DETERMINATION OF THE LEVELS OF INORGANIC ELEMENTS IN ASHES FROM SELECTED AGRO-WASTE BIOMASS FROM GITHURAI MARKET, NAIROBI

BY
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DECLARATION

This is my original work and has not been presented for a degree in any other university

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DEDICATION

To my beloved wife Caro, daughter Haizel, son Enock, parents, brothers and sisters who over the years have given me the right advice and encouragement at the right time during this study.

God bless you all.

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ABBREVIATIONS AND SYNONYMS

AAS	Atomic Absorption Spectroscopy
CBO	Community Based Organization
DOE	Department Of Environment
ECN	Energy Research Centre of the Netherlands
HCL	Hollow Cathode Lamp
ILO	International Labour Organization
JICA	Japan International Cooperation Agency
KPCU	Kenya Planters Cooperative Union
MSW	Municipal Solid Waste
MSWM	Municipal Solid Waste Management
NCC	Nairobi City Council
NGO	Non-Governmental Organization
PAHS	PolyAromatic Hydrocarbons
SWM	Solid Waste Management
XRFS	X-Ray Florescence Spectrophotometry

ABSTRACT

The ashes of different types of agricultural biomasses from Githurai market and rice husks collected from Mwea, have been analyzed for their inorganic elements content using both Atomic Absorption and X-Ray Fluorescence Spectroscopic Techniques. The results show that ash content of various agro-waste ranges from 3.31± 0.10% to 23.92±0.39% with rice husks having 23.92±0.39%. Further analysis on the ashes show that some biomaterials contain very high levels of K_2O and Na_2O, for instance ashes from banana, potato and pineapple peelings were found to have high concentration of K_2O at 63.17± 0.09%, 59.48± 0.77% and 47.05± 0.30% respectively. These were however recovered as the carbonates and thus explain why; ashes were used by the ancients for the manufacture of soap. Ashes from onion stock waste and pigeon pea pods gave high concentrations of CaO at 34.95± 2.28% and 15.20± 5.74% respectively. Rice husks and banana leaves ashes contain over 97% and 61% silica respectively and thus, are important raw materials for pozzolanic cement production. The results of the current study show that the current practice of burying ashes as a waste is not therefore justifiable. They should be treated as a resource rather than a waste.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Biomass is any material of organic origin such as trees, grass, agricultural crops or other biological materials. Biomass waste can be used as solid fuel or converted into liquid or gas form for the production of electric power, heat, chemicals or fuel (Bain, 2004). It is a renewable energy source because we can always grow more trees and crops and thus residue will always exist (Bothum, 1998). Globally, the amount of biomass produced each year through photosynthesis is vast. It has been estimated that net annual photosynthetic production of organic matter amounts to roughly 2 x 10^{11} tones; equivalent to 3 x 10^{21} joules in energy terms, which is approximately 10 times the present world energy consumption (Hall *et al*., 1982).

Biomass-based energy raw materials can be categorized into: natural vegetation, energy crops and organic waste products from industrial, domestic or agricultural sources (Schumacher *et al.*, 1985). Biomass energy sources can also be classified into five main categories namely: wood, crop residues, animal manure, household waste and food waste (Hall *et al.*, 1982). Another source of biomass is garbage generated in towns and cities which is part of what is referred to as Municipal Solid Waste (MSW) (Bothum, 1998).

1.2 Ashes

Ash is an inevitable product of the combustion of solid fuel while Biomass ash is the residue from the combustion of plant biomass which is increasingly being used for heat and electricity production. It can be viewed as a waste to be dispose of; however it also contains valuable minerals and can be used as fertilizer. Ash from combustion of biomass in high efficiency modern combustion equipment such as boilers or stoves primarily consists of non-combustible mineral constituents of the fuel as oxide or salts. It falls into two components, those, primarily large particles that fall through the grate during combustion and are collected as bottom ash, and the very fine particles that are carried away in the flue gases and are known as fly ash. As it contain the minerals taken up by the biomass during growth such as potassium and phosphorous, unless it has been contaminated in some way, bottom ash can form a valuable fertilizer, although it does not contain nitrogen. It can be used as a part of sustainable forestry operations. Owing to the highly concentrated nature of this ash and the presence of oxide of alkali metals such as calcium and potassium, ash tends to have a very high pH, and consequently it is neither necessary nor desirable, to use too much in one place, but it can be very valuable if distributed thinly. In Sweden the maximum allowed dose of wood ash is 3 tones per hectare. It is recommended that in large scale ash application, such as might be associated with forestry, the ash is not applied in the loose form, but in a granulated form developed in Scandinavia having been mixed with water and rolled into small balls. This makes it easier to handle and apply, slows nutrient release, and also reduces damage to ground vegetation, particularly mosses, on application (Pitman, 2006).

Biomass ash contains a wealth of macronutrients and micronutrients. Despite the value of the various elements contained in the ashes, their disposal in landfills is still common practise, generating considerable costs for biomass plant operators and negating the recycling potential of ashes. Appropriate combustion and separation techniques to obtain qualitatively valuable ash fractions are therefore desirable. For this reason, scientists have been searching for alternatives to landfill disposals. Amongst them is Jan Pels from Energy Research Centre of the Netherlands (ECN), who led a research team working on a project, called ‘BIOAS’, while a group of scientist from the University of Leeds did similar work on rice husk ash, which has some importance for developing world. Still, scientist from the Brigham Young University in Utah worked on analyzing whether biomass ash can replace cement (Knapp *et al.*, 2011).

1.3.0 Utilization of ashes

Utilization of ashes is part of sustainable power generation from biomass and contributes to the green image, while landfill of biomass ashes may be interpreted as wasting of valuable nutrients. The search for utilization options must therefore deal with largely different kinds of biomass ash. In the waste management hierarchy, landfill is the least attractive alternative. However for many practical situations it happens to be the most economical alternative. Landfill serves as the bottom-line for comparisons of utilizations options. Any proposed kind of utilization must have economic advantages compared to landfill. As is well known, ashes have been used for soap making for many centuries. Thus in Babylon, there are records of this activity dating back to 2800 BC. No doubt, this was possible because of alkalis in the ashes (Pels *et al*., 2005).

1.3.1 Recycling of nutrients

Returning of biomass ashes to the locations where the biomass was harvested can be regarded as the next best sustainable option. It brings back the nutrients to the original soils and hence closes mineral cycles. In the long run, recycling avoids problems with depletion and exhaustion of the soils, unless the soils are fertilized in other ways. For recycling, combustion ashes seem more appropriate, but in principle, gasification ashes can also be used. The requirements of ashes to be used on trees or crops as sustainable conditioning of the soil should be leading principles. Biomass ashes should be recycled whenever possible, but the ash quality must be high enough to prevent pollution as a result of the spreading of ashes. Most European countries with a history in the use of biomass for energy (Finland, Sweden, Denmark, Austria and Germany among others) have established legislation that enables and controls the recycling of biomass ashes to forests and agricultural areas. Ash recycling is happening in a number of these countries, but the total amounts that are recycled are very small compare to the total production of biomass ash. Often ashes contain too high contents of heavy metals (Cd but also Pb and Zn) even when the ashes originate from clean, untreated biomass (Pels *et al*., 2005).

1.3.2 Bulk utilization options

Despite recycling of ashes being the most sustainable form of ashes utilization, there will be large amount of biomass ash produced that cannot be recycled for a number of reasons. Some landowners do not want to recycle ashes. Also there are large streams of biomass ashes of which it is not possible to trace back the original place of harvest. Finally, there may be no legal possibilities or ashes are simply not clean. For all these streams of biomass ashes, an alternative form of utilization must be found. Three global utilization options have been investigated:

i. Utilization as a raw material for fertilizer
ii. Used as building material or as a component in the manufacture of building material
iii. Re-use as a fuel

(Pels *et al.*, 2005).

1.3.3 Utilization as a fertilizer

Biomass ashes may be used directly as a fertilizer or soil improver or may be used as a raw material in the production of mineral fertilizer. The ashes are returned to the soil, but location is not necessarily the same as where the biomass originated. Utilization as a raw material for fertilizer saves primary resources and can be seen as an example of sustainable use of biomass. Utilization of biomass ashes in all-purpose fertilizer is limited. The three elements in complete fertilizers are N, P and K. Biomass ashes can only be a significant source of potassium, because:

i. Ashes from thermal processes are nearly free from nitrogen, and
ii. Phosphorus is present in a form that has a very poor solubility at soil conditions

There are alternatives in fertilizer production (other than direct utilization as a general-purpose fertilizer). Biomass ashes may be blended with complementary materials, or biomass can be used in the same way as mineral resources; dissolution of K and P at very low PH and then processed in regular fertilizer production. Many ashes contain significant amounts of Ca, Mg, Na and S which represents an agricultural value. In particular when dolomite or limestone is added during gasification or combustion, the ashes can be a valuable source of Ca and Mg and therefore used as soil improver (PH control) (Pels *et al*., 2005).

1.3.4 Utilization as a building material

Utilization of biomass ashes as a building material or as a raw material in the manufacture of building products can be regarded as a sustainable form of utilization when the use of ashes saves the use of non-renewable resources. Bottom ashes are the easiest ashes for utilization as building material. Bottom ashes from fluidized bed combustion or gasification consist of large part of sand and may replace other kinds of sand in road construction or landscaping. Bottom ashes from grate stokers and entrenched flow gasification can be made into granulated and find its way to road constructions and concrete. Direct utilization as a bulk building material replacing sand or gravel is almost not possible, because it is such a fine powder. Utilization as a component in cement or concrete is a more likely option (Pels *et al.*, 2005).

1.4.0 Main ash forming elements

The following elements form the bulk of biomass ashes. They are typically present as oxides and thus the data in the database can be viewed either as elements or as oxides.

1.4.1 Calcium

Calcium is a main ash forming element in biomass ash. Typically the bulk part of ash from woody biomass is a mixture of oxide of elements Ca, Si, Mg and Al. The relation between these oxides is relevant for the melting temperature and the viscosity of the ash and thus important for slagging behavior. CaO increases the melting temperature of ash. Ca can however in special circumstances be a strongly fouling element forming $CaCO_3$ on super heater tubes (http:// www.biolex.dk-teknik.dk, accessed on 16-07-2012).

1.4.2 Silicon

Silicon is the most common bulk ash forming element in biomass. Especially in herbaceous plants, Si is present in significant concentrations as it helps the straw to stay up straight in the wind. SiO_2 forms the main matrix for the ash and slag during biomass combustion. The melting temperature depends strongly on the mixture of other ash forming elements. Especially the alkali metals K and Na lower the ash melting temperatures (http:// www.biolex.dk-teknik.dk, accessed on 16-07-2012).

1.4.3 Aluminium

Aluminium is one of the most common elements on earth. No really biological function in plants and thus significant concentrations together with high ash content in the fuels indicates that large amounts of contamination such as earth are included. Aluminium has no really effect on the combustion. In some cases it can increase the melting temperature of ash and in others decreases it depending on the mixture. Aluminium does generally increase the melting temperature of biomass ash and is sometimes used as an additive for this purpose (http:// www.biolex.dk-teknik.dk, accessed on 16-07-2012).

1.4.4 Magnesium

Magnesium is a component of chlorophyll, which is a part of all green parts of plants; MgO has relevance for ash melting behavior similar to CaO. Green parts of plants are seldom used as fuel and thus the concentration of Mg are typically relatively low in biomass ashes (http:// www.biolex.dk-teknik.dk, accessed on 16-07-2012).

1.4.5 Iron

Iron is very common in earth minerals. Not so biological active and thus does not naturally exist in high concentration in plant material. High concentrations do therefore; suggest that the analyzed samples are contaminated by dirt. Fe can in high concentrations be a significant part in slagging at coal fired units, but is seldom problematic while combusting pure biomass fuels (http:// www.biolex.dk-teknik.dk, accessed on 16-07-2012).

1.4.6 Potassium

Potassium is a major nutrient and very important for growth of plants. High concentrations are also common in fast growing plants such as straw and other agricultural solid biomass fuels. The concentrations does commonly also depends on growing season of the plant that is, in summer and spring when the growth of the plant takes place the concentrations are higher than in the winter when no growth occurs. Potassium is volatile during combustion, and due to that is typically one of the main components that cause fouling on boilers when using solid biomass fuels. For the same reason K is also typically the main component in submicron particle emissions. Moreover, it reacts with other ash forming elements in the ash and in high concentrations it can significantly lower the melting temperature of ash thereby causing slagging (http:// www.biolex.dk-teknik.dk, accessed on 16-07-2012).

1.4.7 Sodium

Sodium is not a nutrient such as potassium. High concentrations are typically due to contamination. Typically, plants growing close to the sea can have significant concentrations of Na. Sodium behaves similar to potassium during combustion and therefore cause the same problems such as fouling, slagging and particle emissions described for potassium (http:// www.biolex.dk-teknik.dk, accessed on 16-07-2012).

1.4.8 Sulphur

Sulphur is relevant as part of Sulphur forms SO_2 emissions while the other parts remain in the ash. The vapourised sulphur is a major part of particulate emissions forming sulphate particles (mainly K_2SO_4). Formed sulphates lower the ash melting temperature and can thus be significant contributors to slagging and fouling problems in biomass boilers. However due to competing reactions with Cl, high S to Cl ratios can in some cases be of advantage as it can decrease Cl corrosion problem (http:// www.biolex.dk-teknik.dk, accessed on 16-07-2012).

1.4.9 Chlorine

Chlorine is relevant as it is directly related to emission of HCl. Formed HCl gas and also chloride particles formed in flue gases are highly corrosive. Cl is typically a major component in particulate emission from biomass combustion units, mainly in the form of KCl. Chlorides has relatively low melting temperatures and thus chloride particles can significantly contribute to fouling. Slagging is less common as typically very low concentrations of Cl remains in the bottom ash due to the relatively high volatility of chlorides compared to oxides and sulphates (http:// www.biolex.dk-teknik.dk, accessed on 16-07-2012).

1.5 Ash content

The ash content is an approximate measure of the mineral content and other inorganic matter in biomass. The ash content is used in conjunction with other assays to determine the total composition of biomass samples. The quantity and quality of ash in biomass depends on a number of factors including its derivation**,** it's growing and harvest conditions, the fertilization type, the harvest techniques, its storage and transportation along with its pretreatment before it is introduced into a bioenergy conversion process. The majority of these factors are manageable, so it is likely to reduce high values of ash content down to an acceptable level. Ash content can originate from the biomass itself or from collection and pretreatment methods and often lead to high disposal costs resulting in a negative economic impact on biomass conversion systems. Ash content values may vary significantly from one biomass resource to another. The main reason that lower ash content values are desirable has to do with its effect on biomass energy value. Similarly to moisture content, since the ash content is a measure of assuming noncombustible inorganics in biomass, it affects significantly its energy content. In general terms, the higher the ash content the lower the energy value. Actually, if ash content and moisture content are not taken into account (ash free & dry basis) most of the biomass resources appear similar energy content values, since they contain in various proportions the same substances (cellulose, hemicelluloses and lignin). The average energy value of ash-free, oven-dry plant residues is about 4.7 kWh/kg. At 15 per cent moisture content, the energy value of the ash-free residue is about 4.2 kWh/kg. Ash content at the level of 2 per cent will reduce the energy value to about 3.9 kWh/kg while biomass with 10 per cent ash content will appear energy content of about 3.6 kWh/kg. It must be noted that ash contents should be compared between biomass samples with the same moisture content. In many energy conversion processes it is not only the amount of ash, but also its chemical properties that must be carefully considered, since ash results in the production of a waste stream that needs to be treated or disposed. Ash content composition affects thermochemical conversion processes (like combustion, gasification or pyrolysis) mainly at higher temperature ranges. In case of ash melting at these increased temperatures, this may affect substantially the operational costs of the plant and thus the whole investment profitability. Molten ash is difficult to be removed and collected and may plug some of the mechanical equipment parts that will increase the maintenance costs. Only under specific conditions biomass ash residues can be considered as a useful byproduct which may have commercial value. For biochemical conversion systems (like fermentation or anaerobic digestion), the impact of ash content value and its composition on those processes isn’t fully clarified. Yet, it has been proved that specific inorganic substances in biomass may lead to fermentation inhibition (depending on the tolerance of the microorganism and the dry matter loading during fermentation). For biomass pellets, it is officially stated the need to have extremely low ash content so as to meet European and national quality standards. The lowest the ash content the less ash is produced from a residential pellet stove or burner so it gets more convenient for the consumer. In case that virgin wood is used as feedstock the standards can be easily meet since the ash content in wood is usually less than 1%, while it can be very high in many agricultural residues. This is why wood pellets quality standards can’t be reached when using agricultural residues as feedstock and another, specified quality standard for agricultural pellets needs to be introduced.

Table 1.1: The ash content of different biomass resources

Biomass Source	Ash content (% weight, dry basis)
Cotton stalk	7
Wheat straw	4
Poplar wood	1
Switch grass	4
Douglas fir wood	1
Barley straw	6
Rice straw	13
Bagasse (sugarcane)	11

(www.biomassenergy.gr, accessed on 16-07-2012)

1.6 Biomass wastes

Biomass wastes are solid organic residues, surplus and by-products of agro-industrial processing available in bulk. In Kenya, biomass wastes produced in large quantities include: coffee husks, tea wastes, maize cobs, rice husks and saw dust. In urban areas, agro-wastes are mainly contributed by foodstuff such as vegetables and fruit peelings (Kibulo, 2004). The quantity of residues produced in a year easily exceeds the production of crop itself (Barnard, 1985). It has been shown that only 5% of plant total biomass is suitable for food. The remaining 95% can be used as animal feed, soil conditioning, building material and fuel (Hankins, 1987).

1.7 Biomass as Fuel

Biomass continues to be a major source of energy in the world today. In the developing countries, biomass accounts for about 70% of the energy generated. In Kenya, for example, Mumias Sugar Company currently uses baggase for generation of electricity. Clayworks Limited in Nairobi buys coffee husks from Kenya Planters Cooperative Union (KPCU) for firing bricks. KPCU has developed a method for making charcoal briquettes from coffee husks. The charcoal is sold in shops rather than by the roadside and is claimed in its advertisement to be “3 times more powerful than ordinary charcoal.” In 1984, more than 36,000 tonnes of these briquettes were exported to the Middle East (Foley, 1986).

1.8 Nairobi City Council

It is the mandate of the Nairobi City Council to ensure collection, transportation, storage, safe treatment and disposal of solid waste. The main responsibilities of NCC towards Solid Waste Management (SWM) are:

i. Provision of services for collection, transportation, treatment and disposal of solid waste
ii. Regulation and monitoring activities of all generators of solid waste
iii. Regulation of private companies engaged in SWM activities
iv. Formulation, enforcement of laws and implementation of SWM policies

The council by-laws deal with some aspects of SWM such as the prohibition of illegal disposal of waste and general provisions for generators of SWM to store and prepare their waste for collection. However, these by-laws do not cover the entire waste management cycle from generation through collection, treatment/separation, to transportation and disposal (ILO, 2001).

1.9 Department of Environment

Until 1996, SWM was under NCC's Public Health Department but as the need for SWM increased, the Department of Environment (DOE) was established in order to focus on SWM activities. The legal responsibilities of DOE towards SWM include:

i. Maintaining public cleanliness, protecting public health and the environment

ii. Implementing NCC's SWM policies formulated by the council's Environmental Committee and enforcement of all laws and regulations relating to SWM

iii. Keeping public places aesthetically acceptable by providing services for the collection, transportation, treatment and disposal of solid waste

iv. Regulating and monitoring generators of solid waste and private companies engaged in SWM activities.

1.10 Statement of the Problem

A recent survey indicates that electricity from the burning of biomass is one of the cheapest. Although when biomass is dried and burnt, energy is generated and ashes are also produced, which creates environmental problem when tones of biomass are burnt. This study was aimed at finding out levels of various inorganic elements in the ashes produced on burning biomass. The reason is that biomass contains inorganic elements such as potassium, sodium, calcium, iron, magnesium which are essential for a plant to grow.

1.11 Scope and limitations

Agro-wastes in urban areas are normally mixed very inhomogeneously with other solid wastes such as broken glass, broken tiles, polythene, scrap metals, waste papers and even hospital wastes, thus making their usefulness very limited. On a similar note, agro-wastes in towns are brought from different regions thus may result in variation of the outcome of our study.

1.12 Relevance of the study

High levels of potassium in ashes could make them useful in glass industry, manufacture of soap and fertilizers. Sodium is also used in glass industry, soap making, water softening and in the manufacture of sodium compounds. Calcium carbonate, Magnesium carbonate, aluminium oxide, iron oxide and silica are components of Portland cement.

1.13 Research statement and justification

Ashes from biomass contain high levels of potassium because it is an essential element for plants to grow. Agricultural biomass wastes are therefore, likely to have high levels of potassium because this is added deliberately as a fertilizer. When biomass is burnt to produce energy, a lot of ashes are generated which creates an environmental problem especially when done in large quantities. Urban and industrial waste have huge amount of these agro-waste biomass because of high population. These can be incinerated to generate electricity and the ashes produced can be used to recover some valuable elements. With knowledge of chemical composition of ashes from selected agro-waste, one can determine the kind of practical application the ashes can be put into.

1.14 Hypothesis

Ashes from agro-waste contain inorganic elements particularly potassium, sodium, calcium, magnesium, iron and silica.

1.15 Objectives

1.15.1 General objective

To investigate chemical composition of ashes from selected biomass waste from Githurai market, Nairobi and rice husk from Mwea.

1.15.2 Specific objectives

i. To determine the ash content from selected agro-waste biomasses from Githurai market and rice husk from Mwea

ii. To determine levels of potassium, sodium, magnesium, calcium, iron, aluminum and silica in ashes from agro-waste biomass from Githurai market and rice husk from Mwea

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Baseline projection of waste generation and population in Nairobi

Municipal Solid Waste refers to the materials discarded in urban areas for which municipalities and cities are usually held responsible for the collection, transportation and the disposal (Medina, 2002). The rate of solid waste generation in urban areas is far greater than the capacity of various city authorities to collect and dispose. These uncollected ‘wastes’ are evidenced in garbage heaps and litter everywhere. The use of the term ‘waste’ is rather inappropriate because several economically useful materials can be recovered from MSW. Examples of such materials include ferrous and non-ferrous metals, polythenes, broken glass, lead batteries, paper, bones, fruits and vegetable peelings (ILO, 2001).

Studies have shown that over 50% of MSW in developing countries is compost of organic material, and therefore, would be ideal for reduction through the process of composting (Zerbock, 2003). The population projection in Nairobi shows a growth rate of 4.7% per annum from 1998 to 2008. Solid waste generation by the year 2008 has been estimated based on this population projection and the field survey results are as shown on Table 2.1. Table 2.2 also indicates waste generation in Nairobi city.

Table 2.1: Baseline projection of population and solid waste generation

Year	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
Nairobi population (‘000)	2,294	2,397	2,500	2,616	2,737	2,867	3,012	3,148	3,300	3,461	3,630
Waste generation (‘000) tonnes/day	1,509	1,595	1,684	1,785	1,893	2,009	2,141	2,269	2,413	2,566	2,730

(Karani *et al.*, 2004).

Table 2.2: Projection of waste generation in Nairobi city in tones

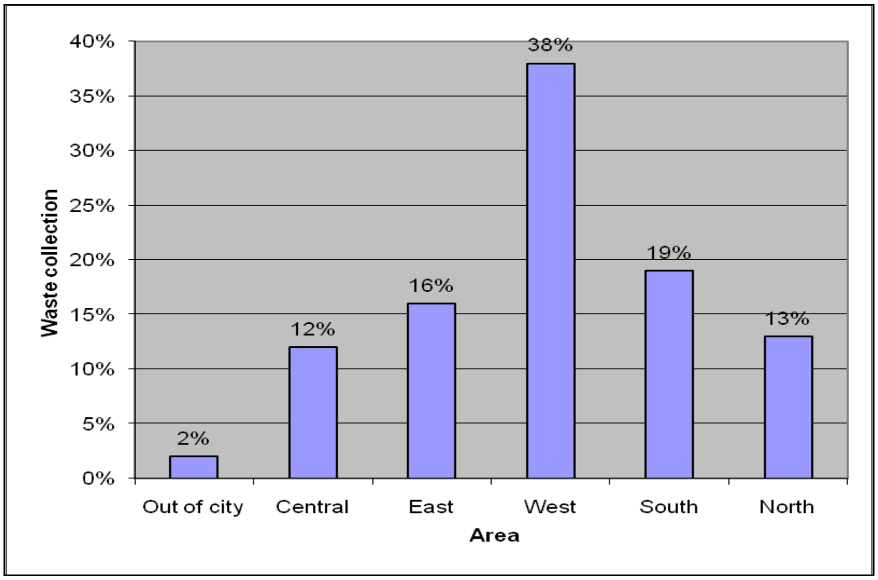
Year	1997	1998	2000	2004	2008
Household	1,181.1	1,251.1	1,398.9	1,784.1	2,283.3
Commerce	93.5	97.9	106.7	128.5	154.9
Market	82.5	86.3	94.1	113.4	136.6
Road	69.0	73.9	84.4	114.4	155.3
Total	1,426.1	1,509.2	1,684.1	2,240.4	2,730.1

(Karani *et al.*, 2004).

2.2 Solid waste collection in Nairobi

In 1999, Nairobi had an estimated population of 2.2 million people with an estimated growth rate of 4-5% per annum. The Japan International Cooperation Agency (JICA) report of 1998, placed production of refuse in Nairobi at approximately 1,530 tonnes per day. The report further showed that 360 tonnes of solid waste were collected per day, or about 25% of the total amount of waste generated in the city. Of this, NCC collected 22% and private firms collected 32%. On average, about 61% of the collected solid waste came from residential areas, 21% from industrial areas and 6% from roads (ILO, 2001).

Low-income areas and informal settlement are poorly serviced by waste collection services. Figure 2.1 shows the comparison in provision of solid waste collection services in different areas of Nairobi and its boundaries.



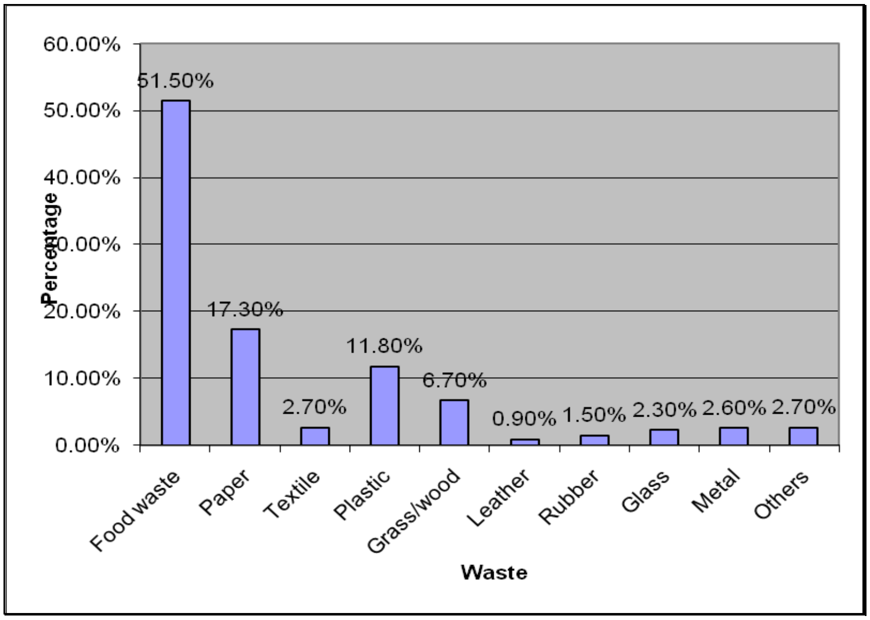
(JICA, 1998)

Figure 2.1: Distribution of solid waste collection services in different areas of Nairobi

It is estimated that between 50% - 75% of the garbage remains uncollected and thus rots close to its source. The rest of the waste is carted into a dumping ground on the arid plains to the south of the city, out of sight and out of mind, where the voiceless reside, Dandora dumpsite which was established by the city council in the mid-1980's (Kantai, 2000). In general, regular private waste collection services are provided in most high income areas. In the middle-income areas, waste is poorly managed with open dumping and burning being a common sight on open spaces and along the roads. Communal containers and refuse in these areas overflow with garbage resulting in the presence of pests and obnoxious odours. In low-income areas and informal settlements, open dumping and burning of waste along roads is widespread with bad odour, pests and scavengers being common characteristics (ILO, 2001).

2.3 Composition of waste

The JICA study further showed that out of 1,530 tonnes of garbage collected per day in Nairobi, the following composition of waste was realized: food waste 51.1%, paper 17.3%, textile 2.7%, plastic 11.8%, grass/wood 6.7%, leather 0.9%, rubber 1.5%, glass 2.3%, metal 2.6% and others 2.7% as shown in figure 2.2.



(JICA, 1998).

Figure 2.2: Composition of solid waste collected in Nairobi (1998)

Recyclable materials such as plastics, paper and glass make up a significant percentage of the waste in Nairobi. The trend is that most of the recyclable waste is found in middle and high income areas. The waste in low-income areas is largely composed of petrucible organic matter suitable only for compost production (ILO, 2001).

2.4 Solid waste management

Waste management is the collection, transportation, processing or disposal, managing and monitoring of waste materials. The term usually relates to materials produced by human activity, and the process is generally undertaken to reduce their effect on health, environment or aesthetics. Waste management is a distinct practice from resource recovery which focuses on delaying the rate of consumption of natural resources. The management of wastes treats all materials as a single class, whether solid, liquid, gaseous or radioactive substances, and tried to reduce the harmful environmental impacts of each through different methods. Waste management practices differ for developed and developing nations, for urban and rural areas, and for residential and industrial producers. Management for non-hazardous waste, residential and institutional waste in metropolitan areas is usually the responsibility of local government authorities, while management for non-hazardous commercial and industrial waste is usually the responsibility of the generator. The management of solid waste is one of the biggest challenge facing any urban authorities and cities all over the world today, especially in the third world countries. The situation of SWM in Kenya is a source of concern. Uncollected solid waste has become a common sight in urban areas with associated public health and environmental risks (Zerbock, 2003).

In Nairobi, for example, less than 20% of the waste generated in 1998 was collected (ILO, 2001). It is estimated that the total amount of municipal solid waste generated worldwide reached 1.84 billion tons in 2004, a 7 per cent increase on the 2003 total (Global Waste Management Market Report 2004). It is further estimated that, between 2004 and 2008, worldwide generation of municipal waste rose by 31.1 per cent, representing an annual rate of increase of some 7 per cent. The city of Nairobi, the capital of Kenya, with a population of more than 3 million people, is a centre of industry, education and culture occupying an area of 696.1 km^2 (0.1 per cent of Kenya's total surface area) and hosting about 25 per cent of Kenya's urban population. The city is currently experiencing waste management problems and the City of Nairobi Environmental Outlook (2007) indicates that increase in solid waste generation has not been accompanied by an equivalent increase in the capacity of the relevant urban authorities to deal with the problem. The current generation rate of garbage in Nairobi is over 2,000 tons per day and waste that finds its way to the final destination is disposed off at the Dandora dumpsite in an environmentally unsustainable manner. UNEP commissioned a study of the Dandora dumpsite in 2006 and the findings suggest that there are severe public health and environmental impacts due to the site. The study shows that the dumpsite is a serious threat to children living nearby and the city's environment in general. During the study, 328 children and youth aged between 2-18 years living around the waste dump were examined. The study also compared soil samples from the site with another location just outside of Nairobi. Half of the children tested had concentrations of lead in their blood exceeding internationally accepted levels while 42 percent of soil samples recorded lead levels almost 10 times higher than what is considered unpolluted soil over 400 ppm as compared to 50 ppm.

During the launch of the report in October 2007, UNEP’s Executive Director pledged his support towards tackling this problem and advised that, "clear urgent action is needed to reduce the health and environmental hazards so that children and adults can go about their daily lives without fear of being poisoned and without damage to nearby river systems." Various reasons have been cited for this situation: inadequate capacity at NCC, lack of finances, inaccessible roads and poor planning. In spite of the rapid increase in urban population, evidence shows that expenditure by the city council on infrastructure and services has been reducing progressively (Kirai, 1996). The situation is not different in other municipalities as seen from piles of garbage and broken down infrastructure. In Nairobi, SWM services are not uniformly distributed. In high income residential areas, SWM by both the NCC and private collectors is more common than in the middle- and low-income residential areas where the communities have been forced to mobilize the local resources to compliment NCC services. As would be expected, the low-income areas of the towns are most affected by poor management of solid waste. In the last 5 years or so, there has been an increase in private sector involvement in solid waste collection. Still, there has been little or no encouragement by NCC to get the private sector involved in SWM. The barriers have been of legislative and economic nature since the present by-laws of the council do not allow private sector involvement in SWM, and also, the distances to the dump sites are prohibitive for most private collectors. There are also physical barriers to waste collection. For instance, in the most low-income areas, roads are almost non-existent, and where they do exist, they are not wide enough to accommodate refuse collection vehicles (ILO, 2001).

Although developing nations do spend between 20-40% of municipal revenues on waste management, this is often insufficient to keep pace with the scope of the problem. In well planned municipalities and cities in western world and Japan, MSW especially the biomass is a source of wealth rather than a waste, in that, it can be used in the following ways:

i. Easily decomposable materials such as fruits and vegetable peelings are made into compost manure
ii. Biomass can also be dried, and heated in absence of air to make charcoal
iii. Biomass can also be dried and burned to generate steam at very high pressure which turns turbines hence generating electricity
iv. Some items such as glass, paper, plastic, metals are recycled to generate income for those involved
v. Other solids are placed in well-engineered landfills (Zerbock, 2003).

2.5 Current methods of garbage disposal

Unfortunately, agro-wastes in urban areas are randomly mixed, and, therefore, their separation to get useful components is very cumbersome. Secondly, they are spread over large areas, which make their collection rather expensive. A natural consequence of careless disposal of MSW is encouragement of vermines like rats. Garbage heaps also provide breeding grounds for mosquitoes and rats. Treatment methods of solid waste in developed countries are used to achieve better environment. Materials that cannot be put into use are dumped in landfills (Bradshaw *et al.*, 1992).

To meet these goals, sustainable SWM systems must be fully embraced by local authorities in collaboration with both the local people and the private sectors. Although in developing countries the quantity of solid waste in urban areas is generally low compared to industrialized countries, Solid Waste Management still remains inadequate. Dandora dump site which is situated 7.5 km South East of Nairobi is the only open dump site in Nairobi (Rotich, 2005). It is supervised by NCC, which provides heavy equipment such as bulldozers to distribute garbage in a controlled manner. It is currently filled with 1.3 million m^3 of waste (Palczynski, 2002). The dumpsite itself is actually multi-million recycling industry for the manufacture of second generation products (Kantai, 2000).

2.5.1 Recycling of municipal solid waste

Recycling is a resource recovery practice that refers to the collection and reuse of waste materials such as empty beverage containers. The materials from which the items are made can be reprocessed into new products. Materials for recycling may be collected separately from general waste using dedicated bins and collection vehicles, or sorted directly from mixed waste streams. The most common consumer products recycled include aluminium such as beverage cans, copper such as wire, old steel furnishings or equipment, polyethene, glass bottles and jars, paperboard cartons, newspapers, magazines and light paper, and corrugated fiberboard boxes. Solid waste recovering and recycling is carried out by many of Nairobi's poor residents who engage in waste picking as a means of income generation. Over 26 companies are engaged in the waste recycling industry such as Nairobi plastics, Central Glass, Kamongo Waste Paper, Madhu Paper, Kenya Reclaim Rubber Company, Premier Rolling Mills among others (Palczynski, 2002). These industries play a key role in resource recovery of solid waste by buying recovered materials from the scavengers for re-processing at their factories. The materials that are often recycled from solid waste include: waste papers, scrap metals, glass bottles, bones, plastics and rubber. Scavengers sell their daily collections to middlemen who in turn sell them to industries for reprocessing into new products. Recycling and resource recovery offers good scope for employment generation and at the same time potentially has positive, economic and environmental impact (ILO, 2001).

2.5.2 Composting of organic solid waste

Organic waste which represents more than half of MSW is not usually scavenged by waste pickers. Before October 2000, Nairobi municipality did not operate any commercial composting plant. According to NCC officials, there was no demand for compost produced at the plants. However, several Community-based Organizations and Non-Governmental Organizations in Nairobi's low-income areas were found to be undertaking composting as an income generating and environmental management strategy. There are composting groups in Nairobi's low-income areas, which are supported by a number of local NGOs. These composting groups were established by the NGOs through existing CBOs, usually women's savings or church groups. Three local NGOs (Uvumbuzi Club, Undugu Society of Kenya and the Foundation for Sustainable Development in Africa) have provided support and training to approximately twelve CBOs doing composting in several of Nairobi's low-income areas. Among the groups are Dandora Women's Group, Korogocho Mbolea Group and City Park Environmental Club among others (Palczynski, 2002).

2.5.3 Landfill

Disposing of waste in a landfill involves burying the waste, and this remains a common practice in most countries. Landfills were often established in abandoned or unused quarries, mining voids or pits. A properly designed and well-managed landfill can be a hygienic and relatively inexpensive method of disposing of waste materials. Older, poorly designed or poorly managed landfills can create a number of adverse environmental impacts such as wind-blown litter, attraction of vermin, and generation of liquid leachate. Another common by-product of landfills is gas (mostly composed of methane and carbon dioxide), which is produced as organic waste breaks down anaerobically. Design characteristics of a modern landfill include methods to contain leachate such as clay or plastic lining material. Deposited waste is normally compacted to increase its density and stability, and covered to prevent attracting vermin (such as mice or rats). Many landfills also have landfill gas extraction systems installed to extract the landfill gas. The gas is pumped out of the landfill using perforated pipes and flared off or burnt in a gas engine to generate electricity (Palczynski, 2002).

2.5.4 Incineration

Incineration is a disposal method in which solid organic wastes are subjected to combustion so as to convert them into residue and gaseous products. This process reduces the volumes of solid waste to 20 - 30 percent of the original volume. Incineration and other high temperature waste treatment systems are sometimes described as "thermal treatment". Incinerators convert waste materials into heat, gas, steam and ash. Incineration is carried out both on a small scale by individuals and on a large scale by industries. It is used to dispose of solid, liquid and gaseous waste. It is recognized as a practical method of disposing of certain hazardous waste materials. Incineration is a controversial method of waste disposal, due to issues such as emission of gaseous pollutants. Incineration is common in countries such as Japan where land is scarce, as these facilities generally do not require as much area as landfills. Japan, which incinerates most of its garbage, is now grappling with a sharp increase in cancer cases linked to dioxins released by burning plastics. Though no environmental assessment has been reported, doctors report a high incidence of respiratory tract infection. Combustion in an incinerator is not always perfect and there have been concerns about pollutants in gaseous emissions from incinerator stacks.

Particular concern has focused on some very persistent organics such as dioxins, furans, PAHs which may have serious environmental consequences. (Kantai, 2000).For many years incineration of waste consisted essentially of open burning in pits (Pavoni *et al*., 1975). It is a disposal method of fairly recent origin practiced by developed countries (Clark, 1978). The remaining heap in Dandora is then set on fire, thus releasing toxic gases into Nairobi's rarefied air. Incineration should not be considered as a disposal option, since following incineration, there is still some quantity of ash to be disposed of via landfill (Zerbock, 2003).

2.6 Analytical Methods and Instrumentation

In order to determine the levels of inorganic elements in ashes, several analytical methods can be employed depending on the type of sample matrix. Several techniques for determining levels of elements like K, Na, Mg, Ca, Fe and Si among others are currently in use or under investigation. The techniques are as varied as the type of sample matrices being analysed (Gary, 1994, Skoog and Leary, 1992). An average chemist does not utilized most of these techniques, either because of the complexity of operations, high cost, limited field of application or other reasons. Spectroscopic methods, particularly atomic absorption (AAS), do not encounter many of these short comings and therefore their use has increased rapidly. Other methods reported in elemental analysis include Atomic Fluorescence Spectroscopy, Atomic Flame Emission Spectroscopy, X-ray Fluorescence and X-ray Emission. In this study, AAS, Flame photometric and X-ray Fluorescence methods were used.

2.6.1 Instruments

Spectrophotometer model 210 VGP Atomic Absorption Spectrophotometer (Varian Manufacturing Col Ltd; Australia) plus the Hollow Cathode Lamps (HCL) for each element to be analyzed were used. Corning 400 Flame Photometer was also used.

2.6.2 Atomic absorption spectroscopy

This is one of the most widely used techniques for the determination of metals at trace levels. Over sixty elements can be determined in most matrices by atomic absorption (Gary, 1994). Examples of these include heavy metals in body fluids, polluted waters, foodstuffs, soft drinks and beer. The method is largely free from spectral or radiation interference because each method has its own characteristic absorption wavelength and the source lamp, the hollow cathode lamp (HCL) composed of the element being determined. The technique is based upon absorption of radiation by free atoms. Atomization of the element is achieved by introducing a fine spray of the test solutions through the nebulizer into an air/acetylene or nitrous oxide/acetylene flame.

2.6.2.1 The lamp system

The Hollow Cathode Lamp is used to produce the required radiation for the element under investigation. It consists of the element to be determined or an alloy of it, and a tungsten anode. These are enclosed in a glass tube usually with a quartz window, since the lines of interest are often in the ultra violet region. The tube is under reduced pressure and filled with inert gas such as argon or neon. A high voltage is impressed across the electrode, causing the gas atoms to be ionized at the anode. The positive ions are accelerated towards the negative cathode. When they bombard the cathode, they cause some of the metals to “sputter” and become vaporized (Gary, 1994). The vaporized metal is excited to higher electronic level by continued collision with the high-energy gas ions. When the electrons return to the ground state, the characteristics lines of the element are emitted.

2.6.2.2 The nebulizer system

The solution under analysis is aspirated into the nebulizer which converts it into a mist. The sample aerosol is mixed with the fuel and oxidant in the nebulizer chamber before being introduced into the flame. The metal ions are then converted into gaseous atoms and subsequently absorption of the relevant energy occurs. The magnitude of absorption of the energy is proportional to the concentration of the metal atoms in the flame and hence the concentration in the sample (Willard *et al*., 1986).

2.6.2.3 The burner system

In order to achieve absorption it is necessary to reduce the sample into atomic state. The flame is used to convert the liquid samples into gaseous state and also for conversion of the molecular entities into atomic vapour. The flame temperature should be in the excess of 2000^0C but too high to cause the ionization of atoms (Skoog and Leary, 1992). Metals that form refractory compounds like aluminium and titanium require high temperatures.

2.6.2.4 The optical cell

The optical cell is fused with silica glass tube, that is transparent in the visible and UV wavelengths and thermally stable at high temperatures. HCL's beam passes through this cell on its way to the monochromator.In hydride generation, the gaseous metalloid hydride flows into the optical cell from the hydride generation module pushed by an inert gas. In this cell the hydrides are decomposed into elemental form, which can be, absorbed by the HCL's beam.

2.6.2.5 The detector, amplifier and read out system

Detectors are made of photomultipliers having cathodes coated with photosensitive materials that amplify optical signals received from the monochrometer. This monochrometer is needed to isolate the resonance line in the transmitted light. In doing this only narrow spectral line impinges on the photomultiplier tube. A photomultiplier tube is coupled with electronic circuitry to enable high speed detection limits and sensitivity to detect it. The photons received strike the photosensitive material and eject electrons. Each electron produced repeats the process until sample amplification is achieved. After amplification, the signal is read out on a digital display as shown in figure 2.3, figure 2.4 also indicates the atomic absorption instrument (Gary, 1994).

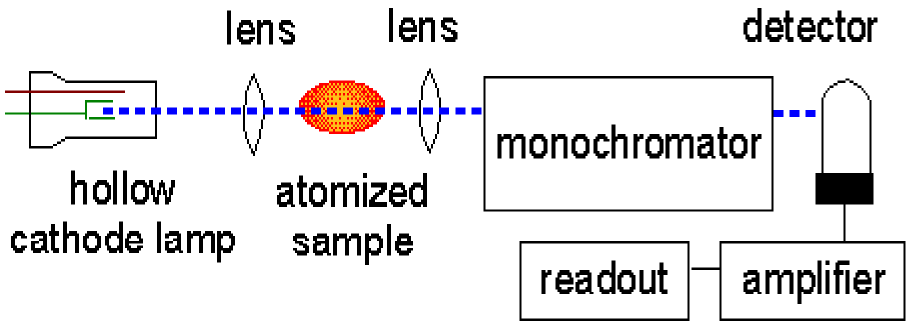


Figure 2.3: Schematic diagram of atomic absorption instrumentation

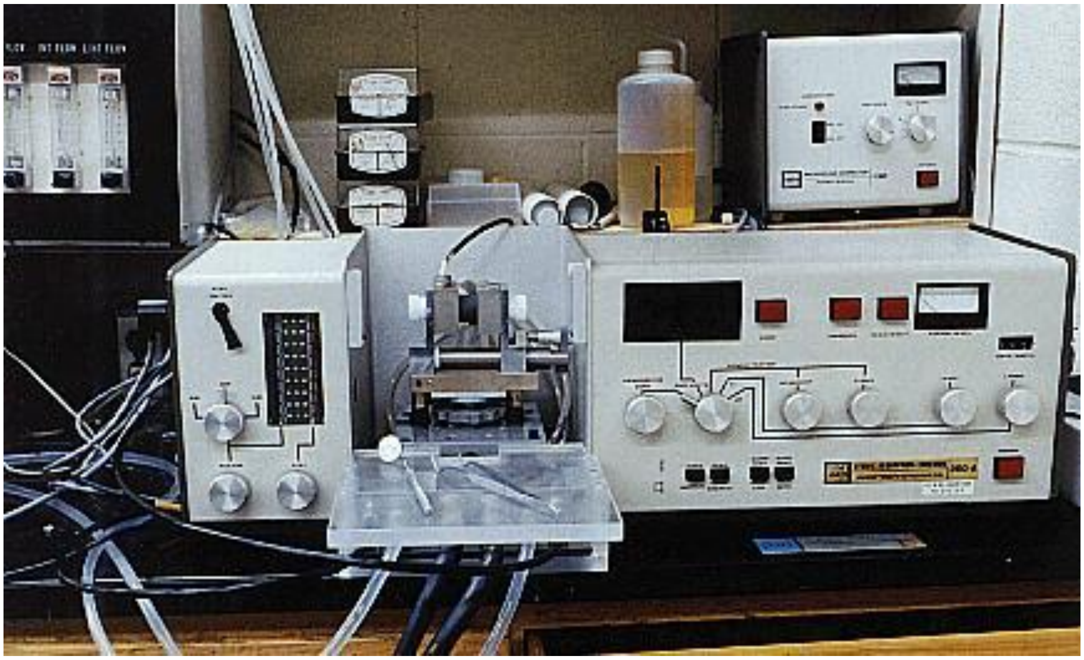


Figure 2.4 Schematic pictures for AAS

2.7 The principles of AAS

Absorption of light is associated with the transition from one state to another. Suppose steady sates 1 and 2 have energies E_1 and E_2 respectively, where $E_2 > E_1$, then the transition from state 1 to 2, results in absorption of light radiation while the transition from sate 2 to 1 results in emission of radiation with frequency (υ) expressed as in equation (2.1) (Skoog *et al.*, 1990).

$$\upsilon_{1 \rightarrow 2} = \frac{E_1 - E_2}{h} \qquad (2.1)$$

Where, h is Planck's constant.

The proportion of excited to the ground state atoms in a population at a given temperature is given by the Boltzman equation (2.1) (Skoog and Leary, 1992 and Skoog *et al.*, 1990).

$$\frac{N_j}{N_O} = \frac{P_j}{P_O} \exp\left(\frac{-E_1 - E_2}{kT}\right) \qquad (2.2)$$

Where;

N_j = Number of atoms in the excited state

N_o = Number of atoms in the ground state

K = Boltzman constant ($1.38 \times 10^{-23} JK^{-1}$)

T = Thermodynamic temperature in Kelvin scale.

E_1-E_2 =Energy difference between the excited and the ground state

P_j =Statistical factor determined by the number of states, having equal energy at the higher quantum level

P_0 =statistical factor determined by the number of states having equal energy at the lower quantum level

The N_j/N_0 ratio for a number of common atoms over a range of temperature has been calculated. The extent to which radiation of a particular frequency is absorbed by an atomic vapour is related to the length of the path traversed and to the concentration of absorbing atoms in the vapour. This is analogous to the Beer-Lambert law relating to samples in solution. Thus for a collimated, monochromatic beam of radiation of incident intensity I_0 passing through an atomic vapour of thickness I is given by equation (2.3).

$$I_{T} = I_{O} \exp^{-k\upsilon l} = I_{O} \exp^{-\varepsilon Cl} \qquad (2.3)$$

Where I_T is the intensity of transmitted radiation at frequency υ and $k\upsilon$ is the corresponding absorption coefficient, ε is the molar absorptivity; C is the concentration of analyte in moles per litre and l is the path length in centimeters. The absorption coefficient or molar absorptivity characterizes absorption lines, just as intensity, characterizes emission lines. For analytical purposes, absorbance, A, is the parameter measured.

$$A = \log \frac{I_O}{I} = \in Cl \qquad (2.4)$$

2.8 Flame photometry

Flame photometry is a spectroscopic technique for determining microgram quantities of elements by measuring directly the intensity of the radiation produced by a flame. The technique is used in the determination of sodium and potassium in inorganic materials, biological specimens and in a variety of natural products. Atomic spectra are composed of separate lines due to transitions between different electronic levels. Atoms do not contain vibrational and rotational levels associated with electronic levels, thus leading to line spectra (Figure 2.5). Atomic spectroscopy is divided into three types which are absorption, emission and luminescence, all yielding line spectra. Flame photometry is an atomic emission technique which may be regarded as the simplest of atomic spectroscopic methods and is similar to the flame test which is applied for detection of alkali metals. Flame photometry is good only for elements that are easily excited and do not require very high temperatures (Na, K, Li, Ca are the most widely determined atoms by this technique) (Berl, 1956).

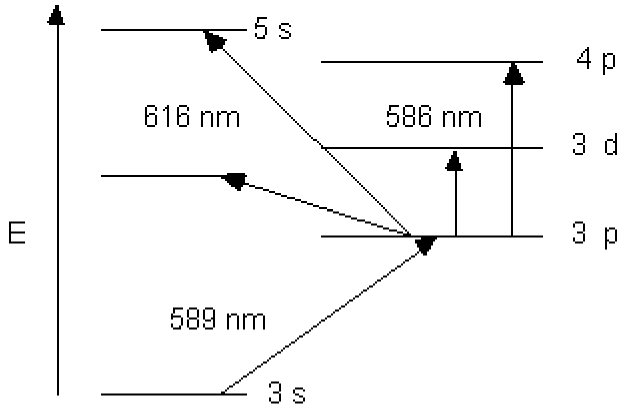


Figure 2.5: Energy level diagram for atomic sodium (Only few lines are shown)

2.8.1 Instrumentation

A flame photometer instrument is extremely simple where the sample in solution is aspirated through an aspirator or nebulizer into the flame which is usually a propane/air fuel or, even, a purified natural gas/air mixture. The sample matrix evaporates followed by atomization of the sample. Atoms present in the high temperature zone of the flame are excited to higher energy levels by absorbing energy from the flame. As excited atoms return to the ground state they emit radiation in definite wavelength depending on the energy level from which each atom drops. This gives rise to a line spectrum. However, in flame photometry a pre-selected filter (depending on the atom in question) is used and it is the intensity of the emission line that is practically measured and is related to the original concentration of the sample in solution. The detector is usually a phototube or a photomultiplier tube depending on the quality of the instrument. A schematic diagram of a simple flame photometer is shown is in Figure 2.6

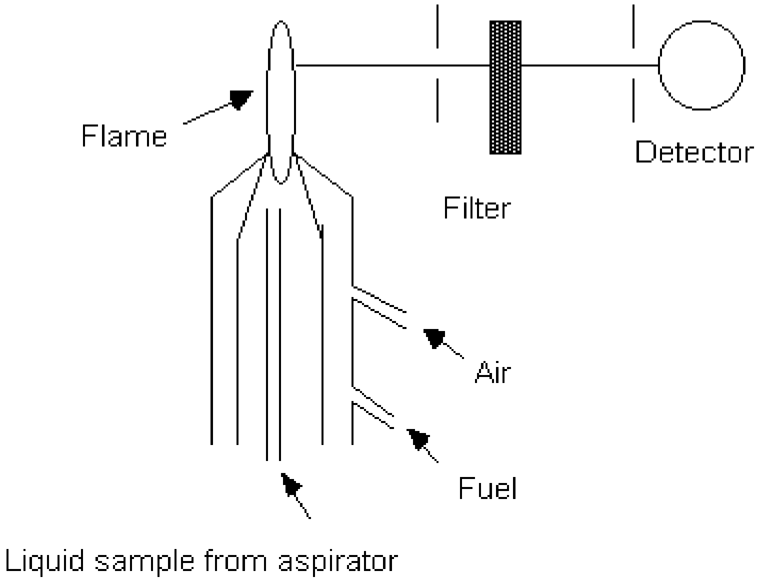


Figure 2.6: A schematic diagram of a simple flame photometer instrument

Filters can be changed or selected to suit the determination of the element in question. Commercial instruments are usually equipped with capabilities to analyze for Na, K, Li and sometimes Ca.

2.8.2 Qualitative versus quantitative

Atomic emission based on flame photometry is used for quantitative determinations only. This is because quantitative analysis using atomic emission requires advanced equipment and measurement of exact location of each emission line followed by comparison with standard line sheets. However, it is possible to use the machine for the qualitative and quantitative determination of the elements of the first and second groups of the periodic table, since these elements exhibit good emission and very intense and few emission lines, using regular flames usually utilized in flame photometry.

2.8.3 Preparation of a calibration curve

A calibration curve should be constructed using standard solutions prepared from the finest grade available. Concentrations covering the regions around the expected analyte signal should be used. It is not wise to try to interpolate or extrapolate a calibration curve of this type since the relationship between the signal and concentration may not be exactly linear, as different factors affect the shape of the calibration plot.

2.9 X-Ray fluorescence

X-ray Fluorescence (XRF) Spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analysis of rocks, minerals, sediments and fluids. It works on wavelength-dispersive spectroscopic principles that are similar to an electron microprobe. However, an XRF cannot generally make analysis at the small spot sizes, so it is typically used for bulk analysis of larger fractions of geological materials. The relative ease and low cost of sample preparation, and the stability and ease of use of X-ray Spectrometers make this one of the most widely used methods for analysis of major and trace elements in rocks, minerals and sediments. However, their accuracy is limited to elements with atomic numbers 12 and higher.

2.9.1 Fundamental Principles of X-Ray Fluorescence

The XRF method depends on fundamental principles that are common to several other instrumental methods involving interactions between electron beams and X-rays with samples, including: X-ray spectroscopy, X-ray diffraction, and wavelength dispersive spectroscopy. The analysis of major and trace elements in geological materials by X-ray fluorescence is made possible by the behavior of atoms when they interact with radiation. When materials are excited with high-energy, short wavelength radiation (X-rays), they become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample. Since, the intensity of a given peak is proportional to the concentration of that element; the technique can be used for determination of the concentration of a given element.

2.9.2 X-Ray Fluorescence Instrumentation

The analysis of major and trace elements in geological materials by XRF is made possible by the behavior of atoms when they interact with X-radiation. An XRF spectrometer figure 2.7 works because if a sample is illuminated by an intense X-ray beam, known as the incident beam, some of the energy is scattered, but some is also absorbed within the sample in a manner that depends on its chemistry. The incident X-ray beam is typically produced from a Rh target, although W, Mo, Cr and others can also be used, depending on the application.

(Wirth *et al.,* 2009)

Figure 2.7: X-Ray Flourescence Spectrometer

When the primary X-ray beam illuminates the sample, the sample is said to be excited. The excited sample in turn emits X-rays along a spectrum of wavelengths characteristic of the types of atoms present in the sample. The atoms in the sample absorb X-ray energy by ionizing, ejecting electrons from the lower (usually K and L) energy levels. The ejected electrons are replaced by electrons from an outer, higher energy orbital. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. This energy release is in the form of emission of characteristic X-rays indicating the type of atoms present. If a sample has many elements present, as is typical for most minerals and rocks, the use of a Wavelength Dispersive Spectrometer allows the separation of a complex emitted X-ray spectrum into characteristic wavelengths for each element present. Various types of detectors (gas flow proportional and scintillation) are used to measure the intensity of the emitted beam. The flow counter is commonly utilized for measuring long wavelength (>0.15 nm) X-rays that are typical of K spectra from elements lighter than Zn. The scintillation detector is commonly used to analyze shorter wavelengths in the X-ray spectrum (K spectra of element from Nb to I; L spectra of Th and U). X-rays of intermediate wavelength (K spectra produced from Zn to Zr and L spectra from Ba and the rare earth elements) are generally measured by using both detectors in tandem. The intensity of the energy measured by these detectors is proportional to the abundance of the element in the sample. The exact value of this proportionality for each element is derived by comparison to mineral or rock standards whose composition is known from prior analyses by other techniques (Wirth *et al.*, 2009).

2.9.3 Sample preparation for X-ray fluorescence

In most cases for rocks, sediments and minerals, the sample is ground to a fine powder. At this point it may be analyzed directly, especially in the case of trace element analyses. However, the very wide range in abundances of different elements, especially iron, and the wide range of sizes of grains in a powdered sample, makes the proportionality comparison to the standards particularly troublesome. For this reason, it is common practice to mix the powdered sample with a chemical flux and use a furnace or gas burner to melt the powdered sample. Melting creates a homogenous glass that can be analyzed and the abundances of the elements calculated. Virtually any solid or liquid material can be analyzed, if adequate standards are available. For rocks and minerals, typical commercial instruments require a sample constituting at least several grams of material, although the sample collected may be much larger. For XRF chemical analyses of rocks, samples are collected that are several times larger than the largest size grain or particle in the rock. This initial sample then undergoes a series of crushing steps to reduce it to an average grain size of a few millimeters to a centimeter, when it can be reduced by splitting to a small representative sample of a few tens to hundreds of grams. This small sample split is then ground into a fine powder by any of a variety of techniques to create the XRF sample as shown in figure 2.8. Care must be taken particularly at this step to be aware of the composition of the crushing implements, which will inevitably contaminate the sample to some extent. The implements,, however need to be clean before putting a fresh sample.

(Wirth *et al.*, 2009)

Figure 2.8: X-Ray Flourescence samples for analysis

2.9.4 Applications

X-Ray fluorescence is used in a wide range of applications, including:

i. research in igneous, sedimentary and metamorphic petrology
ii. soil surveys
iii. mining
iv. cement production
v. ceramic and glass manufacturing
vi. metallurgy
vii. environmental studies
viii. petroleum industry
ix. field analysis in geological and environmental studies

X-Ray fluorescence is particularly well-suited for investigations that involve:

i. bulk chemical analysis of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment
ii. bulk chemical analysis of trace elements (in abundances >1 ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn) in rock and sediment - detection limits for trace elements are typically in the order of a few parts per million

X-ray fluorescence is limited to analysis of:

i. relatively large samples, typically > 1 gram
ii. materials that can be prepared in powder form and effectively homogenized
iii. materials which are similar in composition, well-characterized standards are available
iv. materials containing high abundances of elements for which absorption and fluorescence effects are reasonably well understood

CHAPTER THREE

3.0 METHODOLOGY

3.1 Introduction

This chapter outlines the various chemical methods used in the analysis of ashes of selected biomass waste in order to determine the levels of K, Na, Ca, Mg and Fe. The basic methods that were used in this work, to arrive at the desired results were X-RF, AAS and Flame photometer.

3.2 Study Area

The research study focused on agro- waste mainly collected from Githurai market, which is approximately 12 km on the northern part of Nairobi, the capital city of Kenya along Nairobi – Thika High way. Rice husks were also obtained from Mwea area.

3.3 Experimental Work

The collection of biomass waste samples for elemental analysis is fraught with dangers of contamination. Hence, there was a great deal of care taken in preparation, collection and finally analysis of the ashes. The experiments were carried out at the laboratories of Kenyatta University and mines and geology department laboratories. The biomass waste was sampled during the month of January 2007. It was however observed that most people eating fruits such as oranges, bananas, pineapples threw away their peelings all over making the whole environment messy. As if that was not enough, business men and women dumped vegetable cuttings, potato peelings and other wastes in some sites. However, the less fortunate had used some of the waste especially fruit peelings as food. Some young kids were busy picking items to take as their meals. However some were burning heaps of waste and the ashes produced were scattered all over the entire market place making it look untidy.

3.4 General Practical Preparations

Weighing was done accurately using an electronic balance model AAA 160/L from Adam Equipment Company limited. The mass of the sample was taken as the difference between the weight of the crucible and that of the filled crucible. The procedure was repeated six times for each biomass specimen and the average mass and standard deviation of the ashes produced determined. The ashes produced were kept in a self-sealing polythene bags, labeled and stored.

3.5 Chemicals, reagents and solvent

All reagents used in this study were of analytical grade. Commercially obtained stock solutions for atomic absorption spectroscopy were used to prepare the working solution from which the required standards were made. Distilled water and distilled de-ionized water was used throughout the study.

3.6 Cleaning of glassware and plastic containers

The glassware included: volumetric flasks, pipettes, filter funnels, glass beakers, burettes, conical flasks, measuring cylinders and weighing bottles/ vials. All glassware were cleaned thoroughly by soaking them for about 12 hours in freshly prepared chromic acid and then rinsed several times with distilled de-ionized water. They were then soaked in distilled de-ionized water for about 6 hrs to leach off any adsorbed chromate ions. Finally, they were dried in an open rack after further rinsing with fresh distilled de-ionised water. The plastic containers were first washed with detergent to remove grease then soaked in 2 mol dm^{-3} HNO_3 for 3 days. This was followed by further soaking for about 24 hrs in distilled water. Finally, the bottles were rinsed thoroughly with distilled de-ionised water. Each bottle was placed in a separate plastic bag, sealed and packed. They were stored in dust - proof drawer under lock and key (Millac and Krailj, 2003).

3.7 Sampling

The main objective of obtaining a suitable sample is to take a portion that is representative of all the components and their amounts that are contained in the bulk sample. Three main objectives of sampling are that the cost is lower, data collection is faster and since the data set is smaller it is possible to ensure homogeneity and to improve the accuracy and the quality of the data. Random sampling was however used in collection of the samples within selected sites where the waste had been disposed. The samples are collected on weekly basis using separate labeled polythenes for every biomass waste for a period of 1 month and a total of 150 samples were collected. In this research, the following biomass waste were collected: orange peelings, pineapple peelings, pigeon pea pods, rice husks, banana peels, kale stalks, garden pea pods, potato peels, banana peels and onion stock waste.

3.8 Sample Treatment

Each of the samples was sorted out properly to remove any foreign matter. They were cut into smaller pieces, cleaned thoroughly with distilled water followed by distilled de-ionized water. The samples were then dried in an electric oven at 110^0 C for at least 2-3 hours and cooled in a desicator. They were kept in very clean and separate polythenes to avoid any contamination (Mendham *et al.*, 2000).

3.9 Ashing and Ash content

20g of well-mixed dried biomass samples for each species was accurately weighed using an electronic balance model AAA/160L from Adams Company Limited into six pre-weighed porcelain crucibles. Each crucible was heated at 270^0C, cooled and weighed to determine loss on volatile matter. The residue was then ashed at 560^0C to determine both loss on ignition and the mass of the residue. After each heating, the crucibles were cooled in a well desiccated desicator and weighed to determine the mass of both the ash and the amount of carbon burned in each case mean and standard deviation was determined. The % ash was calculated by difference in weight of the crucibles before and after combustion as follows:

$$\%\ \text{ash} = \frac{W_4 - W_1}{W_2 - W_1} \times 100\% \qquad (3.1)$$

$$\text{Mass of carbon burnt} = W_3 - W_4 \qquad (3.2)$$

$$\text{Organic matter} = 100\% - \%\ \text{ash} \qquad (3.3)$$

Where;

W_1 = Mass of empty, dry crucible

W_2 = Mass of dry crucible + dry biomass

W_3 = Mass of dry crucible + cooled carbonaceous solid

W_4 = Mass of dry crucible + cooled greyish white ash

The ashes produced were then homogenized and put in self-sealing polythene bags, labeled and stored in a dry dust-proof drawer under lock and key awaiting digestion (Okalebo *et al.*, 1993).

3.10 Digestion of the ashes

The ashes were dried in an electric oven at 110°C for 2 hours, cooled in a descicator. About 0.12g of each ash sample was accurately weighed into 100ml glass beakers and digested with aqua regia (3:1 V/V HCl and HNO_3) with constant heating in a fume cupboard until a clear solution was formed. Excessive heating was avoided as it could cause spattering. Samples were then filtered using Whatman No. 41 ashless filter paper into 100 ml volumetric flasks. 4ml of strontium chloride solution was added to each sample to release phosphate during calcium determination. Each filtrate was then adjusted to the mark using distilled de-ionised water for AAS and Flame photometry analysis. This procedure was repeated three times for each sample. Ashes were analyzed immediately or stored in plastic labeled containers at 4°C until analysis was set up (Cid *et al*, 2001).

3.11 Sample preparation for X-Ray Fluorescence Spectrophotometry

10g of each ash sample species was accurately weighed using an electronic balance mode/AAA160L and mixed with 5g of the starch to act as a binder, placed in a suitable die, and compressed to obtain a flat cylindrical pellet. After drying, total elemental analysis was carried out to determine all the elements presents in the ashes. The results are usually expressed in terms of oxides (Townshend *et al*, 1995).

3.12 Preparation of standards

3.12.1 Potassium, sodium, iron, calcium and magnesium standards

From the stock solution (1000ppm), the working solution was prepared by serial dilution using the formula:

$$C_1V_1 = C_2V_2 \qquad (3.4)$$

Where C_1 = concentration of the stock solution (1000ppm)

V_1 = volume required from the stock solution

C_2 = concentration of the working solution in ppm

V_2 = volume of volumetric flask used for dilution

For 100ppm working solution

$$\therefore 1000ppm \times V_1 = 100ppm \times 100ml$$

$$V_1 = \frac{100ppm \times 100ml}{1000ppm}$$

=10ml of 1000ppm were diluted to 100ml in a volumetric flask.

The 100ppm which is the working solution was further diluted to give the required standards within the range 0-25ppm using the same formula:

$$C_1V_1 = C_2V_2$$

25ppm was prepared as follows:

$$100ppm \times V_1 = 25ppm \times 50ml$$

$$V_1 = \frac{25ppm \times 50ml}{100ppm}$$

= 12.5ml of 100ppm working solution were diluted to 50 ml in a volumetric flask.

20ppm was prepared as follows:

$$100ppm \times V_1 = 20ppm \times 50ml$$

$$V_1 = \frac{20ppm \times 50ml}{100ppm}$$

= 10ml of 100ppm working solution were diluted to 50ml in a volumetric flask.

15ppm was prepared as follows:

$$100ppm \times V_1 = 15ppm \times 50ml$$

$$V_1 = \frac{15ppm \times 50ml}{100ppm}$$

= 7.5ml of 100ppm working solution were diluted to 50ml in a volumetric flask.

10ppm was prepared as follows:

$$100ppm \times V_1 = 10ppm \times 50ml$$

$$V_1 = \frac{10ppm \times 50ml}{100ppm}$$

= 5.0ml of 100ppm were diluted to 50ml in a volumetric flask.

5ppm was prepared as follows:

$$100ppm \times V_1 = 5ppm \times 50ml$$

$$V_1 = \frac{5ppm \times 50ml}{100ppm}$$

= 2.5ml of 100ppm were diluted to 50ml in a volumetric flask.

The same procedure was used for the preparation of standards of sodium, iron, magnesium and calcium. In each case 1000ppm stock solution was first diluted to give 100ppm working solution from which the required standards were prepared by serial dilution using the formula above.

3.13 Determination of Sodium and Potassium

Flame Photometer Model Corning EEL 400 was used in the determination of both potassium and sodium. The light emitted by Na and K atoms when these elements are excited in a flame at wavelength 589nm and 769nm respectively was measured as absorbance. The standards for the analysis were made from commercial sodium and potassium standards as describe in equation (3.4). The absorbance of the standards was used to draw the calibration curves from which the concentration of the two metals were determined. The samples were diluted 20 times in the case of K^+ except banana leaves ashes which were diluted 10 times (Golterman, 1971).

3.14 Determination of Iron, Calcium and Magnesium

The concentrations of major cations were determined using atomic absorption spectrophotometry (AAS), Model 210 VGP, interfaced with a computer. This technique is very useful for determining trace elements in environmental samples both qualitatively and quantitatively. The sample solution in an aerosol form was introduced into a flame and vapourized prior to dissociation. At the temperature of the flame, the atoms of the metals initially at the ground state are excited at a given characteristic wavelength called the resonance line upon passing a beam of radiation from a hollow cathode lamp. According to the Beer-Lambert’s Law the absorbance of a metal at a given wavelength is proportional to the number of absorbing species in the light path. Standards for each element were made from commercial standards as describe in equation (3.4). The absorbance for each set of standard was measured and calibration curve was constructed using the computer software from which the concentration of Calcium, Magnesium and total Iron in the samples were determined. The resonance line was set at 248.3nm for iron, 422.7nm for calcium and 285.2nm for magnesium. For all the three elements, air-acetylene flame was used.

Table 3.1 shows the parameters for the determination of Potassium, Sodium, Calcium, Magnesium and Iron.

Table 3.1: Calibrations / Instrument Parameters for each element used

Metals Instrument parameters	Ca	Fe	Mg	Na	K
Mode	F.e	A	A	F.e	F.e
Lamp Current(mA)	3.5	5	3.5	5	5
Flame	N.a	a.a	a.a	a.a	a.a
Wavelength(nm)	422.7	248.3	285.3	589	766.5
Slit width	0.5	0.2	0.5	0.5	1
Photomultiplier(volts)	337.4	349.9	234.6	343.6	349.9
Flame stoichiometry	R	O	O	R	O

Key:

F.e - Flame emission

a.a - Air-acetylene

R - Reducing

O - oxidising

A-Absorbance

N.a- Nitrous-acetylene

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results obtained in the research study in the analysis of ashes of selected biomass waste samples from Githurai market and rice husks from Mwea while determining the ash content as well as the level of Potassium, Sodium, Calcium, Magnesium and Iron. Discussions are also outlined basing on the results obtained in every stage.

4.2 Ash Content

The ash content of selected biomass waste was determined by accurately weighing about 20 g of dry biomass sample into each of the six dry porcelain crucibles. They were subjected to heat in a furnace at a temperature of 270°C, cooled and weighed. The residue was then ashed at 560 °C to determine the mass of the final residue which is the ash. The percentage ash content was worked out from which mean and standard deviation was calculated. Table 4.1 gives a summary of the results of the ash content of various biomass wastes.

Table 4.1: Percentage Ash Content of selected biomass waste

Biomass Materials	% mean ± Sd	n
Orange Peelings	3.81 ± 0.08	6
Pigeon Pea Pods	3.55 ± 0.04	6
Pineapple Peelings	3.31 ± 0.10	6
Rice Husks	23.92 ± 0.39	6
Banana Peelings	12.19 ± 0.11	6
Kales Stalks	14.13 ± 0.18	6
Garden Pea Pods	4.97 ± 0.12	6
Potato Peelings	4.29 ± 0.07	6
Banana Leaves	11.90 ± 0.13	6
Onion Stock Waste	7.59 ± 0.13	6

Figure 4.1 also indicates the bar graph representing the percentage representation of the ash content of the selected biomass waste.

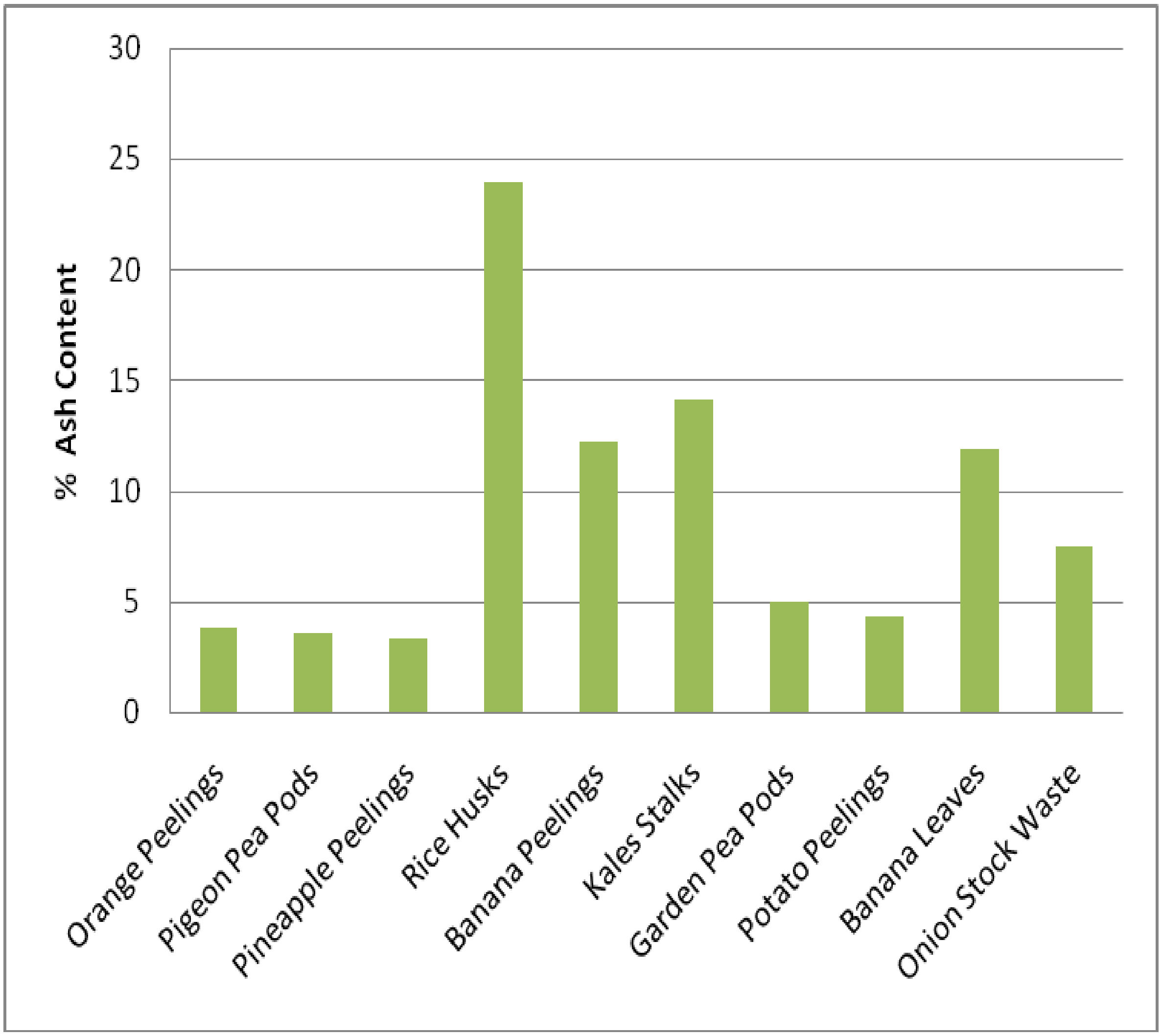


Figure 4.1: Percentage ash content of selected biomass waste

The levels of ashes from different biomass residues varied from 3.31 ± 0.1% to 23.92 ± 0.39%. The ash content from the selected biomass wastes rarely exceeded 15% except for the rice husk which is purely silica and constitutes about 23.92 ± 0.39%. This was the highest ash content among the studied biomass waste as noted from table 4.1 which gives a summary of the results. Kales stalk had ash content of 14.13 ± 0.18%. Banana peelings and banana leaves had 12.20 ± 0.11% and 11.90 ± 0.13% respectively. Pineapple peelings, pigeon pea pods and orange peelings had the lowest ash content of 3.31 ± 0.10%, 3.55 ± 0.04% and 3.81 ± 0.08% respectively.

This actually follows the fact that, the lower the ash content, the higher the carbon content and the better the biomass as a good source of energy. Rice husks should be a poorer form of energy while pineapple peelings, pigeon pea pods and orange peelings should serve as good source of energy because of the fact that they have little amount of ash.

4.3 Levels of Inorganic elements obtained by XRF analysis

Table 4.2 below gives assay analysis done on various samples of ashes of selected biomass waste. The results shown are expressed as oxides of the metals.

Table 4.2: Percentage of the elements as oxides by XRF

Biomass Sample	Na_2O	MgO	MnO	P_2O_5	K_2O	CaO	SiO_2	Al_2O_3	TiO_2	Fe_2O_3
Orange peelings	7.45	1.53	0.041	2.56	33.69	28.05	0.05	1.51	0.30	0.51
Pigeon pea pods	14.69	4.90	0.21	3.76	40.46	12.83	4.54	1.64	0.22	1.73
Pineapple peelings	8.34	0.44	0.53	5.08	43.93	2.68	7.50	1.20	0.08	1.00
Rice husks	bd	bd	0.13	bd	0.98	1.36	97.40	2.97	bd	0.44
Banana peelings	6.48	0.03	0.16	2.75	59.08	2.52	3.33	1.80	0.07	0.44
Kales stalks	14.43	1.75	0.03	1.46	38.02	13.32	0.06	1.96	bd	0.46
Garden pea pods	20.51	5.27	26.41	4.85	26.41	23.36	0.01	0.98	0.04	0.96
Potato peelings	10.50	1.28	0.06	7.21	56.47	2.56	bd	1.45	0.09	1.29
Banana leaves	1.89	0.61	2.60	1.63	9.87	8.68	61.61	1.98	0.01	0.70
Onion stock waste	6.44	1.86	0.28	0.86	7.02	40.14	5.19	2.85	0.28	2.27

bd = below detection

The concentrations of the elements are shown as their oxides in Table 4.2. With the exception of silicon, aluminium and titanium other elements analyzed are essential for healthy animal development. In addition to these elements iodine and selenium are required. The current knowledge of processing of minerals is so advanced that the East Rand Gold and Uranium Company recovers gold from materials with as low a concentration of gold as 0.53 ppm. Lithium is recovered economically from spodumene where it is present only to the extent of 1-3%.The results show that some ashes contain relatively high levels of many essential elements with potential for recovery. For example, the oxides of sodium and potassium are present at very high levels in some of the biomaterials. Potassium oxide, K_2O was generally high in most of the materials except in rice husks ashes where its concentration was 0.98%. Banana peelings, potato peelings, pineapple peelings, pigeon pea pods, kales stalks and orange peelings had the highest levels of K_2O averaging 59.08%, 56.47%, 43.93%, 40.46%, 38.02% and 33.69% respectively.

Onion stock waste, orange peelings and garden pea pods had relatively high levels of calcium oxide at 40.14%, 28.05% and 23.36% respectively. Silica was quite high in rice husks and banana leaves at 97.40% and 61.61% respectively. Other materials had much lower percentage of silica. Orange peelings and banana peelings had combined alkalis of about 41.00% and 65.00% respectively. Calcium oxide, CaO is also another important component in plants. Onion stock waste, orange peelings and garden pea pods had relatively high levels at 40.14%, 28.05% and 23.36% respectively. Al_2O_3, TiO_2, Fe_2O_3, P_2O_5 and MgO were obtained at lower percentages. Garden pea pods had a higher level of MnO at 26.41%. Sodium oxide, Na_2O, is also an important component found in ashes. Garden pea pods, pigeon pea pods, kales stalks and potato peelings had 20.51%, 14.69%, 14.43% and 10.50% Na_2O respectively.

4.4 Levels of inorganic elements obtain by AAS analysis

The concentrations of the elements in ppm in the samples were converted stepwise as shown using the formula:

$$\frac{\text{Volume used in ml x conc. X 100}}{\text{Weight of sample taken x } 10^6} = x \qquad (4.1)$$

Where x is the weight of the element under determination

The value of x obtained was then converted to % oxide for every element being determined.

Percentage Calcium oxide was calculated as follows:

$$\text{Ca} \Rightarrow \text{CaO}$$

$$40\text{g} \Rightarrow 56\text{g}$$

$$\text{X} \Rightarrow ?$$

$$\Rightarrow \frac{56x}{40}\% \qquad (4.2)$$

Percentage iron oxide was evaluated as shown below:

$$2\text{Fe} \Rightarrow \text{Fe}_2\text{O}_3$$

$$112\text{g} \Rightarrow 160\text{g}$$

$$x \Rightarrow ?$$

$$\Rightarrow \frac{160x}{112}\% \qquad (4.3)$$

For potassium, the percentage oxide was calculated as shown below:

$$2K \Rightarrow K_2O$$

$$78g \Rightarrow 94g$$

$$x \Rightarrow ?$$

$$\Rightarrow \frac{94x}{78}\% \qquad (4.4)$$

Percentage sodium oxide was obtained from the calculations show below:

$$2Na \Rightarrow Na_2O$$

$$46g \Rightarrow 62g$$

$$x \Rightarrow ?$$

$$\Rightarrow \frac{62x}{46}\% \qquad (4.5)$$

Finally, percentage Magnesium oxide was obtained from the following conversion formula:

$$Mg \Rightarrow MgO$$

$$24g \Rightarrow 40g$$

$$x \Rightarrow ?$$

$$\Rightarrow \frac{40x}{24}\% \qquad (4.6)$$

In each case of the determination of the element the mean value and the standard deviation was calculated for the % oxide obtained. The overall results obtained from the AAS analysis is shown in table 4.3

Table 4.3: Summary of elemental analysis in percentages as oxides by AAS and Flame Photometry

Biomass Samples	K_2O	Na_2O	MgO	CaO	Fe_2O_3
Orange Peelings	29.42 ± 3.41	13.88 ± 1.40	1.73 ± 0.02	6.32 ± 0.12	0.14 ± 0.01
Pigeon Pea Pods	38.77 ± 1.05	10.48 ± 0.87	0.35 ± 0.07	15.20 ± 5.74	0.83 ± .05
Pineapple Peelings	47.05 ± 0.30	12.89 ± 0.72	1.37 ± 0.09	5.33 ± 2.28	0.84 ± 0.04
Rice Husks	0.49 ± 0.03	0.45 ± 0.03	0.86 ± 0.11	0.98 ± 0.09	0.10 ± 0.01
Banana Peelings	63.17 ± 0.69	16.29 ± 0.54	1.06 ± 0.09	1.53 ± 1.32	0.14 ± 0.01
Kales Stalks	35.47 ± 0.78	14.35 ± 0.51	1.04 ± 0.06	4.92 ± 0.32	0.09 ± 0.01
Garden Pea Pods	25.29 ± 0.73	9.71 ± 0.80	1.79 ± 0.03	5.62 ± 0.11	0.50 ± 0.06
Potato Peelings	59.48 ± 0.77	15.78 ± 1.56	1.41 ± 0.02	2.29 ± 1.32	0.65 ± 0.06
Banana Leaves	6.85 ± 0.77	1.20 ± 0.18	0.28 ± 0.02	6.85 ± 1.32	0.27 ± 0.03
Onion Stock Waste	2.58 ± 0.19	4.30 ± 0.65	0.86 ± 0.19	34.95 ± 2.28	1.04 ± 0.04

4.5.1 Levels of calcium in ashes from biomass waste

The results on the levels of calcium oxide are shown on Table 4.3 and Figure 4.2 also shows the bar graph representation of the same in percentage.

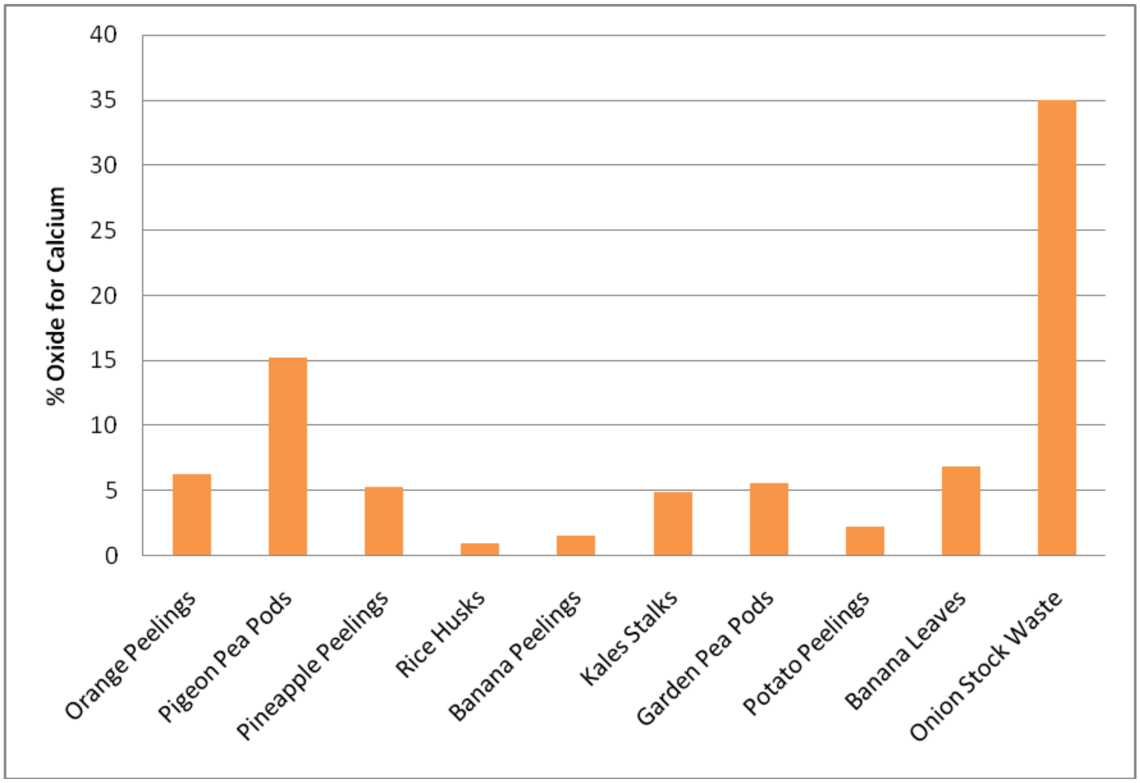


Figure 4.2: Levels of calcium oxide in percentage in ashes from biomass waste

The levels of calcium oxide as shown in Table 4.3 and Figure 4.2 from the samples shows variations from 0.98 ± 0.09% to 34.95 ± 2.28%. Significant levels were however recorded from onion stock waste at 34.95 ± 2.28% followed by pigeon pea pods at 15.20 ± 5.74% and banana leaves at 6.85 ± 1.32%. As low as 0.98 ± 0.09%, 1.53 ± 1.32% were noted from rice husks and banana peelings respectively. However, the rest of the samples had quantities of calcium not exceeding 7% on average.

4.5.2 Levels of iron in ashes from biomass waste

The results on the level of Iron oxide are shown on Table 4.3 and Figure 4.3 also shows the bar graph representation of the same in percentage.

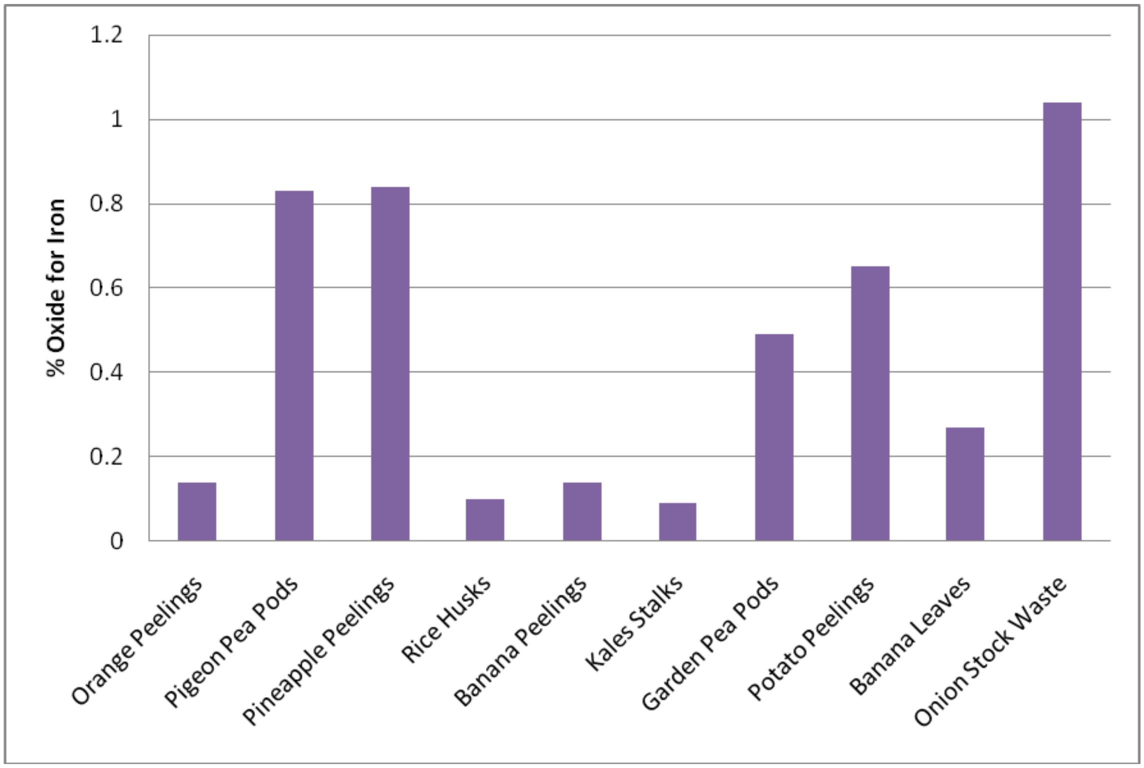


Figure 4.3: Levels of iron oxide in percentage in ashes from biomass waste

The concentrations of iron oxide from all the samples as shown from Table 4.3 and Figure 4.3 was shown to be relatively low. The levels never went beyond 1.04 ± 0.04%. The range was from 0.09 ± 0.01% to 1.04 ± 0.04%. It is only onion stock waste, pineapple peelings and pigeon pea pods that showed amounts at 1.04 ± 0.04%, 0.84 ± 0.04% and 0.83 ± 0.05% respectively Otherwise there levels were minimal.

4.5.3 Levels of potassium in ashes from biomass waste

The results on the levels of potassium oxide are shown on Table 4.3 and Figure 4.4 also shows the bar graph representation of the same in percentage.

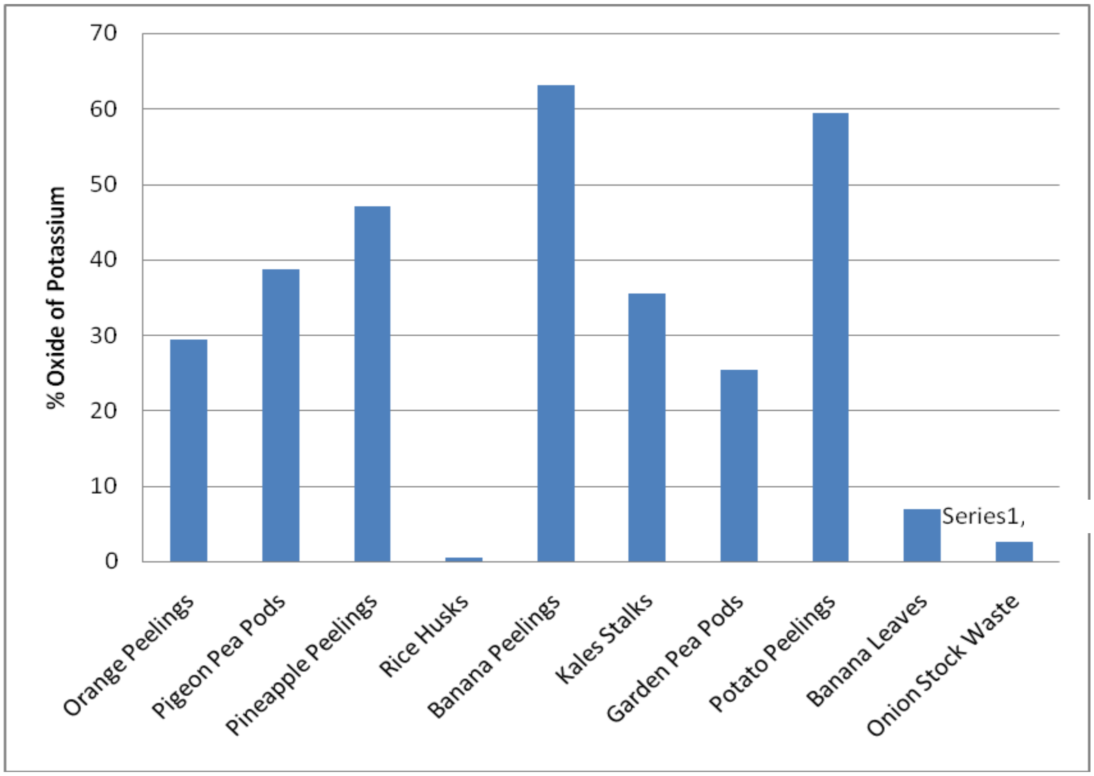


Figure 4.4: Levels of potassium oxide in percentage in biomass waste

The levels of potassium oxide as shown from Table 4.3 and Figure 4.4 varies from 6.85 ± 0.77% to 63.17 ± 0.69%. In general there was high concentration in most of the agro-waste ashes under investigation except rice husk ashes with as low as 0.49 ± 0.03%. The main reason for higher levels could be due to deliberate addition of fertilizers in the farms by farmers either during planting or even top dressing. Since fertilizers contain mainly nitrogen, phosphorous and potassium as the main components. Ashes from banana and potato peelings registered the highest concentration at 63.17 ± 0.69% and 59.48 ± 0.77% respectively. Least amount of potassium oxide was shown by ashes from rice husks, banana leaves and onion stock waste at 0.49 ± 0.03%, 6.85 ± 0.77% and 2.58 ± 0.19% respectively.

4.5.4 Levels of sodium in ashes from biomass waste

The results on the levels of sodium oxide are shown on Table 4.3 and Figure 4.5 also shows the bar graph representation of the same results in percentage.

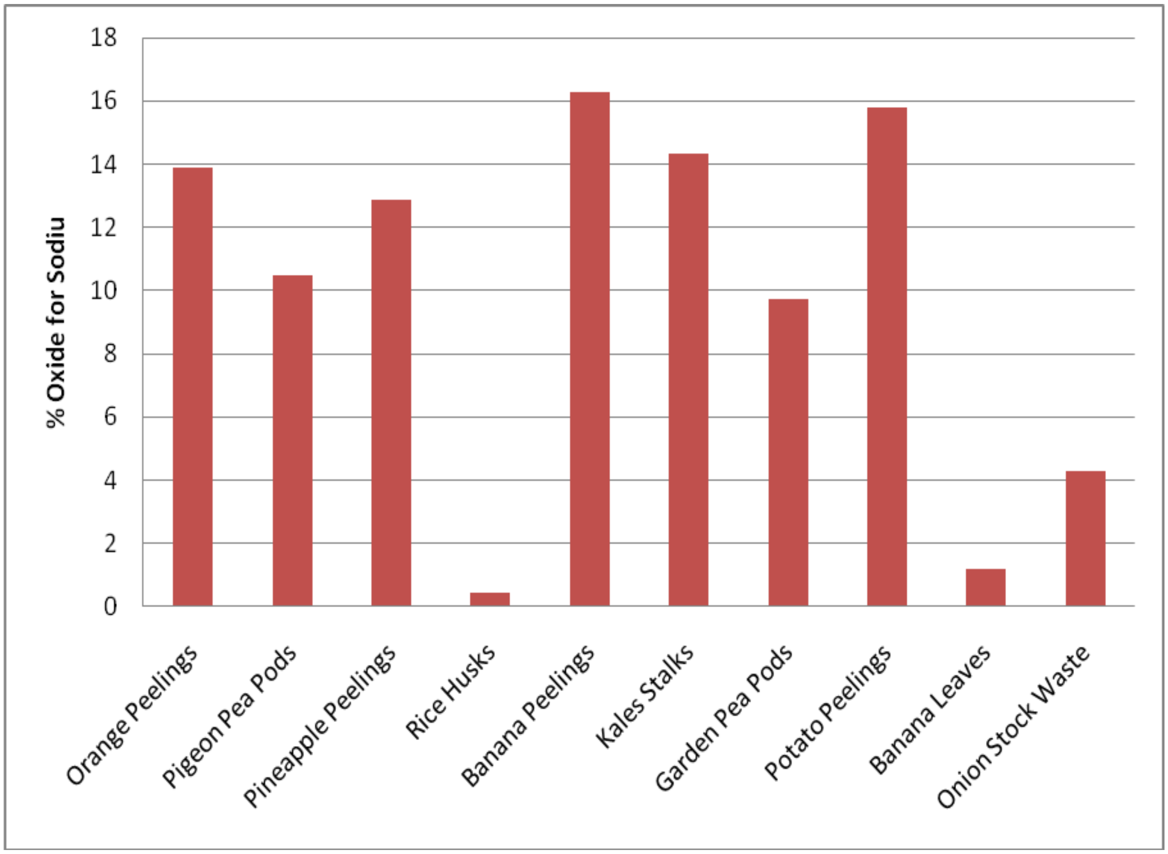


Figure 4.5: Levels of sodium oxide in percentage in ashes from biomass waste

The concentrations of sodium oxide in the biomass waste ashes studied ranged from

0.45 ± 0.03% to 16.29 ± 0.54%. Their levels were a bit lower than potassium oxide in each case, but however ashes from banana and potato peelings showed high concentration on average at 16.29 ± 0.54% and 15.78 ± 1.56% respectively. Ashes from kales stalks and orange peelings on average showed a concentration which was at 14.35 ± 0.51% to 13.88 ± 1.40% respectively. Minimal amount of Sodium oxide was seen from rice husk, banana leaves, onion stock waste and even garden pea pods ashes.

4.5.5 Levels of magnesium in ashes from biomass waste

The results on the levels of Magnesium oxide are shown on Table 4.3 and Figure 4.6 also shows the bar graph representation of the same results in percentage.

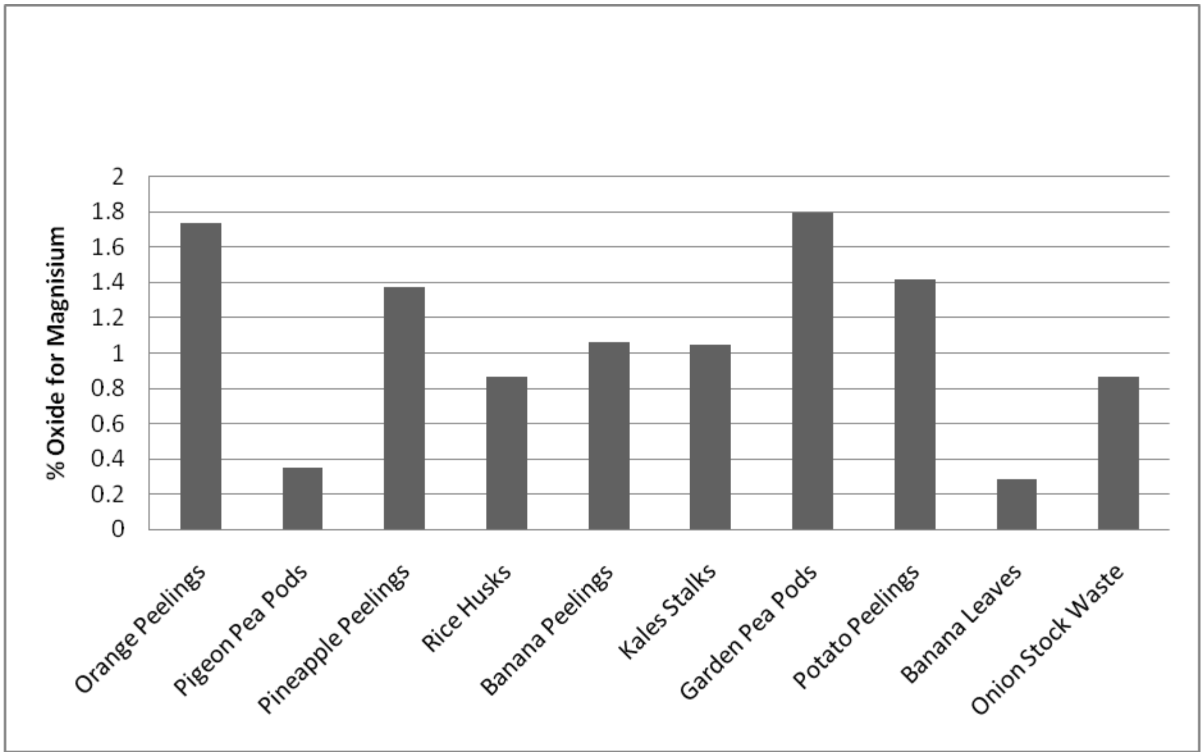


Figure 4.6 Levels of magnesium oxide in percentage in ashes from biomass waste

The concentrations of Magnesium oxide was lower among all the ashes from biomass samples within the range of 0.28 ± 0.02% to 1.79 ± 0.03%.However, some samples were noted to have meaningful levels, for example ashes from garden pea pods and orange peelings showed that they have 1.79 ± 0.03% and 1.73 ± 0.02% respectively. Ashes from banana leaves and pigeon pea pods had the lowest concentrations at 0.28 ± 0.02% and 1.37 ± 0.09% respectively.

4.6 Summary from the findings

Ashes from the agro-waste contain all the major elements in substantial amounts, however, iron oxide and magnesium oxide were found to be at a lower level. It is realized that agro-waste contain several elements that can be recovered for a number of uses. Both XRF and AAS techniques gave values closer to each other. However, XRF usually gives exaggerated values especially for lower atomic weight elements. Potassium oxide, K_2O is generally in higher levels in banana peelings and potato peelings at 63.17 ± 0.69% and 59.48 ± 0.77% respectively. Pineapple peelings, pigeon pea pods and kales stalks were also rich in K_2O at 47.05 ± 0.3%, 38.77 ± 1.05% and 35.47 ± 0.78% respectively. Rice husks, banana leaves and onion stock waste contain the least amount of K_2O among the biomass materials studied. They had 0.49 ± 0.03%, 6.85 ± 0.77% and 2.58 ± 0.19% respectively. Sodium oxide, Na_2O was found to be at 16.29 ± 0.51%, 15.78 ± 1.56%, 14.35 ± 0.51% and 13.88 ± 1.40% in banana peelings, potato peelings, kales stalks and orange peelings respectively. Very low levels of Na_2O were found in rice husks, banana leaves at 0.45 ± 0.03% and 1.20 ± 0.18% respectively. Iron oxide was low compared to the rest of the elements analysed. Onion stock waste and pigeon pea pods were found to be rich in calcium oxide, CaO at 34.95 ± 2.28% and 15.20 ± 5.70% respectively. The values from the two methods of analysis are not far from each other.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The research investigated the levels of inorganic elements particularly potassium, sodium, calcium, iron and magnesium in ashes of selected biomass waste and on the other hand, the ash content of the same agro-waste from Githurai market in Nairobi and rice husks from Mwea. The results revealed that:

i. Ashes of various biomass wastes contained different levels of macro elements which are essential for both plant and animal life. Generally, there were very high concentrations of alkali elements particularly potassium in all the ashes of various biomass materials. Ashes from banana, potato and pineapple peelings showed the highest levels of potassium above all the others. This could be as a result of deliberate addition of fertilizers by farmers either during planting or as top dressing which increases their levels in turn.

ii. Very low concentrations of iron were noted in all the ashes of various biomasses.

iii. A lot of silica was found to be quite high in ashes from rice husks and banana leaves, and therefore such could be an important source for cement production.

iv. Alkalis are important chemicals for instance potassium carbonate and sodium carbonate are used by many industries during the manufacture of different products. The most significant user being glass industry which uses sodium carbonate to decompose silicates for glass making. It is also utilized in water softening. The cosmetic industry uses it for manufacturing soap, while the chemical industry uses it as a precursor to numerous sodium containing reagents. It is also important in photography, textile industry and water treatment. In addition to these industrial applications, sodium carbonate is used in medicine as antacid. The ashes from biomasses containing very high alkali levels mostly potassium carbonate and sodium carbonate contents such as those of banana and potato peelings can be a good source replacing the commercially available alkalis which are expensive.

v. Ash content was generally very low among all the entire samples studied ranging from 3.31±0.10% to 23.92±0.39%. This imp[lies that the samples with lower ash content forms a very good bioenergy material for instance pineapple peelings, pigeon pea pods and orange peelings while rice husks is a poorer form of energy since it has a higher ash content.

5.2 Recommendations for further investigation

High ash content especially in rice husks at the moment is currently used in the production of cement since it has high percentage of silica which is a necessary component in Portland cement. Similarly, the potential of exploiting the high levels of potassium and sodium in soap and glass manufacture is wanting. This is because they are soluble and thus can be leach with water, evaporated to recover the metals. When dry biomass is burnt, they release water and carbon (IV) oxide. One can trap the carbon (IV) oxide, pass through anhydrous calcium chloride and the gas produced can be used to make dry ice which is a very important chemical in most chemical industries. Potassium is one of the six plant macronutrients, the others being nitrogen, calcium, phosphorus and sulphur. Any sulphur and nitrogen in the biomass are readily lost as gases during the ashing process. Further research is also necessary to determine the levels of heavy metals such as cadmium, lead and zinc among others in the ashes of biomasses.

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APPENDIX 1:

Percentage Ash Content of selected Biomasses

Table 5.1: Ash Content of selected Biomasses (Mass in grams)

	Crucible Mass + Sample, W_2	Crucible Mass, W_1	Sample mass, W_2-W_1	Crucible + Sample Mass at 270^0C, W_3	Crucible + Sample Mass at 560^0C, W_4	Mass of the Ash, W_4 -W_1	% Ash Content	Average. % Ash Content	Carbon Mass, W_3 - W_4	Average Carbon Mass
	1. ORANGE PEELINGS									
I	83.02	63.00	20.02	68.29	63.79	0.79	3.95	3.81 ± 0.08	4.50	4.53
ii	85.15	65.02	20.13	70.32	65.77	0.75	3.73		4.55	
iii	87.77	67.32	20.45	72.62	68.08	0.76	3.72		4.54	
iv	87.13	66.92	20.21	72.22	67.69	0.77	3.81		4.53	
V	84.84	64.52	20.32	69.82	65.30	0.78	3.84		4.52	
vi	90.74	70.28	20.46	75.57	71.06	0.78	3.81		4.51	
	2. PIGEON PEA PODS									
I	86.23	66.31	19.92	73.77	67.03	0.72	3.61	3.55 ± 0.04	6.74	7.21
ii	88.07	68.06	20.01	76.81	68.77	0.71	3.55		8.04	
iii	89.42	69.20	20.22	77.17	69.92	0.72	3.56		7.25	
iv	88.24	67.92	20.32	75.90	68.64	0.72	3.54		7.26	
V	90.68	70.12	20.56	78.21	70.84	0.72	3.50		7.37	
vi	91.10	70.38	20.72	77.73	71.11	0.73	3.52		6.62	
	3. PINEAPPLE PEELINGS									
I	89.07	69.36	20.71	77.48	70.03	0.67	3.24	3.31 ± 0.10	7.45	7.43
ii	90.84	70.32	20.52	78.37	71.03	0.71	3.46		7.34	
iii	87.22	66.59	20.63	74.73	67.27	0.68	3.29		7.46	
iv	85.87	65.10	20.77	73.21	65.77	0.67	3.23		7.44	
V	89.41	68.98	20.43	77.07	69.64	0.66	3.23		7.43	
vi	89.71	69.32	20.37	77.47	70.01	0.69	3.38		7.46	
	4. RICE HUSKS									
I	96.94	75.94	21.00	85.62	80.79	4.85	24.25	23.92 ± 0.39	4.83	4.86
ii	92.91	72.38	20.53	82.06	77.22	4.84	23.57		4.84	
iii	91.51	70.41	20.10	80.22	75.31	4.90	24.38		4.91	
iv	90.40	69.68	20.72	79.36	74.52	4.84	23.36		4.84	
V	91.79	71.59	20.20	81.33	76.05	4.86	24.06		4.88	
vi	87.00	66.70	20.30	76.38	71.55	4.85	23.89		4.83	

	Crucible Mass + Sample, W_2	Crucible Mass, W_1	Sample mass, W_2-W_1	Crucible + Sample Mass at 270^{0}C, W_3	Crucible + Sample Mass at 560^{0}C, W_4	Mass of the Ash, W_4-W_1	% Ash Content	Average % Ash Content	Carbon Mass, W_3 - W_4	Average Carbon Mass
	5. BANANA PEELINGS									
I	88.66	68.12	20.54	77.54	70.62	2.50	12.17	12.20 ± 0.11	6.92	6.89
ii	86.98	66.55	20.43	75.90	69.05	2.50	12.23		6.85	
iii	87.99	67.59	20.40	77.00	70.09	2.50	12.25		6.91	
iv	90.43	70.23	20.20	79.65	72.72	2.49	12.33		6.93	
V	89.74	69.32	20.62	78.67	71.83	2.51	12.17		6.84	
vi	88.22	67.40	20.82	76.80	69.90	2.50	12.00		6.90	
	6. KALES STALKS									
I	85.01	65.00	20.01	74.10	67.86	2.86	14.29	14.13 ± 0.18	6.24	6.23
ii	86.68	66.68	20.00	75.78	69.53	2.85	14.25		6.25	
iii	87.78	67.48	20.30	76.58	70.38	2.90	14.29		6.20	
iv	84.43	65.10	20.33	74.20	67.94	2.84	13.96		6.26	
V	87.75	67.28	20.47	76.38	70.19	2.91	13.87		6.19	
vi	89.60	69.38	20.22	78.47	72.24	2.86	14.14		6.23	
	7. GARDEN PEA PODS									
I	87.59	67.38	20.21	75.41	68.42	1.04	5.15	4.97 ± 0.12	6.98	7.07
ii	89.52	69.22	20.30	77.28	70.25	1.03	5.07		7.03	
iii	88.64	68.19	20.45	76.25	69.21	1.02	4.98		7.04	
iv	91.01	70.39	20.62	78.51	71.39	1.00	4.85		7.12	
V	92.23	71.52	20.71	79.64	72.52	1.00	4.83		7.12	
vi	90.69	70.49	20.20	78.61	71.49	1.00	4.95		7.12	

	Crucible Mass + Sample, W_2	Crucible Mass, W_1	Sample mass, W_2-W_1	Crucible + Sample Mass at 270^0C, W_3	Crucible + Sample Mass at 560^0C, W_4	Mass of the Ash, W_4-W_1	% Ash Content	Average % Ash Content	Carbon Mass, W_3 - W_4	Average Carbon Mass
	8. POTATO PEELINGS									
I	88.37	68.11	20.26	72.24	68.99	0.88	4.34	4.29 ± 0.07	3.25	4.75
ii	86.56	66.34	20.22	71.48	67.23	0.89	4.40		4.25	
iii	85.61	65.28	20.33	71.40	66.15	0.87	4.28		5.25	
iv	87.38	66.97	20.41	73.10	67.84	0.87	4.26		5.26	
V	87.81	67.32	20.49	73.45	68.18	0.86	4.19		5.27	
vi	89.78	69.00	20.78	75.13	69.89	0.89	4.28		5.24	
	9. BANANA LEAVES									
I	88.54	68.12	20.42	74.48	70.54	2.42	11.85	11.90 ± 0.13	3.94	3.96
ii	86.86	66.55	20.31	72.96	68.96	2.41	11.87		4.00	
iii	87.61	67.39	20.22	73.74	69.81	2.42	11.97		3.93	
iv	86.60	66.48	20.12	72.83	68.91	2.43	12.08		3.92	
V	88.32	67.70	20.62	74.12	70.11	2.41	11.69		4.01	
vi	89.26	69.01	20.25	75.41	71.43	2.42	11.95		3.98	
	10. ONION STOCK WASTE									
I	86.18	66.36	19.82	71.76	67.87	1.53	7.72	7.51 ± 0.13	3.89	3.89
ii	88.54	68.23	20.31	73.66	69.75	1.52	7.49		3.91	
iii	89.93	69.48	20.45	74.91	70.99	1.51	7.38		3.92	
iv	91.23	70.52	20.74	75.94	72.05	1.53	7.39		3.89	
V	88.15	67.92	20.23	73.28	69.46	1.54	7.61		3.82	
vi	89.14	68.72	20.42	74.16	70.24	1.52	7.44		3.92	

APPENDIX 2:

Absorbance / Calibration curve for Calcium analysis

Table 5.2: Absorbance for Calcium standards

Concentration (ppm)	**Absorbance**
0	0
3	0.08
5	0.13
10	0.27
15	0.40

Equation: y=0.0268x - 0.001 R^2 = 0.9998

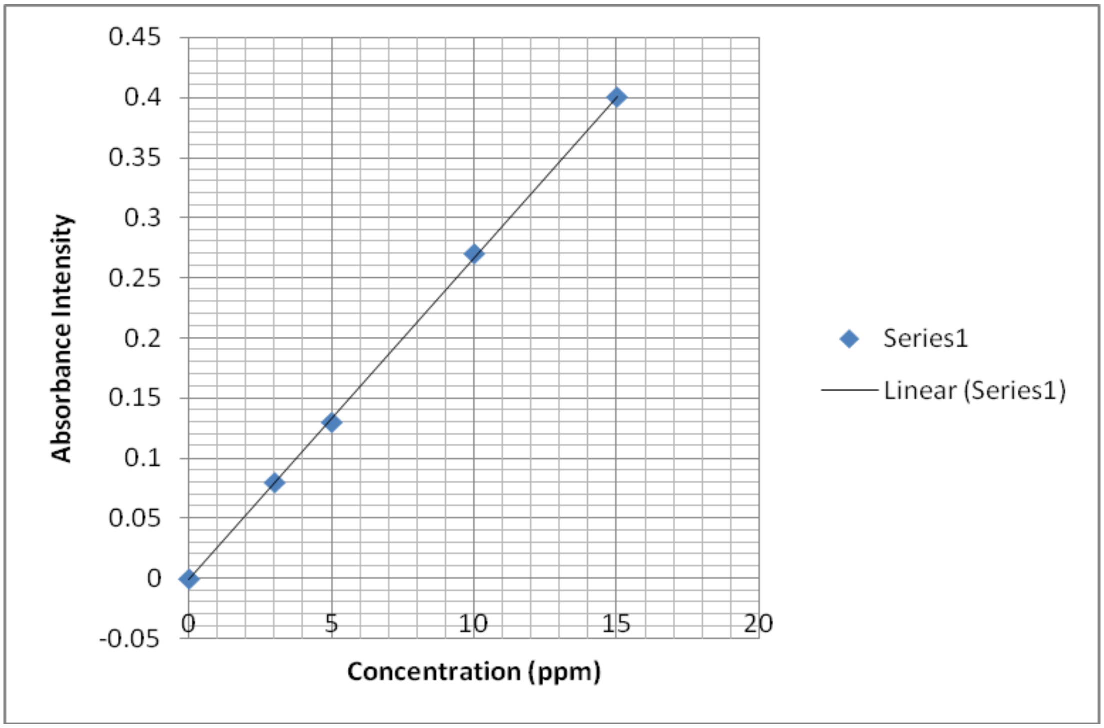

Figure 5.1: Calibration curve for Calcium analysis

APPENDIX 3:

Absorbance / Calibration curve for Iron analysis

Table 5.3: Absorbance for Iron standards

Concentration (ppm)	Absorbance
0	0
5	0.07
10	0.14
15	0.20
20	0.30
25	0.34

Equation: y=0.014x $R^2 = 0.9931$

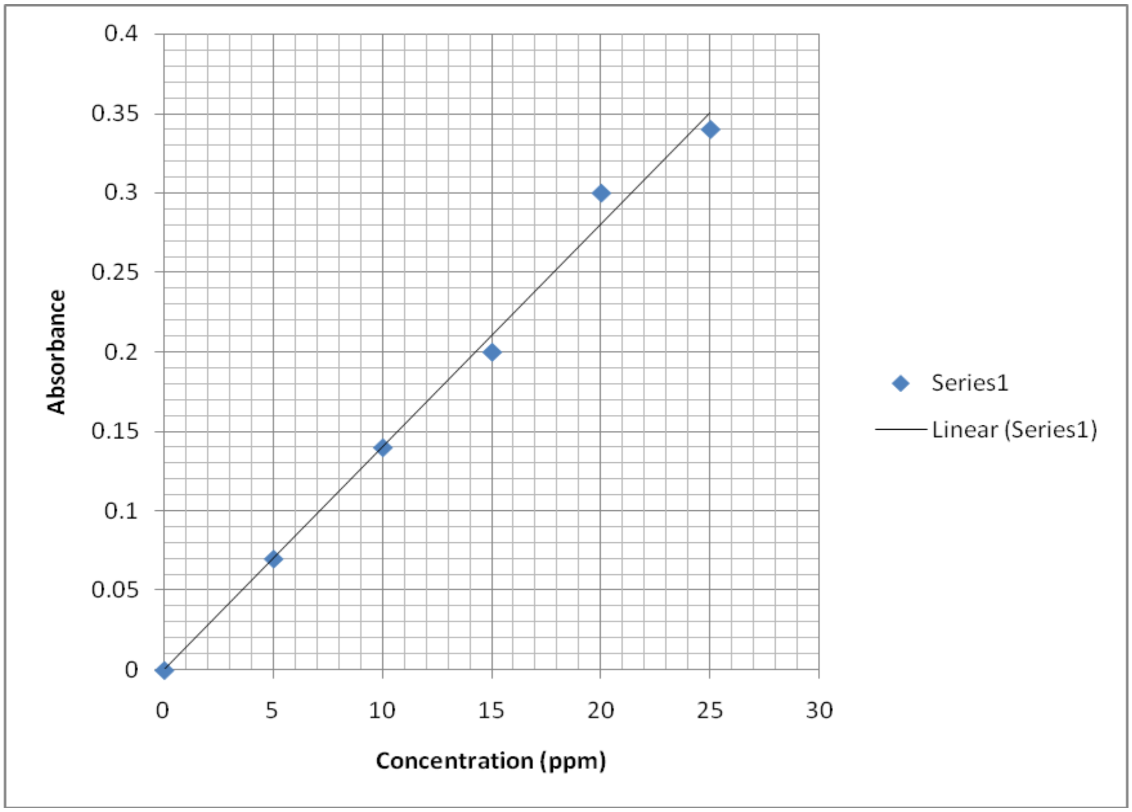

Figure 5.2: Calibration curve for Iron analysis

APPENDIX 4:

Emission Intensity / Calibration curve for Potassium analysis

Table 5.4: Emission Intensity for Potassium standards

Concentration(ppm)	Emission intensity
0	0
5	21
10	46
15	66
20	84
25	100

Equation: $y=4.051x + 2.1905$ $R^2 = 0.993$

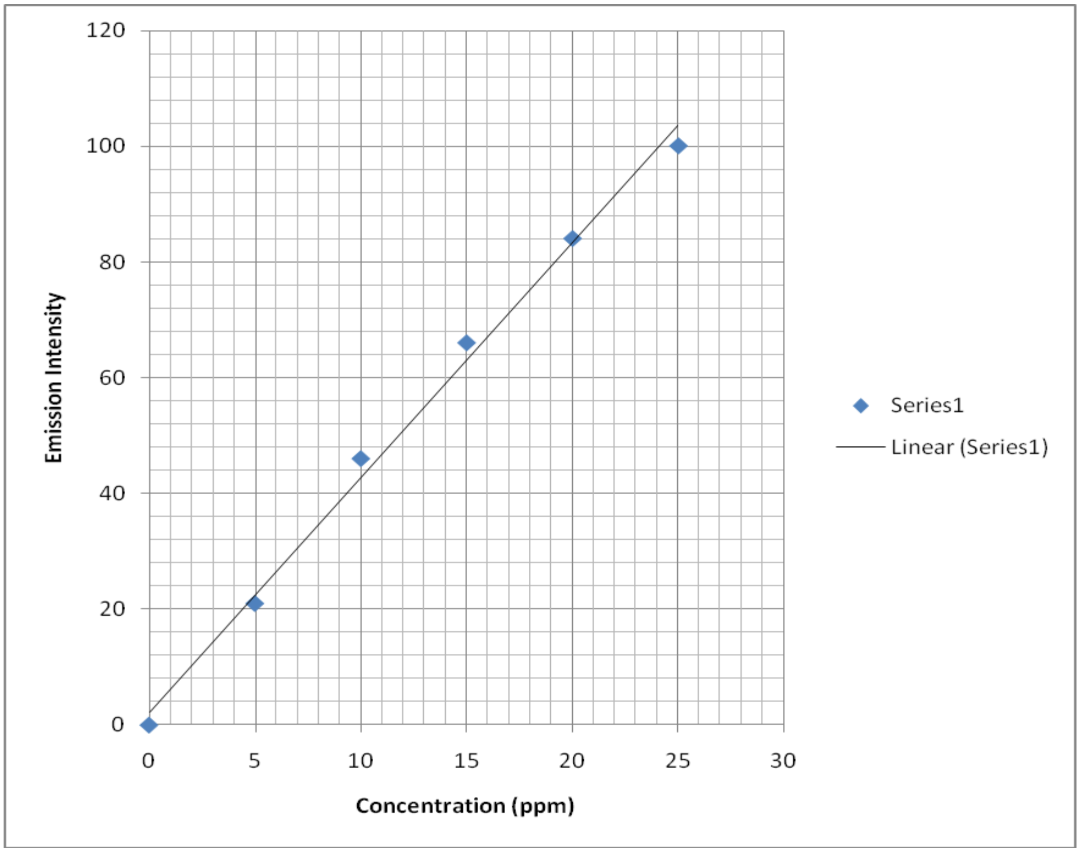

Figure 5.3: Calibration curve for Potassium analysis

APPENDIX 5:
Emission Intensity / Calibration curve for Sodium analysis

Table 5.5: Emission intensity for Sodium Standards

Concentration in ppm	Emission intensity
0	0
5	20
10	42
15	64
20	85
25	100

Equation: $y=4.097x + 0.619$ $R^2 = 0.9972$

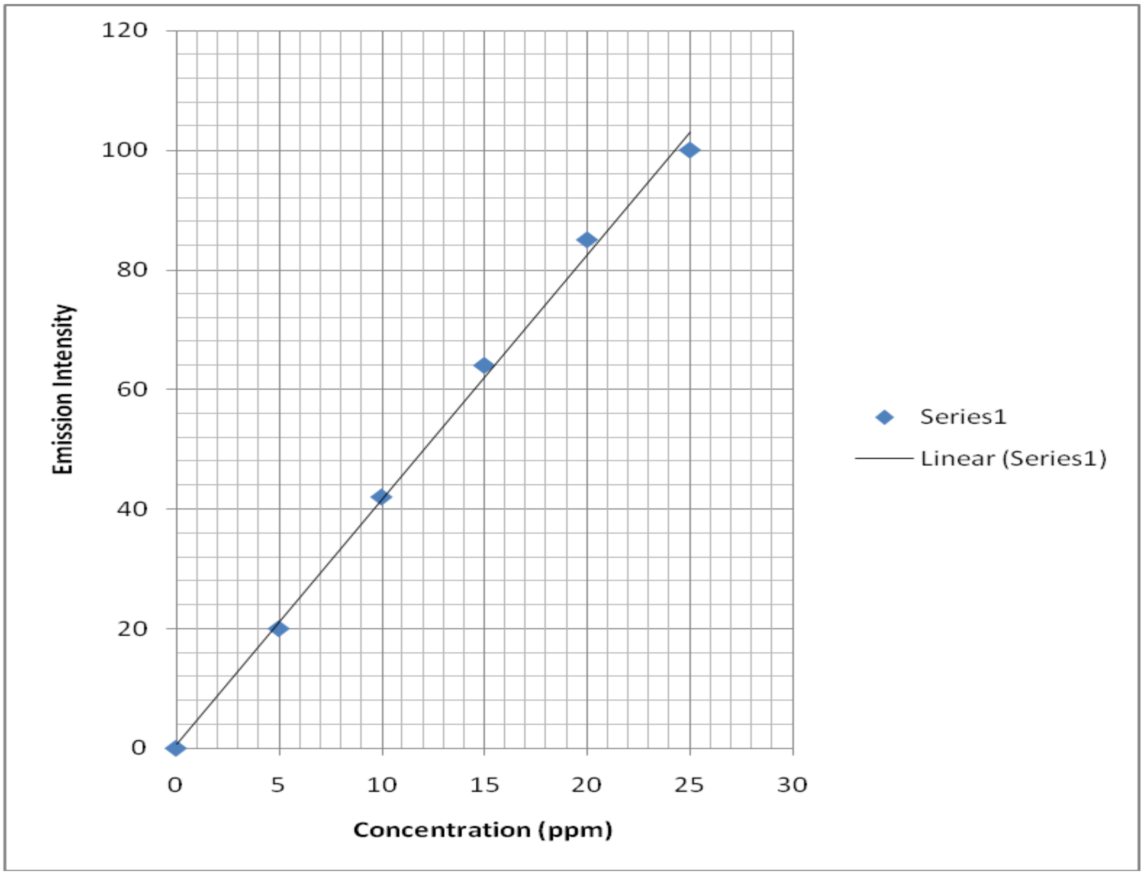

Figure 5.4: Calibration curve for Sodium Analysis

APPENDIX 6:
Absorbance / Calibration curve for Magnesium analysis

Table 5.6: Absorbance for Magnesium Standards

Concentration (ppm)	Absorbance
0	0
3	1.216
5	1.421
7	1.453
10	1.534
15	1.595

Equation: $y = 0.085x + 0.634$ $R^2 = 0.565$

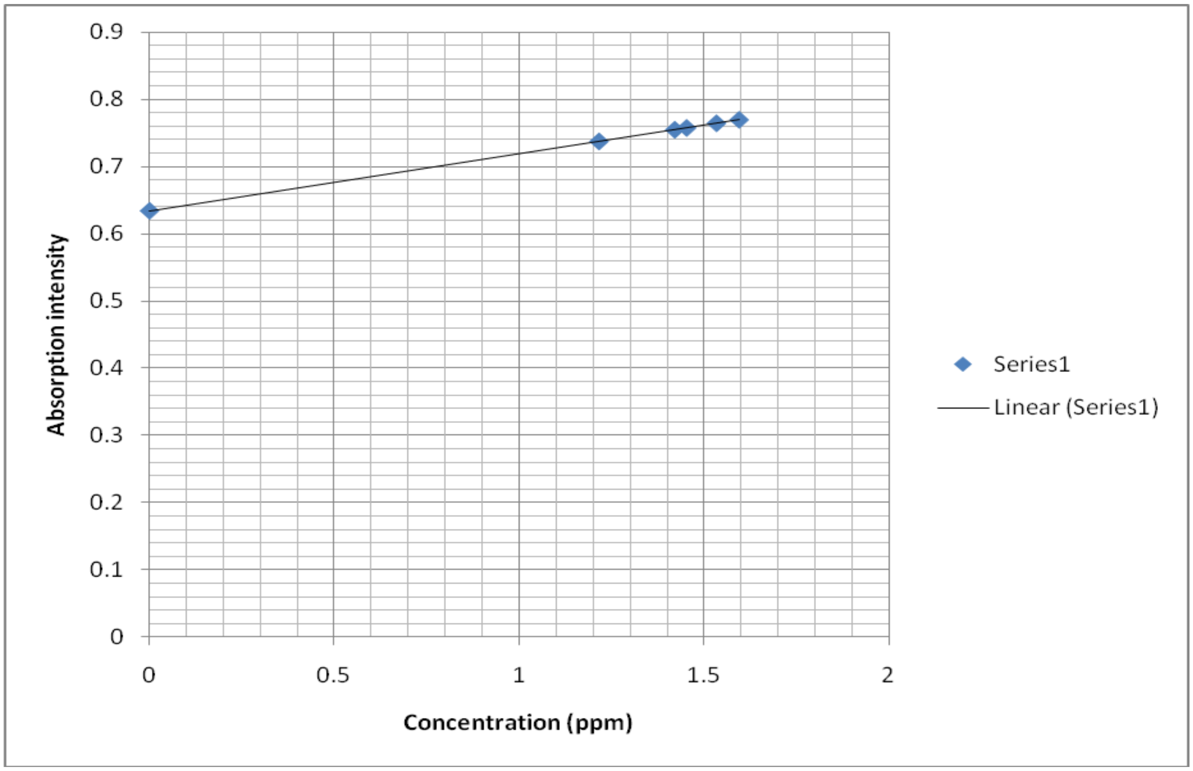

Figure 5.5: Calibration curve for Magnesium analysis

APPENDIX 7:

ANOVA Test

Table 5.7: ANOVA test. Comparing the levels of oxides in the various biomass samples

Oxide		**Sum of Squares**	**df**	**Mean Square**	**F**	**Significant (p-value)**
K_2O	Between Groups	41231.379	9	4581.264	1536.746	0.000
	Within Groups	417.360	140	2.981		
	Total	41648.739	149			
Na_2O	Between Groups	4749.915	9	527.768	723.372	0.000
	Within Groups	102.143	140	0.730		
	Total	4852.058	149			
MgO	Between Groups	35.979	9	3.998	513.010	0.000
	Within Groups	1.091	140	0.008		
	Total	37.070	149			
CaO	Between Groups	774.050	9	86.006	2118.895	0.000
	Within Groups	5.683	140	0.041		
	Total	779.732	149			
Fe_2O_3	Between Groups	17.367	9	1.930	1343.616	0.000
	Within Groups	0.201	140	0.001		
	Total	17.568	149			