Applications of ICP-MS and Isotopic Techniques in Resolving Nuclear Forensic Signatures in Cobalt Processing

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DECLARATION

I, Mr Malayitha Mackson Baloyi, declare herewith that the Mini-dissertation entitled, "Applications of ICP-MS and Isotopic Techniques in Resolving Nuclear Forensic Signatures in Cobalt-60 Mining and Processing", which I herewith submit to the North-West University is in compliance/partial compliance with the requirements set for the degree of Masters of Science in Applied Radiation Science and Technology, is my own work, has been text-edited in accordance with the requirements and has not already been submitted to any other university.

Malayitha Mackson Baloyi

25/07/2018

Date

ABSTRACT

Isotopic techniques in determining elemental composition was evaluated. Gamma Spectrometry was used to determine elemental composition as a non-destructive approach and isotopic signatures were developed to resolve the nuclear library. ICP-MS was another technique to be reviewed for applicability in the field of nuclear forensics. ICP-MS found 57Co; Cu and Ni levels to be at 0.351, 0.468 and 1.589ppm respectively in tailing dam 1 and 0.6725; 0.4597 and 1.3845ppm in tailing dam 2 respectively. Mo and As were present at high concentration levels, this is indicative that there is an unconformity- type ore, impurities were also detected which are a result of processing efforts by the mine, along with lanthanides and RRE. 235U and 238U are mined together, this can be concluded due to cross plots which indicated Co levels being scattered broadly in relation to 235U/238U radioisotopes.208Pb/206Pb isotopic ratio plots can be used as a potential signature to determine sample origins to this specific mine location due to its uniqueness. Using gamma spectrometry, 57Co and 235U signature is around 8.5 (bq) x $10^{(-5)}$) for 235U concentrations less than 0.08, and is around 1.4 x 10(-4) for 235U greater than 0.08 (Bq). The signature of 57Co and 226Ra (238U) is around 8.5 x $10^{(-5)}$ for 226Ra concentrations less that 0.13 (Bq), and is around 1.4 x $10^{(-4)}$ for 226Ra greater than 0.13 (Bq).

DEDICATION

I would like to dedicate this to myself, family and friends, Through The Lord my Savior I have completed milestones in life.

"He will restore you"

To you as well, Funanani, you are dearly missed.

But with on heart, one vision, I move forward.

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LIST OF ABBREVIATIONS

Ci	Curie
DOD	Department of Defense
DOE	Department of Energy
DA	Destructive Analysis
EC	Electron Capture
F6	Fluorine gas
HEU	Highly Enriched Uranium
HPGe	High Purity Germanium
IAEA	International Atomic Energy Agency
ICP-MS	Inductively Coupled Plasma Spectrometry
ITDB	Incident and trafficking Database
ITUE	Institute for Transuranium Elements
LEU	Low Enriched Uranium
NDA	Non-Destructive Analysis
MeV	Million electron volts
NECSA	South African Nuclear Energy Corporation
NNFL	National Nuclear Forensic Library
UF6	Uranium hexafluoride
UOC	Uranium Ore Concentrate
UO2	Uranium dioxide
U3O8	Tri-uranium-octaoxide
UO3	Uranium trioxide
WGPu	Weapons-Grade Plutonium

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1. INTRODUCTION AND PROBLEM STATEMENT

1.1 Introduction

Various physical phenomena have been discovered, new gadgets invented and improved with the changing of time. Among the physical phenomena is *radioactivity* and *nuclear energy*. Antione Henri Becquerel (1896), a French scientist and physicist, during research of phosphorescence in uranium salt, discovered radioactivity accidentally (Nobelprize.org, 2014). This was followed by years of research surrounding radioactivity, resulting in the discovery of nuclear fission. Nuclear fission is an induced or spontaneous reaction (if an element is unstable) where it releases a neutron as well as energy. This discovery comes with both pros and cons, (*with great power comes a great responsibility*).

This process of nuclear fission can be controlled, and the energy released from its reaction produces heat that can produce steam used to run turbines to generate electricity. The advantage of using nuclear powered electricity is that no smoke clouds (carbon pollution) are produced. However useful the process of nuclear fission is, it carries enough potential to become harmful due to the magnitude of power it yields. Any accident could be catastrophic for years, as seen in the Chernobyl accident of 1986, where inadequate personnel coupled with flawed reactor designs resulted in unnecessary casualties and years of major public health concerns (Fischer, 1997), as well as the recent Fukushima nuclear disaster that resulted in massive environmental pollution(Little, 2003; Local, 2015)

The worst case scenario is allowing the process of nuclear fission to occur in an uncontrolled manner, resulting in what is infamously known as nuclear explosions. This uncontrolled fission can be triggered intentionally to use this energy to cause harm. What brought light to the capabilities and the potential destructive nature of nuclear fission, was its deliberate use as a weapon in bombing of Hiroshima and Nagasaki on August 6, 1945. It resulted in an estimated death of 130 000 people in Hiroshima and three days later on August 9, another bomb was dropped resulting in another 60 000 – 70 000 being killed (Fischer, 1997).

From these, emerged the need for nuclear security. The formation of the International Atomic Energy Agency (IAEA) in 1957 was in response to this need and had the intention of easing fears of the world after the discovery of atomic energy and its potential uses not only as a source of clean energy but as a weapon too.

South Africa dismantled its nuclear efforts in 1993 due to increased pressure by the global community, resulting in South Africa joining other member states in the IAEA. These member states commit themselves to use nuclear fission for all purposes but those of causing harm to others. The

IAEA noted that each member state is in charge of the establishment, maintenance and implementation of its own nuclear security regime as a state.

For about 150 years, South Africa was producing gold at a rate of 337 223 kg, that made her the leader in gold production worldwide (Livhuwani, 2010). Whilst producing gold (Au), Uranium (U), an element that has the potential to be altered through various processes (enrichment) to produce weapon grade worthy isotope, is linked to gold production. The ratio of Au:U during gold production can be as close as 1:5 but as large as 1:500 (Livhuwani, 2010). This means the year where production yielded 337 223 kg of gold; at the very least five times that amount of uranium was produced. This uranium can be used for catastrophic activities.

The main point of concern is the radiation released by elements such as U, after it is mined to the surface and processed, and its radiation effects on the environment. Within a year of the discovery of radiation, namely ionizing radiation in the form of X-rays, reports began to come through citing burning of the skin due to a high exposure to X-rays (Gilchrist, 1879; Stevens, 1896). Exposure to high levels of radiation has been known to cause cancer on numerous accounts. Ionizing radiation causes damage to cells, which if not repaired, may either not survive or lose their ability to perform their function normally. In the worst case scenario this damaged cell although modified, is still viable and may lead to cancer formation (Little, 2003). Most of the data we have of the detrimental effects of radiation is mainly from the atomic bomb survivors of the Hiroshima and Nagasaki atomic bombs on Japan in 1945, people who have underwent some form of radiation treatment in a medical establishment, as well as those whose occupation results in radiation exposure (UNSCEAR, 2000). In all three cases, the effects of radiation have been nothing less than shocking and fatal in some events. Let it be noted that these are all man-made radiation sources rather than naturally occurring radioactive material (NORMS). Then as recent as March 2011 we had the Fukushima Nuclear Disaster (Local, 2015).

An element of note, which this research will be focusing on, is Cobalt-60, which will be discussed. Cobalt has physical properties of a solid hard metal with varying colours, generally described as being silver to white shade coloured metal. Cobalt can be found in a mixture of various ores. These ores include calalite; smaltite; erythrite and various other ores. A reduction process is induced in these compounds in the effort of obtaining a more pure form of the cobalt metal. The reduction occurs either with hydrogen, carbon or even aluminium. Due to its similarities to nickel and iron, in regards to its physical and conductivity properties, it is often used in several various alloy mixtures which function at either room temperature or lower temperatures(Swartz, 2009). Cobalt in its essence boasts a set of nine major isotopes which are radioactive, yet only two are worth any interest due to their half-lives. These half-lives are ideal for further investigation. The 7 other isotopes whose half-lives are so short, all no more than 80 days respectively, are rendered not fit for further analysis. The two isotopes that are fit for analysis and thus are of interest are Cobalt 57 as well as Cobalt 60. Cobalt 57 has a half-life of 270 days, just a few days under a full year cycle, whereas Cobalt 60 boasts a half-life of 5.3 years, as shown in the table below (IAEA, 2003; Peek, 2009; Fisher, 2011).

Table 1.1: Cobalt Isotope (Co-57 & Co-60) comparison (IAEA, 2003)

Isotope	$\frac{1}{2} life$	Specific activity (Ci/g)	Decay mode	Radioactive Energy (MeV)		
				Gamma(γ)	Alpha(α)	Beta(β)
Co-57	270 days	8,600	EC	0.13	-	0.019
Co-60	5.3 years	1.100	β	2.5	-	0.097

EC – electron Capture; Ci – curie; MeV – million electron volts (Adapted from Argonne National Laboratory (ANL), 2001)

Cobalt-57 decays through the process of electron capture, whereas cobalt-60 decays through the emission of a β- particle along with 2 gamma (γ) rays with a net sum of 2.5 MeV, each γ ray carries energy of 1.3 and 1.2 respectively.

Amongst the two tabulated isotopes, the isotope of concern in this study is Cobalt-60. This is due to the two γ rays emitted during its decay. These γ rays pose an external threat to human beings in that Co-60 need not be consumed first to cause harm from the inside but can cause harm from external contact, increasing the chances of developing cancer (Brown, 2015).

Table 1.2: Cobalt Isotopes (Co-57 & Co-60) Coefficients for Inhalation and Ingestion (IAEA, 2003)

Isotope	Inhalation (pCi-1)	Ingestion (pCi-1)
Cobalt-57	1.7×10^{-12}	9.0×10^{-13}
Cobalt-60	3.0×10^{-11}	1.4×10^{-11}

Adapted from ANL, 2001

Above are lifetime cancer mortality risk coefficients for cobalt's two radioactive isotopes of concern. It is interesting to see that ingestion has lower risk coefficients for both isotopes even though it is the most common form of contamination.

It is worth mentioning that Cobalt-60 has a parent element in the form of Cobalt-59. Cobalt-59 is found in nature; mainly it can be located in an array of different ores and much less commonly found in soil. Naturally occurring cobalt-59 is found in soil at very low levels, 1-2 mg/kg, this is credited to its stable isotope properties. Cobalt-60 can also be found in nature but at much lower levels and is thus noted as a trace element. This trace element detection could be due to previous weapons tests or ill disposed of nuclear reactor by-product where it is disregarded and viewed as a contaminant. The parent element, cobalt-59, is the main ingredient when aiming to artificially produce its radioactive daughter isotope Cobalt-60 and others. Artificial production of cobalt-60 is achieved through a process known as neutron activation especially in a nuclear reactor. This process is induced within nuclear reactors or even within particle accelerators which are able to of cobalt-60 production (Niemeyer, 1999; Mayer, 2016).

1.2 Problem Statement

Since nuclear energy became public knowledge, major concerns have been voiced about the security and safe keeping of nuclear material. Yet many incidence reports of illicit trafficking of nuclear material have been submitted to the IAEA and countless seizures have occurred. It is imperative that each state has a database and a nuclear forensic library that catalogues signatures of all nuclear materials in the country. These signatures would be for, for example, Uranium, Thorium, Plutonium, HEU, DU, LEU and Cobalt-60 sources in the South African context in order to trace traffickers of radioactive sources back to their origins.

A radioactive dirty bomb dispersal device can be manufactured by nuclear terrorists if they can get access to Co-60. A more recent case is the bomb dispersal in Paris, 14 November 2015, where three teams of coordinated attackers carried out various attacks across Paris. The real danger came from the explosions; one taking place outside the Paris Football stadium where 2 explosions took place but only 1 person was killed. Four more incidents took place, killing as many as 89 people in just one of these attacks. The death total amounted to 129, with over 350 injured placing 99 in critical conditions (Nossiter, 2015; Steafel, 2015).

The explosives used by the suicide bombers were of triacetone triperoxide (TATP) a bomb that can be made from easily obtainable materials that has been used in previous terror attacks. All eight attackers wore the suicide vests and seven of them managed to detonate them. With such an easily obtained bomb, one has to beg the question of how much more damage could have been rendered if nuclear material (Co-60 powder) had been added to the mix and dispersed. All attacks took place in large public areas. This makes for maximum dispersal area, forcing French officials to increase the security at their nuclear plants (Brown, 2015).

These attacks highlight the vulnerability of any state and further demonstrate that the dispersing of nuclear material is possible. Pursing this study will ensure that if any event were to take place, then knowing the signature of the material used only stands to benefit a State and its response time in times of crisis. South Africa is in an ever changing world. Whilst the threat of nuclear war and attacks has not necessarily been directed towards the South African country, in this day and age it is better to be prepared in order to prevent or be prompt in remedying the situation if the need arises. By being able to detect and analyse the radioactive content found in mine dump material, one should be able to transfer this knowledge and apply it in a radiological case like illicit trafficking of radiological material.

Forensic analysis of detected or recovered nuclear material is one emerging tool used for tracing the origin, activity and harmfulness of such material in South Africa. The applicability, flexibility and effectiveness of conventional techniques will be tested in the "normal' respects of detecting radiotoxic elements in mine dumps, but keeping in mind their possible uses in nuclear forensics. This study might seem years ahead of South Africa if not the continent as a whole. (*But a society grows great when old men plant trees whose shade they know they will not sit in*).

Thus developing Nuclear Forensics Library of Co-Pb Ratio and Co-U ratio signatures is one such tree 'planted' for the next generation. This research will evaluate the application of ICP-MS and isotopic ratio techniques in resolving nuclear forensic signatures for Cobalt in relation to the lead and uranium isotopic ratio signatures.

1.3 Aim and Objectives of the Study

1.3.1 Aim

The aim of this study was to investigate the usefulness of nuclear techniques, ICP-MS and Gamma Spectrometry, and their applicability not only in an environmental approach but in a nuclear forensic science approach as well.

1.3.2 Objectives

The objectives of this study were to:

- Evaluate the applicability of inductively coupled plasma mass spectrometry (ICP-MS) isotopic ratio techniques in determining the elemental composition of samples from the mine dump near Carletonville, Gauteng.
- Determine the isotopic ratio of elements by use of non-destructive detection gamma spectrometry in each sample.
- Resolve the nuclear forensic library for cobalt-Pb and Co-U isotopic ratio signatures.

2: LITERATURE REVIEW

2.1 Introduction

Since the 1990s, the issue of illegal trafficking of nuclear material and radioactivity has become household knowledge among nuclear scientists. Authorities all over the world have now taken a major interest in both the use as well as protection from nuclear power. Nuclear energy is an energy source which can propel countries to the forefront of technology and advancement in civilisation. The main concern which arises is that this power has the potential not only to develop a country but more than enough energy to cripple a country for decades on end. Access to such sources of energy should be minimal due to the dangers associated with them, equipment required as well as the high level of expertise needed to convert them into weapons grade sources. A number of specific factors has to be in place in order to launch any activity, especially illegal activities, yet since 1993 there has been more than 130 cases of nuclear material smuggling which have been reported (Wallenius, 2000). In terms of a global view, there is more than 200 tons of plutonium stored in different facilities all over the world, but even a small quantity is a major cause for concern. If any of it is used in any attack or seized during transit it is essential to pin point where it was procured (Baude, 2007). To trace the source of 1kg of plutonium from the 200 tons worldwide can be rather challenging, requiring different elaborate analysis techniques ranging from chemical analysis, physical trait analysis and most importantly, isotopic analysis. In investigating such a case, conventional forensic science is limited due to the extra parameter of radioactivity and the dangers it poses. This is where nuclear forensics comes into play.

Nuclear forensics is the ability to obtain, extract and deduce any relevant information from debris and other radioactive material (Madalia, 2004). Acquired information can be used to determine not only the weapons main constituent element but also for describing the design of the weapon. The IAEA defines nuclear forensics as "*the analysis of intercepted illicit nuclear or radioactive material and any associated material to provide evidence for nuclear attribution. The goal of nuclear analysis is to identify forensic indicators in interdicted nuclear and radiological samples or the surrounding environment, e.g. the container or transport vehicle. These indicators arise from known relationships between material characteristics and process history. Thus, nuclear forensic analysis includes the characterization of the material and correlation with its production history*" (IAEA, 2006).

The main concern with nuclear and radioactive material is not necessarily only its theft from institutions which are regulated but rather other material which is not accounted for and is out of regulatory control (Rhodes, 1995). With unregulated material randomly distributed worldwide, the occurrence of illicit trafficking of nuclear and other radioactive material cannot be comprehended. Adding on, the widespread use of radioactive material for medical purposes, industrial use and for academic and research purposes further highlights the ease of access by terrorists to these radioactive material.

2.2 Nuclear forensics and its role in nuclear security

Nuclear forensics entails two components of science coming together, namely nuclear science and forensic science. If an incident were to occur that involved nuclear material, there would be a better prompt response to tackle the situation if the two components worked together. This is possible if practices are shared, procedures are created and finding common ground on standard operating procedures in each practice. Nuclear forensic science is there to ensure citizens are protected as well as a States' infrastructure and other valuable investments.

Ceased material can thus be analysed in an accredited Laboratory for U, Th, Pb or Co signatures to determine if it has been taken from known locations which, at the time, were considered secure. This information when determined through nuclear forensics can supplement the improvement on nuclear security measures. As an added effect, individuals may be discouraged from engaging in illegal transporting, theft or sale of radioactive material once they discover that a State has its own nuclear forensics division. Once combined with conventional forensic results, a link can be drawn between those involved, the locations which may have been used as preparation bases as well as the possible source (EuropeanCommission, 2009).

Nuclear forensics and traditional forensics are in fact using the same method to extract information from material collected. They both aim to make use of the individual characteristic that each sample has, there being a parameter which fundamentally allows for a conclusion to be drawn (UK-Legislation, 1984). These characteristics and the parameter each exhibits can lead investigators to the possible source of the sample.

With the first analysis of nuclear samples, the age of nuclear forensic was born. The seized material was coded as "Find-1", containing 72 pellets of uranium (Mayer . 2007). With this it was concluded that the pellets were to be used as fuel pellets. From the characteristics even an origin location was suggested. Thus by determining the elemental composition, physical and isotopic characteristics and analysing the results together, the intended use of seized material can be determined as having been for energy production or weapon grade use.

Nuclear forensics is rather young and still in the developmental phases where solid methodologies that have stood the test of time have not necessarily been found yet. A cause for concern has clearly been established by the amount of recorded incidents by the IAEA (IAEA, 2000; IAEA, 2015).

Since the interdiction of nuclear material began, it is very apparent that many of the cases that are opened and looked into begin with either the reporting of missing material, an anonymous informer to the authorities as well as owners who have discarded the property (Potter, 1995; Wallenius, 2006; Baude, 2007). The majority of these incidents took place well within the 1990s but many countries have made the avid effort of putting in place discrete systems in attempts to detect and prevent movement of any illegal radioactive material through traffickers. This is rightfully justified by all too recent incidents that took place in Georgia in the year 2003, 2006 and 2010 where highly enriched uranium was interdicted(Hutcheon, 2015).

Most of these seizures occur whilst the material is well secured and packaged ready for sale, this results in an advantageous position for tactical teams intercepting the package in terms of safety. This is not always assured as the Litvineka interdiction case posed a situation when ^{210}Po poisoning occurred, an example that all possible precautionary steps should be taken (Maguire, 2010). There was an unexpected spill in which public safety and investigators' safety were a concern.

In the response to emergencies that involve material of a nuclear nature, the greatest care is taken and follows a four step plan. Categorization is the first and this seeks to understand the activity level (dose exposure) and take necessary measures. This ensures the safety of the personnel who will most likely be first responders to the scene. This step includes a thorough investigation into the nature of the material, using non-destructive applications, an investigation then follows on to determine the possible device used to disperse the material and the radiation dose dispersed. There after follows the nuclear forensic interpretation. This is where conclusions are made based on results obtained from categorization. The main aim of this step is to try to determine the materials' origin. A number of seizures have taken place over the years. From these seizures investigators were able to determine if the Uranium had been placed through enrichment to make it weapon grade worthy or if the material was uranium or not in the first place. Table 2.1 documents just some of the seizures that have occurred around the world (Brown, 2015; Nossiter, 2015; Steafel, 2015).

TABLE 2 1: Seizures of nuclear material worldwide (Brown, 2015; Nossiter, 2015; Steafel, 2015).

Year	**Location**	**Country**	**Type**	**Enrichment/Pu-239 content**	**Mass**	**Interdiction**
1978	New Mexico	USA	NU	0.72%	1500kg	Theft/Police Investigation
1992	Augsburg	Germany	LEU	2.5%	1.1kg	Police Investigation
1992	Podolsk	Russia	HEU	90%	1.5kg	Theft/Police Investigation
1993	Vilnius	Lithuania	HEU	50%	100g	Police Investigation/ Discovery
1993	AndreevaGuba	Russia	HEU	36%	1.8kg	Theft/Police Investigation
1993	Murmansk	Russia	HEU	20%	4.5kg	Theft/Police Investigation
1994	St. Petersburg	Russia	HEU	90%	3.05	Theft/Police Investigation
1994	Landshut	Germany	HEU	87.8%	0.8g	Police Sting Operation
1994	Munich	Germany	PU	87%	363g	Police Sting Operation
			LEU	1.6%	120g	
1994	Prague	Czech Republic	HEU	87.8%	2.7kg	Police Operation/ Tip-Off
1995	Prague	Czech Republic	HEU	87.8%	0.415g	Police Operation/ Tip-Off
1995	Prague	Ceske Budejovice	HEU	87.8%	17g	Police Operation/ Tip-Off
1995	Moscow	Russia	HEU	20%	1.7kg	Theft/Police Investigation
1999	Ruse	Bulgaria	HEU	72%	0.4g	Border Guards
2001	Paris	France	HEU	72%	0.5g	Police Operation/Tip-Off
2003	Ignalina	Lithuania	LEU	2.0%	60g	Theft/Police Investigation
2003	Rotterdam	Netherlands	NU	0.72%	3kg	Scrap Metal
2006	Tbilisi	Georgia	HEU	~90%	80kg	Police Sting Operation
2007	Pribenik-Lacacseke Border	Slovakia	NU	0.72%	426.5g	Police Operation/Tip-off
2010	Tbilisi	Georgia	HEU	>70%	18g	Police Sting Operation
NU- Natural Uranium; LEU- Low Enriched Uranium; HEU- Highly Enriched Uranium						

In the 2010 Nuclear Security summit in Washington, D.C., the former head of state of the United States of America, President Barrack Obama, in his speech made a statement, "nuclear terrorism is one of the most challenging threats to international security"(Hutcheon, 2015). This statement when analysed makes it clear that in efforts to combat this threat, every State can indeed make its own individual efforts but joint efforts between States will eventually benefit everyone. In order to ensure that responses are indeed prompt and dealt with it is important that the State which has been attacked is able to determine whether the attack and the source used originated from within that State or not. If it originated from within its borders then investigators know where to start with their investigations and prevent further theft if that is the case. Now if the source materials' signatures did not originate from that State in particular then it is up to other States to review these signatures and determine if the source came from their borders or not. This is all part of what President Obama described in 2010, *that fighting a common enemy together could prove much better than individual State efforts*, also described in the U.S 2010 Quadrennial Defence Review, "Improving our ability to attribute nuclear threats to their source can help deter aggressors from considering the use of nuclear weapons, as well as deterring State or non-State actors that may provide direct or indirect support to nuclear terrorism" (GlobalSecurityNewswire, 2010). This statement is relevant for both the prevention and response to attacks if States are able to attribute seized sources and account for what they have within their borders, and then both prevention and reaction are much timelier. From a nuclear explosion a State needs to be able to provide conclusions on certain questions about the attack, such as what was the source used, possible devices that could have been used to spread this source if it is a dirty bomb and if the sophistication of the weapon required State input or not, since it is known that producing and fabricating these devices is not something that can be accomplished in a backyard or garage but often requires expensive equipment which is usually at the disposal of the State rather than individuals. This can help deter any further attacks and attainment of these raw materials used to produce the final product (Brown, 2015; Nossiter, 2015; Steafel, 2015).

After seizure of illicitly obtained sources or samples collected after an attack, it is imperative to obtain preliminary information; this information can include the radioisotopes that have been used and their concentrations. This is possible and can be done within the first 24 hours of obtaining the samples through the use of gamma spectrometry analysis.

Gamma spectrometry is advantageous in that it is a non-destructive analysis and of the five possible analysis types it fits under isotopic analysis, demonstrated in the figure below.

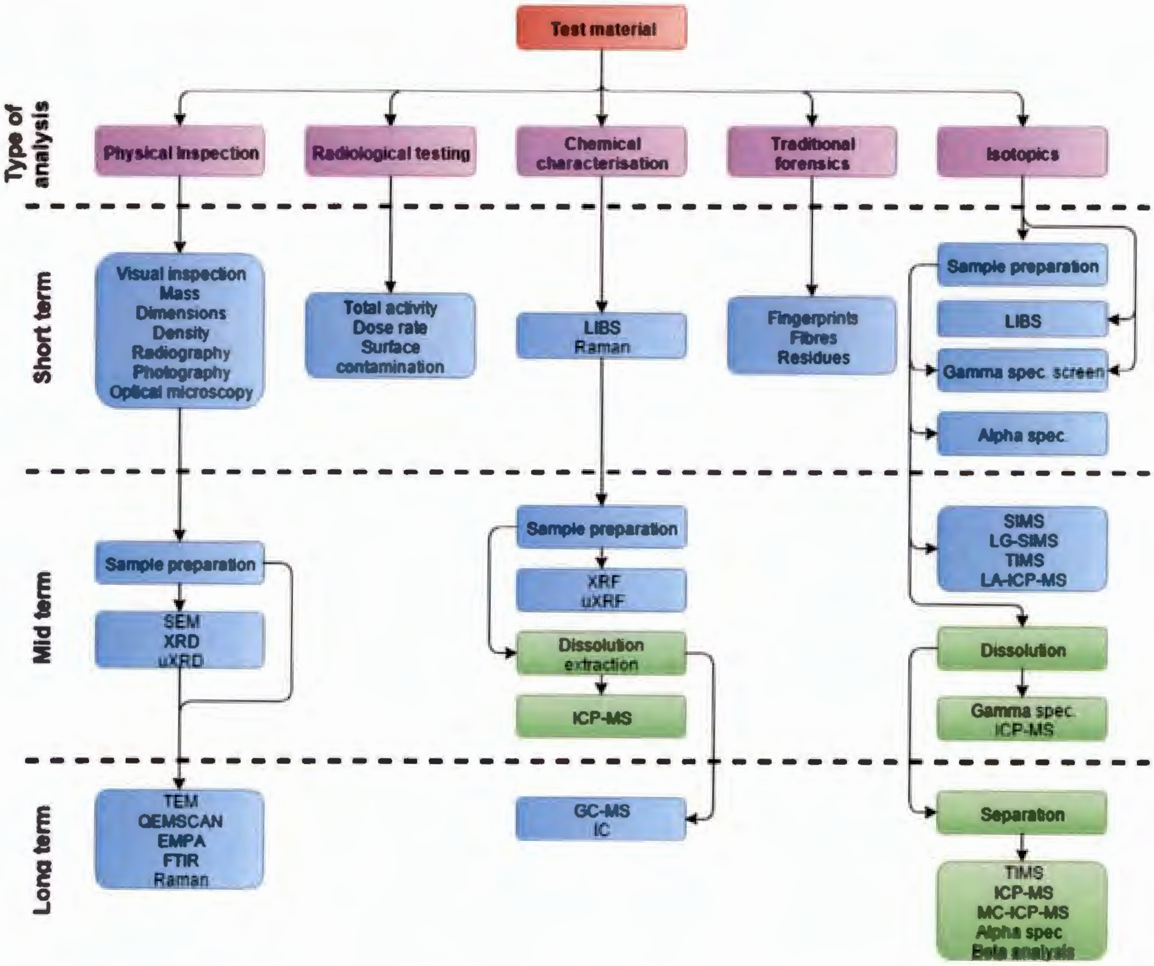


Figure 2.1: Methods used and analytical steps after a nuclear attack or seized material (Mayer, 2005; Hutcheon, 2013).

Similar to conventional forensics, nuclear forensics may begin before an actual attack in the form of prevention and after an attack as a response to solving the case, but the former is the preferred situation in the sense that prevention is truly better than cure.

An analytical methodology is applicable to nuclear forensic situations just as seen in conventional forensic investigations, with a few adjustments, of course. Below is a figure that shows the methodology at tackling the illicit trafficking of stolen nuclear material as well as its propagation for terrorist activities.

Along with nuclear forensic methodology, classical forensic investigation procedures can and most probably should be carried out at the same time. This is primarily due to there being evidence of another nature, biological, other than radioactive sources, this includes DNA, traces of hair, blood and other valuable sources of information which could link individuals to the investigations and lead to prompt attribution.

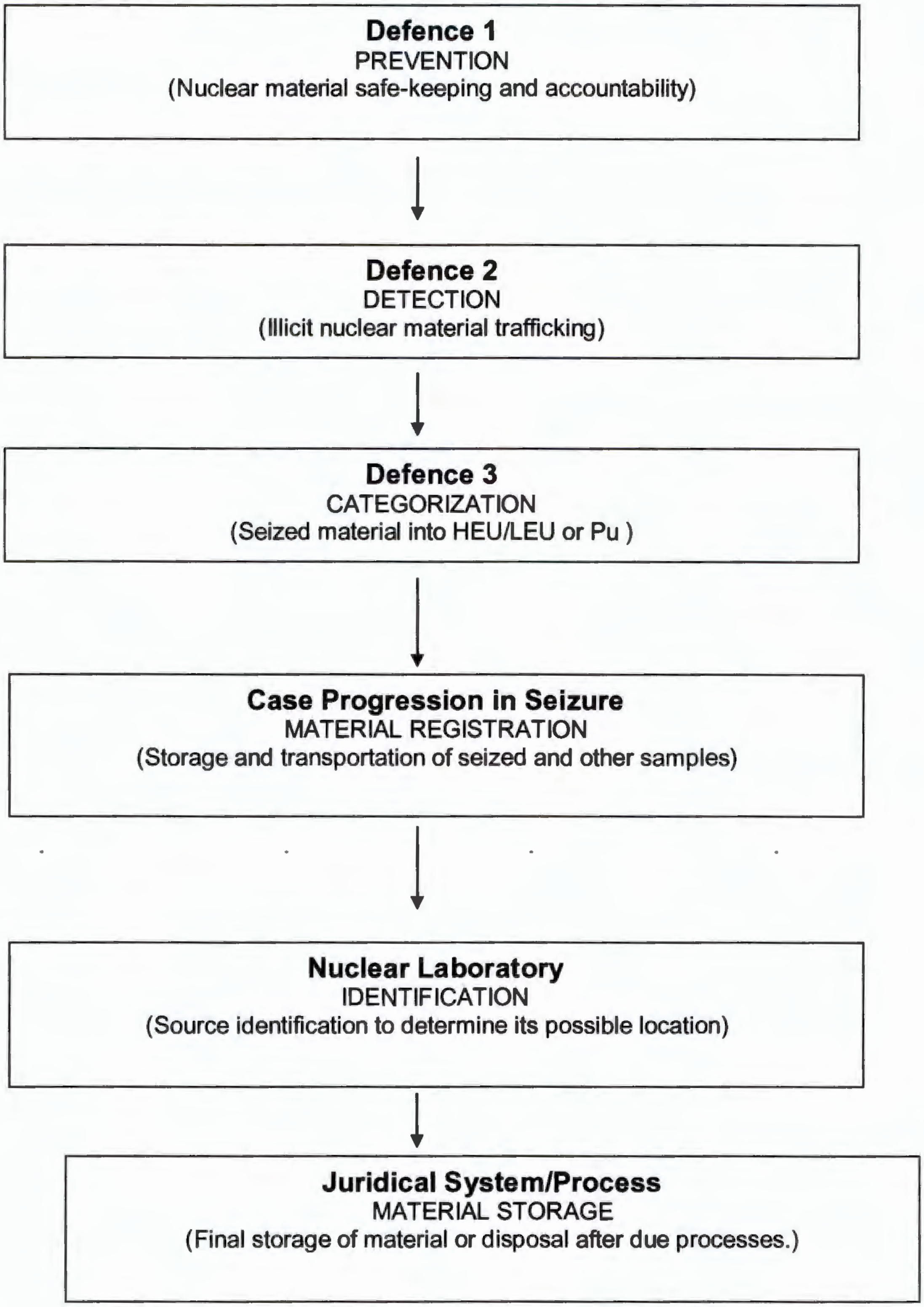


Figure 2.2: Methodology at Tackling Illicit Trafficking of Nuclear material

(Mayer, 2005; Hutcheon, 2013)

Besides these pressing questions, other unknowns also need to be answered, such as who was doing the trafficking, whom was the material meant for and to what avail at the end of the day. Information on the material's origin and production is known as 'Nuclear Fingerprinting'. This fingerprinting is accomplished through various analytical techniques, all in the efforts to extract the maximum amount of information available from the seized nuclear material (Grant, 1998).

The techniques utilized in nuclear forensic investigations are known as radio analytical techniques. These techniques are further assisted by the physical properties of the seized material which are obtainable through physical examinations of the material itself. These inspections need to be done before any analytical techniques are done on the samples. These inspections reveal details on the shape and geometry of the samples, in the case of fuel pellets, measurements on them can help determine the reactor it had once been used in or reactor it was intended for. Now in order to determine the trace signatures and radiation emitted by the seized samples, techniques such inductively coupled plasma mass spectrometry, thermal ion mass spectrometry, and gamma spectrometry as well as alpha spectrometry, as well as chronometry, all radiometric techniques, can be used on the various samples (Niemeyer, 1999).

2.2.1 Gamma spectrometry.

This technique involves the detection of gamma rays or radiation from samples all in the efforts to identify them. Due to its non-destructive property, it is usually the first application in nuclear forensic investigations; especially when dealing with material which has been seized. The tested material remains in its original condition- allowing for further analysis through other analytical methods. These gamma rays are produced when a nucleus goes through a decaying process to a lower energy nucleus. These rays are unique and specific to elements. The rays also carry different energies which assist in element identification.

The information coded into the gamma spectrometry units were obtained from data of ^{238}U and ^{235}U emissions. The peaks observed in a gamma spectrum have intensities which are directly related to the total number of atoms in that sample (FRAM, 1993; Mayer, 2005; Nafaa., 2006). This technique was used in this research.

2.2.2 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS is a technique found to be very useful when aiming to detect (radioactive) elements which are described as trace elements due to their small quantity in nuclear fuels. Nuclear fuel is where nuclear energy is obtained through its burning and going through a process of nuclear fission or fusion. ^{235}U and ^{239}P are the most common isotopes which are used as nuclear fuel inside of reactors. ICP-MS can also detect traces of nuclear fuel, uranium oxide, in the environment, by collecting dust

(Llyod; Mayer, 2005; Wolf, 2005). ICP-MS was used in this research for determining the trace elements of interest.

Calibration

The main analytical problem with ICP-MS is the calibration step, the process of elemental fraction which is dependent on the sample matrix. This implication is that it is implied that standards used for calibration should match the sample matrix. Preparing these standards can prove labour intensive and rather time consuming. The primary approach that has been implored to solve the problem is by completely matching the matrix. This generally offers full elemental coverage. A lot of progress has been made in the last decade in efforts to improve quantification procedures(Gunther, 2000). Taking this into mind it is still worth mentioning that commercial calibration standards are still quite limited. The next option which most laboratories opt for is by preparing their own matrix-matched standards. This is achieved through the mixing of elemental standards as well as samples. This approach is time consuming and often producing unknown homogeneity. This can affect analysis and reduce precision. To correct this short coming or limitation, the micro-homogeneity of the produced standard material has to be optimized and ultimately verified. Below are various calibration approaches for different sample types with their known internal standardization (Hoffmann, 1997; Hattendorf, 2005; Pisonero, 2009).

TABLE 2 2: Calibration approaches for different samples (Gunther, 2001; Bellis, 2006; Kovacs, 2009; Dressler, 2010; Do & Wang, 2011; Pakieła, 2011; Han´c, 2013) .

Type of sample	Method of calibration	Internal Standard
Animal bone	External calibration against reference materials (NYS RMs and NIST SRMs – 1486 Bone Meal and 1400 Bone ash)	Ca
Gold	Solution calibration performed by transferring Ag into a chloro-complex and diluting it with multi-element solutions	N/A
Geological samples	External calibration using NIST SRMs 610 and 612 (glass)	Li, Ca and Si
Sediments, soils, and ashes	Multi-point calibration based on pellet standards prepared by mixing	N/A

	powdered CRMs with zinc oxide (a binder) and solidified by 2-methoxy-4-(2-propenyl)phenol	
Teeth	Calibration with matrix-matched laboratory standards – powdered teeth spiked with standard solutions	Ca
Geological samples (basalt, andesite, ash)	Solution calibration conducted by coupling an ultrasonic nebulizer to a laser ablation cell	N/A
Hair	SRM free, on-line solution based calibration	N/A
Water	Two methods of calibration: external calibration with aqueous standard solutions pipetted onto the PTFE filters and the standard addition method	N/A

Fractionation being very complex is still not understood entirely. This takes place during aerosol formation in the ablation chamber then transporting the aerosol into the ICP. Commonly accepted methods of external calibration for matrix-matched standards often are either from “home-made” standards of from available certified reference material (CRM). If o CRM is available that befits the sample then matrix matching can be achieved through the addition of selected elements into a powdered matrix. This can be done based on available CRMs or the main sample component (Pisonero, 2009).

As previously mentioned matrix-matched calibration is labour intensive though very widely recommended, it also adds a complexity to a rather fast and simple analysis. When CRMs aren’t available, non-matched matrix calibration then becomes an option. The benefit of this method is it helps one avoid time wasting laborious process of laboratory “home-made” standards. These “home-made” standards also pose limited homogeneity obstacles. This lead to the use of aqueous standard solutions for analysis calibration. This comes with its fair share of drawbacks but its simple handling and widespread use has led to a greater focus on them. 3 strategies are for solution based calibration:

- External calibration – if a matrix matched blank is available
- The analyte addition technique – if no blank sample exists
- Isotope dilution technique – for small samples

Depending on the accuracy and precision needed ICP-MS is able to offer different quantification procedures to meet various levels using the isotope dilution mode when analysing provides the highest quality of results. This level of quality can also be achieved through the quantitative approach. This is achieved through external calibration, using standards that include all elements that are desired. The drawback is the time consuming efforts and challenges in producing a multi-elemental standard needed for calibration (Catarino, 2006).

Semi Quantitative approach offers versatility in ICP-MS and its applications.it is suggested that up to 81 elements can be detected by this approach. An additional benefit is the software available which allows for each element and concentration in the sample to be detected also offering automatic isotopic interference correction as well as interfering molecule species; this is then reflected in a comprehensive report (Pisonero, 2009).

Interference

A factor to take into account during analysis is interference. This occurs when other chemical species that are present have the same atomic mass as the analyte of interest, resulting in spectral interferences. This is when other chemical species are present and have the same atomic mass as the analyte of interest resulting in spectral interferences. These isobaric overlaps can be overcome through careful selection of isotopes. Furthermore constituents are able to combine with oxygen and may generate polyatomic ions. This can be overcome by a deep insight into the intensities of parent ions and of the oxides. Interference also depends on the level of interfering species, the ratio at which interference occurs and the intensities of the parent ions. Taking these factors into account, spectral interference though a factor to consider does not mean that all conclusions on a particular element will have been interfered with. Below is a list of isotopes with potential interfering species(Catarino, 2006).

Table 2 3: Isotopes and their interfering species (May, 1998; Catarino, 2006)

Analyte/Isotope	Interfering species
^{53}Cr	$^{40}Ar^{13}C$; $^{35}Cl^{18}O$
^{57}Fe	$^{43}Ca^{16}O^{1}H$
^{59}Co	$^{43}Ca^{16}O$
^{60}Ni	$^{44}Ca^{16}O$

A table of isotopes and interfering species is of benefit to the use of ICP-MS in achieving high quality data.

Aqua Regina is a method of choice when trying to determine selected elements of interest in any study. Taking this into account it is worth mentioning detection limits of the studies elements of interest. These limits are however affected by 2 factors, namely the matric as well as previously mentioned interferences. Below is a table with the detection limits of ICP-MS on the elements of interest in this study.

Table 2 4: Detection Limits of ICP-MS instrument using Aqua Regina

Element	Isotope	Detection limit ug/L
Co	59	0.5
Ni	58	1
	60	3
	61	5
Pb	207	0.2
	208	0.1
Cu	63	1
	65	2
Na	23	10

Zn	64	1
	66	2
	68	3

Now the strengths shown by ICP-MS include the ability to detect up to 70 elements in a single analysis. This ow ever is affected by elemental interferences as well as a rather complex emission spectra.

2.2.3 Alpha spectrometry

The instrument aims to detect alpha particles or helium nuclei. With an atomic number of 2 and a mass number of 4, helium is representative of an alpha particle in that when there is an emission of an alpha particle by a radioactive source, there is a general decrease of 4 units in terms of the mass number and 2 unit decreases in atomic number. During this decay in the nucleus, an alpha particle is released, but these particles due to random combinations of protons and neutrons possess different energies. These random combinations result in characteristic energies, which an alpha spectrometer unit picks up and determines the material from which the radiation comes. Unlike gamma spectrometry, alpha spectrometry requires the samples of interest to go through preparations before analysis occurs, these result in the destruction of the original sample (Mayer, 2005). This technique was not used in this research.

2.2.4 Thermal Ion Mass Spectrometry

This form of analysis is done on a single element; this means that the sample of interest needs to be in its purest form possible. This poses a challenge for samples taken after an attack in that they are often mangled and the purity of the sample is unknown without putting the sample through other tests such as gamma spectrometry in order to preserve the sample in its most original form. Due to its high precision and accuracy it is useful in finding isotopes in uranium, thorium, plutonium and cobalt samples. The only drawback is that before analysis the samples need to go through preparation steps, which make it a destructive process and very labour intensive (Aggarwal, 2003; Mayer, 2005). This technique was not utilized in this research.

2.2.5 Chronometry

This is a dating technique, which is very pivotal and of great importance when dealing with nuclear forensic investigations. Chronometry also offers added advantage of determining the procedures which were used on the material to produce it and alter it. Its main domain where it is used most often is in geology and archaeology where material dates are the fundamental part to their research **(Stanley, 2013).** This technique was not utilized in this research.

2.3 Cobalt-60

When fissile nuclides undergo fission, it has been noted that there is a general uneven split of the nuclide into two fragments. For instance uranium-235 would split into two uneven fission fragments that have varying mass numbers along with two to three neutrons released as well.

Radioactive cobalt-60 has found its place in the world after its discovery in the 1930's by Glenn T. Seaberg and John Livingood(Seaborg, 1970). By bombarding the naturally occurring, non-radioactive, cobalt-59 with a neutron, in a nuclear reactor, radioactive cobalt-60 is produced. Artificially developed and unstable cobalt-60 emits beta and gamma ray to become stable (IAEA, 2003).

$$({}^{59}_{27}Co + {}^{1}_{0}n \rightarrow {}^{60}_{27}Co \rightarrow {}^{60}_{28}Co + {}^{0}_{-1}e + \mathrm{y})$$

$$({}^{60}_{27}Co \rightarrow {}^{60}_{28}Ni + {}^{0}_{-1}e \rightarrow {}^{60}_{28}Ni + \gamma - photon)$$

Various other alloys can be added into reactors in order to achieve similar objectives or any other form of alteration to produce desired isotopic forms of that element. Cobalt-59 is not the only one, elements such as nickel, chromium and irons, just to name a few, are often put through various processes inside nuclear reactors or particle accelerators to produce the desired radioactive element. Cobalt-60 is also produced by this neutron activation process. It is an element of concern when nuclear fuel is used, in certain nuclear reactions and processing plants where it is viewed as a by-product rather than the final product. Cobalt use truly varies and finds its uses in various fields, whether it is in its naturally occurring form of cobalt-59 or any other radio isotopic form. One such case is its addition to various alloys, such as stellite and carloloy, to produce tough rigid machinery that are used where cutting is necessary. Cobalt has also been found to be useful when producing powerful permanent magnets, an alloy combination known as almico. This alloy, almico, includes a mixture of cobalt alongside nickel, aluminium and various other metals (Stanley, 2013; IAEA, 2015; Mayer, 2016).

Cobalt is also used in electroplating, producing oxidation resistant surfaces. In its 'lesser' uses it is used as a blue colourant in glass making and pottery. In its radioactive form of cobalt-60, it has found its place in fault detection of metal components due to its high-energy gamma rays. In the field of medicine, cobal-60 is used in the treatment of cancers of different natures. With this information a lot of input has been put into various forms of therapy, radiation therapy being one of them. Indeed Co-60 was incorporated and has been extensively used as an optional radiation therapy source. After its invention in 1951 in Canada, it became the method of choice (Schreiner, 2003) in a process commonly known as brachytherapy.

Another area where Co-60 has found its place is in radiation processing industry of food products. Aiming to exterminate pests, sterilization and in most cases increase the shelf life of products. This is achieved by having the products undergoing irradiation. Different products undergo radiation treatment at different dose ranges; this is demonstrated in the Table 2.4 (Schreiner, 2003).

Table 2 5: Co-60 dose ranges for different therapeutic effects (Schreiner, 2003)

Product	**Intended effect**	**Dose range (MeV)**
Blood	TA – GVHD prevention	0.020 – 0.040
Potatoes, onions, garlic	Inhibiting sprouting	0.05 – 0.15
Insects	Reproductive sterilization for pest management	0.1 – 0.5
Strawberries and some other fruits	Extending shelf life by delaying mould growth and retarding decay	1 – 4
Meat, poultry, fish	Delaying spoilage, killing certain pathogenic bacteria (e.g. salmonella)	1 – 7
Spices and other seasonings	Killing a variety of microorganisms and insects	1 – 30
Health care products	Sterilization	15 – 30
Polymers	Crosslinking	1 – 250
	Grafting	0.2 – 30

Co-60 has found many applications in the medical field as well as in industrial applications. The use of gamma sterilization offers various positives to wet steam sterilization methods, ranging from easy management, minimal range change in the temperature and the results are constant over time (Schreiner, 2003). The major concern with Co-60 is that it can be fabricated into a radiological dispersal device (RDD), in the so called dirty bomb (Mayer, 2016).

Indeed a dirty bomb is nowhere near to the devastatingly destructive power of a thermonuclear detonation. A dirty bomb is also very easy to make, by simply obtaining a radioactive source (such as Co-60), from various institutions, such as radiology department in hospitals, and simply adding that to any explosive device such as the one used in Paris, TATP, that constitutes a dirty bomb (Economist, 2013).

This simple production of dirty bombs is what caused great concern and panic when a lorry in transit to a nuclear waste facility in Mexico City disappeared on its way from a radiation therapy facility as recent as 2013 (Hall, 2013). This lorry happened to be carrying Co-60 radiation sources and was later found. The thieves were suspected of having received intense exposure and could die well within a few days. This theft brought about great fear that it was a move by terrorists in an attempt to create dirty bombs. The threat of nuclear attack in the form of a dirty bomb is much more eminent than that of a nuclear war-head which not only needs specialized expertize but equipment and infrastructure which cannot be assembled unnoticed.

Co-60 can be seen as the element of choice for dirty bombs due to its extensive uses and availability from hospitals to irradiation and sterilization of food and fruits. With over 2000 reports of radioactive material going missing from regulatory control since 1995, it is safe to assume that taking steps to prevent not only the use but to be prepared for the eminent use of dirty bombs (Hall, 2013), is of utmost priority even for a country like South Africa.

With all the uses of cobalt, interest in it was inevitable. All radioisotopes produced within nuclear reactors or particle accelerators often require further processing, as in the case of cobalt-60 the same is true. It is also worth mentioning that reactors and accelerators account for the majority of radioisotope production as a whole in the world. A Reactor's high production rate is due to its large intake capacity. This is also coupled with its ability to irradiate multiple samples simultaneously. Particle accelerators generally produce accelerated ion particles which nuclear reactors are unable to produce or special radioisotopes which require distinct properties after irradiation (IAEA, 2003).

Several steps are followed during the production of the isotope cobalt-60. These steps include obtaining suitable material in a suitable form depending on whether its introduction for irradiation will be within a nuclear reactor or within a particle accelerator. Then its transport after production, its processing thereafter and quality control checks before being delivered to respective clients (IAEA, 2003). Figures 3 – 8 show different stages and applications of Co-60 production.

Figure 2.3: Type reactor found in irradiation facilities (IAEA, 2003).

Figure 2.4: Radiation core of a swimming pool core in Cerenkov (IAEA, 2003).

Above are figures that depict different types of reactors found around the world, and utilizing water to cool off its processes.

Step one is the procurement of the actual material that is to be entered into the nuclear reactors. When obtaining target material, certain factors described by the IAEA need to be taken into consideration, including guidelines and recommendations. Target material that is to be entered into nuclear reactors needs to be non-volatile, non-explosive and at any point during the irradiation process should not decompose into a gas form of any kind. The target material itself should be of the highest purity achievable if possible with little to no contamination. That is to ensure that no unwanted radioisotopes are produced which will act as a contamination and complicate further processing thereafter. Cobalt in its solid metal form contains certain amount of gases some of which may be hydrogen and or nitrogen. This requires the cobalt target material to be degassed before being packaged, encapsulated, and placed into the reactor for irradiation.

Target materials, require encapsulation before placing them into reactors. These capsules are commonly made of stainless steel or aluminium. Aluminium is the most ideal encapsulation material in that the possible radioisotopes that will be irradiated are rather short lived making post processing and disposal easier.

In the case of cobalt-60 ($^{60}Co_{27}$) production steps after encapsulation, it follows a production flow which is quite unique to its counterparts due to it being a high level radioisotope, often needing heavily shielded hot cells for protection purposes. Below is a figure of cobalt inside heavily shielded hot cells.

Figure 2.5: Technicians manipulating master instrument on hot cells (IAEA, 2003)

Like most radioisotopes produced from reactors, cobalt is produced through radioactive capture. This is a thermal neutron reaction utilizing the (n, γ) reaction, as tabulated below.

Table 2 6: Cobalt-60 (60Co27) decay reaction (Hall, 2013).

Half-life	5.2714 ± 0.0005 a
Nuclear reaction	^{59}Co (n,γ) → ^{60}Co σ = 37.18 + 0.06 (m+g)
Target material	Metallic cobalt
Decay product	Nickel-60

The γ is referred to as a prompt γ and is released when a neutron is absorbed into a nucleus.

$$^{59}_{27}Co + {}^{1}_{0}n \rightarrow {}^{60}_{27}Co + \gamma$$

Cobalt-60 decays into nickel-60, a stable element through beta decay releasing 2 gamma rays in the process.

Table 2 7: Types of decay and energy (MeV) (Kristo, 2012).

Beta (β^-)	1.49 (0.011%)
(E_{max})	0.31 (99.925%)
Gamma (γ)	1332.5 keV 1173.2 keV

Below is a production flow chart of the steps for production of artificial Co-60 radioisotope.

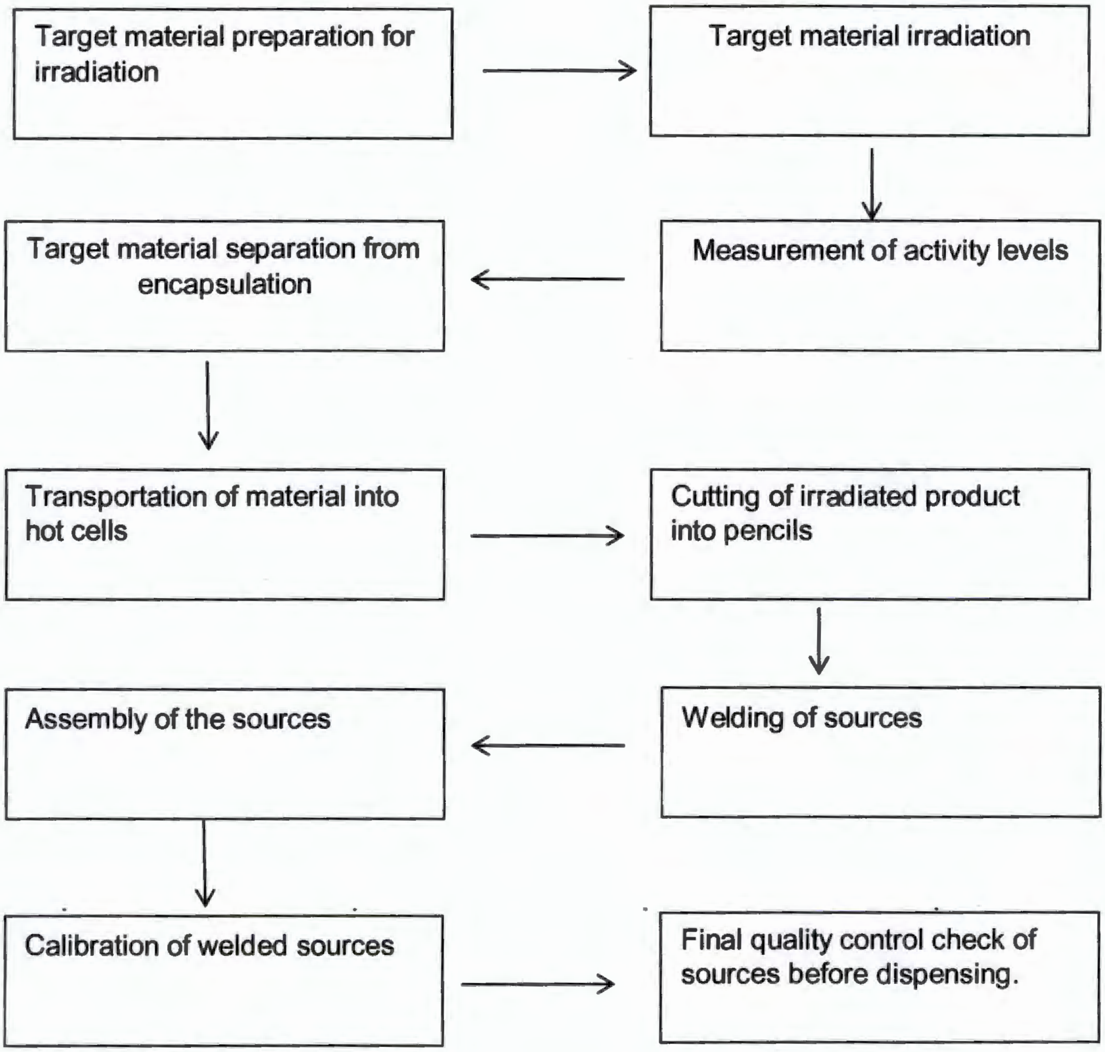


Figure 2.6: Flow diagram of the production of Co-60 (IAEA, 2016).

These various steps require different experts for each of them respectively along with well-equipped facilities as well as supportive structures alongside.

Cobalt target metal consists of cobalt-59 which needs to be higher that 99.7% pure before being placed inside the reactor, again this is to reduce contaminants of unwanted radioisotopes during irradiation. The metal is in a cylinder shape with specific dimensions depending on the reactor used, and is referred to as slugs. Dimensions in this case are 6.4 mm in diameter and 12.7 mm or 25.4 mm in length. There is a choice of pellets, with dimensions 1 mm × 1 mm.

These pellets or slugs are encapsulated with both ends welded shut. The capsule is made of 4 tubes of zircalloy, called pencils. These pencils are arranged in a circle around a centre rod and are held between two plates.

The rod and plates form part of the encapsulation and are also made of zircalloy, with 21 of these cobalt adjuster units being able to be placed in a reactor at a time, as depicted below in the below figure.

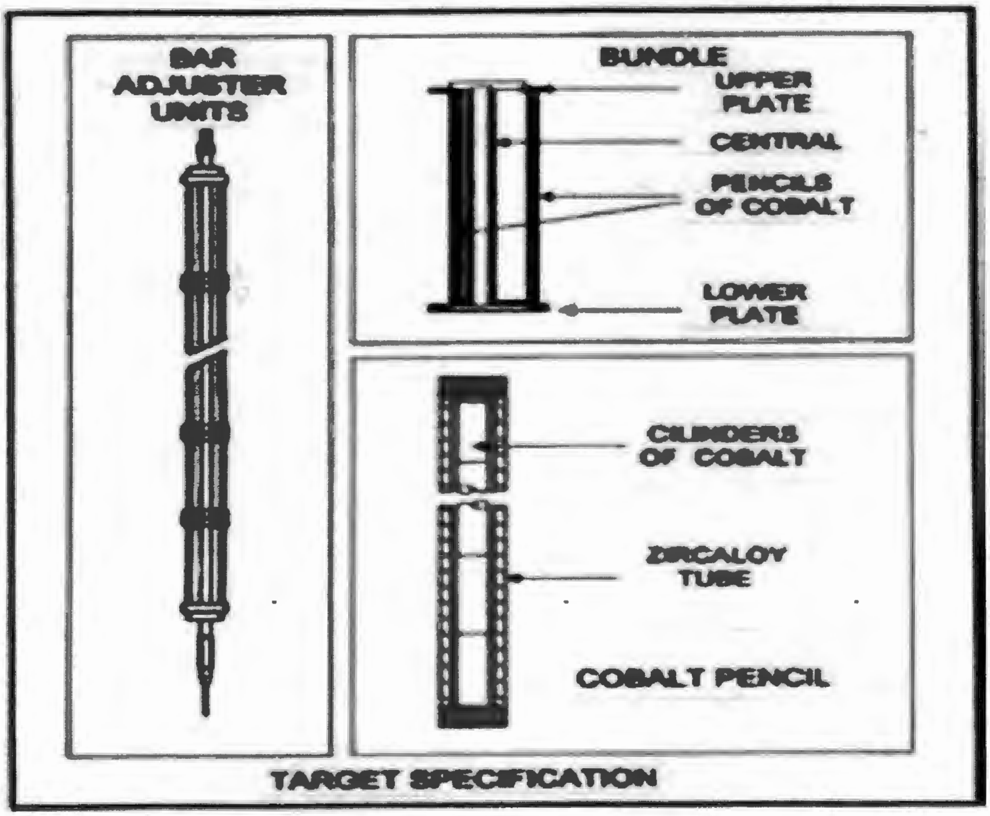


Figure 2.7: Cobalt target assembly (IAEA, 2016).

The pencil masses vary between 52 g and 80 g, this variation can be accredited to the pencil lengths as well as the form of the cobalt.

These pencils go through irradiation for varying periods of 18, 24 or 36 months at an average influx of 2×10^{14}n/cm^2/s (thermal neutrons). This variation in the irradiation period results in specific activity ranging from 120 – 250 Ci/g (IAEA, 2016).

Processing facilities require specialized equipment in the processing of cobalt-60 sources. One such facility, EMBLASE nuclear power plant, utilizes underground water in the efforts for target disassembly and calibration when dealing with cobalt-60 pencils post irradiation.

Hot cells are also required for quality control purposes when dealing with the pencils, especially sources which will later be incorporated in teletherapy units. Below is a figure of Co-60 being handled within its hot cell holdings according for radiation safety measures.

Figure 2.8: Cobalt-60 being handled within a hot cell (IAEA, 2003).

Before final dispensing and delivery to clients, these sources need to adhere to international standards of operation, including an immersion test (ISO 9978 (5.1.1)/ ISO: TR4826 (2.1.3)) and the dry wipe test (ISO 9978 (5.3.2)/ ISO: TR4826 (2.1.2)). The final product needs to comply with these standards respectively before dispensation(IAEA, 2003).

After going through all these steps and meeting the standards set by the international society, then cobalt sources are ready to be incorporated into the various fields for radiological applications. One such field is that of teletherapy, but before delving any further into this topic, it is imperative to define what teletherapy is. Teletherapy is defined as a treatment in which the source of therapy is at some distance from the body, similar to certain radiation therapies. Cobalt-60 and its introduction into cancer therapy could not have occurred at a better time where over 10 million cases of cancer were being reported each year and cancer accounting for 13% of all deaths worldwide (Shedd, 2014; CobaltDevelopmentInstitute, 2015b) .This form of treatment is referred to as radiation therapy, and forms part of three forms of treatment in the battle against cancer today. Chemotherapy and surgery make up the remaining two forms of treatment possible for cancer today.

In radiation therapy; ionizing radiation from radiation sources, such like Co-60, are used to disrupt the genetic material of the cells being targeted all in the efforts to hinder and halt their further propagation. This form of treatment does however affect normal healthy cells as well, but these recover much easier than cancerous cells. An internal form of therapy is also available known as brachytherapy. This involves the placement of small rods or seeds in the affected area in an effort to deliver high doses of radiation therapy also in an effort to halt further propagation of the cancerous cells. The difference between brachytherapy and teletherapy is that the latter is non-invasive, allowing for treatment without the need for surgical procedures anaesthesia and the likes (Schreiner, 2003).

The cobalt unit from their time of introduction until now were appreciated on their compatibility, a wide and easy range of motion as well as better manoeuvrability compared to predecessor units. These features and advantages meant that there was much less damage to unaffected areas and unaffected cells. Units enabled by a cobalt source also rival their counterparts in terms of depth and reaching affected areas, this is clearly depicted in an isodose curve below (Knoll, 1989; Schreiner, 2003).

An isodose curve is represented by a line which notes certain points along a central axis and notes places of similar values. The depth of these curves is readily influenced by the quality of the source being utilized, so the better quality the source the deeper depth it is able to achieve.

The cobalt 60 units comprise of components which are universal throughout all their unit models and ages. It comprises of a bed, where the patient would lay down. Above the bed and along it is a large head part which houses the cobalt-60 source, this head runs along the bed with its manoeuvrability being advantageous.

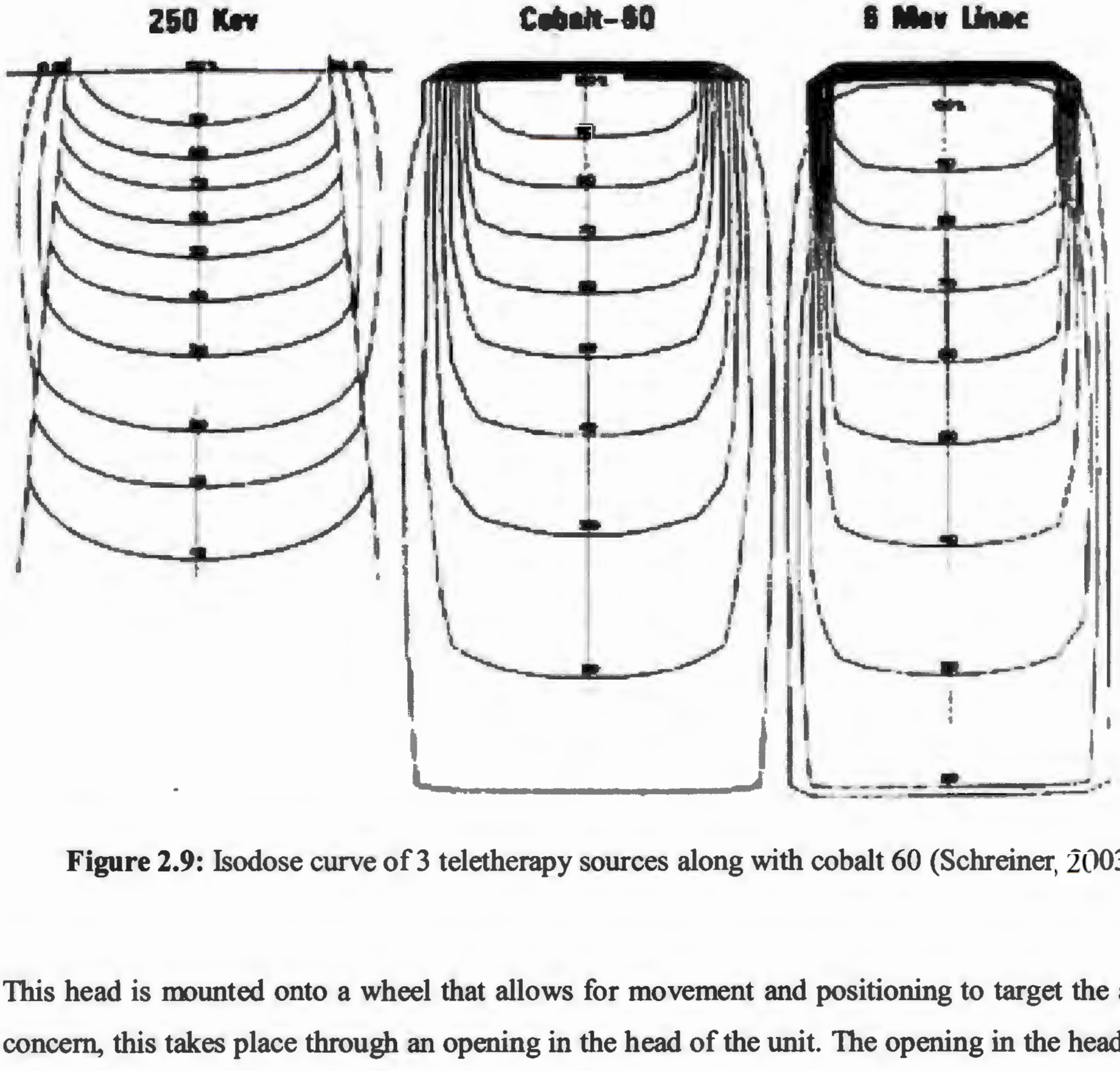


Figure 2.9: Isodose curve of 3 teletherapy sources along with cobalt 60 (Schreiner, 2003)

This head is mounted onto a wheel that allows for movement and positioning to target the area of concern, this takes place through an opening in the head of the unit. The opening in the head of the unit allows for those gamma rays from the cobalt-60 source to pass through and shield the head part and treat the area of concern in the patients.

Due to the nature of the cobalt-60 source units they come with an automatic safety feature incorporated into the unit in order to switch off the beam from the source in case of power failure or any other situation which warrants an emergency. The unit however still experiences leakage, even on standby or off. This leakage is well within international regulation limits of 2mR/h (0.02mSv/h) at 1m from the source, the cobalt-60 unit leakage is at 1mR/h (0.01mSV/h) at 1m from the source (Schreiner, 2003; Peek, 2009).

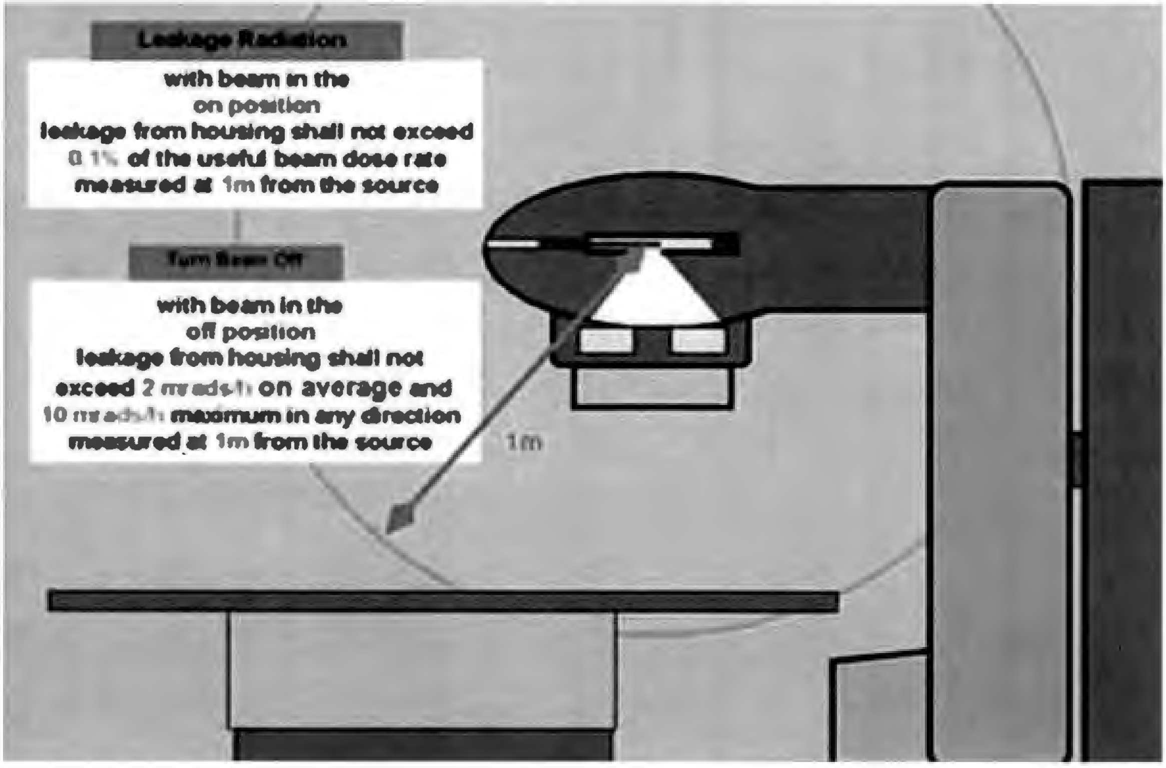


Figure 2.10: International leakage limits for cobalt 60 sources (Schreiner, 2003)

The demand for Cobalt over the last century has increased steadily. However; its demand has not reached what can be referred to as primary commodities level demand such as gold and uranium, largely due to its extraction as a by-product. The extraction of cobalt is achieved during mining of other elements – mainly copper and nickel; and in more recent years the major source being through the nickel industry. The Democratic Republic of Congo has, once again, become the foremost producer of cobalt in recent years through its copper-nickel production efforts (Fisher, 2011).

Cobalt plays a major role for human beings' survival. This is accredited to its participation as the central component in vitamin B_{12}, which is vital in red blood cell formation. Cobalt uses extend further and wider, but not as far reaching as its counterpart macronutrients and major metals iron, copper and nickel, due to its relatively low levels in the Earth's crust. This also contributes to cobalt being recovered as a by-product and seldom being the main objective of mining activities. Since it is was first isolated in a metallic form in 1735, it was only identified as an element in the year 1780 by Torben Bergman and around 1914 only gained traction for its potential uses in the industrial industry(Peek, 2009). Since then, the demand and production rate have since soured, as depicted in the figure below.

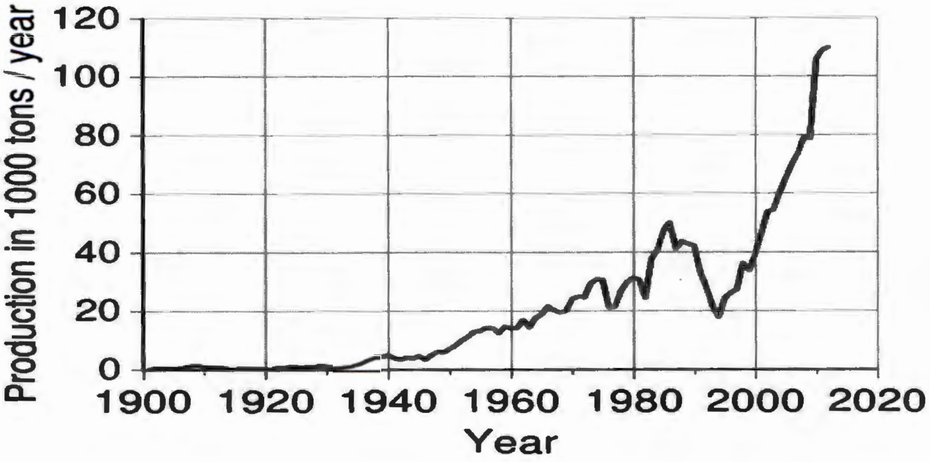


Figure 2.11: Production rate of Cobalt from 1900 to 2009 (Peek, 2009)

Within in the early 19th century, cobalt had been discovered all over the world, including Germany, Spain and England just to name a few. At this time cobalt production was only at approximately 1000 tons/annum (TPA). From the year 1926, mines in Congo began to venture into the exploits of cobalt as a source of profit. To this day its recovery is still in the form of a by-product that is salvaged. This production over the years has increased drastically, peaking just under 60 000 TPA in the year 2010.

According to the Cobalt Development Institute (CDI), responsible for all things cobalt globally from its mining, processing and sales across states, approximately 51% of cobalt has been in metallic form and the remaining 49% has been in chemical form (CobaltDevelopmentInstitute, 2015b). Being a by-product of copper-nickel processes this results in a tilted ratio production in comparison to its counterparts, making it the least produced through these processes, see table below.

Table 2 8: Copper, Nickel and Cobalt production percentage (Peek, 2009; Fisher, 2011)

Element produced/Industry	**Production percentage**	**Total**
Nickel Industry	50%	100%
Copper Industry and other	35%	
Primary cobalt Operations	15%	

Since the year 2010; production has steadily increased worldwide with countries such as Papau, New Guinea; Vietnam and The United States of America venturing into the cobalt production (Table 2.6).

Table 2 9: Cobalt production rates in countries from 2010 to 2014 (AfricanRainbowMineralsLtd., 2015; AquariusPlatinumLtd., 2015)

Country	2010	2011	2012	2013	2014
Australia	3,852	3,848	5,870	6,410	5,978
Botswana	272	149	195	248	196
Brazil	3,139	3,623	2,900	3,500	2,600
Canada	4,636	6,836	6,676	7,168	6,574
China	6,380	6,800	7,500	7,200	7,200
Congo (Kinshasa)	60,000	59,000	51,000	56,000	63,000
Cuba	4,800	5,100	4,900	4,200	3,700
Finland	140	500	635	750	770
Indonesia	1,600	1,600	1,700	1,700	1,300
Madagascar	165	500	630	2,200	3,100
Morocco	3,110	2,160	2,000	2,000	2,100
New Caledonia	2,850	3,100	2,670	3,190	4,040
Papua New Guinea	--	--	469	1,013	2,134
Philippines	2,100	2,000	2,700	2,700	4,600
Russia	6,200	6,100	6,300	6,300	6,300
South Africa	1,800	1,600	2,500	3,000	3,000
United States	--	--	--	--	120
Vietnam	--	--	--	25	223
Zambia	8,648	7,702	5,435	5,919	5,500

Zimbabwe	79	174	195	319	358
Total	110,000	111,000	104,000	114,000	123,000

The DRC in 2014 produced 63 000 tons of cobalt, its highest production rate since the year 2010. The South African story of cobalt is that of a 1.66% increase in production rate since the year 2010, marking 2014 as the highest production year. Of this Nkomah nickel sulphate mine produced 1,096 tons of cobalt, in nickel concentrate format (AfricanRainbowMineralsLtd., 2015).Some cobalt in South Africa, similar to flow sheets utilized in the DRC, is produced as a by-product from its Platinum Group Metals (PGM) operations.

Refined cobalt, in South Africa, is produced by two companies, Rustenburg Base Metals Refineries (proprietary) Ltd (a subsidiary of Anglo American plc.) which produced cobalt sulphate. The other company Impala Platinum Ltd. produces cobalt in a metal powder form. Impala Platinum Ltd. cobalt production was also fed by mines originating from Zimbabwe; namely Mimosa platinum mine produced 90 tons of cobalt concentrate which is then refined in South Africa by Impala Platinum, Lonimin plc., and Northern Platinum Ltd. also produced intermediate nickel sulphate which contained cobalt in it, adding to South Africa's total production rate(AfricanRainbowMineralsLtd., 2015; AquariusPlatinumLtd., 2015).

Primary Cobalt Production Processes

There are four main groups and their activities that account for the significant cobalt production from base metal recovery.

1. Cobalt Arsenide

   These were processes utilized during the 20th Century in order to produce cobalt arsenide ores/concentrates and had variations between approaches towards producing them (Feron 2001). Due to health concerns and environmental issues most of these processes have been abandoned with only a few projects still operational using this approach. The approach featured a roasting stage and a leaching pressure stage for most of the varied methods (Dalvi, 2004).

2. Zambian/DRC copper-cobalt ores (Oxides and Sulphides).

Cobalt in these parts has often been recovered if not solely through copper flotation concentrates. This was achieved through a Roast-Leach-Electrowin (RLE) process. This process involves roasting, direct leaching followed by impurity removal before cobalt can be precipitated as a hydroxide. This often was reprocessed, re-leaching followed by cobalt Electrowinning (EW).

This method is steadily being replaced by copper SX-EW. This is due to the inefficient recovery of cobalt previously experienced. This inefficient recovery is evident in the substantial levels of cobalt found in tailings, which will affect project costs to reprocess from tailings (Dalvi, 2004). This study investigated the level of Cobalt disposed into the Carletonville Gold mine tailings and results are reported in Chapter 4.

3. Nickel Sulphides

   The previous method for processing these sources was also through floatation, followed by smelting. This resulted in platinum group metal (PGM) nickel matte which contained nickel, copper, PGMs and cobalt. This nickel matte was recovered through hydrometallurgical processes. Impala refinery in South Africa is one of many refineries that still utilize this method, through a modified Sherritt-Gordon process (pressure oxidation leaching).

   Due to environmental concerns, new developments are encouraged so as to get alternatives to hydrometallurgical processes. A further pull away from this approach is encouraged by a scarcity of sources in order to push new economically viable sulphide deposits.

4. Nickel Laterites (Oxides).

   Nickel laterites were set to become the world's leading cobalt source from the year 2012. This process was first utilized in Cuba in the year 1959. This came in the form of High Pressure Acid Leach (HPAL) which was employed at the same time in order to further improve cobalt extraction (Dalvi, 2004; Fisher, 2011).

   HPAL is currently the method of choice by a number of projects which aim to process nickel-cobalt production, Butong in 1999 and Gororecenty projects began using HPAL in 2010 just to name a few (Goro et al. 2010)

Cobalt Recovery

1. Generic Flowsheet

   Cobalt, as previously stated, is usually a by-product of nickel and/or copper recovery efforts. In cases where both are target elements, copper is recovered first. This is then followed by the removal of impurities before cobalt can be recovered next. The process follows through and nickel recovery is the last step before what is left is considered debris and sent to tailing dams for disposal and storage. This generic flowsheet for the recovery is shown in figure 2.11 below.

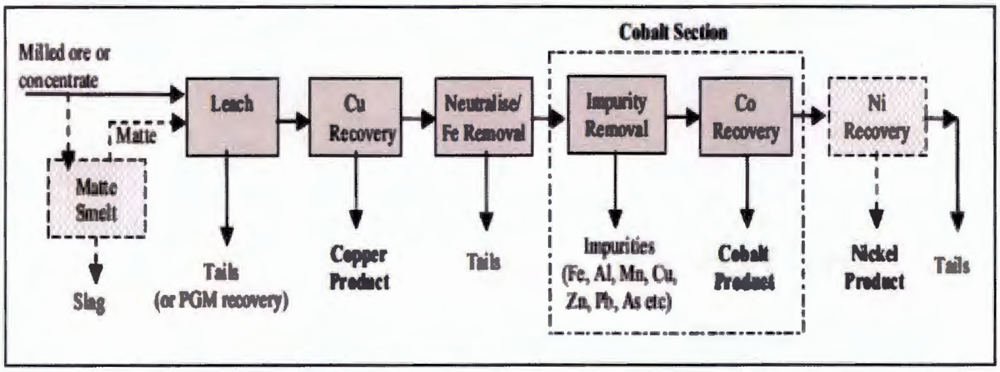


Figure 2.12: Generic flowsheet of copper/cobalt/nickel recovery (Dalvi, 2004; Fisher, 2011)

The cobalt section often contains minor levels of copper and iron elements, along with impurities and sometimes it hosts a large quantity of nickel. This is but a generic representation, a commonality between most if not all process. Actual processes have many steps and are complicated once taken upon by projects aiming to salvage these elements, see figure below.

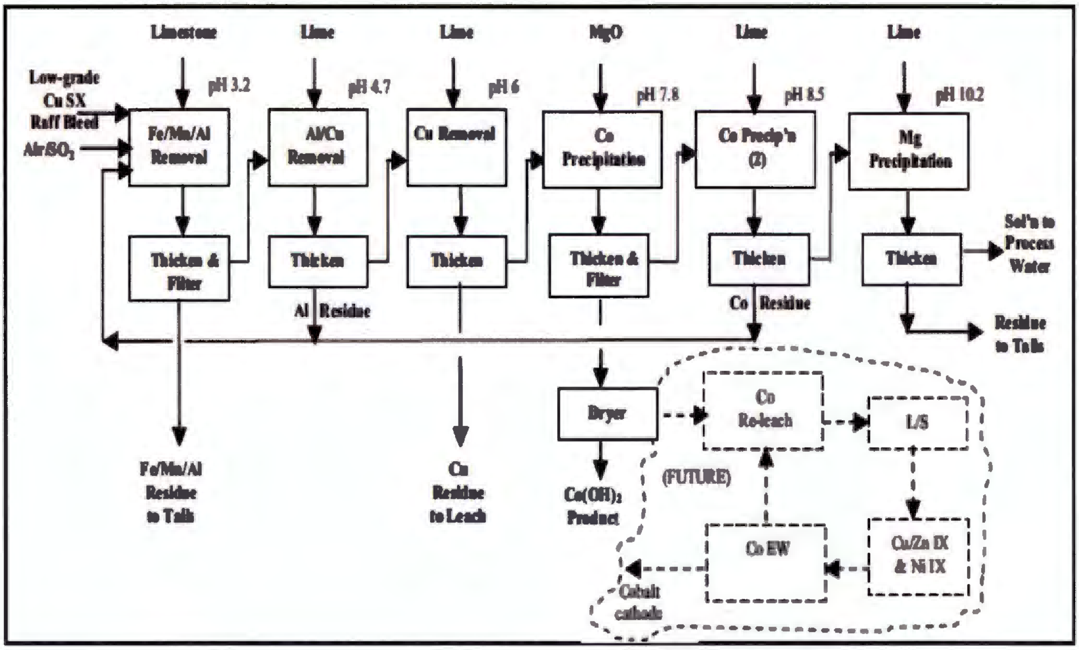


Figure 2.13: Typical Cobalt flowsheet in the DRC (Fisher, 2011)

This is evident in the figure above, which is a proposed flowsheet for DRC project processes. There currently is no preferred process that has yet been developed due to various pros and cons in each flowsheet. It is up to the project leader to choose which process to follow. This is mixed with the complexity of each process (Swartz, 2009)

Product selection

Cobalt comes in various forms as the end product of processing. These forms range from metals and salts of a high purity down to concentrates. The output product is decided during flowsheet development and needs to be finalized before the flowsheet can be finalized. The output options for cobalt vary:

- Cobalt hydroxide (low grade).
- Cobalt hydroxide (high grade) or mixed Ni-Co hydroxide (MHP). (White, 2009)
- Cobalt sulphide or mixed Ni-Co precipitate (MSP).
- Cobalt powder/briquettes, via hydrogen reduction.
- Cobalt sulphate
- Cobalt carbonate
- Cobalt electrowin cathode – HG (99.8%) or LG (99.3)
- Cobalt oxide or oxy-hydroxide

Prior to the world market crash of November 2008; cobalt had reached its peak pricing at US$50/lb, this shown is in the figure 2.13 below.

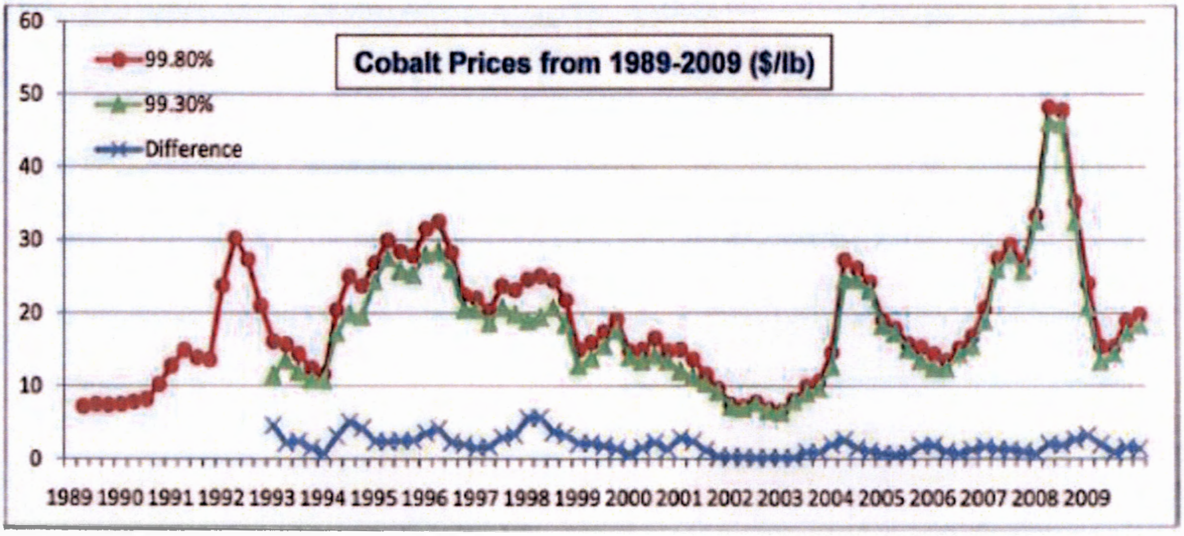


Figure 2.14: Cobalt price from the year (1989 – 2009),(Fisher, 2011)

During that time the focus was on high quality products of carbonate, cathodes or hydroxides. Other factors that now influence its processing are logistics such as site location, whether skilled labour is available and the ruling government policies on cobalt (Peek, 2009).

Role of Cobalt in nuclear forensics

From the literature review above, it is clear that Cobalt can be found in metallic, powder or liquid form. Each of its matrices has accessibility problems when terrorists gain access to the substance. In powder form, and after a neutron activation in a nuclear reactor, it can be fabricated into a dirty bomb. As a solid metal, Cobalt can be smuggled and subjected to reactor activation for illicit purposes. It is therefore not surprising that Cobalt and its radioactive Co-60, are under stringent international safeguards and monitoring.

In a radiological dispersal, it is essential to use the debris to determine the origin of the Co-60 used, through nuclear forensic signatures of either the isotope (Co-60) or the solid metal encapsulation itself. This enables the use of the signature for law enforcement, attribution and possible arrest of the perpetrators and Beneficiaries (M. Mathuthu, 2017).

3: MATERIALS AND METHODOLOGY

3.1 Introduction

The aim of this study was to investigate and determine the usefulness of ICP-MS in nuclear technology application and its potential applicability for resolving and developing nuclear forensics signatures for Co-60 and Uranium mineralisation.

These techniques can produce key information for helping law enforcement agencies in the efforts to intercept illegally obtained nuclear material or material not yet accounted for at any authorized institution or individuals. Seized material, once characterized as evidence there-after needs to be identified.

The material can be identified through various characteristics and various levels of detail. These properties include physical properties, colour and texture, chemical composition, impurities which may present as well as the underlying isotopic composition.

An outcome which was to be reached in this study was producing nuclear signatures in order to form the base for a national nuclear library in the efforts to meet International Atomic Energy Agency (IAEA) compliance standards. With samples obtained from a mine site, whose main activity has to do with gold/uranium extraction from various ores, ICP-MS was the technique applied to determine the elemental composition of the samples from the tailings. From the mining activity employed at the mine, based in Carletonville, North West, it was very possible to obtain data which represents the area's unique geolocation. This geolocation is further aided by the presence of trace elemental impurities whose levels are determined by the processing method of choice employed by the mine. In order to determine signatures as well as the geolocation of the mine, elements of interest were as follows; Na; Ca; Fe; Z; V; Th; sulphates, halogens and phosphates, and finally rare earth elements (Ce, La, Pr, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Sc,Y and Nd) (IAEA, 2003; IAEA, 2015; IAEA, 2016; Mayer, 2016).

3.2 Sampling

Sampling was done at the Gold tailings dump in Carletonville in the western part of the North West Province of South Africa. The samples collected were in the form of soil, water and vegetation with the purpose of detecting the elemental composition therein.

This study would assist in addressing South Africa's nuclear security regime.

The elements which are commonly associated with nuclear weapons are plutonium and uranium. These are hard to obtain and process to weapons grade level. Cobalt-60 however is easily accessible, especially from nuclear waste disposal sites. Co-60 is a very dangerous radioactive material if placed in the wrong hands, as it can be dispersed in a powder form among a crowd increasing exposure rate. This further goes to show the importance of this study, and the necessity to resolve Cobalt-60 signatures for South Africa.

3.2.1 Water sampling

Water that is used for drinking, irrigation at homes and formerly used for irrigation on farms was collected. It is noteworthy to state that the water collected is well within the publics' reach and is used for laundry and also used to irrigate crops which are then fed to sheep. Water is consumed by all living organisms; this shows the significance in sampling water. At each sampling point, along the Klips Drift River, one litre of water was collected in clean plastic bottles and taken to our Radio-analytical and Nuclear Forensics Laboratory at the Centre for Applied Radiation Science and Technology (CARST), where it was treated with 10 ml of HCl acid per 5 litres of water.

3.2.2 Soil Sampling

Our main interest in soil and its interaction with radionuclides is because it is used for agricultural crops which are then consumed by humans and animals at some point in time. The soil was taken from tailings and from living quarters within the mine's property for employees in clean zip-foil plastic bags. Using disposable gloves and plastic bags to avoid contamination between the different soil samples, approximately 2 kg of soil was collected, using an auger with a radius of 10 cm.

3.3 Laboratory sample analysis

3.3.1 Gamma Spectrometry

Each of the soil samples was pulverised and sieved to a fine powder before sealing in Marinelli beakers for 30 days to allow for secular equilibrium between Ra-226 and its daughters. In order to measure the gamma radiation from the samples, gamma ray spectrometry was performed on the samples. For this study, a High-purity germanium (HPGe) detector, by Canberra Industries, was used. It functions at very low temperatures and thus liquid nitrogen was needed to cool it and dropping temperatures to between -201°C and -153°C. However sensitivity efficiency decreases as the temperature drops. Each sample was run for 24 hrs on the gamma spectrometry system and the data was acquired using Gennie 2000 (Vs 3.3) Gamma acquisition Software. The data was then analysed using the Gamma Analysis Software.

Using HPGe the isotopic ratio technique of Co-60 and Ni-60 was determined along with U-235/234 and U-238 ratio. Also lead isotopes (Pb-208, Pb2017, Pb-206, Pb-204) concentration levels (in ppm) were applied to get the ratios for the tailing signatures. The following signature graphs were plotted;

i.) Isotopic ratio of cobalt vs Uranium and Lead isotopes.

ii.) $U^{235/234}/U^{238}$ and $Pb^{206/207}/Pb^{204}$.

iii.) Pb^{208}/Pb^{206} and $Pb^{206/207}$.

3.3.2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The ICP-MS is described as an essential instrument used to determine metal and non-metal concentrations. The advantages of this instrument include the ability to use rather small sample volumes, it has higher sensitivity to signals ratio, a much wider analysis range, high throughput analysis and an ability to perform short analysis times (Ha, 2011).

The Perkin Elmer, NeXION 300Q, Inductively Coupled Plasma Mass Spectrometer (ICP-MS), was used for all sample analysis in this work. It has a Quadrupole ion deflector that focuses the ion beam to the dual mode detector. The Isotope-ratio precision of this instrument is defined for the isotope ratio of $^{107}Ag/^{109}Ag$ internal standard using a 25 µg/L solution, which is achieved by single-point peak hopping with a relative standard deviation (= 100 x SD/AVERAGE, ((0)) of < 0.2% RSD (PerkinElmer, 2010).

Interference reduction

In the ICP-MS analysis of samples, the following molecular ions are potential sources of interferences; oxides, hydrides, hydroxides, and nitrites. The detailed description of the reduction of these elements is found in other works (Mathuthu & Khumalo, 2017).

Chemical separation steps are required before the samples are introduced into the ICP-MS unit for analysis. These chemical separation/digestion steps can greatly influence the detection and sensitivity of the analysed samples. For this work the Perkin Elmer NeXION 300Q (PerkinElmer Inc., UK) was used to determine both the elemental concentrations and the isotopic ratios of the elements of interest for nuclear forensics signatures of Cobalt and Uranium mineralisation. Table 9 below, shows the optimised Parameters of the PerkinElmer ICP-MS Instrument used in this research.

Table 3.1: NexION 300Q ICP-MS Instrumental Parameters (Bosnak & Pruszkowski, 2014)

Parameter	Value
Nebulizer	Glass concentric
Cones (Sampler, Skimmer, super-skimmer)	nickel
Spray Chamber	`glass cyclonic
ample Uptake Rate	300 µL/min
Plasma gas flow	18.0 L/min
Auxiliary gas flow	1.2 L/min
Nebulizer Gas Flow	0.98 L/min (Optimized for 2% CeO^+/Ce^+)
RF Power	1600 W
Cell Gas	99.99% Argon
Detector Type	Dual mode
Sweeps/Reading	200
Readings/Replicate	10
Replicates per sample	3
Mode / Universal Cell Technology™	Isotope Ratio/Collision mode
Total integration time	0.5 s

Water Sample Preparation for ICP-MS

Water samples were acidified with 10 ml of HCl per 5 L of water; this was to prevent radionuclides sticking to the walls of the plastic container. A simple filtering process followed to remove organic solvents from the water and samples were then stored appropriately until further analysis.

Soil Sample Preparation for ICP-MS

Prior to the processing of samples, crucibles were cleaned i.e. they were soaked overnight in used hydrochloric acid and then rinsed with distilled water. The crucibles were dried at 600°C in an oven overnight. They were then placed in a desiccator for cooling for 6 hours. Exactly 1 g of the soil sample was weighed and the measured weight was recorded. The samples were dried in an oven furnace model (G132-002) for 16 hours at 800°C. The dry weight was recorded and the samples were transferred into the rotor vessels. Approximately 1 ml concentrated Nitric acid was added to the samples followed by 10 ml of concentrated Hydrochloric acid. The microwave was placed into the Anton Par 3000 Microwave reactor for 20-45 minutes. The digested samples were transferred into 100-ml volumetric flasks and topped up with water up to the mark. The samples were left to sediment overnight. The supernatant was transferred into the centrifuge tubes for performing ICP-MS analysis.

ICP-MS Isotopic ratio analysis of samples

The ICP-MS was set to isotopic ratio method and then used to analyse all the soil and water samples for isotopic ratios of Co/U; Co/Ni; $^{208}Pb/^{204}Pb$; $^{208}Pb/^{206}Pb$; $^{208}Pb/^{207}Pb$; $^{207}Pb/^{204}Pb$; $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$.

Sample Run

The samples were loaded on to the auto sampler and initialized using the ICP-MS Instrument Control (Data Acquisition) Software. The instrument was set to Isotopic Ratio Method, operated in the Collision Mode for mass energy discrimination and filtration against interferences (Vilta, 2016).

3.3.7 ICP-MS trace calibration for trace element analysis

Quality control samples such as blanks, duplicates, spiked samples and certified reference material were included in the analyses (Keegan *et al.*, 2008) or analysis of trace elements, the Perkin Elmer, NexION 300Q, (ICP-MS), calibration uses a Dual Detector Calibration Solution as the Atomic Spectrometric Standard, whose specifications are defined for the total quantitative method. The standards have 10 mg/L of Al, Ba, Ce, Co, Cu, In, Li, Mg, Mn, Ni, Pb, Tb, U and Zn. For every measurement, the instrument was set to run a blank and a standard check at every ten samples.

4: RESULTS AND DISCUSSIONS

This chapter provides the results of the research in the following order:

- ICP-MS Elemental results for water and soil
- REE results for soil and water
- ICP-MS Isotopic ratio results for U, Co-60 and Pb from water and soil
- Gamma spectrometry results water and soil

4.1 ICP-MS Elemental results for water and soil

Soil sample results from tailing dam 1 and tailing dam 2 showing the provenance of the Co, Cu and Ni group of minerals are shown in Tables 4.1 and 4.2 below. When looking at producing signatures for cobalt at this mine; its important to remember elements recovered along with it, namely copper and nickel. During recovery, as mentioned in Chapter 3; it was mentioned that cobalt is seldom recovered on its own but rather cobalt is recovered as by-product in projects where the ultimate main goal is the recovery of either copper or nickel, or both.

Table 4.1: Provenance of Co, Ni and Cu in the study area of Tailing 1 (in ppm)

Sample ID	**Cu**	**Ni**	**Co**
T1E1	0.491	1.217	0.32
T1E2	0.484	0.92	0.281
T1E3	0.477	1.077	0.325
T1E4	0.53	1.375	0.485
T1E5	0.463	1.113	0.263
T1E6	0.335	0.788	0.233
T1E7	0.405	1.078	0.357
T1E8	0.424	0.996	0.336
T1E9	0.387	4.961	0.275
T1E10	0.516	1.768	0.569
T1E11	0.634	2.187	0.414
AVRG	0.468	1.589	0.351
MAX	0.634	4.961	0.569
MIN	0.335	0.788	0.233
STD.DEV	0.080	1.189	0.102
STD.ERR	0.024	0.358	0.030

Table 4.1 below shows data from 11 samples collected from tailing dam 1. Looking at the data its clear to see that Nickel concentrations are higher than those of Cu and Co. Nickel has a maximum concentration of 4.961ppm and a minimum concentrate of 0.788ppm. Cu has a maximum concentration of 0.643ppm and its minimum concentration level is at 0.335ppm. Co has a maximum of 0.569ppm and a minimum concentration of 0.23ppm. Looking at the average values the order would be Ni>Cu>Co at levels of 1.589ppm, 0.468ppm and 0.351ppm respectively.

Table 4.2: Provenance of Co, Ni and Cu in the study area of Tailing 2 (in ppm)

Sample ID	**Cu**	**Ni**	**Co**
T2E1	0.3520	3.1720	0.1800
T2E2	0.3780	0.6880	0.2100
T2E3	0.7500	1.8470	0.4510
T2E4	0.9750	2.4340	5.1910
T2E5	0.3620	0.9280	0.2260
T2E6	0.3840	0.9380	0.2520
T2E7	0.3430	0.8660	0.2530
T2E8	0.4860	1.4780	0.3330
T2E9	0.3420	0.7780	0.1990
T2E10	0.4550	1.1640	0.3140
T2E11	0.3650	0.8350	0.2380
T2E12	0.2680	0.9740	0.4830
T2E13	0.5170	1.8970	0.4120
AVRG	0.4597	1.3845	0.6725
MAX	0.9750	3.1720	5.1910
MIN	0.2680	0.6880	0.1800
STD.DEV	0.1959	0.7545	1.3612
STD.ERR	0.0543	0.2092	0.3775

Table 4.2 data resulted from 13 samples collected from tailing dam 2. Similar to concentration levels from table 10, Nickel has the highest concentration levels here as well. The average values do however see Cu and Co swopping places. The average concentration values are 1.3845ppm, 0.6725ppm and 0.4597ppm for Ni, Co and Cu respectively.

Ni has a maximum and minimum concentration of 3.1720ppm and 0.6880ppm respectively. Co has a maximum of 5.1910ppm, a level which is higher than any other sample in both tailings and a minimum of 0.1800ppm. Cu has a maximum of 0.9750ppm and a minimum of 0.2680ppm.

Table 4.3: Tailing dam 1: Max, Min and Average concentration (ppm) for soil samples

Element	Maximum	Minimum	Average
Al	896	274	570 ± 60
As	1.5510	0.09790	0.875 ± 0.084
B	0.00901	0	0.00079 ± 0.00008
Ba	0.0800	0.0220	0.0495 ± 0.0041
Ca	656	130	255 ± 28
Cd	0.0010	0	0.00023 ± 0.00006
Co	0.569	0.233	0.351 ± 0.031
Cr	8.826	0.511	4.419 ± 0.039
Cu	0.634	0.335	0.468 ± 0.045
Fe	2420	1127	1782 ± 180
K	94.9	22.82	61.2 ± 6.1
Li	0.143	0.043	0.089 ± 0.009
Mg	553	117	255 ± 23
Mn	23.2	5.9	11.4 ± 1.6
Mo	0.026	0.011	0.018 ± 0.003
Na	11.99	2.22	5.22 ± 0.48
Ni	4.96	0.79	1.59 ± 0.13
P	2.19	0.64	1.55 ± 0.09
Pb	0.131	0.053	0.089 ± 0.007
Rb	0.025	0.006	0.014 ± 0.003
Si	35.6	0	10.6 ± 0.9
Sr	0.282	0.097	0.156 ± 0.016
Th	0.088	0.038	0.047 ± 0.003
Ti	2.89	0.28	1.13 ± 0.12
U	1.365	0	0.530 ± 0.048
Y	0.051	0.015	0.0275 ± 0.002
Zn	1.148	0.274	0.462 ± 0.027

Tailing dam 1 in table 4.3 above shows Al at an average of 570 ± 60ppm; Cr at 4.419 ± 0.039ppm, Cu 0.468 ± 0.045ppm, Zn 0.462 ± 0.027ppm and Fe at 1782 ± 180ppm, when looking at these 5 elements and their composition, their respective levels are considered to be at minor levels with the rest of them being at trace levels, this is indicative of carry through precursor ore. Other averages, namely Sr at 0.156 ± 0.016ppm, Na at 5.22 ± 0.48ppm and Y at 0.0275 ± 0.002ppm, being at such low levels is indicative of the absence of open cast mining. Ni and Fe levels are representative of equipment deteriorating and possible other contaminants during the mining process.

Table 4.4: Tailing dam 2: Max, Min and Average concentrations (ppm) for soil samples

Element	Maximum	Minimum	Average
Al	1324.4180	345.5560	630 ± 63
As	3.01	0.49	1.16 ± 0.17
B	0.0280	0	0.0066
Ba	0.1600	0.0260	0.0655
Ca	566.6030	138.4260	27.1026
Cd	0.0010	0	0.0003
Co	5.1910	0.1800	0.6724
Cr	11.6070	0.5760	4.1201
Cu	0.9750	0.3420	0.4942
Fe	3892.4490	939.0250	1925.7090
K	183.1300	27.3240	72.2848
Li	0.2590	0.0490	0.1006
Mg	1211.0010	266.7930	541.2288
Mn	25.7950	4.5930	12.1445
Mo	0.058	0.011	0.020 ± 0.003
Na	27.9430	4.5040	9.2989
Ni	3.1720	0.6880	1.3845
P	4.1190	0.9270	1.5919
Pb	0.2810	0.0410	0.1109
Rb	0.0390	0.0090	0.0161
Si	149.3070	0.1130	31.4238
Sr	0.3530	0.0930	0.1729
Th	0.0640	0.0300	0.0471
Ti	3.3080	0.1420	0.9581
U	0.8430	0	0.5544
Y	0.0510	0.0120	0.0281
Zn	1.1480	0.2680	0.5205

Boron, in both table 4.3 and 4.4, are at low levels which shows the absence of coal-fired power plant due to a lack of Boon contamination.

When Mo and As present themselves at high concentration levels, this can be linked to an association with unconformity-type ore. This type of ore is characterized by carnotite; uranophane, pitchtitinide and coffinite which are primary elements of U minerals. Cd at high concentrations is linked with a phosphorite deposit which has fluoropatite and apatite that are also indicative of U as a primary mineral.

However due to the intensive, multiple steps and vigorous nature of processing ores, it is expected that there should be some loss of some nuclear forensic fingerprinting characterizing detail. The identification of lanthanides and or rare earth elements (REE) can be used to interpret this loss and add further specification to the fingerprinting of the mine. From these the original deposit type can also be determined.

Four REE have been identified as potential indicators for this mine, namely Ce, Nd, La and Pr, (M. Mathuthu, 2017), both present in tailing dam 1 and 2. Levels in tailing dam 2 are slightly higher than those in tailing dam 1.

Other detections, metazeunerite, urananite as well as REE Rich Uranium phosphate (RRUP) were detected in the samples. Impurities (Fe, Ca and Pb) were detected in this study along with RRUP with a high concentration of Ce and Nd.

When representing the elements detected in graphical form, a better understanding can be ascertained, this approach has been utilized by various authors, including Keegan et al. (2008) in their efforts to do an isotopic and elemental analysis on uranium ores in Australia. This graphical representation has also proved a worthwhile approach for this study as depicted in Figures 4.1 – 4.2 below.

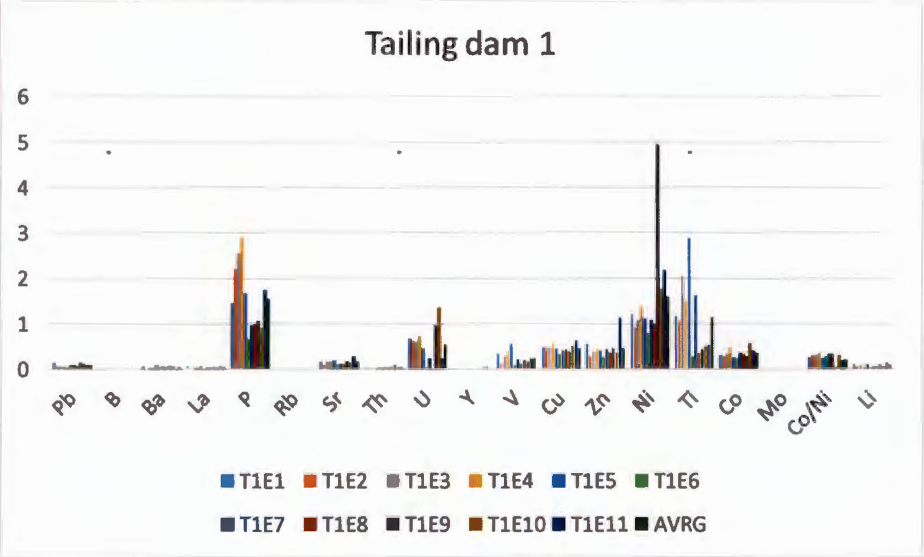


Figure 4.1: Elemental composition of tailing dam 1

Graphical representation of tailing dam 1, above, shows substantial differences between all the elements detected. The concentration of uranium in T1 shows no correlation to the Co/Ni ratio. However in tailing dam 2, there is a noticeable concentration of Co relative to its value in tailing dam 1. This is evident also in the Co/Ni ratios being more correlated to the concentration of uranium.

Fe was found to be the dominant in terms of concentration with other elements following in descending order; Fe > Al > Mg >Ca> K, however due to their very high levels these five elements were removed in order to get a clearly view of the other elements. This was done in both tailing dams graphical representations.

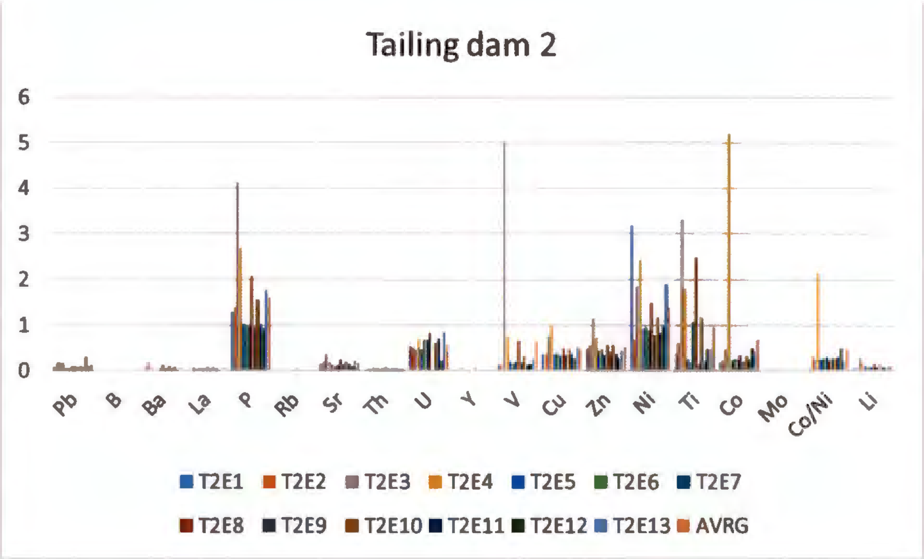


Figure 4.2: Elemental composition of tailing dam 2

Graphical representation of tailing dam 2 above shows a similar trend to tailing dam 1. This is pivotal in confirming that a geolocation can be determined due to similar trends in two locations identified as the mines property, yet boasting a substantial distance of up to 30km between the two locations.

4.1.2 Source guidelines on ICP-MS results

When looking at all the data that was obtained above, it is clear that a set of guidelines to assist with distinguishing the data could be useful, and thankfully previous authors have provided such a guideline. From such guidelines we can determine from the data which part of the data should be considered as an impurity, what should be excluded due to arising through contamination from equipment degradation as well as arising from chemical processes utilized by the mine (Penkin, 2016). This guide was described by Penkin et al. (2016), written on determining source related signatures through utilizing Hf, As, Pb, Mo, Th, W, As and Rr at trace levels, coupling these elements with rare earth elements and platinum group elements can help determine source signatures.

4.2 REE signatures for soil samples

The choice of REE elements is derived from a group of elements known as lanthanides including 2 transitional elements, Sc and Y. The significance of these elements is that due to their chemical stability they are good signatures even though their concentrations vary from location to location. However due to the intensive, multiple steps and vigorous nature of processing ores, it is expected that there should be some loss of some nuclear forensic fingerprinting characterizing detail. This disadvantage can be overcome by using lanthanides or rare earth elements (REE) to add further specification to the fingerprinting of the mine. From these, the original deposit type can also be determined since REE earth elements retain their chemical composition even after uranium processing in the plant.

The results of this work show that the REE levels in tailing dam 2 are slightly higher than those in tailing dam 1 (as shown in Table 4.5 -). Other mineralizations of metazeunerite, urananite as well as REE Rich Uranium phosphate (RRUP) were detected in the samples. Impurities (Fe, Ca and Pb) were detected in this study along with RRUP with a majority of Ce and Nd.

This method was also applied by (Keegan, 2008a), who, through REE concentrations, provided signatures to distinguish between three mines, namely Ranger, Olympic dam and Beverley Dam in Australia. In this study the REE data is presented below.

Table 4.5: REE maximum concentrations

Sample group	No of samples	Max Ce	Max La	Max Pr	Max Nd
Tailing Dam 1	11	0.124	0.061	0.014	0.045
Tailing Dam 2	13	0.154	0.077	0.016	0.051

Looking at the above data for REE maximum concentrations, both tailings seem to be similar but tailing dam 2 having the highest levels for all four REEs, this could be due to sample sizes being slightly different by two extra samples being collected at tailing dam 2.

Table 4.6: REE minimum concentrations

Sample group	No of samples	Min Ce	Min La	Min Pr	Min Nd
Tailing Dam 1	11	0.058	0.03	0.006	0.021
Tailing Dam 2	13	0.049	0.025	0.005	0.018

In the case of the REE minimum concentration levels, tailing dam 2 has the least concentration of Ce and La whereas tailing dam 1 has the lowest minimums for Pr and Nd.

Table 4.7: REE mean concentrations

Sample group	No of samples	Mean Ce	Mean La	Mean Pr	Mean Nd

Tailing Dam 1	11	0.093 ± 0.008	0.046 ± 0.003	0.010 ± 0.003	0.031909
Tailing Dam 2	13	0.097 ± 0.007	0.047 ± 0.006	0.011 ± 0.001	0.033615

Mean concentration levels for both tailings are very similar often being separated by a 0.001 difference.

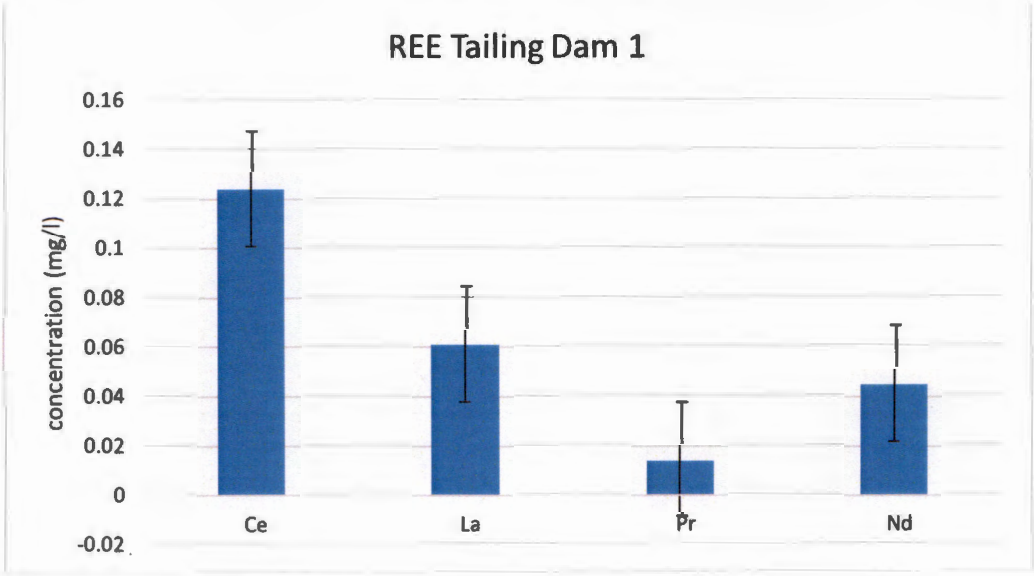


Figure 4.3: REE concentrations for tailing dam 1 (*n=11*)

REE results from Tailing Dam 1, are represented graphically above. Ce dominates in comparison to the other 3 elements in this class of REE chosen. In order of descending order Ce> La >Nd> Pr.

REE results from Tailing Dam 2, are represented graphically above. Again, Ce dominates in comparison to the other 3 elements in this class of REE chosen. In order of descending order Ce > La > Nd > Pr.

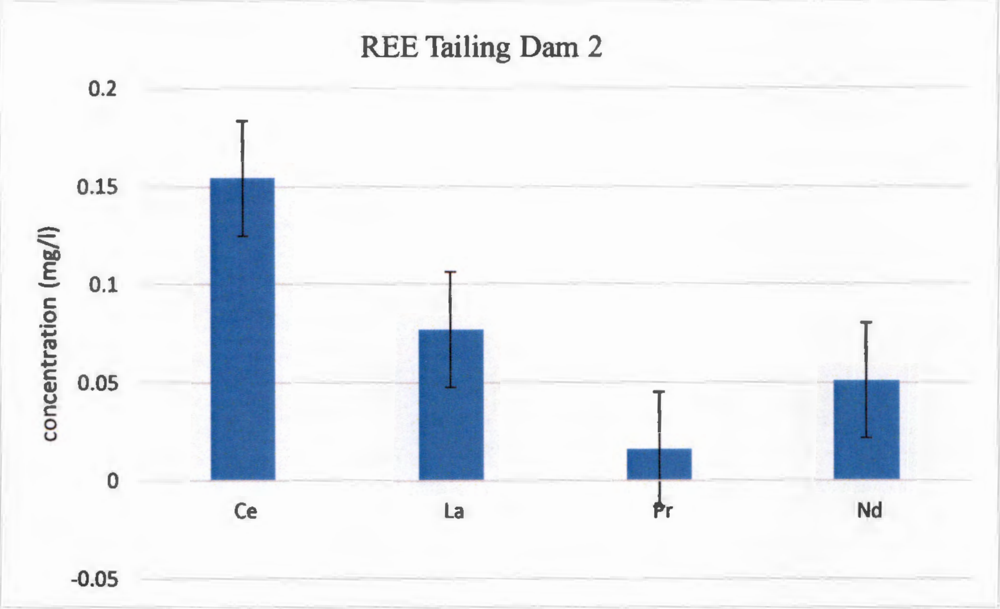
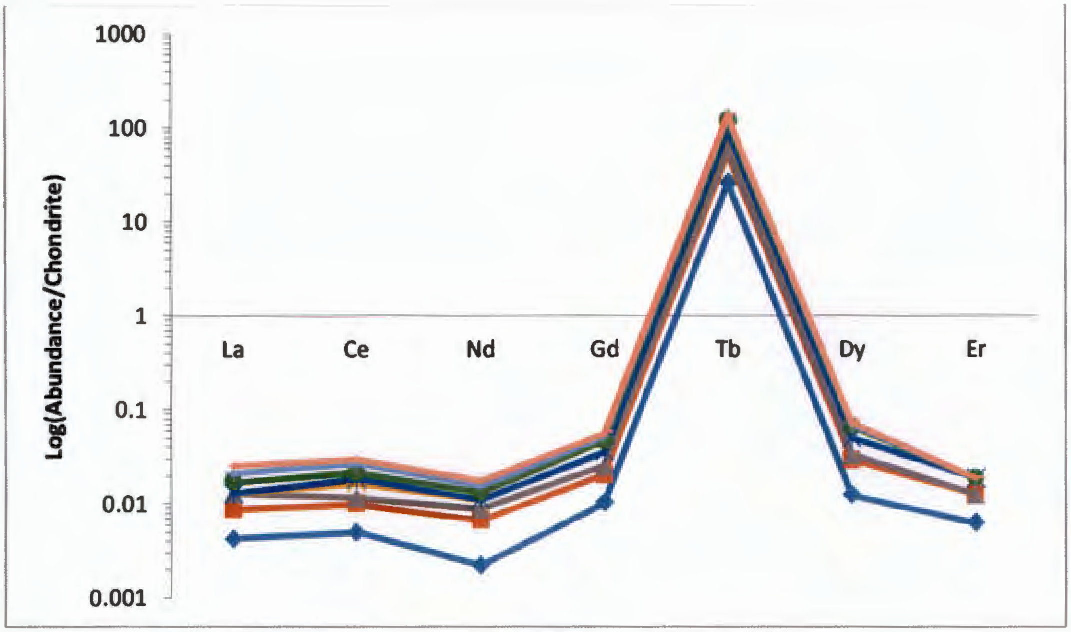


Figure 4.4: REE concentrations for tailing dam 2 (*n=13*)

From the above two tailings' REE results, a clear trend is foreseeable between both tailings which are in two different areas. This similarity, can therefore be established as a signature of this mine and its location (Keegan, 2008b). This method of obtaining a signature has been used by other authors and can be used as a basis for a constructing a nuclear library.

In accordance with Keegan et al (2008), it is essential to follow through in each step at certifying signatures of a mine, as they followed in their study at the 3 mines chosen for their study, namely Beverly, Ranger and Olympic mines. A further step we followed on for this study was the normalization of the mine by using standard chondritic material of known compositions, this method also utilized by Keegan et al (2008). Tailings 3 and 5 were utilized for standardization purposes. See Figure 4.5 a.) – b.) (M. Mathuthu, 2017).

a.)



b.)

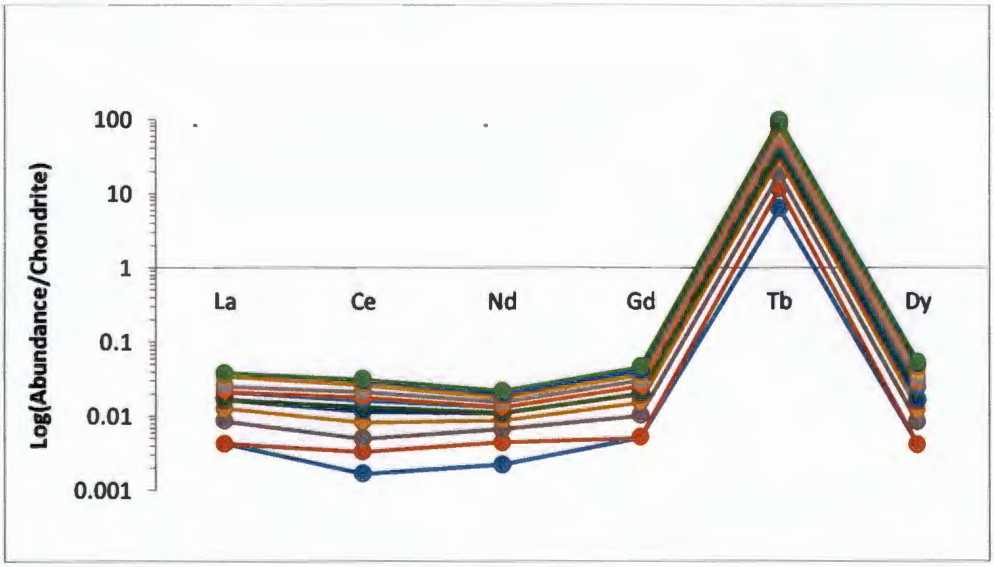


Figure 4.5: REE patterns normalized with Chondrites for a.) Tailing dam 3, and b.) Tailing dam 5

4.3 ICP-MS Isotopic ratio results for U, Co and Pb from soil

4.3.1 ICP-MS Isotopic Analysis

When conventional or traditional forensic investigations are undertaken, key data/evidence is obtained and analysed in order to assist law enforcement in their pursuit for answers. The conventional key evidence/data sought after would be in the form of radioactivity, deoxyribonucleic acids (DNA), REE patterns coupled with fingerprint analysis of all available debris.

In the case of nuclear forensic investigations, isotopic analysis of samples can be regarded as a gold standard approach employed by investigators, similar to that of DNA in conventional forensics. The determination of these isotopic signatures and their representation, have been used to assist in the finding of conclusive decisions for law enforcement agencies around the world (Marin, 2014). The common elements used and sought after by perpetrators are Plutonium, Uranium, Cobalt and Lead. These four heavy metal elements are often seized in sting operations and are measured in post-detonation investigations by law enforcement agencies to assist with investigations.

When the isotopic composition of these four elements are analysed, it can then be applied to decipher certain information, such as the process used for enrichment and from which primary ore. This identifies the geolocation and the origin of the material.

<u>Lead Isotopic ratio Analysis</u>

For this study, lead isotopic analysis as well as their representation were applied in producing further nuclear signatures. Natural lead has four stable isotopes (Reimann, 2012b).

Table 4 .8: Lead isotopes and natural abundances (Reimann, 2012b)

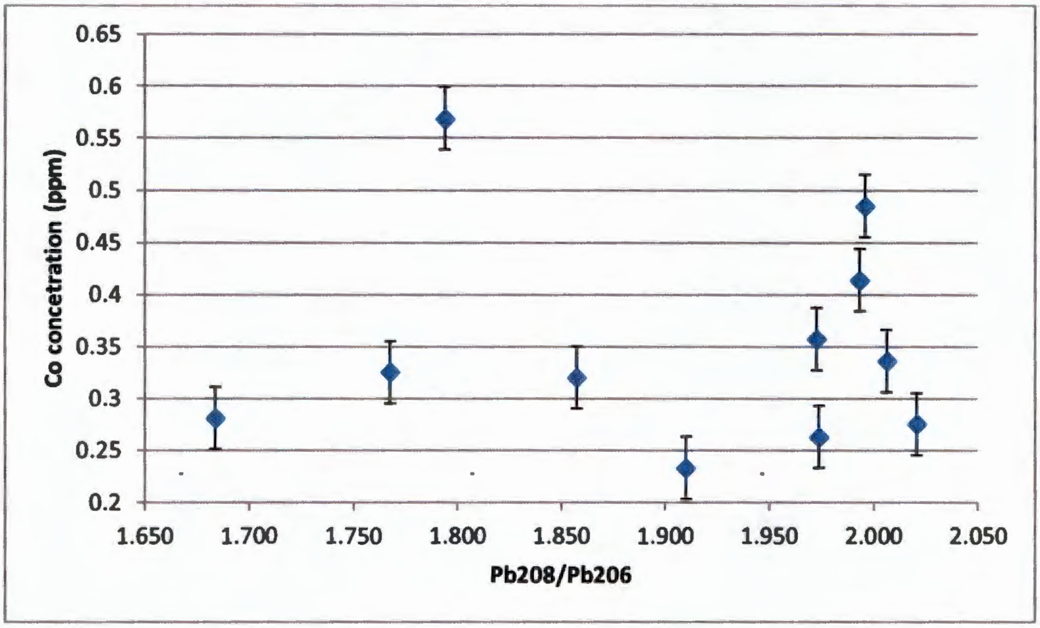
Isotope	Percentage	Total
Pb204	1.4 %	100.0 %
Pb206	24.1 %	
Pb207	22.4 %	
Pb208	52.1 %	

Lead isotopes are used due to two qualities which render them reliable and a gold standard. When introduced to the geological environment lead isotopes are not altered thus allowing for consistency throughout samples obtained from both investigations and those at the site of origin. Another quality is one that is found in three of the four isotopes, namely Pb-208, Pb-207 and Pb-206. These three isotopes are radiogenic and allow for geological processes and sample origin to be determined. These radiogenic isotopes are the result of the decaying process of Th-232, U-235 and U-238 respectively (Švedkauskaite-Legore, 2008; Cheng, 2010).

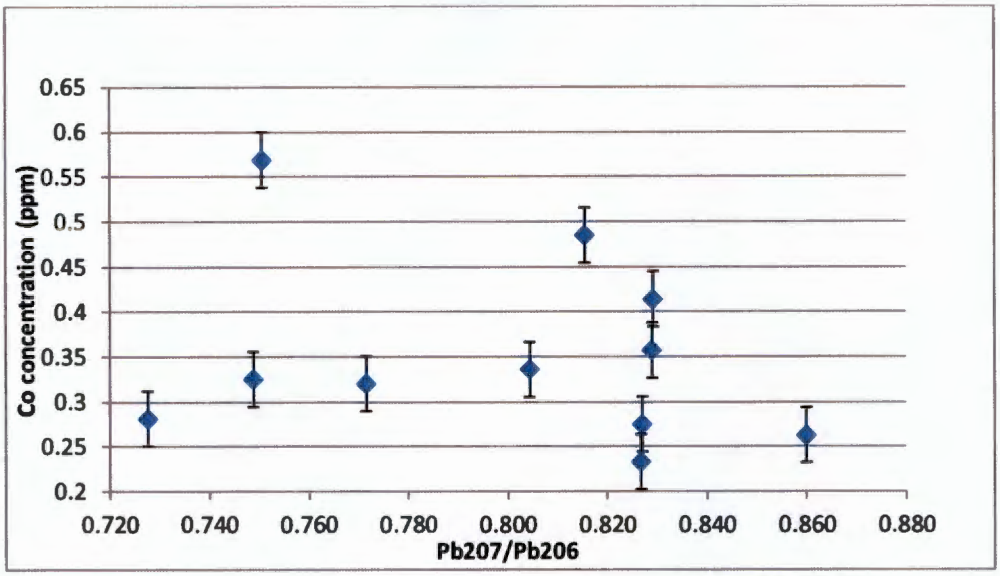
Table 4.9: Decay processes of Th-232, U-235 and U-238 to produce radiogenic lead isotopes

Reaction	Decay Constant	Half-life (years)
${}^{232}_{90}Th \rightarrow {}^{208}_{82}Pb \rightarrow 6{}^{4}_{2}He + 4\beta^{-}$	4.9475×10^{-11}	1.4008×10^{10}
${}^{235}_{92}U \rightarrow {}^{207}_{82}Pb \rightarrow 7{}^{4}_{2}He + 4\beta^{-}$	9.8485×10^{-10}	7.038×10^{8}
${}^{238}_{92}U \rightarrow {}^{206}_{82}Pb \rightarrow 8{}^{4}_{2}He + 6\beta^{-}$	1.55125×10^{-10}	4.468×10^{9}

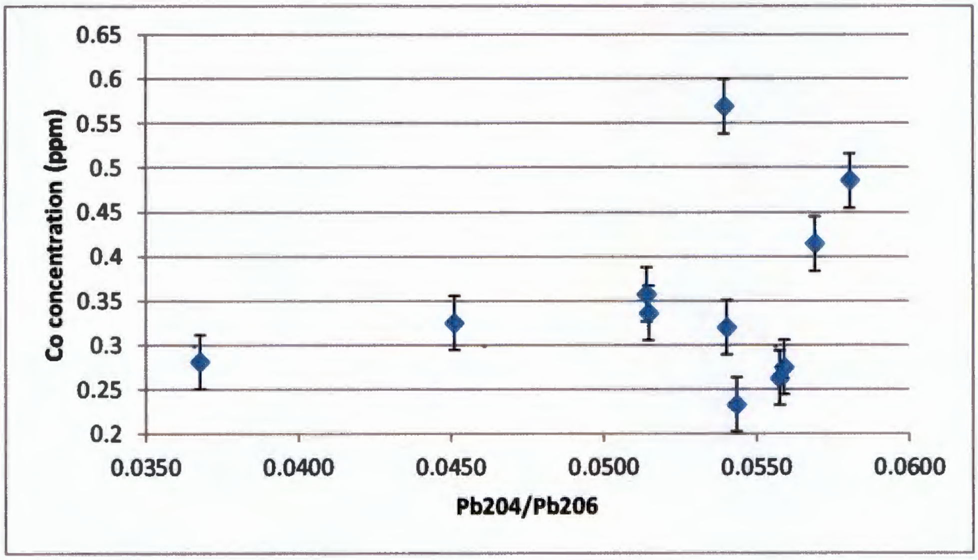
For this mine, the variation of Co concentration with lead isotopic ratios were determined and are displayed in Figure 4.6.



a.)



b.)



c.)

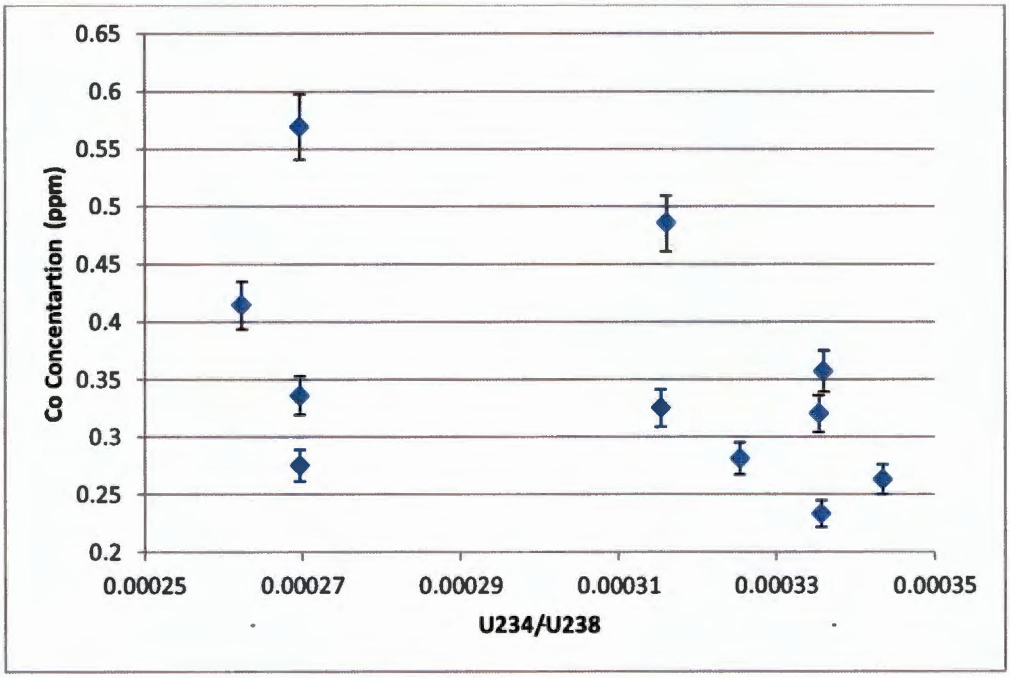
Figure 4.6: Variation of Co vs lead isotopic ratios for a.) $^{208}Pb/^{206}Pb$, b.) $^{207}Pb/^{206}Pb$ and c.) $^{204}Pb/^{206}Pb$ along with standard errors, (± *n=3 for all measured samples*)

The figure above represents the lead isotopic ratios obtained from the Carletonville gold mine. From a.), it is clear that Co concentration varies from 0.2 ppm to 0.55 ppm while the corresponding $^{208}Pb/^{206}Pb$ ratios are mainly around 2.000. From b.), Co ranges from 0.2 to 0.55 while the $^{207}Pb/^{206}Pb$ ratios are around 0.825. In c.), Co has the same range while $^{204}Pb/^{206}Pb$ ratio is around 0.055. These signatures are unique to this South African mine and quite different from those from Beverly, Ranger and Olympic mines (Keegan, 2012). Tailing dam 2 exhibited the same pattern of signatures.

The variation of Co with Uranium ratios is plotted in Figure 4.6 a.) & b.) in the isotopic ratios is accredited to the composition in the ores used, the contamination resulting from the milling process as well as contamination from radiogenic lead removal processes through chemical separation (Varga, 2009).

Looking at the graphs above a similar trend is visible. The average values of Pb206/Pb204 are around 17, Pb207/Pb204 ≈ 14 and Pb208/Pb204 ≈ 35(Varga, 2009; Reimann, 2012a).

a.)



In a.) Co concentrations are correlated to two groups of $^{234}U/^{238}U$ ratios at 0.00027 and 0.00033. While in b.), Co levels are scatterd around a brader group of $^{235}U/^{238}U$ ratio between 0.006 and 0.009. This show validates the fact that ^{235}U and ^{238}U are always mined together. Tailing dam 2 exibitted similar behaviour.

b.)

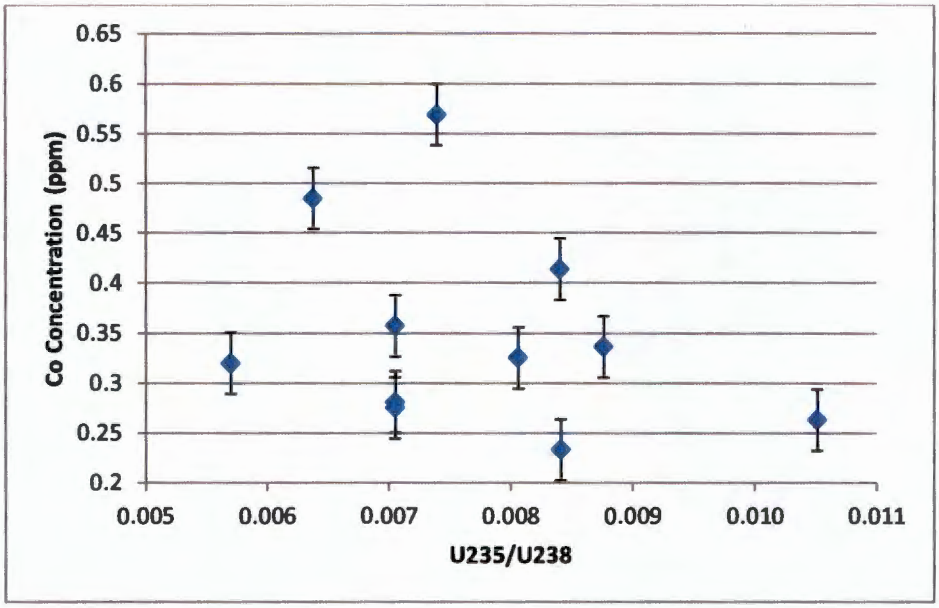


Figure 4.7: Concentartion of Co vs Uranium isotopic ratios. a.) $^{234}U/^{238}U$, b.) $^{235}U/^{238}U$, (for *n=3 repetations)*

The above plots for Pb204/Pb206, Pb207/Pb206 and Pb208/Pb206 also provide conclusions on isotope levels in the Earth crust through consistency. Pb204 plot is the lowest, this is consistent with 1.4% Earth Crust levels. Pb206 presents a higher abundance which is seen in the plots for Pb204/Pb206 and Pb207/Pb206, which present lower levels. Plot for Pb208/Pb206 is higher in comparison to its counter parts, this allows for definite conclusion that Pb208 is the highest in abundance, and rather significantly.(Keegan, 2008b), in their study, concluded that for Ranger Mine, Pb206 was the most abundant. This uniqueness allows for the use of the Pb208/Pb206 plot to be used as a signature for this. Reimann et al (2012) determined lead cross plots which can be used to determine sample origins. The cross plots for this mine follow below. This is to allow future samples seized as evidence to be able to be traced back to this specific mine if they originated from it.

From the above graphs, it is shown that lead detected during analysis came from the mine itself and not from the atmosphere (Cheng, 2010). This is seen by Pb206/Pb207 being the lowest in both graph plots in comparison to its counterpart.

When looking at producing signatures for cobalt at this mine; it is important to remember elements recovered along with it, namely copper and nickel. During recovery, as mentioned in Chapter 3; it was mentioned that cobalt is seldom recovered on its own but rather cobalt is recovered as a by-product in projects where the ultimate main goal is the recovery of either copper or nickel, or both.

In tailing 1; cobalt levels averaged at 0.350727 ppm; with a minimum sample concentration of 0.233 ppm and a maximum of 0.569 ppm. The highest average between the three elements, copper, cobalt and nickel is nickel at an average of 1.58909 ppm; minimum at 0.788 ppm which is higher than any maximum sample concentration for both copper and cobalt respectively.

Table 4.10: Tailing dam 1 Copper, Nickel and Cobalt sample concentrations, min, max, average, standard deviation and standard error

Sample ID	**Cu**	**Ni**	**Co**
T1E1	0,491	1,217	0,32
T1E2	0,484	0,92	0,281
T1E3	0,477	1,077	0,325
T1E4	0,53	1,375	0,485
T1E5	0,463	1,113	0,263
T1E6	0,335	0,788	0,233
T1E7	0,405	1,078	0,357
T1E8	0,424	0,996	0,336
T1E9	0,387	4,961	0,275
T1E10	0,516	1,768	0,569
T1E11	0,634	2,187	0,414
AVRG	0,468	1,589	0,351
MAX	0,634	4,961	0,569
MIN	0,335	0,788	0,233
STD.DEV	0,080	1,189	0,102
STD.ERR	0,024	0,358	0,031

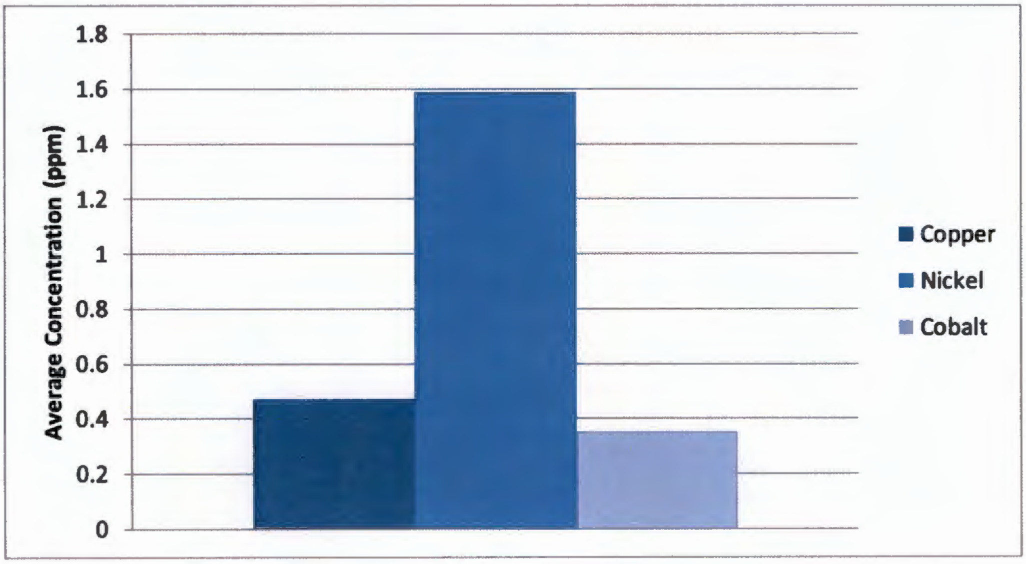
Copper has an average concentration of 0.46782 ppm; a minimum of 0.335 ppm and a sample maximum of 0.634 ppm. This can be summarized as Ni>Cu>Co. This order is expected due to the low levels of cobalt in the Earth's crust to begin with. Tailing 2 boasts a different average order with copper and cobalt switching places, but nickel remains ever dominant by a large extent. The order then becomes Ni > Co > Cu order for tailing 2 averages. Cobalt has an average of 0.67246 ppm and a maximum sample concentration level stands at 5.191 ppm. This maximum is the cause of the skewing in order and graphs. The minimum for cobalt lies at 0.18 ppm. Copper has an average of 0.45977 ppm, its maximum and minimum are 0.975 and 0.268 ppm respectively. This can be seen in the tables below for tailings 1 and 2.

Table 4.11: Tailing dam 2 Copper, Nickel and Cobalt sample concentrations, min, max, average, standard deviation and standard error

Sample ID	Cu	Ni	Co
T2E1	0,352	3,172	0,18
T2E2	0,378	0,688	0,21
T2E3	0,75	1,847	0,451
T2E4	0,975	2,434	5,191
T2E5	0,362	0,928	0,226
T2E6	0,384	0,938	0,252
T2E7	0,343	0,866	0,253
T2E8	0,486	1,478	0,333
T2E9	0,342	0,778	0,199
T2E10	0,455	1,164	0,314
T2E11	0,365	0,835	0,238
T2E12	0,268	0,974	0,483
T2E13	0,517	1,897	0,412
AVRG	0,460	1,385	0,672
MAX	0,975	3,172	5,191
MIN	0,268	0,688	0,18
STD.DEV	0,1960	0,754	1,361
STD.ERR	0,054	0,209	0,378

When represented graphically a trend is visible between the two graphs. Nickel remains dominant and copper and cobalt present similarities between them as well except skewing caused by the Co sample T2E4 at 5.191, which resulted in a shift in order. This irregularity will how ever be replaced by other sample results to correct this very visible irregularity

a.)



b.)

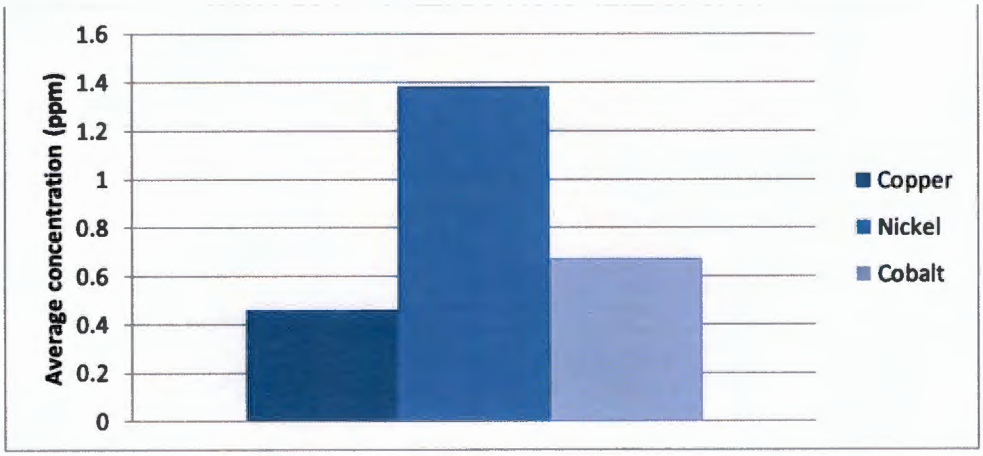


Figure 4.8: Copper, Nickel and Cobalt mean concentrations for a) Tailing 1 and b) Tailing 2

Cross plots have been produced in an efforts to ascertain signatures for cobalt at this mine. These were plotted against previously determined lead levels. This approach is similar to that utilized by Cheng and Hu (2010).

4.4 Gamma Spectrometry isotope ratio results

4.4.1 Gamma Isotopic Analysis

Gamma spectrometry is an ideal first approach technique when an incident takes place involving nuclear material and there is a need for nuclear forensic analysis investigations (Nafaa., 2006; Gregg, 2011). This is accredited to its non-destructive properties. Other properties and qualities of gamma spectrometry that make it ideal are its low operational costs as well as efficiency with time.

In this study samples were first introduced to gamma spectrometry analysis procedures mentioned in Chapter 3. Later these samples being reusable were then sent for ICP-MS analysis which is a destructive technique on samples. Results from gamma spectrometry, shown in the table 4.12 and figure 4.9 below showed the positive presence of our element of interest in this study, Cobalt. Also detecting a wide variety of elements, some of which were of use for this study and others not.

Again it is key to bear in mind that Co-60 was not to be detected in either ICP-MS or Gamma Spectrornetry analysis as Co-60 does not appear in nature, the isotope to be detected was Co-57 which is a stable isotope found in nature. In order to produce Co-60 this is accomplished through neutron activation inside reactors (Schreiner, 2003; Fisher, 2011; Shedd, 2014).Thus Co-57 was a representative of Co-60. To further support signatures for the mine in this study, ^{235}U was looked at as well as ^{238}U. However U238 is presents at very low levels, this makes it very difficult to detect. This difficulty is also to be expected in Cobalt detection which presents itself at a low gamma level.

U238 therefore was represented by its daughter isotope Ra-226. The 226Ra becomes in secular equilibrium with 238U after sealing the samples for 30 days. The equilibrium is between daughter Ra-222 and Ra-226 before analysing the samples with Gamma Spectrometry technique.

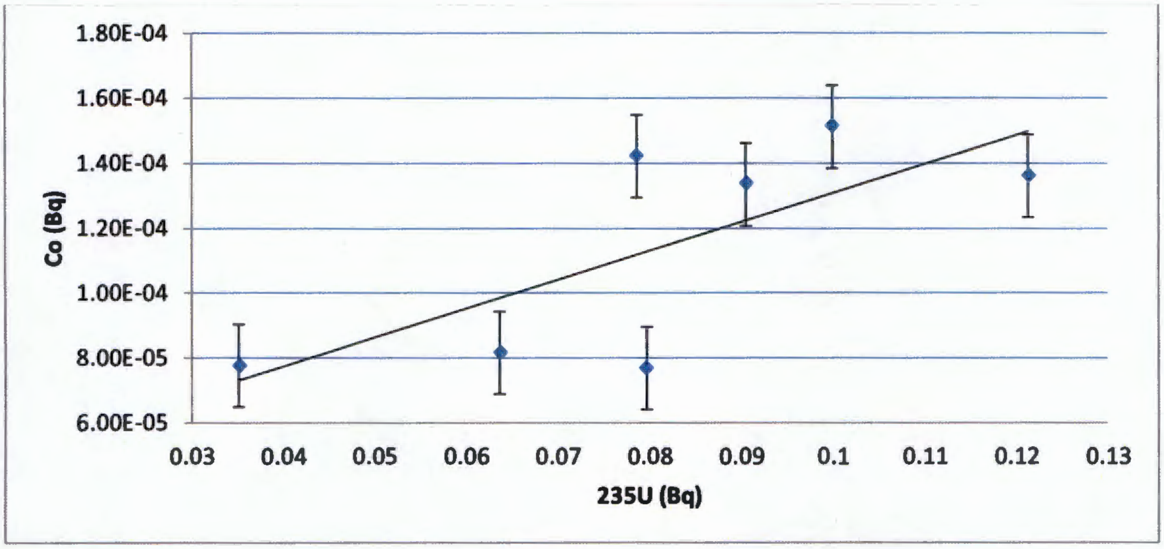
Ra-226 was chosen and detected at its level of 186.31keV bearing in mind that there is possible interference from U235 at this energy.

Table 4.12: Table showing Cobalt and Uranium isotope activity (Bq) in Tailing Dam1

Sample ID	Co-57	U235	Ra226
T1E4	8.163E-05	0.096	0.064
T1E5	7.759E-05	0.126	0.0351
T1E6	14.232E-05	0.140	0.0786
T1E7	7.677E-05	0.115	0.0797
T1E8	13.312E-05	0.157	0.0912
T1E9	15.114E-05	0.142	0.0999
T1E10	13.633E-05	0.223	0.121
MAX	15.114E-05	0.223	0.121
MIN	7.677E-05	0.096	0.0351
AVERAGE	11.414E-05	0.1427	0.0813

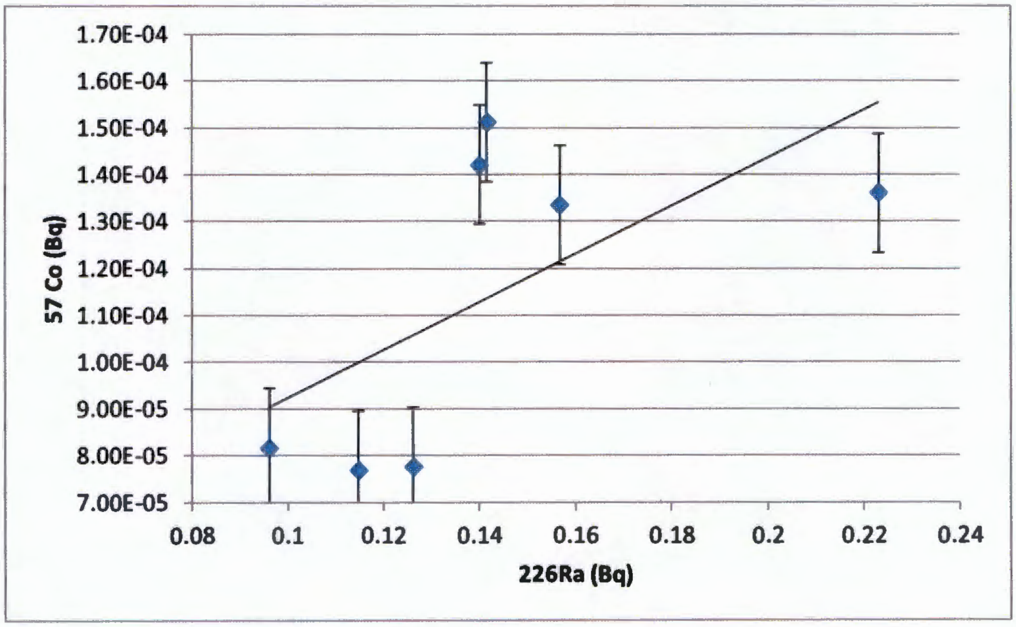
The data above will be presented below in graphical form in order to find correlation and potential signatures for cobalt at this particular mine. Cobalt presents at a maximum of 15 x $10^{(-5)}$ and at a minimum of 7.7 x $10^{(-05)}$. It amounts to an average of 11 x $10^{(-5)}$. U-235 presents at a maximum of 22 x $10^{(-2)}$, minimum of 9.6 x $10^{(-2)}$ and an average of 14 x $10^{(-2)}$. The last isotope being used is 226Ra and presents at a minimum and maximum of 3.5 x $10^{(-2)}$ and 12 x $10^{(-2)}$ respectively. The average for 226Ra is 8.1 x $10^{(-2)}$.

a.)



1.80E-04
1.60E-04
1.40E-04
1.20E-04
1.00E-04
8.00E-05
6.00E-05
Co (Bq)
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
235U (Bq)

b.)



1.70E-04
1.60E-04
1.50E-04
1.40E-04
1.30E-04
1.20E-04
1.10E-04
1.00E-04
9.00E-05
8.00E-05
7.00E-05
57 Co (Bq)
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
226Ra (Bq)

c.)

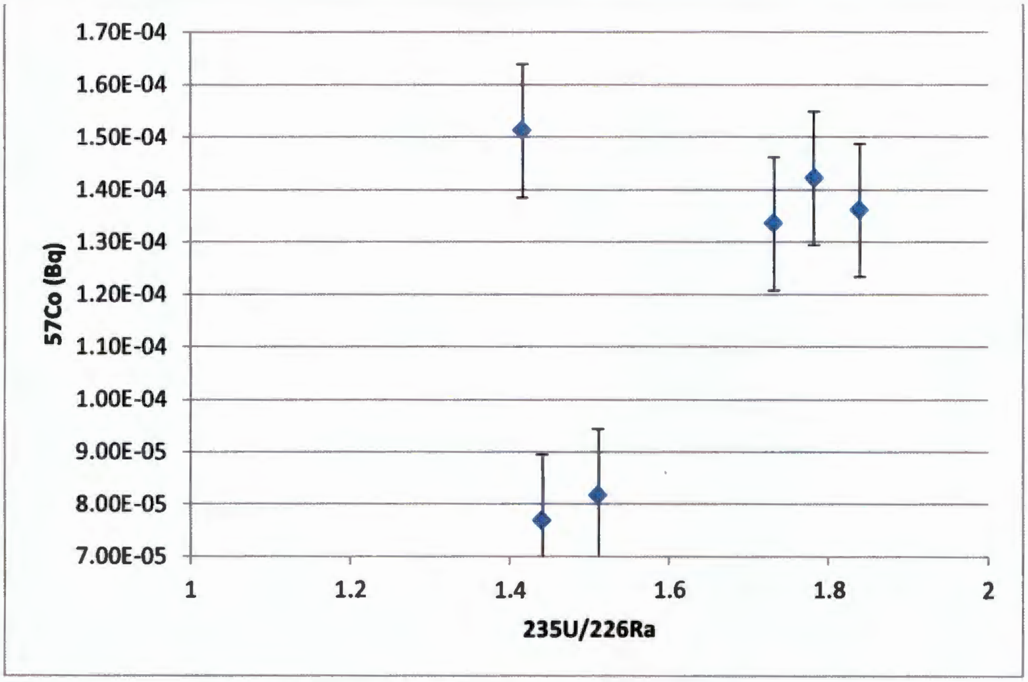


Figure 4.9: Concentration of Cobalt vs isotopes of- a.) 235U, b.) 226Ra and c.) 235U/226Ra

When represented graphically its clear to see a correlation between 57Co (representing Cobalt) and Uranium (represented by isotopes or decay isotopes. In a) it is clear that the signature of ^{57}Co and ^{235}U is around 8.5(Bq) x 10^{-5}) for ^{235}U concentrations less than 0.08, and is around 1.4 x 10^{-4} for ^{235}U greater than 0.08 (Bq).

Similarly from b.) the signature of ^{57}Co and ^{226}Ra (^{238}U) is around 8.5 x 10^{-5} for 226Ra concentrations less that 0.13 (Bq), and is around 1.4 x 10^{-4} for ^{226}Ra greater than 0.13 (Bq).

However in c), *the nuclear forensics signature* of this radioactive element ^{57}Co, is around ^{235}U/^{226}Ra isotopic ratio of about 1.45 for concentrations of ^{57}Co equal to 8 x 10^{-5} Bq, as expected and this ratio jumps to around 1.8 for **57**Co equal to 1.4x10^{-4} Bq.

4.5 Conclusion

4.5.1 Summary of Results

ICP-MS found 57Co; Cu and Ni levels to be at 0.351, 0.468 and 1.589 ppm respectively in tailing dam 1 and 0.673; 0.460 and 1.385 ppm in tailing dam 2 respectively. Mo and As were present at high concentration levels, this is indicative of an or that is an unconformity- type ore impurities were also detected which are a result of processing efforts by the mine, along w ith lanthanides and RRE. ^{235}U and ^{238}U are mined together due to cross plots which indicated Co levels being scattered broadly in relation to ^{235}U/^{238}U radioisotopes. ^{208}Pb/^{206}Pb isotopic ratio plots can be used as a potential signature to determine sample origins due to its uniqueness. Using gamma spectrometry, 57Co and ^{235}U signature is around 8.5 (bq) x 10 $^{(-5)}$) for 235U concentrations less than 0.08, and is around 1.4 x 10$^{(-4)}$ for ^{235}U greater than 0.08 (Bq). The signature of ^{57}Co and ^{226}Ra (^{238}U) is around 8.5 x 10$^{(-5)}$ for ^{226}Ra concentrations less that 0.13 (Bq), and is around 1.4 x 10$^{(-4)}$ for ^{226}Ra greater than 0.13 (Bq).

4.5.2 Role of Nuclear forensics in Law enforcement

When an investigation is taken up, that requires traditional forensic approach, it is of great importance to know how to treat the samples, which process to administer first and which to apply last to the samples. Traditional forensics has become a rather guaranteed if a sample is collected and the perpetrator's sample is obtained as well. This, in television and various forms of media, has made forensics a gold standard almost magical summoning of justice. As a scientist we understand the finer workings of the process and often strenuous efforts that go into justice being delivered promptly. This has been due to years of publications and efforts, leading to new methods being developed, approaches being refined and going as far as databases with profiles of samples that are just waiting for a perpetrator to act again if not caught the first time.

Nuclear forensics is practically the same approach to investigative methods, different sample types but these have been met with equal techniques such as ICP-MS and gamma spectrometry. There are various forms of these techniques that involve coupling extra devices and components. This study fulfils a part of the IAEA member State responsibilities of cataloguing signatures of elements and additional geolocation signatures with our country, South Africa, adding onto our nuclear library.

Nuclear forensics is still very young in development yet such great strides have been made, by utilizing these developments it makes it very possible to catalogue sources that originate from within our own Country to meet international standards of having a nuclear library.

This study has laid grounds to further other studies where other components on nuclear applications can be refined and explored further. Having a nuclear library will allow for a prompt response towards any incident, whether confirming that indeed the sample, example, Cobalt originated from this mine in the west of Gauteng or to eliminate this location allowing for an expedient investigation.

This however can be improved through future studies where age determination processes are coupled with ICP-MS and Gamma Spec in order to further grow this field.

REFERENCES

AfricanRainbowMineralsLtd. 2015. Interim results for the six months ended 31 december 2014. Sandton, South Africa

Aggarwal, A., Govindan. 2003. Ion source chemistry during simultaneous analysis of thorium and uranium by thermal ionisation mass spectroscopy. 249:47-50.

AquariusPlatinumLtd. 2015. Second quarter 2015 production results—production results to 31 december 2014. Bermuda.

Baude, C., Kimmel, Marriotte, Masse, Peron, Tilly, . 2007. The french response in cases of illicit nuclear trafficking. In: Proceedings of the iaea conference on illicit nuclear trafficking. *International Atomic Energy Agency*:363-371.

Bellis, K.M.H., J. Jones, D. Amarasiriwardena and P. J. Parsons. 2006. Calibration of la-icp-ms for quantitative measurements of lead in bone. *J. Anal. At. Spectrom*(21):948.

Bosnak, C. & Pruszkowski, E. 2014. The analysis of drinking waters by u.S. Epa method 200.8 using the nexion 300d/350d icp-ms in standard, collision and reaction modes. *PerkinElmer, Inc.Shelton, CT*, APPLICATION BRIEF ICP - Mass Spectrometry: :1-4.

Brown, S.R. 2015. Paris suicide bombers used tatp, a powerful, homemade explosive: Officials. http://www.nydailynews.com/news/world/paris-suicide-bombers-tatp-homemade-explosive-article-1.2435082 Date of access: 20 November 2015.

Catarino, A.S.C.-G.a., R. Bruno de Sousa. 2006. Measurements of contaminant elements of wines by inductively coupled plasma-mass spectrometry: A comparison of two calibration approaches. *Talanta,*(70):1073-1080.

Cheng, H.H., Y. 2010. Lead (pb) isotopic fingerprinting and its applications in lead pollution studies in china: A review. *Environmental Pollution*, 158:1134-1146.

CobaltDevelopmentInstitute. 2015b. 2015 first half production statistics: Cobalt news.

Dalvi, B.a.O. 2004. The past and the future of nickel laterites. Paper presented at the PDAC 2004 International Convention, Trade Show & Investors Exchange, March 7-10.

Do, H.F.H., W. C. Chang, E. E. Chang and & Wang, C.F. 2011. Analysis of liquid samples using dried-droplet la-icp-ms. *Spectrochim. Acta, Part B,*(66):610.

Dressler, D.P., M. Foster Mesko, A. Matusch, U. Kumtabtime, B. Wue and J. S. Becker. 2010. Bioimaging of metals in thin mouse brain section by la-icp-ms: Novel online quantification strategy using aqueous standards. *Talanta,*(82):1770.

Economist, T. 2013. Dirty bombs: Glowing in the dark29 November 2015.

EuropeanCommission. 2009. Nucleonica, web driven nuclear science. http://www.nucleonica.net/Application/CommunityPortal.aspx Date of access: 18 January 2016.

Fischer, D. 1997. History of the international atomic energy agency: The first forty years. Vienna, Austria: IAEA.

Fisher. 2011. Cobalt processing developments Paper presented at the 6th Southern African Base Metals Conference Southern African Institue of Mining and Metallurgy

FRAM. 1993. Plutonium isotopic analysis system.

Gilchrist, T.C. 1879. A case of dermatitis due to the x rays. *Bull Johns Hopkins Hosp*, 8(71):17-22.

GlobalSecurityNewswire. 2010. Men admit to attempting heu sale in georgia. http://www.nti.org/gsn/article/men-admit-to-attempting-heu-salein-georgia/ Date of access.

Grant, P.M., MOODY, K.J., HUTCHEON, I.D., PHINNEY, D.L., WHIPPLE, R.E., HAAS, J.S., ALCARAZ, A, ANDREWS, J.E., KLUNDER, G.L., RUSSO, R.E., FICKIES, T.E., PELKEY, G.E., ANDRESEN, B.D., KRUCHTEN, D.A. & CANTLIN,. 1998. Nuclear forensics in law enforcement applications,. *JOurnal of Radioanalytical Nuclear Chemistry*, 235(129):1-2.

Gregg. 2011. Comparison of a high purity germanium gamma ray spectrometer and a multidimensional

nai(tl) scintillation gamma ray spectrometer Date accessed: 04 June 2015.

Gunther, A.v.Q., R. Wirz, H. Cousin and V. J. Dietrich. 2001. Elemental analyses using laser abalation-inductivley coupled plasma-mass spectrometry (la-icp-ms) of geological samples fused with li2b4o7 and calibrated without matrix-matched standards. *Mikrochim. Acta*(136):101.

Gunther, I.H.a.B.H. 2000. Recent trends and developments in laser ablation-icp-mass spectrometry. *J. Anal. Chem.*, 4:368.

Ha, T., Churchill. 2011. A tutorial and mini-review of the icp-ms technique for determinations of transition metal ion and main group element concentration in the neurodegenerative and brain sciences142) Date accessed.

Hall, J. 2013. Cobalt 60 theft: Lorry transporting radioactive cargo found empty in mexico, but hijackers expected to die with in days.02-12-2015 2015.

Han´c, A.O.a.D.B. 2013. Quantitative analysis of elements migration i human teeth with and without filling using la-icp-ms. 61(110).

Hattendorf, G.a.B. 2005. Solid sample analysis using laser ablation inductively coupled mass spectrometry *Trends Anal. Chem*, 24:255.

Hoffmann, C.L.a.H.S. 1997. Determination of metalions in single wood fiber by la-icp-ms. *J. Anal. Chem*:359.

Hutcheon, K., Knight. 2013. Nonproliferation nuclear forensics, in: Uranium Paper presented at the Cradle to Grave, Winnipeg.

Hutcheon, M.K., K. Knight. 2015. Nonproliferation nuclear forensics. *Mineralogical Assocaition of Canada*, 43.

IAEA. 2000. Methods of exploitation of different types of uranium deposits. http://www-pub.iaea.org/MTCD/publications/PDF/te_1174_prn.pdf Date of access: 23 September 2017.

IAEA. 2003. Manual for reactor produced radioisotopes. *IAEA NUclear Security Series*.

IAEA. 2006. Iaea nuclear security series no. 2. *Technical Guidance Nuclear Forensics Support Reference Manual. International Atomic Energy Agency Vienna*.

IAEA. 2015. Nuclear forensics in support of investigations - implementing guide. Paper presented at the IAEA, Vienaa.

IAEA. 2016. Nuclear forensics support. Reference manual. Paper presented at the IAEA NUclear Security Series, IAEA, Vienna.

Keegan, E., Richter, S., Kelly, I. & Alonso-Munoz, A. 2008. The provenance of australian u ore concentrates by elemental and isotopic analysis. *Applied Geochemistry*, 23(4):765-777.

Keegan, E., RICHTER, S., KELLY, I., WONG, H., GADD, P., KUEHN, H. & ALONSO-MUNOZ, A. 2008a. The provenance of australian uranium ore concentrates by elemental and isotopic analysis. *Applied Geochemistry*, 23:765-777.

Keegan, E., RICHTER, S., KELLY, I., WONG, H., GADD, P., KUEHN, H. & ALONSO-MUNOZ, A. 2008b. The provenance of australian uranium ore concentrates by elemental and isotopic analysis. *Applied Geochemistry,*, 23:762-777.

Keegan, E., WALLENIUS, M., MAYER, K., VARGA, Z. & RASMUSSEN, G. 2012. Attribution of uranium ore concentrates using elemental and anionic data. *Applied Geochemistry*, 27:1600-1609.

Knoll, G.F. 1989. Radiation detection and measurement 2.

Kovacs, S.S., S. P. Staub, A. Schmiderer, E. Pernicka and D. G¨unther. 2009. Characterization of calibration materials for trace element analysis and fingerprint studies of gold using la-icp-ms *J. Anal. At. Spectrom*(24):476.

Kristo. 2012. Nuclear forensics *Handbook of Radioactivity Analysis*

Little, M. 2003. Risks associated with ionizing radiation. *Impact of environmental pollution on health: Balancing risk*, 68(1):259-275.

Livhuwani, M. 2010. Tailings dams and radioactive bricks – acid water in gauteng. http://www.bdlive.co.za/articles/2010/12/08/tailings-dams-and-radioactive-bricks---acid-water-in-gauteng Date of access: 10 June 2015 2015.

Llyod, P., Horstwood. Nuclear forensic application of la-mc-icp-ms. Paper presented at the Thermo Fisher Scientific, Bermen, Germany

Local, T. 2015. Security tight at france's nuclear power plants. http://www.thelocal.fr/20151125/france-ramps-up-security-at-nuclear-power-stations-terrorism Date of access: 27 November 2015.

M. Mathuthu, N.K. 2017. Determination of lead isotope ratios in uranium mine products in south africa by means of inductively coupled plasma mass spectrometry. *J Radioanal Nuch Ch*:1-12.

Madalia. 2004. Nuclear terrosim: A brief review of threats and responses http:/digital.library.unt.edu/ark:/67531/metacrs6190/ Date accessed: 22 July 2015.

Maguire, H., Fraser, G., Croft, J., Bailer, M., Tattersall, P., Morrey, M., Turbitt, D., Ruggles, R., Bishop, L., Giraudon, I., et al.,. 2010. Assessing public health risk in the london polonium-210 incident, 2006. *Public Health*, 124(6):313-318.

Marin, R.C., SARKIS, J. E. & PESTANA, R. C. 2014. Nuclear forensics: Strategies and analytical techniques. Paper presented at the International Nuclear Atlantic Conference, Recife, PE, Brazil.

Mathuthu, M. & Khumalo, N. 2017. Determination of lead isotope ratios in uranium mine products in south africa by means of inductively coupled plasma mass spectrometry. *Journal of Radioanalytical and Nuclear Chemistry*:1-12.

May, R.H.W. 1998. A table of polyatomic interferences in icp-ms. *At. Spectrosc*, 5(19):150.

Mayer ., W.M.a.F.T. 2007. Nuclear forensic science - from cradle to maturity *Journal of Alloys and Compounds* 50-56.

Mayer, a.M.W. 2016. Nuclear forensics. *RADIOCHEMISTRY AND NUCLEAR CHEMISTRY*, 2:1-7.

Mayer, M.W., I. Ray, Nuclear forensics. 2005. A methodology providing clues on the origin of illicitly trafficked nuclear materials, . *Analyst 130*, 130:433-441.

Nafaa., R. 2006. Gamma ray spectrometry-a practical information.

Niemeyer, S., Hutcheon, I. 1999. Geolocation and route attribution in illicit trafficking of nuclear materials, 21st esarda symposium. Sevilla, Spain. (Report EUR 18963 EN).

Nobelprize.org. 2014. Henri becquerel - facts. http://www.nobelprize.org/nobel_prizes/physics/laureates/1903/becquerel-facts.htmlMedia Date of access: 21 September 2015.

Nossiter, A., Breeden, A., and Bennhold, K.,. 2015. Three teams of coordinated attackers carried out assault on paris, officials say; hollande blames isis. *New York Times*.

Pakieła, M.W., B. Wagner and E. Bulska, J. 2011. A novel procedure of powdered samples immobilization and multi-point calibration of la-icp-ms. *J. Anal. At. Spectrom*(26):1539.

Peek, A.a.A. 2009. Technical considerations of cobalt hydrometallurgy. *Journal of Metallurgy*, 61(10).

Penkin, M., BOULYGA, S. & FISCHER, D. 2016. Application of uranium impurity data for material characterization in nuclear safeguards. *Journal of radioanalytical and nuclear chemistry,*, 307(1995-1999).

PerkinElmer, W. 2010. Nexion 300q icp-ms specifications icp-ms spectrometry. *PerkinElmer, Inc. Waltham,*:1-2.

Pisonero, B.F.a.a.D.G.u. 2009. Critical revision of gd-ms, la-icp-ms and sims as inorganic mass spectrometric techniques fro direct solid analysis *J. Anal. At. Spectrom*, 24:1145.

Potter, W.C. 1995. Before the deluge? Assessing the threat of nuclear leakage from the post-soviet states. *Arms Control Today*:9-16.

Reimann, C., FLEM, B., FABIAN, K., BIRKE, M., LADENBERGER, A., NÉGREL, P., DEMETRIADES, A., HOOGEWERFF, J. & TEAM, T. G. P. 2012a. Lead and lead isotopes in agricultural soils of europe–the continental perspective. *Applied Geochemistry,*, 27:532-542.

Reimann, C., FLEM, B., FABIAN, K., BIRKE, M., LADENBERGER, A., NÉGREL, P., DEMETRIADES, A., HOOGEWERFF, J. & TEAM, T. G. P. . 2012b. Lead and lead isotopes in agricultural soils of europe–the continental perspective. . *Applied Geochemistry*, 27:532-542.

Rhodes, R. 1995. Dark sun: The making of the hydrogen bomb. New York: Simon and Schuster.

Schreiner, L.J., Kerr, A., Salomons, G., Dyck, C., Hajdok, G. 2003. The potential for image guided radiation therapy with cobalt-60 tomotherapy *Medical Image Computing and Computer assisted Intervention-MICCAI* 2879:5, 6, 108.

Seaborg. 1970. Reminiscences on the development of some medically useful radionuclides 2015.

Shedd, K.B. 2014. Cobalt *U.S. GEOLOGICAL SURVEY MINERALS YEARBOOK-2014*.

Stanley, S., A.M ; Spitz, H.B. 2013. A brief introduction to analytical methods in nuclear forensics. *Journal of Radioanalytical and Nuclear Chemistry*, 295(2):1385-1393.

Steafel, E., Mulholland, R., Sabur, R., Malnick, E., Trotman, A., Harley, N. 2015. Paris terror attack: Everything we know on saturday afternoon. http://www.telegraph.co.uk/news/worldnews/europe/france/11995246/Paris-shooting-What-we-know-so-far.html Date of access: 29 November 2015.

Stevens, L.G. 1896. Injurious effects on the skin. *BMJ*, 1:998.

Švedkauskaite-Legore, E., J., RASMUSSEN, G., ABOUSAHL, S. & VAN BELLE, P. . 2008. Investigation of the sample characteristics needed for the determination of the origin of uranium-bearing materials. *Journal of radioanalytical and nuclear chemistry,*, 278:201-209.
Swartz, D.a.A. 2009. Processing considerations for cobalt recovery from congolese copperbelt ores. Paper presented at the SAIMM Southern African Hydrometallurgy Muldersdrift, Johannesburg, RSA.
UK-Legislation. 1984. Criminal justice act 2003 10(2) amending s.63 of police and criminal evidence act 1984. Applicable to england, wales and northern ireland, but not scotland.
UNSCEAR. 2000. United nations scientific committee on the effects of atomic radiation (unscear). Sources and effects of ionizing radiation. Unscear 2000 report to the general assembly, with scientific annexes. New York: United Nations
Varga, Z., WALLENIUS, M., MAYER, K., KEEGAN, E. & MILLET, S. 2009. Application of lead and strontium isotope ratio measurements for the origin assessment of uranium ore concentrates. *Analytical chemistry*, 81:8327-8334.

Vilta, M. 2016. Nexion 300 icp-ms instruments animation. https://www.youtube.com/watch?v=L-FYh2z9mi0 Date of access: 15 November 2016 2016.

Wallenius, M., Mayer, K., Ray, I., . 2006. Nuclear forensic investigations: Two case studies. *Forensic Science International*, 156:55-62.

Wallenius, M., Peerani, P., Koch, L. 2000. Origin determination of plutonium material in nuclear forensics *Journal of Radioanalytical and Nuclear Chemistry*, 246(2):317-321.

White. 2009. Commercial development of the magnesia mixed hydroxide process for recovery of nickel and cobalt from laterite leach solutions. Paper presented at the CIM Hydrometallurgy of Nickel and Cobalt 2009, Sudbury, Canada.

Wolf, S.F.B., D.L; Cunnane, J.C. 2005. Analysis of high burnup spent nuclear fuel by icp-ms. *Journal of Radioanalytical and Nuclear Chemistry*, 263:581-586.

APPENDIX A: PUBLICATIONS

M. Mathuthu, N. Khumalo, **M. M. Baloyi**, R. N. Maretela; (07/2017). Resolving nuclear forensic signatures from a uranium and Thorium mine in South Africa using the ICP-MS Isotopic Ratio technique. In IAEA TECDOC 1820: Identification of High Confidence Nuclear Forensics Signatures *Results of a Coordinated Research Project and Related Research,* pp 70 – 77. http://www-pub.iaea.org/books/IAEABooks/12231/Identification-of-High-Confidence-Nuclear-Forensics-Signatures.