LEVELS OF SELECTED ESSENTIAL ELEMENTS IN FOUR PARTS OF THREE VARIETIES OF WATERMELONS SOLD IN GITHURAI AND MWEA MARKETS IN KENYA

BY

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REG. NO: I56/CE/12245/2009

A thesis submitted in partial fulfillment of the requirements for the award of the degree of Master of Science in Applied Analytical Chemistry in the School of Pure and Applied Sciences of Kenyatta University

JUNE 2012

DECLARATION

I hereby declare that this is my original work and has not been presented for the award of a degree or any other award in any other university.

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DEDICATION

This work is dedicated to my beloved and supportive husband Boniface and our children Johnpeter and Joan.

ACKNOWLEDGEMENTS

First and foremost I would like to thank the almighty God for enabling me to come this far. My gratitude goes first to my supervisors Prof. Jane Murungi and Dr. Ruth Wanjau for their encouragement, support, guidance and advice throughout the research stage. Their useful suggestions, comments and timely corrections after patiently reading each of this thesis made it possible for me to complete my work in good time.

I am also grateful to lecturers and technical staff of Chemistry Department, Kenyatta University and staff of Department of Geology and Mines, Ministry of Environment and Natural Resources for their substantial help during this study.

I would also like to acknowledge the support I have received from my colleagues at work and my course mates for supportive ideas and advice throughout the course.

Finally am deeply grateful to my husband Boniface Kimeu, for his support both academically and financially and our children Johnpeter and Joan for their encouragement, patience and understanding during my absence.

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ABBREVIATIONS AND ACRONYMS

AHR	APPLIED HORTICULTURAL REPORT
AMA	AMERICAN MEDICAL ASSOCIATION
DF	DEGREES OF FREEDOM
DW	DRY WEIGHT
EDXRF	ENERGY DISPERSIVE X-RAY FLUORESCENCE
FAAS	FLAME ATOMIC ABSORPTION SPECTROSCOPY
FAO	FOOD AGRICULTURAL ORGANIZATION
FNB	FOOD AND NUTRITIONAL BOARD
ICP-AES	INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY
ICP-MS	INDUCTIVELY COUPLED PLASMA MASS SPECTROSCOPY
IPCS	INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY
KSC	KENYA SEED COMPANY
MII	MINERAL INFORMATION INSTITUTE
NRC	NATIONAL RESEARCH COUNCIL
RDA	RECOMMENDED DAILY ALLOWANCES
SCF	SCIENTIFIC COMMITTEE FOR FOODS
UL	UPPER LIMIT
USDA	UNITED STATES DEPARTMENT OF AGRICULTURE
WHF	WORLD HEALTHIEST FOODS
WHO	WORLD HEALTH ORGANIZATION

ABSTRACT

Watermelons belong to the family cucurbitaceous, they are fruits like cantaloupe, pumpkin and similar to plants that grow on vines on the ground. There are over 1,200 varieties of watermelons in the world, several of these varieties have been recommended for Kenya range of climate, however only three varieties are commercially grown in Kenya namely; the Charleston Grey (Sugar F1), Crimson sweet (Zebra) and Sugar baby. Watermelon has four distinct parts; the seeds, the pink flesh, the white flesh and the peel. Watermelon has high content of water of about 93%. It is a rich source of essential minerals such as calcium, magnesium, phosphorous, potassium, sodium and smaller amounts of copper, iron, zinc and selenium. Watermelons have substantial amounts of boron, iodine, chromium, silicon and molybdenum. The levels of nutrients in different parts of the watermelons may be different. Different people consume different parts and varieties of watermelon and thus depending on the part/variety of watermelon consumed these people may get different nutrients and levels of the same. However, levels of nutrients in various parts/varieties of watermelon have not been documented. There is need to have nutrient of various parts/varieties determined and documented. This study therefore determined the levels of Si, Ca, B, Mo, Cr and V in the four parts of Charleston grey, Crimson sweet and Sugar baby watermelons. The samples were obtained from Githurai and Mwea markets from different vendors. The elements were analyzed using atomic absorption spectrophotometer and data analyzed using ANOVA. The results of this study showed that there were variations in levels of essential elements the parts and varieties of watermelons bought from Githurai and Mwea markets. Significant high mean levels ($p = 0.002$) of 1.28±0.02 mg/g B and ($p = 0.001$) in 471.89±13.89 µg/g V, 40.33±1.58 µg/g Mo and 44.67±1.10 µg/g Cr were recorded in seeds compared to other parts of Sugarbaby watermelons samples. Significantly high mean levels of 1.44±0.12 mg/g Si ($p = 0.001$) were recorded by the peel/rind compared to other parts of Charleston grey watermelons samples. Compared to other varieties of watermelon the Crimson sweet recorded significantly high amounts of 31.11±1.81 µg/g Mo, 297.67±8.28 µg/g V and 1.15±0.05 mg/g B ($p = 0.001$). Charleston grey watermelons samples bought form Mwea market recorded significantly high amount of Cr of 28.89±3.33 µg/g ($p = 0.002$) compared to those obtained from Githurai market. It would be recommended that people find ways of eating all the parts and varieties of watermelons.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background information

Availability of high quality, nutritious food is something most people take for granted. To be healthy and active, one requires food in adequate quantity, quality and variety to meet energy needs and nutrients. About 850 million people in the world today are chronically undernourished and unable to obtain sufficient food to meet minimum energy needs and this number increases during seasonal food shortages, in times of famine and social unrest (FAO, 2007). The majority of the undernourished people come from developing countries which accounts for 95% (798 million) (FAO, 2007). In Kenya there are about 9.7 million people who are undernourished (FAO, 2007). Most common deficiencies are those from iron, zinc, iodine, selenium and vitamin A. As a result high quality analysis of food is essential. It enables us to determine its safety, nutritional value and monitor its quality. Essential elements such as B, Si, Ca, V, Mo and Cr are good for health for they reduce risk of non communicable chronic diseases such as cancer, diabetes, osteoporosis and cardiovascular diseases (Sandstorm and Walter, 2001).

Inappropriate dietary and lifestyle patterns such as regular consumption of diet high in processed food, refined food, white sugar, flour and junk food, decreased physical activities and increased tobacco use has lead to increase in diet-related chronic non communicable diseases such as obesity, osteoporosis, diabetes mellitus, cardiovascular disease (CVD), hypertension and stroke, and some types of cancer which are becoming increasingly significant causes of disability and premature deaths (WHO/FAO, 2003). Nutrition is coming to the force as a major modifiable determinant of chronic disease, with scientific evidence

increasingly supporting the view that alterations in diet have strong effects, both positive and negative, on health throughout life (WHO/FAO, 2003).

Consumption of fruits and vegetables plays a vital role in providing a diversified and nutritious diet (WHO, 2005). Daily intake of fresh fruits and vegetables in adequate quantities is recommended to reduce risk of coronary heart diseases, stroke and high blood pressure (WHO/FAO, 2003). Chromium plays a role in the management of heart diseases by regulating fat and cholesterol synthesis in the liver (WHO, 1999), Calcium lowers cholesterol levels and helps cardiovascular disease (Balch, 2006) and boron has been shown to support the functions of calcium (Schaafsma, 2001). Cancer is the leading cause of death globally. The world health organization estimated that 7.6 million people died of cancer in 2005 and 84 million people will die in the next ten years if action is not taken (WHO, 2007).

Eating a daily diet that includes a variety of foods from plant sources, such as fresh fruits, vegetables, whole grains, and whole grain breads and cereals can reduce risks of cancer. Fruits and vegetables contain calcium which reduces the risk of colon cancer (NADC, 1998) and boron which reduces the risk of prostate cancer (Zhang *et al.,* 2001). More than 220 million people worldwide have diabetes. In 2005, an estimated 1.1 million people died from diabetes. WHO projects those diabetes deaths will double between 2005 and 2030 (WHO, 2005). About 3.5 million Kenyans are thought to be suffering from diabetes and 10% of whom are young people with type 1 diabetes (WHO, 2006). Diabetes is characterized by raised blood glucose levels which results from lack of a hormone insulin which controls the blood glucose levels (WHO, 2005). Healthy diet, regular physical activity, maintaining a normal body weight and avoiding tobacco use can prevent or delay the onset of diabetes (WHO, 2006). Fruits and vegetables are rich sources of chromium which regulates blood

sugar, thereby reducing insulin needs in diabetic patients (Bahkru, 2006) and vanadium which mimics the action of insulin, stimulates glucose uptake into cells and enhancing glucose metabolism (Nielson, 2001).

Osteoporosis is a disease affecting many millions of people around the world. It is characterized by low bone density which leads to fragile bones and this may result in bone fracture. About 1.66 million hip fractures occur each year in the word and this is set to increase by fourfold in year 2050 (WHO/FAO, 2003). Calcium which is one of the bone forming minerals and other minerals such as zinc, copper, manganese, boron and silicon have been found to reduce osteoporosis (WHO/FAO, 2003).

Watermelon *(Citrullus lunatus)* is one of the most cultivated and consumed crops in the world (Huh *et al.*, 2008). The global consumption of watermelon is greater than any other cucurbit with China leading in its production followed by Turkey, United States, Iran and Republic of Korea (Huh *et al.*, 2008). There are over 1,200 varieties of watermelons worldwide with wide variety of watermelons being cultivated in Africa (Zohary and Hopf, 2000). Several of these varieties have been recommended for Kenya range of climate and they include Sugarbaby, Crimson Sweet (zebra), Charleston Grey (sugar F1), Chilean black, Congo, Fairfax and Tom Watson (Tindall, 1983). However, among these cultivators only the first three are available in Kenyan markets with Sugarbaby being the most popular (HCDA, 2006). The demand for watermelons in Kenya is higher than the production resulting in the fruit being unaffordable by most Kenyans (HCDA, 2006). However, there is very little information on the dietary benefits of the watermelon grown and consumed in Kenya.

Watermelons have four distinct parts namely the rind/peel, the seed, the fleshy white and the fleshy red/pink/yellow parts. The seeds can be brown, white green, or yellow and a few varieties are actually seedless (Murray *et al.*, 2005). Watermelon pink flesh part is used make wine, as ingredients in salads and juices or just eaten as raw or as sweet juicy treat, while the rind and flesh white part are used as skin smoothers (Mayo, 2007).

Minerals such as silicon, boron and molybdenum have been found to have effects of reducing cancer in the body while vanadium and chromium regulates blood glucose levels in the body reducing effects of diabetes (Sareen *et al.*, 2008). The amounts of mineral nutrients in plants vary with species and genotype, age of plant, site and season and they vary in different organs and tissues of the same plant (Pallardy and Theodore, 2008). Watermelons and other cucurbits are medium accumulators of silicon after wheat, rice and sugarcane which are high accumulators of silicon. Plants take up silicon in form of silic acid from the soil (Ellioh *et al*., 1991). Calcium accumulation within watermelon occurs quite early during the fruit development; about 80% of the calcium found in the ripe fruit was already there 20 days after anthesis (Bemadac *et al*., 1999). Calcium moves to the seeds as the fruit matures and its utilization requires adequate boron (AHR, 2007).

Fruits and vegetables are composed of edible and non edible parts. The non edible parts are termed as food waste. The food waste is divided into three broad categories: avoidable food waste, unavoidable food waste and possibly avoidable food waste. Avoidable food waste is comprised of truly edible food items which are frequently discarded as inedible, but can actually be eaten by humans. Some examples of possibly avoidable food waste include potato peels and beetroot greens. Unavoidable food waste is comprised of inedible parts of food products, such as egg shells, bones and banana peels. A product is considered a ‘food waste’

when it is not consumed by a human, but this does not imply that the food does not mean that it can fully be utilized for another purpose. For example, food which is turned into compost or digested into biogas would be considered a food waste even though it is utilized in another way (Morgan, 2007).

In Kenya fresh produce flows into Nairobi from over 45 districts plus Tanzania and Uganda throughout the year. There are several local markets for watermelons in Kenya. These include supermarkets, Aghakhan market, city markets, Kangemi, Gikomba, Githurai market among others in Nairobi and other towns such as Embu, Mwea among others. (Ayieko *et al*., 2005).

1.2 Problem statement and justification

Incidences of cancer, diabetes, osteoporosis and hypertension are on the rise in Kenya, this is due to regular consumption of diet high in processed food, refined food, white sugar, flour and junk food, all in the name of civilization. Research has shown that most of these foods are low in nutrients and high in fats and sugar (Balch, 2006). Management and control of cancer, diabetes, osteoporosis, hypertension and cardiovascular diseases is very expensive and has lead to pain and suffering to patients and their families yet these diseases can be managed through sound dietary intervention (WHO/FAO, 2003). Daily intake of fresh fruits and vegetables in adequate quantities is recommended to reduce risk of cancer, diabetes, osteoporosis, hypertension and cardiovascular diseases (WHO/FAO, 2003).

Watermelons just like other plants accumulate essential elements in varying amounts depending on several factors such as their accumulation in soils, the pH of the soil and their forms of occurrence and physical conditions of the soil (Underwood, 1977). Watermelons contain substantial amount of calcium which is essential to the body. Limited information is

available about silicon, chromium, vanadium, molybdenum and boron in fruits and vegetables grown in Kenya. This is because the role of some of these micronutrients in the body was recently discovered for example the role of silicon was discovered in 1970's (Van *et al.*, 1999), boron in 1980's (Nielson, 1996) and molybdenum in the past few decades (FNB, 2010).

Different parts of different varieties of watermelons could have varying amounts of essential elements since their accumulation vary with species, genotype, age of plant, site and season, organs and tissues of the same plant (Pallardy and Theodeore, 2008). Studies done on nutritional value of watermelons do not specify the nutrients in all the parts (USDA, 2008). In Kenya most people consume only the red fleshy part of watermelons and discard the other parts as waste.

The role played by calcium, silicon, chromium, vanadium, molybdenum and boron in reducing cholesterol levels, regulation of blood sugar and reducing effect of prostate cancer cannot be overlooked. Watermelons are becoming popular with urban population making their demand higher than their supply as result they are very expensive compared to other fruits (HCDA, 2006). Most people only eat the fleshy parts throwing away the other parts. There is need to establish the nutrients in each part of watermelon in order to optimize their nutritional benefits. This study was therefore carried out to determine the levels of silicon, vanadium, chromium, molybdenum, boron and calcium in the four parts of watermelons that is the peel/rind, seeds, red flesh and white fleshy parts in three varieties of watermelons from Githurai and Mwea markets in Kenya.

1.3 Hypotheses

Levels of essential elements do not vary in parts and varieties of watermelons and in those sold in Githurai and Mwea markets.

1.4 Objectives

1.4.1 General objective

To determine the levels of selected essential elements in four parts of three varieties of watermelons from two markets in Kenya.

1.4.2 Specific objectives

i) To determine levels of Mo, Si, V, Ca, B and Cr in the peel/rind, the fleshy red, fleshy white and the seeds of Sugarbaby, Crimson Sweet (zebra) and Charleston Grey (SugarF1) watermelons.

ii) To determine levels of Mo, Si, V, Ca, B and Cr in Sugarbaby, Crimson Sweet (zebra) and Charleston Grey (SugarF1) watermelons.

iii) To determine levels of Mo, Si, V, Ca, B and Cr in watermelons bought from Githurai and Mwea markets.

1.5 Significance of the study

The study was done to determine levels of chromium, silicon, boron, calcium, molybdenum and vanadium in watermelons in four parts of three varieties of watermelons and provide information on the levels. The information will be used to encourage the general public to grow watermelons in their home gardens and to eat all the parts. The results of this study will be forwarded to the relevant authorities for documentation purposes.

1.6 Scope and limitations

Watermelons are sold in many markets all over the Kenya; however, samples were obtained from Mwea and Githurai markets this is because the three varieties of watermelons are available in these markets throughout the year. This study determined the levels of silicon, molybdenum, boron, calcium, chromium and vanadium in parts of watermelons. There are several varieties of watermelons but only three varieties which were available in the two markets were considered. Soils and fertilizers and pesticides residues were not considered, since it was difficult to establish the exact location where these watermelons were obtained.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Watermelons

Watermelon (*Citrullus lanatus*) is an annual plant of the Cucurbitaceae family. The edible fruit is produced on trailing vines that may reach 15 ft. (4.6 m) or more in length. Fruit vary in shape from globular to oblong. Watermelon fruits have a thin, firm outer rind, a layer of white-fleshed inner rind that may be up to about one inch thick and an interior edible pulp containing seeds, a few varieties are actually seedless. Pulp color of most commercial varieties is some shade of yellow or red (Sackett, 1974). It is related to cucumber, cantaloupe, squash and pumpkin. Watermelons are largely enriched with minerals (Murray *et al.*, 2005). The four parts of watermelons are shown in Plate 2.1

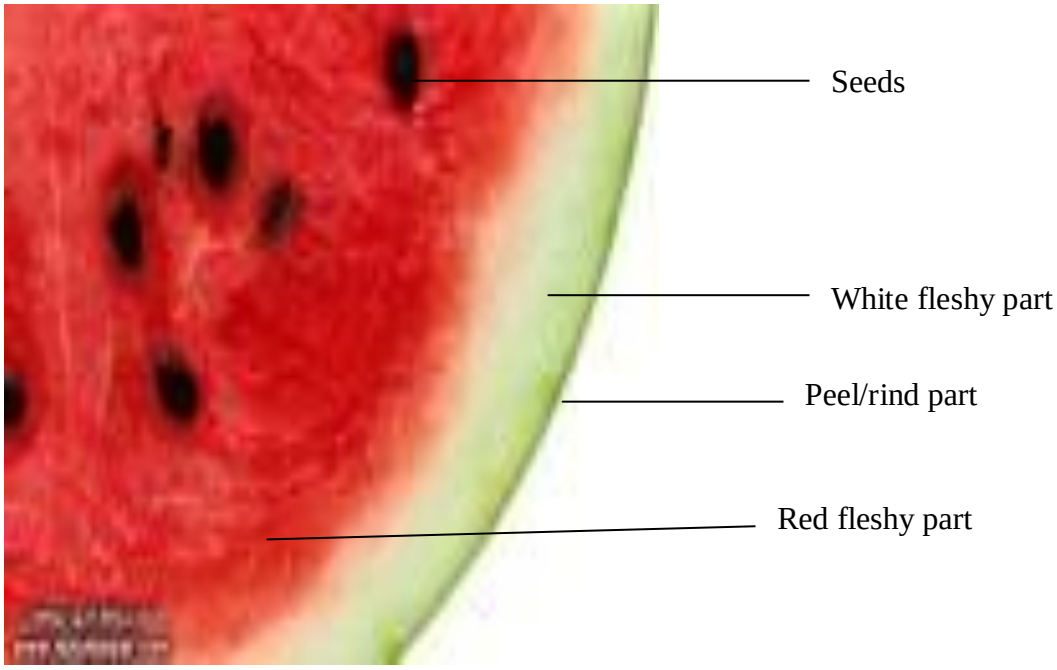

Plate 2.1: Parts of a watermelon

Plate 2.1 show watermelons have four distinct parts. Of these, the red fleshy part is commonly eaten followed by the seeds, the white fleshy part and peel/rind are normally thrown away as waste.

Several of varieties watermelons have been recommended for Kenya range of climate and they include Sugarbaby, Crimson Sweet (zebra), Charleston Grey (sugar F1), Chilean black, Congo, Fairfax and Tom Watson (Tindall, 1983). Watermelons require relatively long hot seasons for good fruit development; they do well in sandy and loam soils though they also grow well on wide range of well drained soils. This study considered the commercially grown varieties; Sugar baby, Charleston grey and Crimson sweet watermelons shown in plates 2.2-2.4. The Sugarbaby is round in shape and dark green in colour and can be cultivated all year round. It weighs about 7-9 Kg and matures in 80 days. Crimson Sweet (Zebra) medium sized, relatively striped and with dark rose juicy part. Crimson Sweet matures in 85 days. Charleston Grey (SugarF1) is oblong, has light green stripes and red flesh colour. It matures in 90 days (KSC, 2010).

High quality watermelons should be well formed, symmetrical and uniform in shape with a waxy, bright appearance. The rind/peel should be free of scars, sunburn, and abrasions with no bruising or other physical injury, free from anthracnose or other decay, and not overripe Watermelons are not suited to very long term storage; the fruit should be consumed within 2 to 3 weeks following harvest. The ideal storage temperature is in the range of 10 to 15 °C (Hardenburg *et al*., 1986).

Plate 2.1: Charleston Grey (Sugar F1)

Plate 2.2 Crimson Sweet (Zebra

Plate 2.3 Sugarbaby

Watermelons can be eaten as a whole without discarding any part (waste). For example, in China even the rind/peel is either pickled or stir fried, stewed to make it a delicious serving

and its seeds are also found useful as a snack (Mayo, 2007).). The pickles are used to prepare cakes in United State, can also be dried and the resulting brown circlets which are sweet are eaten or cooked in times of draught in Africa, the flesh rind are often curved as table decorations.(NRC, 2008). The de-skinned and de-fruited white fleshy part is cooked with Olive oil, garlic, chili peppers and sugar in Southern US, Russia Ukraine and Romania (Collins, *et al.*, 2005

The seeds of watermelon can be bruised and rubbed up with water to form an emulsion, which can be used to cure catarrhal infections, disorders of the bowels, urinary passage and fever. It is also being used as worm expeller; for example, tapeworms (Sodeke, 2005). In Nigeria the watermelons seeds are used to treat diarrhea and gonorrhea (Grubben and Denton, 2004). In Senegal, Niger, Chad and Cameroon seeds are roasted and eaten as nuts, some are powdered into a paste resembling peanut butter, while others are ground and baked into bread into which flavor is added and a number is added in soups or stews or perched and eaten with cereal products. The Yoruba ferment the cannels to produce a favorite food flavoring known las Ogiri (NRC, 2008). Sudan exports watermelon to France for snack food, to be eaten out of hand and to China's southern province where roasted watermelon seeds are an essential part of meal for special occasions including weddings, funerals and New Year celebrations (NRC, 2008). Watermelon seed oil is light, penetrating and rich in essential fatty acids (Cho and Ensminger, 2004). The seeds contain cucurbocitrin a compound that dilates capillaries and can lower blood pressure. In Chinese medicine the rind is used to treat diabetes, hypertension and it is rubbed on acne to help decrease the blemishes with its cold nature (Ellen, 2009).

Watermelon is a good source of water, it is a thirst quencher that may also reduce the inflammation that contributes to conditions like asthma, atherosclerosis, diabetes, colon

cancer and arthritis and an excellent diuretic (Murray *et al.*, 2005). Watermelons play a very important role in Africa as they are used to quench thirst when there is a shortage of water (Sodeke, 2005). The watermelon is packed with some important antioxidants in nature, for example the fleshy red part of watermelon is a source of potent caretonoid antioxidant, lycopene that reduces man's risk of prostate cancer when combined with drinking green tea (Holden *et al.,* 1999).

The nutritional profile of watermelons and related vegetables as provided by United States Department of Agriculture are provided in Table 2.1

Table 2.1: Minerals present in cucurbits

Cucurbits/ Mineral	Amount in mg/100 g				
	Watermelon (red fleshy part)	Cucumber (without peel)	Pumpkin seeds	Cantaloupe	Squash
Calcium	12.16	16.64	14.84	14.40	45.10
Copper	0.05	0.04	0.43	0.07	0.17
Fluoride	ND	0.00	ND	0.00	ND
Iodine	ND	ND	ND	0.0064	ND
Iron	0.26	0.29	2.84	0.34	0.90
Magnesium	16.72	13.52	190.92	19.20	26.65
Manganese	0.06	0.08	1.47	0.07	0.38
Molybdenum	ND	0.00052	ND	ND	ND
Phosphorus	13.68	24.96	397.64	24.00	38.94
Potassium	176.32	152.88	260.90	427.20	494.05
Selenium	0.00015	0.00031	0.00303	0.00064	0.00082
Sodium	3.04	2.08	2.26	25.60	2.05
Zinc	0.11	0.21	2.52	0.29	0.45

ND: Not Determined
Source: (USDA, 2008).

Table 2.1 shows that even those parts regarded as waste can have nutrients. Like pumpkin seeds and red fleshy part of watermelons as in Table 2.1 other parts of watermelons can be nutritious. Research has shown that fruits and vegetable waste such as tomato peels, apple, plum peach, grape and apricot peel have been found to contain antioxidants (SA, 2010).

2.3 Essential elements for human body

Essential minerals, including trace elements are inorganic elements that have a physiological function within the human body. They must be supplied in the diet either in food or fluid and vary from grams, through milligrams to micrograms per day per day. They categorized as major (macro) minerals such as calcium, magnesium, sodium, potassium and phosphorus and trace elements such as silicon, boron vanadium, chromium, iodine, germanium, manganese, molybdenum, sulphur and zinc are required in minute quantities for good health (Michael *et al*., 2005).

Man obtains essential elements from plants which accumulates them from the soil which is their major source. The uptake of essential elements from the soil is determined by many factors including their amounts in the soil, genetic makeup of the plant species, physical condition of the soil and soil pH of soil (Underwood, 1977). The roles of some of these essential elements in the body have been discussed in the following subsections

2.3.1 Silicon

Silicon (Si) is the second most abundant element in the Earth's Crust and although there has been interest in the biological role of Si since the beginning of the century, it is only in the

last three decades that it has been suggested as an essential trace element (Jugdaohsingh *et al*., 2004). Silicon (Si) is rarely found in its elemental form as it readily reacts with atmospheric oxygen and water to produce silicates which vary in composition from simple orthosilic acid which is the most readily absorbed form of silicon and silicate in man (Jugdaohsingh *et al*., 2002). Silicon (Si) is present in almost pure form in sand as well semiprecious stones such as opal, a great variety of silicates which are the major constituents of rocks and soils.

In the human body silicon content (0.002% or about 1.5 g in an adult) ranks in abundance just below magnesium but surpasses that of iron, zinc, copper and boron. The plants can incorporate silicates in their insoluble matter often in association with certain types of fibers. Since silicon has an electron shell distribution similar to that of carbon, the chemistry of the two elements are parallel and therefore silicon forms atom to atom bonds with hydrogen, carbon, nitrogen, oxygen and other silicon atoms. Humans and animals ingest silicon from various types of vegetables and fruits (Insel *et al*., 2010).

Silica improves hair health by helping hair grow thicker and stronger. It prevents alopecia or thinning of hair, the common hair problems which occur due to deficiency of nutrients especially silica in the body (Balch, 2006). Hence, silica encourages healthy and thick hair growth and also increases the luster and shine of hair. Likewise silica is also good for nail as it protects nails from getting brittle and improves their quality. Silicon is often used in various skin beauty products to treat skin disorders like sunburn, eczema, acne, aging and even insect bites. As one advances in age the silica levels in the body decreases which is also one of the major causes for aging, it is vital to maintain normal silica level in the body to avoid aging signs like dry and wrinkled skin (Jugdaohsingh *et al*., 2002). Hence, a body having a healthy

level of silica benefits by retarding the process of aging as the mineral aids in enhancing the skin elasticity and retaining the moisture which keeps the skin young and glowing (Kanika, 2010).

Silica/silicon maintains flexible arteries and plays a significant role in cardiovascular health. It is responsible for connective tissue growth and health (Insel *et al*., 2010). There is evidence that silicon content of the aorta declines with age and those concentrations in the arterial wall decrease with development of atherosclerosis and as a result elderly people require silicon in large amounts (Linda, 2002). Findings in animal experiments indicate that silicon is necessary for collagen synthesis, regenerates body infrastructure including skeleton, tendons, ligaments and cartilage. There are suggestions that a deficiency may be related to the development of certain conditions observed especially in the elderly such as hypertension and Alzheimer's disease (Conor, 2004). A number of studies have found evidence of a possible protective role for silicon against the effects of aluminum neurotoxicity and accumulation in the brain and it is important in prevention of Alzheimer's disease and osteoporosis. A connection between silicon and selenium in relation to the control of the production of free radical formation and lipid peroxidation in animals has been postulated (Conor, 2004).

Experimental diets lacking silicon caused poor growth and skeletal abnormalities in baby chickens. However there are no known symptoms of silicon deficiency in humans. Studies suggest that silicon may prevent atherosclerosis in the elderly (Insel *et al*., 2010). This element is essentially non toxic when ingested orally; magnesium tri-silicate, an over the counter antacid has been used by humans for more than 40 years without obvious deleterious effects, other silicates are food additives used as anti-caking or antifoaming agents however;

breathing airborne silicon particles may cause silicosis, a type of silicon toxicity (Insel *et al*., 2010).

A study conducted on silicon on foods consumed in United Kingdom suggested that fruits and vegetables were highly variable sources of silicon ranging from 0.01 – 16.61 mg/100g with substantial amounts present in Kenyan grown; beans, French beans, runner beans, spinach, dried fruits, bananas and red lentils. However, there were undetectable amounts in tomatoes, oranges and onions. Silicon levels of 1.82 mg/100 g have been reported in cantaloupe and 2.53 mg/100 g in fresh raw cucumbers (Powell *et al*., 2005).

2.3.2 Vanadium

Vanadium element exists in several oxidation states from V^{2+} to V^{5+}. In solution vanadium produces a range of colours with V^{5+} being yellow and V^{2+} being blue. The V^{3+} forms complexes with amino acids such as alonine and aspartate (Bukietynska *et al.,* 2003). In biological systems including the serum, vanadium primarily exists in pentavalent state V^{5+}, known as vanadate or monovanadate and tetravalent state V^{4+} known as vanadyl and in alkaline conditions as the ortho-monovanadate ion. Vanadium is a trace mineral that plays numerous important roles in the body, including blood sugar regulation, proper bone growth and cofactor in multiple enzymatic reactions. Excess of vanadium in the body can lead to kidney dysfunction, gastrointestinal upset and central nervous system depression (Chris and Jason, 2004). Vanadium is involved in lipid and catecholamine metabolism, cholesterol production, thyroid function, growth, reproduction, calcium metabolism, red blood cell production and bone and tooth formation (Bukietynska, 2003).

Vanadium is active pharmacologically exerting a broad assortment of effects that are well documented. Vanadium as vanadate mimics the action of insulin, stimulates glucose uptake into cells, enhances glucose metabolism and inhibits catecholamine induced lipolysis in adipose tissue (Nielson, 2001). Vanadium stimulates glycogen synthesis in the liver. Insulin works by binding insulin receptors, which span the lipid membranes of cells. Insulin binding to cell membrane receptors results in tyrosine residues on the receptor (Sareen, 2008).

The recommended daily values for vanadium from diet have been estimated to about 10 µg to 2 mg (Rodney *et al.,* 2002). A study on elements in seeds of watermelon (variety not specified) and pumpkin seed in Kenya reported 1.54 mg/Kg of vanadium in pumpkin seed and 8.5 mg/Kg of vanadium in watermelon seeds (Muchemi, 2006). Beverages, fats, oils, fruits and vegetables contain <1-5 mg/Kg of vanadium (Myron *et al*., 2010).

2.3.3 Boron

Boron is a trace mineral that is essential to plant growth and in turn finds its way into the human diet. Prior to 1981 boron was not considered as an essential element (Nielson, 1996).Boron is present in plant foods such as fruits (especially plums, grapes, and avocados), vegetables, nuts, and legumes. Despite its availability in nature, ingesting adequate amounts of boron can be difficult. Boron levels in plant foods are rather low (Harvey, 2006). Moreover, modern dietary habits almost ensure boron deficiency, as many people do not eat nearly enough fruits and vegetables. In the United States, estimated daily boron intake ranges from 0.5 mg to 3 mg, with 1 mg being average (Harvey, 2006).

Ensuring optimal boron intake becomes increasingly important with age, especially in light of boron's critical role in safeguarding bone health. Calcium fructoborate is a plant form of boron which is a complex of calcium, fructose, and boron found naturally in fruits, vegetables and other foods (Harvey, 2006). This innovative form of boron is not only safe and well tolerated, but has been shown to be much more bioavailable than other commercial forms of boron (Harvey, 2006). Ensuring healthy bones is fundamental to any anti-aging program, since weak bones can lead to disabling and even life-threatening bone fractures. Boron plays an integral part in bone metabolism, as it supports the functions of calcium, magnesium, and vitamin D, all of which are crucial to promoting dense, healthy bone tissue (Schaafsma *et al.*, 2001). Boron has important applications in helping women preserve bone mass and prevent osteoporosis following menopause. Boron may likewise help to alleviate the detrimental effects of vitamin D deficiency on calcium metabolism. Vitamin D is Crucial to bone health because it helps to support calcium absorption (Hegsted *et al*., 1991).

Osteoarthritis is the most common form of joint disease, a source of daily pain, stiffness, and decreased range of motion. Emerging research indicates that, in addition to preserving bone health, boron may help relieve the debilitating symptoms of osteoarthritis (Gaby, 1999). Examining the relationship between boron intake and osteoarthritis prevalence around the world, researchers have uncovered epidemiological evidence demonstrating that in areas where boron intake is 1 mg or less per day, the estimated incidence of arthritis ranges from 20% to 70% (Balch, 2006). Conversely, in areas of the world where boron intake is usually 3-10 mg per day, the estimated incidence of arthritis is dramatically lower, ranging from zero to just 10%. This remarkable finding is compelling evidence that abundant intake of dietary boron may confer powerful protection against the development of osteoarthritis (Balch, 2006).

Boron may play an underappreciated role in protecting men against prostate cancer. As men grow older, their risk for prostate cancer increases. Fortunately, growing research indicates that boron may help prevent prostate cancer. Studies have revealed that prostate cancer risk can be reduced simply by consuming a greater amount of boron-rich foods (Zhang *et al.*, 2001). Studies have revealed a possible mechanism by which boron may reduce the incidence of prostate cancer. Boron compounds inhibit the activity of many serine protease enzymes, including prostate-specific antigen (PSA). Elevated PSA may promote prostate cancer via its degradation effects on the extra-cellular protein matrix (the protein surrounding the cell) within the prostate gland. Breaking down these cellular barriers may enable prostate cancer cells to more readily invade healthy tissue and spread (metastasize) beyond the prostate gland (Faloon and Strum, 2005).

Researchers have found that oral administration of various concentration of a boron-containing solution may help to shrink prostate tumors and decrease levels of PSA, an important prostate cancer marker. Recent discoveries have shown that PSA itself may contribute to prostate cancer promotion. Ensuring adequate boron intake should thus be considered a critical component of any strategy to prevent prostate cancer and maintain optimal PSA levels (Gallardo *et al.*, 2004).

Boron is necessary to allow the brain to function properly. Boron increases mental alertness, low boron intake by humans caused decreased brain activity. People on low boron diet have lower brain performance on attention and short term memory tests (MII, 2011). This essential mineral may also have important applications in helping aging adults preserve cognitive function (Penland, 1998). Calcium fructoborate decreases the production of intracellular

reactive oxygen species; this antioxidant activity has clinical significance in protecting skin cells from oxidation-induced injury (Scorei *et al*., 2005).

Boron affects the metabolism and utilization of numerous other substances involved in life processes including macro minerals, energy substances such as triglycerides and glucose, nitrogen containing substances such as amino acids and proteins, reactive oxygen species and estrogen. Through this effect boron can affect several body systems including brain, skeleton and immune system (Heiner, 2002). Substituted carboranes and polyhedral hydroborate salts are potent anti-neoplastic agents inhibiting the growth of human leukemia, uterine carcinoma, colon adenocarcinoma, lung brochogenic tumor and gliomas (Hall *et al*., 1998).

Food and drinks of plant origin, especially non-citrus fruits, leafy vegetables, nuts, pulses, legumes and beer are sources of boron (Michael *et al*., 2005). Levels of boron in pumpkins, squash, cucumbers and cantaloupe have not been reported (WHF, 2010). Fruits and vegetables contain 0.1- 0.6 mg/100g of boron and levels of 4.5 mg/100g are reported in avocados (Devirian and Volpes, 2003).

2.3.4 Calcium

The major function of calcium to build and maintain strong bones and teeth and for maintenance of healthy gums (Balch, 2006). It is also important in maintenance of regular heartbeat and in the transmission of nerve impulses. Calcium lowers cholesterol levels and helps cardiovascular disease and it is also needed for muscle growth and contraction for the prevention of muscle cramps. It may also increase the rate of bone growth and bone mineral density in children (Balch, 2006).

It is essential for healthy blood, milk production, enzyme activation and help to regulate the heart beat. Calcium aids in the process of blood clotting and helps in regulation of accumulation of acid or alkali in the blood and regulates the passage of nutrients in and out the cell wall. Calcium is present in milk and dairy product, bones, meats, eggs and vegetables. Chronic dietary deficiency of calcium results in osteoporosis either by inadequate accumulation of bone mass during growth or increase rate of bone loss at menopause. Dietary calcium deficiency also has been associated with increased risk of hypertension and colon cancer. Excess calcium supplementation has been associated with some mineral imbalances such as Zinc (Jackman *et al.*, 1997).

Calcium has been shown to prevent colon cancer (Balch, 2006). Supplemental calcium seems to suppress changes in the lining of colon associated with the onset of cancerous changes. Experiments have shown that human colon cancer cells replicate rapidly when deprived of calcium but slow their replication when calcium is restored (Kally, 2000). Recommended daily allowance of 1000 mg/day has been set (FNB, 2004). Tolerable upper intake levels of calcium of 2500 mg/day have been recommended (Michael *et al.*, 2005).

2.3.5 Chromium

Chromium is essential for plants and animal growth. Most plants contain chromium in levels less than 1 ppm while in others it ranges from 4 ppm to 6 ppm (Underwood, 1977). It is widely distributed in human tissue in extremely low and variable concentration, with total body content of less than 6 mg (Underwood, 1977). Chromium of the plasma is bound to transferring component of β-globulin fraction of the plasma protein. Biological activity of chromium is demonstrated by the trivalent state. In foods, chromium exists both in poorly

absorbed inorganic form and biologically active complex. Hexavalent chromium is better absorbed than the latter (Mindell and Mundis, 2004).

Research has showed a strong connection between whole grain intake and health, including up to 50% reduction of risk of ischemic stroke and 36% reduction of heart diseases (AMA, 2000). Chromium regulates blood sugar, thereby reducing medication and insulin needs in diabetic patients (Bahkru, 2006). It also works with insulin in metabolism of sugar, thus normalizing blood sugar levels. Maintenance of blood sugar levels stems from the fact that the active agent (glucose tolerance factor) consists of chromium chemically bound with nicotinic acid, a member of vitamin B complex. If a person has mild diabetes, chromium may save him/her from getting full-fledged disease and can help improve glucose tolerance. Diabetes responds to chromium supplementation thus occurrence of diabetes may be due to lack of chromium in the body (Mindel and Mundis, 2004).

Lack of chromium also appears to be involved in the development of maturity onset diabetes, since it has been found that levels of the mineral in tissues drop with age. Chromium also helps the body keep fat in small particles since when fat globules get too large causing narrowing and hardening of arterial walls (Al Durtsch, 1999). Chromium also plays a role in the management of heart diseases by regulating fat and cholesterol synthesis in the liver (WHO, 1999).

The LDL (low density lipoprotein) cholesterol in diabetes is more susceptible to oxidation and thus more likely to become toxic. The oxidized LDL cholesterol is more likely to clog arteries thus diabetics are 2 to 3 times at high risk of development heart diseases (Bakhru, 2006). The dangerous oxidized LDL cholesterol is caused by high levels of sugar in the

blood. However, as sugar is metabolized it releases oxygen free radicals that tend to make cholesterol toxic. Chromium activates vitamin C which is beneficial to human health since it increases resistance to infections and prevents cancer. It also aids in iron absorption and reduces oxidative stress and HIV viral load (WHO, 1999).

The estimated safe and adequate daily dietary intake of chromium is 50 to 200 µg for adult and adolescents (Bakhru, 2006). In the United States adult women consume about 23 µg to 29 µg of Cr per day from food while men consume an average of 39 µg to 54 µg per day (IM,FNB, 2001) and infants obtain about 0.2 µg from breast milk (NRC, 1989). No tolerable upper intake level for this mineral has been established (Stoecker, 2001). A recent study on analysis of a bitter cucumber *(momordica charantia*) grown in south Nigeria showed that it contains 162.00 mg/Kg of Cr (Ayoola *et al*., 2010). A study in Kenya has shown that watermelon seeds contain 6.20 µg/g of chromium while pumpkin seeds contain 5.26 µg/g of chromium (Muchemi, 2006). Levels of 22 µg/g of chromium are reported in broccoli (Anderson *et al*., 1992).

2.3.6 Molybdenum

Molybdenum is a trace element that is an essential nutrient for plants and animals. Serious research on the importance of molybdenum in human body begun in the past few decades (FNB, 2010). It is a component of several mammalian metalloenzymes including xanthine oxidase, aldehyde oxidase, and sulphite oxidase (Emsley, 2003). Human body contains only 9 mg of molybdenum, where it is present in the liver, kidney adrenal glands, bones, skin and tissues (Ahmed, 2005). Molybdenum is essential in tiny amounts and can be highly toxic in large amounts. Animal experiments have shown that too much of molybdenum causes fatal

deformities and interfere with absorption of copper. The parts of the body with most molybdenum are the bones, skin, liver and kidney (Emsley, 2003).

Molybdenum is very important in enzyme system, for example molybdenum triggers the mammalian enzyme xanthine oxidase which eliminates the toxic nitrogen waste by turning it into uric acid. The uric acid can easily be processed and flushed out of the system. Molybdenum also aids in carbohydrate metabolism (Emsley, 2003). Dental enamel is rich in molybdenum. Molybdenum helps to induce sleep and also helps promote general sense of well being (Balch, 2006).

Molybdenum regulates the pH balance in the body. For each one tenth of a pH point difference, the oxygen level in the blood may increase or decrease by ten times (Emsley, 2003). This has a different change on the metabolism and the body's ability to burn fat. If the body doesn't have enough oxygen, the metabolism cannot oxidize enough burn fat. Molybdenum's ability to change the body's pH is very important in treatment of many severe illnesses and in control of viruses and parasites. Symptoms of deficiency of molybdenum includes; acne, cavities, flu, cold, depression, diabetes, eczema, liver damage, Lyme disease, obesity, prostate infection and ringworms (Lynell, 2011).

Aldehyde oxidase converts aldehyde into acids and sulphide oxidase which detoxifies sulphite (SO_3^{2-}) by oxidizing it to harmless sulphate (SO_4^{2-}). Both of these elements are found in the liver. Aldehyde oxidase is needed in metabolism of alcohol which is converted first to acetaldehyde by zinc containing enzyme, then to acetic acid by molybdenum containing enzyme. Acetic acid is used by cells as a source of energy (Emsley, 2003).

The average human intake is 0.3 mg of molybdenum a day (Balch, 2006). The absolute minimum intake that is needed is not known, although it may be as low as 0.05 mg. In any case the intake should not regularly exceed 0.4 mg because above this level molybdenum can provoke a toxic response (Namin and Yavuz, 2006). Foods with molybdenum are vegetables with 4 – 90 mg/100g, potatoes 3- 60 mg/100g and fruits berries with 0.15 – 9 mg/100g (Kaslow, 2011). In 2001 the US Food and Nutritional Board (FNB) established the recommended daily dietary intake for Mo to be 2-50 mg (FNB, 2004) and its deficiencies in older males have also been linked to impotence and may be of value in fighting mouth and gum disorders (Michael *et al.*, 2005).

2.4 Methods of analysis

Several techniques for determination of metallic elements are currently in use. These include the atomic absorption spectroscopy (AAS) (Taylor *et al*., 2006), inductively coupled plasma hypermated with mass spectroscopy (ICP-MS) (Conor, 2004), the inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Pavel *et al.*, 2005) and energy dispersive X-ray fluorescence (EDXRF) spectroscopy (Beckhoff *et al*., 2006).

2.4.1 Principles of AAS

The AAS is a single elemental method in which one element is determined in a series of samples and instrumental parameters optimized for the next element and can easily be automated. In AAS a substance is vaporized and decomposed into gaseous atoms in flame or electrothermal atomizer.

The concentration of an element is measured by the absorption of radiation with characteristic frequency by free atoms of an element. Light of certain wavelength produced by monochromatic or hollow cathode lamp emits spectral lines corresponding to energy required for excitation of an element of interest. The analytical signal is obtained from the difference between the intensity of the source in the absence of the element of interest and the decreased intensity obtained when the element of interest is present in the optical path. Absorption of light is associated with transition process from one steady state to another , for instance the case of a steady state O and J where Eo< Ej, the O-J transition results in the absorption of light with the frequency given in Equation (2.1).

$$\nu_{oj} = \frac{E_j - E_o}{h} \quad \text{.....Eq.2.1}$$

Where
h - Plank's constant
V - Frequency
E_o - Energy at ground state
E_j - Energy at the excited state
O - J – the transition stimulated by absorption of external radiation.

The number of atoms in the excited state relative to the number in the ground state is given by Maxwell –Boltzmann law (Skoog *et al.*, 1998), given by Equation 2.2.

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} \exp\left(\frac{E_0 - E_1}{KT}\right) \text{.....Eq.2.2}$$

Where
N_1 - Number of atoms in the excited state
N_0 - Number of atoms in the ground state
g_1 and g_0 – Statistical weight of excited and ground state respectively
K - Boltzmann′s constant
T - Absolute temperature
E_0 - Energy at the ground state
E_1 - Energy at excited state

The relative fraction of atoms in excited state is dependent on temperature whereas intensity is independent of temperature. Sample solution is aspirated through nebulizer into the air/acetylene or nitrous oxide/acetylene flame (Taylor *et al.*, 2006). An electrically heated graphite furnace is used when very high sensitivity is required. The sample solution gets dispersed into mist of droplets and then evaporated into dry salt. The dry salt goes into vapor and dissociates into atoms that absorb resonance radiation from external source. The unabsorbed radiation is allowed to pass through the monochromator which isolates spectral lines. The isolated analyte line falls on the detector and the output of which is amplified and recorded. The parameter measured is absorbance (*A*) and related to concentration by the Equation 2.3.

$$A = \log I_0 / I = \varepsilon c l \quad \text{.....Eq. 2.3}$$

Where;
A - Absorbance
I_0 - Incidence radiation
I - Attenuated radiation
ε - Molar absorptivity ($Lmol^{-1}cm^{-1}$)
c - Concentration ($moldm^{-3}$)
l - Path length (cm)

Since the relationship between absorbance (*A*) and concentration (*c*) is linear over a wide range of levels (Beer's law), standards are used to obtain calibration curve from which levels of analyte is established through interpolation method (Van loon, 1980). The most important components of atomic absorption spectrophotometer are:

(a) Radiation source

Hollow cathode source

It is commonly used in atomic absorption spectroscopy (AAS) instrument and made up of metallic or alloy of element of interest. Hollow cathode lamp consists of a tungsten anode and

cylindrical cathode sealed in a glass tube that is filled with neon or argon gas at a pressure of 1-5 torr.

(b) Atomizer

The two types of atomizers are flame and electrothermal atomizers. In flame atomizer, the temperature is determined by flow rate and ratio of oxidant and fuel. In flame atomizer solvent is evaporated to produce solid molecular aerosol during dissolving process. Dissociation leads to atomic gas whereas some of the atoms ionize to give cations and electrons. In electrothermal atomizer, few molecules of the solvent are first evaporated at low temperature and ashed at higher temperatures in electrically heated graphite. After ashing, the temperature is increased to 2000-3000 °C to cause atomization of the sample.

(c) Monochromators

They are analyzers that present monochromatic radiation to the detector. They are filters, prisms or gratings that disperse or separate radiation so that selected wavelength corresponding to particular energy of the samples is transmitted. Diffraction grating is preferred to prisms as they offer a wide range of wavelengths.

(d) Detectors

Detectors convert radiation energy into electrical signal and include phototube, photomultiplier tube and photodiode array detectors.

(e) Read out system

These are digital and interfaced with microprocessors that allow the programming of various aspects, bringing simplicity in operation. However AAS is a single elemental method in which one element is determined in a series of samples and instrumental parameters optimized for the next element.

In this study the AAS was used due to its availability, sensitivity, selectivity, reproducibility and time efficiency.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Research design

The experimental design involved the determination of levels of the selected metals in four parts of watermelon namely; the peel/rind, white fleshy part, the red fleshy part and seeds of three varieties of watermelons. The three varieties of watermelons; Charleston Grey (SugarF1), Crimson Sweet (zebra) and Sugarbaby were obtained from Mwea and Githurai market in Kenya.

3.2 Sampling procedure and Pre-treatment

Purposive strategy was used to select the sampling sites. The sampling sites were Mwea and Githurai markets; the main criterion for selection of sampling sites was the availability of the three varieties of watermelons. Sampling for the each variety was done for six times at intervals of two months for a period of twelve months. This was done to avoid biasness due to seasonal variations. Each time three watermelons of the same variety were bought from three different vendors. The selection of vendors was subject to availability of the variety of watermelon being bought. The watermelons were selected randomly from the vendor. This was repeated for six times in each sampling site (market).

The obtained watermelon samples were packed in plastic bags and transported to laboratory. The three watermelons of the same variety sampled were cleaned using distilled water, four parts were extracted namely the peel/rind, fleshy red part, fleshy white part and seeds and dried at 105 °C in a gravity oven until there was no further change in weight. Each of the dry parts from the three watermelons was homogenized by grinding to form one sample; a total

of four samples (four parts). The ground samples were stored in well labeled plastic bags awaiting digestion and analysis. This was repeated each time sampling was done.

3.3 Chemicals and Reagents

All reagents used in this study were of analytical grade. Concentrated nitric acid, sulfuric acid, hydrogen peroxide, potassium nitrate and hydrochloric acid were sourced from Thomas Baker Chemicals Ltd Mumbai India whereas sodium borate ($Na_2B_4O_7.10H_2O$), calcium carbonate decahydrate ($CaCO_3.10H_2O$), silicon dioxide (SiO_2), molybdenum (Mo) metal, vanadium metal (V) and Chromium (Cr) metal strips were purchased from Fluka Chemie GmbH Aldrich chemical company, Inc. USA.

3.4 Equipments and AAS operating conditions

The equipments used in this study include the analytical balance (Model AAA, Adam Co Ltd.) from Britain, water distillation machine (Model WSB/4) from England and Varian Atomic Absorption Spectrophotometer (Model AA-10) from Australia. The operating conditions for the AAS are given in Table 3.1.

Table 3.1: The AAS operating conditions

Operating parameters	B	Ca	Cr	Mo	Si	V
Wavelength (nm)	249.8	422.7	357.9	313.3	251.6	318.5
Slit width (nm)	0.2	0.5	0.2	0.5	0.5	0.2
Flame type	N_2O-acetylene	N_2O-acetylene	Air-acetylene	N_2O-acetylene	N_2O-acetylene	N_2O-acetylene
Oxidant flow rate (l/min)	4.5	4.5	1.5	4.5	4.5	4.5
Sensitivity (ppm)	8.4	0.021	0.055	0.33	1.6	0.88
Detection limit (ppm)	2	0.0005	0.005	0.04	0.3	0.11
Lamp current (mA)	15	3	5	5	15	20
Optimum working range (ppm)	400-1600	1-4	2.0-8.0	15-60	70-280	40-120

3.5 Cleaning of Apparatus

All plastic ware and glass ware apparatus were washed with liquid detergent and hot water then rinsed severally with tap water followed by soaking overnight in 10 % analytical grade nitric acid. Apparatus were rinsed with distilled water. The glass ware were dried in an oven at 105 ℃ and the plastic bottles in open racks and stored in lockable drawers.

3.6 Preparation of standards

Stock solutions were prepared from analar grade granulated metals and salts of high purity (99.9%). Each metal or salt was first dried at 105 $^{\circ}$C, cooled in desiccators prior to weighing and transferred into 1 litre volumetric flasks. Molybdenum stock was prepared by dissolving 1.000 g Molybdenum metal strip in hot concentrated nitric acid, cooled and diluted to 1 litre using distilled water to give 1000 µg/ml of molybdenum. Vanadium stock solution was

prepared by dissolving 1.000 g of vanadium metal granules in 40 ml nitric acid and diluted using distilled water to 1 litre to give 1000 µg/ml Vanadium.

For boron stock solution 44.095 g of $Na_2B_4O_7.10H_2O$ was dissolved 500 ml of distilled water and then diluted to 1 litre to give 5000 µg/ml B, whereas Ca stock solution was prepared by dissolving 2.497 g of $CaCO_3$ in a minimum volume of 1:4 nitric acid and then diluted to 1 litre to give 1000 µg/ml of Ca. For chromium stock solution, 1.000 g of chromium metal was dissolved in 1:1 hydrochloric acid with gentle heating, cooled and diluted to 1litre with distilled water to give 1000 µg/ml chromium. A stock solution of silicon was prepared by fusing 2.140 g of silicon dioxide with 8 g of sodium hydroxide in a zirconium Crucible at dull red heat until a clear melt was obtained. It was then cooled and the cake was dissolved in 100 ml of 1:3 hydrochloric acid and made to 1 litre using distilled water to give 1000 µg/ml silicon.

During serial dilution and subsequent dilution of stock solutions, the final acid concentration was maintained at about 1% to keep the metal in free ionic state. The stock solutions were stored in plastic bottles and labeled appropriately. Working standards were freshly prepared from stock solutions each time an analysis was carried out. Calibration graphs were established from a plot of absorbance readings of standards against their concentration were used to determine the concentration of B, Ca, Cr, Mo, Si and V.

3.7 Digestion of watermelon samples

A 0.500 g of each sample was weighed accurately using electronic balance (model AAA, Adam Co ltd). A 9 ml mixture of HNO_3 and H_2SO_4 in the ratio 2:1 were first added to the 0.500 g of sample in Kjeldahl flask and then gently heated on hot mantle until the dense

brown fumes began to appear. Hydrogen peroxide was added drop wise to clear the brown fumes. Digestion was allowed to continue until the solution was clear and white fumes observed. The digested sample was cooled and filtered using filter paper (whatman No 42) into 100ml clean dry volumetric flask and then diluted to the mark with distilled water. They were then transferred into separate plastic bottles, labeled and appropriately stored under refrigeration until analysis.

3.8 Digestion of the blank samples and calculation of detection limit

In order to account for the background effects from the acids and to correct for changes resulting from digestion procedures, six blank samples were digested following the same procedures as the samples and each of the blank samples were determined for the elements of interest (Ca, Mo, Cr, Si, B and V) by atomic absorption spectrophotometer. Their absorbance's were recorded. Their means and standard deviations were calculated and used for calculating limit of detection using the Equation 3.1 as described by Christian (2005).

$$\text{Limit of detection} = \frac{3\text{x}\text{Standard deviation of blank readings}}{\text{Absorbance of standard} - \text{Mean absorbance of six blanks}} \quad \ldots\text{Eq. 3.1}$$

3.9 Instrument and Method Optimization

Instrument optimization involves the analytical sequence to demonstrate that the instrument is working properly during the analysis of the elements. In this study the instrument was calibrated by analysing calibration solutions that produced responses of 0.000 absorbance and standards of known concentration for each element. Regression analysis was done where the slope (m), and intercept (b) of linear equations ($y = mx + c$) that best fits data from calibrations were determined and the correlation coefficients(r). If x and y have a strong positive correlation r is close to 1 (Gareth, 2011). Where errors in preparations of calibration

standard solutions, deviations from linearity and contamination were observed new solutions were prepared correctly and the calibration was repeated.

To determine the accuracy of the analytical procedure a recovery test was conducted. The recovery test was investigated by spiking a suitable known amount of the analyte metals into a test portion of the sample having a known concentration of the analyte and analyzing the spiked test portion along with the original sample. The precision of the method was expressed as a percent relative standard deviation (% RSD) of the triplicate analyses. In cases where the test solutions did not agree with the recommended range of 90-110 % recovery and ± 5 % relative differences (Hight, 1998) the test solutions were prepared again and re-calibration of instrument done to analyze the test solutions.

For this research, in order to demonstrate the validity of whole analytical procedure, the recovery test was done as follows: A 10 ml aliquot of 5 µg/ml Cr, 20 µg/ml Mo, 5 µg/ml Ca, 100 µg/ml Si, 50 µg/ml V and 500 µg/ml B were spiked into a conical flask containing 0.5 g of dried watermelon samples. Then same digestion procedure was followed for non-spiked and spiked watermelon samples side by side. Each sample was analyzed for their respective spiked metals by atomic absorption spectrophotometer. The concentration of un-spiked sample was subtracted from the concentration of the spiked sample to determine the amount recovered. The recovered amount was divided by the concentration of the known standard added (spiked) and multiplied by 100 and expressed as a percentage recovery.

3.10 Determination of the metals

Determination of the silicon, molybdenum, vanadium, boron and chromium was done in replicates using computerized Varian Atomic Absorption Spectrometer model AA-10. The

samples were analyzed in replicates under the same conditions as standards and blanks. For precision, standards were measured before and after the sample solution. The calibration of the instrument using standards and blank was frequently done between samples to ensure stability of the base line.

3.11 Calculations of concentration in elements

The concentration of essential elements in the samples was worked out from the obtained AAS analytical results (read out) using the Equation 3.2.

$$Actual\ Concentration(\mu g/g) = \frac{Concentration(\mu g/ml)xVolume\ digested(ml)}{Weight\ of\ dried\ sample(g)} \quad \text{.....Eq.3.2}$$

In cases of dilution (determination of concentration of calcium), the actual concentration was obtained by multiplying the read out results with the dilution factor. The means of the replicate measurements were then calculated from the actual concentration obtained. The concentrations of B, Ca, Cr, Mo, Si and V in the samples were worked out by calculating their means and standard deviation values.

In cases where the sample readings were below the optimum working range (determination of concentration of boron), standards of known concentrations were added to bring the sample reading to the range. The absorbances were recorded for the original sample and after the addition of the standard. Equation 3.4 described by Skoog *et al*. (1992) was used to calculate the actual concentration of the sample.

$$C_x = \frac{A_1 C_s V_s}{(A_2 - A_1)V_x} \quad \text{.....Eq.3.3}$$

Where;
C_x - Concentration of sample
C_s - Concentration of the standard
A_1 - Absorbance of the sample before addition of standard
A_2 - Absorbance of sample after addition of standard
V_s - Volume of standard added
V_x - Volume of sample solution

3.12 Data analysis

Mean values obtained for silicon, molybdenum, boron, calcium, Chromium and vanadium studied in the four parts of watermelons and the three varieties of watermelon samples were compared by One-Way ANOVA at 95% level using SPSS (version 18.0). The assumption was that there were no significant differences among them when the statistical comparison gives $p < 0.05$. Whenever a significance difference exists, the means were compared at $p = 0.05$ significance level which accounts for errors since a sample was used to represent a population (Sawyer *et al.*, 2004).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Introduction

The levels of silicon, boron, vanadium, calcium, chromium and molybdenum from selected samples of peel, rind, flesh and seeds of Charleston Grey, Crimson Sweet and Sugarbaby watermelons were determined in triplicates using AAS. Signal responses of AAS obtained are discussed in the following sub sections.

4.2.0 Method validation

4.2.1 Regression Analysis and Detection limit

Regression analysis was used to evaluate the linearity of AAS using the established calibration curves. The absorbance readings and concentration of ideal standards were used to calculate the correlation coefficients (r). The detection limits were calculated as the concentration that give signals equal to three times the standard deviations of the six blanks as described in section 3.8. The calibration curves were established by a plot of absorbance readings(y-axis) against the corresponding concentration (x-axis) of standards with optimized instrumental conditions. The detection limits, the correlation coefficients, the equations of the calibration curves and the range of standards used to establish them in are represented in Table 4.1.

Table 4.1: Detection limits, correlation coefficients and equations of the calibration curves for the determination of metals in watermelon samples by AAS

Element	Method Detection limit(µg/ml)	Concentration range of standards (µg/ml)	Correlation Coefficient of calibration curve	Equations for calibration Curve
Ca	0.0027	0.0-5.0	0.9991	Y=0.010x+0.003
Cr	0.003	0.0-70.0	0.9998	Y=0.019x+0.001
Mo	0.016	0.0-10.0	0.9998	Y=0.058x+0.059
Si	0.061	0.0-300.0	0.9991	Y=0.001x+0.003
V	0.008	0.0-150.0	0.9998	Y=0.001x+0.001
B	0.01	0.0-2000	0.9992	Y=0.001x+0.003

In Table 4.1; x-concentration, Y- absorbance

From Table 4.1 the correlation coefficients of all calibration curves were ≥ 0.9991, which shows that there was a very good correlation (relationship) between concentration and absorbance (Gareth, 2011). The method detection limits for all the metals were < 0.1 µg/ml which indicate that the method is applicable for the determination of metals at trace levels. The performance of AAS spectrophotometer was therefore good and reliable to warrant its use in the analysis of the selected essential elements in the watermelon samples.

4.2.2 Recovery test

The recovery test for watermelon samples was performed in triplicates. The recovery test results are indicated in Table 4.2.

Table 4.2: Recovery test results for the metals (percentage)

Metal	Concentration (µg/ml)			Mean % Recovery	(%)RSD
	Un-spiked sample Mean±SE	Standard added to the sample	Spiked sample Mean±SE		
Cr	0.15±0.01	5.00	5.13±0.02	99.87	0.62
Mo	0.10±0.01	20.00	20.09±0.06	99.75	0.39
Ca	3.90±0.02	5.00	8.91±0.01	100.12	0.06
Si	4.73±0.02	100.00	104.72±0.04	100.02	0.04
V	0.53±0.02	50.00	50.55±0.08	99.91	0.14
B	18.97±0.21	500.00	518.00±0.46	99.74	0.07

Results in Table 4.2 indicate that the percentage recovery lies within the range (99.74−100.12) % this was within the acceptable range for percentage recovery of 90-110 % and RSD (0.04−0.62 %) which is within the acceptable range for all metals ±5 % (Hight, 1998). This confirms that the method is of good precision and accuracy and therefore the results presented in this thesis are valid.

4.3 Mean levels of calcium in watermelons

4.3.1 Mean levels of calcium in parts of watermelons

The results for mean levels of calcium in the parts of various varieties of watermelons samples obtained from Mwea and Githurai market are discussed in the following subsections. The results of the mean levels of calcium in the rind/peel, white flesh, red flesh and seeds of Charleston Grey, Crimson Sweet and Sugarbaby watermelons bought from Mwea and Githurai markets were calculated and compared at α=0.05 level as shown in Table 4.3.

Table 4.3: Mean levels of calcium in parts of varieties of watermelons (range)

Varieties of watermelons/sampling sites		Concentration (mg/g) Mean ±SE (Range)				P-value
		Peel/rind	White flesh	Red Flesh	Seeds	
Charleston Grey	Githurai n=6	19.01±1.57[a] (0.39-20.76)	18.62±1.38[a] (0.63-21.03)	15.65±0.97[a] (0.41-20.75)	15.89±0.80[a] (0.39-19.23)	0.133
	Mwea n=6	14.69±2.08[a] (8.51-22.33)	13.59±1.10[a] (8.73-15.76)	14.10±1.63[a] (10.17-20.16)	16.02±1.29[a] (11.14-20.40)	0.723
	Overall mean n=12	16.80±1.40[a] (8.51-24.23)	16.10±1.13[a] (8.73-23.23)	14.87±0.93[a] (10.17-20.16)	15.9±0.72[a] (11.14-20.40)	0.638
Crimson Sweet	Githurai n=6	19.47±1.78[a] (12.90-24.59)	17.35±1.03[a] (15.35-19.89)	16.88±1.80[a] (8.51-20.65)	14.86±1.86[a] (8.76-19.85)	0.308
	Mwea n=6	17.15±2.19[a] (12.04-22.52)	17.98±1.09[a] (14.99-22.06)	16.68±2.14[a] (10.16-22.84)	14.19±1.86[a] (5.96-17.41)	0.528
	Overall mean n=12	18.3±11.39[a] (12.04-24.59)	17.70±0.72[a] (14.99-22.06)	16.78±1.33[a] (8.51-22.84)	14.53±1.26[a] (5.96-19.85)	0.150
Sugarbaby	Githurai n=6	12.71±0.94[a] (10.20-15.51)	15.91±1.21[a] (12.20-18.95)	15.25±1.12[a] (11.76-19.86)	12.37±1.43[a] (8.10-17.61)	0.114
	Mwea n=6	19.20±1.19[b] (8.51-22.33)	15.43±1.38[ab] (8.73-15.76)	15.19±1.40[ab] (10.17-20.16)	11.90±1.04[a] (11.14-20.40)	0.006
	Overall mean n=12	15.96±1.22[b] (10.2-22.76)	15.67±0.88[b] (10.19-19.97)	15.22±0.86[b] (9.52-19.86)	12.14±0.85[a] (8.10-17.61)	0.027

In Table 4.3 mean values with the same small letters within the same row are not significantly different at α =0.05.

The results in Table 4.3 shows that in Charleston Grey, calcium mean levels in the peel/rind, white flesh, red flesh and seeds of the samples obtained from Githurai market, Mwea market

and the overall mean did not differ significantly ($p > 0.05$). This implies that any of the four parts provide equivalent nutritional benefits with respect to calcium.

One way ANOVA reveals P values of 0.308, 0.528 in parts of Crimson Sweet watermelons samples bought from Githurai and Mwea market respectively. Mean levels of calcium recorded in the peel/rind, white flesh, red flesh and seeds of Crimson sweet water melons bought from Githurai and Mwea markets that did not differ significantly. The overall mean levels of calcium in four parts of Crimson sweet watermelons obtained from the two markets did not differ significantly ($p = 0.15$). Any of the four parts would provide equivalent dietary values of calcium.

For the Sugarbaby, samples obtained from Githurai market recorded calcium mean levels that did not differ significantly ($p = 0.114$) in the peel/rind, white flesh, red flesh and seeds. Samples bought from Mwea market, the peel/rind, white flesh and the red flesh parts recorded Ca mean levels which did not differ significantly. Calcium mean levels recorded by the peel were significantly higher than those recorded by the seeds ($p = 0.006$). Considering the overall mean of Sugar baby watermelons, samples obtained in the two markets recorded calcium mean levels in the seeds which were significantly lower than those recorded by the peel/rind, white flesh and red flesh ($p = 0.027$).

The means levels of calcium in the peel/rind, white flesh, red flesh and seeds in three varieties watermelons ranged from (8.51-24.59) mg/g, (8.73-23.23) mg/g, (8.51-22.84) mg/g and (5.96-20.40) mg/g respectively. The range can be attributed to the fact that the watermelons may have been grown in soils of varying levels of calcium, seasons in which the watermelons were planted, the water used or soil pH (Underwood, 1977). The variations of

calcium mean levels in different parts of the same variety of watermelon can be attributed to fruit maturity (AHR, 2007), seasons, tissue differences in the four parts (Pallardy and Theodore, 2008., 1979)

4.3.2 Mean levels of calcium in varieties of watermelons

The results of calcium mean levels obtained in Charleston Grey, Crimson Sweet and Sugarbaby watermelons samples bought from Mwea and Githurai markets were compared as shown in Table 4.4.

Table 4.4: Mean levels (mg/g) calcium varieties of watermelons

Varieties of watermelons/ Sampling sites	Concentration (mg/g)			p-value
	Charleston Grey	Crimson Sweet	Sugarbaby	
Githurai market Mean±SE (n=24)	17.29 ± 0.65^{b} (12.16-24.23)	17.13 ± 0.87^{b} (8.51-24.59)	14.06 ± 0.64^{a} (8.10-19.86)	0.030
Mwea market Mean±SE (n=24) (Range)	14.60 ± 0.76^{a} (8.51-22.33)	16.50 ± 0.92^{a} (5.96-22.84)	15.43 ± 0.80^{a} (8.89-22.76)	0.272
Overall mean Mean±SE (n=48) (Range)	15.94 ± 0.53^{ab} (8.51-24.23)	16.81 ± 0.63^{b} (5.96-24.59)	14.75 ± 0.52^{a} (8.10-22.76)	0.035

In Table 4.4 mean values with the same small letters within the same row are not significantly different at α =0.05.

Results in Table 4.4 indicate that the Sugarbaby watermelon samples bought from Githurai market recorded calcium mean levels which were significantly lower than those recorded by samples from Charleston Grey and Crimson Sweet watermelons (p = 0.03). Mean levels of calcium in Charleston Grey, Crimson Sweet and Sugarbaby watermelon samples from Mwea market did not differ significantly (p = 0.272). The overall calcium mean levels recorded in both markets, Crimson Sweet watermelon samples recorded calcium mean levels of calcium

which were significantly higher than mean levels of Sugarbaby (p = 0.035). However, calcium mean levels in Charleston Grey did not differ significantly from the other two varieties.

The variations in the mean levels of calcium in varieties of watermelons could be as a result of differences in their genotype, levels of calcium, pH and physical conditions of soils in which the watermelons were grown (Pallardy and Theodore, 2008). Calcium mean levels reported in this study are comparable to levels reported in cucumbers, watermelon, pumpkin seeds and cantaloupe respectively (USDR, 2008).

4.3.3 Mean levels of calcium in varieties of watermelons in the markets

Calcium was detected in all the samples obtained in from Githurai and Mwea markets. Mean levels of calcium in the parts of each variety of watermelons were used to determine the mean levels of calcium in each variety of watermelons samples obtained from Githurai and Mwea markets. The mean levels of calcium in watermelons bought from the two markets were compared at α =0.05 level as shown in Table 4.5.

Table 4.5: Mean levels (mg/g) calcium varieties of watermelons from the markets

Varieties of watermelons	Concentration (mg/g)		p- value
	Githurai Market Mean±SE n = 24	Mwea Market Mean±SE n = 24	
Charleston Grey	17.29±0.65[b]	14.60±0.76[a]	0.010
Crimson Sweet	17.13±0.87[a]	16.50±0.92[a]	0.960
Sugarbaby	14.06±0.64[a]	15.43±0.80[a]	0.187

In Table 4.5 mean values with the same small letters within the same row are not significantly different at α =0.05.

Results in Table 4.5 indicates that Charleston Grey watermelon, samples obtained from Githurai market recorded calcium mean levels that were significantly higher than those recorded by watermelon samples obtained in Mwea market (p=0.010). For Crimson Sweet, watermelon samples obtained from Githurai and Mwea markets recorded mean levels of calcium that did not differ significantly (p=0.960). There was no significant difference in calcium mean levels recorded by Sugarbaby watermelon samples obtained from Githurai and Mwea markets (p = 0.187). The variation in the mean levels calcium in the same variety of watermelons could be due to the site, amount of calcium, soil pH, physical conditions of the soils where the watermelons were grown (Underwood, 1977).

4.4 Mean levels of chromium in watermelons

4.4.1. Mean levels of chromium in parts of watermelons

Chromium was found in all the parts of the three varieties of watermelons that were analyzed. The mean levels of chromium in the peel/rind, white flesh, red flesh and seeds of each variety of watermelon from each sampling sites, and an average of mean levels in parts of samples collected from the two sites were compared at α =0.05 level and the mean levels in each part are recorded in Table 4.6.

Table 4.6: Mean levels and range (µg/g) of chromium in parts watermelons

Varieties of watermelons /sampling sites		Concentration (µg/g) Mean ±SE (Range)				P- value
		Peel/rind	White flesh	Red flesh	Seeds	
Charleston Grey	Githurai n=6	12.89±1.15^{a} (14.10-23.32)	16.89±2.41^{a} (13.66-24.23)	16.13±6.05^{a} (12.16-19.41)	19.78±0.76^{a} (12.84-17.93)	0.549
	Mwea n=6	21.11±4.14^{ab} (6.67-34.00)	40.11±2.63^{c} (32.67-48.67)	36.78±9.86^{ab} (2.67-60.67)	17.56±2.70^{a} (6.67-24.00)	0.024
	Overall mean n=12	17.00±2.39^{a} (6.67-34.00)	28.50±3.89^{a} (8.00-48.67)	26.46±6.33^{a} (2.67-60.67)	18.67±1.38^{a} (6.67-24.00)	0.121
Crimson Sweet	Githurai n=6	18.00±0.91^{c} (16.00-21.33)	3.47±0.25^{a} (2.67-4.00)	9.22±1.51^{b} (4.67-13.33)	25.33±1.42^{d} (20.67-29.33)	0.001
	Mwea n=6	16.00±0.46^{c} (14.67-18.00)	5.56±0.37^{a} (4.67-7.33)	12.00±0.96^{b} (10.00-15.33)	23.34±1.45^{d} (19.33-29.33)	0.001
	Overall mean n=12	17.00±0.57^{c} (14.67-21.33)	4.61±0.40^{a} (2.67-15.33)	10.61±0.95^{b} (4.67-15.33)	24.34±1.01^{d} (19.33-29.33)	0.001
Sugarbaby	Githurai n=6	17.56±2.54^{a} (10.00-26.00)	25.00±4.86^{ab} (10.00-36.00)	29.44±1.97^{b} (20.00-33.33)	44.67±1.10^{c} (40.67-48.00)	0.001
	Mwea n=6	15.56±1.10^{a} (12.67-20.00)	27.33±4.22^{bc} (12.00-38.00)	22.00±1.72^{ab} (16.00-27.33)	34.17±3.39^{c} (25.00-48.67)	0.002
	Overall mean n=12	16.56±1.35^{a} (10.00-26.00)	26.17±3.9^{b} (10.00-38.00)	25.72±1.68^{b} (16.00-33.33)	39.42±2.32^{c} (25.00-48.67)	0.001

In Table 4.6 mean values with the same small letters within the same row are not significantly different at α =0.05.

Results in Table 4.6 indicates that samples of Charleston Grey from Githurai market, chromium mean levels recorded by the peel/rind, white flesh, red flesh and the seeds did not differ significantly (p = 0.549). Charleston grey, samples bought from Mwea market recorded

chromium mean levels of white flesh were significantly higher than those recorded by the peel/rind, red flesh and seeds ($p = 0.024$). Chromium mean levels in the peel/rind and flesh did not differ significantly, however they were significantly higher than those recorded by the seeds. The overall mean levels of chromium in the peel/rind, white flesh, red flesh and the seeds of Charleston grey watermelons samples from both markets did not differ significantly ($p = 0.121$). Consuming any of the four parts statistically it means that one gets the same nutritional values of chromium.

In Crimson Sweet watermelons, samples obtained from Githurai market, Mwea market and overall mean of chromium mean levels in the four parts (peel/rind, white flesh, red flesh and the seeds) differed significantly since ($p = 0.001$).

In Sugarbaby watermelons, the samples obtained from Githurai market recorded chromium mean levels in the seeds which were significantly higher than those recorded by the red flesh, white flesh and the pee/rind ($p = 0.001$). However, chromium mean levels in the white flesh and the red flesh did not differ significantly as well as mean levels in the peel/rind and white flesh part. Sugar baby watermelon samples from Mwea market, chromium mean levels recorded by the seeds were significantly higher than those recorded by the peel/rind and red flesh ($p = 0.001$) but did not differ significantly with those recorded by the white flesh. The overall mean for all Sugar baby watermelons samples obtained the two markets, the seeds recorded the significantly high mean levels of chromium followed by the white flesh and the red flesh and the peel/rind which recorded the lowest mean level of chromium ($p = 0.001$). The mean levels of chromium in white flesh and the red flesh did not differ significantly.

The range of chromium mean levels in the peel/rind, flesh and seeds of the three varieties were (6.67-34.00) µg/g, (2.67-48.67) µg/g, (2.67-60.67) µg/g and (6.67-48.67) µg/g respectively. The variation in chromium mean levels in parts of the same variety of watermelon and also the range in the mean levels could have been contributed by such factors as difference in levels of chromium, pH and condition of soils where the watermelons were grown, the maturity of the watermelon and the season the watermelons were grown (Underwood, 1977).

4.4.2 Mean levels of chromium in varieties of watermelons

Chromium mean levels in Charleston grey, Crimson sweet and Sugar baby watermelons samples obtained from Mwea and Githurai markets were determined from the mean levels in four parts of each variety. Overall mean in each variety obtained in the two markets was determined from mean level of chromium in all the parts of watermelons obtained from both markets and compared as shown in Table 4.7.

Table 4.7: Mean levels (µg/g) of chromium in varieties of watermelons

Varieties of watermelons/ Sampling sites	Concentration (µg/g)			p-value
	Charleston Grey (SugarF1)	Crimson Sweet (Zebra)	Sugarbaby	
Githurai market Mean±SE (n=24) (range)	16.42±1.63[a] (2.67-60.67)	14.46±0.84[a] (4.67-29.33)	29.17±2.49[b] (10.00-48.00)	0.001
Mwea market Mean±SE (n=24) (Range)	28.89±3.33[b] (8.51-22.33)	14.23±1.41[a] (5.96-22.84)	24.76±1.96[b] (8.89-22.76)	0.001
Overall Mean±SE (n=48) (Range)	22.66±2.05[b] (2.67-60.67)	14.34±1.14[a] (2.67-29.33)	26.97±1.60[b] (10.00-48.67)	0.001

In Table 4.7 mean values with the same small letters within the same row are not significantly different at α =0.05.

Results in Table 4.7 indicate that the watermelons samples obtained in Githurai market, the Sugarbaby watermelon samples recorded chromium mean levels which were significantly higher than these recorded by Charleston Grey and Crimson Sweet watermelons samples ($p = 0.001$). In watermelon samples obtained from Mwea market, Charleston Grey recorded chromium mean levels which were significantly higher than those recorded by Crimson Sweet ($p = 0.001$) but did not differ significantly with mean levels recorded by Sugarbaby. The overall mean for all watermelon samples obtained in the two markets, the Sugarbaby recorded the highest mean levels followed by the Charleston Grey and Crimson Sweet watermelons which recorded the lowest chromium mean levels ($p = 0.001$).There was no significant difference chromium mean levels in Charleston Grey and the Sugarbaby watermelons samples.

The variations in chromium mean levels in the varieties of watermelons can be attributed to such factors as the genetic makeup of the watermelons, the sites, amounts of chromium, pH and the physical conditions of the soils the watermelons were grown in (Pallardy and Theodore, 2008).

Mean levels of chromium reported in this study were higher than those reported in watermelons and pumpkin seeds (Muchemi, 2006) but were lower than those reported in bitter cucumber (Ayoola *et al*., 2010). However, they were comparable to those reported in broccoli of 22 µg/g (Anderson *et al*., 1992).

4.4.3 Comparison of chromium mean levels in watermelons in markets

Chromium mean levels in Charleston grey, Crimson sweet and Sugar baby watermelon samples obtained from Githurai and Mwea markets were determined from the means of chromium levels the four parts of each variety bought from each market and compared at α =0.05 level as shown in Table 4.8.

Table 4.8: Mean level (µg/g) of chromium in watermelon from Githurai and Mwea markets

Varieties of watermelons	Concentration (µg/g)		p-value
	Githurai Market Mean±SE n = 24	Mwea Market Mean±SE n = 24	
Charleston Grey	16.42±1.63[a]	28.89±3.33[b]	0.002
Crimson Sweet	14.46±1.84[a]	14.23±1.41[a]	0.921
Sugarbaby	29.17±2.49[a]	24.76±1.96[a]	0.171

In Table 4.8 mean values with the same small letters within the same row are not significantly different at α =0.05.

The results in Table 4.8 in Charleston Grey, watermelon samples obtained in Mwea market recorded chromium mean levels which were significantly higher than chromium mean levels recorded by watermelon samples obtained in Githurai market ($p = 0.002$). The mean levels of chromium in Crimson Sweet and Sugar baby watermelons samples from Githurai and Mwea markets did not differ significantly ($p > 0.05$). The variation in chromium mean levels same variety of watermelons could be as a result of the sites, the amount of chromium in soils where the watermelons were grown, the soil physical conditions or the pH of the soil (Underwood, 1977).

4.4 Molybdenum in watermelons

4.4.1 Mean levels of molybdenum in parts watermelons

The levels of molybdenum were determined in the peel/rind, white flesh, red flesh and the seeds of Charleston Grey. Crimson Sweet and Sugarbaby watermelons samples obtained from Githurai and Mwea markets. The mean levels of molybdenum obtained in the four parts of the three varieties of watermelons obtained from the two sampling sites were compared at α =0.05 level and their mean and their corresponding p-values recorded in Table 4.9.

Table 4.9: Mean levels and range (µg/g) of molybdenum in the parts of watermelons

Varieties of watermelons/sampling sites		Concentration (µg/g) Mean ±SE (Range)				p value
		Peel/Rind	White flesh	Red flesh	Seeds	
Charleston Grey	Githurai n=6	16.67±0.54^{ab} (13.66-24.23)	24.00±0.99^{c} (14.10-23.32)	14.44±1.31^{a} (12.16-19.41)	18.78±1.27^{b} (12.84-17.93)	0.001
	Mwea n=6	18.67±2.64^{b} (7.33-24.00)	5.00±0.66^{a} (3.33-7.33)	5.33±0.34^{a} (4.00-6.00)	8.78±0.72^{a} (6.00-10.67)	0.001
	Overall mean n=12	17.67±1.32^{a} (7.33-24.00)	14.50±2.92^{a} (3.33-28.00)	9.89±1.52^{a} (4.00-18.00)	13.78±1.66^{a} (6.00-23.33)	0.059
Crimson Sweet	Githurai n=6	17.44±1.09^{b} (14.00-22.00)	21.60±1.19^{c} (18.00-24.67)	9.67±1.48^{a} (4.67-14.00)	9.22±1.65^{a} (5.33-16.67)	0.001
	Mwea n=6	12.33±1.83^{b} (5.33-18.00)	5.22±0.44^{a} (4.00-6.67)	6.33±1.00^{a} (2.00-8.67)	11.33±0.54^{b} (9.33-12.67)	0.001
	Overall mean n=12	14.89±1.27^{b} (5.33-22.00)	12.67±2.64^{b} (4.00-24.67)	8.00±0.99^{a} (2.00-14.00)	10.28±0.89^{ab} (5.33-16.67)	0.018
Sugarbaby	Githurai n=6	21.22±0.53^{a} (10.20-15.51)	25.00±1.01^{b} (12.20-18.95)	41.33±1.14^{d} (11.76-19.86)	36.89±1.79^{c} (8.10-17.61)	0.001
	Mwea n=6	18.22±1.88^{a} (12.67-24.00)	25.78±3.07^{a} (17.33-36.67)	25.44±3.14^{a} (20.00-40.00)	40.33±1.58^{b} (34.00-44.67)	0.001
	Overall mean n=12	19.72±1.03^{a} (12.67-24.00)	25.39±1.55^{b} (17.33-36.67)	33.39±2.88^{c} (20.00-46.00)	38.61±1.25^{d} (32.00-44.67)	0.001

In Table 4.9 mean values with the same small letters within the same row are not significantly different at α =0.05.

The results in Table 4.9 show that in Charleston Grey watermelons samples obtained from Githurai market, the white flesh recorded the highest molybdenum mean levels followed by the seeds and the red flesh recorded the lowest ($p = 0.001$). Molybdenum mean level in the peel/rind, red flesh and seeds of Charleston Grey did not differ significantly, however they were significantly lower than those recorded by the pee/rind of Charleston grey watermelons samples obtained in Mwea ($p = 0.001$). The overall mean for all the samples of Charleston Grey watermelon obtained in the two markets, the peel/rind, white flesh, red flesh and seeds recorded molybdenum mean levels that did not differ significantly ($p = 0.059$). Statistically any of the four parts would provide equivalent amount of molybdenum in the body.

In Crimson Sweet watermelons samples obtained from Githurai market, molybdenum mean levels in the peel/rind were the significantly higher than those recorded by the red flesh and seeds, however they were significantly lower than those recorded by the white fleshy part ($p = 0.001$). Molybdenum mean levels recorded by the seeds and red flesh did not differ significantly. Crimson sweet watermelons samples bought from Mwea market, the peel/rind recorded the highest molybdenum mean levels which did not differ significantly with those recorded by the seeds, however, they were significantly higher than those recorded by the white flesh and red flesh ($p = 0.001$). The mean levels of molybdenum in the red flesh and white did not differ significantly. Considering the overall mean of molybdenum in Crimson sweet watermelons bought in both markets, the red flesh recorded significantly lower mean levels compared to the peel/rind and white flesh ($p =0.018$). There was no significant difference in molybdenum mean levels in the peel/rind, white flesh and seeds as well as between red flesh and seeds.

In the Sugarbaby watermelons samples obtained from Githurai market recorded molybdenum mean levels which differed significantly in peel/rind, white flesh, red flesh and seeds ($p = 0.001$). Sugar baby watermelons samples obtained from Mwea market, molybdenum mean levels in the seeds were significantly higher than those recorded by the other three parts ($p = 0.001$). Molybdenum mean levels in the peel/rind and white flesh and red flesh did not differ significantly. The overall Molybdenum mean levels in Sugar baby watermelon samples from the two markets, differed significantly in the four parts ($p = 0.001$).

The range of mean levels of molybdenum in the peel, the rind, the flesh and the seeds were (5.33-24.00) µg/g, (3.33-36.67) µg/g, (2.00-46.00) µg/g and (5.33-44.6) µg/g. The range and variation in the parts could be attributed to variation of the levels of molybdenum in soils where the watermelons samples were grown (Underwood, 1977).

4.4.2 Molybdenum mean levels (µg/g) in varieties of watermelons

The mean levels of molybdenum in Charleston Grey, Crimson Sweet and Sugarbaby watermelon were obtained from the mean levels recorded in the four parts of each variety of watermelons. Molybdenum mean levels in the three varieties of watermelons from each market and overall mean in both markets were compared using one way ANOVA and results recorded in Table 4.10.

Table 4.10: Mean levels (µg/g) of molybdenum in varieties of watermelons

Varieties of watermelons /sampling sites	Concentration (µg/g)			p-value
	Charleston Grey	Crimson Sweet	Sugarbaby	
Githurai market Mean±SE(n=24) (Range)	18.47±0.89[b] (10.00-28.00)	14.17±1.27[a] (4.67-24.67)	31.11±1.81[c] 20.00-46.00	0.001
Mwea market Mean±SE(n=24) (Range)	9.44±1.33[a] (3.33-24.00)	8.81±0.82[a] (2.00-18.00)	27.44±2.04[b] (12.67-44.67)	0.001
Overall mean Mean±SE (n=48)(Range)	13.96±1.03[a] (3.33-28.00)	11.43±0.84[a] (2.0-24.67)	29.28±1.38[b] (12.67-46.00)	0.001

In table 4.10 mean values with the same small letters within the same row are not significantly different at α =0.05.

The results in Table 4.10 show that watermelons samples obtained from Githurai market, molybdenum mean levels recorded in the three varieties of watermelons differed significantly (p = 0.001). Molybdenum mean level in Sugar baby watermelons samples obtained from Mwea market as well as those obtained in both markets(overall mean) were significantly higher than mean levels recorded by Crimson sweet and Charleston grey (p = 0.001). Molybdenum mean levels in Charleston Grey and the Crimson Sweet watermelons samples did not differ significantly. The variation in the mean levels of molybdenum in different varieties of watermelon can be attributed to their genetic makeup, amounts of molybdenum, the pH and physical conditions of the soils where the watermelons were grown in (Pallardy and Theodore, 2008).

Mean levels of molybdenum reported in this study were significantly higher than those reported in cucumbers (USDA, 2008), but were lower than those reported in potatoes and vegetables however they are comparable to those in fruit berries (Kaslow, 2011).

4.4.3 Molybdenum mean levels (µg/g) in watermelons in markets

Molybdenum mean levels in Charlton Grey, Crimson Sweet watermelons and Sugar baby watermelons samples were determined from the means of levels the parts of each obtained from Githurai and Mwea markets. The mean levels of each variety in the two markets were compared at α =0.05 level as recorded in Table 4.11.

Table 4.11: Mean levels (µg/g) of molybdenum in watermelons from Githurai and Mwea markets

Varieties of watermelons	Concentration (µg/g)		p-value
	Githurai Market mean±SE n = 24	Mwea Maeket mean±SE n= 24	
Charleston Grey	18.47±0.89[b]	9.44±1.33[a]	0.001
Crimson Sweet	14.17±1.27[b]	8.81±0.82[a]	0.001
Sugarbaby	31.11±1.81[a]	27.44±2.04[a]	0.187

In Table 4.11 mean values with the same small letters within the same row are not significantly different at α =0.05.

Results in Table 4.11 show that, the Charleston Grey and Crimson sweet watermelon samples from Githurai market recorded molybdenum mean levels which were significantly higher than samples from Mwea market (p = 0.001). In Sugarbaby, the results indicate that the mean levels of molybdenum in watermelon samples obtained from Githurai and Mwea markets were not significantly different (p = 0.187). The variation in the mean levels of molybdenum in the same variety of watermelon samples in the two markets could have been brought about by differences in the sites, soil pH, physical conditions of soils and amounts of molybdenum in the soils the watermelons were grown in (Pallardy and Theodore, 2008).

4.5 Silicon in watermelons

4.5.1. Mean levels of silicon in parts of watermelons

Silicon levels in the peel/rind, white flesh red flesh and seeds of Charleston Grey, Crimson Sweet and Sugarbaby watermelons samples obtained from Githurai and Mwea markets were determined and the overall mean levels of silicon in all the four parts of samples obtained in the two sampling sites and their means compared at α =0.05 level as shown in Table 4.12

Table: 4.12: Mean levels (mg/g) of silicon in parts of watermelons

Varieties of watermelons		Concentration (mg/g) Mean ±SE (Range)				P-value
		Peel/Rind	White flesh	Red flesh	Seeds	
Charleston Grey	Githurai n=6	1.44±0.12^{c} (1.08-1.81)	0.82±0.03^{b} (0.70-0.90)	0.32±0.03^{a} (0.25-0.42)	0.66±0.05^{b} (0.49-0.85)	0.001
	Mwea n=6	0.51±0.10^{a} (0.23-0.79)	0.52±0.04^{a} (0.38-0.69)	0.60±0.05^{a} (0.45-0.73)	0.81±0.07^{b} (0.50-0.96)	0.028
	Overall mean n=12	0.97±0.16^{b} (0.23-1.81)	0.67±0.18^{ab} (0.38-0.90)	0.46±0.17^{a} (0.25-0.73)	0.73±0.16^{ab} (0.49-0.96)	0.030
Crimson Sweet	Githurai n=6	0.61±0.07^{a} (0.39-0.76)	0.86±0.06^{ab} (0.63-1.03)	0.61±0.05^{a} (0.41-0.75)	0.95±0.12^{b} (0.39-1.23)	0.013
	Mwea n=6	1.01±0.04^{b} (0.94-1.14)	0.64±0.05^{a} (0.46-0.79)	0.61±0.04^{a} (0.45-0.72)	0.48±0.10^{a} (0.32-0.96)	0.001
	Overall mean n=12	0.81±0.07^{a} (0.39-1.14)	0.74±0.05^{a} (0.46-1.03)	0.61±0.03^{a} (0.41-0.75)	0.71±0.10^{a} (0.32-1.23)	0.223
Sugarbaby	Githurai n=6	0.70±0.02^{a} (0.65-0.74)	0.60±0.03^{a} (0.47-0.67)	0.79±0.12^{a} (0.27-0.99)	0.63±0.02^{a} (0.55-0.70)	0.192
	Mwea n=6	0.78±0.05^{a} (0.56-0.90)	0.63±0.09^{a} (0.39-1.05)	0.86±0.07^{a} (0.58-1.01)	0.62±0.08^{a} (0.32-0.83)	0.099
	Overall mean n=12	0.74±0.09^{ab} (0.56-0.90)	0.62±0.05^{a} (0.39-1.05)	0.83±0.07^{b} (0.27-1.01)	0.63±0.04^{a} (0.32-0.83)	0.009

In Table 4.12 mean values with the same small letters within the same row are not significantly different at α =0.05.

From Table 4.12 the results show that in Charleston Grey, watermelon samples obtained from Githurai market recorded silicon mean levels in the peel/rind which were significantly higher than those recorded by the other three parts and the flesh recorded silicon mean levels which were significantly lower than those recorded by the other three parts ($p = 0.001$). Silicon mean levels in the seeds and white flesh did not differ significantly. In Charleston grey watermelon samples from Mwea market, the seeds recorded silicon mean levels which were significantly higher than those recorded by the rest of the parts ($p = 0.028$). Silicon mean levels in the peel/rind and white flesh and the red flesh did not differ significantly. The overall mean levels of silicon in Charleston grey watermelon samples obtained in the two markets, there was no significant difference in the mean levels of silicon in the peel/rind, white flesh and seeds. However, Silicon mean levels in the peel/rind were significantly higher than mean levels recorded by red flesh ($p = 0.03$).

For Crimson Sweet, watermelon samples obtained in Githurai market recorded silicon mean levels in the seeds were significantly higher than those recorded by the red flesh and the peel/rind ($p = 0.013$) but did not differ significantly from those recorded by the white flesh. Silicon mean levels in the red flesh and peel/rind did not differ significantly. In watermelon samples obtained from Mwea market the peel/rind recorded silicon mean levels which were significantly higher than those recorded by the other three parts ($p = 0.001$). Silicon mean levels in the rind/peel white flesh and seeds did not differ significantly. The overall mean levels of watermelon samples obtained from the two markets, there was no significant difference in silicon mean levels between the four parts since ($p = 0.223$). It means that consuming any of the four parts would provide equivalent amount of silicon in the body.

In Sugarbaby, watermelon samples obtained from Githurai market and Mwea recorded silicon mean levels that did not differ significantly in the peel/rind, white flesh, red flesh and seeds ($p > 0.099$). The overall mean for silicon in Sugar baby watermelon samples obtained in the two markets, there was no significant difference in mean level recorded by the peel/rind, white flesh and the seed and also between peel/rind and red flesh. Silicon mean levels in seeds were significantly higher than those recorded by the white flesh and red flesh ($p = 0.009$).

Results in Table 4.12 indicate that in all the three varieties, the range in silicon mean levels in the peel/rind, the white flesh, red flesh and the seeds were (0.23-1.81) mg/g, (0.38-1.05) mg/g, (0.15-1.01) mg/g and (0.32-1.23) mg/g respectively. The range is an indication that the watermelons may have been grown in soils of varying silicon levels (Underwood, 1977). The variation in parts of the same variety of watermelon could be as a result of seasonal variation and maturity of the fruit (AHR, 2007). Consuming any part would provide equivalent amount of silicon in the body.

4.5.2 Mean levels (mg/g) of silicon in varieties of watermelons

The mean levels of silicon in the four parts were used determine the mean levels of silicon in the variety of watermelon. This was done for watermelon samples of each variety and in each and both markets. The mean levels of silicon in Charleston Grey, Crimson Sweet and Sugar baby watermelons form Githurai and Mwea markets were compared statistically as shown in Table 4.13.

Table 4.13: Mean levels (mg/g) of silicon varieties of watermelons

Varieties of watermelons /sampling sites	Concentration (mg/g)			p-value
	Charleston Grey	Crimson Sweet	Sugarbaby	
Githurai market Mean±SE(n=24) (Range)	0.80±0.09[b] (0.25-1.81)	0.75±0.05[b] (0.39-1.23)	0.68±0.03[a] (0.27-0.99)	0.001
Mwea market Mean±SE(n=24) (Range)	0.61±0.04[a] (0.23-0.96)	0.68±0.05[a] (0.32-1.14)	0.72±0.04[a] (0.32-1.05)	0.283
Overall mean Mean±SE (n=48)(Range)	0.71±0.05[a] (0.23-1.81)	0.72±0.04[a] (0.32-1.23)	0.70±0.03[a] (0.27-1.05)	0.963

In Table 4.13 mean values with the same small letters within the same row are not significantly different at α =0.05

Table 4.13 indicate that in watermelon samples obtained Githurai market, silicon mean levels in Charleston Grey and Crimson Sweet were significantly higher than those recorded by Sugarbaby (p = 0.001). Silicon mean levels in Charleston Grey and Crimson Sweet did not differ significantly. Watermelons samples obtained from Mwea market recorded mean levels of silicon that did not differ significantly in the three varieties (p =0.283). In overall mean for watermelon samples bought from the two markets, silicon mean levels in Crimson Sweet, Charleston Grey and Sugarbaby did not differ significantly (p = 0.963). Statistically it means that Charleston Grey, Sugarbaby and Crimson Sweet provide equivalent amount of silicon in the body. The variations in mean levels of silicon observed in the varieties could have resulted due factors such as genetic makeup of the watermelons, the soils (silicon content, pH and physical condition) in which watermelons were grown (Pallardy and Theodore, 2008).

Mean levels of silicon reported in this study were significantly lower than those reported in cucumbers and cantaloupe; however, the mean levels of silicon in the three varieties of watermelons are comparable to the mean levels reported in fruits and vegetables (Powel *et al*., 2005).

4.5.3 Silicon mean levels (mg/g) in watermelons in the markets

The mean levels of silicon obtained in the four parts of each variety were used to determine the mean levels of in all samples obtained from one market and they were compared with the silicon mean in the other market. Silicon mean levels recorded by Charleston grey, Crimson sweet and sugar baby watermelons obtained from Githurai and Mwea markets were compared at α =0.05 level as shown in Table 4.14

Table 4.14: Mean levels (mg/g) silicon in watermelons from Githurai and Mwea markets

Varieties of watermelons	Concentration (mg/g)		p-value
	Githurai Market Mean±SE n = 24	Mwea Market Mean±SE n = 24	
Charleston Grey	0.81±0.09[b]	0.61±0.04[a]	0.049
Crimson Sweet	0.75±0.05[a]	0.68±0.05[a]	0.342
Sugarbaby	0.68±0.03[a]	0.72±0.04[a]	0.457

In Table 4.14 mean values with the same small letters within the same row are not significantly different at α =0.05.

Table 4.14 shows that in Charleston Grey, watermelon samples obtained from Githurai market recorded mean levels of silicon which were significantly higher than those of Mwea market (p = 0.049). The mean levels of silicon in Crimson Sweet watermelon samples from Githurai market did not differ significantly from those obtained from Mwea market (p = 0.342). The mean levels of silicon in Sugarbaby watermelon samples obtained from Githurai market did not differ significantly from those recorded by watermelon samples from Mwea market (p = 0.457). The variations noted in Charleston grey watermelon could have been as a results of melons having been grown in soils of varying silicon levels, differences in soil pH,

sites where the watermelons were grown or silicon content water used to grow the watermelons (Underwood, 1977).

4.6 Vanadium in watermelons

4.6.1 Mean levels of vanadium in parts watermelons

The levels of vanadium were determined in the pee/rind, white flesh, red flesh and the seeds of Charleston Grey. Crimson Sweet and Sugarbaby watermelons samples obtained from Githurai and Mwea markets. The mean levels of vanadium obtained in the four parts of the three varieties of watermelons obtained from the two sampling sites were compared at α =0.05 level and their means and their corresponding p-values recorded in Table 4.15.

Table 4.15: Mean levels and range (µg/g) of vanadium in parts of watermelons

Varieties of watermelon /sampling sites		Concentration (µg/g) Mean ±SE (Range)				p-value
		Peel/Rind	White flesh	Red flesh	Seeds	
Charleston Grey	Githurai n=6	307.33±23.58^{b} (266.00-20.00)	129.67±23.10^{a} (70.00-220.00)	250.56±24.85^{b} (190.00-350.00)	453.00±5.88^{c} (438.00-474.00)	0.001
	Mwea n=6	31.67±2.66^{a} (22.00-40.00)	194.78±17.53^{b} (119.33-46.67)	231.67±15.27^{b} (166.00-273.33)	202.89±62.88^{b} (6.00-342.00)	0.002
	Overall mean n=12	169.50±43.07^{a} (22.00-420.00)	162.22±16.96^{a} (70.00-246.67)	241.11±14.19^{ab} (166.00-350.00)	327.94±48.25^{b} (6.00-474.00)	0.004
Crimson Sweet	Githurai n=6	30.78±4.48^{a} (23.33-50.00)	104.27±20.58^{b} (58.00-177.33)	54.11±16.12^{a} (20.67-132.00)	471.89±13.81^{c} (418.00-522.00)	0.001
	Mwea n=6	256.00±13.74^{a} (212.00-302.67)	312.33±9.92^{b} (270.00-340.00)	304.78±21.88^{b} (242.00-390.00)	317.67±4.11^{b} (306.00-334.00)	0.020
	Overall mean n=12	143.39±34.64^{a} (23.33-302.67)	217.75±34.31^{a} (58.00-340.00)	179.44±39.95^{a} (20.67-390.00)	394.78±24.24^{b} (306.00-22.00)	0.001
Sugarbaby	Githurai n=6	105.11±9.68^{a} (68.00-34.00)	70.44±30.25^{a} (16.67-210.00)	383.67±9.43^{b} (342.00-406.00)	347.33±13.14^{b} (302.00-390.00)	0.001
	Mwea n=6	74.44±21.42^{a} (14.00-131.33)	26.33±9.58^{a} (3.33-70.00)	266.00±36.41^{b} (170.00-410.00)	355.17±27.17^{c} (276.33-41.33)	0.001
	Overall mean n=12	89.78±12.12^{a} (14.00-134.00)	48.39±16.53^{a} (3.33-210.00)	324.83±25.22^{b} (170.00-410.00)	351.25±14.44^{b} (276.33-441.33)	0.001

In Table 4.15 mean values with the same small letters within the same row are not significantly different at α =0.05.

Results recorded in Table 4.15 shows that in Charleston Grey, watermelon samples obtained from Githurai market recorded vanadium mean levels in the seeds which were significantly higher than those in the other parts, while those recorded by the white flesh were significantly lower than those recorded by the other parts since ($p = 0.001$). Mean levels in the red flesh and the peel/rind did not differ significantly. Watermelons samples obtained from Mwea market the peel/rind recorded vanadium mean levels that were significantly lower than those recorded by the rest of the parts since ($p = 0.002$). Vanadium mean levels in the peel/rind, red flesh and seeds did not differ significantly. The overall mean of vanadium recorded by watermelon samples obtained from the two markets, the seeds recorded mean levels of vanadium that were significantly higher than the peel/rind and white flesh part ($p = 0.004$). There was no significant difference in the mean levels of vanadium in the peel/rind, white flesh and the red flesh parts.

In Crimson Sweet, watermelon samples obtained from Mwea market recorded vanadium mean levels in the peel/rind that were significantly lower than those recorded by the other three parts ($p = 0.020$). Vanadium mean levels in the white flesh, red flesh and seeds did not differ significantly. Watermelon samples obtained from Githurai market recorded mean levels of vanadium in the peel/rind and red flesh parts that did not differ significantly however, they were significantly lower than those recorded by the seeds and white flesh parts ($p = 0.001$). Vanadium mean levels recorded by the seeds were significantly higher than those recorded by the other parts. The overall mean levels of vanadium in watermelon samples obtained from the two markets, the mean levels recorded by the seeds were significantly higher than those recorded by the other three parts ($p = 0.001$). The vanadium mean levels in the peel/rind, white flesh and red flesh did not differ significantly. Seeds of the Crimson Sweet are the best sources of vanadium compared to the other three parts.

In Sugarbaby, watermelon sample obtained from Githurai market, the red flesh recorded the mean levels of vanadium which were significantly higher than the mean levels recorded by the peel/rind and white flesh (p = 0.001). Vanadium mean levels in the peel/rind and white as well as red flesh and seeds did not differ significantly. Watermelon samples obtained from Mwea market recorded vanadium mean levels in the seeds were significantly higher than those recorded by the other three parts and also those recorded by the flesh were significantly higher than those recorded by the pee/rind and white flesh (p = 0.001). Mean levels of vanadium in the peel/rind and white flesh did not differ significantly. The overall mean levels of vanadium in Sugar baby watermelon samples obtained from the two markets, the seeds recorded mean levels of which were significantly higher than mean levels recorded by the white flesh and the peel/rind parts (p = 0.001). Vanadium mean levels in the peel/rind and white flesh and also those of seed and red flesh did not differ significantly.

The range of levels of peel, the rind, the flesh and the seeds for all the varieties studied were (14.0-420.00) µg/g, (3.33-340) µg/g, (20.67-420.00) µg/g and (6.00-522.00) µg/g respectively. The range in the parts could be attributed to variation of the levels of vanadium in soils where the watermelons samples were grown (Underwood, 1977).

4.6.2 Comparison of mean levels of vanadium in varieties of watermelons.

The mean levels of V in all the parts of each variety of watermelon were obtained and used to determine vanadium mean levels in each of watermelons from each market. Vanadium mean levels in the three varieties bought from each market and both markets were compared α =0.05 level. Table 4.16 shows the mean levels of V in each variety and the p values. Mean levels were based on dry weight.

Table 4.16: Mean levels (µg/g) of vanadium in varieties of watermelons

Varieties of watermelons/ sampling sites	Concentration (µg/g)			p-value
	Charleston Grey	Crimson Sweet	Sugarbaby	
Githurai market Mean±SE(n=24) (Range)	285.14±26.12^{ab} (70.00-474.00)	164.93±38.56^{a} (20.67-522.00)	226.64±30.35^{b} (16.67-406.00)	0.035
Mwea market Mean±SE(n=24) (Range)	165.25±22.62^{a} (6.00-342.00)	297.69±8.28^{b} (212.00-390.00)	180.49±30.56^{a} (3.33-441.33)	0.001
Overall Mean±SE (n=48) (Range)	225.19±19.20^{a} (6.00-474.00)	234.18±21.76^{a} (20.67-522.00)	203.56±21.57^{a} (3.33-441.33)	0.567

In Table 4.16 mean values with the same small letters within the same row are not significantly different at α =0.05

The results in Table 4.16 indicate that vanadium mean levels in watermelon samples obtained from Githurai markets, the Sugarbaby watermelon recorded significantly higher mean levels than those recorded by Crimson Sweet (p = 0.035). Vanadium mean levels in the Charleston Grey and the other two varieties did not differ significantly. Watermelon samples bought from Mwea market, Vanadium mean levels recorded by Crimson Sweet were significantly higher than those recorded by the other two varieties (p = 0.001). The overall mean levels of vanadium in watermelon samples obtained in the two markets did not differ significantly in the three varieties of (p = 0.567). The variations in mean levels of vanadium observed in the varieties could have resulted due factors such as genetic makeup of the watermelons, vanadium content, pH and physical condition of the soils in which watermelons were grown (Pallardy and Theodore, 2008).Statistically, the Charleston Grey, Crimson Sweet and the Sugarbaby provide equivalent nutritional values of vanadium.

Vanadium mean levels reported in this study were within the range of concentration of vanadium in fruits and vegetables as reported by Myron *et al.*, (2010).

4.6.3 Concentration of vanadium in varieties of watermelons in markets

The average of the mean levels of vanadium in watermelons samples of each variety from Githurai and Mwea markets were obtained using mean levels of vanadium obtained in parts of the watermelons and compared and the results recorded in Table 4.17.

Table 4.17: Mean concentration (µg/g) vanadium in watermelons from Githurai and Mwea markets

Varieties of watermelons	Concentration (µg/g)		p-value
	Githurai Mean±SE n = 24	Mwea Mean±SE n = 24	
Charleston Grey	285.14±26.12[b]	165.25±22.62[a]	0.001
Crimson Sweet	167.91±39.46[a]	297.69±40.59[b]	0.004
Sugarbaby	226.64±30.35[a]	180.49±30.56[a]	0.290

In Table 4.17 mean values with the same small letters within the same row are not significantly different at α =0.05.

Results in Table 4.17 indicate that Charleston Grey watermelon samples obtained from Githurai recorded the highest mean levels of vanadium compared to mean levels recorded by watermelons samples obtained in Mwea market (p = 0.001). Crimson Sweet watermelons samples obtained from Mwea market recorded the highest mean levels of vanadium compared to those from Githurai (p = 0.004). The mean levels of vanadium in Sugarbaby watermelon samples from Githurai and Mwea market did not differ significantly (p = 0.290). The Sugarbaby watermelon obtained from Mwea and Githurai would provide equivalent amount of dietary vanadium. The variations noted in Charleston grey and Crimson sweet watermelon could have been as a result of melons having been grown in soils of varying vanadium levels, differences in soil pH, sites where the watermelons were grown or vanadium content water used to grow the watermelons (Underwood, 1977).

4.7 Boron in watermelons

4.7.1 Levels of boron in parts of watermelons

The results of the analysis of boron in part of various varieties of watermelon from Githurai and Mwea markets are discussed in the following subsections. The means obtained in each part were compared at α =0.05 level as shown in Table 4.18.

Table 4.18: Mean concentration and range (mg/g) of boron in parts watermelons

Varieties of watermelons/sampling sites		Concentration (mg/g) Mean ±SE (Range)				p-value
		Peel/rind	White flesh	Red flesh	Seeds	
Charleston Grey	Githurai n=6	1.20 ± 0.26^{b} (0.23-1.93)	0.73 ± 0.05^{b} (0.52-0.89)	0.20 ± 0.01^{a} (0.19-0.22)	1.21 ± 0.20^{b} (0.61-2.09)	0.001
	Mwea n=6	0.39 ± 0.08^{c} (0.15-0.65)	0.09 ± 0.01^{a} (0.07-0.11)	0.03 ± 0.01^{a} (0.00-0.05)	0.24 ± 0.03^{b} (0.18-0.39)	0.001
	Overall mean n=12	0.79 ± 0.18^{b} (0.15-1.93)	0.41 ± 0.10^{ab} (0.07-0.89)	0.12 ± 0.03^{a} (0.01-0.22)	0.72 ± 0.17^{b} (0.18-2.09)	0.003
Crimson Sweet	Githurai n=6	0.80 ± 0.20^{b} (0.12-1.49)	0.94 ± 0.11^{b} (0.60-1.31)	0.39 ± 0.05^{a} (0.18-0.55)	0.96 ± 0.07^{b} (0.69-1.19)	0.013
	Mwea n=6	1.16 ± 0.13^{ab} (0.61-1.37)	1.07 ± 0.11^{ab} (0.53-1.23)	1.38 ± 0.02^{b} (1.34-1.46)	1.01 ± 0.05^{a} (0.81-1.20)	0.037
	Overall mean n=12	0.98 ± 0.13^{a} (0.12-1.49)	1.01 ± 0.08^{a} (0.53-1.31)	0.88 ± 0.15^{a} (0.18-1.46)	0.98 ± 0.04^{a} (0.69-1.20)	0.854
Sugarbaby	Githurai n=6	0.64 ± 0.29^{a} (0.01-1.35)	0.16 ± 0.07^{a} (0.01-0.37)	0.34 ± 0.22^{a} (0.00-1.38)	1.28 ± 0.02^{b} (1.22-1.36)	0.002
	Mwea n=6	1.27 ± 0.06^{c} (1.02-1.43)	0.38 ± 0.02^{b} (0.31-0.44)	0.23 ± 0.02^{a} (0.17-0.28)	1.21 ± 0.05^{c} (1.06-1.40)	0.001
	Overall mean n=12	0.95 ± 0.17^{b} (0.01-1.43)	0.27 ± 0.05^{a} (0.01-0.44)	0.28 ± 0.11^{a} (0.00-1.38)	1.24 ± 0.03^{b} (1.06-1.40)	0.001

In Table 4.18 mean values with the same small letters within the same row are not significantly different at $\alpha = 0.05$.

The result recorded in Table 4.18 indicate that in Charleston Grey, the watermelons samples obtained from Githurai market boron mean levels recorded by the seeds, peels/rind and white flesh did not differ significantly, however boron mean levels recorded by the flesh were significantly lower than the other three parts ($p = 0.001$). Watermelon samples obtained from Mwea market recorded mean levels of boron in the peel/rind which were significantly higher than those recorded by the other three parts and also mean levels recorded by the seed were significantly higher than those recorded by the white flesh and red flesh ($p = 0.001$). Boron mean levels in the white flesh and red flesh parts did not differ significantly. The overall mean levels of boron in Charleston grey watermelon samples obtained in the two markets, the peel/rind recorded the highest mean levels of boron which did not differ significantly with the levels in the seeds and the white flesh part but were significantly different from the levels recorded by the red flesh ($p = 0.003$).

In Crimson Sweet watermelons, samples obtained from Githurai market, the reported boron mean levels in the red flesh part which were significantly lower than those obtained from the other parts ($p = 0.013$). Boron mean levels in the seed, peel/rind, white flesh and seeds did not differ significantly. Samples obtained from Mwea market recorded boron mean levels in the peel/rind, seed and white flesh parts that did not differ significantly, however the mean levels recorded by the seed were significantly lower than those recorded by the red flesh ($p = 0.037$). The overall mean levels of boron from crimson sweet watermelon, samples obtained from the two markets recorded mean levels that did not differ significantly ($p= 0.854$) in the peel/rind, white flesh, red flesh and the seeds. This means that the four parts provided equivalent amount of boron in the diet when equal quantities are consumed.

In Sugarbaby watermelons, samples obtained from Githurai the seeds had significantly higher boron mean levels compared to the other three parts ($p = 0.002$). Boron mean levels in the peel/rind, white flesh and red flesh did not differ significantly. Samples obtained from Mwea market, the peel/rind part recorded the highest mean level of boron followed by the white flesh and the seeds recorded the lowest mean levels ($p = 0.001$). Mean levels of boron in the peel/rind did not differ significantly with those recorded by the seeds. The overall mean of boron in all the Sugar baby watermelon samples obtained from the two markets, the seeds recorded the highest mean levels of boron which did not differ significantly with the mean levels in peel/rind but were significantly higher than mean level in the white flesh and the red flesh parts ($p = 0.001$). Boron mean levels in the red flesh and white flesh did not differ significantly.

From the results Table 4.18, the mean levels of boron for the three varieties of watermelons in the peel, the rind, the flesh and the seeds recorded ranges of (0.01-1.93) mg/g, (0.01-1.31) mg/g, (0.01-1.46) mg/g and (0.18-2.09) mg/g respectively. The range in the parts could be attributed to variation of the levels of boron in soils where the watermelons samples were grown (Underwood, 1977).

4.7.2 Mean levels of boron in varieties of watermelons

Mean levels of boron each variety of watermelons was determined from the mean levels of boron in the four parts of watermelons. Boron mean levels in Charleston grey, Crimson sweet and Sugar baby watermelon samples obtained from Githurai and Mwea market were compared at $\alpha = 0.05$ level as shown in Table 4.19.

Table 4.19: Boron mean levels (mg/g) in varieties of watermelons

Varieties of watermelons /sampling sites	Concentration (mg/g)			p-value
	Charleston Grey	Crimson Sweet	Sugarbaby	
Githurai market Mean±SE (n=24) (Range)	 0.83±0.12[a] (0.19-2.09)	 0.76±0.08[a] (0.12-1.49)	 0.60±0.12[a] (0.00-1.38)	 0.307
Mwea market Mean±SE (n=24) (Range)	 0.19±0.04[a] (0.00-0.65)	 1.15±0.05[c] (0.53-1.46)	 0.77±0.10[b] (0.17-1.43)	 0.001
Overall Mean±SE (n=48) (Range)	 0.51±0.08[a] (0.01-2.09)	 0.96±0.05[b] (0.12-1.49)	 0.69±0.18[a] (0.01-1.43)	 0.001

In Table 4.19 mean values with the same small letters within the same row are not significantly different at α =0.05

The results in Table 4.19 indicate that watermelon samples obtained from Githurai market, boron mean levels recorded in the three varieties did not differ significantly since (p = 0.307). Samples obtained from Mwea market recorded boron mean levels in the three varieties differed significantly (p = 0.001). The overall mean levels of boron from watermelon samples obtained from the two markets indicate that the crimson sweet watermelon had significantly higher amounts compared to the other two varieties (p = 0.001). The mean levels of boron in Charleston Grey and Sugarbaby did not differ significantly. The variations in mean levels of boron observed in the varieties could have resulted due factors such as genetic makeup of the watermelons, the soils (boron content, pH and physical condition) in which watermelons were grown (Pallardy and Theodore, 2008).

Levels of boron reported in the three varieties of watermelons in this study were comparable to those reported in fruits and vegetables of 0.1 – 0.6 mg/ 100g, however, they were lower than those reported in avocados of 4.5 mg/100g (Devirian and Volpe, 2003).

4.7.3 Comparison of mean levels of boron in the market

Boron levels in each variety of watermelon samples ware determined from the mean levels of boron recorded in the four parts of watermelons. The mean level of boron obtained in the three varieties of watermelons samples obtained from Githurai and Mwea markets were compared at α =0.05 level as shown in Table 4.20.

Table 4.20: Mean concentration (mg/g) boron in watermelons from Githurai and Mwea markets

Varieties of watermelons	Concentration (mg/g)		p-value
	Githurai Market mean±SE n = 24	Mwea Market mean±SE n = 24	
Charleston Grey	0.83 ± 0.12^{b}	0.19 ± 0.04^{a}	0.001
Crimson Sweet	0.76 ± 0.08^{a}	1.15 ± 0.05^{b}	0.001
Sugarbaby	0.60 ± 0.12^{a}	0.77 ± 0.10^{a}	0.299

In Table 4.20 mean values with the same small letters within the same row are not significantly different at α =0.05.

Results in Table 4.20 indicate that in the Charleston Grey watermelons, boron mean levels in samples obtained from Githurai market were significantly higher than those of Mwea market($p = 0.001$). In Crimson Sweet watermelon, the mean levels of boron recorded by samples obtained from Mwea market was significantly higher than those obtained from Githurai market ($p = 0.001$). This variation in levels of boron in the same variety of watermelon could have resulted from the boron levels, pH and physical conditions of the soils where the watermelons were grown (Underwood, 1977). There was no significant difference in the mean levels of boron in Sugarbaby watermelons samples obtained from Githurai and Mwea markets ($p = 0.299$). This indicated that the Sugarbaby watermelons may have grown in soils with similar levels of boron. The variations noted in levels of boron in

Charleston grey and Crimson sweet watermelon samples could have been as a result of melons having been grown in soils of varying boron levels, differences in soil pH, sites where the watermelons were grown or silicon content water used to grow the watermelons (Underwood, 1977).

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

With respect to the results obtained from this study, the following conclusions were made.

i) All the parts of watermelon samples analyzed in this study were found to contain the selected essential elements (Ca, Cr, B, Si, V and Mo.) determined.

ii) The seeds of Sugar baby watermelons samples recorded chromium, boron, molybdenum and vanadium mean levels which were significantly higher than those recorded by the other parts of watermelons while the seeds of Charleston grey watermelon samples recorded mean levels of silicon which were significantly higher than those recorded by the other parts of watermelons.

iii) Crimson sweet watermelons samples recorded molybdenum, vanadium and boron mean levels which were significantly higher than those recorded by the other two varieties of watermelon samples and the Sugar baby watermelons samples recorded mean levels of chromium which were significantly higher than the other two varieties of watermelon samples.

iv) Charleston grey watermelon samples obtained in Mwea market recorded significantly high amounts of chromium compared to those recorded by samples obtained from Githurai market.

5.2 Recommendations

5.2.1 Recommendations from this study

i) The Kenyan population should be sensitized on the use of watermelon as a fruit and as a vegetable just like cucumbers, cantaloupe and squash. Like in China the pee/rind to be added in stew, pickled and added to cakes, the seeds to be eaten when roasted or added in porridge flour.

ii) People and especially those who are aging and are at a risk of osteoporosis, hypertension, prostate cancer and diabetes to regularly consume watermelons.

iii) Use of fruits and vegetable like watermelons should be encouraged instead of food supplements which in most cases are out of reach for most Kenyan population.

5.2.2 Recommendations for further work

i) Correlation between the levels of essential elements, water used for irrigation and soils should be investigated by planting the watermelons in controlled conditions.

ii) Studies on more fruits and vegetables to determine levels of essential elements.

iii) Studies on other essential elements in watermelons.

iv) Studies on other varieties of watermelons grown in Kenya.

v) Speciation studies on these elements.

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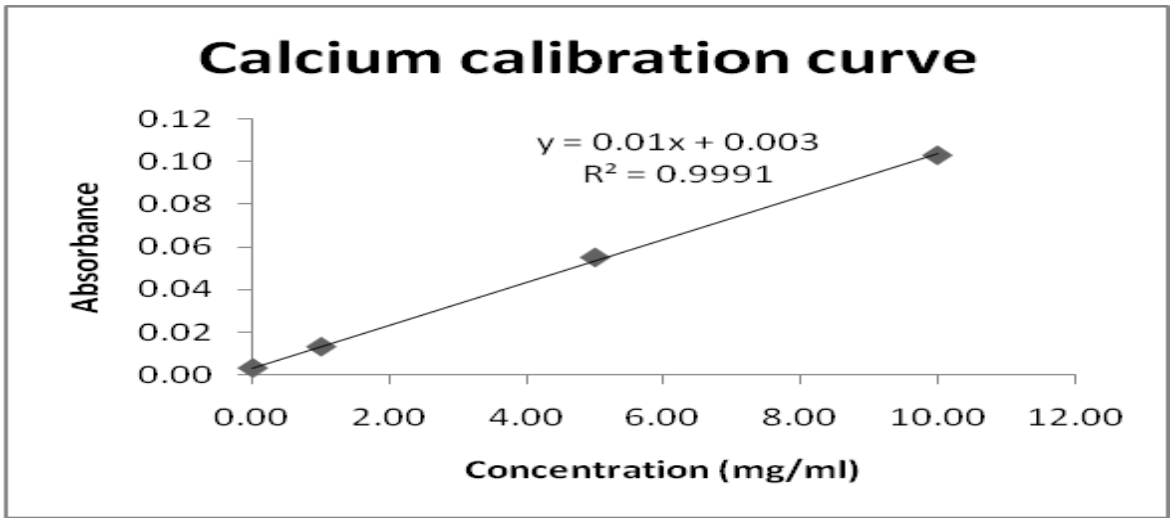
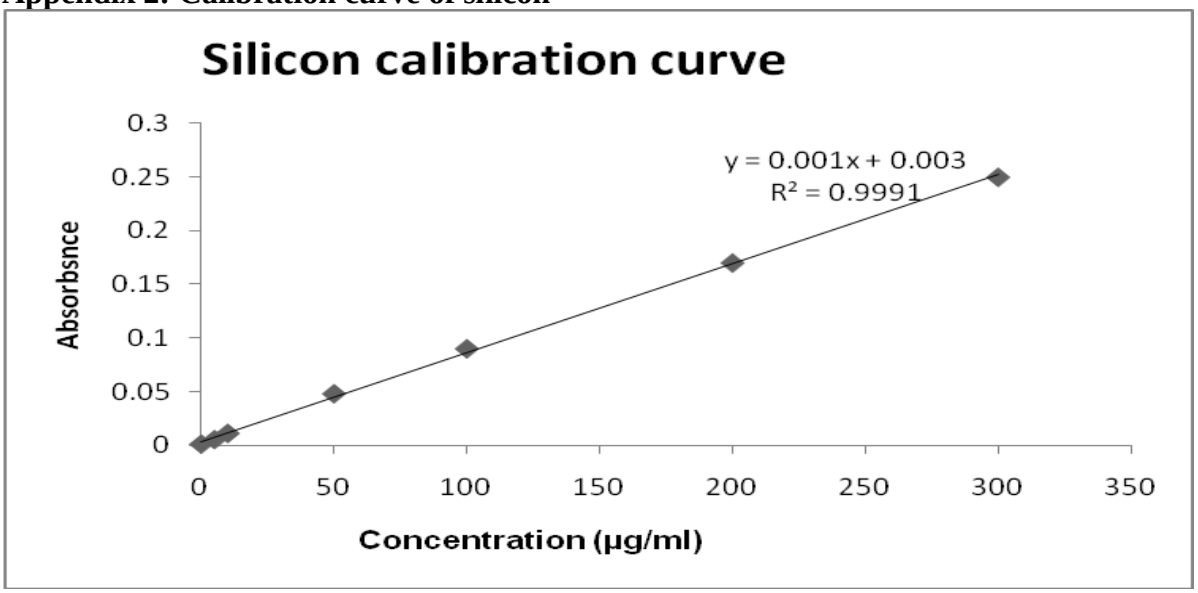
APPENDICES

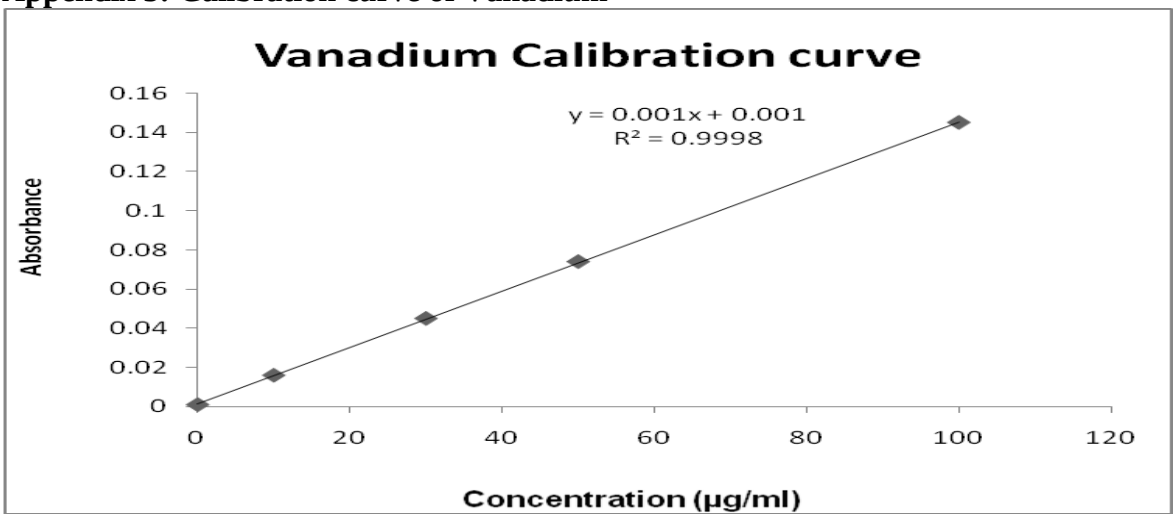
Appendix 1: Calibration curve of calcium



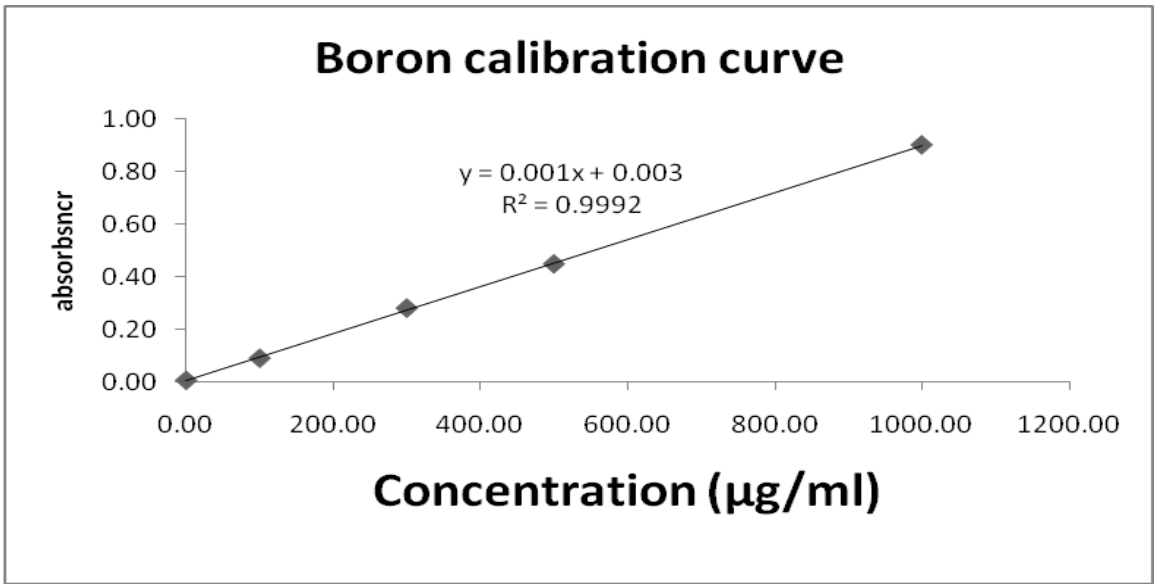
Appendix 2: Calibration curve of silicon



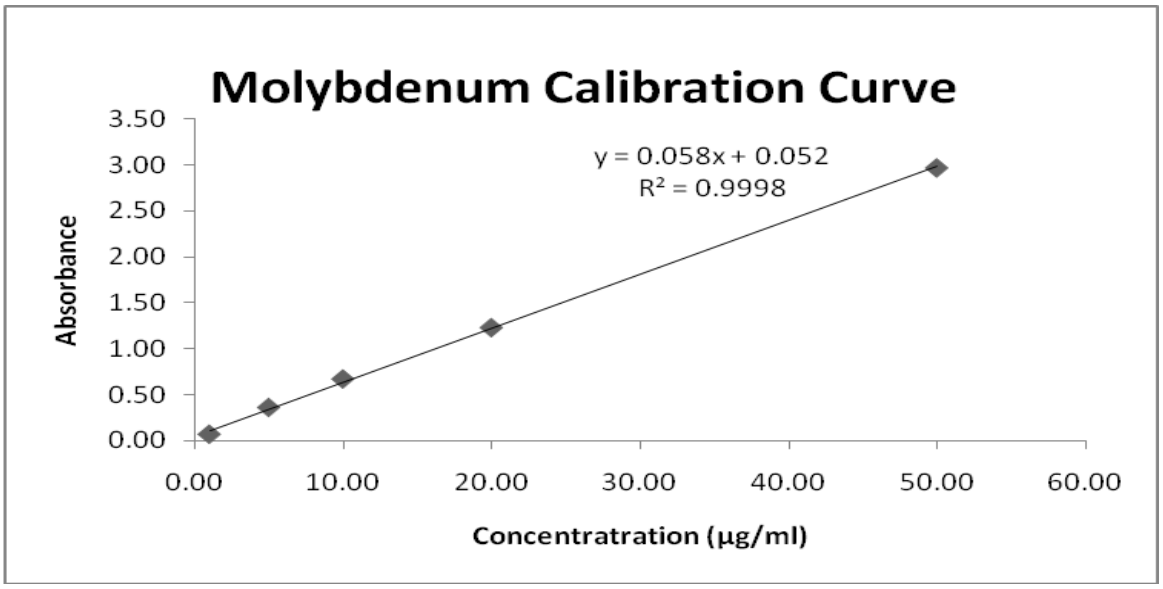
Appendix 3: Calibration curve of Vanadium



Appendix 4: Calibration curve of boron



Appendix 5: Calibration curve of molybdenum



Appendix 6: Calibration curve of chromium