Comparative Study of Portable X-Ray Fluorescence (p-XRF) and Atomic Absorption (AAS) Spectrometry Techniques for Soil Environmental Study

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Being a MSc Thesis Submitted to the Department of Chemical Sciences (Chemistry Unit), Faculty of Natural & Applied Sciences, Lead City University, Ibadan, Oyo State, Nigeria

In Partial Fulfillment of the Requirements for the Award of Master of Science Degree (MSc) in Environmental and Analytical Chemistry

2023

Certification

This attests that Oluremi, Omoniyi, OLALEKAN with matriculation number LCU/PG/001194, conducted the research project titled " **Comparative Study of X-Ray Fluorescence and Atomic Absorption Spectrometry Techniques for Environmental Study of Soils from selected Sites In Ibadan Metropolis"** in the Department of Chemical Sciences (Chemistry Unit), Faculty of Natural and Applied Sciences, Lead City University, Ibadan, Oyo State, Nigeria, for the award of Master Degree (MSc) in Environmental and Analytical Chemistry and that this work has not been previously submitted.

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Dedication

I dedicate this thesis to the glory of God the giver of all things, provider of wisdom and knowledge.

Acknowledgement

I sincerely express my gratitude to Lead City University Ibadan and Institute of Agricultural Research & Training Moor Plantation Ibadan for their assistance in this write up

My special appreciation goes to my supervisor, Dr. Olumuyiwa O. Ogunlaja, for the inspiration, useful remarks, and prized suggestions. Thank you, Sir. My appreciation also goes to my H.O.D., Prof. O.M. Ighodaro, and to all other lecturers Professors, Assistant Professors and Doctors in our enviable department. Also, I valued the support rendered by all the non-academic staff in the department. My appreciation also goes to all non-academic staff of the Department of Chemical Sciences Lead City University, and Post graduate college, I love you all.

I deeply appreciate my Wife, Dr. (Mrs.) T.E. Olalekan, children biological and spiritual, Mr. Olatunbosun, Dr (Mrs) Oluremi Ojo, Joel Ekemezie, Felix Akpaka, Nurudeen Abiodun and Pastor George Godwin, I am grateful.

"Even though the above-mentioned institutions and persons have assisted in the process of this research work, I alone stand responsible for the errors, if any, found in the work."

Abstract

Routinely in Nigeria, elemental quantification of environmental samples such as soil samples is often done using standard techniques such as atomic absorption spectrometry (AAS). Despite the extensive application of AAS due to its relatively low cost and accuracy, the main standard operation procedure (SOP) involves the use of non-environmentally friendly chemicals like HNO_3 and high energy. Consequently, the SOP exposes the users and the environment to the detrimental effects of such chemicals. Additionally, AAS is a cumbersome, destructive technique that requires the use of lamps which are often not available at the time of analysis. Hence this study assessed the potential of Portable X-Ray Fluorescence (p-XRF) as an alternative technique to AAS by statistically comparing elemental results obtained from both techniques. In total, 66 grab soil samples were randomly collected from a minimum of two geo-referenced points at a depth of 0-15 cm each from solid waste dumpsites, auto-mechanic workshops and farmlands in the Ibadan metropolis in June 2021. The analytical techniques were validated via recovery tests (≥ 96.5 %). The results of the T-test analysis showed that AAS and p-XRF interchangeably quantified Cu ($p = 0.06$) and Zn ($p = 0.14$) in the dumpsite, Cu ($p = 0.96$), Zn ($p = 0.98$), Cd ($p = 0.16$), Pb ($p = 0.30$), Ni ($p = 0.10$), Mg ($p = 0.16$), Mn ($p = 0.23$) and Fe ($p = 0.08$) in auto-mechanic and Ca ($p = 0.16$), Cu ($p = 0.25$), Cd ($p = 0.24$) and Pb ($p = 0.06$) in farmland soil samples. Although statistical data from this study showed that there were some similarities in the two techniques, suggesting that some elements can be quantified with either p-XRF or AAS, the overall result indicates that p-XRF can be used in screening for all these studied elements in these environmental samples.

Keywords: Correlation study, Environmental samples, Elemental analysis techniques, Non-destructive elemental quantification, Regression analysis, Statistical analysis.

Word Count: 300

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List of Acronyms

Abbreviation	Meaning
SOP	Standard Operation Procedure
AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Mass Spectroscopy
XRF	X-ray Fluorescence
p-XRF	Portable X-ray Fluorescence
NAA	Neutron Activation Analysis

Chapter One

Introduction

1.1 Background to the Study

The campaign for safe environment has necessitated alternative ways of analyzing different forms of objects and materials (soils, water, and air) in the environment. It has become necessary for scientists and technologists to put the safety of the environment and all its inhabitants into consideration when thinking about methods or techniques to be used in carrying out analytical procedures. Universally, Spectrometry techniques like Atomic Absorption (AA), Atomic Fluorescence (AF), Inductively Coupled Plasma Optical Emission (ICP-OES) and Inductively Coupled Mass (ICP-MS) are conventional techniques used in many laboratories and industries for elemental quantitative analysis[1,2,3,4]. These conventional techniques of evaluation involve usage of toxic as well as hazardous mineral acids in both extraction and digestion of samples to be analyzed. This technique gives room for errors such as parallax errors. The procedures for these types of methods take a long time and the chemicals involves are very expensive which makes the cost of analysis to be high. Each of these techniques has several merits and demerits which engender the analyst the workability of choosing the best equipment for the elemental analysis of interest.

Most recognized laboratories in developing countries such as Nigeria use acidulous chemicals like HNO_3 and H_2SO_4 for preparation of sample materials and destructive methods like Atomic Absorption Spectrometry (AAS) for all forms of empirical procedures for elemental evaluation in different sample matrices[5,6,7]. These mineral acids are toxic and hazardous to the user and the environment at large. The normal convention is to take precautionary measures while handling these chemicals in the laboratory as well as while disposing them in the environment. Despite all the recommended precautions and procedural handling of mineral acids, oftentimes users fall victim to their toxicity by way of accidents, mishandling and carelessness[8].

The use of alternative means of determining metals especially trace and heavy metals in soils apart from conventional means requires in-depth study. In developing sustainable environmentally friendly analytical methods, precision and accuracy of the parameters being evaluated are of high priority to the scientists and environmentalists; hence the need for comparison with the already established conventional techniques of analytical procedure in order to calibrate and validate the new technique. It also involves the drastic reduction of the use of toxic concentrated minerals acids and other hazardous chemicals[9]. Furthermore, this method is highly repeatable and reproducible, unlike conventional methods.

Contrary to other routinely used methodologies such as: AAS, AFS, ICP-OES and ICP-MS, XRF spectroscopy does not require sample dissolution or digestion, thereby sample materials are not destroyed in the event of running the analysis[10]. X-ray fluorescence is an atomic emission method, similar in operation to optical emission spectroscopy, and neutron activation analysis (gamma spectroscopy). This method calculated the wavelength and intensity of 'light' evolved by energized molecule in the sample. X-ray fluorescence has grown over years from instance to being one of the major techniques being engaged in field geochemical analyses in the mining and environmental applications[10]. XRF notwithstanding may not totally displace atomic spectrometry techniques such as ICP-MS for light level analyses, but it significantly has some merits including, little or no sample preparation, combination of high capacity, output, efficiency, productivity and performance. These analyzers have been consistently used for geological, environmental and industries matters in the past[11,12,13]. By circumventing the possibilities for inexactness caused by partial dissolution and large dilutions, the complete analysis by XRF helps to ensure the accuracy and repeatability of results. Until quite recently XRF machines were limited to bench-top units which often required that samples be removed from an object for analysis. Nevertheless, the portable X-ray fluorescence (p-XRF) machine ensure a fast and cheaper alternative to some other established techniques such as AAS, and ICPs[3,4]. XRF can be engaged when demanding limits of quantifications that are above 1 ppm (µg/g), or when sample materials is to be preserved, especially when analyzing solids, powders, slurries, filters and oils that are in smaller quantities.

In the recent happenings, soil heavy-metal pollution was observed to be one of several global problems confronting the environment. Heavy metal Pollution of soil contributed exceedingly to its deterioration, and its remediation and risk management need apt attention[8]. The need for intentional risk control and methodical repair requires lofty-precision characterization of pollution[9].

1.2 Statement of Problem

Although there are many established scientific spectrometry techniques like Atomic Absorption (AAS), Atomic Fluorescence (AFS), X-Ray Fluorescence (XRF), Neutron Activation Analysis (NAA), Inductively Coupled Plasma Optical Emission (ICP-OES), and Inductively Coupled Mass (ICP-MS). In developing countries like Nigeria, AAS is one of the vastly used technique for the assessment and evaluation of heavy metals of environmental matrices. This is as a result of AAS been substantiated to be accurate, relatively cheap, non-time consuming, and easy to operate than other spectroscopic techniques for elemental analyses. Despite these advantages, the AAS standard operation procedure (SOP) involves the use of toxic concentrated mineral acids such as HNO_3 and H_2SO_4 that are toxic and hazardous to the user and the environment at large. Additionally, AAS is a destructive technique with a cumbersome procedure for different heavy metal specie. It requires the availability of lamps for different metal specie which is most often not available at the time of analysis. On the other hand, the alternative technique being study is a non-destructive technique with a relatively simple SOP and sample preparation. It is generally used in the analysis of rock samples with little application in routine laboratory analysis. Therefore, in this study, AAS and p-XRF techniques were used to quantitatively analyze the heavy metal contents of soil from different sources in Ibadan.

1.3 Justification of the Study

In Nigeria, elemental analysis is often done using atomic absorption spectrophotometry (AAS) as it is the preferred technique. However, the initial cost, as well as the operational cost (acids, gasses, lamps, electricity and fume hoods), make usage impossible for some laboratories. Additionally, the cumbersome of the SOP and non-environmentally friendly practices expose the operator to toxic and harmful chemicals but, the XRF spectrophotometry technique can offer a comparative alternative. X-Ray Fluorescence spectrophotometer is producing good results without costing a lot of money than AAS. It does not require any use of toxic acids, gasses and fume hoods. Its only require basic electricity, calibration and in some cases helium to enhance the sensitivity of light elements in the sample. Additionally, the individual components in XRF spectrometers are not subjected to friction or heat and in effect can last for many years.

Decades ago, p-XRF has metamorphosed from being a prototype to being a key technique used in areas such as geochemical and mining analyses but, with little application in routine environmental analysis, especially in Nigeria. P-XRF does not need daily routine calibration as a result of non-usage of gasses or liquids in operation which may introduce impurity and instability. Similarly, oils evaluation only requires the use of disposable liquid cups that are cheap and solid samples, like metals, can be scanned directly without necessarily preparing the object of analysis.

Hence, this study was conducted to comparatively explore p-XRF with an established atomic absorption spectrophotometry (AAS) technique to determine selected metals in diverse samples of soils from auto-mechanic workshops, solid waste dumpsites and agricultural farmlands located in Ibadan, Oyo State.

1.4 Aim and Objectives of the Study

The research aims to assess concentrations of selected metals, heavy metals inclusive in potentially polluted diverse soil samples collected from auto-mechanic workshops, solid waste dumpsites and farmlands located in Ibadan, Oyo State using AAS and p-XRF techniques.

The specific objectives were:

i. determine the concentration of selected heavy metals in potentially polluted soil types using the p-XRF technique.

ii. determine the accuracy and precision of the p-XRF technique by comparing its results with the conventional atomic absorption spectrometry (AAS) method.

iii. determine if the two methods (AAS and p-XRF) are not significantly different.

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Chapter Two

Literature Review

2.1 Digestion-Based Technique for Elemental Analysis

Compounds of metals are abundant in our environment and so many kinds of metals have been discovered over time and grouped together. Heavy metals like lead (Pb) and chromium (Cr), are one of such group and are reconned as toxic if found in abundant in the body[1]. The excess of heavy metals in the body typified bioaccumulation, which means the concentration of such metallic elements in the body increases over time. Bioaccumulation of metal in the body can occur as a result of eating foods contaminated by heavy metals as well as drinking heavy metals polluted water[1]. However, some metals are also needed for life sustainability, for example iron (Fe) and copper (Cu). The Scientist reported that, Cu in trace levels is necessary for maintaining good metabolic health, and that Fe carries oxygen to all the cells inside our bodies. Metals play a major role in global technological advancement, and mining companies routinely search for it in other to drive world economies[1].

Generally, elemental quantification required the sample to be in solution forms by means of digestion for a wide variety of analytical sample materials, hence standard scientific procedure is to be followed before analysis. Sample matrix digestion for metals investigation in qualitative and quantitative evaluation play a significant role. This is also referred to as the step-by-step sample preparation technique that involves decomposition and dissolution of organic and inorganic materials prior to detection and quantification[2,3,4]. The basic reagents used for breaking down metal-containing materials are concentrated mineral acids such as hydrogen trioxonitrate (HNO_3), hydrogen chloride (HCl), dihydrogen sulfate (H_2SO_4), hyperchloric acid ($HClO_4$), and hydrofluoric acid (HF). These forms of acids can be use single or can be combined to digest multifarious of samples and release the metals within. Also, these four acids can be combined together in the digestion of the toughest compounds like silica[1]. The knowledge of which acids to combine in order to obtain optimal results when digesting metals is very important.

2.1.1 Microwave Acids Digestion

Microwave digestion is now being engaged in digesting organic and inorganic matrices and it has become a routine method of analysis. This improved type of digestion has the merit of high sample output, loss of volatile species is drastically reduced and of little contamination levels[5]. "Microwave acid digestion is a technique to dissolve metals, bound within a sample matrix, into liquid". This is realized by subjecting a sample to a strong acid, in a closed vessel and raising the temperature and pressure through microwave glow as shown in Figure 2.1. Microwave enhanced the speed of heat decomposition of the sample and the dissolution of heavy metals are increased. The quantification of heavy metals released into solutions is accomplished through elemental techniques[6]. The microwave debonding method involves the use of a blend of some mineral acids that are freshly prepared, for example: concentrated HNO_3–H_2O_2, HNO_3–HCl, and HNO_3 in accordance with the standard operating procedure of recommended 6:2, v/v and 8 mL of the acids respectively, and this blend are freshly prepared mixture each time to be used[6,7]. These mixed mineral acids usually added to certain specified milligrams of sample to be digested and placed in a microwave. The temperature can be adjusted to 120 °C in 5 min with a power not exceeding 1000 W, and this can be maintained at 120 °C for 2 min. Then the temperature is increased to 210 °C in 10 min, and allow to remain at 210 °C for 15 min. At the end of the heating procedure, vessels are allowed to stabilize at room temperature for about 15 minutes, however, the oven is not allowed to exceed 1600W throughout the process. Digested samples are usually marked up to 25 mL with ultrapure water[6].

Figure 2.1: A Typical Microwave Digestor

Source[8].

As reported in the determination of “multi-element contents in Tamarind (*Tamarindus indica*), star fruit (*Averrhoa carambola*), golden berry (*Physalis peruviana*), kumquat (*Citrus japonica*), dragon fruit (*Hylocereus undatus*), and passion fruit (*Passiflora edulis*)”[5]. “The six procedures used to determine the element contents of these fruits includes; 8 mL HNO_3, 6 mL of HNO_3 + 2 mL of H_2O_2; 6 mL of HNO_3 + 2 mL of HCl, 8 mL of HNO_3 + 4 mL of H_2O_2, 8 mL of HNO_3 + 4 mL HCl, and, 12 mL of HNO_3”[2]. The acid mixture of 6 mL of HNO_3 + 2 mL of H_2O_2 in the experiment indicated the best digestion for all the fruits[5]. Microwave assisted digestion as described here has been successfully applied to biodiesel digestion prior to the determination of trace elements[9,10]. Moreover, it was reported that digestion method, based on microwave-assisted in closed vessels offers advantages over conventional open systems wet digestion that is characterised with loss of species, this method of digestion minimizes the risk of analyte loss, ameliorate contamination, sample throughput is improved, and digestion effectiveness is enhanced[9,10].

2.1.2 Coldblock Digestion

Coldblock digestion system make use of short-wave infrared radiation to precisely heat the sample and provision of a cooling block to improve condensation of fumes, thereby minimizing volatile components loss (Figure 2.2)[1]. Infrared radiation has attracted growing recognition based as a result of its fast heating of solutions, as it quickens the vibratory and rotational motion of the molecules[11,12]. The additional advantage of Coldblock digestion system is the volume of acids being used for digestion as a result of heating the sample directly and often times usage of dangerous acid like hydrogen fluoride and hypochlorite are removed[1]. Coldblock digestion system uses focused short-wave infrared lamps as a heat source, this heat source allows common aqua-regia to be used in digestion thereby eliminating hazardous chemicals[1]. The time required for Coldblock digestion is in minutes, speed of processing is coupled with reliability. The system is consistently accurate and precise across a range of sample types. Figure 2.2 show the application of Coldblock digestion.

2.1.3 Microwave Assisted Ultraviolet Digestion

"Ultraviolet radiation is the portion of the electromagnetic spectrum extending from the violet, or short-wavelength, end of the visible light range to the X-ray region" as shown in Figure 2.3[13,14]. The production of ultraviolet radiation is from sun of high-temperature surfaces, in a continuous spectrum and also by a gaseous discharge tube where atomic excitation takes place as a single spectrum of wavelengths[10]. Ultraviolet radiation has always been in used in research and as a sterilizer, as well as in fluorescent lamps a more energy-efficient form of artificial lighting compared with flickering lamps[13].

Ultraviolet radiation situates between about 400 nanometers (nm) and 10 nm wavelengths on the visible-light side and on the X-ray side respectively, though some scientists extend the short-wavelength limit to 4 nm. The ultraviolet radiation is conventionally split into four regions: near-infrared (400–300 nm), mid-infrared (300–200 nm), far-infrared (200–100 nm), and extreme (below 100 nm)[13,14]. Wavelengths of UV radiation has been categorized into three: UVB radiation which make up about 5% of the UV rays but very high in energy is effect affected most organisms and UVA radiation that make up 95% of all the UV rays that reaches the earth, this kind can penetrates deep into human's skin resulting in a tan and the third one is called UVC which is the highest energy portion of the UV radiation spectrum and it is blocked from reaching the earth surface by the ozone layer[13].

Figure 2.2: Coldblock Digestion Set Up

Source[14].

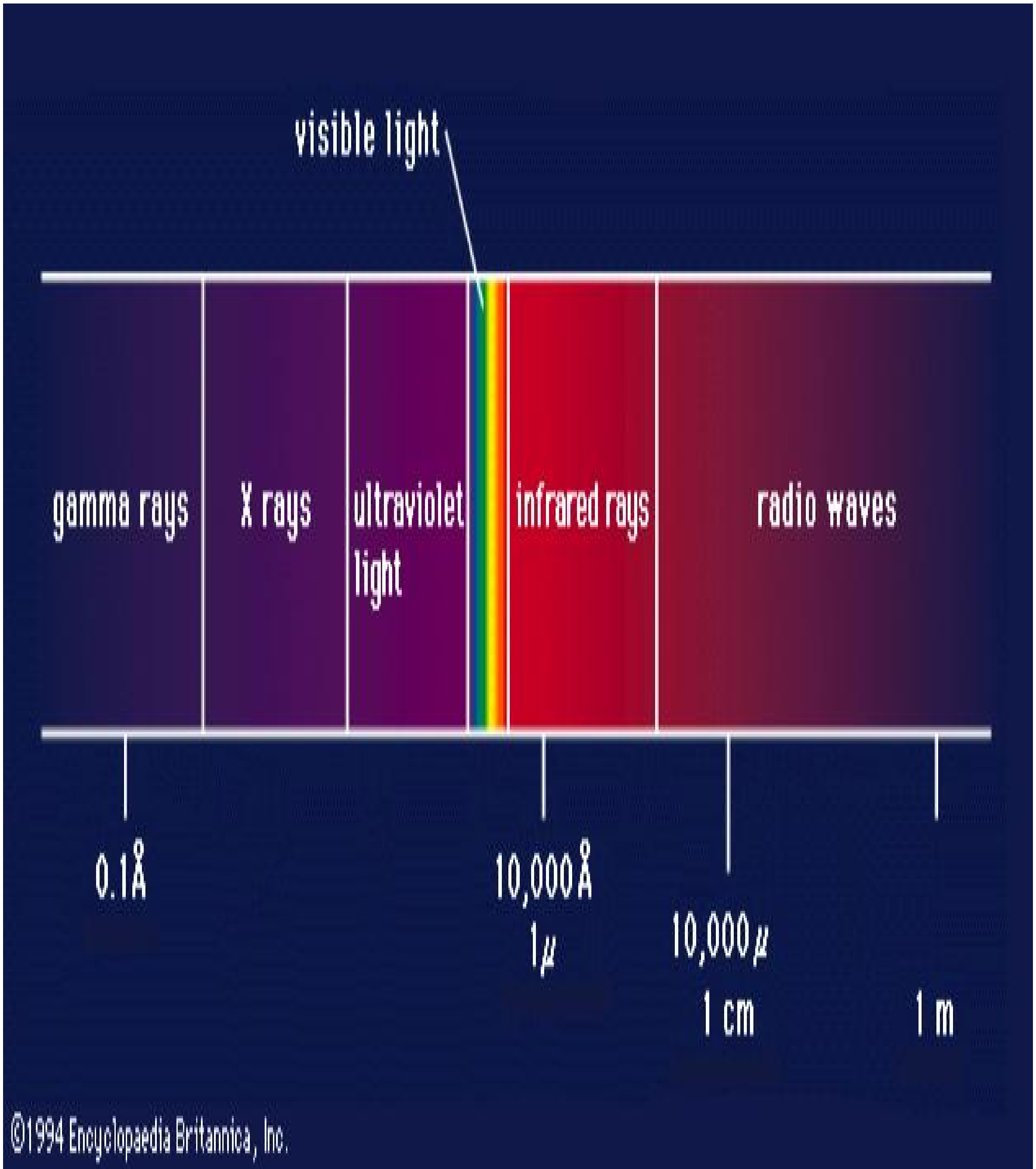

Figure 2.3: Electromagnetic Spectrum

Source[15].

It has been reported that ultraviolet digestion method is not used solely but in combination with another method like microwave digestion[16]. The system set up revealed the introduction of an electrodeless discharge lamp directly into the digestion vessel, while under a microwave field region the emission of UV radiation is triggered[16,17]. The following radicals are formed as a result of decomposition process in a microwave ultraviolet digestion; hydroxyl radicals ($OH^{\cdot}$) from the water (H_2O), hydrogen peroxide (H_2O_2) or nitrate ion (NO_3) as a result of addition of nitric acid. These $OH^{\cdot}$ radicals, that was generated during photochemical process, trigger the oxidation reactions, thereby accelerating the breaking down of the organic matter and whereby releasing the analyte from the matrix[18]. Relationship effect of the simultaneous application of ultraviolet and microwave-assisted digestion reduces the sample preparation time, thereby becoming an option to increasing the effectiveness of digestion and to minimize the use of concentrated reagents. This method has been used successfully in the process of digesting the biodiesel matrices for evaluation of trace elements by spectrometric methodology[19,20].

2.1.4 Dry Ashing Digestion2.1.4

Dry ashing digestion is mostly used for the digestion of food items as well as plant materials, the number of chemical reagents required for the method of digestion is minimal as well as the related hazards involved; this method requires simple equipment and better recovery is achieved[21].

High-temperature muffle furnace is usually set at 500°C to ash a sample placed inside a platinum crucible for at least 5 hours until the sample turns to white or grey ash residue, this procedure converts most minerals to sulfate, phosphates, oxides or silicates in dry ashing technique. In this digestion procedure new reagents are required; many samples can be analyzed simultaneously and it is not laborious[22]. The muffle furnace in dry ash method make room for large samples to be process at the same time and removal organics in the cause of ashing reduces the use of strong oxidizing acid and allow high sample processing[23]. However, this method requires relatively expensive apparatus like platinum crucibles and muffle furnace, some losses also occurred due to volatilization, some materials are difficult

to ash as well as dissolved and also high contamination is inevitable[24]. Research had been carried out to evaluate the effect of the dry ashing method on Cd isotope measurements of soil and plant samples[23].

Keshun Liu, has used the effect of dry ash temperature, sample size and duration in determining ash content of algae and other biomass, and, it was discovered that all the three factors had significant effects ($p < 0.05$) on ash measurement of algae samples[25].

2.1.5 Wet Acid Digestion

"Wet digestion methods for elemental analysis involve the chemical degradation of sample matrices in solution, usually with a combination of acids to increase solubility"[26]. It is a decomposition method of transforming the elements of a matrix into simple chemical forms. The decomposition takes place by means of mineral acids, or by supplying heat energy, or by combining the both. In this method of digestion, the choice of reagent to be used will depends upon the nature of sample matrices The amount of reagent used is consequent upon the size of the sample, which also depends on the sensitivity of the method of determination. Generally, wet decomposition technique will always use combination of some oxidizing acids such as concentration HNO_3, concentrated, $HClO_4$, as well as concentrated H_2SO_4, and nonoxidizing acids like HCl, HF, H_3PO_4, dilute H_2SO_4, dilute $HClO_4$ including hydrogen peroxide. Wet digestion has an advantage of being effective on both the inorganic and organic materials. Most often matrix in the sample is destroyed or remove thereby helping to eliminate some kinds of interference.

The procedures of conducting wet digestion often times are dangerous considering the high temperature involves and the kinds of reagents to be used[26]. In carrying out this digestion materials such as flasks, crucibles, etc., to be used are chosen carefully according to the particular procedure to be employed. Dissolution/desorption of elements happened from the surface[27]. It has been established that when considering materials to be used heat resistance, conductance, mechanical strength, resistance to acids and alkaline as well as surface properties and reactivity of that materials must be considered, and the organic and inorganic material as well should be given consideration. The nitric acid is accepted universally to be disintegration agent and it is widely used as primary oxidizer for the dissolution of organic matter because it does not interface with most results and commercially available[27]. The combination of hydrogen peroxide and hydrochloric acid with nitric acid enhances the quality of a decomposition. The general rule in wet digestion is to mix hydrochloric acid with other acids for samples containing principally inorganic matrices, and combinations of this with hydrofluoric acid are used to decompose silicate insolvable in the other acids[27].

Digestion method explained above has been used to digest several sample matrixes in different kinds of research work[28,29,30,31,32].

2.2 Techniques for Elemental Quantitative Analysis

Techniques used for elemental quantitative analysis are generally based on atomic spectroscopy in the form of absorption, emission, and fluorescence[33].

2.2.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a multi-elements technique that can detect majority of the periodic table elements at milligram to nanogram levels per liter. “ICP-MS is a type of mass spectrometry that uses an inductively coupled plasma to ionize the sample”[34]. It works on the principle of sample atomization that creates atomic and small polyatomic ions, which are then detected. ICP-MS is used to detect metals and several non-metals as well as different isotopes of same elements in liquid samples at very low concentrations [34].

ICP-MS is highly precise, sensitive and of great speed in analyzing elemental ions unlike atomic absorption spectrophotometer[34].

The plasma in ICP-MS is inductively heated by the gas with an electromagnetic coil thereby ionizing the plasma that contains a sufficient concentration of ions and electrons to make the gas electrically conductive from where it derives its name[34]. It has been reported that little gas is needed for ionization to take place in order to have a characteristic plasma[34]. Electrically neutral plasmas is used in the spectrochemical analysis, with each positive charge on an ion balanced by a free electron, there are almost equal numbers of ions and electrons in each unit volume of plasma[34].

The ICPs operate under capacitive (E) mode with low plasma density and inductive (H) mode with high plasma density, and the transition of these two modes occurs with external inputs[35]. In the case of ICP-MS, inductive mode is operational. ICP-MS differs from other forms of inorganic mass spectrometry because of its ability to auto-sample analyte continuously, without interruption[34].

The coupling of mass spectrometry with ICP is such that the ions from the plasma are extracted through a series of cones into a quadrupole usual called mass spectrometer[36]. The separation of ions is on the basis of their mass-to-charge ratio and the signal receives by a detector harmonious with the concentration as shown in Figure 2.4.

The concentration of a sample can be determined through calibration using certified reference material such as single or multi-element reference standards. ICP-MS through isotope dilution also lends itself to quantitative determinations, a single-point method based on an isotopically enriched standard. Data in ICP-MS is generally analyzed either quantitatively or semi-quantitatively, as isotope ratio measurements or in isotope dilution analyses[37]. The loudness of ICP-MS includes its multi-elements capability for almost all elements in the periodic table at concentrations in the low ng/L range with a high dynamic range. High sample output is another specialty which is particularly important in industrial applications. Low quantity of sample volumes, often with reasonably simple preparation methods, are usually adequate to produce the required results[38]. The method also has the ability of characterizing isotopes, both stable and radioactive, for high-precision measurement of isotope ratios. Furthermore, ICP-MS is also qualified as a selective detector in hyphenated methods using some form of separation technique to allow the determination of analyte species. Its constraints include the relatively high cost of the equipment which requires a high level of staff proficiency. Some of the most common problems related to ICP-MS usually are at the nebulizer or the cone ion optics elements, peristaltic pump which may lead to inconsistencies in the ion count rates and precision repeatedly measured from the same sample are likely to be observed if these elements are dirty or damaged[39,40]. As the technique is so sensitive and at the same time it may be prone to memory or carryover effects whereby the detection limits for an analyte may be artificially increased by its residual presence in the instrument resulting from previous analysis of samples or calibration standards with high concentrations of that same element. Though collision and reaction cells in single quadrupole systems are effective at eliminating elemental and molecular ion mass interferences, they are far less effective when it comes to eliminating isobaric mass interferences (two elemental ions with the same isotopic mass e.g., ^{58}Ni and ^{58}Fe) or interferences at m/z caused by doubly charged ions (z = 2; eg.$^{56}Fe^{2+}$ and $^{28}Si^{+}$). Separating these types of interferences typically requires triple quadrupole systems[39].

ICP-MS was explored in the quantitative assessment of trace elements in serum and whole blood, classification of wines according to several factors, heavy metals concentration in soil, heavy metal contents of different cereals and so many other elemental analysis[40,41,42,43].

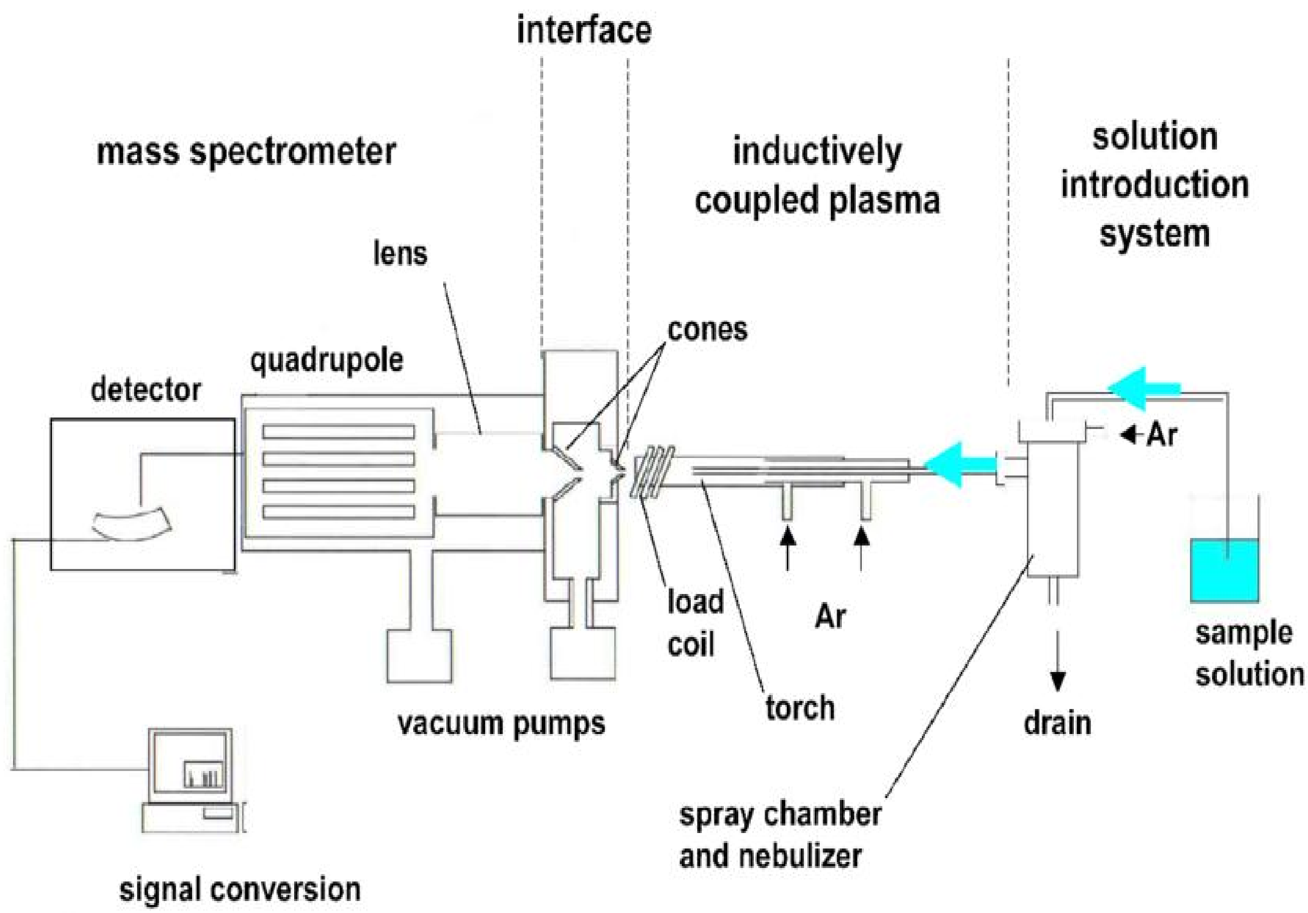

Figure 2.4: Schematic Diagram of an Inductively Coupled Plasma Mass Spectrometer ICP-MS
Source[44].

2.2.2 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also known as inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique used for the detection of chemical elements. This is a type of emission spectroscopy that utilizes the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The plasma is a high-temperature source of the ionized source gas and relies on optical emission for analysis. The plasma is sustained and maintained by inductive coupling from cooled electrical coils at megahertz frequencies. The source temperature is in the range of 6000 to 10,000 K. The intensity of the emissions from various wavelengths of light is proportional to the concentrations of the elements within the sample[34].

The ICP-OES is composed of two parts: the ICP and the optical spectrometer. The ICP torch consists of three concentric quartz glass tubes[45]. The output or "work" coil of the radio frequency (RF) generator surrounds part of this quartz torch.

The torch is operated in the H mode just like ICP-MS. When the torch is turned on, an intense electromagnetic field is generated within the coil by the high-power radio frequency signal flowing in the coil. This RF signal is prompted by the RF generator which is, effectively, a high-power radio transmitter driving the "work coil" the same way a typical radio transmitter drives a transmitting antenna. Typical instruments run at either 27 or 40 MHz[46,47]. The argon gas flowing through the torch is kindled with a Tesla unit that creates a brief discharge arc through the argon flow to initiate the ionization process. Once the plasma is kindled, the Tesla unit is turned off.

The ionization of argon gas takes place in the intense electromagnetic field and flows in a particular rotationally symmetrical pattern towards the magnetic field of the RF coil. A 7000 K of a stable and high temperature plasma is then generated as the result of the inelastic collisions created between the neutral argon atoms and the charged particles[34].

An aqueous or organic sample is pumped into an analytical nebulizer by means of a peristaltic pump where it is transformed into mist and migrated directly to the plasma flame. The sample immediately collides with the electrons and charged ions in the plasma and is itself broken down into charged ions. These various molecules break up into their respective atoms which then lose electrons and repeated recombination occurred in the plasma, giving off radiation at the characteristic wavelengths of the elements involved[34]. One or two transfer lenses are then used to focus the emitted light on a diffraction grating where it is separated into its component wavelengths in the optical spectrometer. At the optical chambers, the light is separated into its different wavelengths (colours), the light intensity is measured with a photomultiplier tube or tubes physically positioned to identified the specific wavelength(s) for each element line involved, or, charge-coupled (CCDs) with an array of semiconductor photodetector in a more modern equipment performed this functions of colour separation. In units using these detector arrays, the intensities of all wavelengths within the system's range can be measured simultaneously, allowing the instrument to analyze every element to which the unit is sensitive all at once, by this, samples can be analyzed very quickly[34].

ICP-OES is presently being employed in pharmaceutical analysis due to its accuracy and sensitivity[48]. Also, it is beneficial for sample preparation because making multiple dilutions is eliminated as it can detect multiple elements from an analysis. Besides, it is being successfully used in the analysis of DNA, protein, and trace elements in the human body[49,50]. The ICP-OES has been reported to have played a major role in the analysis of complex samples and has been used in procedure for trace elements analysis in the human brain, determining the chemical composition of electronic cigarettes, screening of pesticides and assessing the purity of pharmaceutical compounds[51,52]. The technique has also found routine utility in the analysis of drinking water, wine, petrochemicals composition of crude oil, contaminated soil and heavy metal mixtures, all of which would be difficult to analyze by other methods[52,53,54,55].

Notable among ICP-OES merits include the ability to identify the types and ratios of elements in complex samples, as well as the ability to detect multiple elements simultaneously, researchers reported analytical procedure where ICP-OES was able to detect up to 19 elements [56,57]. ICP-OES was generally accepted because of its ability to aerosolize a wider variety of samples and also has advantage in spectral deconvolution and calibration procedures to facilitate effective detection[58,59]. Moreover, ICP-OES can still be used to determine the elemental composition of radioactive samples[60]. One of the limitations of ICP-OES include the fact that samples must be aerosolized, though aerosolization procedures have taken new trends, it means solid and liquid samples cannot be analyzed while they are still in their solid and liquid forms. Moreover, analytical procedure in ICP-OES does not take preservation of samples in consideration, meaning that the sample cannot be recovered after analysis[52]. As a result, highly valuable or rare samples cannot be analyzed via this method. Moreover, method development using ICP-OES can be a time-consuming process, as it necessarily involves multiple steps: like doing crude analysis to obtain a basic idea of the elements present in the sample; initial knowledge is needed to be able to select wavelength; separation optimization to prevent signals from the various wavelengths from overlapping; an internal standard is required to validate the method and system performance; and analysis for spectral interferences and ways to eliminate those from the read-out without eliminating target signals some of the drawbacks[60]. Finally, ICP-OES requires costly instrumentation for plasma generation, sample aerosolizing, and signal analysis, albeit at a relatively lower cost than other comparable methods such as ICP-MS, which means that access to this technique is necessarily limited[52].

It offers the least detection time, lower detection limits, a broader linear dynamic range, and greater matrix tolerability as well as negligible chemical interferences. Beyond this, it can handle multiple varieties of samples including aqueous, inorganic, organic liquids, and solids as well[61,62]. Among other things poor precision, sample drift, non-ideal detection limits, and inaccurate identification are familiar problems with ICP-OES[60]. Figure 2.5 showed a typical part of ICP-OES in diagram.

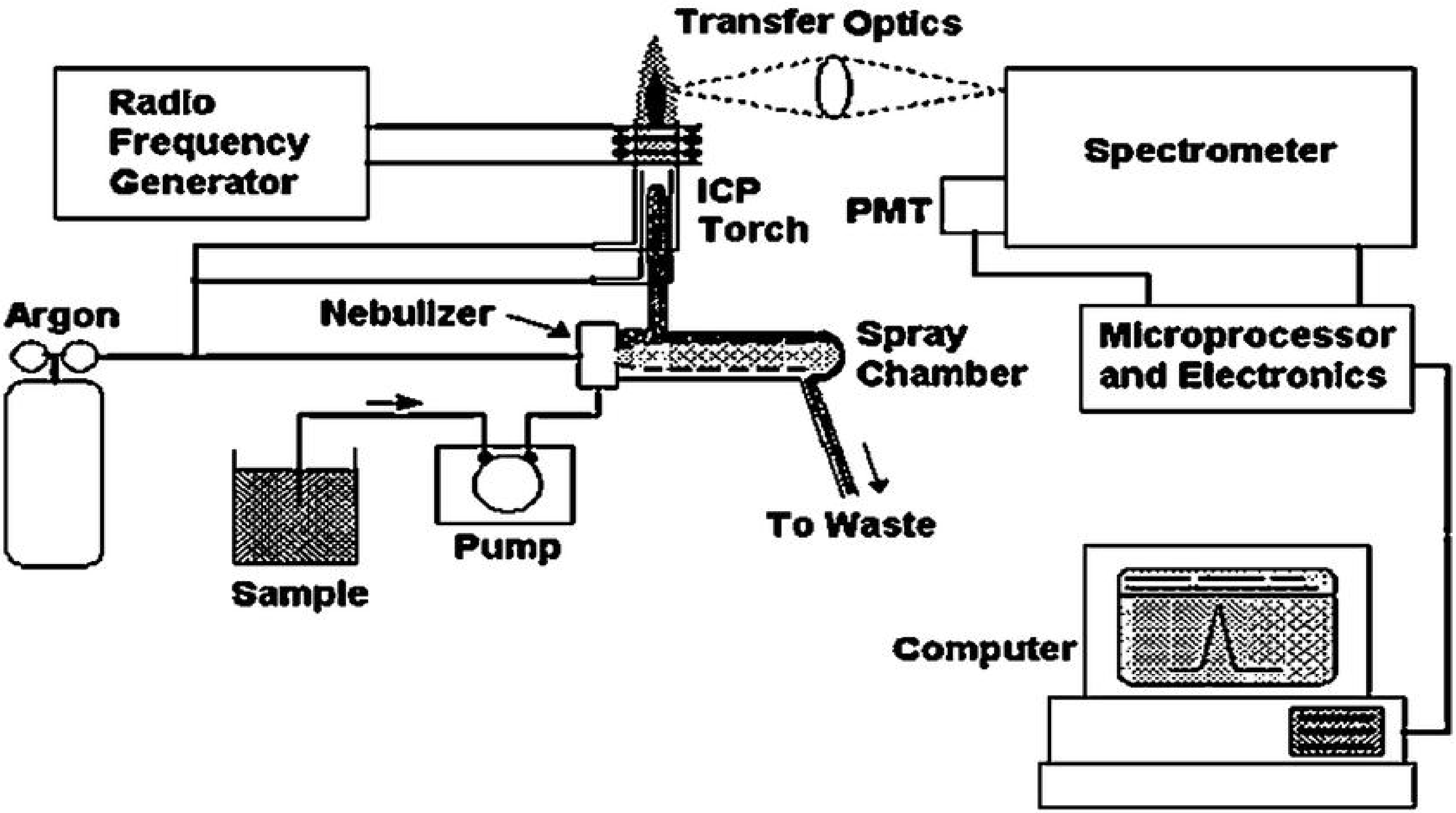

Figure 2.5: Inductively Coupled Plasma Optical Emission Spectroscopy

Source[63].

2.2.3 Atomic Emission Spectrometry (AES)

Atomic emission spectroscopy (AES) is a chemical method of analysis that uses the intensity of light emitted from a source (flame, plasma, arc, or spark) at a particular wavelength to determine the quantity of a metal in a sample. The atomic spectral line wavelength in the emission spectrum gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms of the element[34]. Atomic emission occurs when a valence electron in a higher energy atomic orbital return to a lower energy atomic orbital[64]. An atomic emission spectrometer is similar in design to the instrumentation for atomic absorption and it is convenient to adapt most flame atomic absorption spectrometers for atomic emission by turning off the hollow cathode lamp and monitoring the difference in the emission intensity when aspirating the sample and when aspirating a blank. Many atomic emission spectrometers, however, are dedicated instruments designed to take advantage of features unique to atomic emission, including the use of plasmas, arcs, sparks, and lasers as atomization and excitation sources, and an enhanced capability for multi-elemental analysis[65]. Atomic emission uses flames and plasmas for converting a solid, liquid, or solution analyte into a free gaseous atom as shown in Figure 2.6. The same source of thermal energy usually serves as the excitation source. Solid samples may be analyzed by dissolving in a solvent and using a flame or plasma atomizer[64]. The same nebulization and spray chamber assembly used in atomic absorption for atomization and excitation is used in flame atomic emission[64]. The main components of AES are the same as atomic absorption spectrometry (AAS), the difference is that in AAS, the amount of absorbed energy is measured whereas, in AES, the amount of emitted energy by the atoms is measured[34]. The wavelength of the atomic spectral radiation informs the identity of each element[34]. AES most of the times is used in combination with other equipment like ICP[65,66].

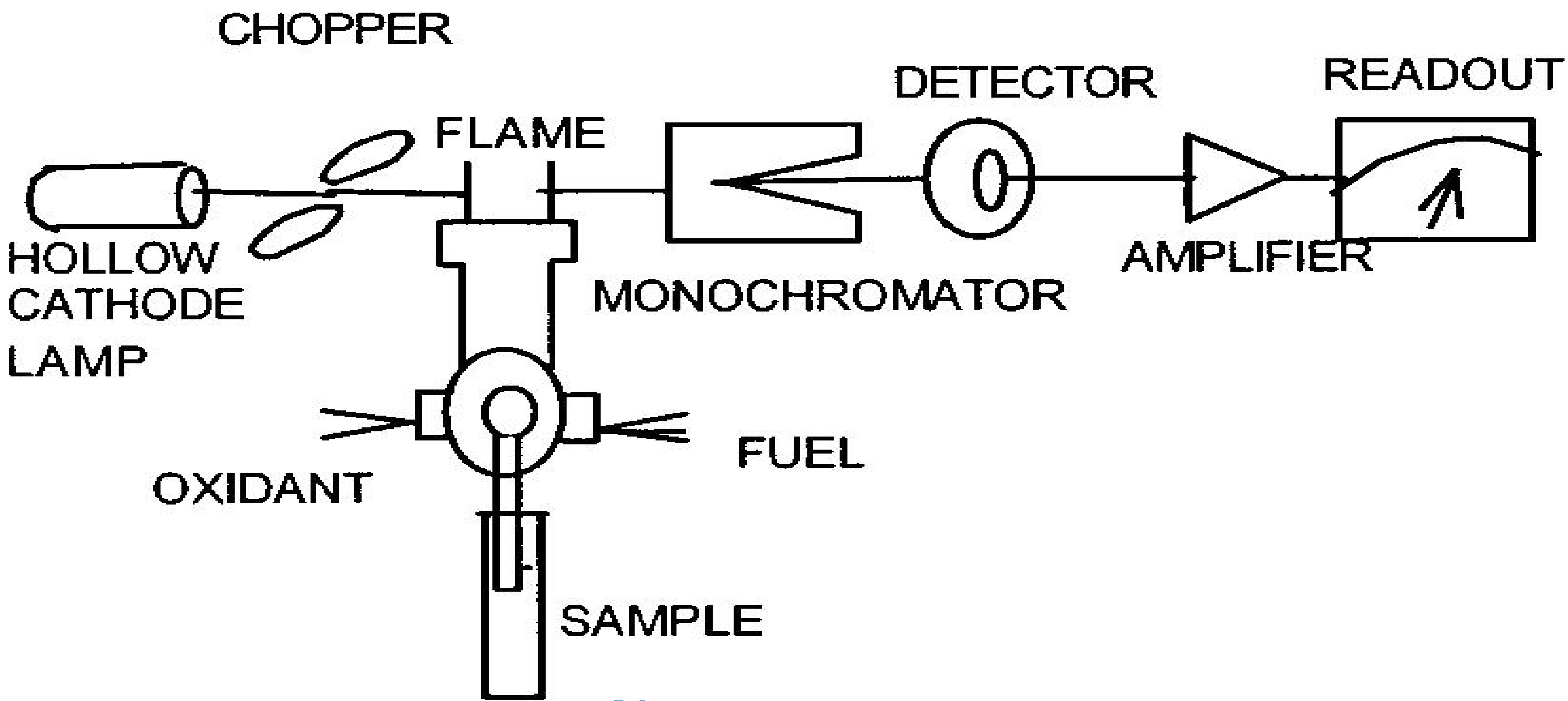

Figure 2.6: Schematic Diagram of Atomic Emission Spectrophotometer

Source[67].

2.2.4 Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry (AAS) is an analytical technique used to determine the concentration of metal atoms/ions in a sample by measuring the absorbed radiation by the metal[68,69]. Metals make up around 75% of the earth's chemical elements. Metal content in a material in most cases is desirable, but can also be contaminants, and, as a result, measuring metal content is critical in many different applications. To measure the metal content in a sample is by reading the spectra produced when the sample is excited by radiation. The atoms absorb ultraviolet or visible light and make transitions to higher energy levels[69]. Atomic absorption methods determined the amount of energy in the form of photons of light that are absorbed by the sample. The light transmitted by the sample is measure by a detector and compares them to the wavelengths which has passed through the sample initially. A signal processor then incorporates the changes in wavelength absorbed, which appear in the readout as peaks of energy absorption as single wavelengths. The energy needed for an electron to leave an atom is known as ionization energy and is specific to each chemical element[69]. When an electron moves from one energy level to another within the atom, a photon is emitted with energy. Every atom has its own distinct pattern of wavelengths at which it will absorb energy, due to the unique configuration of electrons in its outer shell[69]. A typical atomic absorption spectrometer consists of four main components: the light source, the atomization system, the monochromator and the detection system[68].

Atomization of solid or liquid materials is done either in the flame or graphite furnace. The free atoms are then exposed to light, typically produced by a hollow-cathode lamp, and undergo electronic transitions from the ground state to excited electronic states. The light produced by the lamp is emitted from excited atoms of the same element that is to be determined, therefore the radiation energy corresponds directly to the wavelength absorbed by the atomized sample[68]. A monochromator is placed between the sample and the detector, whose function is to measure the intensity of the beam of light and converts it to absorption data. Monochromator was so positioned to reduce the background interferences. AAS is used mainly to analyze metals atoms this is because metals have narrow, bright and clear single emission and absorption lines[68]. The process of turning a liquid sample into an atomic gas are desolvation, vaporization and volatilization. Desolvation is the evaporation of liquid solvent into the dry sample, which vaporizes to a gas, while volatilization is the breaking down of compounds that compose the sample into free atoms[69]. Flame and furnace spectroscopy has been used for the analysis of metals over the years, and nowadays they are being used in materials and environmental applications. This is due to the need for lower detection limits and for trace analysis in a wide range of samples[69]. AAS has larger specificity that ICP does not have[69].

Light of a specific wavelength, selected appropriately for the element being analyzed, is given off when the metal is ionized in the flame; the absorption of this light by the element of interest is proportional to the concentration of that element. Quantification in AAS is accomplished by preparing standards of the elements.

2.2.5 Flame Atomic Absorption Spectrometry

Flame atomic absorption methods are referred to as direct aspiration determinations and is a very common technique for detecting metals and metalloids in environmental samples. They are normally completed as single element analyses and are relatively free of interelement spectral interferences[69]. In this method, the temperature or type of flame used for some elements is sacrosanct. It is also important that flame and analytical conditions are met for elements to be determined so as to prevent chemical and ionization interferences. Different flames can be achieved using different mixtures of gases, depending on the desired temperature and burning velocity. Some elements can only be converted to atoms at high temperatures. Even at high temperatures, if excess oxygen is present, some metals form oxides that do not re-dissociate into atoms. To inhibit their formation, conditions of the flame may be modified to achieve a reducing, non-oxidizing flame. The flame is produced by a burner for atomization as shown in figure 2.7. Methods used in the determination of metals in flame AAS could be one of the three pattern-matching; calibration curve generated by a series of patterns, standard addition and internal standard. The most widely used method is calibration curves generated from a series of patterns, which involves measuring the sample of interest in a series of samples of known concentration prepared under the same conditions[69].

Flame atomic absorption spectrophotometers are being used widely in the determination of various chemical and environmental materials[70,71,72,73].

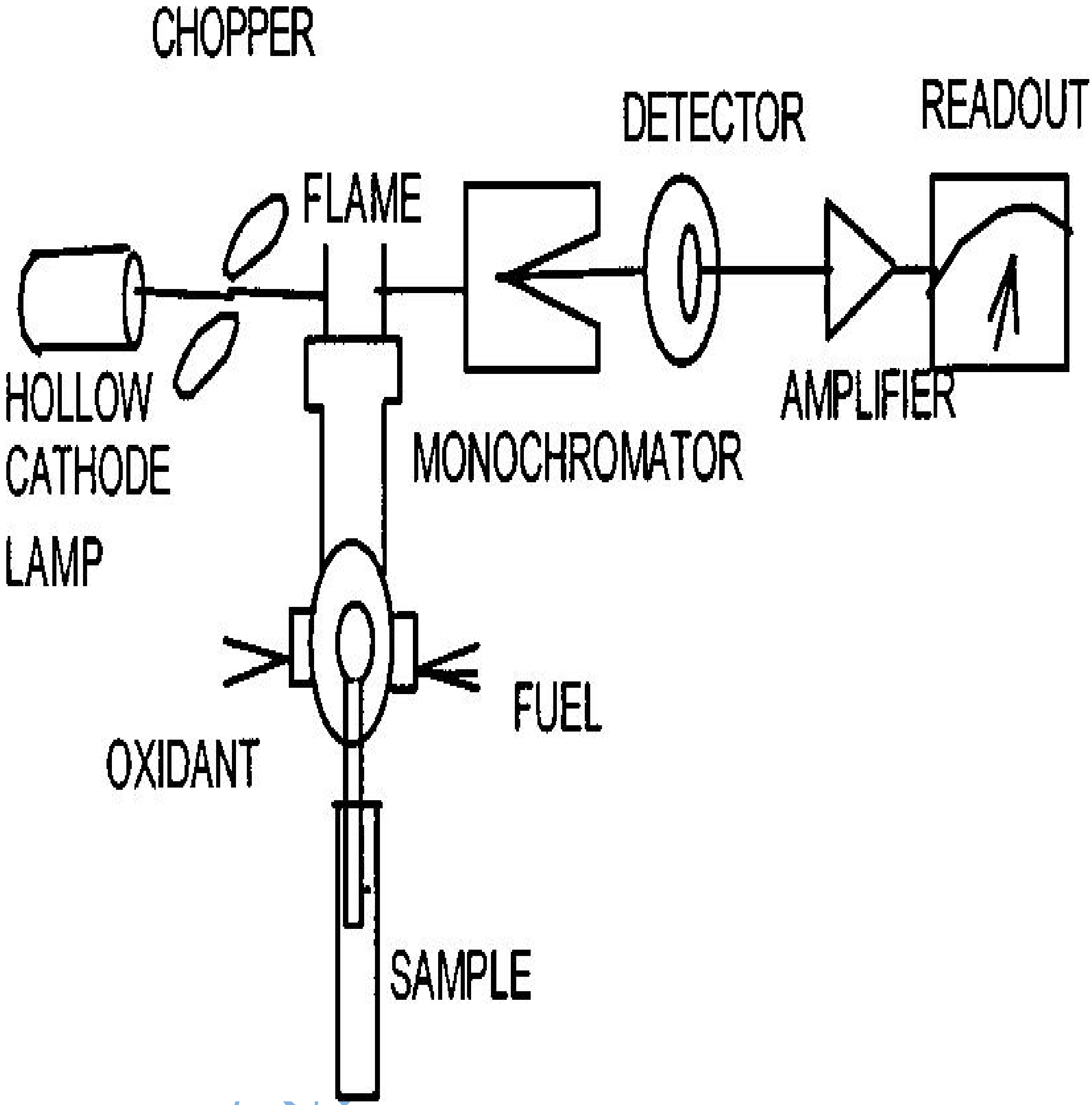

Figure 2.7: Schematic Diagram of Flame Atomic Spectrometry

Source[74].

2.1 Difference between Atomic Absorption Spectrophotometer and Atomic Emission Spectrophotometer

S/N	Atomic Absorption Spectrophotometer (AAS)	Atomic Emission Spectrophotometer (AES)
1.	It depends upon the number of atoms in ground state	It depends upon the number of atoms present in excited state
2.	It measures the radiations absorbed by the atoms in ground state	It measures the radiations emitted from atoms in excited state
3.	Light source is present	Light source is absent
4.	There is a separate chamber for atomization of the sample.	Atomization takes place step by step upon the introduction of the sample to the flame
5.	AAS employs the method of absorption of light by the atoms.	In AES, the light emitted by the atoms is what is taken into consideration.

Source[75].

2.3 Drawback of Digestion Based Technique

The reagents used in digestion-based techniques are potentially hazardous as well as instruments and operations employed, even when used as directed[76]. It is paramount that the operator must put on laboratory protection like coat, gloves, and safety glasses properly when handling wet digestion procedures[76]. A well-ventilated hood is needed when using concentrated fuming acids (HF, HNO_3, HCl), while oxidizing acids (HNO_3, $HClO_4$) which are more hazardous than non-oxidizing acids like HCl, H_3PO_4, and HF are prone to explosion, especially in the presence of reducing agents like organic matter.

Digestion of acids that are conducted in a fume cupboard must be combined with efficient scrubbers. It is reported that great care should be taken when using pressure digestion methods because pressure digestion vessels (bombs) contain acid fumes which are useful for rapid, one-step digestions without losses, but in reactions that are spontaneous, potentially explosive gases are produced that may exceed the safety limits of the vessels thereby leading to explosion[76]. For instance, nitric acid and especially the spontaneous HNO_3 and H_2O_2 decomposition of organic matter in a closed vessel may result in an explosion due to unintended pressure build-up within the vessel. These systems produce high-pressure spikes, which can be avoided by decreasing the sample weight or by applying a gradual temperature increase.

2.4 Alternative Method for Elemental Quantitative Analysis

2.4.1 X-rays Absorption Analysis Method

Wilhelm Röntgen in 1895 discovered X-rays and it was defined as a short wavelength form of electromagnetic radiation[77]. An X-ray is a high-frequency electromagnetic radiation of energy intertwined between the far ultraviolet and gamma-ray regions of the spectrum[78]. X-rays evolved from electron transitions between discrete orbitals shells of an atom, for example, gamma-rays are emitted by the nucleus[78]. An X-ray's energy is measured in unit of an electron volt this presupposes that one electron volt is an energy impacted to an electron after acceleration through a potential field of one volt[78].

X-ray waveform is sinusoidal in nature like every other electromagnetic radiation[78]. As a result of this, an X-ray can also be typified by its wavelength.

$E = hv = hv/\lambda$

Where E is energy, λ is wavelength and *h* are the Planck constant = 6.626 X 10^{-34} joules s^{-1}, c is the velocity of light in vacuum = 2.998 x 108 ms^{-I}, and v is the frequency of the waveform (cycles per second)[78].

X-ray fluorescence analysis is consistent and predictable when it comes to variation in the energy of X-ray emissions from atom to atom when compared with other X-ray analytical techniques[78]. Moseley (1913, 1914) observed this uniqueness and formulated a formular that related the wavelength of an X-ray emission (A.) to the atomic number of an element (Z)[75].

$I/\lambda = k\,(Z- \sigma)^2$ where k is a constant for a particular series of lines (K, L, M, etc.), and σ is a shielding constant.

Moseley findings were eventually used to confirm the atomic number of new elements in the Periodic Table (from their appropriate X-ray signature) and can be appropriated as the foundation of analytical X-ray spectrometry[78]. This fundamental is related to transitions of electrons between orbitals of discrete energy in an atom.

X-rays form part of the electromagnetic spectrum and are characterized by energies lying between ultraviolet and gamma radiation. Wavelengths are usually in the range of 0.01 to 10 nm, which is equivalent to energies of 125 keV to 0.125 keV[79].

Generally, in society today X-rays are used for medical imaging in hospitals and airport baggage screening at gates. It is being used for elemental and structural analytical techniques in science[80]. X-rays are produced when accelerated electrons within an X-ray tube interacted[78]. X-ray absorption spectroscopy (XAS) is a widely used technique for determining the local geometric and/or electronic structure of matter[81]. The analysis is usually performed at synchrotron radiation facilities, which provide intense and tunable X-ray beams. Samples are usually in the gas, solutions, or solids phases[81].

X-ray spectroscopy run on the principle of the excitation of core electrons that are rotating in the subordinate shell(s). As the electron absorbs X-rays, it becomes excited and hop to a higher level. The X-ray zone used ranges from 1 to 100 nm. When X-rays associate with electrons it excites them to higher levels. Energy absorbed by the electrons has a peculiar value for each element one can differentiate with the X-ray absorption spectrum[82].

2.4.2 Genesis of X-ray Fluorescence (XRF)

X-ray fluorescence is now a popular well-known method of analysis in both the laboratory and industry[83]. X-rays were first identified by the German physicist Wilhelm K. Röntgen (1845–1923), for which he won the Nobel Prize in 1901. Charles, G. Barkla in 1909 found a connection between X-rays radiating from a sample and the atomic weight of the sample. In 1913, Henry G. J. Moseley helped number the elements with the use of X-rays, by observing that the Kline transitions in an X-ray spectrum moved the same amount each time the atomic number increased by one, a primary theoretical precept in XRF physics. He demonstrated that when a chemical element emits certain characteristic X-rays, the frequencies of these X-rays are proportional to the square of a number close to the element's atomic number. This became Moseley's Law. He later laid the foundation for identifying elements in X-ray spectroscopy by establishing a relationship between frequency (energy) and atomic number, which form the basis of modern X-ray spectrometry[84].

Scientists experimented with primary x-rays instead of electrons to excite samples in the 1920s, and in 1928, pioneered XRF as a means of performing the quantitative analysis of materials.

However, it was not until the 1940s that detector technology developed to an extent that turned XRF into a more practical technique for elemental analysis[84].

By the 1950s, there were the first commercially-produced X-ray spectrometers using crystals to separate X-ray energies as their wavelengths with simple X-ray detectors.

The development of a high-tech lithium-drifted silicon detector took place in 1970 and this inform the basis for detecting energies of x-rays directly as Energy Dispersive XRF technology still in use today[84].

2.4.3 Categories of XRF Spectrometers

XRF is classified into energy dispersive (EDXRF) and wavelength dispersive (WDXRF). Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS or XEDS), sometimes called energy dispersive X-ray analysis (EDAX or EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characteristic of a sample[85]. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum (which is the main principle of spectroscopy)[85]. The peak positions are predicted by Moseley's law with accuracy much better than the experimental resolution of a typical EDX instrument. Energy Dispersive X-Ray Fluorescence (ED-XRF) is an express, multi-element and non-destructive analytical technique that does not involve sample preparation or any pollution due to the use of chemical extractant[86]. EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements ($Z < 10$). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition[87].

The wavelength-dispersive X-ray spectroscopy (WDXS or WDS) is a non-destructive analysis technique used to obtain elemental information about a range of materials by measuring characteristic X-rays within a small wavelength range. The technique generates a spectrum in which the peaks correspond to specific X-ray lines and elements can be easily identified.

WDS is primarily used in chemical analysis, wavelength-dispersive X-ray fluorescence spectrometry, electron microscope, scanning electron microscope, and high-precision experiments for testing atomic and plasma physics[88].

This technique is complementary to energy-dispersive spectroscopy (EDS) in that WDS spectrometers have significantly higher spectral resolution and enhanced quantitative potential. Many scanning electron microscopies (SEM) and electron probe micro-analyzer (EPMA) instruments have EDS systems mounted to the column, and an EPMA typically has an array of several WDS spectrometers for simultaneous measurement of multiple elements. In typical EPMA applications, EDS is used for quick elemental scans to find out what material contains, and WDS is then used to acquire precise chemical analyses of selected phases[89].

The main difference between EDS and WDS is that energy dispersive spectrometers (EDS) sort the X-rays based on their energy; while wavelength dispersive spectrometers (WDS) sort the X-rays based on their wavelengths[90]. A wavelength dispersive spectrometer distinguishes X-rays by moving a crystal through a range of angles until the Bragg angle is matched for the wavelength distinguished. Only one element per spectrometer can be measured at a time. An energy dispersive system uses solid-state detector and associated electronics to sort the entire range of emitted X-rays by their energy[83]. With both methods, the energy (or wavelength) of an X-ray "peak" is characteristic of the emitting atom and the intensity is proportional to that atom's weight fraction in the sample. In general, WDS provides higher peak-to-background ratios than EDS and therefore lower detectabi1ity limits and is thus preferred for work involving near-trace concentrations[91].

Some of the advantages and disadvantages of modern EDS and WDS includes: (a) Elemental detection range; EDS is usually limited to elements heavier than Na, WDS will detect metals down to Be with introduction of appropriate crystals, (b) Limits of detection: depends on the smallest weight percent detectable depends upon operating conditions and the chemical matrix of the specimen, WDS will normally detect lower concentrations in sequence of importance. (c) Operating sensitivity: Solid-state EDS detectors are more sensitive than WDS detectors; as a result, beam currents can be 30x to 50x lower. This risk of damage to beam-sensitive samples is being reduced by this detector. (d) Instrument adaptibi1ity: Most scanning electron microscope(s) (SEM) readily accept an EDS system, whereas some may not have the proper ports or geometry for WDS. In addition, some smaller SEMs may not be able to generate beam currents high enough for WDS[91]. In terms of cost WDS cost much more than EDS. The lower price and the portable and simultaneous multi-elemental capabilities of EDXRF put the energy-dispersive system several steps ahead of the WDXRF in environmental applications[92].

2.4.4 Basic Principles of XRF Spectrometers

XRF works on techniques that engages interactions among electron beams and X-rays with samples. This is made possible by the atoms' behavior when they interact with radiation. When materials are excited with high-energy, short-wavelength radiation such as X-rays, they can become ionized. An electron is in motion to higher energy level from the inner shell of an atom when excited by the energy of a photon. When it returns to the low energy level, the energy which it previously gained by the excitation is emitted as a photon which has a wavelength that is specific for the element under investigation. Thus, atomic X-rays are emitted during electronic transitions to the inner shell states in atoms of modest atomic number. These X-rays have characteristic energies related to the atomic number, and each element, therefore, has a characteristic X-ray spectrum which can be used to identify the element[93].

2.4.5 X-ray Acquisition

X-rays make up X-radiation, a form of electromagnetic radiation. Most X-rays have a wavelength ranging from 0.01 to 10 nanometers, corresponding to frequencies in the range 30 petahertz to 30 exahertz (3×1016 Hz to 3×1019 Hz) and energies in the range 100 eV to 100 keV, produced by the deceleration of high-energy electrons[93]. An X-rays tube is a vacuum tube that uses a high voltage to accelerate the electrons released by a hot cathode to a high velocity thereby generating X-ray. The high-velocity electrons collide with a target metal in the sample, the anode, creating the X-rays[93]. The production of X-rays passes through three stages: the charged particle is accelerated, atomic transitions between discrete energy levels, and some atomic nuclei decay radioactively. Each mechanism leads to an identifiable spectrum of X-ray radiation[94]. As noticed in the theory of classical electromagnetism, accelerating electric charges emit electromagnetic waves. In the most common terrestrial source of X-rays, the X-ray tube, a beam of high-energy electrons collides on a solid target. As the fast-moving electrons in the beam interact with the electrons and nuclei of the target atoms, they are repeatedly deflected and slowed. During this abrupt deceleration, the beam electrons emit bremsstrahlung (German: “braking radiation”) — a continuous spectrum of electromagnetic radiation with a peak intensity in the X-ray region. Most of the energy radiated in an X-ray tube is contained in this continuous spectrum[93,94]. Far more powerful and far larger sources of a continuum of X-rays are synchrotron particle accelerators and storage rings. In a synchrotron, charged particles normally electrons are accelerated to very high energies of billions electron volts and then captured in a closed orbit by strong magnets[94]. In an X-ray tube, in addition to the continuous spectrum of radiation emitted by the decelerating electrons, there is also a spectrum of distinct X-ray emission lines that is characteristic of the target material. This "characteristic radiation" results from the excitation of the target atoms by collisions with the fast-moving electrons. Most commonly, a collision first causes a tightly bound inner-shell electron to be ejected from the atom; a loosely bound outer-shell electron then falls into the inner shell to fill the vacancy. In the process, a single photon is emitted by the atom with an energy equal to the difference between the inner-shell and outer-shell vacancy states. This energy difference usually corresponds to photon wavelengths in the X-ray region of the spectrum. Discrete X-ray radiation can also evolve from a target material when it is exposed to a primary X-ray beam. In this case, the primary X-ray photons initiate the sequence of electron transitions that result in the emission of secondary X-ray photons.

2.4.6 Instrumentation

Handheld/Portable XRF is a rapid, mobile, high throughput, and potentially cost-effective instrumental analytical technique capable of elemental assessment. It is widely used for environmental assessment of soils in a variety of contexts such as agriculture and pollution both in-situ and ex-situ, to varying levels of success[95]. The process of X-ray Fluorescence as shown in Figure 2.7 commences with an excitation X-ray which is normally generated using an X-ray tube. This excitation X-ray collides with an inner shell electron of the atom and displaced the electron from the atom. The vacant position is filled by an electron from a further outer shell and fluorescence radiation is emitted[96]. The power of this radiation is unique to the specific atom and indicates what atom is present in the sample. X-rays with different energies will be emitted, notwithstanding the number of atoms contained in a sample.

Relating to an energy-dispersive XRF instrument, the fluorescence radiation is collected by a semi-conductor detector. The X-rays create signals in the detector, which are dependent on the energy of the incoming radiation. The signals are collected using a multi-channel-analyzer, and converted into a spectrum. These spectral are inform of peaks in counts per seconds and emission energies. Using the energies of the peaks, the elements present in the sample can be identified. The process handles each X-ray one by one but with high speed. Modern detectors can handle 1 million counts per second and more, consequent upon which the spectrum can be recorded quasi-simultaneously. Even with a short measurement time, the spectrum can give sufficient information to calculate intensities, which can be used to determine the composition of the sample[96]. Calibrated machine for a longer measurement time allows for better statistics resulting in good precision as well as peak-to-background thus resulting in improved detection limits.

Modern energy-dispersive X-ray fluorescence is available as a portable instrument with a tube-based X-ray source, as opposed to a radioactive isotope source shown in Figure 2.8. The introduction of Peltier–cooled silicon drift detectors (SDD), has helped in the effective measurement of incoming photons energy via the ionization produced in the detector and accomplished impressive resolution and can identify elements as light as carbon[97]. A handheld XRF is capable of detecting low atomic number elements as low as to either Mg or Na, depending on the configuration of the system cum type of matrix. The presentation of portable ED-XRF systems, also known as p-XRF, affords new opportunities for rapid, low-cost plant nutritional analysis, both as a traveling laboratory system and as an on-the-spot analyzer[98].

Sample preparation of XRF techniques is characterized by sample homogenization, while the processing is fast and capable of multi-elemental analysis over a large concentration range, which makes the procedure fast and cheap, and therefore suitable for application to a large number of samples[99].

Figure 2.8: Handheld TRACER 5i XRF

Source[100].

The technique involves a procedure in which electrons of a given energy range interact with an X-ray source called anode to produce an X-ray spectrum. The configuration of p-XRF devices is more or less the same like that of benchtop instruments except for their sizes. Photons are emitted from an X-ray tube using Rh, Ag, Mo, Cr, or W, as an anode. These photons interact with the atoms within a sample, which in turn emit photons specific to each element. These photons then pass through a Peltier-cooled SDD to reach a detector, where photons are identified as counts within a particular channel, which can be converted in a computer into a spectrum of energy with elements clearly identifiable as peaks.

The range of elements currently analyzable using the p-XRF method range from neon to plutonium and on to synthetic elements. Detection of lighter elements requires modification of atmospheric parameters, as the nitrogen and oxygen in the air readily absorb their relatively lower energy emissions.

It has been accounted for that sample preparation is required for optimizing the sensitivity, reliability and elemental detection from p-XRF. Though applications of p-XRF to archaeology, geochemistry and other disciplines show a range of sample preparations available and may use reduced protocols when analyzing soil. Some studies reported that p-XRF can be used directly on object of analysis in-situ[101]. However, a researcher was of the opinion that the comparison of different sediment preparations when interplaying with p-XRF will give a reasonable result[102]. Three clear-cut procedures: in-situ, in-field and ex-situ can be used to analyze archaeological soil using p-XRF. The in-situ technique had been done by some researchers and it is carried out by holding the p-XRF pointedly against the soil and analysis is done without extraction or sample preparation[103,104,105]. Some researchers reported that the in-field method involves extracting a soil sample into a clear plastic bag and analyzing it with the p-XRF in contact with five different locations of the bag[103,104,105]. The ex-situ method involves extracting, fully drying, sieving and homogenizing soil before putting it into plastic XRF sample cups, typically in lab-based applications[102,105,106,107,108]. There is a range of protocols encapsulated within ex-situ methods, such as milling, pressing and pelleting[109,110].

The ex-situ procedure used in this research involves manual grinding without pelleting because this does not require access to additional instrumentation. The in-situ method is used for applications such as archaeometry, geology, mapping contaminated soils and sample screening due to the desire to exploit the rapid, simple and portable nature of p-XRF in site-wide analyses as commented by scientists[108,110]. Also, some researchers, commented that moisture enhances the absorption of X-rays and scatters the primary X-rays, which together attenuate the refracting X-rays and effectively under-detect the 'true' value[112]. However, several investigations into moisture content suggested that the matrix effects and moisture in unprocessed soil have more impact than reported, but can be accounted for with correction formulae irrespective of the soil and archaeological site as commented[112]. Figure 2.9 showed how a typical X-ray passed through a sample material and detected on a detector.

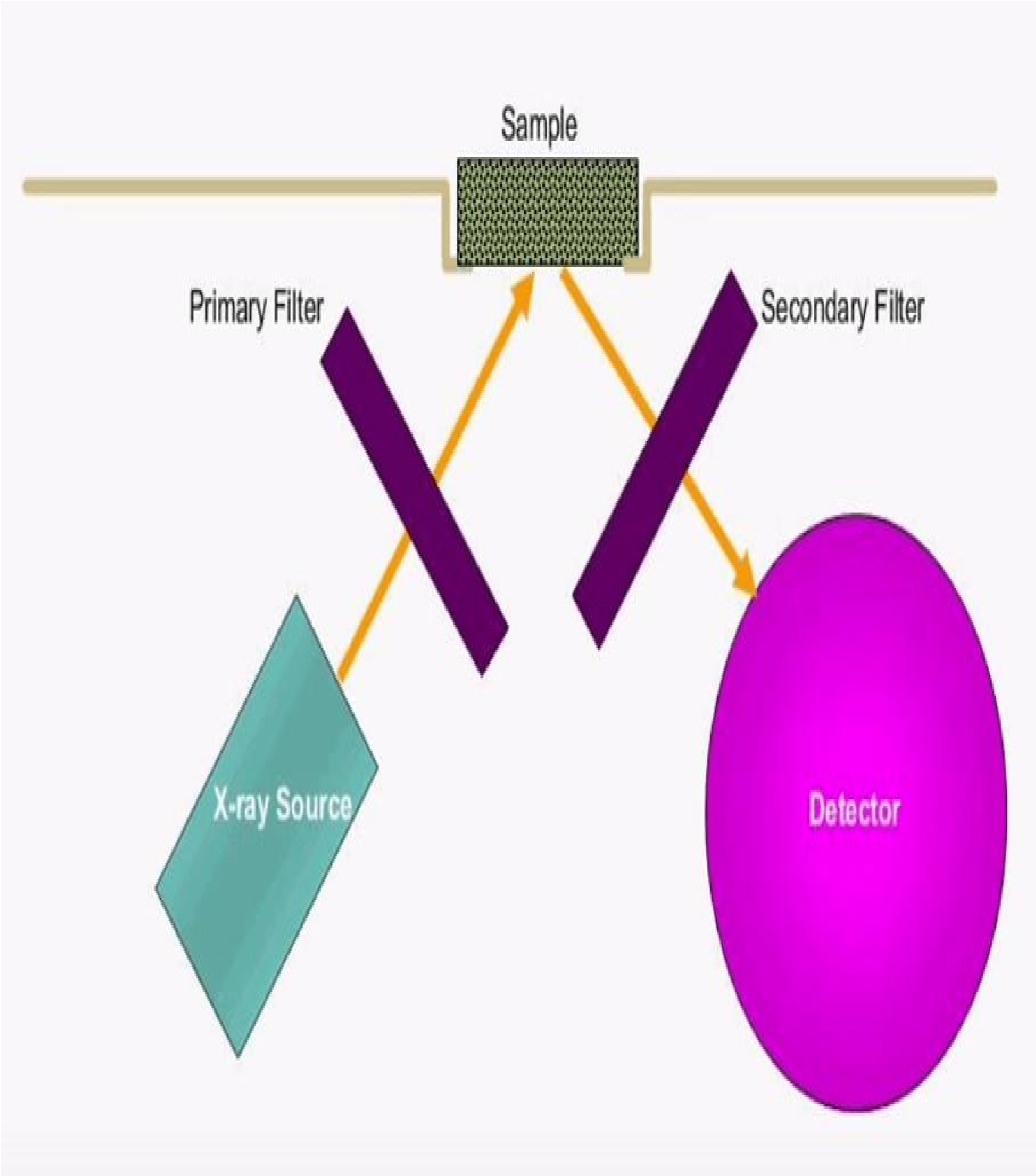

Figure 2.9: Schematic X-ray Fluorescence

Source[113].

2.4.7 Sample Preparation

The sample preparation procedure as regards p-XRF is as important as the analytical technique itself and it has powerful influences on the final quantitative result. The use of an inappropriate sampling or sample preparation method can introduce large errors in the final results[114]. The acceptable sample for XRF analysis must have a perfectly flat surface, taking into account that XRF systems are calibrated based on a fixed geometry (sample-to-source and sample-to-detector distances). Even for largely flat samples, the surface finish can affect the analysis results, particularly for lighter elements. Another important feature in XRF analysis is the effective thickness of the measured samples which is controlled by the density of the sample and its ability to absorb the characteristic fluorescence X-rays from the elements present. Pressed pellet is the usual and well-established XRF sample preparation technique, in which the final analytical result is one of the best in terms of repeatability. For the pelletization of some types of samples, such as soil and geological ones, the addition of a binder like; wax, cellulose, boric acid, starch is usually required to avoid pellet breakage. As highlighted earlier, another technique is to point the machine to powder materials directly to the as loose powders, packed in cells or spread out on film materials. Although the repeatability of the results obtained by the loose powder method is not as good as in the case of pressed pellets due to surface prone effects, the time-saving in the sample preparation is significant and it is a method for consideration. Samples exhibiting difficulties to go into solution easily or tending to remain heterogeneous after grinding and pelletizing are often treated by the technique of flux fusion. This sample preparation method is mostly applied for geological and soil sample analysis[114]. This method affords the most homogeneous sample preparation and additionally offers matrix effect diminishing. Meanwhile, the fusion techniques have the demerit of the time and material costs involved and due to the dilution effects, and thus the trace determination in the sample is critically constrained[114]. Therefore, this sample preparation strategy is mostly reduced to the determination of major components in solid samples.

2.4.8 XRF Calibration

Calibration is the way and process by which one can confirm that the measurements are true by measuring against a standard. XRF calibration is normally done on the instrument before it is shipped from the manufacturer to the end user. The p-XRF analyzers are expectedly quite rugged, especially since they are sometimes used in harsh environments, equipment degrades over time and should be periodically recalibration[115].

It is important then, to check, adjust, or determine by comparison with a standard the accuracy of your instrument on a regular period basis, and as a result the manufacturer's recommendation for recalibration, operating environment, the extent of use, and the history of the instrument should be strictly followed. Companies is expected to comply with a calibration schedule to ensure compliance with an ISO Quality Document. For instance, ISO/IEC 17025:2005 specifies "the general requirements for the competence to carry out tests and/or calibrations, including sampling. It covers testing and calibration performed using standard methods, non-standard methods, and laboratory-developed methods"[115]. The recalibrations should be done annually to ensure that measurements are accurate within the specification limits that led you to selecting the instrument in the first place. The manufacturer's, calibration is consequence upon the purpose for which the machine was requested for; for instance, over 3000 different soil standards and fertilizers were used to calibrate Tracer5 portable XRF from Brokers.

2.4.9 XRF Limitation

The fluorescent x-rays from lighter elements ($Z<18$) are less energetic and are greatly attenuated as the x-rays pass through air, meaning analysis of these elements with handheld XRF can be challenging.

Spectral effects are a form of limitation to XRF due to overlapping lines that some elements have, which can make detection challenging – especially when two overlapping elements are present. This limitation can be removed with the introduction of software that will separate out and correct most of these overlaps assuming the interfering element is in the mode being used. Another limitation is matrix effects, this refers to any other element present in the sample, other than the one element being considered. The use of fundamental parameters-based calibration with all the necessary elements present, enhancement and absorption effects are typically taken care of in the software[116].

Enhancement effects are also some of the limitations of XRF, some fluorescent X-rays have more energy than the binding energy of other elements present in the sample, so their energy will excite those other elements. These elements will give a greater signal return to the detector, therefore "enhancing" the reading. Absorption effects can also occur if the fluorescent X-ray is scattered or absorbed by other elements present in the sample, it will not reach the detector so the signal is weaker[116].

XRF is a surface analysis technique, so if the surface of the material being analyzed is not representative of the entire sample i.e., particle size, in homogeneity, surface contamination among others, the results will be skewed and this will result in sample effects.

The single most effective method of enhancing the quality of X-ray fluorescence technology results is utilizing robust sample preparation methodologies to remove complex heterogeneities that could cause undesirable attenuation or enhancement of the emission spectrum. Using a eutectic flux, small volumes of sample material can be fused into a glass bead or pellet which eliminates matrix effects while offering an almost perfect homogenous representation of the raw sample material[117].

2.4.10 XRF Detection Limit

An XRF spectrometer detects and measures X-rays emitted from atoms of a sample that has been irradiated.

Some atoms in a sample are stimulated to a greater energy level using a beam of X-rays directed into them. It is related to the concentration of the element in the sample, but the intensity of the fluorescent radiation depends on several factors. Detection limits for most elements are 2-20 ng/cm^2 for micro samples, thin samples, aerosols, and liquids[101]. Most metals and elements starting with Titanium (Z = 22) exhibit detection limits in the 10-150 ppm range if they are present in a material consisting mainly of light elements[117].

In the case of a heavy element mixture, such as an alloy, the level of detection can be higher. For example, while lead in soil can be detected below 20 ppm in the absence of interferences, lead in tin becomes hard to detect below 500 ppm (0.05%), based on experiments with standards in Analytical Mode. For standard analytical mode, a number of metals in alloys appear to have a level of detection in the 200-ppm range (acquisition time of 180 s) based on analysis of certified reference standards, but there is significant variability depending on the specific metal and alloy. Detection capability of ED XRF is typically in the low-ppm (pg/g) range in the solid material. Furthermore, it can achieve lower detection limits if the measurement time is extended. Typical measurement times are in the range of 10-30s, but a fivefold to tenfold increase in integration time can show an improvement[118]. However, it should be emphasized that this represents detection capability directly in the solid material. For plasma spectrochemistry to achieve similar performance, the solution detection limit must be in the order of 10 ppb (pg/L), if the EDXRF detection limit is 1 ppm, assuming a sample weight of 1 g is digested and made up to 100 mL (100-fold dilution factor)[118].

2.4.11 Applications of XRF

XRF is emerging as a promising method for the rapid quantification of heavy metals in vegetables due to its non-destructive nature of analysis as demonstrated by recent work that showed that lead and heavy metals are taken up and translocated from soil into consumable vegetable tissues[119,120].

The United States of America Environmental Protection Agency, recognized the p-XRF for the determination of elemental concentrations in soils and sediments (method 6200) and the USDA established the protocol method for using it[121,122]. Weindorf and Chakraborty published the chapter Portable X-ray fluorescence spectrometry analysis of Soils in the Methods of Soil Analysis by the Soil Science Society of America[123].

X-ray fluorescence as a nondestructive analytical technique is mostly being used in many areas. It had been used for elemental and chemical analysis in the investigation of metals, glass, ceramics and building materials, and in research areas such as geochemistry, forensic science, archaeology and art projects[124].

One of the applications of the XRF technique is in the determination of the chemistry of a sample by measuring the fluorescent X-ray emitted when it is excited by a primary X-ray source. However, fluorescent X-rays from each element correlate with the intensity of the primary X-ray source and the element concentration in the sample. This juxtaposed that each of the elements present in a sample produces a set of characteristic fluorescent X-rays called “a fingerprint” that is unique for that specific element[125]. This makes XRF spectroscopy an excellent technology for qualitative and quantitative analysis of material composition.

p-XRF was reported to be the first analytical technique that was able to provide relevant information on-site to field geochemists, and as a result broke the time barrier between sampling, results and decisions, first in environmental investigations, then in mineral exploration[126].

Portable XRF which offers multi-element analysis had been found to be capable of giving results at all stages of any food production process, from the presence of required elemental nutrients to threats from elemental and metal contaminants[127]. Energy-dispersive XRF which was used to determine the elemental concentration of olive oil has revealed that EDXRF can be an effective tool to discriminate olive oils of Maltese origin[128].

Some researchers also indicated that ED-XRF can be used as a rapid offline analytical technology for minerals like Na, Mg, K, P, and Ca in skim milk powders[129]. XRF has proven to be a good tool for routine analysis in the dairy industry[130].

Scientist has analyzed the heavy metals concentration using ED-XRF in soil and food crops and found that the elements are highly related to mining activities which might pose a threat to human health[131].

In a study on heavy metal contamination of soils in mining facilities, determining Pb, As, Cu and Zn concentrations were analyzed by using FPXRF and AAS. The result demonstrated an excellent correlation of FPXRF with the AAS method[131].

Robert H. Tykot, reported the use of XRF to determine different components in artifacts in-situ[132]. Scientists had informed that sources of heavy metals in soils are manifold. Heavy metals are naturally occurring in the ecosystem with huge concentration variations as retorted by researchers[133].

Atomic absorption spectroscopy techniques in comparison with XRF are the main focus of this research. The quantity of interest in atomic absorption measurements is the amount of light at the resonant wavelength which is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others. Many authors had used AAS in the quantitative determination of individual elements from different materials media; such as water, foods, air, and soil etc., this research intends to use atomic absorption spectrophotometer to elucidate individual elements present in soils from three different sources.

Soil is the material that is found on the earth's surface and is made of organic and inorganic materials. The typical soil consists of about 45% mineral, 5% organic matter, 20-30% water, and 20-30% air. It is a blend of natural issues, minerals, gases, fluids, and living beings that together help to the existence of many life forms that have evolved on our planet.

The Earth's body of soil is the pedosphere, which has four vital functions: it is a medium for plant growth, it is a means of water storage, supply and purification, and it is a modifier of Earth's atmosphere. It is natural surroundings for living beings. It would be very wrong to think of the land as a simple collection of fine mineral particles. The soil also contains air, water, dead organic matter and various types of living organisms. The soil interfaces with the lithosphere, the hydrosphere, the atmosphere and the biosphere[93]. Soil is a major component of the Earth's ecosystem.

Different analytical techniques have been employed for heavy metals determination in biological samples and these include Atomic Absorption Spectrophotometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES)[134]. Atomic absorption spectroscopy (AAS) is an analytical technique widely used for elemental determination because of its simplicity, sensitivity, low limit of detection, cost-effectiveness and ability to determine over 70 elements in solution and in different matrices including biological fluids, water, air particulates and pharmaceutical products to mention a few. Apart from the free access to AAS, other characteristics and advantages of the technique had led to the choice of the equipment for heavy metals analysis in suspected contaminated soils in the present study.

According to the United States Environmental Protection Agency (USEPA), a portable XRF can successfully measure Hg, with detection limits typically ranging from 10–20 mg/kg. Other studies have found Hg detection limits of 7.4 mg/kg or less than 5 mg/kg[135]. Some studies have found that XRF has a poor correlation with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for measuring Hg. When compared to Cold Vapor Atomic Absorption (CVAA), studies have found variable correlations for XRF analysis of Hg. However, the erroneous correlation is believed to be caused by soil samples' heterogeneity and mercury beads within the samples in that particular study[135]. Good correlations between XRF and CVAA methods have been found while accurately measuring 93% of soil samples in one study[135].

The municipal solid wastes are heterogeneous in nature and may include used batteries, electronics waste, old clothes, plastics bags, chemical waste, organic materials, vegetables and food, syringes, automobile junks, and painting wastes[136].

The alarming importation and influx of used vehicles popularly called "Tokunbo" have caused a proliferation of many auto-mobile mechanic workshops all over the country.

Many unused plots of lands and farmlands have been converted to auto-mechanics workshops and other specialized individuals who engage in auto repair[137]. Activities carried out in the workshops include: general servicing inclusive of engine and air condition cleaning and washing of engine parts, welding, panel beating, painting and body spraying, electrical repair, vulcanizing and battery charging[137]. Several studies conducted on auto-mobile mechanic workshops in Nigeria had indicated heavy metals such as copper, lead, chromium, cadmium and zinc, hydrocarbons such as oil and grease, volatile organic compounds (VOCs), poly-aromatic hydrocarbons (PAHs)) and toxic chemicals inclusive of solvents, chlorinated compounds, glycols as major pollutants of groundwater around these workshops[137].

Over the years it has been observed that as mechanic workshop owners conduct their daily operations they dumped their used oil, grease and toxic liquids indiscriminately in the environment. These substances are usually high in hydrocarbons and heavy metals which have adverse effects on the natural well-being of the environment. Most operators drop these waste materials uncoordinated whereby they are later absorbed by the soil or washed into the nearby water bodies which in turn contaminate the water rendering it harmful when consumed or used in without treatments[138].

It was reported that the presence of residual hydrocarbon spills and oil may have had some direct impact in lowering the pH of the soil samples[139]. It is also more likely that the production of organic acid by microbial metabolism may account for the difference in pH. However, a significant ($p < 0.05$) difference in physicochemical properties between the auto mechanic soil and some control soil had been reported[139].

The report of WHO/FAO in 2001 put the permissible limit of mercury to 2.0 mg/kg and according to their findings, the mercury contents in auto-mechanic workshop soil was far above this limit[139]. Moreover, it was also reported that arsenic recorded the highest metal detected but below the permissible limit of 20 mg/kg set by the WHO/FAO in 2001[139].

The high Cd, As and Hg levels obtained from the soil samples of auto-mechanical workshop sites may be due to the motor vehicle repair such as bodywork, painting, soldering, brake fluid, engine oils, shear off from metal plating, leachates from used oils and old tyres frequently burnt on these sites, corrosion of metal, batteries and metal parts such as radiators and indiscriminate dumping of waste products are likely sources of cadmium[139].

Also reported in a journal was the mean lead values (22.4 mg/Kg) in most auto-mechanic sites is lower than the value recommended by WHO/FAO (50 mg/kg)[140]. While mineral elements such as phosphorous, potassium and magnesium are usually required by living systems in relatively large amounts for the normal physiological processes of the living organism due to the role they play in building up and proper functioning of living tissues, elements like manganese, zinc and iron are required in very minute quantities for the proper growth, development and physiology of the organism[141]. Silicon is termed a beneficial element yet not essential as it aid plant's ability to resist infection. However, all heavy metals constitute an ill-defined group of inorganic chemical hazards and those commonly found at contaminated sites include lead, chromium, arsenic, cadmium, mercury as well as zinc and copper at elevated concentration[141]. Soils are the major reservoir for heavy metals released into the environment by activities mentioned above and most metals do not undergo microbial or chemical degradation hence their total concentration in soils may persist for a long time after their introduction likewise changes in their chemical forms and bioavailability are, however, possible.

The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants as well as pose risks and hazards to humans and the ecosystem through direct ingestion or contact with contaminated soil, the food chain, drinking of contaminated groundwater, reduction in food quality, reduction in land usability for agricultural production causing food insecurity[141].

Furthermore, as revealed by research carried out by Scientists, soil pollution in farmlands soil is caused by heavy metals like cadmium, nickel, mercury, arsenic, and lead; while the pollution rates of zinc, chromium, and Copper were low[142]. The contamination of soils by heavy metals noticeable in farmlands and urban farmland has negatively affected human health and environmental security all over the world[143].

For example, heavy metal, in particular cadmium, contamination in soils in the United States, European, Australia, Russia, and India were severe[144].

To this end there is the need to explore and utilize a method of determining these heavy metals in soils in such a way that the means of determination will be fast, accurate and free of hazardous mineral acids as compared to conventional methods which are slow, and use hazardous mineral acids. The research explores the comparison of the XRF technique with the AAS technique using selected soils from dumpsites, auto-mechanic workshops and farmlands in the Ibadan metropolis.

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Chapter Three

Methodology

3.1 Description of Study Area

The study area is located within Ibadan city, a cosmopolitan city and the capital as well as the most populous city in Oyo State, Nigeria[1]. It is the third most populous city in Nigeria after Lagos and Kano; with a total population of 3,649,000 as of 2021, and over 6 million people within its metropolitan area, and the second most populous in Africa after Cairo[2]. The population of the urban area is 3,742,273 according to a 2023 estimate[3]. Ibadan is located in Southwestern Nigeria in the Southeastern part of Oyo State, approximately on long. 3°55 E of the Greenwich Meridian and Lat. 7°23 N of the Equator at a distance of about 150 km Northeast of Lagos[1,2]. The metropolis area is 1,190 sq. mi while the urban area is 2,600 sq. mi[3].

Ibadan consists of a total of eleven (11) Local Government Areas (LGAs), comprising of five (5) urban (metropolitan Ibadan) local governments in the city namely: North East, Ibadan North, Northwest Ibadan, Southeast Ibadan, and Southwest Ibadan[1,2]. The remaining six (6) are located in a semi-urban local governments part of the city namely: Akinyele, Ido, Egbeda, Ona-Ara, Lagelu, Oluyole[1,2]. Ibadan is located approximately 120 km east of the border with the Republic of Benin in the forest zone with a mean annual rainfall of about 1,205 mm, a mean temperature of 28°C, ranging from 18°C and 37°C, while relative humidity is high all year round at about 74.55%[4,5,6].

The study was carried out across eight (8) LGAs in Ibadan with soil samples obtained from twelve (12) solid wase dumpsites, nine (9) auto-mechanic workshops and nine (9) agricultural farmlands (Figure 3.1).

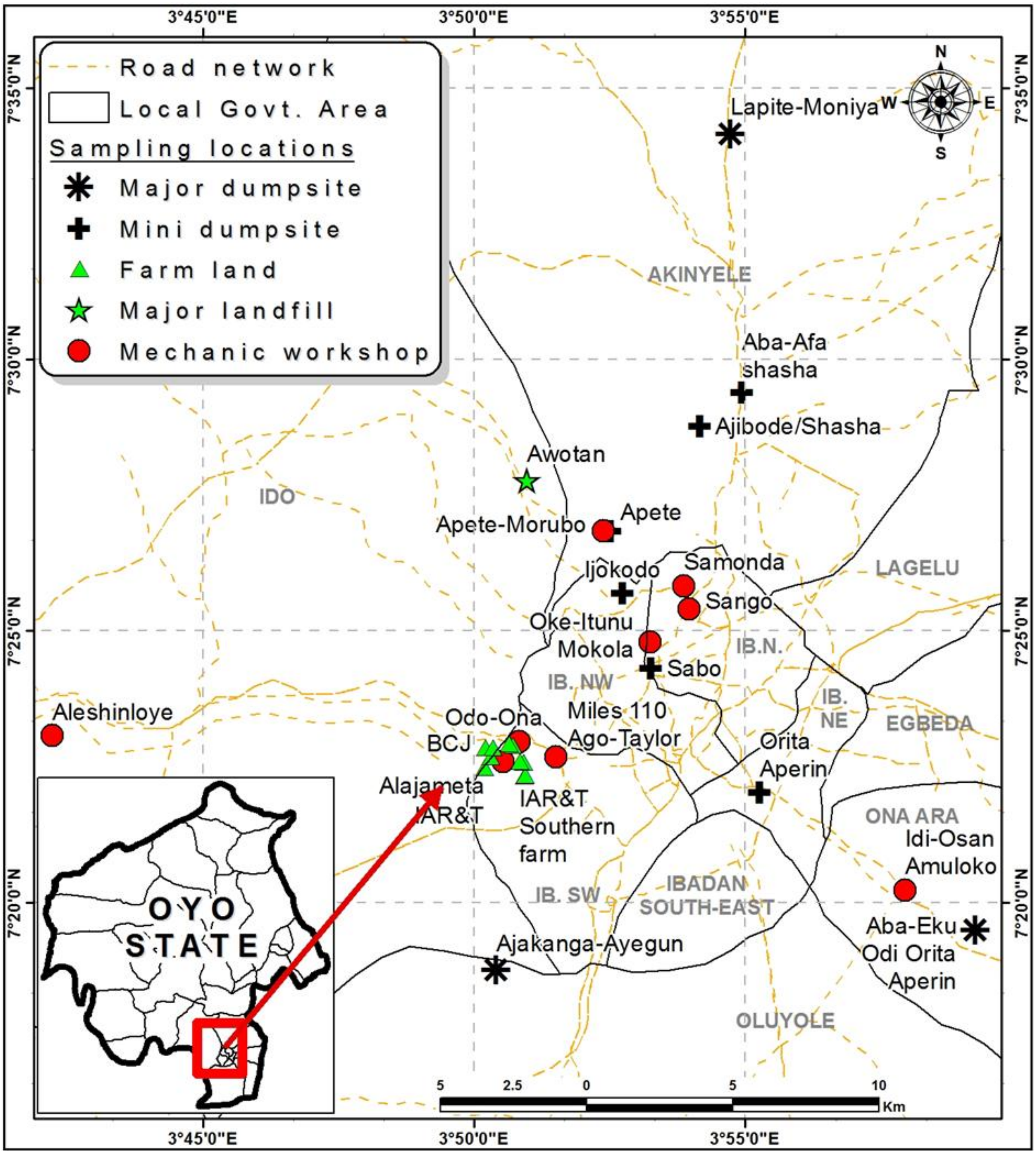

Figure 3.1: Sample Locations Showing the General Study Area

Source: Author’s Analysis, 2023

3.2 Sample Collection and Preparation

Grab soil samples were collected from a minimum of two geo-referenced points at a depth of 0-15 cm each from landfills/dumpsites (approved and illegal) (Table 3.1), auto-mechanic workshops (Table 3.2) and agricultural farmlands (Table 3.3) within the metropolis and then bulked into one composite sample for each site. The collected composite soil samples were put in a well-labeled polyethylene bag and then stored in a refrigerator prior to analysis.

3.2.1 Sample Preparation for Atomic Absorption Spectrophotometer (AAS) Quantification

Based on the procedure described by Ogunlaja and associates, a representative soil sample from the composited sample from each sampling site was dried overnight in an oven at 40^{o}C[7]. The dried representative was then passed through a 2 mm mesh sieve to remove all the organic matter and gravel present in the soil sample[7]. By means of conning and quartering, one portion was stored away why the other portion was kept for digestion. After 10 g of each processed soil sample was crushed with mortar and pestle to reduce the particle size for thorough digestion. The digested soil samples were kept in a refrigerator before AAS analysis.

3.2.1.1 Aqua Regia Digestion of Soil Samples

Dried ground sample of 0.5g was weighed using an analytical balance and placed in a 250 mL beaker which has been previously washed with nitric acid and rinsed with distilled water. The sample was reacted with a freshly prepared mixture of 2 mL HNO_3 + 6 mL HCl + 2 mL of $HClO_4$ using dropping pipette[3]. The mixture was digested in a fume cupboard, heating continued until a dense white fume appeared which was then ingested for 15 minutes, set aside to cool and diluted with distilled water. The mixture was filtered through acid washed Whattman No.44 filter paper into a 100 mL volumetric flask and diluted to mark volume[8,9,10,11].

Table 3.1: Dumpsite Soil Samples with Geo-Referenced Points

Sampling Locations	Local Government Areas	Latitudes N	Longitudes E
Lapite Major Dumpsite	Akinyele	7° 34'10" 7°34'11" 7°34'09"	3°54'39" 3°54'43" 3°54'48.9"
Aba Alfa	Akinyele	7°29'27" 7°29'21" 7°29'23.1"	3°54'57" 3°54'57.3" 3°54'54.7"
Ajibode	Akinyele	7°28'50" 7°28'46.2" 7°28'43.7"	3°54'10" 3°54'9.6" 3°54'10.2"
Awotan Landfill	Ido	7°27'47.6" 7°27'50.4"	3°51'1.9" 3°51'0.5"
Awotan Blanket	Ido	7°27'41.3" 7°27'41.8"	3°50'54.9" 3°50'55.9"
Ajakanga	Oluyole	7°18'46.5" 7°18'47.9" 7°18'44.7" 7°18'41.5"	3°50'27.7" 3°50'24.4" 3°50'19.6" 3°50'24"
Aba-Eku	Ona-Ara	7°19'30 7°31'31.94″ 7°19'28.53″ 7°19'26.27″	3°59'18.50″ 3°59'15.81″ 3°59'14.10″ 3°59'11.56″
Orita Aperin	Ibadan South East	7°22'1.82″	3°55'16.20″
Sabo	Ibadan North West	7°24'18.82″ 7°24'19.05″	3°53'16.34″ 3°53'15.40″
Ijokodo	Ido	7°25'41.70″ 7°25'43.03″	3°52'44.46″ 3°52'44.38″
Apete	Ido	7°26'49.44″ 7°26'52.08″	3°52'35.97″ 3°52'24.27″
Apete-Morubo	Ido	7°26'51.15″ 7°26'50.37″	3°52'23.08″ 3°52'22.78″

Source: Author's Analysis, 2023

Table 3.2: Auto-Mechanic Workshops Soil Samples with Geo-Referenced Points

Sampling Locations	Local Government Areas	Latitude N	Longitude E
Alasa Akoyoyo	Ona-Ara	7°20'9.8″ 7°20'16.4″	3°58'2.75″ 3°57'51.04″
Moor Plantation	Ido	7°22'36.63″ 7°22'34″	3°50'32.07 3°50'31.29″
Oke-Itunu	Ibadan North West	7°24'46.6″ 7°24'48.5″	3°53'15.39″ 3°53'13.75″
Apete-Morubo	Ido	7°26'51.15″ 7°26'50.37″	3°52'23.08″ 3°52'22.78″
Alesinloye	Ibadan North West	7°23'6.55″ 7°23'4.9″ 7°23'0.55″	3°52'13.38″ 3°52'12.30″ 3°52'28.95″
Mile-10	Ibadan South West	7°22'40.2″ 7°22'40.19″	3°51'49.09″ 3°51'28.95″
Samonda	Ibadan North West	7°25' 54.8″ 7°25'54.8″ 7°25'49.9" 7°25'38.5"	3°54'0.6″ 3°53'54.2" 3°53'43" 3°53'50.6
Odo-Ona	Ibadan South West	7°22'57.32″ 7°22'57.91″	3°50'49.09″ 3°50'49.57″
Sango	Ibadan North	7°25'23.95″	3°50'13.21″

Source: Author's Analysis, 2023

Table 3.3: Farmlands Soil Samples with Geo-Referenced Points

Sampling Locations	Local Government Areas	Latitude (N)	Longitudes E
Alajameta	Ido	7°22'28.99″	3°50'13″
IAR&T Land Use	Ido	7°22'40.07″	3°50'18″
		7°22'41.87″	3°50'17.87″
BCJ/IBEDC	Ido	7°22'52.54″	3°50'12.77″
		7°22'49.20″	3°50'12.77″
Opposite NCRI	Ido	7°22'51.30″	3°50'18.75″
		7°22'51.07″	3°50'22.44″
Southern Farm 1	Ido	7°22'19.10″	3°50'54.51″
		7°22'19.19″	3°50'56.98″
Southern Farm 2	Ido	7°22'20.58″	3°50'57.92″
		7°22'20.52″	3°50'54.76″
IAR&T/FCA	Ido	7°22'34.34″	3°50'55.51″
		7°22'35.75″	3°50'54.34″
IAR&T/OSADEP	Ibadan South West	7°22'34.62″	3°50'51.72″
		7°22'36.08″	3°50'49.25″
NCRI Rice Plantation	Ibadan South West	7°22'51.17″	3°50'37.39″

Source: Author's Analysis, 2023

3.2.2 Sample Preparation for Portable X-Ray Fluorescence (p-XRF) Quantification

Similarly, the second part of the sample was ground with the aid of agate mortar and pestle, then was allowed to pass through a 5 mm sieve. These samples were then mixed very well and using conning and quartering were divided into two. One was kept away for storage, while the other portion was further subjected to further grinding with agate mortar and pestle until a powdering form of soil was achieved. This was kept in a Ziplock polytene bag ready for loading into the p-XRF sample cups.

3.3. Reagents and Chemicals

All chemicals used were supplied by Merck (Kenilworth, USA) and Sigma-Aldrich (St. Louis, USA) Chemical Companies and were of analytical-reagent grade. Elemental calibration standards were prepared from spectroscopic grade stock standard solutions of 1000 mg L^{-1} (Sigma-Aldrich, Buchs, Switzerland).

3.4. Quality Control and Analytical Quality Assurance

All glassware were soaked in 10% HCl overnight and later washed with a detergent solution and rinsed with deionized water in order minimize the risk of contamination before use. Blank reagents and certified reference material (CRMs) for AAS and p-XRF procedures were used to verify the accuracy, precision, and efficiency of the analytical method (Table 3.4). All analytical procedures were done in triplicates.

The instrumental calibration for the study of heavy metals was carried out using a working spectroscopic grade stock standard solution and a coefficient of correlation of $r^2 \geq 0.993$ was obtained for all calibration curves (Table 3.5).

Table 3.4: Validation of the Analytical Method using Certified Reference Materials

Metals	p-XRF (Sd AR-H1)			AAS (ISE 999)		
	Measured	**Certified**	**Recovery (%)**	**Measured**	**Certified**	**Recovery (%)**
Cd	25.4	25.0	101.6	0.09	0.07	128.57
Cr	223.7	209.7	106.7	319	321	99.38
Cu	1216	1190	102.2	18.67	16.8	111.1
Co	55.6	57.6	96.5	21.2	20.8	101.92
Ni	230	230	100	123	121	101.7
Pb	3965	4035	98.3	6.40	6.25	102.4
Zn	3807	3780	101	22.5	21.5	104.65

Values are in mg kg^{-1}, dry mass (mean 95% confidence interval, n = 3),

Source[12,13].

Table 3.5: Elemental Wavelength Calibration Curve Correlation Coefficients

Element	Wavelength (nm)	LOD	Conc. of working standard (mg/L)	R^2
Ca	422.7	0.06	1.0, 3.0, and 9.0	0.999
Cd	228.8	0.012	0.2, 0.6, and 1.2	0.997
Co	240.7	0.06	0.2, 0.6, and 1.2	0.997
Cu	324.7	0.04	0.2, 0.6, and 1.2	1.000
Cr	357.9	0.08	0.2, 0.6, and 1.2	0.999
Fe	248.3	0.08	1.0, 3.0, and 9.0	1.000
Mg	285.2	0.0035	1.0, 3.0, and 9.0	0.993
Mn	279.5	0.028	1.0, 3.0, and 9.0	1.000
Mo	313.3	0.5	0.2, 0.6, and 1.2	0.999
Ni	232.0	0.08	0.2, 0.6, and 9.0	0.997
Pb	283.3	0.25	1.0, 3.0, and 9.0	1.000
Zn	213.9	0.011	1.0, 3.0, and 9.0	1.000

Source[14].

3.5. Elemental Analysis

All digested soil samples were analyzed for Ca, Mg, Cd, Pb, Ni, Cr, Cu, Zn, Co, Mn, Mo, and Fe by flame Atomic Absorption Spectrophotometer (ACUSY 210 Buck Scientific). Analytical wavelengths were chosen from the three most sensitive lines that showed no interfering elements and that had minimal spectral or matrix interferences

3.6. Statistical Analysis

The studied elemental concentrations were subjected to descriptive statistics (Microsoft Office Excel 2016) as well as inferential (ANOVA) statistical analyses with a significance level of $p < 0.05$ using GraphPad Prism 6.

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Chapter Four

Results and Discussion of Findings

4.1 Elemental Concentration in Dumpsite Soils

Table 4.1 and Figure 4.1 summarizes average elemental concentrations and the distribution by atomic absorption spectrophotometer (AAS) across different dumpsites respectively. The table showed that soil samples from Lapite major dumpsite have the highest concentration of Ca, followed by the Ijokodo mini dumpsite while the least is from the Orita-Aperin mini dumpsite. Chromium was highest in Apete mini soils (1059 mg/kg) while Ajakanga and Aba-eku soil samples have the same concentration of Cr (281mg/kg). Cadmium was highest in Ajibode (883 mg/kg) while it was least at Aba-eku dumpsite (31mg/kg), the highest concentration of Cd in Ajibode deviates from what literature reported for dumpsites in Nigeria[1,2,3]. Iron is contained in several household and industrial materials. It also occurs in high concentrations in some soils, so, the high concentrations of Fe in the soils are not uncommon. Sabo has the highest concentration of iron (33793mg/kg) followed by the Awotan blanketed landfill (29280mg/kg)[4].

The high concentration of heavy metals indicated that leachate from these dumpsites may find their ways into the nearby well or water body which leads to contamination.

The mean elemental concentrations in the soil were in the order: Ca (7500 mg/kg) > Mg (6510 mg/kg) > Zn (1260 mg/kg) > Fe (657 mg/kg) > Pb (562 mg/kg) > Cu (357 mg/kg) > Mn (233 mg/kg) > Mo (231 mg/kg) > Cr (229 mg/kg) > Co (185 mg/kg) > Ni (154 mg/kg) > Cd (114 ug/g) for Lapite, while for Ajakanga we have Mg (10500 ug/g) > Fe (10100 ug/g) > Ca (4000 mg/kg) > Mn (3433 mg/kg) > Zn (1307 mg/kg) > Ni (1187 mg/kg) > Co (442 mg/kg) > Cu (417 mg/kg) > Pb (397 mg/kg) > Cd (353.33 mg/kg) > Cr (281 mg/kg) > Mo (66 mg/kg). In Aba eku site Fe (27380 mg/kg) > Mg (7222 mg/kg) > Ca (4300 mg/kg) > Mn (3813 mg/kg) > Zn (2293 mg/kg) > Ni (1013 mg/kg) > Pb (773 mg/kg) > Co (579 mg/kg) > Cr (281 mg/kg) > Cu (214 mg/kg) > Mo (123 mg/kg) > Cd (31 mg/kg). Some of these sites followed the trends of Fe > Zn > Pb > Cd as reported in literature while few did not for heavy metals, however, it was also reported in the literature that Cr was greater than Cu in an abandoned industrial waste dumpsite in Ibadan, as we have it in Aba-eku site[4,5]. The estimated data were compared with the levels allowed by the Pakistan Environmental Protection Agency (Pak-EPA) and the United States Environmental Protection Agency (USEPA). The maximum allowable limit for Cd is 3; Cr, Cd, and Pb are 100 for Ni is 50 and 300 mg/kg for Zn[1].

Awotan blanketed and Awotan landfills samples were taken from the Oyo State major dumpsite at Awotan, one aspect of the site was turned with a tractor and covered with sand (blanketed) while the other was left untouched (landfill). Samples were taken from each of the sites and the distribution of metals in Awotan blanketed shows that Fe (29280 mg/kg) > Mg (5483 mg/kg) > Zn (3427 mg/kg) > Mn (3407 mg/kg) > Ca (3033 mg/kg) > Ni (1296 mg/kg) > Pb (978 mg/kg) > Cd (788 mg/kg) > Co (267 mg/kg) > Cu (499 mg/kg) > Cr (319 mg/kg) > Mo (131 mg/kg), while in Awotan landfill Fe (1091 mg/kg) < Mg (10850 mg/kg), Mn (4160 mg/kg) > Zn (2787 mg/kg), Ca (3467 mg/kg) > Ni (148 mg/kg), Pb (2059 mg/kg) > Cd (285 mg/kg), Cu (456 mg/kg) > Co (41 mg/kg), Cr (239 mg/kg) > Mo (37 mg/kg)[1,3]. The comparison of blanketed and landfill reveals that the concentration of Fe in the blanketed side is higher than in the unblanketed site, while Mg in the unblanketed side is higher than the blanketed side. However, Cd in blanketed is higher than unblanketed. In the same vein Co in the blanketed side is higher than the one in the unblanketed side same goes for Cr. Also, Mo in blanketed is higher than unblanketed. This showed that heavy metals concentration is likely to be much in disturbed soil than in undisturbed one. In Orita-Aperin Mg (3395 mg/kg) > Zn (2339 mg/kg) > Fe (1290 mg/kg) > Ca (1133 mg/kg) > Pb (803 mg/kg) > Cd (685 mg/kg) > Mn (341 mg/kg) > Cu (197 mg/kg) > Cr (161 mg/kg) > Ni (128 mg/kg) > Mo (80 mg/kg) > Co (41 mg/kg). The elemental concentrations in Aba Alfa is as follows: Mg (8960 mg/kg) > Ca (4533 mg/kg) > Zn (1280 mg/kg) > Fe (927 mg/kg) > Pb (903 mg/kg) > Mn (325 mg/kg) > Co (227 mg/kg) > Cr (192 mg/kg) > Ni (181 mg/kg) > Cd (96 mg/kg) > Mo (55 mg/kg) > Cu (49 mg/kg)[4].

Table 4.1: Elemental Concentrations of Dumpsite Samples by Atomic Absorption Spectrophotometer (AAS)

Dumpsite Samples	Ca	Cu	Zn	Cr	Cd	Pb	Ni	Mg	Mn	Co	Mo	Fe
Lapite	7500 (4.00)	357 (2.70)	1260 (5.37)	229 (2.21)	114 (1.19)	562 (5.93)	154 (1.10)	6510 (7.95)	233 (4.20)	185 (6.00)	231 (2.40)	12713 (3.82)
Ajakanga	4000 (8.54)	417 (6.10)	1307 (2.01)	281 (2.90)	353 (1.40)	397 (4.90)	1187 (1.50)	10500 (3.50)	3433 (27.25)	442 (8.70)	66 (6.00)	10100 (3.82)
Aba-Eku	4300 (8.54)	214 (8.56)	2293 (1.63)	281 (6.00)	31 (9.65)	773 (6.10)	1013 (1.22)	7222 (5.53)	3813 (5.13)	579 (1.10)	123 (5.95)	27380 (7.20)
Awotan Blanketted	3033 (7.77)	499 (1.33)	3427 (6.99)	319 (6.00)	788 (1.20)	978 (7.40)	1296 (1.70)	5483 (5.34)	3407 (17.44)	627 (2.80)	131 (1.70)	29280 (6.01)
Awotan landfill	3467 (1.15)	456 (2.30)	2787 (5.81)	239 (2.01)	285 (6.56)	2059 (1.58)	148 (2.30)	10850 (3.50)	4160 (3.69)	143 (1.60)	37 (0.16)	1091 (6.10)
Orita-Aperin	1133 (2.08)	197 (1.30)	2339 (3.03)	161 (3.10)	685 (2.61)	803 (1.00)	128 (1.00)	3395 (1.52)	341 (1.26)	41 (1.00)	86 (1.45)	1290 (1.30)
Aba-Alfa	4533 (2.31)	49 (8.00)	1280 (1.63)	192 (1.55)	96 (3.85)	831 (8.60)	181 (2.11)	8960 (1.77)	325 (5.80)	227 (3.11)	55 (8.92)	927 (5.01)
Ajibode	3267 (2.31)	292 (1.56)	933 (1.22)	214 (4.71)	882 (5.22)	903 (1.03)	177 (2.52)	13650 (7.00)	1140 (9.11)	183 (1.99)	326 (2.21)	1347 (1.85)
Apete Mini	2300 (1.73)	393 (6.78)	1373 (6.21)	1059 (2.33)	50 (7.00)	267 (4.23)	5913 (1.41)	6288 (9.06)	2040 (3.32)	356 (2.00)	141 (1.00)	23133 (8.44)
Sabo	4567 (1.15)	173 (7.72)	2940 (1.11)	855 (1.13)	53 (2.16)	839 (9.11)	4800 (1.31)	2100 (6.06)	2047 (3.60)	414 (1.61)	46 (4.94)	33793 (1.73)
Ijokodo	5467 (8.08)	342 (2.00)	2373 (2.68)	1012 (1.87)	208 (1.4)	1632 (12.88)	304 (5.11)	18200 (10.50)	3200 (6.10)	808 (3.10)	359 (3.71)	21787 (26.69)
Apete Morubo	3533 (8.14)	190 (1.22)	1340 (2.02)	335 (4.34)	241 (1.32)	279 (7.00)	222 (1.90)	7233 (5.34)	1167 (8.00)	423 (5.52)	66 (1.31)	23380 (84.47)

Values are in mg/kg and Mean (SD)
Source: Author's Analysis, 2023

However, in Ajibode dumpsite Ca (3266 mg/kg) > Mg (13650 mg/kg) > Fe (1346 mg/kg) > Mn (1140 mg/kg) > Zn (933 mg/kg) > Pb (903 mg/kg) > Cd (883 mg/kg) > Mo (326 mg/kg) > Cu (292 mg/kg) > Cr (214 mg/kg) > Co (183 mg/kg) > Ni (177 mg/kg). In Apete mini, Fe (23133 mg/kg) > Mg (6288 mg/kg) > Ni (5913 mg/kg) > Ca (2300 mg/kg) > Mn (2040 mg/kg) > Zn (1373 mg/kg) > Cr (1053mg/kg) > Cu (393 mg/kg) > Co (356 mg/kg) > Pb (267 mg/kg) > Mo (141 mg/kg) > Cd (50 mg/kg), while in Sabo site, Fe (33793 mg/kg) > Ni (4800 mg/kg) > Ca (4566 mg/kg) > Cu (2940 mg/kg) > Zn (2940 mg/kg) > Mg (2100 mg/kg) > Mn (2047 mg/kg) > Cr (855 mg/kg) > Pb (839 mg/kg) > Co (414 mg/kg) > Cu (173 mg/kg) > Cd (53 mg/kg) > Mo (46 um/kg). The mean of metals in Ijokodo site reveals that Fe (21786 mg/kg) > Mg (18200 mg/kg) > Ca (5467 mg/kg) > Mn (3200 mg/kg) > Zn (2373 mg/kg) > Pb (1632 mg/kg) > Cr (1012 mg/kg) > Co (808 mg/kg) > Mo (359 mg/kg) > Cu (342 mg/kg) > Ni (304 mg/kg) > Cd (208 mg/kg). The mean concentration of Fe (23380 mg/kg) in Apete Morubo is greter than Mg (7233 mg/kg), while Ca (3533 mg/kg) > Mn (1167 mg/kg) > Zn (1340 mg/kg) > Co (423 mg/kg) > Cr (335 mg/kg) > Pb (279 mg/kg) > Cd (241 mg/kg) > Cu (190 mg/kg) > Mo (66 mg/kg). The differentiation in different dumpsite was also reported in dumpsites of Southeastern Nigeria[1,3].

Figure 4.1 below showed the distributions of various elements across the dumpsite investigated; the chart showed that iron is highest in Ijokodo dumpsite site this site happened to be a mini dumpsite situated around residential/commercial area where household wastes among other materials are dumped. It can also be seen that iron from Apete mini and Apete Morubo are the same, these dumpsites are also situated around residential area.

The dumpsites in Lapite, Awotan landfill, Orita Aperin, Aba Alfa and Ajibode recorded the lowest concentration of iron. Out of these five sites two happens to be major dumpsites which are Lapite, and Awotan landfill. Nickel, Copper, Cobolt, Zinc, Molybdenum and Chromium

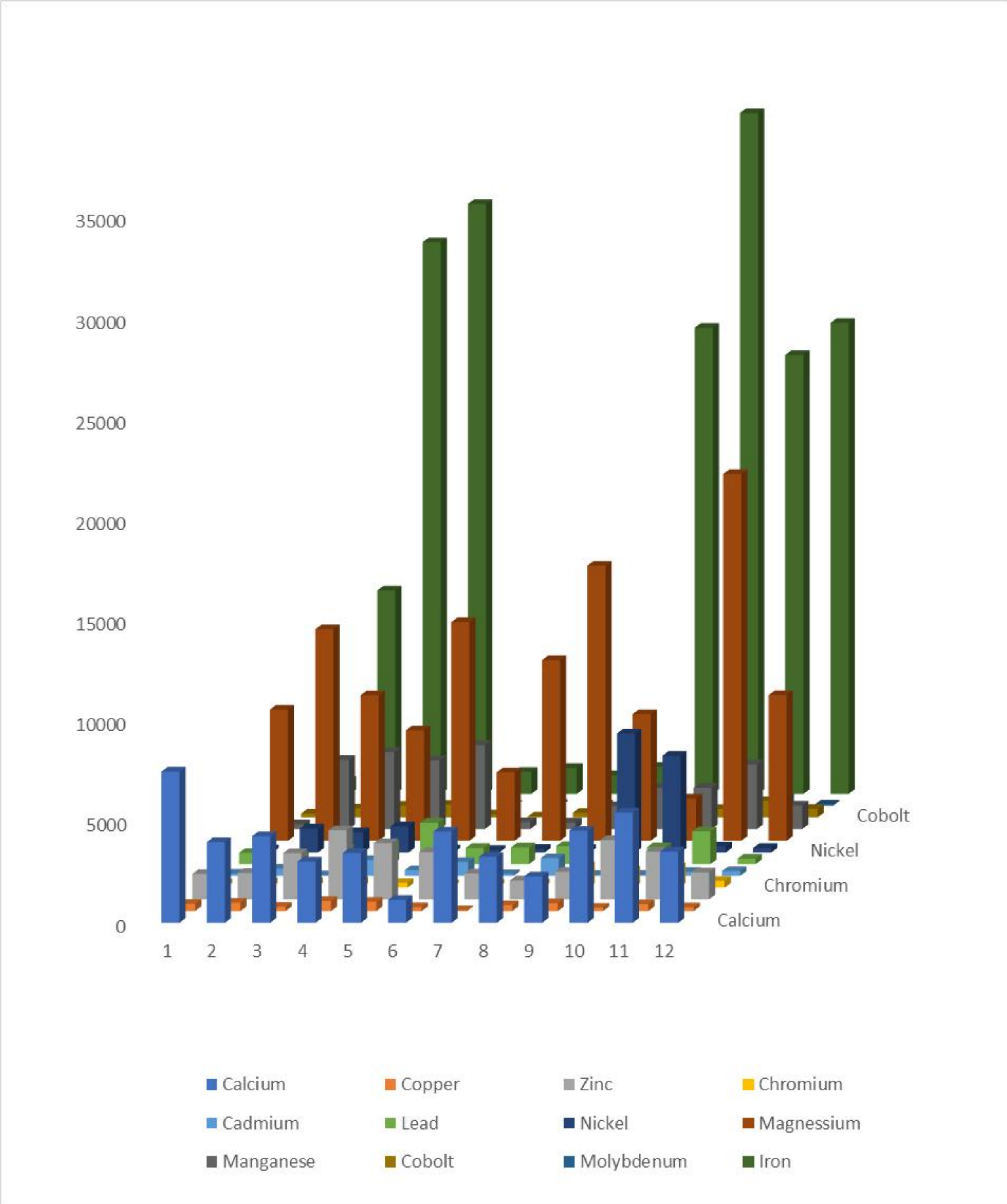

Figure 4.1: Elemental Distribution Across Dumpsites by Atomic Absorption Spectrophotometer (AAS)

Lapite, 2 = Ajakanga, 3 = Aba-Eku, 4 = Awotan blanketed, 5 = Awotan landfill, 6 = Orita Aperin, 7 = Aba-Alfa, 8 = Ajibode, 9 = Apete mini, 10 = Sabo, 11 = Ijokodo, 12 = Apete Morubo

Source: Author’s Analysis, 2023

are generally high across the twelve sites, based on the W.H.O permissible limit of 1996: Zn (0.6 mg/kg), Cu (10 mg/kg), Cr (1.6 mg/kg), Pb (2 mg/kg) and Ni (10 mg/kg).

Table 4.2 below showed the elemental concentrations in dumpsite at Lapite as analysed by X-ray fluorescence spectrophotometer (XRF), showed that Ca (60591mg/kg) > Fe (37082 mg/kg) > Zn (1813 mg/kg) > Mn (1449 mg/kg) > Cu (637 mg/kg) > Pb (455 mg/kg) > Cr (81 mg/kg) > Ni (31 mg/kg) > Co (7 mg/kg) while, Cd, Mg and Mo were below detection limit, this also follow the trend as we have it in AAS analysed samples except for Cd, Mg, Mo that were below detection level which may be due to low nutrient retention capacity of the soil as reported in literature[6]. However, in Ajakanga Fe (28663 mg/kg) > Ca (24400 mg/kg) > Mn (645 mg/kg) > Zn (593 mg/kg) > Cu (224 mg/kg) > Pb (83 mg/kg) > Cr (48 mg/kg) > Ni (17 mg/kg) > Co (8 mg/kg) while Cd, Mg and Mo were below detection limit[6]. Aba eku dumpsite showed that mean concentration of Fe (37069 mg/kg) > Ca (28940 mg/kg) > Zn (1813 mg/kg) > Mn (1456 mg/kg) > Mg (1291 mg/kg) > Cu (641 mg/kg) > Pb (452 mg/kg) > Cr (79 mg/kg) > Ni (30 mg/kg) > Co (9 mg/kg). At Awotan blanketed, Ca (94468 mg/kg) > Fe (37778 mg/kg) > Zn (3457 mg/kg) > Mn (2040 mg/kg) > Cu (933 mg/kg) > Pb (593 mg/kg) > Cr (93 mg/kg) > Ni (48.00 mg/kg) > Co (13 mg/kg). Awotan landfill also shown that Ca (96982 mg/kg) > Fe (30610 mg/kg) > Mg (5816 mg/kg) > Mn (2678 mg/kg) > Zn (1415 mg/kg) > Cu (562 mg/kg) > Pb (510 mg/kg) > Cr (74.67 mg/kg) > Ni (35 mg/kg) > Co (10 mg/kg)[7]. The mean concentration of metals at Orita Aperin shown that Fe (39352 mg/kg) > Ca (33538 mg/kg) > Mn (1042 mg/kg) > Zn (993 mg/kg) > Pb (449 mg/kg) > Cu (341 mg/kg) > Cr (64 mg/kg) > Ni (26 mg/kg) > Co (4 mg/kg). At Aba-Alfa Fe (94023 mg/kg) > Ca (86855 mg/kg) > Mg (4101 mg/kg) > Mn (434 mg/kg) > Zn (155 mg/kg) > Cr (109 mg/kg) > Pb (93 mg/kg) > Ni (68 mg/kg), however, Cd, Co and Mo, are below detection limit. Mean concentration of metals at Ajibode shown that Fe (35568 mg/kg) > Ca (33496 mg/kg) > Mg (6589 mg/kg) > Zn (1290 mg/kg) > Mn (974 mg/kg) > Cu

(227 mg/kg) > Pb (150mg/kg) > Cr (61 mg/kg) > Ni (21 mg/kg) > Co (13 mg/kg). The XRF could not however detect Cd and Mo. At Apete-mini Ca (80581 mg/kg) > Fe (31570 mg/kg) > Zn (2544 mg/kg) > Mn (1290 mg/kg) > Pb (618 mg/kg) > Cu (292 mg/kg) > Cr (129 mg/kg) > Cd (45 mg/kg) > Ni (21 mg/kg) > Co (12 mg/kg). Mo was however below detection limit.

Table 4.2: Elemental Concentrations of Dumpsite Samples by X-ray Fluorescence Spectrophotometer (XRF)

Dumpsite	Ca	Cu	Zn	Cr	Cd	Pb	Ni	Mg	Mn	Co	Mo	Fe
Lapite	60591 (4.80)	637 (4.85)	1813 (4.90)	81 (2.85)	< LOD	455 (3.59)	31 (0.01)	< LOD	1449 (7.25)	7.00 (0)	< LOD	37082 (0.01)
Ajaganga	24400 (5.23)	224 (0)	593 (0)	48 (0.58)	< LOD	83 (0.57)	17 (0.01)	< LOD	645 (0.01)	8 (0)	< LOD	28663 (0.58)
Aba-Eku	28940 (2.47)	641 (3.95)	1813 (3.68)	79 (4.58)	< LOD	452 (1.00)	30 (0)	1291 (0.58)	1456 (0.58)	9 (0)	< LOD	37069 (0.01)
AwotanBlanketed	94468 (3.19)	933 (4.85)	3457 (9.00)	93 (0.58)	< LOD	593 (4.55)	48 (0.58)	< LOD	2040 (0.58)	13 (0)	< LOD	37778 (0.01)
Awotan landfill	96982 (3.25)	562 (0.58)	1415 (3.59)	75 (0.58)	< LOD	510 (6.89)	35 (0.06)	5816 (3.21)	2678 (0.79)	11 (0)	< LOD	30610 (0.01)
Orita-Aperin	33538 (1.09)	341 (2.78)	993 (4.56)	64 (0)	< LOD	449 (5.67)	26 (0)	< LOD	1042 (0.01)	4 (0)	< LOD	39352 (0.01)
Aba-Alfa	86855 (1.64)	< LOD	155 (0.58)	109 (0.90)	< LOD	93 (1.00)	68 (0.05)	4101 (0)	434 (0.01)	LOD	< LOD	94023 (0.01)
Ajibode	33496 (2.18)	227 (0.58)	1290 (2)	61 (2)	< LOD	150 (0.05)	21 (0.05)	6589 (0.01)	974 (0)	13 (0)	< LOD	35568 (0.01)
Apete Mini	80581 (1.73)	292 (1.00)	2544 (3.00)	129 (1.00)	45 (0.57)	618 (4.56)	41 (0)	< LOD	1290 (0.01)	12 (0)	< LOD	31570 (0.01)
Sabo	96642 (1.69)	< LOD	3050 (5.52)	113 (0.57)	< LOD	770 (6.52)	44 (0.05)	1714 (0)	1673 (0.01)	13 (0)	< LOD	32082 (0.01)
Ijokodo	10696 (2.00)	459 (2.98)	644 (1.00)	90 (0)	39 (0)	188 (2.98)	28 (0)	3879 (0.01)	1170 (0)	9 (0)	< LOD	29888 (0.01)
Apete Morubo	80581 (1.73)	599 (3.98)	1043 (1.92)	59 (0.01)	< LOD	179 (3.56)	26 (0)	7490 (0.05)	941 (0.1)	12 (0)	< LOD	33756 (0.01)

Values are in mg/kg and Mean (SD)

Source: Author's Analysis, 2023

The mean concentration of metals at Sabo revealed that Ca (96642 mg/kg) > Fe (32082 mg/kg) > Zn (3050 mg/kg) > Mg (1714 mg/kg) > Mn (1673 mg/kg) > Pb (770 mg/kg) > Cr (113 mg/kg) > Ni (44 mg/kg) > Co (13 mg/kg). However, Cu and Mo are below detection limit.

The mean concentration of metals at Ijokodo shown that Fe (29888 mg/kg) > Ca (10696 mg/kg) > Mg (3879 mg/kg) > Mn (1170 mg/kg) > Zn (644 mg/kg) > Cu (459 mg/kg) > Pb (188 mg/kg) > Cr (90 mg/kg) > Cd (39 mg/kg) > Ni (28 mg/kg) > Co (9 mg/kg). Mo was below detection limit. At Apete Morubo, Ca (80581 mg/kg) > Fe (33756 mg/kg) > Mg (7490 mg/kg) > Zn (1043 mg/kg) > Mn (941 mg/kg) > Cu (599 mg/kg) > Pb (179 mg/kg) -> Cr (59 mg/kg) > Ni (26 mg/kg) > Co (12 mg/kg). Cd and Mo are below detection limit. Generally, the elemental concentrations as analysed by XRF followed the trend of that of AAS except for few elements that are eighter above or below detection limit which may be as results of low retention capacity of the soil, and soil matrix[6,7,8].

The figure 4.2 below showed the bar chart distribution of means concentration of metals across the selected sites. It is evidently shown as explained above that Ca and Fe spread across the sites evenly. Aba Alfa has the highest concentration of Fe followed by Orita Aperin. The least Fe mean concentration was Ijokodo, while Awotan landfills had the highest mean concentration of Ca, followed by Sabo. However, Ijokodo had the least concentration of Ca. Awotan landfills recorded the highest mean concentration of Mn followed by Awotan blanketted, while the least concentration was found in Aba Alfa. Cd was detected by XRF in only Apete mini and Sabo, while Mo was not detected in any of the selected sites by XRF unlike AAS.

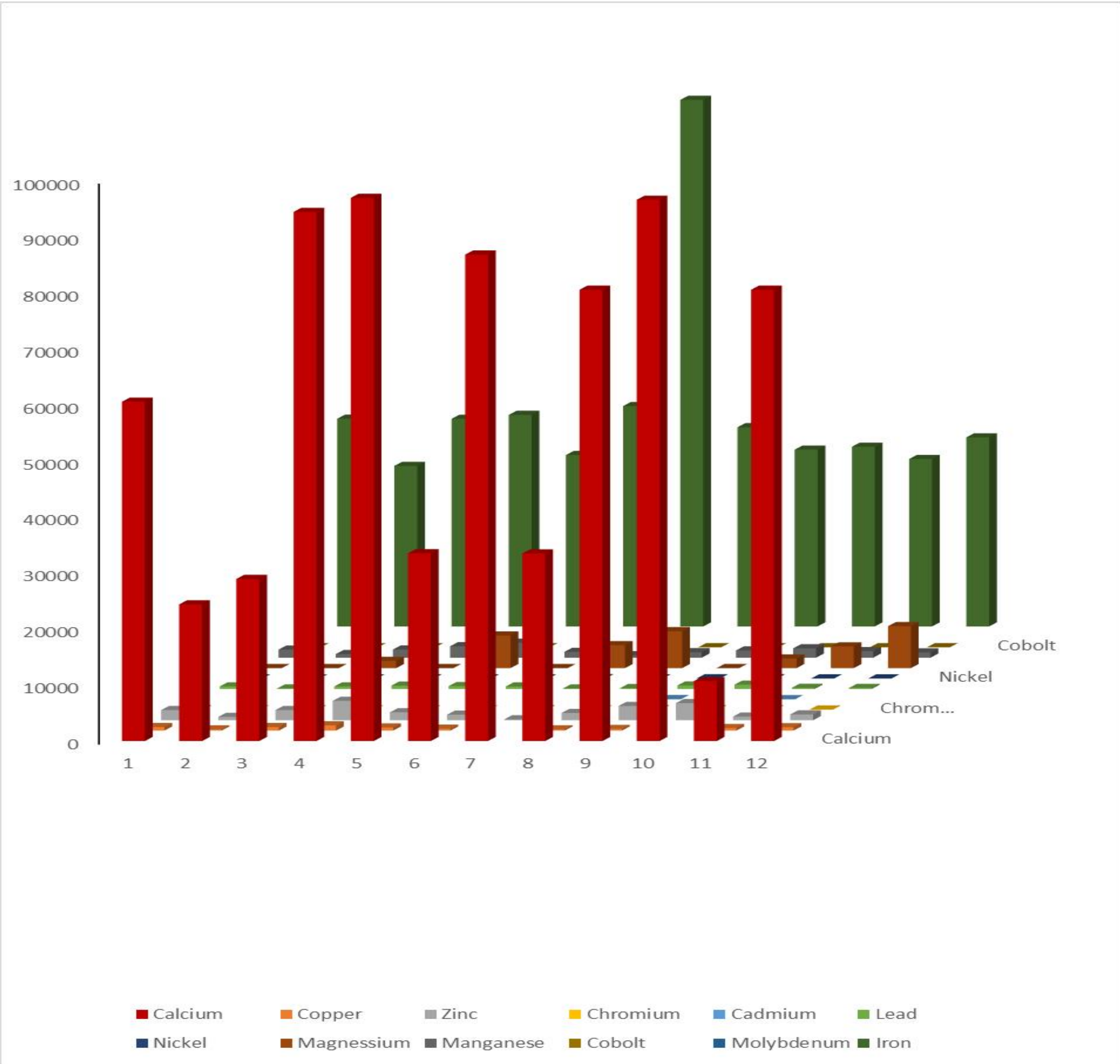

Figure 4.2: Distribution of Elements Across Dumpsites by X-ray Fluorescence Spectrophotometer (XRF)

1 = Lapite, 2 = Ajakanga, 3 = Aba-Eku, 4 = Awontan Blanketted, 5 = Awotan Landfills, 6 = Orita Aperin, 7 = Aba Alfa, 8 = Ajibode, 9 = Apete mini, 10 = Sabo, 11 = Ijokodo, 12 = Apete Morubo

Source: Author's Analysis, 2023

4.2 Elemental Concentration in Auto-mechanic Workshops Soil Samples

The concentration of investigated elements from auto-mechanic workshop villages can be seen in Table 4.3 below and it shown that in Alasa Akoyoyo site Mg (64400 mg/kg) > Mn (3407 mg/kg) > Fe (3075 mg/kg) > Ca (2147 mg/kg) > Zn (401 mg/kg) > Co (387 mg/kg) > Cd (285 mg/kg) > Cr (200 mg/kg) > Pb (181 mg/kg) > Ni (149 mg/kg) > Mo (135 mg/kg) > Cu (87 mg/kg). Moor Plantation mechanic workshop showed that Fe (47680 mg/kg) > Mn (1587 mg/kg) > Ca (1833 mg/kg) > Mg (1167 mg/kg) > Mo (619 mg/kg) > Cr (325 mg/kg) > Zn (245 mg/kg) > Pb (146 mg/kg) > Cu (132 mg/kg) > Cd (109 mg/kg) > Ni (97 mg/kg) > Co (77 mg/kg). Oke-Itunu site shown that Fe (104000 mg/kg) > Mg (42700 mg/kg) > Cr (11160 mg/kg) > Ni (6287 mg/kg) > Ca (2667 mg/kg) > Mn (2100 mg/kg) > Mo (485 mg/kg) > Zn (476 mg/kg) > Cu (263 mg/kg) > Cd (172 mg/kg) > Co (43 mg/kg). At Samonda auto-mechanic workshop, Fe (77707 mg/kg) > Cr (8140 mg/kg) > Ca (4100 mg/kg) > Mg (1540 mg/kg) > Mn (1240 mg/kg) > Ni (1127 mg/kg) > Cu (940 mg/kg) > Zn (880 mg/kg) > Cr (8140 mg/kg) > Cd (181 mg/kg) > Pb (177 mg/kg) > Co (141 mg/kg). In Apete Morubo, Fe (43493 mg/kg) > Mg (22867 mg/kg) > Cr (4973 mg/kg) > Ca (2500 mg/kg) > Ni (2127 mg/kg) > Mn (960 mg/kg) > Mo (521 mg/kg) > Zn (387 mg/kg) > Co (150 mg/kg) > Cu (137 mg/kg) > Pb (111 mg/kg) > Cd (51 mg/kg). All the elemental concentrations followed the trend as reported in literature[9,10]. Odo-ona auto-mechanic workshop revealed that Mg (38733 mg/kg) > Fe (35787 mg/kg) > Ca (2667 mg/kg) > Mn (813 mg/kg) > Zn (499 mg/kg) > Cr (396 mg/kg) > Cd (211 mg/kg) > Pb (194 mg/kg) > Ni (167 mg/kg) > Cu (117 mg/kg) > Mo (73 mg/kg) > Co (50 mg/kg), however, Alesinloye sites showed that Mg (23193 mg/kg) > Fe (24200 mg/kg) > Cr (8813 mg/kg) > Ca (2767 mg/kg) > Mn (413 mg/kg) > Ni (412 mg/kg) >

Mo (343 mg/kg) > Zn (290 mg/kg) > Co (219 mg/kg). Meanwhile, mean concentration of Cu and Pb were the same (108 mg/kg).

Sango auto-mechanic workshop soils indicated that Fe (18600 mg/kg) > Mg (13510 mg/kg) > Pb (7167 mg/kg) > Ca (2700 mg/kg) > Zn (1587 mg/kg) > Mn (787 mg/kg) > Cr (607 mg/mg) > Cu (356 mg/kg) > Mo (219 mg/kg) > Ni (182 mg/kg) > Co (126 mg/kg) > Cd (32 mg/kg)[10].

Table 4.3: Elemental Distribution Across Auto-Mechanic Workshops by Atomic Absorption Spectrophotometer (AAS)

Auto-Mechanic	Ca	Cu	Zn	Cr	Cd	Pb	Ni	Mg	Mn	Mo	Co	Fe
AlasaAkoyoyo	2147 (0.58)	87 (0.44)	401 (1.10)	200 (6.08)	285 (0.23)	181 (0.64)	149 (0.26)	64400 (1.15)	3407 (0.39)	135 (0.05)	387 (0.01)	3075 (0.55)
MoorPlantation	1833 (5.77)	132 (5.20)	245 (5.96)	325 (0.39)	109 (0.39)	146 (5.77)	97 (0.46)	1167 (0.35)	1587 (0.26)	619 (0.75)	77 (0.52)	47680 (0.58)
Oke-Itunu	2667 (0.30)	263 (0.22)	476 (7.51)	11160 (57.74)	172 (7.51)	159 (5.20)	6287 (5.79)	42700 (66.58)	2100 (55.08)	485 (5.65)	43 (1.21)	104000 (58.32)
Samonda	4100 (10)	940 (25.98)	880 (47.63)	8140 (11.55)	181 (0.51)	177 (5.68)	1127 (3.58)	1540 (0.58)	1240 (0.58)	379 (0.70)	141 (0.53)	77707 (0.45)
Apete Morubo	2500 (5.51)	137 (0.06)	386 (0.16)	4973 (0.23)	50 (0.18)	111 (0.20)	2126 (0.18)	22866 (0.35)	960 (1.55)	521 (0.35)	150 (0.58)	43493 (0.23)
Odo-Ona	2667 (0.66)	117 (0.29)	499 (0.20)	396 (0)	211 (0.61)	194 (0.01)	167 (0.42)	38733 (0.53)	813 (0.20)	73 (0)	50 (0.58)	35787 (0.57)
Alesinloye	2767 (0.44)	108 (2.08)	290 (0.58)	8813 (0.56)	91 (0.46)	108 (0)	412 (0)	23193 (2.37)	413 (0.52)	343 (0.40)	219 (0.49)	24200 (57.74)
Sango	2700 (1)	356 (4.16)	1587 (0.43)	607 (0.20)	32 (0)	7167 (0.51)	182 (0.58)	13510 (0.58)	787 (0.23)	219 (0.05)	126 (0.58)	18600 (0.58)
Mile-10	2567 (0.23)	389 (5.20)	1313 (0.20)	5253 (0.25)	119 (0.05)	1213 (0.58)	853 (0.20)	5857 (0.58)	1360 (0.58)	215 (0.58)	231 (0.58)	58933 (1.73)

Values are in mg/kg and Mean (SD)

Source: Author’s Analysis, 2023

Mile – 10 auto-mechanic workshop site in table 4.3 above indicated that Fe (58933 mg/kg) > Mg (5857 mg/kg) > Cr (5253 mg/kg) > Ca (2567 mg/kg) > Mn (1360 mg/kg) > Zn (1313 mg/kg) > Pb (1213 ug/g) > Ni (853ug/g) > Cu (389ug/g) > Co (231ug/g) > Mo (215ug/g) > Cd (119 mg/kg)[9,10].

The figure 4.3 below showed the distribution of mean concentration of metals across the selected sites. It can be seen that Fe was distributed substancially across all the selected sites and Oke Itunu had the highest mean concentration of Fe followed by Samonda and the least was recorded in Alasa Akoyoyo. Mg followed Fe closely with the highest recorded in Alasa Akoyoyo, followed by Oke Itunu and the least was recorded in Moor Plantation auto-mechanic workshop. Cr also was spread across all the sites though not pronounced like Fe and Ca but was significant in Oke Itunu, Samonda, Apete Morubo, Alesinloye and Mile-10 these areas are major mechanic workshops that comprises of panel beaters, auto-mechanic, painter, battery charger and car rewire.

It can also be seen from the chart that Ca spread across all selected sites, with the highest from Samonda, followed by Alesinloye, while the least was recorded in Moor plantation. However, Zn and Cu were more or less the same in quantity across all the selected sites. Same thing with Pb except at Sango auto mechanic workshop. The findings corroborated the findings in Benin City and Orgi in Imo state both in Nigeria that Fe concentration was highest in auto-mechanic[9,10]. There were death of literature on auto-mechanic workshop soil analysis by both AAS and XRF.

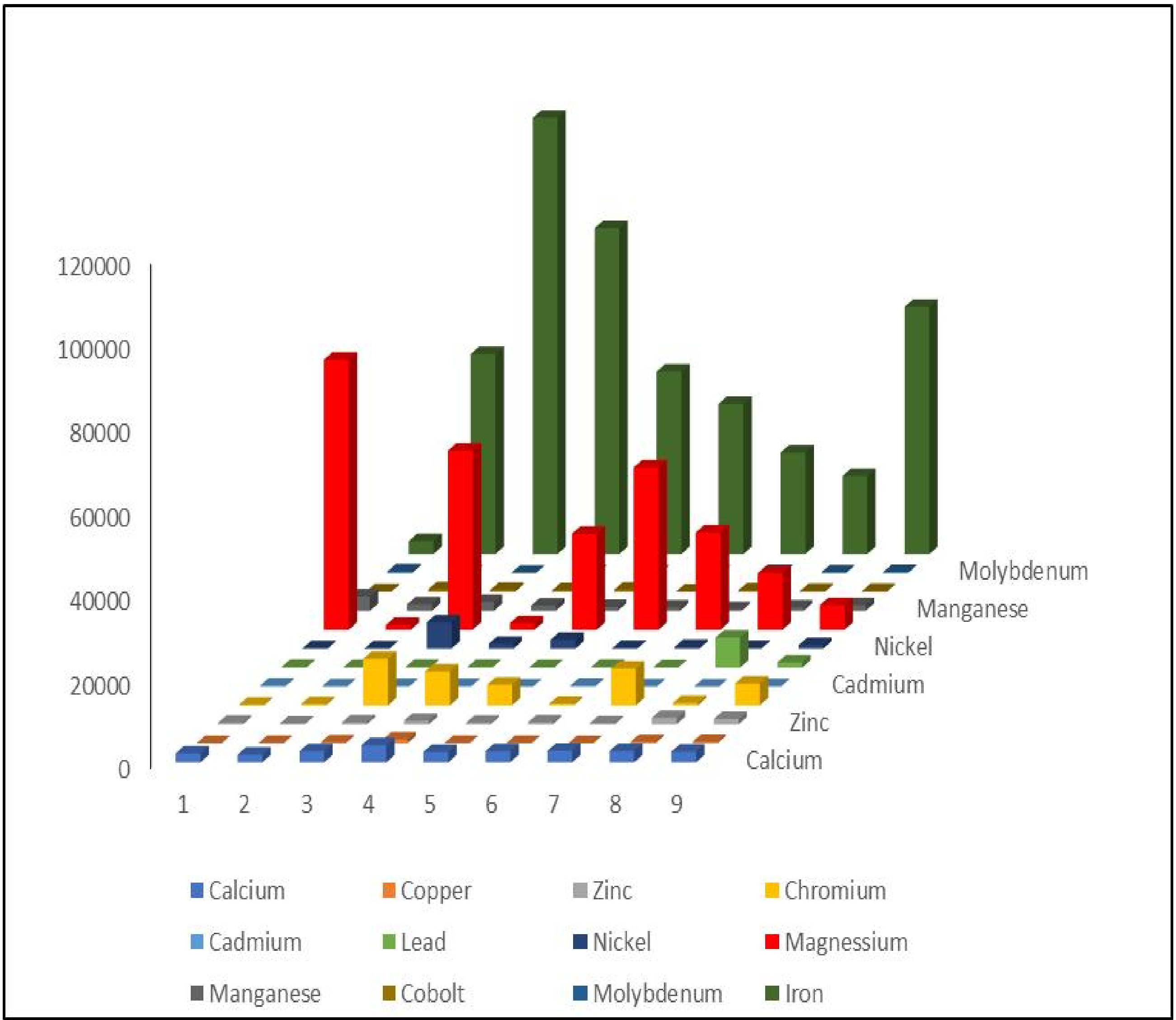

Figure 4.3: Distribution Elements Across Auto-Mechanic workshops by Atomic Absorption Spectrophotometer (AAS)

Note: 1 = Alasa Akoyoyo, 2 = Moor Plantation, 3 = Oke Itunu, 4 = Samonda, 5 = Apete Morubo, 6 = Odo-Ona, 7 = Alesinloye, 8 = Sango, 9 = Mile-10

Source: Author's Analysis, 2023

The table 4.4 below showed the mean concentration of metals from selected auto-mechanic workshop in Ibadan metropolis. Alasa Akoyoyo sites indicated that Fe (31769 mg/kg) > Ca (11481 mg/kg) > Mn (1476 mg/kg) > Mg (1415 mg/kg) > Zn (415 mg/kg) > Cu (185 mg/kg) > Pb (100 mg/kg) > Cr (44 mg/kg) > Ni (16 mg/kg) > Co (15 mg/kg). Cd and Mo are below detection limit of the spectrophotometer. The findings followed the trend in AAS analysed soil[9,10].

Moor plantation site revealed that Ca (79579 mg/kg) > Fe (31769 mg/kg) > Mg (2923 mg/kg) > Mn (2041 mg/kg) > Zn (1163 mg/kg) > (Cu (694 mg/kg) > Pb (251 mg/kg) > Cr (102 mg/kg) > Ni (71 mg/kg) > Co (8 mg/kg), Cd and Mo are below detection limit.

At Oke-Itunu workshops Fe (49087 mg/kg) > Ca (46339 mg/kg) > Mg (11671 mg/kg) > Zn (2135 mg/kg) > Mn (1676 mg/kg) > Cu (571 mg/kg) > Pb (369 mg/kg) > Cr (81 mg/kg) > Co (18 mg/kg) > Mo (2 mg/kg). The mean concentration of metals at Samonda indicated that Fe (16135 mg/kg) > Ca (9820 mg/kg) > Mg (7234 mg/kg) > Zn (225 mg/kg) > Mn (188 mg/kg) > Cu (81 mg/kg) > Pb (41 mg/kg) > Cr (20 mg/kg) > Ni (6 mg/kg) > Co (5 mg/kg). Cd and Mo are below detection limit.

Apete morubo auto-mechanic workshop soil samples revealed that Fe (33593 mg/kg) > Ca (26597 mg/kg) > Mg (3014 mg/kg) > Mn (1259 mg/kg) > Zn (1119 mg/kg) > Cu (345 mg/kg) > Pb (170 mg/kg) > Cr (49 mg/kg) > Ni (28 mg/kg) > Co (13 mg/kg). Like the previous sites Cd and Mo are below detection limits. Odo-ona mechanic workshop shops soils revealed that the mean concentration of Fe (20511 mg/kg) > Ca (3052 mg/kg) > Mn (1008 mg/kg) > Cu (89 mg/kg) > Zn (64 mg/kg) > Cd (51 mg/kg) > Pb (44 mg/kg) > Cr (32 mg/kg) > Ni (13 mg/kg) > Co (6 mg/kg). Mg and Mo could not be determined by XRF spectrometer. Alesinloye site indicated that Fe (16168 mg/kg) > Ca (5400 mg/kg) > Mn (545 mg/kg) > Zn (66 mg/kg) > Cu (55 mg/kg) > Cd (45 mg/kg) > Pb (43 mg/kg) > Cr (34 mg/kg) > Ni (13 mg/kg) > Co (7 mg/kg). However, Mg and Mo are below detection limit of

XRF spectrophotometer. Furthermore, at Sango Fe (17987 mg/kg) > Ca (2025 mg/kg) > Mn (716 mg/kg) > Zn (69 mg/kg) > Cu (59 mg/kg) > Cd (44 mg/kg) > Pb (34 mg/kg) > Cr (28 mg/kg) > Ni (14 mg/kg) > Co (9 mg/kg). Mg and Mo are below detection limit of XRF spectrometer.

Table 4.4: Elemental Concentration across Auto-mechanic Workshops by X-ray Fluorescence Spectrophotometer (XRF)

Auto-Mechanic	Ca	Cu	Zn	Cr	Cd	Pb	Ni	Mg	Mn	Co	Mo	Fe
AlasaAkoyoyo	11481 (1.73)	185 (0.40)	415 (0)	44 (0.58)	LOD	100 (0.58)	16 (0)	1415 (0.58)	1476 (0.58)	15 (0)	LOD	31769 (0.58)
MoorPlantation	79579 (0.58)	694 (0.58)	1163 (0.58)	102 (0.57)	LOD	251 (0.70)	71 (0.57)	2923 (0.58)	2041 (0.56)	8 (0.58)	LOD	23645 (0.58)
Oke-Itunu	46339 (0.70)	571 (0)	2135 (3.79)	81 (0)	LOD	369 (0.58)	65 (0.76)	11671 (1.52)	1676 (3.79)	18 (0)	2 (0)	49087 (0.61)
Samonda	9820 (0.55)	81 (0.58)	225 (0.58)	20 (0)	LOD	41 (0)	6 (0.43)	7234 (8.67)	188 (0.58)	5 (0)	LOD	16135 (0.61)
Apete Morubo	26597 (4.93)	345 (0)	1119 (0.23)	49 (0)	LOD	170 (0.58)	28 (0.39)	3014 (3.79)	1259 (5.77)	13 (0)	LOD	33593 (2.08)
Odo-Ona	3052 (0.70)	89 (0)	64 (0.32)	32 (0)	51 (0.58)	44 (0)	13 (0)	LOD	1008 (1)	6 (0)	LOD	20511 (5.77)
Alesinloye	5400 (1.53)	55 (0.38)	66 (0)	34 (0.83)	45 (8.71)	43 (0.51)	13 (0)	LOD	545 (0.58)	7 (1.00)	LOD	16168 (0.47)
Sango	2025 (0.46)	59 (0.40)	69 (0)	28 (0)	44 (0.45)	34 (0)	14 (0)	LOD	716 (0.28)	9 (0)	LOD	17987 (0.58)
Mile-10	25939 (2.65)	391 (3.06)	883 (2.52)	44 (8.71)	48 (7.72)	514 (0.70)	24 (0)	LOD	788 (0.47)	13 (0)	LOD	41442 (2.06)

Values are in mg/kg and Mean (SD)
Source: Author’s Analysis, 2023

Mile-10 in table 4.4 above indicated that Fe (41442 mg/kg) > Ca (25939 mg/kg) mean concentrations as analysed by XRF spectrometer. However, Ca (25939 mg/kg) > Zn (883 mg/kg) > Mn (788 mg/kg) > Pb (514 mg/kg) > Cu (391 mg/kg) > Cd (48 mg/kg) > Cr (44 mg/kg) > Ni (24 mg/kg) > Co (13 mg/kg). Mg and Mo are below detection limit of XRF spectrometer. This also follwed the trend as seen in AAS analysis.

Moreover, the figure 4.4 below showed the distribution of elements, where Fe and Ca are substantially distributed across all the selected sites. Oke-Itunu had the highest concentration of Fe closely followed by Mile-10 while the least recorded mean concentration was found in Aleshinloye. Moor plantation recorded the highest concentration of Ca closely followed by Oke Itunu while the least was recorded in Sango auto-mechanic workshop. The chart indicated that Mg is highest in Oke Itunu followed by Samonda. Mo, Co, Pb and Cu are evenly distributed across all the sites. Oke Itunu also recorded the highest concentration of Zn, while Alasa Akoyoyo recorded the highest concentration of Mn.

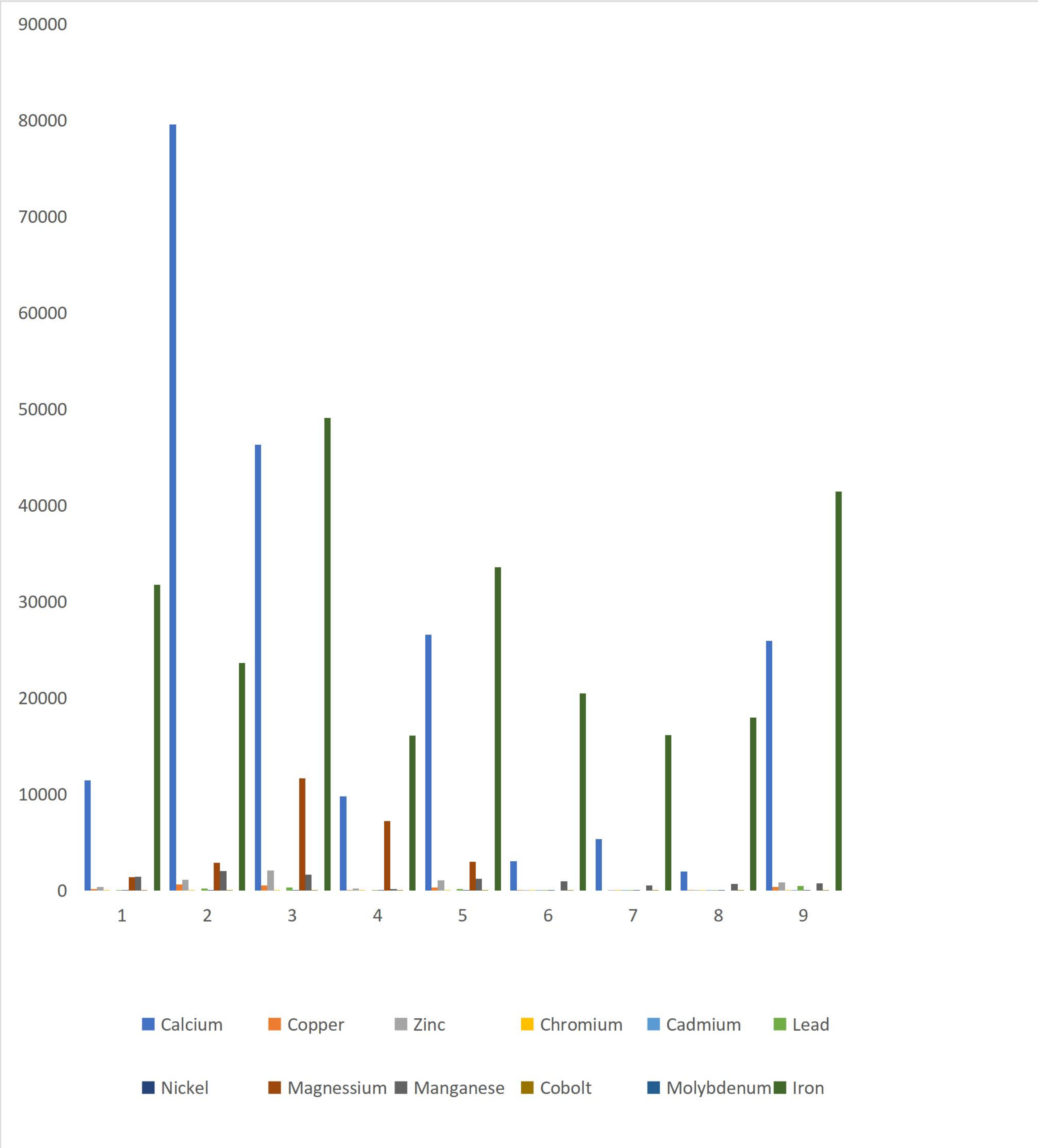

Figure 4.4: Distribution of Elements across Auto-Mechanic Workshops by X-ray Fluorescence Spectrophotometer (XRF)

1 = Alasa Akoyoyo, 2 = Moor Plantation, 3 = Oke Itunu, 4 = Samonda, 5 = Apete Morubo, 6 = Odo-Ona, 7 = Alesinloye, 8 = Sango, 9 = Mile-10

Source: Author's Analysis, 2023

4.3 Elemental Concentration of Farmlands Soil Samples

Table 4.5 below showed the elemental concentrations from selected farmland soils as analysed by AAS. Alajameta farmland showed that Fe (12713 mg/kg) > Mg (3150 mg/kg) > Ca (873 mg/kg) > Mn (567 mg/kg) > Co (165 mg/kg) > Mo (155 mg/kg) > Cr (123 mg/kg) > Pb (79 mg/kg) > Ni (69 mg/kg) > Cd (44 mg/kg) > Cu (20 mg/kg) > Zn (12 mg/kg). Moor Plantation clinic (M.P. Clinic) farmland soil indicated that Mg (14023 mg/kg) > Ca (8433 mg/kg) > Fe (239 mg/kg) > Mn (154 mg/kg) > Co (137 mg/kg) > Mo (131 mg/kg) > Cr (102 mg/kg) > Ni (83 mg/kg) > Cd (59 mg/kg) > Zn (46 mg/kg) > Pb (43 mg/kg) > Cu (28 mg/kg). BCJ/IBEDC farmland indicated that the mean concentration of Ca (10277 mg/kg) > Fe (7840 mg/kg) > Mg (7037 mg/kg) > Mn (680 mg/kg) > Mo (166 mg/kg) > Cd (145 mg/kg) > Cr (125 mg/kg) > Co (124 mg/kg) > Pb (81 mg/kg) > Ni (71 mg/kg) > Cu (24 mg/kg) > Zn (12 mg/kg). As reported in literature the concentration of elements in soil does not follow particular orders, the order depends on so many factors like type of fertilizer applied, Cation Exchange Capacity of the soil, pH, Soil particle sizes, level of contamination and length of usage among others[12,13,14]. NCRI farm revealed that mean concentration of Fe (10400 mg/kg) > Mg (5810 mg/kg) > Mn (3100 mg/kg) > Ca (837 mg/kg) > Mo (411 mg/kg) > Cr (142 mg/kg) > Ni (137 mg/kg) > Cd (123 mg/kg) > Co (50 mg/kg) > Cu (37 mg/kg) > Pb (29 mg/kg) > Zn (26 mg/kg). However, Southern farm 1 indicated that Mg (28700 mg/kg) > Fe (11260 mg/kg) > Ca (8600 mg/kg) > Ni (3673 mg/kg) > Cr (3020 mg/kg) > Mn (2873 mg/kg) > Co (366 mg/kg) > Mo (109 mg/kg) > Cu (79 mg/kg) > Cd (63 mg/kg) > Pb (29 mg/kg) > Zn (26 mg/kg). At NCRI rice farm, Mg (42677 mg/kg) > Fe (22280 mg/kg) > Cr (4953 mg/kg) > Ca (3433 mg/kg) > Ni (2273 mg/kg) > Mn (2313 mg/kg) > Mo (185 mg/kg) > Co (151 mg/kg) > Cu (139 mg/kg) > Cd (83 mg/kg) > Pb (43 mg/kg) > Zn (39 mg/kg). The IAR&T/FCA farmland showed that Fe (18067 mg/kg) > Cr (11280 mg/kg) > Mg (3267 mg/kg) > Ni (2240 mg/kg) > Ca (1900 mg/kg)

Table 4.5: Elemental Concentrations across Farmlands by Atomic Absorption Spectrophotometer (AAS)

Farm Lands	Ca	Cu	Zn	Cr	Cd	Pb	Ni	Mg	Mn	Co	Mo	Fe
Alajameta	873	20	12	123	44	79	69	3150	567	165	155	12713
	(1.95)	(0)	(0)	(0.20)	(0)	(0)	(0)	(32.15)	(1.89)	(0.58)	(0)	(1)
M.P. Clinic	8433	28	46	102	59	43	83	14023	154	137	131	239
	(3.79)	(0.58)	(1.15)	(5.20)	(8.70)	(0.38)	(2.31)	(4.59)	(0)	(0.58)	(0.58)	(1.15)
BCJ/IBEDC	10277	24	12	125	145	81	71	7037	680	124	166	7840
	(0.70)	(0)	(0)	(0.61)	(0.58)	(0)	(0.58)	(0.58)	(0.58)	(2.08)	(1.15)	(1)
Opp. NCRI	837	37	26	142	123	29	137	5810	3100	50	411	10400
	(3.57)	(0)	(0)	(1.53)	(2.83)	(0)	(1.53)	(23.09)	(5.77)	(0)	(2.69)	(5.03)
Southern Farm 1	8600	79	19	3020	63	29	3673	28700	2873	366	109	11260
	(23.09)	(0.58)	(0)	(0.58)	(8.70)	(0)	(2.31)	(5.77)	(2.89)	(5.77)	(0.58)	(5.77)
NCRI Rice	3433	139	39	4953	83	43	2273	42677	2313	151	185	22280
	(2.89)	(1.15)	(0)	(5.51)	(0)	(8.70)	(1)	(2.65)	(0.58)	(1)	(1.73)	(0.58)
I.A.R.&. T/FCA	1900	211	69	11280	73	38	2240	3267	1607	201	95	18067
	(5.77)	(5.20)	(0)	(5.29)	(0)	(0)	(0.58)	(1.15)	(1)	(4.62)	(0.38)	(0.58)
I.A.R.&T/OSADEP	1967	169	37	10533	64	47	5073	3640	1507	239	144	25827
	(0.55)	(1.92)	(0)	(5.03)	(0)	(8.70)	(5.29)	(2.89)	(2.31)	(1.73)	(0)	(6.08)
Southern Farm 2	2433	173	48	8922	73	42	3196	16528	1809	197	141	22058
	(1.53)	(2.69)	(0)	(5.51)	(0)	(0)	(2.65)	(1.73)	(0.61)	(0)	(0)	(1.73)

Values are in mg/kg and Standard Deviation (SD)
Source: Author's Analysis, 2023

> Mn (1607 mg/kg) > Cu (211 mg/kg) > Co (201 mg/kg) > Mo (95 mg/kg) > Cd (73 mg/kg) > Pb (38 mg/kg). IAR&T/OSADEP follow trends of other farms. The mean concentration of Southern farm 2 in table 4.5 above indicated that Fe (22058 mg/kg) > Mg (16528 mg/kg) > Cr (8922 mg/kg) > Ni (3196 mg/kg) > Ca (2433 mg/kg) > Mn (1809 mg/kg) > Co (197 mg/kg) > Cu (173 mg/kg) > Mo (141 mg/kg) > Cd (73 mg/kg) > Zn (48 mg/kg) > Pb (42 mg/kg)[15].

The figure 4.5 below showed the distribution of mean concentration of metals across farmlands as analysed by AAS spectrophotometer. The figure indicated that Fe was highest in IAR&T/OSADEP farmlands closely followed by NCRI rice farmlands, then Southern farmlands 2. The least of Fe was recorded in M.P. Clinic. The chart further revealed that Mg was highest in NCRI rice farmlands followed by Southern farm 1, then Southern farm 2. The least Mg was noticed in IAR&T/FCA farmlands. Following these two highest concentrations of metals was Cr which was highly significant in IAR&T&FCA farmlands, closely followed by IAR&T/OSADEP farmlands. The least was recorded at M.P. Clinic. It interesting to note that where all these highest records of Fe, Mg, and Cr were noticed those farms are within the same region and close to river Odo-Ona that normally overflooded during raining season, the abnormality in this increase may be due to deposition from overflooded rivers. Ca was also significant at BCJ/IBEDC, followed by Southern farm 1, them M.P. Clinic farmland. The least Ca was recorded at Opposite NCRI. It can also be deduced from the chart that Mn was noticed to be highest in Opposite NCRI and least at M.P. Clinic.

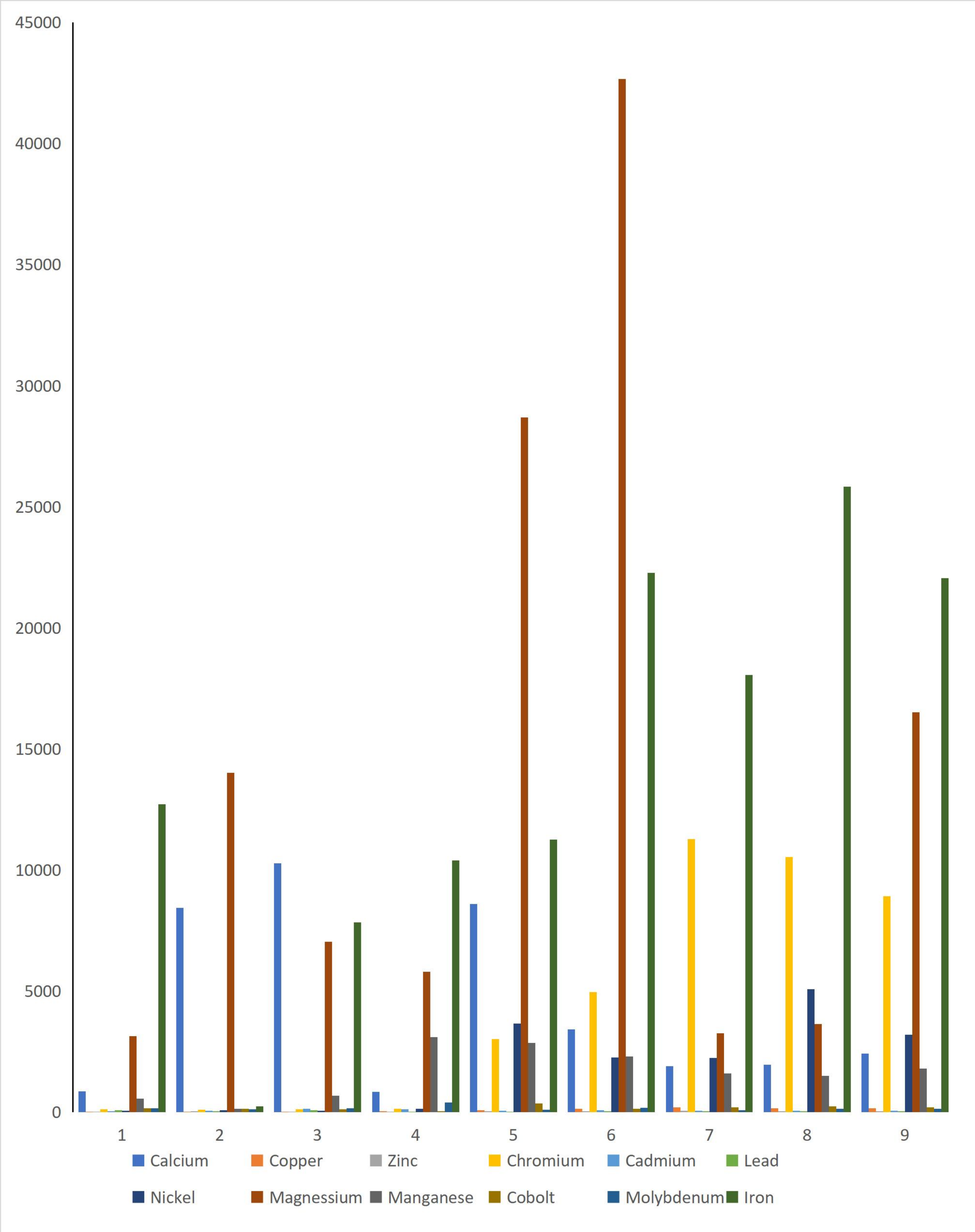

Figure 4.5: Distribution of Elements across Farmlands by Atomic Absorption Spectrophotometer (AAS)
Note: 1 = Alajameta, 2 = M.P. Clinic, 3 = BCJ/IBEDC, 4 = Opposite NCRI, 5 = Southern Farm 1, 6 = NCRI Rice, 7 = IAR&T/FCA, 8 = IAR&T/OSADEP, 9 = Southern Farm 2
Source: Author's Analysis, 2023

The table 4.6 below showed the mean concentrations of metals from selected farmlands analysed by XRF spectrometer. The table indicated that at Ca (59440 mg/kg) > Fe (34994 mg/kg) > Zn (1757 mg/kg) > Mg (1415 mg/kg) > Mn (1331 mg/kg) > Cu (658 mg/kg) > Pb (353 mg/kg) > Cr (82 mg/kg) > Ni (30 mg/kg) > Co (12 mg/kg). However, the XRF could not detect Cd and Mo.

At M.P. Clinic Fe (24013 mg/kg) > Ca (1390 mg/kg) > Mn (1081 mg/kg) > Zn (65 mg/kg) > Cd (53 mg/kg) > Pb (50 mg/kg) > Cu (49 mg/kg) > Cr (37 mg/kg) > Ni (16 mg/kg) > Co (5 mg/kg). The BCJ/IBEDC farmlands revealed that Fe (11999 mg/kg) > Mn (596 mg/kg) > Ca (491 mg/kg) > Zn (56 mg/kg) > Cu (47 mg/kg) > Cd (36 mg/kg) > Pb (26 mg/kg) > Cr (16 mg/kg) > Ni (7 mg/kg). However, XRF could not determine Mg and Mo, which may be above detection limit or below detection limit respectively[16].

The farmland opposite NCRI indicated that Fe (18380 mg/kg) > Ca (3070 mg/kg) > Mn (865 mg/kg) > Zn (62 mg/kg) > Cu (59 mg/kg) > Pb (52 mg/kg) > Cd (50 mg/kg) > Cr (33 mg/kg) > Ni (14 mg/kg). XRF spectrometer could not detect Mg, Mo and Co, which may either be above limit of detection as the case may be in the Mg metal or below detection limit in the case of Mo and Co. Southern Farm 1 showed that Fe (33391 mg/kg) > Ca (27165 mg/kg) > Mn (1183 mg/kg) > Zn (1119 mg/kg) > Cu (362 mg/kg) > Pb (157 mg/kg) > Cr (47 mg/kg) > Ni (28 mg/kg) > Co (11 mg/kg). XRF however could not detect Cd, Mg, and Mo, from Southern Farm 1 this could be as a result of what was stated in farmland opposite NCRI. The NCRI rice farmland indicated that Fe (24840 mg/kg) > Ca (9207 mg/kg) > Mn (618 mg/kg) > Zn (407 mg/kg) > Cu (119 mg/kg) > Cd (93 mg/kg) > Pb (91 mg/kg) > Cr (50 mg/kg) > Ni (16 mg/kg) > Co (5 mg/kg). As witnessed in the previous sites XRF could not detect Mg and Mo from the NCRU rice farmland.

Table 4.6: Elemental Concentration of Farmlands by X-ray Fluorescence Spectrophotometer (XRF)

Farm lands	Ca	Cu	Zn	Cr	Cd	Pb	Ni	Mg	Mn	Co	Mo	Fe
Alajameta	59440 (2.08)	658 (1.53)	1757 (0.95)	82 (0)	LOD	353 (2.52)	30 (0)	1415 (2.51)	1331 (2.08)	12 (0)	LOD	34994 (2.31)
M.P. Clinic	1390 (4.04)	49 (0)	65 (0)	37 (0)	53 (2.4)	50 (1)	16 (0.58)	LOD	1081 (4.73)	5 (0)	LOD	24013 (5.77)
BCJ/IBEDC	491 (2.10)	47 (0)	56 (8.72)	16 (0)	36 (0)	26 (0)	7 (1.09)	LOD	596 (3.79)	LOD	LOD	11999 (1)
Opp. NCRI	3070 (5.77)	59 (0.57)	62 (1.70)	33 (1.73)	50 (0)	52 (1.73)	14 (0)	LOD	865 (5.77)	LOD	LOD	18380 (2.08)
Southern Farm 1	27165 (2.08)	362 (4.51)	1119 (1.15)	47 (8.71)	LOD	157 (5.20)	28 (0)	LOD	1183 (4.62)	11 (0)	LOD	33391 (1.53)
NCRI Rice	9207 (2.08)	119 (0.58)	407 (1.73)	50 (8.72)	93 (0)	91 (0.58)	16 (0.19)	LOD	618 (5.77)	5 (0)	LOD	24840 (2.65)
I.A.R.&T./FCA	3097 (1.53)	92 (0)	198 (8.65)	42 (0)	54 (8.73)	42 (0)	8 (0)	LOD	352 (5.51)	LOD	LOD	19467 (5.77)
I.A.R.&T./OSADEP	33962 (10.06)	317 (0.58)	1195 (2.31)	53 (8.72)	148 (0.58)	490 (5.20)	21 (0)	LOD	634 (1.15)	16 (0.58)	LOD	39410 (5.77)
Southern Farm 2	2013 (0.58)	63 (0)	72 (0)	28 (0)	79 (0.58)	27 (0.58)	14 (0)	LOD	712 (4.58)	LOD	LOD	18018 (6.08)

Values are in mg/kg and Standard Deviation (SD)
Source: Author’s Analysis, 2023

IAR&T/FCA farmlands showed that Fe (19467 mg/kg) > Ca (3097 mg/kg) > Mn (352ug/g) > Zn (198ug/g) > Cu (92ug/g) > Cd (54ug/g) > Cr (42ug/g) > Pb (42 mg/kg) > Ni (8 mg/kg). Mg, Co and Mo are not detectable by XRF spectrometer as explained earlier on. The IAR&T/OSADEP follows trend of other farmlands. Southern Farm 2 as shown in Table 4.6 above revealed that the mean concentration of Fe (18018 ug/g) > Ca (2013 mg/kg) > Mn (712 mg/kg) > Cd (79 mg/kg) > Zn (72 mg/kg) > Cu (63 mg/kg) > Cr (28 mg/kg) > Ni (14 mg/kg), however, XRF spectrometer could not detect Mg and Mo unlike in the case of AAS spectrometer. This may be due to over range limit of Mg and the under-range limit of Mo in the soil samples[16,17,18,19].

Table 4.6 below described the distribution of metals across all the selected sites graphically. The chart showed that Fe was highest in IAR&T/OSADEP, followed by Alajameta farmland then Southern farm 1, however, BCJ/IBEDC had the least concentration of Fe. The chart also indicated that Ca was highest in Alajameta farmland samples, closely followed by IAR&T/OSADEP then Southern Farm 1. The least Ca was recorded at M.P. Clinic. Alajameta and IAR&T/OSADEP have a substantial amount of Zn concentration.

The XRF spectrometer could not detect Mg which was not the case with AAS, this may be as a result of the high concentration of Mg in all the selected soil samples as revealed by AAS. XRF spectrometers are calibrated to be able to measure certain values of concentration from samples, and as a result, any concentration above or below the value of standard used to calibrate the machine may not be detected.

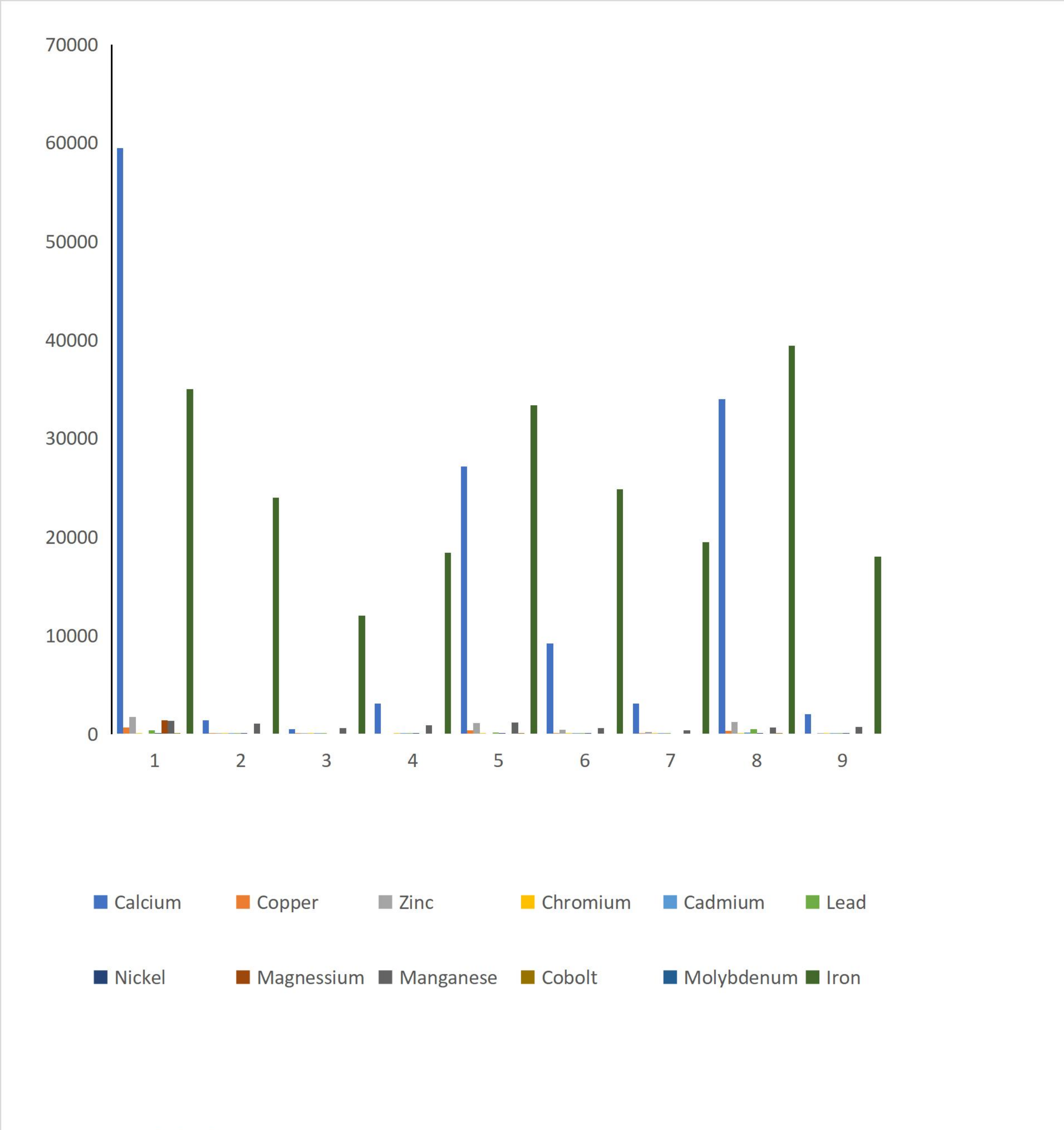

Figure 4.6: Distribution of Elements Across Farmlands by X-ray Fluorescence Spectrophotometer (XRF)

1 = Alajameta, 2 = M.P. Clinic, 3 = BCJ/IBEDC, 4 = Opposite NCRI, 5 = Southern Farm 1, 6 = NCRI Rice, 7 = IAR&T/FCA, 8 = IAR&T/OSADEP, 9 = Southern Farm 2

Source: Author's Analysis, 2023

4.4 Statistical Analysis

The statistical analysis of data obtained was done using GraphPad Prism 6 and Microsoft Excel Analysis Toolbar, 2016. The paired t-test showed that there is no statistically significant difference from copper metal in dumpsite soil samples analyzed with both AAS and XRF spectrophotometers at significance levels $p > 0.060$, ss shown in Figure 4.7a, especially for Aba-alfa samples.

The remaining elements showed significant differences in Lapite a major dumpsite, Ajakanga a major dumpsite, Awotan blanketed and Awotan landfill a major dumpsite. Also included are Aba Eku, Ajibode, Sabo, Orita Aperin, Apete, Apete Morubo, and Ijokodo mini dumpsites. These findings informed that the two machines cannot be used interchangeably for Ca, Cr, Mn, Mg, Co, Pb, Mo, and Fe, analyzed from dumpsite soils. Also, there is no statistically significant difference for zinc elements analyzed by AAS and XRF spectrophotometers at significance level of $p > 0.143$, as shown in Figure 4.7b especially for Awotan blanketed, Ajibode, Sabo and Apete morubo. However, the results showed statistically significant difference for Lapite a major dumpsite, Ajakanga a major dumpsite, Awotan landfill a major dumpsite, Orita – Aperin an old major dumpsite, as well as Aba - Alfa, Apete, and Ijokodo unauthorized dumpsites. This implied that AAS and XRF cannot be used interchangeably to determine elements contents of soils from these sites mentioned. The findings are in agreement with the reports from literature[20,21].

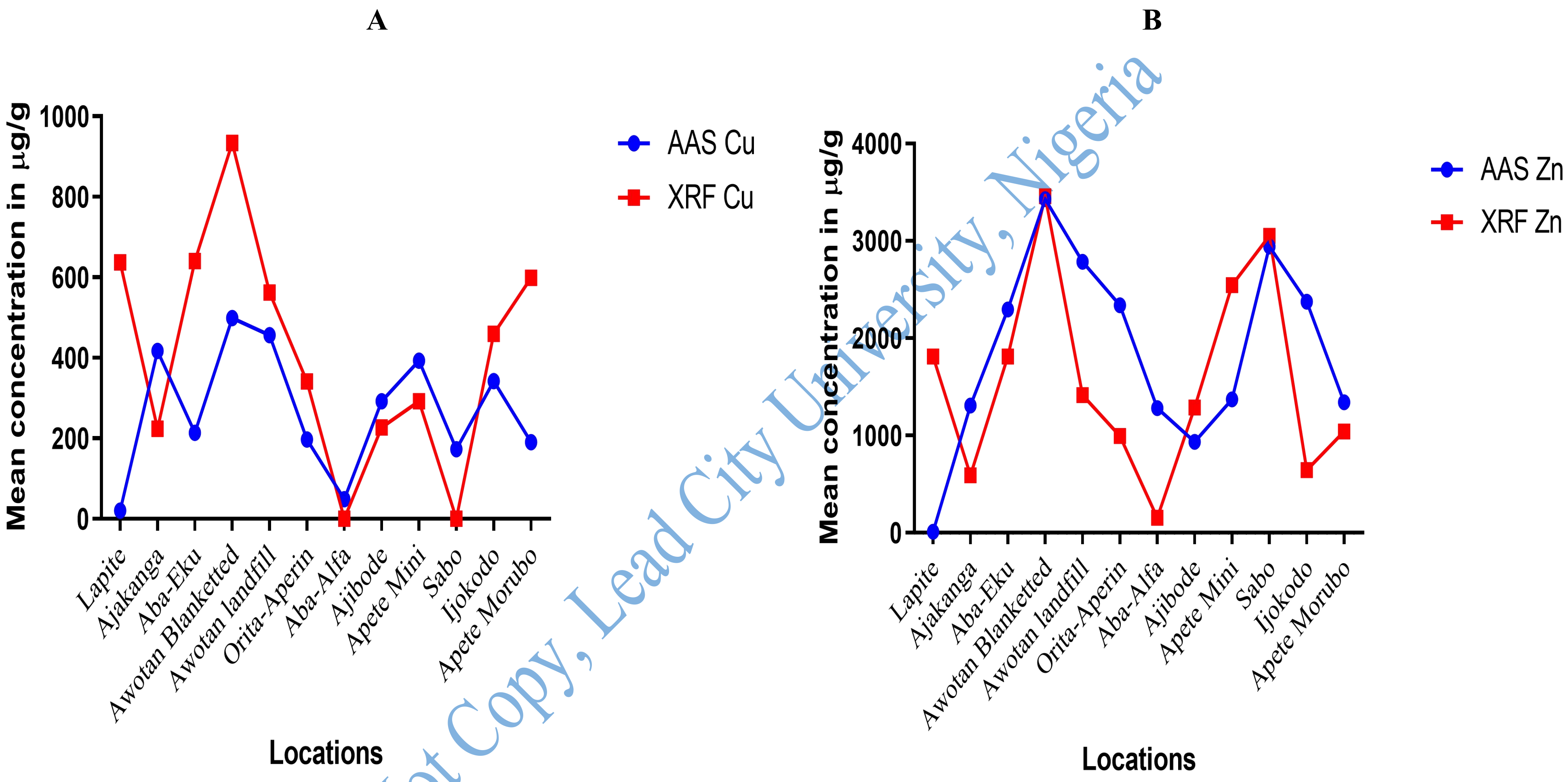

Figure 4.7: Mean of Differences of Cu and Zn with AAS and XRF Methods

Source: Author's Analysis, 2023

The statistical analysis of Cu concentration for auto-mechanic workshops samples (table 4.3 & 4.4) shows no significant differences at significance level $p > 0.960$ between AAS and XRF spectrophotometer of auto-mechanic soil samples (Figure 4.8a) especially for Odo-Ona, Alesinloye and Mile 10 Ago-Tylor.

Also, there is no significant differences between paired Zn mean concentration determined by AAS and XRF spectrophotometer, at significance level $p > 0.9834$, (Figure 4.8b) especially for Alasa & Akoyoyo[20,21].

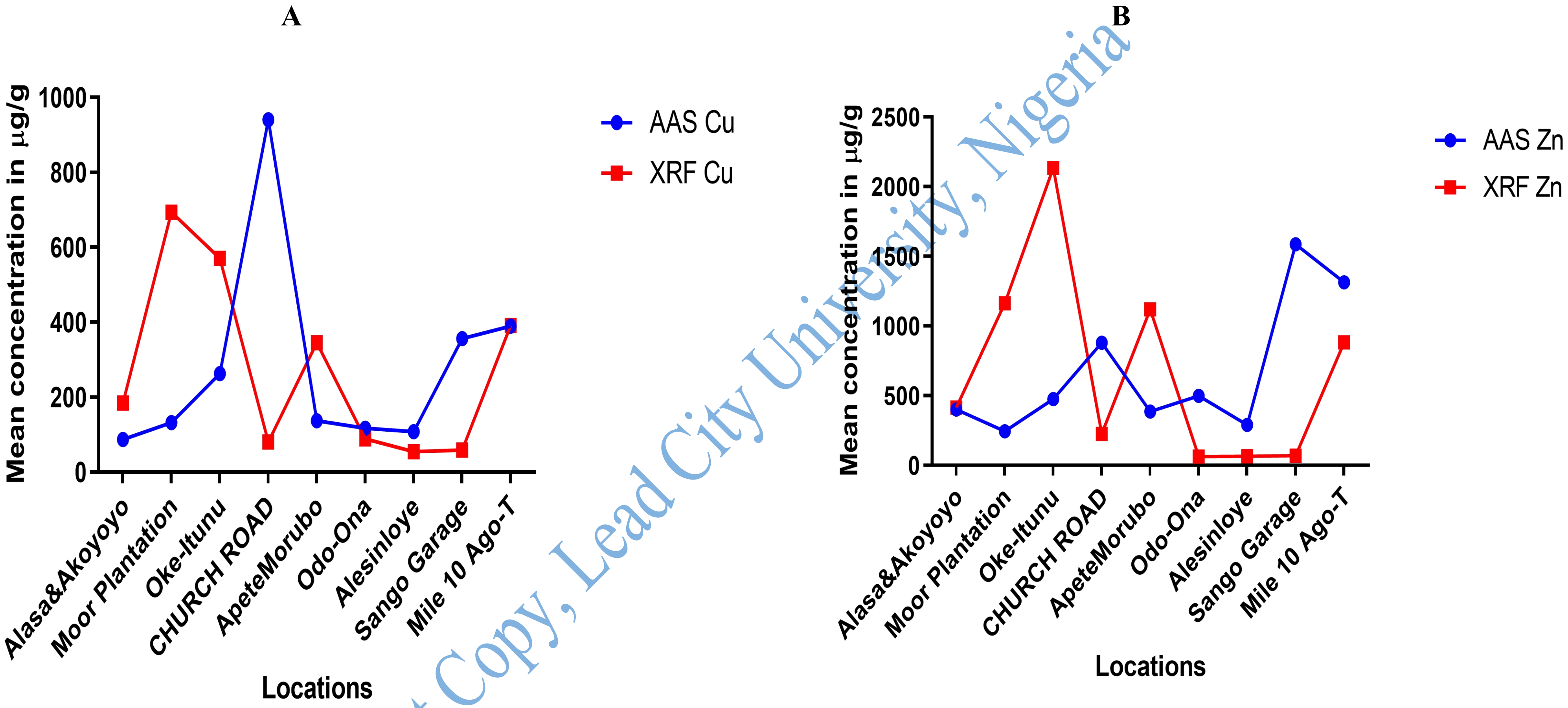

Figure 4.8: Mean of Difference of Cu & Zn by AAS and XRF Methods.
Source: Author's Analysis, 2023

The t-test for Pb as shown in Figure 4.9a below, indicated no significant differences at significance level $p = 0.2975$, this was noticed in all the selected sites (Alasa Akoyoyo, Moor Plantation, Oke Itunu, Samonda (Church Road), Apete Morubo, Odo-Ona, Aleshinloye, and Mile-10) except Sango garage meaning the AAS and XRF can be used interchangeably to determine Pb from auto-mechanic workshops soil samples.

The result in Figure 4.9b showed that there is no significant difference between the mean concentration of Ni determined by AAS and XRF spectrometer, at significances level $p = 0.0978$, for Alasa Akoyoyo, Moor Plantation, Odo-Ona, Aleshinloye and Sango garage.

Furthermore, Mn and Fe mean concentration determined by the two equipment showed no significant differences at level $p = 0.2335$ and $p = 0.0813$, respectively as shown in Figure 4.9c and 4.9d below, especially for Odo-Ona, Aleshinloye and Sango garage.

However, Cr and Co showed significant differences at level $p = 0.0149$ and $p = 0.0008$ respectively.

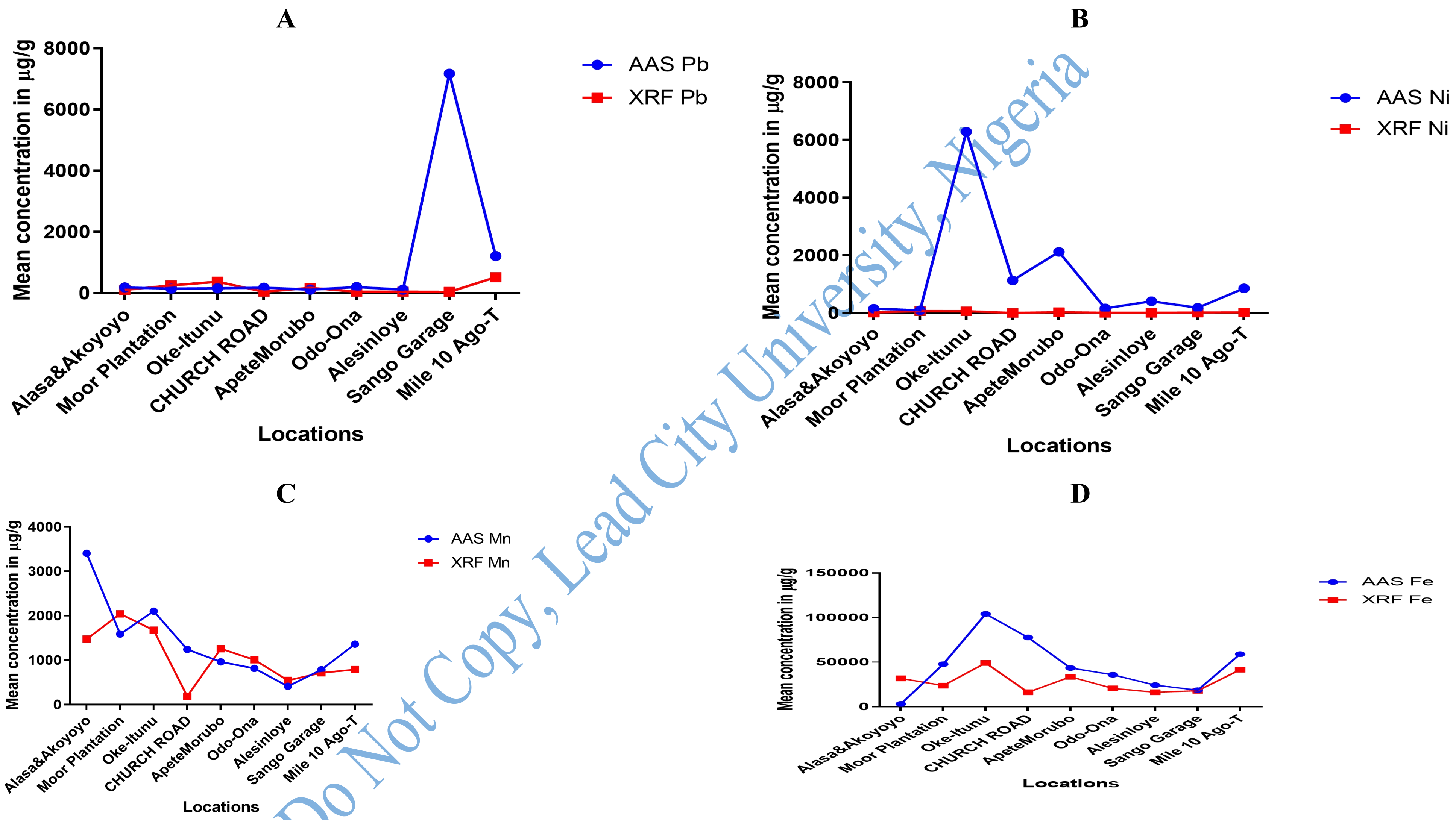

Figure 4.9: Mean of differences of Pb, Ni, Mn & Fe with AAS and XRF Methods

Source: Author's Analysis, 2023

The result of the t-test of farmlands indicated in Figure 4.11a below showed that there are no significant differences in the result of Ca at significance level $p = 0.1630$, by both AAS and XRF for Opposite NCRI, Southern farm 1, NCRI Rice plantation, IAR&T/OSADEP and Southern farm 2. It can also be seen in Figure 4.11b below that there are no significant differences in Cd analyzed by both AAS and XRF at significance level $p = 0.2440$, especially for Moor Plantation Clinic land use, Southern farm 1, and Southern farm 2. It can also be seen from figure 4.11c that Pb showed no significant difference in the results of both AAS and XRF, at significance level $p = 0.0619$.

Figure 4.11d showed that there is no significant difference in Cu mean concentration as analyzed by both AAS and XRF, the significance level is $p = 0.2473$ especially for Moor Plantation clinic land use, BCJ/IBEDC, Opposite NCRI, NCRI rice plantation and Southern farm 2.

However, there are statistically significant differences in the pairing of Zn, Cr, Ni, Mg, Co, Mo and Fe. The implication of these findings is that AAS and XRF can be used interchangeably to determine Cu, Cd, Pb and Ca in farmland soils.

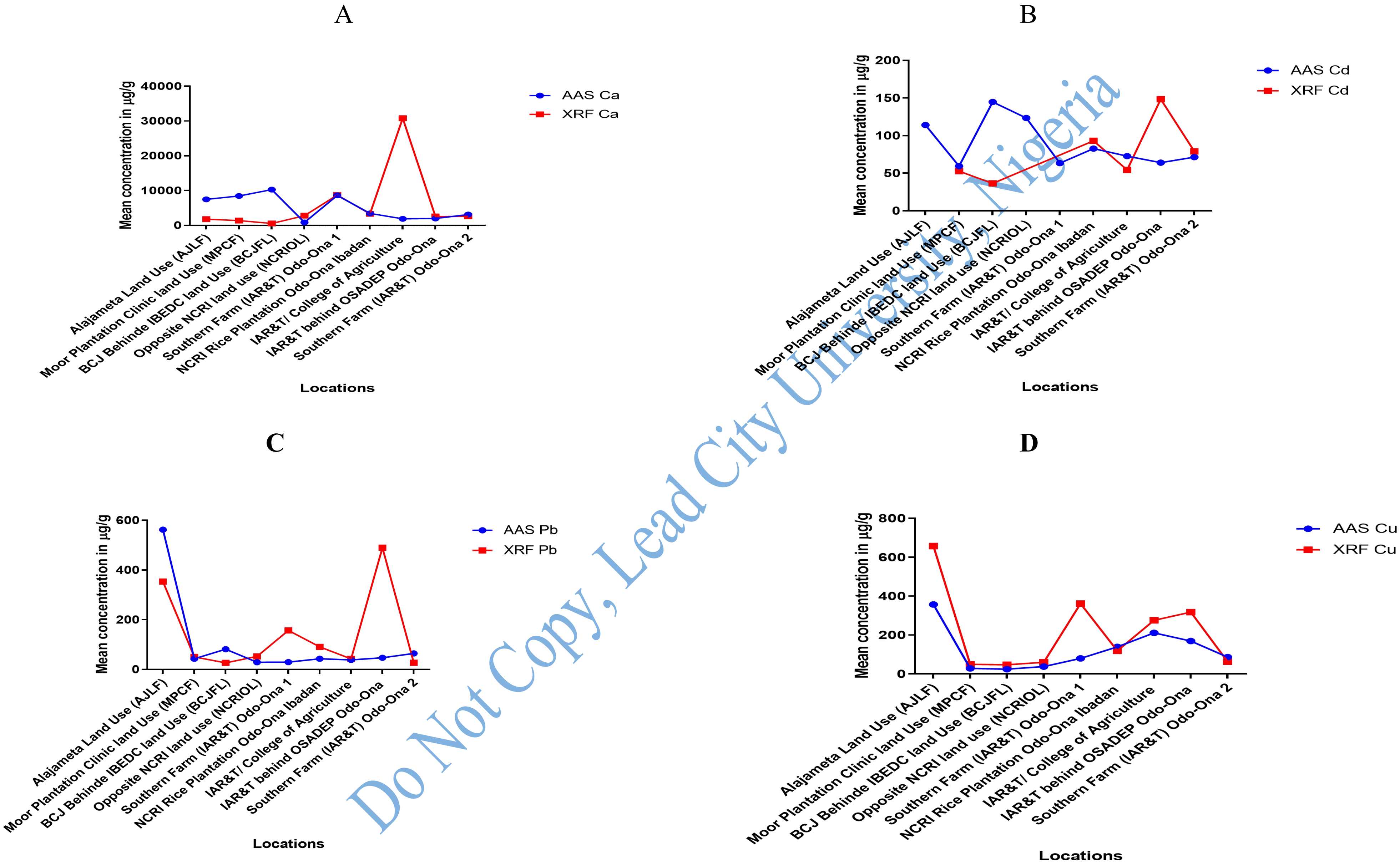

Figure 4.10: Mean Concentrations of Ca, Cd, Pb & Cu with AAS and XRF Methods

Source: Author's Analysis, 2023

4.5 Statistical Analysis

4.5.1 One-way Analysis of Variance (ANOVA) for AAS Method

The mean concentrations of the same elements from the dumpsites, auto mechanic villages and farmlands soils were conducted using one-way analysis of variance (ANOVA) to determine their significant differences ($p < 0.05$)

ANOVA test revealed that there was no statistically significant difference in the mean concentration of Ca, Cu, Pb, Mg, Mn, Co, and Mo. between at least two sites. (Table 4.7) Bonferroni correction was used for post-hoc analysis.

The test revealed that there was a statistically significant difference between Ca of farmland and auto-mechanic workshop, as well as dumpsites and auto-mechanic workshop. However, there is no statistically significant difference between the Ca of farmland and dumpsites.

The Bonferroni post-hoc test showed that there was no statistically significant difference between Cu of dumpsite and auto-mechanic, as well as farmland and auto-mechanic workshop. However, there is a statistically significant difference between the Cu of farmland and dumpsites.

Post-hoc test revealed that there was no statistically significant difference between Pb of dumpsite and auto-mechanic, as well as farmland and auto-mechanic sites. However, there was a statistically significant difference between the Pb of farmland and dumpsite. Meanwhile, post-hoc tests of Ni, Mg, Mn, Co and Mo revealed that there was no statistically significant difference between the three sampled sites. However, a post-hoc test of Fe revealed that there was a statistically significant difference between dumpsite and auto-mechanic, as well as auto-mechanic and farmland sites, while there was no statistically significant difference between the Fe of farmland and dumpsite sites.

Table 4.7: ANOVA Table of Metals using Atomic Absorption Spectrophotometer (AAS)

Elements	P - value	F - value	F – critical
Calcium	0.290	1.295	3.354
Cupper	0.061	3.153	3.403
Lead	0.251	1.463	3.404
Nickel	0.717	0.337	3.403
Magnesium	0.186	1.805	3.403
Manganese	0.108	2.442	3.403
Cobalt	0.066	3.043	3.403
Molybdenum	0.590	0.539	3.403
Iron	0.002	8.282	3.354

Source: Author’s Analysis, 2023

4.5.2 One-way Analysis of Variance for XRF Method

A one-way ANOVA revealed that there was a statistically significant difference in the mean concentration of Ca, Cu, Zn, Cr, Pb and Mg in at least two sites, while there were no statistically significant differences between Cd, Mn, Co and Fe. (Table 4.8)

ANOVA post-hoc tests (Bonferroni correction) were performed to know which two sites are significant differences and which are not.

The test revealed that there was a statistically significant difference between the Ca of dumpsite and auto-mechanic, as well as farmland and dumpsite sites. However, there was no statistically significant difference between the Ca of farmland and auto-mechanics. In the case of post-hoc test carried out on Cu test revealed that there was no statistically significant difference between dumpsite and auto-mechanic, as well as auto-mechanic and farmland. However, there was a statistically significant difference between the Cu of farmland and dumpsite sites.

Post-hoc test revealed that there was no statistically significant difference between Zn of dumpsite and auto-mechanic, as well as auto-mechanic and farmland. However, there was a statistically significant difference between the Zn of farmland and dumpsite sites. Moreover, the post-hoc test revealed that there was a statistically significant difference between Cr of dumpsite and auto-mechanic, as well as farmland and dumpsite sites. However, there was no statistically significant difference between the Cr of farmland and auto-mechanics.

The post-hoc test for Cd and Pb indicated statistically no significant difference between the three sites for the number of samples that XRF was able to determine. The post-hoc test also revealed that there was no statistically significant difference between Mn, Co as well as Fe of the dumpsite, auto-mechanic, and farmlands.

The test revealed that there was no statistically significant difference between Ni of dumpsite and auto-mechanic, as well as farmland and auto-mechanic. However, there was a statistically significant difference between the Ni of farmland and dumpsite.

The test revealed that there was no statistically significant difference between Mg of dumpsite and auto-mechanic, as well as farmland and dumpsite sites. However, there was a statistically significant difference between the Mg of farmland and auto-mechanic workshop.

There are deaths of literature on the comparison of elements from three different soil sites.

4.5.3 Linear Regression and Correlation Studies of XRF and AAS Methods

Results showing comparison of the two methods using linear regression are presented in figure 4.11, to 4.13 below, for dumpsite, auto-mechanic and farmlands respectively. Although there was a high degree of agreement ($R^2 > 0.7$) between the two methods (XRF and AAS) for Cu, Zn, Cr, and Mn from Dumpsites and Mn and Fe from Auto-mechanic workshops samples, there regression lines showed some deviations.

Similarly, correlation study suggested that the two methods can be interchangeably used to quantify Cu (0.56), Zn (0.55), Cr (0.65) and Mn (0.55).

Table: 4.8 ANOVA Table of Metals using X-ray Fluorescence Spectrophotometer (XRF)

Elements	P - value	F - value	F - critical
Calcium	0.00	8.802	3.403
Cupper	0.013	5.364	3.443
Zinc	0.017	4.835	3.403
Chromium	0.001	9.791	3.403
Cadmium	0.609	0.519	3.982
Lead	0.020	4.553	3.354
Nickel	0.066	3.010	3.354
Magnesium	0.008	6.069	3.422
Manganese	0.127	2.228	3.354
Cobalt	0.050	3.365	3.369

Iron	0.065	3.030	3.354

Source: Author's Analysis, 2023

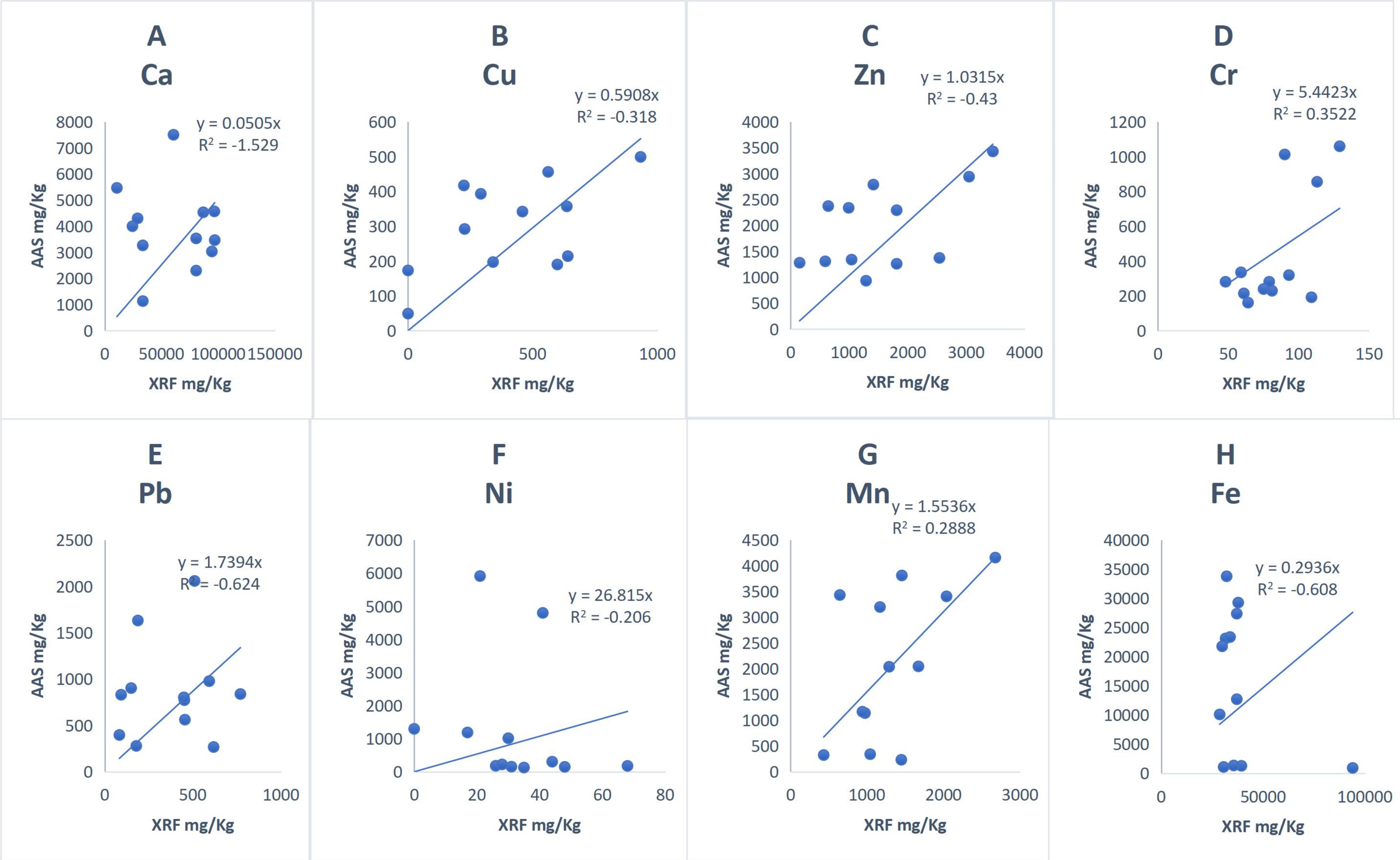

Figure: 4.11, Dumpsite regression results for XRF and AAS for (A) Ca, (B) Cu, (C) Zn, (D) Cr, (E) Pb, (F) Ni, (G) Mn, (H) Fe. XRF indicate X-ray fluorescence and AAS atomic absorption spectrophotometer

Source: Author’s Analysis, 2023

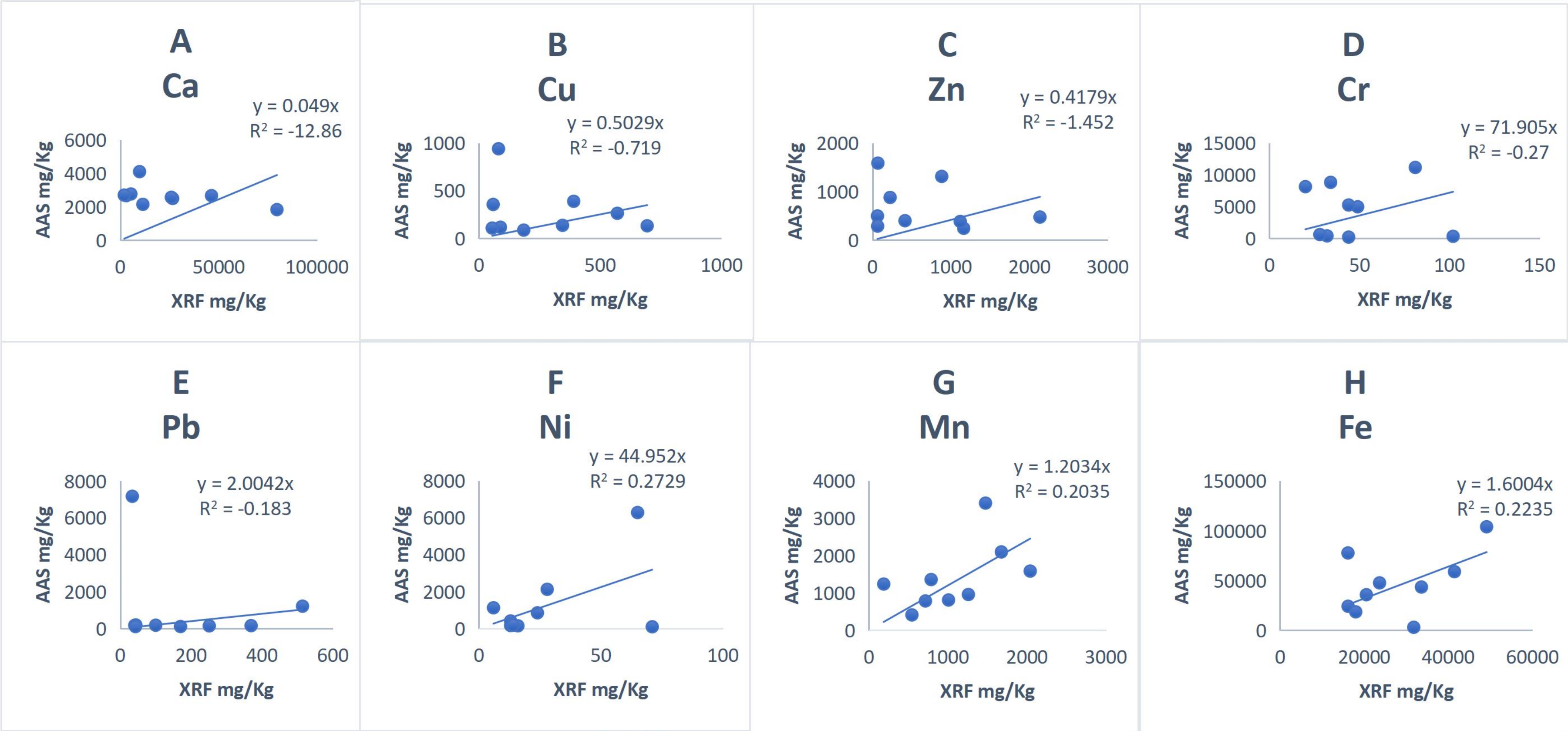

Figure: 4.12 Auto-mechanic regression results for XRF and AAS for (A) Ca, (B) Cu, (C) Zn, (D) Cr, (E) Pb, (F) Ni, (G) Mn, (H) Fe. XRF indicate X-ray fluorescence and AAS atomic absorption spectrophotometer
Source: Author's Analysis, 2023

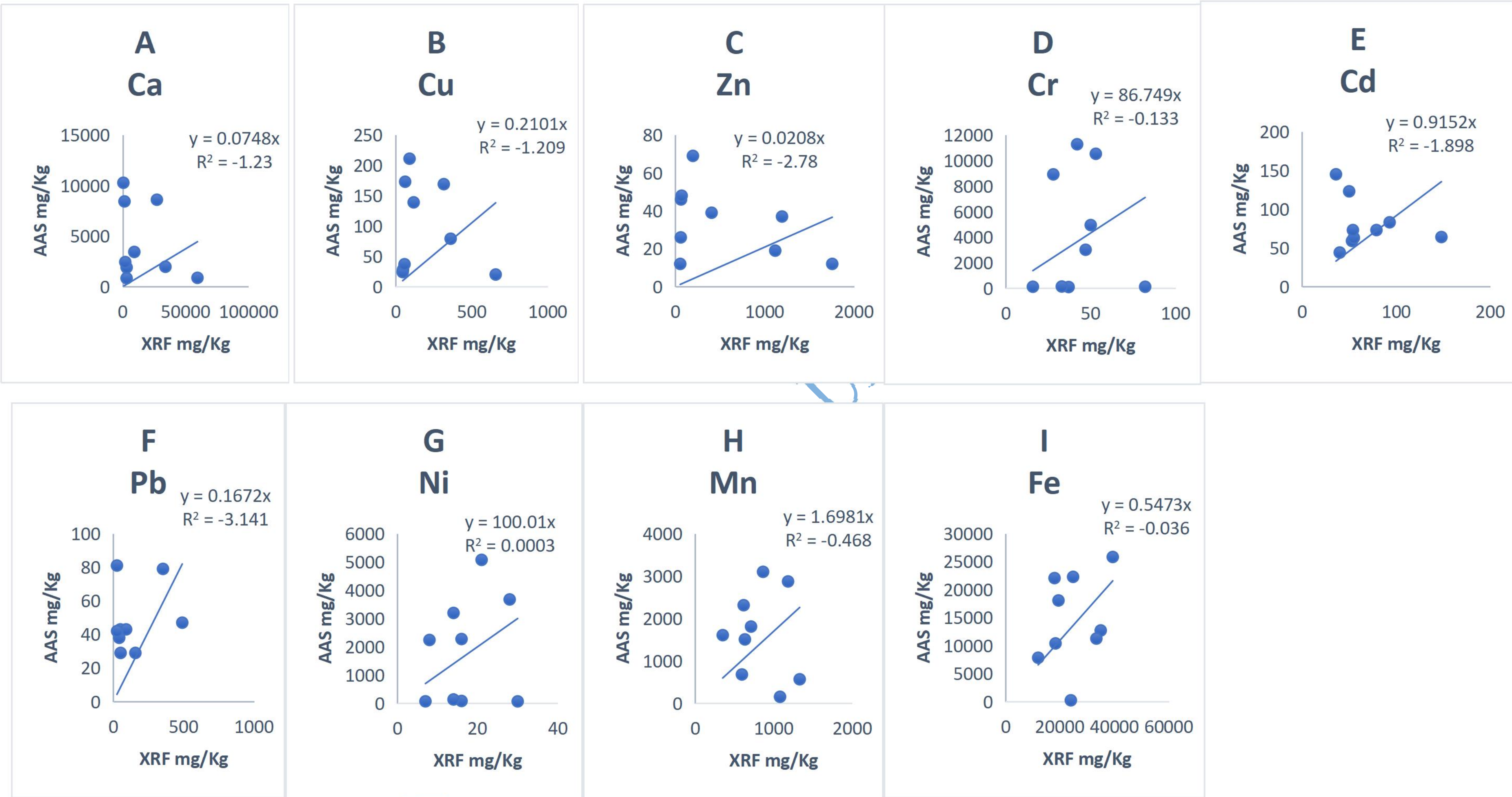

Figure:4.13 Farmland's regression results for XRF and AAS for (A) Ca, (B) Cu, (C) Zn, (D) Cr, (E) Cd, (F) Pb, (G) Ni, (H) Mn, (I) Fe. XRF indicate X-ray fluorescence and AAS atomic absorption spectrophotometer.

Source: Author's Analysis, 2023

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Chapter Five

Conclusion

5.1 Summary of Findings

Reproducibility results of XRF and AAS analyses in this study were dependent on the element being quantified, although the former technique underestimated assayed trace element concentrations. Underestimation was possibly due to differences in equipment sensitivity in the two methods.

XRF has low sensitivity to light elements like lithium, beryllium, sodium, and high detection limits to trace metals like Ca, Cu, Zn, Mn, Pb, Fe Co, in low concentrations while the sensitivity of AAS is high and enhanced by aqua regia digestion.

Based on the comparative studies of atomic absorption spectrophotometer (AAS) and X-ray Reflectance Fluorescence (XRF) on soil from dumpsites, auto-mechanic workshop and farmlands to determine twelve elements, the results of dumpsites samples showed that only Zn and Cu can be determined interchangeably with AAS and XRF, while Cu, Zn, Cd, Pb, Ni, Mg, and Fe from auto-mechanic workshop soil samples can be determined interchangeably with XRF and AAS. Furthermore, farmland soils indicated that Ca, Cu, Cd, Pb and Mn could be determined interchangeably with AAS and XRF.

The ANOVA analysis was carried out for the three sites to know the relationship between the quantities of metal elements. The result revealed that the quantity of Ca in farmland and dumpsites was the same for AAS while farmland and auto-mechanic are the same for XRF. For Cu, dumpsites and auto-mechanic as well as farmland and auto-mechanic are the same for both AAS and XRF.

Zn was the same for dumpsite and auto-mechanic as well as auto-mechanic and farmland for XRF, while none was the same for AAS.

Cr was the same in farmland and auto-mechanic for both AAS and XRF, while Cd was not the same for the three sites with the two methods. Mn, Co and Mo are not the same with the two methods.

However, Fe was not the same in farmland soil and dumpsites soil with XRF and AAS.

5.2 Conclusion

The studied samples indicated that AAS and XRF machines could be used interchangeably for some elements determination in dumpsite (Zn & Cu), auto-mechanic (Cu, Zn, Cd, Pb, Ni, Mg & Fe) and farmland (Ca, Cu, Cd, Pb & Mn). However, XRF can be used to screen for available elements in a particular sample before embarking on chemical analysis for elements that cannot be determined interchangeably with the machine.

5.3 Recommendations

The fact that XRF has low sensitivity and high detection limits to trace metals in low concentrations it can be used to determine trace metals that are suspected to be of high quantity in a sample without necessarily using AAS.

5.4 Contribution to Knowledge

The study has been able to establish the fact that concentration of Cu, Zn, Cr, Mn, Fe, and Co, elements in dumpsite, farmland and auto-mechanic are the same as confirmed by the two methods of analysis. Furthermore, using the two methods to determine several elements in most especially auto-mechanic and farmlands yielding more than two elements that can be determined interchangeably is germane to this study.

5.5 Area(s) for Further Research

Area of further research is the calibration of XRF to be of high sensitivity to light and trace elements in small quantity in a sample.

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Appendix I

Means, Standard Deviation and Standard Error Mean of Paired Elements of Dumpsites

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	Ca_{AAS}	3925	12	1599	461.5
	Ca_{XRF}	60647	12	32372	9345
Pair 2	Cu_{AAS}	298.2	12	135.1	38.99
	Cu_{XRF}	491.6	12	226.0	71.47
Pair 3	Zn_{AAS}	1971	12	819.1	236.5
	Zn_{XRF}	1568	12	1016	293.2
Pair 4	Cr_{AAS}	431.4	12	334.9	96.67
	Cr_{XRF}	83.31	12	24.61	7.11
Pair 5	Cd_{AAS}	315.6	12	303.1	87.49
	Cd_{XRF}	41.75	12	3.889	2.75
Pair 6	Pb_{AAS}	860.2	12	526.8	152.1
	Pb_{XRF}	378.5	12	231.1	66.7
Pair 7	Ni_{AAS}	1294	12	1961	566.1
	Ni_{XRF}	34.72	12	13.82	3.99
Pair 8	Mg_{AAS}	8366	12	4455	1286
	Mg_{XRF}	2573	12	2866	827.3
Pair 9	Mn_{AAS}	2109	12	1459	421.1
	Mn_{XRF}	1316	12	612.6	176.9
Pair 10	Co_{AAS}	368.9	12	225.9	65.22

	Co_{XRF}	10	12	2.85	.86
Pair 11	Mo_{AAS}	138.9	12	109.5	31.6
	Mo_{XRF}	.0000	12	.00000	.00000
Pair 12	Fe_{AAS}	14514	12	13093	3780
	Fe_{XRF}	38953	12	17682	5104

Appendix II

Paired samples correlations of Dumpsites

		N	Correlation	Sig.
Pair 1	Ca_{AAS} & Ca_{XRF}	12	-0.08122	.0001
Pair 2	Cu_{AAS} & Cu_{XRF}	12	0.2176	0.0596
Pair 3	Zn_{AAS} & Zn_{XRF}	12	0.5511	0.1431
Pair 4	Cr_{AAS} & Cr_{XRF}	12	0.6489	0.0031
Pair 5	Cd_{AAS} & Cd_{XRF}	2	linear	0.4793
Pair 6	Pb_{AAS} & Pb_{XRF}	12	0.0778	0.0124
Pair 7	Ni_{AAS} & Ni_{XRF}	12	0.2464	0.0477
Pair 8	Mg_{AAS} & Mg_{XRF}	12	0.4923	0.0003
Pair 9	Mn_{AAS} & Mn_{XRF}	12	0.5491	0.0478

Pair 10	Co_{AAS} & Co_{XRF}	11	0.2904	0.2904
Pair 11	Mo_{AAS} & Mo_{XRF}	12		
Pair 12	Fe_{AAS} & Fe_{XRF}	12	-0.3437	0.0066

Appendix III

Paired Samples T-test

	Paired Differences					t	df	Sig. (2 -tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence interval of the Difference				
				Lower	Upper			
Ca_{AAS}-Ca_{XRF}	56722	32541	9394	36047	77398	6.038	11	0.0001
Cu_{AAS}-Cu_{XRF}	155.9	228.8	72.35	-7.766	319.6	2.155	9	**0.060**
Zn_{AAS}-Zn_{XRF}	-403.5	886.3	255.8	-966.6	159.6	1.577	11	**0.143**
Cr_{AAS}-Cr_{XRF}	-348.1	319.5	92.22	-551.1	-145.1	3.774	11	0.0031
Cd_{AAS}-Cd_{XRF}	-87.25	115.6	81.75	-1126	951.5	1.067	1	0.4793
Pb_{AAS}-Pb_{XRF}	-481.7	558.7	161.3	-836.7	-126.7	2.987	11	0.0124
Ni_{AAS}-Ni_{XRF}	-1259	1958	565.2	-2503	-15.02	2.228	11	0.0477

Mg_{AAS}-Mg_{XRF}	-5793	3936	1136	-8293	-3292	5.098	11	0.0003
Mn_{AAS}-Mn_{XRF}	-792.8	1234	356.1	-1576	-9.021	2.226	11	0.0478
Co_{AAS}-Co_{XRF}	-371.8	231.8	69.79	-527.3	-216.3	5.328	10	0.0003
Fe_{AAS}-Fe_{XRF}	24440	25362	7321	8326	40554	3.338	11	0.0066

Appendix IV

Mean and standard deviation of soil samples from Auto-mechanic villages

	N	Mean		Std. Deviation
	Statistic	Statistic	Std. Error	Statistic
Ca_{AAS}	9	2661	206.4	619.3
Ca_{XRF}	9	23395	8515	25545
Cu_{AAS}	9	566.7	137.7	413.1
Cu_{XRF}	9	333.3	81.65	244.9
Zn_{AAS}	9	1878	365.1	1095
Zn_{XRF}	9	933.3	299.5	898.6
Cr_{AAS}	9	14244	4526	13579
Cr_{XRF}	9	56.67	8.165	24.49
Cd_{AAS}	9	321.1	64.02	192.1
Cd_{XRF}	9	94.44	14.25	42.75
Pb_{AAS}	9	3222	2844	853.2
Pb_{XRF}	9	282.2	90.29	270.9
Ni_{AAS}	9	2947	1612	4836
Ni_{XRF}	9	23.67	6.12	18.35
Mg_{AAS}	9	56000	16707	50120

Mg_{XRF}	9	7744	1382	4146
Mn_{AAS}	9	4044	405.2	1216
Mn_{XRF}	9	1367	255.0	764.9
Co_{AAS}	9	767.8	151.4	454.3
Co_{XRF}	9	8.778	2.332	6.992
Mo_{AAS}	9	370	84.97	254.9
Mo_{XRF}	9	.0000	.00000	.00000
Fe_{AAS}	9	54511	121582	36475
Fe_{XRF}	9	28644	2757	8271
Valid N (listwise)	9			

Appendix VI

Standard deviation and standard error means of paired elements of auto-mechanic soil samples

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	Ca_{AAS}	3.0556	9	.62472	.20824
	Ca_{XRF}	3.3144	9	3.33395	1.11132
Pair 2	Cu_{AAS}	.0567	9	.04131	.01377
	Cu_{XRF}	.0333	9	.02449	.00816
Pair 3	Zn_{AAS}	.1878	9	.10952	.03651
	Zn_{XRF}	.0933	9	.08986	.02995
Pair 4	Cr_{AAS}	1.4244	9	1.35788	.45263
	Cr_{XRF}	.0057	9	.00245	.00082
Pair 5	Cd_{AAS}	.0321	9	.01921	.00640
	Cd_{XRF}	.0094	9	.00428	.00143
Pair 6	Pb_{AAS}	.3222	9	.85318	.28439
	Pb_{XRF}	.0282	9	.02709	.00903
Pair 7	Ni_{AAS}	.2947	9	.48361	.16120

	Ni_{XRF}	.0024	9	.00184	.00061
Pair 8	Mg_{AAS}	5.6000	9	5.01203	1.67068
	Mg_{XRF}	.4056	9	.48583	.16194
Pair 9	Mn_{AAS}	.4044	9	.12156	.04052
	Mn_{XRF}	.1367	9	.07649	.02550
Pair 10	Co_{AAS}	.4044	9	.12156	.04052
	Co_{XRF}	.0009	9	.00070	.00023
Pair 11	Mo_{AAS}	.0370	9	.02549	.00850
	Mo_{XRF}	.0000	9	.00000	.00000
Pair 12	Fe_{AAS}	5.4511	9	3.64746	1.21582
	Fe_{XRF}	2.8644	9	.82709	.27570

Appendix VII

Correlation of paired elements of auto mechanic soil samples

		N	Correlation	Sig.
Pair 1	Ca_{AAS} & Ca_{XRF}	9	-0.501	0.0431
Pair 2	Cu_{AAS} & Cu_{XRF}	9	-0.0238	0.960
Pair 3	Zn_{AAS} & Zn_{XRF}	9	-0.2681	0.983
Pair 4	Cr_{AAS} & Cr_{XRF}	9	-0.0123	0.0149
Pair 5	Cd_{AAS} & Cd_{XRF}	9	0.9857	0.1601
Pair 6	Pb_{AAS} & Pb_{XRF}	9	-0.1964	0.298

Pair 7	Ni_{AAS} & Ni_{XRF}	9	0.5175	0.0978
Pair 8	Mg_{AAS} & Mg_{XRF}	5	-0.05198	0.1623
Pair 9	Mn_{AAS} & Mn_{XRF}	9	0.5338	0.2335
Pair 10	Co_{AAS} & Co_{XRF}	9	0.1181	0.0008
Pair 11	Mo_{AAS} & Mo_{XRF}	9	.	.
Pair 12	Fe_{AAS} & Fe_{XRF}	9	0.4904	0.0813

Appendix VII

Paired Sample Test for Auto-mechanic Workshop

	Paired Differences					t	df	Sig. (2 -tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence interval of the Difference				
				Lower	Upper			
Ca_{AAS}-Ca_{XRF}	20698	25861	8620	820.1	40577	2.401	8	0.0431
Cu_{AAS}-Cu_{XRF}	-6.959	402.0	134.0	-315.9	302.0	0.052	8	**0.960**
Zn_{AAS}-Zn_{XRF}	6.814	954.3	318.1	-726.8	740.4	0.021	8	**0.9834**
Cr_{AAS}-Cr_{XRF}	-4382	4256	1419	-7653	-1110	3.089	8	0.0149
Cd_{AAS}-Cd_{XRF}	-66.33	71.40	35.70	-179.9	47.28	1.858	3	**0.1601**

Pb_{AAS}-Pb_{XRF}	-876.7	2360	786.7	-2691	937.4	1.114	8	**0.2975**
Ni_{AAS}-Ni_{XRF}	-1239	1983	661.2	-2764	285.6	1.874	8	**0.0978**
Mg_{AAS}-Mg_{XRF}	-21283	27815	127815	-55820	13254	1.711	4	**0.1623**
Mn_{AAS}-Mn_{XRF}	-329.9	768.0	256.0	-920.2	260.4	1.289	8	**0.2335**
Co_{AAS}-Co_{XRF}	-321.5	185.4	61.81	-464.1	-179.0	5.202	8	0.0008
Fe_{AAS}-Fe_{XRF}	-18127	27278	9093	-39094	2841	1.994	8	**0.0813**

Appendix IX

Mean, standard deviation and standard error mean for paired elements determined from farm land soil.

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	Ca_{AAS}	4306	9	3716	1239
	Ca_{XRF}	15537	9	20499	6833
Pair 2	Cu_{AAS}	97.70	9	75.34	25.11
	Cu_{XRF}	196.3	9	209.8	69.94
Pair 3	Zn_{AAS}	34.34	9	18.84	6.281
	Zn_{XRF}	548.0	9	641.0	213.7
Pair 4	Cr_{AAS}	4356	9	4753	1584
	Cr_{XRF}	43.15	9	18.44	6.147
Pair 5	Cd_{AAS}	80.79	9	32.44	10.81
	Cd_{XRF}	57.04	9	46.28	15.43
Pair 6	Pb_{AAS}	47.83	9	19.25	6.415
	Pb_{XRF}	143.1	9	166.3	55.45

Pair 7	Ni_{AAS}	1868	9	1879	626.4
	Ni_{XRF}	17.11	9	8.073	2.691
Pair 8	Mg_{AAS}	13870	9	13695	4565
	Mg_{XRF}	157.3	9	471.3	157.3
Pair 9	Mn_{AAS}	1623	9	1027	342.2
	Mn_{XRF}	819.1	9	320.0	106.7
Pair 10	Co_{AAS}	181.2	9	87.80	29.27
	Co_{XRF}	5.481	9	6.249	2.083
Pair 11	Mo_{AAS}	170.9	9	94.03	31.34
	Mo_{XRF}	.0000	9	.00000	.00000
Pair 12	Fe_{AAS}	14520	9	8192	2731
	Fe_{XRF}	24946	9	9159	3053

Appendix X

Paired sample correlations of paired samples for farmlands

		N	Correlation	Sig.
Pair 1	Ca_{AAS} & Ca_{XRF}	9	-0.3086	**0.1630**
Pair 2	Cu_{AAS} & Cu_{XRF}	9	-0.2029	**0.2473**
Pair 3	Zn_{AAS} & Zn_{XRF}	9	-0.4521	0.0451
Pair 4	Cr_{AAS} & Cr_{XRF}	9	0.01155	0.0262

Pair 5	Cd_{AAS} & Cd_{XRF}	9	-0.005588	**0.2440**
Pair 6	Pb_{AAS} & Pb_{XRF}	9	0.2350	**0.1175**
Pair 7	Ni_{AAS} & Ni_{XRF}	9	0.2139	0.0182
Pair 8	Mg_{AAS} & Mg_{XRF}	9	-0.2935	0.0178
Pair 9	Mn_{AAS} & Mn_{XRF}	9	-0.1231	**0.0619**
Pair 10	Co_{AAS} & Co_{XRF}	9	0.5352	0.0003
Pair 11	Mo_{AAS} & Mo_{XRF}	9	.	.
Pair 12	Fe_{AAS} & Fe_{XRF}	9	0.2870	0.0168

Appendix XI

Paired samples test for mean concentration elements of farmland soils.

	Paired Differences					t	df	Sig. (2 - tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence interval of the Difference Lower	Upper			
Ca_{AAS}-Ca_{XRF}	11231	21933	7311	-5628	28091	1.536	8	**0.1630**
Cu_{AAS}-Cu_{XRF}	98.55	236.9	78.9	-83.53	280.6	1.248	8	**0.2473**
Zn_{AAS}-Zn_{XRF}	513.7	649.7	216.6	14.21	1013	2.372	8	0.0451
Cr_{AAS}-Cr_{XRF}	-4313	4753	1584	-7966	658.9	2.722	8	0.0262

Cd_{AAS}-Cd_{XRF}	-23.75	56.67	18.89	-67.31	19.80	1.258	8	**0.2440**
Pb_{AAS}-Pb_{XRF}	95.25	162.9	54.30	-29.97	220.5	1.754	8	**0.1175**
Ni_{AAS}-Ni_{XRF}	-1851	1877	625.8	-3294	-408.2	2.958	8	0.0182
Mg_{AAS}-Mg_{XRF}	-13713	13841	4614	-24352	-3074	2.972	8	0.0178
Mn_{AAS}-Mn_{XRF}	-804.2	1112	370.8	-1659	50.89	2.169	8	**0.0619**
Co_{AAS}-Co_{XRF}	-175.8	84.62	28.21	-240.8	-110.7	6.231	8	0.0003
Mo_{AAS}-Mo_{XRF}	-170.9	94.03	31.34	-243.2	-98.61	5.452	8	0.0006
Fe_{AAS}-Fe_{XRF}	10425	10389	3463	2439	18411	3.010	8	0.0168

Appendix XII

ANOVA Table of Ca from the Three Sample Sites using AAS

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	13584352.55	2	6792176	1.294655	0.290463	3.354131
Within Groups	141650651.6	27	5246320			
Total	155235004.2	29				

Appendix XIII

ANOVA Table of Cu from the Three Sample Sites using AAS

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	205580.984	2	102790.5	3.15336	0.060823	3.402826
Within Groups	782331.2808	24	32597.14			
Total	987912.2649	26				

Appendix XIV

ANOVA Table of Pb from the Three Sample Sites using AAS

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5509071	2	2754536	1.463387	0.251375	3.402826
Within Groups	45175230	24	1882301			
Total	50684301	26				

Appendix XV

ANOVA Table of Ni from the Three Sample Sites using AAS

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2698071	2	1349036	0.337429	0.716934	3.402826
Within Groups	95951707	24	3997988			
Total	98649778	26				

Appendix XVI

ANOVA Table of Mg from the Three Sample Sites using AAS

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	510554223.4	2	255277111.7	1.804905	0.186112	3.402826
Within Groups	3394444045	24	141435168.5			
Total	3904998269	26				

Appendix XVII

ANOVA Table of Mn from the Three Sample Sites using AAS

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5843240	2	2921620	2.442073	0.108298	3.402826
Within Groups	28712851	24	1196369			

Total	34556091	26

Appendix XVIII

ANOVA Table of Co from the Three Sites using AAS

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	207632.6	2	103816.3097	3.043881	0.066352	3.402826
Within Groups	818557.6	24	34106.56465			

Total	1026190	26

Appendix XIX

ANOVA Table of Mo from the Three Sample Sites using AAS

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	10265.36	2	5132.681	0.539289	0.590065	3.402826
Within Groups	228420	24	9517.5			

Total	238685.4	26

Appendix XX

ANOVA Table of Fe from the Three Sample Sites using AAS

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6221470407	2	3110735204	8.282163586	0.001567	3.354131
Within Groups	10141051867	27	375594513.6			

Total	16362522275	29

Appendix XXI

ANOVA Table of Ca from the Three Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	13043923816	2	6521961908	8.80217	0.00136	3.40283
Within Groups	17782786562	24	740949440.1			

Total	30826710378	26

Appendix XXII

ANOVA Table of Cu from the Three Sample Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	486115.9034	2	243058	5.36446	0.01266	3.44336

Within Groups	996796.8236	22	45308.9			
Total	1482912.727	24				

Appendix XXIII

ANOVA Table of Zn from the Three Sample Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6782126.6	2	3391063	4.8349	0.0172	3.40283

Within Groups	16832911	24	701371			
Total	23615038	26				

Appendix XXIV

ANOVA Table of Cr from the Three Sample Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*

Between Groups	10857.52	2	5428.758	9.790549	0.000778	3.402826
Within Groups	13307.75	24	554.4896			
Total	24165.27	26				

Appendix XXV

ANOVA Table of Cd from the Three Sample Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1275.74	2	637.868	0.51905	0.60896	3.9823
Within Groups	13518	11	1228.91			
Total	14793.7	13				

Appendix XXVI

ANOVA Table of Pb from the Three Sample Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	352481.2	2	176240.6	4.553314	0.019769	3.354131
Within Groups	1045062	27	38706.01			
Total	1397543	29				

Appendix XXVII

ANOVA Table of Ni from the Three Sample Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1596.827	2	798.4136	3.010442	0.066033	3.354131
Within Groups	7160.797	27	265.2147			
Total	8757.625	29				

Appendix XXVIII

ANOVA Table of Mg from the Three Sample Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	85716725.52	2	42858363	6.069315	0.007644	3.422132
Within Groups	162414090.4	23	7061482			
Total	248130815.9	25				

Appendix XXIX

ANOVA Table of Mn from the Three Sampled Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1274029	2	637015	2.22786	0.12719	3.35413
Within Groups	7720155	27	285932			
Total	8994184	29				

Appendix XXX

ANOVA Table of Co from the Three Sampled Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	142.687	2	71.3434	3.36483	0.05017	3.36902
Within Groups	551.27	26	21.2027			
Total	693.957	28				

Appendix XXXI

ANOVA Table of Fe from the Three Sampled Sites using XRF

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1175230317	2	587615159	3.029568969	0.06501	3.35413
Within Groups	5236919656	27	193959987			
Total	6412149973	29				

Appendix XXXII

Awotan Landfill

Appendix XXXIII

Lapite Major Dumpsite at Moniya

Appendix XXXIV

Appendix XXXIV

Ajakanga Major Dumpsite at Ayegun Oleyo

Appendix XXXV

Aba-Eku Major Dumpsite at Odi Orita Aperin

Appendix **XXXV**

Appendix **XXXVI**

Map showing Mechanic Workshops Locations

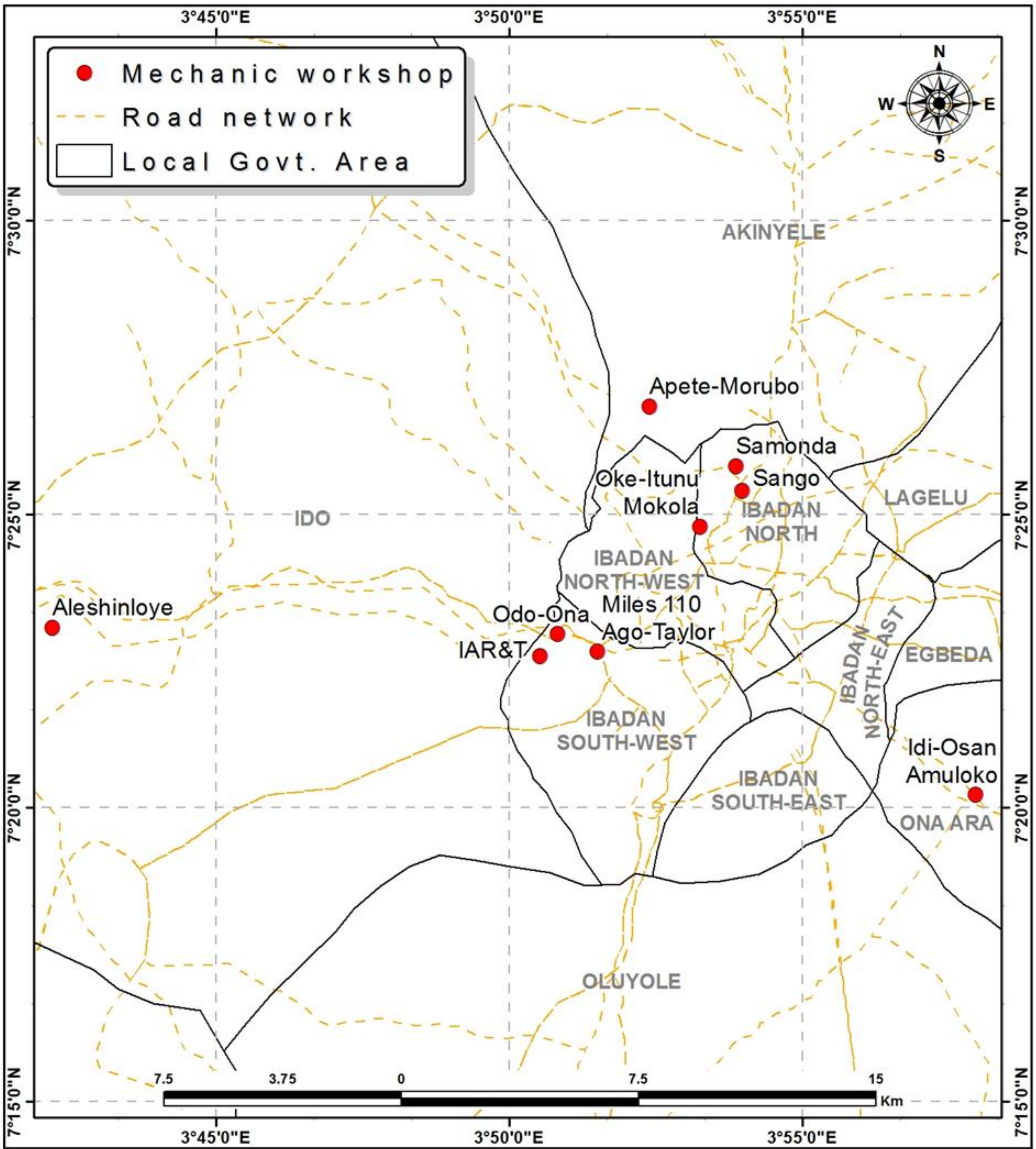
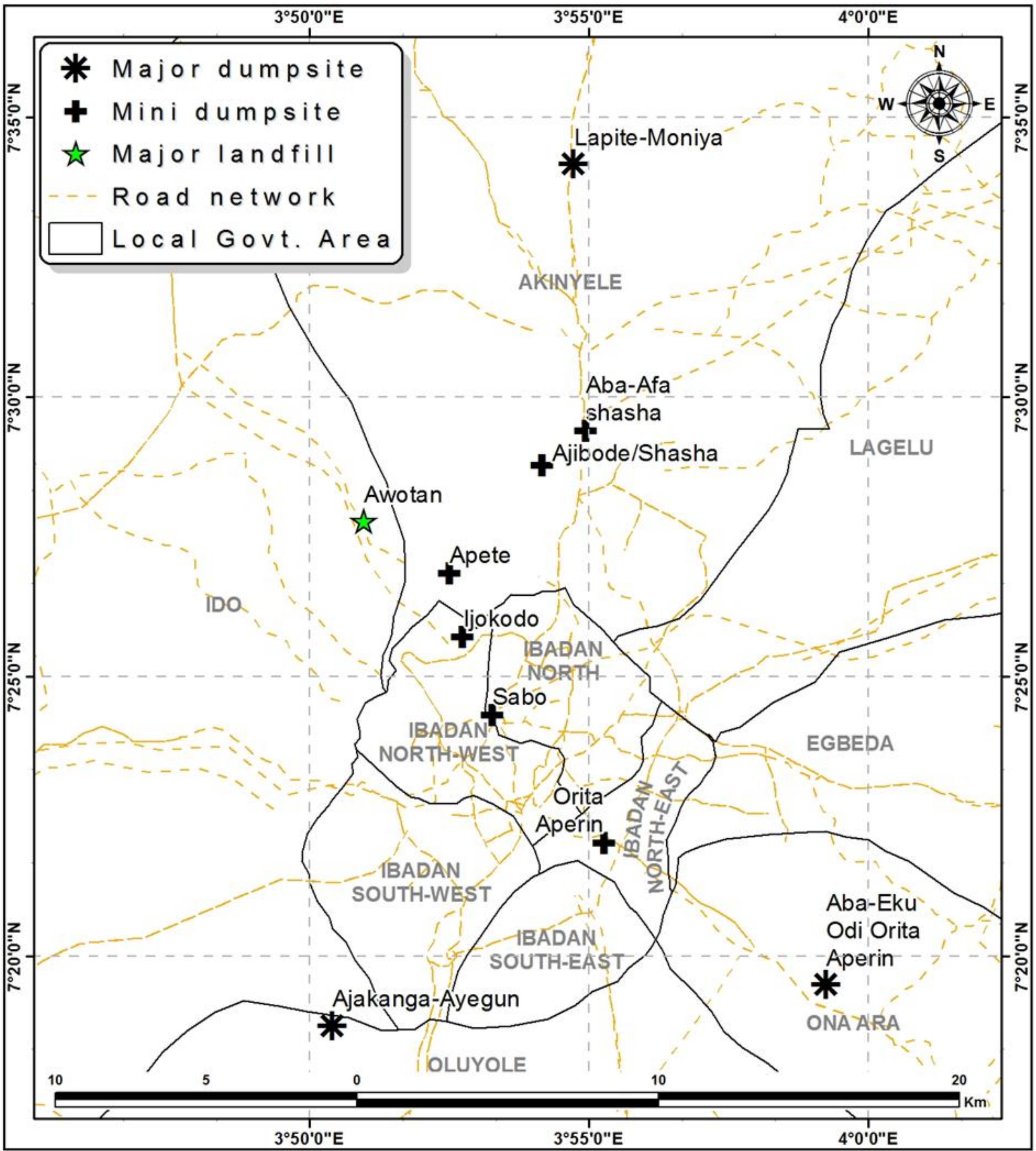


Figure: 3.2 Mechanic Workshops Locations

Appendix **XXXVII**

Map showing Dumpsites and Landfills Locations



Appendix **XXXVIII**

Map showing Farmlands Locations

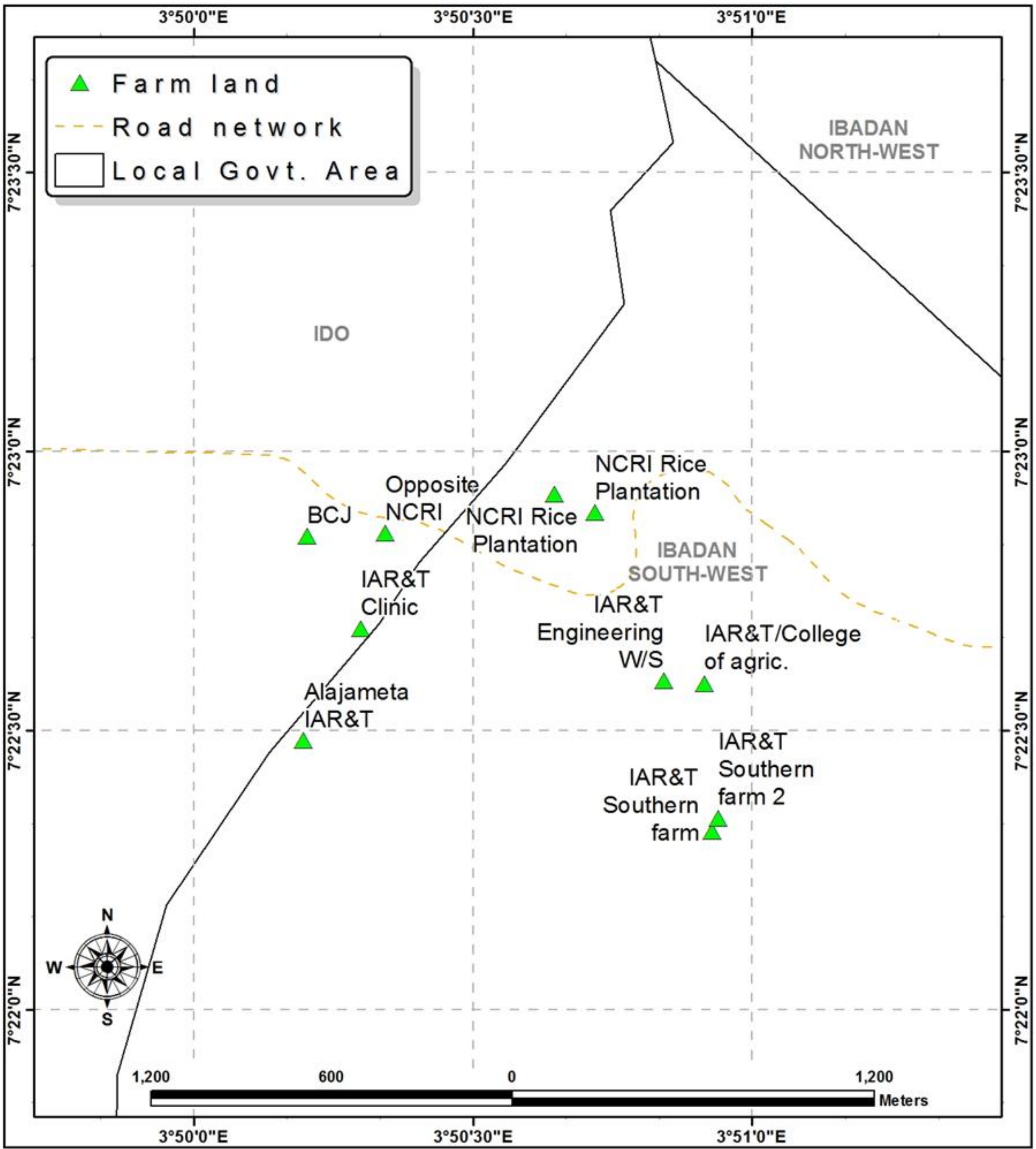
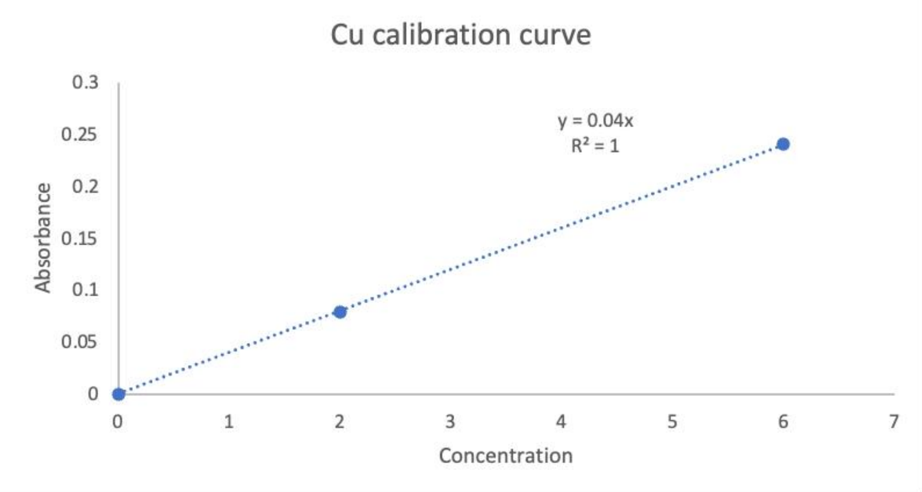
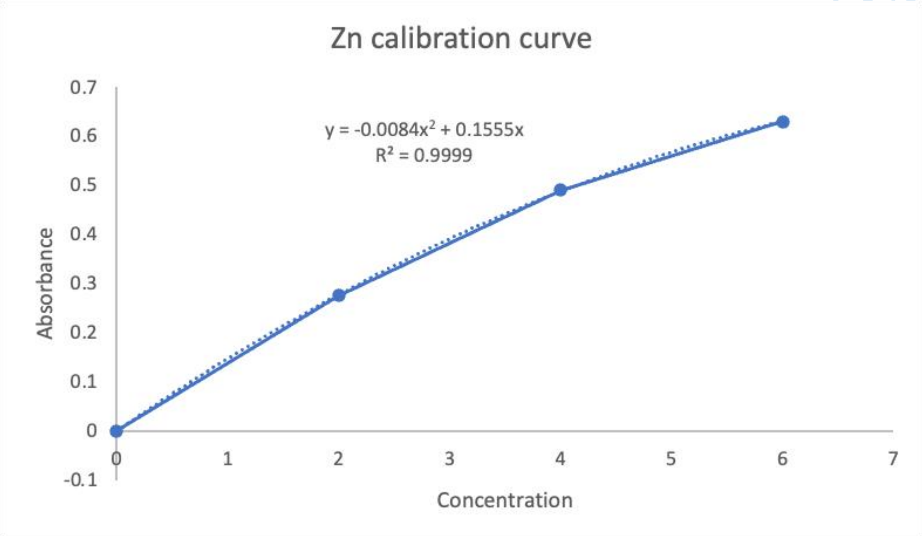
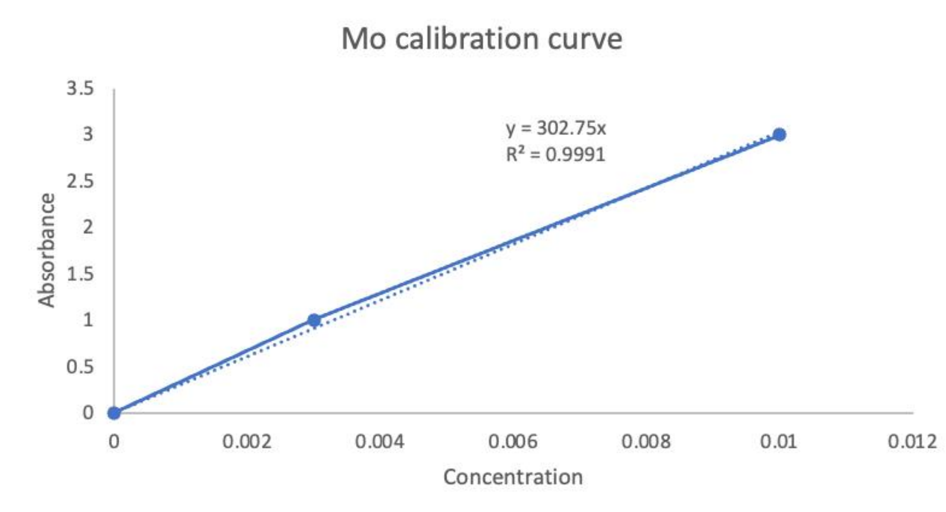


Figure 3.4 Map showing Farmlands Locations

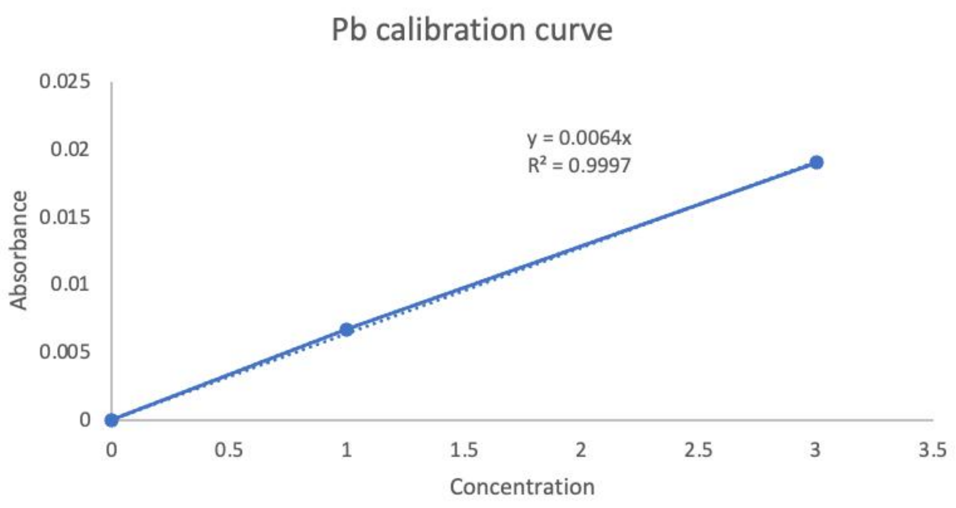
Appendix **XXXIX**

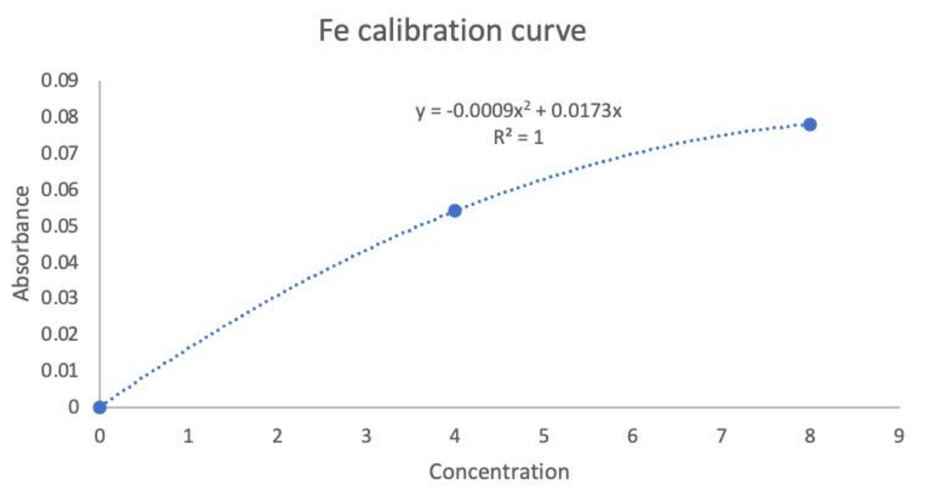

Cu calibration curve
y = 0.04x
R² = 1
Absorbance
Concentration

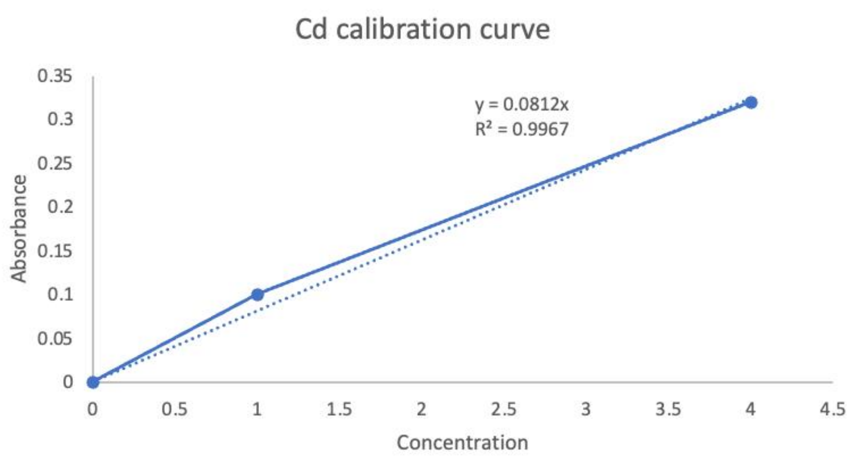

Zn calibration curve
y = -0.0084x² + 0.1555x
R² = 0.9999
Absorbance
Concentration


Mo calibration curve
y = 302.75x
R² = 0.9991
Absorbance
Concentration

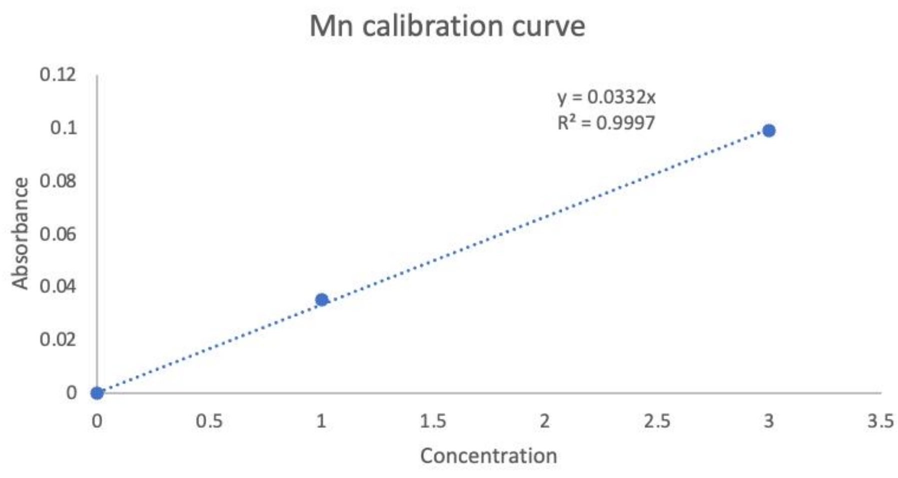
Appendix XL

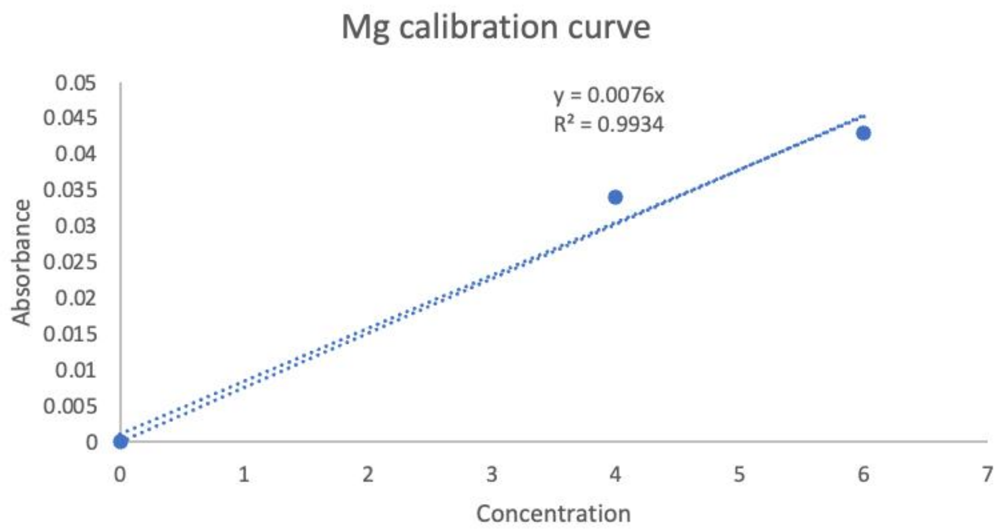


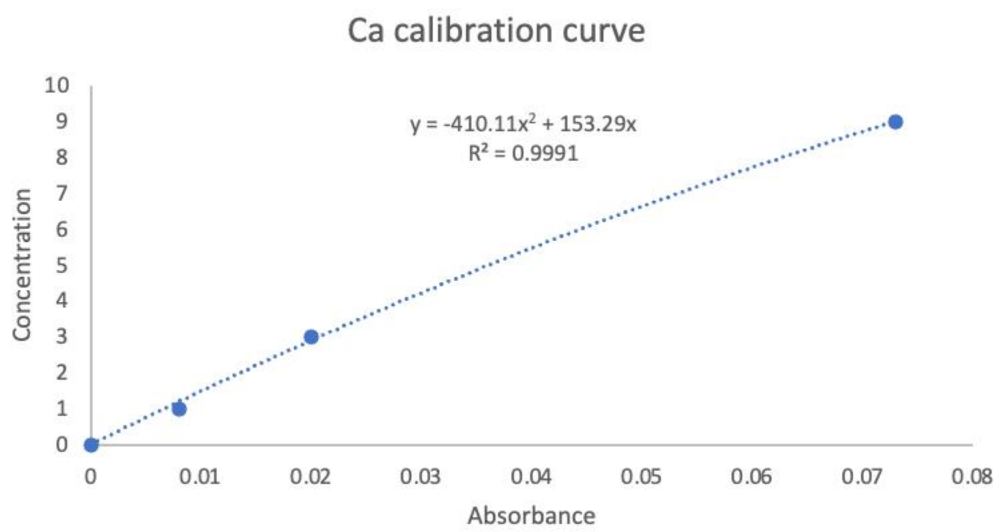




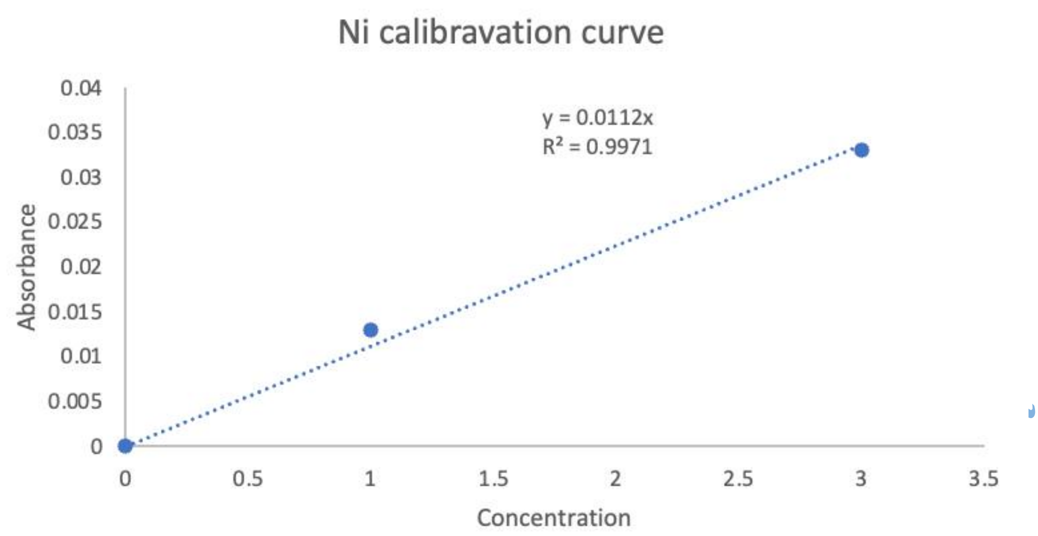
Appendix XLI







Appendix XLII


Ni calibravation curve
y = 0.0112x
R² = 0.9971
Absorbance
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
3.5
Concentration

Bio-data

A. PERSONAL DATA

Full Name	OLUREMI, Omoniyi Olalekan
Permanent Address	N5A/351A, Oke-Apon Total Garden Ibadan
E-mail Address	prayingcard@gmail.com
Telephone Number	08034700275
Date of Birth	January 30th 1971
Place of Birth	Ibadan
Nationality	Nigerian
Next of Kin	Dr (Mrs.) Temitope E. Olalekan
Address	House 1A Akuro Olokun Apapa Moniya, Ibadan

B. EDUCATIONAL BACKGROUND

Educational Institutions Attended with Dates and Qualifications

Ladoke Akintola University of Technology	PGD Environmental Chemistry	2002-2012
University of Ibadan, Ibadan	Final Diploma in Sci. Lab. Technology	1992-1998
St. Mary's Grammar School, Iwo	West African School Certificate	1984-1989

C. AWARDS AND FELLOWSHIPS

EU H2020 Integrated Nitrogen Studies in Africa (INSA) Project secondment to Laboratoire d'Aerologie, Universite de'Toulouse France 2023

D. WORK EXPERIENCE WITH DATES

Institute of Agricultural Research & Training, Obafemi Awolowo University Moor Plantation Ibadan 2022 till date

E. MEMBERSHIP OF ACADEMIC PROFESSIONAL BODIES

(1)	Nigeria Institute of Science Laboratory Technology	2015-Till Date
(2)	Institute of Chartered Chemists of Nigeria	2009-Till Date
(3)	Institute of Science Technology London	2008-Till Date

F. PUBLICATIONS

Thesis/Dissertation

1. Production of Ethanol using Cassava.

Papers Accepted for Publication:

(1) A.O Ojo, O.O Olalekan, O.T Ande, O.D. Adeoyolanu, K.S. Are, A.O. Adelana, A.O. Oke, O.A. Denton, & A.O. Oyedele. "Comparative study of the Mid-IR spectroscopy and chemical method for soil physical and chemical properties." *Ife Journal of Agriculture* 29 (1), 2017, 52-62.

G. MAJOR CONFERENCES/WORKSHOPS ATTENDED

(1) Took part in a training on "Good Laboratory Practices" organized by the Institute in collaboration with the International Institute of Tropical Agriculture (IITA) in 2022.

(2) Certificate of attendance of GLOSOLAN Webinar on the implementation of the standard operating procedure for soil electrical conductivity (Soil/Water, 1:5) held virtually in English on 14 December 2021

(3) Participated in the fourth meeting of the Global Soil Laboratory Network (GLOSOLAN) implemented by FAO from 11 to 13 November 2021.

(4) Participated in the 6th session of the GLOSOLAN soil spectroscopy webinar on Measuring reflectance of the undisturbed soil surface in the field under laboratory quality: A protocol to assess soil properties that are sensitive to the soil sealing phenomenon held virtually on 28 October 2021

(5) Participated in the third session of the GLOSOLAN soil spectroscopy webinar on "A future for soil spectral inference" held virtually on 23 September 2021.

(6) Participated in the second session of the GLOSOLAN soil spectroscopy webinar on "Soil spectroscopy for accurate measurement of soil physical and chemical soil properties" held virtually on 16 September 2021.

(7) Participated in the fourth meeting of the Global Soil Laboratory Network (GLOSOLAN) implemented by FAO from 11 to 13 November. (2020)

(8) A one-day workshop on the use and operation of a portable X-ray fluorescence spectrometer organized by AfSiS-NiSiS at IITA. (2019)

(9) Workshop training on quality assurance and quality control on soil and plant analysis, by AGRA/IITA in conjunction with Obafemi Awolowo University Ile-Ife. (2015)

(10) 2nd Hands-on soil infrared spectroscopy training course, ICRAF Nairobi Kenya. (2014)

(11) Training on capacity building for soil and plant analysis organized by AGRA/IITA in conjunction with NISLT. (2014)

(12) Hands-on soil infrared spectroscopy training course, ICRAF Nairobi Kenya. (2013)

(13) Workshop training on FT-IR, AAS, and HPLC principles and applications organized by the Multidisciplinary Central Research Laboratory of the University of Ibadan. (2013)

(14) Training on principles and application of PG500 atomic absorption spectrophotometer organized by WINTECK Nig. Ltd/ARCN. (2012)

(15) Training on the operation of the mid-infrared FT spectrophotometer at I.A.R Zaria. (2011)

(16) 26th Annual National Conference/Workshop of Nig. Inst. of Sci. Lab. Techn. (2011)

(17) Mandatory Training workshop on the principles of chemicals management and environmental impact assessment of the institute of Chartered Chemists of Nigeria ICCON (2008)

(18) Certificate of Training on Modern Trends in Sci. Lab. Techn. Practice. (2006)

(19) 22 Annual National Conference/Workshop of Nig. Inst. Of Sci. Lab. Techn. (2006)

F. REFEREES

1. Prof. Oyebamiji Jonathan Babalola

   Department of Chemistry, Physical Unit

   University of Ibadan,

   Ibadan, Oyo-State.

2. Prof. Louis Nwokocha

   Industrial Chemistry

   Department of Chemistry, Industrial Unit

   University of Ibadan,

   Ibadan, Oyo-state.

3. Dr. Kayode Are

   Institute of Agricultural Research & Training,

   Obafemi Awolowo University, Moor Plantation

   Apata Ibadan

   Ibadan, Oyo-State.

………………………… …………………………

Signature **Date**

The University Compliance Certification

This is to certify that, this Thesis was written by **Oluremi Omoniyi, OLALEKAN with Matric Number LCU/PG/002183** of the Department of Chemical Sciences, Faculty of Natural and Applied Sciences, Lead City University, Ibadan and it is in full compliance with the approved University format and style.

……………………………......   ………………………………….......

Signature   **Date**