL; vortex rate, 3500 rpm.

5.2.3.1.6. Effect of volume of receiver solvent

To determine the optimal volume of receiver solvent, different volumes of receiver solvent were investigated. Volumes of receiver were varied between 150-1000 µL **(**Figure 24). The increase the volume of receiver initially increased the enrichment factors until at 400 µL where it reaches the maximum, then decreased afterwads. Smaller volumes (< 400 µL) of the receiver solvent solvent are not sufficient to properly extract the palladium-dithizone complex in solution. Probably, the droplets formed lack intensity and energy to penetrate the large surface scale of the samples. When quantities of receiver higher than 400 µL are used, there is a significant dilution of the dithizone-palladium complex in the solvent. This decreased the impregnation and, consequently, the measured enrichment factors. The enrichment factors of the complex decreased likewise probably following the Beer's law of relationship between the absorbance and/or concentration and volume. The volume of 400 µL was selected as the optimum for use in the subsequent experiments. Kozani et al. [3] reported similar trend. However, their extraction efficiencies increased with the volume increase of receiver solvent. This was probably due to the difference in range of volumes that was investigated. Saçmacl et al. [46] got an optimum volume of 100 µL that gives high pre-concentration factor using similar set up. This difference is probably due to the receiver solvent volumes (smaller volumes) that were used. Using DLLME, Chaiyamate et al. [18] reported an optimum volume of 300 µL with 1-dodecanol as a receiver solvent, although their focus was on cadmium. This is comparable to the optimum volume that was obtained in this study.

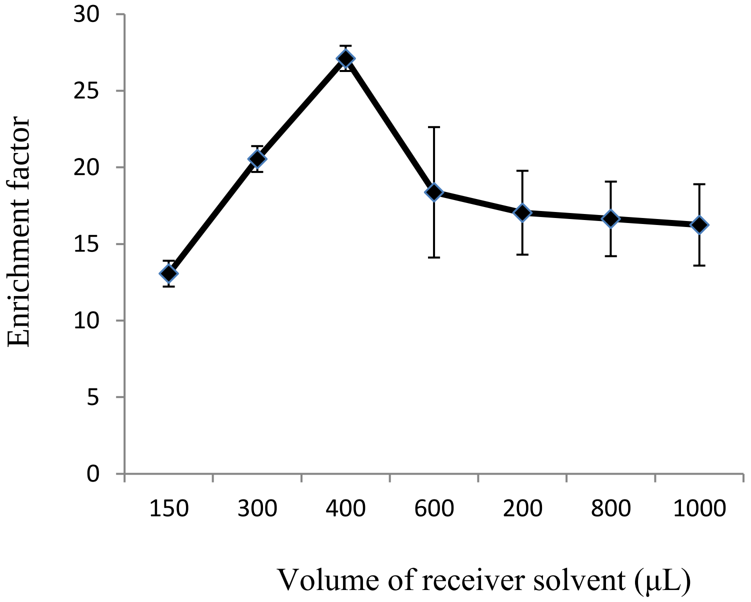

Figure 24: Effect of volume of receiver solvent (chloroform) on the enrichment factor of palladium (n = 3, SD). Experimental conditions: Sample volume, 7.5 mL; type of receiver, chloroform; vortex time, 3 min; type of complexing/diluent agent, acetone; volume of complexing/diluent (acetone), 600 µL; vortex rate, 3500 rpm; volume of dispenser solvent (methanol), 500 µL.

5.2.3.1.7. Effect of sample volume

In the analysis of environmental samples, sample volume is one of the most critical parameters influencing the enrichment factors. Therefore, the effect of sample volume on the enrichment factors of palladium was studied in the range of 4.5-10.5 mL, while other DLLME parameters were kept constant. The enrichment factors of palladium from the different volumes of aqueous solutions are shown in Figure 25. It was found that enrichment factor of palladium generally increase with the increase in sample volume. Maximum enrichment factor was obtained when sample volume was at 10.5 mL. The increase in sample volume increased the number of moles of palladium in the mixture, thereby resulting in an increase in enrichment factors. The trend can be further explained by the high interaction between extraction solvent and metal chelates in higher sample volume. Therefore, sample volume of 10.5 mL was selected for further study. Bahadir et al. [11] reported maximum quantitative extraction of palladium at aqueous sample volume of 10 mL. Pouyan et al. [22] also found that 10 mL sample give maximum extraction efficiency of palladium. This is comparable with optimum volume obtained in this work.

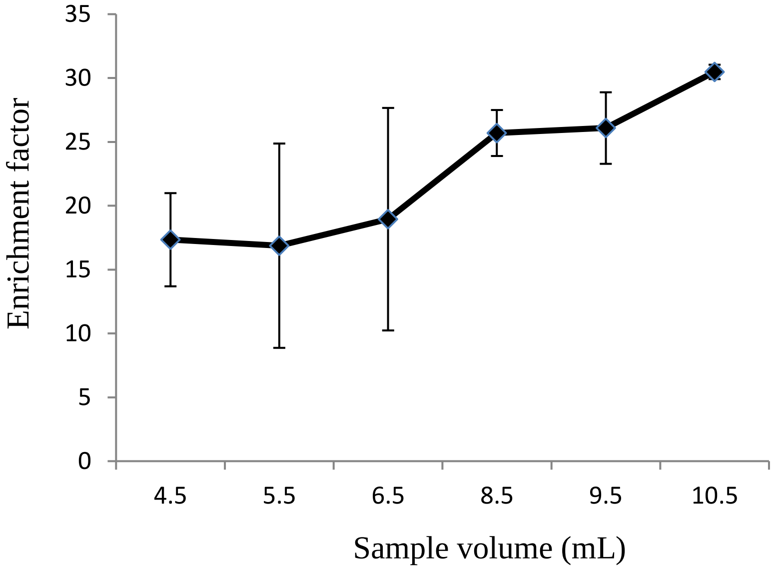

Figure 25: Effect of sample volume on the enrichment factor of palladium (n = 3, SD). Experimental conditions: Type of receiver, chloroform; vortex time, 3 min; type of complexing/diluent agent, acetone; volume of complexing/diluent (acetone), 600 µL; vortex rate, 3500 rpm; volume of dispenser solvent (methanol), 500 µL; volume of receiver solvent (chloroform), 400 µL.

5.2.3.1.8. Effect of type of receiver solvent

It's crucial to choose extraction solvent carefully, paying attention to its qualities. It must be denser than water, be capable of extracting the dithizone-palladium complex, and have low solubility in water. Tetrabutylphosphate, hexane, chloroform, dichloromethane and tetrachlorocarbon were compared for their extraction efficiency (Figure 26). From the results, it was observed that chloroform give the highest enrichment factor followed by dichloromethane, tetrachlorocarbon, TBP, and hexane the least enrichment factor. This was due to the reason that the complex formed between dithizone and palladium is neutral and non-polar.

Chloroform is a non-polar solvent with low dielectric constant, and with relatively lower solubility in water (8.09 g L^{-1}) as compared to the other organic solvents, like dichloromethane with a solubility of 17.5 g L^{-1}, used during the assessment of the effect of receiver solvents on enrichment factor. Thus, it effectively interacts with the non-polar organic solvents such as chloroform through Van der waals forces resulting in high enrichment factor. Solvents such as TPB, however, have a lower density (0.9727 g mL^{-1}) than water (0.9982 g L^{-1}). The bulky nature of TBP probably prevented the close packing of it with the dithizone-palladium complex, thereby weakening the intermolecular forces between them such that sedimentation does not occur during centrifugation. This probably hampered the extraction process when this solvent was used leading to lower enrichment factors. Thus, chloroform was selected as the optimum receiver solvent.

Many researchers have used chloroform as the extraction solvent during the pre-concentration of palladium in different matrices using DLLME. Using similar set up, Kozani et al. [3] compared the effect of carbon tetrachloride, chloroform, and dichloromethane on the extraction of palladium from water samples, and reported that chloroform gave the highest quantitative recovery. Using DLLME, Lemos et al. [16] found that chloroform gave the highest absorbance in an enriched phase over trichloroethylene and dichloromethane. However, their focus was on cobalt metal. Özdemir et al. [48] also used chloroform in DLLME as an extraction solvent and successfully pre-concentrated palladium and gold ions in environmental samples. This is comparable because palladium and cobalt almost share similar characteristics. Bahadir et al. [11] reported that chloroform had high capacity extraction for the pre-concentration of palladium over carbon tetrachloride, dichloromethane, and carbon disulphide.

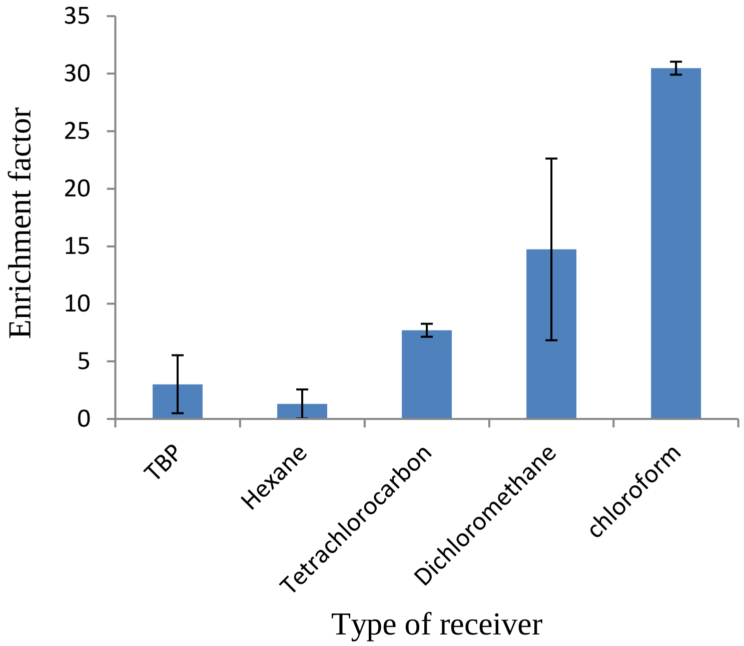

Figure 26: Effect of type of receiver on the enrichment factor of palladium (n = 3, SD). Experimental conditions: Vortex time, 3 min; type of complexing/diluent agent, acetone; volume of complexing/diluent (acetone), 600 µL; vortex rate, 3500 rpm; volume of dispenser solvent (methanol), 500 µL; volume of receiver solvent (chloroform), 400 µL; sample volume, 10.5 mL.

5.2.3.2. Physico-chemical propaties

The pH (9.0), EC (1334.0 µS cm^{-1}), temperature (25.5°C) and total dissolved solids (TDS) (270.0 mg L^{-1}) were obtained in the soil surounding Medupi Power Station. The pH value showed that the soil was alkaline, and this means that the soil was rich in ions, which might be due to the presence of magnesium, sulphate, carbonate, chloride and calcium from limestone and clay. The alkalinity of the soil might be due to the presence of high content of lime and coal fly ash. The EC value also confirms the soil was predominantly loaded with ions.

5.2.5. Conclusion

The impotant DLLME parameters were successfully optimesed prior to analysis of real samples. The studied DLLME scheme offers significant advantages including simplicity, low operation cost, and as well as short extraction time (approximately 3 min). The sample preparation time as well as the consumption of harmful organic solvents was reduced without altering the sensitivity of the method. The effectiveness of the method was improved by using dithizone as a metal chelator reagent which increases the affinity of palladium towards chloroform. This pre-concentration technique proves to be simple, rapid and cost-effective. Since the method validation and application was not achived in this study, future work will attempt to analyse the concentration of palladium in real samples obtained from the proposed sampling area using the proposed procedure for method validation and application. The quantification of palladium in real samples with ICP-OES and GFAAS for the purpose of comparison of detection techniques will be excuted in the future work of this study.

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5.3. Paper V

This paper “The applications of membrane assisted solvent extraction for the analysis of cobalt in environmental samples” outlined pre-concentration of palladium using MASE in environmental matrix was investigated.

The applications of membrane assisted solvent extraction for the analysis of cobalt in environmental samples

Abstract

Amongst radioactive metals, cobalt is considered the most common cause of pollution to the environment. Membrane assisted solvent extraction (MASE) was applied as a pre-concentration and enrichment technique of cobalt from environmental samples. The pre-concentrated cobalt has been detected by graphite furnace atomic absorption spectrometry (GFAAS). Variables affecting MASE comprising sample pH, extraction time, stirring rate, addition of salt, extraction solvent and volume of buffer solution were optimised for the purpose of increasing the extraction efficiency of the method. Results showed significant effect of the optimised parameters for the extraction of cobalt. The method showed high effectiveness of the following optimised conditions: sample pH, 3.5; extraction time, 60 min; stirring rate, 2 rpm; addition of salt, 0 mol L^{-1}; extraction solvent, hexane; and 1.0 mL volume of buffer solution. The R^2 value was 0.9964. Finally, the method has been applied pre-concentration of cobalt from environmental water sample, and the measured concentration was was 12.7 ± 5.6 mg L^{-1} (n =3; RSD). The MASE method has been found sensitive, the limit of detection and quantification were 9.6625 µg L^{-1} and 32.2081 µg L^{-1}, respectively. For these reasons, this method can be further used for other application.

Keywords: Radioactive, Environmental samples, Cobalt, MASE, GFAAS, Pre-concentration, Pollution.

5.3.1. Introduction

Toxic radioactive metals are becoming a human and environmental threat and their level are increasing at alarming rate, due to the growth of the traditional industries and their applications in nuclear sectors [1, 2]. Environmental ecosystems are frequently contaminated as a result of human activities, which occur in parallel with expanding human population, continued urbanization, technological development, and an increase in industrial effluent discharges and waste generation. As a result of human health issues associated with the accumulation of dangerous materials in the food chain, the removal of these contaminants using recent developed technologies has been investigated and evaluated [2-4].

Amongst radioactive metals, cobalt is considered the most common cause of pollution to the environment, because of its several applications and emission of radionuclides (e.g., ^{60}Co, ^{57}Co and ^{59}Co) formed from industries, nuclear power plants and during nuclear accidents [4, 5]. Cobalt is used in a variety of alloys, including superalloys for parts in gas turbine, aviation engines, corrosion resistant alloys, high-speed steels, cemented carbides, magnets and magnetic recording media, petroleum and chemical industry catalysts, and paint and ink drying agents. It is also a target species that must be removed during the maintenance or decommissioning of nuclear reactors [6]. Also, radioactive cobalt is widely utilized as a useful radiation source in several industrial applications that include security screenings, sterilization, food irradiation, and radiation therapy [7, 8]. Cobalt is mainly deposited in the environmental medium normally by leaching of ores from mining industries [9].The wide use of such radionuclides requires efficient decontamination processes for managing radioactive waste [6].

Apart from that, cobalt is a naturally occurring earth metal found in trace levels in the air, plants, soil and water. The main concern is that, when cobalt concentrations are too high, it may become toxic to human health. [10]. Interstitial lung disease, vasodilation, flushing, and cardiomyopathy are among the toxicological effects of excessive cobalt consumption in humans and animals [11-13]. Since one of the routes of incorporation of cobalt into the human body is by ingestion, its determination in environmental samples becomes important. Cobalt concentration levels are very low in other environmental samples, and therefore, simple and sensitive analytical techniques are required to carry out its detection [12]. Recently, a number of methods based on graphite furnace atomic absorption spectrometry (GFAAS) have been developed for cobalt detection due to its advantages such as ease of operation, lower sample requirements, and high sensitivity [10, 14-16]. However, due to interference from other metal ions and its occurrence at a low level in environmental samples, quantification of cobalt might be problematic at times. Prior to the instrumental measurements, a separation and pre-concentration phase is always required in these situations.

Several methods of membrane extraction have been developed in the last decade among the new methodologies [17]. Membrane extraction methods are efficient in reducing solvent usage and allow for the exclusion of matrix components, resulting in high accuracy and reduced matrix effect. In this class of extraction methods, membrane-assisted solvent extraction (MASE) is the most promising pre-concentration technique [18]. During the operation of this method, a dense polypropylene membrane bag is affixed to a metal funnel with a Teflon ring. The funnel and lid are crimped to the top of a standard 20 mL headspace vial. The membrane bag filled with the extraction solvent is immersed in the vial filled with the sample. The appropriate volume of extraction solvent is poured into a membrane bag. It has the advantages of simplicity, solvent-sparing, fully automatable, low sample volume, low cost, high recovery, a good enrichment factor, and its modern technique [19-22].

MASE has been widely used for the extraction of organic compounds (polycyclic aromatic hydrocarbons (PAHs)) from different aqueous matrices [21]. However, it has not been applied for the extraction of inorganics. Therefore, this study aims to attempt to use MASE for extraction of inorganic substance (cobalt) by incorporating the metal chelator and the extractant into the nanocomposite membrane bag, which can rapidly trap cobalt from the environmental matrices.

5.3.2. Experimental

5.3.2.1. Chemicals and instruments

All reagents and solvents used were of analytical quality grade. Stock solutions of 1000 mg L^{-1} of cobalt were purchased from Sigma-Aldrich (Johannesburg, South Africa). Working standard solutions of cobalt were obtained by appropriate dilution of stock solutions. This aqueous solution of cobalt was used for the during the development of MASE and optimization of extraction parameters. Ultrapure water (MilliQ Plus system, Millipore Corp., Bedford) was used for dilutions, and for standard preparations in all experiments. Dithizone, ammonium chloride, sodium chloride, sodium hydroxide, carbon tetrachloride, ammonia, hexane, nitric acid, and toluene were purchased from Sigma-Aldrich (Johannesburg, South Africa). The membrane bags (4 cm length, 0.03 mm thickness, and 6 mm i.d.) were from Gerstel (Mühleim, Germany). The quantification of cobalt in analytes was performed using a graphite furnace equipped PerkinElmer PinAAcle 900T atomic absorption (AA) spectrometer (PerkinElmer Inc., Shelton, CT, USA), advanced with the intuitive Syngistix™ for AA software for sample analysis, quantification of analytes and achieving results.

5.3.2.2. Sampling and real sample preparation

Minerals and river waters were sampled from the area suspected to be exposure to radioactive metals, passed through 0.45-mm cellulose membrane filters (Millipore), and were acidified with 1% (v/v) nitric acid. The samples were stored in a polyethylene container in darkness at 4°C.

5.3.2.3. MASE procedure

The method described by Mañana-López et al. [21] was used but with slight adjustment and modification. Briefly, a 20 mL headspace vial was filled with a mixture of 6 M ammonium chloride buffer solution containing 15 mL of the sample. The membrane bag was attached to a steel funnel with a polytetrafluoroethylene ring introduced into the vial, and a mixture of 800 μL of solvent with 200 μL of dithizone (complexing agent) was added inside the membrane bag. The vial was then closed with a crimp cap, placed inside the stirring oven for 20-60 min at room temperature, and shaken at rate of 0.5-6.0 rpm.

After extraction is complete the vial was removed and the organic solvent was withdrawn and transferred to a 2-mL vial, and analysed with GFAAS system.

5.3.3. Results and discussion

5.3.3.1. Optimization of DLLME parameters

5.3.3.1.1. Effect of the sample pH

The pH of the sample solution is an important parameter for the extraction of metals because metals can exist in different forms at different pH levels. The effect of pH change on the dissociation equilibrium of chemicals in an aqueous sample has been investigated. Apart from this, at a favourable pH metal ions can form complex with the chelating reagent used. Thus analytes were investigated in the pH range from 1.5-8.0 (Figure 27). The enrichment factors increased from pH 1.5 to pH 3.5 then remained constant. After pH 4.5, a decreasing trend was observed which further decreased under basic conditions may be due to the formation of metal hydroxides that reduce the formation of metal-chelate complex in the extraction mixture. This is because of hydroxides bonding with the dithizone, which lowers the bonding availability for cobalt ions. Moreover, at higher pH values, metals exist as their hydroxide, and precipitation of the metals may occur which could have resulted in the decrease of cobalt enrichment factors.

At lower pH values (< 3.5), the less enrichment factors could be due to the competition of the proton with the cobalt ions for reaction with dithizone in the extraction phase [10, 23]. At the pH, 3.5 probably the cobalt metal ions are sufficient enough to exist in cationic form, which makes it easier to be attracted towards the metal chelator to form central atom, hence the high enrichment factors were obtained. The sample pH of 3.5 was therefore selected as an optimum. Researchers such a Sajid et al. [24] found the optimum sample pH of 4.5 during the extraction of cobalt and other metals. In this case, membrane-based inverted liquid–liquid extraction (MILLE) was used as the extraction technique. The work of Kumbasar and Tutkun [25], have also found the optimum pH of 4.5 during cobalt extraction using liquid membranes. These values are in agreement with the optimum sample pH obtained from this study.

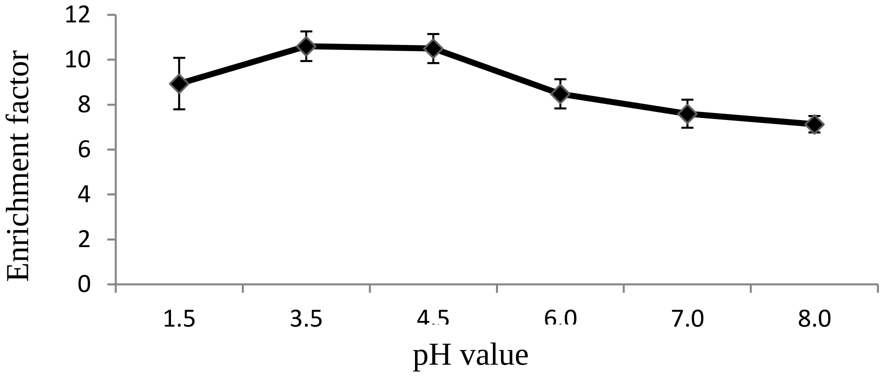

Figure 27: Effect of sample pH on the enrichment factor of cobalt (n = 3, SD). Experimental conditions: cobalt concentration, 0.1 mg L^{-1}; volume of buffer solution, 2 mL; extraction time, 20 min; extraction solvent, acetone; stirring rate, 4 rmp, amount of salt added, 0 mol L^{-1}.

5.3.3.1.2. Effect of addition of salt (sodium chloride)

The salting out effect on the enrichment factors of cobalt was investigated. The amount of salt addition was investigated in the range of 0-4 mol L^{-1} (Figure 28). The results showed that, no significant change was observed on the enrichment factors of cobalt with addition of different amounts of sodium chloride from 0-4 mol L^{-1}. Thus cobalt erichment factors are not sensitive to the sodium chloride salt at the range concentrations investigated. This could be due to the increase in ionic strength of the aqueous solution as sodium chloride concentration increases, whereas the presence of Na^{+} ion decreases the ability of the dithiozone in the extraction phase to form a complex with cobalt ions. As a result, sodium chloride was not used to adjust the ionic strength of next experiments.

Popp et al. [21] and Sajid et al. [24] also found that, the addition of salt to have no effect on the extraction cobalt. Furthermore, the addition of a salt to the aqueous solution can decrease the quantity of solvent (water) to dissolve the cobalt. This happens because of the formation of hydration spheres over ions which are formed from the salt molecules. Based on research by Sorouraddin and Mogaddam [26] addition of sodium chloride into the sample did not have a significant impact on extraction efficiency. Ying [27] also reported the same results, but the focus was on the strontium.

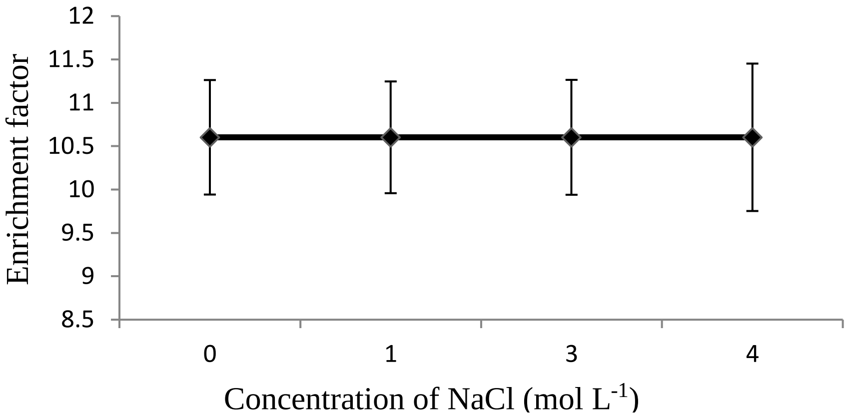

Figure 28: Effect of salt addition (sodium chloride) on the enrichment factor of cobalt (n = 3, SD). Experimental conditions: cobalt concentration, 0.1 mg L^{-1}; volume of buffer solution, 2 mL; extraction time, 20 min; extraction solvent, acetone; stirring rate, 4 rmp, sample pH, 3.5.

5.3.3.1.3. Effect of extraction time

Extraction time was studied in the range of 20-60 min (Figure 29). The results showed that enrichment factors insignificantly increased with the increase in the extraction time. The highest enrichment factors were obtained at the maximum contact time of the investigated range. Meaning that, the longer the contact time, the more the cobalt ions that are extracted into the membrane bag, resulting in high enrichment factors. Sufficient contact time allows the cobalt ions opportunity to penetrate through the membrane pores into the extraction mixture. Thus, 60 min contact time was selected as an optimum extraction time. Mostly during MASE procedure, the extraction time takes about 30 or 60 min [21, 28]. When the partition equilibrium for the analytes is attained, a long extraction period allows for the highest extraction yield. Zante et al. [29] also investigated the effect of the contact time on the extraction of cobalt using ionic membrane; the amount of cobalt extracted followed the same trend as observed in this study, with 60 min reported to be the optimum

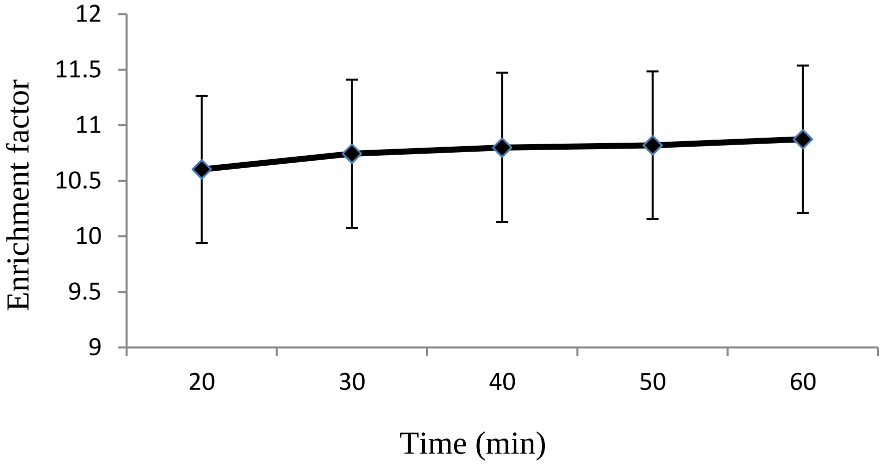

Figure 29: Effect of extraction time on the enrichment factor of cobalt (n = 3, SD). Experimental conditions: cobalt concentration, 0.1 mg L^{-1}; volume of buffer solution, 2 mL; extraction solvent, acetone; stirring rate, 4 rmp, sample pH, 3.5; amount of salt added, 0 mol L^{-1}.

5.3.3.1.4. Effect of stirring rate

In order to improve the transport of the cobalt through the membrane into the organic phase, the sample must be well mixed and the boundary walls of the membrane bag. The stirring rate of sample was varied between 0.5 and 6.0 rpm. Cobalt enrichment factors increased from 0.50 to 2.0 rpm, while enrichment factors decreased when the stirring rate was above 2.0 rpm (Figure 30). The increase in agitation rate would favour the increase of interfacial area and mass transfer coefficient up to some level of agitation, beyond which, further increase in rate may result to the cobalt ions to pass through the membrane pores, thereby lowering the enrichment factors. It is observed that increasing agitation speed from 0.5 to 2.0 rpm increased the enrichment factors. This is due to an increase in volumetric mass transfer coefficient, kLa, in the aqueous feed phase [30]. Further increase in stirring speed beyond 2.0 rpm resulted in a reduction in the enrichment factors. This suggest that vigorous stirring may result cobalt in ions not able to get in through the membrane bag pores, thereby binding with the metal chelating agent, and to an extent that it result in leaching of some cobalt metals ions from the membrane bag. Above 2.0 rpm, the solution is moving fast, as a result cobalt ions pass the membrane pores hence resulting in enrichment factors dropping. Therefore, 2.0 rpm was selected as the optimum stirring rate. Thien et al. [30], and Kumbasar and Tutkun [25] also reported the similar trend during the extraction of cobalt ions using liquid membranes.

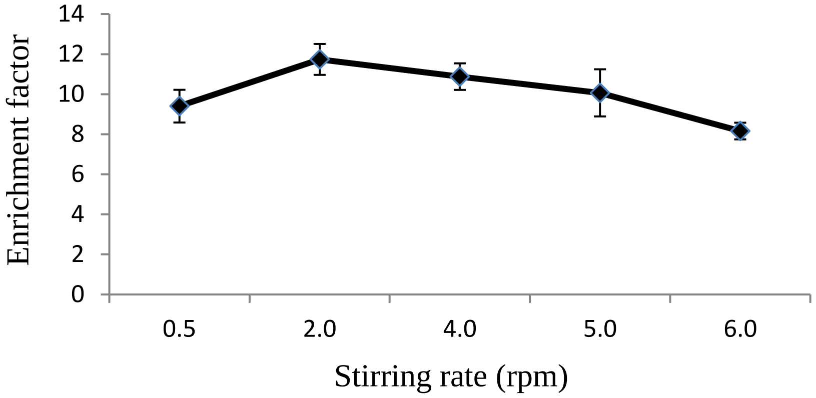

Figure 30: Effect of stirring rate on the enrichment factor of cobalt (n = 3, SD). Experimental conditions: cobalt concentration, 0.1 mg L^{-1}; volume of buffer solution, 2 mL; extraction solvent, acetone; sample pH, 3.5; amount of salt added, 0 mol L^{-1}; extraction time, 60 min.

5.3.3.1.5. Effect of type of extraction solvent

The selection of a suitable extraction solvent to mix with complexing agent to extract cobalt into the mixture is critical in MASE, as the extraction solvent must not deviate/leach from the membrane bag. Also, the cobalt should have a high affinity for the receiver solvent, allowing for an effective concentration in the organic phase to become attainable. In this work, different solvents, namely acetone, hexane, toluene and carbon tetrachloride, were studied. As can be seen from Figure 31, the high enrichment factors results were achieved using hexane and thus it was selected as the optimum solvent to be used in the subsequent experiments. The enrichment factors were in the following order: hexane > acetone > carbon tetrachloride > toluene. This indicated that hexane has high affinity toward cobalt when mixed with metal chelating complex compared to other extraction solvents. Therefore, based on high enrichment factors, hexane was used as an optimum solvent to be used in the subsequent experiments. Hexane is one of the solvents commonly used with MASE technique [21], compared to other solvents such as toluene that contains a π bond with high polarity. This reduces the strengath of the organic properties of extraction solvent and weakens the distribution coefficient of cobalt complex in the organic phase, thus lowering cobalt extraction efficiency. The result is similar to the findings of Wang et al. [31]; whose studies also found that high extraction efficiencies of cobalt are obtained when n-hexane is used.

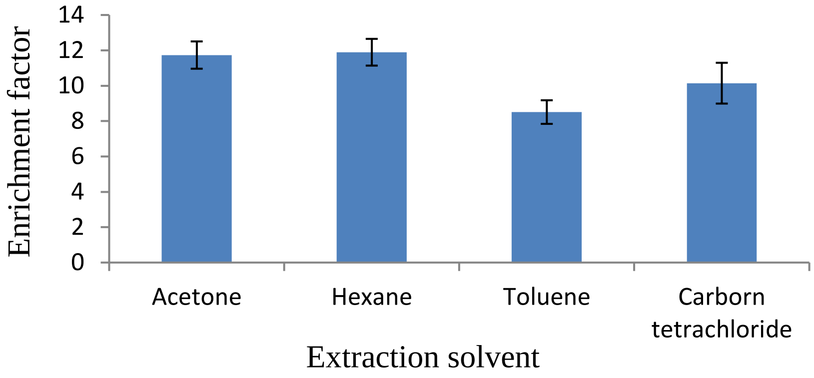

Figure 31: Effect of stirring rate on the enrichment factor of cobalt (n = 3, SD). Experimental conditions: cobalt concentration, 0.1 mg L^{-1}; volume of buffer solution, 2 mL; sample pH, 3.5; amount of salt added, 0 mol L^{-1}; extraction time, 60 min; stirring rate, 2 rmp.

5.3.3.1.6. Effect of volume of buffer solution

The ammonium chloride buffer solution was used to precisely maintain constant sample pH at nearly optimal value [32]. Figure 32 shows the effect of volume of ammonium chloride buffer solution that was investigated in the range of 0.5-4.0 mL. The enrichment factors initially increased then decreased with the increase in the volume of ammonium chloride buffer solution. The decrease in enrichment factors is probably due to the increase in moles of ammonium chloride. At high volume of ammonium chloride precipitation is more likely to occur during fixation which hinders the selectivity of the extraction. Unexpected behavior was observed at volume of 3.0 mL because the enrichment factors increased and then decreased at 4 mL. This may be due to the inferference in the instrument and/or in the samples. Hence a volume of 1.0 mL was selected as an optimum. Hossein and Elnaz [33] used a volume of 1.2 mL acetate/acetic acid buffer solution during the extraction of cobalt metal ions from the environmental samples. Sirotiak et al. [34] used 2.5 mL of ammonium chloride solution, but their focus was on magnesium metal ions.

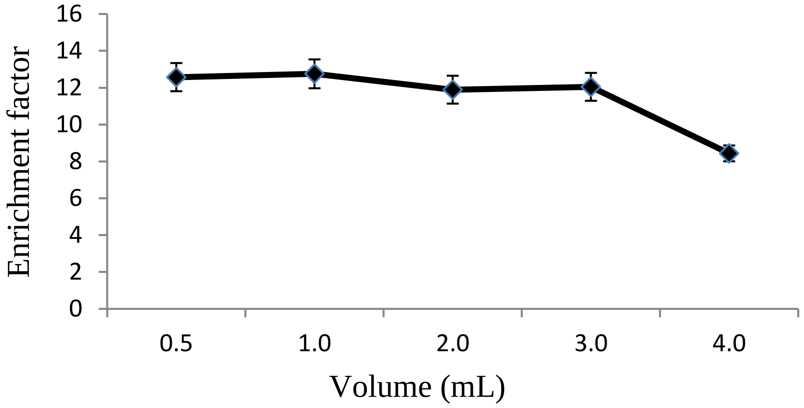

Figure 32: Effect of volume of buffer on the enrichment factor of cobalt (n = 3, SD). Experimental conditions: cobalt concentration, 0.1 mg L^{-1}; sample pH, 3.5; amount of salt added, 0 mol L^{-1}; extraction time, 60 min; stirring rate, 2 rmp; extraction solvent, hexane.

5.3.3.2. Physico-chemical parameters

The pH, total dissolved solids (TDS), electrical conductivity (EC) and temperature of water samples collected from Nandoni dam ware measured. The pH of 8.48 was recorded which is above the neutral pH of 7. This may be due to seasonal effect as sampling was done during the raining period in summer season, during which most of materials and contaminants were flooded in to the dam by the rain. However, the pH value fell within the guidelines of 6–8.50 set by the WHO and accepted by the South African Department of Water Affairs and Forestry [35] for agricultural water, recreation and domestic use.

EC and TDS are water quality parameters which indicate the level of salinity (Jemily et al., 2019). The EC and TDS values measured at Nandoni dam were 139.4 µS cm^{-1} and 83.8 mg L^{-1} respectively. The EC measured was within the maximum allowable limit of 70 mS/m and 600 mS/m, proposed by DWAF [35] and WHO [36], respectively. The TDS which was measured was in compliance with the recommended limit of DWAF [37] for domestic water use 450 mg L^{-1} and higher than the guideline value of (0.4 mg L^{-1}) for use in irrigation. The temperature of the water was 28.9 °C. The dam is open to direct sunlight which increases the temperature of water.

5.3.3.3. Method validation

An analytical curve, with a maximum point of 0.30 mg L^{-1}, was constructed. The developed method was validated before its application to determine cobalt species in real environmental water samples. The following figures of merits were used during the validation process: linear range, linearity, limit of detection (LOD) and limit of quantification (LOQ). The equation of the slope is given by $y = 1.1643C_{Co} + 0.0084$, where y is the AAS signals and C_{Co} is the cobalt concentration in mg L^{-1} under the optimum conditions of the proposed method. The linear range of the developed method was from 0.05 to 0.3 mg L^{-1}. The LOD and LOQ were 9.6625 µg L^{-1} and 32.2081 µg L^{-1}, respectively. The correlation coefficient (R^2) was found to be 0.9964 and therefore the calibration curve can be used for external quantification.

To evaluate the applicability and accuracy of the proposed method, under the optimized condition, the method was used to extract cobalt in real environmental samples from the Nandoni dam. The measured average concentration of cobalt in the Nandoni dam was 12.7 ± 5.6 mg L^{-1} (n =3; RSD). According to ambient Water Quality Guidelines for cobalt by a report of British Columbia Report [38], the maximum acceptable limit for cobalt is 110 µg L^{-1}. Therefore, the measured concentration is in compliance to the maximum allowable limit of cobalt for environmental water quality.

5.3.4. Conclusion

Cobalt was successfully removed from water samples using the MASE process. MASE method is a practical and reliable analytical approach for extracting and pre-concentrating cobalt from environmental water samples prior to GFAAS for quantification. A mixture dithizone and hexane was used to selectively extract and pre-concentrate cobalt ions in the presence of ammonium buffer solution. The method is easy, eco-friendly, and of low cost as it does not need the use of special laboratory equipment or too much of organic solvents and tedious agitations. The mixture of extraction solvent and complexing agent containing cobalt ions can be directly introduced to the analytical instrument analysis at micro-liter level to determine cobalt concentration with no requirement for further treatment. Furthermore, there was no interference effect that was observed.

The validity of this method was confirmed by analysing real water samples from the area expected exposure to radioactivity. This method proved high extraction efficiency of cobalt ions in the environmental samples. Therefore, it can be further used for other applications. The future wotk of this study will attempt to quantify the cobalt in pre-concentrated environrmtal samples using ICP-OES to compare its detection with GFAAS.

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Chapter 6: Conclusion and future work

This chapter gives general conclusions and future work based on the research findings of this work.

6.1. Conclusion

It is difficult to treat and handle radioactive metals because of their uncertainties. Different strategies that attempt to treat radioactive metals for the radiation and protection purposes as criteria for use in exceptional circumstances have been provided in Chapter 2 including the overview of the radioactive waste management, and strategies to treat the trace occurrence of the radioactive metals. Various methods are used for pre-concentration for the trace analysis of radioactive metals in aqueous and solid environmental matrix (paper II and II). These methods have different categories, and their modes of approach differ depending on the type of extraction technique. These extraction methods they all strive to achieve common goal; which is to develop a safe, efficient, simple, rapid, inexpensive, sensitive, and environmental-friendly extraction procedure for trace level concentration determination of in various environmental samples. These goals hold to the principles of green chemistry (paper I). The most recently studies demonstrate high commitment on the development of efficient modern analytical methods which fulfil the principles of green chemistry during the trace analysis of environmental samples. The concept of efficient analytical techniques in area of analytical chemistry continue to grow, and have now comprised of features such as the use of environmentally friendly solvents, shortening of the extraction time, and elimination of tedious steps, the use of ionic liquids and deep eutectic solvents. The application of some of these aspects in DLLME have been reviewed in paper I, for the purpose of adopting to the efficient analytical techniques during the analysis of radioactive metals in environmental samples. The DLLME technique is a miniaturised, modern sample pre-concentration analytical technique that is based on a miscibility and immiscibility of dispersion solvent and extraction solvent in the aqueous environmental samples, respectively. It has been widely used for the pre-concentration of radioactive metals in various environmental samples (paper I and II).

When pre-concentrating radioactive metals in environmental matrix the modifications of extraction system is crucial to increase the effectiveness of the extraction technique. Usually, metal chelators such as dithizone (paper IV and V), and xylenol orange (paper III) are used to enhance the affinity of target metal ions to the receiver solvent. All the parameters that affect MASE, VA-LLME and DLLME should be carefully optimised in order to establish the favourable conditions which the modern analytical technique is effective during the extraction of radioactive metals in environmental samples. DLLME was successfully applied for the pre-concentration of palladium in environmental samples (paper IV). When the analytes are not/or compatible with the instrument, a complexing agent/diluent can be added in order to increase the volume of the analyses for the successful determination by the instrument. The type of complexing agent/diluent can affect the quantification of the radioactive metals; hence its optimisation is of importance. The MASE technique was successfully used for the extraction of cobalt in water and mineral samples (paper V). The MASE method is a practical and reliable analytical technique for the extraction and pre-concentration of cobalt from environmental water samples. The important step in MASE is the selection of the receiver solvent to inject inside the membrane bag. The receiver solvent should not leach into the sample solution. Thus it is imperative to pay attention in this area during the trace analysis of radioactive metals. MASE can be modified with the addition of a buffering solution in order to increase the effectiveness of the analytical technique. VA-LLME was successfully used for the pre-concentration of cobalt in environmental matrix (paper II). Under the optimized conditions, the technique provided acceptable precision, high enrichment factors, and a relatively low limit of detection. Therefore, this method was suitable for the determination of trace radioactive metals in environmental samples.

6.2. Future work

The future work will look in to the following aspects:

- To cary out the the recovery experiments by spiking the samples with different amount of cobalt (paper III and V) and palladium (paper IV) before pre-concentration step to confirm and validate the accuracy of the developed methods.
- To genetrate the figures of merits using standard deviation of the blank signal for the proposed DLLME procedure (paper IV).
- To use gamma ray spectroscopy identify and quantify radionuclides isotopes species such ^{60}Co, ^{57}Co, ^{107}Pd and ^{105}Pd in the pre-concentrated analytes, since the instrument used for this study only give the total element composition. The application of MASE, VA-LLME and DLLME for the removal of other radioactive metals in different matrix, such as water and soil since procedure have been done in only selected metals containing radioisotopes species. Reduce the longer the extraction time in MASE, since a longer time does not comply with the authors' objective of developing a shorter extraction method.
- To eliminate of use of organic solvents in modern analytical technique during analysis of radioactive metals in environmental samples. The application of general procedure of these for the removal of radioactive metals in a large quantity scale.
- To develop a new/improved methods that allows the shorter analysis of solids by GFAAS, as well as coupling methods for determining different chemical forms of these elements with other determination techniques that were not used in this study. The future endeavours should be looking forward for solvents that are less toxic used in pre-concentration techniques as well as cost reduction. Thus, the researchers should direct their new developments towards enhancement of the efficient of pre-concentrations techniques. To utilize the proposed DLLME method to demonstrate its applicability and performance in real soil samples (paper IV).
- To utilize ICP-OES to quantify cobalt and palladium concentration in real samples after application of VA-LLME, DLLME and MASE in paper III, IV and V, respectively.

Appendix

This section gives supplementary data for the manuscripts in this dissertation.

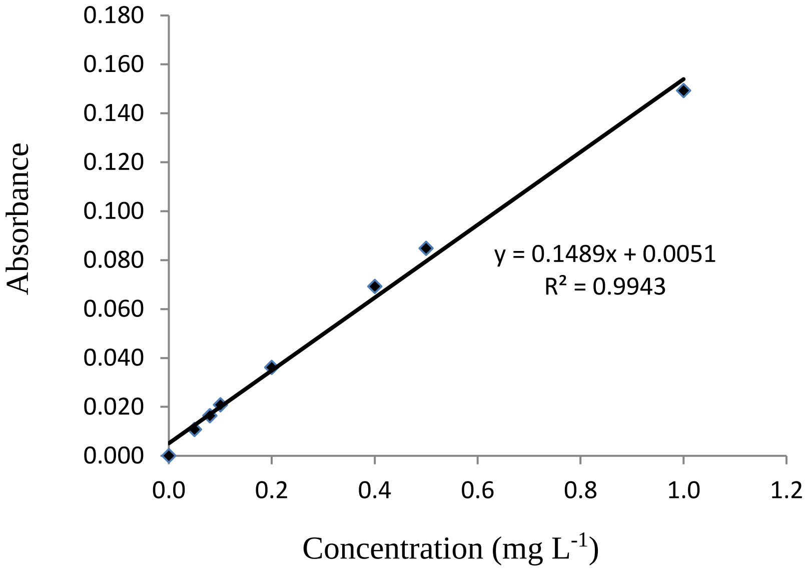

Figure 33: The calibration curve for prepared cobalt standards (paper III).

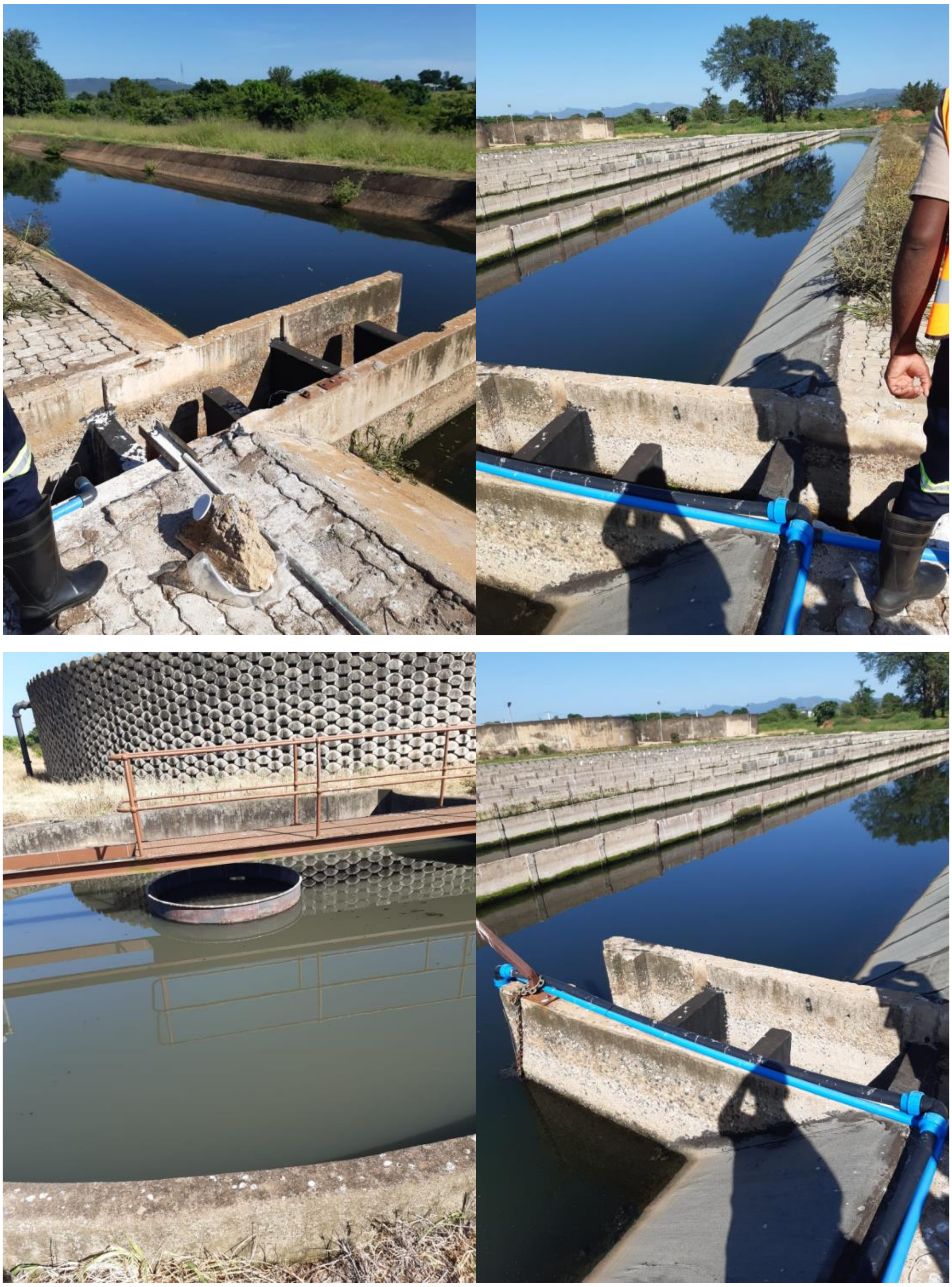

Figure 34: Sampling area; Tswinga (WWTP), Limpopo, South Africa (Paper III).

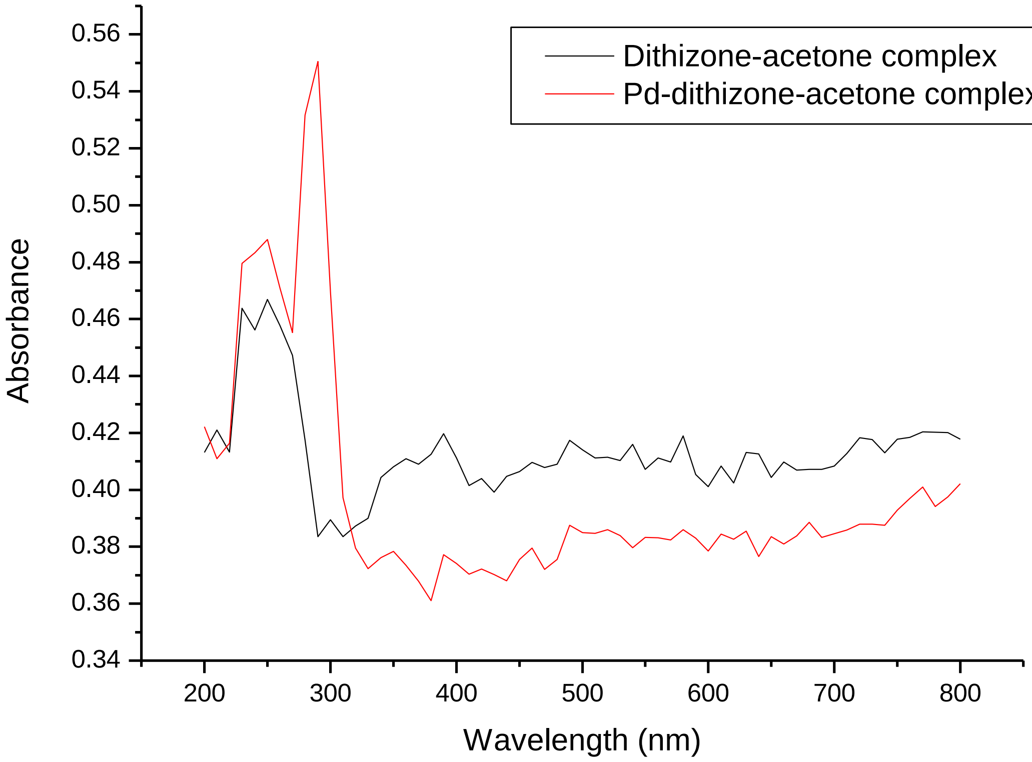

Figure 35: UV-vis spectra of dithizone-acetone and Pd-dithizone acetone complex (paper IV).

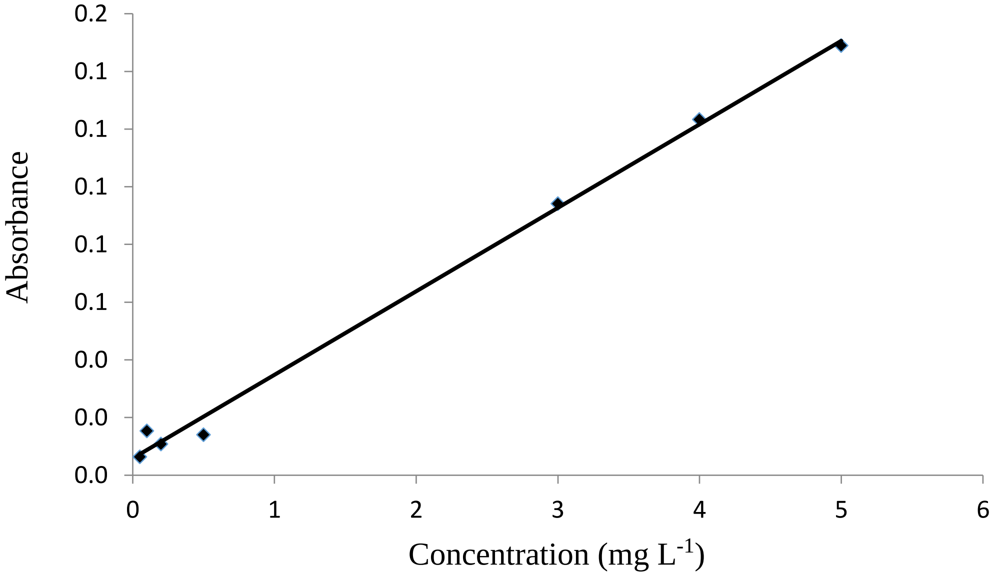

Figure 36: Calibration curve for palladium standards (paper IV).

Figure 37: Sampling area; Lephalale, Limpopo, South Africa (Paper IV).

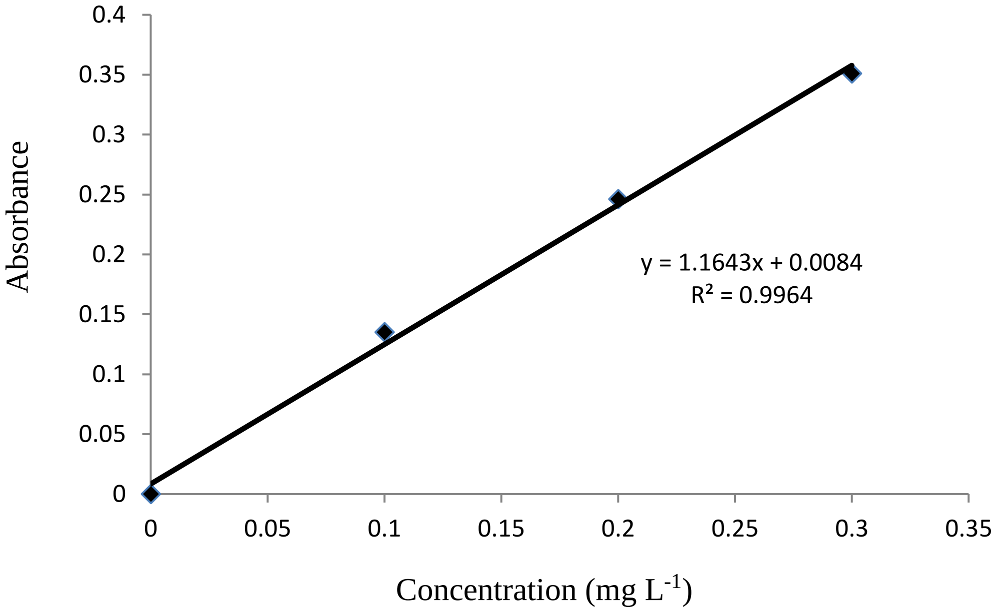

Figure 38: The calibration curve for cobalt standards (paper V).

Figure 39: Sampling area Nandoni dam, Limpopo, South Africa (Paper V).