

Applying nuclear forensics in fingerprinting of uranium-bearing materials from a South African mine

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Applying nuclear forensics in fingerprinting of uranium-bearing materials from a South African mine

DECLARATION

I, at this moment, declare that the title of the thesis presented in this thesis is my work and that all the sources I have used are indicated in the references. This thesis has never been submitted for a degree at any other university elsewhere and this university before.

Name: ...Tebogo Gilbert Kupa.....

A handwritten signature in black ink, appearing to read 'Tebogo Gilbert Kupa', written over a horizontal line.

Signature:

Date: ...15 September 2022.....

DEDICATION

This work is dedicated to my wife and daughter, Boipelo Alinah Kupi and Omogolo Kupi, for their love, encouragement, and support during my PhD studies.

ACKNOWLEDGEMENTS

I am thankful to God Almighty for enabling me to complete this work. This work would not have been possible without Him. I want to express my sincere gratitude to the following:

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ABSTRACT

In this work, three samples selected for investigation, originated from the Nufcor uranium plant and were analyzed for nuclear forensics using ICP-MS and SEM with EDS functionality. The samples were uranium ore, ammonium diuranate slurry, and triuranium octoxide. This research aimed to apply nuclear forensics to fingerprint uranium ores from a South African mine. The study was motivated by the fact that no previous studies had been carried out to develop forensics signatures for a nuclear forensic library for South African uranium mines.

For the three samples used in the study, each sample was duplicated and labelled. Then, each duplicated sample was diluted ten times, making 60 sub-samples for analysis. Depending on the form samples were received from Nufcor, samples were crushed and pulverized before digested with a PerkinElmer Titan MPS™ microwave and subsequently analyzed with NexION 2000 ICP-MS and SEM/EDS.

The ICP-MS was used to measure the concentration of rare-earth elements and lead isotopic ratio in each sample. The typical within-run precision measurement was less than 0.02%. Verification measurements on reference standard as a sample were performed successfully and showed good agreement with the reference values. To avoid mass biased results, mass fractionation corrections were performed using lead NIST 981 certificate reference standard and rare-earth elements SRM traceable to NIST. The lead isotopic ratio and REE results measured showed unique signatures for South Africa compared to literature. The REE patterns obtained showed that origin location reflect significant variation within the mine and thus provided valuable information about the geochemical formation and origin.

The FEI Quanta™ FEG 250 electron microscope with EDS capabilities was used to perform morphology and elemental characterization of the samples. The results obtained for analysis showed large grains size distribution in micromillimeter range for all the samples. For EDS analysis in all the samples, uranium was identified as the most dominant mineral ranging from 51.6 wt.% to 56.9 wt.%. Overall, the characterization, lead isotopic ratio, REE pattern, and SEM-EDS measurements implied in uranium ore, ADU, and U₃O₈ are a powerful geographical signature in uranium ore, ADU, and U₃O₈ for uranium attribution and a powerful approach for nuclear forensics studies. The results obtained can be added into a national

nuclear forensics library for reference purposes; since South Africa is embarking on developing and establishing a national nuclear forensic library, these results support and strengthen the initiatives.

Keywords: Nuclear forensics, uranium, lead, rare-earth elements, fingerprints

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LIST OF ACRONYMS

ADU	Ammonium diuranate
ALI	Annual limit of intake
AMS	Accelerator mass spectrometry
CARST	Centre for Applied Radiation Science and Technology
DNA	Deoxyribonucleic acid
DRC	Dynamic reaction cell™
CRM	Certified reference material
EDS	Energy dispersive X-ray spectroscopy
EDX	Energy dispersive X-ray analysis
FGPU	Fuel grade plutonium
RDD	Radiological dispersal device
GC	Gas chromatography
GC-MS	Gas chromatography/mass spectrometry
GICNT	Global initiatives to combat nuclear terrorism (GICNT)
HEU	Highly enriched uranium
HREE	Light rare earth elements
ITDB	Illicit trafficking database
IAEA	International Atomic Energy Agency
ICD	In column detector
IRMS	Isotope ratio mass spectrometry
ICP-MS	Inductively coupled mass spectrometry
ICRP	International Commission on Radiological Protection
IDMS	Isotope dilution mass spectrometry

IUPAC	International Union of Pure and Applied Chemistry
KED	Kinetic energy discrimination
LEU	Low enriched uranium
LREE	Heavy rare earth elements
MC-ICPMS	Multi-collector inductively coupled mass spectrometry
MS	Mass spectrometry
MGPU	MOX grade plutonium
NSCT	National strategy for combating terrorism
NDA	Non-destructive analysis
NIST	National Institute of Standards and Technology
NECSA	South African Nuclear Energy Corporation
NFL	Nuclear forensic library
NNFL	National nuclear forensics library
NNR	National Nuclear Regulator
NORM	Naturally occurring radioactive material
NPT	Non-proliferation treaty
NUFCOR	Nuclear Fuel Corporation of South Africa
NWU	North-West University
OM	Optical microscopy
PDI	Polydispersity index
PPB	Parts per billion
PPE	Personal protective equipment
POC	Point of contact
PPM	Parts per million

PTFE	Polytetrafluoroethylene
Q-ICPMS	Quadrupole inductively coupled mass spectrometry
RGPU	Reactor grade plutonium
REE	Rare earth element
RTG	Radioisotope thermoelectric generators
SA	South Africa
SAPS	South African Police Service
SED	Secondary electron detector
SEM	Scanning electron microscopy
SGPU	Weapons grade plutonium
SIMS	Secondary ion mass spectrometry
SNM	Special nuclear material
SRM	Standard reference material
TEM	Transmission electron microscopy
TIMS	Thermal ionization mass spectrometry
TREE	Total rare earth element
UCT	Universal cell technology™
UF ₆	Uranium hexafluoride
US	United States of America
UK	United Kingdom
U ₃ O ₈	Triuranium octoxide
UOC	Uranium ore concentrates
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic

Radiation

V-CDT	Vienna canyon diablo troilite
WGPU	Weapons grade uranium
WMS	Weapon of mass destruction
WNA	World Nuclear Association
XRD	X-ray diffraction
XRF	X-ray fluorescence

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1 CHAPTER ONE: INTRODUCTION

1.1 General background

Throughout the world, nuclear and radioactive materials are used daily for beneficial purposes, in industry, medicine, agriculture and research. However, the use of nuclear and radioactive material generates some risk because these materials emit radiation and are harmful to human health especially if they enter the human body even at low levels (i.e. microgram amounts) (Aggarwal, 2016a). The main security concerns relating to their use, are perceived as ease of access to them, the culture of personnel responsible for managing the material, and the potential for theft and construction of radiological dispersive devices (RDDs) also referred to as “dirty” bombs (Hutcheon *et al.*, 2013; IAEA, 2007).

In our society today, the term radiation usually carries thoughts of a dangerous substance produced in nuclear power plants or nuclear explosions. In reality, however, only a very small fraction of the radiation on earth comes from these two sources (Ali, 2020; O'Doherty *et al.*, 2018). Most of the radiation comes from natural sources, such as outer space, which strikes the earth every second of every day (Nelson, 2016).

Radiation refers to the energy that comes from a source and travels through space at the speed of light and may be able to penetrate various materials (Martin *et al.*, 2018). Also radiation occurs when a radioactive material (atom with unstable nuclei) gives off or emits excess energy or mass (Rosen *et al.*, 2015). This energy is emitted from the nucleus or electron shells of certain nuclides. A nuclide that spontaneously emits radiation from its nucleus is called a radioactive nuclide. The term spontaneous means that the radiation is emitted without any outside forces causing the emission.

Exposure to radiation especially ionising radiation is a health hazard. High doses of ionising radiation can cause acute radiation syndrome, known as “radiation sickness”, while lower doses carry a risk of radiation-related cancer and heritable ill health (Kamiya *et al.*, 2015). Ionising radiation is also detrimental to materials and can cause damage to polymers, lubricants as well as semiconductor electronic components (Algadir, 2017).

Radiation is divided into two categories, ionising and non-ionising radiation. Ionising radiation occurs as either electromagnetic rays (such as X-rays and gamma rays, i.e. ionising photons) or particles (such as alpha and beta particles as well as neutrons and photons) (Schmid *et al.*, 2019). Non-ionizing radiation includes electric and magnetic fields, radio frequency, microwaves, infrared, ultraviolet, and visible light. This study only dealt with ionising radiation.

1.2 Ionising radiation

Ionising radiation refers to the emissions from the radioactive nuclei. This radiation has a number of beneficial uses in our daily lives such as use in smoke detectors, cancer treatment, research or sterilization of medical equipment etc. Nonetheless, the use of ionising radiation is potentially harmful if not used correctly. As a result, the National Nuclear Regulator (NNR) of South Africa, strictly regulates commercial and institutional uses of nuclear materials (GUIDE, 2018; Liefferink, 2011). Ionising radiation may be characterised as neutrons, alpha, beta and gamma radiation depending on its behaviour in a magnetic field.

1.2.1 Neutron

Neutrons are particles with no electrical charge, found within an atom's nucleus. Because they are neutral in their charge, they have a strong penetrating power and are not easily stopped by thin materials. When they are emitted from the nucleus, they are called neutron radiation. Neutrons are highly energetic particles that induce severe deoxyribonucleic acid (DNA) double-strand breaks, a highly toxic form of DNA damage (Moore *et al.*, 2014). The eleventh report on carcinogens list neutrons as a carcinogen (El Ghissassi *et al.*, 2009; Smoke & Oncology, 2007).

Exposure to neutrons can either cause cells to change in their functionality or to completely stop replicating, resulting in damage to the body over time. Neutrons are particularly damaging to soft tissues like the cornea of the eye (Kleiman *et al.*, 2017; Roth *et al.*, 1976). Incidents such as the tsunami-induced radiation leak at the Fukushima Daiichi site in Japan, in March 2021 and the Hiroshima-Nagasaki atomic bomb explosions in 1945, resulted in exposure to neutron radiation (Kleiman *et al.*, 2017).

Neutrons can be emitted as a result of nuclear interactions, e.g. (p,n) reactions or from a nuclide that is fissioning (i.e. fission process). Because neutrons have no charge, they are typically more penetrating than either the alpha or beta particles. They are best shielded by light material such as water in which a hydrogen atom absorbs a fast moving neutron, thus reducing its penetrating power.

1.2.2 Alpha particles

Alpha particles (α) are positively charged particles emitted from naturally occurring materials (such as uranium, radium and thorium) and man-made elements (such as americium and plutonium) (Fano, 1963). Alpha particles are made up of two protons and two neutrons from the atom's nucleus. Alpha particles are very energetic and heavy particles. Because of that, they are unable to travel very far from the atom, so they use up their energy over short distances.

The health impact from exposure to alpha particles depends mainly on how a person is exposed. Since alpha particles are unable to travel very far, they lack the energy to penetrate even the outer layer of skin, as a result exposure to the outside of the body is not a main concern. However, if exposed inside the body either through a cut, injection or inhalation, they can be very harmful resulting in damage to sensitive living tissue (Brooks *et al.*, 2016).

1.2.3 Beta particles

Beta (β) particles are high energy electrons emitted from the nucleus of an atom. They are small, fast-moving particles emitted at a velocity approaching the speed of light by certain unstable atoms such as hydrogen-3 (tritium), carbon-14 and strontium-90 (Popov & Vasenkov, 2015). They are negatively charged particles with kinetic energy between 0.2 MeV and 3.2 MeV released from an atom's nucleus during radioactive decay.

Beta particles are more penetrating and can travel far in air compared to alpha particles. However, they can be stopped by a thin layer of a substance such as aluminium. Some beta particles are capable of penetrating the skin and causing damage such as skin burns. The ionisation radiation produced by beta particles is widely spread out, resulting in less

damaging to living tissue and DNA. However, when inhaled or swallowed, beta-emitters are most hazardous (Ruff, 2017).

1.2.4 Gamma and X-rays

Gamma rays (γ) and X-rays are high energy waves called photons. Photons are high energy electromagnetic quanta that move at the speed of light in a vacuum (Attix & Tochilin, 2016). Gamma rays (γ) and X-rays are highly penetrating, but not as penetrating and problematic as neutrons. These photons can be attenuated to low enough dose rates by adequate thicknesses of shielding material such as lead. Gamma rays and X-rays are similar to visible light, they can travel great distances and have a great ability to penetrate other materials. Gamma rays are often emitted from the nucleus, along with alpha or beta particles during radioactive decay. However, X-rays originate from the electron cloud, when energy moves from a higher energy level to a lower one, causing the excess energy to be released (Garman & Weik, 2019).

Gamma radiation is difficult to stop because of its high energy; it has no mass nor any electrical charge. Gamma rays are a radiation hazard for the entire body. As they pass through the human body; they can cause ionizations that damage tissue and DNA. High exposures to X-rays can cause direct acute effects through immediate damage to cells while low level exposure may cause stochastic health effect which might cause cancer (Kamiya *et al.*, 2015).

1.3 Health risk of ionising radiation

When radiation pass through human body it might cause damage to the cell or it might pass through without any damage occurring. The damaged cell might repair or not repair themselves then replicates itself in the damaged form or else it might die (Lomax *et al.*, 2013). Radiation damage in human cell is divided into two groups, somatic damage (harmful to either the whole body) and genetic damage (harmful to some parts, e.g. eggs and sperm) (Martincorena & Campbell, 2015; Mousseau & Møller, 2014).

When ionising radiation interacts with target atoms, energy is deposited, resulting in ionisation or excitation. The absorption of energy from ionising radiation produces damage to molecules by direct or indirect actions. For direct action, damage occurs as a result of

ionisation of atoms on key molecules in the biologic system (Lomax *et al.*, 2013). This causes inactivation or functional alteration of the molecule. Indirect action involves the production of reactive free radicals which then damages key molecules in cells, so causing biologic effects (Alizadeh *et al.*, 2015). Ionising radiation can have two general categories of health effects on irradiated persons, namely deterministic effects and stochastic effects (Mettler, 2012).

1.3.1 Deterministic effects

Deterministic effects result from radiation-induced cell death, as a result of high radiation dose (Kamiya *et al.*, 2015). When it occurs, it may result in compromising the functioning of organs and tissues. The early tissue reactions include bone marrow failure, gastrointestinal symptoms, skin disturbance and various other symptoms while the late tissue reactions may include cataracts, necrosis and cardiovascular disorders (Kamiya *et al.*, 2015). The dose thresholds for this category of radiation effects is high, which only manifest at very high radiation doses, far above legal dose limits (Desouky *et al.*, 2015).

1.3.2 Stochastic effects

Stochastic effects of radiation refer to damage to the genetic material in cells, which might result in risk of radiation-related cancer, risk of heritable ill health or possibly to some developmental effects under specific conditions (Mettler, 2012). Stochastic effects are related to DNA damage and their effects cannot be certainly predicted, as the risk increases with the dose increase. However, there are a range of detrimental health effects such as an increased incidence of heart disease, strokes, lung disease, liver disease, systemic inflammation, which might arise in a single cell damage (Aggarwal, 2014).

1.4 Recommended and legal dose limits

The International Commission on Radiological Protection (ICRP) is an international, independent, non-governmental body, with the aim to protect people, the environment and animal from the harmful effects of ionising radiation (Kang, 2016). The body provides recommendations (the radiological protection framework) and guidance on protection against the risks associated with ionising radiation. The ICRP recommendation is based on

research on the biological effects of ionising radiation, the scientific results of which are reviewed regularly by major international organisations, such as the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (Cléro *et al.*, 2019). Since the formation of ICRP in 1925, quantification of biological effects associated with ionisation radiation exposure has been an issue of great concern for the organization.

The ICRP's 2007 dose limits for occupational exposure to ionising radiation, which are also the present (2021) legal dose limits in South Africa set by the Directorate of Radiation Control in the Department of Health, Bellville, South Africa, are summarised in Table 1.1.

Table 1. 1: Legal dose limits for occupational exposure to ionising radiation (Boal & Pinak, 2015).

Type of dose	Maximum permissible dose
Effective dose (excluding pregnant women)	20 mSv per year
Dose to the skin, hands and feet	500 mSv per year
Dose to lens of eye	150 mSv per year
Effective dose to pregnant women	1 mSv from diagnosis of pregnancy to its end
Radionuclide intake by pregnant woman	$\frac{1}{20}$ of normal Annual Limit of Intake (ALI) for duration of pregnancy.

1.5 Problem statement

Illicit trafficking of radioactive material and especially nuclear material (thorium, uranium, and plutonium) has been an issue of concern since the beginning of the 1990s, when the first seizures of nuclear material were reported to the International Atomic Energy Agency (IAEA) (Wallenius *et al.*, 2006). Since 1993, over 2889 illicit trafficking of nuclear materials and radiological materials have been recorded by the incident and trafficking database (ITDB) and reported to the IAEA mostly involving low-enriched, natural, and depleted uranium (Balatsky & Severe, 2019). To date the ITDB record stands at 3686 (General, 2020).

In South Africa, there have been several incidents of illicit trafficking reported with criminal cases under South African Police Services (SAPS) custody (Mogafe *et al.*, 2015). Two

containers containing uranium of 1.2 kg and 0.5 kg were confiscated in Sandton area on Tuesday 10th January 2012. Three days later, on Friday 13th January 2012, one container containing uranium was seized in the same area of Sandton weighing about 0.8 kg. On the 14th of November 2013, SAPS arrested two men on suspicion of possessing uranium and some pills, which were stored in a plastic bag. The non-destructive analysis (NDA) screening revealed that the material consisted of depleted uranium with the radiation dose of approximately 0.58 $\mu\text{Sv/h}$ (Mogafe *et al.*, 2015).

As a counter-response to this risk, the September 2006, national strategy for combating terrorism (NSCT), declared intentions to develop a system that will rapidly identify source and perpetrator of use of weapon of mass destruction (WMS) including biological, chemical, nuclear, radiological and high-yield-explosive, using a combination of scientific analyses, law enforcement and intelligence in the determination of provenance (Frost, 2020). This has resulted in the development of a new branch of science called “nuclear forensics” with the intent not only to identify and characterize illicit nuclear or radioactive material but also to learn more about the intended use of the seized material as well as its origin and about the potential trafficking route (Hutcheon *et al.*, 2013; Jariwala, 2014). In South Africa, the nuclear forensics’ efforts are still in a developing stage.

The importance of this type of study cannot be overemphasized as the threat is very real and require immediate attention. This study focused on applying nuclear forensics in fingerprinting of uranium-bearing materials from a South African mine. The number of mines investigated depended on the number of samples given for this study by the Nuclear Fuel Corporation of South Africa (NUFCOR). The targeted mine was in the Witwatersrand basin (First Uranium province in SA). This research work focused on the first stage (Geological deposition) and second stage (mining and milling) of the nuclear fuel cycle.

1.6 Research aim and objectives

1.6.1 Research aim

The aim of this study was to apply nuclear forensics to fingerprint uranium-bearing material from a South African mine.

1.6.2 Research objectives

The specific objectives were to:

- Investigate the assay of uranium samples produced from South African mine using Inductively coupled plasma mass spectrometry (ICP-MS) and scanning electron microscopy (SEM) / energy dispersive X-ray spectroscopy (EDS),
- Evaluate the isotopic composition of the uranium samples using ICP-MS Isotopic ratio technique,
- Resolve the Pb isotopic ratios as nuclear forensics signatures for the South African mine, and
- Evaluate the concentration of rare earth elements (REE) patterns measured in the uranium samples produced from South African mine using ICP-MS.

2 CHAPTER TWO: LITERATURE REVIEW

2.1 Discovery of uranium

Uranium was discovered in 1789 by Martin Heinrich Klaproth, a German chemist, while analysing mineral samples from the Joachimstal silver mines in the present day Czech Republic (Karol, 2018). Uranium is an element that is widespread in the earth's crust, in most rocks and soils, in many rivers and in sea water (Degueldre, 2017). It is the last naturally occurring element in the periodic table. It is a hard, malleable, ductile, dense, silvery-grey, radioactive metal that is chemically highly reactive and forms a number of brightly-coloured oxides and salts (Dinocourt *et al.*, 2015). It reacts with almost all the non-metallic elements and their compounds, especially at elevated temperatures. Uranium is primarily used as a nuclear fuel in a nuclear reactor to produce electricity. Other uses of uranium outside nuclear power industry includes, as a target for X-ray production, as ammunition for some types of military weaponry, as a shield against radiation, as a counterweight for aircraft control surfaces and in the gyroscopes of inertial guidance systems (Habashi, 2015).

Uranium occurs in different geological environments or uranium deposits. According to the IAEA, uranium deposits world-wide can be grouped into 15 major categories of deposit types, based on the geological setting of the deposits (Bruneton & Cuney, 2016a; Bruneton *et al.*, 2018). The 15 major categories of deposit are intrusive, granite-related, polymetallic iron oxide breccia complex, volcanic-related, metasomatite, metamorphite, proterozoic unconformity, collapse breccia pipe, sandstone, palaeo-quartz-pebble conglomerate, surficial, lignite–coal, carbonate, phosphate and black shale. The classification of uranium deposits found worldwide is based on the size of the deposit and the amount of uranium (U_3O_8) in it (Dahlkamp, 2013). Table 2.1 shows the general description of uranium deposit types with common impurities in different types of uranium ores.

Table 2. 1: Different type of uranium ores deposit and their common impurities (Švedkauskaitė-Le Gore, 2008; Tauchid & Underhill, 1997).

Elements	Type of Uranium deposit													
	Unconformity-related	Sandstone	Quartz-pebble conglomerate	Vein	Breccia complex	Intrusive	Surficial	Collapse breccia pipe	Volcanic	Phosphorite	Metasomatic	Metamorphics	Lignite	Black shale
Ag	X		X	X	X	X		X			X			X
Al							X		X					
As		X	X				X		X	X			X	X
Au	X		X	X	X	X		X			X			
Ba		X					X						X	
Be						X							X	
Bi	X			X		X								
Ca							X		X		X	X		
Cd													X	
Ce			X		X		X			X	X		X	
Co	X		X	X	X			X		X			X	
Cr			X										X	X
Cu	X	X	X	X	X	X	X	X	X	X	X		X	X
Dy			X		X		X			X	X		X	
Er			X		X		X			X	X		X	
Eu			X		X		X			X	X		X	
Fe		X		X	X		X	X	X		X			
Gd			X		X		X			X	X		X	
Ge													X	
Ho			X		X		X			X	X		X	
Ir			X											
K											X			
La			X		X		X			X	X		X	
Li						X			X					
Lu			X		X		X			X	X		X	
Mg							X							
Mn							X							X
Mo	X	X		X		X	X	X	X	X	X	X	X	X
Na							X				X			
Nb											X			
Nd			X		X		X			X	X		X	
Ni	X		X	X	X			X				X	X	
P		X												
Pb	X	X	X	X				X	X	X		X	X	
Pd						X								
Pr			X		X		X			X	X		X	
Pt	X		X			X								
Re						X							X	
Sb	X	X						X	X					
Sc										X				
Se	X	X				X	X						X	
Si						X	X							
Sm			X		X		X			X	X		X	
Sn									X					
Sr							X			X				
Tb			X		X		X			X	X		X	
Te	X													
Ti							X						X	
Tm			X		X		X			X	X		X	
V	X	X					X	X					X	X
W									X					
Y			X							X			X	
Yb			X		X		X			X	X		X	
Zn	X	X	X	X				X	X	X		X	X	
Zr			X						X				X	

Uranium is ubiquitous in the environment due to natural and anthropogenic activities. It is of natural isotopic composition consisting of three isotopes with their approximate relative natural abundance as follows: ^{238}U – 99.27%, ^{235}U – 0.724% and ^{234}U – 0.006% (Zheng & Yamada, 2006). ^{238}U is an alpha emitter, decaying through the 18-member uranium natural decay series into ^{206}Pb . The decay series of ^{235}U (the actinouranium series) has 15 members that ends in stable ^{207}Pb . This series includes only two long lived (> several days) radioactive members, namely ^{231}Pa (T = 3.28years) and ^{227}Ac (T = 21.77days). Only ^{235}U is a valuable fuel for electricity production (Fry & Thoennessen, 2013).

The proportion of these isotopes is constant in nature regardless of the type of mineral or deposit in which the uranium is found. Uranium does not occur in native state. It has affinity for oxygen and occurs in nature mostly as oxides, phosphates, sulphates, vandates, arsenates, carbonates and silicates (Dahlkamp, 2013).

One of the main interest in uranium, is the trace elements or impurities (Švedkauskaitė-Le Gore, 2008). These trace elements are of great interest to nuclear forensics, because they can be used to attribute the uranium material to its geological source, i.e., to a uranium ore deposit type (Keegan *et al.*, 2012).

2.2 Uranium discovery in South Africa

In South Africa, the presence of the uranium bearing material was noted in 1923 on a sample analysed in the United State of America (US). The uranium exploration in South Africa begun in 1944, followed by the uranium production in 1952 with the highest peak production in the early 1980s with over 6000 tonnes of uranium per year (Kenan & Chirenje, 2016a). However, uranium production in South Africa has gradually declined and reached 448 tonnes in 2015 (Kenan & Chirenje, 2016a). The South African government has approved the Integrated Resources Plan 2010-2030, with a vision that uranium production will increase soon. The Integrated Resources Plan 2010-2030 is expected to enable the increase in nuclear energy capacity from the current 1.8 GWe to 9.6 GWe by the year 2030. The present nuclear energy capacity needs about 294 tonnes of uranium per annum and the expected expansion will require a total of 1536 tonnes per annum (Rennkamp & Bhuyan, 2016; Tshelane, 2018).

The uranium produced in South Africa is a by-product of gold or copper (Mogafe *et al.*, 2015; NEA, 2006). South Africa's uranium resources and reserves occur in five deposit types:

quartz-pebble conglomerate, carbonatite, sandstone, coal, and surficial deposits. Other, less significant, uranium occurrences are hosted in granites and gneisses, as well as in marine phosphate deposits (Dahlkamp, 2013; Rantzschi *et al.*, 2011). The major uranium deposits in South Africa which contribute to the nation's uranium identified resource inventory are found in Witwatersrand Basin (quartz-pebble conglomerate hosted deposit), Springbok flats basin (carbonaceous shale- and coal-hosted deposit), Namaqualand region (surficial deposit) and Karoo uranium province (sandstone-hosted deposit) (Bruneton & Cuney, 2016a; Kinnaird & Nex, 2016a). The major uranium deposits in South Africa are demonstrated in Figure 2.1 followed by summary of each deposit.

Figure 2. 1: Map showing major uranium deposits in South Africa (Kenan & Chirenje, 2016a).

The Witwatersrand basin is situated in the central parts of South Africa, and spreads into Gauteng, North West, Mpumalanga and Free State provinces. It has an area of more than 30,000 km² (Fuchs *et al.*, 2016a; Kenan & Chirenje, 2016b). Historically, majority of uranium

produced in South Africa came from the Witwatersrand basin as a by-product of gold, with a small proportion being from the Palaborwa carbonatite complex, as a by-product of copper. At present, all the uranium production in South Africa is sourced from the Witwatersrand Basin, both from the underground operations and related tailing dam facilities. The current operational facilities are Vaal river by processing the reef material from Moab Khotsong, Great Noligwa and Kopanang in the Noligwa gold plant or South uranium plant circuit by reverse leach process (Kenan & Chirenje, 2014; Winde *et al.*, 2017b).

2.2.2 Springbok flats basin

The Springbok flats basin occurs in the northern part of South Africa. Uranium was discovered in the basin in 1976 during the exploration drilling for coal. The uranium exploration continued sporadically until it stopped in 1988 (Randabel & Lusambo, 2018). In 2012, a pre-feasibility study was completed in the basin. The uranium in the Springbok flats basin is believed to have started from granites of the Bushveld complex, Settlers area, with uranium distributed in the coal and carbonaceous shale (Kenan & Chirenje, 2016a).

2.2.3 Namaqualand uranium

The Namaqualand region is in the north-western part of South Africa. The region is a known uranium enrichment in metamorphic rocks, granite gneiss and pegmatites of the Namaqualand Metamorphic complex (Kinnaird & Nex, 2016c). The existence of uranium in the Namaqualand region was discovered by the Anglo American Limited, following the airborne radiometric survey in 1975 (Vance, 2014). The feasibility study was completed in 1979, however, due to low uranium prices the project was shelved in the mid-1980s (Kenan & Chirenje, 2016a). In 2007 the Namakwa uranium was granted the prospecting rights, then conducted desktop studies by reviewing previous work by Anglo American Limited. At present, Xtract Resources Ltd is conducting exploration in the Namaqualand region (Hanly, 2014; Vance, 2014).

2.2.4 Karoo uranium province

The Karoo uranium province occurs in the south-western part of South Africa. The presence of uranium in the Karoo uranium province was first noted by Southern Oil Exploration Corporation in 1967 during a search for oil (Bruneton & Cuney, 2016b; Issah & Umejesi, 2018). In 1970, the Union Carbide Exploration Corporation begun with the exploration. By the year 1976, 11 companies were exploring in the Karoo uranium province. Due to low uranium prices, the exploration work stopped in 1986 and re-started in 2005. Uranium mineralization in the Karoo occurs in alternating layers of sandstone and mud stone and/or siltstone (Kinnaird & Nex, 2016b).

2.3 The nuclear fuel cycle

The nuclear fuel cycle is the series of industrial process which involve various stages to produce electricity from uranium in nuclear power reactor. Uranium is the main raw material for nuclear fuel. It is processed through a series of steps to produce an efficient fuel for the nuclear reactor for generating electricity. The cycle consists of the nuclear power reactor facility, the reprocessing facility, and the fuel fabrication facility. The cycle starts with the mining of uranium and ends with the disposal of nuclear waste (spent fuel and other radioactive waste). The fuel cycle is often described in terms of the “front-end” activities, which involves the preparation of uranium for the use in a nuclear reactor, the “service period” in which fuel is used during reactor operation to generate electricity and the “back-end” activities, in which majority of the waste is isolated and the unburned uranium and/or plutonium recovered (Zohuri & Fathi, 2015).

South Africa has been involved in the nuclear fuel cycle since its very beginning, feeding the nuclear weapons programmes of the US and United Kingdom (UK) during the 1950s and 1960s (Ford, 1993; Postar, 2017). In South Africa, the nuclear fuel cycle has been classified into the 8 different stages leading to the production of electricity from the use of uranium: mining, milling, conversion, enrichment, fabrication of the fuel, electricity generation, reprocessing of spent fuel, and finally, disposal of two classifications of waste (low/intermediate level and high-level waste). The main stages of the nuclear fuel cycle are illustrated in Figure. 2.2, followed by main various stages of the nuclear fuel cycle described below (Borg & Hutcheon, 2013).

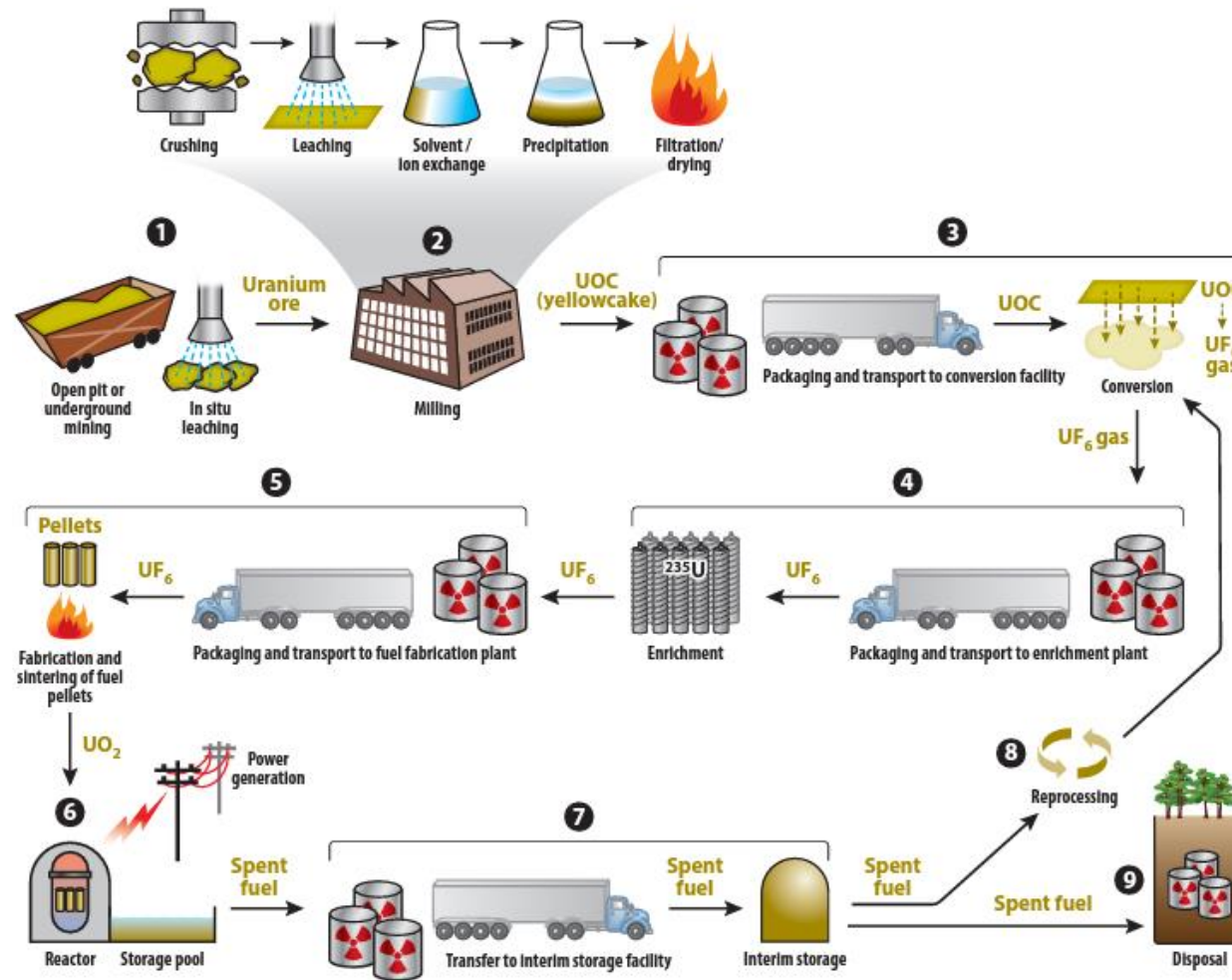


Figure 2. 2: Simple flow sheet of the nuclear fuel cycle (Kristo *et al.*, 2016b).

2.3.1 Uranium mining

Uranium is mined in three ways, depending on the type of deposit: underground mining, open pit mining and *in-situ* leaching, where the uranium is leached directly from the ore (Carvalho, 2011). According to the World Nuclear Association (WNA), in 2019, the globally produced uranium with total annual production of 54,752 tonnes came from Kazakhstan (41,7%), Canada (12,7%), Australia (12,1%), Namibia (10,0%), Uzbekistan (6,4%), Niger (5,4%), Russia (5,3%), China (3,4%), Ukraine (1,5%), USA (0,1%), India (0,6%), South Africa (0,6%), Iran (0,1%) and Pakistan (0,1%). The mining of uranium begins with recovering uranium from ore deposits and is taken to a mill (Kinnaird & Nex, 2016a).

2.3.2 Uranium milling

In a mill, uranium is extracted from the crushed and ground-up ore by leaching, usually by addition of acid or alkaline solution to chemically dissolve the uranium (together with other metals) into a liquid solution (Toman & Vinkler, 2019). Once this solution dries, the product is the highly concentrated uranium known as "yellow cake". In *yellow cake*, the uranium concentration is raised to more than 80% to obtain almost pure uranium in the form of triuranium octoxide (U_3O_8). The products of the milling process are highly impure and have numerous potential signatures, which includes the type of uranium compound that is present, the abundances of key trace elements, the lead, uranium and strontium isotopic composition of the uranium ore concentrates (UOC) (Hausen, 1998; Kim, 2018). Uranium ore concentrates (UOC), included triuranium octoxide (U_3O_8), ammonium diuranate (ADU) and sodium diuranate. The remaining crushed rocks after the uranium is extracted, are known as "tailings". They are pumped as slurry to the tailings dam, which is built to keep them secured (Eidemüller, 2021; Gil, 2018). After milling, the yellow cake concentrate is shipped to a conversion facility.

2.3.3 Uranium conversion process

At a conversion facility, uranium is converted to a form suitable either for enrichment or fuel fabrication. Natural uranium only consists of two isotopes, namely, uranium-238 (^{238}U) (99.3%) and uranium-235 (^{235}U) (0.7%). The ^{235}U is the isotope that maintains a nuclear reactor's chain reaction, through the fission process by which heat energy is released in a

nuclear reactor (Kristo *et al.*, 2016a). Most nuclear power plants, however, require enriched uranium, meaning to increase the ratio of ^{235}U against ^{238}U , usually to a level of 3–5%. At this stage, the yellowcake is then converted into a gaseous form called uranium hexafluoride (UF_6) which is a desired product suitable for use in enrichment operation (Lesiak *et al.*, 2021). The UF_6 exits the process as a gas which is loaded into special storage cylinders, then cooled to a liquid and into a solid. The solidified UF_6 is then shipped to an enrichment facility (Nash & Lumetta, 2011).

2.3.4 Uranium enrichment process

At an enrichment facility, the solidified UF_6 is transformed back into a gas and the uranium concentration is increased so that it is usable for nuclear fuel. Uranium is enriched in ^{235}U by introducing the gas into fast spinning cylinders, known as centrifuges, where heavier isotopes are pushed out to the cylinder walls (Ko *et al.*, 2012). The enrichment process separates gaseous uranium hexafluoride into two streams, namely, low-enriched uranium and depleted uranium (Silvennoinen, 2013). After enrichment, the UF_6 is converted to uranium dioxide (UO_2) in powder form then shipped to a fuel fabrication plant.

2.3.5 Fuel fabrication

Enriched UF_6 is converted to uranium dioxide powder and sintered at temperatures of over 1400°C to achieve high density and stability (Stevenson, 2017). The UO_2 is then formed into small, solid, cylindrical pellets, which are then encased in metal tubes to form fuel rods. The fuel rods are arranged into a fuel assembly ready for introduction into a reactor. The fuel assemblies are used in the reactor to generate electricity for 3 to 6 years with 25% to 30% of the fuel being replaced each year (Park *et al.*, 2011).

2.4 The production process of U_3O_8 in South Africa

Uranium is currently produced in the Witwatersrand basin of South Africa at the Vaal river (near Orkney) and Cooke operations (near Carletonville). The Moab Khotsoeng, Great Noligwa, and Kopanang are among the Vaal river enterprises. The mine waste solution facility processes ore from Vaal river tailings dams. The Noligwa gold plant/South uranium plant circuit processes

reef materials from Moab Khotsonq, Great Nologwa, and Kopanang. Cooke 4, Ezulwini gold, and Uranium plant treat ore resources from the Cooke operations (Kenan & Chirenje, 2016a).

South Africa recovers uranium from the mines as a by-product during gold extraction, and this uranium by-product is converted at the Nuclear Fuel Corporation of South Africa (NUFCOR) into different uranium oxides (UOC) such as triuranium octaoxide (U_3O_8) and uranium dioxide (UO_2) (Marks *et al.*, 2015). Figure 2.3 illustrate the process for the NUFCOR plant and the samples used in this study were provided by the plant operator and believed to represent a flow of material originating from the same feed.

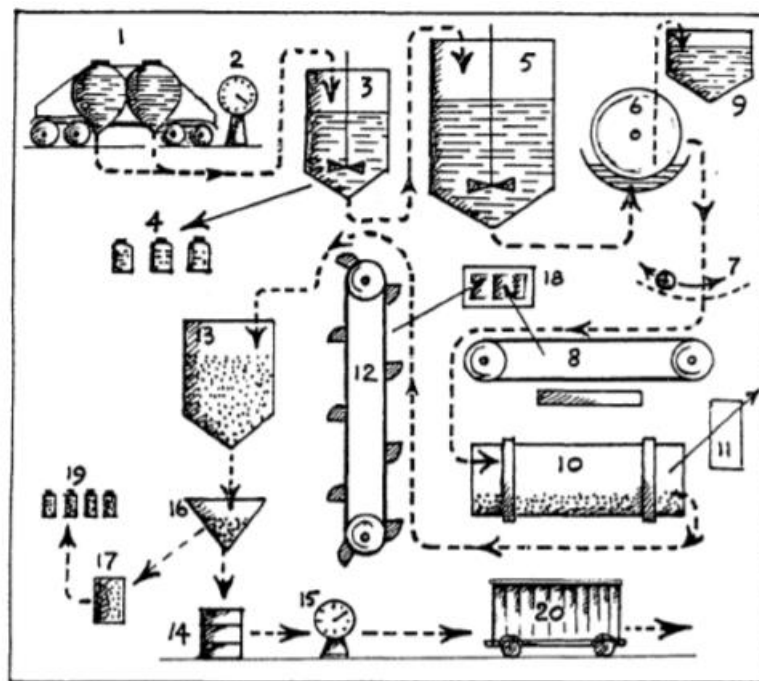


Figure 2. 3: Flow diagram of the processing steps from the ADU to the final U_3O_8 product at the NUFCOR plant (Kim, 2018).

The underground mining method is used to recover uranium oxide ore using traditional brutal rock methods. The uranium oxide ore is ground into a powder to form "pulped" ore, while the gold is separated by mechanical separation. Subsequently, the pulped ore is conveyed as a thick slurry suspended in water to the South uranium facility (Winde *et al.*, 2017a).

The uranium and other metals included in the comminuted ore slurry are subsequently leached off in sulfuric acid. The leaching period is 18 hours at 50-60 degrees Celsius (Krajko *et al.*, 2016). The uranium solution is separated from the waste solids bypassing the leach discharge slurry through a series of thickeners (counter-current decantation). A sample of the cleared

leachate solution (including some recycled raffinate from the solvent extraction circuit) will be uranium ore material passed through the sulfuric acid leach. After thickening, the cleaned leachate solution is fed through a fluidized counter-current ion exchange circuit (Marks *et al.*, 2015). Ambersep 400, an SO₄ strong base anion resin, developed for uranium recovery, is used in the CCIX circuit. Uranium is extracted using a 12 percent sulfuric acid solution (Kenan & Chirenje, 2016a).

After that, the ion exchange eluate goes through a three-stage solvent extraction circuit. The organic acid alamine 336 removes uranium from the eluate, subsequently stripped with ammonium sulphate. Uranium is extracted using solvents and then precipitated with ammonia to generate an ammonium diuranate (ADU) slurry. Later, the ADU slurry is transferred to the NUF COR facility from the South uranium plant. A filtering circuit is used to filter the ADU slurry. The feed ADU slurry was collected first at the NUF COR plant as part of the sampling process. The slurry is dried to ADU powder in a rotating vacuum filter furnace. Finally, the ADU powder is calcined for 6 hours at 490°C to get U₃O₈ powder (Kim, 2018).

2.5 Nuclear forensics

Nuclear forensics is defined as a measure put in place for the examination of nuclear or other radioactive material seeking to identify what the materials are, how, when and where the materials were made, and what their intended uses were (IAEA, 2015). Aggarwal (Aggarwal, 2016a) defines nuclear forensics as the collection and analysis of nuclear and radioactive materials (e.g., actinides) to support investigation into diversion, trafficking and illicit use to find out the origin of the interdicted, stolen, or lost material to eliminate its accessibility to illicit traffickers. Nuclear forensics is a key tool in the fight against illicit trafficking of nuclear and other radioactive material and can help authorities to see if a law has been broken.

Applying nuclear forensics allows by using fingerprinting or signature and comparison with reference data, to determine the origin, the intended use, the last legal owner and the smuggling route of the nuclear or radioactive material (Schwerdt, Olsen, *et al.*, 2018). Nuclear forensics is an important element of nuclear security. Nuclear security is defined as the measures put in place for the prevention, detection of and response to theft, sabotage, unauthorized access, illegal transfer or other malicious acts involving nuclear material, other radioactive sources or their associated facilities (IAEA, 2011).

Nuclear forensics often combines laboratory methods used for ordinary analysis of nuclear and other radioactive material and interpretation of the analysis results to provide technical conclusions about, for example, seized illicit nuclear or radioactive materials (Kristo & Tumey, 2013). Nuclear forensic investigation is considered as part of a comprehensive set of measurements for detection, interception, categorization and characterization of illicit nuclear material (Smith *et al.*, 2008). The investigations make use of the information inherent to the material.

Hence, nuclear forensic analysis results are an important conclusion on the origin of the material and thus provide the most essential contribution to the prevention of future diversions from the same source. Table 2.2 summarizes the analytical techniques commonly used in nuclear forensic investigation.

Table 2. 2: Analytical techniques typically applied in nuclear forensic investigations (Smith *et al.*, 2008).

Techniques/ Methods	First Analysis	Information	Detailed Analysis	Information
Radiological	Estimated total activity Dose rate (α , γ , n) Surface contamination	Radiological hazard Precautions		
Physical characterization	Visual inspection Photography Size measurement Optical microscopy Radiography Weighing	Macroscopic dimensions Mass	SEM (EDX) XRD TEM	Microstructure and elemental composition Crystal structure Microstructure
Traditional forensic analysis	Fingerprints, fibers etc.			
Isotopes analysis	γ -spectroscopy	Isotopic composition	Mass spectrometry (SIMS, TIMS, MC-ICP-MS) Radiochemical separations α -spectrometry	Accurate isotopic composition

Elemental/Chemical analysis			ICP-MS XRF Assay (titration, IDMS) GC/MS	Chemical impurities Chemical composition
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This study focused only on parameters and signatures that are related to uranium ore and ore concentrate in the first and second step in the nuclear fuel cycle. In the fuel cycle, each step provides important signatures that can be used to determine the source of the material. The first step in the nuclear fuel cycle is uranium ores deposit. Important signatures associated with uranium ores include mineralogy, bulk chemical composition and stable isotopic compositions (Borg & Hutcheon, 2013).

Table 2.3 summarizes the different analytical techniques used to characterize signatures in first two stages of the fuel cycle (Borg & Hutcheon, 2013).

Table 2. 3: Nuclear fuel cycle and associated signatures (Borg & Hutcheon, 2013).

Process	Materials	Signatures	Analytical techniques
Geologic deposition	Ore, ore body	Mineralogy, U concentration, U isotopes, non-U isotopes, trace elements	OM, XRD, XRF, Q-ICPMS, SEM/EDS, Photography
Mining and milling	Ore concentrate, yellow cake	Compound, U concentration, U isotopes, non-U isotopes, trace elements, morphology, size distribution, color	XRD, XRF, Q-ICPMS, MC-ICPMS, TIMS, SEM, Photography, Optical Spectroscopy, IRMS

The IAEA categories nuclear forensic investigation into three parts, namely, categorization, characterization and nuclear forensic interpretation (do Nascimento *et al.*, 2011).

2.5.1 Categorization

Categorization of nuclear material refers to a quick assignment of the material to a predefined group and thus determining its further handling during a nuclear security events (Fedchenko, 2014). The aim of categorization is to identify the bulk constituents of the material in order to understand the threat posed by the material, assess the risk to safety of first responders (law enforcement personnel or member of public) and confirm whether the seized evidence is contraband and also if there is criminal activity or threat to a national security (Kristo, 2020).

Categorization involves the use of non-destructive analysis (NDA) techniques such as field-portable nuclide identifier, gamma-ray spectrometry, or X-ray fluorescence to classify the suspected material without affecting the evidence. The basic information obtained during non-destructive analysis can assist to know whether seized material is naturally occurring radioactive material (NORM), contaminated radioactively material, commercial radioactive source or a special nuclear material (SNM) (Kristo, 2020). The IAEA categorize nuclear materials as SNM, reactor fuel, and commercial radioactive sources (Lee *et al.*, 2017; Smith *et al.*, 2008). Table 2.4 show IAEA categorization of nuclear materials.

Table 2. 4: Categories of nuclear materials as classified by the IAEA (Smith *et al.*, 2008).

Special Nuclear Materials (SNM)	
IAEA categories	Characteristics
High enriched uranium (HEU)	>20% U-235
Weapons-grade uranium (WGU)	Pure uranium metal, >93% U-235
Weapons-grade plutonium (WGPu)	Pure plutonium metal, <7% Pu-240
Super-grade plutonium (SGPu)	Pure plutonium metal, <3% Pu-240
Reactor fuel	
IAEA categories	Characteristics
Low enriched uranium (LEU)	<20% (typically 3–5%) U-235
Reactor-grade plutonium (RGPu)	Produced in nuclear power reactors, >19% Pu-240
Fuel-grade plutonium (FGPu)	Produced in nuclear reactors, >7% and <19% Pu-240

MOX-grade plutonium (MGPu)	Recycled from mixed (uranium + plutonium) oxide fuel, >30% Pu-240
Radioactive sources	
Typical uses	Common constituents
Medical diagnostic sources	Short-lived radioisotopes
Radiotherapy sources	Co-60 and Cs-137
Irradiators/sterilizers	Co-60 and Cs-137
Radiography	Ir-192
Gauging	Co-60, Cs-137, Am-241
Radioisotope thermoelectric generators (RTG)	Pu-238, Cm-244, and Sr-90

2.5.2 Characterization

Characterization is performed to determine the nature of the nuclear material under investigation following the on-scene categorization performed during the nuclear security event. The goal of characterization is to determine the complete elemental analysis including isotopic, chemical, minor, major and trace constituents of the nuclear material (Gregoric, 2011; Guide). Characterization provides detailed results for officials to make informed decision with regard to the nature and associated evidence of the nuclear material. Characterization usually take more time than categorization, approximately 1 to 4 weeks after receiving of the samples, but less time than the full nuclear forensics analysis (Fedchenko, 2014).

Characterization may aid in uncovering basic signatures (e.g. amount, chemical, physical, isotopic and elemental) of a nuclear material and may lead to precise interpretation of the sample and methods for measuring forensic signatures (Fedchenko, 2015). The basic information obtained is often sufficient for making proper judgment regarding how to proceed with nuclear forensic examination.

2.5.3 Nuclear forensics interpretation

Nuclear forensics interpretation is the process of correlating analytical data with the characteristics of the sample on existing information (type of material, use, handling, origins

and method of production) (Hutcheon *et al.*, 2015). Mayer (2011) defines nuclear forensics interpretation as the re-establishment of nuclear or radioactive material's history based on indicators that arise from known relationships between material characteristics and process history (Mayer *et al.*, 2011). The aim of nuclear forensic interpretation is to determine the method and time of production. Nuclear forensic interpretation is one of the four key elements of nuclear forensic analysis.

Nuclear forensic analysis includes categorization, characterization, nuclear forensic interpretation, and reconstruction of the history of the nuclear material. Nuclear forensic analysis has a key technical capability that utilises signatures inherent to nuclear or other radioactive material to provide information on its source, production and history (Borg & Hutcheon, 2013). Nuclear forensic analysis use fingerprinting to determine the origin, mode of production and the composition of nuclear material (Jariwala, 2014). In the context of this work, fingerprinting refers to the process of identifying signatures, which are measurable attributes of the nuclear fuel cycle (Borg & Hutcheon, 2013). Nuclear forensic interpretation provides context, explanation and form the basis of nuclear forensic finding from the analytical results. The results obtained as a result of nuclear forensic interpretation are the end product for the nuclear forensic library (Fedchenko, 2014).

2.6 Material signatures

The term “signatures” in the field of nuclear forensics, describes material characteristics that potentially link sample to location, people and processes, similarly like a written signature can be used to link a particular individual (Hutcheon *et al.*, 2015). Material characteristics of the sample may also include physical dimension, chemical form, elemental concentration or isotopic abundance. In the nuclear fuel cycle, nuclear material processes can create, destroy or carry over signatures as they move through the cycle, however, generally each cycle produces a unique set of signatures (Keegan *et al.*, 2016).

Each nuclear forensic signature reveals specific information concerning material under investigation. *“Signatures” explain any characteristic or group of characteristics that can be used to help distinguish materials from one another or identify the processes history of a material* (Hutcheon *et al.*, 2013; Redermeier, 2009). Signatures are combinations of variables used to make comparisons or an information that is obtained by nuclear forensic

analysis. Table 2.5 shows the examples of potential material characteristics to become signatures.

Table 2. 5: Typical example of signatures in nuclear forensics (Kimura *et al.*, 2017b).

Signatures	Example of material characteristics
Appearance	▪ Shape, ▪ geometry, ▪ color (photo)
Physical characteristics	▪ Physical form, ▪ Mass, ▪ density, ▪ radioactivity, ▪ mechanical properties
Chemistry	▪ Chemical form, ▪ elemental compounds, ▪ isotopic compositions, ▪ trace impurities, ▪ material age (chemical separation date), ▪ fuel burnup
Morphology	▪ Grain size (mean, histogram), ▪ shape description, ▪ homogeneity, ▪ inclusions, ▪ crystal structure, ▪ porosity
Others	▪ Packaging and containers (geometry, material, serial numbers)

Signatures can be divided into two groups, namely, comparative (also known as empirical) and predictive signatures (Hutcheon *et al.*, 2015; Redermeier, 2009). Comparative signatures are discovered by comparison of an unknown sample with one or more known samples and can also be through systematic measurement of the nuclear or radioactive material (Fedchenko, 2014). For example, the "age" of nuclear material (i.e., the time elapsed since the previous chemical purification or last geological activity can be deduced directly from the measured data or calculated directly from relative concentrations of

radionuclides present in the sample. Comparative approach depends mostly on the relevance and comprehensiveness of the sample archive or database.

An example of comparative signatures to identify an interdicted sample is shown in Figure 2.4, which relied on the inter-comparison of two or more closely matched samples of highly enriched uranium (HEU) interdicted in Ruse, Bulgaria in 1999 and in Paris, France in 2001 (Keegan *et al.*, 2016; Kristo *et al.*, 2016b).

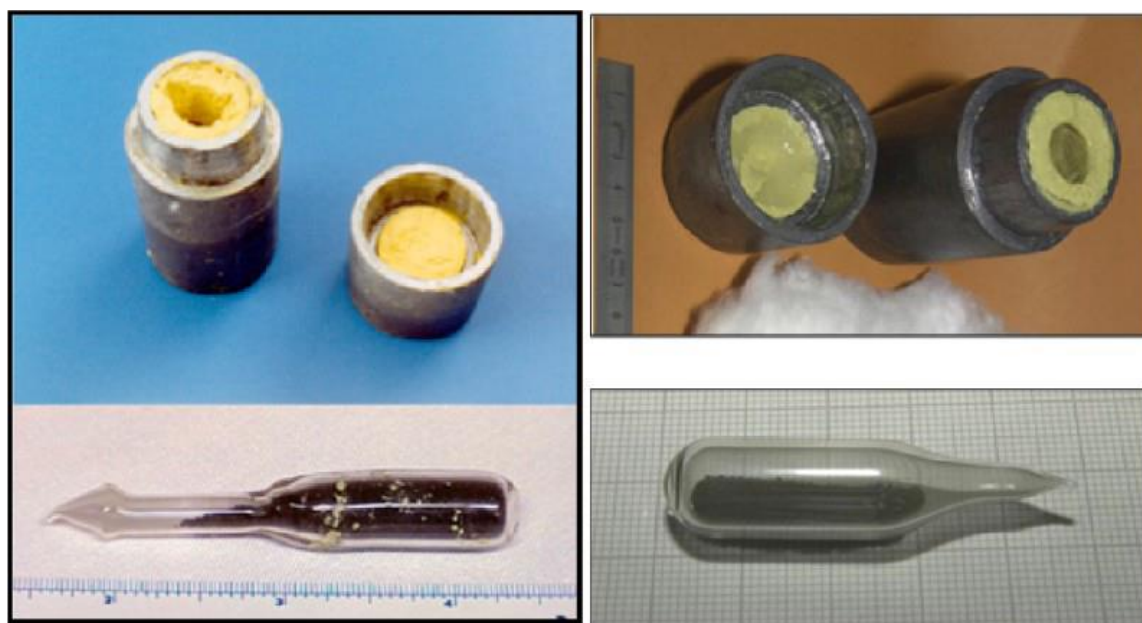


Figure 2. 4: Comparison of the lead containers, glass ampules and black powders of the seizures in Ruse, Bulgaria (left) and Paris, France (Right) (Keegan *et al.*, 2016).

Predictive signature, in contrast, use both modelling and empirical approach to predict relevant signatures based upon the chemistry and physics of nuclear processes used to create it and the previous analysis of the nuclear material (Fedchenko, 2014). If the measured characteristic of the sample matches the predictive signature, the determination of the sample's origin is simplified (Fedchenko, 2015). Predictive signatures, usually come into play when representative data for a suite of appropriate reference materials are unavailable. Predictive signatures seek to analyze signatures useful for attribution based on underlying scientific principles such as isotopic and chemical fractionation in the example of uranium ore and ore concentrate (Hutcheon *et al.*, 2015).

Summarized below in Table 2.6 is an example of predictive and comparison signatures mentioned above, including some properties of the material characteristics, such as morphology, structure, minor and major elements, impurities, and isotopes.

Table 2. 6: Summary of nuclear forensic signatures developed during the past years (Fahey *et al.*, 2010; Fayek *et al.*, 2011a; Keegan *et al.*, 2016; Krajko, 2016; Kristo *et al.*, 2016b; Redermeier, 2009; Švedkauskaite-LeGore *et al.*, 2007a; Wallenius *et al.*, 2006).

Group of parameters	Signature		Technique(s) used to determine analyte(s)	Information derived from analysis	Predictive / Comparative
Physical appearance (morphology)	Appearance		Optical microscopy	Material type (powder/pellet)	Comparative
	Dimension (pellet)		Comparison to data base	Reactor type	Comparative
	Surface roughness		Profilometry, comparison to data base	Production plant	Comparative
	Microstructure		SEM, TEM	Production process	Comparative
Elemental content	Major elements	U, Pu	Titration, hybrid K-edge densitometry, isotope dilution, mass spectrometry	Chemical concentration, nuclear fuel type	Predictive / comparative
	Impurities	Anionic (F^- , Cl^- , Br^- , NO_3^- , SO_4^{2-} , PO_4^{3-})	FTIR combined with multivariate statistical analysis methods, IC	Composition of major and minor phases, identification of the type of uranium compound, production method of the material	Predictive / comparative
		Metallic (e.g. REE)	ICP-MS	Possible identification of the type of uranium deposit	Comparative

		Organic (Alamine [®] 336, Decanol)	GC-MS	Possible indication of processing history based	Predictive / comparative
Isotope ratios (IR)	Major Isotopic composition	²³⁸ U, ²³⁵ U	Gamma spectrometry, TIMS, ICP-MS, SIMS	Enrichment–intended use/reactor type, nuclear fuel type, weapon type, and device type	Predictive / comparative
	Minor isotope ratio	²³⁵ U/ ²³⁴ U, ²³⁴ U/ ²³⁸ U, ²³⁶ U/ ²³⁸ U	MC-ICP-MS, TIMS, AMS	Possible identification of type of uranium deposit & type of depositional settings	Comparative
	Trace elements	⁸⁷ Sr/ ⁸⁶ Sr, ²⁰⁷ Pb/ ²⁰⁶ Pb	MC-ICP-MS	Possible identification of origin of mine and the ore type	Predictive (Pb age) / comparative
	Stable isotopes	¹⁸ O/ ¹⁶ O	TIMS	Possible indication of processing history of UOC & location of the facility	Comparative
	Age	²³⁰ Th/ ²³⁴ U, ²²⁸ Th/ ²³² Th, ²³¹ Pa/ ²³⁵ U	Alpha spectrometry, TIMS, ICP-MS	Production date	Predictive

2.6.1 Age

The age of a sample in the nuclear forensics context is defined as the time elapsed since the last separation of the progeny isotopes from the radioactive parent (usually uranium or plutonium), referred to as the production, purification or reprocessing date (Keegan *et al.*, 2016). The separation of the progeny isotopes from the radioactive parent set the clock to “zero”; the subsequent ingrowth of the progeny isotope allows the age of the sample to be measured (via measurement of progeny to parent ratio) and calculated based on radioactive decay equations (Keegan *et al.*, 2016). The age of the material may serve as exclusion parameter in the search for the production or reprocessing plant. The age determination of material is an extremely useful nuclear forensic signature as it is “predictive”, it does not require comparison with other material in a database.

Since radioactive isotopes decay or grow in at a rate determined by the initial amount and the half-life of the isotope, the relative amounts of decay products (daughters) in comparison to the parent isotope can be used as a chronometer. The age of the material is short in comparison to the half-life of the observed nuclides. Uranium has two candidate parent/daughter relations mostly used in nuclear forensics for the age determination: $^{234}\text{U}/^{230}\text{Th}$ and $^{235}\text{U}/^{231}\text{Pa}$ (Varga *et al.*, 2018). The radioactive decay of uranium isotope is unique, therefore measuring the parent/daughter ratio provides a chronometer that is inherent to the material. The age of uranium material is calculated from the equation of basic radioactive decay, $N = N_0 \times e^{-\lambda t}$ (Mayer *et al.*, 2011).

The example of calculated parent/daughter mass ratios of uranium as function of age is shown in Figure 2.5.

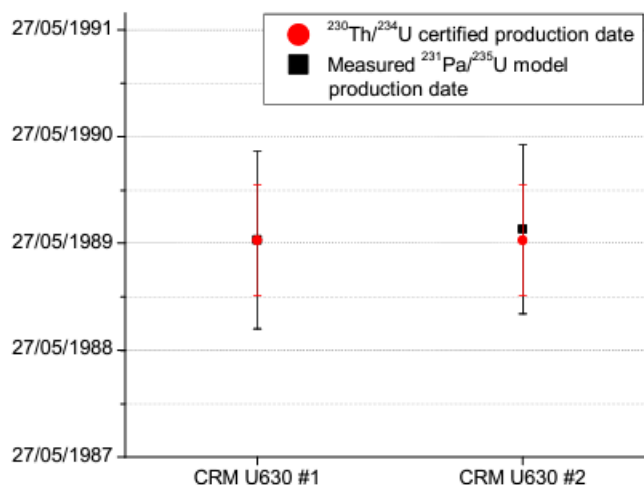


Figure 2. 5: Calculated parent/daughter mass ratios of uranium as function of age (decay time) (Varga *et al.*, 2018).

2.6.2 Isotopic composition of stable elements

Measurements of isotopic composition of specific elements such as uranium (U), plutonium (Pu), lead (Pb), strontium (Sr), sulphur (S), neodymium (Nd) and oxygen (O) in any uranium bearing material can be used to trace the origin of uranium samples. These elements have been successfully validated as signatures for use in nuclear material attribution (Mishra *et al.*, 2017).

2.6.2.1 Uranium isotope ratio

Uranium is abundant in the environment due to natural processes and anthropogenic activities such as nuclear, natural gas, oil, coal, mineral processing, phosphate fertilizer industries and ore refining. Releases of U from anthropogenic nuclear activity can significantly alter the isotopic ratios in environmental samples. The use of ICP-MS to measure variety of environmental samples and to determine $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios has been reported in the literature (Veerasamy *et al.*, 2020). Uranium material present of enriched ^{235}U isotope indicative of weapons production type material, while low $^{235}\text{U}/^{238}\text{U}$ ratios shows depleted uranium or waste from nuclear fuel enrichment process (Eppich, 2020; Sharp *et al.*, 2014).

The determination of uranium is important for not only nuclear forensics purposes but also for environmental radioactivity monitoring, which studies the releases of uranium from

nuclear facilities and of naturally occurring radioactive materials (NORM). While the release of NORM could enhance the radioactivity level in the environment, the isotopic compositions of $^{235}\text{U}/^{238}\text{U}$ ratio remains unaltered and the $^{234}\text{U}/^{238}\text{U}$ ratio may vary due to the natural causes (Baloyi, 2018; Fons, 2016).

Studies have revealed that the $^{234}\text{U}/^{238}\text{U}$ activity ratio varies significantly in many uranium ore samples of different geographical origins (Bajoga, 2016). Therefore, uranium isotope ratios, give information concerning the source of the uranium in the environment and are important for studying its geochemical behaviour.

Uranium isotopic ratios are used to give information regarding the source of uranium in the environment (Karpas, 2014). The three naturally occurring isotopes of U: ^{234}U , ^{235}U and ^{238}U with their corresponding isotopic abundances means the $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios in uranium of natural origin are 0.00725 and 0.0000552, respectively. The enriched ^{235}U is indicative of weapons production or reactor fuel, while low $^{235}\text{U}/^{238}\text{U}$ ratios, depleted U, is indicative of nuclear fuels that have been burnt up, reprocessed, or waste from fuel enrichment process (Mayer *et al.*, 2013; Zheng & Yamada, 2006). The other information which can be obtained by investigating the isotopic patterns is the presence of small amounts of ^{236}U which indicate a contamination with recycled uranium and hence point at reprocessing activities. Also, by investigating the isotopic patterns, uranium oxide can be found in different forms, for example, UO_2 or U_3O_8 , which give information on various points of origin in the uranium fuel cycle.

2.6.2.2 Lead isotope ratio

Pb-bearing material has a time-dependent Pb isotopic composition that definite the relative abundances and decay schemes of ^{232}Th , ^{235}U and ^{238}U , the parent isotopes, producing ^{208}Pb , ^{207}Pb and ^{206}Pb . On a geological time-scale, over 90% of the ^{235}U has decayed to ^{207}Pb and about half the amount of ^{238}U has decayed to ^{206}Pb . Pb isotopes are mostly changed by radioactive decay or mixing not by fractionation, natural chemical or physical processes (Wiederhold, 2015). Since ^{204}Pb is non-radiogenic, not produced by radioactive decay, it is therefore used to estimate the quantities of ^{206}Pb and ^{207}Pb that of non-radiogenic origin (Awadh, 2020).

Measuring the stable isotope such as lead (Pb) is an established technique in geolocation (Apostol *et al.*, 2016; Mathuthu & Khumalo, 2018). Natural Pb is composed of four stable isotopes, and the International Union of Pure and Applied Chemistry (IUPAC) (Margui *et al.*, 2007) reports small natural variations on the representative isotopic composition: ^{204}Pb - 1.4%, ^{206}Pb - 24.1%, ^{207}Pb - 22.1% and ^{208}Pb - 52.4%. Therefore, the stable lead isotope composition gives information on the initial U/Th ratio in the ore deposits and on the age of the ore. Since the variations in the composition for different mines are significant, investigating the stable lead isotopes can locate the original mine.

The variability of the isotopic composition of lead in ores and yellow cakes and the applicability of this signature for nuclear forensic investigation has been discussed by Svedkauskaite-LeGore *et al.* (Švedkauskaite-LeGore *et al.*, 2007a). They found that uranium ore bodies can have different Pb-isotope signatures. Figure 2.6 shows an example of Pb isotopes for natural Pb in yellow cake samples from different production plants.

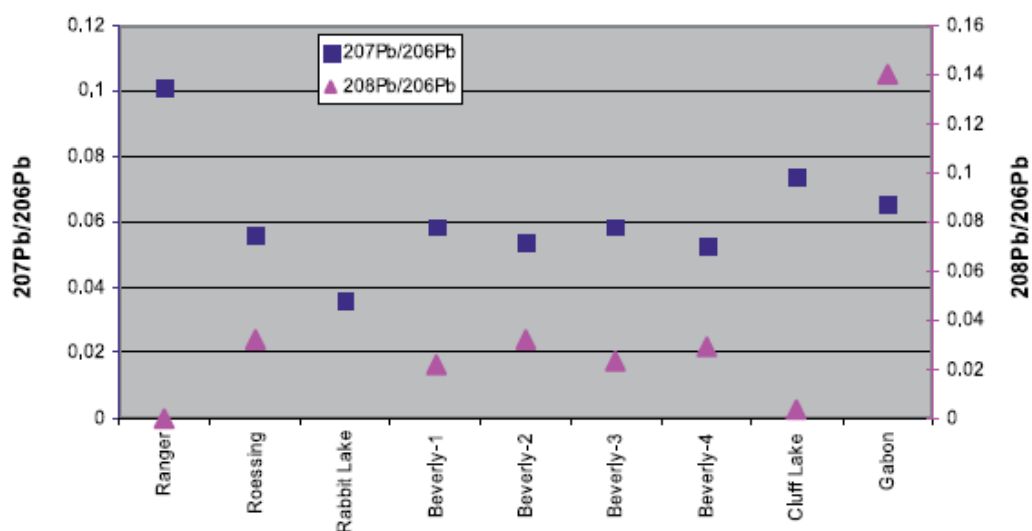


Figure 2. 6: Pb isotope ratio for natural Pb in yellow cake samples from different production plants (Švedkauskaite-LeGore *et al.*, 2007a).

2.6.2.3 Oxygen isotope ratio

Oxygen consists of three stable isotopic compositions: ^{16}O , ^{17}O , and ^{18}O , and varies by almost 5% (relative) in nature (Dierick *et al.*, 2017). The variations are as a results of natural isotopic fractionation or different chemical and physical behaviour of the isotopes (Pajo *et al.*, 2001). The isotopic composition of oxygen is an important diagnostic tool in nuclear

forensics for characterization of samples. For the past twenty years, advances in the use of thermal ionisation mass spectrometry (TIMS) and secondary ion mass spectrometry (SIMS) have made possible for precise measurement for resolving small differences in $^{18}\text{O}/^{16}\text{O}$ on a microscale in solids (Siron *et al.*, 2017). The $^{18}\text{O}/^{16}\text{O}$ isotope amount ratio in the actinides oxides can be used to trace their geographical location (Krajko *et al.*, 2014; Varga *et al.*, 2009). Oxygen isotopic ratios for UO_2 fuels have been observed to vary slightly with the geo-location of the fuel production facility, and these variations show a range in $^{18}\text{O}/^{16}\text{O}$ of $\sim 3\%$ (Wotzlaw *et al.*, 2017). Also with the use of SIMS and TIMS, small changes in $^{18}\text{O}/^{16}\text{O}$ isotope amount ratios (less than 3%) were observed in uranium oxide samples of different origins (Sevastyanov, 2016).

2.6.2.4 Sulphur isotope ratio

The relatively high variation of sulphur (S) isotope abundance in nature and sulphur ratio applicability as a nuclear forensic signature have been studied (Krajko *et al.*, 2016). This variation can be exploited to differentiate samples of different origin, for example, to exclude or verify an assumed origin. The variations in sulphur isotope ratio is usually expressed as $\delta^{34}\text{S}$, the amount ratio of $n(^{34}\text{S})/n(^{32}\text{S})$ of the sample relative to the IAEA Vienna canyon diablo troilite (V-CDT) standard, expressed in ‰ (Leyden *et al.*, 2021).

Signatures for nuclear forensics in sulphur isotope ratio variation in uranium deposits are related to only UOC samples originating from sandstone type uranium deposits, where the uranium is leached with alkaline lixiviant and not with sulphuric acid (Han *et al.*, 2013b). Determination of $^{34}\text{S}/^{32}\text{S}$ ratio in uranium ore concentrates of world-wide origin shows that process reagents have a significant effect on the $n(^{34}\text{S})/n(^{32}\text{S})$ ratio, confirming that sulphur isotope ratio is in most cases a process-related signature (Han *et al.*, 2013a).

2.6.2.5 Neodymium isotope ratio

Neodymium is composed of seven natural isotopes, ^{142}Nd (27.153 %), ^{143}Nd (12.173 %), ^{144}Nd (23.798 %), ^{145}Nd (8.293 %), ^{146}Nd (17.189 %), ^{148}Nd (5.756 %), and ^{150}Nd (5.638 %) (Meija *et al.*, 2016). The stable isotopes of Nd are ^{142}Nd , ^{143}Nd , ^{145}Nd , ^{146}Nd and ^{148}Nd , with ^{142}Nd being the most abundant (27.153% natural abundance). Neodymium (Nd) isotope belongs to the lanthanide series or rare-earth element (REE). The variation of $^{143}\text{Nd}/^{144}\text{Nd}$

isotope ratio in various uranium-bearing materials, such as uranium ores and ore concentrates (UOC) has been studied and has provided a reliable forensic signature for provenance assessment in nuclear forensics (Krajko *et al.*, 2014). The $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratio is a reliable forensic signature since it is not prone to weathering and is dependent on the type and age of the minerals (Jung *et al.*, 2001). The Nd isotope ratio ranges from 0.511 to 0.516 (1%), with Sm/Nd ratio varying from 0.05 to 0.8 in various uranium ores and ore concentrates samples (Aggarwal, 2016b; John *et al.*, 2021).

2.6.3 Rare earth elements

The rare-earth elements (REE) are a set of fifteen chemical elements in the periodic table. They are also known as lanthanides (with the addition of scandium and yttrium forms the REE) and are present in nuclear materials (uranium and plutonium) in widely variable concentrations. REE, consists of Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Certain REE may be added intentionally to the nuclear materials to improve certain properties of the final product, such as to control the reactivity of the fuel in nuclear reactors (Varga *et al.*, 2010). Rare-earth element (REE) patterns often remain unaltered during deposition of uranium bearing sediments or during metamorphism, thus they provide information on the history and provenance of geologic samples.

A large amount of uranium is found in REE deposits and may be extracted as a by-product. As a result, REE in uranium compounds can be used as an evidence of uranium origin. The REE share numerous common physical and chemical properties that make them difficult to chemically separate from each other. The atomic number (Z) for the REE ranges from 57 to 71 and they are divided into two sub-groups, namely the light rare earth elements (LREE) and the heavy rare earth elements (HREE). The LREE consists of the following metals namely, lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu) and gadolinium (Gd). The HREE include metals such as terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Table 2.7 summaries the REEs with respect to their atomic number, atomic weight and their crystal abundance in nature.

Table 2. 7: List of the rare-earth elements found in natural deposits (Schulz *et al.*, 2018).

Element	Atomic number	Atomic weight	Crustal abundance (ppm)
Light rare-earth elements (LREEs)			
La	57	138.91	39
Ce	58	140.12	66.5
Pr	59	140.91	9.2
Nd	60	144.24	41.5
Sm	62	150.36	7.05
Eu	63	151.96	2.0
Gd	64	157.25	6.2
Heavy rare-earth elements (HREEs)			
Y	39	88.91	33
Tb	65	158.92	1.2
Dy	66	162.50	5.2
Ho	67	164.93	1.3
Er	68	167.26	3.5
Tm	69	168.93	0.52
Yb	70	173.04	3.2
Lu	71	174.97	0.8

Promethium (Pm), with atomic number 61, is extremely rare in nature, therefore, not included in the list. Variations in the REE pattern of UOC samples may reflect differences in the geologic origin of the uranium deposit (Varga *et al.*, 2011; Varga *et al.*, 2010).

2.6.4 Impurities and trace elements

Impurities can also be introduced into the material unintentionally as contaminants from the uranium feed material or from the processes used throughout the fuel cycle to convert uranium ore into targeted items. Analyzing for trace impurities in uranium bearing materials from different stages throughout the fuel cycle is essential for nuclear forensics as it may provide details about the origins of materials or insight into the production processes.

During the production of uranium, unwanted elements called “impurities” are created as a by-product or deliberately introduced to enhance the performance of the material (Stanley *et al.*, 2013). Impurities in various uranium products are generally considered as a signature, which may reveal information about the process used to produce the nuclear material. Impurities study in UOCs was first commissioned in 1978 and was associated with the “Great Yellowcake Caper,” theft of five barrels of UOC in New Mexico (Kristo *et al.*, 2016a).

2.7 Nuclear forensic library

The IAEA has recommended that each of its member states should establish a national register of nuclear material and radioactive sources known as the national nuclear forensic libraries (NNFL). This will enable the State to ensure accountability of all nuclear material that is under their control. In addition, the NNFL provides a credible assessment of whether or not nuclear and other radioactive material encountered out of regulatory control is consistent with material produced, used or stored within the state (IAEA, 2015). A national nuclear forensics library is an administratively organized collection of information on nuclear and other radioactive material produced, used or stored within a state, which may come from different and diverse sources, to assist in queries regarding a sample’s origin, its history, intended use and point at which legitimate control was lost (Moody *et al.*, 2014). This library may facilitate comparisons of measured characteristics of nuclear and other radioactive material with signatures of classes of known materials (e.g. physical characteristics, chemical and elemental composition, and isotopic ratios). Scientists and experts contribute to the development of the state’s nuclear forensic libraries. The NNFL may ensure that nuclear material and radioactive sources are identifiable and traceable, or when this is not practicable, ensure that there are alternative processes for identifying and tracing sources. The creation and development of nuclear forensic library was recognised as an important international issue by IAEA, the global initiative to combat nuclear terrorism, and the Nuclear Security Summit of 2010 and 2012 (Findlay, 2014).

One of the objectives of this study is to develop nuclear forensic signature that can be recommended for nuclear forensic libraries for uranium material produced in South Africa mines. The results of the study will contribute significantly to the development of South Africa’s national nuclear forensics libraries. It provides an overview of the South Africa’s

NNFL development programme, including a discussion regarding the instruments that enable it. Table 2.8 details requirements of development of the nuclear forensic library.

Table 2. 8: Requirements of nuclear forensic library (Davydov & Smith, 2020; Davydov *et al.*, 2016).

Requirements	Necessary data types	Necessary system functions
Collection of Information on NMs	- General information (facility, process, process duration, intended use, history, shape etc...) - Material data (elemental, isotopic, chemical, physical, microscopic etc...)	Data entry, search, update
Interpretation and accumulation of NF measurement data	- Sample general information (archive, collected situation, transportation etc...) - Measurement data (sample shape, chemical, physical, elemental, isotopic, microscopic, radiation, analyst, uncertainty etc...) - Burnup analysis data - Age determination data	- Analysis data entry, search, update - Graphing - Age calculation by analysis data - Statistical analysis

The development of NNFL is still new phenomena as no country has developed its own except development of case studies and exercise to evaluate their expertise and capabilities (Kimura *et al.*, 2017a; Kips *et al.*, 2019; Nelwamondo *et al.*, 2014). The summary list of information required in the NNFL is listed in Table 2.9 below.

Table 2. 9: List of information required in the national nuclear forensic library.

Material information	Signature	Intended used
Sample identity number	Age	Natural
Categorization	Isotopic composition	Depleted
Characterization	Chemical composition	Highly enriched
	Morphology	Low enriched
	Elemental composition	Spent fuel

The developed NNFL must consists of data query and database (Kimura *et al.*, 2017a). The data query is a user interfaces function designed to obtain necessary information from database rapidly and accurately, while a database is an organized collection of data according to its objectives and kinds.

2.7.1 Data query

For an efficient NNFL, a state must appoint a national point of contact (POC) to facilitate communication through official channels and serve as an interface to its NNFL. The POC must be responsible to receive and reply to queries or request about nuclear material in the country's NNFL. The NNFL must be controlled and managed by the state since it is likely to contain proprietary or sensitive information. However, queries about exchange of expertise and information about material must be maintained in the library without revealing detailed information about the database or library content. These approaches will provide an effective and more comprehensive way to facilitate information to support an investigation (Davydov *et al.*, 2016).

2.7.2 Database

A database consists of information pertaining to the inventory of nuclear material manufactured, stored, or used by the state. The data items included in the database assist to identify discriminative characteristics, history, origin and intended use of illicit nuclear materials (Apostol & Fugaru, 2019).

2.7.3 Nuclear forensics policy instruments

In South Africa (SA), the nuclear forensics approach and its functions are managed and hosted by the South African Nuclear Energy Corporation (Necsa). These includes support of any nuclear security investigations, handling and storage of nuclear material out of regulatory control (Phuti *et al.*, 2015). The main aim of this approach is to increase credibility status of the chain of custody of the material. The NNFL not only allows a state quick access to see whether material is consistent with its own holdings but form an integral part of a framework for governments to cooperate in investigating illicit uses of nuclear material.

Although, illicit trafficking of radiological and nuclear terrorism is an issue of global concern, South Africa has a well-established and defined system for combating illicit trafficking of nuclear material. The South African government has a robust nuclear regulatory framework, which is derived from a set of comprehensive legislation, which includes the: Nuclear Energy Policy of 2008, Nuclear Energy Act, 1999 (Act 46 of 1999), Non-Proliferation of Weapons of Mass Destruction Act, 1993 (Act 87 of 1993); the National Nuclear Regulatory Act, 1999 (Act 47 of 1999), the Hazardous Substances Act, 1973 (Act 15 of 1973); National Radioactive Waste Disposal Institute Act, 2008 (Act 53 of 2008); National Strategic Intelligence Act, 1994 (Act 39 of 1994); Disaster Management Act, 2002, (Act 57 of 2002); National Key Points Act, 1980 (Act 102 of 1980); and the Protection of Constitutional Democracy Against Terrorist and Related Activities Act, 2004 (Act No. 33 of 2004).

The outcome of the Nuclear Security Summit of 2010 organised by the former United States of America (USA) President Barack Obama, pledged to secure all vulnerable nuclear material around the world within a space of four years with a goal to address the threat of nuclear terrorism and to prevent the illicit acquisition of nuclear material by non-state actors and taking steps to strengthen the global nuclear security regime (Sorvillo, 2009; Yan, 2010).

3 CHAPTER THREE: METHODOLOGY

3.1 Certified reference materials (CRMs)

Certified reference materials (CRMs) are defined as standards used to check the quality and metrological traceability of products and are characterized by a metrologically valid procedure for one or more specified properties, accompanied by a reference material certificate (ILAC, 2005). These CRMs are used globally to provide a benchmark for analytical laboratories and to deliver accurate and comparable results (Weber *et al.*, 2015). They are produced by accredited national and international institutions such as the standard reference material (SRM), National Institute of Standards and Technology (NIST) and International Atomic Energy Agency (IAEA) to calibrate measuring instrument, evaluate test procedures and for quality control purposes and are subject to strict testing (Inn *et al.*, 2013b; Jakopič *et al.*, 2013). CRMs usually contain a certificate with information on traceability, validated methods, and measurement uncertainty.

CRMs, produced by national and international organizations, serve as critical standards in research work. This is vital for instrument calibration and method validation, to ensure the integrity of critical forensic measurements (Fahey *et al.*, 2010; Morgenstern *et al.*, 2002). The United States of America has spearheaded a multi-agency program for identifying and prioritizing the development of radio-analytical CRMs for field and laboratory nuclear measurement, that meet the emerging needs of the nuclear forensic community and are available to both the United States and international community (Inn *et al.*, 2013a).

3.2 Study area

The study area is one of the uranium mines situated in *Witwatersrand basin uranium province*, in the in North West province of South Africa. It is found near the towns of Klerksdorp and Orkney, approximately 180 kilometers southwest of Johannesburg. The exact location, where uranium ore samples were collected cannot be revealed due to confidentiality agreement signed with the mines. The uranium ore, ammonium diuranate (ADU) and triuranium octoxide (U_3O_8) samples were provided by the NUFCOR on request through the Department of Mineral Resources (see Appendix A). This research work

focused only on the first stage (geological deposition) and second stage (mining and milling) of the nuclear fuel cycle.

3.2.1 Sample collection

The samples selected for this study were uranium ore, ammonium diuranate (ADU) slurry and triuranium octoxide (U_3O_8). The samples in this case were part of the first and second stages of the front end in nuclear fuel cycle. Figure 3.1 shows samples collected and analyzed in this study.

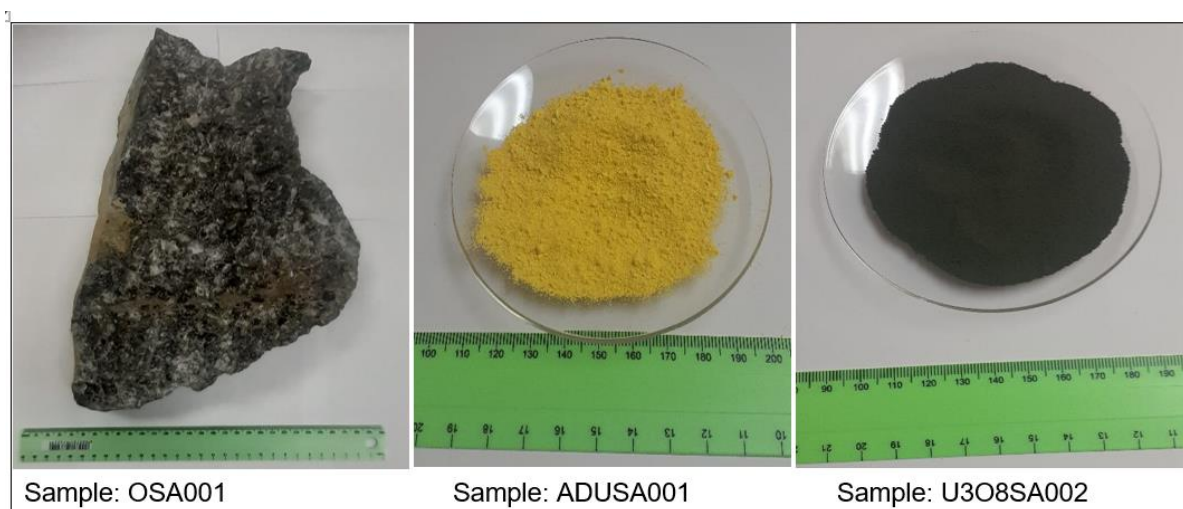


Figure 3. 1: Samples collected from the South African uranium facility used for analyses in the study.

At the Centre for Applied Radiation Science and Technology (CARST), samples were given unique identity number: uranium ore - OSA001, ammonium diuranate (ADU) - ADUSA001, and triuranium octoxide (U_3O_8) - U3O8SA002.

3.2.2 Sample preparation

Sample preparation refers to the process in which a representative piece of material is extracted from a larger amount and readied for analysis (Zivuku, 2020). Sample preparation is a critical key element of the analytical process, as it is considered one of the major contributors of errors if not done in an accurate and precise manner, thus leading to wrong results, conclusions and recommendations (Keith, 2017).

In the nuclear forensic laboratory, the material is first subjected to visual inspection as this may reveal useful information on the material itself and thus provide the starting point for further analysis. Preparation and analysis of samples for ICP-MS analysis were carried out at the North-West University's Centre for Applied Radiation Science and Technology (CARST) nuclear forensics laboratory. At CARST, the samples were first subjected to weighing, photography and dose rate measurement, followed by crushing and grinding, then digestion and analysis.

Table 3.1 below lists all the apparatus used for the first examination of the samples and the measurement results are presented in Table 3.2

Table 3. 1: List of apparatus used in physical characterization of the samples.

Apparatus		
Dose rate measurement device	Forceps	Surface contamination device
Gloves	Permanent marker pen	Camera
Glove box	Identifying tags	Swipe sampling material
Caliper	Petri-dish	Ruler
Plastic bags with slick locks	Millimeter paper	Isotope identifier device
Weighing balance		

Table 3. 2: Sizes and dimensions of the sample.

Sample ID	OSA001	ADUSA001	U3O8SA002
Type	Rock	Sludge	Powder
Form	Ore	ADU	U ₃ O ₈
Mass*	24.59 kg	3 kg	1 kg
Expanded uncertainty	0.0003	0.0002	0.0002
Colour code	RAL 9007	RAL 1026	RAL 9005

*Mass measured by analytical scales (mass included weight of the container).

The aim of nuclear forensics is to provide as much information as possible about the seized material so that the expert matters can use it to formulate their response to the event or action and therefore identify and remedy vulnerabilities in a State's nuclear security infrastructure. According to the Nuclear Forensics International Technical Working Group (ITWG), the designed nuclear forensic laboratory should provide their findings in three different types of reports (24h report, 1-week report and 2-months report) (Schwantes *et al.*, 2017; Taylor *et al.*, 2020).

3.2.2.1 Weight and dose rate measurements

The background radiation is a measure of the level of ionizing radiation present in the environment at a particular location which is not due to deliberate introduction of radiation sources (Hosoda *et al.*, 2021; Kendall *et al.*, 2021). For this study, within 24 hours of receiving samples at the CARST facility, the natural radiation background check was performed in the area where the samples were received, and the samples were surveyed for radiation leak and dose rate measurement using the RedEye-G10 and Electra-GM radiation monitoring instrument shown in Figure 3.2 and Figure 3.3 respectively. The RedEye-G10 and Electra-GM instrument used in the investigation were calibrated before it was used for radiation measurement (See Appendix B).

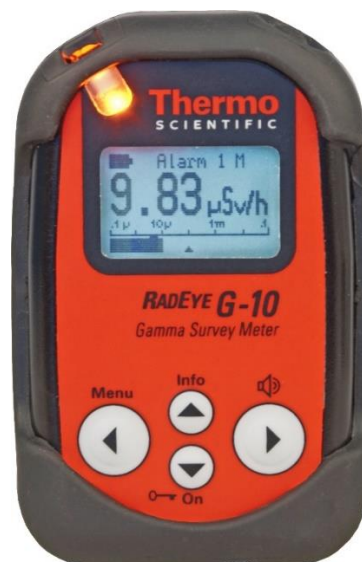


Figure 3. 2: RedEye-G10 radiation monitoring instrument used for dose rate measurement.



Figure 3. 3: Electra-GM radiation instrument used for contamination monitoring.

The natural background check and radiation survey were performed to ensure if there is no radiation leak on the sample and to confirm if any radioactive or nuclear material is present at the scene as well as to check contamination of the area or the samples.

The samples were uncovered from the sample container using manipulator in a fume hood. The photograph of the samples was taken at all stages of examination, including during receiving, opening, and transporting of the samples for analysis. The samples were weight on the weighing balance to obtain their weights. The samples were weight using the Adam TCS150 platform scale equipped with stainless steel platform and fitted with an internal rechargeable battery with up to 80 hours lifetime. The Adam TCS150 platform scale is shown in Figure 3.4. Once the survey was completed, the samples were then secured in plastic bags, sealed, labeled, and transported to the laboratory for digestion and analysis.



Figure 3. 4: The Adam TCS150 platform scale used for weighing the samples.

3.2.2.2 Crushing, drying and milling

Before digestion, the uranium ore sample were crushed into small grain sizes using mortar, pestle and Polymix (PX-MFC 90 D), Kinematica, dispersing and mixing technology. The collected ammonium diuranate (ADU) slurry sample were first spread out on petri dish and allowed to air dry for 60 days. The grinding and milling instrument used is shown in Figure 3.5. To avoid cross contamination between samples during milling, the sieve kernel, hammer and blade grinding were washed with ethanol after every sample run.



Figure 3. 5: Milling and crushing instrument used in sample preparation.

Once milled, each samples was then gently disaggregated and sieved through a 2 mm mesh to obtain a homogenous sample matrix (Luo *et al.*, 2018; Rasmussen, 2020). Each sample was transferred into new sample holder, re-tagged and moved to storage awaiting analysis. All samples were homogenous prior to analysis to ensure better precision and an accurate presentation.

3.2.2.3 Digestion

The PerkinElmer, titan MPS™ microwave digester and high-pressure vessel was used for complete dissolution of the samples. The instrument employs high pressure and temperature to accelerate the process. The digester employs 16-position pressure vessel, which allows preparation of samples for subsequent inorganic analysis (Pruszkowski *et al.*, 2015; Stacey *et al.*). The PerkinElmer titan MPS™ microwave is a flexible easy-to-use sample preparation system, with dual magnetrons with a 1,500 Watts peak output microwave power delivered in 1% output increments (Eid *et al.*, 2020; Luenam). The titan MPS™ is made of stainless-steel outer case, which encloses a cylindrical corrosion resistant Perfluoroalkoxy (PFA) coated oven cavity that ensures homogeneous microwave distribution. The digestion process is the chemical reaction of the sample with in an effort to remove the sample matrix and leave analyte ions suspended in solution (Furmuly *et al.*, 2020).

For the three samples used in the study, each sample was duplicated and labelled. Then each duplicated sample was diluted ten times making a total of 60 sub-samples for analysis. For each type of sample, a certified reference material was used to correct the mass biased effect during measurements. These CRMs are an assay (elemental concentration) and isotopic standard primarily for use in uranium determinations.

For actual measurement, 2 grams (g) of pulverised sample were weighed accurately and transferred in pre-cleaned polytetrafluoroethylene (PTFE) microwave sample vessels, to which 5 ml of 65% nitric acid (HNO₃) (Sigma–Aldrich, Inc., USA, 01 February 2022) and 2 ml of 32% hydrochloric acid (HCl) (VWR Prolabo Chemicals) were added. The mixture was gently swirled and allowed to reflux for 10 minutes before putting the seals in place and closing the vessels. The digester instrument used is shown in Figure 3.6.



Figure 3. 6: The titan MPS™ microwave digester used in sample digestion.

The digestion program consisted of 30 min of heating, as shown in Table 3.3. When opening the samples after digestion, the vessels were allowed 30 minutes to cool, enough to avoid foaming and sample loss. The samples were then opened in a fume hood wearing personal protective equipment (PPE), since a large amount of gas can be produced during the digestion process.

Table 3. 3: The PerkinElmer titan MPS™ microwave digestion program using HNO₃ and HCl.

Step	Target temp (°C)	Pressure, max (bar)	Ramp time (min)	Hold time (min)	Power (%)
1	150	35	5	5	80
2	195	35	2	20	100
3	50	35	1	15	0

All samples were completely dissolved, resulting in clear solutions that were diluted to a final volume of 50 mL with 18.2 MΩ HHITECH laboratory ultrapure water, 2020 model. The

ultrapure water purification system used is shown in Figure 3.7. No further sample dilutions were necessary.



Figure 3. 7: Ultrapure HHitech laboratory water purification system.

The sample preparation by microwave digester significantly reduced the sample preparation time, acids usage, hazardous emissions and other reagents and the waste generated during sample preparation (Mohagheghi *et al.*, 2000).

3.2.3 Analysis of samples

Once the sample preparation was complete, the analysis was carried out by use of ICP-MS and SEM with EDS functionality. Digested samples in this study were analyzed for lead isotopic composition and ratios and rare-earth elements using inductively coupled plasma-mass spectrometry (ICP-MS), model PerkinElmer (NexION 2000C). A 10 ml of each sample was packaged in clean plastic vial for elemental analysis. The ICP-MS is a powerful tool for analysing isotopic ratios and rare-earth elements in nuclear fuel cycle samples. The ICP-MS system can quantitatively measure various elements and produce a value of the total amount of a specific element of interest (Bazilio & Weinrich, 2012).

Solid samples were further examined for morphology, major and minor elements to determine the chemical and physical properties of a material using SEM/EDS system available at the Laboratory for Electron Microscopy of the North-West University (NWU).

The solids samples were scooped into clean sample containers using a spatula, and then the containers were appropriately labeled and referenced with their contents. Nuclear forensics sampling and analysis of nuclear material is performed with due regard for preservation of evidence. All the collecting apparatus, including radiation detectors were decontaminated and other disposed of as radioactive waste.

During the analysis, the sequence of analysis was based upon the ultimate goals of the investigation. Table 3.4 shows the sequence followed and the analytical techniques used during the investigation of signatures for nuclear forensic examination.

Table 3. 4: Sequence followed, and the analytical techniques used during the nuclear forensics' investigations.

Parameter	Possible signature	Analytical technique used
Radiological	Total activity Dose rate Surface contamination Isotope	RadEye-G10 Electra-GM Inspector 1000
Physical	Visual inspection Photography Weight Optical microscopy Morphology	SEM Camera
Isotopic analysis	Lead isotopes Uranium isotopes	ICP-MS
Elemental/chemical	Concentration Major element Minor element Rare earth element Chemical properties	ICP-MS SEM/EDS

The nuclear forensics examinations of samples included methods for preventing contamination or cross-contamination of the evidence.

3.3 Analytical method

A wide range of analytical tools are available and used in nuclear forensics examination for fingerprinting or detecting signatures in nuclear or other radioactive material. These analytical tools can be grouped into three wide categories, namely, bulk analysis tools (e.g. inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence(XRF)), imaging tools (e.g. optical, scanning, and transmission electron microscopy), and microanalysis tools (e.g. electron beam energy dispersive analysis) (Kristo & Tumey, 2013).

Bulk analysis tools allow to characterize isotopic and elemental composition of the sample. Bulk analysis involves the physical destruction of the sample (Gaffney *et al.*, 2016). Imaging analyses provide high magnification pictures, images, or maps of the sample (material). Microanalysis tools are used to quantitatively or semi-quantitatively characterize the individual constituents of the bulk material (Kristo, 2020).

3.3.1 ICP-MS technique

The ICP-MS technique has been increasingly used during the last years in nuclear forensics analysis to perform isotope ratio measurements (Marin *et al.*, 2013). The advantages of the ICP-MS technique are ease of operation, low detection limits, good precision and accuracy, and its high degree of sensitivity multi-elemental analysis (Frei & Gerdes, 2009; Woodhead, 2002; Zheng & Yamada, 2006). In this study, the ICP-MS analyses of the uranium samples were performed using the NexION 2000C shown in Figure 3.8, after the samples were digested. The samples were analysed for isotopic composition and ratio of uranium, natural variation of lead and rare-earth element concentrations (Bazilio & Weinrich, 2012).



Figure 3. 8: The ICP-MS NexION 2000C instrument at CARST for multi-elemental analysis.

The ICP-MS NexION 2000C system is a quadrupole ion deflector, consisting of a benchtop ICP-MS instrument, data acquisition and analysis software, cooler, re-circulator and roughing pump. It can be operated in three modes using the universal cell technology™ (UCT™) functionality: Standard mode for routine analyses, dynamic reaction cell™ (DRC™) mode for ultimately low detection limits and kinetic energy discrimination (KED) mode for rapid analysis. The NexION produces minimal background interferences and low levels of oxides and doubly charged ions while providing excellent signal to noise ratio (sensitivity), precision and outstanding stability.

The PerkinElmer NexION 2000C ICP-MS (PerkinElmer Inc., Connecticut, USA) spectrometer was equipped with PerkinElmer auto sampler, (S10 Autosampler), nebulizer, spray chamber and quadrupole ion deflector that focuses the ion beam to the dual mode detector. The equipment uses a helium gas collision system that greatly reduces the spectral interference caused by argon and chlorine. Argon gas with 99.999% ultra-high purity, supplied by African Oxygen Limited (Afrox), was used for plasma, sample nebulisation, and as auxiliary gas.

3.3.1.1 Instrument setting

The instrument was optimized using the automated SmartTune™ procedure. A PerkinElmer NexION setup solution (Smart Tune solution, N8145051) was used for daily performance calibration. The instrument was rinsed using a PerkinElmer Rinse solution

(Rinse solution, N8145051) and the sample and standard solutions were aspirated into the ICP-MS flow through a peristaltic pump with 1 mL/min carrier flow rate and the isotopes selected were measured using the experimental conditions indicated in Table 3.5. The ICP-MS running conditions used in the investigation are reported in peer reviewed journal attached in the appendix (see Appendix G).

Table 3. 5: NexION 2000C ICP-MS operating conditions and settings for the determination of uranium, lead and REE (Kupi *et al.*, 2020a).

ICP-MS running conditions	
RF frequencies	27.12 MHz
RF power	1.2 kW forward, <10 W reflection
Outer	Argon plasma flow
Intermediate	Nebulizer flow
Central	AUX flow
Nebulizer	Manhard type C
Spray chamber	Dual sychronic/double Scott glass chamber (ambient temperature)
Sample uptake	50 μ L/min (free aspiration)
Number of sweeps	1000
Number of replicates	5
Ion energy	10,000 V
Extraction	2000 V

The data were acquired and processed using the equipment's Syngistix™ Nano Application Software Module Version 3.5 software (PerkinElmer Inc.). Solutions, standards, and dilutions were prepared with ultra-pure water (18.2 M Ω .cm) obtained from HHITECH laboratory ultrapure water purification systems.

3.3.1.2 Mass bias correction

The mass bias is explained as a measure of the deviation between the measured and true isotopic ratios. Due to the space charge effect, when the positively charged ions of an elements formed in the plasma leave the skimmer cone, the lighter isotopes are deflected from the central ion beam more than the heavier ions (Yang *et al.*, 2018). The differential transmission efficiencies of ions and the space charge effect leads to mass discrimination, results in mass biased in the measured isotope ratios (Mathuthu *et al.*, 2017).

To accurately perform isotope ratio measurement, the isotope ratios must be corrected for mass bias. Therefore, to achieve mass bias correction, a standard solution of known isotopic composition (e.g., NIST SRM 981) is analysed before and after the measurement of the sample. In this work, a mass biased correction was calculated using the following equation (1) and (2) respectively (Narukawa *et al.*, 2014).

$$K_f = \frac{R_{\text{true}}(\text{NIST SRM 981})}{R_{\text{measured}}(\text{NIST SRM 981})} \dots\dots\dots (1)$$

$$R_{\text{corrected}(\text{sample})} = K_f \cdot R_{\text{measured}(\text{sample})} \dots\dots\dots (2)$$

where K_f , is the mass bias correction factor, $R_{\text{corrected}}$, the mass corrected isotope ratio, R_{true} is the ratio of the isotope amount fractions calculated from known composition data and R_{measured} is the experimental ratio of the isotope amount fractions measured by the ICP-MS.

3.3.1.3 Interferences

The NexION 2000C ICP-MS uses quadrupole ion deflector and collisions of polyatomic interferences to reducing the interference and improve the results (Chen, 1996; Pruszkowski *et al.*, 2017). The quadrupole ion deflector only allows ions to enter the quadrupole while photos and neutrals are prevented by geometry from entering the quadrupole and impacting the detector. The collisions of polyatomic interferences are used in the NexION 2000C ICP-MS to reduce their kinetic energy which are prevented from entering the quadrupole mass spectrometer. The collisions of polyatomic interferences can also use different gases to react with polyatomic interferences to neutralize the mass or change them. The use of dual

detector mode in NexION allows for quantitation over a large dynamic range (Pruszkowski *et al.*, 2017).

3.3.2 Scanning electron microscope (SEM)

The FEI Quanta™ FEG 250 electron microscope, a non-destructive technique, was used to characterize material structure and elemental composition in each sample. In this study, the state-of-the-art high-resolution SEM system available at the Laboratory for Electron Microscopy, North-West University (NWU) shown in Figure 3.9 was used.



Figure 3. 9: The FEI Quanta FEG 250 Electron microscope at North-West University (<http://natural-sciences.nwu.ac.za/laboratory-electron-microscopy/home-0>: 01 February 2022).

The FEI Quanta FEG 250 electron microscope features Everhardt Thornley secondary electron detector (SED), suitable for high and low vacuum modes to provides topographical and compositional contrast (Olsen *et al.*, 2017). It consists of 4 quadrants solid-state BSED and in-column detector (ICD) for secondary electrons in BD mode. The FEI Quanta FEG 250 electron microscope uses Oxford EDS on INCA software and Oxford EBSD detector on AzTec platform. It has a resolution of 0.8 nm at 30 kV for high vacuum, 2.5 nm at 30 kV for SE and 3.0 nm at 1 kV (SE) for BSE (Mazumder *et al.*, 2018).

SEM is a widely used technique in nuclear forensics investigation (Keegan *et al.*, 2014; Mayer *et al.*, 2005). SEM provides pictures of the surface of objects at high magnification and with a large depth of field. SEM also detects the electrons that are backscattered or emitted (i.e., secondary electrons) from the specimen's surface. In nuclear forensics, the application of SEM is particularly interesting for powder samples or inhomogeneous samples. Figure 3.10 and Figure 3.11 show examples of reference samples of a known fabrication plant and of a sample seized at Munich airport in 1994, which consisted of a powder mixture of three components: uranium, plutonium rod shaped particles and plutonium platelets.

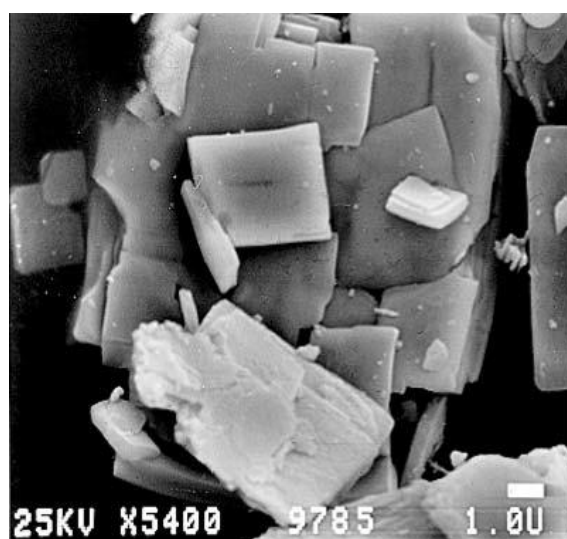


Figure 3. 10: SEM picture of a PuO₂ reference sample of a known fabrication plant (Mayer *et al.*, 2005).



Figure 3. 11: SEM picture of PuO₂ platelets from a sample seized in 1994 at Munich airport, Germany (Ho, 2015).

Scanning electron microscope (SEM) was used in this study to conduct a nuclear forensic investigation to assess the similarity or difference between the samples' morphology and elemental composition. Preparation and analysis of the samples using SEM/EDS following procedures described by Pidchenko (Pidchenko *et al.*, 2020) were adopted for this study. The measurement time set for most nuclear forensic scenarios required to collect spectra for a detailed nuclear forensic analysis in the laboratory is on the order of hours to days (Apostol *et al.*, 2016).

3.3.3 Isoplot code

Isoplot code 3.75, is a free and open-source tool for data analysis, graphical presentation and interpretation of radiogenic-isotope data (Paul *et al.*, 2021). The code is an add-in software program for microsoft excel, which allows geologists to visualise and calculate geochronological data within a familiar spreadsheet environment. The software provides tools for the manipulation and plotting of radiogenic-isotope ratios, particularly U-Pb concordia plots, uranium-series isochron ages and calculate ages using conventional concordia intercepts (Harvati *et al.*, 2021; Ludwig, 2012). The research chose this Isoplot software to validate the results from the ICP-MS ratio technique, following the procedure adopted by Schoene (2014).

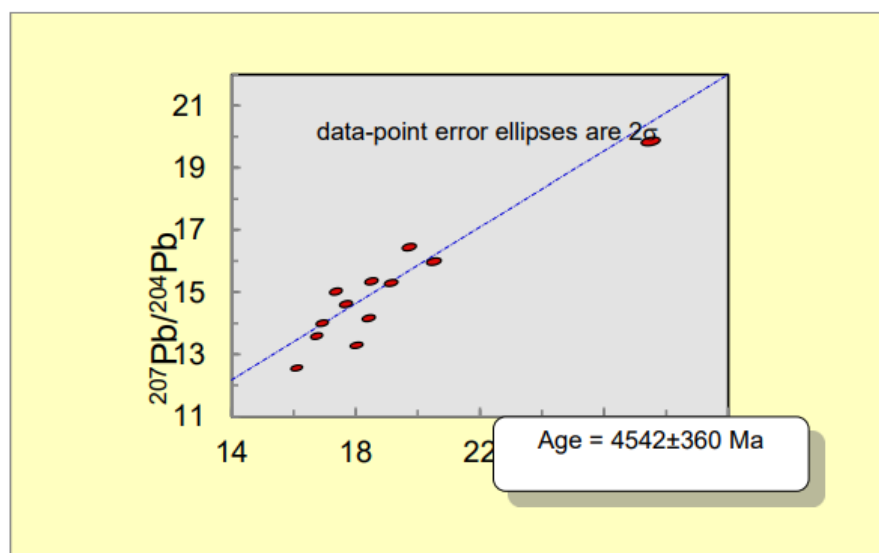


Figure 3. 12: Example of a lead-lead Isochron (Khumalo, 2017).

4 CHAPTER FOUR: RESULTS AND DISCUSSION

This chapter presents the results and discussions on the analysis of uranium ore, ammonium diuranate (ADU), and triuranium octoxide (U_3O_8). The results of the radiological measurement and physical characterization of the samples are presented first. The results of the isotopic composition of Pb (atom percentage) in the natural lead and lead ratios performed by means of inductively coupled plasma mass spectrometry (ICPMS) are presented second, followed by the rare-earth elements analysis. Results from the SEM/EDS measured for morphology and elemental or chemical characterization in uranium ore, ADU and U_3O_8 are also presented and discussed.

4.1 Physical characterization and radiological measurements

4.1.1 Physical characterizations

All samples were photographed upon receipt and subsamples were then crushed and pulverized for ICP-MS and SEM/EDS analysis. Pulverized aliquots were then dissolved into liquid using nitric acid and hydrochloric acid; and used for destructive elemental analysis by ICP-MS, lead (Pb) and rare-earth elements (REE) measurements. The goal of categorization was to identify the bulk constituents of the material and to determine whether it is SNM, naturally occurring radioactive material, radioactively contaminated material, a commercial radioactive source, or nuclear reactor fuel. Figure 4.1 shows physical characterization of the samples used in this study.

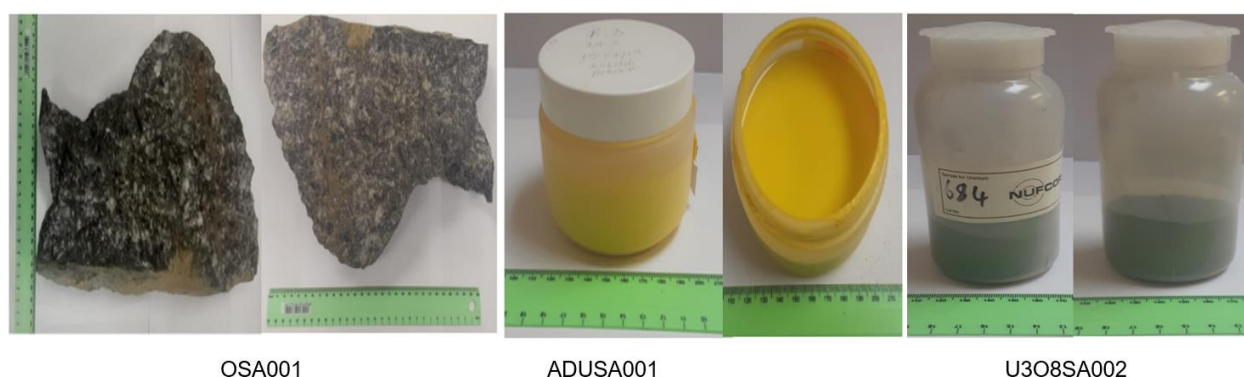


Figure 4. 1: The physical characterizations of the samples used in the study.

The physical examination of the sample, OSA001, revealed that the sample was a black rock with description written on top. Sample ADUSA001 was contained in 500 ml plastic container. The lid of the container had markings on top. The sample inside the container was in thick liquid form and yellow in colour. The physical examination of the sample, U3O8SA002, revealed that the sample was enclosed in a 250 mL plastic bottle container with marking sign on the outside. The sample inside the container was in powdered form and black in colour.

The colour code match for each sample was determined using RALcolorchart (www.ralcolorchart.com: Accessed, 10 March 2021). The characterization of the samples OSA001, ADUSA001, and U3O8SA002 revealed the color codes RAL 9007, RAL 1026, and RAL 9005, respectively. This indicates a stage level and manufacturing process for the samples, which revealed a unique signature for the U₃O₈ samples.

4.1.2 Radiological measurements

Table 4.1 below shows the gamma dose rate and contamination measurements collected during physical characterization of the samples in the laboratory. The contamination measurements were performed using the Electra-GM instrument. The instrument used was calibrated for radiological measurement.

Table 4. 1: Radiological measurements for gamma and contamination dose rate.

Radiological measures			
Sample ID	OSA001	ADUSA001	U3O8SA002
Dose rate (background)	0.26 µSv/h	0.26 µSv/h	0.26 µSv/h
Gamma/outside	0.87 µSv/h	0.56 µSv/h	0.46 µSv/h
Gamma/samples	48.84 µSv/h	64.42 µSv/h	79.94 µSv/h
Surface contamination	<2 cps	<2 cps	<2 cps

The radiological measurement revealed that the samples were radioactive, with the count rate on the instrument more than three time of the natural background. There was no surface contamination on the sample's containers, indicating no radiation leakage.

4.2 Isotopic and elemental concentration results by ICP-MS

The inductively coupled plasma-mass-spectrometry (ICP-MS) was employed to examine the isotopic ratio of Pb in the investigated samples. The ICP-MS techniques was also used to measure the rare-earth elements (REE) in the investigated samples.

4.2.1 Lead isotopic composition

Measured results for relative abundance of stable lead isotopes, ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb expressed in atom percent measured in sample OSA001, ADUSA001 and U3O8SA002 using ICP-MS are presented in Tables 4.2, 4.3 and 4.4. The dissolved uranium ore, ADU slurry, and U_3O_8 samples, the relative isotopic abundances of the stable lead isotopes ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb were measured. Each sample's results are discussed separately below. Because of the mass bias effect, the measured NIST SRM 981 and certified NIST SRM 981 results differ slightly. The mass bias effect is used as a correction factor for mass bias correction. For an expanded source of information, Appendix C (Table C1 – C3) is referred to.

Table 4. 2: Results of ICP-MS analysis of the isotopic composition of Pb (atom percentage) in the natural lead from a uranium ore sample.

Sample	Type	^{204}Pb (%)	^{206}Pb (%)	^{207}Pb (%)	^{208}Pb (%)
OSA001	Ore	1.0766 ± 0.0004	40.9392 ± 0.0013	22.9538 ± 0.0008	35.0305 ± 0.0013
NIST981 STD (Measured in this study)		1.4540 ± 0.0012	24.0140 ± 0.0012	22.1190 ± 0.0012	52.4130 ± 0.0012
NIST981 STD (Certificate)		1.4255 ± 0.0012	24.1442 ± 0.0057	22.0833 ± 0.0027	53.3470 ± 0.0086
Natural Pb (IUPAC)		1.4245 ± 0.0012	24.1447 ± 0.0057	22.0827 ± 0.0027	52.4000 ± 0.0086

(Brand <i>et al.</i>, 2014)					
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Sample OSA001, was a sample of the feedstock ore processed for uranium extraction at the South uranium plant. Table 4.2 displays the sample's measured isotopic composition of lead in the sample (expressed as an atom percentage). This result indicates that only a trace amount of ^{204}Pb was present. This was to be expected for a uranium-rich mineral.

This result suggests that the lead in the sample was of natural origin (primordial lead), and it was present as a trace element in the rock. Because ^{204}Pb does not accumulate through radioactive decay, it allows measure of the amount of primordial lead initially present in the rock sample. The amount of natural lead in the uranium ore was thus estimated from the observed amount of ^{204}Pb , and an appropriate correction for the natural lead contribution was applied.

Table 4. 3: Results of ICP-MS analysis of the isotopic composition of Pb (atom percentage) in the natural lead in ADU slurry sample.

Sample	Type	^{204}Pb (%)	$^{206}\text{Pb}(\%)$	$^{207}\text{Pb}(\%)$	$^{208}\text{Pb}(\%)$
ADUSA001	ADU	1.4025 ± 0.0004	25.6817 ± 0.0009	21.9786 ± 0.0011	50.9375 ± 0.0011
NIST981 STD (Measured in this study)		1.4540 ± 0.0012	24.0140 ± 0.0012	22.1190 ± 0.0012	52.4130 ± 0.0012
NIST981 STD (Certificate)		1.4255 ± 0.0012	24.1442 ± 0.0057	22.0833 ± 0.0027	53.3470 ± 0.0086
Natural Pb (IUPAC) (Brand <i>et al.</i>, 2014)		1.4245 ± 0.0012	24.1447 ± 0.0057	22.0827 ± 0.0027	52.4000 ± 0.0086

The relative isotope abundance of Pb isotopes in the ADU slurry is shown in Table 4.3. The isotopic composition of the sample was comparable to that of natural Pb. On the one hand,

this suggests that the Pb isotopes formed by uranium decay had only a minor impact on the isotopic composition of these samples. The small contribution of radiogenic lead isotopes showed that a low uranium concentration in the ore. Other samples, on the other hand, with lower ^{204}Pb levels, indicated a low natural Pb content (or a high content of uranium in the source material).

Table 4. 4: Results of ICP-MS analysis of the isotopic composition of Pb (atom percentage) in the U_3O_8 sample.

Sample	Type	^{204}Pb (%)	^{206}Pb (%)	^{207}Pb (%)	^{208}Pb (%)
U3O8SA002	U_3O_8	1.4131 ± 0.0004	25.7348 ± 0.0010	21.9428 ± 0.0010	50.9094 ± 0.0014
NIST981 STD (Measured in this study)		1.4540 ± 0.0012	24.0140 ± 0.0012	22.1190 ± 0.0012	52.4130 ± 0.0012
NIST981 STD (Certificate)		1.4255 ± 0.0012	24.1442 ± 0.0057	22.0833 ± 0.0027	53.3470 ± 0.0086
Natural Pb (IUPAC) (Brand <i>et al.</i>, 2014)		1.4245 ± 0.0012	24.1447 ± 0.0057	22.0827 ± 0.0027	52.4000 ± 0.0086

The relative isotope abundance of Pb isotopes in the U_3O_8 are shown in Table 4.4. Similarly, like in ADU slurry in Table 4.3, the isotopic composition of the sample was comparable to that of natural Pb, suggesting that the Pb isotopes formed by uranium decay had only a minor impact on the isotopic composition of those samples. The small contribution of radiogenic lead isotopes indicated an ore with low uranium concentration.

4.2.1 Lead isotopic ratio

The results of lead isotopic ratios are tabulated in Tables 4.5, 4.6, and 4.7. Table 4.5 summarizes the results of ICP-MS measurements of Pb isotopic ratios, $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$ in sample OSA001. For an expanded source of information, Appendix D (Table D1 – D3) is referred to.

Table 4. 5: Results of ICP-MS analysis of the isotopic ratio of Pb in the uranium ore sample.

Sample ID	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
OSA001	0.0263 ± 0.0002	0.5607 ± 0.003	0.8557 ± 0.0054
Measured NIST SRM 981 (this work)	0.0589 ± 0.0001	0.9144 ± 0.0036	2.1706 ± 0.0013
Certified NIST SRM 981 (Lancellotti <i>et al.</i>, 2020)	0.059042 ± 0.000037	0.91464 ± 0.00033	2.1681 ± 0.0008

The uranium ore sample's $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$ compositions were essentially identical to average crustal lead (i.e. common Pb), indicating that the ore body was either young or not significantly enriched in uranium relative to lead. This was consistent with the concentration of uranium in the Witwatersrand basin formation from which this ore was derived (Fuchs *et al.*, 2016b).

Table 4. 6: Results of ICP-MS analysis of the isotopic ratio of Pb in the ADU slurry sample.

Sample ID	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
ADUSA001	0.0546 ± 0.0005	0.8558 ± 0.0095	1.983553 ± 0.0317
Measured NIST SRM 981 (this work)	0.0589 ± 0.0001	0.9144 ± 0.0036	2.1706 ± 0.0013
Certified NIST SRM 981 (Lancellotti <i>et al.</i>, 2020)	0.059042 ± 0.000037	0.91464 ± 0.00033	2.1681 ± 0.0008

The $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratio for the ADU sample was comparable result to the common Pb certificate results, indicating that the ADU was made of natural uranium ore sample. The ratios also suggest that the uranium sample used were of low uranium content.

Table 4. 7: Results of ICP-MS analysis of the isotopic ratio of Pb in the U₃O₈ sample.

Sample ID	²⁰⁴ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb
U3O8SA002	0.0549 ± 0.0003	0.8527 ± 0.0050	1.9783 ± 0.0107
Measured NIST SRM 981 (this work)	0.0589 ± 0.0001	0.9144 ± 0.0036	2.1706 ± 0.0013
Certified NIST SRM 981 (Lancellotti <i>et al.</i> , 2020)	0.059042 ± 0.000037	0.91464 ± 0.00033	2.1681 ± 0.0008

The results for samples U3O8SA002 compared to the NIST 981 reference standard; the isotopic ratios ²⁰⁴Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb were slightly lower, however the results demonstrated the spread of data was close or like the NIST 981 certificate reference value.

4.2.1.1 Comparison of the results within the production plant

To look for similarities or differences in the samples, the ratios ²⁰⁴Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb, and ²⁰⁸Pb/²⁰⁶Pb were measured on OSA001, ADUSA001, and U3O8SA002. The results of lead isotopic composition measurements are shown in Tables 4.8 and 4.9. Each sample's results are discussed separately below.

Table 4. 8: Results of ICP-MS analysis of the isotopic composition of Pb (atom percentage) in the natural lead in uranium ore, ADU slurry and U₃O₈ samples.

Sample	Type	²⁰⁴ Pb (%)	²⁰⁶ Pb(%)	²⁰⁷ Pb(%)	²⁰⁸ Pb(%)
OSA001	Ore	1.0766 ± 0.0004	40.9392 ± 0.0013	22.9538 ± 0.0008	35.0305 ± 0.0013
ADUSA001	ADU slurry	1.4025 ± 0.0004	25.6817 ± 0.0009	21.9786 ± 0.0011	50.9375 ± 0.0011
U3O8SA002	U ₃ O ₈	1.4131 ± 0.0004	25.7348 ± 0.0010	21.9428 ± 0.0010	50.9094 ± 0.0014
NIST981 STD (Measured in this study)		1.4540 ± 0.0012	24.0140 ± 0.0012	22.1190 ± 0.0012	52.4130 ± 0.0012
NIST981 STD (Certificate)		1.4255 ± 0.0012	24.1442 ± 0.0057	22.0833 ± 0.0027	53.3470 ± 0.0086
Natural Pb (IUPAC) (Brand <i>et al.</i>, 2014)		1.4245 ± 0.0012	24.1447 ± 0.0057	22.0827 ± 0.0027	52.4000 ± 0.0086

Table 4. 9: Results of ICP-MS analysis of the isotopic ratio of Pb in the uranium ore, ADU slurry and U₃O₈ samples.

Sample ID	²⁰⁴ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb
OSA001	0.0263 ± 0.0002	0.5607 ± 0.0028	0.8557 ± 0.0054
ADUSA001	0.0546 ± 0.0006	0.8558 ± 0.0095	1.9836 ± 0.0317
U3O8SA002	0.0549 ± 0.0006	0.8527 ± 0.0095	1.9783 ± 0.0317

Mine Tailing Waste Solution (Kupi <i>et al.</i> , 2020b)	0.0494 ± 0.0017	0.8201 ± 0.0194	2.0172 ± 0.0606
Measured NIST SRM 981 (this work)	0.0589 ± 0.0001	0.9144 ± 0.0036	2.1706 ± 0.0013
Certified NIST SRM 981 (Lancellotti <i>et al.</i>, 2020)	0.059042 ± 0.000037	0.91464 ± 0.00033	2.1681 ± 0.0008

When the results of the mine or production plants were compared to the results of the certified NIST SRM 981 reference standard, the isotopic composition of Pb (atom percentage) and lead isotopic ratios varied significantly from the ore samples, while ADU, U₃O₈, and water samples recovered from mine tailings for reuse in the plant showed no variation. The water samples in this case were collected as part of the reprocessing of mine waste, which is an intermediate step in the nuclear fuel cycle's front end. The lack of variation in the results could be attributed to the same technological processes used to make the yellow cakes and also the stage of nuclear fuel cycle the sample was collected.

The ²⁰⁴Pb/²⁰⁶Pb ratio for uranium ore samples was significantly lower, whereas the ratios for ADU slurry, U₃O₈, and mine tailing waste solution were marginally lower to the common lead values. The isotopic ratios of samples OSA001, ADUSA001, and U3O8SA002 in relation to the common lead value indicating that the source of the U had a higher U/Pb ratio than the average continental crust. The lower U/Pb ratio i.e., below those of continental crust preserved REE compositions typical of igneous zircon from crustal rocks and yield nearly concordant U/Pb ages from 4.4 Ga to 3.9 Ga (Pidgeon *et al.*, 2017).

4.2.1.2 Comparison of the results from various production plants

The measured isotopic composition (expressed in atom percent) and isotopic ratios of lead isotopes in uranium ore and U₃O₈ samples are shown in Tables 4.10 and 4.11 respectively, followed by a discussion of the possible trend observed on the dependency of the isotope ratio measurements on the ratio value. When the results from different mines or production plants were compared, the isotopic composition of Pb (atom percentage) and lead isotopic ratios differed significantly. The data showed that the samples were distinctive for the different geological locations and thus could be used as a nuclear forensic signature.

Table 4. 10: Results of ICP-MS analysis of the isotopic composition of Pb (atom percentage) in the natural lead in uranium ore samples from different mines (Švedkauskaite-LeGore *et al.*, 2007b).

Sample origin	²⁰⁴ Pb (%)	²⁰⁶ Pb(%)	²⁰⁷ Pb(%)	²⁰⁸ Pb(%)
South Africa (OSA001)	1.0766 ± 0.0004	40.9392 ± 0.0013	22.9538 ± 0.0008	35.0305 ± 0.0013
Australia, Olympic Dam	0.1162 ± 0.0024	85.2800 ± 0.0027	8.1000 ± 0.0015	6.5100 ± 0.0015
Australia, Ranger	0.0200 ± 0.0012	89.0480 ± 0.0061	9.7250 ± 0.0055	1.2073 ± 0.0066

Table 4. 11: Results of ICP-MS analysis of the isotopic composition of Pb (atom percentage) in the natural lead in U₃O₈ ore samples from different mines (Švedkauskaite-LeGore *et al.*, 2007b).

Sample origin	²⁰⁴ Pb (%)	²⁰⁶ Pb(%)	²⁰⁷ Pb(%)	²⁰⁸ Pb(%)
South Africa (U3O8SA002)	1.4131 ± 0.0004	25.7348 ± 0.0010	21.9428 ± 0.0010	50.9094 ± 0.0014
Gabon, Mounana	1.3199 ± 0.0037	29.4380 ± 0.0038	20.7080 ± 0.0025	48.5340 ± 0.0067
Germany, Truenzig	1.3963 ± 0.0024	25.6820 ± 0.0017	21.2310 ± 0.0017	51.6910 ± 0.0033
Namibia, Roessing	0.4810 ± 0.0030	69.0500 ± 0.0085	10.8600 ± 0.0032	19.6000 ± 0.0095
Canada, Cluff Lake	0.2262 ± 0.0068	82.8200 ± 0.0020	8.5145 ± 0.0063	8.4400 ± 0.0020
Canada, Rabbit Lake	1.2720 ± 0.0012	30.1200 ± 0.0017	19.8200 ± 0.0012	48.7900 ± 0.0030
Australia, Beverly-1	0.4460 ± 0.0018	71.5340 ± 0.0016	10.5673 ± 0.0071	17.4530 ± 0.0020

Australia, Ranger	0.1054 ± 0.0051	86.0306 ± 0.0089	10.0594 ± 0.0080	3.8045 ± 0.0071
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The isotopic composition of Pb (atom percentage) in the natural lead and isotopic ratios of the stable lead isotopes ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb in uranium ore and U_3O_8 samples from different geological locations differed significantly, as showed in Tables 4.10 and 4.11. Only where there were similarities, the results showed that the samples had only trace amounts of ^{204}Pb present, indicating that the mineral was rich in uranium/thorium and thus contained significant amounts of radiogenic lead. Furthermore, in the simple case of the Roessing and Beverly-1 mines, the isotopic composition of Pb (atom percentage) in the natural lead and U_3O_8 ore samples was nearly similar. This could be related to the technological processes used to create U_3O_8 . The use of a specific Pb composition allows for the formation of a distinct pattern. This pattern could be useful in nuclear forensics investigations, complementing the lead isotopic signature.

The isotopic composition and atomic weight of lead isotopes are variable in terrestrial materials because the heaviest lead isotopes (^{206}Pb , ^{207}Pb and ^{208}Pb) are stable end-products of the radioactive decay of uranium and thorium. Lead (^{204}Pb) is the lightest stable isotope, non-radiogenic and primordial. In other words, ^{204}Pb can be used to estimate how much Pb has been produced by decay in the ore body since it was formed. The variations in these isotopes and atomic weight give useful information for use in forensic science, geochronology, environmental studies, and archaeology.

4.2.1.3 Summary of South Africa lead results

The ICP-MS results for the average isotopic composition of Pb (atom percentage) in natural lead for ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb plotted in Figures 4.2 and 4.3 shows that sample, OSA001, ADUSA001 and $\text{U}_3\text{O}_8\text{SA002}$ results were comparable to published data from IUPAC and NIST 981 reference standards and revealed that samples were comparable to natural uranium sample. This was attributed to the concentration of enriched uranium/thorium in the mine area.

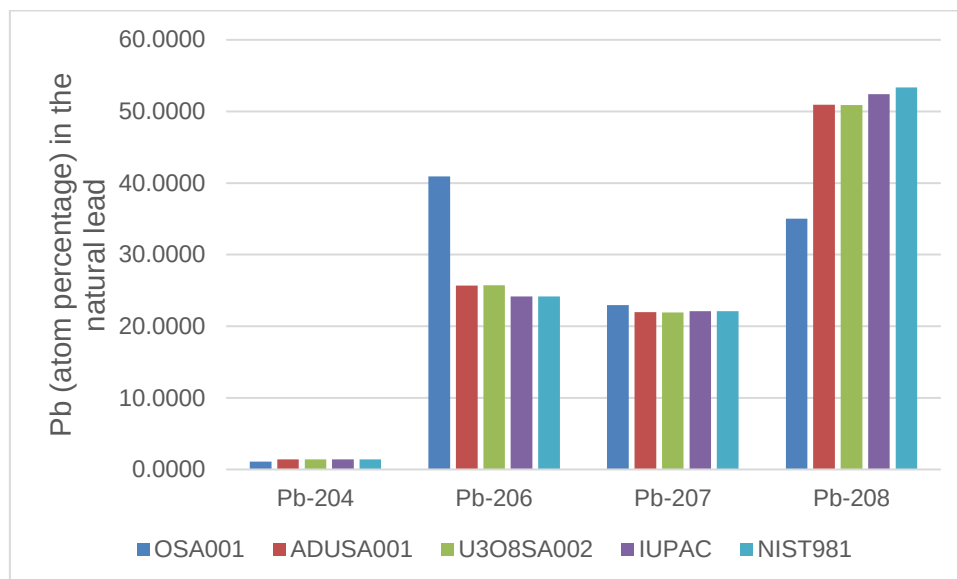


Figure 4. 2: The average isotopic composition of Pb (atom percentage) in natural lead.

According to the study's findings, sample OSA001 (i.e., uranium ore) in the mining area has a lower ^{204}Pb and ^{208}Pb isotopic composition when compared to sample ADUSA001, U3O8SA002 and IUPAC values however has a higher ^{206}Pb and ^{207}Pb isotopic composition atom percentage in the natural lead. The results obtained in sample OAS001 revealed that the average Pb isotopic compositions of ^{204}Pb and ^{208}Pb were slightly less when compared to the Natural Pb observed in IUPAC.

In contrast, the results obtained in samples ADUSA001 and U3O8SA002 revealed that the ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb were the same. The lead isotopic composition of ^{204}Pb was slightly less than NIST 981 certificate values in all the three samples measured. The obtained results were compared to the natural Pb observed in the IUPAC and NIST 981 reference standards, demonstrated that all samples were made of natural uranium and were never subjected to any nuclear enrichment activity in order to increase their concentration for the purpose of developing weapons of mass destruction.

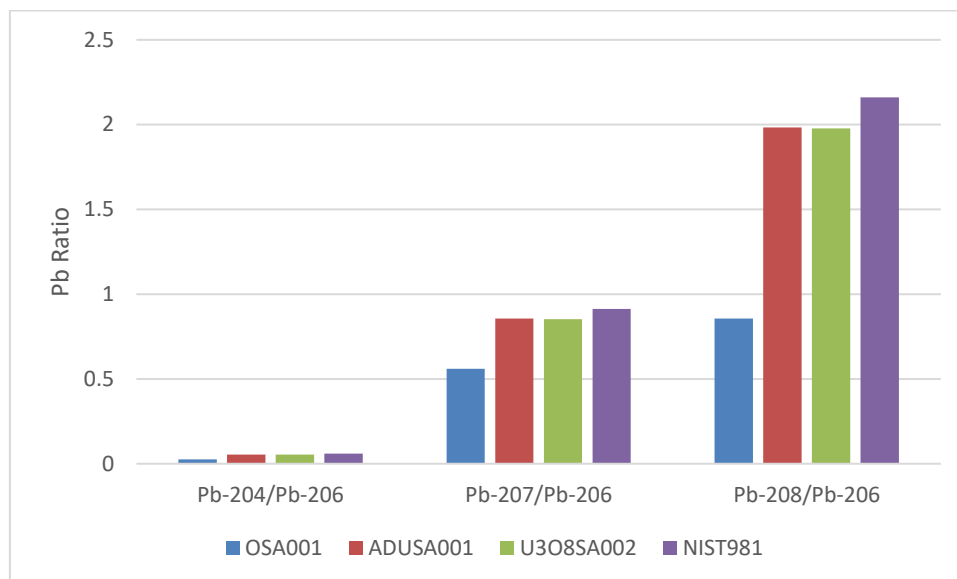


Figure 4. 3: The average Pb isotopic ratios of measured samples.

The ICP-MS results for the average Pb isotopic ratios for $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ plotted in Figures 4.3 shows that sample, OSA001, ADUSA001 and U3O8SA002 is comparable to natural uranium sample; the spread of data was close or like the NIST 981 certificate reference values. The $^{204}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of the measured NIST 981 reference material was slightly lower than the certificate certified value. This deviation was not significant, it might had been due to smaller ion beam intensity for a less abundant Pb isotope.

4.2.2 Rare-earth element (REE) concentration results

The contents of the rare-earth elements in uranium ore, ADU and U_3O_8 sample were determined by ICP-MS. The aim of REEs measurement in samples OSA001, ADUSA001 and U3O8SA002 was to determine the concentration and REE patterns measured at any stage of a nuclear fuel cycle and use the information to look for variations or similarities in each sample. To study if the information obtained can be used to attribute the sample to the production stage in the fuel cycle.

The comparison of the three samples, uranium ore, ADU slurry, and U_3O_8 , provided some insight into the behavior of rare-earth elements in uranium materials as the uranium is concentrated. Table 4.12 shows the concentrations of REE results of the samples OSA001, ADUSA001 and U3O8SA002. For an expanded source of information, Appendix E (Table E1 – E3) is referred to.

Table 4. 12: REE concentrations in ppm measurements of uranium ore, ADU and U₃O₈ samples by ICP-MS.

Element	OSA001	ADUSA001	U3O8SA002
La	9.1570 ± 1.4913	0.0003 ± 0.0001	0.00170 ± 0.00011
Ce	15.8673 ± 3.9757	0.0000 ± 0.0000	0.00309 ± 0.00024
Pr	1.6444 ± 0.2593	0.0000 ± 0.0000	0.00040 ± 0.00004
Nd	6.2358 ± 1.0142	0.0000 ± 0.0000	0.00162 ± 0.00014
Sm	1.7364 ± 0.3345	0.0000 ± 0.0000	0.00019 ± 0.00008
Eu	0.3167 ± 0.0561	0.0000 ± 0.0000	0.00007 ± 0.00002
Gd	1.8829 ± 0.3534	0.0000 ± 0.0000	0.00032 ± 0.00006
Tb	0.3882 ± 0.0695	0.0000 ± 0.0000	0.00006 ± 0.00002
Dy	2.4810 ± 0.4483	0.0000 ± 0.0000	0.00035 ± 0.00005
Ho	0.4366 ± 0.0775	0.0000 ± 0.0000	0.00006 ± 0.00001
Er	1.1342 ± 0.2052	0.0000 ± 0.0000	0.00014 ± 0.00004
Tm	0.1603 ± 0.0301	0.0000 ± 0.0000	0.00003 ± 0.00001
Yb	0.9681 ± 0.1786	0.0000 ± 0.0000	0.00015 ± 0.00004
Lu	0.1143 ± 0.0213	0.00001 ± 0.000001	0.00004 ± 0.00001
ΣLREE	36.84049	0.00034	0.00739
ΣHREE	5.68269	0.00001	0.00081

ΣTREE	42.52318	0.00035	0.00820
ΣLREE/ΣHREE	6.482934	34.0000	0.91235

Table 4.12 presents the analytical data for the concentrations of REEs obtained in this study for the samples collected at different stages of the nuclear fuel cycle. In this study, the sum of concentration of the LREE, HREE and total rare-earth element (TREE) were calculated. The ratios Σ LREE/ Σ HREE of the samples ranged from 0.91235 to 34, which indicates high fractionation of REEs in the samples. The Σ LREE/ Σ HREE ratio of sample U3O8SA002 was the lowest among the samples. The lowest Σ TREE concentration was observed in sample ADUSA001 at 0.00035 ppm and the highest was for sample, OSA001 at 42.52318 ppm. The highest observed REEs concentration in OSA001 sample was expected since the ore was still at the mining stage, the first stage of the nuclear fuel cycle.

Sample ADUSA001 depicted the efficiency with which various REEs are removed from the ADU slurry during sample processing. Nearly all rare-earth element concentrations were removed in the ADU slurry sample compared to the uranium ore and U₃O₈ samples. La and Lu were notable exceptions, as they remained during processing. These results showed that REEs concentrations decreased progressively during the leaching, ion exchange, and solvent extraction steps before becoming enriched during the calcination process.

As another means of looking for variations or similarities in the measurements of the samples, the REE patterns were determined. Figures 4.4 and 4.5 illustrated the data from the analyses of results of the samples OSA001 and U3O8SA002, and shows very interesting results. The REE pattern for sample ADUSA001 could not be plotted due to insufficient REEs data.

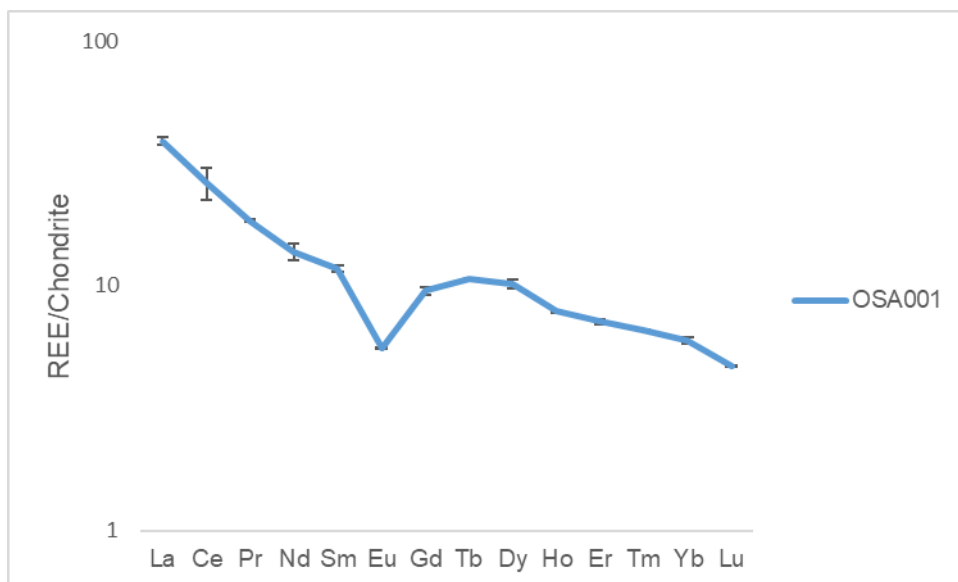


Figure 4. 4: REE pattern normalised to chondrite for OSA001 sample.

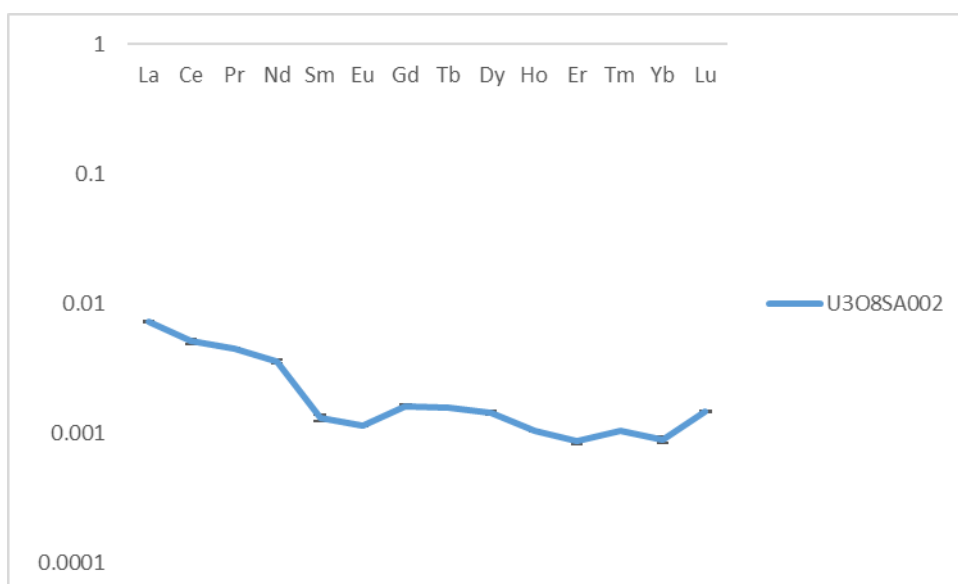


Figure 4. 5: REE pattern normalised to chondrite for U3O8SA002 sample.

The concentrations of rare earth elements, which are plotted on chondrite normalized diagrams in Figures 4.4 and 4.5, showed different abundances of REEs as well as the highly fractionated REE patterns. The REE patterns for the ore sample, OSA001, in Figure 4.4 exhibited an enriched positive anomaly of Tb and a pronounced negative Eu anomaly when normalized to their chondrite values. The sample showed fractionation of HREE with a flat downward from Ho to Yb while the LREE were heavily depleted. The REE patterns for sample U3O8SA002 showed an enriched positive anomaly of Tm and a pronounced negative Eu, Er and Yb anomaly when normalized to their chondrite values.

The REE pattern from the OSA001 sample was not preserved in the U3O8SA002 sample. The changes indicate that, the REE patterns did not remain the same during the processing stages and at different stages of the nuclear fuel cycle. The REE concentrations were enriched during the ore phase and slightly reduced at the U₃O₈ production phases.

Although the reductions in concentration at the U₃O₈ production phase was not as dramatic as was in the ADU slurry process. The chondrite-normalized abundances of rare-earth elements patterns in the uranium ore samples from South Africa, Nigeria, and Namibia illustrated in Figures. 4.4 4.6 and 4.7 showed that the distribution of patterns was quite different.

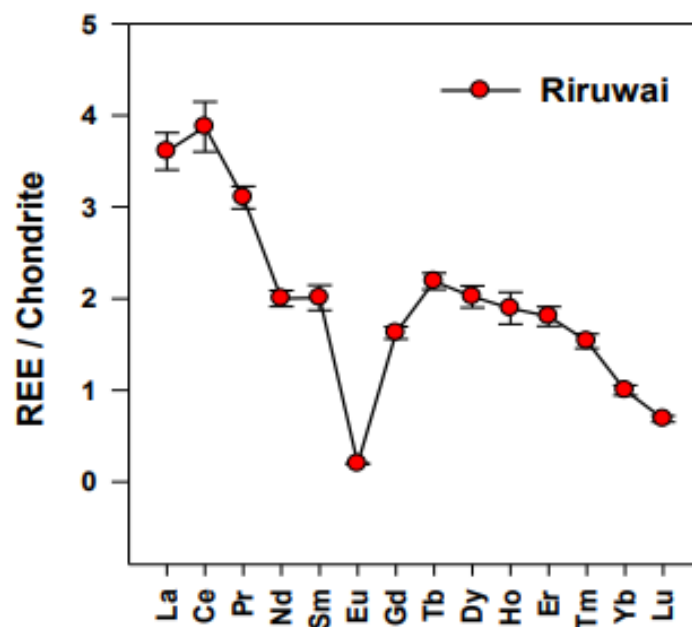


Figure 4. 6: REE pattern normalised to chondrite for uranium ore sample from Riruwai, Nigeria (John *et al.*, 2021).

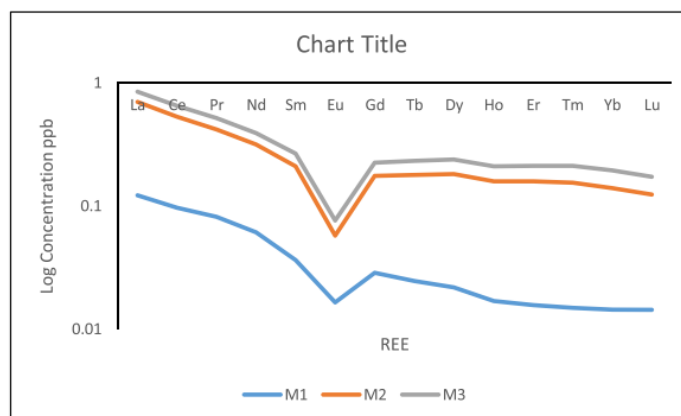


Figure 4. 7: REE patterns normalised to chondrite for uranium ore Mines 1, 2 and 3 in Namibia (Madzunya *et al.*, 2021).

Figure 4.6 showed a positive and negative anomaly at Ce and Eu with a decrease in order of LREE to HREE. The negative slope of LREE is a characteristic of LREE enrichment (Qiu *et al.*, 2019). The REE pattern in Figure 4.7 the REE patterns were broadly similar across all samples, with LREE having a negative slope and HREE having a relatively flat slopes. The LREE dominates the uranium ore samples, accounting for more than 80% of the $\sum \text{REE}$ in all mines. Ce is the dominant LREE element, accounting for more than 40% of the $\sum \text{LREE}$, while Dy is the dominating HREE element, accounting for more than 40% of the $\sum \text{HREE}$ in all mines (Madzunya *et al.*, 2021). The dominant LREE is primarily due to the presence of minerals that are not easily leachable and have a higher LREE (Varga *et al.*, 2017).

The distribution patterns of REEs in Figures 4.4, 4.6 and 4.7 showed that the uranium-bearing materials could thus be used as fingerprints to identify the source of some uranium nuclear materials. These findings support the validity of the REEs distribution pattern in related nuclear materials for nuclear forensics purposes. The REEs pattern was, therefore, a viable fingerprint for source attribution. The REE patterns normalized chondrite for uranium ore samples from these countries followed a distinctive trend. The REEs patterns often remain unchanged during the deposition of uranium-bearing sediments or metamorphism, providing information on the history and provenance of geologic samples. Variations in the REE pattern of uranium samples reflected differences in the uranium deposit's geologic origin.

4.3 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) results

Scanning electron microscopy (SEM) and electron dispersion spectroscopy (EDS) were used in this study to determine the signatures of uranium ore, ADU slurry, and U_3O_8 samples for nuclear forensic applications. SEM and SEM/EDS provided detailed information on the morphology and elemental composition of the sample. The SEM is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface morphology and composition of the sample. The distinct qualitative and quantitative differences are presented in Figures 4.8, 4.9, 4.10, 11, 12, 13 and Table 4.13.

In this study, scanning electron microscopy (SEM) analysis of the surface morphology of three uranium samples (SA001, ADUSA001 and U3O8SA002) believed to originate from the same mine was performed to determine if the morphology remain constant in different stages of the nuclear fuel cycle. To provide a framework for forensic analysis of samples from different stages of the nuclear fuel cycle sample. The sample distributions at each stage of the fuel cycle were compared to each to determine if they were any morphological difference. The texture, size, and form of the particles of the samples differed noticeably. The samples revealed different characteristics at different stages of the fuel cycle, from the ore to U_3O_8 .

The topography, surface features, for samples OSA001 revealed relatively smooth dark area and one big pore while for sample ADUSA001 and U3O8SA002 consisted of clean surfaces with no fractures. The morphology (shape, size and arrangement of the particles) for sample OSA001 consisted of homogenous spherical particles, with dispersed individual grains while for sample ADUSA001 and U3O8SA002 showed homogenous fine-grained particles with dispersed individual grains and clumps of grains. The darker areas reveal that the samples were positively charged while the hole in the samples indicates melting.

In this study, morphological variations in U_3O_8 based on calcination temperature, were determined, allowing the morphological feature to be used as a fingerprint of processing history in nuclear forensics (Olsen *et al.*, 2017). Results from this study provided the morphology of uranium samples and reveal the potential strength of morphological particle

analysis in nuclear forensics as a framework for more rapid characterization of interdicted uranium samples.

4.3.1 Scanning electron microscope results

4.3.1.1 SEM images analysis

SEM image analysis of uranium ore, ADU and U_3O_8 samples surface characteristics were performed to identify forensic signatures indicative of the stages of the nuclear fuel cycle. The SEM/EDS images in Figures 4.8 and 4.9 were taken at the same magnification of 20 000 x 10.0 mm and particle size of 5 μm while in Figure 4.10, the magnification was taken at 20 000 x 9.4 mm and particle size of 5 μm .

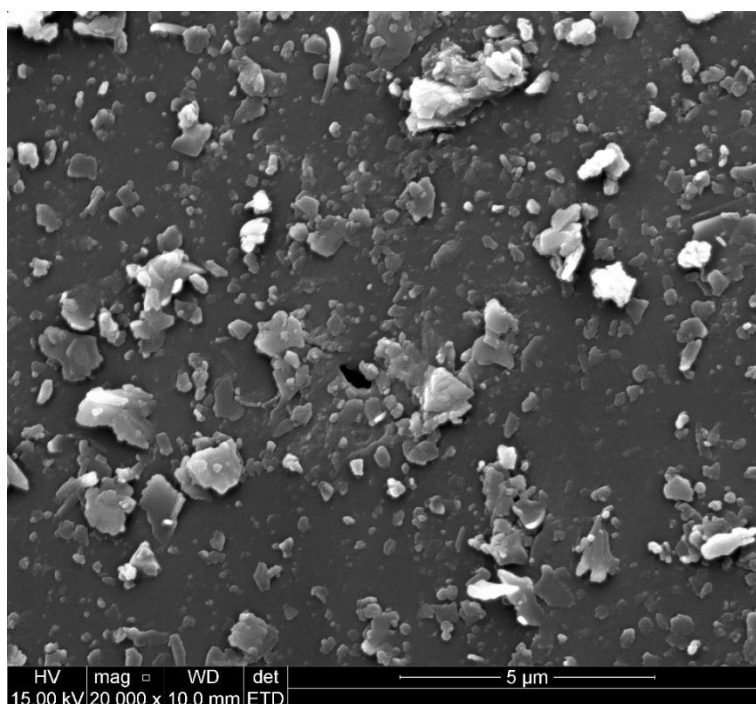


Figure 4. 8: The scanning electron microscope image of OSA001 sample.

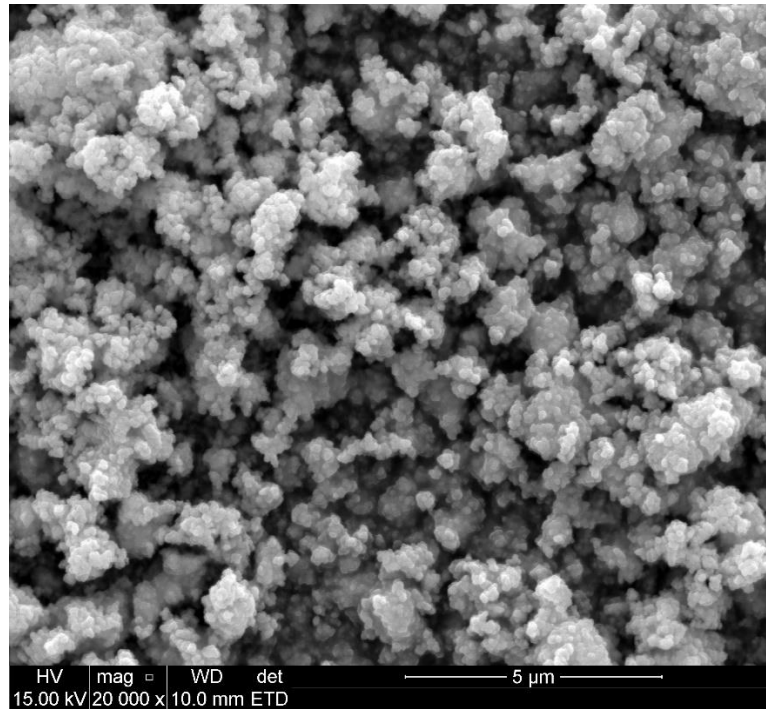


Figure 4. 9: The scanning electron microscope image of ADUSA001 sample.

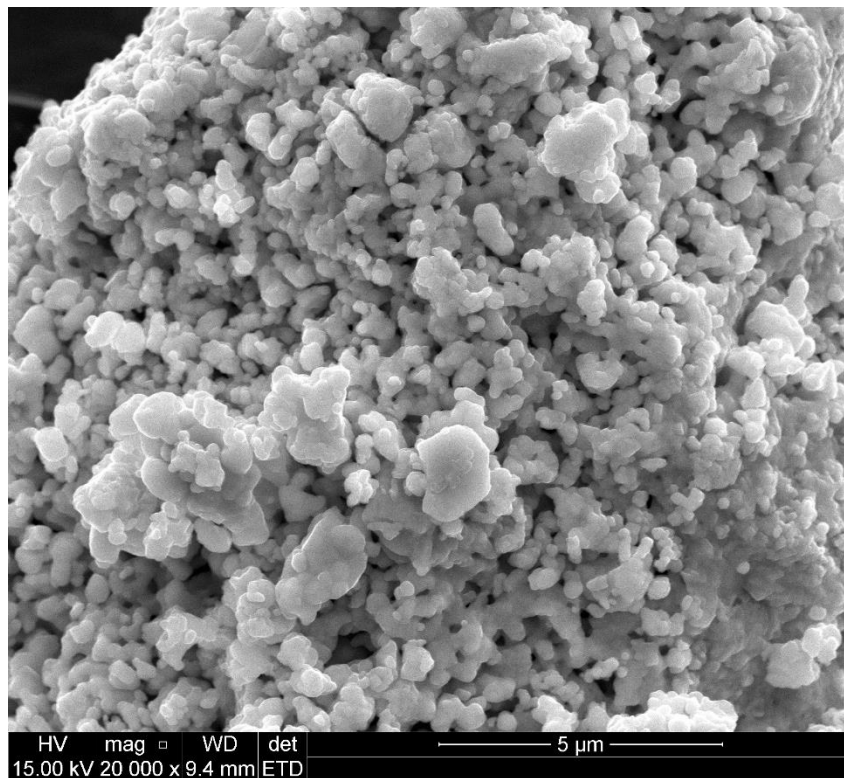


Figure 4. 10: The scanning electron microscope image of U3O8SA002 sample.

The imaged results composed of dispersed individual grains and clumps of grains observed in samples ADUSA001 and U3O8SA002 were common with various ore from uranium plants that uses an acid leaching process (e.g. H_2SO_4) in the production of uranium oxide (Huang

et al., 2017). The morphological difference between samples OSA001 and U3O8SA002 validates the proof of concept, the ability of impurities to change the surface morphology of U_3O_8 , as processed sample will likely contain new or removed impurities (Hanson *et al.*, 2019). This study is an important first step in the investigation of impurities in uranium oxides as it demonstrates the power of quantitative morphology on nuclear material processing history (Schwerdt, Brenkmann, *et al.*, 2018).

4.3.1.2 Intercomparison of SEM Images at 100,000 x 10 mm magnification

The SEM/EDS images in Figures 4.11, 4.12 and 4.13 were taken at the same magnification of 100 000 x 10.0 mm and particle size of 1 μm .

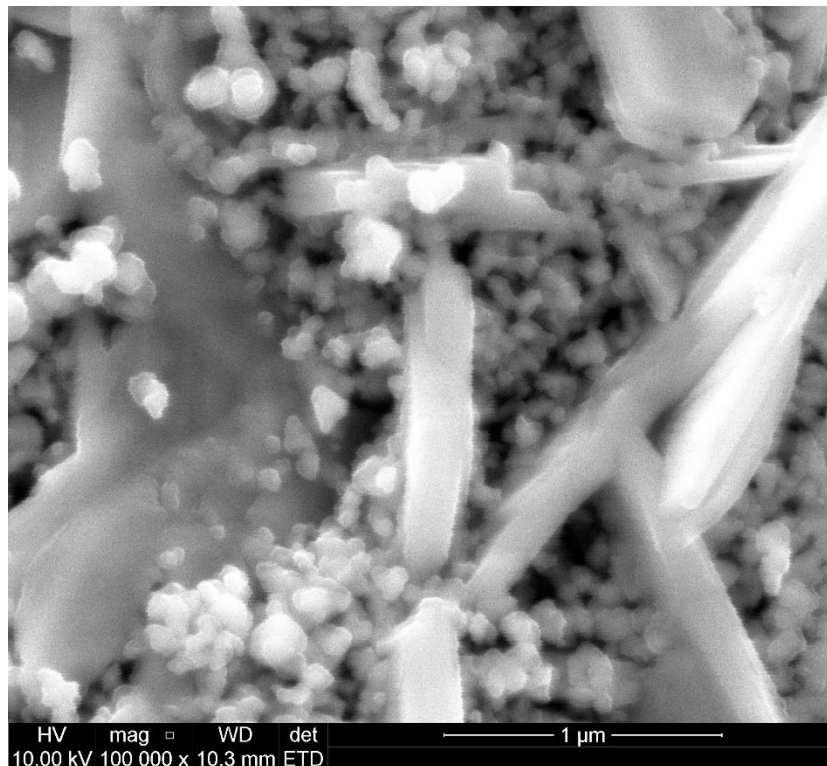


Figure 4. 11: The SEM Image of OSA001 sample at 100,000 x 10 mm magnification.

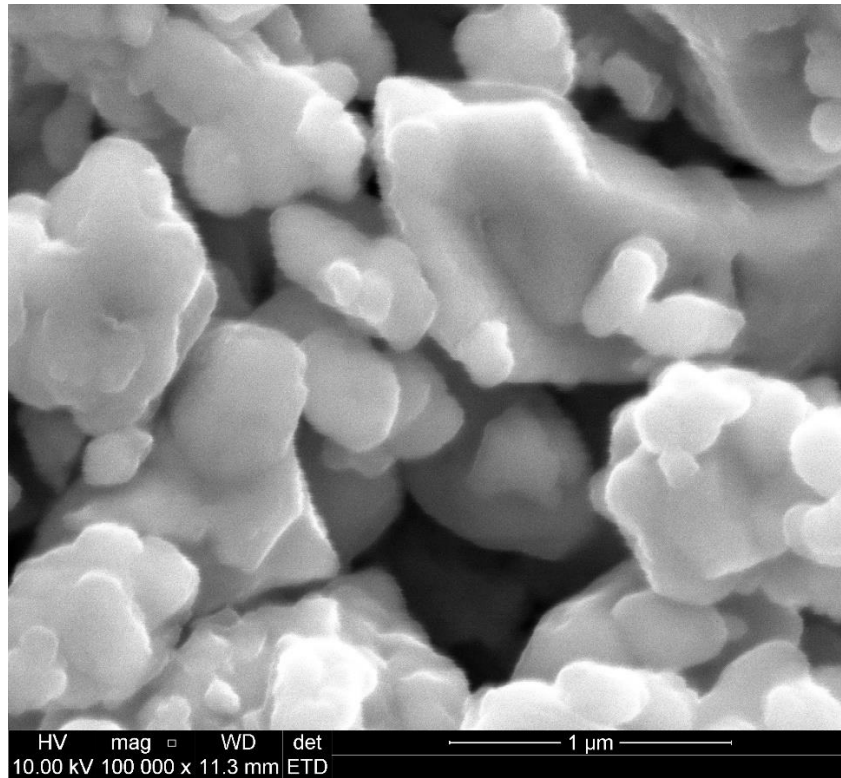


Figure 4. 12: The SEM Image of ADUSA001 sample at 100,000 x 10 mm magnification.

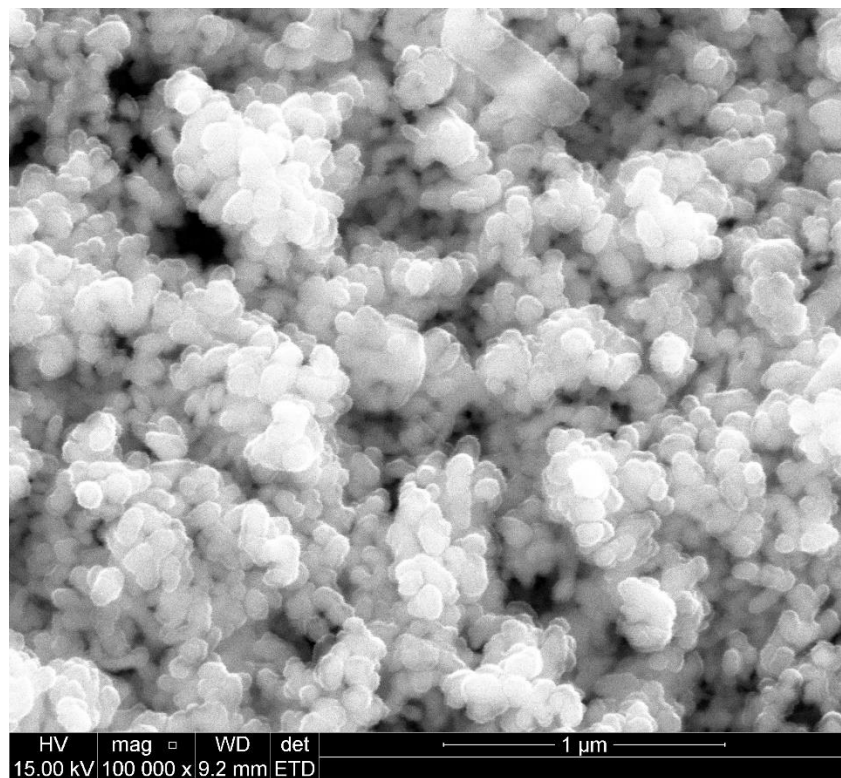


Figure 4. 13: The SEM Image of U3O8SA002 sample at 100,000 x 10 mm magnification.

Sample OSA001 shows irregular structure, consisting of rounded particles, sandwiched between platelets and agglomerated particles. Samples ADUSA001 and U3O8SA002 were

mainly boulders with their smaller particles and clusters adhering to their surface. They have seemingly very compact boulders and sharp-edged fragments. Sample ADUSA001 and U3O8SA002 revealed smaller primary particle size distribution and aggregates with a very low polydispersity index (PDI) (Colmenares Roldán *et al.*, 2018). The primary particles are also very evident in most of their surfaces which implies that the agglomeration process was not yet completed. It is therefore, suspected that these samples went through a thermal diagenesis process.

4.3.2 SEM/EDS analysis results

The interaction of the electron beam of the SEM with the powder samples allowed for the EDS to utilize the X-ray signals produced to analytically identify the elements present in any given sample. The chemical characterization of uranium samples investigated using SEM-EDS is shown in Table 4.13. All the elements analysed were normalised with results in weight %.

Table 4. 13: SEM/EDS results in atom wt.% of the measured samples.

Elements								
Sample	C	O	Al	Si	K	Fe	Cu	U
OSA001	12.1	53.81	2.09	30.46	0.84	0.7		
ADUSA001	24.16	19.91	1.11				3.22	51.6
U3O8SA002	22.26	17.98	0.78				2.08	56.9

The combined elements composition in samples, OSA001, ADUSA001, and U3O8SA002 were carbon (C), oxygen (O), aluminium (Al), silicon (Si), potassium (K), iron (Fe), copper (Cu) and uranium (U). The identified carbon element was a result of carbon coating prior to the analysis. The elements composition in the sample OSA001 were C, O, Al, Si, K and Fe with the atom wt.% of 12.1, 53.81, 2.09, 30.46, 0.84 and 0.7. The elements composition Al, Si, K and Fe were impurities identified in the South African uranium ore sample.

Samples ADUSA001 and U3O8SA002 contained elements C, O, Al, Cu and U with corresponding atom wt.% of 24.16, 19.91, 1.11, 3.22, 51.6 and 22.26, 17.98, 0.78, 2.08, 56.9 respectively. The analysis also revealed that during the production process of the

ADUSA001 and U3O8SA001 samples, impurities such as Si, K, Fe were removed and only Al remained as the impurity of the initial uranium ore sample.

The presence of Al may be the result of residuals from uranium ore processing or feed material (Hanson *et al.*, 2019). The removal of impurities is an important signature and shows that no memory of the starting Si, K and Fe isotopes signature for sample OSA001 is expressed in the final U₃O₈ product. The impurities in the samples provides information regarding the production process and thus can be regarded as a production signature for nuclear forensic investigation (Assulin *et al.*, 2022). The elemental composition Cu was identified as an added impurity during the production process of samples ADUSA001 and U3O8SA002, implying that a new impurity was added during the ADU and final U₃O₈ production stages and can thus be used as a process signature in nuclear forensics (Crean *et al.*, 2015). The results of wt.% of ADUSA001 and U3O8SA002 indicating that the samples were uranium oxide compounds, constituting on over 50% of uranium. The uranium was not detectable in OSA001 sample, this might be as a results of instrument detection limit.

Impurities detected by SEM-EDS in sample OSA001 are unevenly and widely distributed around the uranium ore-hosting deposits shown in Table 2.1. The results show that impurity Fe widely occurs in Sandstone, Vein, Breccia complex, Surficial, Collapse breccia pipe, Volcanic and Metasomatic type of uranium deposit. Additionally, the impurities, Al occurs in Volcanic and Surficial deposits, Si occurs in Surficial and Intrusive deposits and K occurs in Metasomatic types of uranium deposits. Moreover, the dominance of Fe impurities in uranium deposits indicates that Fe plays a major role in uranium mineralization, as impurities such as Fe and Si can affect the thermodynamic properties of uraninite and the rate of alteration (Fayek *et al.*, 2011b). This results, to some extent can provide a guide for understanding the metallogenic mechanism (Zhang *et al.*, 2022).

5 CHAPTER FIVE: CONCLUSION AND RECOMMENDATION

Finally, the fifth chapter looks at the summary of the study findings, conclusions, and recommendations.

5.1 Conclusion

The principal aim of this study was to apply nuclear forensics in fingerprinting of uranium material from a South African mine. The study was motivated by the fact that no previous research had been carried out in this area to develop data for use in nuclear forensic library for nuclear material produced from South African mines. Uranium ore, ADU and U_3O_8 samples were collected for this purpose. ICP-MS and SEM/EDS were used to measure the isotopic composition, rare-earth elements, morphology, and elemental composition of the samples.

The result of the isotopic ratio and isotopic composition of Pb (atom percentage) in the natural lead in uranium samples from the study could be used to distinguish between the different ore samples and thus form part of the nuclear forensic signature of the South African uranium bearing materials. The results for samples OSA001, ADUSA001 and U3O8SA002 shown that, samples were comparable to the NIST 981 common Pb certificates. The comparison of South Africa's uranium material with other countries shown a distinct pattern which could be useful in nuclear forensics investigations, complementing other nuclear forensic signatures.

For the rare-earth element measurements, the concentrations of Σ LREE in samples OSA001, ADUSA001 and U3O8SA002 was higher than the concentrations of Σ HREE. In the Σ LREE, the REE with odd atomic number had the highest concentration and compared to the REE with even atomic number, while in the Σ HREE, the REE with odd atomic number had the highest concentration as compared with the REE with even atomic number. REEs of odd atomic number (La, Pr, Eu, Tb, Ho) were less abundant than those of even atomic number (Ce, Nd, Sm, Gd, Dy, Er Yb). The concentration of heavy rare earth elements (Σ HREE) (Gd, Tb, Dy, Ho, Er and Yb) was less than those of light rare-earth elements (Σ LREE) (La, Ce, Pr, Nd and Sm) in all the samples.

The concentration of REE decreased as they moved at different stages of the nuclear fuel cycle, even though, in the case of sample ADUSA001, the concentration showed a zero measurement in elements Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb. This might also be as a result of some elements sticking on the side of the container, holding the sample, then during preparation of the sample for digestion, those elements could not be recovered.

The high enriched Σ LREEs compared to Σ HREE with an Eu_A negative anomaly for OSA001, and U3O8SA002 samples indicated that their origin might be attributed to the parent material, mostly granitic rocks or the felsic rock type (Liu *et al.*, 2019). For samples, OSA001, ADUSA001 and U3O8SA002, their chondrite normalized REE pattern revealed a unique nuclear forensic signature for the South Africa's nuclear material.

These results confirmed that, the REE patterns used for the origin location did reflect significant variation within the mine and thus provided valuable information about the geochemical formation and origin. The composition of the REEs in this work can be applied to nuclear forensic investigations as a viable signature.

For SEM analysis, the results for samples OSA001, ADUSA001, and U3O8SA002 revealed large grain size distributions with distances in the millimeter range for all three samples. The smallest grains were measured in micrometers. Except for one large and small pore in sample OSA001, no porosity was observed in ADUSA001 and U3O8SA002. Uranium was identified as the most dominant element in the EDS analysis for samples OSA001, ADUSA001, and U3O8SA002, ranging from 51.6 wt.% for ADUSA001 to 56.9 wt.% percent for U3O8SA002.

The abundance of oxygen ranged from 17.98 wt.% for U3O8SA002 to 19.91wt.% for ADUSA001 and uranium ranged from 51.6 wt.% for ADUSA001 to 56.9 wt.% for U3O8SA002 indicating that the samples were uranium oxide compounds, constituting on over 50% of uranium.

The major elements identified in sample OSA001 were C, O, Al, and Si; minor elements being K and Fe. Only major elements were identified in sample ADUSA001, with no minor elements observed. The major elements identified in sample U3O8SA002 were C, O, Cu, and U, with only Al regarded as a minor element. There were no trace elements found in

any of the three samples. The absence of trace elements indicates that no residual chemicals or initial feed materials were used during production.

Overall, the characterization, lead isotopic ratio, REEs pattern, and SEM-EDS measurements, implied in uranium ore, ADU, and U_3O_8 attribution are powerful geographical signatures in uranium ore, ADU, and U_3O_8 attribution and are an effective significant nuclear security tool for nuclear forensics studies. The mineralogy of OSA001, ADUSA001, and U3O8SA002 samples revealed that, despite minor differences in mineral concentrations, the samples were of the same origin. This information can be added in a nuclear forensic library for future reference.

SEM with EDS was successfully used in fingerprinting uranium ore, ADU slurry, and U_3O_8 samples, to investigate the shape, appearance, and particle size of nuclear material derived from the various stages of the nuclear fuel cycle. The morphology and composition of the materials led to the conclusion that they originated from the same processing facility. The study's goal was to resolve nuclear forensics signatures based on sample morphology and compositional elemental analysis.

Finally, the IAEA has recommended that each member states establishes a national registry of nuclear material and radioactive sources known as the NNFL. Since South Africa is embarking on developing and establishing a national nuclear forensic library, these results support and strengthen the initiatives. The NNFL is useful in deterring theft of nuclear material by nuclear terrorist for non-peaceful purposes within the country and elsewhere. South Africa will be able to ensure accountability for their nuclear material under their control due to results of this study. Furthermore, the NNFL offers a credible assessment of whether nuclear and other radioactive material encountered outside of the regulatory authority is consistent with material produced, used, or stored within the state.

5.2 Recommendation

From the findings of this study, the following recommendations should be considered for future studies:

- Based on the results obtained from ICP-MS and SEM-EDS measurements of uranium ore, ADU and U_3O_8 samples from different nuclear fuel cycle stages, future projects should be based on other stages of fuel cycle to provide a near complete

overview of the signatures. Therefore, a nuclear forensic database to include all other signatures. Where uranium exploration is feasible, it is recommended for future research highlights.

- It was also observed that the nuclear fingerprints obtained did not only vary for the different countries, but also varied locally and can be used to distinguish between mines within a country. Hence, a study of the viable signatures that can be used to distinguish between mines in the same country is recommended. This necessitates that all the other three uranium provinces of South Africa should be investigated.
- A study on the $^{18}\text{O}/^{16}\text{O}$ ratio for geolocation of uranium origin should be considered in future, as it may be used as a signature. For this type of measurement, TIMS and SIMS show a better performance.
- As mining of the ore body is not a “static” process, the composition (fingerprint) of the various stage will shift continuously. It is therefore, recommended that more studies be carried out to link or identify common denominators between the various phase of the mining and mineral processing.
- Lead, uranium, thorium and REE separation in the study area should be considered in future work. This requires resins from accredited vendors like Triskem international.

This study has demonstrated that the NexION 2000 ICP-MS and SEM-EDS are a rapid and accurate method for determination of nuclear forensic signatures of lead and REEs in the first and second stages of the nuclear fuel cycle.

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7 APPENDICES

Appendix A: Authorisation for North-West University to acquire, possess, use and transport source material as uranium ore, uranium oxide and processed uranium.



energy

Department:
Energy
REPUBLIC OF SOUTH AFRICA

DE 10

Private Bag x 96 Pretoria, 0001, 192 Visagie Street, Cnr Visagie and Paul Kruger Street, Pretoria
Enquiries: Ms Elsie Monale, Tel: 012 406 7499, fax: 012 323 5637, Email: Elsie.Monale@energy.gov.za

13/2/1/1

Prof. Victor Tshivhase
Director
North West University
Centre for Applied Radiation Science and Technology, CARST
Private Bag X2046
Mmabatho
2735

Dear Prof. Tshivhase

**AUTHORISATION FOR NORTH WEST UNIVERSITY TO ACQUIRE, POSSESS, USE
AND TRANSPORT SOURCE MATERIAL AS URANIUM ORE, URANIUM OXIDE AND
PROCESSED URANIUM**

Your application received on 09 March 2017 regarding the above matter has reference.

Attached please find the following authorisation for North West University to acquire, possess, use and transport source material as uranium ore, uranium oxide and processed uranium.

- 13/2/1/1/DEPARTMENT OF ENERGY/NORTH WEST UNIVERSITY,CARST/001/2017

The North West University is hereby authorised in terms of the above-mentioned authorisation to acquire, possess, use and transport such source material from the following mines: Beatrix Mine, Blyvooruitzicht Gold Mine, Buffelsfontein G M, East Rand Proprietary Mines Limited, Ezulwini Mining Company, Freegold Operations, Freestate, Randfontein Operations, South Deep Gold Mine, Vaal River Operations, West Wits Operations, Mogalakwena Mine, Shiva Uranium Limited and Palabora Mining CO LTD.

Your attention is drawn to the conditions set out in the authorisation.

Yours Sincerely,

MS E MONALE

CD: NUCLEAR NON-PROLIFERATION AND RADIATION SECURITY

DATE: 20/06/2017

Appendix B: Instrument calibration certificates.

A) Radeye-G10 annual calibration certificate.

ANALYTICAL & CALIBRATION SERVICES

A DIVISION OF NECSA

Elias Mokoaledi Street Ext Brits District Pelindaba, North West Province, Republic of South Africa

Building X1, Second Floor, Room 419

Telephone: (012)305 3091

Fax: (012)305 3185

E-Mail : calibration@necsa.co.za

necsa
We're in your world



CERTIFICATE OF CALIBRATION
"a SANAS Accredited Calibration Laboratory, No 1203"
NECSA Calibration Laboratory, V-X1 Building

Certificate No. : CQ-KVG-16/10568

Technical Enquiries Tel. : (012)305 3153

Calibration of : Raydetector
Manufacturer : Canberra France
Instrument serial No : 00000167/03069783
MTE number : 00000167/03069783
Calibrated for : North-West University Mfikeng Campus Carst Facilities
Client's address : Cnr Dr Albert Luthuli & University Drive, Private Bag X2046,
Mmabatho, 2735
Calibration procedure : CAL-WIN-0032 Rev 02
Calibration Spreadsheet : Raydetector Spreadsheet Rev 05
Date of Calibration : 2016-12-13
Date of Issue : 2016-12-13

Validity of calibration:

The measurement results recorded in this certificate were correct at the time of calibration. The subsequent accuracy will depend on factors such as care, handling and frequency of use. It is recommended that recalibration be undertaken at an interval that will ensure that the instrument remains within the desired limits.

This certificate may not be reproduced other than in full without written approval of the issuing laboratory.

Page 1 of 3		Certificate No: CQ-KVG-16/10568
Calibrated by: P.P. Sebata	Checked by: T.M. Ramashidzha	Approved by: R.A. Mofokeng
Metrologist	Technical Signatory	Laboratory Manager
		

① Directors

Dr KR Kemm (Chairperson), Dr NT Magau, Dr XH Mkhwanazi, Dr AS Tsela, Mr MPK Tshivhase, Mr N Ngcobo, Mr ZC Ngidi, Ms P Bosman, Ms RP Mosia, Mr GP Tshelane (CEO)

② Company Secretary

First Corporate Secretaries (Pty) Ltd

REG. 2000/003735/06



B) Electra-GM annual calibration certificate.

ANALYTICAL AND CALIBRATION SERVICES
A DIVISION OF NECSA
Elas Motsoaledi Street Ext Brits Districts Pretoria, North West Province, Republic of South Africa
Building Beva-C5, Pretoria 001
Telephone: (012)305 3091
Fax: (012)305 3135
E-Mail: calibration@necsa.co.za



CERTIFICATE OF CALIBRATION

"a SANAS Accredited Calibration Laboratory, No 1203"
NECSA Calibration Laboratory, Building Beva-C5

Certificate No. : CQ-KVG-21/8300
Technical Enquiries Telephone : 012 305 3153

Calibration of : Electra Ratemeter with a Dual Scintillation Probe DP2R/4A
Manufacturer : NE Technology
Instrument serial No. : 654
MTE number : 654/9782
Probe serial No : 9782
Calibrated for : North-West University
Address client : Private Bag X60014, Potchestroom, 2520
Calibration procedure : CAL-QMS-WIN-0019 Rev 02
Calibration Spreadsheet : Electra Rev 07
Date of Calibration : 2021-03-08
Date of Issue : 2021-03-08

Validity of calibration:

The measurement results recorded in this certificate were correct at the time of calibration. The subsequent accuracy will depend on factors such as care, handling and frequency of use. It is recommended that recalibration be undertaken at an interval that will ensure that the instrument remains within the desired limits.

This certificate may not be reproduced other than in full without written approval of the issuing laboratory.

Page 1 of 4		Certificate no: CQ-KVG-21/8300
Calibrated by: B Ramaphakela	Checked by: P.P Sebata	Approved by: R.A Mofokeng
Metrologist	Technical Signatory	Laboratory Manager

Directors: Ms A Choswan, Dr GJ Davids, Mr M J Maboa, Dr N T Magau, Ms B M Makgope, Ms K N Masango, Ms P E Monale, Ms L Noge-Tungamirai, Mr L J Shayi, Mr D R Nicholls (Chairman) Mr L Tyabashe (CEO)

Company Secretary: FGCLA (Pty) Ltd (Interim)

REG. 2006/003736/08



Appendix C: Details isotopic composition of Pb (atom percentage) in the natural lead, in OSA001, ADUSA001, and U3O8SA002 samples.

Table C1: Measured isotopic composition of Pb (atom percentage) in the natural lead, in the OSA001 sample.

Sample ID	²⁰⁴ Pb (%)	²⁰⁶ Pb (%)	²⁰⁷ Pb (%)	²⁰⁸ Pb (%)
OSA001-1	1.0680 ± 0.00045	40.840 ± 0.00134	22.921 ± 0.00084	35.171 ± 0.00114
OSA001-2	1.0700 ± 0.00045	40.870 ± 0.00114	22.988 ± 0.00084	35.072 ± 0.00179
OSA001-3	1.0740 ± 0.00045	40.908 ± 0.00179	22.994 ± 0.00071	35.023 ± 0.00164
OSA001-4	1.0740 ± 0.00045	40.955 ± 0.00055	22.937 ± 0.00089	35.034 ± 0.00084
OSA001-5	1.0730 ± 0.00045	40.891 ± 0.00110	23.005 ± 0.00100	35.031 ± 0.00084
OSA001-6	1.0770 ± 0.00045	40.920 ± 0.00179	22.969 ± 0.00071	35.034 ± 0.00164
OSA001-7	1.0760 ± 0.00045	41.049 ± 0.00114	22.916 ± 0.00084	34.960 ± 0.00114
OSA001-8	1.0730 ± 0.00045	40.971 ± 0.00114	23.015 ± 0.00110	34.941 ± 0.00251
OSA001-9	1.0750 ± 0.00045	40.983 ± 0.00100	22.996 ± 0.00071	34.946 ± 0.00114
OSA001-10	1.0760 ± 0.00045	40.941 ± 0.00114	22.962 ± 0.00089	35.021 ± 0.00100
OSA001-11	1.0790 ± 0.00045	40.872 ± 0.00130	22.954 ± 0.00055	35.095 ± 0.00130
OSA001-12	1.0740 ± 0.00045	41.013 ± 0.00148	22.940 ± 0.00055	34.973 ± 0.00114
OSA001-13	1.0820 ± 0.00045	41.044 ± 0.00089	22.880 ± 0.00084	34.994 ± 0.00100
OSA001-14	1.0760 ± 0.00045	40.963 ± 0.00055	22.945 ± 0.00055	35.016 ± 0.00071
OSA001-15	1.0820 ± 0.00045	41.007 ± 0.00110	22.980 ± 0.00084	34.931 ± 0.00114
OSA001-16	1.0750 ± 0.00045	40.921 ± 0.00268	22.915 ± 0.00045	35.089 ± 0.00261
OSA001-17	1.0830 ± 0.00045	40.897 ± 0.00084	22.901 ± 0.00122	35.119 ± 0.00134
OSA001-18	1.0830 ± 0.00045	40.851 ± 0.00259	22.965 ± 0.00114	35.101 ± 0.00277

OSA001-19	1.0780 ± 0.00045	41.000 ± 0.00141	22.909 ± 0.00084	35.013 ± 0.00045
OSA001-20	1.0830 ± 0.00045	40.888 ± 0.00071	22.984 ± 0.00084	35.045 ± 0.00055
Mean	1.0766 ± 0.00043	40.9392 ± 0.000632	22.9538 ± 0.000382	35.0305 ± 0.000638

Table C2: Measured isotopic composition of Pb (atom percentage) in the natural lead, in the ADUSA001 sample.

Sample ID	²⁰⁴ Pb (%)	²⁰⁶ Pb (%)	²⁰⁷ Pb (%)	²⁰⁸ Pb (%)
ADUSA001-01	1.393 ± 0.00045	25.163 ± 0.00455	21.992 ± 0.00045	51.453 ± 0.00462
ADUSA001-02	1.386 ± 0.00045	25.557 ± 0.00114	21.987 ± 0.00045	51.071 ± 0.00089
ADUSA001-03	1.387 ± 0.00045	25.573 ± 0.00089	21.982 ± 0.00130	51.058 ± 0.00230
ADUSA001-04	1.396 ± 0.00045	25.736 ± 0.00134	22.048 ± 0.00089	50.819 ± 0.00148
ADUSA001-05	1.401 ± 0.00045	25.748 ± 0.00055	22.005 ± 0.00084	50.846 ± 0.00114
ADUSA001-06	1.395 ± 0.00045	25.651 ± 0.00089	22.005 ± 0.00084	50.949 ± 0.00152
ADUSA001-07	1.398 ± 0.00045	25.757 ± 0.00055	21.977 ± 0.00084	50.868 ± 0.00084
ADUSA001-08	1.402 ± 0.00045	25.747 ± 0.00089	21.979 ± 0.00055	50.872 ± 0.00055
ADUSA001-09	1.398 ± 0.00045	25.65 ± 0.000550	21.91 ± 0.000450	51.042 ± 0.00089
ADUSA001-10	1.404 ± 0.00045	25.756 ± 0.00045	21.963 ± 0.00055	50.877 ± 0.00045
ADUSA001-11	1.407 ± 0.00045	25.712 ± 0.00045	21.985 ± 0.00084	50.896 ± 0.00122
ADUSA001-12	1.405 ± 0.00045	25.757 ± 0.00045	21.953 ± 0.00055	50.885 ± 0.00071
ADUSA001-13	1.408 ± 0.00045	25.706 ± 0.00045	21.966 ± 0.00084	50.92 ± 0.000450
ADUSA001-14	1.408 ± 0.00045	25.708 ± 0.00100	21.98 ± 0.000450	50.905 ± 0.00045
ADUSA001-15	1.408 ± 0.00045	25.725 ± 0.00084	21.951 ± 0.00055	50.917 ± 0.00084
ADUSA001-16	1.412 ± 0.00045	25.776 ± 0.00045	21.949 ± 0.00114	50.864 ± 0.00084
ADUSA001-17	1.409 ± 0.00045	25.744 ± 0.00084	22.003 ± 0.00447	50.843 ± 0.00045

ADUSA001-18	1.410 ± 0.00045	25.695 ± 0.00084	21.991 ± 0.00447	50.905 ± 0.00045
ADUSA001-19	1.410 ± 0.00045	25.733 ± 0.00045	21.967 ± 0.00055	50.890 ± 0.00045
ADUSA001-20	1.413 ± 0.00045	25.740 ± 0.00055	21.979 ± 0.00055	50.869 ± 0.00055
Mean	1.4025 ± 0.00008	25.6817 ± 0.001357	21.9786 ± 0.000279	50.93745 ± 0.001401

Table C3: Measured isotopic composition of Pb (atom percentage) in the natural lead, in the U3O8SA002 sample.

Sample ID	²⁰⁴ Pb (%)	²⁰⁶ Pb (%)	²⁰⁷ Pb (%)	²⁰⁸ Pb (%)
U3O8SA002-01	1.406 ± 0.00045	25.678 ± 0.00164	22.005 ± 0.00122	50.911 ± 0.00217
U3O8SA002-02	1.408 ± 0.00045	25.630 ± 0.00192	21.918 ± 0.00207	51.044 ± 0.00351
U3O8SA002-03	1.412 ± 0.00045	25.750 ± 0.00089	21.884 ± 0.00130	50.954 ± 0.00114
U3O8SA002-04	1.409 ± 0.00045	25.693 ± 0.00148	21.878 ± 0.00182	51.020 ± 0.00179
U3O8SA002-05	1.415 ± 0.00045	25.729 ± 0.00089	21.819 ± 0.00141	51.037 ± 0.00152
U3O8SA002-06	1.407 ± 0.00045	25.753 ± 0.00130	21.894 ± 0.00212	50.946 ± 0.00241
U3O8SA002-07	1.416 ± 0.00045	25.829 ± 0.00100	21.908 ± 0.00130	50.847 ± 0.00084
U3O8SA002-08	1.414 ± 0.00045	25.765 ± 0.00114	21.935 ± 0.00089	50.886 ± 0.00122
U3O8SA002-09	1.418 ± 0.00045	25.792 ± 0.00179	21.932 ± 0.00114	50.859 ± 0.00219
U3O8SA002-10	1.404 ± 0.00045	25.732 ± 0.00114	21.990 ± 0.00084	50.874 ± 0.00110
U3O8SA002-11	1.410 ± 0.00045	25.665 ± 0.00055	21.927 ± 0.00055	50.998 ± 0.00071
U3O8SA002-12	1.414 ± 0.00045	25.742 ± 0.00114	22.016 ± 0.00084	50.827 ± 0.00114
U3O8SA002-13	1.419 ± 0.00045	25.751 ± 0.00089	21.973 ± 0.00164	50.857 ± 0.00179
U3O8SA002-14	1.414 ± 0.00045	25.733 ± 0.00110	21.968 ± 0.00045	50.885 ± 0.00122
U3O8SA002-15	1.421 ± 0.00045	25.767 ± 0.00089	21.934 ± 0.00045	50.878 ± 0.00089
U3O8SA002-16	1.410 ± 0.00045	25.715 ± 0.00045	21.982 ± 0.00071	50.893 ± 0.00100

U3O8SA002-17	1.416 ± 0.00045	25.751 ± 0.00089	21.948 ± 0.00055	50.884 ± 0.00084
U3O8SA002-18	1.419 ± 0.00045	25.738 ± 0.00055	21.962 ± 0.00084	50.882 ± 0.00130
U3O8SA002-19	1.416 ± 0.00045	25.763 ± 0.00045	21.958 ± 0.00055	50.863 ± 0.00055
U3O8SA002-20	1.414 ± 0.00045	25.719 ± 0.00071	22.025 ± 0.00045	50.842 ± 0.00055
Mean	1.4131 ± 0.00005	25.73475 ± 0.00045	21.9428 ± 0.00051	50.90935 ± 0.00067

Appendix D: Details isotopic ratios measurement in OSA001, ADUSA001 and U3O8SA002 samples by ICP-MS.

Table D1: Measured isotopic ratio in OSA001 sample using ICP-MS technique.

Sample ID	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
OSA001-01	0.026150	0.561260	0.861200
OSA001-02	0.026180	0.562470	0.858170
OSA001-03	0.026250	0.562100	0.856170
OSA001-04	0.026220	0.560060	0.855430
OSA001-05	0.026250	0.562610	0.856690
OSA001-06	0.026310	0.561320	0.856180
OSA001-07	0.026210	0.558270	0.851670
OSA001-08	0.026190	0.561760	0.852850
OSA001-09	0.026230	0.561120	0.852700
OSA001-10	0.026280	0.560860	0.855390
OSA001-11	0.026400	0.561610	0.858660
OSA001-12	0.026180	0.559350	0.852740
OSA001-13	0.026360	0.557450	0.852610
OSA001-14	0.026260	0.560140	0.854810
OSA001-15	0.026380	0.560390	0.851850
OSA001-16	0.026270	0.560010	0.857550
OSA001-17	0.026490	0.559980	0.858740
OSA001-18	0.026510	0.562200	0.859310
OSA001-19	0.026290	0.558780	0.853990
OSA001-20	0.026490	0.562120	0.857100
Mean	0.026295 ± 0.000213	0.560693 ± 0.002816	0.8556905 ± 0.005377

Table D2: Measured isotopic ratio in ADUSA001 sample using ICP-MS technique.

Sample ID	²⁰⁴ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb
ADUSA001-01	0.05536	0.87421	2.04563
ADUSA001-02	0.05421	0.86031	1.99834
ADUSA001-03	0.05424	0.85959	1.99658
ADUSA001-04	0.05425	0.85671	1.97467
ADUSA001-05	0.05441	0.85466	1.97482
ADUSA001-06	0.05438	0.85788	1.9863
ADUSA001-07	0.05427	0.85325	1.97493
ADUSA001-08	0.05446	0.85367	1.97588
ADUSA001-09	0.05449	0.85418	1.98993
ADUSA001-10	0.05450	0.85273	1.97535
ADUSA001-11	0.05471	0.85502	1.97947
ADUSA001-12	0.05453	0.85228	1.97557
ADUSA001-13	0.05477	0.85451	1.98088
ADUSA001-14	0.05475	0.85503	1.98016
ADUSA001-15	0.05472	0.85331	1.97932
ADUSA001-16	0.05477	0.85151	1.97328
ADUSA001-17	0.05473	0.85468	1.97494
ADUSA001-18	0.05487	0.85583	1.98112
ADUSA001-19	0.05479	0.85363	1.97762
ADUSA001-20	0.05489	0.85388	1.97627
Mean	0.054605 ± 0.000555	0.855844 ± 0.009515	1.983553 ± 0.031739

Table D3: Measured isotopic ratio in U3O8SA002 sample using ICP-MS technique.

Sample ID	²⁰⁴ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb
U3O8SA002-01	0.05477	0.857	1.98278
U3O8SA002-02	0.05495	0.85518	1.99168
U3O8SA002-03	0.05485	0.8499	1.97884
U3O8SA002-04	0.05485	0.85159	1.98583
U3O8SA002-05	0.05499	0.84807	1.9837
U3O8SA002-06	0.05463	0.8502	1.97836
U3O8SA002-07	0.05484	0.84824	1.96864
U3O8SA002-08	0.05489	0.85136	1.97506
U3O8SA002-09	0.05497	0.85035	1.97196
U3O8SA002-10	0.05457	0.85459	1.97708
U3O8SA002-11	0.05496	0.85434	1.98706
U3O8SA002-12	0.05494	0.85529	1.97453
U3O8SA002-13	0.05509	0.85329	1.97497
U3O8SA002-14	0.05495	0.85368	1.97745
U3O8SA002-15	0.05516	0.85127	1.9746
U3O8SA002-16	0.05481	0.85482	1.97911
U3O8SA002-17	0.055	0.8523	1.976
U3O8SA002-18	0.05513	0.85329	1.97697
U3O8SA002-19	0.05497	0.85229	1.97428
U3O8SA002-20	0.055	0.8564	1.97686
Mean	0.054916 ± 0.000288	0.8526725 ± 0.004975	1.978288 ± 0.010707

Appendix E: Details of rare-earth elements (REE) concentrations in ppm of measurements in OSA001, ADUSA001 and U3O8SA002 samples by ICP-MS.

Table E1: REE concentrations in ppm of measurements in OSA001 sample using ICP-MS technique.

Sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
OSA001-01	9.8195	19.0346	1.8422	7.0765	1.9608	0.3700	2.2526	0.4603	2.9169	0.5202	1.3491	0.1893	1.1314	0.1334
OSA001-02	8.3874	14.1422	1.5754	5.9992	1.6952	0.3016	1.7987	0.3722	2.3138	0.4077	1.0584	0.1469	0.8898	0.1055
OSA001-03	7.1513	12.7649	1.4059	5.3235	1.4458	0.2676	1.5860	0.3300	2.1239	0.3721	0.9690	0.1349	0.8193	0.0975
OSA001-04	11.9975	24.3405	2.1976	8.3668	2.4682	0.4332	2.6213	0.5329	3.4270	0.5938	1.5531	0.2236	1.3429	0.1598
OSA001-05	10.2532	19.9955	1.8324	6.9614	2.0053	0.3578	2.0844	0.4293	2.7854	0.4918	1.2734	0.1807	1.0950	0.1289
OSA001-06	9.3389	14.8948	1.6412	6.2104	1.6983	0.3136	1.8586	0.3844	2.4354	0.4276	1.1234	0.1585	0.9643	0.1140
OSA001-07	8.7662	13.8015	1.5020	5.6193	1.5354	0.2821	1.6816	0.3485	2.2217	0.3949	1.0218	0.1437	0.8643	0.1028
OSA001-08	7.0014	11.6861	1.2988	4.8803	1.3147	0.2444	1.4232	0.2976	1.9051	0.3352	0.8625	0.1220	0.7346	0.0861
OSA001-09	8.8299	13.2438	1.4919	5.6251	1.5311	0.2822	1.6513	0.3415	2.2083	0.3896	0.9995	0.1421	0.8665	0.1013
OSA001-10	10.0246	14.7694	1.6563	6.2956	1.7090	0.3143	1.8718	0.3849	2.4726	0.4334	1.1319	0.1614	0.9725	0.1139
Mean	9.1570 ±	15.8673 ±	1.6444 ±	6.2358 ±	1.7364 ±	0.3167 ±	1.8829 ±	0.3882 ±	2.4810 ±	0.4366 ±	1.1342 ±	0.1603 ±	0.9681 ±	0.1143 ±
	1.4913	3.9757	0.2593	1.0142	0.3345	0.0561	0.3534	0.0695	0.4483	0.0775	0.2052	0.0301	0.1786	0.0213

Table E2: REE concentrations in ppm of measurements in ADUSA001 sample using ICP-MS technique.

Sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
ADUSA001-01	0.00055	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
ADUSA001-02	0.00043	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
ADUSA001-03	0.00036	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
ADUSA001-04	0.00039	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
ADUSA001-05	0.00036	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
ADUSA001-06	0.00034	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
ADUSA001-07	0.00028	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
ADUSA001-08	0.00024	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
ADUSA001-09	0.00025	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
ADUSA001-10	0.00016	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00001
Mean	0.0003 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.0000 ±	0.000001 ±
	0.00001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table E1: REE concentrations in ppm of measurements in U3O8SA002 sample using ICP-MS technique.

Sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
U3O8SA002-01	0.0018	0.00318	0.00039	0.00179	0.00017	0.00003	0.00033	0.00008	0.00041	0.00007	0.00018	0.00002	0.00009	0.00003
U3O8SA002-02	0.00188	0.00349	0.00045	0.00168	0.00035	0.00006	0.00028	0.00009	0.00031	0.00007	0.00012	0.00002	0.00014	0.00002
U3O8SA002-03	0.00181	0.00328	0.00045	0.00176	0.00029	0.00007	0.00043	0.00006	0.00044	0.00005	0.00016	0.00003	0.00021	0.00005
U3O8SA002-04	0.00166	0.00309	0.00034	0.00138	0.00013	0.00007	0.00031	0.00005	0.00031	0.00004	0.00012	0.00003	0.00019	0.00002
U3O8SA002-05	0.00158	0.00265	0.00038	0.00164	0.00021	0.00007	0.00035	0.00004	0.00032	0.00006	0.00008	0.00003	0.00012	0.00004
U3O8SA002-06	0.00176	0.00314	0.00043	0.00157	0.00019	0.00009	0.00032	0.00006	0.00037	0.00007	0.00014	0.00002	0.0002	0.00003
U3O8SA002-07	0.00164	0.00296	0.00038	0.00152	0.00009	0.00007	0.00025	0.00005	0.0004	0.00006	0.00012	0.00004	0.00012	0.00005
U3O8SA002-08	0.00171	0.00327	0.00045	0.00171	0.00025	0.00005	0.00028	0.00006	0.0003	0.00006	0.00021	0.00004	0.00014	0.00003
U3O8SA002-09	0.00153	0.00281	0.00035	0.00173	0.00017	0.00006	0.00024	0.00005	0.00033	0.00005	0.00008	0.00003	0.00014	0.00004
U3O8SA002-10	0.00165	0.00305	0.00038	0.00144	0.00009	0.00008	0.00037	0.00003	0.00029	0.00005	0.00016	0.00002	0.0001	0.00005
Mean	0.00170 ±	0.00309 ±	0.0004 ±	0.00162 ±	0.00019 ±	0.00007 ±	0.00032 ±	0.00006 ±	0.00035 ±	0.00006 ±	0.00014 ±	0.00003 ±	0.00015 ±	0.00004 ±
	0.00011	0.00024	0.00004	0.00014	0.00008	0.00002	0.00006	0.00002	0.00005	0.00001	0.00004	0.00001	0.00004	0.00001

Appendix F: List of publications, conference presentations, workshops, technical trainings, and technical meetings.

Peer reviewed publications from this work

1. Vera Uushona, Heike Wanke, Innocent Shuro, Manny Mathuthu, Naomi Mokhine, **Tebogo Gilbert Kupi**, Age Estimation of Uranium Ore Mineralization using Lead Isotopic Ratios as A Nuclear Forensic Tool **(2022)** Journal of Earth Sciences & Environmental Studies 6(2) :162-16
2. **Kupi, T.G.**, Uushona, V., Mathuthu, M. et al. Using lead isotope ratios to distinguish between samples of different uranium mines. J Radioanal Nucl Chem 324, 1–5 **(2020)**. <https://doi.org/10.1007/s10967-020-07048-1>.

Conference presentations

1. **Kupi T.G.**, Mathuthu M., and Seemela K., **(2022)**, Safe and secure management of sealed radioactive sources at the Centre for Applied Radiation Science and Technology, International Conference on the Safety and Security of Radioactive Sources - Accomplishments and Future Endeavors, Safe and secure management of radioactive sources at CARST, IAEA Headquarters, Vienna, Austria from 20 - 24 June 2022.
2. **Kupi T.G.**, Mathuthu M., and van Tonder D., **(2021)**, Investigation of the Rare Earth Elements Pattern for uranium attribution in nuclear forensics environment, South African Institute of Physics conference, North-West University, Potchefstroom Campus, 11 Hofman Street, Potchefstroom 2531, South Africa.
3. V Uushona, N D Mokhine, M Mathuthu, I Shuro and **T G Kupi**, **(2021)**, Analysis of UOC for nuclear forensics using Scanning Electron Microscope, South African Institute of Physics conference, North-West University, Potchefstroom Campus, 11 Hofman Street, Potchefstroom 2531, South Africa.
4. **Kupi T.G.**, Mathuthu M. **(2020)**, International Conference on Nuclear Security: Sustaining and Strengthening Efforts (ICONS 2020), IAEA, Vienna, Austria, 10 - 14 February 2020.
5. **Kupi T.G.**, **(2018)**, Age determination of uranium in mine tailing using Inductively Coupled Plasma Mass Spectrometry for Nuclear Forensic purpose, UESM Prestigious PhD Conference, 30 Augusts, 2018, North-West University, Potchefstroom Campus, 11 Hofman Street, Potchefstroom 2531, South Africa,
6. **Kupi T.G.**, **(2018)**, Assessment of Radiation Doses for NORM storage facility at the Centre for Applied Radiation Science and Technology, International Youth Nuclear

Congress, Conference, Bariloche, Argentina, International Youth Nuclear Congress (IYNC), 2018, 11th – 17th March 2018.

Workshops

1. **Kupi T.G., (2017)**, Workshop, Radisson Blu Edwardian Hotel, London, United Kingdom Fundamentals of Physical Protection at Facilities Holding Nuclear and Radioactive Materials Workshop, 29th January - 3rd February 2017

Training

1. **Kupi T.G., (2019)**, International Training Course, Budapest, Hungary, Advance Training Course on Practical Introduction to Nuclear Forensics 16th Sep – 30th Nov 2019
2. **Kupi T.G., (2019)**, International Training Course, Budapest, Hungary, International Training Course on Practical Introduction to Nuclear Forensics, 9th – 13th September 2019
7. **Kupi T.G., (2018)**, Regional Training Course, Centurion, South Africa, Regional Training Course on Nuclear Safeguards and Non-Proliferation for South African Region, 12th – 16th February 2018.

Technical meetings

1. **Kupi T.G., (2022)**, Annual Meeting of the International Nuclear Security Education Network (INSEN), IAEA Headquarters in Vienna, Austria, 18 to 22 July 2022
2. **Kupi T.G., (2022)**, Second Research Coordination Meeting on Applying Nuclear Forensic Science to Respond to a Nuclear Security Event, IAEA, Vienna, Austria, 12 - 15 July 2022
3. **Kupi T.G., (2022)**, Technical Meeting on Nuclear Forensics from National Foundations to Global Impact, IAEA, Vienna, Austria, 11 - 14 April 2022
4. **Kupi T.G., (2018)**, The Third International Galaxy Serpent exercise on Nuclear Forensics Libraries (NNFL), The Nuclear Forensics International Technical Working Group (ITWG) and U.S. Department of State, online training, 2018
5. **Kupi T.G., (2017)**, Annual Meeting, International Atomic Energy Agency (IAEA), Vienna, Austria, Annual Meeting of the International Security Education Network (INSEN), 24th - 28th July 2017

6. **Kupi T.G., (2017)**, Technical Meeting, IAEA, Vienna, Austria, Technical Meeting on Developing a Systematic Education and Training Approach Using Personal Computer Based Simulators for Nuclear Power Programme, 15th – 19th May 2017.

Appendix G: Journal article on using lead isotopes ratios to distinguish between samples of different uranium mines.

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Using lead isotope ratios to distinguish between samples of different uranium mines

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Abstract

In this work, a total of twenty samples selected for investigation originate from South Africa and Namibia uranium mines. The aim of this study was to determine whether the lead ratios measured in particular samples could be used to attribute the uranium sample to the production or reprocessing plant. Measurements were carried out using an inductively coupled plasma mass spectrometer PerkinElmer NexION 2000. The precision obtained for the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio, the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio and the $^{204}\text{Pb}/^{206}\text{Pb}$ ratio values was considerably lower than 0.02% demonstrating the applicability of the technique for Pb isotope ratio studies.

Keywords Lead isotopic ratio · Nuclear forensic signatures · ICP-MS

Introduction

Illicit trafficking of radioactive material and especially nuclear material (thorium, uranium, and plutonium) has been an issue of concern since the beginning of the 1990s, when the first seizures of nuclear material were reported to the International Atomic Energy Agency [1]. However throughout the world, nuclear and radioactive materials are used daily for beneficial purposes, in industry, medicine, agriculture and research. The use of nuclear and radioactive material generates some risk due to radiation being emitted, which is harmful to human health especially if they enter the human body even at low levels (i.e. microgram amounts)

[2]. The main security concerns relating to their use, are perceived ease of access to them, the culture of personnel responsible for managing the material, and the potential for theft and construction of radiological disperse devices (RDDs) also referred to as “dirty” bombs [3, 4].

The clear evidence of significant amount of nuclear material outside regulatory control has created international concern over the importance of maintaining global nuclear order [4]. This has resulted in the development of a new branch of science called “Nuclear Forensics” with the intent not only to identify and characterize illicit nuclear or radioactive material but also to learn more about the intended use of the seized material as well as its origin and about the potential trafficking route. [4, 5].

Applying Nuclear Forensics as a fingerprinting tool to compare with reference data allows the researcher to determine the origin, the intended use, the last legal owner and the smuggling route of the nuclear or radioactive material [6]. This makes Nuclear Forensics to be a key element of Nuclear Security.

In South Africa, the Nuclear Forensics efforts are still in a developing stage. In nuclear forensics, the isotopic composition of nuclear material aid as one of the parameters that contribute to “nuclear fingerprint” of the material and thereby provide a basis for drawing conclusions on the potential origin of the material. Nuclear fingerprinting refers to the determination of origin, mode of production from the composition of nuclear material [5]. In the context of this

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work, fingerprinting would refer to the process of identifying signatures in the nuclear fuel cycle.

Signatures are measurable attributes of nuclear fuel cycles [7]. Therefore nuclear forensic analysis is a key technical capability that utilizes signatures inherent to nuclear or other radioactive material to provide information on its source, production and history [8, 9]. This study investigates the application of lead isotopic ratios and lanthanides pattern in nuclear forensics.

Lead isotopic composition

In South Africa, the uranium is produced as a by-product of gold or copper mining [10, 11] while in Namibia uranium is directly mined from the uranium mine. The proportion of the lead isotopes is constant in nature regardless of the type of mineral or deposit in which the uranium is found [12]. Another parameter of main interest in uranium/gold mining, is the level of trace elements or impurities [13]. These trace elements are of great interest to nuclear forensics, because they can be used to attribute the uranium material to its geological source, i.e., to a uranium ore deposit type [14].

Measuring the stable isotope such as Lead (Pb) is an established technique in geolocation [6, 15]. Natural Pb is composed of four stable isotopes, and the International Union of Pure and Applied Chemistry (IUPAC) [16] reports small natural variations on the representative isotopic composition: ^{204}Pb —1.4%, ^{206}Pb —24.1%, ^{207}Pb —22.1% and ^{208}Pb —52.4%. Therefore the stable lead isotope composition gives information on the initial U/Th ratio in the ore deposits and on the age of the ore. Due to the fact that the variations in the composition for different mines are significant, investigating the stable lead isotopes can locate the original mine.

Methodology

Measurement of nuclear material is the backbone of the verification measurements in the nuclear forensics environment and thus provide clue for determination of sample origin. Measurements of nuclear material can provide information on the uranium content, as well as uranium isotopic composition in a given material. However, the measurements methods of nuclear material is an elaborate and time-consuming process. The measurements requires clean working environment to monitor the impurity levels that arise from any working procedure involved.

Samples

Samples selected for this study are water samples recovered from the mine tailings for reuse in the plant samples

collected from the uranium mines areas. The water samples in this case was part of the reprocessing from the mine waste which is an intermediate step of the front end in nuclear fuel cycle. The origin for all samples used in this work cannot be revealed due to confidentiality agreements with the mines.

Samples preparation

A total of 20 water samples from two mines area were collected and used for analysis with inductively coupled plasma mass spectrometer (ICP-MS). A set of ten samples were collected from South African uranium mine area and another ten set of samples from Namibian mine area. A water sample of 5 mL each were mixed with 1 mL of 70% high purity nitric acid (HNO_3) (Sigma Aldrich, South Africa). All solutions were prepared with 18 M Ω Millipore Milli-Q system distilled water (Millipore, USA). For analysis of Pb isotope ratio, about 0.8 g of high-purity Pb metal (NIST SRM 981 standard) purchased from the National Institute of Standards and Technology (NIST) was used as a Pb isotope ratio standard. The Pb standard were dissolved in 1 M HNO_3 to prepare a stock solution.

During the analysis, quality control samples such as blanks and certified reference materials were included in the analyses. The ICP-MS were set to run a blank and a standard check at every ten samples for every set of measurement.

Instrumentation

All analyses were conducted at North-West University's Centre for Applied Radiation Science and Technology. The instrument used in this study is a NexION 2000 ICP-MS (PerkinElmer Inc., Connecticut, USA) which is equipped with a Quadrupole ion deflector that focuses the ion beam to the dual mode detector. In addition to being highly sensitive, the NexION 2000 ICP-MS uses a helium gas collision system that greatly reduces the spectral interference caused by argon and chlorine. The instrument were optimized using the automated SmartTune™ procedure. All the data acquired were processed using the Syngistix™ Nano Application Software Module (PerkinElmer Inc.). The instrumental operating conditions and signal measurement settings are summarized in Table 1.

Results

A major advantage of the ICP-MS is sensitivity and before the start of the analysis the instrument were allowed to run for 30 min following plasma ignition to reach thermal stability. For lead isotopic ratio measurement, a 20 ppb solution of NIST SRM 981 isotope ratio standard were measured for 5 replicates. The Pb NIST SRM 981 was used to

Table 1 Nexion 2000 ICP-MS instrumental operating conditions

RF frequencies	27.12 MHz
RF power	1.2 kW forward, < 10 W reflection
Outer	Argon plasma flow
Intermediate	Nebulizer flow
Central	AUX flow
Nebulizer	Meinhard type C
Spray chamber	Dual sychnic/double Scott glass chamber (ambient temperature)
Sample uptake	50 μ L/min (free aspiration)
Number of sweeps	1000
Number of replicates	5
Ion energy	10,000 V
Extraction	2000 V
Typical transmission Pb	90,000 counts (cps/ppb)

MHz, Megahertz; W, watts; μ L/min, microliters per minute; V, volt; cps, counts per second; ppb, parts per billion

correct the mass bias of the ICP-MS instrument used for the isotope ratio analysis. The instruments showed excellent precision as provided in Tables 2 and 3. The typical within-run precision of the isotope ratio measurement of NIST SRM 981 was less than 0.02% for ratio $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. All of the laboratory utensils used in the preparation of standard and digestion were properly washed, acid-soaked and finally rinsed with 18 M Ω Millipore Milli-Q system distilled water prior to use.

Discussion and conclusion

The aim of this study was to determine whether the lead ratios measured in particular samples could be used to attribute the uranium sample to the production or reprocessing

plant. As a means of looking for variations or similarities in the measurements of South African and Namibia water samples recovered from the mine tailings for reuse in the plant, the ratios $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ were determined. In both Tables 2 and 3 the measured NIST SRM 981 and certified NIST SRM 981 [17] results are different as a results of the mass bias effect. The mass bias effect is used as a correction factor for mass bias correction. Tables 2 and 3 illustrates the data from the analyses of both South African and Namibia mine tailings and shows very interesting results. For example, the isotopic ratios $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ measurements results for South African mine are 1% less than the measured NIST SRM 981 isotope ratio standard while the Namibia mine results are 1% more than the measured NIST SRM 981 isotope ratio standard.

These results confirm that, lead isotopic ratio used for origin location do reflect significant variation within mine and thus provide valuable information about the geochemical formation and origin. The difference of both results is distinct and shows that it is possible to distinguish between South Africa and Namibia uranium samples from different sources.

The South African results are similar to those obtained by Khumalo and Mathuthu [18]. These results support and strengthen national nuclear security in deterring theft of nuclear material by nuclear terrorist for non-peaceful purposes within the country, as South Africa seek to develop and establish a national nuclear forensic library.

It is recommended that comprehensive sampling be undertaken to give the full view of the forensics signatures in different stage of the nuclear fuel cycle (cradle to grave and mining to waste characterization). However, this study has clearly demonstrated that the nuclear forensics signatures from the gold/uranium mine can be distinguished

Table 2 Results of Pb isotope ratio measurements of South African mine tailing samples

Sample ID	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
C5W-1	0.0482	0.8159	2.0108
C5W-2	0.0484	0.8115	1.9457
C5W-3	0.0498	0.8221	2.0326
C5W-4	0.0507	0.8269	2.0349
C5W-5	0.0488	0.8144	2.0434
C5W-6	0.0488	0.8221	2.0217
C5W-7	0.0496	0.8193	1.9589
C5W-8	0.0495	0.8192	2.0331
C5W-9	0.0510	0.8304	2.0427
C5W-10	0.0487	0.8187	2.0481
Mean	0.04935 ± 0.0017	0.82005 ± 0.0194	2.01719 ± 0.0606
Measured NIST SRM 981 (this work)	0.05888 ± 0.0001	0.91441 ± 0.0036	2.17061 ± 0.0013
Certified NIST SRM 981 [17]	0.059042 ± 0.000037	0.91464 ± 0.00033	2.1681 ± 0.0008

Table 3 Results of Pb isotope ratio measurements of Namibia mine tailing samples

Sample ID	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
TSF2-1	0.0589	0.9672	2.3113
TSF2-2	0.0612	1.0153	2.4330
TSF2-3	0.0584	0.9658	2.3160
TSF2-4	0.0614	1.0148	2.4278
TSF2-5	0.0610	1.0111	2.4209
TSF2-6	0.0606	0.9993	2.4004
TSF2-7	0.0605	1.0059	2.4007
TSF2-8	0.0605	1.0045	2.4075
TSF2-9	0.0606	1.0065	2.4037
TSF2-10	0.0606	1.0020	2.3969
Mean	0.0604 ± 0.00091	0.9992 ± 0.01708	2.3918 ± 0.04078
Measured NIST SRM 981 (this work)	0.05888 ± 0.0001	0.91441 ± 0.0036	2.17061 ± 0.0013
Certified NIST SRM 981 [17]	0.059042 ± 0.000037	0.91464 ± 0.00033	2.1681 ± 0.0008

using isotopic profiles and the ICP-MS PerkinElmer NexION 2000 is a good choice for isotope ratio analysis since it has very good nebulization efficiency and stability. Further improvements in precision of results may be carried out by slightly modifying the method used in this study. For example, Tl may be added to the sample as an internal standard [19].

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