PROXIMATE AND HEAVY METALS ANALYSIS OF COMMONLY CONSUMED TUBERS IN KANO METROPOLIS AND ENVIRONS

BY

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DECLARATION

I hereby declare that this work is the product of my research efforts undertaken under the supervision of Prof. M.D. Saeed and has not been presented anywhere for the award of a degree or certificate. All sources have been duly acknowledged.

…….. …….

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CERTIFICATION

This is to certify that the research work for this thesis and subsequent write up (SANUSI ADEBAYO BUARI SPS/13/MCH/00069) were carried out under my supervision

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DEDICATION

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ABSTRACT

A comparative analysis of the proximate composition and heavy metals concentrations of tubers and root crops commonly consumed in Kano and its envirDGDSGons was carried out. The tubers analyzed include yam, cocoyam, sweet potato, irish potato and cassava while the root crops include carrot, ginger, garlic and onion. All samples were washed, dried, digested and concentration of heavy metals was determined using atomic absorption spectrophotometer (AAS). Proximate analyses procedures including the percentage of carbohydrate, crude protein, crude fat, crude fiber, ash content and moisture content in the samples were carried using the Association of Analytical Chemists methods. Among the tubers analyzed, the carbohydrate content decreased in the order: Yam (66.58%) >Irish (65.85%) > cassava(64.63%) >sweet potato(64.33%) >cocoyam(62.78%). Crude protein was in the order: yam(5.02%) > irish (3.59%) >sweet potato(3.29%) > cocoyam(3.18%) >cassava(2.52%). Fat content was highest in cocoyam(4.74%) and lowest in cassava(3.16%). The moisture content was in the order irish potato (20.21%) > yam(18.11%) > cassava(13.07%) > sweet potato(3.39%) > cocoyam(1.39%). Ash content was highest in cocoyam(2.81%) and lowest in Irish potato (1.04%). Crude fibre was highest in cocoyam(25.45%) and lowest in Irish potato (4.10%). Cadmium (1.44mg/kg), Lead (0.89mg/kg) and chromium (0.62mg/kg) were highest in cocoyam. Copper was highest in Yam (2.87mg/kg) while Iron(10.26mg/kg)and zinc (9.85%) were highest in sweet potato. It can be inferred that apart from these tubers being a good source of carbohydrate in the daily diet, they also supply reasonable quantities of other nutrients.The proximate analysis of the spicy root crops shows that moisture and ash contents were highest in Carrot. Carbohydrate content was as follows; ginger (67.79%) > garlic (67.48%) > Onion (66.69%) > carrot (53.27%). Crude protein content decreased in the order: garlic (10.64%)>ginger(4.69%) > carrot(4.28%) > onion (2.42%). The result also shows that the spices are generally higher in mineral contents but lower in Carbohydrates.

CHAPTER ONE

1.0 Introduction

Root crops and tubers are used in the preparation of the major staples eaten in Nigeria and are estimated to contribute about 15% of the total calories and 8% of the total protein (Odebumi et al, 2004) in the daily diet of the average Nigerian. Tubers are the most efficient carbohydrates Producers. Tuber crops have been lesser attended to by the researchers the world over, being considered inferior food stuffs. The consequence of trace metals in foods such as tubers has been a considerable interest because of their toxic effects which are important to human beings (Sharma *et al*, 2004). Trace metals analysis is an important part of environmental pollution studies (Loska *et al*., 2004; Chibowski, 2000; Solecki *et al*, 2000; Narin *et al*., 1998; Czarrnowska and Milewska, 2000). Some trace metals are essential in plant nutrition, but plants growing in a polluted environment can accumulate trace elements at high concentrations, causing a serious risk to human health (Vousta *et al*. 1996; Sharma *et al*.,2004). Heavy metals are among the major contaminants of food supply and may be considered the most important problem to the environment (Zaidi *et al*, 2005). Such a problem is becoming more serious all over the world especially in developing countries. Considering the level of technological advancement in the developing world, it becomes very necessary to obtain accurate and reliable data on the concentrations of elements in the commonly consumed foods.

Food safety is a major public health concern worldwide and food consumption has been identified as the major pathway for human exposure to certain environmental contaminants, accounting for over 90% of intake compared to inhalation or dermal routes of exposure (Fries, 1995). About 30% of human cancers are caused by low exposure to initiating carcinogenic

contaminants in the diet (Tricker *et al*, 1990). Such contaminants include micro minerals (when higher than normal) and heavy metals. Micro minerals, also known as trace elements or trace minerals, include those nutrients that are required in milligram or microgram quantities by organisms on a daily basis (Berdanier *et al*, 2009). The chief function of microminerals, except boron and chloride, is to serve as constituents of prosthetic groups in metalloproteins and as activators of enzyme reactions. Without trace elements as a ‘‘spark plug’’, the enzyme system in organisms would simply be an inert mass of proteins (Gupta *et al*, 2008).

Heavy metals are among the major contaminants of food supply and may be considered as the most important problem to the environment. Such a problem is becoming more serious all over the world especially in developing countries. Heavy metal contamination of agricultural products may occur due to contamination with irrigation water, the addition of fertilizers and metal-based pesticides, industrial emissions, transportation, harvesting processes, storage and/or sale (Radwan and Salama, 2006). The ingestion of heavy metals (Cd, Ni, Pb, etc.) can cause depletion of some essential nutrients in the body, which in turn causes a decrease in immunological defences, intrauterine growth retardation, psychosocial dysfunctions, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer (Turkdogan *et al,* 2003).

In many plant species, there is restricted translocation of metals including copper, cadmium, lead and zinc from roots to shoots. Concentration of metals is low in shoots of tolerant plants. The metals are retained in cell wall in roots. The main sources of trace metals to plants are the air and soil from which metals are taken up by the root or foliage. The uptake of metal concentration by roots depends on speciation of metal and soil characteristics and type of plant species etc. Consequently, metal mobility and plant availability are very important when assessing the effect

of soil contamination on plant metal uptake, as well as translocation and toxicity or ultra structural alterations (Chandra *et al*., 2001). Airborne submicron particles are also filtered out on plant surfaces, constituting a substantial, but unknown contribution to the atmospheric supply. Indirect effects of air pollutants through the soil are also great interference, because of the large scale sustained exposure of soil to both wet and dry depositions of trace elements (Bernard *et al*., 2004). Information on the distribution of some of these metals in the various components of tubers contains the highest level of minerals and in assessing the nutritional and medicinal value of the various components for appropriate application. Equally, any component could serve as pollution indicators for some metals. The Heavy metals such as cadmium and lead are released mainly from the manufacture of batteries and zinc from zinc plating Industries. Zinc and copper were predominant in sewage sludge and is released in to the soil. The threshold value of acid soils is less because of greater solubility of metals (Zaidi, *et al*. 2005)

1.1 TUBERS

Tubers are enlarged structures in some plant species used as storage organs for nutrients. They are used for the plants perennation to provide energy and nutrients for regrowth during the next growing season and as a means of asexual reproduction. They can be in the stem or the root of the plant. African yam (Dioscorea rotundata), Cocoyam (Xanthosoma sagittifolium), water yam (Dioscorea alata), Cassava (Manihot esculenta), Sweet Potato (Ipomoea batatas) and Irish potato (Solanum tuberosum) are all grown widely and used in the preparation of a variety of foods in Nigeria (Olayide *et al* 1979; Ogunmodede, 1983).

1.2 COMMON TUBER

Common tubers in Nigeria include foods like yam, cassava, sweet potatoes, Irish potatoes and cocoyam, spices like garlic, onion, and ginger as well as vegetables like carrot.

1.2.1 Yam (Dioscorea rotundata)

Nigeria is the leading world producer of African Yam, responsible for about 71 % of world production (Onwueme, 1978). It is also known as the White Yam. The tuber is eaten mostly as boiled or pounded yam or processed into yam flour and reconstituted with boiling water into a paste known as *"amala*". Yam can be eaten fresh or used in the preparation of a porridge locally known as "*paten doya*" in Hausa or made into a pudding and fried as ojojo. (Imdiversity, 2006).

1.2.2 Cocoyam (Xanthosoma sagittifolium)

Cocoyam is a variant of yam and is used in essentially the same way as yam, although it is not considered as prestigious as yam. Cocoyam flour has the added advantage that it is highly digestible and so is used for invalids and as an ingredient in baby foods (Onwueme, 1978).

1.2.3 Cassava (Manihot esculenta)

Cassava is another very important staple food of Nigerians. It is grown for its enlarged starch-filled roots which contain nearly the maximum theoretical concentration of starch on a dry weight basis among food crops (Onwueme, 1978). Dried cassava roots can be milled into flour or it can be peeled, grated and washed with water to extract the starch which can be used to make bread, crackers, pasta and pearls of tapioca. Unpeeled roots can be grated, dried and used as animal feed. Cassava is used in the industry in the processing or manufacture of paper, textiles, adhesives, high fructose syrup and alcohol (O'Hair, 1995; Cock, 1985).

1.2.4 Sweet potato (Ipomoea batatas)

Sweet potato can also be used to prepare a variety of foods. It can be baked, boiled, fried, broiled, canned or frozen. Sweet potato originates from tropical America, but has been cultivated in most regions of the world (Onwueme, 1978; Yen, 1982).

1.2.5 Irish potato (Solanum tuberosum)

The Irish potato is originally a temperate crop but grows in high altitudes in tropical Africa such as the Plateau in Nigeria. The Irish potato can also be boiled, fried, baked or canned (Kay, 1973).

Some other root crops find application mainly as spices in food preparations and are very high in volatile oils. Many of these spices also have medicinal values and find wide application as therapeutic agents. The spices that were examined in this work include onion (Allium cepa), garlic (Allium sativum), ginger (Zingiber officinale) and carrot (Daucus carota).

1.2.6 Ginger (Zingiber officinale)

Ginger is used as an essential spice in curry powder, gingerbread and in some beers and other drinks. It helps to allay motion sickness and is used, especially in the Far East, as a digestive aid and a food preservative (Macrae *et al* 2002).

1.2.7 Onions (Allium cepa)

Onions are popular flavourings for soups and stews and are used medicinally to prepare the allium remedy which is used to treat complaints that make the eyes and nose water, such as colds and fever (Macrae *et al* 2002; Purseglove, 1972).

1.2.8 Garlic (Allium sativum)

Garlic, which belongs to the same family as onions, is used as a flavouring in cooking and pickling, sometimes in the form of whole or grated cloves and sometimes in the form of a cooked extract, as in sauces and dressings (Macrae et al 2002; Purseglove, 1972). In medicine, garlic is used as a digestive stimulant, diuretic, and anti-spasmodic.

1.2.9 Carrot (Daucus carota)

Carrot is a popular table vegetable and is a very rich source of vitamin A. Carrots are widely used in many cuisines, especially in the preparation of salads. Salads are a tradition in many regional cuisines. Carrots can be eaten in a variety of ways such as boiling, pulping, frying or steaming. It is also used in soups and in baby and pet foods (Purseglove, 1968).

1.3 PROXIMATE ANALYSIS

Proximate analysis is the partitioning of compounds in a sample into various categories based on the chemical properties of the compounds. Although proximate analysis does not give the entire nutritional essay, they are an inexpensive way to track deviations from the quality of foods. The analysis should always add to 100% and any deviation from this may arise from the resolution of chemical test i.e. small variations in the way each test is performed (Der *et al*., 2012).

Analytically, six constituents are obtained via chemical reactions and experiments. They include

1. Carbohydrates
2. Crude protein
3. Crude fat
4. Crude fibre
5. Moisture
6. Ash

1.3.1 Carbohydrates

Carbohydrates are the most abundant biomolecules on earth. Each year, photosynthesis converts more than 100 billion metric tons of CO_2 and H_2O into cellulose and other plant products. Certain carbohydrates (sugar and starch) are a dietary staple in most parts of the world, and the oxidation of carbohydrates is the central energy yielding pathway in most non-photosynthetic cells (Michelle et al., 1993). Carbohydrate polymers (also called glycans) serve as structural and protective elements in the cell walls of bacteria and plants and in the connective tissues of animals. Other carbohydrate polymers lubricate skeletal joints and participate in recognition and adhesion between cells. Complex carbohydrate polymers covalently attached to proteins or lipids act as signals that determine the intracellular location or metabolic fate of these hybrid molecules, called glycol conjugates. Carbohydrate are polyhydroxy aldehydes or ketones, or substance that yields such compounds on hydrolysis. Many, but not all, carbohydrates have the empirical formula $(CH_2O)_n$ and also contain nitrogen phosphorous or sulphur. (Nelson and Cox, 2008).

There are three major size classes of carbohydrates: monosaccharide, oligosaccharides, and polysaccharides. Carbohydrates perform numerous roles in living organisms. Polysaccharides serve for the storage of energy (e.g. starch and glycogen), and as structural components (e.g. cellulose in plants and chitin in arthropods). The 5-carbon monosaccharide ribose is an important component of coenzymes (e.g. ATP, FAD and NAD) and the backbone of the genetic molecule known as RNA. The related dioxyribose is a component of DNA. Saccharides and their derivatives includes many other important bio-molecules that play key roles in the immune system, fertilization, preventing pathogenesis, blood clotting, and development (Michelle *et al.,* 1993).

1.3.2 Crude Protein

Crude protein is the measurement of protein content in a sample. Proteins are body-building substances which are necessary to build up new cells and replace old ones. It is calculated mineral nitrogen value obtained by the kjeidahl method, or by a method giving similar results after correction, such as the Dumas method. They occur in the protoplasm of the plant cells, muscles i.e., flesh of vertebrate (as myosin), milk and cheese (as casein) as well as eggs (as albumin) (Ihekoronye et al., 1985). The elements contained in the proteins are carbon, hydrogen, oxygen and nitrogen. Someproteins also contain sulphur and phosphorous. Proteins are polymers of amino acids, with each amino acid residue joined to its neighbor by a specific type of covalent bond. Proteins can be broken down (hydrolyzed) to their constituent amino acids by a variety of methods.

Many proteins are enzymes that catalyze biochemical reactions and are vital to metabolism.Other proteins are important in cell signaling, immune responses, cell adhesion and cell cycle in animals, amino acids are obtained through the consumption of foods containing proteins.Ingested proteins are then broken into amino acids through digestion, whichtypically involves denaturation of the protein through exposure to acid and hydrolysis by enzymes called proteases, (Brosnan, 2003).

1.3.3 Crude Fat

Crude fat is the term used to refer to the crude maximum of fat soluble material present in a sample. Crude fat is also known as ether extractor the free lipid content, is a traditional measure of fat in food product. Lipids or fats can be broadly defined as hydrophobic naturally occurring molecules. The term is more specifically used to refer to fatty acids and their

derivatives (including tri-; di-;mono-glycerides anj phospholipids) as well as other fat soluble sterol-containingmetabolites such as cholesterol (Maton, 1993). Lipids serve many functions in livingorganisms including energy storage, serve as structural components of cell membranes, and constitute important signing molecules (Fahy*et al,* 2009) and (Subramania and Manoharan*, 2011)*. Chemically, fatty acids can be described as long-chain mono carboxylic acids, the saturated examples of which have a general structure of CH_3 $(CH_2)_nCOOH$. The length of the chain usually ranges from 12-24, always with an even number of carbon atoms the carbon chain contains no double bonds, and it is a saturated chain. If it contains one or more double bonds it is unsaturated. The presence of double bond reduces the melting point of fatty acids (Fahy *et al,* 2009).

Lipids play diverse and important roles in nutrition and health. Many lip absolutely essential for life; however, there is also considerable awareness that let certain lipids particularly cholesterol (in hypercholesterolemia) and, more recently fatty acids are risk factors for heart diseases among others (Micha and Mozaffarian, 2008).

1.3.4 Crude Fibre

Crude fibre is a measurement of indigestible cellulose, pentosans and lignin present in food. It is the insoluble residue of an acid hydrolysis followed by an alkaline one. This residue contains true cellulose and insoluble lignin. Fibres are structural components of plants. The type and amount of plants vary from one species to another. Dietary fibers are also the indigestible portion offood derived from plants (Parisi *et al*, 2002). There are two main fibre components; soluble and insoluble fibre. Soluble fiber dissolves in water; and it is readily fermented in the colon into and physiologically active by-products, and can be prebiotic and/or viscous. Soluble tend to slow

the movement of food through the system. Insoluble fiber does not dissolve in water. Bulking fibers absorb water as they move throuh the digestive system, easing defecation (Higgins, 2004), Dietary fibers can act by changing the contents of the gastrointestinal tract and by changing the way other nutrient chemicals are absorbed (Tungland and Meyer, 2002). Some types of insoluble fiber have bulking action and are not fermented (Parisi *et al,* 2002). Constipation can occur if insufficient fluid is consumed with a high fiber diet. (Leung, 2007).

1.3.5 Moisture Content

Moisture content is the quantity of water contained in a material, such as soil, rock, ceramics, fruit or wood. Water content is used in a wide range of scientific and technical areas, The level of moisture in foods varies depending on certain factors like storage, variety, geographical location and time of the year. The moisture content is often an important aspect of various food stuff and other dried goods, such as tea, where excess moisture can promote bacterial growth, decay, and molding overtime. Excessive moisture is usually undesirable and can also cause rot on wood or other organic materials, corrosion in metals and electrical short circuits (Nijjar, 1990).

1.3.6 Ash Content

Ash is the inorganic residue remaining after the water and organic matter have been removed by heating in the presence of oxidizing agents, which provides a measure of the total amount of minerals within a food. Analytical techniques for providing information about the total mineral content are based on the fact that that the minerals can be distinguished from all other components within a food in some measurable way. The most widely used methods are

based on the fact that minerals are not destroyed by heating, and that they have low volatility compared to other food components (Mc Clement, 2005)

1.9 Heavy Metals

Heavy metal is defined as a metal with specific density more than 5g/cm^3. Micro minerals, also known as trace elements or trace minerals, include those nutrients that are required in milligram or microgram quantities by organisms on a daily basis (Berdanier and Zempleni, 2009). Heavy metals are natural components of the earth crust. They cannot be degraded or destroyed. They enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc etc.) are essential to maintain the metabolism of the human body. However at higher concentrations they can lead to poisoning. Heavy metals are dangerous because they tend to bio accumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time. Compared to the chemicals Concentration in the environment, Heavy metal compounds accumulate in living things any time they are taken up and stored faster than they are broken (metabolized) or excreted. (Akubor *et al,* 2000).

Heavy metals such as zinc, copper, iron, manganese, lead, chromium, cadmium, nickel and cobalt are potential bio-accumulative toxins as soil tends to act as long term sinks for these metals (Alloway, 1995). Although different heavy metals display a range of different properties in the soil, loses are generally low and may occur through crop removal, leaching and soil erosion (Aldrich et al., 2002). Lead poisoning in humans causes severe dysfunction in the kidneys, reproductive system, liver and the brain and central nervous system; causing sickness or death (Manahan, 1997).

1.9.1 Nickel

Nickel is a naturally occurring element with many industrial uses, including the production of stainless steel, electroplating, pigments and ceramics. Nickel sulfide fumes and dust are believed to be carcinogenic (Dunnick *et al*., 1995) Nickel carbonyl {$Ni(CO)_4$, is an extremely toxic gas. The toxicity of metal carbonyls is a function of both the toxicity of the metal as well as the carbonyls ability to give off highly toxic carbon monoxide gas, and this one is no exception; nickel carbonyl is also explosive in air (Barceloux 1999). The most toxic form of nickel is its tetra carbonyl derivatives. Exposure to excess of this derivative causes dermatitis, respiratory disorder, lung cancer, dizziness, nausea, vomiting followed by rapid respiration and death (Eisenberg *et al.,* 1994).

Nickel has been noted as an essential trace metal in experimental animals. Though nickel has occupational and inhalation effects, nickel compounds are also potent carcinogens in experimental animal models (Costa, 2000).

1.9.2 Copper

Copper is an essential micro-nutrient in humans as it functions as a factor for many enzymes (Chancy, 1992). It is not very toxic to animals, plants and algae at moderate levels. However in sufficient concentration, copper compounds are poisonous to higher organisms. It used as bacteriostatic substances, fungicides and wood preservatives (Manahan, 1997). The main areas where copper is found in humans are liver, muscle and bone (Johnson and Larry, 2008)

1.9.3 **Lead** (Pb)

Lead has since been known to mankind as a non-essential element since it has no specific function in the body system. Its natural concentrations are not high in the environment (Ewers and Schlipkoter, 1991). Atmospheric lead is an important component of street dust. Other sources are leaded gasoline, tyre wear, lubricating oil, grease and metal bearing wear. The improper disposal of leaded batteries is another source of lead pollution (Hodel and Chang 2004). Lead gets into man through his diets and by inhalation. It has been found that one-third of the daily lead intake by man comes through inhalation and the remaining two-thirds from diets. Thus, it accumulates to cause toxicity and can be found prevalently in soft tissues of the body such as the liver, kidneys and brain (Ademoroti, 1991). When ingested to certain amount, lead becomes a poisonous substance to animals as well as for human beings. It damages the nervous system and causes brain disorder, Excessive lead also causes blood disorders in mammals. Animal tissues with the highest concentrations are liver, kidney and bone and lead concentrations in milk are usually much lower than blood levels. Bl'uthgen (2000) reported a carry-over percentage from feed to milk of 0.1-1%.

1.9.4 **Cobalt** (Co)

Cobalt is present in trace amounts in soil, plants and in our diets, It usually occurs in association with other metals such as copper, nickel, manganese and arsenic. Cobalt is an element that occurs naturally in many different chemical forms throughout the environment. Small amounts of cobalt are essential for good health. Natural sources of cobalt in the environment are soil, dust, seawater, volcanic eruptions and forest fires. (Vouk and Piver, 1983).

Cobalt and its salts are used in a variety of processes to make super alloys, which maintain their strength at high temperature; as paint drier; as a ground coat for porcelain enameling used on steel bathroom fixtures and large appliances, and as an ingredient of colored pigment. Co, a radioactive isotope of cobalt is an important source of gamma rays and is used to treat some form of cancer and as a medical tracer. (Audi *et al*, 2003).

Cobalt inhibits cellular respiration and enzymes of the citric acid cycle. Workers exposed to cobalt containing dusts develop progressive pulmonary fibrosis and other forms of lungs damages. It is weakly mutagenic (Gennart *et al* 1993). Cobalt is beneficial for humans because it is a part of vitamin B (cyanocobalamin), which is essential for human health. Cobalt is used to treat anemia in pregnant women, because it stimulates the production of red blood cells. (Cracan and Banerjee, 2013).

1.9.5 Manganese (Mn)

Manganese is found in nature (often in combination with iron), and in many minerals. Manganese is a metal with important industrial metal alloy uses particularly in stainless steel. Manganese phosphate is used as a treatment for rust and corrosion prevention on steel. Depending on their oxidation state, manganese ions have various colors and are used industrially as pigments. The permanganates of alkali and alkaline earth metals are powerful oxidizers. Manganese dioxide (MnO_2) is used as the cathode (electron acceptor) material in standard and alkaline disposable dry cells and batteries.

In Biology, manganese (II) ion functions as cofactors for a large variety of enzymes with many functions (Roth *et.al,* 2013). Manganese enzymes are particularly essential in detoxification of superoxide free radicals in organisms that must deal with elemental oxygen. Manganese also

functions in the oxygen evolving complex of photosynthetic plants. Manganese is an important metal for human health, being absolutely necessary for development, metabolism and the antioxidant system. Nevertheless, excessive exposure or intake of manganese may lead to a condition known as manganism, a neurodegenerative disorder that causes dopaminergic neuronal death and parkinsonian-like symptoms (Daiana *et al*., 2013).

1.9.6 Zinc (Zn)

Zinc is an essential trace element involved in major metabolic functions in all living organisms. It is found in all human tissues and body fluids (Ohnesorge and Wilhelm, 1991). Zinc is a component of over 300 enzymes needed to repair wounds, maintain fertility in adults and growth in children, synthesize protein, helps in reproduction of cells, preserve vision, boost immunity and protect against free radicals (Ohnesorge and Wilhelm,1991). It is "typically the second most abundant transition metal in organism" after iron andit is the only metal which appears in all enzyme classes (Broadley *et al,* 2007). There are 2-4 grams of zinc (Rink and Gabriel, 2000) distributed throughout the human body. Most zinc is in the brain, muscle, bones, kidney and liver, with the highest concentrations in the prostate and parts of the eye (Wapnir, 1990). Semen is particularly rich in zinc, which is a key factor in prostate gland function and reproductive organ growth (Berdanier et al., 2007).

The toxicity of zinc is low and with certain exception of importance compared with the significance of its deficiency (Ohnesorge and Wilhelm, 1991).

1.9.7 Cadmium (Cd)

Cadmium occurs as a minor component in most zinc ores and therefore is a by-product of zinc production. It was used for a long time as a pigment and for corrosion resistant plating on steel, while cadmium compounds were used to stabilize plastic. With the exception of its use in nickel-cadmium batteries and cadmium telluride solar planets, the use of cadmium is generally decreasing. Although these declines have been due to competing technologies, cadmium's toxicity in certain forms and concentration and resulting regulations (Marrow, 2010), Cadmium has no biological function in higher organism. Cadmium-dependent carbonic anhydrate has been found in marine diatoms (Micheal, 2010). The diatoms live in environments with very low zinc concentration.

Inhaling cadmium-laden dust quickly leads to respiratory tract and kidney problems which can be fatal (often from renal failure). Ingestion of any significant amount of cadmium causes immediate poisoning and damage to liver and kidneys. Compounds containing cadmium are also carcinogenic.

1.9.8 Chromium (Cr)

Chromium is a metal that exists in different forms, divalent, trivalent and hexavalent. Trivalent chromium (Cr^{3+}) occurs in trace amounts in foods and water, and appears to be benign (Mertz, 1993). In contrast, hexavalent chromium (Cr^{6+}) is very toxicand mutagenic when inhaled. Cr^{6+} has not been established as a carcinogen in solution, although it, may cause Allergic Contact Dermatitis (ACD) (ATSDR, 2001). Hexavalent chromium has many uses. It is used as pigment in paints, inks and plastics, as an anticorrosion agent in protective coating, and

in chromate plating. Textile dyes e.g. ammonium dichromate $(NH_4)_2Cr_2O_7$, sodium chromate Na_2CrO_4, potassium chromate K_2CrO_4 contain hexavalent chromium.

Chromium has no verified biological role and has been classified by some as not essential for mammals (Bona et al., 2011).

Aim and Objectives of the Research

This research is aimed at analyzing the concentration of heavy metals commonly consumed tubers in Kano. The objectives of the study are as follows:

1. To ascertain the proximate composition of some common tubers in Kano Metropolis and its environs.
2. To determine the level of Heavy metals in the Tubers using Atomic Absorption Spectrometry (AAS) technique.
3. To find out whether these heavy metals are within the permissible limit or not by comparing with limits set by regulatory bodies.

CHAPTER TWO

2.0 Literature Review

A lot of research works have been conducted on the analysis of tubers. Among them is the assessment of tubers obtained from five different markets from Kumasi, Ghana by Apauet *et al* (2014). The pulverized samples were digested with concentrated nitric acid. Heavy metals Zn, Fe, Cu and Cd were analyzed using Atomic Absorption Spectroscopy in four tubers which include yam, cassava, cocoyam and sweet potatoes. The metals were analysed using Atomc Absorption Spectrophotometer 220. The concentration ranges were 0.862 to 2.144 mg/kg for Cu, 0.476 to 0.778 mg/kg for Cd, 11.246 to 58.728 mg/kg for Zn and 27.918 to 45.872 mg/kg for Fe. Health risk assessment showed that consumers are not in danger as far as these metals are concerned.

Divya *et al* (2015), conducted a study in three different markets of Ernakulam district, India to check the concentration of heavy metal in tuber foods. The accumulation of heavy metals was studied in the tubers which included elephant yam, potato, sweet potato, tapioca and yam, were collected from three different markets of Ernakulam district (Cochin, Thripunithura, Ernakulam). All the collected samples were washed, dried, digested and the concentration of heavy metals was found out using atomic absorption spectrophotometer (AAS). They observed that the peeled samples were having less concentration of metals than the unpeeled samples collected from three markets. The samples were collected from Thripunithura market showed more contamination than other two samples. The Zinc content of few samples exceeded the Food Adulteration Act (PFA) limit. The copper content was not that much high compared to PFA limit in all the

observed samples. The cadmium content of most samples exceeded the PFA Limit while the lead content of all samples were above the PFA limit.

Alinnor *et al* (2010) analyzed Dioscorea rotundata (white yam) and Colocasia esculenta (white cocoyam) for their proximate and mineral compositions. The result showed that Dioscorea rotundata had moisture content of 54.50%, ash content 1.4%, crude fat content 2.70%, crude protein content 0.087%, crude fibre content 0.70%, carbohydrate content 40.61%, available energy 731.75 kJ; while Colocasia esculenta had moisture content 38.50%, ash content 1.60%, crude fat content 1.05%, crude protein content 0.066%, crude fibre content 1.0%, carbohydrate content 57.78%, available energy 1022.27 kJ. Heavy metals were determined with Atomic Absorption Spectrophotometer (AAS). The mineral content of the analyzed samples showed that Dioscorea rotundata and Colocasia esculenta were rich in iron with values of 81.85mg/100 g and 59.07mg/100g respectively. The copper content of the samples were 10.06 mg/100 g and 6.72mg/100g for Dioscorea rotundata and Colocasia esculenta respectively. Similar results were obtained during the evaluation of the proximate and mineral element composition of sweet cassava specie (Mannihot esculenta) from Ohaukwu and Iboko communities of Ebonyi State, Nigeria by Madubuike *et al* (2014). Proximate analysis results of cassava specie from Ohaukwu were as follows; Crude protein (0.96%), moisture (5.00%), carbohydrate (83.84%), Crude fibre (7.60%), Ash (2.00%), and Lipids (0.60%). Its cyanide content was obtained as 1.91mg/kg, while the mineral elements composition were as follows, Ca (0.28mg/kg), Cu(1.49mg/kg), Mn(6.20mg/kg), Mg (0.50mg/kg), Na(0.04mg/kg), Fe(7.88mg/kg), Zn(10.01mg/kg), Pb(0.25mg/kg), Cd(0.006mg/kg) and K(5.28mg/kg). The cassava specie from Iboko had its proximate composition as follows: Crude protein (0.8%), moisture (6.4%), Crude fibre (7.35%), Ash (2.40%), Lipids (0.34%), and Carbohydrate (82.33%), while the Cyanide content was

2.02mg/kg. Its mineral element compositions were as follows; Ca (0.32mg/kg), Mg (0.54mg/kg), Na (0.03mg/kg), Fe (7.31mg/kg), Zn (8.03mg/kg), Mn (6.75mg/kg), K (5.04mg/kg), Pb (0.23mg/kg), Cd (0.011mg/kg), and Cu (1.50mg/kg).

Soil and crop samples collected during the 2005/2006 rainy and dry seasons were treated and digested using standard wet digestion methods (Olayemi *et al*, 2008). Heavy metals were determined with Atomic Absorption Spectrophotometer (AAS). Analytical results of soil from landfill indicated that in the wet and dry seasons, values for Cd, Cu, Fe, Ni, Cr, Zn, Co and Pb were higher than normal levels of a typical agricultural soil, but As (3.20 and 4.13mg/kg) was found to be within the acceptable range while Mn values of 597.00 - 828.37 mgkg-1 were slightly above the usual background levels. The study showed highest concentrations of As (8.31mg/kg), Cr (9.00 mg/kg) and Ni (40.00 mg/kg) in Manihot esculenta leaves; Cu (25.0 0 mg/kg) and Fe (176.00 mg/kg) in Xantosoma mafaffa tuber; Cd (14.50 mg/kg), Co (22.50 mg/kg), Mn (189.50 mg/kg), Pb (680.00 mg/kg) and Zn (440.59 mg/kg) in Talinum triangulare. In general, the levels of heavy metals in soil and crops were higher in the dry season than in the wet season, but this difference is not statistically significant. Particularly, the levels of As, Cd, Cr, Ni, and Pb were above the critical toxiclevel in plant leaves in both dry and wet seasons while Zn and Cu occurred at toxic levels only in the dry season.

The concentrations of heavy metals (Ni, Zn, Cu, Pb and Fe) were determined in cassava from farmlands in kaani and Kpean Communities in Khana Local Government Area of Rivers State, Nigeria by Kalagborka, 2015. Samples were collected, prepared, digested and analyzed using AAS. The levels of heavy metals obtained for cassava samples from Kaani were Ni (5.71 mg/kg), Cu (2.45 mg/kg), Fe (92.4 mg/ kg), Pb (6.57 mg/kg), Zn (9.64 mg/kg) were recorded. The levels of heavy metals obtained for samples from Kpean were Ni (4.09 mg/kg), Cu (9.64

mg/kg), Fe (6.34 mg/ kg), Pb (13.44 mg/kg), Zn (0.22 mg/kg). Results showed that the levels of these heavy metals Ni, Cr, Cu, Pb and Fe in these food crops were found to be relatively high when compared with FAO/WHO recommended values with crops from Kpean farms having higher values. The most essential element Zn was found to have values below the acceptable limits for cassava and plantain from both farmlands. Proximate analysis of yam (D. cayenensis, D. dumetorum, and D. bulbifera) and cocoyam (Xanthoso mamaffa) was carried out and the average proximate composition of the yams and cocoyam samples were as follows: moisture 665gkg-1, crude protein 52.4gkg-1, crude fiber 52.5gkg-1, crude fat 3.4gkg-1, ash 31.5gkg-1 and carbohydrate 195gkg-1 (Anthony N. Ukom et al, 2014).

The levels of heavy metals in Dioscorea rotundata (white yam) and Ipomoea batatas (sweet potato) by Wilberforce (2013) were examined using X-ray Fluorescence (XRF) technique. The results revealed that heavy metal decreased in the order Pb> Zn > Cu >Mn>Cd >Ni > As > Cr. The mean concentration (mg kg-1) of metals was found in the range of Pb (0.04-0.14); As (0.02-0.04): Cd (0.02-0.04); Cu (40.12-62.12); Cr (0.01-0.21); Zn (24.18-74.60); (Mn 18.46-84.90); and Ni (8.24-14.86).

Analysis of yam tubers was done in Ibadan by Adepoju et al (2012). The yam was peeled and cut into small pieces, then divided to eight portions. One portion was treated as raw sample while others were processed into roasted, fried, boiled, pounded yam (two samples), *amala* and porridge. All samples were analysed for proximate, energy and mineral composition using standard methods of AOAC (2005) and atomic absorption spectrophotometric methods. Raw yam was very low in crude protein (2.3%), lipid (0.8%), and fibre (1.4%) moderate in ash (3.4%), iron (4.1mg/kg) and zinc (5.6mg/kg), high in carbohydrates (33.3%), energy (369.6kcal), sodium (580mg/kg) and potassium (470mg)/kg) edible portion. Roasting and frying brought

significant improvement on crude protein, lipid and energy content of the products ($p<0.05$). Boiling yam caused significant reduction in all nutrient content except fibre, while boiling and pounding yam significantly improved its crude lipid, ash and energy content with $p>0.05$ showing there was a significant difference. Frying and using water for boiling yam in pounded yam preparation brought significant retention of nutrients in yam. Processing yam to *amala* and porridge resulted in significant improvement in nutrient content of the diets. Diets from yam can serve as good source of energy and minerals, and their 100g portion can contribute between 12.4 to 20.9% gross energy, 11.0 to 46.0% iron and 17.3 to 48.7% zinc to recommended dietary allowances (RDAs) of consumers.

According to Martin *et.al* (2010), some biochemical parameters of different parts of two varieties of edible yams tuber "Florido" (Dioscorea alata) and "Krenglè" (Dioscorea cayenensis-rotundata) were monitored during storage. The statistical analyses related to analysis of variance (ANOVA) carried out on these eleven variables showed that the proximate and mineral composition of different parts of yam tuber were significantly different at 0.05 level between them and during the storage. Indeed, the total ash and carbohydrate contents increased significantly ($P > 0.05$) during the conservation from month 0 to month 6 and varied from one tuber part to another. The ash content was highest in the proximal parts, while the carbohydrate contents were higher in the distal parts. Contrary to these variables, the lipids and the crude protein contents didn't vary significantly at 0.05 level from a tuber part to another one during the storage period which lasted six months.

A study by Öztürket. al (2011) examined concentrations of some heavy metals (Fe, Cu, Zn, Mn, Pb, Ni and Cd) from sixteen potato cultivars grown at Erzurum, Turkey using atomic absorption spectrophotometry (AAS). The study revealed that the potato cultivars had a considerable

variation in heavy metal concentrations. The contents of heavy metals in the potato cultivars were found in the ranges: 48.87-72.64 mg kg^{-1} for iron, 3.07-5.43 mg kg^{-1} for copper, 13.80-18.89 mg kg^{-1} for zinc, 6.93-13.06 mg kg^{-1} for manganese, 0.51-0.77 mg kg^{-1} for lead, 2.02-3.55 mg kg^{-1} for nickel and 0.08-0.32 mg kg^{-1} for cadmium. The accumulation pattern for the metals in the potato tubers was in the order; Fe>Zn>Mn>Cu>Ni>Pb>Cd.

According to a study by Meludu (2010) sweet potato was processed and toasted into granules. The proximate analysis performed on the toasted granules showed protein, fat, ash, fiber, starch, moisture and low sugar content after processing. It was discovered that the more fermented the paste before toasting the lower the sugar content and more acceptable the taste. Therefore, the remarkable low sugar content indicates potential usefulness as a dietary supplement for diabetic patients. Its fiber content will add bulk and aid digestion, thus preventing constipation. Therefore, awareness should be created on this innovation for the management of the diabetics.

The proximate and elemental composition of some standardized sweet potato dishes in Kwara state was determined using official methods of analysis (Abubakar 2010). The indigenous sweet potato dishes analysed included pounded sweet potato/yam; sweet potato leaf soup; boiled sweet potato; fried sweet potatoes and sweet potato/beans pottage. There were significant differences ($p < 0.05$) for proximate analysis as well as mineral contents of the sweet potato dishes. The moisture contents varied between 35.15% in sweet potato and pounded yam to 70.54% in sweet potato leaf soup. The highest protein content of 12.21% was found in sweet potato leaf soup and least value of 1.42% in sweet potato and pounded yam. The fat content of the samples ranged from 0.30% in sweet potato boiled to 3.88% in sweet potato leaf soup. Sweet potato boiled sample had the highest carbohydrate content of 70.54% while sweet potato leaf soup sample had the least value of 25.74%. The ash contents varied from 1.13% in sweet potato boiled to 8.83%

in sweet potato leaf soup. The sweet potato leaf sample had the highest content of iron 8.82 ± 0.05 mg/100g while boiled sweet potato sample was highest in zinc (0.26 ± 0.01mg/100g) among all the dishes. The contributions of these varied nutrient contents to reducing the nutritional problems in the society were discussed.

The levels of some trace metals (Fe, Zn, Cu, Ni, Cd) were quantitatively determined in raw and heat processed staple food cultivars (yam, cassava and cocoyam) from oil producing areas of part of the Niger Delta and compared with a non-oil producing area of Ebonyi State as control using atomic absorption spectrophotometer (AAS) (Akaninwor, 2006). The survey was conducted to evaluate the role of foods as exogenous source of these metals among the inhabitants. The data showed that metal levels in all the raw staple foods from oil producing areas were significantly different at ($p<0.05$) than those from non-oil producing areas. However, lead levels of all the raw staple foods in all the studied areas were below detectable levels. Exceedingly higher levels of these metals characterized the raw staple food cultivars from oil producing areas than those from non-oil producing area and on heat treatment the levels were reduced. These high levels are indicative of extensive pollution in these areas under study suggesting possible health risks in consumption of food cultivars from such areas.

Analysis was carried out on the cassava flour to ascertain the levels of some toxic contaminants like cyanide lead, cadmium and nickel introduced into the food naturally or as a result of human activities (Abimbola, 2009). At selected sites, twenty samples were collected, digested and analyzed. Cyanide in the cassava flour was determined by UV-Visible spectrophotometer. Lead, cadmium and nickel were determined using Atomic Absorption Spectrophotometer (AAS). The mean concentration levels in mg/kg of cyanide, lead, cadmium and nickel in the cassava flour from the urban areas were 0.07±0.03, 0.13±0.14, 0.03±0.02 and 0.60±0.18 respectively. These

were higher than the mean concentration levels, 0.03±0.02, 0.04±0.10, 0.02±0.01 and 0.36±0.11 respectively determined in the cassava flour from the rural areas. However, all the determined levels of these elements from both urban and rural areas are far below the WHO guideline values or permissible levels of cyanide and metal in food. This implies that cyanide and the metal toxicants are present in the cassava flour in such low concentrations that render the food non-toxic.

CHAPTER THREE

3.0 Methodology

3.1 Material and Methods

All the plastic and glass wares were washed with detergent and rinsed with water before immersion in 10% nitric acid solution. They were finally rinsed with deionized water. Analytical grade reagents and deionized water were used throughout the analysis.

3.2 Preparation of reagents

3.2.1 Preparation of 0.1mol/dm^3 HNO_3 acid

6.30cm^3 of Concentrated HNO_3 **(S.G** 1.42; 70% v/v) was gradually added to water into half filled 1000cm^3 volumetric flask and then made up to the mark.

3.2.2 Preparation of 0.13M H_2SO_4 acid

6.93cm^3 of Concentrated H_2SO_4 (S.G 1.84, 97% v/v) was gradually added to water into half filled 1000cm^3 volumetric flask and then made up to mark.

3.2.3 Preparation of 40% NaOH (w/v)

40g of solid NaOH was dissolved in a 100ml volumetric flask with deionized water and made up to the mark.

3.2.4 Preparation of 0.02MHC1 acid

1.72cm^3 of Concentrated HCl (S.G 1.18, 36% v/v) was gradually added to water into half filled 1000cm^3 volumetric flask and then made up to mark.

3.2.5 Preparation of 0.313M NaOH

2.504g of solid NaOH was dissolved in 200cm^3 of deionized water in a volumetric flask.

3.2.6 Preparation of 2% H_3BO_3

2g of solid H_3BO_3 acid was dissolved in 100ml volumetric flask with deionized water and made up to the mark.

3.3 Sampling

Nine tuber crops; five foods (yam, cocoyam, sweet potato, Irish potato, cassava) and four spices(carrot, ginger, onion, garlic) commonly consumed by Kano populace were purchased from major food markets in the state which include Yan Kaba market, Yan Kura Market and Dambatta Market.

3.4 Proximate Analysis

Proximate analysis is the partitioning of compounds in a sample into various categories based on the chemical properties of the compounds. Although proximate analysis does not give the entire nutritional essay, they are an inexpensive way to track deviations from the quality of foods (Der et al., 2012). The samples were subjected to proximate analysis in accordance with standard methods described by (AOAC, 2005). Each of the samples was oven dried at about 80ºC for 24 hours and then ground into a powder which was then used for the analyses.

3.4.1 Moisture content Determination

A clean Petri-dish with lid was dried in an oven at 105^0C for 3hours and then transferred to a desiccator to cool and weighed (W_1). The sample (3g) was weighed in a 2x2 Petri-dish (W_2). The dish was then placed in an oven and dried at 105°C until a constant weight was achieved. After drying, the dish was then transferred to a desiccator to cool and then reweighed with its content (W_3) (AOAC, 2005).

Calculation:

$$\%\text{moisture} = \frac{\text{loss of weight in drying}}{\text{Weight of sample taken}}$$

$$= \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

Where W_1= weight of empty petri-dish

W_2= weight of petri-dish + sample

W_3= weight after drying

3.4.2 Crude Fat Determination

The sample (3g) was carefully weighed (W_1) into a folded fat-free filter paper. This was properly folded and weighed (W_2), and was carefully placed in a soxhlet extractor. The whole apparatus was then connected after addition of about 300ml of 60°-80°C petroleum ether into the weighed extraction flask. The extraction was then carried out for 3 hours using the heating mantle and making sure there was continuous flow of water in the condenser. The sample was then removed, air-dried and then

placed in an oven at 80°C until a constant weight was obtained (W_3). The extractible lipid was then calculated as percentage Crude fat (%) (AOAC, 2005).

$$\% \text{ Crude fat (w/w)} = \frac{W_2 - W_3 \times 100}{W1}$$

Where W_1= weight of sample

W_2= weight of sample + filter paper

W_3= weight of "sample + filter" after extraction

3.4.3 Crude Fiber Determination

Crude fiber was determined by subjecting 3g of the dried samples from moisture analysis and ether extraction to successive treatments with boiling 200cm^3 of 0.13M H_2SO_4 acid under reflux for 30mins, washed several times with hot water until it was acid free (litmus paper was used to check). The residue was again subjected to the same treatment using 200cm^3 of 0.31M NaOH solution, washed thoroughly with hot water until it was base free. It was then dried to a constant weight in an oven at 100^0C, cooled in desiccators and weighed. The weighed sample was incinerated in a muffle furnace at 550°C until a constant weight was obtained. The crude fibre was calculated as the loss in weight on ashing (AOAC, 2005).

Calculation

$$\% \text{ crude fiber} = \frac{W_1 - W_2 \times 100}{W3}$$

W_1 = weight of sample extracted + filter paper

W_2 = weight of "Wl" after ashing

W_3 = weight of sample used (3g)

3.4.4 Crude Protein Determination

Exactly 0.15g of dried (moisture free) sample was weighed and the content was transferred into the Kjeldahl digestion flask. 0.8g of the catalyst (mixture of 0.7g sodium sulphate, 0.06g copper sulphate, and 0.04g mercury (II) oxide was added into the digestion flask; $2cm^3$ of conc. sulphuric acid was also added. The mixture was heated on the heating mantle at an inclined position until the liquid became clear. The digest was cooled and made alkaline with $15cm^3$ of 40% NaOH. The digest was then transferred to the steamed out apparatus. The ammonia steam was distilled into $10cm^3$ of 0.32M boric acid solution with 5 drops of methyl red, indicator for 15minutes. The distilled ammonia was the titrated with 0.02M HCI prepared by dilution of the 1M stock. (AOAC 1894)

i) Digestion

$$\text{Sample-N} + H_2SO_{4\,(aq)} \xrightarrow{CuSO_4\text{-}TiO_2} (NH_4)_2\,SO_{4\,(aq)} + H_2O_{(l)} + CO_{2(g)}$$

ii) Distillation

$$(NH_4)_2\,SO_{4\,(aq)} + 2NAOH_{(aq)} \longrightarrow 2NH_{3(g)} + Na_2SO_{4(aq)}$$

iii) Absorption

$$2NH_{3(g)} + H_3BO_{3(aq)} \longrightarrow NH_4^+H_2BO_3^-{}_{(aq)}$$

iv) Back titration

$$H_3BO_{3(aq)} + HCl_{(aq)} \longrightarrow H_4BO_3^+Cl^-{}_{(aq)}$$

Calculation:

$$\%\ \text{Crude Protein} = \frac{Xcm^3 \times \text{NgN} \times \text{factor (6.25)}}{\text{Weight of Sample}} \times 100$$

Where Xcm^3 = titrated value

6.25 = Conversion factor

N = Molecular weight of Nitrogen (14)

3.4.5 Total Ash Determination

Crucible was dried in the oven for 24hours, cooled and weighed (W_1). 2g of dried (moisture free) sample (W_2) was placed in the crucible and heated in the muffle furnace at 550°C until a constant weight is obtained. The ash was then covered with a lid and placed in desiccators prior to weighing. This was then measured as W_3. (AOAC, 2005).

Calculation

$$\%Ash = \frac{W_3-W_1}{W_2-W_1} \times 100$$

Where W_3 = weight after ashing

W_2 = weight of crucible + sample

W_1 = weight of crucible

3.4.6 Carbohydrate content Determination

The carbohydrate content was determined by difference i.e.

Carbohydrate % = 100-(crude fibre + lipids + crude protein + moisture content + Ash) as reported by (Akubor et al., 2000).

3.5 Dry Ashing Digestion

The residual of ashes from total ash determination were dissolved using 5ml of 30% HCl (0.1M) prepared by dilution of the 1M stock and then filtered using Whatman filter papers. The filtrates were individually poured into 50cm^3 volumetric flasks and made up to mark with deionized water. The sample solution was then kept in sample bottles for further analysis using AAS.

3.6 Determination of heavy Metal Concentration

The samples were analyzed using Atomic Absorption Spectroscopy (AAS) for cadmium, cobalt, copper, iron, manganese, nickel, lead, chromium and zinc levels at various wavelengths.

3.7 INSTRUMENTATION

The atomic absorption Spectroscopy is a process which involves absorption of energy by free atoms (produced by the evaporation of the solvent in the air acetylene flame) of element with light at resonance wavelength. The light or energy should be characteristic of that element concerned. The sample is converted into atomic vapor by aspirating the sample solution into the flame. A hallow cathode lamp containing cathode made of the element to be determined is used as the light sources. The atoms of the analyte in the flame absorb at precisely the wavelength emitted by the hollow cathode lamp source. The samples were aspirated and the absorbance readings recorded. The procedure was performed using different lamps and samples. Mean readings of both standards and samples were collected as well as the blank. Calibration curves of absorbance versus concentration were plotted for the standards of each metal. The slope was taken and used to determine the concentrations of each metal under investigation in mg/L using the beer lambert law.

$$\text{Concentration in mg/kg} = \frac{\text{concentration in mg/l x vol. of solution (ml)x Dilution factor}}{\text{Mass of sample (g)}}$$

$$[\text{Analyte}]\text{mg/kg} = \frac{[\text{AAS}]\ \text{mg/L}}{[\text{Sample}]} \times 10^6$$

3.7Preparation of Standard Solution

3.7.1 1000mg/l Lead (Pb)

l.5986g of $Pb(NO_3)_2$ was dissolved in a beaker using deionized water and the content was transferred into 1000cm^3 volumetric flask, 10cm^3 of 0.1M nitric acid was added to prevent hydrolysis in the solution, and made to mark with deionized water.

3.7.2 100mg/l Lead (Pb)

10cm^3 of the stock solution was transferred into a 100cm^3 volumetric flask; deionised water was added to the solution to make it to the mark.

3.7.3 10mg/l Lead (Pb)

5cm^3 of 100mg/l lead solution was transferred using pipette into 50cm^3 volumetric flask and this was made-up to mark with deionized water.

3.7.4 1mg/1 Lead (Pb)

5cm^3 of 10mg/1 lead solution was transferred using pipette into 50cm volumetric flask and this was made to mark with deionized water. Serial dilution was carried out for 0.8, 0.6, 0.4, 0.2, and 0.1 from 1mg/l.

3.8 1000mg/l Cobalt (Co)

63.546g of Cobalt oxide (CoO) was dissolved in 20cm^3 Conc. HCl (sp. Gr.1.18), the solution was then cooled and transferred into 1000cm^3 volumetric flask, deionized water was added to the solution to make it to the mark.

3.8.1 100mg/l Cobalt (Co)

10cm^3 of the stock solution was transferred into a 100cm^3 volumetric flask; deionised water was added to the solution to make it to the mark.

3.8.2 10mg/l Cobalt (Co)

5cm^3 of 100mg/l cobalt solution was transferred using pipette into 50cm^3 volumetric flask and this was made-up to mark with deionized water.

3.8.3 1mg/1 Cobalt(Co)

5cm^3 of 10mg/l cobalt solution was transferred using pipette into 50cm^3 volumetric flask and this was made to mark with deionized water. Serial dilution was carried out for 0.8, 0.6, 0.4, 0.2, and 0.1 from 1mg/1.

3.9.0 1000mg/l Manganese (Mn)

1.5818g of MnO_2 was dissolved in a beaker using deionized water and the content was transferred into 1000cm^3 volumetric flask, more deionized water was added to the solution to make it to the mark.

3.9.1 100mg/l Manganese (Mn)

$10cm^3$ of the stock solution was transferred into a $100cm^3$ volumetric flask; deionised water was added to the solution to make it to the mark.

3.9.210mg/l Manganese (Mn)

$5cm^3$ of 100mg/l manganese solution was transferred using pipette into $50cm^3$ volumetricflask and this was made-up to mark with deionized water.

3.9.31mg/1Manganese (Mn)

$5cm^3$ of 10mg/l manganese solution was transferred using pipette into $50cm^3$ volumetric flask and this was made to mark with deionized water. Serial dilution was carried out for 0.8, 0.6, 0.4, 0.2, and 0.1 from lmg/1.

3.10 1000mg/1 Chromium (Cr)

4.9038g of $K_2Cr_2O_7$ was dissolved in a beaker using deionized water, $10cm^3$ of 0.1 M nitric acid was added and the content was transferred into $1000cm^3$ volumetric flask, and made up to the mark with deionized water.

3.10.1 100mg/l Chromium (Cr)

$10cm^3$ of the stock solution was transferred into a 100cm" volumetric flask; deionised water was added to the solution to make it to the mark.

3.10.2 10mg/l Chromium (Cr)

5cm^3 of 100mg/l chromium solution was transferred using pipette into 50cm^3 volumetric flask and this was made-up to mark with deionized water.

3.10.3 1mg/1 Chromium (Cr)

5cm^3 of 10mg/l chromium solution was transferred using pipette into 50cm^3 volumetric flask and this was made to mark with deionized water. Serial dilution was carried out for 0.8, 0.6, 0.4, 0.2 and 0.1 from 1mg/1.

3.11 1000mg/l Cadmium (Cd)

1.142g of Cadmium oxide (CdO) was dissolved in a beaker using deionizedwater and the content was transferred into 1000cm^3 volumetric flask, more deionised water was added to the solution to make it to the mark.

3.11.1100mg/l Cadmium (Cd)

10cm^3 of the stock solution was transferred into a 100cm^3 volumetric flask; deionised waterwas added to the solution to make it to the mark.

3.11.2 10mg/1 Cadmium(Cd)

5cm^3 of 100mg/l cadmium solution was transferred using pipette into 50cm^3 volumetric flask and this was made-up to mark with deionized water.

3.11.3 1mg/I Cadmium (Cd)

5cm^3 of 10mg/l cadmium solution was transferred using pipette into 50cm^3 volumetricflask and this was made to mark with deionized water. Serial dilution was carried out for0.8, 0.6, 0.4, 0.2 and 0.1 from 1mg/1.

3.11.0 1000mg/l Iron (Fe)

8.6361g of $FeNH_4(SO_4)_2.12H_20$ was dissolved in a beaker using 0.1M $HN0_3$ and the content was transferred into 1000cm^3 volumetric flask, deionized water was added to the solution to make it to the mark.

3.11.1 100mg/l Iron (Fe)

10cm^3 of the stock solution was transferred into a 100cm^3 volumetric flask; deionised water was added to the solution to make it to the mark.

3.11.2 10mg/l Iron (Fe)

5cm^3 of 100mg/l Iron solution was transferred using pipette into 50cm^3 volumetric flask and this was made-up to mark with deionized water.

3.11.3 1mg/l Iron(Fe)

5cm^3 of 10mg/l iron solution was transferred using pipette into 50cm^3 volumetric flask and this was made to mark with deionized water. Serial dilution was carried out for 0.8, 0.6,1.4, 0.2 and 0.1 from lmg/l

3.12 1000mg/l Copper (Cu)

1.2520g of CuO was dissolved in a beaker using deionized water and the content was transferred into 1000cm^3 volumetric flask, more deionized water was added to the solution to make it to the mark.

3.12.1 100mg/l Copper (Cu)

10cm^3 of the stock solution was transferred into a 100cm^3 volumetric flask; deionised water was added to the solution to make it to the mark.

3.12.2 I0mg/l Copper (Cu)

5cm^3 of l00mg/l copper solution was transferred using pipette into 50cm^3 volumetric flask and this was made-up to mark with deionized water.

3.12.3 mg/1 Copper (Cu)

5cm^3 of 10mg/l copper solution was transferred using pipette into 50cm^3 volumetric flask and this was made to mark with deionized water. Serial dilution was carried out for 0.8, 0.6, 0.4, 0.2 and 0.1 from 1mg/l.

3.13 l000mg/l Zinc (Zn)

1.2447g of ZnO was dissolved in a beaker using deionized water and the content was transferred into a 1000cm^3 volumetric flasks, more deionized water was added to the solutionto make it to the mark.

3.13.1100mg/l Zinc (Zn)

10cm^3 of the stock solution was transferred into a 100cm^3 volumetric flask; deionised water was added to the solution to make it to the mark.

3.13.2 10mg/l Zinc (Zn)

5cm^3 of 100mg/l zinc solution was transferred using pipette into 50cm^3 volumetric flask and this was made-up to mark with deionized water.

3.13.3 1mg/l Zinc (Zn)

5cm^3 of 10mg/l zinc solution was transferred using pipette into 50cm^3 volumetric flask and this was made to mark with deionized water, Serial dilution was carried out for 0.8, 0.6, 0.4, 0.2 and 0.1 from 1mg/l.

3.14 1000mg/l Nickel (Ni)

2.0225g of $NiCO_3$ was dissolved in a beaker using deionized water and the content was transferred into a 1000cm^3 volumetric flask, more deionized water was added to the solution to make it to the mark.

3.14.1100mg/I Nickel (Ni)

10cm^3 of the stock solution was transferred into a 100cm^3 volumetric flask; deionised waterwas added to the solution to make it to the mark.

3.14.2 10mg/l Nickel (Ni)

5cm^3 of 100mg/l Nickel solution was transferred using pipette into 50cm^3 volumetric flask and this was made-up to mark with deionized water.

3.14.3 1mg/l Nickel (Ni)

5cm^3 of 10mg/l nickel solution was transferred using pipette into 50cm^3 volumetric flask and this was made to mark with deionized water. Serial dilution was carried out for 0.8, 0.6, 0.4, 0.2 and 0.1 from 1mg/1.

CHAPTER FOUR

4.0 Results and Discussion

The results of the analyses are presented in figures 4.1-4.24 below. The results indicate proximate composition and heavy metal concentration of the tuber samples and spices.

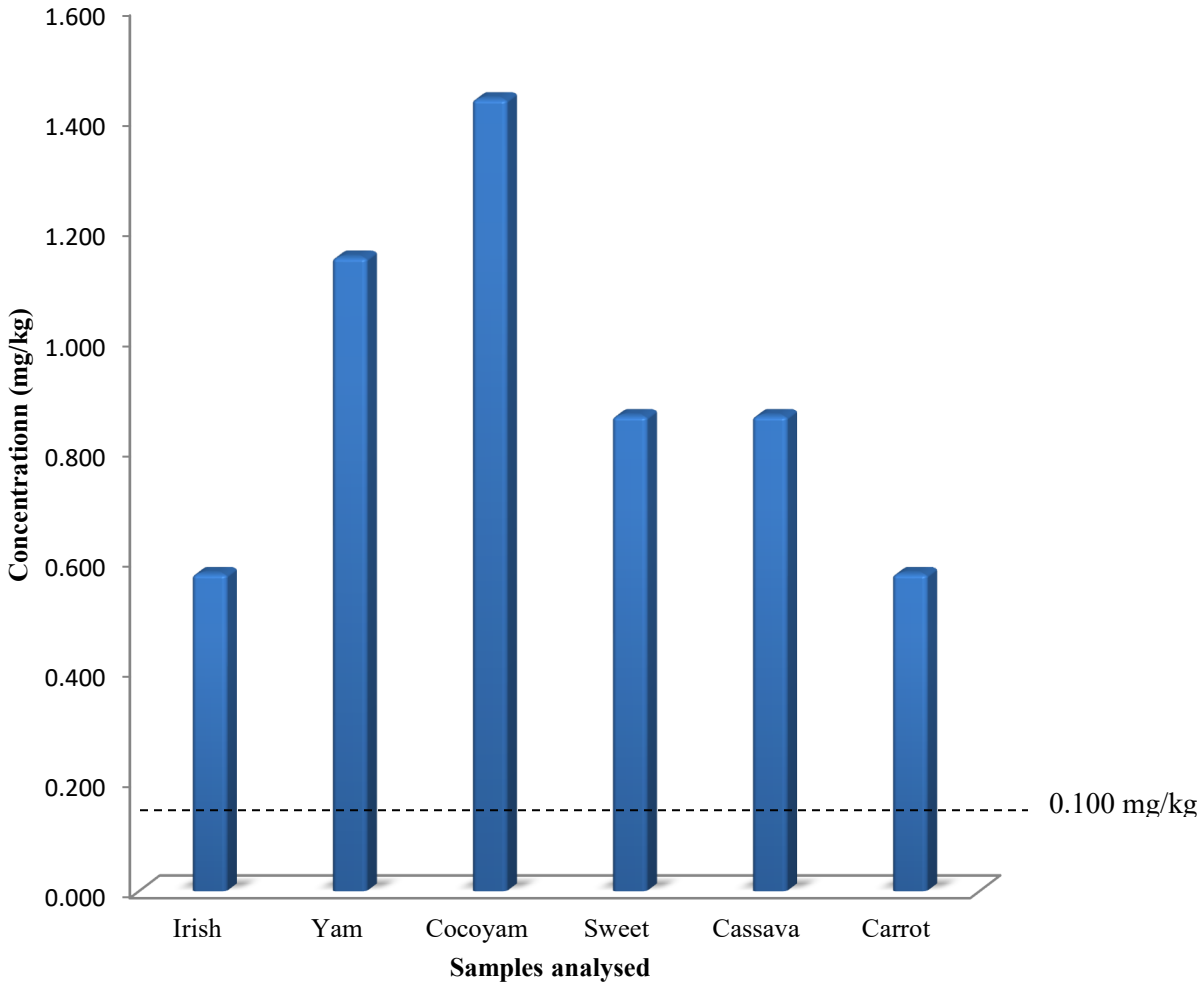

Fig. 4.1: Concentration of Cd (mg/kg)

■ MPL – Food and Agricultural Organization Maximum permissible level (FAO/WHO, 1991)

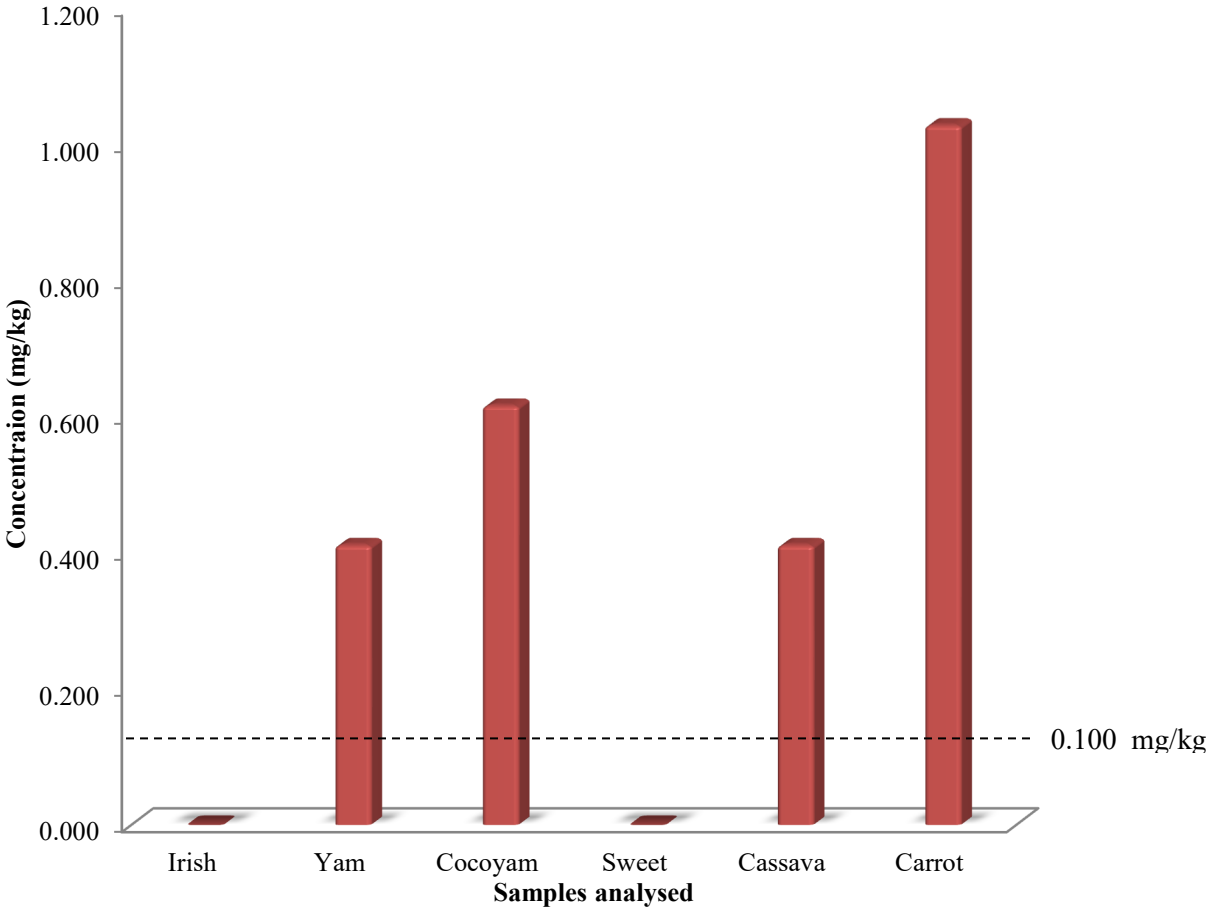

Fig. 4.2: Concentration of Cr (mg/kg)

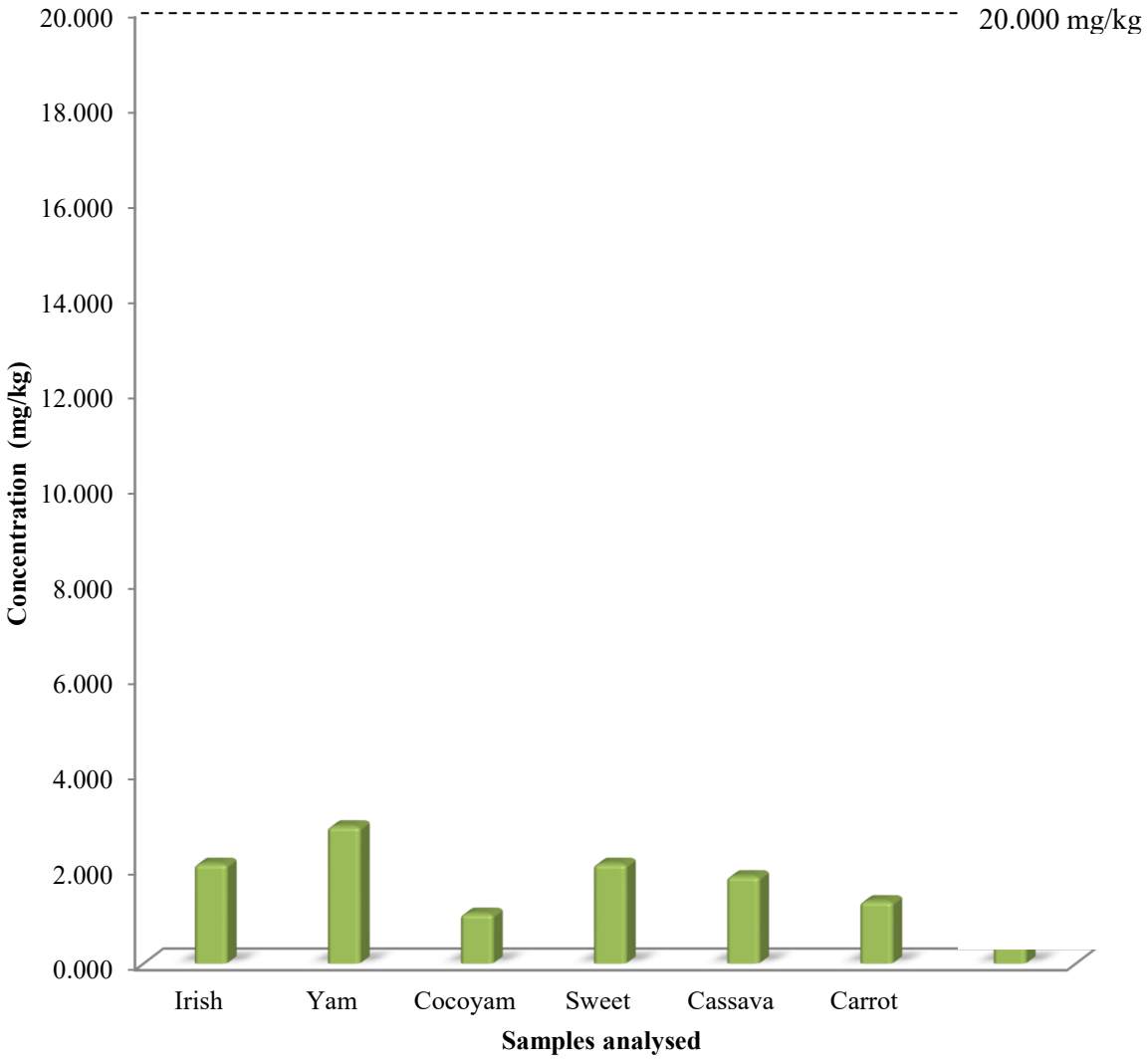

Fig. 4.3: Concentration of Cu (mg/kg)

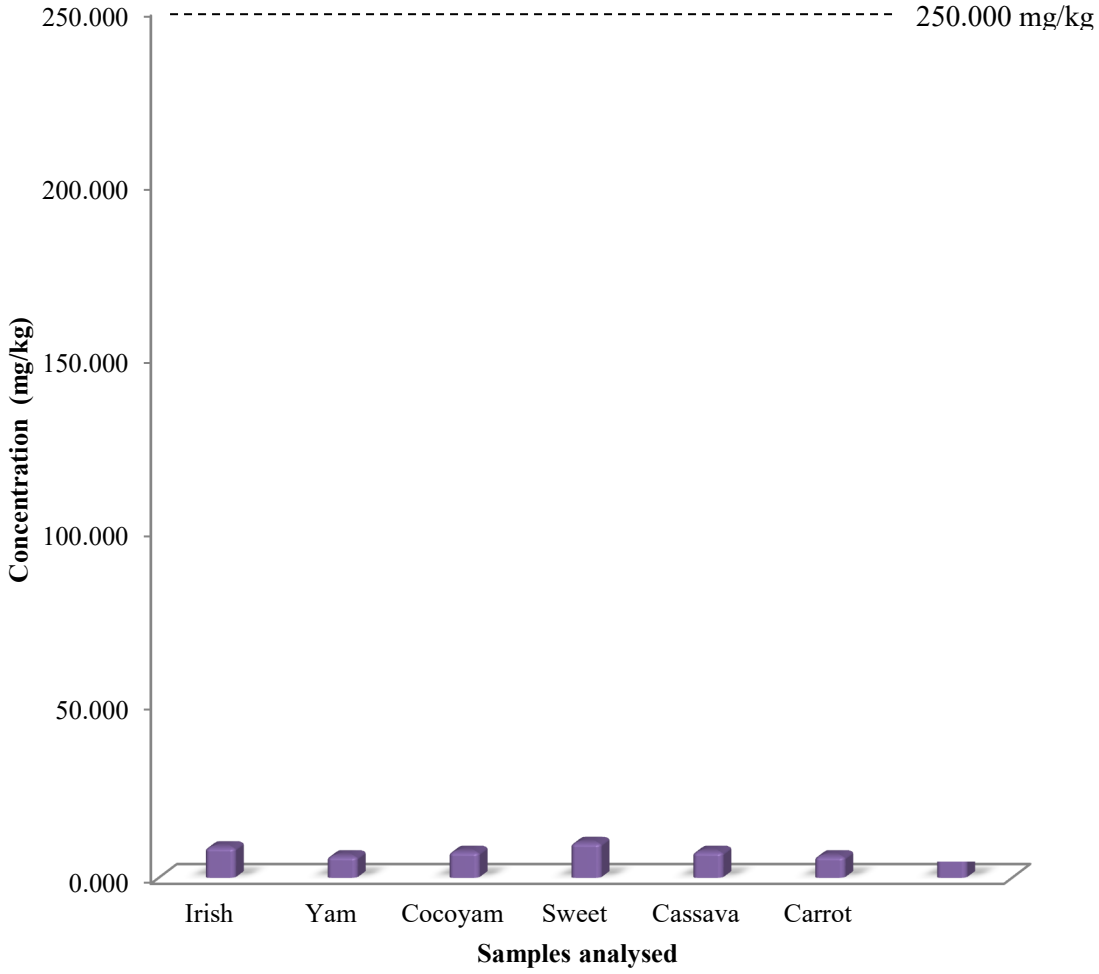

Fig. 4.4: Concentration of Fe (mg/kg)

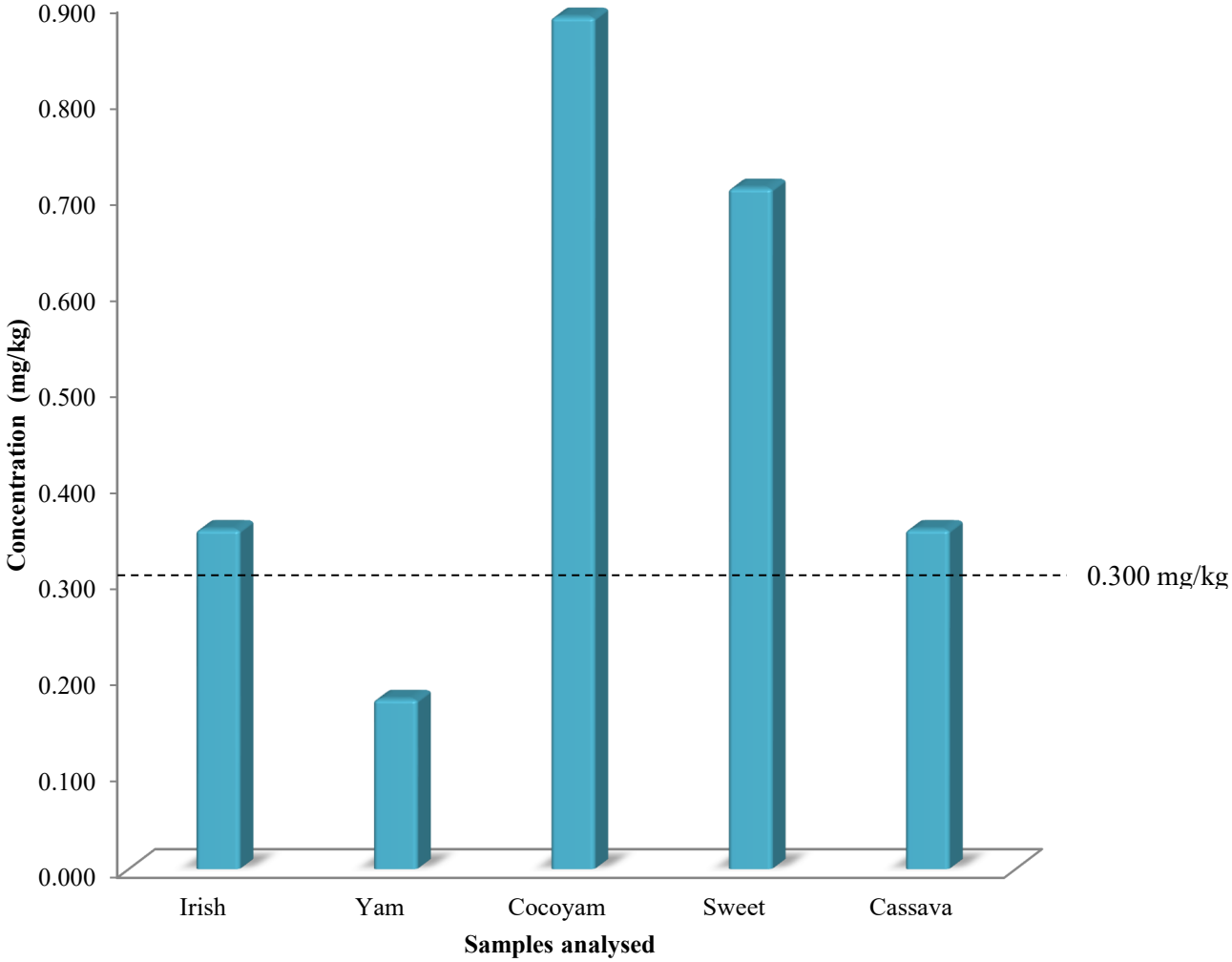

Fig. 4.5: Concentration of Pb (mg/kg)

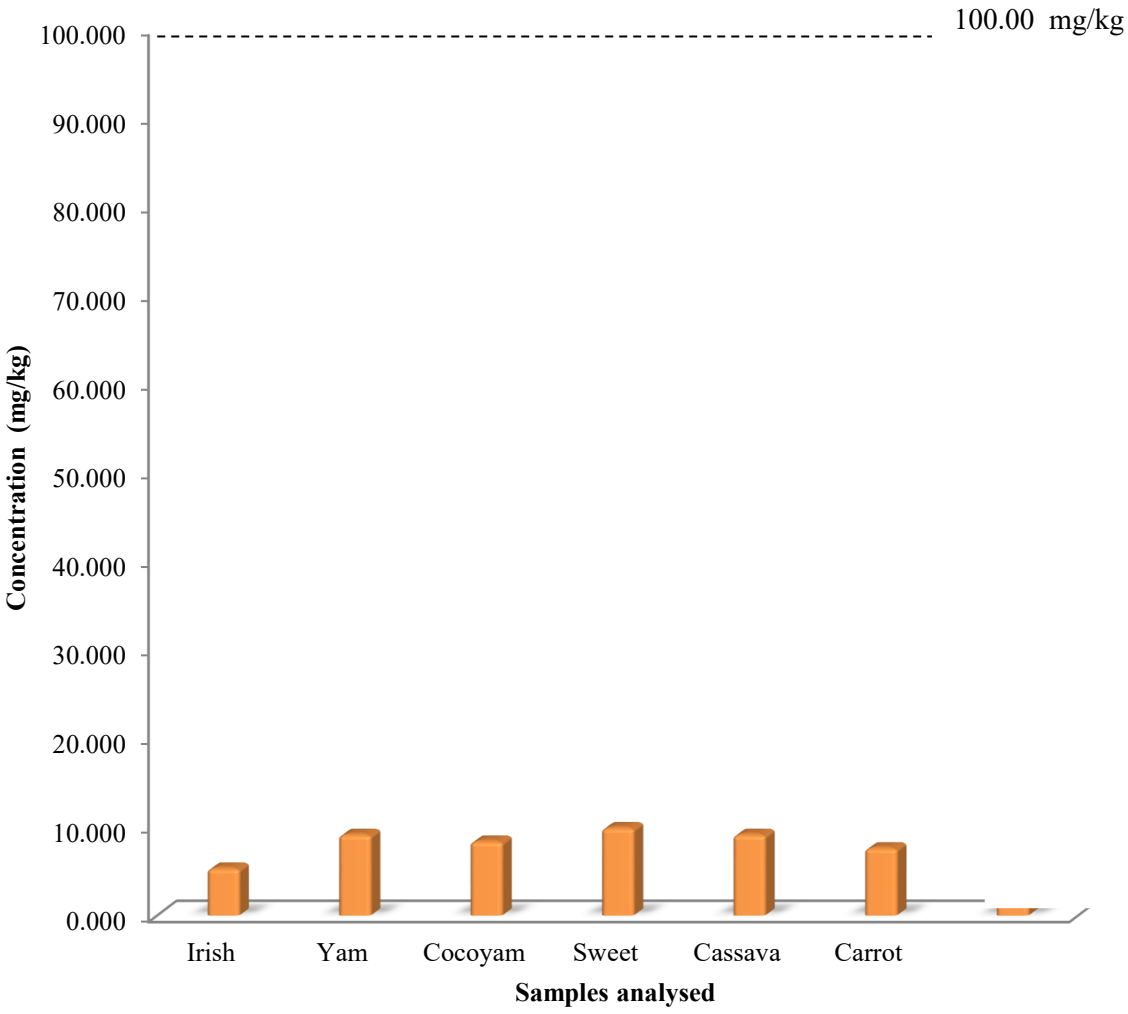

Fig. 4.6: Concentration of Zn (mg/kg)

4.2.2 Heavy metals in Spices

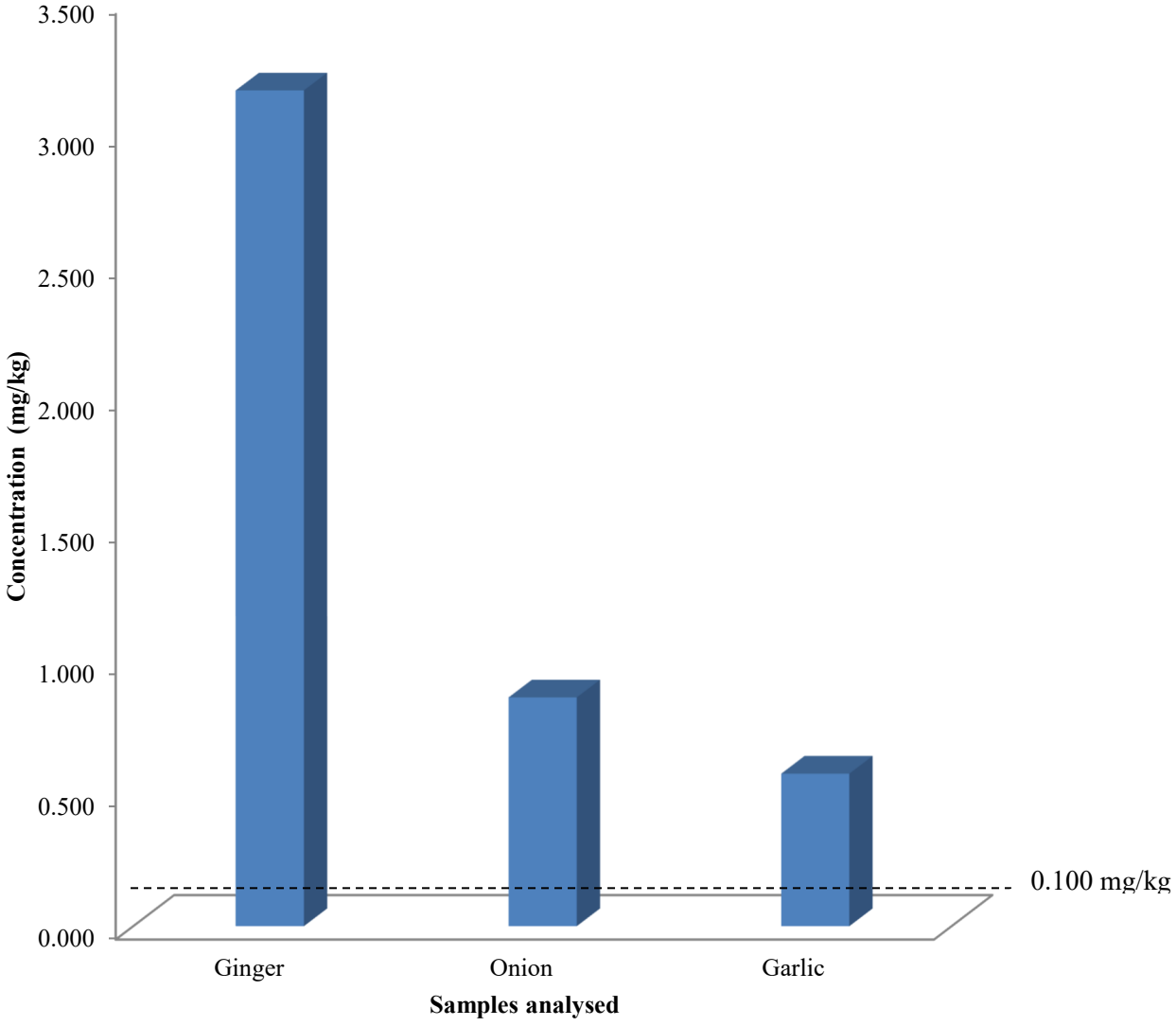

Fig. 4.7: Concentration of Cd (mg/kg)

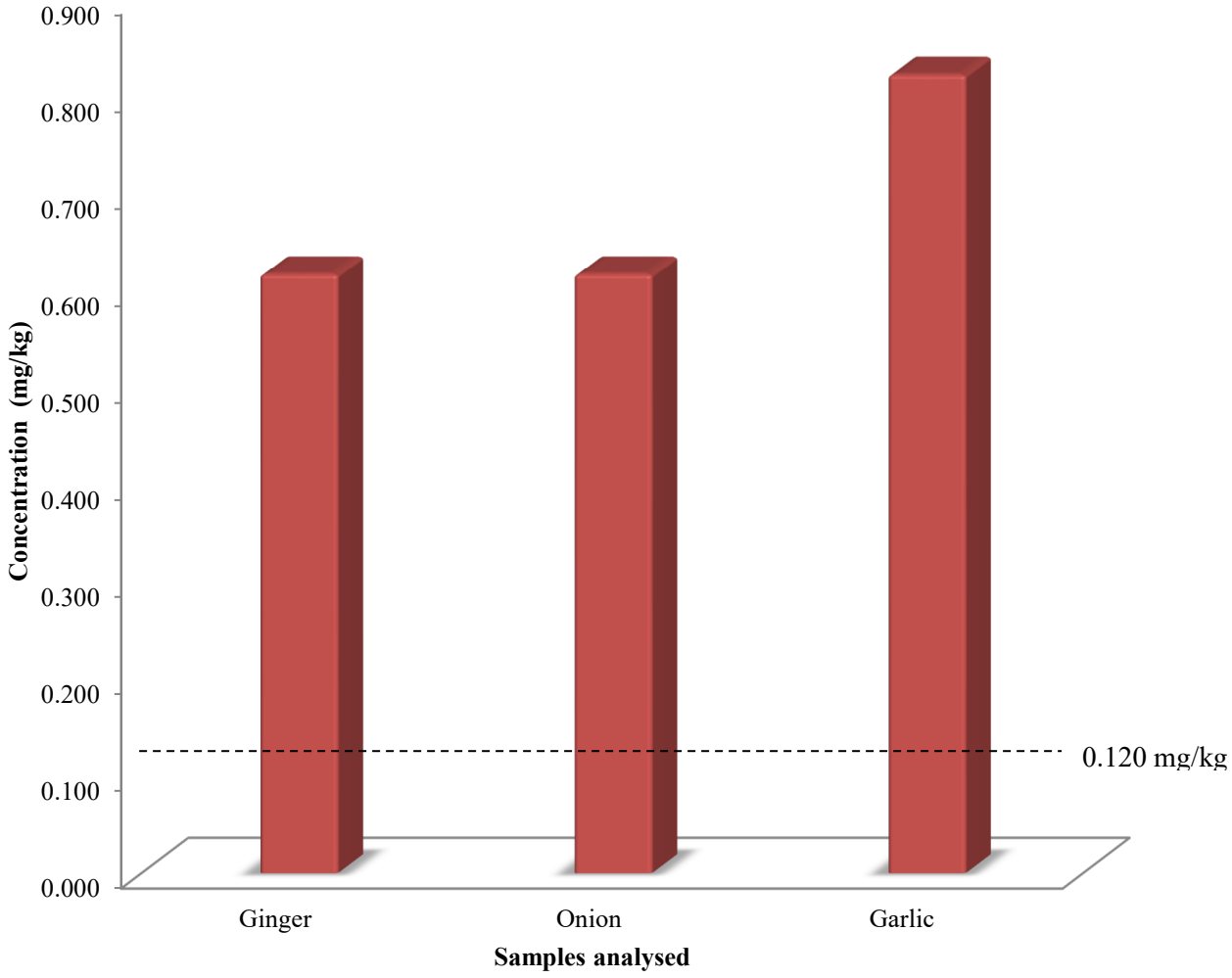

Fig. 4.8: Concentration of Cr (mg/kg)

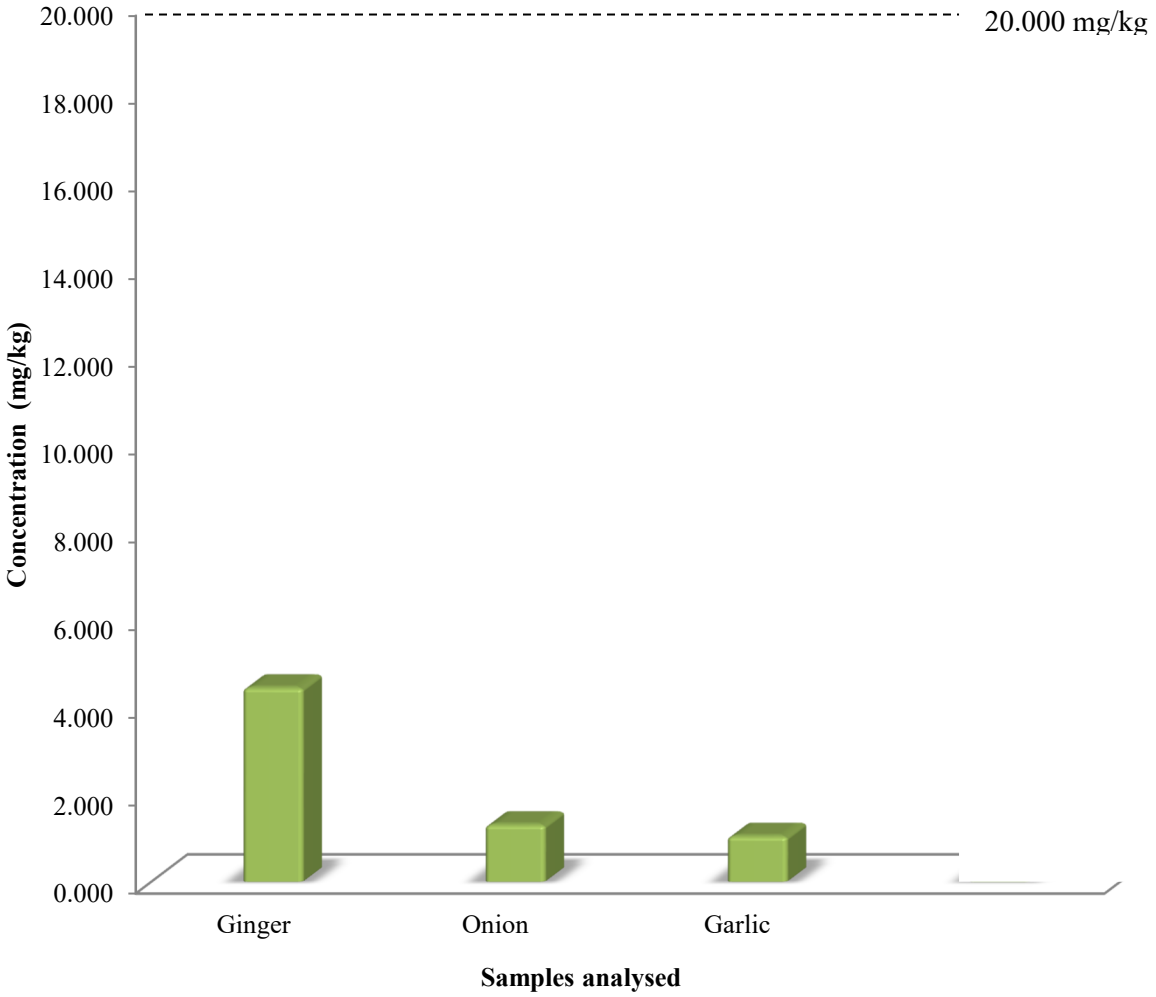

Fig. 4.9: Concentration of Cu (mg/kg)

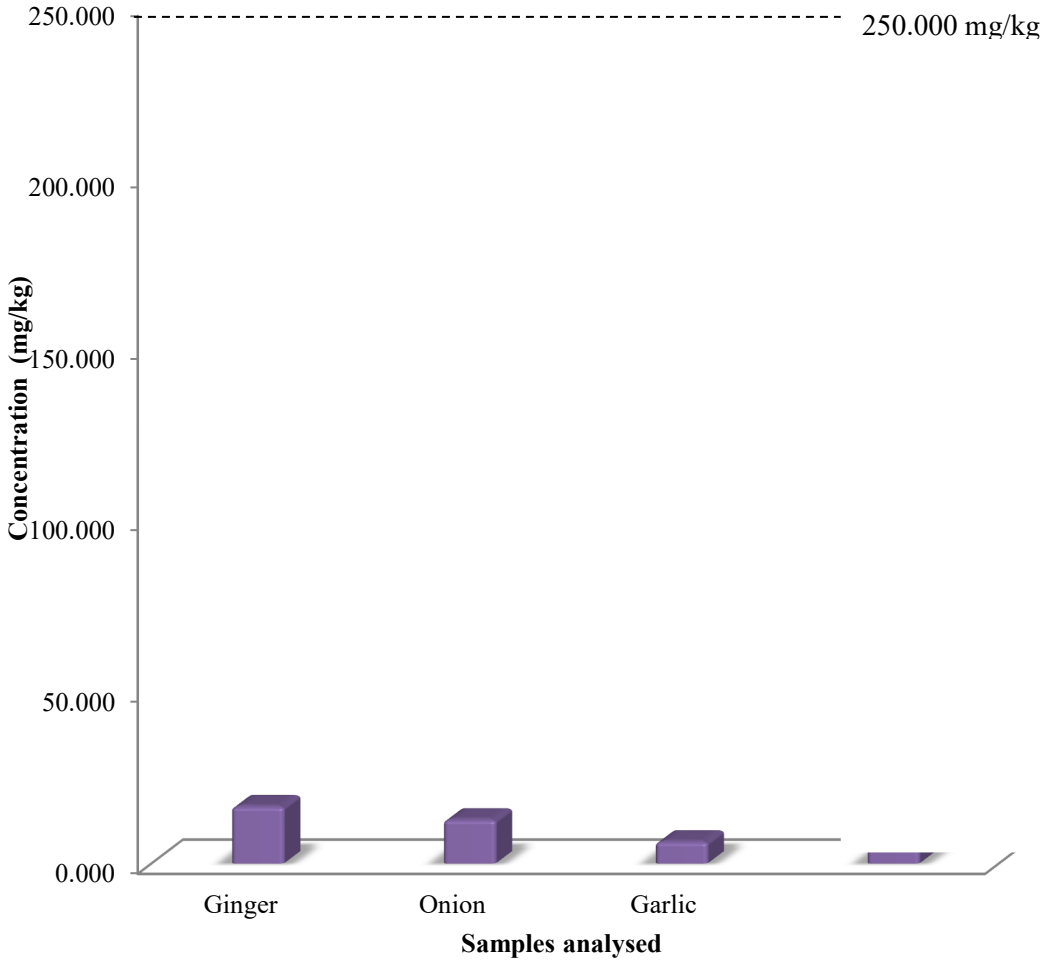

Fig. 4:10 Concentration of Fe (mg/kg)

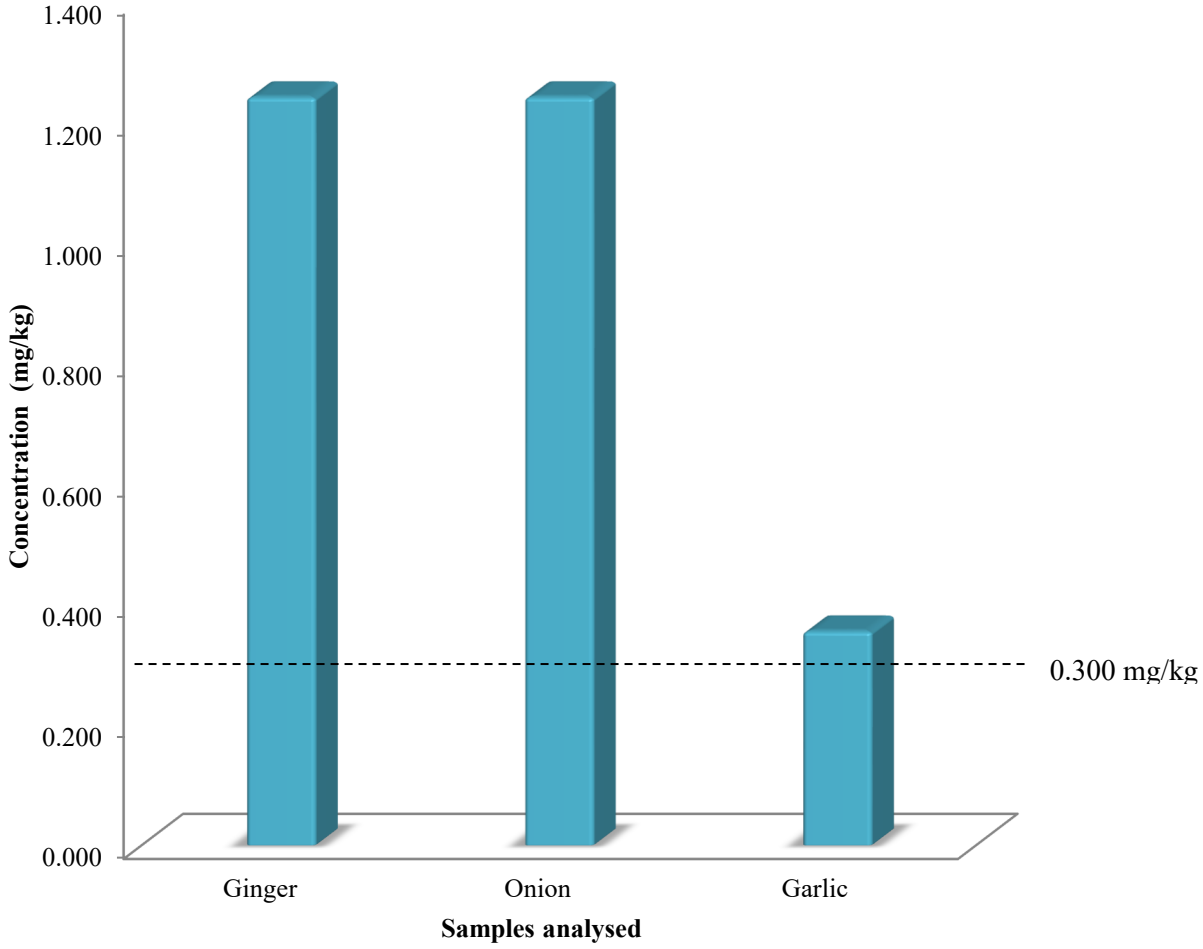

Fig. 4.11: Concentration of Pb (mg/kg)

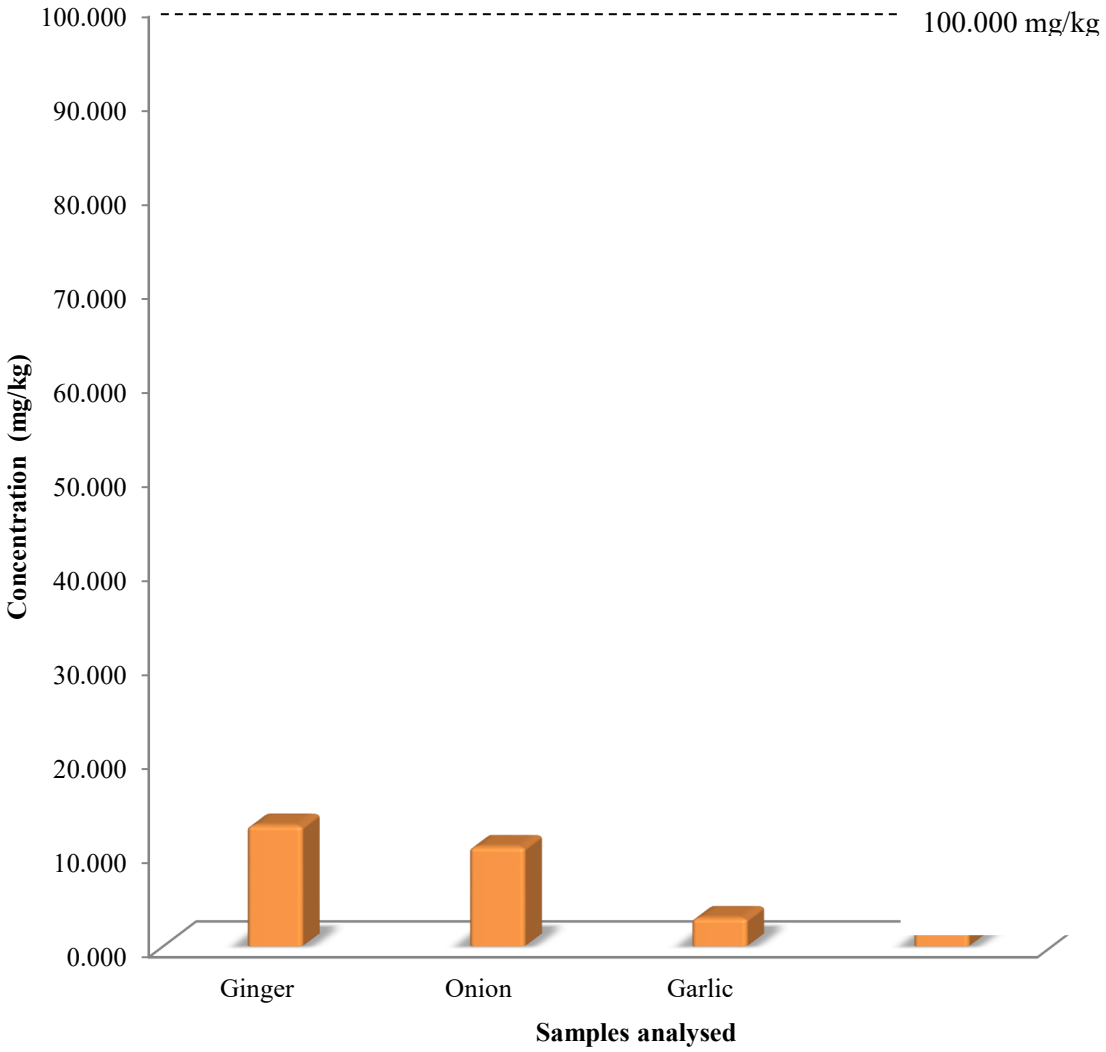

Fig. 4.12: Concentration of Zn (mg/kg)

4.2.3 Proximate analysis of Tubers

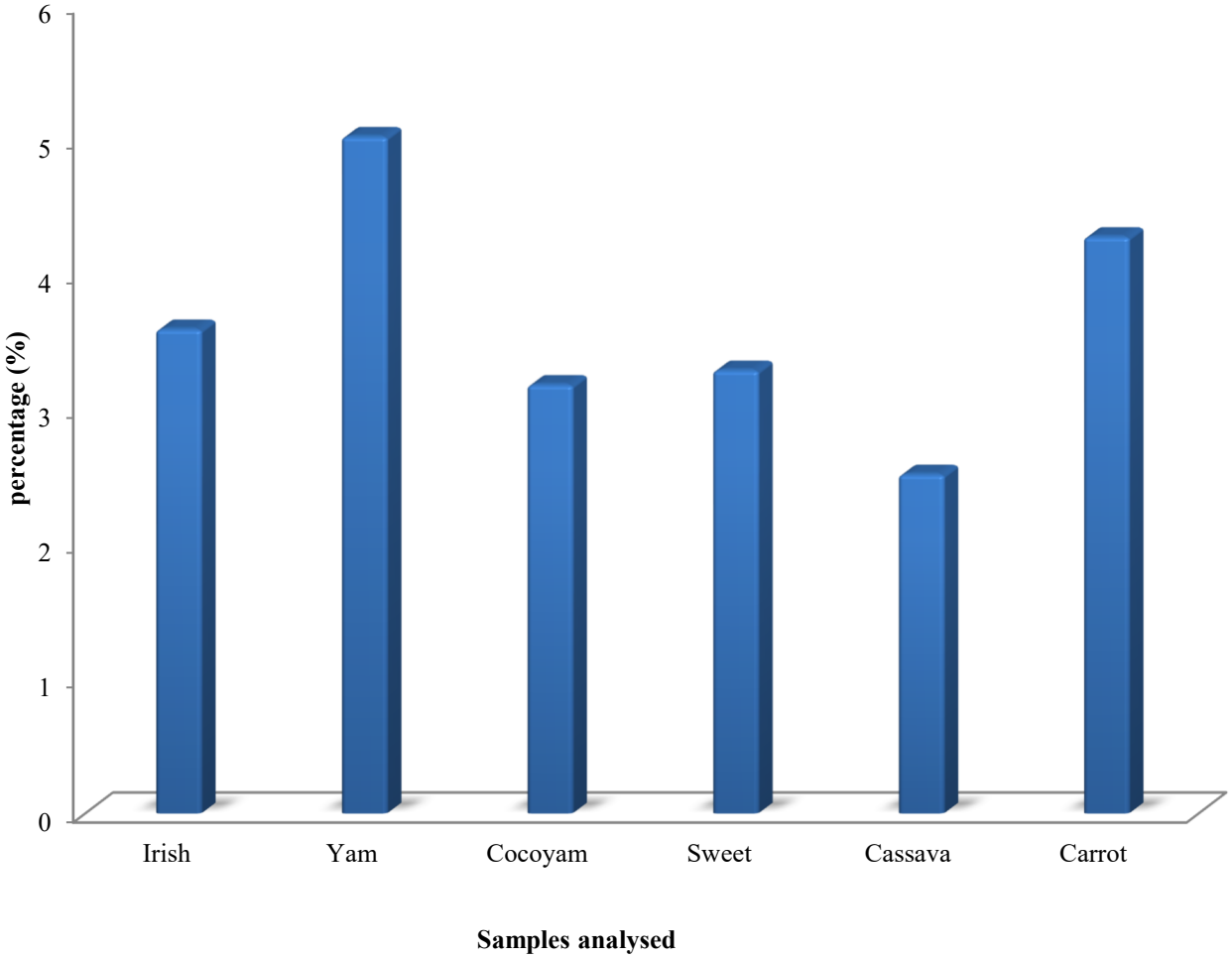

Fig. 4.13: Percentage of Crude Protein

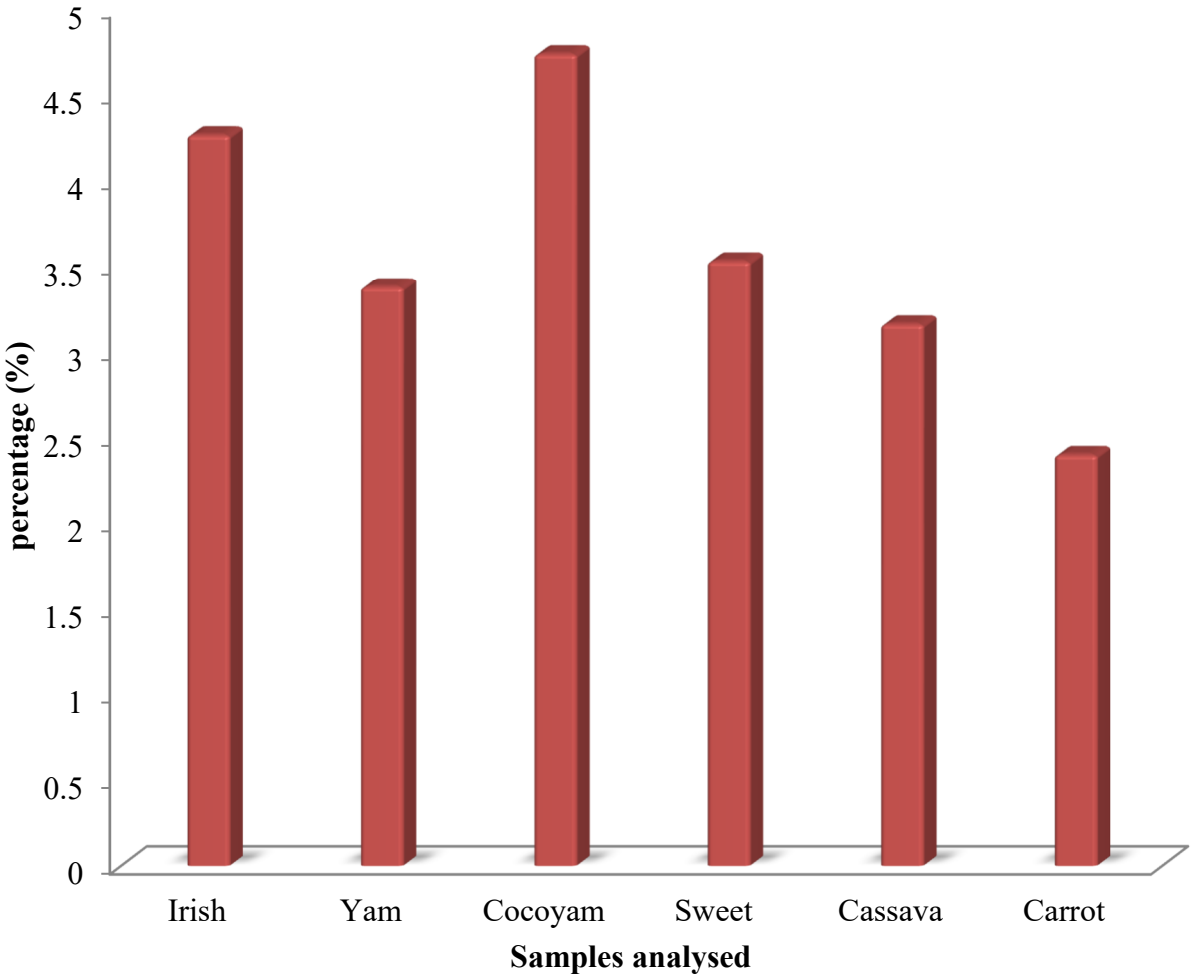

Fig. 4.14: Percentage of Fat

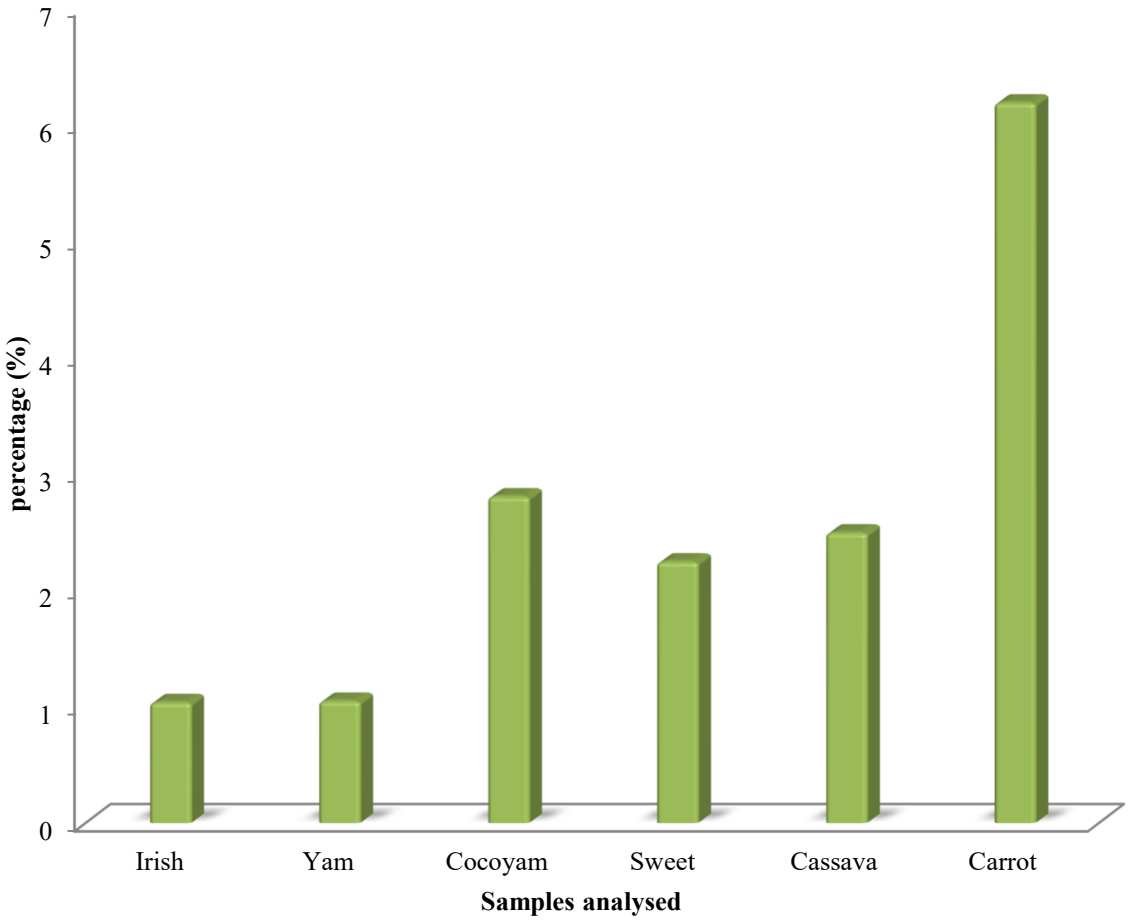

Fig. 4.15: Percentage Ash content

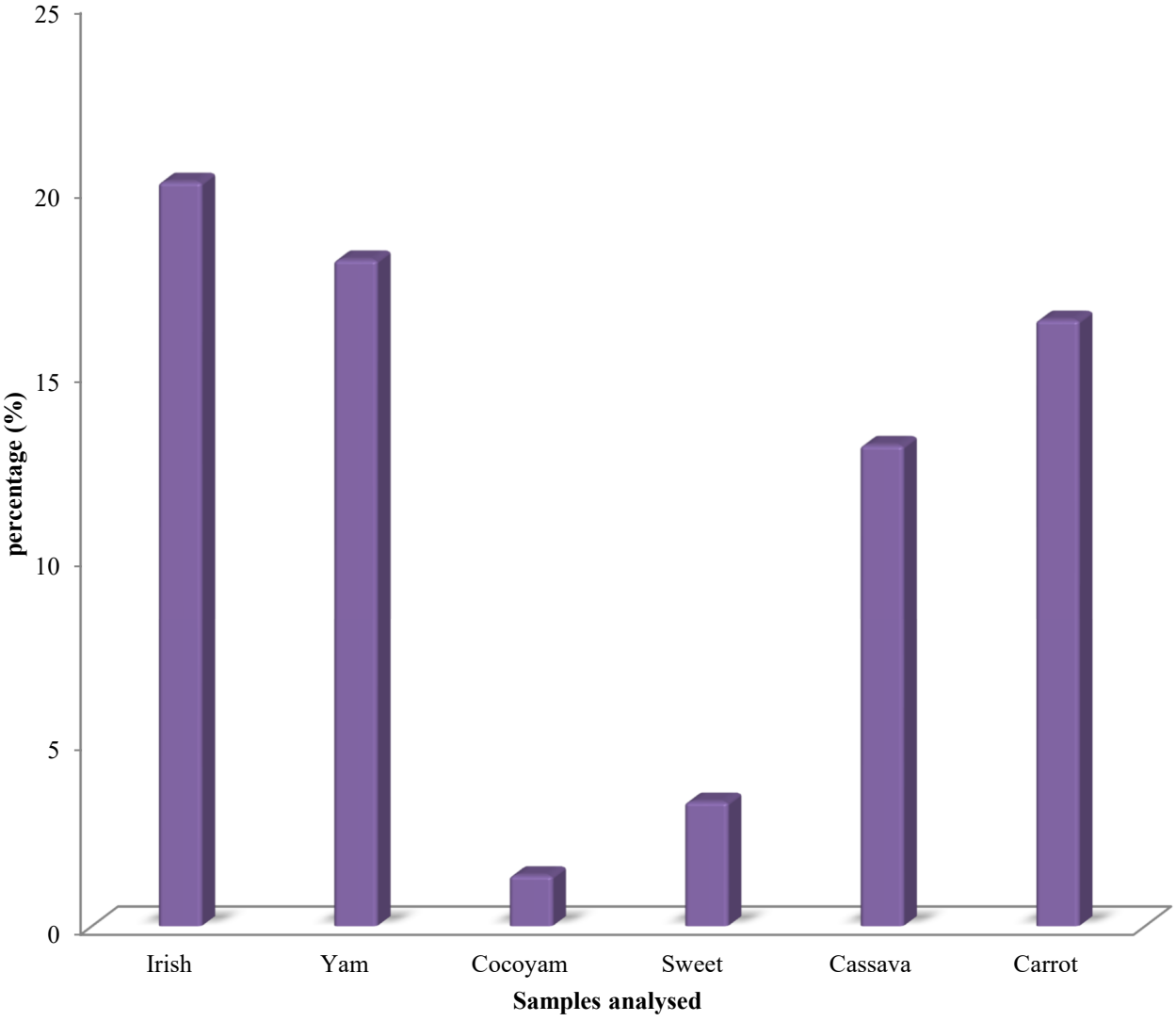

Fig. 4.16: Percentage of Moisture

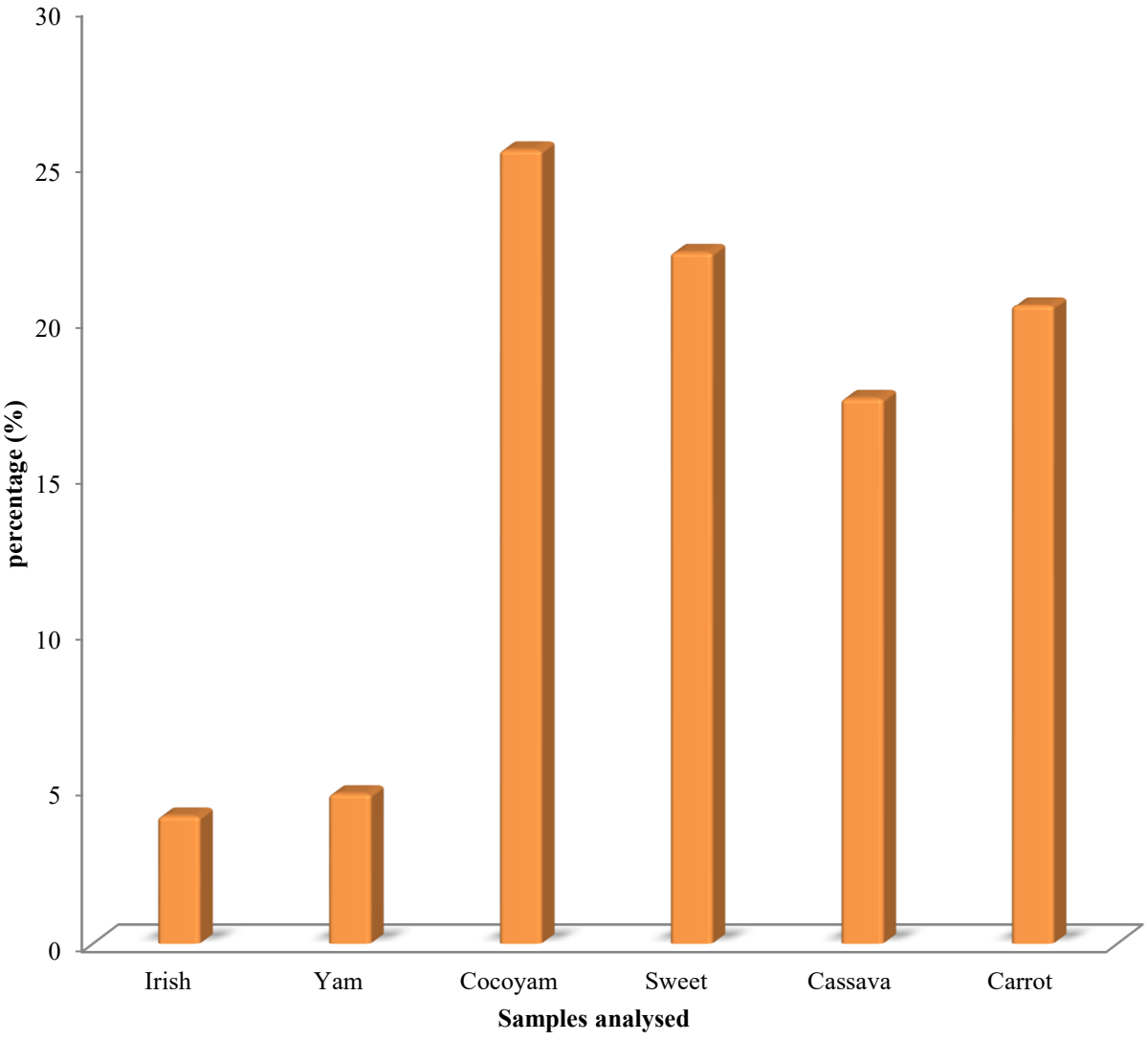

Fig. 4.17: Percentage of Crude Fibre

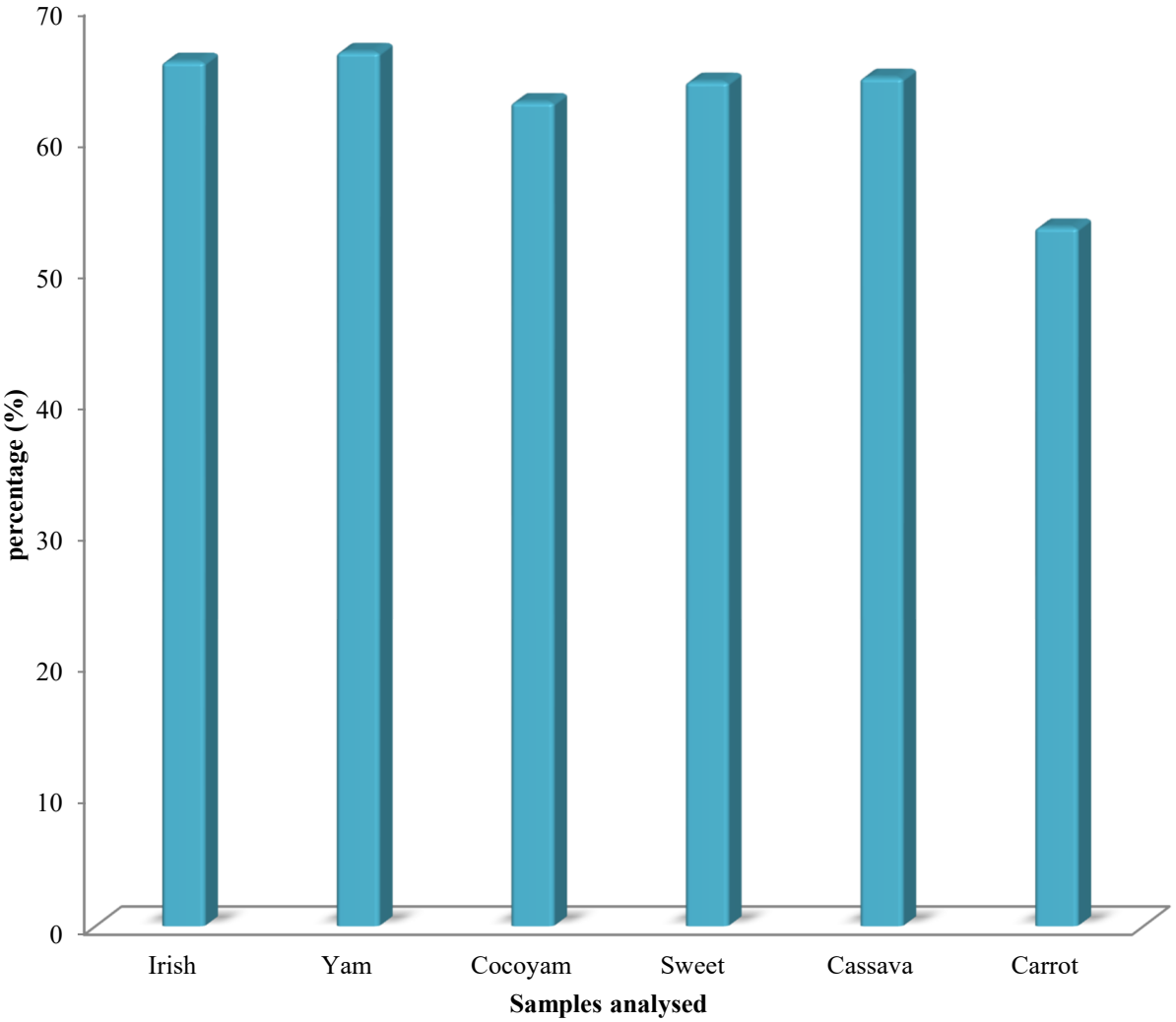

Fig. 4.18: Percentage of Carbohydrate

4.2.4 Proximate analysis of Spices

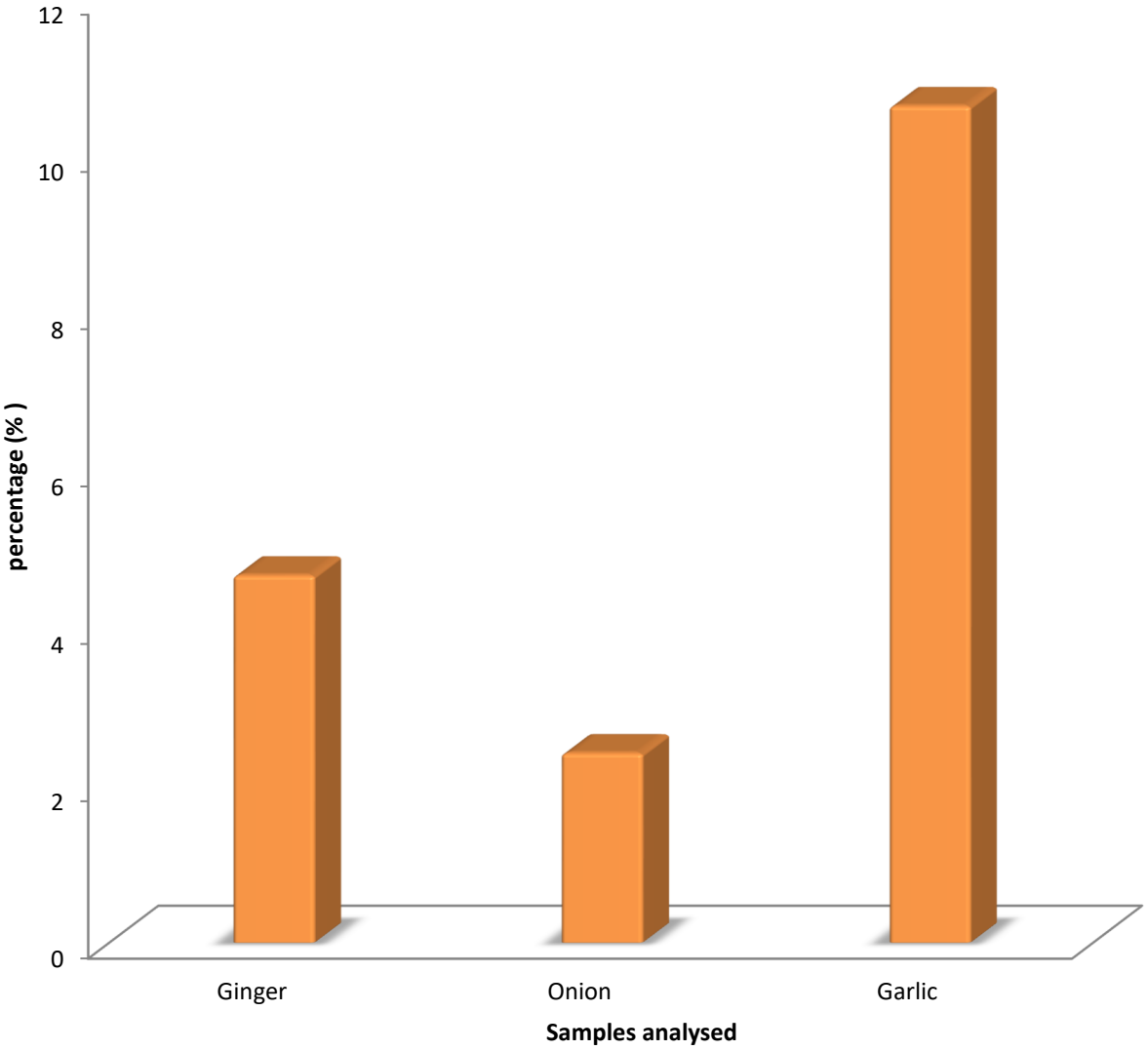

Fig. 4.19: Percentage of Crude Protein

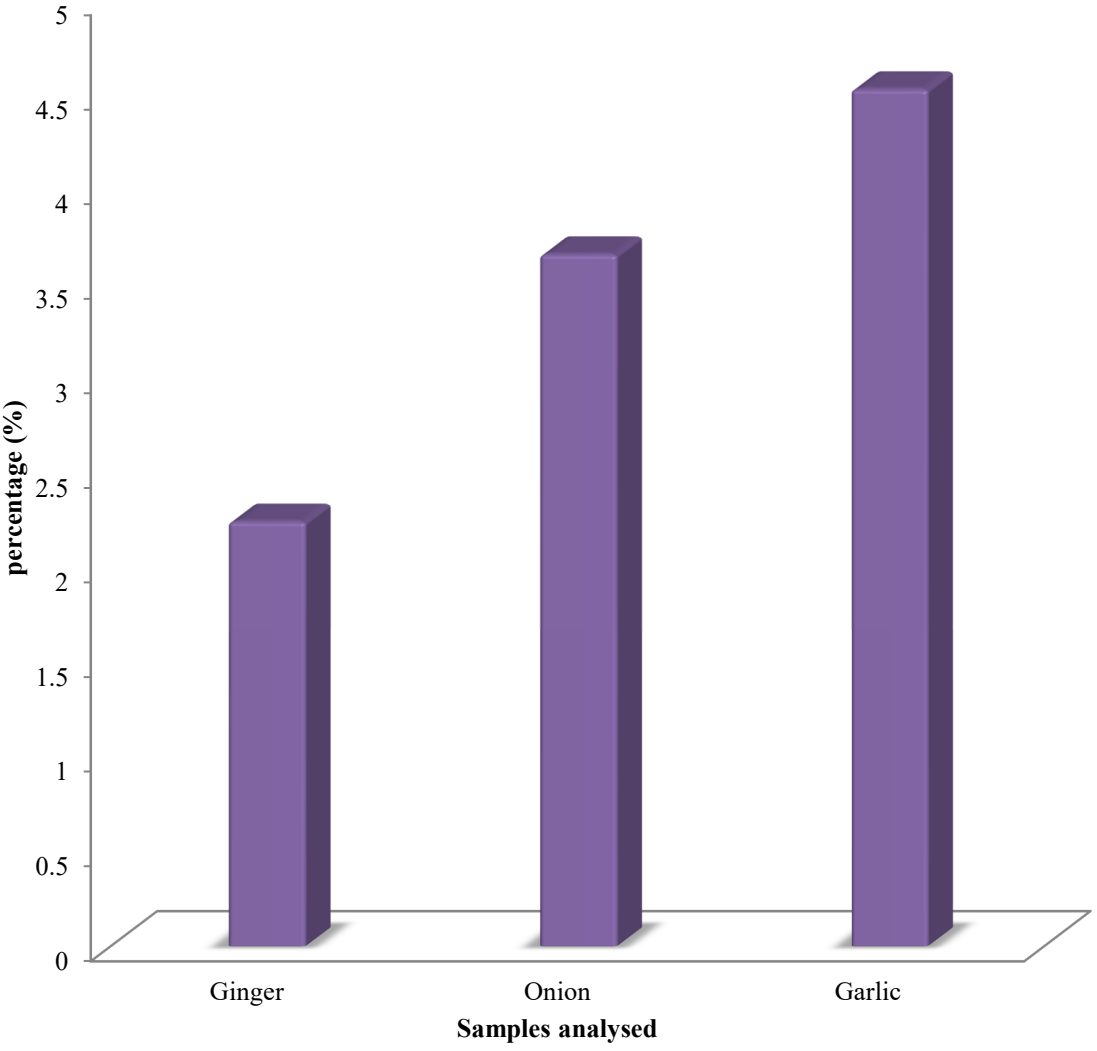

Fig. 4.20: Percentage Fat content

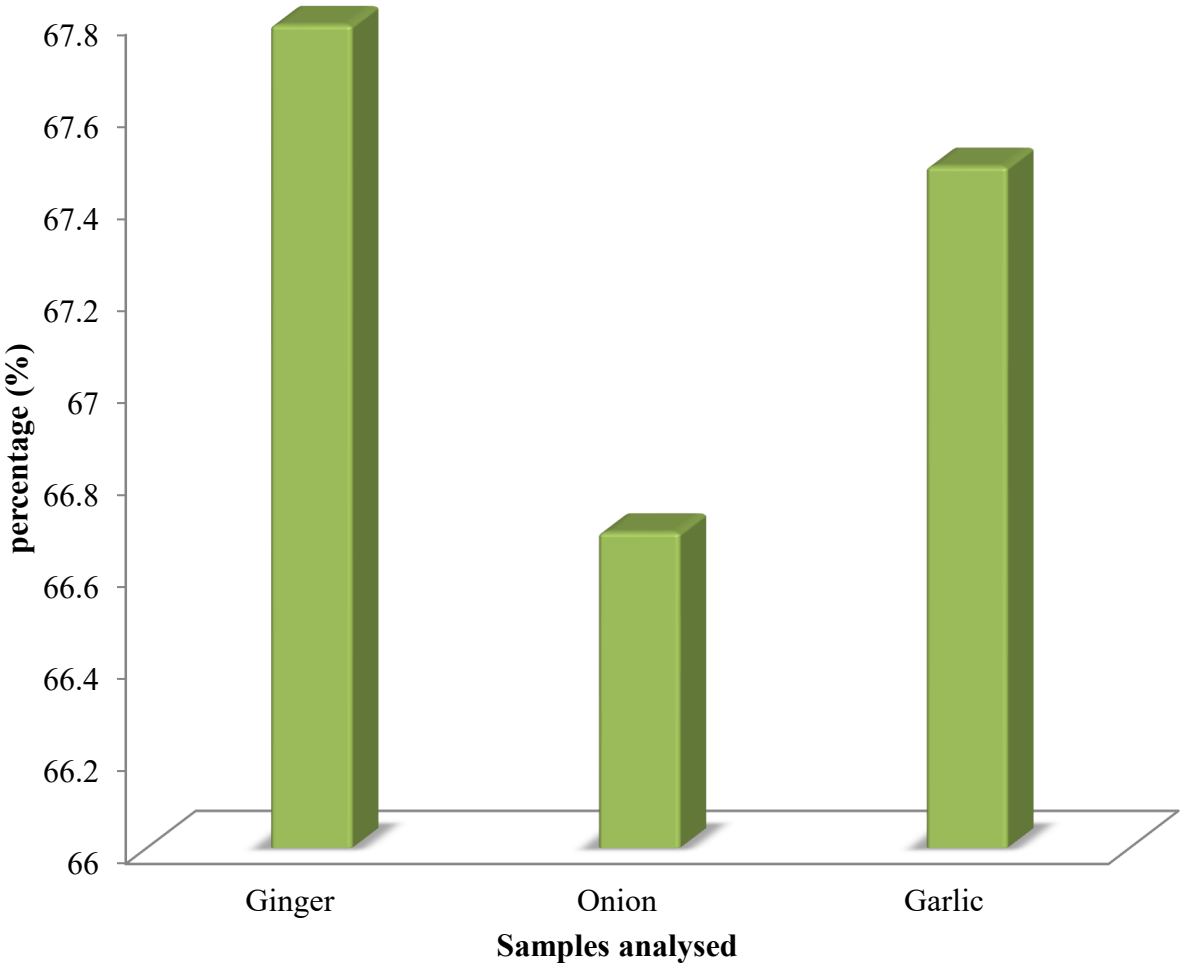

Fig. 4.21: Percentage of Crude Protein

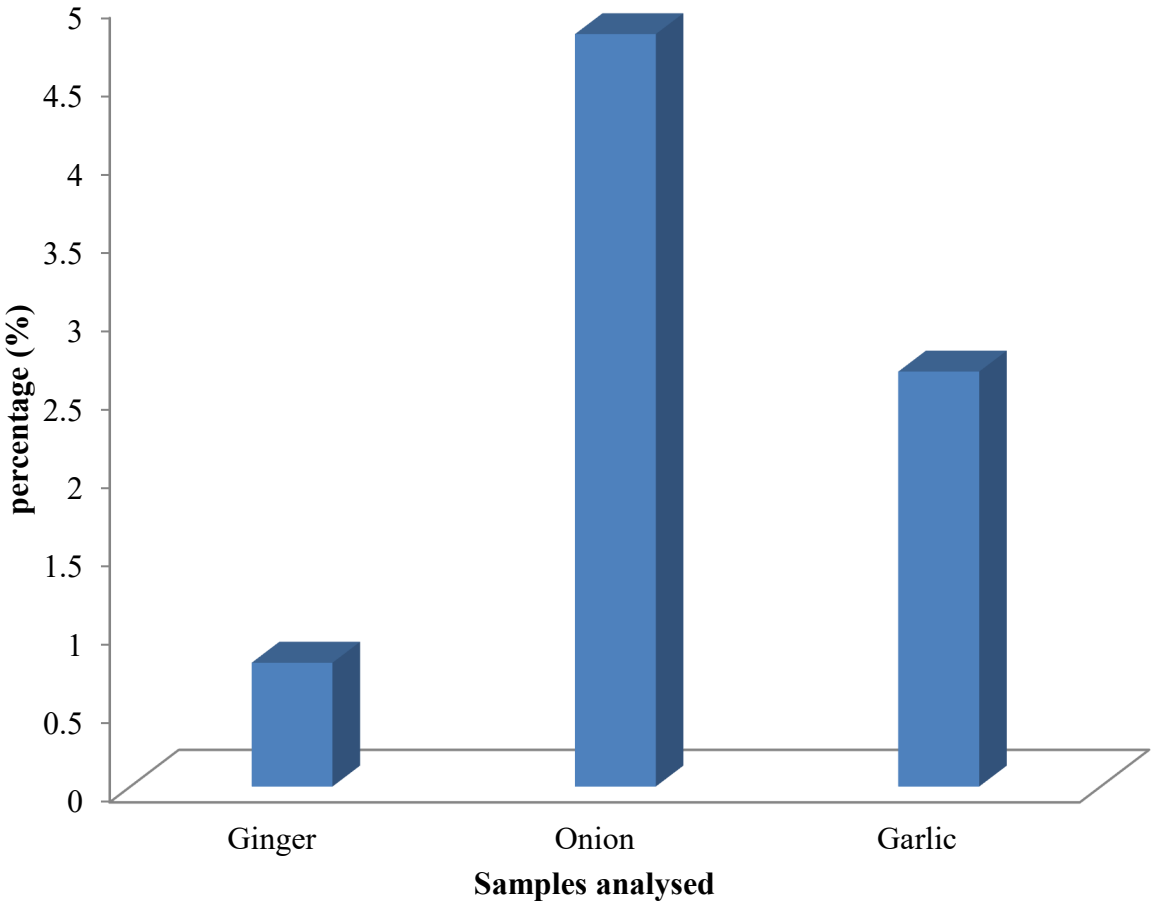

Fig. 4.22: Percentage Ash content

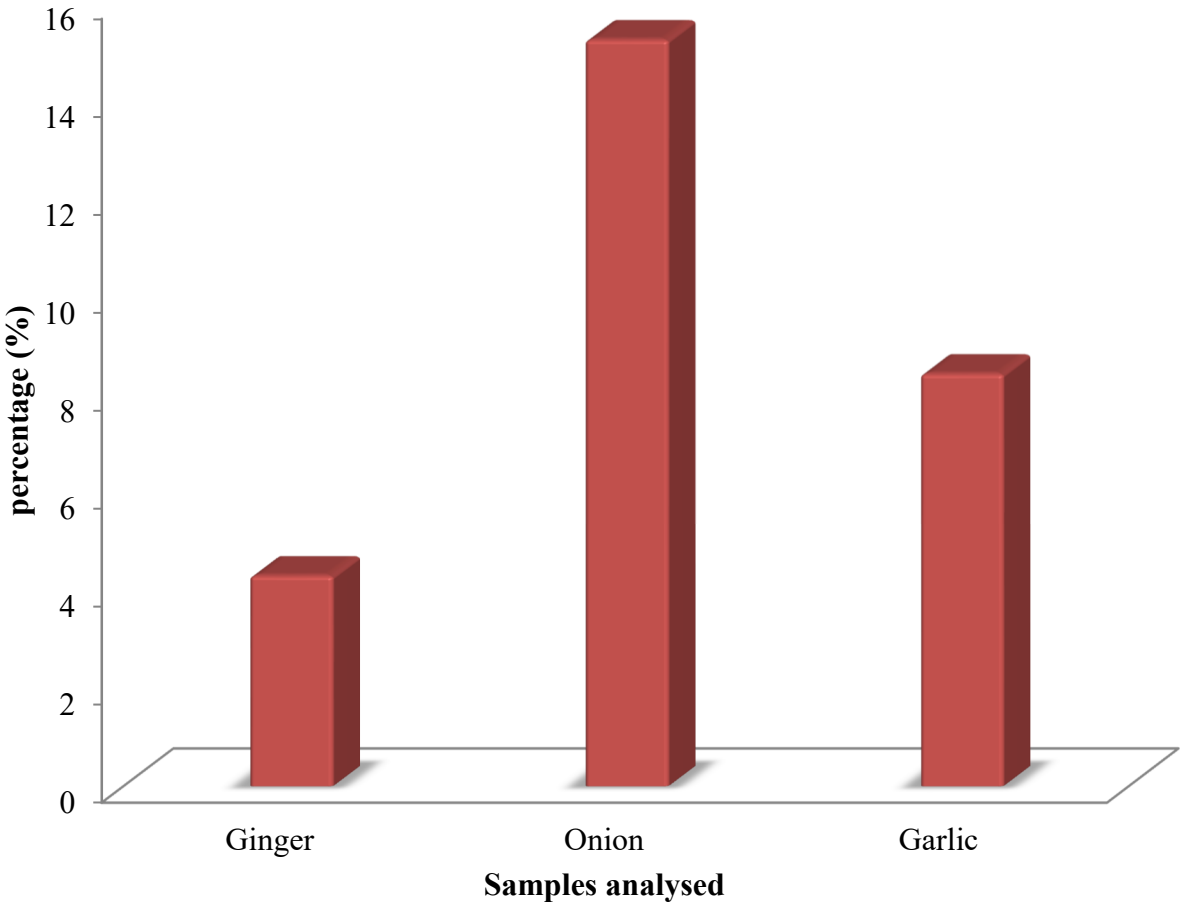

Fig. 4.23: Percentage Moisture content

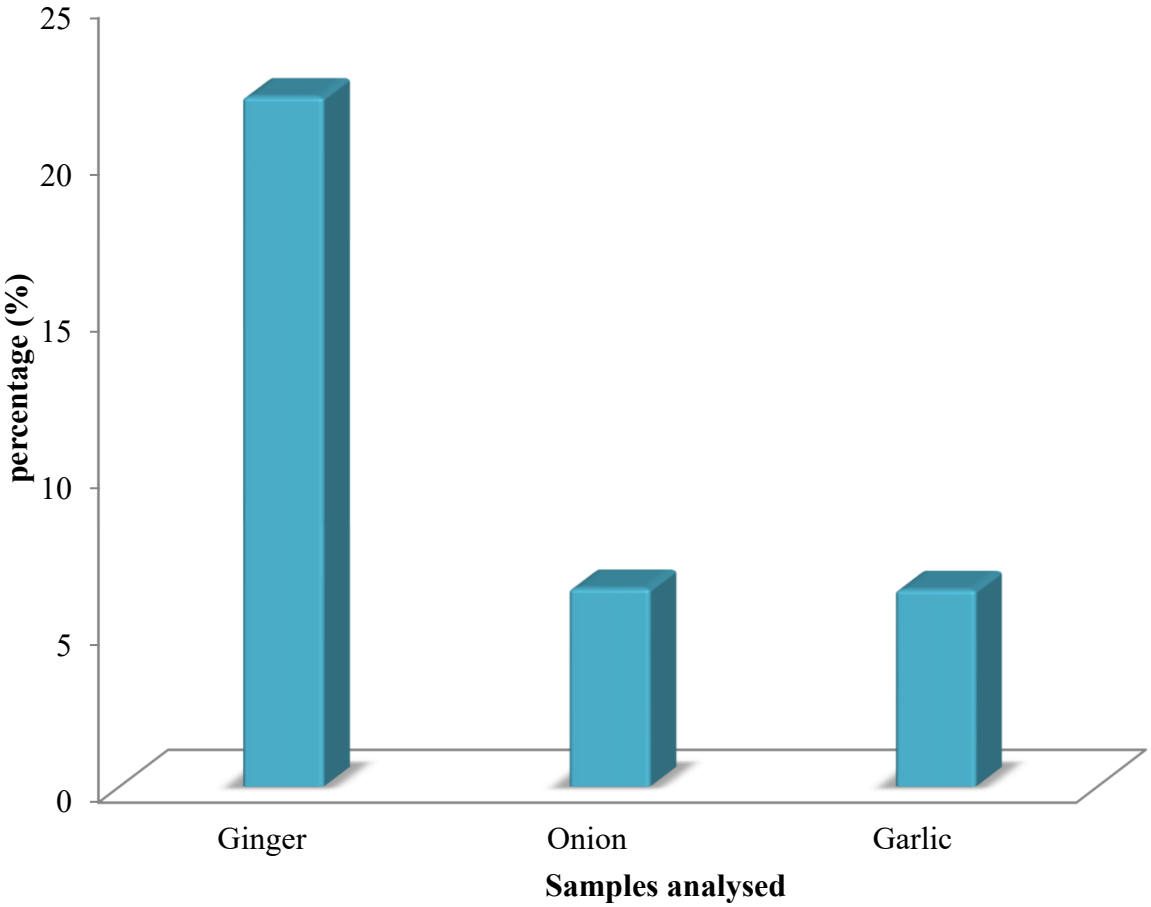

Fig. 4.24: Percentage of Crude Fibre

The figures above (4.1-4.12) show the concentrations of the heavy metals in mg/kg for the various tuber samples. Generally low level concentrations of the metals were recorded for all the samples. The concentrations of cadmium, chromium and lead were highest in cocoyam while sweet potato had the highest concentrations of iron and zinc. Lead (Pb) concentration was highest in cocoyam (0.887±0.418mg/kg) and lowest in yam (0.177±0.227mg/kg) among the tuber foods as seen in fig. 4.11. All the samples, with the exception of ginger, onion, cocoyam and sweet potato recorded mean values within the permissible limit (0.3mg/kg) set by the Food and Agricultural Organization (FAO/WHO, 2011). There was no significant difference observed ($p<0.05$). Cadmium levels ranged from 1.437±0.412mg/kg in cocoyam, followed by 1.149±0.392mg/kg in yam and least in 0.575±0.408mg/kg in Irish potato although all the samples recorded mean values of cadmium well above standard limits (0.10mg/kg) set by FAO (FAO/WHO, 2011) for safe consumption as shown in fig. 4.7. There was no significant difference observed at $p<0.05$. The copper concentration levels in the tubers were in the following order among the food tuber crops;

Cocoyam < Carrot <Cassava<Sweet Potato <Irish Potato <Yam.

All the samples fall within the permissible limit (20mg/kg) for safe consumption (FAO, 2008). There was no significant difference observed ($p< 0.05$). Chromium concentrations were the lowest of all the metals in the tuber samples, however the concentration of chromium was noticed to be highest in carrot (1.029±0.356mg/kg) among the tuberswhile undetectable levels were recorded for sweet potato and Irish potato. With the exception of sweet and irish potato, all

other samples recorded levels higher than the permissible limit (0.10mg/kg) for safe consumption (FAO, 1991). A significant difference was observed at $p>0.05$.

Among the food tubers, zinc concentrations ranged from 9.848±1.312mg/kg in sweet potato to 5.303±2.624mg/kg in Irish potato although they all fall within the standard (100mg/kg) permissible limit (FAO, 2008). There was no significant difference observed when comparing all the zinc concentrations across all the tubers ($p<0.05$). Iron concentrations was high in all the tubers with concentrations of 10.256±2.221mg/kg (sweet potato) followed by 8.974±4.441mg/kg (irish potato) recorded, however it decreased in the other samples as follows

Sweet potato>Irish potato>Cocoyam>Cassava>Yam>Carrot

All the samples fall within the permissible limit (250mg/kg) for consumption of iron set by the Food and Agricultural Organization (FAO, 2008) as shown in fig.4.4. There was no significant difference observed when comparing the Iron concentrations across all the tubers ($p<0.05$). From all the figures, chromium had the lowest mean values while iron had the highest concentration among all the tubers.

Among the spices, iron (Fe) had the highest average concentrations followed by Zinc (Zn) while the least concentrations recorded were those of Chromium (Cr). Copper concentrations were highest in ginger (4.427±0.902 mg/kg) and least in 1.042±0.45. There was a significant difference observed ($p>0.05$). High levels of Iron were recorded in ginger (16.667±2.221mg/kg) and lower concentrations were recorded in garlic (6.710+0.021mg/kg).

Ginger had the highest concentration of most of the heavy metals. Lead concentrations in the samples ranged from 0.350±0.007mg/kg to 1.271±1.007mg/kg in the order below.

Garlic>Onion>Ginger. The high concentration may be as a result of contamination during harvesting, processing or preparation.

However these results were not in full agreement with what has been recorded in previous literatures for tubers. For instance, Nson et al., (2014) reported highest Copper concentration in cocoyam, followed by yam, cassava and potato with values of 2.062mg/kg, 2.144 mg/kg, 1.768 mg/kg and 0.862 mg/kg respectively. He also reported higher mean values of Zinc (11.264mg/kg-30.772 mg/kg) and Iron (27.918-45.872 mg/kg) in tuber samples. Zurera et al. (1989) have reported that the difference in metal contents present in food samples depended on the physical and chemical nature of the soil and absorption capacity of each metal by the plant, which is altered by various factors like environmental and human interference, and nature of the plant (Zurera et al., 1989). The foods may also be contaminated during harvesting, storage, transportation, processing and preparation (Ward, 1995).

Figures 4.13 – 4.24 above show the proximate analysis of the various samples (food tubers and spices) showing the proximate chemical composition of each sample.

Crude protein contents ranged from 2.137-5.153%. Yam was highest in protein with cassava recording the lowest protein content. All the samples had low protein percentage as expected. There was significant difference observed for the entire tuber samples at $p>0.05$. Fat content in the tubers ranged from $3.160\pm0.046\%$ (Cassava) to $4.740\pm0.5454\%$ (Cocoyam) as seen in fig. 4.14. All the samples were low in fat and there was no significant difference observed ($p<0.05$).

Most tubers are grown for their starch filled roots and eaten predominantly as carbohydrate source in foods (Onwueme, 1998; O'Hair, 1995).The carbohydrate content is also known as Nitrogen free extract and was found to be high among all the samples. Fig. 4.18 shows

the carbohydrate concentration which is the major proportion of the tubers and was found to be highest in yam (66.58%) and lowest in cocoyam (62.78%). There was significant difference observed ($p>0.05$). Percentage ash of the tubers relates to its inorganic content. The percentage of the ash content in the samples was highest in cocoyam (2.807%) and lowest in yam (1.047%). There was a significant difference observed ($p>0.05$). The moisture content was highest in Irish potato (20.210%) closely followed by yam (18.10$\pm$0.915%) and least in cocoyam (1.387%). Cocoyam with very lower moisture content would store for a longer time without spoilage while irish potato with a higher moisture will spoil faster due to increased microbial action (Onyieke et al.,1995).There was a significant difference observed at $p>0.005$. Fibre content was highest in cocoyam (25.447%) and least in Irish potato (4.096%) among the tuber crops. A significant difference was observed at $p>0.05$. These values may indicate the digestibility of the crops since food fibres are known to aid digestion (Ihekoronye and Ngoddy 1985).

Crude protein contents ranged from 2.420% -10.643% among spice samples. Garlic was observed to have the highest protein content (10.64%) while onion had the lowest protein percentage (2.42%). There was significant difference observed in the moisture content of the entire spice samples ($p>0.005$).

All the spices had relatively low fat content. The fat content of the spices samples ranged from 2.400% - 4.530%. Garlic had the highest fat content (4.53%) while ginger had the lowest (2.25%). There was a significant difference observed at $p>0.05$. The carbohydrate concentration which was the major proportion of the spice tubers was found to be highest in garlic and lowest in onion with values of 67.480% and 66.687% respectively. There was a significant difference observed at $p>0.005$. Ash content in the spices ranged from 0.787$\pm$0.021 in Ginger to 4.797$\pm$0.176 in Onion. The Ash content indicates the level of inorganic matter in the samples.

Fibre content was highest in ginger (21.990%), and least in garlic (6.270%). A significant difference was observed at $p>0.05$.

These results are not in full agreement with what has been recorded in previous literatures for tubers. For instance, Osagie and Eka (1998) reported the carbohydrate content of tubers on fresh weight basis to be in the following order

CS>CY>AY>SP>IP

Where CS>Cassava AY>African Yam CY-Cocoyam

SP>Sweet potato IP> Irish Potato

However, the crude protein content was also reported to be highest in yam and lowest in cassava. These variations may be as a result of the species or variety of plant investigated, season of cultivation or other factors such as geographical location since these factors have been known to affect the chemical composition of plant materials (Ibiyemi, 1988; Faloye et al, 2002) and tubers are known to have different varieties with corresponding different composition (Kissai, 2004; Zuirera et al., 1989).

CHAPTER FIVE

5.0 Conclusion and Recommendation

5.1 Conclusion

From the data obtained, it can be concluded that all the tubers and spices had good essential nutrient content. The proximate analysis represents variations in the dietary quality of the various tubers and spices. The analysis showed that the levels of cadmium, chromium, and lead were all above the Food and Agricultural (FAO) standard of maximum permissible limit while all the other heavy metals were within safe limits in the spices. With the exception of lead, all the heavy metals were within the FAO standard of maximum permissible levels in the tubers.

5.2 Recommendation

It is recommended that more comparative studies be done on similar samples from farms, after processing, after storage and after preparation to ascertain the true source of the heavy metals.

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APPENDICES

APPENDIX I: HEAVY METAL CONCENTRATION

Appendix IA: Heavy Metal Concentration in Food Tubers

Sample	Cd	Cr	Cu	Fe	Pb	Zn
Irish	0.575±0.498	ND	2.083±0.451	8.974±0.441	0.316±0.107	5.303±2.624
Yam	1.149±0.498	0.412±0.113	2.865±0.451	6.410±0.221	0.177±0.307	9.091±2.273
Cocoyam	1.437±0.498	0.617±0.000	1.042±0.451	7.692±3.846	0.887±0.307	8.333±5.249
Sweet	0.862±0.000	ND	2.083±0.451	10.256±2.221	0.709±0.307	9.848±1.312
Cassava	0.862±0.000	0.412±0.356	1.823±0.451	7.692±0.662	0.355±0.307	9.091±1.013
Carrot	0.575±0.498	1.029±0.356	1.302±0.451	6.410±2.221	0.355±0.307	7.576±2.624

Appendix IB: Heavy Metal Concentration in Spice Tubers

Sample	Cd	Cr	Cu	Fe	Pb	Zn
Ginger	3.161±0.498	0.617±0.017	4.427±0.902	16.667±2.221	1.241±0.307	12.879±3.472
Onion	0.862±0.130	0.617±0.030	1.302±1.193	12.821±1.006	1.241±0.107	10.606±1.312
Carlic	0.575±0.198	0.823±0.356	1.042±0.451	6.410±2.221	0.355±0.014	3.030±1.312

APPENDIX II: PROXIMATE ANALYSIS

APPENDIX IIA: Proximate analysis of food tubers

Sample	% Protein	%fat	% Cabohydrate	%Ash	% Moisture	% fibre
Irish	3.590±1.688	4.267±0.157	65.847±0.930	1.036±0.031	20.210±1.544	4.096±0.234
Yam	5.023±0.131	3.377±0.275	66.580±0.531	1.047±0.032	18.107±0.915	4.813±0.198
Cocoyam	3.180±0.161	4.740±0.545	62.780±3.344	2.807±0.050	1.387±0.085	25.447±1.820
Sweet	3.287±0.418	3.530±0.399	64.327±3.398	2.240±0.151	3.390±0.157	22.167±0.897
Cassava	2.517±0.380	3.160±0.046	64.630±2.389	2.497±0.274	13.070±8.124	17.477±4.254
Carrot	4.280±0.252	2.400±0.431	53.270±1.012	6.190±0.199	16.457±2.697	20.453±2.898

APPENDIX IIB: Proximate analysis of Spice Tubers

Sample	% Protein	%fat	% Cabohydrate	%Ash	% Moisture	% fibre
Ginger	4.687±0.316	2.247±0.162	66.687±2.817	0.787±0.021	4.303±0.201	21.990±0.202
Onion	2.420±0.026	3.660±0.520	66.687±2.817	4.797±0.176	15.247±0.072	6.313±0.012
Galic	10.643±1.286	4.530±0.409	67.480±0.471	2.643±0.200	8.433±0.350	6.270±1.563

APPENDIX III: ANOVA RESULT FOR PROXIMATE ANALYSIS OF TUBERS

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	1.724138	0.574713	0.247721
Yam	3	3.448276	1.149425	0.247721
Cocoyam	3	4.310345	1.436782	0.247721
Sweet	3	2.586207	0.862069	1.85E-32
Cassava	3	2.586207	0.862069	1.85E-32
Cd 1	5	6.034483	1.206897	0.222949
Cd 2	5	3.448276	0.689655	0.148633
Cd 3	5	5.172414	1.034483	0.148633

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	1.288149	4	0.322037	3.25	0.073213	3.837853
Columns	0.693619	2	0.346809	3.5	0.080909	4.45897
Error	0.792707	8	0.099088			
Total	2.774475	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	0	0	0
Yam	3	1.234568	0.411523	0.508053
Cocoyam	3	1.851852	0.617284	0
Sweet	3	0	0	0
Cassava	3	1.234568	0.411523	0.127013
Cr 1	5	0.617284	0.123457	0.076208
Cr 2	5	2.469136	0.493827	0.266728
Cr 3	5	1.234568	0.246914	0.114312

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.914495	4	0.228624	2	0.1875	3.837853
Columns	0.355637	2	0.177818	1.555556	0.268739	4.45897
Error	0.914495	8	0.114312			
Total	2.184626	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	6.25	2.083333	0.203451
Yam	3	8.59375	2.864583	0.203451
Cocoyam	3	3.125	1.041667	0.203451
Sweet	3	6.25	2.083333	0.203451
Cassava	3	5.46875	1.822917	0.203451
Cu 1	5	10.15625	2.03125	0.793457
Cu 2	5	7.8125	1.5625	0.305176
Cu 3	5	11.71875	2.34375	0.305176

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	5.126953	4	1.281738	21	0.000266	3.837853
Columns	1.546224	2	0.773112	12.66667	0.003318	4.45897
Error	0.488281	8	0.061035			
Total	7.161458	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	26.92308	8.974359	19.72387
Yam	3	19.23077	6.410256	4.930966
Cocoyam	3	23.07692	7.692308	14.7929
Sweet	3	30.76923	10.25641	4.930966
Cassava	3	23.07692	7.692308	44.3787
Fe 1	5	23.07692	4.615385	10.35503
Fe 2	5	50	10	11.83432
Fe 3	5	50	10	4.43787

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	25.64103	4	6.410256	0.634146	0.652338	3.837853
Columns	96.64694	2	48.32347	4.780488	0.043069	4.45897
Error	80.86785	8	10.10848			
Total	203.1558	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	1.06383	0.35461	0.094311
Yam	3	0.531915	0.177305	0.094311
Cocoyam	3	2.659574	0.886525	0.094311
Sweet	3	2.12766	0.70922	0.094311
Cassava	3	1.06383	0.35461	0.094311
Pb 1	5	1.06383	0.212766	0.08488
Pb 2	5	3.191489	0.638298	0.056587
Pb 3	5	3.191489	0.638298	0.198053

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	1.01856	4	0.25464	6	0.015625	3.837853
Columns	0.603591	2	0.301796	7.111111	0.016796	4.45897
Error	0.33952	8	0.04244			
Total	1.961672	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	15.90909	5.30303	6.887052
Yam	3	27.27273	9.090909	5.165289
Cocoyam	3	25	8.333333	27.54821
Sweet	3	29.54545	9.848485	1.721763
Cassava	3	27.27273	9.090909	36.15702
Zn 1	5	22.72727	4.545455	10.33058
Zn 2	5	47.72727	9.545455	3.615702
Zn 3	5	54.54545	10.90909	6.198347

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	37.87879	4	9.469697	1.774194	0.227126	3.837853
Columns	112.259	2	56.12948	10.51613	0.005765	4.45897
Error	42.69972	8	5.337466			
Total	192.8375	14				

APPENDIX IV: ANOVA RESULT FOR HEAVY METAL CONCENTRATION

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
0.862069	2	0.862069	0.431034	0.371581
3.448276	2	6.034483	3.017241	0.371581
0.862069	2	1.724138	0.862069	0
0.862069	2	0.862069	0.431034	0.371581
Cd 2	4	6.034483	1.508621	1.672117
Cd 3	4	3.448276	0.862069	1.486326

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	9.196641	3	3.065547	33	0.008487	9.276628
Columns	0.836058	1	0.836058	9	0.057669	10.12796
Error	0.278686	3	0.092895			
Total	10.31139	7				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	3.08642	1.028807	0.127013
Ginger	3	1.851852	0.617284	0.381039
Onion	3	1.851852	0.617284	0
Carlic	3	2.469136	0.823045	0.127013
Cr 1	4	2.469136	0.617284	0
Cr 2	4	3.08642	0.771605	0.349286
Cr 3	4	3.703704	0.925926	0.127013

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	0.349286	3	0.116429	0.647059	0.612811	4.757063
Columns	0.19052	2	0.09526	0.529412	0.614125	5.143253
Error	1.079612	6	0.179935			
Total	1.619418	11				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	3.90625	1.302083	0.203451
Ginger	3	13.28125	4.427083	0.813802
Onion	3	3.90625	1.302083	1.424154
Carlic	3	3.125	1.041667	0.203451
Cu 1	4	9.375	2.34375	4.882813
Cu 2	4	7.8125	1.953125	1.831055
Cu 3	4	7.03125	1.757813	2.593994

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	23.34595	3	7.781982	10.2	0.009024	4.757063
Columns	0.712077	2	0.356038	0.466667	0.648078	5.143253
Error	4.577637	6	0.762939			
Total	28.63566	11				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	19.23077	6.410256	4.930966
Ginger	3	50	16.66667	4.930966
Onion	3	38.46154	12.82051	64.10256
Carlic	3	19.23077	6.410256	4.930966
Fe 1	4	30.76923	7.692308	29.5858
Fe 2	4	46.15385	11.53846	49.30966
Fe 3	4	50	12.5	33.28402

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	230.5227	3	76.84089	4.348837	0.059716	4.757063
Columns	51.77515	2	25.88757	1.465116	0.303295	5.143253
Error	106.0158	6	17.6693			
Total	388.3136	11				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	1.06383	0.35461	0.094311
Ginger	3	3.723404	1.241135	0.094311
Onion	3	3.723404	1.241135	1.226045
Carlic	3	1.06383	0.35461	0.377245
Pb 1	4	3.723404	0.930851	1.202467
Pb 2	4	1.595745	0.398936	0.259356
Pb 3	4	4.255319	1.06383	0.188622

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	2.357779	3	0.785926	1.818182	0.244158	4.757063
Columns	0.990267	2	0.495134	1.145455	0.379007	5.143253
Error	2.593557	6	0.432259			
Total	5.941603	11				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	22.72727	7.575758	6.887052
Ginger	3	38.63636	12.87879	12.05234
Onion	3	31.81818	10.60606	1.721763
Carlic	3	9.090909	3.030303	1.721763
Zn 1	4	34.09091	8.522727	39.17011
Zn 2	4	34.09091	8.522727	21.95248
Zn 3	4	34.09091	8.522727	8.178375

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Rows	163.1371	3	54.37902	7.288462	0.019991	4.757063
Columns	0	2	0	0	1	5.143253
Error	44.76584	6	7.460973			
Total	207.9029	11				

APPENDIX IV: ANOVA RESULT FOR THE PROXIMATE ANALYSIS

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	10.77	3.59	2.8483
Yam	3	15.07	5.023333	0.017033
Cocoyam	3	9.54	3.18	0.0259
Sweet	3	9.86	3.286667	0.174433
Cassava	3	7.55	2.516667	0.144233
% Protein A	5	19.54	3.908	1.57867
% Protein B	5	16.98	3.396	1.32663
% Protein C	5	16.27	3.254	0.98503

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	10.32489	4	2.581223	3.943488	0.046851	3.837853
Columns	1.183373	2	0.591687	0.903955	0.442644	4.45897
Error	5.236427	8	0.654553			
Total	16.74469	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	12.8	4.266667	0.024633
Yam	3	10.13	3.376667	0.075433
Cocoyam	3	14.22	4.74	0.2971
Sweet	3	10.59	3.53	0.1591
Cassava	3	9.48	3.16	0.0021
%fat A	5	20.07	4.014	0.67688
%fat B	5	19.63	3.926	0.39933
%fat C	5	17.52	3.504	0.33868

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	5.28604	4	1.32151	28.30392	8.99E-05	3.837853
Columns	0.743213	2	0.371607	7.95902	0.012516	4.45897
Error	0.37352	8	0.04669			
Total	6.402773	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	197.54	65.84667	0.865033
Yam	3	199.74	66.58	0.2821
Cocoyam	3	188.34	62.78	11.1841
Sweet	3	192.98	64.32667	11.54743
Cassava	3	193.89	64.63	5.7061
%Cabohydrate A	5	324.59	64.918	4.14222
%Cabohydrate B	5	320.11	64.022	6.86717
%Cabohydrate C	5	327.79	65.558	8.73872

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	25.77576	4	6.44394	0.96871	0.474857	3.837853
Columns	5.952853	2	2.976427	0.447443	0.654333	4.45897
Error	53.21668	8	6.652085			
Total	84.94529	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	3.109	1.036333	0.00096
Yam	3	3.14	1.046667	0.001033
Cocoyam	3	8.42	2.806667	0.002533
Sweet	3	6.72	2.24	0.0229
Cassava	3	7.49	2.496667	0.075233
%Ash A	5	9.539	1.9078	0.672919
%Ash B	5	9.66	1.932	0.66647
%Ash C	5	9.68	1.936	0.78478

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	8.293684	4	2.073421	81.71418	1.6E-06	3.837853
Columns	0.002328	2	0.001164	0.045876	0.95541	4.45897
Error	0.202993	8	0.025374			
Total	8.499005	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	60.63	20.21	2.3839
Yam	3	54.32	18.10667	0.837233
Cocoyam	3	4.16	1.386667	0.007233
Sweet	3	10.17	3.39	0.0247
Cassava	3	39.21	13.07	65.9959
% Moisture A	5	51.68	10.336	70.23353
% Moisture B	5	52.87	10.574	82.27658
% Moisture C	5	63.94	12.788	94.79672

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	869.014	4	217.2535	14.45786	0.000984	3.837853
Columns	18.28457	2	9.142287	0.608404	0.567594	4.45897
Error	120.2134	8	15.02667			
Total	1007.512	14				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Irish	3	12.289	4.096333	0.05474
Yam	3	14.44	4.813333	0.039033
Cocoyam	3	76.34	25.44667	3.311633
Sweet	3	66.5	22.16667	0.805033
Cassava	3	52.43	17.47667	18.09543
% fibre A	5	73.279	14.6558	100.3583
% fibre B	5	70.81	14.162	101.8451
% fibre C	5	77.91	15.582	99.46477

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	1167.257	4	291.8144	59.22919	5.54E-06	3.837853
Columns	5.196808	2	2.598404	0.527395	0.609322	4.45897
Error	39.41494	8	4.926867			
Total	1211.869	14				

Proximate analysis of Spice Tube

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	12.84	4.28	0.0637
Ginger	3	14.06	4.686667	0.099633
Onion	3	7.26	2.42	0.0007
Galic	3	31.93	10.64333	1.653333
% Protein A	4	23.48	5.87	18.24507
% Protein B	4	21.03	5.2575	9.760692
% Protein C	4	21.58	5.395	11.02037

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	114.2699	3	38.08996	81.3748	2.99E-05	4.757063
Columns	0.82625	2	0.413125	0.882594	0.461315	5.143253
Error	2.808483	6	0.468081			
Total	117.9046	11				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	7.2	2.4	0.1857
Ginger	3	6.74	2.246667	0.026233
Onion	3	10.98	3.66	0.2709
Galic	3	13.59	4.53	0.1675
%fat A	4	13.14	3.285	1.4041
%fat B	4	13.02	3.255	0.927367
%fat C	4	12.35	3.0875	1.600892

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	10.58703	3	3.529008	17.49849	0.002268	4.757063
Columns	0.090617	2	0.045308	0.22466	0.805215	5.143253
Error	1.21005	6	0.201675			
Total	11.88769	11				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	159.81	53.27	16.0951
Ginger	3	200.06	66.68667	7.934033
Onion	3	200.06	66.68667	7.934033
Galic	3	202.44	67.48	0.2223
%Cabohydrate A	4	252.98	63.245	71.4057
%Cabohydrate B	4	246.45	61.6125	51.09803
%Cabohydrate C	4	262.94	65.735	28.25903

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	422.3976	3	140.7992	28.26279	0.000616	4.757063
Columns	34.48022	2	17.24011	3.460628	0.100124	5.143253
Error	29.89072	6	4.981786			
Total	486.7685	11				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	18.57	6.19	0.0397
Ginger	3	2.36	0.786667	0.000433
Onion	3	14.39	4.796667	0.031033
Galic	3	7.93	2.643333	0.040133
%Ash A	4	14.63	3.6575	5.667225
%Ash B	4	13.91	3.4775	5.268092
%Ash C	4	14.71	3.6775	6.076625

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	50.91029	3	16.9701	811.104	3.25E-08	4.757063
Columns	0.097067	2	0.048533	2.319703	0.17935	5.143253
Error	0.125533	6	0.020922			
Total	51.13289	11				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	49.37	16.45667	7.275233
Ginger	3	12.91	4.303333	10.24923
Onion	3	45.74	15.24667	0.005233
Galic	3	821.26	273.7533	210871.2
% Moisture A	4	40.15	10.0375	33.76943
% Moisture B	4	48.07	12.0175	18.12283
% Moisture C	4	841.06	210.265	156727.9

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	154424.6	3	51474.87	0.977635	0.463188	4.757063
Columns	105862.7	2	52931.36	1.005297	0.420203	5.143253
Error	315914.6	6	52652.44			
Total	576202	11				

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
Carrot	3	61.36	20.45333	8.400633
Ginger	3	65.97	21.99	1.4439
Onion	3	18.94	6.313333	0.000133
Galic	3	18.81	6.27	2.4421
% fibre A	4	56.64	14.16	103.0162
% fibre B	4	55.43	13.8575	68.66349
% fibre C	4	53.01	13.2525	60.02863

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	672.2595	3	224.0865	58.80142	7.69E-05	4.757063
Columns	1.708117	2	0.854058	0.224109	0.805628	5.143253
Error	22.86542	6	3.810903			
Total	696.8331	11				