Estimation of elemental concentrations of Ethiopia Coffee Arabica on different coffee bean Varieties (Subspecies) Using Energy Dispersive X-ray Florescence

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Abstract: Using Energy Dispersive X-ray Florescence (EDXRF) Elemental analysis, Coffee cherry of Arabica subspecies produced in crop years of 2015/2016 in nine different parts of coffee growing Area in Ethiopa were analyzed and has been found four major elements P, K, Ca, S and eight minor elements Mn, Fe, Cu, Zn, Se, Sr, Rb, Br from Twenty coffee Arabica subspecies. The Samples were washed; dried; Grinding with mortar and finally pelletized. EDXRF analysis were carried the energies of the X-rays emitted by the sample are measured using a Si-semiconductor detector and are processed by a pulse height analyzer. Computer analysis of this data yields an energy spectrum which defines the elemental composition of the sample. The system detection calibration and accuracy check was performed through different countries reported values and analysis of NIST certified reference materials SRM 1515 (Apple leaves). Most of coffee beans sample were found to be a good agreements towards NIST standards and different countries reported values. Meanwhile discussed the elemental concentration and their biological effects on human physiology.

Keywords: Coffee Cherry, Subspecies coffee, Elemental Concentration and EDXRF

1. INTRODUCTION

According to International Organization for Standardization (ISO) definition of coffee is: The fruits and seeds of plants of the genus “Coffea” usually of the cultivated species, and the products from these fruits and seeds, in different stages of processing and use intended for human consumption. [1]. the fruits of coffee are often called cherries, once the cherries have been harvested, coffee processing begins. The cherries are pulped (the seed is removed from the fruit), the mucilage is removed and the seeds are dried finally ready for roasting, it is called raw coffee or gold coffee [2] Nowadays, Coffee is one of the most important agricultural products in the international business next to petroleum the major species of commerce are known as Arabica and Robustas. Coffee Arabica predicted to be originated in the mountain forests of Ethiopia and then domesticated by Arabians to Yemen, once of the varieties named as Bourbon. From Yemen, Arabica seeds were spread globally through the colonization. [3, 4]

Coffee is the single most important crop in the Ethiopian economy as it contributes over 60% of the national foreign exchange earnings, 30% of government direct revenue, and Subsistence earnings of about 25% of the population (Institution of Agriculture research, 1983) [5]. There are several subspecies of coffee Arabica in different parts of Ethiopia some of them are (74148, Forest in Metu), (F-59,7454,Gesha, yellow in Tepi),(K-2, K-1, Gesha, Catinol in Bebeka),(74165, 7410 in Limu),(741, 7576, Abbaa Buunaa in Jimma),(Welisho, Deega, Kurmee in Yirgachefee),(Derasicho, Sidancho in Sidama),(Abadir, shumburee, Masala in Harare),(Mana Sibuu, 7576 in Welega), these all subspecies name given by the local farmer, agricultural research center and some of them internationally known like Gesha. In general, all Ethiopian coffee cultivation systems appear to be under the same system of cultivation techniques. However, the major conventional production systems include: i) forest

coffee (10%); ii) semi-forest coffee (35%); iii) garden coffee (50%); and iV), plantation coffee (5%) [6]

Nowadays, many people are interested in healthy food. The analysis of individual components of raw and processed products is necessary in the food industry mainly to control the food safety [7]. To guarantee quality and safety of a final coffee product and protect well-being and health of consumers, different parameters responsible for the wholesomeness of green coffee beans, have to be measured using suitable analytical methods. [8]. Although there is less information is available on the levels of major and trace element contents of Ethiopian coffee beans of different subspecies. but in the literature, a number of studies with different analytical techniques have been carried out to determine the level of minerals (major, minor and toxic metals) in green and roasted coffee types in different parts of the world (such as Brazil, Nigeria, India, etc.) [9] Using different analytical techniques like flame atomic absorption spectrometry (FAAS) [10], inductively coupled plasma optical emission spectrometry (ICP OES) [11] and neutron activation analysis [12].

In the present investigation EDXRF methods has been employed for the estimation of major and minor elemental constituents of Ethiopian subspecies green coffee beans. Energy Dispersive X-Ray Fluorescence apparatus can be used for a tremendous variety of elemental analysis applications, because almost every element from Na to Pu in the periodic table can be measured, in concentrations ranging from a few ppm to nearly 100 percent. EDXRF provides has the following Advantage as follow Multi-elemental, non-destructive, minimal sample preparation, shorter analysis time, high sensitivity for many elements, good accuracy and precision, automation possible, new large irradiation facility required. This study might be a good indicator of the Ethiopian Coffee authenticity meanwhile it could bring the useful information about individual elemental patterns that are distinctive to the origin of growing soils for coffee plants in addition to cultivation and environmental conditions used

2. MATERIALS AND EXPERMENTAL METHODS

2.1. Sampling and preparation

The green coffee seed (coffee cherry) samples and its soil samples were collected from different parts of The green coffee seed (coffee cherry) samples and its soil samples were collected from different parts of Ethiopia. The green coffee seed were obtained (harvested) from each subspecies trees and besides the soil samples was taken from nearby from each subspecies coffee trees. The analysis was conducted on 20 coffee cherry subspecies and 9 soil samples which available in different parts of Ethiopia such as Eastern, Southern and South West. Specifically were collected from nine sampling sites. (Chiro, Aleta wendo, Yirgachefe, Limu, Godere Mexi, Bebeka, Haru Gimbi, Metu and Agaro coffee bean).

Chiro (Harare coffee) is a town and separate woreda (district) in eastern Ethiopia. Located in the Amhar Mountains, it has a latitude and longitude of 9°05′N 40°52′E and an Altitude of 1500 – 2800 meter above sea level. It is the administrative center of the West Hararghe Zone 318 km from addis abeba. The weather condition of this area are, average rain fall 900ml – 1800ml and temperature 27.5 ℃ – 39℃. The soil types are black 32%, red 25.5% and loamy 42.5%. The coffee subspecies has been found in Chiro are Abadir, Buunna buracha and buunna shumbre. [13]

Godere (Tepi coffee) is one of the woredas(districts) in the Gambela Region of Ethiopia. Part of the Mezhenger Zone, Godere is bordered on the south and east by the Southern Nations, Nationalities and Peoples Region (SNNPR), and on the west by Mengesh. The largest town in Godere is Meti. The latitude and longitude 7° 20′ 0″ N, 35° 10′ 0″ E and the average elevations 500 to 1000 meter over 40 % of the area is covered by forest. The available coffee subspecies are F-59, 7454, Gesha, yellow and so on.[14]

Aleta Wondo(Sidamo coffee) is in the SNNP Region, Sidama Zone, Aleta Wondo Woreda. 300 miles (338km) south of Addis Ababa There are three distinct agro-ecological zones; 12 % of the Woreda is classified as Dega (highlands), 71 % as Woinadega (midlands), and 17 % dry Kolla (lowlands) situated about 7000 feet

above sea level. Located in a fertile and forested area near Lake Abaya, not far from the sources of the Ganale Dorya and Dawa Rivers this town has a longitude and latitude of 6°36′N 38°25′E with an elevation of 2037 meters above sea level. The annual rainfall 1400ml, the temperature min to max 10, 18, 23℃ and its altitude 1858m, 1942m, 2026m. The coffee subspecies has been found Miqe, Logomma, dobancho, Sidancho and Derasicho. however I was collected only sidancho and Derasicho from weto kebele.[15]

Yirgachefe (Yirgachefe coffee) is a town in central southern Ethiopia in Yirgachefe District. Located in the Gedeo Zone of the Southern Nations, Nationalities and Peoples' Region, this town has an elevation between 1,880 and 1,919 meters (6,168 and 6,296 ft) above sea level. It is the administrative center of Yirgachefe woreda (or district), an important coffee growing area latitude and longitude 6° 10′ 0″ N, 38° 12′ 0″ E distance from addis abeba 409.2 km. There are two distinct agro – ecological zones: 8% Dega (highland) and 92% Woinadega (midlands) the annual rainfall 1500ml – 1700ml and its temperature 16 – 28℃ the coffee subspecies has been found Kurumee, Deega and Welisho.[16]

Haru,Gimbi (Wellega coffee) is one of the 180 woredas in the Oromia Region of Ethiopia. Part of the west Welega Zone, Haru is bordered on the south by Nole Kaba, on the southwest by Dale Lalo, on the west by Yubdo, on the north by Gimbi, on the east by an exclave of the Benishangul-Gumuz Region, and on the southeast by the Illubabor Zone. Coffee is an important cash crop of this woreda. Over 50 square kilometers are planted with this crop. The annual rainfall 1700ml, temperature min 12 and max 27 and the altitude 1950m. there are three distinct agro – ecological zones: Dega 849.46 hectare, Woinadega 469,894.6 hectar and desert 80,970.54 hectare. The soil type is loamy. The coffee subspecies has been grown sende, mana sibu, chala, Haru 1 and 75227 but I had collected Mana sibu and 75227 from were baro kebele.[17]

Metu (Illubabor coffee) is a market town and separate woreda in south-western Ethiopia. Located in the Illubabor Zone of the Oromia Region (or kilil) along the Sor River, this town has a latitude and longitude of 8°18′N 35°35′E and an altitude of 1605 meters. Metu has been an important market of the coffee trade, with several foreigners residing in the town as early as the 1930s to buy the crops from local farmers. Distance from Addis abeba to Metu 541.5 Km. the annual rainfall 1800ml, temperature 20℃ and altitude 1600m – 1710m and its soil type loamy. There are two distinct agro – ecological zones; 17% kola (lowland) and 83% Woinadega (midlands).the coffee subspecies has been grown 74148 and forest.[18]

Mizan Tefere (Bebeka coffee) is a town in southern Ethiopia. The largest town, and the administrative center, of the Bench Maji Zone of the Southern Nations, Nationalities, and Peoples Region (SNNPR), and located about 160 kilometers southwest of Jimma, Mizan Tefere has a latitude and longitude of 7°0′N 35°35′E . distance from addis ababa to Mizan Teferi 564.8 km Altitude 950 – 1120 meter, average temperature 32 ℃ and annual rainfall 1700 mm Some subspecies of coffee are Catinol , K-1, K-2 and Gesha but I had got K- 2.[19]

Limu Kosa(Limu coffee) is one of the woredas in the Oromia Region of Ethiopia Part of the Jimma Zone, The altitude of this woreda ranges from 1200 to 3020 meters above sea level. Latitude: 8° 09' 60.00" N Longitude**:** 37° 09' 60.00" E 426 kilometers south west of Addis Ababa. Average max temp 28℃ – min 12℃, and annual rain fall 1500ml – 1800ml .the coffee

subspecies has been grown 7410, 74165, F – 59, 75227,74148 and 6510.[20]

Agaro (Jimma coffee) is a town and separate woreda in south-western Ethiopia. Located in the Jimma Zone of the Oromia Region, it sits at a latitude and longitude of 7°51′N 36°35′E, and an elevation of 1560 meters above sea level. The annual rainfall 1400ml – 1650ml, temperature max 28.9℃ – min 13.4℃ and altitude 1400m – 2700m. the coffee subspecies has been grown 7576, Meleko, F – 59, Abaa bunna and 741.[21]

First of all In a laboratory the collected coffee subspecies were removed the outer layers of coffee cherry (Pulp, Skin and Mucilage) and the soil samples were cleaned from stones, a piece of roots and sediments by using stainless steel forceps and next the removed outer layer (green coffee beans) can be washed with tap water and followed by de-ionized water to decrease contamination. Later both samples can be dried in ovens at temperatures within 60–103 °C in order to avoid water contents. Finally both samples were powdered; homogenized using a mortar and pestle and 200mg of each powdered sample weighed and compressed using a 150 ton hydraulic press for coffee beans buts 100 ton for soil and both made into pellets of 13mm diameter and 1- 2mm thickness. Triplicates of each sample were done.

3. EXPERIMENTAL METHODS

3.1 Energy Dispersive X-ray Fluorescence

EDXRF spectrometry is well recognized as a tool for the qualitative and quantitative determination of major and minor elements in a wide range of sample types.

A typical spectrometer uses an X-ray tube to bombard the sample which was positioned at angle of 450 to the beam direction with X-rays of sufficient energy to knock out the inner shell electrons of the sample atoms. Electrons from outer shells then drop down into the vacant inner-shell positions, and characteristic X-rays are given off. This is known as X-ray fluorescence (XRF). In the energy-dispersive technique (EDXRF), the characteristic energies of the X-rays emitted by the sample are measured using a high resolution Si-semiconductor detector which has a sensitive area of 30 sq mm thickness and are processed by a pulse height analyzer. Computer analysis of this data yields an energy spectrum which defines the elemental composition of the sample. Essentially, the energy of the peak gives the element identification, and the number of X-rays counted in the peak gives the amount of the element present in the sample. This quantitative analysis is carried out by using the software nEXT.

3.2 Operational Parameters

These elemental analysis of green coffee bean and soils samples was carried out at trace element laboratory UGC-DAE Consortium for Scientific Research, Kolkata Centre by using a Xenemetrix (erstwhile Jordan Valley) EX 3600 EDXRF spectrometer which consists of an X-ray tube with a Rh anode as the source of x-ray with a 50V, 1mA power supply, Si (Li) detector with a resolution of 143 ev at 5.9 kev and 10 sample pellets analyzing at a time. The quantitative analysis is carried out by the in- built software nEXT.

Parameters	e_1	e_2	e_3
Voltage (kv)	6	14	23
Current (mA)	200	900	200
Time (sec)	200	300	600
Atmosphere	Vacuum	Vacuum	Vacuum
Energy range (kev)	10	10	40
Through put	Low	Low	Low
Filter	none	Titanium	iron

Table 1. The working operational parameter of EX 3600 EDXRF spectrometer (for coffee samples)

Parameters	e_1	e_2	e_3
Voltage (kv)	6	14	37
Current (mA)	100	800	41
Time (sec)	200	400	300
Atmosphere	Vacuum	Vacuum	Vacuum
Energy range (kev)	10	10	40
Through put	Low	Low	Low
Filter	none	Titanium	iron

Table 2. The working operational parameter of EX 3600 EDXRF spectrometer (for soil samples)

Where e_1, e_2 , e_3 is spectrum 1, 2, 3

4. DATA AND DATA ANALYSIS

Minerals are inorganic substances, present in all body tissues and fluids, and their presence is necessary for the maintenance of certain physicochemical processes which are essential to life. Although minerals yield no energy, they have important roles to play in many biological activities in the body [22, 23]. Minerals are involved in metabolic, enzymatic and biochemical reactions needed for feed efficiency, growth and reproduction. Human body requires certain essential elements in limited quantities and their absence or excess may result in severe malfunctioning of the body and even death in extreme cases because these essential trace elements directly influence the metabolic and physiologic processes of the organism. Poor nutrition can lead to reduced immunity, augmented vulnerability to various oral and systemic diseases, impaired physical and mental growth, and reduced efficiency. [24, 25]

Similarly Chemical composition of coffee, namely the presence of essential, non-essential, and toxic elements, has to be known because of its habitual consumption. These elements have to be kept under control in terms of its safety and to assist its quality, nutritional value, and certain sensorial properties (P. Pohl, 2013)[8, 26]. Coffee contains various elements such as Na, B, Mg, Fe, Ca, and K. These elements have various effects on human health. In present study the outcomes of energy dispersive x-ray florescence (EDXRF) measurements for the determination of the concentration of major and minor essential elements in subspecies of coffee beans are presented in table below. In this study were twelve different elements determine namely P, S, K, Ca, Mn, Fe, Cu, Zn, Se, Br, Rb and Sr. four of these elements are major minerals included P, S, K, Ca and the reset eight elements are micro – minerals they are important in human metabolisms and essential for the growth of living organisms.

The concentrations of twelve different elements (P, S, K, Ca, Mn, Fe, Cu, Zn, Se, Br, Rb and Sr) in green coffee beans subspecies were showed in Table 1. The level of potassium (K) elemental concentration appears to be highest value was 15645.9 µg/g(ppm), followed by Ca, P, S, Fe, Rb, Mn, Cu, Sr, Zn, Br and Se with concentrations of 2288.8, 1535.9, 1317.3, 211.7, 67.94, 54.5, 18.4, 9.39, 6.0, 4.68 and 0.8 µg/g(ppm).

Phosphorus:

Phosphorus content was ranged between 599.6 – 1535.9 µg/g(ppm). The highest amount was found in subspecies 7576 and followed Abaa buunaa about 1535.9 and 1482.5 µg/g(ppm) collected from Agaro. The lowest amounts was found in yallow and 7454 about 680.99 and 599.6 µg/g(ppm) Collected Godere Mexi. The amounts of standards were recorded above the present value NIST Standard 1500 ppm.

Phosphorus is one of the most essential minerals as it ranks second only to calcium in total body content. It is found in every cell in the body and is also part of our DNA and RNA that are the building blocks of life and growth. However, phosphorus participates in many other body functions including energy metabolism, DNA synthesis, and calcium absorption and utilization. Phosphorus is plentiful in most foods, but main sources include milk, cheese, and meat. Adults need 700 milligrams of phosphorus a day. If Phosphorus levels that are too high or too low can cause medical complications, such as heart disease, joint pain, or fatigue. [27, 28]

Sulfur:

The concentration of Sulfur was ranged between 880.0 – 1317.3 µg/g(ppm). The highest amount was found in subspecies K – 2 and followed Abaa buunaa about 1317.3 and 1304 µg/g(ppm) collected from Bebeka coffee farm and Agaro respectively. The lowest amounts was found in forest coffee and yallow about 1026.3 and 880.0 µg/g(ppm) Collected from Metu and Godere Mexi. The amounts of standards were recorded above the present value NIST Standard 1800 ppm.

Ranking number four in mineral abundance in the body is sulfur. It is a component of amino acids as part of thus sulfur containing amino acids; it performs a number of important functions, such as providing a place these amino acids to bond together, solidifying a protein structure. It is found in high concentrations in the protein structure of the joints, hair, nails, and skin. In the case of arthritis, cartilage can be repaired by adequate sulfur intake through supplementation.

The hormone insulin is a protein based hormone rich in sulfur-containing amino acids. Although there is no official recommended intake for sulfur, it is a critical nutrient. Daily intake is usually 800-to-900 mg of sulfur per day. Certain health conditions, such as arthritis and liver disorders, may be improved by increasing the intake of sulfur to 1500 mg per day in supplemental form. Sulfur rich foods include eggs, legumes, whole grains, garlic, onions, Brussels sprouts, and cabbage will provide an adequate amount of sulfate. [27]

Potassium:

The present study potassium were the richer elements than any other elements. Its amount was ranged 10176.3 – 15645.9 µg/g(ppm). The maximum amounts of potassium were detected in coffee subspecies 74165, 741… the value were recorded 15645.9 ppm in Limu and 14796.4 in Agaro respectively while the minimum amounts were recorded 10176.3 ppm, 11022.6 ppm in subspecies yellow and 7454 coffee beans both are in Godere (Tepi coffee).the present value has fairly agree with different country earlier reported value 13836.98 – 15092.21 ppm [29] and 13500 – 17120 ppm [30]. The amounts of standards were recorded slightly above the present value NIST Standard 16100 ppm. The concentration of potassium were found in agricultural soils of the study area are 14073.87 ± 339.09 ppm (Agaro), 8861.62 ± 318.6 ppm (Limu) and 7028.93 ± 430.58 ppm (Godere).

The third most abundant mineral in the body is potassium. Potassium is an electrolyte, a chemical that dissolves in water and turns into charged particles called ions. These circulate in the blood, in and out of the fluid of the cells, and help with proper nerve and muscle functions. The beating of the heart is based on impulses that require electrolytes. Potassium is plentiful in all living plant and animal cells, but fresh fruits and vegetables are the richest sources of potassium. Broccoli, carrots, strawberries, bananas, and artichokes are excellent sources of potassium. Adults require 4700 milligrams of potassium each day. [27]

Calcium:

Calcium is the second most ranking elements in this study its amount was ranged between 1588.7 – 2288.8 µg/g(ppm). The maximum amounts of calcium were detected with similar to potassium i.e. in coffee subspecies 74165, 741… the value were recorded 2288.8 ppm in Limu and 2268.3 in Agaro respectively while the minimum amounts were recorded 1588.7 ppm, and 1722.4 ppm in subspecies yellow and 7454 coffee beans both are in Godere (Tepi coffee).the present value has higher than with different country earlier reported value 741.51 – 793.23 ppm [29] and 760 - 1200 ppm [30]. The amounts of standards were recorded much higher than the present value NIST Standard 15260 ppm. The concentration of Calcium were found in agricultural soils of the study area are 10406.3 ± 512.75 ppm (Agaro), 8473.35 ± 577.44 ppm (Limu) and 3208.89 ± 55.76 ppm (Godere)

Calcium is the body's most abundant mineral about 2% of body weight is calcium in bones and teeth. A little is scattered in soft tissue like muscles and organs. It is important for optimal bone health throughout your life. Your body needs calcium to build and maintain strong bones. Your heart, muscles and nerves also need calcium to function properly. If you don't get enough calcium, you could face health problems related to weak bones and muscles:

Although diet is the best way to get calcium, calcium supplements may be an option if your diet falls short. Most calcium comes from dairy foods like milk, cheese, and yogurt. While those who don't like dairy products can get calcium from bokchoy, broccoli, kale, and spinach. The amount of Ca is required to our body depending on age and sex. In general Adult has required a minimum of 1000 mg/day of Ca.

Excessively high levels of calcium in the blood known as hypercalcemia can cause renal insufficiency, vascular and soft tissue calcification, hypercalciuria (high levels of calcium in the urine) and kidney stones. High calcium intake can cause constipation. It might also interfere with the absorption of iron and zinc, though this effect is not well established. [27, 31]

Manganese:

The concentration of Manganese was found highest in coffee subspecies K – 2 (54.5 ppm) from Bebeka and Gesha (28.1 ppm) from Godere. While the lowest was found in subspecies 74165 (15.2 ppm) from Limu and yellow (14.6 ppm) from Godere. When we compare the present experimental value with different country earlier reported value in this case slightly higher than reported value 9.96 – 18.05 ppm [29] and fairly agrees with this range 11 - 98 ppm [30]. The amounts of NIST standards 54 ppm were fairly agree with K – 2 Subspecies. The concentration of Manganese were found in agricultural soils of the study area are 8468.45 ± 69.74 ppm (Bebeka), 2206.84 ± 92.77 ppm (Godere), and 6143.79 ± 134.64 ppm (Limu)

Manganese is a trace mineral that is vital to life. The human body contains about 15 to 20 milligrams of it. Most of it is found in the bones, with the rest distributed throughout the body in tissues like the pancreas, kidneys, liver, adrenal glands and pituitary glands. Manganese is an essential nutrient in many ways. Its key role is in the activation of enzymes that are needed for the digestion and utilization of foods and nutrients. It also plays a role in reproduction and bone growth. It is sometimes called the 'brain' mineral, as it is important to mental function. Manganese deficiency is very rare and hard to determine. However there is no specific RDA for manganese, it is estimated that most people require between 2-to-5 mg per day. The most common cause of low manganese is poor dietary intake, either due to a diet lacking in manganese food sources, or because of intestinal tract disorders that hinder the absorption of nutrients from food. Although. This can easily be met by regularly

consuming nuts, Whole grains, leafy vegetables, and tea as these are the best sources of manganese. [27]

Iron:

The highest concentration of iron has found in K -2, Degaa, Forest coffee bean subspecies… and the values in ppm are 211.7 from Bebeka , 152.8 from Yirgachefe and 134.4 from Metu forest coffee respectively in decreasing order. Whereas the lowest concentration has found in subspecies Sidancho and Yellow coffee beans sample and its recorded values are 74.5 ppm from Aleta wendo and 67.95 ppm from Godere. This results has higher than reported values 40.72 – 44.47 ppm [29] and slightly agree with other reported values 21 – 105 ppm [30]. The amounts of NIST standards 83 ppm were good agreements with Kurmee Subspecies from Yirgachefe. The concentration of Iron were found in agricultural soils of the study area are 126823 ± 829.93 (Bebeka), 129695.3 ± 2706.839 (Yirgachefe), 129278.2 ± 1945.89 (Metu), 115624.6 ± 2937.15 (Aleta wendo) and 132942.2 ± 4519.05 (Godere).

Iron is critical to human life. It plays the central role in the hemoglobin molecule of our red blood cells (RBC), where it functions in transporting oxygen from the lungs to the body's tissues, and also transports carbon dioxide from the tissues to the lungs. In addition, iron also functions in several key enzymes in energy production and metabolism including DNA synthesis.

Iron is a mineral that is naturally present in many foods such as red meat, Beef liver, Cereal, soybean, white beans and flour products, seafood, sunflower seeds and so on, and it's added to some food products, and available as a dietary supplement. Most of the 3 to 4 grams of elemental iron in adults is in hemoglobin which is the compound that transmits oxygen in the blood to the cells. Much of the remaining iron is stored in the form of ferritin or hemosiderin (a degradation product of ferritin) in the liver, spleen, and bone marrow or is located in myoglobin in muscle tissue. Humans typically lose only small amounts of iron in urine, feces, the gastrointestinal tract, and skin. Losses are greater in menstruating women because of blood loss. If an excess amount of iron can cause to the human body such as it causes the enzyme to malfunction, it also causes inflammation. Iron attracts oxygen and when in excess, the free radical oxygen damages the surrounding body tissue. In addition, as a carrier for oxygen, iron promotes bacterial growth by feeding it oxygen, leading to chronic infections [27, 32]

Copper:

In this study the amounts of copper was ranged between 9.9 – 18.4 µg/g (ppm). The maximum amounts of copper were detected in coffee subspecies K - 2, Abadir, Mana Sibu and 7576 value were recorded 18.4 ppm in Bebeka and the rest three of them similar value 17.1 ppm in Chiro, Haru and Agaro respectively while the minimum amounts were recorded 11.8 ppm, and 9.9 ppm in subspecies yellow and 7454 coffee beans both are in Godere (Tepi coffee).the present value has a good agreement with different country earlier reported value 16.69 – 18.05 ppm [29] and fairly agree 5 – 23 ppm [30]. The amounts of NIST standard value 5.6 ppm were smaller than the present value. The concentration of copper were found in agricultural soils of the study area are

47.58 ± 6.49 (Bebeka), 126.7 ± 6.46 (Chiro), 82.55 ± 6.64 (Haru), 45.98 ± 8.99 (Agaro), and 84.96 ± 7.13 (Godere).

Copper is a trace element also essential for the human body to function properly. Copper is present in all body tissues and plays a role in the formation of connective tissue, and in the normal functioning of muscles and the immune and nervous systems.

The human body requires copper for normal growth and health. Copper, along with iron, is a critical component in the formation of red blood cells. Copper also influences the functioning of the heart and arteries, helps prevent bone defects such as osteoporosis and osteoarthritis, and promotes healthy connective tissues (hair, skin, nails, tendons, ligaments and blood vessels). (Source: Dr. Andrew Weil, Internet)

Copper deficiency is characterized by anemia, fatigue, poor wound healing, chronic diarrhea, elevated cholesterol levels, and poor immune function. Signs of deficiency include bleeding under the skin, damaged blood vessels, hair loss, pale skin, and an enlarged heart. Symptoms include fatigue and, because copper plays a role in immunity, imbalances can make you more susceptible to infections.

Good food sources include vegetables, legumes, beans, nuts and seeds, mushrooms, shellfish, avocado and whole grains.

opper is toxic in large amounts, and acute poisoning can lead to nausea, vomiting, diarrhea and even kidney damage, anemia and death. The toxic amount for adults is 10000 micrograms. One should not take more than that amount daily. For younger people smaller amounts become toxic. [27]

Zinc:

Zinc content was ranged between 2.6 – 6.0 µg/g (ppm). The highest amount was found in subspecies Welisho and followed Kurmee about 6.0 and 5.6 µg/g (ppm) collected from Yirgachefee. The lowest amounts was found in subspecies 7576 from Agaro and 74165 from Limu with both are the same values about 2.6

µg/g(ppm). The present value has a good agreement with different country earlier reported value 5.71 – 6.23 ppm [29] and slightly below the reported value 5 – 32 ppm [30]. The amounts of NIST standards were recorded 12.5 ppm greater than the present results. The concentration of Zinc were found in agricultural soils of the study area are 208.33 ± 6.28 ppm (Yirgachefe), 244.21 ± 12.37 ppm (Agaro), and 132.52 ± 10.49 ppm (Limu)

Zinc is another mineral that must be absorbed in small amounts to keep humans healthy. The trace mineral zinc is essential for body growth, maturation and development, as well as tissue repair and resistance to disease. Zinc is an important mineral for children and the elderly. It is involved in numerous aspects of cellular metabolism. It is required for the catalytic activity of approximately 100 enzymes and it plays a role in immune function, protein synthesis, wound healing, DNA synthesis, and cell division. Zinc also supports normal growth and development during pregnancy, childhood, and adolescence and is required for proper sense of taste and smell. A daily intake of zinc is required to maintain a steady state because the body has no specialized zinc storage system. Zinc is an essential mineral that is naturally present in some foods such as meats, specifically organ meats, poultry, and seafood. The body needs 15.0 milligrams of zinc per day.

Zinc deficiency is characterized by growth retardation, loss of appetite, and impaired immune function. In more severe cases, zinc deficiency causes hair loss, diarrhea, delayed sexual maturation, impotence, hypogonadism in males, and eye and skin lesions. Weight loss, delayed healing of wounds, taste abnormalities, and mental lethargy can also occur. Many of these symptoms are non-specific and often associated with other health conditions; therefore, a medical examination is necessary to ascertain whether a zinc deficiency is present.

Zinc toxicity can occur in both acute and chronic forms. Acute adverse effects of high zinc intake include nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches. One case report cited severe nausea and vomiting within 30 minutes of ingesting 4 g of zinc gluconate (570 mg elemental zinc). Intakes of 150–450 mg of zinc per day have been associated with such chronic effects as low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins. . [27][33]

Selenium (Se):

In this study Selenium were the lest amounts than any other elements. Its amount was ranged 0.12 – 0.8 µg/g (ppm). The maximum amounts of Selenium were detected in coffee subspecies Derasicho, Sidancho… the value were recorded 0.8 and 0.6 ppm in Aleta wendo (Sidama coffee) respectively while the minimum amounts were recorded 0.12 ppm in subspecies 7576 and 74148 coffee beans collected from Haru (welega coffee) and Metu respectively. I could not get earlier reported values of green coffee beans regarding to selenium elements. The amounts of NIST standards were recorded 0.05 ppm which is slightly below the present study value. The concentration of Selenium were found in agricultural soils of the study area are 2.82 ± 3.68 ppm (Aleta wendo), 4.93 ± 6.5 ppm (Haru), and 1.23 ± 1.41 ppm (Metu)

Selenium, as a component of the antioxidant enzyme glutathione peroxidase, works with vitamin E in preventing free radical damage to cell membranes. It also defends against oxidation and regulates the thyroid hormone. Low levels of selenium render people at higher risk for cancer; cardiovascular disease; inflammatory diseases, such as asthma; and other conditions associated with increased free radical damage, including premature aging and cataract formation. Selenium supplementation of 100-to-250 mcg or more per day is often used in the treatment of these disorders. Although there is no specific RDA for selenium, a daily intake of 200 mcg is often recommended. selenium is found in Whole grains, fish, meat, eggs, fruits, and vegetables grown in selenium-rich soil are the richest sources, However, be aware that daily intake in excess of 2,000 mcg can produce toxicity.[27]

Bromine (Br):

In the present study amount Bromine was ranged 0.0 – 4.68 µg/g (ppm). The maximum amounts of Bromine were detected in coffee subspecies Mana Sibbu, K - 2… the value were recorded 4.68 and 4.53 ppm in Haru (Welega coffee) and Bebeka respectively while the minimum amounts were recorded 0.0 ppm in subspecies 7410 and Derasicho coffee beans collected from Limu and Aleta wendo (Sidama coffee) respectively. I could not get earlier reported values of green coffee beans regarding to Bromine elements. The amounts of NIST standards were recorded 1.80 ppm which is a good agreement to the present study value.

Bromine is possibly important to basement membrane architecture and tissue development, as a needed catalyst to make collagen IV. Basement membranes (BMs) are specialized extracellular matrices that are key mediators of Signal transduction and mechanical support for epithelial cells. Intake of excessive bromide can induce a condition termed bromism, with neurological, psychiatric, dermatological, and possibly endocrine effects. [34, 35]

Rubidium (Rb):

The highest concentration of Rubidium has found in 74148 and 7576 coffee bean subspecies… and the values in ppm are 67.94 from Metu (Ilubabor coffee) and 53.5 from Haru (Welega coffee) respectively in decreasing order. Whereas the lowest concentration has found in subspecies Degaa and Abadir coffee beans sample and its recorded values are 6.69 ppm from Yirgachefee and 5.96 ppm from Chiro (Harare coffee).The amount of this results has a good agreement with earlier reported values 6.0 - 42 ppm [23]. The amounts of NIST standards 10.2 ppm were slightly agree with Welisho Subspecies 8.32 ppm from Yirgachefee. The concentration of Rubidium were found in agricultural soils of the study area are 0.0 ppm in Metu, 63.1 ± 0.78 ppm (Haru), 42.94 ± 3.08 ppm (Chiro) and 7.92 ± 0.97 ppm (Yirgacheffe)

Rubidium is found in animal tissue and it resembles potassium in its distribution and excretory pattern. Relatively high levels can be found in the soft tissue, while the skeletal tissue contains low level. Rubidium, like sodium and potassium, almost always has +1 oxidation state when dissolved in water, even in biological contexts. The human body tends to treat Rb^+ ions as if they were potassium ions, and therefore concentrates rubidium in the body's intracellular fluid (i.e., inside cells). The ions are not particularly toxic; a 70 kg person contains on average 0.36 g of rubidium, and an increase in this value by 50 to 100 times did not show negative effects in test persons. The biological half-life of rubidium in humans measures 31–46 days. [36][37]

Subspecies name	Sample code	P	S	K	Ca	Mn	Fe	Cu	Zn	Se	Br	Rb	Sr
74148 Metu	M74c	1422.4±220.6	1203.6±57.1	11825.7±675.1	1747.9±104.99	22.5±1.6	94.7±2.9	16.8±0.9	3.7±1.4	0.12±0	1.23±1.13	67.94±6.07	1.65±1.85
74165 Limu	L74C	1224.8±143.3	1193.7±56.5	15645.9±707.9	2288.8±66.7	15.2±2.0	126.7±3.3	14.3±0.9	2.6±2.4	0.13±0.01	0.6±0.65	45.1±0.8	1.78±2.58
741 Agaro	G74C	1330.6± 32.0	1292.3±18.2	14796.4±113.2	2268.3±67.1	27.3±1.5	113.9±1.2	13.3±1.1	3.2±1.0	0.46±0.6	2.72±0.6	17.1±0.84	4.24±0.57
Derassicho Aletawendo	ADCB	1383.3± 74.9	1159.4±6.5	14257.6±312.6	2212.9±47.4	25.6±0.8	78.0±1.9	12.3±0.5	3.4±0.6	0.8±0.7	0.0±0.0	17.66±2.35	5.52±0.64
K – 2 Bebeke	BK2	1374.2 ± 38.5	1317.3±22.6	14097.6±139.4	2236.6±44.3	54.5±1.0	211.7±1.6	18.4±0.9	4.9±1.1	0.57±0.4	4.53±0.14	18.1±1.24	4.67±2.13
Welisho Yirgacheffe	YWCB	1330.7 ± 29.96	1259.4±29.2	13784.5±72.8	2043.0±60.0	26.4±0.5	77.1±1.8	11.8±1.2	6.0±1.4	0.46±0.4	0.8±1.1	8.32±1.54	4.89±1.47
F – 59 Godere	TF59	1262.3 ± 87.7	1274.7±42.0	14578.6±521.5	2116.4±81.3	18.0±4.9	89.2±11.3	14.0±3.0	4.1±2.9	0.19±0.12	2.45±1.06	40.47±0.37	3.89±3.28
Sidancho Aletawend	ASIC	1324.4± 146.6	1152.9±22.9	14493.5± 400.4	2260.81±33.5	21.3±0.5	74.5±1.4	12.5±1.0	5.3±1.2	0.6±0.5	0.78±0.7	16.6±1.04	4.2±1.95
Mana Sibu Harru	HMSC	1335.6± 9.5	1271.5±35.3	11064.7±221.0	1811.5±74.1	25.8±1.6	101.0±2.3	17.1±1.0	4.6±0.4	0.3±0.05	4.68±0.64	46.85±5.13	4.49±1.43
Gesha Godere	TGC	1333.7± 48.99	1264.3±42.7	14349.6±372.4	2104.5±42.4	28.1±0.6	90.7±0.9	16.1±0.8	4.7±0.6	0.16±0.06	3.1±0.3	35.3±0.44	5.22±1.34
Kureme Yirgacheffe	YKC	1389.4± 24.04	1273.2±8.0	14148.9±139.9	2060.8±12.7	26.1±0.3	83.1±0.7	13.4±0.8	5.6±1.5	0.3±0.2	0.41±0.37	7.14±1.82	4.65±0.27
7410 Limmu	L740	1237.3± 127.8	1144.1±72.5	14631.0±1004.7	2188.8±186.2	15.5±1.1	116.3±3.8	12.1±1.2	3.1±1.3	0.38±0.2	0.0±0.0	37.28±1.72	2.5±2.6
Abadir Chiro	WHVC	1260.9± 49.6	1094.9±36.7	13066.6±427.1	2222.0±52.7	21.6±1.8	91.2±2.7	17.1±1.7	4.1±0.5	0.5±0.6	1.75±0.41	5.96±0.49	6.08±0.38
7576 Agaro	G75C	1535.9± 79.8	1229.5±58.9	14770.7±725.96	2227.99±125.6	26.0±1.2	100.4±3.3	17.1±0.9	2.6±1.2	0.4±0.4	1.31±1.85	29.68±0.8	2.9±3.3
Degaa Yirgacheffe	YDCB	1381.7± 66.6	1286.7±40.3	14092.8±411.98	2067.05±46.7	27.9±1.9	152.8±7.5	14.8±0.9	4.9±0.4	0.55±0.6	0.52±0.89	6.69±1.0	5.45±1.5
7576 Harru	H75C	1262.1± 28.5	1251.5±10.9	12447.2±217.4	2030.0±5.4	22.2±1.2	93.5±1.9	15.8±0.6	4.8±1.6	0.12±0.0	2.13±0.63	53.5±3.2	5.0±2.1
Abaa Buna Agaro	GABC	1482.5± 57.4	1304.3±49.0	14210.4±545.4	2231.3±83.3	25.4±1.0	92.8±4.1	12.9±0.8	3.9±0.8	0.123±0.0	0.55±0.96	26.07±1.68	6.79±1.06

Table 3. Average elemental concentration with (±) standard deviation in ppm of different Coffee Bean varieties (Sub - Species)

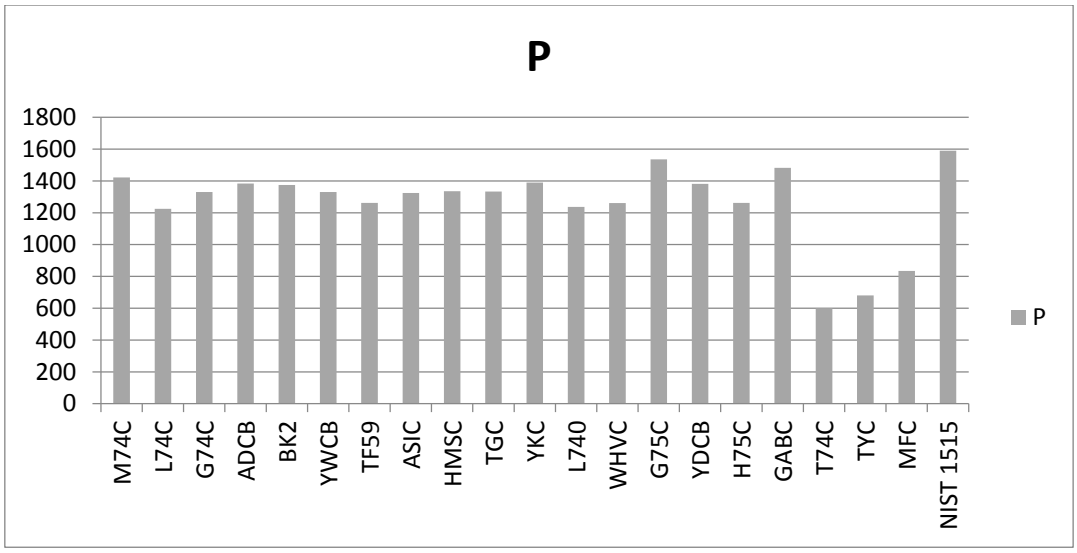

Figure 1. Elemental concentration of phosphorus in coffee subspecies of different parts of Ethiopia

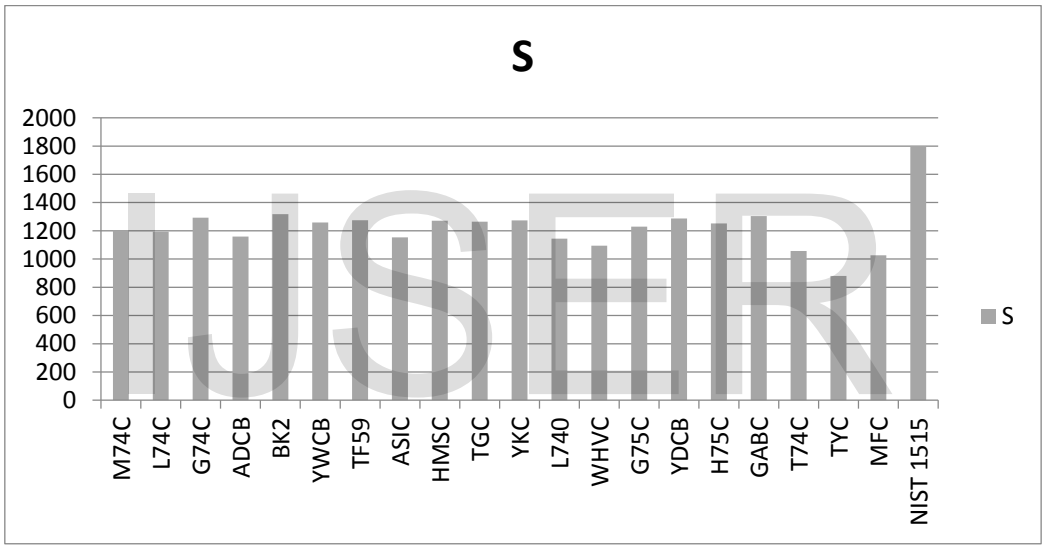

Figure 2. Elemental concentration of sulfur in coffee subspecies of different parts of Ethiopia

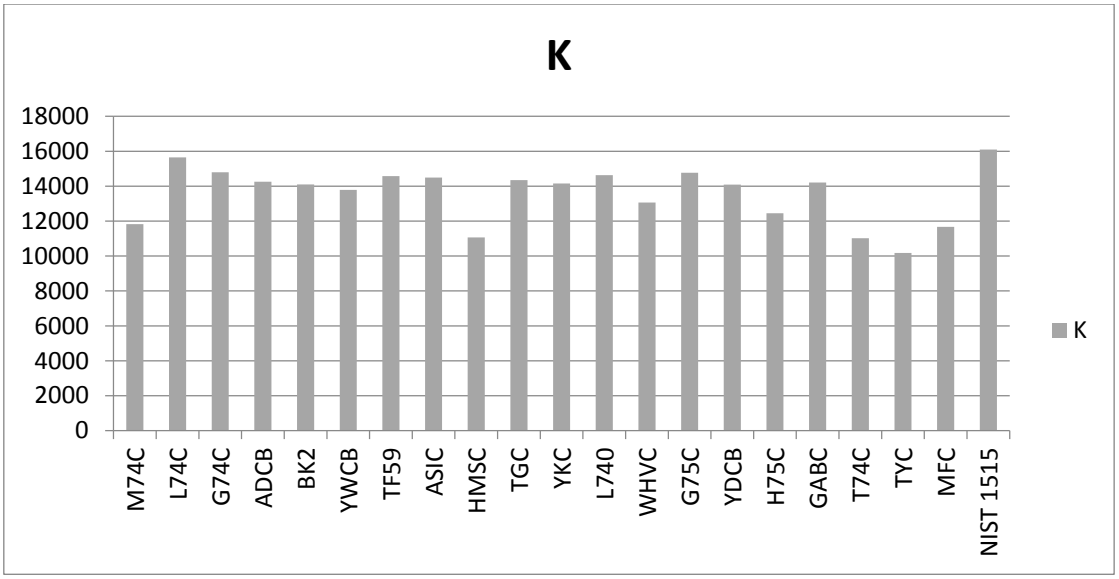

Figure 3. Elemental concentration of Potassium in coffee subspecies of different parts of Ethiopia

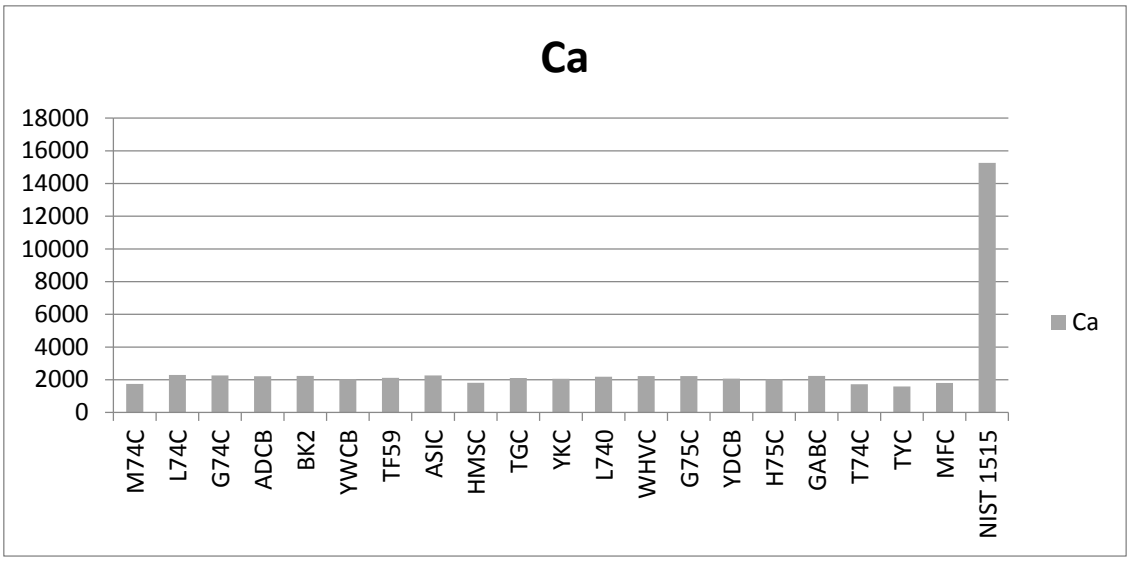

Figure 4. Elemental concentration of Calcium in coffee subspecies of different parts of Ethiopia

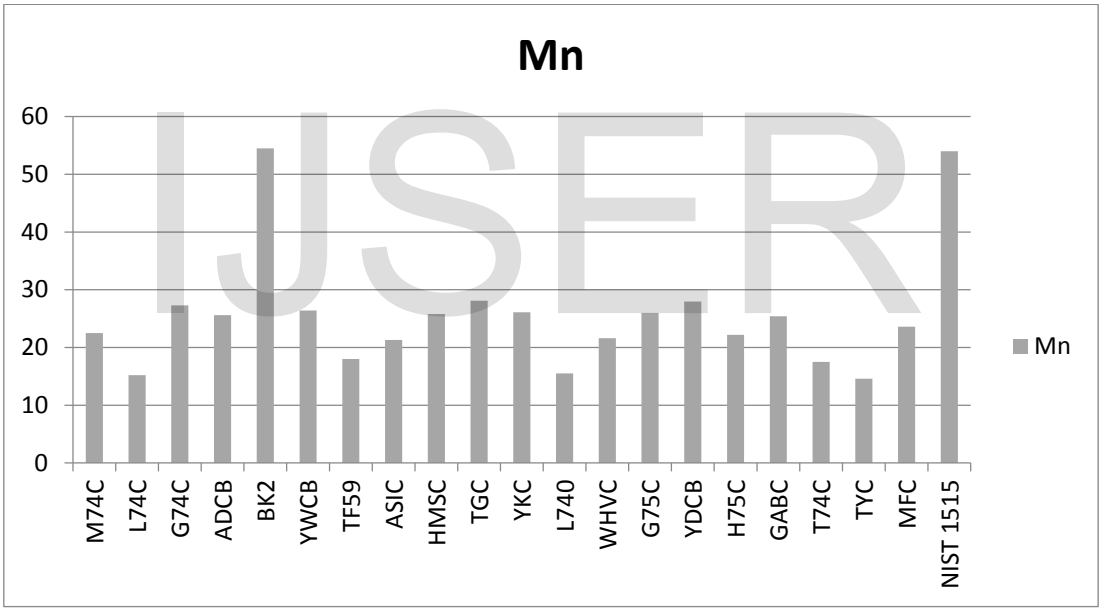

Figure 5. Elemental concentration of Manganese in coffee subspecies of different parts of Ethiopia

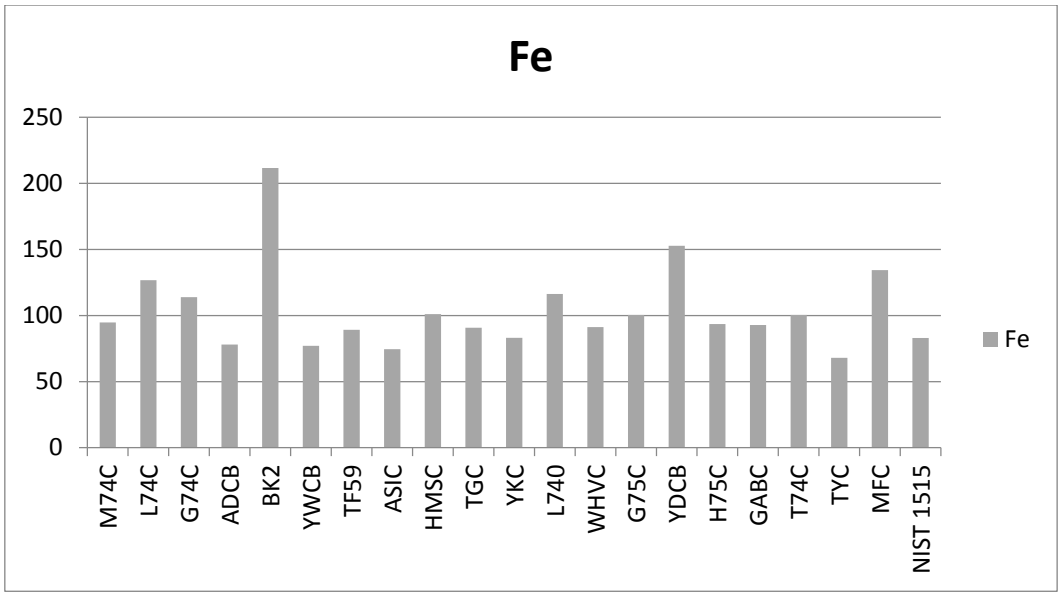

Figure 6. Elemental concentration of Iron in coffee subspecies of different parts of Ethiopia

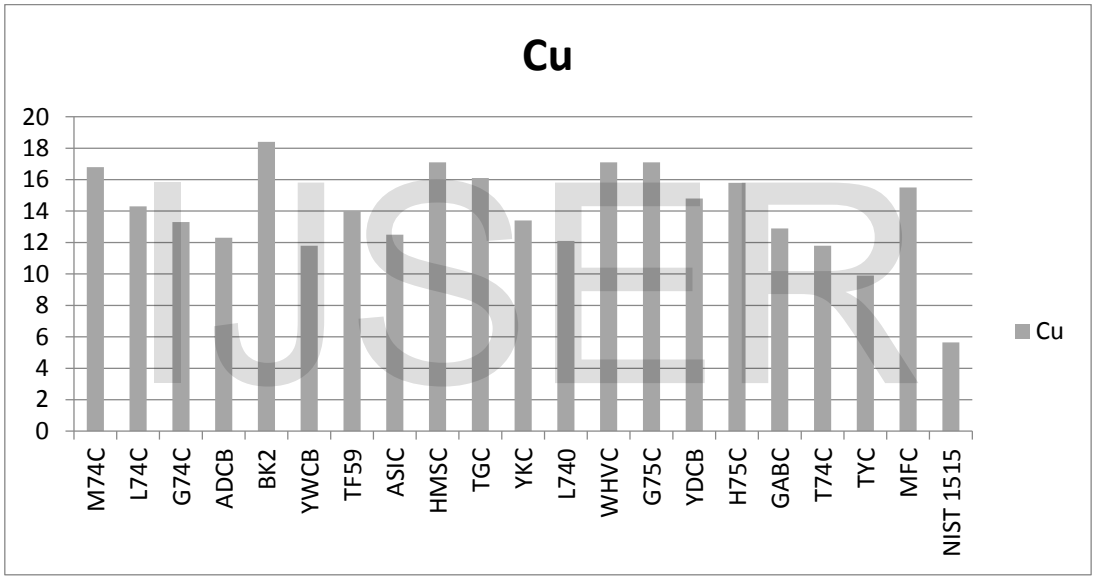

Figure 7. Elemental concentration of Copper in coffee subspecies of different parts of Ethiopia

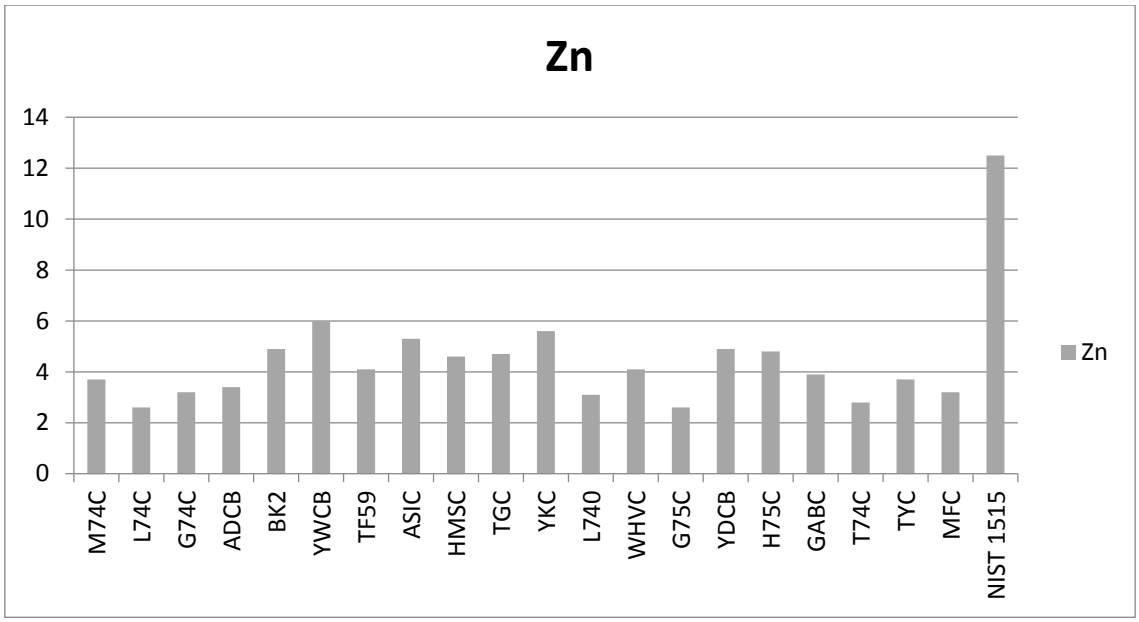

Figure 8. Elemental concentration of Zinc in coffee subspecies of different parts of Ethiopia

Figure 9. Elemental concentration of Selenium in coffee subspecies of different parts of Ethiopia

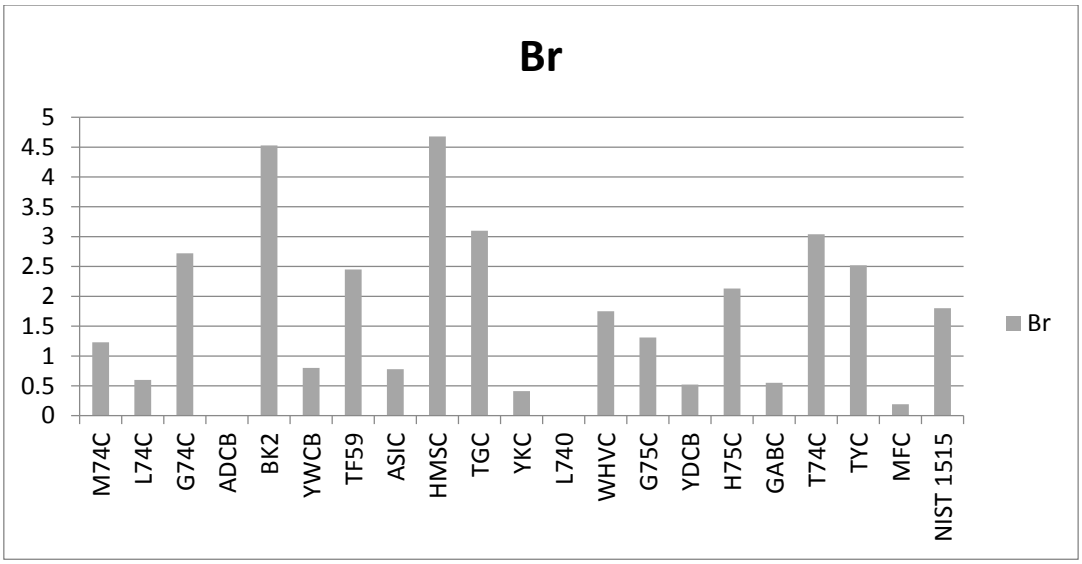

Figure 10. Elemental concentration of Bromine in coffee subspecies of different parts of Ethiopia

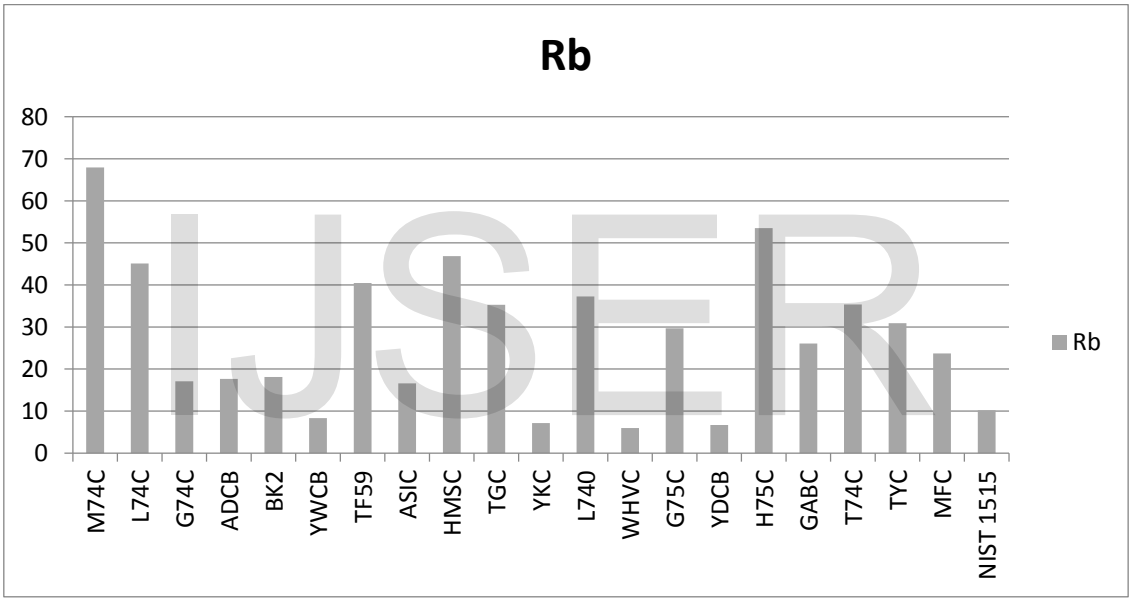

Figure 11. Elemental concentration of Rubidium in coffee subspecies of different parts of Ethiopia

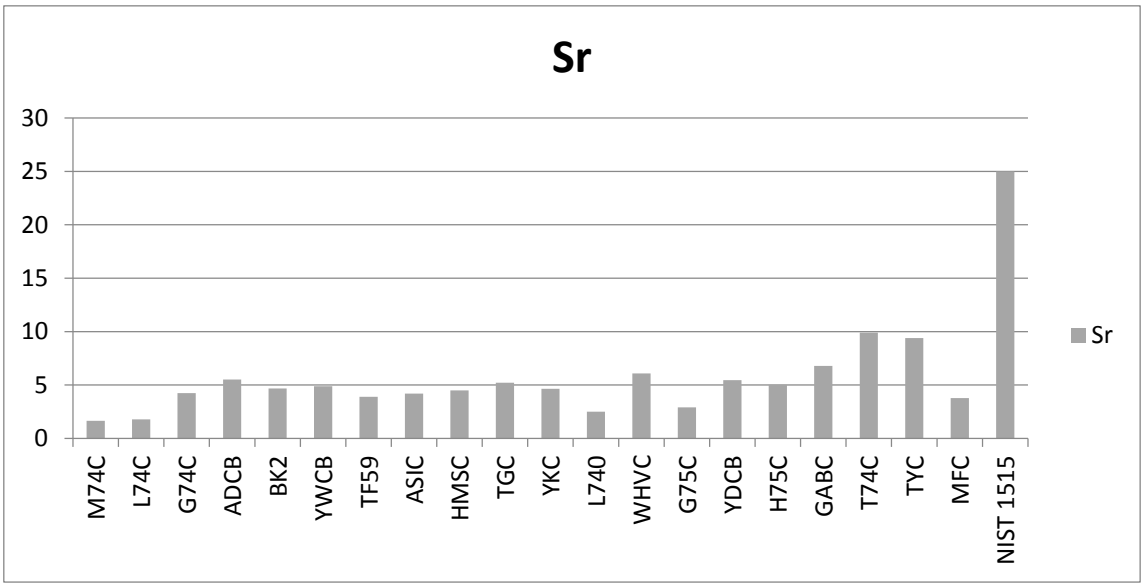

Figure 12. Elemental concentration of Strontium in coffee subspecies of different parts of Ethiopia

Strontium (Sr):

Strontium content was ranged between 1.65 – 9.39 µg/g(ppm). The highest amount was found in subspecies Yellow and followed 7454 about 6.0 and 5.6 µg/g(ppm) respectively both are collected from Godere(Tepi coffee). The lowest amounts was found in subspecies 74165 from Limu and 74148 from Metu with the values about 1.78 and 1.65 µg/g(ppm) respectively. The present value has a good agreement with different country earlier reported value 4 - 13 ppm [29] . The amounts of NIST standards were recorded 25.0 ppm which is above the present study value. The concentration of Strontium were found in agricultural soils of the study area are 191.22 ± 10.88 ppm (Godere), 24.52 ± 1.3 ppm (Limu) and 27.2 ± 3.46 ppm (Metu)

Strontium has been found to be involved in the utilization of calcium in the body. It has promoting action on calcium uptake into bone at moderate dietary strontium levels, but a rachitogenic (rickets-producing) action at higher dietary levels [38]. The omission of strontium caused an impairment of the calcification of the bones and teeth and a higher incidence of carious teeth. 90Sr is one of the most abundant and potentially hazardous radioactive byproducts of nuclear fission and plants are more efficient than animals in the absorption of strontium. Radioactive strontium is absorbed and deposited in tissues especially the bones, and is also readily transmitted to the foetus and secreted in the milk. Strontium is preferentially excreted, especially in the urine, thereby providing some means of protection against 90Sr. [36]

5. CONCLUSION

Coffee plays a significant role in human nutrition even though Effects of coffee on human health are still under strong debate. In the present study twelve essential elements such as P, S, K, Ca, Mn, Fe, Cu, Zn, Rb, Br, Sr, and Se are analyzed in coffee Arabica subspecies those collected from coffee growing area in different parts of Ethiopia using energy dispersive x-ray fluorescence spectroscopy. In this result the order of elements concentration from highest to lowest are K > Ca > P > S > Fe > Rb, > Mn > Cu > Sr > Zn > Br > Se it can be classified major such as P, S, K, Ca and the rest eight are minor elements. From the present investigation shows that variation of elemental concentration of coffee subspecies which is collected from the same soil composition, from the same environment and agricultural practices. There have been suggestions that certain minerals predispose to higher quality and others to lower quality due to ability to uptake mineral from the soil through their roots and transport them to coffee bean. Finally the investigation of the present study concluded that from the analysis in various coffee bean subspecies constituents it showed that coffee bean is a good source of essential minerals. For further studies it could be suggested that coffee beans under investigation could be a source of dietary minerals and complementing food composition.

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