

Development of a quantitative method for the analysis of zinc in various ores by spectroscopy



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by

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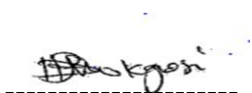
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March 2025

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other university. This research was conducted at Mintek, (Council for Mineral Technology) Analytical Chemistry Division.

A handwritten signature in black ink, appearing to read 'B. Kgosi', is written over a horizontal dashed line.

(Signature of a candidate)

06 Day of March 2025

ABSTRACT

Zinc is the most used non-ferrous metal in modern society and it has the major ability to prevent steel from corrosion which has significant positive effects on the economy and environment. Given the vital role of zinc in such applications, the inconsistent results produced necessitated further investigation on the zinc analysis. Inductively coupled plasma optical emission spectroscopy and X-ray fluorescence spectroscopy were used in this study to investigate sample preparation and develop a comparative approach for determining zinc concentrations in various ores.

This study emphasised the determination of Zinc from different zinc ores by the conventional and new technology methods, which include X-ray fluorescence spectroscopy, inductively coupled plasma optical emission spectroscopy and X-ray diffractometer techniques. Mineral abundance was shown by analytical data from the x-ray diffractometer including sphalerite, pyrite, dolomite, chalcopyrite and calcite. The X-ray fluorescence spectroscopy data indicated that the elemental compositions had high concentrations ranging from 50 to 0.07% for (Zn, S, Fe, Ca, Cu, Mg and Si) as major elements. Certified reference materials were used to validate the methods and compare the results produced by the two techniques.

The instrumental analysis results demonstrated that inductively coupled plasma emission spectroscopy by microwave acid digestion performed better than the X-ray fluorescence spectroscopy pressed pellet approach. The results showed that inductively coupled plasma optical emission spectroscopy is more efficient method for obtaining zinc ore samples. Both techniques achieved good recovery rates ranging from 80 to 120%. Inductively coupled plasma optical emission spectroscopy revealed a higher concentration of zinc ore in the samples investigated than X-ray fluorescence spectroscopy. Microwave acid digestion with inductively coupled plasma optical emission spectroscopy acquired 99.64 and 100.4%

whereas the pressed pellet approach with X-ray fluorescence technique obtained 98.89 and 99.22% recoveries. The results of the two techniques were in good agreement; however, the inductively coupled plasma optical emission spectroscopy outperforms the X-ray fluorescence spectroscopy. Overall performance of the methods was satisfactory, demonstrating consistency and reliability in achieving accurate zinc recoveries.

DEDICATION

To my loving family
Ba ga Mokgosi le Mogatwe

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption spectroscopy
ACD	Analytical Chemistry Division
CRM	Certified reference material
CuS	Covellite
EDXRF	Energy dispersive X-ray fluorescence
EPMA	Electron Probe Microanalysis
EDTA	Ethylenediaminetetraacetic Acid
FeCO ₃	Siderite
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
ICP–AES	Inductively coupled atomic emission spectrometer
ICP–MS	Inductively coupled plasma mass spectrometer
ICP–OES	Inductively coupled plasma optical emission Spectrometer
ISP	Imperial Smelting Process
M/t	Millions of tons
Mt/a	Millions of tons per annum
MIP-OES	Microwave-Induced Plasma Optical Emission Spectrometry
PTFE	Polytetrafluoroethylene
PXRF	portable X-ray fluorescence
SARM	South African reference material
SDD	Silicon Drift Detector
TXRF	Total Reflection X-ray Fluorescence
WDXRF	Wavelength dispersive X-ray fluorescence
XRD	X-ray Diffraction
XRF	X-ray fluorescence
ZnFe ₂ O ₄	Franklinite
ZnS	Sphalerite
ZnO	Zincite

CHAPTER ONE: INTRODUCTION

Chapter One presents the overall background and motivation of the origin of zinc, its properties and uses, the problem statement, aim, objectives, hypotheses, research questions and dissertation layout.

1.1 Background

Zinc (Zn) is an element with atomic number 30, making it one of the most utilised metals in the world, followed by iron (Fe), aluminum (Al) and copper (Cu). The unique properties of Zn include distinct chemical, electrical, thermal, physical and insulating qualities. It is used in several industries, including mechanical engineering, aircraft, automotive, electrical and energy facilities (Nilsson et al., 2017). Due to the demand and vast application in industry, the sourcing of Zn in post mine dumps, open casts and underground mining has increased significantly. This study is motivated by the repurposing of mines that are reopening old pits due to advancements in technology and the demand (Roberts & Thornton, 2014). There are opportunities for industry and government cooperation over the next five to ten years to unleash South African high potential mining assets such as iron ore, manganese (Mn) and Zn reserves. Renewed exploration initiatives can enhance the understanding of the country's resource potential, as Northern Cape is home to significant deposits of these minerals. In the future, stakeholders in the South African mining industry must adopt a long-term perspective to ensure relevance beyond 2030.

This entails undertaking large-scale exploration and embracing new technologies to assess prospective valuable minerals. A stable regulatory regime maintained by the government is essential to facilitate the necessary long-term investment for exploration (Goodman et al., 2019). It is one of the most commonly produced metal in the world and is an essential nonferrous raw material. Its significant qualities lead to its broad use across multiple industries (Chen et al., 2024). While the initiative is positive, there is a need to ensure that the design of process projects will last and resist corrosion, particularly in coastal areas. Dip galvanising is a process in which steel is coated with Zn to prevent corrosion, has emerged as a cost-effective and sustainable solution. It is an essential element because it is both abundant and recyclable. Strong infrastructure and sustainable economic growth in South Africa can be achieved through the use of galvanised steel and the optimisation of local galvanising capabilities (Goodman et al., 2019).

Additionally, alloying Zn with other metals, such as Cu and Al produces compounds with exceptional mechanical and chemical qualities that are perfect for slicing, drilling and use, such as seamless pipes, valves and fitting casting (Chen et al., 2024). Unlike other base metals, Zn is used primarily as an alloying or plating material (Lu et al., 2022) and as a nonferrous metal (Sabnavis, 2018). It is highly desirable because of its physical, chemical, thermal, electrical and isolating properties. Due to its resistance to corrosion and capacity to combine with other metals to form alloys, Zn is utilised in the automotive industry to produce parts and components for automobiles (Nilsson et al., 2017). It is also widely used in construction for roof cladding and structural elements because of its long-lasting nature and attractive appearance.

The electrical and electronics industries rely on Zn for batteries, coatings, and electronic components, capitalising on its conductivity and protective properties (Kania & Saternus, 2023). Furthermore, Zn is crucial in energy production and storage systems, including solar panels and batteries. It can be found in mechanical engineering machinery, equipment and tools which contributes to their longevity and performance (Gordon et al., 2003). The mining industry, fossil fuel burning, metallurgy and Zn ore processing are the main human sources of Zn. The majority of its uses involve making cars, alloys, paints, lacquers, ointments and galvanisation processes (Aliu et al., 2010). Hot dipping steel in molten Zn is the conventional method of galvanising it. Recently, some users have started using electrolytic coatings rather than those attainable through dipping methods. Galvanised steel as described by Chen et al. (2013), which consists of 50% of the end-used product illustrated in Figure 1.1, is used for safety barriers, street lamp posts, car bodies, and suspension bridges.

The automotive, electrical and hardware sectors rely heavily on die-casting, which requires large amounts of Zn. Owing to its many benefits and uses, it is sought after by the majority of mining firms. One of its qualities is that it can blend flawlessly with other metals that have various characteristics. Additionally, it can be combined with Al to create highly useful alloy components. The

production of brass, which contains 17% of a Cu–Zn alloy, from pure Cu, a less desirable metal, sparked the initial interest in Zn. The majority of Zn on earth existed mostly in various natural Zn compounds before the discoveries made by metallurgists (Barak & Helmke, 1993). The main form of Zn in nature is sulfide, which is usually found with sulfides of lead (Pb), Fe and Cu (Van Niekerk & Begley, 1991).

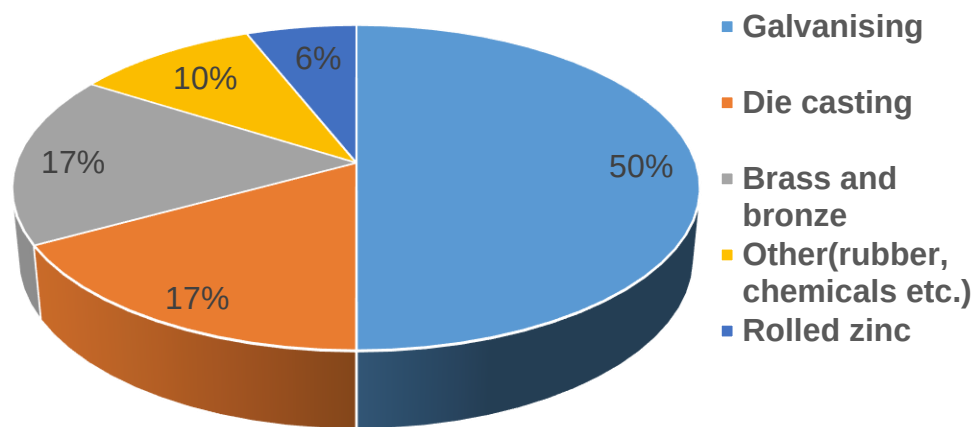


Figure 1.1. Percentages of various Zn end products (Chen et al., 2013).

1.2 Motivation of the Study

The motivation behind this study arises from the widespread application of Zn in the steel industry as a means of corrosion prevention. Zn is used in a variety of innovative energy-related technologies, including fuel cells, renewable energy sources, solar panels and automotive industries (Jones et al., 2014). A growing number of high-performance businesses, such as the steelmaking sector, which also needs clean scrap, are in need of speciality alloyed steels (Persson, 2020). Power deposits have become one of the main technological foundations of modern civilisation, and South Africa is experiencing an electricity crisis (Perez-Antolin et al., 2022). Infrastructure development is closely linked to the demand for Zn and is constantly increasing in both industrialised and emerging economies (Grund et al., 2019). The quantification of high concentrations of Zn in

various ores by different sample dissolution strategies and analytical instrumentation approaches is economically important.

1.3 Problem Statement

Sphalerite (ZnS), which is primarily composed of Zn and S, is a significant mineral because of its association with different elements, particularly Fe. These factors that highlights the necessity of studying the mineral characteristics and elemental composition. The Kipushi Mine provided a high-grade Zn sample that was treated by sodium peroxide fusion and determined by inductively coupled plasma optical emission spectroscopy. The procedure yielded inconsistent results, which necessitated the investigation of sample preparation methods to achieve satisfactory results. Inconsistent results could lead to flawed conclusions, impacting both the accuracy of zinc concentration measurements and subsequent applications.

1.4 Aim and Objectives

The aim of this research was to optimise sample preparation techniques for inductively coupled plasma optical emission spectroscopy (ICP-OES) and to develop a quantitative procedure for assessing Zn ores with high S by utilising X-ray fluorescence (XRF). To accomplish this, the following objectives have been defined:

- To evaluate sample dissolution methods, sodium peroxide fusion, microwave acid digestion and hot plate digestion by exploring mass as well as flux variations for analysis by ICP-OES.
- To develop a pressed pellet approach for the investigation of Zn by XRF
- To carry out a comparative study of the results acquired from the XRF and ICP-OES instruments.

1.5 Hypothesis

The recovery of Zn in various ores in geological samples can be determined quantitatively by ICP-OES with different dissolution techniques.

1.6 Research Questions

The project aim to answer the following questions:

- How do spectroscopic techniques perform in quantitative analysis across different zinc ores?
- How do different sample preparation methods influence the accuracy and reliability of zinc analysis using ICP-OES?
- Which analytical technique is best suited for the quantification of Zn in various ores?

1.7 Thesis Layout

Chapter One: Introduction

This chapter includes a background summary, an introduction, a problem study, aim and objectives, a hypothesis, and research questions.

Chapter Two: Literature Review

The background information and literature related to the current study are thoroughly reviewed in this chapter.

Chapter Three: Methodology

This chapter addresses the methodology, experimental set-up, and chemicals and reagents applied in the experiments. Different sample dissolution methods were investigated by XRF and ICP-OES.

Chapter Four: Results and Discussion

This chapter provides the findings from all the sample preparation procedures as well as a review of the XRD, EDXRF and ICP-OES techniques.

Chapter Five: Conclusion and Recommendation

The last chapter provides an overview of the entire investigation by summarising the outcomes of this study and provides a prospective future that will motivate more research on Zn ore.

CHAPTER TWO: LITERATURE REVIEW

This chapter provides an overview of zinc mining and extraction processes, focusing on global production and South Africa's role in industry. This section discusses the demand for zinc, the geological history of zinc deposits and the use of spectroscopic techniques to quantify zinc ores. Overall, these findings emphasise the economic importance of zinc as well as the need for sustainable mining and extraction practices.

2.1 Process of Zinc Mining and Extraction

The Zn ore was used to make brass alloys and medicinal salts before it was recognised as a metal (Sabnavis, 2018). According to (Gordon et al., 2003), Zn was first made available in India in the 12th century AD. Indian crafts men melted at least 1000 kg of Zn in Zawar from the 12th to 16th centuries. Heavy metals are classified as heavy metals because of their harmful effects on living organisms and disruption of essential ecological balance. Human activities such as mining, chemical industries, metallurgy and fossil fuel waste disposal have introduced heavy metals that contaminate and disrupt ecosystems (Alsaleh et al., 2018). Heavy metals in topsoil might be attributed to different sources, including soil formation processes, agricultural practices, human activities, and natural variations in concentration. It is challenging to determine accurately how many heavy metals are present in each ecosystem segment.

The process of mining involves taking precious minerals or geological substances from the Earth's surface or interior, usually from an orebody. Additionally, mining creates jobs, supplies society with necessary raw materials, and has the potential to develop infrastructure, the economy, and society in underdeveloped and isolated areas (Grund et al., 2019). Technologically and economically valuable metals are extracted from mined ore by the mining industry. Each mined ore body has a different concentration of valuable metals, and the remaining material becomes mining waste, primarily mine tailings, which are stored underwater in tailings dams and have limited commercial value (Kiventerä et al., 2020). Traditional Zn mining techniques include flotation, which is the most straightforward way to extract sulfide minerals (Van Niekerk & Begley, 1991). There are two methods used in the mining of Zn ore, open cast mining and underground mining. Approximately 80% of the Zn ore used in the world's Zn industry comes from underground mines, whereas 20% comes from open pit mines (Genderen et al., 2016).

Two typical mining processes are underground pit mining and open pit mining. Underground mining can be accessed through inclined roads or vertical shafts. There are typically two types of access for ventilation safety and convenience, one is for the ore, while the other is for mining personnel and supplies. (Taylor et al., 2014). The level tunnels are dug out to access the mineral resources once the correct depth is achieved by open pit mining. A crushed ore is lifted and loaded onto trucks or conveyors for transport to the open-cut processing plant. This process may involve blasting, drilling, or a combination of the two. A front end loader and an electric or hydraulic excavator with a shovel or backbone design are usually used for this lifting (Genderen et al., 2016). Naturally occurring in compounds with sulphur (S) or oxygen (O), Zn is highly abundant and is found in various ores, such as ZnS, zincite (ZnO) and franklinite (ZnFe_2O_4).

Sulphide minerals account for nearly 90% of the metal Zn produced. The different forms of Zn minerals are shown in Table 2.1. The most prevalent of the three ZnS polymorphs, ZnS, crystallises as a face-centered cubic lattice of tetrahedral coordinated Zn and S ions (Cook et al., 2009). The most common mineral of Zn is ZnS, which is often found in base metal deposits such as vein-type deposits, stratiform Cu, carbonate-hosted Pb-Zn (Mississippi Valley-type), skarn deposits, sediment-hosted massive sulfides (SEDEX) and volcanogenic massive sulfides (VMS). (Onuk et al., 2017). Wurtzite is a less common mineral with a hexagonal shape while ZnS is popular type of Zn ore and is identified by the high Zn content. During mineralisation, the Fe atoms that form marmatite replace the Zn atoms in ZnS to build marmatite. The crystal structure and cell characteristics of marmatite are still the same as those of ZnS, as studied by (Lai et al., 2019).

Table 2.1. Various mineral forms containing Zn

Mineral	Chemical formula
Sulfides (sphalerite and wurtzite)	ZnS
Sulfates (zincosite; goslarite)	ZnSO ₄ ; ZnSO ₄ .2H ₂ O
Oxides (zincite; franklinite; gahnite)	ZnO; ZnFe ₂ O ₄ ; ZnAl ₂ O ₄
Carbonates (smithsonite)	ZnCO ₃
Phosphates (hopeite)	Zn ₃ (PO ₄) ₂ . 4H ₂ O
Silicates (willemite; hemimorphite)	Zn ₂ SiO ₄ ; Zn ₄ Si ₂ O ₇ . (OH) ₂ .H ₂ O

2.2 The Processes of Zinc Production and Future Trends

The three primary steps in the production of Zn are mining, smelting, and refining. It is widely acknowledged that the production of Zn from its mineral concentrates is a challenging process and that the concentrate must first be reduced to zinc oxide. There are two methods for achieving reduction: hydrometallurgical and pyrometallurgical (Guo et al., 2010). The processes used in hydrometallurgy include fluid roasting in addition to leaching under high pressure, while re-distillation and the imperial smelting process (ISP) are two pyrometallurgical techniques. The electrolytic refining process, electrolysis, or smelting are the usual final steps used to create metallic zinc.

The ore is the primary material input during the mining stage, and tailings and concentrates of Zn are the main material outputs. South African Zn production stage primarily involves domestic and imported ores with refined Zn, tailings, slag and lost metal, accounting for most outflows. A decrease in Zn prices occurred following the global COVID-19 pandemic and government lockdowns, which resulted in decrease in the production of mines across several countries in 2021, particularly in South America (Kania & Saternus, 2023). Mine production, refined Zn production and its use all noticeably declined from January–September 2023 compared with the same period in 2021 (Kania & Saternus, 2023). Global mine production is predicted to reach a peak of more than 14 million tons (Mt) in 2024. Since reserves for Zn are

currently depleted and ores are becoming lower in quality, mining is likely to decrease. The estimated total amount of Zn reserves in the world is 250 million tons, which is estimated to last for only the next 17 years because of the comparatively high demand for Zn metal (Kania & Saternus, 2023).

2.3 Mining Production of Zinc in South Africa

South African Zn production is a notable contributor to both the regional and global Zn markets. Predominantly ranked as the eighth largest Zn resource holder globally, it boasts significant reserves and important deposits, including the Gamsberg, Black Mountain and Broken Hill mines in northern Cape Province (Kania & Saternus, 2023). The Gamsberg Zn deposit is the largest undeveloped deposit in the country and has the potential to produce up to 400,000 tons of Zn metal annually, although its economic feasibility is still being evaluated as shown Figure 2.1. In 2008, South Africa played a crucial role in the Southern African Development Community (SADC) Zn market, contributing approximately 90,000 tonnes of refined primary metal out of a total output of 240,000 tonnes (White, 2011). This highlights South Africa's importance as a major player in regional Zn production. The outlook for Zn production in South Africa is positive, with ongoing expansions at mines such as Hindustan Zn operations expected to contribute to increased production, aligning with the broader trend of rising Zn output in the country and other key global producers such as Australia and India (White, 2011).

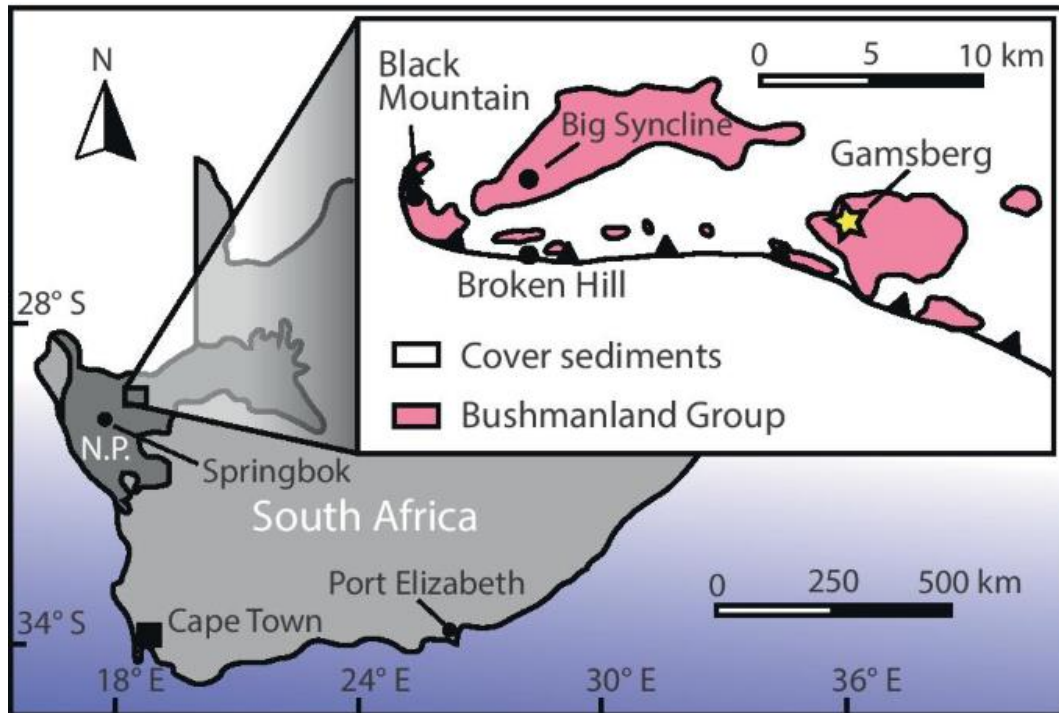


Figure 2.1. Locations of Zn mines in South Africa (Höhn et al., 2021)

2.4 The Demand for Zinc Production

Rich and manageable Zn ore is becoming less abundant as the mining sector grows; however, the demand is rising daily. China was the main producer and consumer of Zn in 2022, it provided 6.29 M/t of refined Zn, in contrast of the need of more than seven million tons. The increasing output of Zn highlights the challenges of supply versus demand. It is necessary to take advantage of the numerous low-grade complicated Zn ores (Elsayad et al., 2024). The growing demand for metals coupled with advancements in modern technologies linked to economic progress has created new requirements for the exploration and extraction of raw metals. The production and exploration of raw materials are increasing (Henning et al., 2019).

Infrastructure development is closely linked to the demand for Zn and is constantly increasing in both industrialised and emerging economies (Grund et al., 2019). It is one of the most widely used metals in civilisations because of its unique technical and chemical characteristics. Rust and corrosion in steel

are the primary factors driving the increase in Zn consumption and will continue to do so (Sabnavis, 2018). There is no anticipated physical shortage of Zn in the future, but significant price hikes are expected due to rising demand and decreasing resource quality. The price of Zn is predicted to rise dramatically over the next several decades. The scarcity of Zn will primarily show up as higher metal prices, which will have an impact on demand, and recycling will rise in the future due to the anticipated price increase (Sverdrup et al., 2019).

Over 13.67 M/t of Zn were required in 2016, and by 2021, that number is expected to surpass 14 M/t. The economic downturn resulting from the lockdown and the COVID-19 pandemic in 2022 led to a decrease in the demand for Zn in the market (Kania & Saternus, 2023). The substance needed to maintain and improve the human-made inventory of commodities that meet societal needs might be considered the reason for the demand for Zn. It is predicted that by 2050, the demand for Zn in first-use products will rise from 17.5 Mt/a in 2019 to 29 Mt/a (Rostek et al., 2023).

2.5 Geological Background of Zinc Ores

Nature sources of Zn include ores like ZnS, ZnO and ZnFe₂O₄. The common ore, ZnS, is found in base metal deposits such as volcanogenic massive sulfides (VMS), sediment-hosted massive sulfides (SEDEX), carbonate-hosted Pb–Zn such as Mississippi Valley-type deposits, stratiform copper deposits, vein-type deposits, and skarn deposits (Onuk et al., 2017) and (Ye et al., 2011). Furthermore, as a key industrial mineral for Zn, it also contains scattered metals such as cadmium (Cd), gallium (Ga), germanium (Ge) and indium (In), as well as occasionally silver (Ag) and gold (Au) (Duan et al., 2023). The structure of ZnS can contain a wide range of elements, with Fe and Cd being important (Ye et al., 2011). During the process of mineralisation, the substitution of Zn atoms with Fe atoms in ZnS leads to the production of marmatite. The crystal structure and cell characteristics of marmatite are still the same as those of ZnS (LAI et al., 2020).

2.6 Determination of the Zinc Concentrations by Spectroscopy

This study offers a thorough summary of the approaches commonly used to measure zinc, along with the theories and findings related to this area of research. However, in this summary, a review was performed on sample materials with low concentrations, mostly at the ppm level. This is because it was challenging to obtain ores that were at the same level and had an appropriate matrix. Materials related to soil, sludge, sediment, sewage sludge, soil dust and topsoil were used. A range of analytical techniques, such as XRD, XRF and ICP-OES, were employed in this investigation. However, other methods for measuring Zn include atomic absorption spectroscopy (AAS), polarography, anodic stripping, ICP-MS, atomic fluorescence spectrometry (AFS) and neutrons (Baker & Amacher, 2015). In addition to other spectrometric methods, microwave-induced plasma optical emission spectrometry (MCP-OES) was utilised in evaluation of elemental contents in a variety of samples.

There are several sample preparation and analysis techniques that can be used to determine Zn, each of which has advantages and disadvantages. These methods include open digestion methods, such as hotplate digestion; closed vessels, microwave acid digestion; alkali peroxide fusion; borate fusion; and pressed pellets by XRF. Most of the elements in most materials could be determined by both the open acid digestion method and the microwave acid digestion method, which yielded comparable findings. The benefits of microwave acid digestion include the use of reduced amounts of reagents and faster digestion times. A range of sample preparation methods was employed to obtain quantitative data for all the elements studied. Sample preparation methods are used to obtain quantitative results for all the elements examined in a variety of materials.

The sequential extraction method stipulated by the group of Bureau of Reference (BCR) contracts was conducted by (Kazi et al., 2006). They used

flame atomic absorption spectrometry (FAAS) to create a rapid ultrasound-accelerated method for the discovery of Zn and Cu. Materials were obtained from untreated sewage sludge in a city called Hyderabad in Pakistan. These materials were then compared with those obtained from ultrasonic treatment for the separation of (Cu, Cd, chromium (Cr), Pb, nickel (Ni) and Zn). Based on the results of the partitioning study conducted on unprocessed raw sewage, the most common forms of Cd and Zn were those that were more easily mobilised. Additionally, the organic matter/sulphur dioxide (SO₂) and Fe or manganese oxide (MnO₂) fractions had the highest concentrations of Pb and Cr. Overall, metal recoveries ranging from 95 to 100% were achieved with the traditional BCR technique.

Total reflection X-ray fluorescence spectrometry (TXRF), a novel technique for directly identifying the elemental composition of oxide and sulfide Cu-Zn ores in the solid state, was examined previously (Sharanov et al., 2019). The elements of interest were S, Zn, Fe, Cu and arsenic (As) from materials with various matrices, such as ferrous sulfide (FeS) and silicon dioxide (SiO₂). The procedure did not require a sample digestion step; instead, prepared suspensions in high viscosity liquids were used. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) utilised to verify the TXRF results. The significant element concentrations in the Cu-Zn ore identified by the TXRF were consistent with those produced by ICP-AES, with a relative standard deviation (RSD) of below 10%. The TXRF can be used to quantify S, Fe, As, Zn, and Cu, the elements that are most significant in Cu-Zn ores.

Dust and topsoil samples collected were used to examine how wind contributes to the dispersion of heavy metals in an area surrounding an Iranian mining region by (Mokhtari et al., 2018). Marble dust collectors were used to determine the quantity of Zn and Pb dispersed by wind because of mining operations. A combination of hydrochloric (HCl), hydrofluoric (HF), perchloric (HClO₄) and nitric (HNO₃) acid was used in the four acid digestion methods to break down the soil and dust samples for the analysis of total Pb and Zn

concentrations by the ICP-OES technique. These findings demonstrated that there was important variation between Zn and Pb levels in the dust and topsoil but not between the dust and subsoil. The concentrations of Zn and Pb were 19.83 and 102.0 ppm for the subsoil and 29.2 and 91.1 ppm for the topsoil, respectively.

Ballito, Zinkwazi, Tugela, Mtunzini and Durban North are five different Kwazulu Natal beach locations that were the subject of the investigation reported by (Vetrimurugan et al., 2019). The value of sediment metals such as (Zn, Cu, Cr, cobalt (Co), Ni, manganese (Mn), magnesium (Mg), Pb, molybdenum (Mo), arsenic (As) and mercury (Hg) and Fe) were determined by ICP-OES. Sediments were decomposed together with the CRMs for quality and precision of the analytical procedure. In addition to confirming the precision of the measurements, the approach offered a trustworthy comparison of the metal recovery rates. A procedure highlighted the effectiveness of the digestion and analysis process while demonstrating the potential for metal accumulation in the coastal sediments. The results revealed percentage recoveries ranging from 77.68 to 106.96%.

The metal concentrations of (Mn, Mg, Cu, Fe, Co, Ni, Cr, Mo, Cd, Pb and Zn) and their sustainable effects on sand sludges close to South Africa's marine protected areas, Sodwana Bay and St Lucia were examined by (Vetrimurugan et al., 2018) using ICP-OES. An investigation of the possible ecological effects on sensitive coastal environments was also conducted. The EPA 3051A approach was used to digest the collected sediment materials and the recoveries ranged from 85.6 to 105.2%. The results produced showed that the analytical process is highly reliable and efficient. These findings demonstrated the high level of accuracy of the employed analytical technique. In addition, it is essential to have important information for understanding the metal distribution in ecosystems and emphasising the necessity of continuous monitoring to protect coastal biodiversity and ecosystems is needed.

A heavy metal sediment concentration comparison between the alkaline fusion dissolution technique and aqua regia-assisted microwaves in a closed vessel was performed by (Chand and Prasad 2013). Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) was used to prepare (Al, Co, Zn, As, Pb, Fe Cr, Cu, Ni and Mn) by alkaline fusion with acid digestion using a microwave approach. Microwaves were selected so that the lowest quantity of acids could be used, followed by ICP-OES. The sediment CRM was employed to verify the precision and accuracy of the digestion methods. Statistical evaluation revealed no marked difference in metal concentrations between the two digestion methods, with the recovery values obtained for most metals being >82% for both methods, with an RSD of less than 6%. Alkaline fusion worked well for refractory and silicate-bound metals, but microwave-assisted aqua regia digestion worked better for detecting volatile and minor elements such as As.

A straightforward analysis of Zn and Co in materials of various volatilities with solid sampling graphite atomic absorption spectrometry (GFAAS) was performed by (Belarra et al., 2003). The investigation was based on establishing the importance of maintaining Argon flow during atomisation to increase the signal-to-background ratio during simultaneous matrix and analyte release. The soil and vitamin samples were cut by a ceramic knife and then added to an atomiser using a traditional micropipette. After being suspended in the water, the sample was aspirated and swept into the tube platform. Both samples were dissolved to evaluate the results. The resulting solutions were then examined by GFAAS, with differences of less than 6% from the reference values, the results demonstrated excellent agreement with those from acid digestion. An RSD of approximately 8% further demonstrated the acceptable precision of the analysis.

Heavy metals (Cr, Zn, Pb and Cu) were identified in soil and sediment by Güven and Akinci (2011) utilising acid digestion techniques followed by ICP-OES. San Joaquin Soil-2709 and Estuarine Sediment-1646a were used as CRMs, and three low-pressure microwave heating procedures (P1, P2 and P3)

were adjusted and compared with the Environmental Protection Agency (EPA) acid digestion procedure 3050A. The results revealed that P2 efficiently extracted San Joaquin soil with a recovery percentage ranging from 90% to 102%, while the highest accuracy findings for Estuarine Sediment ranging from 96% to 104% were obtained from the P3 microwave extraction technique.

The simultaneous quantification of (Zn, Cr, Ni, Cd, Pb, Cr, and Cu) concentrations was conducted by (Barańkiewicz et al., 2010) using ICP-OES. Sewage sludge was also microwave digested and added to the plasma as an aqueous solution, followed by the utilisation of a standard with aqueous solution for calibration. The CRM for sewage sludge was used to confirm that the process was correct. At the 95% confidence level, the values obtained by slurry were found to be nearly identical to the certified values used by Student's t-test. The slurry procedure can be efficiently used to ascertain the content of each element in sewage, as evidenced by the RSD being found to be less than 3%.

The FAAS technique was used by Viets et al., (1984) to examine the levels of (Zn, As, Ag, Cu, Cd, Pd, Mo, Bi and Sb) in geological samples. Fusion with potassium pyrosulphate was used to prepare the samples, and the resulting mixture was then broken down into liquids that contained potassium iodide (KI), ascorbic acid ($C_6H_8O_6$) and HCl. An organic phase of 10% V/V aliquat 336-isobutyl methyl ketone was used to shake the solutions and separate the nine targeted elements. The FAAS was used to identify nine elements in the organic phase, and the method allows fast analysis and can accept detection limits as low as 0–5 ppm.

The determination of quality CRM values for 16 elements, including Zn, in Cuban soils and their geochemical associations was reported previously (Alfaro et al., 2015). An index for determining soil background metal concentrations was provided to examine the connection between trace elements and Fe. Surface samples were taken from 33 soil profiles, most of

which were found in regions with natural forests or little human influence. The ICP-AAS was used to examine the metal content after the samples were subjected to digestion (USEPA method 3051A). The results indicated that only had recoveries of 100% for Zn and 108 for Cr and Pb%, respectively. These findings support the theory that national soils naturally have heavier metal concentrations on average than average for the world.

The use of ICP-MS technique with the microwave acid digestion method for the multielemental analysis of various metals in soils and sediments was explained by (Falciani et al., 2000). The instrument parameters were improved and adjusted to the ideal level to guarantee accurate quantitative data. Multiple elemental acid solutions were used for calibration without the need for sample matrix matching. Metals with large ionisation potentials, such as Cd, Zn, As and Cd, experienced signal suppression when HNO₃ was utilised. Consequently, calibration solutions were prepared using the same acids employed for sample mineralisation. Four CRMs were analysed to evaluate the process. The analytical results indicated notably low quantification limits, typically below 100 ppm, with accuracies exceeding 80% for the most components. Overall, good precision was shown, with values ranging from 0.3 to 14%.

2.7 Detailed Chemical Analysis by Energy Dispersive Spectroscopy

Chemical contents of sample materials can be determined by handheld or bench-top EDXRF. Handheld or portable instruments have been utilised since their introduction in many geoscientific domains, such as mineral exploration, environmental investigations and process monitoring, in both solid, liquid and powder forms (Laperche & Lemièrre, 2020). Analysing with a handheld device is becoming increasingly common for various materials and matrices within a minimum time. Portable techniques are quick, dependable and affordable with accuracy and precision similar to benchtop instruments (Caporale et al., 2018). The limits of detection of XRF are less

sensitive for most of trace elements than those of laboratory-based approaches. However, it provides accurate total elements concentrations for samples of solid soil.

The energy and intensity of distinctive X-rays in X-ray fluorescence spectra are essential for elemental analysis of different kinds of samples. This technology is very responsive and works on the basis of atoms interacting with radiation (Garg et al., 2020). It is capable of offering a multielemental quantitative analysis and even unexpected additional non-targeted components that are more accurate and dependable than the XRF quantification software (Kallithrakas-Kontos et al., 2016). The matrix effect, overlap interference, and difficulty with deconvolution and background fitting can all limit accuracy when working with solid samples. However, this can be rectified by methods such as automatic XRF quantification software and the influence coefficient and fundamental parameter constant. The concentration can be obtained during sample preparation, such as by pressing pelleted fused glass beads or directly on a sample without destruction (Mejía-Piña et al., 2016).

2.8 Mineral Characterisation by X-ray Diffraction

Minerals are identified qualitatively, semi qualitatively or quantitatively by using XRD spectroscopy. Identification of a single-phase mineral is very simple to achieve and combinations involving two or more phases are more complicated. Several factors can lead to errors in the determination by XRD, including unfamiliar substances that are present in mixtures in trace amounts, with structures with variable compositions. Inadequate sample preparation and problems with their appearance can also contribute to errors. Semiconductor analysis, especially the measurement of the mineral composition of rocks and soils, can cause these problems. (Hupp & Donovan, 2018).

Atomic positions, arrangements inside the unit cell and separation between atomic planes can be analysed reported by (Ali et al., 2022). It is a useful technique for identifying the crystalline phase or phases that are present in a material. The diffraction method is influenced by the crystal structure rather than solely by the composition, and it is possible to distinguish between compounds because each phase has a distinct powder diffraction pattern (Loubser & Verry, 2008). Additionally, it is feasible to distinguish between various polymorphic forms of an identical compound. Furthermore, each component's pattern intensity corresponds to its quantity.

Powder XRD is a small and sophisticated tool that is used for phase identification and mineral determination. It contains several notable features and innovative attachments, such as a variable temperature and humidity chamber, which can broaden its application by providing information on how temperature and humidity influence the properties of materials. The XRD pattern intensities are used to determine the atomic structures. (Ali et al., 2022). Chemical studies of ores and quantitative mineralogical data are essential for effectively surveying and following mining and extraction procedures (Secchi et al., 2018). The mineral phases in mine drill cores have been identified by preparing thin sections of samples for analysis using a variety of techniques, such as electron microprobe analysis and scanning electron microscopy (SEM). The mining industry makes extensive use of X-ray techniques such as XRD and XRF.

The mineralogy, geology and element mobility of the sulfide-rich Excelsior waste rock dump, which is connected to the polymetallic Zn-Pb-(Ag-bismuth (Bi)-Cu) deposit from Cerro de Pasco mine and central Andes in Peru, were examined by (Smuda et al., 2007). The purpose of the investigation was to ascertain the ore that was discovered in the Excelsior waste dump and to investigate the mineralogy and geochemical characteristics. It was discovered that the main ore minerals were Hematite (Fe_2O_3), siderite (FeCO_3), muscovite ($\text{KAl}_2 (\text{Si}_3 \text{Al}) \text{O}_{10} (\text{OH})_2$), and quartz (SiO_2) while the deposit contains trace

amounts of tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), covellite (CuS), and cerrusite (PbCO_3). That made it suitable to characterise a Zn ore by XRD analysis.

Different types of ZnS crystals were identified by examining the intergrowth associations of ZnS samples and the mineralogical texture under a polarising microscope. Mineral phases were investigated using in situ micro-XRD, and the chemical composition was assessed by polished section electron probe microanalysis (EPMA). The majority of the naturally occurring ZnS samples that were gathered had close dispersed structures and were reddish-brown or yellow brown in color with high purity. An EPMA and XRD measurements revealed that all the naturally occurring ZnS from different locations had crystallised in cubic phases with specific chemical compositions. These findings indicate that natural ZnS with high Cd and moderate levels of Fe has the most desirable photocatalytic properties.

2.9 Dissolution Techniques of Samples for Instrumental Analysis

Various methods exist for the preparation of mineral ore samples for quantification employing techniques such as ICP-OES and XRF. These methods include peroxide fusion, microwave acid digestion, hot plate digestion, pressed pellets and glass beads. However, the type of test sample, as well as the necessary degree of exactness and specificity in the analysis, typically determines the precise method of analysis (Hossner, 2018). Most commonly, wet dissolution is the preferred method, which is based on the digestion of samples by using different acids, heat and pressure to convert complex ore into simple chemical compounds. Reaching complete dissolution is difficult and necessitates the creation of a drawn-out process that typically involves the use of dangerous chemicals (Belarra et al., 2003).

One common technique for dissolving metals, alloys, geological samples (rocks, minerals, soils, sediments and ores) and organic materials is to attack them with strong inorganic acids (HCl , HNO_3 , HClO_4 and H_2SO_4), and others (H_3O_4 and HF) have been successfully broken down by the right acid combinations (Hu & Qi, 2013). Certain requirements concerning solid samples must be met, including the need for the sample to be pulverised to a specific particle size, homogenised and representative of the whole material before sample preparation to minimise errors in the quantification process. Complete dissolution is required to for the elemental and isotopic compositions to be accurately determined. There are main factors to consider when a sample is dissolved, to guarantee complete dissolution, the adopted procedure must first guarantee that the portion of the material chosen is representative of the field (Balaram & Subramanyam, 2022a).

2.9.1 Sodium Peroxide Fusion Digestion Technique

Alkali peroxide fusion is a sample preparation method in which a sample is dissolved at high temperature with alkali salts. These salts include sodium hydroxide (NaOH) pellets, anhydrous sodium peroxide (Na_2O_2), sodium carbonate (Na_2CO_3) and lithium metaborate (LiBO_2) to dissolve the sample at high temperature. The Na_2O_2 and Na_2CO_3 are commonly used over LiBO_2 and $\text{Li}_2\text{B}_2\text{O}_7$ because minimal loss of analytes at low temperatures and decomposition of Na_2O_2 results in a simpler matrix (Bokhari & Meisel, 2017). Major and minor soil constituents can typically be determined by commercial sources of Na_2CO_3 and Na_2O_2 , as they are typically sufficiently pure (Hossner, 2018).

Fusion dissolution is employed in certain cases when open acid and microwaves are insufficient to fully dissolve certain refractory minerals (Hu & Qi, 2013). The Na_2O_2 sintering experiments can be conducted using crucibles made of Au, Ag, Ni, platinum (Pt), zirconium (Zr), and Fe. Crucibles made of Fe or Ni may be thrown away after few applications because of the strong corrosion that occurs in these materials. Crucibles made of Zr can withstand temperatures up to 700°C during the process of fusion and have been demonstrated to have high resistance to molten Na_2O_2 flux (Balaram & Subramanyam, 2022b).

2.9.2 Microwave-assisted Acid Digestion Approach

Digestion with the assistance of microwaves is based on the exposure of a sample to strong acids, temperature and pressure under microwave irradiation. It has been used for over 30 years in chemical laboratories as a source for sample decomposition (Balaram & Subramanyam, 2022a). This method is capable of digesting various mineral ores, as it allows the temperature and pressure to be increased without the loss of volatile elements,

as it is a closed vessel digestion technique. The microwave digestion method can vary in the number of steps, in which more than one step (temperature ramping) is used when the analytes respond to a broad temperature range. The advantages include that it is fast, offers decreased loss of volatile analytes and often leads to complete dissolution of the mineral ores; however, the disadvantage is that, depending on the model of the instrument, acids such as (HClO₄) and sulphuric acid (H₂SO₄) cannot be used, as demonstrated in Table 2.2.

Table 2.2. Disadvantages and advantages of sample preparation

Method	Advantage	Disadvantage
Hotplate digestion	Simplicity and easy to operate	Loss of volatile elements
	Inexpensive method	Incomplete dissolutions
	Suitable for all sample types	Time consuming
		Attracting contamination
Microwave digestion	Rapid digestion process	Uneven heating
	Low salts matrix contamination	Possible explosion
	Low risk of contamination	Expensive equipment
	High purity acids used	Loss of volatile elements
	Decomposition of resistant solids	
	Low temperature required	
Peroxide fusion	Total dissolutions	Contaminations from flux
	Effective for refractory materials	Highly reactive and attract contaminant
	Silicate, complex matrix	High temperature
	Capable of complete dissolution	
	Minimum loss of volatile elements	

The investigation of the microwave-assisted digestion using sulfide ore and concentrate of various Zn ores containing ZnS, chalcopyrite (CuFeS_2), SiO_2 , FeS_2 , pyrrhotite (Fe_7S_8) and calcite (CaCO_3) were analysed as Cu, Zn, S and Fe (Al-Harashseh and Kingman 2007). The samples were diluted with HNO_3 in digestion vessels. However, this method led to incomplete dissolution, which was also observed in Tanner, Leong, and Pan (2000). Small amounts of HF and extra HNO_3 are frequently added to overcome incomplete dissolution. Another disadvantage of microwave acid digestion is that fluoride-based minerals can precipitate out of the solution; however, this is often avoided by the addition of a complexing step using boric acid (H_3BO_3). Research has revealed that the experimental results match the certified values and that successful recoveries are achieved.

Heavy metals in sewage sludge have been found to be detectable using (B) ignition and microwave digestion, (A) drying and microwave digestion, and (C) drying and conventional digestion methods (Turek et al., 2019). An amount of sample was weighed into polytetrafluoroethylene (PTFE) storage containers, mixed with concentrated HNO_3 and HCl, and then digested by a microwave. The solution was transferred into a 100 mL bottle and diluted with ultrapure water to the desired level. Second process followed the same steps, except that the material was roasted before digestion. After digestion, the solution was diluted with deionised water and filled to the appropriate level in a 100 mL flask. The third approach involved digesting the sample sludge with concentrated solutions of HNO_3 and HCl after it was dried to a consistent load. Materials were boiled in closed containers on a hotplate. The containers were diluted to the appropriate level after all the solutions containing undissolved materials were added. The solutions were then filtered through medium filters into polyethylene bottles.

Three standard digestion methods, ISO14869-1, ISO11466 and EPA3050B, to extract heavy metals from calcareous soils were compared by (Shahbazi & Beheshti, 2019). Additionally, ICP-OES and GFAAS instruments were used to

examine the amounts of (Zn, As, Cr, Mn, Cd, Co, Ni, Pb, V and Cu) and evaluated the influence of lime on the extraction process. It was discovered that the results of most elements were within the acceptable value of the CRMs for all the three techniques. The findings showed that the ISO 14869-1 method demonstrated the highest recovery rates of 94 to 107.8%, for ISO 11466 as 90.3 to 101.7% and for the EPA 3050B was 84.6 to 105.9%

The distribution of Zn by Aliu et al., (2010) in surface soils of the K. Mitrovica region in Kosovo was examined by using the ICP-MS and ICP-OES methods. An amount of weighed sample was digested by the addition of HNO₃ or HCl followed by the addition of HClO₄ on a hotplate and then transferred to a volumetric flask. The solutions were subjected to microwave acid digestion with aqua regia and followed by ICP-OES. Both techniques resulted in similar average mean values. The determination of heavy metals (Zn, Fe, Cu, Mn, Co, Cd, Cr, Ni and Pb) for contamination in sediments of the Qinjiang River in China was conducted by (Zhang et al., 2022). The sediment aliquots were digested by a combination of HNO₃, HClO₄ and HF with samples that were boiled in a microwave, purified, diluted, filtered and analysed by ICP-OES. The CRM was used to confirm the precision and correctness of the heavy metals test, and it was discovered that the relative error was less than 10 and the recovery was 80-120%

2.9.3 Hotplate Acid Digestion Approach

Hotplate acid digestion is an analytical method for decomposing solid samples into solutions. It involves heating a solid sample in an appropriate vessel, such as Teflon, together with a combination of strong mineral of HNO_3 , HClO_4 , HCl and HF . Sample preparation with hotplate acid digestion is essential, particularly for solid samples that have complex matrices that must be broken down to liberate the desired elements. Acid digestion of a hotplate has the potential for incomplete dissolution of sample material. This process is time consuming and limited to the maximum temperature. Through the process of increasing the solubility of different elements and homogenisation the sample, this technique enables precise and accurate analytical measurements

The effectiveness of four different microwave acid digestion techniques, open nitric, open aqua regia, microwave aqua regia and microwave acids, on seven topsoil materials employing ICP-OES was investigated by (Tighe et al., 2004). Compared with those of 18 elements, including Zn, the relative strength and analytical precision were investigated. The use of aqua regia with microwave acid digestion demonstrated superior elemental extraction and analytical consistency. The broad range of substances demonstrated excellent consistency when CRMs and other sample types were measured, with RSD values below 20%.

The effectiveness of two USEPA 3050A, 3051B and total digestion methods 3052 for the analysis of Ni, Pb, Cd, Cu and Zn and mercury (Hg) in soil samples using AAS with the flame technique was investigated by (Da Silva et al., 2014). The measured Hg was used to identify the apparatus connected to an electrodeless discharge lamp and a hydride generator. The extraction of (Zn, Cu, Cd, Pb, and Ni) at ecologically accessible levels was therefore more effective using USEPA method 3051A than with USEPA method 3050B. In addition to yielding a greater recovery of these components, the procedure has a shorter digestion period, uses minimal acids, and has a lower risk of

contamination. The USEPA method 3051A extracted Hg more efficiently in soils with higher concentrations. This approach is appropriate for situations in which different types of soils and minerals are analysed or to reduce losses due to evaporation of elements in an open system.

A gel preparation technique for the examination of (Zn, Fe and Pb) in Zn concentrate material utilising WDXRF spectrometry was studied by (Zhang et al., 2009). A weighed sample with the concentrated HCl and HNO₃ mixture was transferred into a vessel, which was then closed and heated in an electric oven. After cooling and inclusion of the Co internal standard, the pH was set at 4 with NaOH, and an Ethylenediaminetetraacetic acid (EDTA) sodium citrate buffer solution was added. Gelose was added, and the mixture was stirred until it was fully dissolved to create a gel. Elements distributed in the gel medium were identified by the WDXRF spectrometry. The results displayed excellent accuracy and precision with a limit of quantification of 0.1%, a linear of 0.5 to 100%, and the RSD of less than 4%.

An investigation of (Cd, Fe, Cr, Pd and Zn) from surface dust using AAS was conducted by (Ehi-eromosele et al., 2012). Three methods were used for acid digestion, dry ashing with aqua regia (B), HNO₃ digestion and aqua regia (A), and HCl extraction. The most effective method for the recovery of Pb and Fe was HNO₃ digestion, followed by HCl extraction. Extraction of Zn from aqua regia validated to be the best approach however, HNO₃ digestion and subsequent HCl extraction worked well for Cd.

2.10 Energy Dispersive and Wavelength Dispersive X-ray Spectroscopy.

The widespread use of XRF for chemical studies started in the 1950s. They can be utilised in a way that is prominent or even harmful, depending on the features of the artefact and the precision of the necessary data. This analytical method determines the chemical compositions of a substance. The materials may be powder, liquid, solid, filtered, or other forms (Margu  et al., 2022).

Commercial XRF systems come in a range of models and the best spectrometer for a given application depends on its specific needs. Two main types of detection systems are used to determine fluorescent XRF, WDXRF and EDXRF. The fundamental difference between them is how they discriminate the energy of the X-ray photons that come from the sample. A semiconductor detector is used in the latter system, whereas a crystal is used in the former to create a high-resolution system.

The EDXRF systems are superior to WDXRF systems in environmental applications because of their portable nature and simultaneous multielemental capabilities. The most widely used method for spectrochemical analysis by XRF, which entails exposing a sample to primary XRF radiation in order to examine the secondary X-ray spectrum that the samples emits was investigated by (Brouwer, 2010). Electromagnetic radiation with a wavelength (λ) ranging from 0.01 to 10 nm is known as X-rays. Their energy (E) has a direct relationship with the vibration frequency and an inverse relationship with the wavelength and is expressed in electron volts (Ev) with a few fixed exceptions as in equation 2.1. The h is expressed as the Planck's constant, c is denoted as the speed of light and λ is the wavelength.

$$E = \frac{hc}{\lambda} \quad \text{Equation (2.1)}$$

The X-rays are produced in a tube known as an X-ray tube under extremely high vacuum. Compton scatter, Rayleigh scatter and fluorescence are the three main mechanisms through which they interact with matter. Then, an X-ray photon beam is pointed at a slab of material, some of the photons will pass through the material, some will be absorbed, produce fluorescent light and some will be scattered back (Li et al., 2020). The WDXRF uses spectrophotometric crystals and Bragg's law to disperse X-rays of various wavelengths (energies). The distinctive X-rays of the element are emitted into the detector during the WDXRF process, where the optical signals are transformed into electrical signals. Analogue-to-digital converter (ADC)

loose powders, and pressed pellets are some of the techniques used to prepare samples for XRF determination. However, pressed powder pellets and fused glass beads are the most favoured methods for qualitative geological sample analysis by traditional XRF equipment (Marguí & Queralt, 2024).

Powder samples can be pressed into pellets with or without a binder, which can then be analysed instantly or fused with an appropriate flux (Shaltout et al., 2020). The fused beads method is preferred because it can lessen matrix interference and remove particle size impacts. The samples must be homogeneous for the pressed pellet to be effective. A larger amount of sample is required to make a pellet, and a sample of known material or CRM is frequently used for corrections of matrix effects (Sharanov et al., 2019). Tungsten carbide mills are recommended because of their hardness and ability to reduce contamination in the pelletising process. The binding agent used in pressed pellets should be clear of significant elemental pollution, have low absorption, remain stable under vacuum, and exhibit good self-bonding properties. Despite the sample gaining strength and potentially minimising interelement effects, careful consideration of these factors is necessary for accurate XRF analysis (Shaltout et al., 2020).

The pressed pellet approach is very popular and provides quality data. The drawback of pressed pellets is heterogeneity effects, which are mineralogical effects and particle size. The XRF is capable of providing a high level of accurate quality results (Messenger et al., 2021). The report from Wien et al. (2005) and Mori et al. (1999) indicated that XRF is frequently employed in most analytical laboratories. It is used to investigate a variety of substances, including pharmaceuticals, alloys, ceramics, slags, rocks, metals, food, minerals, and fuels. Essentially it can analyse almost anything that can be sufficiently exposed to X-ray beams provided sufficient calibration is performed beforehand, it can completely replace the traditional elemental analysis of other approaches. A non-destructive and nearly constant XRF observations

have steadily increased in efficiency for obtaining high-resolution elemental records. (Mccomb et al., 2014).

They offer immediate analysis of solid samples for multiple elements, along with semi quantitative, quantitative and qualitative measurements throughout a broad spectrum. The techniques are cost effective and easy to operate, and owing to their potential for non-destructiveness, it is possible to re-measure the same sample over again, which can be important for quality assurance (Weinberger et al., 2024). The wide use of XRF technology has been encouraged by the easy sourcing of powerful radioisotopes, excessively sensitive detectors and wavelength dispersive circuits. The XRF methods allow for rapid and damage-free measurement of the total concentrations of several elements. Rapid and damage-free measurements of the total concentrations of multiple elements are made possible with XRF methods.

An improved method for XRF analysis was developed by Ling et al.,(2014) using sulfide ores with different concentrations, including two Cu-Ni-FeS samples and four ore CRMs (Zn, Cu and FeS). The optimal conditions for homogeneous stable glass disc fusion were determined. The samples were combined with different silica weights, and a lithium borate flux ($\text{Li}_2\text{B}_4\text{O}_7$) used to fuse them together. The ratio of silica ranged from 1:20 in materials with low S contents to 1:5 in samples with excessive amounts. The mass of each sample in the presence of $\text{Li}_2\text{B}_4\text{O}_7$, including silica, was 1:14. Lithium nitrate (LiNO_3), a peroxidising reagent, was used to prevent the deterioration of the Pt-Au crucibles. The RSD of major and minor element contents improved by 5–10%, respectively after a 13 min peroxidation period at 580°C whereas temperature was raised to 1100°C for 12 min. The precisions of the Zn, Co, Cu, Ni and Bi results were well below the expected values.

The validation of (Pb, Cu, Cd and Zn) in environmental samples employing different extraction techniques was investigated by (Sastre et al., 2002). They compared HNO_3 extraction and aqua regia extraction for complete microwave

assisted digestion. Microwave digestion process involved the use of specific acids (70% HNO₃, 40% HF, 70% perchloric acid (HClO₄) and 30% H₂O₂, whereas aqua regia and HNO₃ extraction involved the use of different acid mixtures. After digestion, the solutions were analysed using FAAS for Zn and Cu and with ICP-MS for Pb and Cd. The study revealed that the microwave-assisted digestion method had low RSD values of less than 5%, indicating good precision. The results further indicated that the microwave-assisted technique was reliable and accurate for heavy metal determination of environmental sample data, as the results were highly consistent with the acceptance or guideline values.

The total amount of (Zn, Cu, As, Pb, Ni, Mn, Fe and Cd) in 81 soil samples were investigated by utilising dual isotope and X-ray tube field portable X-ray fluorescence (FPXRF) systems by (Kilbride et al., 2006). A statistically comparison was made between the metal concentrations derived from the FPXRF and the aqua regia extractions results, which were examined by ICP-OES. High-quality analytical data were obtained for Pb and Fe at levels commonly associated with contaminated soil components using the X-ray tube and FPXRF approach. High-quality data for Zn, Fe, Cu, Pb, Cd and Mn were produced by duplex source FPXRF. Along with FPXRF analysis, confirmation analysis with ICP-OES with aqua regia extract operations should be performed on a collection of materials representing concentrations levels.

Elemental compositions of solid samples from the metallurgical industry, such as copper-zinc ore, coal and coke, have been reviewed by (Sharanov et al. 2019). The results from the total reflection X-ray spectrometer (TXRF) were compared to ICP-AES analysis. The phenomenon of the TXRF occurs when primary X-ray radiation is focused on a sample in the TXRF spectrometer at a glancing angle (approximately 0.1°C). A range of samples in various stages of aggregation are analysed by the TXRF method. Samples can be applied to the sample holder in suspensions, powders, films, or other forms, or they can be prepared as solutions following sample decomposition. Solid powders can be

applied straight to a sample holder for qualitative analysis. The samples were decomposed by a combination of concentrated acid and H_2SO_4 . The TXRF concentrations and the ICP-OES concentrations were in strong agreement. Majority of the elements determined had RSDs of less than 10%. The results from both approaches agreed very well for the three most significant factors defining the quality of the ore type (Fe, Cu, and Zn).

The evaluation of various digestion techniques for precisely determining the elemental concentrations of (Al, Ba, Ca, Fe, potassium (K), Mg Mn, phosphorus (P), Ni, Zn, As, Cr, Pb, Cd, Cr, selenium (Se) and Cu) in soils using GFAAS and ICP-OES was conducted by (Alsaleh et al., 2018). Microwave aqua regia, microwave aqua regia-HF and hotplate aqua regia are the three digestion methods used to degrade Florida soils and CRM. Compared with the other two methods, the microwave aqua regia HF process demonstrated marginally greater precision and accuracy. However, the total-total digestion method (microwave aqua regia HF) understates the total concentrations of Pb, Al, Ca, Fe, Mg, and Ba in Florida soils in the Florida Paleudults.

The analysis of sewage sludge samples from various sources and evaluation of the slurry as an alternative method was conducted by (Barańkiewicz et al., 2010). The calibration and determination of simultaneous amount of (Cd, Zn, Cu, Ni, Pb, and Cr) were performed by water standard solutions, which were measured by ICP-OES, with calibration conducted with aqueous solutions. The microwave digestion of sewage sludge was also analysed, and the resulting aqueous solution was introduced into the plasma. A sewage sludge CRM was analysed to verify the reliability of the method. Student's t-test revealed that the values produced by slurry nebulisation were at the 95% confidence level, which were comparable to the certified values and RSD values of less than 3%.

A reliable technique was used by Asare et al., (2019) to determine the concentrations of toxic metals (Ca, As, Cu Fe, Ni, Al, Mn, Cd, Cr, Co, Zn and

Pb). After the extraction process, ICP-OES was used to analyse the sediments from Malaysia's Sadong. Quality control procedures were followed, and the analytical methodology was validated to provide accurate data. The prerequisites for precision reproducibility were met by estimating duplicate analyses. A CRM was utilised to assess the correctness of the findings. Sediments samples under investigation had detection and quantification levels for each of the chosen metals that were below permissible limits. Since the recoveries fell between the specified range of 90.0 and 110.0%, the matrix effect is not thought to be major. The mean RSDs were less than 10% for all the elements.

The outcome of the study comparing fused beads and pressed powder pellets employing XRF with CRM as a standard for evaluating the precision of the analysis was conducted by (Rohiman & Arifin, 2020). The pressed powder pellet was made by weighing the sample and mixing it with Cellulose Mycro Crystalline, and the blend was homogenised with two procedures. The first procedure involved the use of a mortar and pestle, and the second procedure involved the use of a shaker. The homogenous mixture was then pressed with a Herzog press machine with boric acid applied to the instrument's pellet ring before the sample was inserted uniformly. The pellet ring was then removed from the sample and placed in a container after the crossbar has closed. After that, the sample ring pellet was labelled and dried in an oven for 15 min. The used glass beads were prepared by mixing LiB_4O_7 and LiBO_2 into a Pt-Au crucible. A spatula was used to blend the mixture, and 10% each of LiBr and LiNO_3 was added. A fusion machine melts a mixture, and after the fusion is completed, the fused glass disk is labelled and analysed by XRF. Compared with the fused glass beads, the pressed powder pellets resulted in the most elements being most closely related to the CRM.

The elemental composition and sample characteristics of a complex sulfide ore deposit in Nigeria were studied by Olubambi et al.,(2008) using EDXRF, XRD and SEM. The powdered ore samples were combined with Herzog

organic binder, which consisted of 90% cellulose and 10% wax, for EDXRF analysis. A hydraulic press was utilised to compress the combination at high pressure after it had been ground and homogenised. It was transferred into an aluminium cup. The presence of common constituents such as SiO_2 , ZnS , PbS and FeCO_3 was found in the ore along S, CaCO_3 and oxide. The different proportions of Zn and Fe in the Fe-rich ZnS were identified by XRD. Less complex intergrowth, low interpenetrations between crystalline phases and fine to coarse grained compositions of the ore were all revealed by SEM analysis. The imprecise quantification of minor elements by XRF makes accurate determination of their composition difficult.

The minor and major concentrations of metals in the Trepca ore deposit in Kosovo and correlations between chemical data were studied (Gashi et al., 2017). Abundance metals such as (Pb, Zn, and Fe) as well as minor companion metals such as (Cd, As, antimony (Sb), bismuth (Bi), silver (Ag) and Cu) were present in significant amounts in the concentrate produced by the flotation process of the Trepca Metallurgical Corporation. The pseudo total metal content was determined by digesting the samples in an aqua-regia mixture (a solution of HNO_3 and HCl) and shaking them for one hour at room temperature. The AAS concentrations were chemically determined and order of Pb concentrate elements was found as $(\text{Pb} > \text{Fe} > \text{Zn} > \text{Ag} > \text{As} > \text{Sb} > \text{Cd})$, whereas for the Zn concentrate sample was $(\text{Zn} > \text{Fe} > \text{Pb} > \text{Ag} > \text{As} > \text{Cd})$ with RSDs less than 1.5%.

The analysis of high quantities of Zn and Pb in polluted soil utilising EDX was studied by (Sitko et al., 2004). Calibration was executed by using soil samples where Pb and Zn contents were ascertained with the AAS method because the CRMs for soils with high Zn and Pb concentrations were not available. The repeatability of the results was determined by varying the position of the sample holder in the EDXRF analyser, including the repeatability during sample insertion and removal as well as during calibration. Following material drying and powdering, soil analysis was performed by filling the sample holder

with powdered soil and manually pressing the powder in the sample holder. Comparisons were made between the results of the EDXRF and WDXRF analyses. The soil samples were prepared for WDXRF analysis with the same sample holders as those used for EDXRF. The results acquired from the EDXRF procedure were compared with those obtained from AAS and WDXRF.

The preparation of fused beads by Norman et al., (2003) utilising a variety of sulfide ores was investigated. The ores of Fe sulfides, silicate matrices, Pb-Zn sulfides and Cu-Mo sulfides were determined by XRF and laser ablation (ICP)-MS for the trace and major element contents. Fused glass beads were prepared and dissolved with acid digestion and analysed by ICP-MS, and the solid beads were examined using XRF technique. The comparative findings revealed that matrix effects were not the underlying issue. There was strong consistency between the XRF and ICP-MS results with RSDs of 2 to 8%.

The determination of the different quantification techniques for easy and trustworthy methods of (Cd, Zn and Pb in soil suspensions utilising TXRF was investigated by (Bilo et al., 2019). The TXRF analysis of the soils was tested for analytical performance by commercial CRMs with varying heavy metal contents from low to high. The application of these methods to soil suspensions was found to have limitations and was addressed by exploring alternative quantification methods. External calibration, combined with soil elimination preparation and TXRF analysis, are used to achieve metal assessment in soils. The findings indicated that internal standardisation with TXRF result correction with the calibration curve derived from recommended techniques. The digestion and ICP-OES analysis yielded accurate quantitative results for the studied metals, including (Pb, Zn and Cd), with recovery values of approximately 95%.

The evaluation of the Zn contents in Pakistan soil through FAAS of three different digestion processes was reported previously (Yawar et al., 2010). The

digestion methods include two leaching techniques and a total dissolution process across 21 soil samples. Soil CRMs were used for quality control during the analysis, with a specific focus on Zn levels measured by FAAS. The leaching and total dissolution processes in the CRM and the soil samples both yielded precision levels better than 4.7% in the analysis. The $\text{HNO}_3\text{-H}_2\text{O}_2$ and $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-HCl}$ methods yielded similar results, with a few samples exhibiting slight variations; the HF-HClO_4 procedure was significantly more accurate in terms of precision. Both dissolution procedures achieved a precision level better than 4%.

The development of a more reliable database for portable X-ray fluorescence spectrometry (PXRF) by examining massive sulfide ores and host sequences was conducted by (Toniazzi & Lentz, 2018). Using a matrix of Geochem REE (2) and soil extraction modes, they analysed five CRMS (OREAS-146, OREAS-620, MP-1b, CZN-4 and OREAS-622) were used to investigate representative calibrations for (Zn, Co, Cu and Pb). They then compared the results of PXRF analysis with those of other analytical techniques in a laboratory setting. Three X-ray beam intensities were sequentially utilised in soil extraction mode to determine a wide range of elements. Inaccurate data (>10%) were yielded from Cu, Zn and Ag whereas Pb performed best with an RSD of 3.27%. This study evaluated the composition of PXRF by analysing core samples multiple times and comparing the results with those of conventional assays. The PXRF was found to be an extremely useful geological tool for gathering geochemical data in real time and supporting different phases of exploration projects.

2.11 Inductively Coupled Plasma Optical Emission Spectroscopy

The identification and measurement of metals in a variety of sample matrices can be accomplished by an essential technique (Goodman et al., 2019). The method features a polychromator and can quickly and accurately perform many elemental analyses ranging from parts per billion (ppb) to parts per

million (ppm) with minimal interference (Khan et al., 2022). Recently, it has been used extensively for a variety of chemical elemental analysis. These include heavy metals such as Cd and Zn as well as valuable metals such as Au. It has the advantages of shorter detection periods, lower detection limits, broader linear dynamic ranges and increased accuracy.

As shown in Figure 2.3, the liquid was introduced into the instrument through the sample introduction system, which comprises the nebuliser, spray chamber and torch. The nebulised samples then interact with the argon plasma, where molecules are atomised, ionised and ultimately excited. Ionic or atomic emission occurs when electrons drop from a higher energy level when excited to a lower energy level. A detector that uses Echelle or Rowland circle optics, which distinguish between various emission wavelengths, captures the emission. The detector then measures the intensity of the discharged signals at each wavelength as shown in Table 2.3. The emission wavelength is related to the vitality contrast between the energised and ground states of the electron, and the concentration of the outflow signals corresponds to the component wealth within the plasma. In Table 2.3, the key components of an ICP-OES are tabulated with their functions.

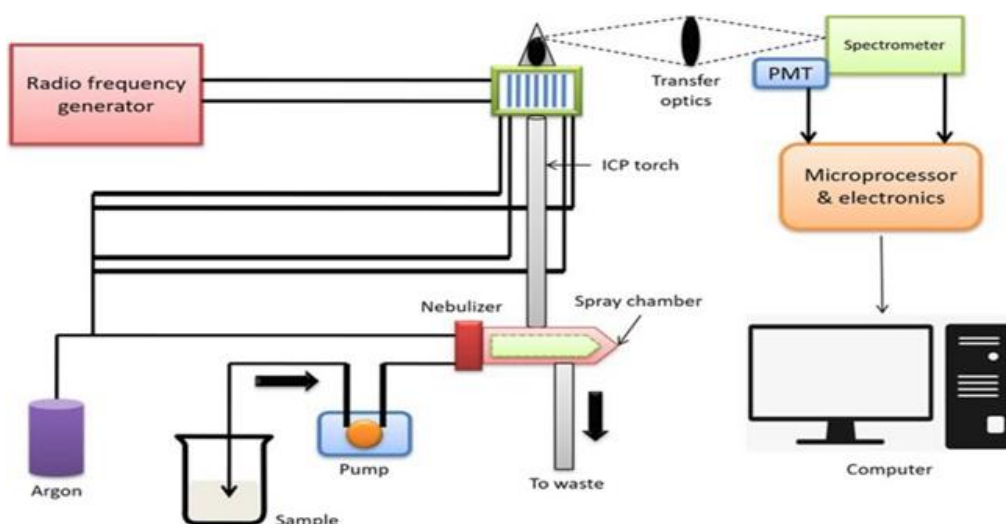


Figure 2.3. Schematic illustration of ICP-OES instrument components (Khan et al., 2022).

Table 2.3. Components and functions of an ICP–OES instrument.

ICP-OES Component	Function
Nebuliser	Converts liquid samples into aerosol
Spray Chamber	Carries nebulised sample from the nebuliser to the torch
Sample injector	Introduces the liquid samples into the nebuliser
Torch	Vaporise and ionising particles in the eluent
Radiofrequency Generator	Provides the power to the plasma
Optics and spectrometer	Separate light wavelengths specific to each element
Emission Detector	Measure the intensities of the scattered ICP radiation
Signal Processing	Process data from emission detectors for spectral analysis

It usually requires sample preparation by pre-treatment before the analysis takes place; therefore, this can result in under recoveries and/or loss of sample (Axelsson & Rodushkin, 2001) and (Gundewar, 2012). The results of two commonly used sample preparation techniques and ICP-OES analysis are critically evaluated in this study. The comparison used nine CRMs which are known to contain Zn, among other elements. The spectroscopy method with the correct sample preparation method was able to accurately quantify the targeted analytes, which also included rare earth elements. The benefits and drawbacks of the two methods of analysis are tabulated in Table 2.4.

Table 2.4. Advantages and disadvantages of the ICP-OES and XRF techniques

Spectroscopy	Advantage	Disadvantage
XRF	Non-destructive analysis	Poor sensitivity to low atomic number elements
	Fast and easy to use	Poor surface sensitivity can lead into inaccurate surface composition due to interferences
	Minimal sample preparation	Matrix effect problem
	Portable equipment	Quantification Challenges
	Wide elemental range	
	Cheap	
ICP-OES	Good Precision, accuracy	Destructive
	Wide elemental range	Complex sample preparation
	High sensitivity	Expensive
	Multielemental capability	Instrument complexity
	Lower detection limit	Time consuming

A study conducted by (Sahraoui & Hachicha, 2016) compared ICP-OES and portable XRF for the determination of trace elements in mine soil materials. A pressed pellet served as a basis for the XRF analysis, whereas an acid digestion technique was used for the ICP-OES analysis. The results indicated a decreasing trend in all the elements. However, the results were in good agreement for both techniques with Cd. The correlations were good for Cd and lower for Zn and Cd. Student t-test was carried out to perform whether there was any slightly variation between the two analysis techniques, and it was found that the concentrations were significantly different for elements such as Zn and Pb.

The use of ICP-OES and ICP-MS was studied for the quantification of various metals in polluted soil samples, such as (Mg, calcium (Ca), titanium (Ti), Cr, Co, Zn, Mn, V, Fe, Cu, strontium (Sr), and P), from a land fill in a different investigation by (Nyika et al., 2019). The samples for instrumental analysis emanated from an acid digestion method, which included drying the samples. After drying the samples were stored for metal analysis. The results for metal concentrations for the techniques were then compared with three different

statistical techniques: coefficient of variation (CV), t-tests, and linear regression analysis. Compared with those of the other elements, the Fe concentrations were the highest.

Compared with ICP-MS, ICP-OES showed higher average values for most components. Furthermore, the determination of (Mg, Ca, Fe, Ti and Mn) had great reproducibility but displayed deviations in their regression lines, whereas the analyses of (Cu, Pb, Co, Sr, Ni, Cr, Zn and V) had absolute reproducibility. Standard deviation (SD) values of the two analyses were substantial and showed significant dispersion in the mean concentration ratios for all the components at the different soil sampling locations. However, not all elements were acquired with statistical analysis by these two approaches. The superiority of ICP-MS over ICP-OES technology was proven by its high sensitivity and precision. (Tanaka & Orihashi, 1997). However, since Zn is often found at high concentrations, it is more suitable for analysis with ICP-OES than for analysis with ICP-MS.

The study by Mokoena et al.,(2019) described the methodology for extracting trace metals (Zn, Cr, Pb, Fe, Cd, Cu, and As) from fresh sediment. Hotplate digestion method was utilised by diluting HNO₃ solutions, followed by analysis by ICP-OES. The one-factor-at-a-time (OFAT) technique was used to optimise the temperature, HNO₃ concentration, volume, and other factors impacting the digestion process. A (CRM015) pertaining to freshwater sediment was used for the optimisation process. The efficiency of hotplate digestion depends largely on temperature, as is common with open acid digestion systems, where the digestion temperature is typically determined by the boiling points of acids.

Higher temperatures were found to extend to normal levels, leading to increased collisions between the corrosive and soil tests, which encouraged the disintegration of the metals. This highlighted the significant influence of the hotplate temperature on the extraction process. Interestingly, previous findings indicated that the test volume had a small impact on the disintegration of

metals from freshwater slits. These studies demonstrated that dilute HNO_3 was an effective agent for digesting various sample matrices. Additionally, the results demonstrated that between 30 and 45 minutes of digestion, the quantitative extraction of trace metals from sediments improved, with most investigated metals yielding similar results between 45 and 60 minutes. Moreover, the accuracy and precision were confirmed by the recovered values being close to the CRM values, with RSDs ranging from 1.2 to 5.8% and recovery percentages ranging from 98 to 110%.

CHAPTER THREE: METHODOLOGY

The goal of this section is to provide a thorough explanation of the methods and techniques used to accomplish the stated goals and objectives of this study. This provides a full description of the methods, processes and instruments used for data collection.

3.1 An illustration of the processes used for the quantification of Zn

A flow chart shows the sample preparation process of the CRMs and samples V2 and V4 for analysis using spectroscopy, as shown in Figure 3.1. A back loading approach was utilised in the mineralogy of a sample by XRD. The samples were prepared using the pressed pellet technique and analysed by a method developed by EDXRF. A powder sample was screened for elemental composition by employing handheld and benchtop instruments. The sample material was prepared utilising microwave acid digestion, hotplate acid digestion and sodium peroxide followed by ICP-OES as presented in Figure 3.1.

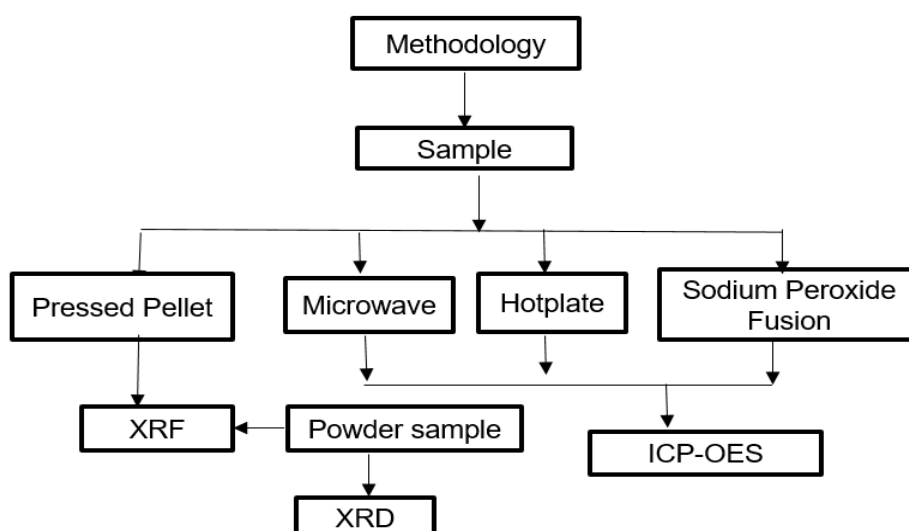


Figure 3.1. A flow diagram that provides an overview of the research approach

3.2 Reagents and Materials Utilised in this Investigation with CRMs

All the experiments in this study were prepared with high-quality ultrapure water with a resistivity of 18.2 MW at 25°C, which was made with a Type 1 Millipore purification system. Sodium nitrate (NaNO_3) UNIV AR with a purity of 98.5% and Hoechst wax C micro powder were purchased from Merck Life Science (Pty) Ltd, in Modderfontein, South Africa. The 65% HNO_3 , 37% HCl , NaOH , NaCO_3 , Na_2O_2 and hydrogen peroxide with 50% purity (H_2O_2) by platinum lines were purchased from Associated Chemical Enterprises (ACE Limited, Johannesburg, South Africa). A pure 99.999% Zn stock solution in a 5% HNO_3 matrix was bought from De Bruyn Spectroscopic Solutions (Kyalami, South Africa). Two certified reference materials, CZN-4 (55.07%), which is a zinc sulfide (ZnS) flotation concentrate from Xstrata Cu manufactured in Canada, and AMIS0620 (47.04%) purchased from African Minerals Standards, which is a Zn concentrate from Black Mountain in Northern Cape, South Africa, were used in this investigation.

3.3 X-ray Diffraction Analysis for Mineralogy Determination

The phase distribution of a sample was analysed by using XRD to assess optimal methods and any limitations that might occur during sample preparation. Both qualitative and quantitative mineralogical procedures were carried out precisely with XRD which was conducted by back loading sample preparation. A Malvern Analytical Aeris diffractometer (Malvern Pan Analytical Ltd., Worcestershire, United Kingdom) was used for the analysis. The XRD instrument consists of a PIXcel detector, fixed slits, and Fe-filtered $\text{Co-K}\alpha$ radiation, ensuring high sensitivity and accuracy in detecting mineral phases. The X'Pert High Score plus software, which enabled precise phase identification based on diffraction patterns was used to determine the identification of the phases. Furthermore, the relative phase amounts in weight percent were estimated by the Rietveld method.

3.4 Sample Dissolution for X-ray Fluorescence

Two CRMs and Zn ore samples (V2 and V4) were used for XRF and ICP-OES determination in this investigation. The samples were pulverised at 90% with a particle size distribution of 75 µm. Development and assessment of the accuracy of the XRF method depend on the grinding approach. The use of CRMs also helped verify the reliability of the procedures, and a detailed analysis is provided in Appendices 3 and 4. The identification of the samples as ZnS ore by semi-quantitative XRD analysis further validated the experimental procedures and findings.

3.4.1 Powder Scan Sample Preparation for Benchtop

The elemental analysis process involved transferring approximately 2.0 g of a powder material (CRMs and samples) into a 32 mm double open-ended plastic cup fitted with polypropylene, as shown in Figure 3.4. The elemental analysis was performed by using EDXRF (Xepos He bench top and Hitachi X-Met8000 handheld) techniques for comparison of chemical information. For the benchtop, the instrument was calibrated by running a multichannel analyser (MCA) disk, which was analysed once per month to fix the peaks. The samples were analysed under a Turboquant (Tq-powder. and Liquid.60 F) mode, which boasts high sensitivity across all elements from sodium (Na) to uranium (U).

Excitation source used was a palladium (Pd) anode X-ray end window tube operating at 40 kV with air cooling. This provides the optimal excitation conditions for accurate measurements. A 12-position autosampler was used to load the samples, followed by instrument measurement. Helium gas flushing was utilised to minimise interference during analysis, and measurements were conducted under air atmosphere conditions. Turbo Quant Quantification software 155309 and X-Lab Pro 4.0 were used for data processing and collections.

3.4.2 Powder Scan Sample Preparation for Handheld

Sample was prepared by placing about 2 g of powdered material into a plastic cup that was fitted with polypropylene film. The material was then analysed by the handheld EDXRF, whereby it was fitted on a stand that enables it to load only one sample at a time. The device has a silicon drift detector (SDD), a 4 W Rh target X-ray tube and a maximum voltage of 50 kV. It is facilitated by standard less fundamental parameter (FP) programs. The LE-FP mining program, which uses a low energy of 10 keV for determining elements with a low atomic number and high energy at 40 keV, was selected. The instrument was calibrated by using a mining and soil CRM (316 SS) disc provided by the supplier before the investigation samples were analysed.



Figure 3.2. Hitachi X-met8000 used for elemental composition

3.4.3 Preparation of Pressed Pellets

Approximately 7.9990 to 8.0010 g of the sample and 1.7990 to 1.8010 g of a Hoechst wax C micro powder ($\text{CH}_{38}\text{H}_{76}\text{N}_2\text{O}_4$) was transferred into a clean, dried squat beaker. The component was mixed with a spatula until a homogenised mixture was achieved. The mixture was then transferred into a clean tungsten carbide bowl where it was milled for 90 s by a six-pod swing mill, as indicated in Figure 3.3 (a and b). Once milled, the homogenised mixture was transferred into a clean, labelled 32 mm aluminum cup with a plastic rod. The aluminum cup was pressed into a 32 mm die using a Herzog HTP 20 pressing machine (Dickie & Stocker Pty, Ltd., Johannesburg, South Africa), with a pressure of 10 tons for 2 min. After labelling, a pressed pellet were stored inside tiny zip-lock plastic bag to prevent contamination prior to analysis.



Figure 3.3. Tungsten carbide bowl used for sample preparation (a) and the obtained pressed pellets (b).

3.4.4 Preparation of Calibration Standards for X-ray Fluorescence

The new calibration method was developed by using standards of different ores with known concentrations of Zn ranging from low to high, as shown in Table 3.1. A calibration was created for the development of a new pressed pellet method. This is due to the difficulty in acquiring standards with the same matrix. The CRMs were used since they determine the correlation between elemental concentrations and X-ray intensities with known compositions. A total of 12 CRMs were selected to develop a calibration for a new pressed pellet.

The following CRMs were identified as standards: CZN-4, A590, AMIS0620, AMIS0A429, A590, 15_69, 3_98, AMIS0429, 2_83, 31_74, 5_78 and 4_77. A sample of 853_4 was used as a standard because it was previously analysed via ICP-OES. The uncertified value was used to calibrate the new method as one of the standards. This choice was made to expand the range of CRM points used in the calibration procedure, allowing for a more comprehensive evaluation of the accuracy of the method.

Table 3.1. CRM was used as a standard for calibrating the EDXRF method.

CRM ID	Certified value 95% confidence Limits (Zn)	Mineral composition
AMIS 0429	0.0126 ± 0.0026	Gold and uranium ore
2_83	2.15 ± 0.057	Zn-Pb carbonate
4_77	4.23 ± 0.05	Pb–Zn-vanadium ore
15_69	5.3 ± 0.38	Cu-Zn ore
3_98	15.3 ± 0.26	Enviro slag
AMIS0147	28.17 ± 1.48	Zn-Pb sulfide ore
A_590	34.65 ± 0.15	Zn-Pb-Sn-Ag ore
31_74	44.77 ± 0.95	Zn concentrate
AMIS0620	47.04 ± 0.17	Zn concentrate
5_78	50.7 ± 0.90	Zn concentrate
CZN-4	55.07 ± 0.49	Zn-sulfide concentrate
853_4	57 ± 0.245	Semi-massive ZnS

* Zn-Pb-Sn-Ag ore Certified value 95% confidence Limits (Pb=2.24, Sn=0.61, Ag=0.167%)

The standards were first analysed with the Turboquant screening method (Tq) pellets and Solids 60 F (A2) and copied to the new method, and accurate values were manually entered in each Zn standard for evaluation. Xepos He has Empirical Lucas Tooth Price calibration for overlapping element and matrix element corrections with measuring conditions, as indicated in Figure 3.4. The system evaluated the given concentration and the analysed value that was used to calculate or plot the calibration graph. After that, a calibration curve (intensity vs. concentration) was developed. A multichannel analyser (MCA) was used to calibrate the instrument library once a monthly to track instrumental drift and evaluate the EDXRF instrument's validity.



Figure 3.4. Xepos He EDXRF was utilised in the analysis of the pressed pellets

Table 3.2. Measuring conditions applied during the XRF analysis.

Xepos HE Measurement Conditions	Settings
Voltage	45.1 kv
Average Current	0.707 Ma
Atmosphere	Vacuum
X-ray tube	Palladium and Cobalt
Plate Correction Factor	1
Spectrometer Resolution (FWHM) at 5.89 Kev (Mn K α)	131 Ev
Lifetime	131.4 Ev
Relative Dead Time	53.20%
Zero Peak Rate	2000000 CpS
Target Current	0.708 Ma
Duration	90 s
Number of Channels	4096
Input Count Rate	651149 CpS
Lifetime (ZPR corrected)	42.1 s

3.5 Sample Preparation by Sodium Peroxide Fusion

Approximately 0.0990 to 0.1010 g and 0.1990 to 0.2010 g of Zn ore samples for different ICP-OES experiments were weighed into Zr crucibles. The samples were combined with 1.5 g of Na₂CO₃ and 0.5 g of Na₂O₂ with a spatula (method C). A Nieka G8-Series fusion machine was used to fuse the mixture at 480°C under the conditions listed in Table 3.3. During the fusion process, the samples were heated for approximately 3 min until complete melt was achieved, indicating dissolution of the sample components.

Table 3.3. Nieka fusion machine operating conditions

Gas Power (W)	Rotation speed	Cooling power	Time (min)	Temperature (°C)
10	00:00	00:00	03:30	
15	15	0	01:30	480
20	0	02:00		

Following peroxide fusion, the melt was leached with 50 mL of ultrapure water into a 250 mL beaker. After the reaction stopped, 40 mL of 65% HNO₃ was added to the beaker and left for approximately 10 min to cool, as demonstrated in Figure 3.5. A plastic rod was used to carefully remove the crucible and any remaining material by rinsing with ultrapure water. The solution was transferred into 200 mL volumetric glass flask containing 10 mL 0.2 g/L (Sc) internal standard, diluted with highly purified water with resistivity of 18.2 MΩ.cm at 25°C to the mark and analysed by using ICP-OES. In a different experiment in which the flux components were varied, three pellets of NaOH were mixed with 1.4990 to 1.5010 g of Na₂O₂ (method A) and weighed into a Zr crucible.

The same peroxide fusion procedure was followed; however, the solutions were milky, and 2 drops of hydrogen peroxide (H₂O₂) solution were added and placed on a hotplate to dissolve for 2 min. After the solution had cleared, it was allowed to cool at ambient temperature, transferred into a 200 mL volumetric flask containing 10 mL of 0.2 g/L Sc solution and diluted to appropriate volume with deionised water. Method B, approximately 0.0990 to 0.1010 g and 0.1990 to 0.2010 g were weighed into Zr crucibles and mixed with Na₂O₂. The same procedure was used to complete peroxide fusion by fusion, leaching and transfer of the mixture to a 200 mL volumetric flask containing 10 mL of 0.2 g/L Sc solution.

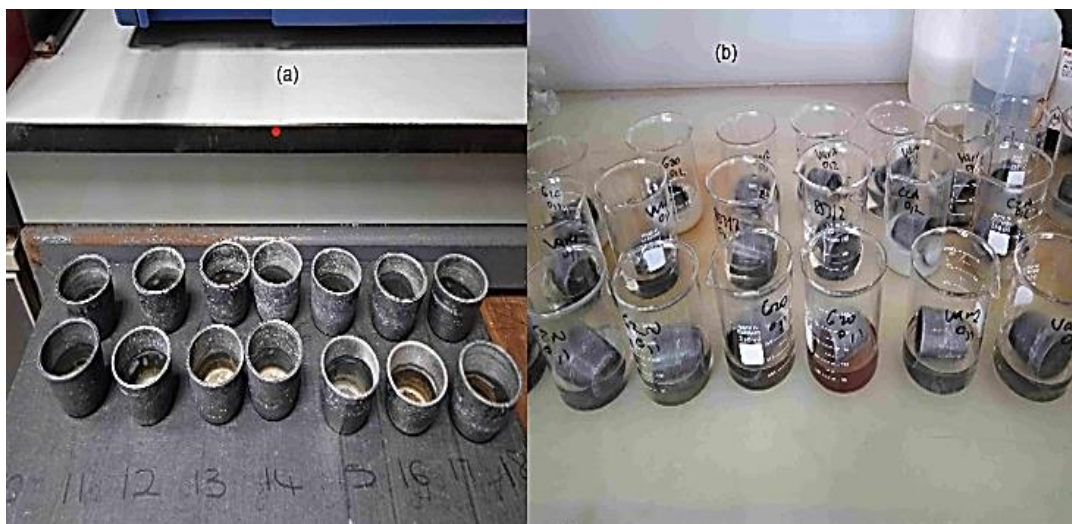


Figure 3.5. Peroxide fusion samples showing the melt in the crucible (a) and crucibles in beakers showing the leaching process (b).

3.6 Microwave-Assisted Acid Digestion Dissolution

About 0.0990 to 0.1010 g and 0.1990 to 0.2010 g samples were weighed directly into PTFE vessels, followed by the addition of concentrated 12 mL HCl and 4 mL HNO₃ to each vessel. The samples were kept in a ventilated fume hood for 15 min at ambient temperature to allow fumes to be released before sealing the vessels. The sealed vessels were then subjected to microwave digestion using the CEM MARS 6 iWave model manufactured by (CEM Corporation, Matthews, NC 28104, United States of America), as shown in Figure 3.6. The samples were subjected to microwave digestion at a maximum temperature of 200°C for 20 min, followed by a 15-min ramp-down period to cool the samples. Once the digestion was complete, the vessels were cooled and opened in a fume hood to release pressure, and the digests were quantitatively transferred into 50 mL glass volumetric flasks containing 2.5 mL of 0.2 g/L Sc solution. The solutions were diluted to the designated volume with purified water, and the digests were left overnight in a fume hood before analysis by ICP-OES.



Figure 3.6. CEM Mars6 microwave digestion instrument

3.7 Dissolution by Hotplate Acid Digestion

Approximately 0.0990 to 0.1010 g and 0.1990 to 0.2010 g were weighed directly into PTFE beakers. The samples were treated with 12 mL of concentrated HCl and 4 mL of HNO₃. Prior to digestion, the samples were kept at ambient temperature for 15 to 30 min to allow the reaction to complete. Containers were covered and refluxed on a hotplate for two hours (h) at 230°C to ensure thorough digestion. After 2 h, 15 mL of purified water was transferred in the beakers, covered with lids inside the fume hood at ambient temperature. Materials were partially dissolved, and all residues that remained at the bottom of the containers were placed inside 100 mL flasks with 5 mL of 0.2 g/L Sc solution as shown in Figure 3.7. The solutions were stored in a fume hood overnight before being analysed by ICP-OES.



Figure 3.7. Teflon beakers with acid-digested samples

3.8 Conditions of Inductively Coupled Plasma Optical Emission Spectroscopy

An Agilent 5900 ICP-OES instrument (Agilent Technologies Inc., California, United States of America) equipped with ICP-Expert software (version 7.5.4.11997) was used for the analysis of Zn, as shown in Figure 3.8. The operating conditions used were an RF power of 1.20 kW, a plasma current of 12 L.min⁻¹, an auxiliary flow of 1.00 L min⁻¹ and a sample flow rate of 0.3 mL min⁻¹. The full operating conditions are shown in Table 3.4. Analysis was performed in radial mode with high purity of 99.9998% argon 5.0 gas supplied by Afrox (Johannesburg, South Africa), which was used as the carrier gas source in the plasma. The wavelengths used to measure the analytes were selected because they gave strong signals and were less likely to be affected by interferences that could affect the results. Five wavelengths for Zn, 202.548 nm, 206.200 nm, 213.857 nm, 334.502 nm and 472.215 nm, were selected on the Agilent ICP-OES and used for the analysis, as indicated in Table 3.5.



Figure 3.8. Agilent 5900 ICP-OES instrument

Table 3.4. Agilent 5900 ICP-OES measurement conditions

Parameters	Conditions
Plasma gas	Argon
Pump speed (rpm)	12
Uptake delay (s)	25
Rinse time (s)	30
Read time (s)	5
RF power (kW)	1.2
Stabilisation time (s)	15
Viewing mode	Radial
Viewing height (mm)	8
Nebuliser flow (L/min)	0.7
Plasma flow (L/min)	12
Aux flow (L/min)	1

Table 3.5. Wavelength and intensity of the Agilent 5900 ICP-OES

Wavelength (nm)	Intrinsic Intensity
202.548	25904.6
206.2	7588.4
213.857	42500.9
334.502	2591.2
472.215	1129.2

3.9 Preparations of Calibration Standards for ICP-OES

Calibration standards for Zn ranging from 10 to 60% were prepared from single-element stock solutions. The standards were prepared from a Zn stock solution of 10 000 ppm with a matrix of HNO₃ and scandium (Sc) and topped with ultrapure water. To enable analysis throughout a concentration

range of 10 to 60%, two quality control (QC) check standards with concentrations of 15 and 50% Zn were prepared from 10000 ppm purchased from LGC Standards (Kyalami Park, Midrand). A reagent blank was prepared by concentrated HCl, internal standard and diluted to the mark by ultrapure water. The sodium in the samples from the flux was matched by the addition of about 11.0010 g of sodium chloride salt to each calibration standard. The flasks were then filled with ultrapure water and analysed with the calibrated standard with acceptance criteria as shown in Table 3.6.

Table 3.6. Acceptance Criteria for the calibration standard

Standard	Concentration (%)	Acceptance criteria (error)
STD1	60	<5%
STD2	40	<10%
STD3	20	<10%
STD4	10	<15%

3.10 Limit of detection and Limit of Quantification

Analytical performance is necessary to ensure that the instrument is suitable for its intended use and sensitivity assessment to understand its possibilities and limitations. The LOD and LOQ are used to describe the lowest concentration of the analyte that can be accurately detected by using analytical instruments. They were determined by measuring the intensities of the blanks for both ICP-OES and EDXRF techniques. The blanks were analysed in 10 replicates for both methods and used to calculate the SD. The slope was determined from both calibration curves by using equations 3.1 and 3.2.

$$\text{LOD} = (3 \times S_b) / m \quad \text{Equation (3.1)}$$

where m represents the slope of the calibration curve and S_b represents the standard deviation of the blank.

The LOQ was determined similarly to the LOD by using 10 blank replicates and standard deviations with slopes from the linear calibration curve (Equation 3.2).

$$\text{LOQ} = (10 \times S_b) / m \quad \text{Equation (3.2)}$$

3.11 Statistical Analysis by Student's t-Test

The statistic for the t-test is based on the average of the two groups. A t-test is used to determine whether a sample mean deviates from a known average. Statistical methods that compare samples provide a test critical ratio associated with the probability level (p-value). The p-value is the probability that two groups are selected that are representative of the same population, and the variation within the groups is less in comparison with the defined group. The P-value greater than 0.05 indicates that the two groups can be sampled from the same population with an equal or lower probability. Critical value for the Student's t-test, for an alpha of 0.05 in a dataset including many samples, is 1.96, as determined with the t-test table. Similar to the t-test, statistical significance is reached when the p-value is less than 0.05 and more than 95% of the standard population is on the side of the mean. Statistical comparisons (Student's t-test) were performed, and microwave acid digestion, hotplate acid digestion, peroxide fusion and pressed pellets were carried out for the determination of Zn. Student's t-test was used to evaluate the analytical results obtained.

CHAPTER FOUR: RESULTS AND DISCUSSION

This chapter aim to address the outcomes obtained and answer them according to the objectives of this study. The mineral characteristics, elemental composition, pellet method by EDXRF, peroxide fusion with various fluxes and varying masses, microwave acid digestion and hotplate acid digestion by ICP-OES have been fully explored in comparative studies of spectroscopy

4.1 Sample Characterisation of V2 and V4 by XRD

A detailed examination of the mineral structure of materials V2 and V4 is given in Table 4.1. The phase amounts and chemical formulas given as weight percentages of the important minerals that make up these samples are demonstrated in Figure 4.1. In both V2 and V4, ZnS was the major mineral as 55.7 and 55.3%, respectively. Minerals that were found in the samples were chalcopyrite (1 to 2%), pyrite (14.1 to 19.7%), quartz (0.5 to 3.9%), and calcite (1 to 1.65%) between the two samples as illustrated in Figure 4.1. Although ZnS is the major component of the samples, there are mineralogical difference between them in that V2 contains higher amounts of pyrite and chalcopyrite while V4 contains more dolomite, quartz and calcite. These indicated that the compositions of both samples are not the same. The other findings are available in Appendix 3.

Table 4.1. Chemical formulas and phase amounts of V2 and V4

Mineral	Chemical formula	V2 (wt %)	V4 (wt %)
Sphalerite	ZnS	55.7	55.3
Dolomite	CaMg(CO ₃) ₂	14.9	22.7
Pyrite	FeS ₂	19.7	14.1
Chalcopyrite	CuFeS ₂	3.8	2
Quartz	SiO ₂	0.5	3.9
Calcite	CaCO ₃	1	1.6

There is a noticeable difference in the dolomite $\text{CaMg}(\text{CO}_3)_2$ composition between the two samples, V4 has a peak of 22.7%, whereas V2 has a peak of 14.9%, as demonstrated in Figure 4.1. Pyrite compound, which is a sulfide mineral, has a high content of 19.7% in V2 and 14.1% in V4. The samples show varying weight percentages of minor chalcopyrite, with V2 containing 3.8% and V4 comprising 2%. The amount of quartz in V4 was 3.9%, whereas that in V2 was only 0.5%. Almost all the mineral characteristics were identified by Mongoljiibuu,(2022) on a complex skarn ore.

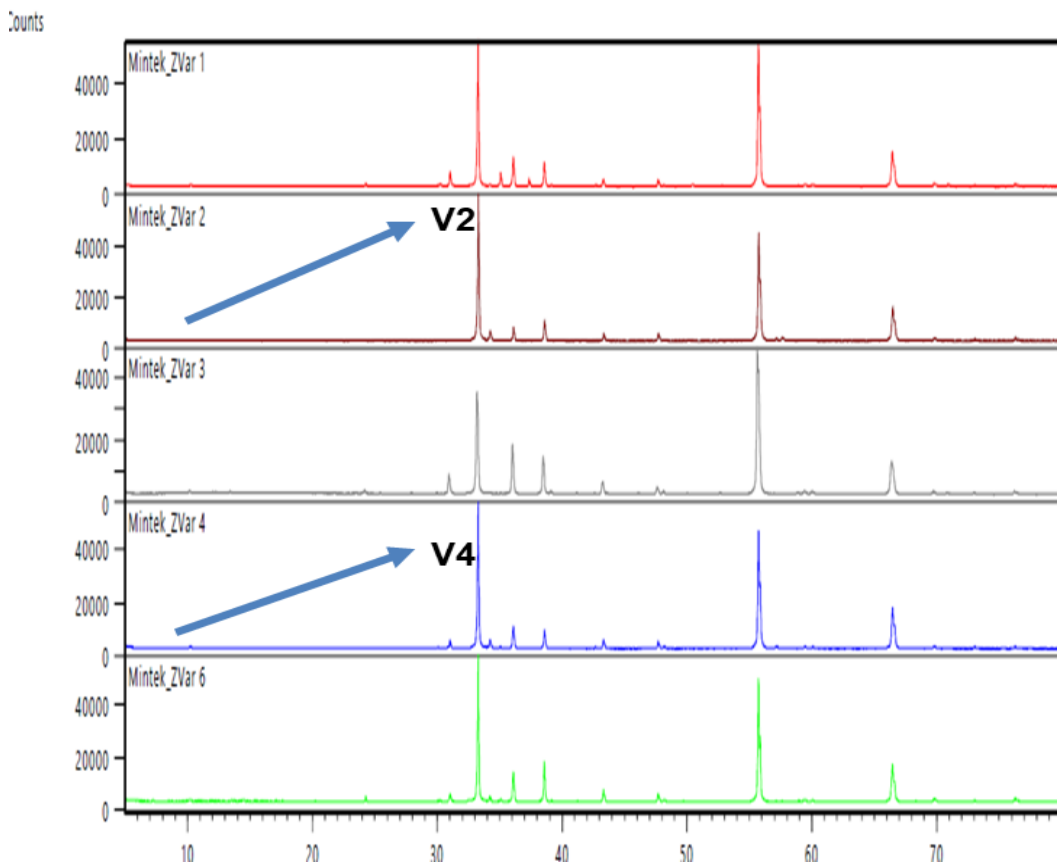


Figure 4.1. Characteristic diffraction pattern of the ore displaying the mineral phases

4.2 Elemental Composition of V2 and V4 by EDXRF and a Handheld X-Met 8000 by Powder Scan

The X-Met8000 (handheld) and Xepos He (benchtop) EDX analyses were utilised to compare the chemical analysis results of the two Zn ore samples (V2 and V4) and CZN-4 and AMIS0620. The CRMs were included for validation of the results acquired. V2 has high (Zn, S, Fe, Ca, Cu, Mg and Si) contents, whereas V4 has (Zn, S, Fe, Si, Ca, Mg and Cu) contents as shown in Figure 4.2. The findings revealed the same trend in elemental concentrations for major elements from Zn to Fe; however, a minor variation in Ca, Cu, Si and Mg was observed. The difference in elemental composition between the two forms may indicate distinct geological origins or depositional settings. Additionally, they noted certain mineralogical differences between the two types, and these findings aligned with the XRD analytical results.

All samples acquired Cd content of less than 0.2%, as reported by Tembo et al., (2006) when AAS was used, and Cook et al., (2009) reported the same results when ICP-MS was used. Comparing benchtop and handheld methods for all the CRMs and Zn ore samples, it was observed that the benchtop method resulted in higher concentrations of most of the elements than the handheld analyser. This is because benchtop instruments are more sensitive, have lower detection limits and better detector resolutions than handheld techniques are. Benchtop methods take longer in sample measurement, which increases the accuracy of the results and may lead to higher recorded concentrations.

A handheld analyser often has issues with matrix effects, whereas a benchtop analyser is better equipped to correct for matrix effects. As shown in Figure 4.3 the results for Fe, Cd, Ca and Cu, are comparable. The results obtained were lower than the CRM values. This might be because in powder samples, there is a possibility of spaces between the coarse grains and

large particles, whereas in pressed pellets with a binder, the binder fills in the gaps within the coarse grains, possibly minimising the amount of pores and particle sizes (Mijatović et al., 2023). Handheld measurement were found to be accurate and less variable than the benchtop values (Bliujienė et al., 2023). However, this was due to the shavings material, which was not homogenous during the analysis. This highlights one of the limitations of using XRF dependability as a surface measurement technique.

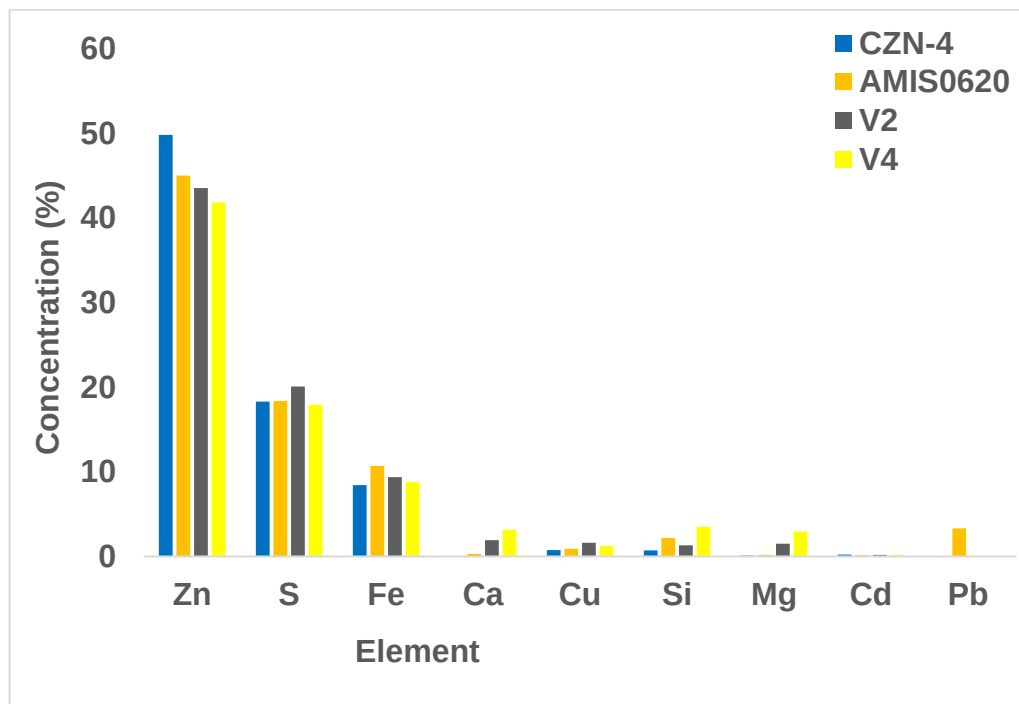


Figure 4.2. Elemental composition at the benchtop

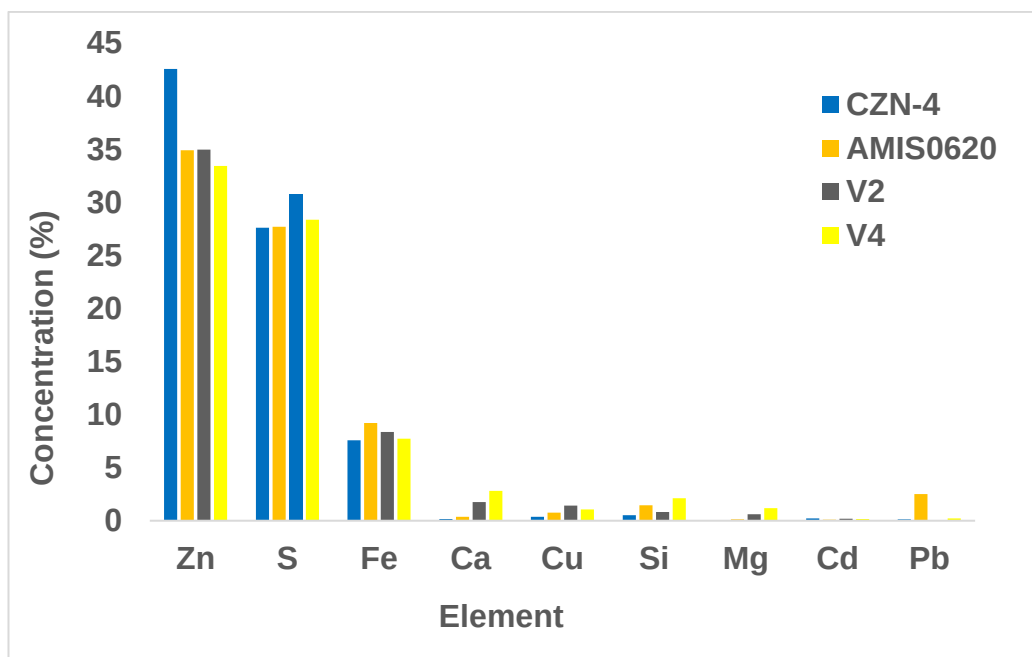


Figure 4.3. Elemental composition by handheld

4.3 Linear Calibration Curve for the Pressed Pellet Method by X-ray Fluorescence

Spectro software was used to create a calibration curve based on the given and calculated values of Zn concentrations according to the different mineral compositions of the standards. The acquired values of the standards after evaluation are demonstrated in Table 4.2. Standard 2_83 has high variations in results obtained and this could be due to the matrix effect as it can change the x-ray absorption or fluorescence yield by causing a higher reading because the standard density or composition differs from the calibration standards. Regardless of the standards used that were not of the same matrix, the correlation coefficient (R^2) was 0.999, which indicates good linearity of the calibration curve, as demonstrated in Figure 4.4. The R^2 was closer to one, which showed that the concentration of Zn is directly proportional to the X-ray intensity. This finding showed that the method is robust, and it can accommodate different sample compositions while maintaining high linearity.

Table 4.2. The Obtained results of the XRF calibration standards

Standard	Certified value 95% confidence Limits	Obtained results (%)
AMIS 0429	0.0126 ± 0.0026	0.01
2_83	2.15 ± 0.057	4.35
4_77	4.23 ± 0.05	4.15
15_69	5.3 ± 0.38	5.44
3_98	15.3 ± 0.26	14.77
AMIS0147	28.17 ± 1.48	33.34
A_590	34.65 ± 0.15	36.41
31_74	44.77 ± 0.95	42.87
AMIS0620	47.04 ± 0.17	44.63
5_78	50.7 ± 0.90	47.67
CZN-4	55.07 ± 0.49	55.04
853_4	57 ± 0.245	56.43

4.3.1 Limit of Detection and Limit of Quantification

The limit of detection (LOD) and limit of quantification (LOQ) characterise good sensitivity, accuracy and dependability of a measurement technique. The LOD and LOQ are very important for evaluating method sensitivity, especially for low concentrations. However, they can also influence the determination of high-concentration materials. It is crucial that the method maintains accuracy and precision across its calibration range and effectively handles any potential matrix effects or high concentration.

The slopes for both techniques were 12159 and 6884 for EDXRF and ICP-OES, respectively, as shown in Table 4.3. This result revealed how the measured signal changes with concentration and was crucial for quantifying analyte concentrations based on the calibration data. The LOD for EDXRF was 0.1533%, with a LOQ of 0.511% whereas for the ICP-OES method, the LOD was 0.0108%, with a LOQ of 0.0350%. The R^2 values for both the

instruments calibrations were found to be similar at 0.9993. These findings indicate that the techniques have great linearity and are capable of detecting the Zn concentration.

Table 4.3. LODs and LOQs for Zn determined by EDXRF and ICP-OES

Zn	EDXRF	ICP-OES
Slope	12159	6884
Intercept	8698.2	1668.7
R 2	0.9993	0.9993
Concentration range	0-60%	0-60%
LOD	0.1533	0.0108
LOQ	0.511	0.036

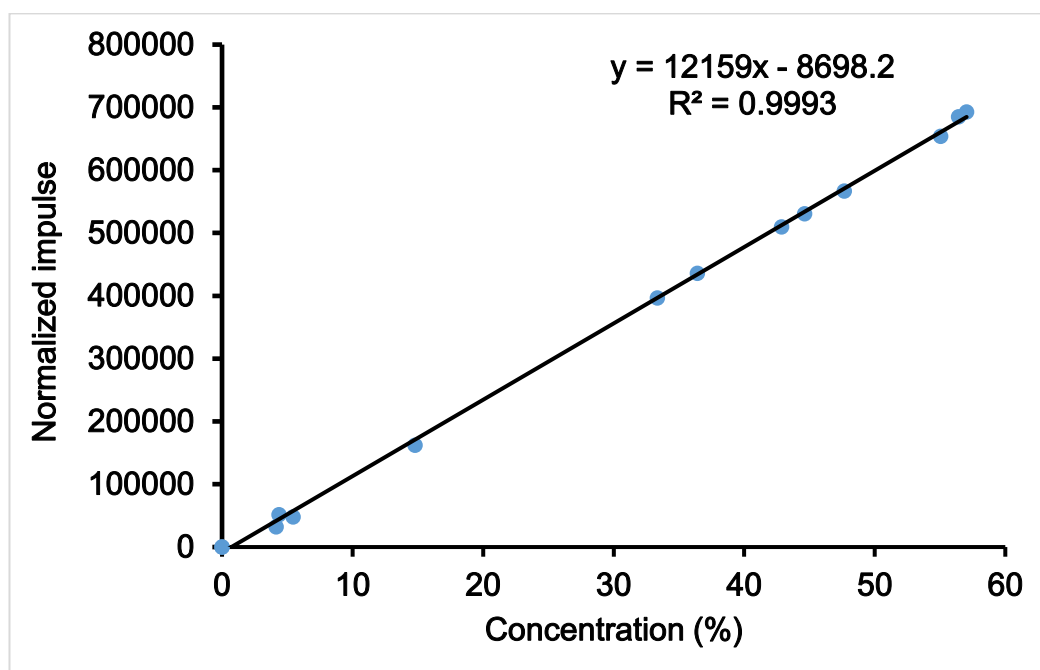


Figure 4.4. Zn linear calibration curve obtained by EDXRF

4.4 Performance of the CRMs by the Pressed Pellets Method

Two CRMs with different mineral characteristics, CZN-4 and AMIS0620, were used to validate the pressed pellet method. The RSD was used to

demonstrate how precise and reproducible the measurement values reflected the reliability and consistency of the method. The result obtained from the pressed pellet method for CZN-4 was 54.64%, which is the mean average concentration, as presented in Figure 4.5. The data indicated the extent to which the method is reproducible and repeatable, with a good RSD of 0.95% and a percentage recovery of 99.22%. The obtained value is close to the accurate value and within the CRM boundaries.

A pressed pellet approach was chosen over the fused beads because of the high amount of pyrite in the materials that can potentially damage the Pt crucibles. The samples used in this study contained high levels of Zn, S and Fe, which are poisons and can progressively penetrate into the Pt grain boundaries at high temperatures. Processing the S minerals in Pt crucibles is dangerous, as single fusion can destroy the crucibles by Lupton et al., (1997) and Willis, (2010). Accuracy was assessed by comparing obtained values with verified values. Precision with reproducibility were evaluated by RSD and percentage recovery calculations. The percentage recovery of each value was determined using six replicates, as expressed in Equation (4).

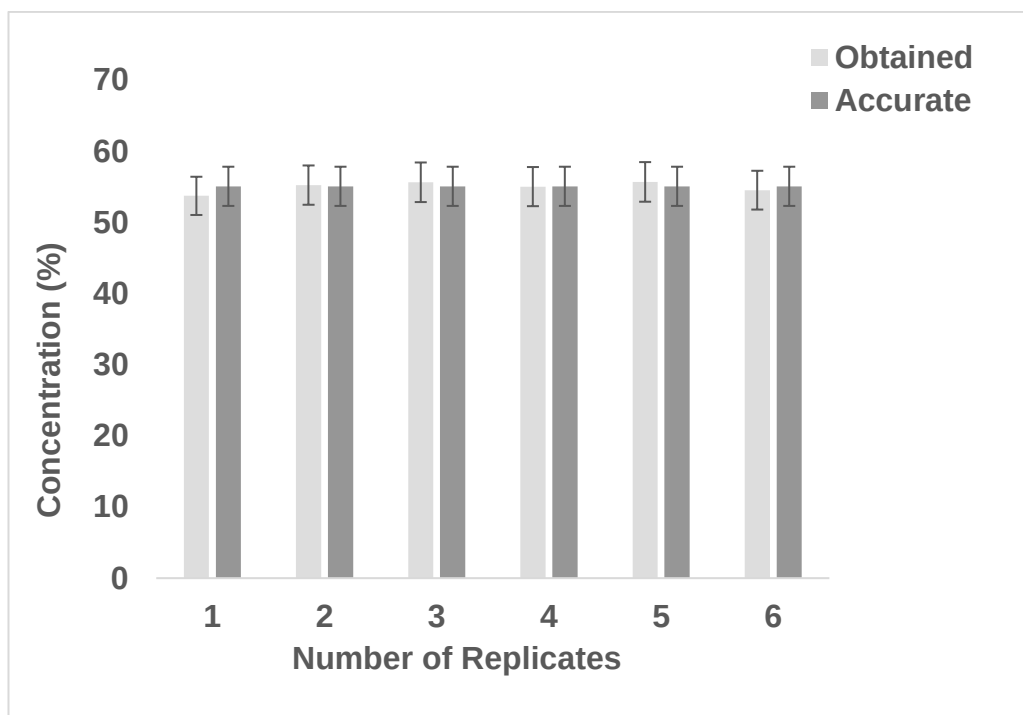


Figure 4.5. CZN-4 performance for the pressed pellet method

The concentration of Zn for AMIS0620 was 46.52%, with an RSD of 1.66%, which appeared to be slightly outside the boundaries but very close to the accurate value of 47.04%, as shown in Figure 4.6. However, AMIS620 produced a slightly lower level of accuracy and precision than with CZN-4, which was demonstrated by the higher RSD obtained. The results revealed that the percentage recovery of CZN-4 was greater than that of AMIS0620 with 99.22 to 98.89% respectively. There was a difference in the percentage recovery rate, which suggests that CZN-4 was more efficient at extracting Zn during the analysis. The results obtained by Toniazzo & Lentz, (2018) indicated high recovery of Zn by greater than 10% compared with that of the CRMs used while in this study the data were lower. The overall performance of both CRMs was satisfactory, with percentage recoveries within the acceptable range of 80 to 120%, which confirms the reliability of the pressed pellet method.

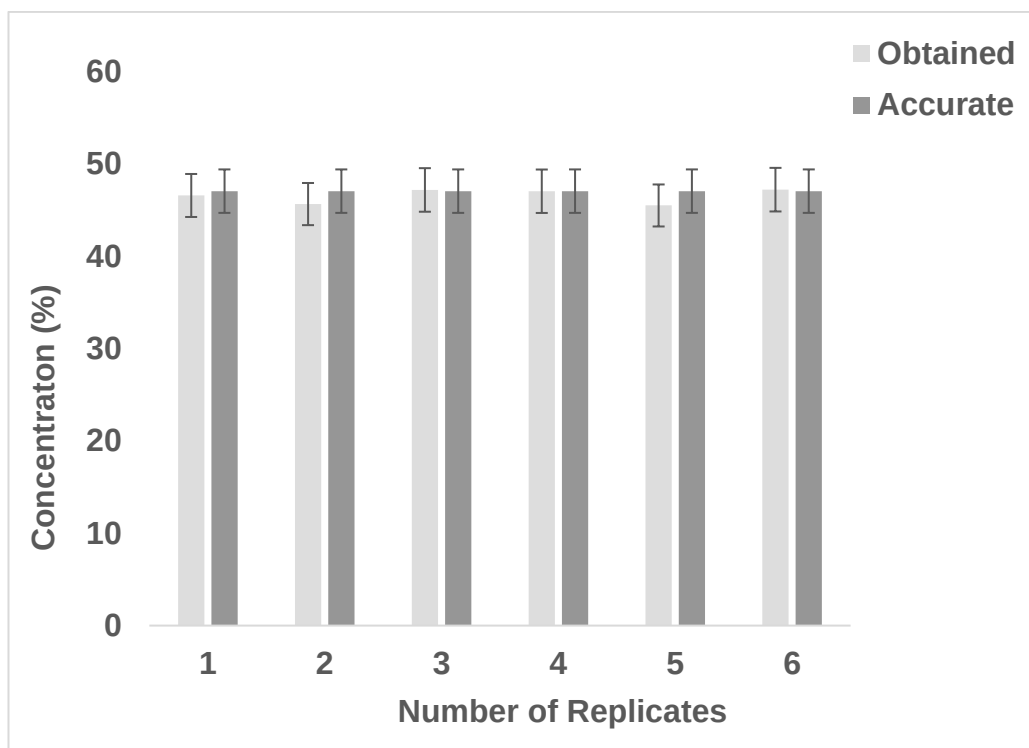


Figure 4.6. The performance of AMIS0620 by the pressed pellet method

4.4.1 Limitation of Wavelength Dispersive X-ray Fluorescence

The calibration was developed in a WDXRF Primus IV ZSX, Rigaku with ZSX Guidance expert system software. It is a sequential instrument with an empirical calibration method, and the results acquired for the CRMs were overestimated using the same standard as of EDXRF. The R^2 was 0.996. However, the instrument issued an error of intensities larger than the upper limit of counting loss corrections, which seemed to be one of the limitations of the WDXRF. The mean average concentration of CZN was 60.66%, with an RSD of 1.11%, whereas that of AMIS0620 was 84.97%, with an RSD of 0.11. Most of standards in the calibration curve had calculated values that did not agree well with the true values hence the EDXRF was used. The full outcomes are presented in Appendix 2.

$$\% \text{ Recovery} = \frac{\text{Experimental value}}{\text{Certified value}} \times 100 \quad \text{Equation (4.1)}$$

4.5 Determination of Zinc by Inductively Coupled Plasma Optical Emission Spectroscopy

The CRMs and Zn material were first investigated using all five wavelengths available on the Agilent 5900 ICP-OES instrument, which were used to guarantee a thorough analysis of the analytical data. This approach aim to capture any potential variables or trends across different wavelengths of samples and internal standards. The different wavelengths of Zn available in the instrument were (202.548 nm, 206.200 nm, 213.857 nm, 334.502 nm and 472.215 nm), whereas the wavelengths (335.372, 357.253, 361.383 and 363.074 nm) were for the Sc internal standard. The CRMs were examined using all wavelengths to determined and verify which one had the highest recovery of Zn. An internal standard of 361.383 nm and a wavelength of 472.215 nm were chosen due to the consistency and accuracy of the findings produced, as demonstrated in Figure 4.7. Performance of the calibration curve served as a critical tool in determining the most accurate and reliable wavelength for quantifying the element of interest. No interference corrections were applied in the evaluation of the analyte peaks in the samples since there was no possibility of interference.

The wavelength of 472.215 nm resulted in the best linearity, sensitivity, and accuracy for the quantification of high Zn concentrations. This wavelength proved the quality of the components across a variety of various sample preparations, ensuring consistent and reliable findings. Furthermore, there was a strong degree of linear relationships with the obtained measurements and actual concentrations at the chosen wavelengths, as evidenced by R^2 of 0.989 to 0.999. However, the high errors were only noticeable at wavelengths other than 472.215 nm. Compared with standard addition and direct calibration methods, the internal standard calibration technique is regarded as the most recommended method for matrix correction because of its precision, accuracy and cost effectiveness (Chiweshe et al., 2016).

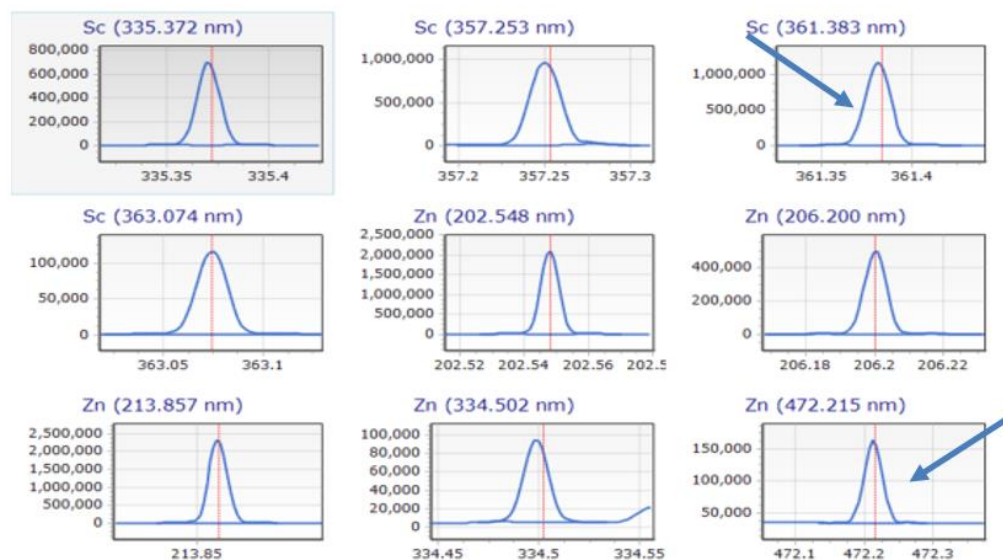


Figure 4.7. Peaks of the analyte and internal standard showing no interference in a sample

4.5.1 Linear Calibration Curve for Inductively Coupled Plasma Optical Emission Spectroscopy

Four standards ranging from 10 to 60% were used to develop a calibration curve and analysed by ICP-OES. Standard 1 achieved a concentration of 59.64%, standard 2 reached 40.65%, standard 3 reached 20.03% and standard 4 reached 10.02%, as tabulated in Table 4.4. The obtained data were very close to the true values, with errors of less than 2% across all the standards. Low percentage error produced indicated that the calibration curve is highly accurate and linear. Linearity of the curve demonstrated that the method is well suited for quantifying analyte concentrations in a variety of applications. Additionally, the method is more precise, reliable and effective. The R^2 was 0.999, which validated good linearity and accuracy of the method, as demonstrated in Figure 4.8.

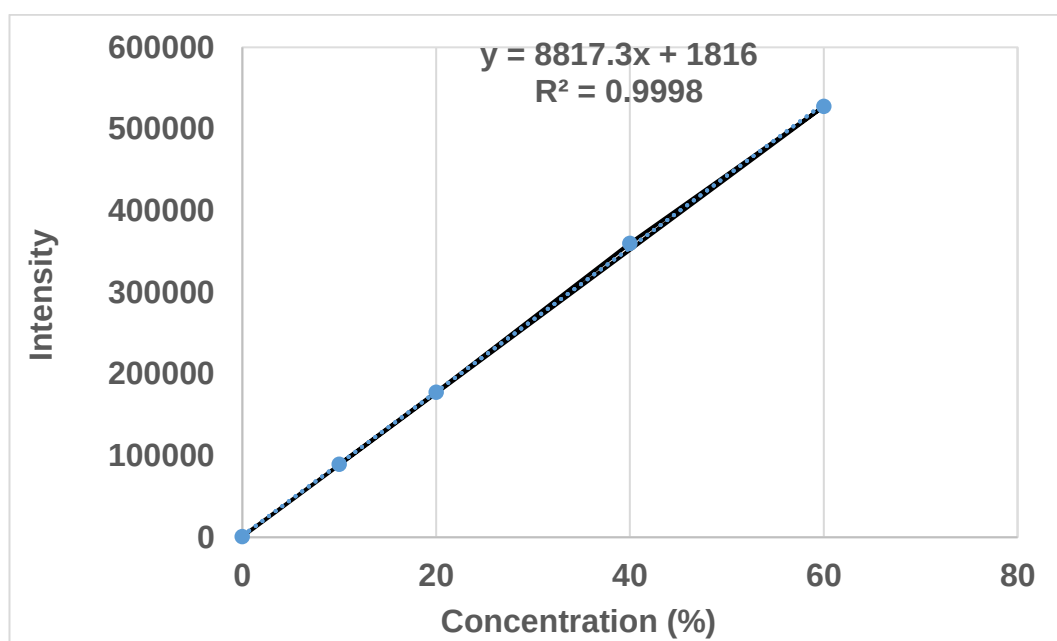


Figure 4.8. Wavelength of 472.215 nm used for Zn determination

Table 4.4. Obtained results for the calibration standards

STD	Concentration		% Error
	(%)	Obtained Concentration (%)	
Blank	0	0.00	
STD1	60	59.64	0.61
STD2	40	40.65	1.62
STD3	20	20.03	0.14
STD4	10	10.02	0.2

4.5.2 Performance of the Certified Reference Materials by ICP-OES

The findings obtained from mass variation experiments between 0.1 and 0.2 g were based on how well the CRMs performed. Precision was assessed as a percentage recovery by comparing the measured concentrations with the approved values. All the wavelengths were used for the analysis of the reagent blank, CZN-4 and AMIS0620 until 472.215 nm was satisfactorily identified as an appropriate line for the investigation. The wavelength used was selected on the basis of the stable internal standard, the passing quality check standards of 15 and 50 concentrations, the low concentration of the reagent blank and the passing CRMs. The wavelength of 472.215 nm ensured reliable and precise quantification of Zn by meeting precise quality control standards and providing accurate results compared with the verified values.

4.5.3 Performance of CZN-4 and AMIS0620 by Microwave Acid Digestion

The effectiveness of the microwave acid digestion technique was assessed by CRMs to validate the process. The results obtained indicated that CZN-4 produced a Zn concentration of 54.98% with an RSD of 1.16 and a percentage recovery of 99.84% at 0.1 g and 100.4% with an average measured concentration of 55.30% and an RSD of 0.45 at 0.2 g. There was no significant difference in the outcome, as demonstrated in Figure 4.10. The results indicated that the performance of the method for both masses was consistent and did not significantly differ, as shown in Figure 4.9 and Table 4.5. The findings investigated by (Florian et al., 1998) indicated that the effectiveness of the microwave-assisted leaching method for quantifying heavy metals in sediments, soils and sludge was investigated. The research has examined how leaching temperature and duration affect element recovery in the extraction of eight elements, including Zn, using aqua regia and the improved nitric acid (HNO_3) procedure (EPA method 305) for four certified reference materials (CRMs). The findings showed that the overall extraction efficiency was improved by increasing the temperature and duration, although this effect varied with respect to the particular components and techniques used.

Microwave acid digestion has the advantages of complete dissolution of the material. It is efficient in digesting the materials in different tubes and has the ability to break down complicated matrices, such as sediments and soils, that contain organic materials, silicates and oxides Hassan et al., (2007). However, it is expected that the results from this technique should yield higher recoveries, as Chen & Ma (2001) and Florian et al., (1998) obtained the same analytical results. This could be attributed to the smaller and lower volatilisation losses of components during the microwave acid digestion approach.

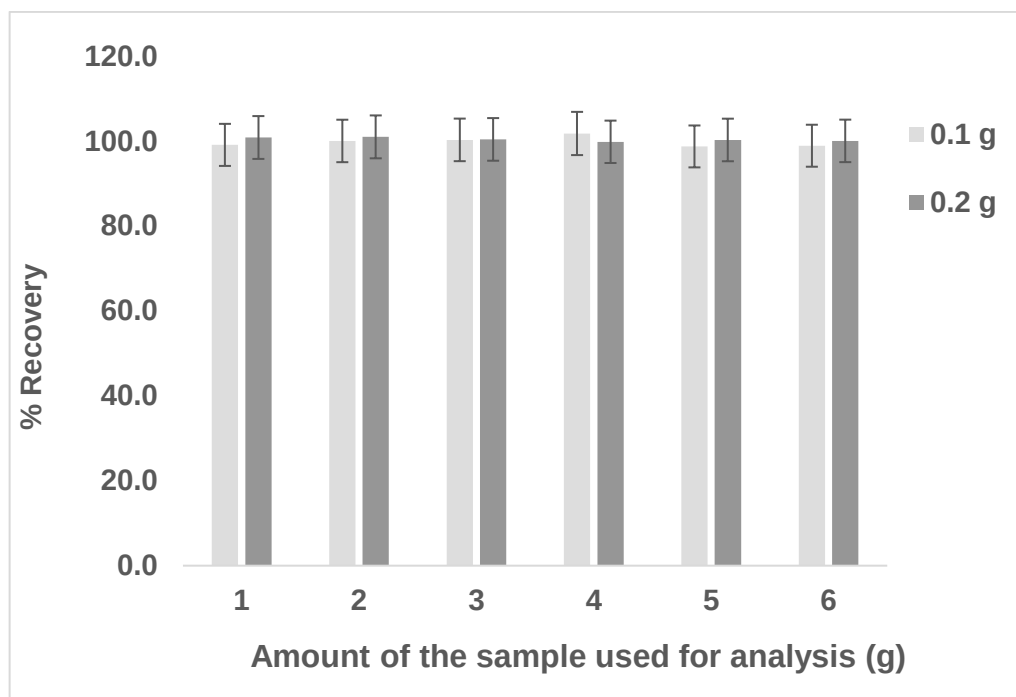


Figure 4.9. Performance of CZN-4 at 0.1 and 0.2 g for microwave energy

4.5.4 Statistical Results for CZN-4 after Microwave Acid Digestion

The t-test results do not support the null hypothesis because there is no variation in the two masses. The p-value was 0.17 for one-tailed and 0.34 for two-tailed, which is significantly greater than one normal significance level of 0.05, indicating that the difference between the means was not statistically significant, as shown in Table 4.5.

Table 4.5. Performance of microwaves for CZN-4

CZN-4	0.1 g	0.2 g
Mean	54.98	55.3
Variance	0.404	0.06
Observations	6	6
Pearson Correlation	-0.33	
Hypothesised Difference	Mean 0	
df	5	
t Stat	-1.05	
P(T<=t) one-tail	0.17	
t Critical one-tail	2.02	
P(T<=t) two-tail	0.34	
t Critical two-tail	2.57	

4.5.5 Performance of AMIS0620 at 0.1 and 0.2 g for Microwaves

The concentration of AMIS062 was found to be 46.87 and 46.91% with recovery rates of 99.64 and 99.72% at 0.1 and 0.2 g respectively as demonstrated in Figure 4.10. Obtained outcomes indicate that the approach was robust because there was no effect on mass variations which demonstrated high precision, with an RSD of less than 0.60%. The percentage recovery was within 80 to 120% as this was also reported by Florian et al.(1998), who reported that aqua regia was more effective leaching reagent for removing metals from geological samples.

Aqua regia is capable of breaking down ores, sulfides, silicates and alloys Hu & Qi, (2013). The RSDs produced were less than 5% when microwave acid digestion was used, which was also reported by Sastre et al. (2002). A lower RSD of less than 2% and high percentage recoveries demonstrated

the good precision of the results. Hassan et al., (2007) reported high recoveries of almost all the elements, including Zn, by using HNO₃ and HCl for different matrices of samples with ICP-MS.

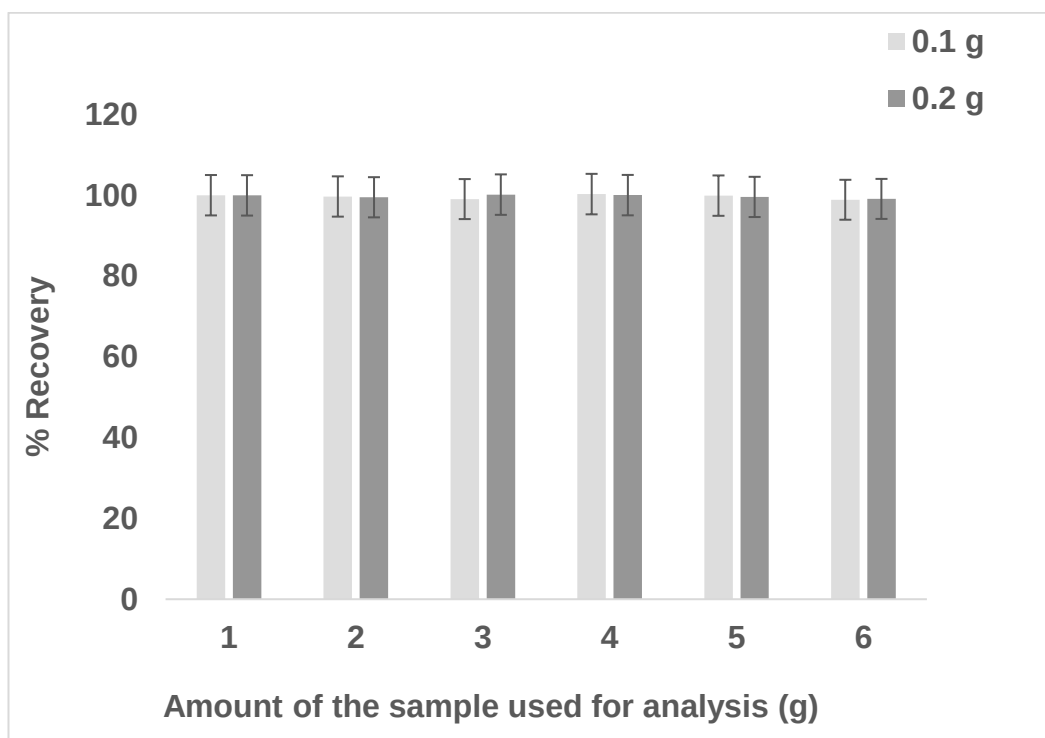


Figure 4.10. Performance of AMIS0620 at 0.1 and 0.2 g for microwave acid digestion

4.5.6 Statistical results for AMIS0620 by Microwave Acid Digestion

The null hypothesis cannot be excluded because there was no considerable variation of the masses used. Observed variation of 46.87% and 46.91% demonstrated no remarkable variations since the p-values of 0.36 and 0.71 for two-tailed analyses. They are both above the accepted significance level of 0.05. The p-value was discovered as greater than 0.05, which indicated that there was no major difference in acquired findings, as illustrated in Table 4.6.

Table 4.6. Statistical results for AMIS0620 for microwave acid digestion

AMIS0620	0.1 g	0.2 g
Mean	46.87	46.91
Variance	0.07	0.04
Observations	6	6
Pearson Correlation	0.41	
Hypothesised Mean Difference	0	
df	5	
t Stat	-0.39	
P(T<=t) one-tail	0.36	
t Critical one-tail	2.01	
P(T<=t) two-tail	0.71	
t Critical two-tail	2.57	

4.5.7 Performance of CZN-4 and AMIS0620 by Hotplate Acid Digestion.

The results produced are very close to the accuracy for CZN-4 at 0.1 g, with a measured average concentration of 53.76%, an RSD of 2.13 and 97.62% recovery. At 0.2 g, the concentration was recovered to 53.48%, with an RSD of 2.85% and a percentage recovery of 97.11%. The results showed that the method is robust. Both results are lower and out of the CRM bound, as indicated in Figure 4.11. Using aqua regia digestion to dissolve samples normally results in a stable process that only permits partial digestion Mijatović et al., (2023) when hotplate acid digestion is used.

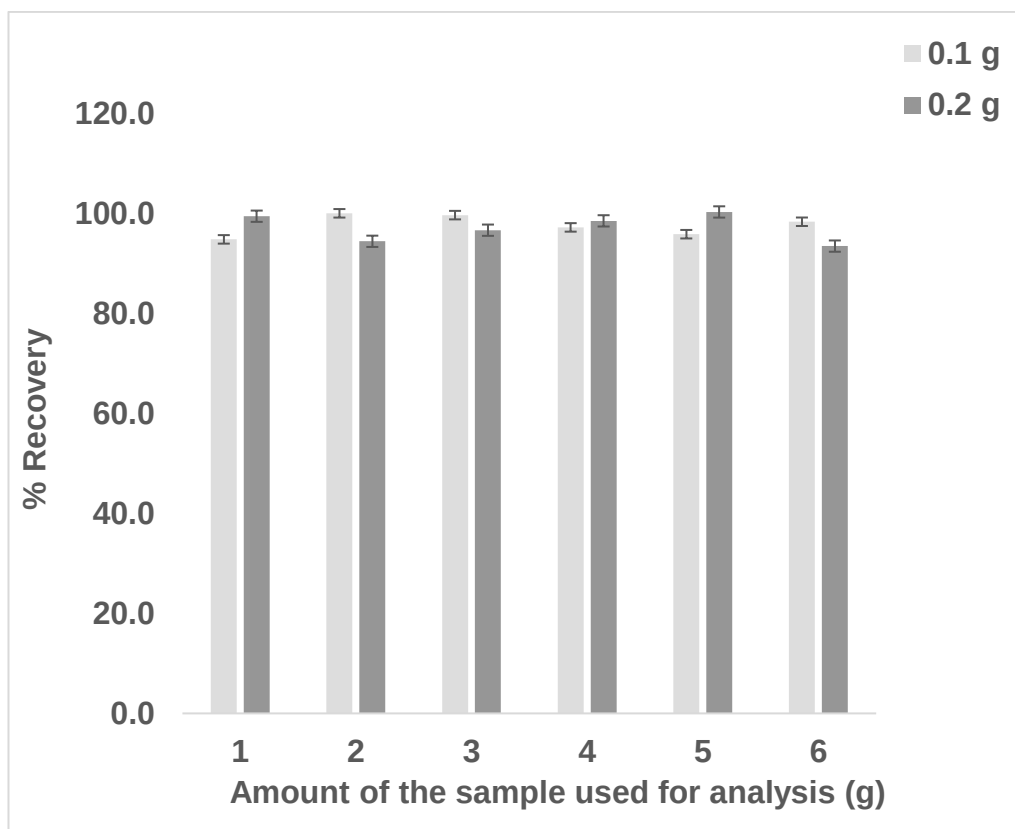


Figure 4.11. The performance of CZN-4 at 0.1 and 0.2 g masses for the hot plate.

4.5.8 Statistical Results for AMIS0620 by Hotplate Acid Digestion

The null hypothesis cannot be rejected for one-tailed and two-tailed due to both one-tail and two-tail p-values (0.40 and 0.79). Various masses do not significantly affect the results since the p-value is greater than 0.05, indicating that the two groups do not differ statistically, as demonstrated in Table 4.7.

Table 4.7. Statistical results for CZN-4 for hotplate acid digestion

CZN-4	0.1 g	0.2 g
Mean	53.76	53.48
Variance	1.31	2.32
Observations	6	6
Pearson Correlation	-0.79	
Hypothesised Mean Difference	0	
df	5	
t Stat	0.27	
P(T<=t) one-tail	0.4	
t Critical one-tail	2.02	
P(T<=t) two-tail	0.79	
t Critical two-tail	2.57	

4.5.9 Comparison of Masses for AMIS0620 for Hotplate

An average percentage recovery of 98.19% with an RSD of 2.40% at 0.1 g was acquired, and at 0.2 g, a recovery of 97.53% was produced with an RSD of 3.88% for AMIS0620. The results indicated notable variations in terms of differences in the masses and the measured values, as shown in Figure 4.12. Overall, the analysis demonstrated that the analytical technique employed is accurate and precise. However, the percentage recoveries of AMIS0620 are within 80 to 120% with RSD values of less than 5%. The majority of rock and tailings samples are unsuccessfully to go under digestion process using hotplate technique discovered by (Han et al., 2021). The slightly higher RSD achieved by the hotplate acid digestion method than the other methods might be due to inconsistency in the results caused by partial digestion, oxidation or loss of volatile components in this process, as also observed by Balaram, (2021) and Da Silva et al., (2014).

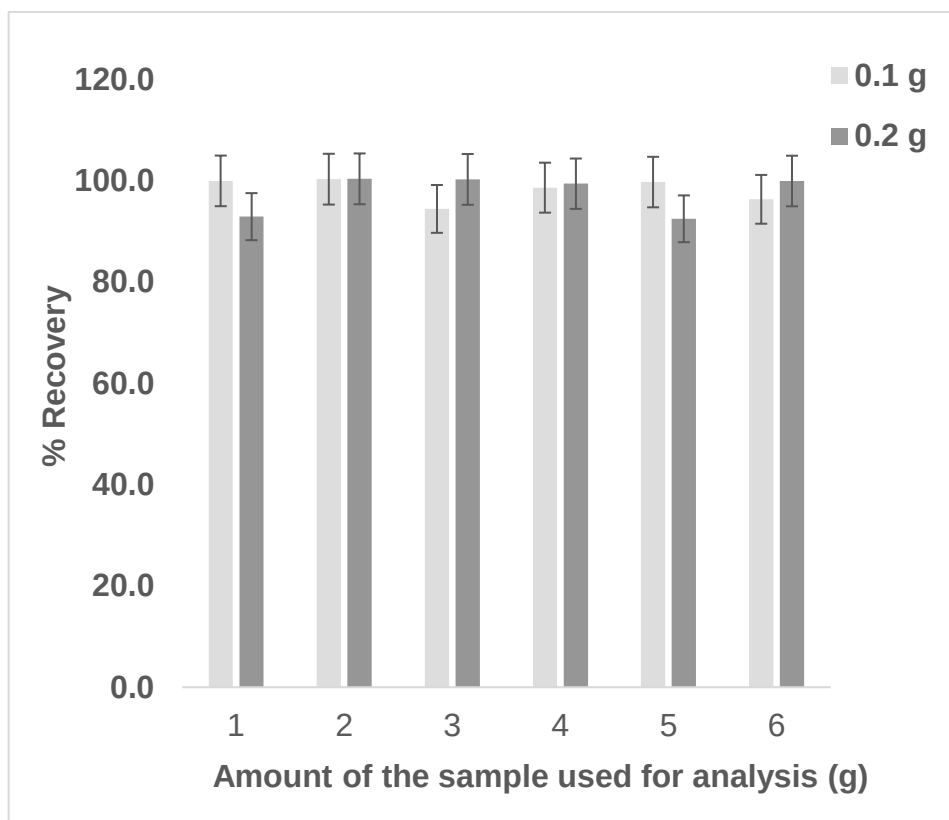


Figure 4.12. Comparison of various sample masses (0.1 g, 0.2 g) of AMIS0620 analysed by hotplate digestion, demonstrating how sample mass affects accuracy and recovery rates.

4.5.10 Statistical Results for AMIS0620 by Hotplate Acid Digestion.

The hypothesis was not rejected based on results obtained as shown in Table 4. P-value of 0.30 and 0.39 for the one-tail test and 0.77 for the two-tail test indicate that the difference between the mean values (46.19 and 45.88%) was not statistically significant.

Table 4.8. Statistical results for AMIS0620 by hotplate digestion

AMIS0620	0.1 g	0.2 g
Mean	46.19	45.88
Variance	1.23	3.17
Observations	6	6
Pearson Correlation	-0.54	
Hypothesised Mean Difference	0	
df	5	
t Stat	0.3	
P(T<=t) one-tail	0.39	
t Critical one-tail	2.02	
P(T<=t) two-tail	0.77	
t Critical two-tail	2.57	

4.5.11 Performance of CZN-4 and AMIS0620 by Peroxide Fusion

Methods

Three Na_2O_2 fusion techniques were investigated by an ICP-OES instrument with different sample masses and various combinations of fluxes. The Na_2O_2 is a strong oxidising agent for sulfide materials, Pt alloys and minerals such as Zr, Cr and Sn. These Na_2O_2 fusion methods include Na_2O_2 and NaOH pellets (method A), Na_2O_2 granules (method B) and Na_2CO_3 and Na_2O_2 (method C) with sample masses of 0.1 and 0.2 g,

respectively. One of the most widely used digestive reagents HNO_3 , served as the main oxidant for the breakdown of organic materials.

The performances of the two different CRMs were used to select the most effective method. Method A for CZN-4, yielded percentage recovery of 98.82 and 99.07%, with RSDs of 1.33 and 1.23%, at 0.1 g and 0.2 g, respectively. A recovery of 99.49% was acquired and an RSD of 0.55 was achieved at 0.1 g for AMIS0620 while at 0.2 g the recovery rate produced was 99.09% and an RSD of 0.87%. The variation in mass utilised showed no effect on the results obtained.

A CZN-4 using method B had a recovery of 89.92% at 0.1 g, with a mean average of 49.63% and an RSD of 0.23, whereas the mean of 50.76% at 0.2 g had an RSD of 1.72% and a percentage recovery of 92.17%, as indicated in Figure 4.13. The recovery was 91.28% for 0.1 g, with a measured value of 42.94% and an RSD of 0.34 for AMIS0620, as shown in Figure 4.14. At 0.2 g, the recovery was 88.63%, with an RSD of 3.26 and an average of 41.69%. Method C resulted in a percentage recovery of 86.16% at 0.1 g for CZN-4 and 84.58% at 0.2 g, whereas the recoveries rate for AMIS0620 were 88.50% at 0.1 g and 82.29% at 0.2 g, with an RSD of less than 6%. However, all the methods resulted in good recoveries ranging from 80 to 120% for all the CRMs. There was no significant variation between the recoveries obtained from 0.1 and 0.2 g. Overall the findings of peroxide fusion techniques indicated lower recovery of Zn with CRMs results not comparing with the accurate values.

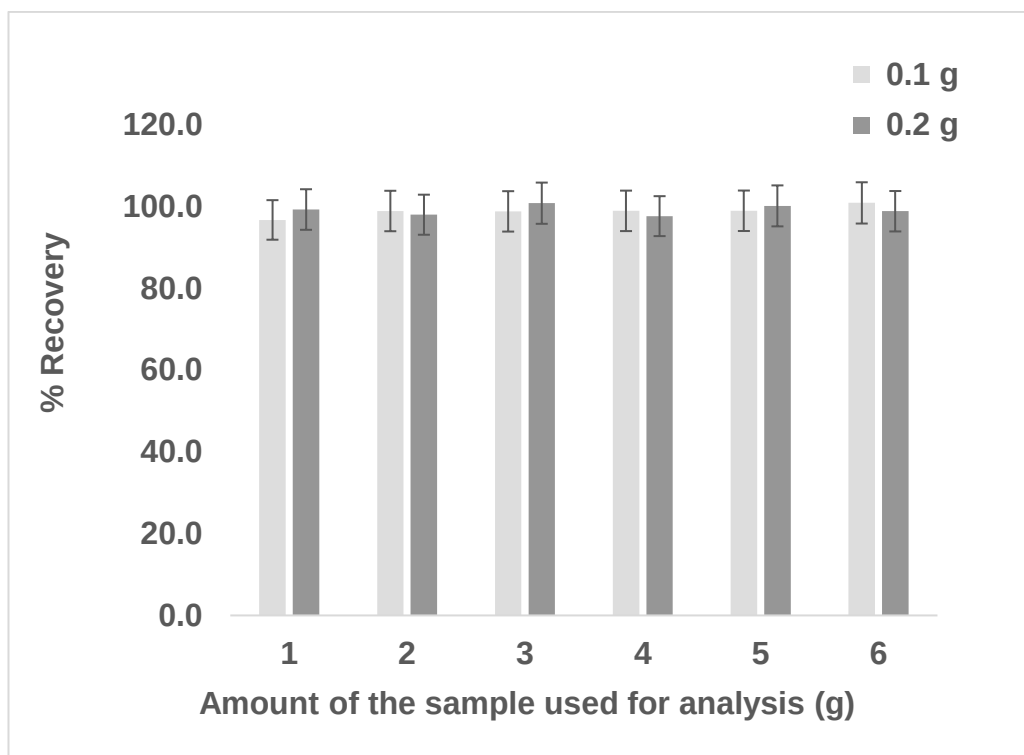


Figure 4.13. Performance of CZN-4 for Method A at 0.1 and 0.2 g

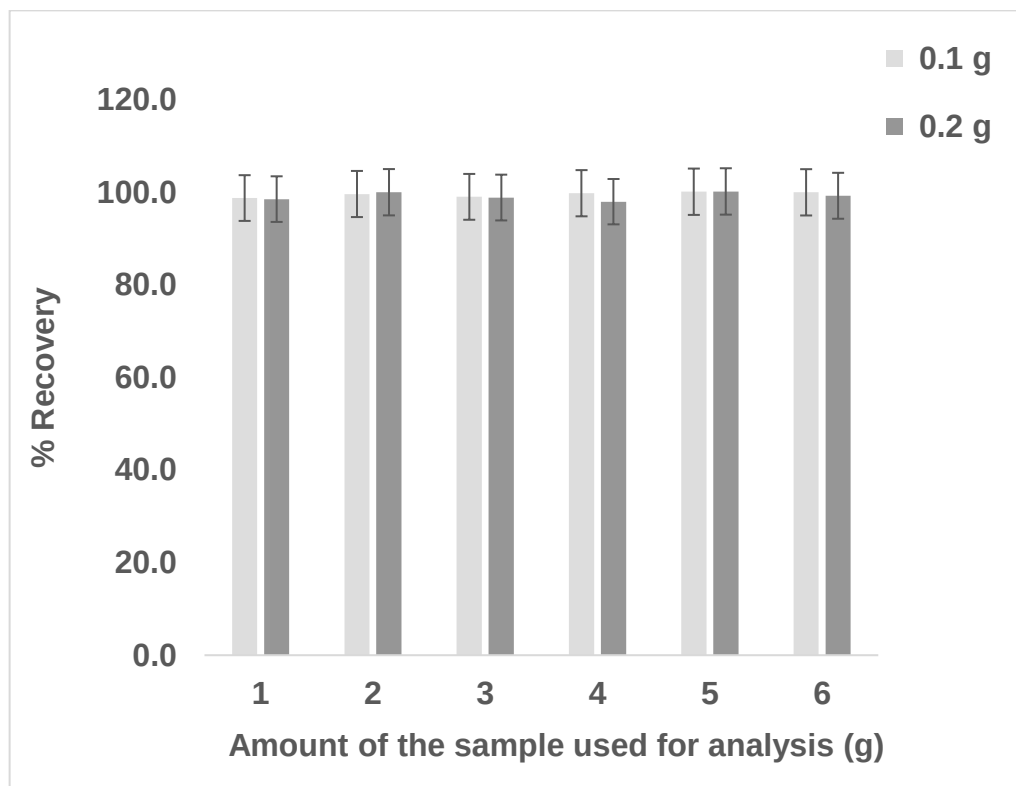


Figure 4.14. Performance of AMIS0620 for 0.1 and 0.2 g for Method A

4.5.11.1 Effects of Various Fluxes and Masses on Peroxide Fusion

The Na_2O_2 fusion guarantees that every component in the solution will dissolve completely. It is employed in this investigation because of its ability to break complex geological materials that are challenging to digest in acids. Flux variation of the Na_2O_2 and NaOH pellets resulted in excellent recoveries of the high concentration of Zn as also discovered by Bokhari & Meisel, (2017). Method A obtained recovery rate of 98.82 and 99.47%, with RSDs below 1.35%, followed by those of Method B, with recoveries of 88.63 to 92.17%, with RSDs below 3.5%. Method C acquired the lowest recoveries of 84.57 and 86.17% for CZN-4 at 0.1 and 0.2 g, respectively.

The recoveries of AMIS0620 were within the range of 82.3 and 88.50% at 0.1 g, with RSDs of below 6% for all the masses. Method A was chosen as the best method because it had the highest recovery among all three approaches. However, most commercial sources of the combination of fluxes used are sufficiently pure to identify the major and minor components of soil Hossner, (2018). No trend was observed in mass variation, as the results produced with various combinations of fluxes indicated no significant differences. This means that all the fluxes used are capable of recovering from high Zn concentrations.

4.5.12 Comparison of the Performance of the Certified Reference Materials for all Sample Preparations

Two CRMs with different compositions, CZN-4 and AMIS0620, were analysed using hotplate acid digestion, microwave acid digestion and peroxide fusion methods. Three various sample preparations with a sample mass of 0.1 g obtained recoveries ranging from 97.53 to 100.4% and 0.2 g obtained 97.11 to 101.4% for CZN-4. The recovery produced for AMIS0620 was 88.50 to 99.49% at 0.1 g, whereas at 0.2 g, it was between 82.30 and

99.49%. Microwave acid digestion approach produced the highest percentage recoveries for both CZN-4 and AMIS0620 across all masses compared with the other two methods.

The hotplate acid digestion method resulted in slightly lower results, which might be due to inconsistency in the results achieved. Additionally, peroxide fusion method consistently yields lower recoveries, indicating less accurate results than the other methods. The 0.2 g sample mass and the analysis of the CRMs with the hotplate, microwave, and peroxide fusion methods indicate varying levels of accuracy, as shown in Figures 4.15 and 4.16. The CZN-4, for both the hotplate and microwave acid digestion methods resulted in good recoveries close to 100% or slightly above. The peroxide fusion method, however, results in a slightly lower recovery percentage indicating less accurate results.

Overall, the microwave method to demonstrated the highest accuracy for both CZN-4 and AMIS0620 at both sample masses, providing consistent and reliable measurements. The microwave method seems to be the best option for both CZN-4 and AMIS0620 according to the findings of this study. All the methods showed good efficiency for the determination of high Zn contents, with recoveries between 80 and 120% and RSDs below 5%. This findings was also observed by (Oduoza & Miaphen, 1993) when AAS was used, whereby the peroxide fusion method performed very poorly compared with the microwave acid digestion approach.

All the sample preparation methods were capable of successfully recovering the concentration of Zn, with percentage recoveries ranging from 80 to 120%. This result was discovered by (Wei et al., 1997), whereby the Zn concentration was successfully determined by hotplate and microwave acid digestion techniques. All the methods resulted in good recoveries and effectively facilitated the analysis of Zn using ICP-OES. Therefore, the microwave method stands out among all the techniques as the most reliable

and accurate technique for the analysis of the amount of Zn in both CZN-4 and AMIS0620 samples at the 0.2 g sample mass. Similar outcome was observed when HF was mixed with aqua regia using the same techniques on sulphide ore material by (Al-Harashsheh et al., 2009).

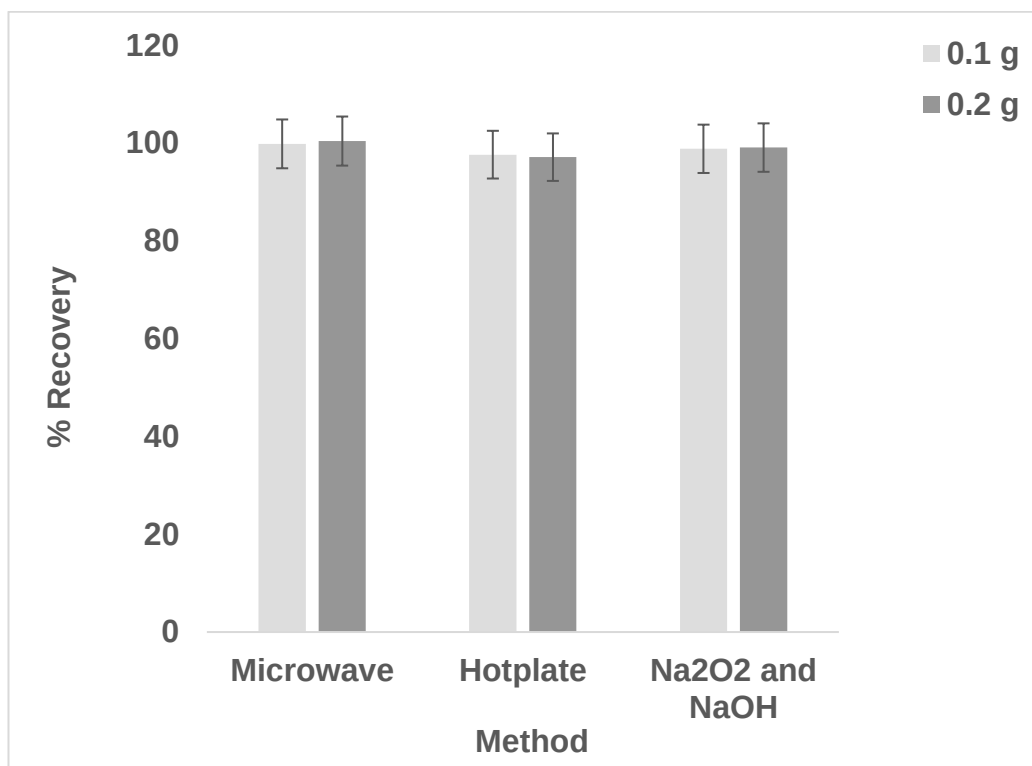


Figure 4.15. Comparison of CZN-4 for ICP-OES sample preparation at 0.1 and 0.2 g

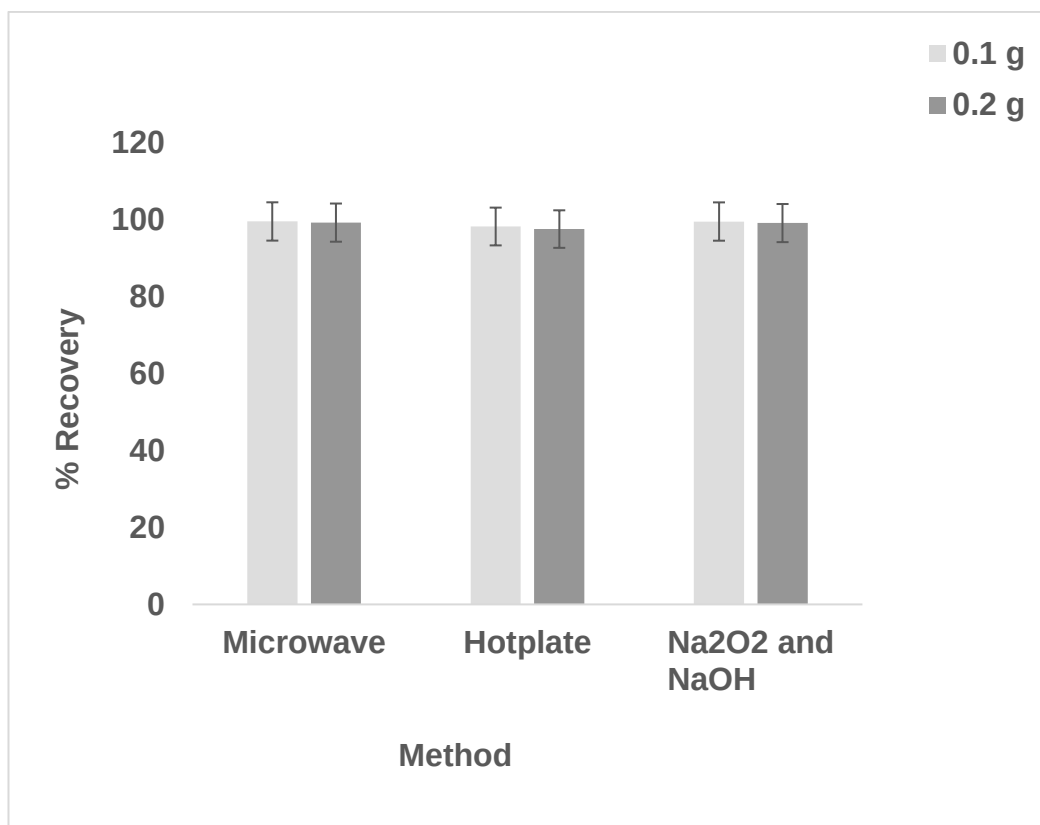


Figure 4.16. Comparison of AMIS0620 at 0.1 and 0.2 g for ICP-OES methods

4.5.13 Comparison of the Statistical Results for ICP-OES Methods

There were notable variations between methods B and C for both CZN-4 and AMIS0620. Method B and C showed a significant difference with p-values as 0.02 for CZN-4 while for AMIS0620 there was a variation of p-values for 0.03 and 0.09 by method B and C, as indicated in Table 4.9. Minimal differences were indicated by the p-values of the other approached which were greater than 0.05 demonstrating no variations.

Table 4.9. Statistical results for sample preparation by ICP-OES

Sample	Method	Conc (%) 0.1 g	Conc (%) 0.2 g	t- start	P(T<=t) two- tail
CZN-4	Microwave	54.98	55.3	-1.05	0.34
AMIS0620		46.87	46.91	-0.04	0.71
CZN-4	Hot plate	53.76	53.48	0.27	0.79
AMIS0620		46.19	45.88	0.3	0.77
CZN-4	Method A	54.42	54.56	-0.32	0.76
AMIS0620		46.8	46.61	1.31	0.25
CZN-4	Method B	49.63	50.76	-3.47	0.02
AMIS0620		42.94	41.69	2.07	0.09
CZN-4	Method C	47.45	46.58	2.59	0.02
AMIS0620		41.63	38.71	3	0.03

4.5.14 Recovery of Zinc Concentrations in V2 by ICP-OES Methods

A small increase in V2 measurement across the microwave acid digestion and alkaline peroxide fusion method was observed but not with hotplate acid digestion when the mass was doubled from 0.1 to 0.2 g. The microwave and peroxide fusion method achieved good precision, with an RSD of <0.90%, whereas the hotplate method yielded lower precision, with a high RSD of <2.3%. The results of the microwave acid digestion method were consistent for both masses with lower RSDs. The trend observed for the results was microwave acid digestion, hotplate acid digestion and peroxide fusion methods in terms of percentage recoveries. Peroxide fusion results were consistently lower, as shown in Figure 4.17.

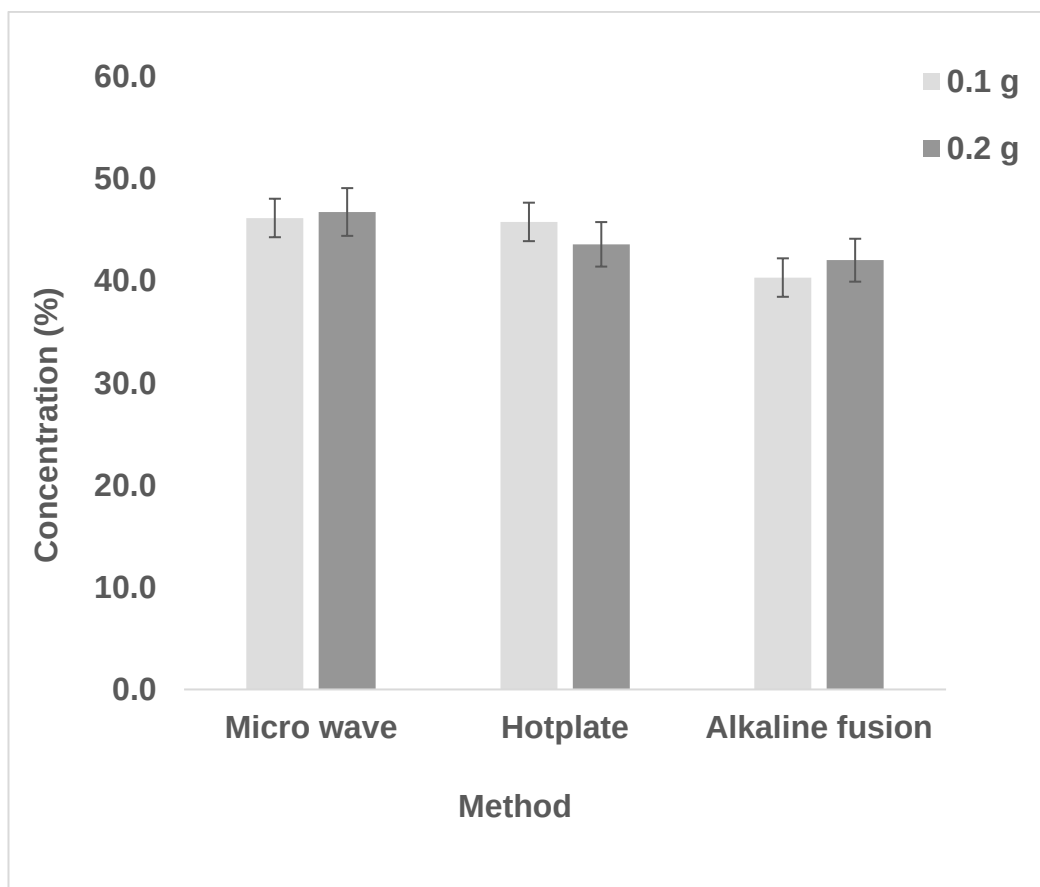


Figure 4.17. Comparison of V2 sample by ICP–OES methods

4.5.15 Recovery of Zinc Concentrations in V4 by ICP-OES Methods

The results of two masses obtained by microwave aqua regia were 43.58 and 44.07%, with an RSD of <0.75% for V4, as illustrated in Figure 4.18. The analytical outcome displayed that the concentrations for different masses did not differ significantly. The concentration of 44.71 and 42.14% with of RSDs of <2.70 was produced by hotplate acid digestion whereby peroxide fusion produced the lowest concentrations of 37.82 and 39.09%, with RSDs of less than 0.50% for both 0.1 and 0.2 g respectively. The microwave method consistently outperformed the hot plate and peroxide fusion methods for both samples across both 0.1 and 0.2 g sample masses. It consistently yielded the highest recovery values, indicating better extraction and quantification of the Zn concentration in the samples. The

hotplate method closely follows the microwave method, showing slightly lower values but still demonstrating reliable performance with slightly higher RSDs.

There is a similar trend in V2 and V4 for microwave and peroxide fusion at a concentration of 0.2 g. Peroxide fusion method also showed a similar pattern of the lowest CRMs values for V2 and V4 samples, as demonstrated in Figures 4.17 and 4.18. Overall, the microwave method emerged as the most effective and reliable technique for the Zn concentration analysis of the V2 and V4 samples. The results of the Zn samples indicated that all methods were capable of producing acceptable results since the recovery percentage was within 80 to 120%.

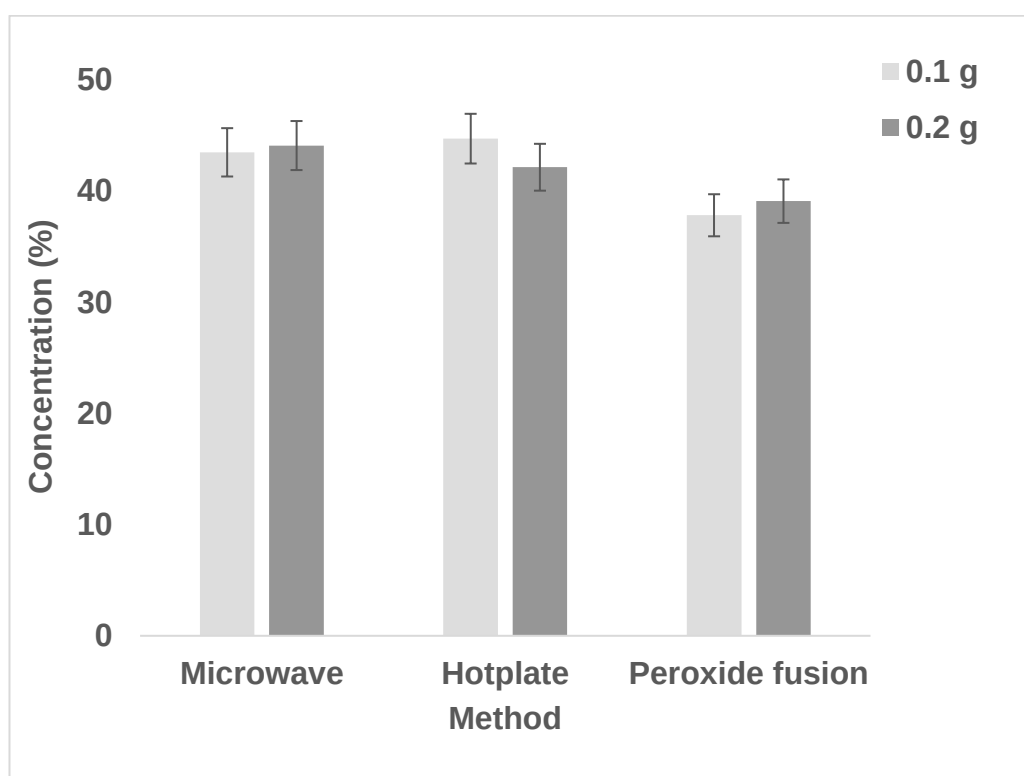


Figure 4.18. Comparison of the ICP-OES results for the V4 sample

4.5.16 Comparison of X-ray Fluorescence and Inductively Coupled Plasma Emission Spectroscopy

A comparison of the Zn findings obtained by microwave acid digestion and the pressed pellet approach for the Zn or CRMs was performed using ICP-OES and EDXRF investigations. Statistically, the results achieved by both techniques showed no noticeable variation. P-value for CZN-4 for both the techniques was found to be 0.39 and greater than 0.05 which demonstrated that there is no difference in the results produced as shown in Table 4.10. The techniques are cable of determining Zn precisely and accurately.

Table 4.10. Statistical comparison of the effects of microwave and pressed pellets on CZN-4

CZN-4	Microwave acid digestion	Pressed pellet
Mean	55.3	54.98
Variance	0.06	0.56
Observations	6	6
Pearson Correlation	-0.22	
Hypothesised Mean Difference	0	
Df	5	
t Stat	0.95	
P(T<=t) one-tail	0.19	
t Critical one-tail	2.02	
P(T<=t) two-tail	0.39	
t Critical two-tail	2.57	

The Zn results for AMIS0620 by microwave and pressed pellet are comparable as 46.91 and 46.52% respectively. Statistically the p-value acquired 0.26 which is more than 0.05 as represented in Table 4.11. That demonstrated that there is no significant variation between the approaches. The results indicated that both techniques are efficient and more reliable for the recovery of Zn

Table 4.11. Comparison of AMIS0620 by microwave and pressed pellet methods

AMIS0620	Microwave digestion	acid Pressed pellet
Mean	46.91	46.52
Variance	0.04	0.6
Observations	6	6
Pearson Correlation	0.24	
Hypothesised Mean Difference	0	
df	5	
t Stat	1.27	
P(T<=t) one-tail	0.13	
t Critical one-tail	2.02	
P(T<=t) two-tail	0.26	
t Critical two-tail	2.57	

4.5.17 Performance of V2 and V4 by Microwave acid digestion and Pressed Pellet

The performance of V2 and V4 was compared in the study using pressed pellets and microwave acid digestion with ICP-OES and XRF. The findings indicated that V2 had a 45.61 and V4 45.35% for pressed pellet while microwave acquired 46.75% for V2 and V4 as 44.09% as shown in Table

4.12. The results of microwave acid digestion were slightly different for V2 and V4, whereas the EDXRF results are similar. A study reported by (Mongoljiibuu, 2022) for sulfide skarn ore indicated that microwave acid digestion outcome were in strong agreement with the XRF results. These results offer important insights into the effectiveness and precision of various digestive techniques across various samples. The overall RSD for all the results was less than 2%, this was also discovered by (Kilbride et al., 2006) in a study of comparing dual source FPXRF results and acid digestion results by ICP-OES spectroscopy.

Table 4.12. Comparison results of ICP-OES and EDXRF

Sample	Technique	Zn (%)	Percent Recovery	RSD (%)	95% Confidence
CZN-4	ICP-OES	55.3	100.4	0.45	54.58-55.56
	XRF	54.64	99.22	0.95	
AMIS0620	ICP-OES	46.91	99.72	0.403	46.87-47.21
	XRF	46.52	98.98	1.66	
V2	ICP-OES	46.75		0.31	
	XRF	45.61		1.37	
V4	ICP-OES	44.09		0.72	
	XRF	45.35		0.51	

4.5.18 Overall Performance of V2 and V4 for both Techniques

The P-value of greater than 0.05 for the CRMs indicated that both methods and techniques are capable of analysing high Zn concentrations. P-value results obtained by V2 was 0.01 and V4 was 0 as indicated in Table 4.13 and Table 4.14. The findings indicated that the p-value was <0.05, which demonstrated that there was notable variation in the findings produced. The same discovery was found when field XRF was compared with ICP-OES in soil trace metals by (Sikora et al., 2021 ; Sahraoui & Hachicha, 2016). There is a similar trend of V2 results slightly higher than V4 for both techniques and this is also confirmed by the elemental composition.

Microwave acid digestion was found to be the greatest efficient technique for the analysis of Zn concentration by using ICP-OES based on the performance of the CRMs. This technique demonstrated precision in the extraction of Zn from various samples with varying masses as it reliably yielding the highest amounts of Zn. Additionally, microwave digestion produces accurate and reliable results making it appropriate for high Zn concentrations. Therefore, the microwave acid digestion method was selected as the best choice for determining the Zn concentration by using the ICP-OES technique.

Table 4.13. Comparison of V2 for Pressed Pellets and Microwave acid digestion

V2	Pressed pellet	Microwave acid digestion
Mean	45.61	46.75
Variance	0.39	0.02
Observations	6	6
Pearson Correlation	0.01	
Hypothesised Mean Difference	0	
df	5	
t Stat	-4.37	
P(T<=t) one-tail	0	
t Critical one-tail	2.02	
P(T<=t) two-tail	0.01	
t Critical two-tail	2.57	

Table 4.14. Comparison of V4 by Pressed pellet and Microwave acid digestion

V4	Pressed pellet	Microwave acid digestion
Mean	45.35	44.09
Variance	0.05	0.102
Observations	6	6
Pearson Correlation	0.24	
Hypothesised Mean Difference	0	
df	5	
t Stat	8.86	
P(T<=t) one-tail	0	
t Critical one-tail	2.02	
P(T<=t) two-tail	0	
t Critical two-tail	2.57	

CHAPTER FIVE: CONCLUSION AND RECOMMENDATION

This chapter offers a through conclusive analysis of the outcomes of the conducted experiments. The answers to the aim and objectives of work were obtained, including goals that were met. A concise summary of possible future studies is needed.

5.1 Conclusion

The purpose of this investigation was to create a quantitative approach for analysing the concentration of Zn in various ores using XRF and to optimise sample dissolution for ICP-OES. The aim and objectives of this study were satisfactorily met and demonstrated. The most abundant mineral characteristic compositions of the Zn ore samples were sphalerite, dolomite, pyrite, chalcopyrite, quartz and calcite, as determined by XRD. A comparative study of the handheld and benchtop techniques revealed that the benchtop technique resulted in higher recoveries than with the handheld technique. The optimisation of sample dissolution using microwave, hotplate acid digestion and Na_2O_2 fusion was effective as evidenced by selected Zn CRMs using ICP-OES. The pressed pellet method was successfully developed using EDXRF and microwave acid digestion by ICP-OES, achieving high percentage recoveries within the 80 to 120% range.

The spectroscopy techniques were utilised to fulfil the aim and objectives of the study by validating methods with CRMs. Based on the findings achieved Zn analysis in various ores was successfully accomplished by both techniques. The benchtop method is more effective than the handheld method because more recoveries of the elemental composition were acquired. Microwave acid digestion with aqua regia was the most effective method for accurately determining the concentration of Zn in various ore types and masses, yielding accurate results. Statistically, the validation of CRMs using both spectroscopy approaches showed no measurable difference. However, for samples the results exhibited some variation, though they remained in reasonable agreement for both techniques. Both techniques are capable of analysing high Zn concentrations in various ores due to the techniques achieved recoveries between 80 and 120%. The concentrations of Zn in V2 and V4 was between 40% and 50%. Compared to EDXRF with pressed pellets, ICP-OES with microwave acid digestion is

more efficient since it produces excellent recoveries of high Zn for both CRMs used.

5.2 Recommendations

It is recommended that additional investigations be performed in Na_2O_2 fusion to improve the ability of the method to accurately recover more Zn with ICP-OES. This indicates that further work should be done to improve the analytical process and raise the accuracy of Zn by using the ICP-OES approach. Additionally, by adjusting mass ratios and binder usage for XRF pressed pellet method.

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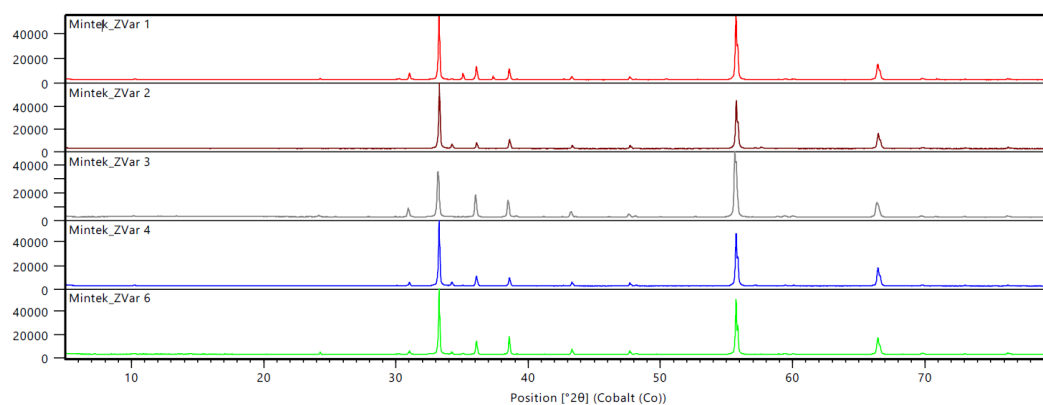
APPENDIX

Appendix 1

Qualitative and quantitative XRD results

	Quartz	Sphalerite]	Galena	Pyrite	Dolomite	Calcite	Muscovite	Chalcopyrite	Siderite
Mintek_ZVar 1	7.6	52	0.8	15.6	23.4	0	0.2	0	0.3
Mintek_ZVar 2	0.5	59.7	0	19.7	14.9	1	0	3.8	0.4
Mintek_ZVar 3	9.1	37.9	0	17.6	34.9	0	0.1	0.1	0.3
Mintek_ZVar 4	3.9	55.3	0	14.1	22.7	1.6	0	2	0.4
Mintek_ZVar 6	4.5	45.9	0.1	21.8	25	0.8	0.5	0.9	0.4

0 = n.d. – not detected above the detection limit of 0.5-3 weight percent



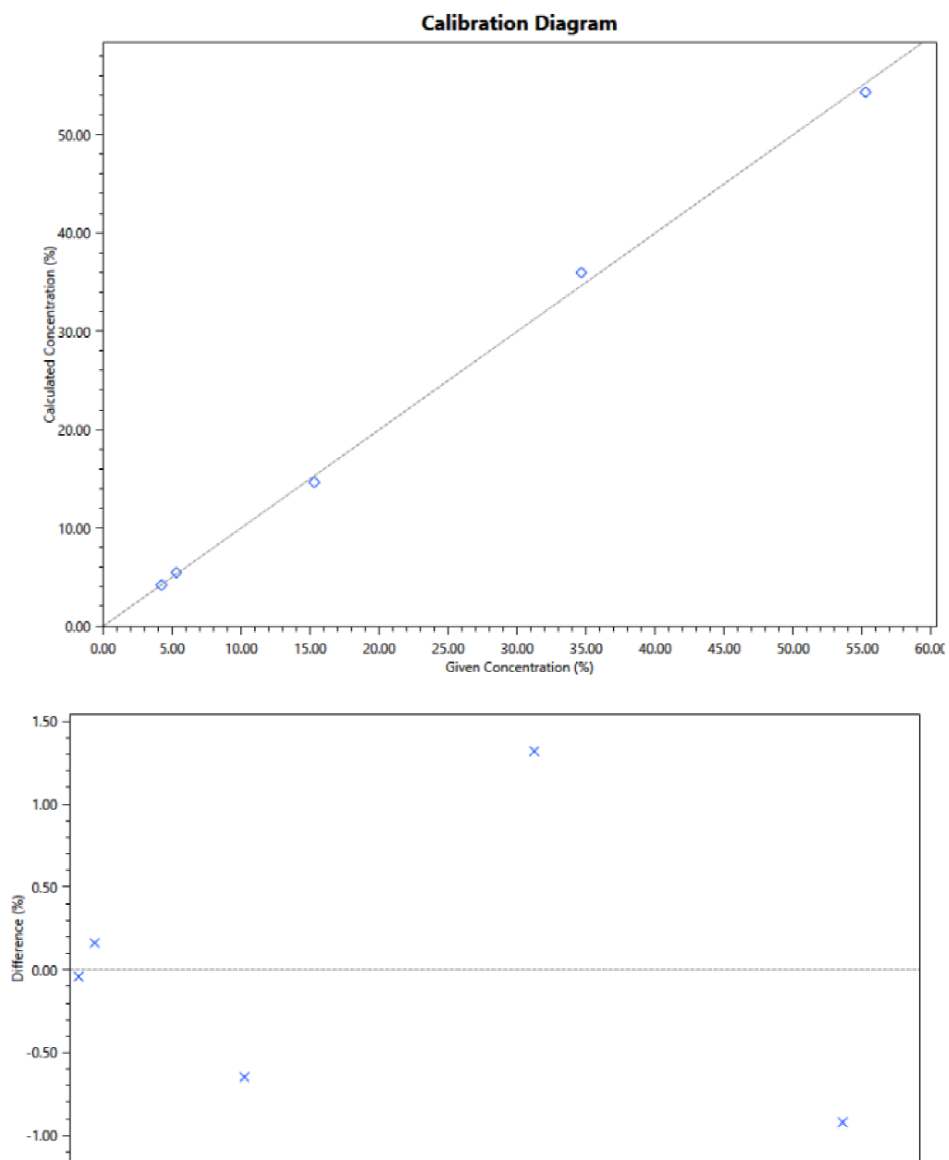
Peak List
Quartz low: O2 Si1
Sphalerite: S1 Zn1
Galena: Pb1 S1
Pyrite: Fe1 S2
Dolomite: C2 Ca1 Mg1 O6
Calcite: C1 Ca1 O3
Muscovite 2M1: H2 Al2.83 Fe0.07 K0.92 Mg0.07 Na0.08 O12 Si3.03 Ti0.02
Chalcopyrite: Cu1 Fe1 S2
Siderite: C1 Fe1 O3

Appendix 2

2.1 Calibration curves for Zn by the EDXRF

XRF Analyzer Pro

Calibration Data



Certification

◆ - Not Certified

x - Info

+ - Certified

Method

Zinc Pellets

Element

Zinc (30)

Number of Standards

5

Sample State

Pressed Tablet

Correlation Coefficient

0.999211

Creator

Admin User

Deviation

8716.4

Description

Calibration Standards

Concentrations in µg/g

Sample Name	Certification	Norm. Imp.	Given Conc.	Calc. Conc.	Deviation
4_77	None	32573.820	42300.0	41889.8	-410.2
15_69 (2)	None	48356.738	53000.0	54621.3	1621.3
3_98 (2)	None	162286.128	153000.0	146523.4	-6476.6
A_590_STD	None	435852.440	346500.0	359704.4	13204.4
CZN 4	None	654027.569	552400.0	543191.2	-9208.8

Empirical Calibration Results -LucasTooth

Offset 1.2746E+004
Slope 6.5850E-001

2.2 Calibration curves for Zn by ICP-OES

Test Report



Agilent Technology

Summary

Worksheet Name	ZINC TEMPLATE 21_11_2023..esws	Created Date/Time (local)	2023-04-25 10:46:20
Instrument Name	MY2333CQ21	Created Date/Time (GMT)	2023-04-25 08:46:20
Software Version	7.6.2.12331	Workstation Name	AGILENT-5800
Firmware Version	5590	Report Generated By	MNTK\Agilent5800
File Path	Y:\Agilent ICP\DIMAKATSO\ICP-OES\ZINC TEMPLATE 21_11_2023..esws		

Notes

Configuration

Sample Introduction	Agilent SPS 4	Drift Correction Argon Lines	True
AVS67 Enabled	False	Peak Lines Used	Initialized
AVS4 Enabled	False	QC Enabled	True
IsoMist Enabled	False	IEC Enabled	False
Oxygen Injection On	False	Custom Replicates Enabled	False

Elements

Element	Wavelength (nm)	Label	Type	Internal Standard	Background Correction	Pixels	Calibration Fit	Condition Set
Zn	206.200	Zn A (206.200 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	1
Sc	335.372	Sc (335.372 nm)	Internal Standard		Fitted	2	Linear Weighted	1
Sc	357.253	Sc (357.253 nm)	Internal Standard		Fitted	2	Linear Weighted	1
Zn	472.215	Zn A (472.215 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	1
Zn	334.502	Zn A (334.502 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	1
Sc	361.383	Sc (361.383 nm)	Internal Standard		Fitted	2	Linear Weighted	1
Zn	213.857	Zn A (213.857 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	1
Sc	363.074	Sc (363.074 nm)	Internal Standard		Fitted	2	Linear Weighted	1
Zn	202.548	Zn A (202.548 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	1
Zn	202.548	Zn B (202.548 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	2
Zn	206.200	Zn B (206.200 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	2
Sc	335.372	Sc (335.372 nm)	Internal Standard		Fitted	2	Linear Weighted	2
Sc	363.074	Sc (363.074 nm)	Internal Standard		Fitted	2	Linear Weighted	2
Zn	213.857	Zn B (213.857 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	2
Zn	334.502	Zn B (334.502 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	2

Test Report



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Element	Wavelength (nm)	Label	Type	Internal Standard	Background Correction	Pixels	Calibration Fit	Condition Set
Sc	361.383	Sc (361.383 nm)	Internal Standard		Fitted	2	Linear Weighted	2
Zn	472.215	Zn B (472.215 nm)	Analyte	Sc (361.383 nm)	Fitted	2	Linear Weighted	2
Sc	357.634	Sc (357.634 nm)	Internal Standard		Fitted	2	Linear Weighted	2

Common Conditions

Replicate Count	3	Intelligent Rinse Enabled	False
Pump Speed (rpm)	12	AVS67 Enabled	False
Sample Uptake Time (s)	25	Uptake Delay (s)	
Sample Uptake Fast Pump	True	Uptake Rate (mL/min)	
Rinse Time (s)	30	Injection Rate (mL/min)	
Rinse Time Fast Pump	True	Bubble Injection Time (s)	
Rinse Port Position		Preemptive Rinse Time (s)	

Condition Set Title Condition Set: 1

Read Time (s)	5
RF Power (KW)	1.2
Stabilization Time (s)	15
Viewing Mode	Radial
Viewing Height (mm)	8
Nebulizer Flow (L/min)	0.7
Plasma Flow (L/min)	12
Aux Flow (L/min)	1
Makeup Flow (L/min)	0
Oxygen Percent (%)	0

Test Report



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Condition Set Title Condition Set: 2

Read Time (s)	5
RF Power (KW)	1.35
Stabilization Time (s)	15
Viewing Mode	Radial
Viewing Height (mm)	8
Nebulizer Flow (L/min)	0.55
Plasma Flow (L/min)	12
Aux Flow (L/min)	1
Makeup Flow (L/min)	0
Oxygen Percent (%)	0

Calibrations

Standard Concentrations By Element

Solution Label	Zn (%)
Blank	0.00
Standard 1	60.00
Standard 2	40.00
Standard 3	20.00
Standard 4	10.00

Calibration Parameters

Label (Wavelength nm)	Calibration Fit	Minimum Concentration	Maximum Concentration	Calibration Error	Excess Curvature	Upward Curvature	%RSE Limit
Zn B (202.548 nm)	Linear Weighted	0.00 %	66.00 %	20 %			
Zn A (202.548 nm)	Linear Weighted	0.00 %	66.00 %	20 %			
Zn B (206.200 nm)	Linear Weighted	0.00 %	66.00 %	20 %			
Zn A (206.200 nm)	Linear Weighted	0.00 %	66.00 %	20 %			
Zn A (213.857 nm)	Linear Weighted	0.00 %	66.00 %	28.5 %			
Zn B (213.857 nm)	Linear Weighted	0.00 %	66.00 %	28.5 %			
Zn B (334.502 nm)	Linear Weighted	0.00 %	66.00 %	20 %			
Zn A (334.502 nm)	Linear Weighted	0.00 %	66.00 %	20 %			
Zn B (472.215 nm)	Linear Weighted	0.00 %	66.00 %	20 %			
Zn A (472.215 nm)	Linear Weighted	0.00 %	66.00 %	20 %			

Detailed Calibration Results

Zn B (202.548 nm)

Standard	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	217.94	0.00	0.00	N/A
Standard 1	10550447.02	60.00	51.18	14.70
Standard 2	7853178.92	40.00	38.10	4.76
Standard 3	4205064.24	20.00	20.40	1.99
Standard 4	2224337.02	10.00	10.79	7.90

Zn A (202.548 nm)

Standard	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	95.27	0.00	0.00	N/A
Standard 1	4630790.24	60.00	49.21	17.98
Standard 2	3484126.28	40.00	37.02	7.44
Standard 3	1847797.06	20.00	19.64	1.82
Standard 4	990066.97	10.00	10.52	5.20

Zn B (206.200 nm)

Standard	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	50.15	0.00	0.00	N/A
Standard 1	2889355.63	60.00	56.34	6.11
Standard 2	2038927.07	40.00	39.75	0.62
Standard 3	1028737.75	20.00	20.06	0.29
Standard 4	529304.04	10.00	10.32	3.19

Zn A (206.200 nm)

Standard	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	25.56	0.00	0.00	N/A
Standard 1	1378812.02	60.00	56.01	6.65
Standard 2	969278.16	40.00	39.37	1.56
Standard 3	484134.75	20.00	19.67	1.67
Standard 4	249835.36	10.00	10.15	1.48

Zn A (213.857 nm)

Standard	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	153.38	0.00	0.00	N/A
Standard 1	6129398.90	60.00	49.60	17.34
Standard 2	4821640.43	40.00	39.01	2.46
Standard 3	2798924.15	20.00	22.65	13.23
Standard 4	1522821.94	10.00	12.32	23.21

Zn B (213.857 nm)

Standard	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	205.06	0.00	0.00	N/A
Standard 1	7832292.44	60.00	49.24	17.93
Standard 2	5902396.25	40.00	37.11	7.22
Standard 3	3307888.68	20.00	20.80	3.99
Standard 4	1761660.92	10.00	11.08	10.75

Test Report



Zn B (334.502 nm)

Standard	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	170.56	0.00	0.00	N/A
Standard 1	374398.39	60.00	60.13	0.21
Standard 2	251068.67	40.00	40.31	0.78
Standard 3	124058.76	20.00	19.91	0.47
Standard 4	61999.28	10.00	9.93	0.65

Zn A (334.502 nm)

Standard	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	102.52	0.00	0.00	N/A
Standard 1	369041.92	60.00	61.00	1.67
Standard 2	247347.23	40.00	40.88	2.20
Standard 3	119138.56	20.00	19.68	1.59
Standard 4	58718.88	10.00	9.69	3.08

Zn B (472.215 nm)

Standard	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	849.43	0.00	0.00	N/A
Standard 1	527546.52	60.00	59.64	0.61
Standard 2	359835.86	40.00	40.65	1.62
Standard 3	177741.28	20.00	20.03	0.14
Standard 4	89353.50	10.00	10.02	0.20

Summary Calibration Results

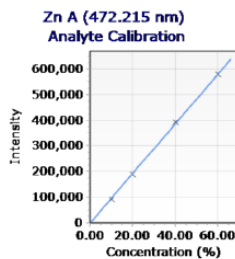
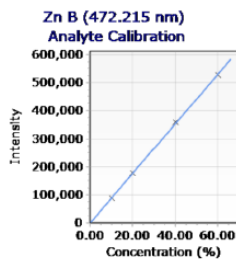
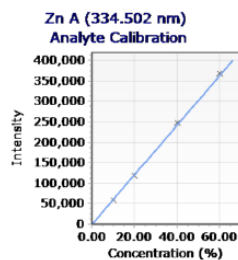
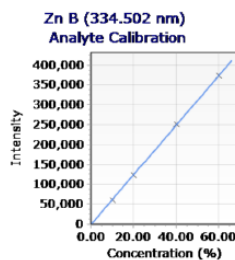
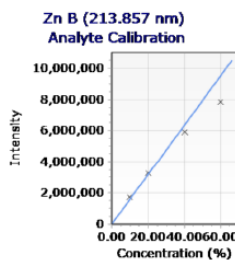
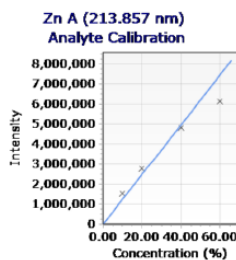
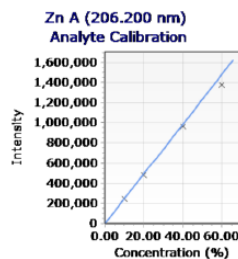
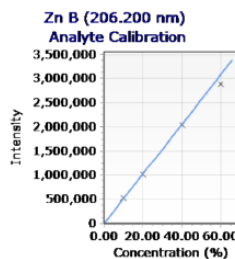
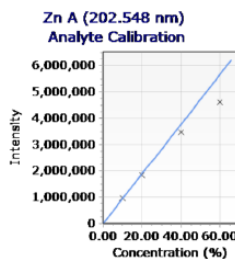
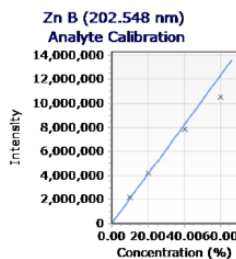
Element and wavelength	Type	Units	Equation	Correlation Coefficient	%RSE
Zn B (202.548 nm)	Analyte	%	206136.67414119 * Concentration + 218.10299838	0.99596	12.34943357
Zn A (202.548 nm)	Analyte	%	94101.04839750 * Concentration + 95.56268942	0.99539	14.30294949
Zn B (206.200 nm)	Analyte	%	51287.50988657 * Concentration + 50.70437463	0.99917	4.89699534
Zn A (206.200 nm)	Analyte	%	24616.38280194 * Concentration + 25.61941384	0.99932	5.08080747

Test Report

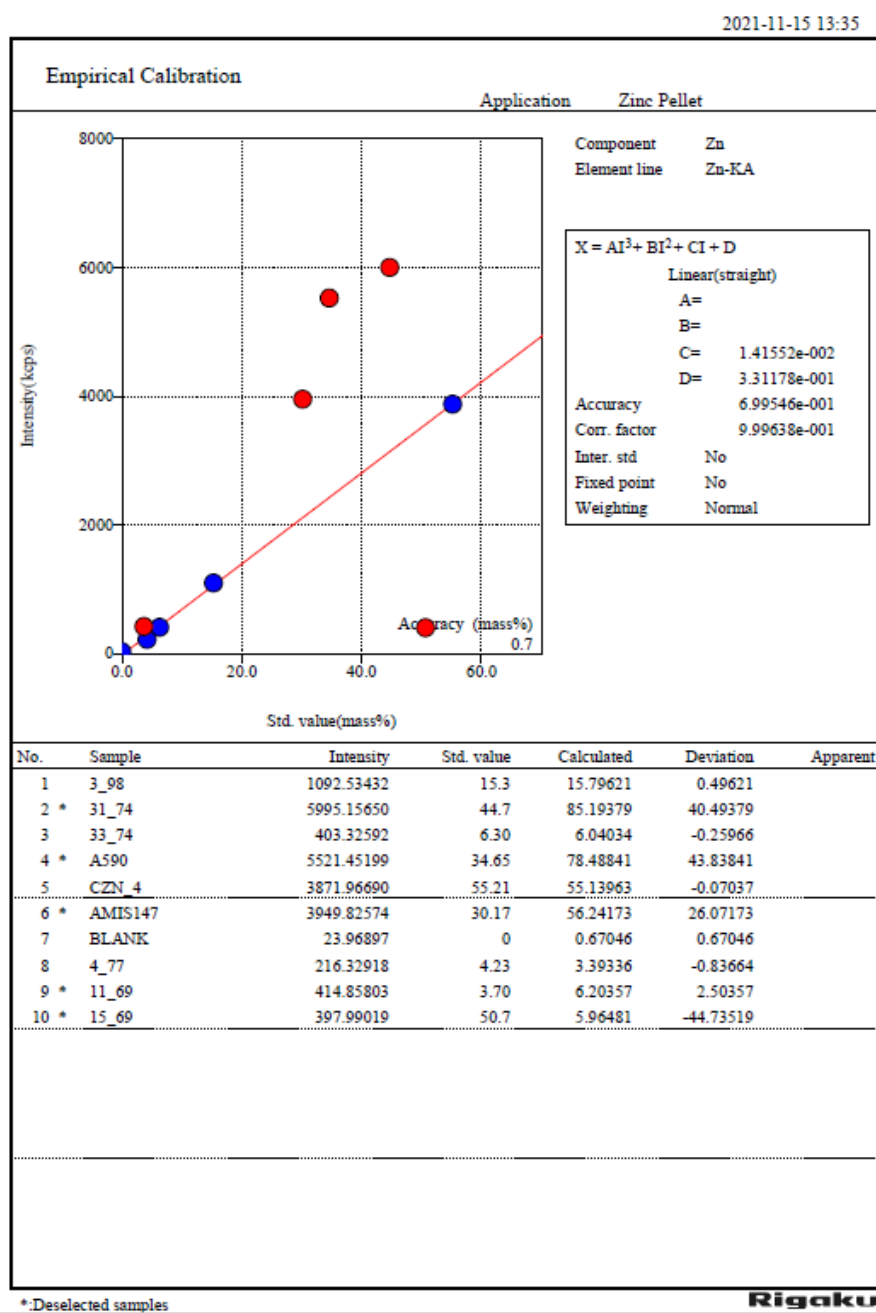


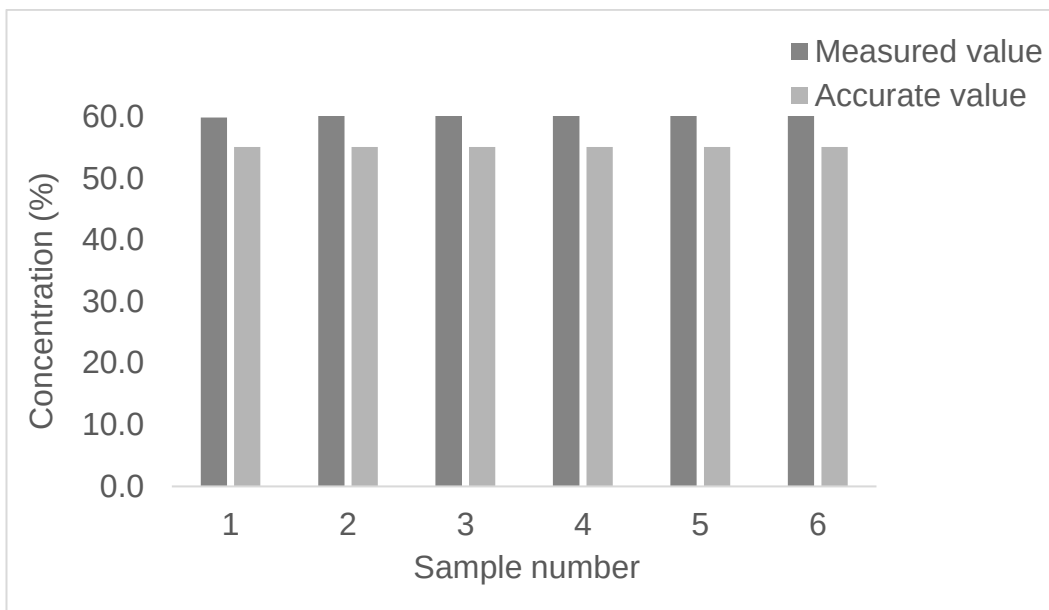
Agilent Technologies

Element and wavelength	Type	Units	Equation	Correlation Coefficient	%RSE
Zn A (213.857 nm)	Analyte	%	123582.73850285 * Concentration + 153.40220397	0.98827	22.58997944
Zn B (213.857 nm)	Analyte	%	159044.81313767 * Concentration + 205.52503708	0.99387	15.89059005
Zn B (334.502 nm)	Analyte	%	6224.09330895 * Concentration + 163.91252590	0.99999	0.80604849
Zn A (334.502 nm)	Analyte	%	6048.21556174 * Concentration + 102.43776548	0.99991	3.13539343
Zn B (472.215 nm)	Analyte	%	8831.72786630 * Concentration + 857.30831032	0.99989	1.23307982
Zn A (472.215 nm)	Analyte	%	9657.23669402 * Concentration + 270.52020385	0.99985	3.18061776

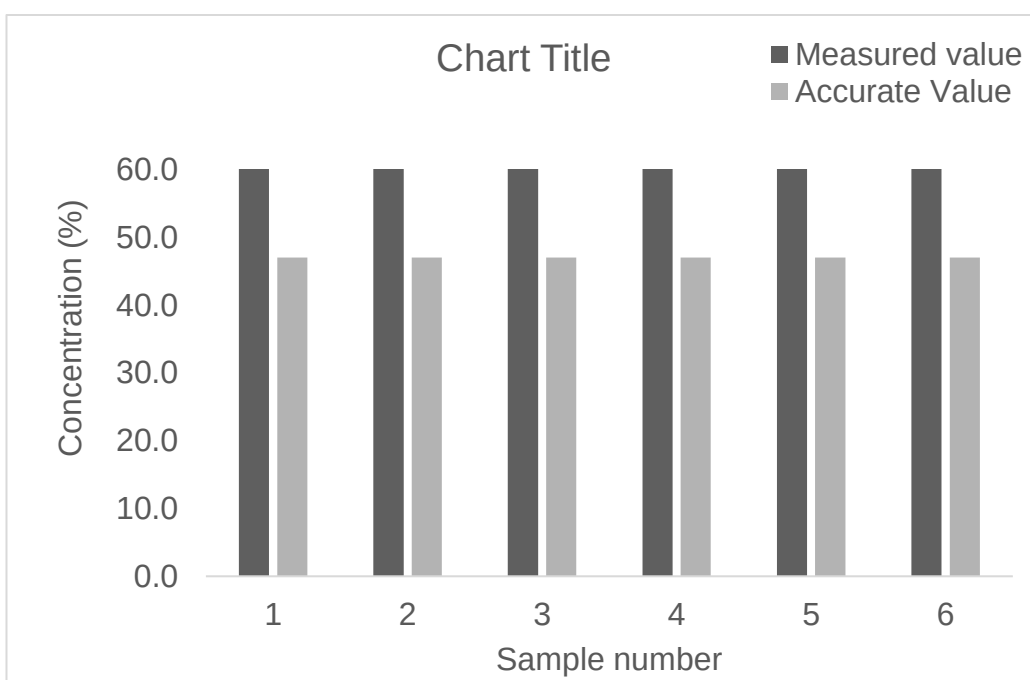


2.3 Calibration curves for Zn by WDXRF





Performance of CZN-4 at WDXRF



Performance of AMIS0620 at WDXRF

Appendix 3

Reference material certificate CZN-4

	CCRMP Canadian Certified Reference Materials Project CANMET Mining and Mineral Sciences Laboratories 555 Booth Street, Ottawa, Ontario, Canada K1A 0G1 Tel.: (613) 995-4738, Fax: (613) 943-0573 E-mail: ccrmp@nrcan.gc.ca www.ccrmp.ca	PCMRC Projet canadien de matériaux de référence certifiés Laboratoires des mines et des sciences minérales de CANMET 555, rue Booth, Ottawa (Ontario) Canada K1A 0G1 Tél. : (613) 995-4738, Téléc. : (613) 943-0573 Courriel : pcmrc@nrcan.gc.ca www.pcmrc.ca
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Certificate of Analysis

First issued: January 2010 Version: January 2010

CZN-4

Certified Reference Material for a Zinc Concentrate

Table 1 – CZN-4 Certified Values

Element	Units	Mean	Within-lab Standard Deviation	Between- labs Standard Deviation	95% Confidence Interval of Mean
Ag	µg/g	51.4	1.3	1.4	0.7
Al	%	0.0715	0.0027	0.0086	0.0063
As	%	0.0356	0.0009	0.0015	0.0011
Cd	%	0.2604	0.0046	0.0141	0.0074
Co	µg/g	93.5	3.3	6.4	3.7
Cu	%	0.403	0.011	0.010	0.006
Hg	µg/g	4.54	0.28	0.57	0.40
Pb	%	0.1861	0.0059	0.0085	0.0044
S	%	33.07	0.23	0.56	0.34
Se	µg/g	86.7	2.7	6.1	4.5
Si	%	0.295	0.013	0.026	0.019
Zn TITN	%	55.24	0.06	0.24	0.12

TITN = titration methods


 Natural Resources
Canada

Ressources naturelles
Canada



Table 2 – CZN-4 Provisional Values

Analyte	Units	Mean	Within-lab Standard Deviation	Between- labs Standard Deviation	95% Confidence Interval of Mean
Ca*	%	0.0419	0.0021	0.0057	0.0061
Fe TITN	%	9.086	0.062	0.055	0.052
Fe non TITN	%	9.02	0.07	0.33	0.22
Mg*	%	0.0352	0.0010	0.0014	0.0014
Moisture	%	0.149	0.014	0.012	0.012
Zn non TITN	%	55.07	0.38	0.56	0.49

* statistical analysis of the results warrants classification as provisional, despite only 6 sets of data for calcium and 7 data sets for magnesium
 Moisture was determined at 100-107°C for up to 24 hours on varying sample masses without use of nitrogen
 TITN = titration methods
 Non TITN = non titration methods

Table 3 – CZN-4 Informational Values

Element	Units	Mean	Number of accepted sets/values
Au	µg/g	0.04	3 / 15
Bi	µg/g	10	5 / 25
C	%	0.09	4 / 20
Cl	%	0.003	4 / 17
F	%	0.004	7 / 35
In	%	0.020	8 / 40
Mn	%	0.009	5 / 25
Ni	µg/g	16	7 / 35
Sb	µg/g	10	5 / 25
Sn	%	0.05	6 / 30

SOURCE

CZN-4 is a zinc sulphide flotation concentrate donated by Xstrata Copper Canada Division, Kidd Metallurgical Site, Timmins, Ontario, Canada. The raw material was obtained from the same source as its predecessor, CZN-3.

DESCRIPTION

The mineral species include: sphalerite (90.6%), pyrite (4.1%), pyrrhotite (3.3%), iron oxides (0.5%), quartz (0.5%), chalcopyrite (0.3%), various other silicates (0.2%), ankerite (0.1%), arsenopyrite, cassiterite, chlorite and galena (all at 0.1%).

INTENDED USE

CZN-4 is suitable for the analysis of zinc and various other elements at major, minor and trace levels in zinc concentrates. Examples of intended use include quality control and method development.

Appendix 4

Reference material certificate AMIS0620

Summary Statistics

Recommended Concentrations and Limits (at two Standard Deviations) Certified Concentrations

Analyte	Method	Certified (μ) ⁶	(2s) ⁸ $\pm$	Unit
Zn	Titration ¹	47.04	0.17	%
SG	SG ²	4.08	0.15	Dimensionless
S	Combustion/LECO ³	29.88	1.8	%
Ag	4A_MICP ⁴	52	5	ppm
As	4A_MICP	64	15	ppm
Ba	4A_MICP	192	32	ppm
Be	4A_MICP	1	0.3	ppm
Bi	4A_MICP	205	11	ppm
Ca	4A_MICP	2944	213	ppm
Cd	4A_MICP	1443	73	ppm
Ce	4A_MICP	15	2	ppm
Co	4A_MICP	1137	69	ppm
Cr	4A_MICP	104	30	ppm
Cs	4A_MICP	1	0.09	ppm
Cu	4A_MICP	9708	1349	ppm
Cu	XRF ⁵	9591	1079	ppm
Fe	4A_MICP	10.69	0.28	%
In	4A_MICP	110	11	ppm
La	4A_MICP	7	2	ppm
Mg	4A_MICP	1610	125	ppm
Mn	4A_MICP	1.27	0.10	%
Mo	4A_MICP	36	3	ppm
Nb	4A_MICP	2	0.1	ppm
Ni	4A_MICP	83	5	ppm
P	4A_MICP	195	20	ppm
Pb	4A_MICP	3.67	0.39	%
Pb	XRF	3.52	0.15	%
Rb	4A_MICP	3	0.2	ppm
Sb	4A_MICP	25	5	ppm
Sr	4A_MICP	5	1	ppm
Th	4A_MICP	1	0.2	ppm
Ti	4A_MICP	202	9	ppm
Tl	4A_MICP	1	0.1	ppm
U	4A_MICP	2	0.3	ppm
W	4A_MICP	7	1	ppm
Y	4A_MICP	4	0.9	ppm
Zr	4A_MICP	12	5	ppm

1. Certified Concentrations and Uncertainties

AMIS0620 is a new standard material, developed and certified in June 2019. Table 1 gives the certified concentrations, confidence interval, combined and expanded uncertainty for the certified reference material. Table 2 shows the certified major oxides concentrations, two standard deviations, confidence interval, combined and expanded uncertainty.

Table 1. Certified concentrations, two standard deviations, combined and expanded uncertainty.

Analyte	Method	Certified (μ) ⁶	N	n	k	% RSD	(u_c) ⁷	(2s) ⁸ ±	(CI) ⁹ 95%	(U) ¹⁰ ±	Unit
Zn	Titration ¹	47.04	2	16	12.706	0.2	0.087	0.17	0.51	1	%
SG	SG ²	4.08	4	32	3.182	2	0.074	0.15	0.11	0.2	Dimensionless
S	Combustion/LECO ³	29.88	7	53	2.447	3	0.88	1.8	0.83	2	%
Ag	4A_MICP ⁴	52	6	48	2.571	5	3	5	3	7	ppm
As	4A_MICP	64	6	48	2.571	12	7	15	8	19	ppm
Ba	4A_MICP	192	4	32	3.182	8	16	32	25	51	ppm
Be	4A_MICP	1	4	31	3.182	13	0.1	0.3	0.2	0.4	ppm
Bi	4A_MICP	205	4	32	3.182	3	5	11	8	17	ppm
Ca	4A_MICP	2944	5	39	2.776	4	106	213	117	295	ppm
Cd	4A_MICP	1443	5	38	2.776	3	37	73	43	101	ppm
Ce	4A_MICP	15	3	23	4.303	8	1	2	2	5	ppm
Co	4A_MICP	1137	6	48	2.571	3	35	69	35	89	ppm
Cr	4A_MICP	104	5	40	2.776	15	15	30	18	42	ppm
Cs	4A_MICP	1	3	21	4.303	3	0.04	0.09	0.08	0.2	ppm
Cu	4A_MICP	9708	6	48	2.571	7	675	1349	698	1734	ppm
Cu	XRF ⁵	9591	4	32	3.182	6	540	1079	853	1717	ppm
Fe	4A_MICP	10.69	4	32	3.182	1	0.14	0.28	0.086	0.5	%
In	4A_MICP	110	4	30	3.182	5	6	11	9	18	ppm
La	4A_MICP	7	3	24	4.303	16	1	2	3	5	ppm
Mg	4A_MICP	1610	5	37	2.776	4	62	125	57	173	ppm
Mn	4A_MICP	1.27	5	40	2.776	4	0.048	0.10	0.058	0.1	%
Mo	4A_MICP	36	4	32	3.182	4	1	3	2	4	ppm
Nb	4A_MICP	2	2	16	12.706	4	0.06	0.1	0.4	0.7	ppm
Ni	4A_MICP	83	7	54	2.447	3	2	5	2	6	ppm
P	4A_MICP	195	3	24	4.303	5	10	20	23	42	ppm
Pb	4A_MICP	3.67	5	40	2.776	5	0.19	0.39	0.24	0.5	%
Pb	XRF	3.52	4	32	3.182	2	0.075	0.15	0.12	0.2	%
Rb	4A_MICP	3	3	22	4.303	4	0.1	0.2	0.2	0.5	ppm
Sb	4A_MICP	25	3	24	4.303	9	2	5	6	10	ppm
Sr	4A_MICP	5	4	32	3.182	10	0.5	1	0.8	2	ppm
Th	4A_MICP	1	3	22	4.303	7	0.1	0.2	0.09	0.4	ppm
Ti	4A_MICP	202	4	32	3.182	2	5	9	7	15	ppm
Tl	4A_MICP	1	3	24	4.303	4	0.06	0.1	0.07	0.3	ppm
U	4A_MICP	2	3	23	4.303	7	0.1	0.3	0.2	0.6	ppm
W	4A_MICP	7	3	24	4.303	9	0.6	1	1	3	ppm
Y	4A_MICP	4	3	24	4.303	11	0.5	0.9	1	2	ppm
Zr	4A_MICP	12	4	32	3.182	19	2	5	3	7	ppm

Table 2. Certified major oxides concentrations, two standard deviations, combined and expanded uncertainty.

Analyte	Method	Certified (μ) ⁶	N	n	k	% RSD	(u_c) ⁷	(2s) ⁸ ±	(CI) ⁹ 95%	(U) ¹⁰ ±	Unit
CuO	XRF	1.20	4	32	3.182	6	0.068	0.14	0.11	0.2	%
PbO	XRF	3.79	4	32	3.182	2	0.081	0.16	0.13	0.3	%
SiO ₂	XRF	2.63	5	40	2.776	2	0.061	0.12	0.049	0.2	%

1. Titration
2. SG is Specific Gravity
3. Combustion/LECO
4. 4A_MICP is a Multi-acid digestion with either ICPOES/ICPMS/AAS finish
5. XRF is X-ray Fluorescence
6. The certified value μ , is an unweighted grand mean of the means of N accepted sets of data from different laboratories and n number of test sample replicates. The certified value is traceable to SI units and is reported on a dry basis.
7. The combined uncertainty of the certified value is the within-laboratory reproducibility standard deviation derived from the analysis of variance of results from N number of laboratories and n number of sample replicates. (u_c)
8. Two standard deviations (2s)
9. Confidence interval at 95% level of confidence.
10. Expanded uncertainty (U) at a confidence level of 95% is determined by multiplication of the combined uncertainty (u_c) with a coverage factor (k) found from N-1 degrees of freedom (see Appendix 7 for t-distribution table). Example: $U = 2.36 \times 0.23 = 0.5\%$