REPUBLIC OF TURKEY
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COMPARISON OF METAL CONTENT OF COFFEE SAMPLES GROWN IN DIFFERENT COUNTRIES BY ICP-OES

Sabah Hassan Mohammedazeez Al-JAF
(151117109)

Master Thesis
Department: Chemistry
Supervisor: Prof. Dr. Sinan SAYDAM

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Sabah Hassan Mohammedazeez Al-JAF
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Supervisor:	**Prof. Dr. Sinan SAYDAM (Firat Uni.)**
Member:	**Prof. Dr. Habibe ÖZMEN (Firat Uni.)**
Member:	**Prof. Dr. Firat AYDIN (Dicle Uni.)**

MAY 2017

DECLARATION

I declare that the Master Thesis entitled **"Comparison of Metal Content of coffee Samples Grown In Different Countries By ICP-OES"** is my own research and prepared by myself, and hereby certify that unless stated, all work contained within this thesis is my own independent research and It is being submitted for the Degree of Master of Science (in analytical chemistry) at the Firat University, and has not been submitted for the award of any other degree at any institution.

DEDICATION

This thesis is dedicated to my beloved family, and I would like to thank them for their understanding, moral supports, encouragements, prayers, patience and all kind of support. It is also dedicated to my faithful friends.

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First of all, I would like to express my deep thanks to merciful **Allah**, who enabled me to perform and complete my scientific project successfully.

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Sincerely

SABAH HASSAN AL-JAF

Elazig - 2017

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ABSTRACT

Coffee is the one of the most consumed beverage across the world. Therefore, it has enormous commercial value and social importance. Coffee consumption continues to increase due to its physiological effects, its pleasant taste, aroma and many health benefits. Robusta and Arabica are two basic types of coffee beans. Turkish coffee is a method of preparation, not a kind of coffee bean grown in Turkey. The coffee beans used for Turkish coffee is generally Arabica type coffee beans.

This study was aimed to determine the concentrations of some major, minor and trace elements in six different coffee samples from six different origins (Brazil, Colombia, Ethiopia, Guatemala, Kenya, and Yemen) where the coffee plants grown. The coffee samples were analyzed for seventeen elements (Al, As, Ba, Ca, Cr, Cu, Fe, K, Mn, Na, Ni, P, Se, Sn, Sr, Zn, and Mg) by using inductively coupled plasma optical emission spectroscopy (ICP-OES). Prior to the analysis by ICP-OES, all coffee samples were completely digested in aqua regia. According to the obtained results, the determined elements were classified into three groups (macro, micro, and trace) elements according to their concentration in different coffee samples; among the macro elements potassium (K) showed the highest levels in all coffee samples whereas the concentration of calcium (Ca) were found to be lowest in the group of macro elements. Micro elements showed the concentration order of: Sr > Mn > Fe > Al > Ba > Cu > Zn in all coffee samples. Concentrations of nickel (Ni) were higher than all other elements in the group of trace elements. The results obtained in present study showed good agreement with previously reported studies for most of the elements especially micro and trace elements while the results for macro elements were generally lower than reported values.

Statistical analysis of the results showed significant differences in the concentration of each element in different coffee samples of different origins.

Key Words: Coffee, Trace element, elements, analysis, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

ÖZET

FARKLI ÜLKELERDE YETİŞEN KAHVE ÖRNKLERİNİN METAL İÇERİKLERİNİN ICP-OES İLE KARŞILAŞTIRILMASI

Kahve dünya çapında en fazla içilen içeçeckelrden biridir. Bu yüzden, çok büyük ticari ve sosyal öneme sahiptir. Kavhe, hoş kokusu ve aroması, içenler üzerindeki fizyolojik etkileri, gibi sağladığı faydaları sebebi ile, kullanımı günden güne gittikçe artmaktadır. Kahve genel itibarı ile ikiye ayrılmaktadır; Robusta ve Arabika olmak üzere. Türk kahvesi, Türkiye'de yetişen bir kahve türü olmayıp, kahve hazırlama yöntemini ifade etmektedir. Türk kahvesi, genellikle Arabica türü kahve çekirdeklerinden hazırlanır.

Bu çalışmada, altı farklı ülkede (Birezilya, Colombiya, Etiyopya, Gutemala, Kenya ve Yemen) altı farklı kahve örneklerinde, onyedi elementin analizi (Al, As, Ba, Ca, Cr, Cu, Fe, K, Mn, Na, Ni, P, Se, Sn, Sr, Zn, and Mg) Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) tekniği ile yapıldı. Bu amaçla bütün kahve örnekleri kral suyunda çözünürleştirildi. Elde adilen sonuçlardan, analiz edilen elementler konsantrasyonlarına göre üç ana gruba ayrıldı, makro, mikro ve eser olmak üzere. Bunlarda potasyum (K) elementi bütün örneklerde makro element olarak ortaya çıkarken, kalsiyum elementi ise, makro elementlerin içinde en düşük konsantrasyona sahip olduğu gözlendi. Bütün kahve örneklerindeki mikro elementlerin sırası Sr > Mn > Fe > Al > Ba > Cu > Zn şeklinde tespit edilmiştir. Nikel (Ni) elementi ise, eser elementler grubundaki elementlerden konsantrasyonu en fazla element olarak bulunmuştur. Elde edilen sonuçların daha önceden yapılmış olan benzer çalışmalardaki sonuçlar ile genel itibarı uyum halinde olduğu özellikle mikrno ve eser elementlerde gözelenmektedir. Diğer taraftan ise, makro elementlerin genel itibarı ile daha önceki yapılan çalışmalardan daha düşük seviyede olduğu gözlenmektedir.

Sonuçların istatistiki değerlendirilmesinden çıkan sonuç ise, kahve örneklerin orijinlerine göre element konsantrasyonlarının önemli derecede farklılık gösterdiği bulunmuştur.

Anahtar Kelimeler: Kahve, eser element, element, analiz, spektroskopi, Emisyon spektroskopisi, (ICP-OES).

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1. INTRODUCTION

1.1. General Introduction

Food samples are commonly analyzed for determining different elements to estimate probable toxicological or nutritional indication and also to assure conformity with government supervisions or quality of the product [1–3] in addition to determination of authenticity or geographical source [4]. Amount of a specific element fluctuates enormously among different types of food but commonly it is invariable for specific type food. Elements that satisfy the nutrient requirement or that considered as safe at specific concentration can be toxic at higher concentration [5–8]. A number of elements are generally observed in analyzed food samples but they have not been identified as nutrients and they are not toxic at the concentration that ordinarily present in food samples. Ranges of the mass fractions of the elements in food samples are conveniently described by the term listed in Table 1.1.

One of the sources of exposing to toxic elements is contaminated food. Thus it is so crucial to perceive the dangers to human well-being and take proper measures as soon as possible [9]. People are encouraged for more consumption of food materials like fruits and vegetables that are good sources of some minerals that useful for human health and vitamins. [10]. Trace quantity of some elements like zinc (Zn), manganese (Mn), cobalt (Co), selenium (Se), iron (Fe), and copper (Cu) are considered as essential micro-nutrients which they have different biochemical action in all living organisms. Although they are essential, if taken in excess they may be toxic. Some other elements like cadmium (Cd) lead (Pb), and arsenic (As), are non-essential elements, these elements even in traces amount are toxic. [11]. throughout the environment elements like cadmium (Cd), aluminum (Al), and lead (Pb) are present and these elements are virtually found in most of the food samples in very low concentration [12].

Trace elements can enter our foods from different sources such as: (i) from the soil, (ii) from irrigation and water that used in cooking or food processing, (iii) pesticides and the chemicals that used to farmlands, (iv) from the equipment, utensils, and containers that used in the processing of the food; and also (v) from storing, packing, and cooking. One of the essential problems in most of the countries around the world is the presence of toxic elements or even nontoxic elements that present at higher concentration than allowed level in the environment and foodstuff. The danger related to exposing to the toxic trace elements in that found in different foodstuffs has raised widespread concern in human health. Some acute and chronic symptoms such as, diarrhea, vomiting, nausea, dizziness, reduced conception rate, sleeping disorders, and appetite loss are some symptoms of the toxicity of heavy metals,

Heavy metals are defined as elements in the periodic table having densities more than 5.0 g/mL; generally excluding alkali metals and alkaline earth metals [97]. Heavy metals are individual metals and also metal compounds, which can affect human health. Generally, humans are exposed to heavy metals by the way of ingestion (drinking or eating) or inhalation (breathing) [98]. Some other health problems such as cardiovascular disease, nervous and immune system disorders, impaired fertility, depressed growth, elevated death rate among infants, and increased spontaneous abortions are also connected to trace metals [13].

TABLE 1.1. Ranges of mass fraction of elements found in most food stuff [115].

Term	**Mass Fraction**	**Mass Fraction (%)**
Major	1–1000 g/kg	0.1–100
Minor	10–1000 mg/kg	0.001–0.1
Trace	0.01–10 mg/kg	0.000001–0.001
Ultratrace	10 μg/kg	0.000001

The steady increase in the contamination of food products requires the investigation and determining amount of toxic elements that can turn out to be a serious potential hazard if not controlled. In recent years many researches have been carried out at different countries on the kind, source, quantity, and precaution of toxic elements in the contaminated food samples [14].

Concentrations of a number of trace elements in food samples from Nigeria have been determined by Onianwa et al. [15]. Voegborlo et al. investigated amount of lead (Pb), mercury (Hg), and cadmium (Cd) in some canned Tuna fish [16]. Sample preparation procedures were examined by Doner and Akman for the determining concentration of zinc (Zn) and iron (Fe) in bulgur (boiled pounded) wheat samples using graphite furnace atomic absorption spectrometry [17]. Aluminum content of fish samples were investigated by Ranau et al. [18]. Fernandez et al. determined some trace elements in tea beverages from Spain by using inductively coupled plasma atomic emission spectrometry [19]. Racz et al. determined concentration of some trace element in culture mushrooms [20]. The contents of some heavy metals in fish samples were determined by Tuzen [21]. Table 1.2 shows the elements that most generally monitored in different food samples, the normal range of interest, and the usual purpose for their monitoring [22].

TABLE 1.2. Elements commonly monitored in different food samples [115].

Elements	**Range**	**Primary Purpose**
Aluminum	Trace	Toxicity
Arsenic	Trace/ultratrace	Toxicity
Boron	Trace	Nutrition
Cadmium	Trace/ultratrace	Toxicity
Calcium	Major/minor	Nutrition
Chromium	Trace/ultratrace	Nutrition/toxicity
Copper	Minor/trace	Nutrition
Fluorine	Trace	Nutrition/toxicity
Iodine	Trace	Nutrition/toxicity
Iron	Minor/trace	Nutrition
Lead	Trace/ultratrace	Toxicity
Magnesium	Minor/trace	Nutrition
Manganese	Minor/trace	Nutrition
Mercury	Trace/ultratrace	Toxicity
Molybdenum	Trace/ultratrace	Nutrition
Nickel	Trace/ultratrace	Toxicity
Phosphorus	Major/minor	Nutrition
Potassium	Major/minor	Nutrition
Selenium	Trace/ultratrace	Nutrition/toxicity
Sodium	Major/minor	Nutrition
Tin	Minor/trace	Toxicity
Zinc	Minor/trace	Nutrition

1.2. Coffee

Coffee beverage is one of the most consumed drinks in world and it is ranked after petroleum as the second most traded global commodity [53] and it is exporting to more than 167 different countries with more than 9.0 million ton annual consumption in recent years [63]. Coffee is an agricultural product that plays an important role in the international trade [54]. Arabic word Quahweh is the word in which the word Coffee has originated from. Nowadays its popularity is identified by different terms in many countries like caffe (Italian), kaffee (German), café (French), koffie (Dutch) and coffee [55].

Coffee beverage prepared from soluble (instant) powder or brewed from ground roasted coffee beans is one of the most extensively and habitually consumed non-alcoholic drinks over the world. Its growing popularity is mainly owing to its unique flavor, taste, and aroma as well as recognized health effects [62]. It is suggested by recent researches that drinking two to four cups of coffee per day provides a number of health benefits like decrease of mortality risk [101], colorectal cancer development [111], liver cancer [112, 113], hepatic injury and cirrhosis [108, 109, 110], degenerative, progressive and chronic diseases such as Alzheimer's [99, 100] Parkinson's disease [105, 106, 107], type 2 diabetes [102, 103, 104] coronary heart disease and stroke [114, 66].

Coffee is an important plantation crop which belongs to the Rubiaceae and genera Coffea family, they are shrubs or small trees (Figure 1.1). Usually the coffee plant is a woody perennial tree that is growing at region of higher altitudes [57]. Food industry uses fruits (berries) parts of coffee plants for the coffee production [58]. after collecting green coffee beans from dried and hulled barries, the coffee beans will be roasted at high temperature of about 100-230 °C, for achieving full aroma of the coffee. Roasting caused the color of the coffee beans to change significantly from the light brown into the dark brown, and chemical composition of beans also changed, particularly the amount of volatile compounds [61]. Coffea Arabica (Arabica coffee) and Coffea canephora (Robusta coffee) are two most important types among 70 different species of genera Coffea that have been reported. There is difference in caffeine contents, taste, and appearance between these two varieties. Arabica coffee is favored by a hedonic trend of consumers as compared to Robusta coffee [57].

Figure 1.1. Arabica coffee plants [57].

Turkish coffee is not a type of coffee plant grown in Turkey; it is a different method of preparation of coffee than other type of coffee. Thus, there are no different kinds of coffee beans. For the preparation of Turkish coffee, coffea Arabica is used. For preparing Turkish coffee, the coffee Beans will be ground or pounded in order to get the finest possible powder as compared to other preparation method. The coffee bean is grinded by either pounding it in a mortar in which this method is the original way or by the burr mill. Except traditional Turkish hand grinders, most of the domestic coffee grinders are unable to grind coffee beans finely enough. After roasting and grinding, the coffee beans will be boiled usually in a pot (cezve), frequently with sugar, then it will be served in a cup in which the grounds will be allowed to settle (called telve). For achieving the best results, cold water is better to be used. Therefore, in case when addition of sugar is preferred you should choose the form of sugar which dissolved easily. The cups used for serving the coffee, can also be used to measure the quantity of necessary water.

For preparing each cup of coffee between one and two Turkish teaspoons of the coffee are used. The best Turkish coffee as any other type of coffee is prepared from freshly roasted beans ground just before brewing. Like other types of coffee, you can buy and store Turkish-ground coffee, although its flavor will be lost with the time. This way of coffee preparation is found in the Middle East, North Africa, the Caucasus, and also some other different locations within Eastern Europe [59].

1.3. Elemental Coffee Analysis

In order to guarantee the safety and the quality of the final products of coffee and also to protect the health and well-being of coffee consumers, suitable analytical techniques have to be used to measure different parameters that detect wholesomeness of the green, and roasted coffee beans, and also prepared coffees and their infusions. As an example, in the analysis of organoleptic in green beans, the taste, and odor of the green beans and also some information about their color, size, cross-section and the shape are confirmed as a part of assessment of their quality [61]. Important characteristics for finding the best roasting degree of green coffee beans are Color and flavor [61].

For the evaluating the coffee infusions quality, the taste of the prepared beverages is generally termed under some standardized situations [69]. All the different notes are collected from each coffee sample and then their unique profile will be evaluated. However, it is notable that evaluations of the coffee testers on the aroma and taste of the coffee might be subjective [70]. Chemical methods that used for analysis coffee are similar to the methods that used in the assessment and quality control of food samples [71]. They depend on the determining of various compounds, such as caffeine, tannins, polyphenols, lipids, and volatile compounds, different carbohydrates such as glucose, galactose, fructose, sucrose, arabinose, and some poly-saccharides such as cellulose, vitamins B_3, amino acids, chlorogenic acid, trigonelline, and minerals [72]. These chemical compounds are measured generally for the identification of brands and varieties of the coffee or for the determination of the origin of the coffee [72]. However, it must be noted that the composition of the final coffee product may be changed in all steps involved in the coffee production, from harvesting to roasting of the coffee beans [73]. Among different substances that present in the coffee, only amount of caffeine will be stable to the high roasting temperature [74]. Other chemical compounds present in coffee may be degraded during the production and conditions of storage [73].

1.4. Element Contents of Coffee

It is recognized that the coffee beverage is a rich source of elements, including those that are essential for the human health, in addition to non-essential elements and even toxic to human take up from a polluted soil. [54]. Coffee contains various elements such as Na, B, Mg, Fe, Ca, K and many other elements. These elements have various effects on human health such as Na helps to regulate the body's water balance. [55, 64]. Mg is a cofactor of enzyme systems [65]. Fe is an important for normal human physiology and for most life forms [67]. Therefore, the determination of total concentrations of elements in coffee enables to assess its nutritive quality and also helps to judge its possible ill-effect that may cause to the human health [54]

1.5. Literature Review

Information available in literature about the levels of the trace elements present in coffee beans from different origins is limited, different analytical techniques in a number of studies have been used for determination the amount of some elements (major, minor and toxic element) in different types of roasted, and green coffee beans in different countries around the world (like India, Nigeria, Brazil, etc.) [58].

There are various studies about element contents of coffees. Concentration of l4 elements (Ca, Cd, Pb, Mn, Fe, Na, K, P, Mg, Cr, Ni, Co, Cu, Zn) in coffee were determined by Grembecka et al. [62]. Oliveira et al. determined amount of 9 elements (Mg, Na, Fe, Ca, K, P, Cr, Ni, and Mn) in soluble powdered instant coffees [56]. The levels of some bioactive amines, five elements (K Na, Mg, Zn, and Mn), total ash content, pH values, and total dry matter content in ground coffee and brewed Turkish coffees were investigated by Ozdestan [75]. Krejcova and Cernohorsky determined Boron (B) in coffee and tea by ICP-AES [76]. Stelmach, Pohl and Szymczycha-Madeja measured total concentrations of Mn, Cu, Mg, Fe, and Ca, in the green coffee infusions by using high resolution-continuum source flame atomic absorption spectrometry [93]. Oleszczuk, Nédio, et al. determined concentration of copper, manganese, and cobalt in samples of green coffee by using direct solid sampling electrothermal atomic absorption spectrometry (SS-ET AAS) [84].

green Arabica coffee species produced in crop year 1987/88 in Costa Rica, Colombia, El Salvador, Cuba, Panama, Mexico, Papua New Guinea, and Nicaragua were analyzed by Krivan et al. 1993 for determination of concentration of (Mg, Na, K, C, Mn, Cr, H, Co, Br, Ba, Ca, Fe, Rb, Cs, Sc, N, Cu, Zn, La, and Sr) using different techniques like flame and graphite furnace atomic absorption spectrometry, and instrumental neutron activation analysis (INAA), [70].

Ashu and Chandravanshi determined the concentrations of 11 elements (Cd, Cu, Co, Ca, Mn, K, Fe, Pb, Na, Zn, Mg) in three different brands of roasted coffee powders from Ethiopia and their infusions by flame atomic absorption spectrometry (FAAS) [58]. Habte, Girum, et al. determined 45 elements in the 129 different coffee samples by using inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and direct mercury analyzer (DMA) [94]. Szymczycha-Madeja, Welna and Pohl, compared six procedures for sample preparation, for determining the amount of (Ca, Pb, Mg, Ba, Ni, Fe, Cd, Mn, P, Cr, Sr, Zn and Cu) in slim instant coffees by inductively coupled plasma optical emission spectrometry (ICP-OES), they established that the extraction with aqua regia provides better results as compared to other digestion procedures [95]. Concentration of 27 elements (K, Ni, P, Mg, Sb, Ca, Li, Al, Be, Mn, Sr, Cr, B, Se, Co, Hg, Zn, Mo, Cu, As, Sn, Pb, Ba, U, Bi, Cd, and Th) in green coffee samples and their infusions were determined by Şemen, Sevcan, et al. by inductively coupled plasma-mass spectrometry (ICP-MS) [96].

1.6. Spectroscopy

In analytical chemistry measurements that based on light and other forms of electromagnetic radiation are widely used. Spectroscopic science is dealing with the interaction of radiation with matter. Spectroscopic analytical methods are based on measuring the quantity of radiation formed or absorbed by atomic or molecular species of interest, We can classify spectroscopic methods according to the region electromagnetic spectrum that involved in the measurement, The regions of the spectrum that have been used include γ-ray, X-ray, ultraviolet (UV), visible, infrared (IR), microwave, and radio-frequency (RF). Actually, the meaning of spectroscopy have been extended further by the current usage to include the techniques that do not even involve electromagnetic radiation, like electron, acoustic, and mass spectroscopy [68].

Spectroscopy played significant role in the development of modern atomic theory. In addition, spectrochemical methods have provided as one of the most widely used tools for the explanation of molecular structure as well as the quantitative and qualitative determination of both inorganic and organic compounds [68].

Spectroscopy can be divided into two main groups of techniques. In the first techniques group, the energy transfers between the photon and the sample. In absorption spectroscopy the atom or molecule absorb a photon, by which it will transit from a lower to a higher energy state (excited state) (Figure 1.2). The kind of transition depends on the photon's energy. For example, when an atom or a molecule absorbed a photon of the visible light, one of their electrons promotes to a higher energy level, on the other hand, when infrared radiation absorbed by a molecule, vibrational energy of one of its chemical bonds will be changed [37].

By absorbing an electromagnetic radiation by the sample, the number of the photons that passing through it will be decreased. Measurement of this decrease in the number of photons passing is called absorbance, and it is a useful analytical signal. Absorption occurs only when the energy of the photon, $h\nu$, matches the energy difference, ΔE, between the two energy levels [37].

When the atom or molecule in the excited state returns back to the lower energy state, excess of the energy is frequently released as photon, this process is called emission (Figure 1.2). Atom or molecule might end up in the excited by a number of ways, such as absorption of a photon, chemical reaction, or by thermal energy. Emission following photon absorption called photoluminescence, and emission following the chemical reaction is called chemiluminescence [37].

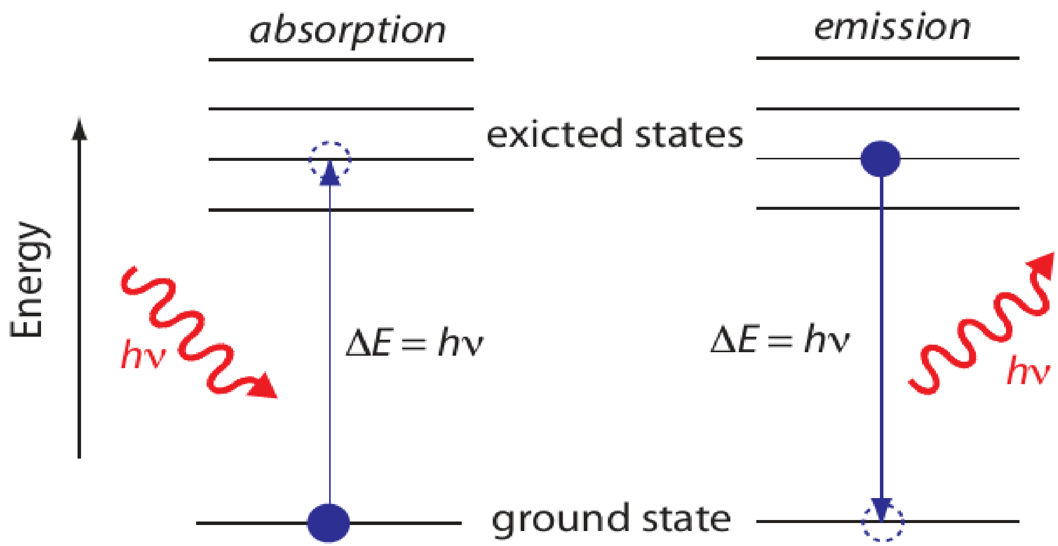

Figure 1.2. Energy level diagram showing the absorption and emission processes [37].

In the second techniques group, the amplitude, phase angle, polarization, or direction of propagation of the electromagnetic radiation will be changed when it is refracted, reflected, scattered, diffracted, or dispersed by the sample [37].

2. ANALYTICAL TECHNIQUES USED FOR TRACE ELEMENT DETERMINATION IN VARIOUS FOOD SAMPLES

2.1. Atomic Absorption Spectrometry

Atomic Absorption Spectrometry is one of the oldest techniques that are still used for determining amount different elements in food samples, even though it's using is decreased as compared to other simultaneous multielement techniques. AAS techniques are used for determining concentration elements in different food samples in many laboratories by using flame or electro thermal atomization atomic absorption spectroscopy ((FAAS or ETA-AAS); Pb and Cd determined in food by ETA-AAS; mercury (Hg) determined in food by using CV-AAS; determination of Se and As in food sample using HG-AAS or ETA-AAS. A proficiency testing report on analysis of the food samples for determination of As, Sn, Pb, Hg, and Cd showed that the results from the techniques related to AAS like (ETA-AAS and FAAS) were not good as compared to the results obtained from the techniques related to inductively coupled plasma such as (ICP-MS and ICP-OES). However, they caution that the staff specialization that used ICP techniques might be the cause of the better performance, not the difficulty or ease of the techniques [23].

2.1.1. Flame Atomic Absorption Spectroscopy (FAAS)

Flame atomic absorption spectroscopy (FAAS) can be used for determining many nutritional and toxic elements at different levels in different food samples. In flame atomic absorption spectroscopy, flame is used as atomizer in which the sample will be aspirated into the flame in the form of solutions and converted to free atom by high temperature of the flame that may reaches up to 2300 °C with air-acetylene flame and up to 2700 °C with nitrous dioxide system (N_2O)-acetylene flame. Dry ashing or wet digestion methods are used for digesting the samples and preparing analytical solutions. For determining the low concentration of some elements in food samples, enriching the analytical solutions with chelation-solvent extraction might be required. Operating the FAAS instrument is simple as compared to other techniques, and in the case when concentration of only one or two elements are required to be determined FAAS technique might be faster than other multielement techniques [25]. Some of the standard methods that are used FAAS are determination of Cd in the food sample [26]; Fe, Zn, and Cu in different food samples [24]; determination of Zn in food [27], determination of Fe in vegetables and fruits [28]; determination of Zn contents of milk [29], and determination of amount of Mn, Fe, Ca, Mg, Cu, Zn, K, and Na in infant formula [38]. Rains determined concentration of (Cr, K, V, Se, Ca, Mn, Al, Fe, Na, Co, Zn, Ni, Cd, As, Sn, Mo, Cu, and Mg) in food sample by using flame atomic absorption spectroscopy (FAAS) with hydride generator [28]. Ability of FAAS for the analysis food was established by Miller-Ihli for the determination of (Mn, Fe, Mg, Zn, Cr, Ca, and Cu) by either wet digestion or dry-ashing procedures [30].

Flame atomic absorption spectrometry (FAAS) is one the techniques that quite often used for determining the major (Na, K, Mg, Ca,), minor (Zn, Fe, Mn, Cu) and trace (Ni, Co, Pb, Cr, Cd) elements in different coffee samples [70]**.** High-resolution continuum source flame atomic absorption spectrometry (HR-CS-FAAS) is also used for determining concentration of (Na, Mn, Fe, Mg, Ca, and K) in coffee samples [56]. Concentrations of Na and K are determined by using flame atomic emission spectrometry (FAES) [80].

Unfortunately, FAAS do not have enough sensitivity for quantification some important elements that exist traces in amount [62] therefore for determining such elements like (Pb, Ni, Cr, and Cd) using more sensitive technique such as inductively coupled plasm optical emission spectrometry (ICP-OES) is preferred [83].

Simple standard solutions are usually used for calibrating FAAS [80]. As an exception, in the determination of sodium (Na), and potassium (K) we can add a chemical suppressor such as cesium chloride ($CsCl_3$) as an ionization buffer to the samples and standard solutions [56]. By the same way, lanthanum (La) salts such as lanthanum nitrate $La(NO_3)_3$[58] or a solution of lanthanum chloride $LaCl_3$[62], will be added to the sample and standard solutions to minimize the effect of chemical interferences in the case of determination of Mg and Ca.

2.1.2. Electrothermal Atomization Atomic Absorption Spectroscopy (ETA-AAS)

ETA (generally called graphite furnace) AAS is also used for determining many nutritional and toxic elements at different levels in different food samples. A small amount of the sample will be added to the graphite tube, and then it is electrically heated in three steps, in the first step the solution will be dried, secondly the sample residues will be ashed or pyrolyzed, and finally the analyte will be atomized. a chemical matrix modifier is Usually added to the analytical to retain the analyte while removing the matrices at the time of ashing step. Different matrix modifiers can be used depending on the element that determined [25, 31].

Electrothermal atomic absorption spectrometry (ETA-AAS) is less frequently used compared to other multielement techniques. High-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS-GFAAS) can be used as an alternative [56]. Both aforementioned techniques are primarily used for the determining trace and minor elements like Cu, Al, Cr, Mn, Co, Ni, Sr, and Fe in coffee samples. Similarly to FAAS technique coffee samples to be analyzed must be digested first [56]. An interesting approach for determining concentration of the elements by using ETAAS without the initial sample digestion have been reported in which the solid samples analyzed directly [84] direct measurement of solid samples without digestion offer higher sensitivity, as compared to analyzing the solution of the digested sample, because there is no sample dilution in direct analysis and also the risk of error (lower blanks) and losses of the elements is minimum because lower amount of reagent is used for sample preparation. External calibration curves are commonly used with simple standard water solutions in ETAAS measurements [56]. In the direct measurement of the solid sample or their slurries, the calibration will be done by using an aqueous solution as in the case of Mn and Co or by addition of a solid certified reference material (CRM) as in the case of Cu [84]. Chemical modifier is necessary for stabilizing the element species and modifying the matrices of the coffee samples at high pyrolysis temperature, i.e., a mixtures of $Mg(NO_3)_2$, $Pd(NO_3)_2$, and the Triton X-100 in the measurement of manganese (Mn) [84], $Mg(NO_3)_2$ in the measurements of Ni and Cr [56] or in the measurement of Al [85].

2.1.3. Hydride Generation Atomic Absorption Spectroscopy (HG-AAS)

Hydride generation atomic absorption spectrometry (HG-AAS) is generally used for determining the concentration of selenium (Se) and arsenic (As) in various food samples. Food samples should be digested rigorously for oxidizing organometallic compounds, particularly organoarsenic compounds. Digestion of the samples are usually performed by using H_2SO_4–$HClO_4$–HNO_3 or it will be dry ashed with magnesium oxide (MgO), and magnesium nitrate ($Mg(NO_3)_2$) and analytical solutions are prepared with hydrochloric (HCl) solution [32]. As an alternative only HNO_3 can be used for digesting the sample, but it must be accomplished at high temperature for accurate measurement of arsenic (As) [33]. Analytical solutions must be warmed for prereducing Se from Se(VI) to Se(IV), and prereducing As from As(V) to As(III), generally with NaI or KI before generation of their hydrides by addition of sodium borohydride, then these hydrides will be transported to the graphite furnace or quartz tube where it will be heated for atomization to occur for atomic absorption. HG-AAS is used in standard methods for determining concentration of Se and As in food samples [34].

2.1.4. Cold Vapor Atomic Absorption Spectroscopy (CV-AAS)

For determining the amount of mercury (Hg) in different samples, many analytical techniques can be used but the technique that still being mainly used for determining concentration of mercury (Hg) in different food samples is CV-AAS. Mercury vapor will be formed from analytical solution by using either sodium borohydride ($NaBH_4$) or stannous chloride ($SnCl_2$) and then it will be transported to a cell for measuring its atomic absorption. Usually, the cell will be maintained at temperature of the room, but the reliability of the technique can be enhanced by heating the cell [35]. Sometimes incorrectly "hydride generation" term is used to describe the technique when for producing Hg vapor sodium borohydride is used. Standard methods that available for determining amount of mercury (Hg) in vegetables and fruits samples [36].

2.2. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Since its development in the early 1980s, ICP-MS became a well-known multielement analytical technique for determination of trace elements. This technique is able to detect many elements at very low levels (trace and ultratrace) with large dynamic range [46]. The sensitivity of this technique has been improved by two to three orders of magnitude as compared to ICP-AES. However, operation of the instrument is complicated and more costly, and spectral interference is possible from other molecular species. A quadrupole ICP-MS used to overcome the isobaric interferences, dynamic reaction cell [48] or collision and reaction cells [47] are being used now. Double-focusing magnetic-sector ICP-MS is still the ultimate means of suppression of the isobaric interference, but the price of the instrument is much greater than other ICP-MS instruments [22].

Cubadda et al. determined 15 different elements in some food reference materials by using micro wave-assisted digestion procedure and quadrupole ICP-MS [49]. ICP-MS and ETA-AAS has been compared by Zhang et al. for determining amount of Pb and Cd in some duplicate diets, they found that ICP-MS technique was much faster, and provides higher accuracy and precision as compared with ETA-AAS, they concluded that ICP-MS technique can be used as a routine method of analysis for analyzing different food samples [50]. Zbinden and Andrey determined elements such as (As, Pb, Cd, Al, Se, and Hg) in the samples of food by using high-pressure device for ashing the samples and ICP-MS technique. They added isopropanol to the analytical solutions to overcome the residual carbon interference on Se, As, and Pb [51]. D'Ilio et al. determined ten elements in rice sample by using double-focusing magnetic-sector ICP-MS and they compared their results to the results obtained by the ICP-AES and quadrupole ICP-MS [52].

2.3. Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP- OES)

Inductively coupled plasma optical emission spectroscopy is one of the most effective techniques that can be used for determining the elements in different samples. in ICP-OES technique, first step is injection of the sample solution into to the radiofrequency (RF) induced argon plasma by a nebulizer or by techniques of sample introduction. The sample mists reach into the plasma and then rapidly they will be dried, vaporized and finally energized by collisional excitation at high temperature. Then atomic emissions that originating from the plasma are observed, collected by a mirror or lens, then they will be imaged into the entrance slit of the monochromator (wavelength selector). Measurements of single element could be done cost effectively by combining simple monochromator with a photomultiplier tube (PMT), and determining multielements simultaneously are achieved for more than 70 different elements by combining polychromator with an array detector. Performance of a system like this is competitive with most of other techniques of analysis, particularly with respects to the sensitivity and sample throughput [77]. ICP-OES technique can be used generally for analyzing different food samples, mainly for major and minor levels of elements [39]. multielement capability of this technique makes it beneficial for the dietary studies. Some improvements in the instrument such as axially viewed plasma and charge transfer device as a two-dimensional detector have upgraded the efficiency of ICP-OES technique [40].

Some of the standard methods that used ICP-OES technique are, determination of Cu, Mg, Ca, Fe, P, Na, Mn, Zn and K in sample of infant formula [43]; determination of amount of Ca, K, B, P, Cu, Mn, Zn, and Mg in some plant samples [41]; and concentration of phosphorus (P) were determined in some samples of animal and vegetable fat and oil [42]. The ability of ICP-OES for the analysis of food were demonstrated by Miller-Ihli for determining amoun of Co, V, Ca, Mn, Cu, Mg, Ni, Fe, Cr, Zn, and P by either wet digestion or dry-ashing [30]. Dolan and Capar determined concentration of 20 elements in the food samples by using ICP-OES [44]. ICP-OES used determining concentration of 13 elements in different animal and plant samples by Carrilho et al. by using micro wave for digestion of the samples but they dried and grinded the samples before digestion [45].

ICP-OES is one of the best techniques that can be used for determining elemental contents of different samples of coffee. It is particularly attractive and useful for determining amount of some elements at different levels, including major elements (Na, K, Ca, Mg, S, and P), minor elements like (B, Cu, Al, Co, Mn, Zn, Fe, and Sn) and trace elements like (Ba, Cr, Se, Cd, Pb, Ni, Sb, As, Sr, and Si) [73]. Some other benefits of ICP-OES technique over other techniques of atomic spectrometry such as ETAAS and FAAS are that ICP-OES provides higher sensitivities, Lower detection limits, faster measurements and wider linear dynamic ranges [82]. Due to the absence of the ionization and spectral interferences, in the analysis with ICP-OES the calibration is generally performed with standard solutions [73]. Same quantity of

HNO_3 that have been used for digestion of the samples will be added into the standard solutions for controlling matrix effects [76]. Additionally, internal standard might be added into the samples and standard solutions for controlling instabilities of signal throughout the analysis [76].

2.3.1. Principle

ICP-OES technique is based on the sponteneous emission of photons by the atoms and the ions exited in a radiofrequency discharges. Sample solutions can be directly inserted to the instrument, but the samples in the solid form must be digested for extracting the analytes into the solution. Then sample solutions will be transformed to an aerosol then it will be directed into plasma. essentially inductively coupled plasma sustains temperature of about 10000 K. there is an area called preheatng zone (PHZ) where removing the solvent from the sample aerosol (desolvation) is performed at this zone and in which the sample is leaft as microscopic salt particle. And also in this zone the salt particles will be decomposed into the individual gas phase molecules (viporization), in which they are subsequently broken down into the single atoms (atomization). After that desolvation, vaporization, and atomization of the sample aerosols have been done, only one thing is left to be done by the plasma dicharge which is excitation and ionization/excitation. The processes of ionization and excitation will be done mainly in initial radiation zone (IRZ) and normal analytical zone (NAZ). Then both atomic and the ionic species in the excited state are then relaxed back into the ground state by emitting a photon. So, the wavelength of the photons could be used for identification of the element from which the emission is originated. Concentration of the element from which the emission is originated in the sample is directly proportional to the the amount of the emitted photons. the amount of the emitted photons by the ICP will be collected by a concave mirror or a lens. This focusing optic forms an image of the ICP on the entrance slit of the wavelength selector (monochromator). photodetector will convert specific wavelength that exiting from the wavelength selector to the electrical signals. improvement and processing of the signal is performed by the detector, then it will be displayed and stored by the computer [60].

2.3.2. Inductively Coupled Plasma Characteristics

The major benefits of the inductively coupled plasma over other different sources of excitation, is the efficiency and reproducibility of the ICP source for vaporizing, atomizing, exciting, and ionizing many elements in different samples. And this is chiefly due to its high temperature of about, 7000 – 8000 K, in the zone of exitation of ICP source. Which is considerably higher than the highest temperature of the furnaces and flames which is about (3300 K). This high temperature make ICP to be able to excite refractory elements, and makes it to be less prone to the matrix interference. In addition, contaminations from impurities that exist in the electrode materials will not be present because the ICP is an electrodeless source. And relatively it is not dificult to build up an ICP assembly and it is cheaper comparing to other sources, like LIP. Some of the most advantageous characteristics of ICP sources are listed as follows.

- higher temperatures of about (7000 – 8000 K)
- high electron density of (10^{14}–10^{16} cm^3)
- significant degree of ionizations for most of the elements
- simultaneous multielements capabilities (more than 70 elements including S and P)
- lower background emissions, and lower chemical interferences
- higher stability that leads to higher precision and accuracy
- lower detection limit for most of the elements (0.1 –100 ng/mL)
- wider linear dynamic range (LDR)
- appropriate for determining the refractory elements
- cost-effective analysis [77].

2.3.3. Instrumentation

In ICP-OES, the samples will be injected into instrument in the form of a liquid stream. After that, the sample solution will converted to an aerosol by nebulisation process. Then the aerosol sample is transported into the plasma where desolvation, vaporization, atomization, and excitation and/or ionization of the sample solution performed by the plasma. Then the atoms and ions that excited will emit their specific radiation that collected by the optical devices and the radiation will isolated by the monochromator to individual wavelength. Then the detector detect the radiation and convert it into the the electrical signals after that it will be changed to information about the concentration by the computer [78]. A representation of the layout of a typical ICP-OES instrument is shown in Figure 2.1.

2.3.3.1. Sample Introduction

Liqiuds are the most common form to be analyzed by plasma emmision. These are usually introduced with a nubilizer and spray chamber combination, similar to that used for AAS. An Aerosol is formed and introduced to the into the plasma by nebulizer gas stream through the injector tube [78].

2.3.3.2. Nebulizer

The device that converts liquid samples to the sample aerosol which is then transported into the plasma is called nebulizer. One of the most critical processes in the ICP-OES is nebulization process. Commercial instruments uses only two type of nubilizers with an ICP: (i) pneumatic nubilizer and (ii) ultrasonic nubilizer [79].

2.3.3.3. Detectors

After the isolation of the proper emission line by spectrometer, intensities of the emission lines are measured by the detector and its associated electronics. Most commonly used detectors are [79]:

- Photo multiplier tube
- Array detectors
- Photodiode array
- Charge-injection devices (CID)
- Charge-coupled devices (CCD)

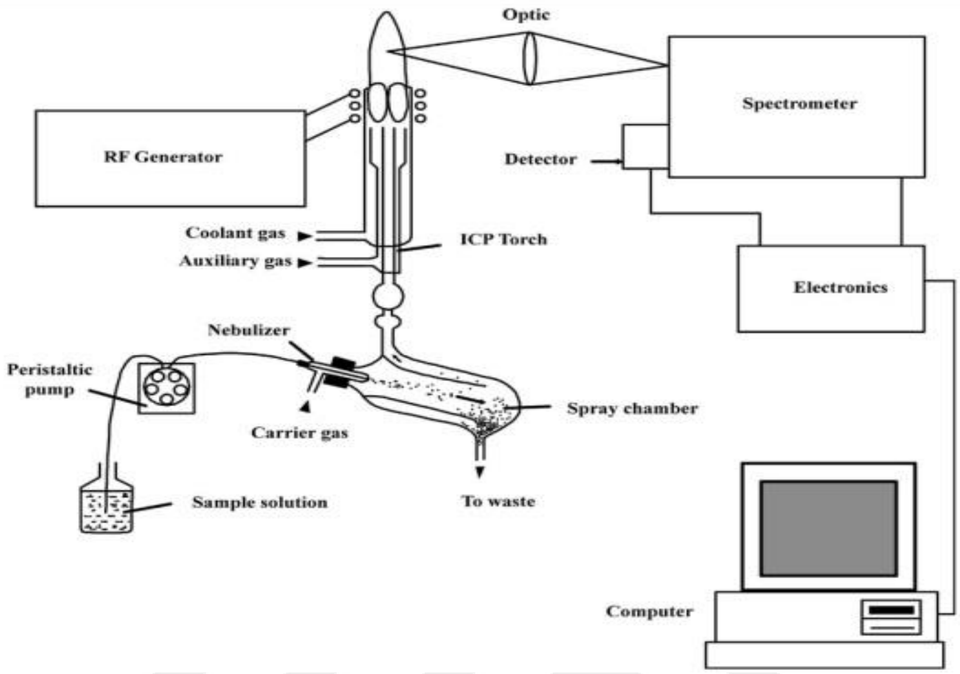

Figure 2.1. The major components and layout of a typical ICP-OES instrument [77].

3. MATERIAL AND METHODS

3.1. Coffee Samples

Six coffee samples (Figure 3.1) from six different origins of coffee beans were selected for the analysis. All coffee samples were purchased from local markets of Turkey, detailed description of coffee samples and their sample ID are given in Table 3.1.

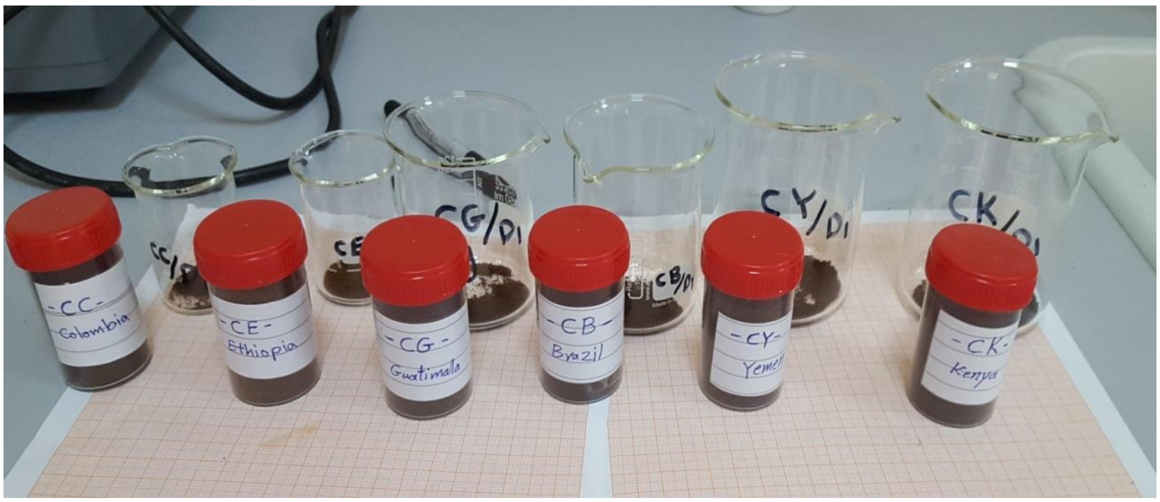

Figure 3.1. Coffee samples used for analysis

Table 3.1. Coffee samples and their sample ID

No.	Sample	Sample ID
1	Coffee beans from Brazil	CB
2	Coffee beans from Colombia	CC
3	Coffee beans from Ethiopia	CE
4	Coffee beans from Guatemala	CG
5	Coffee beans from Kenya	CK
6	Coffee beans from Yemen	CY

3.2. Sample Preparation

Digestion of the coffee samples were done in triplicate by taking 0.500g of each coffee sample into a beaker and 2 ml of aqua regia (1:3 HNO_3: HCl) were added then the resulting mixture were sonicated in ultrasonic bath for 1 hour, after that 10.0 ml of deionized water were added, filtrated to remove any undissolved particle then diluted to 25 ml with deionized water Figure 3.2 shows coffee sample after digestion.

Figure 3.2. Coffee Samples after Digestion

3.3. Chemical Reagents

All of the reagents that have been used in present study were of the analytical grades. All of the prepared aqueous solutions prepared by deionized water. Concentrated HNO_3 and HCl (Merck, Darmstadt- Germany) solutions were used for the digesting the coffee samples. All of the standard solutions prepared by diluting multi-element (1000µg/mL) ICP standard (Bernd Kraft der standard). Deionized water was obtained from (Thermos – Germany) water purification system. All glassware and plastic bottles that used in this work were washed by 10% (m/v) HNO_3 and rinsed many times with deionized water.

3.4. Operating Conditions for ICP – OES Instrument

An ICP – OES instrument (Spectro-Arcos – Germany) used for the analysis of elements under study. The conditions of the operation of ICP – OES instrument for determination of elements in samples are shown in Table 3.2 and a photographic picture of the instrument is shown in Figure 3.3.

Table 3.2. Operating conditions for ICP – OES instrument

Parameters	Descriptions
Power	1400 Watts
Coolant flow	13 L/min
Auxiliary flow	1 L/min
Nebulizer flow	0.83 L/min
Plasma Torch	Quartz, demountable
Injector tube	2.0 mm
Spray chamber	Glass Cyclonic
Nebulizer	Concentric nebulizer
Sample uptake rate	1.2 mL/min
Replicate read time	60 sec per replicate

Figure 3.3. Photographic picture of ICP – OES instrument

3.5. Calibration Curves for Determination of Elements in Coffee Samples

In this study, 17 elements at major, minor and trace levels in six coffee samples from six different origins of the coffee beans have been determined successfully using ICP-OES with acceptable accuracy and precision. For determining the elements in the coffee samples we prepared a calibration curve for each element by preparing a series of standard solution and measuring the emission intensity for each solution, calibration curves were made by plotting of emission intensity in counts per second (cps) versus concentration in (mg/l). Figure 3.4 , Figure 3.5, Figure 3.6, Figure 3.7, Figure 3.8, Figure 3.9, Figure 3.10, Figure 3.11, Figure 3.12, Figure 3.13, Figure 3.14, Figure 3.15, Figure 3.16, Figure 3.17, Figure 3.18, Figure 3.19, and Figure 3.20) shows the calibration curves for (Al, As, Ba, Ca, Cr, Cu, Fe, K, Mn, Na, Ni, P, Se, Sn, Sr, Zn, and Mg) respectively and Table 3.3 shows the characteristics data of the calibration curves of elements using ICP-OES,

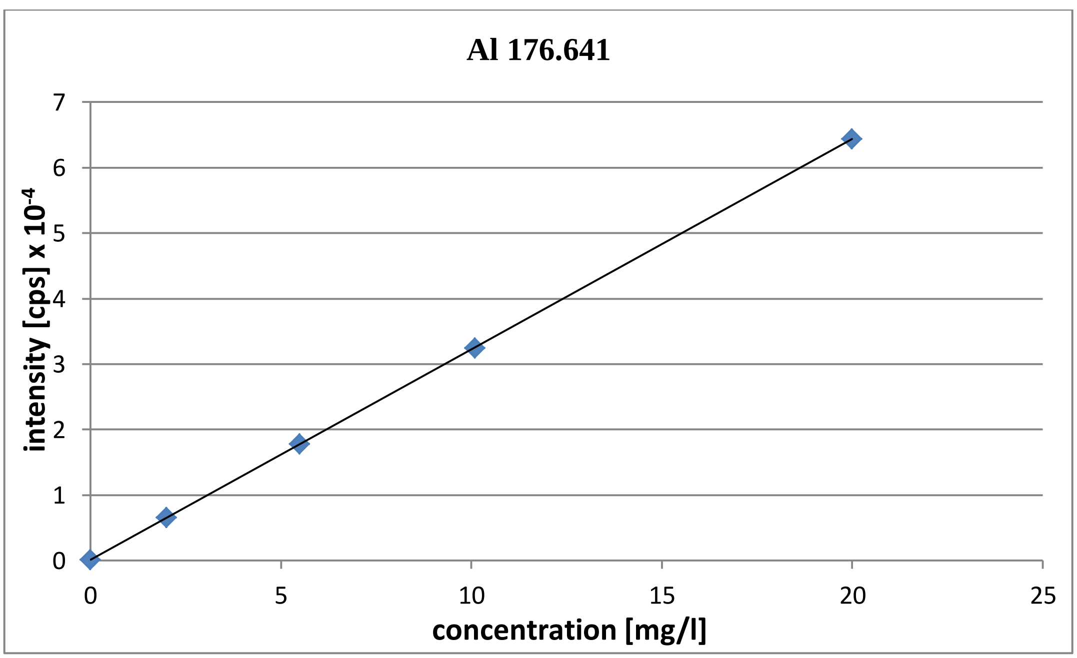

Figure 3.4. Calibration curve for Aluminum (Al) by ICP-OES

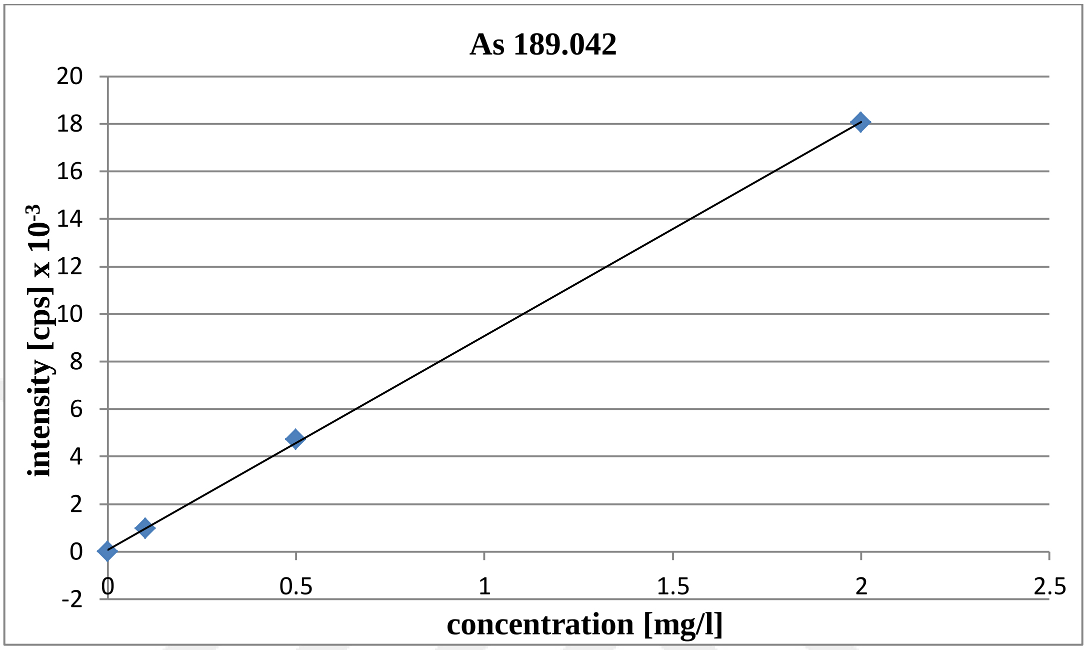

Figure 3.5. Calibration curve for Arsenic (As) by ICP-OES

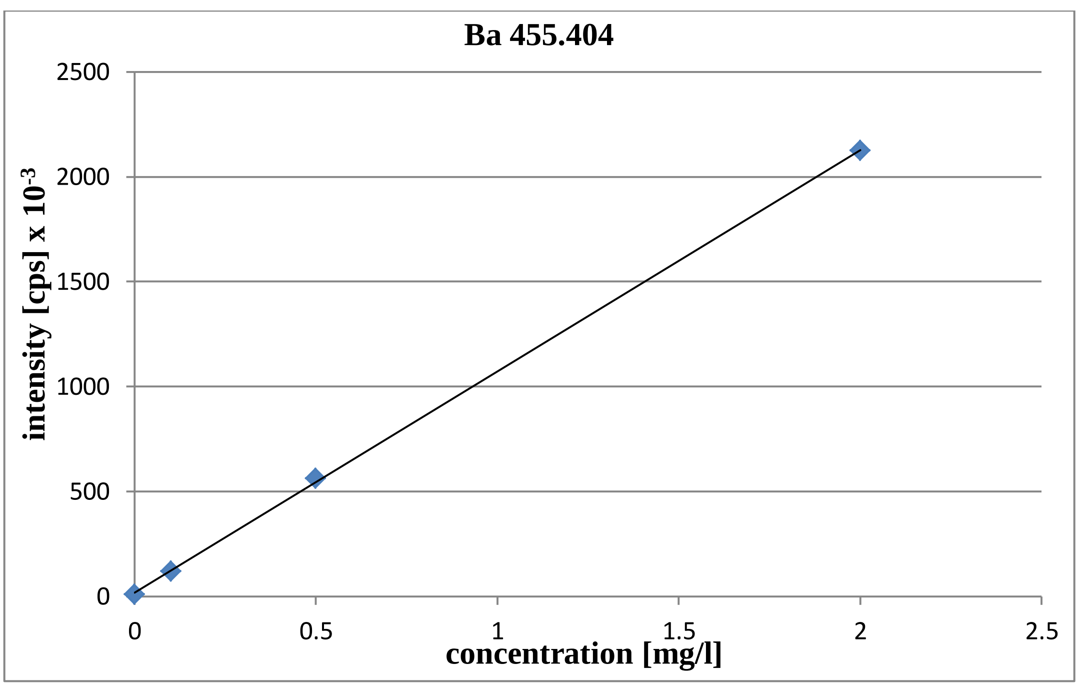

Figure 3.6. Calibration curve for Barium (Ba) by ICP-OES

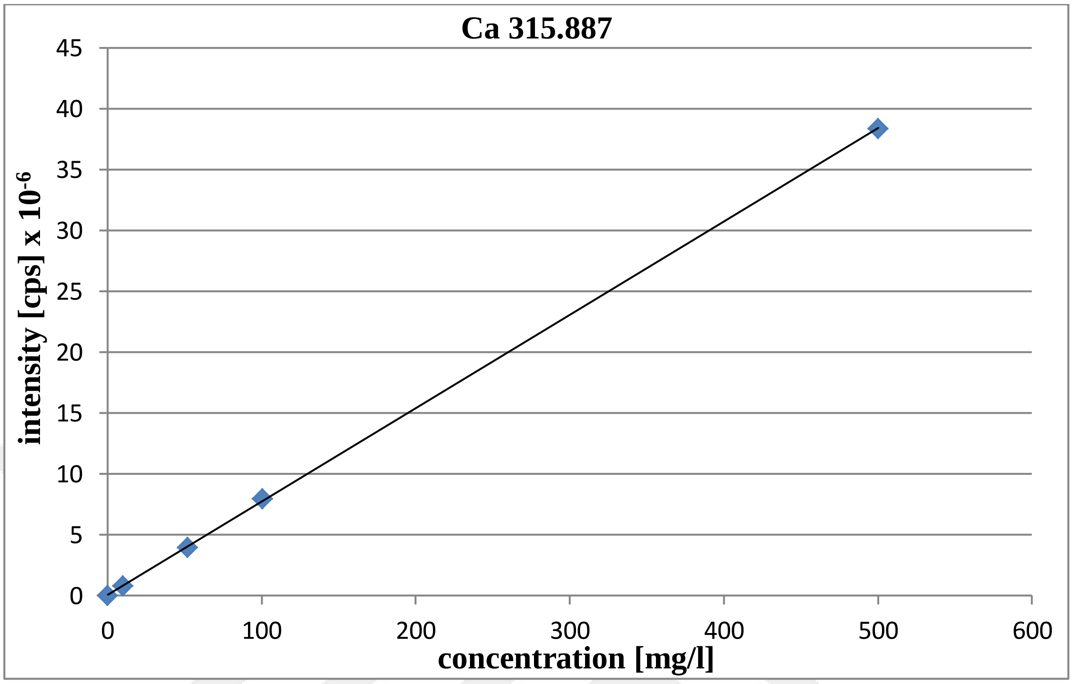

Figure 3.7. Calibration curve for Calcium (Ca) by ICP-OES

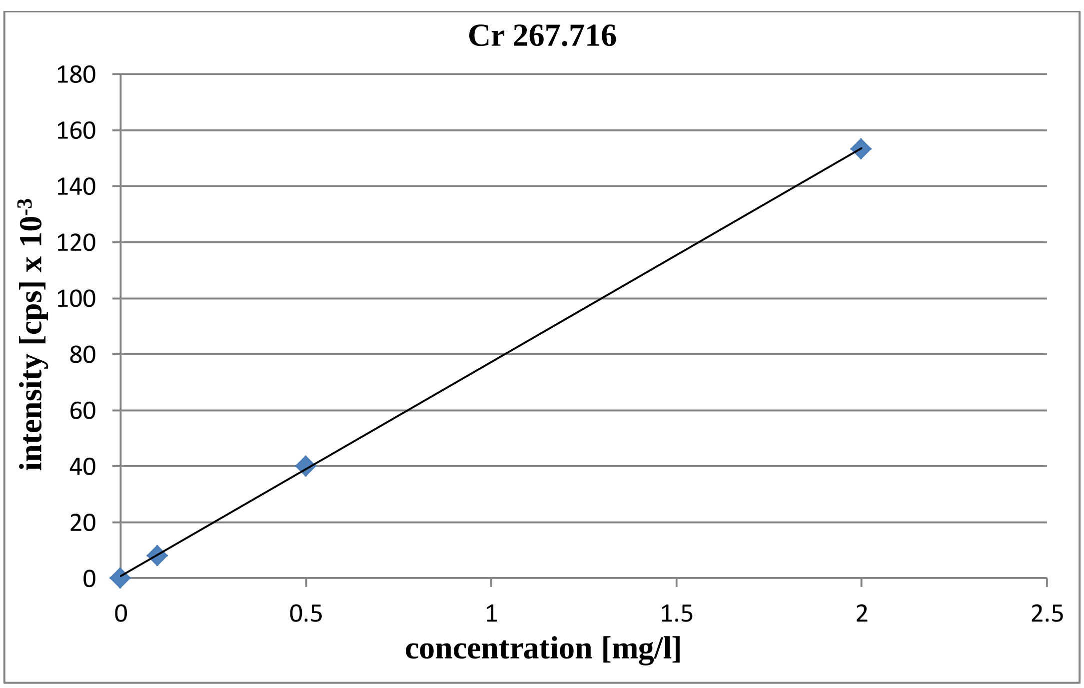

Figure 3.8. Calibration curve for Chromium (Cr) by ICP-OES

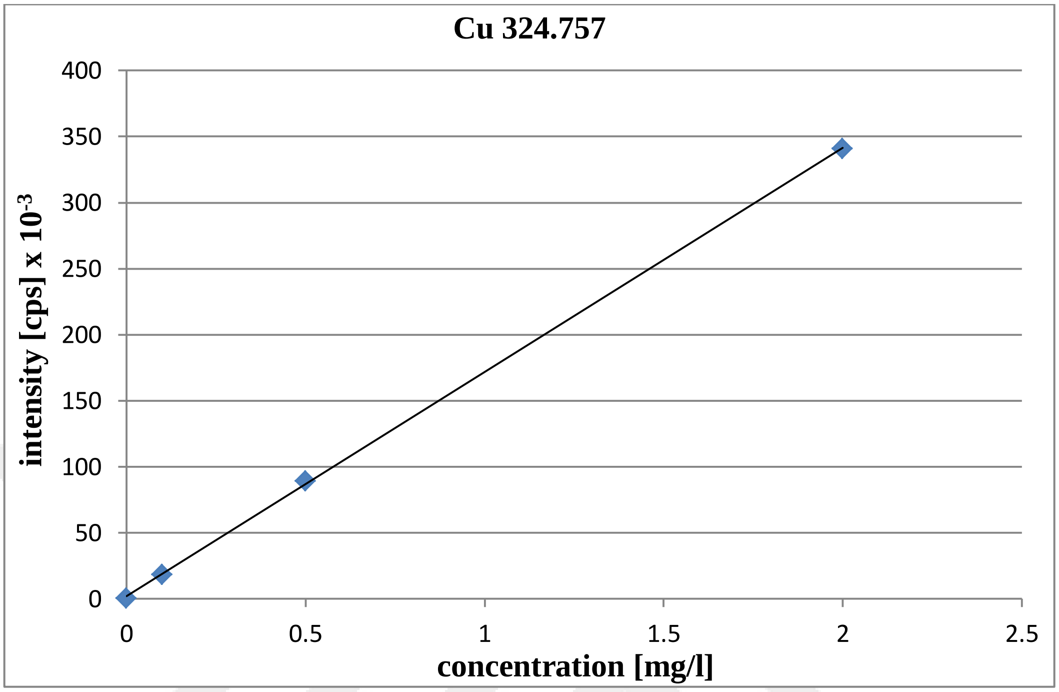

Figure 3.9. Calibration curve for Copper (Cu) by ICP-OES

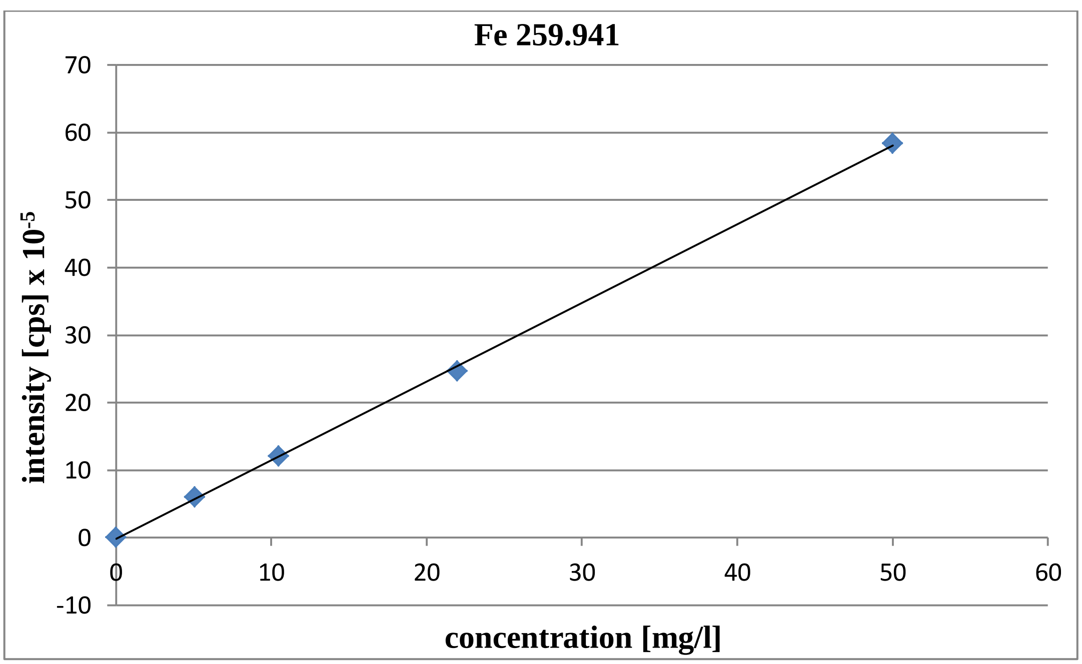

Figure 3.10. Calibration curve for Iron (Fe) by ICP-OES

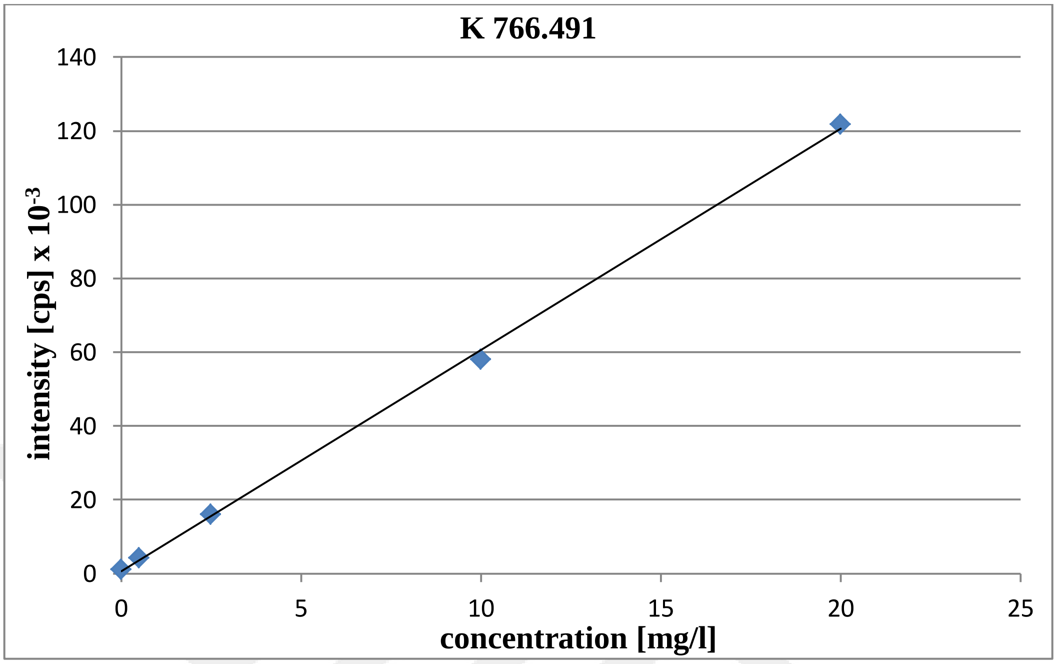

Figure 3.11. Calibration curve for Potassium (K) by ICP-OES

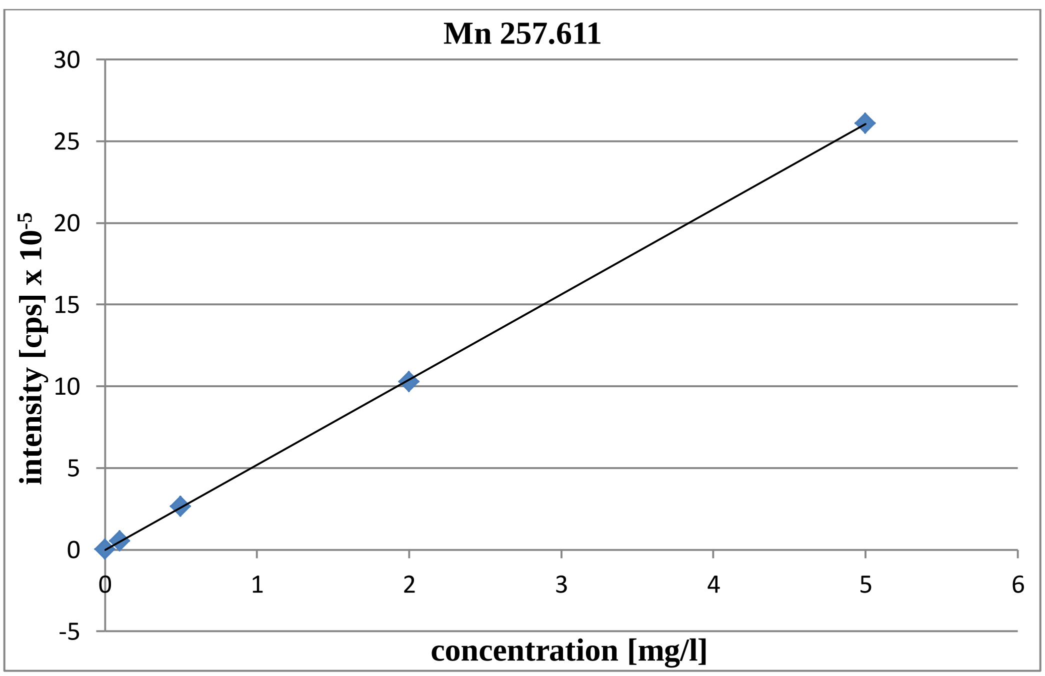

Figure 3.12. Calibration curve for Manganese (Mn) by ICP-OES

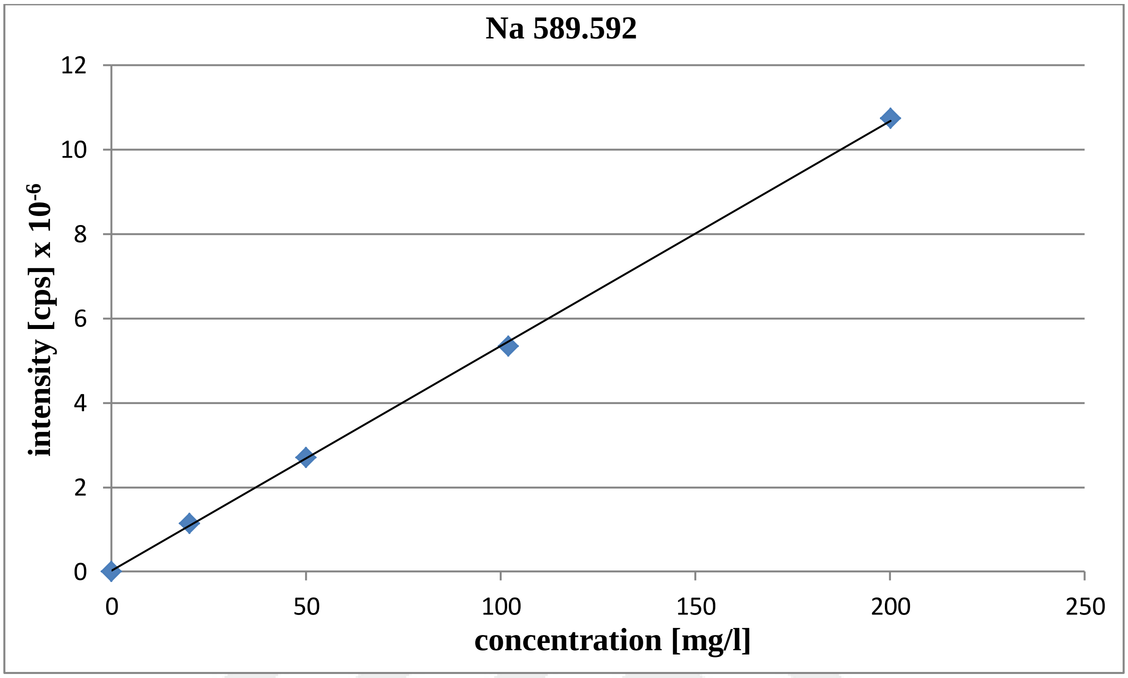

Figure 3.13. Calibration curve for Sodium (Na) by ICP-OES

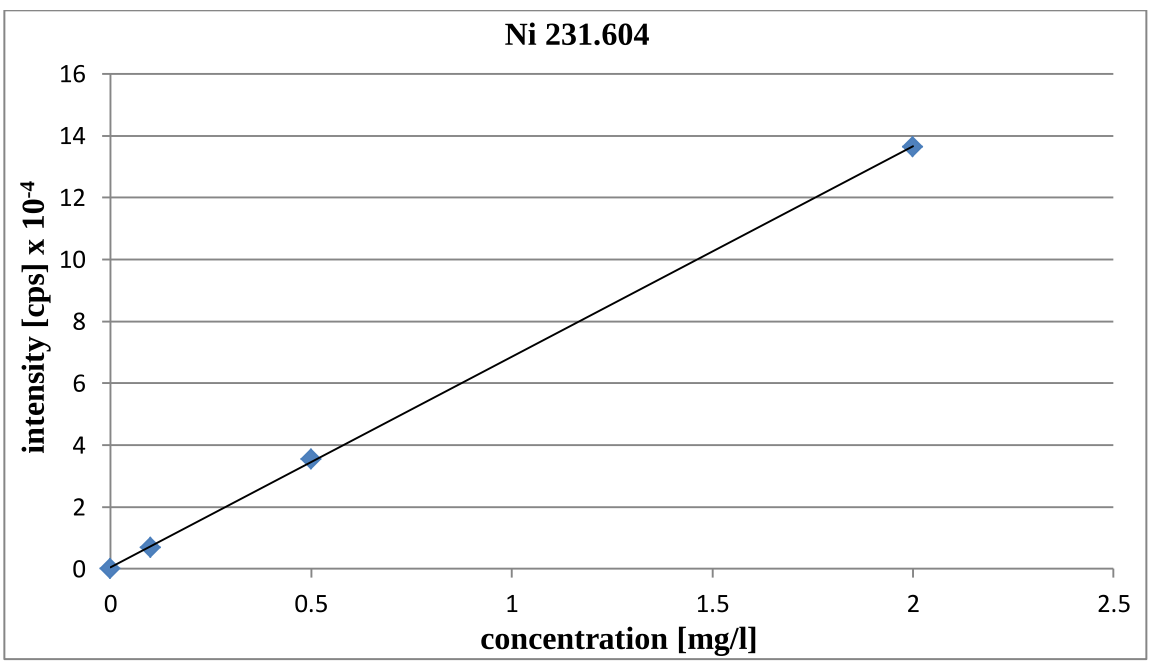

Figure 3.14. Calibration curve for Nickel (Ni) by ICP-OES

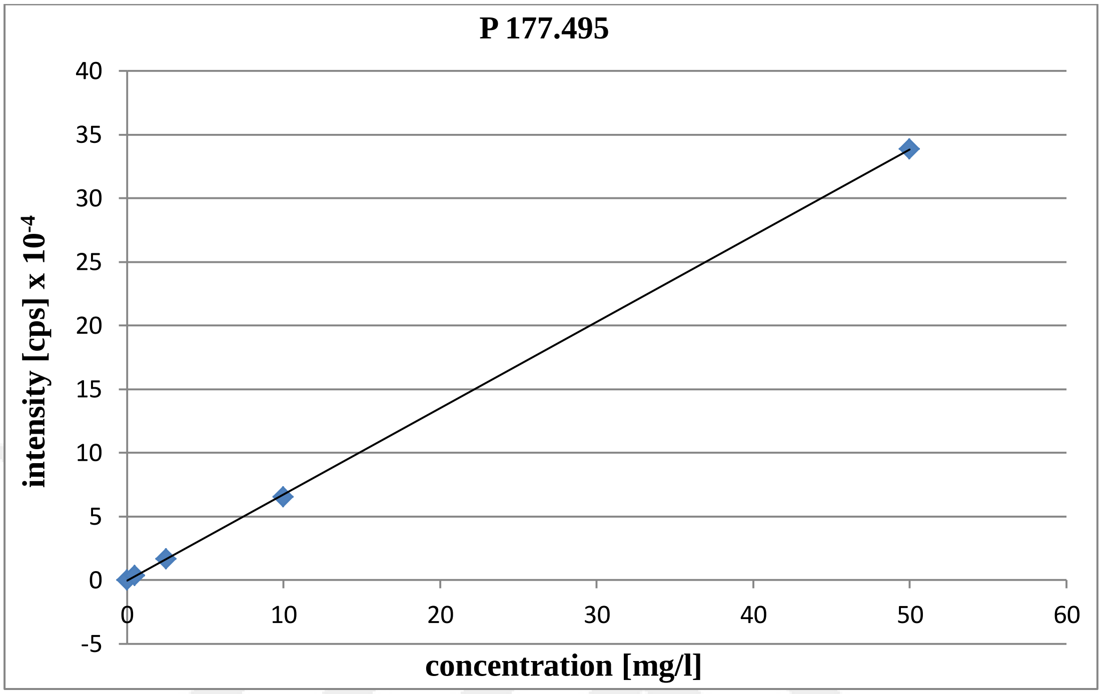

Figure 3.15. Calibration curve for Phosphorus (P) by ICP-OES

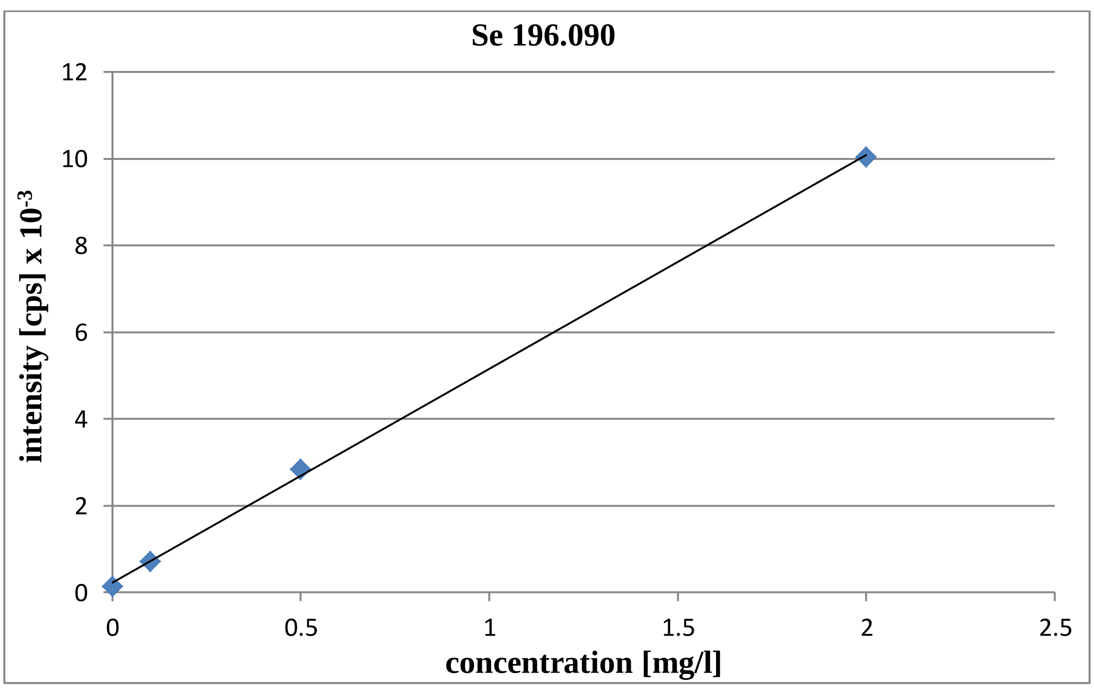

Figure 3.16. Calibration curve for Selenium (Se) by ICP-OES

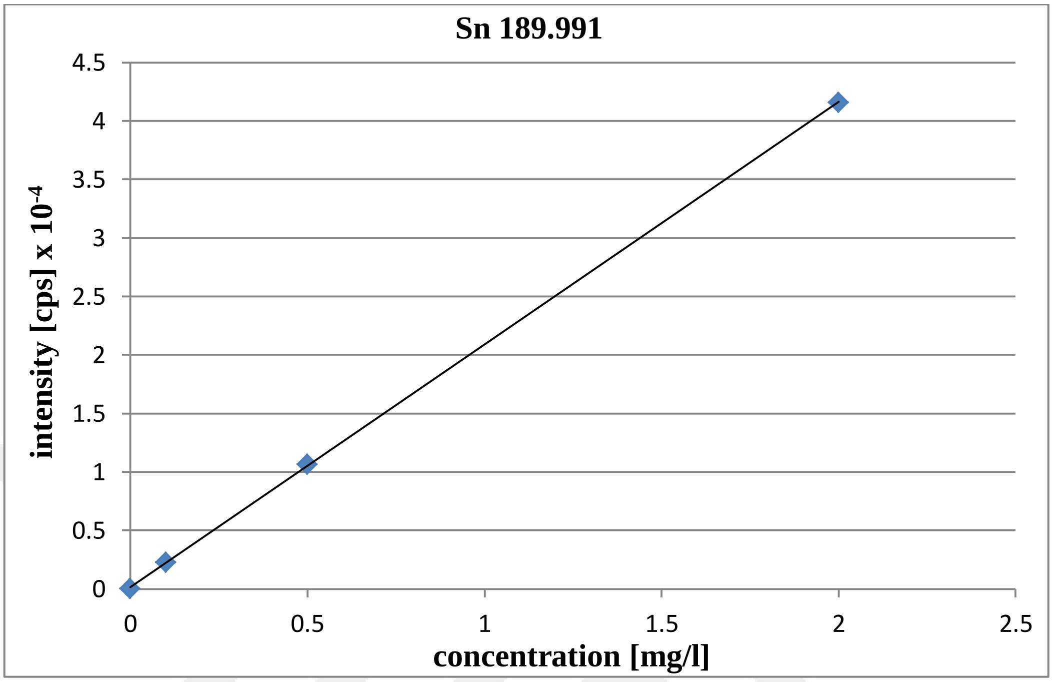

Figure 3.17. Calibration curve for Tin (Sn) by ICP-OES

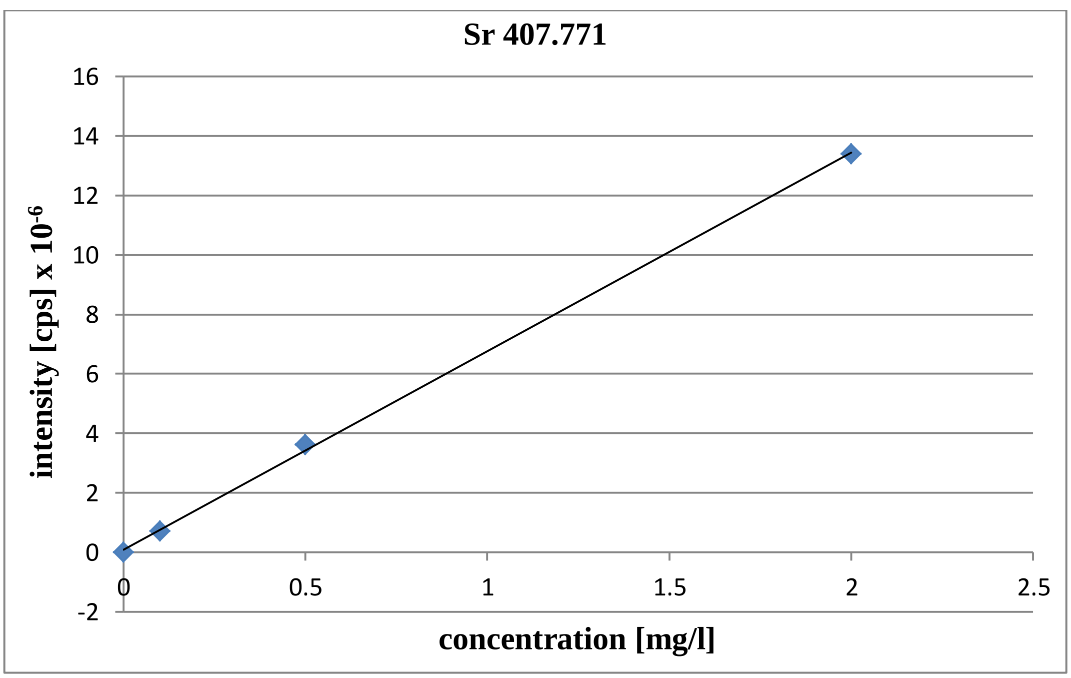

Figure 3.18. Calibration curve for Strontium (Sr) by ICP-OES

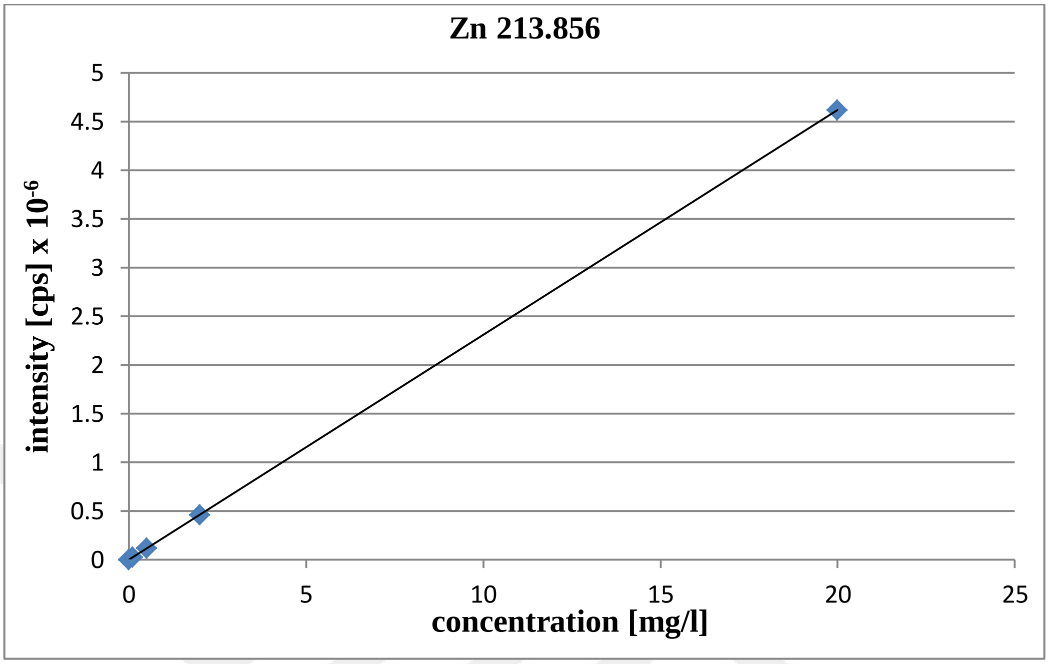

Figure 3.19. Calibration curve for Zinc (Zn) by ICP-OES

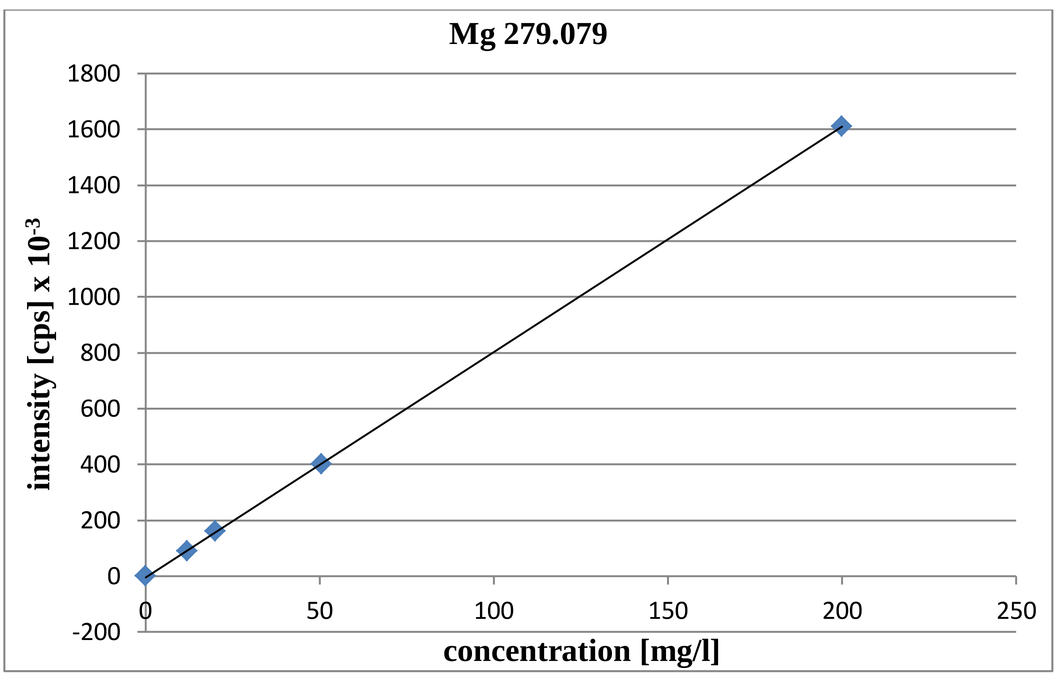

Figure 3.20. Calibration curve for Magnesium (Mg) by ICP-OES

Table 3.3. Characteristics data of the calibration curves of elements using ICP-OES

Elements	Equation	R^2	Wave length(nm)	Linear range ($mg.L^{-1}$)	DL ($mg.L^{-1}$)
Al	y = 3.2113x + 0.1235	1.00000	176.641	0.00355 – 24	0.00355
As	y = 9.0001x + 0.0804	0.99994	189.042	0.00264 - 2.4	0.00264
Ba	y = 1055.1x + 16.513	0.99994	455.404	0.000441- 2.4	0.000441
Ca	y = 0.0767x + 0.0524	0.99998	315.887	0.00419 – 600	0.00419
Cr	y = 76.47x + 0.6904	0.99993	267.716	0.000457 - 2.4	0.000457
Cu	y = 169.69x + 2.0525	0.99995	324.754	0.00126 - 2.4	0.00126
Fe	y = 0.1165x - 0.0181	0.99982	259.941	0.00145 – 60	0.00145
K	y = 5.9976x + 0.7163	0.99957	766.491	0.0316 – 24	0.0316
Mn	y = 0.5213x - 0.0009	0.99997	257.611	0.000226 – 6	0.000226
Na	= 0.053x + 0.0606	0.99987	589.592	0.0552 – 240	0.0552
Ni	y = 68.03x + 0.4872	0.99996	231.604	0.000974 - 2.4	0.000974
P	y = 6.7779x - 0.5846	0.99998	177.495	0.00245 – 60	0.00245
Se	y = 4.9216x + 0.2345	0.99976	196.090	0.0087 - 2.4	0.0087
Sr	y = 6.6695x + 0.0972	0.99978	407.771	9.63e-005 - 2.4	9.63e-005
Sn	y = 20.731x + 0.1671	0.99998	189.991	0.00194 - 2.4	0.00194
Zn	y = 0.2307x + 0.0011	1.00000	213.856	0.000633 – 24	0.000633
Mg	y = 0.0081x - 0.0028	0.99999	279.079	0.00576 – 240	0.00576

3.6. Statistical Analysis

The data of the study was statistically analyzed using statistical package for social science (SPSS, Version 16), which is a software package used for statistical analysis. The obtained data was expressed as (Mean ±St Dev). Differences in mean values of each element in all six coffee samples were analyzed by one-way ANOVA and Duncan test and relationships between concentrations of the elements in analyzed coffees were assessed by using the Pearson's linear correlation coefficient. The probably level of P - value ($P < 0.05$) level of significant was considered to be statistically significant.

4. RESULTS AND DISCUSSION

4.1. Concentration of Elements in Analyzed Coffee Samples

In this study, concentration of 17 elements (Al, As, Ba, Ca, Cr, Cu, Fe, K, Mn, Na, Ni, P, Se, Sr, Sn, Zn and Mg) were determined in coffee samples by inductively coupled plasma optical emission spectroscopy (ICP-OES). According to the obtained results in this study the measured elements can be classified into three main group, due to their concentration, the first group will be named as macro or essential element because their concentrations are too high in coffee as compared to other elements and include five elements which are (Ca, K, Na, P and Mg), the concentration trend of macro elements were fund to be as follows: K > Mg > Na > P > Ca.

Coffee beverages are one of the important sources of some micro elements like Mn, Zn and Cu which are necessary for the metabolic processes in human. Second group of elements determined in coffee in present were some micro elements and including elements like (Zn, Al, Cu, Ba, Sr, Fe, and Mn). The order of mean concentrations of the micro elements in all analyzed coffee samples was found to be: Sr> Mn> Fe> Al> Ba> Cu> Zn.

The third and final group of elements determined is trace elements in which coffee samples contain some essential trace elements like Ni, Cr, and Se which are essential nutrients that are cofactors for the metabolism and some other biological processes. Trace elements like (Ni, As, Se Cr, and Sn) were determined in coffee samples in present study, among trace elements, Se is the highest concentration followed by Ni, Cr, Sn and As. The analysis results of the coffee samples for all the elements studied are given in Table 4.1 as mg/l.

Table 4.1. Concentrations (mean ± standard deviation) in (mg/l) of elements in six coffee samples

	CB	CC	CE	CG	CK	CY
Al	3.633 ±0.160	4.250±0.050	2.950±0.100	2.950±0.132	4.500±0.450	4.583±0.104
As	0.166±0.076	0.116±0.125	0.050±0.043	0.050±0.000	0.083±0.028	0.083±0.057
Ba	0.933±0.028	6.916±0.028	3.200±0.050	6.450±0.050	3.983±0.057	1.300±0.000
Ca	283.82±14.07	306.87±17.25	243.93±9.93	298.03±10.97	310.88±14.54	334.73±9.70
Cr	0.066±0.0763	0.300±0.100	0.116±0.057	0.050±0.025	0.083±0.028	0.150±0.050
Cu	2.850±0.100	3.266±0.202	2.916±0.076	2.966±0.104	3.016±0.125	3.333±0.076
Fe	5.166±0.650	7.033±0.828	5.183±0.664	5.533±0.505	7.100±0.785	8.100±0.427
K	10357±21	10012±161	10723±68	11635±154	9360±83	10964±216
Mn	11.667±0.562	13.483±0.825	7.283±0.404	12.650±0.541	14.617±0.709	14.000±0.436
Na	302.82±3.87	293.45±1.89	240.73±4.58	333.42±2.60	294.57±1.80	353.38±0.65
Ni	0.150±0.050	0.333±0.076	<DL	0.016±0.028	0.216±0.028	0.366±0.028
P	295.27±12.82	299.73±10.38	325.98±14.84	251.07±5.09	342.38±11.98	283.67±6.23
Se	0.616±0.125	0.700±0.229	0.533±0.125	0.450±0.132	0.733±0.057	0.633±0.160
Sn	0.066±0.076	0.133±0.763	0.083±0.028	0.100±0.050	0.083±0.057	0.150±0.000
Sr	9.583±0.029	16.783±0.252	9.733±0.126	15.767±0.104	12.967±0.076	11.183±0.208
Zn	2.266±0.175	2.816±0.175	1.900±0.132	2.416±0.104	3.250±0.180	3.050±0.132
Mg	463.48±18.64	455.35±25.14	420.63±21.24	447.75±16.50	500.77±24.18	493.60±14.08

4.2. Comparison of Elemental Content of Coffee Samples

Generally, the chemical composition of the coffee is mostly related to the origin in which the coffee plants grown. The primary factor connected with the elements is the soil conditions, variety of the coffee, and the methods of cultivation of the coffee plants [73]. Procedures included in the green and roasted coffee beans processing or even the methods of the brewing of the coffee are also important [62]. In this study we measured elemental content of six different coffee samples from six different countries (Brazil. Colombia, Ethiopia, Guatemala, Kenya and Yemen). The obtained results show significant difference for elemental content for different coffee samples. Figure 4.1, Figure 4.2, Figure 4.3, Figure 4.4, Figure 4.5, Figure 4.6, Figure 4.7, Figure 4.8, Figure 4.9, Figure 4.10, Figure 4.11, Figure 4.12, Figure 4.13, Figure 4.14, Figure 4.15, Figure 4.16, and Figure 4.17) shows the difference among these coffee samples in the content of (Ca, K, Na, P, Mg, Al, Ba, Cu, Fe, Mn, Sr, Zn, As, Cr, Ni, Se and Sn) respectively.

Figure 4.1 shows that the highest value for calcium (Ca) content was observed for (CY) with concentration of 334.73 mg/l and the lowest was CE with concentration of 243.93 mg/l. Figure 4.2 shows that the highest value for potassium (K) content was observed for CG (11635 mg/l), and the lowest amount observed for CK with concentration of 9360 mg/l. highest concentration for sodium (Na) as shown in Figure 4.3 observed in CY (353.38 mg/l) and lowest sodium content for CE (240.73 mg/l), the highest concentration of phosphorus (P) and magnesium (Mg) as shown in Figure 4.4 and 4.5 obtained in CK with concentration of (342.38 and 500.77 mg/l) and the lowest amount observed in CG (251.07 mg/l) and CE (420.63) for P and Mg respectively.

For micro elements CY contains highest amount of aluminum (Al), copper (Cu), and iron (Fe) with concentration of 4.5833, 3.3333, and 8.1 mg/l respectively as shown in Figure 4.6, 4.8, and 4.9, and lowest amount found in each of CE, CG for Al (2.95 mg/l), CB for Cu (2.85 mg/l), and Fe (5.1667 mg/l), while CC contains highest amount of both barium (Ba) and strontium (Sr) with concentration of (6.9167 and 16.783 mg/l) respectively as shown in Figure 4.7 and 4.11, and CB contains lowest concentrations for both elements (0.9333 mg/l) for Ba and (9.583 mg/l) for Sr. highest amount of manganese (Mn) and zinc (Zn) were observed in CK as shown in Figure 4.10 and 4.12 with concentration of (14.617 and 3.25 mg/l) and the lowest concentration observed in CE for both elements (7.283 mg/l) for Mn and (1.9 mg/l) for Zn.

In the results obtained for trace elements CY contains the highest amount of chromium (Cr), nickel (Ni), and tin (Sn) with concentration of (0.15, 0.36667, and 0.15 mg/l) respectively as shown in Figure 4.14, 4.15, and 4.17, while the minimum concentration observed in CG for Cr (0.05 mg/l), CE for Ni (<DL), and CB for Sn (0.06667 mg/l). Highest arsenic (As) amount were found in CB (0.16667 mg/l) while lowest arsenic observed in CE and CG (0.05 mg/l) as shown in Figure 4.13. CK contains highest amount of selenium (Se) 0.7333 mg/l and lowest amount were found in CG 0.45mg/l as shown in Figure 4.16.

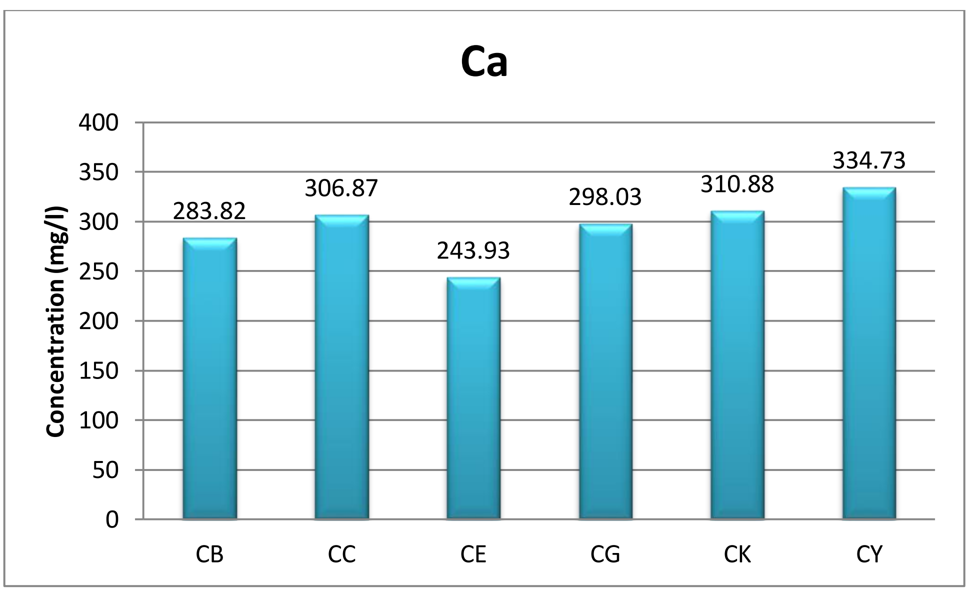

Figure 4.1. Calcium levels in different coffee samples

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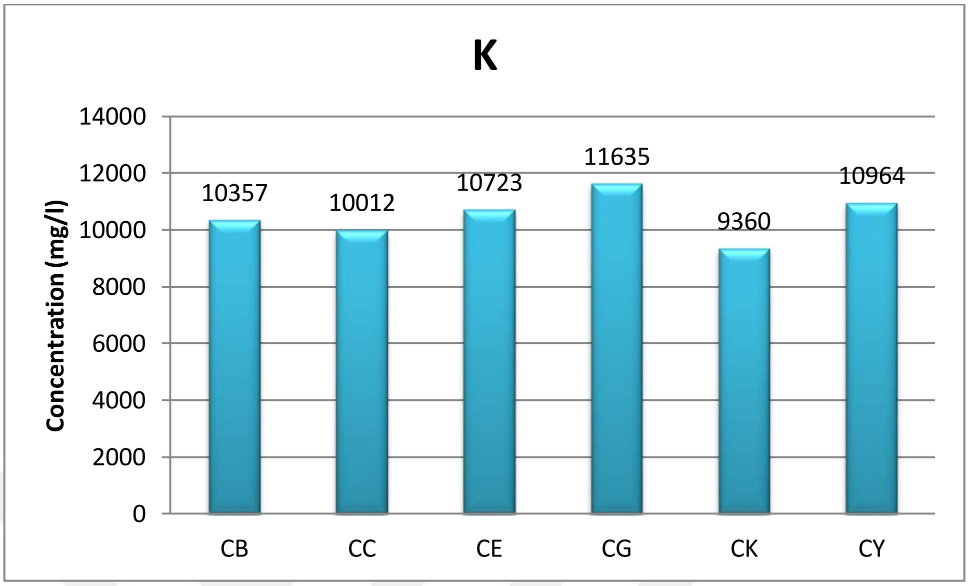

Figure 4.2. Potassium levels in different coffee samples

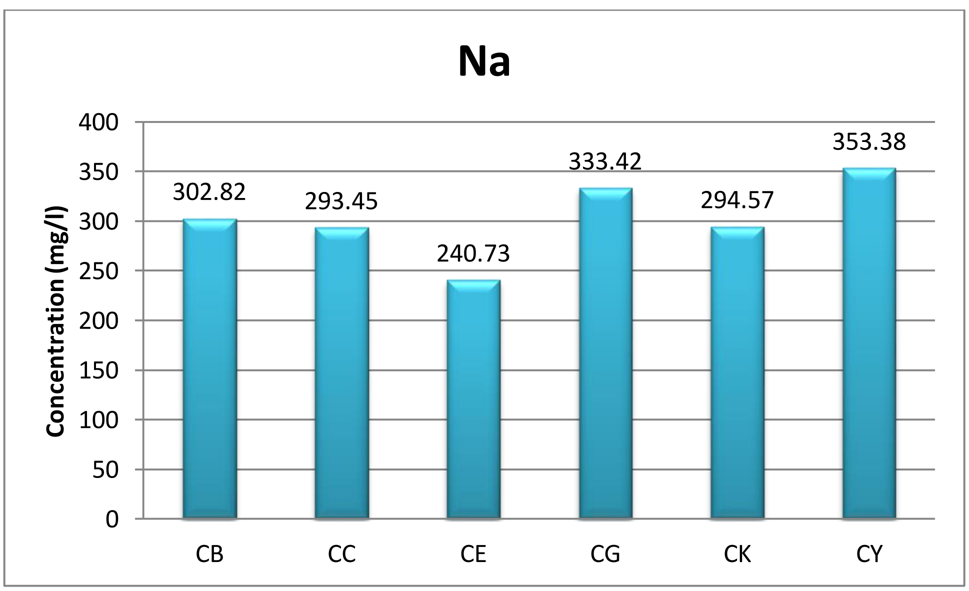

Figure 4.3. Sodium levels in different coffee samples

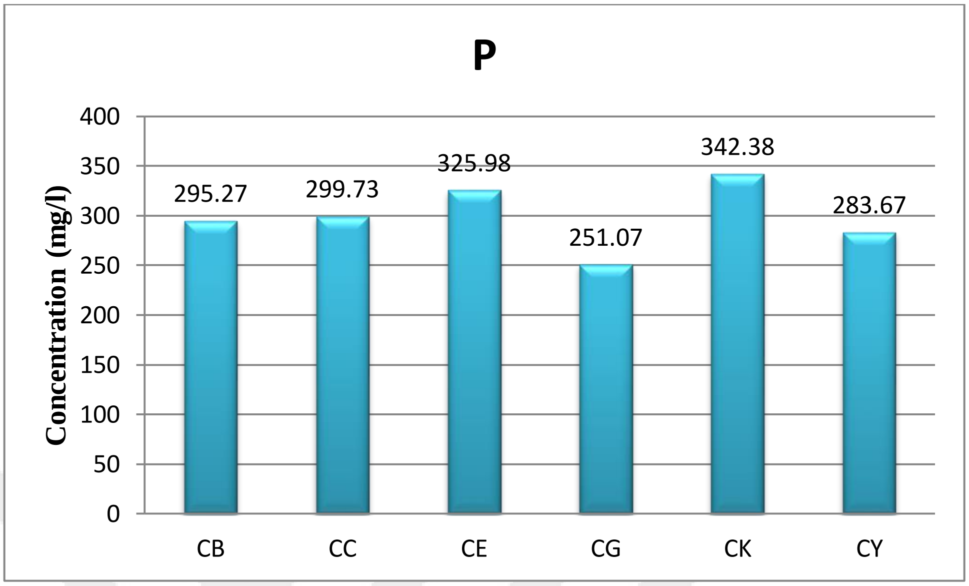

Figure 4.4. Phosphorus levels in different coffee samples

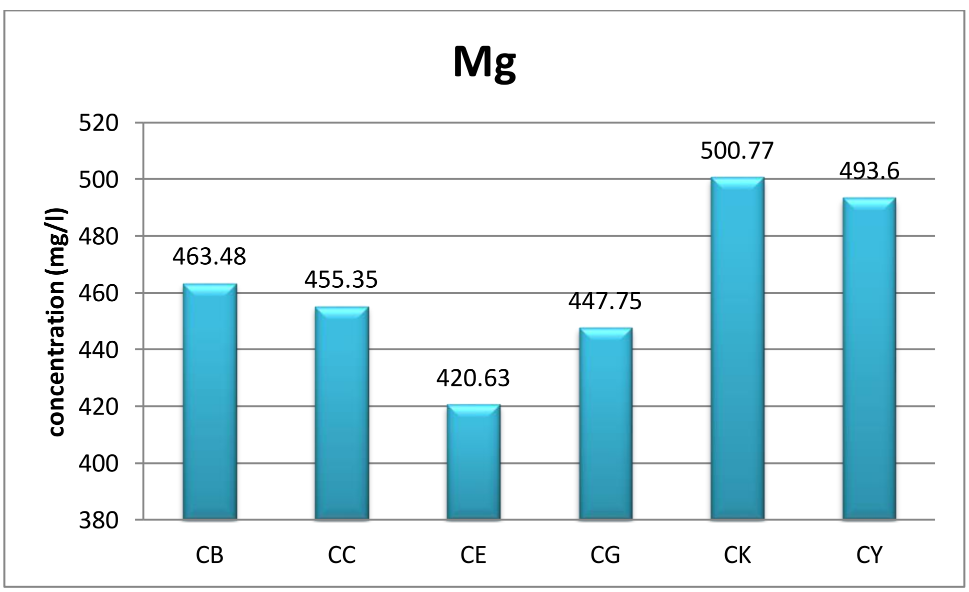

Figure 4.5. Magnesium levels in different coffee samples

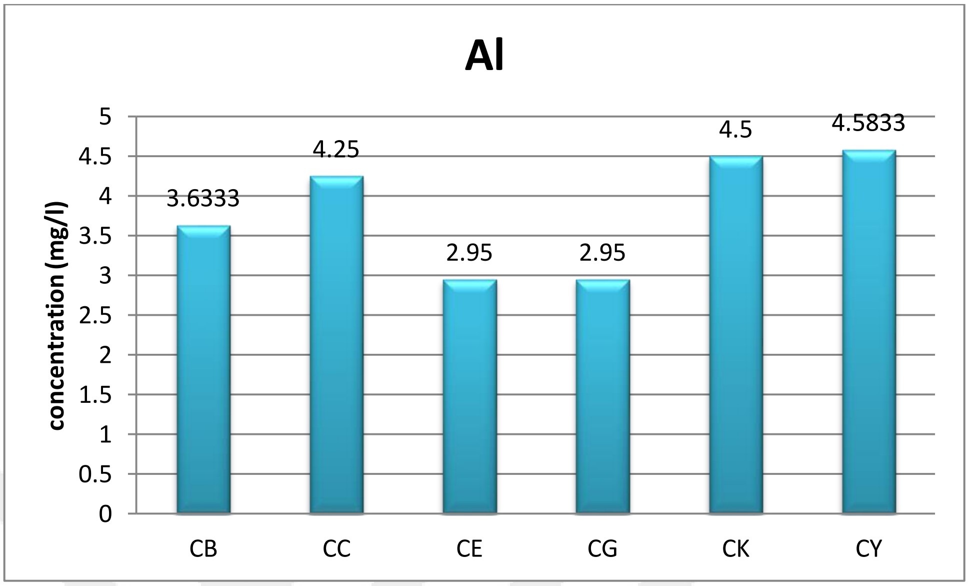

Figure 4.6. Aluminum levels in different coffee samples

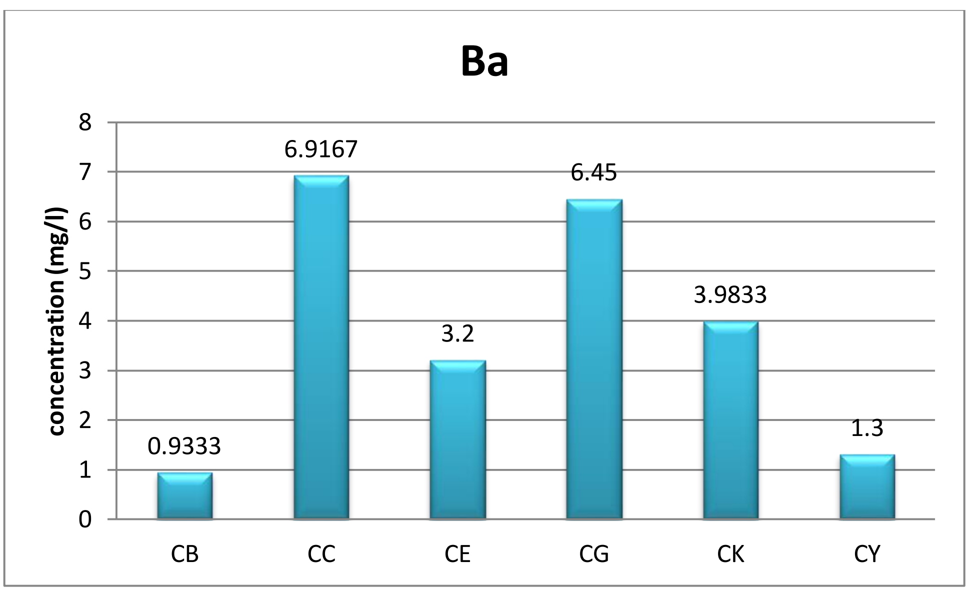

Figure 4.7. Barium levels in different coffee samples

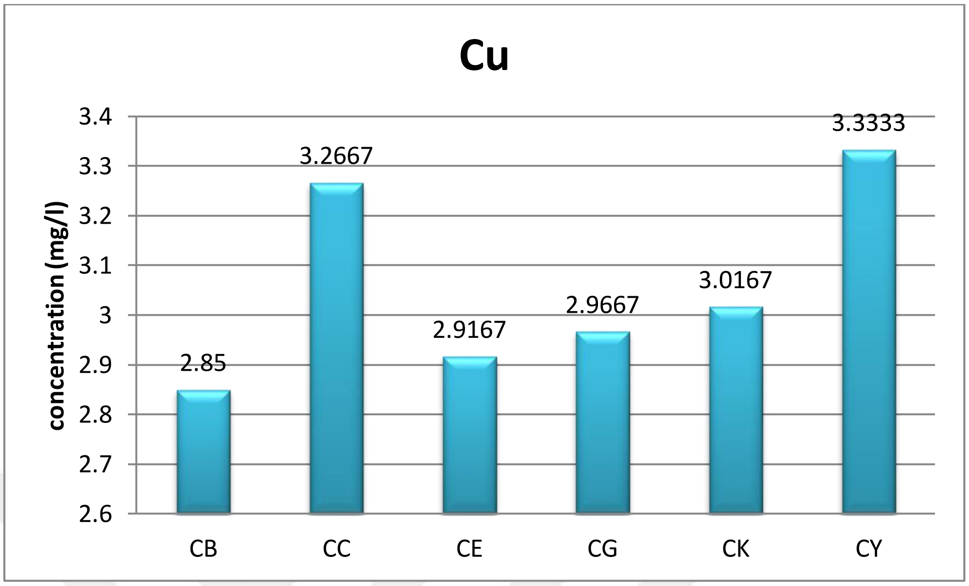

Figure 4.8. Copper levels in different coffee samples

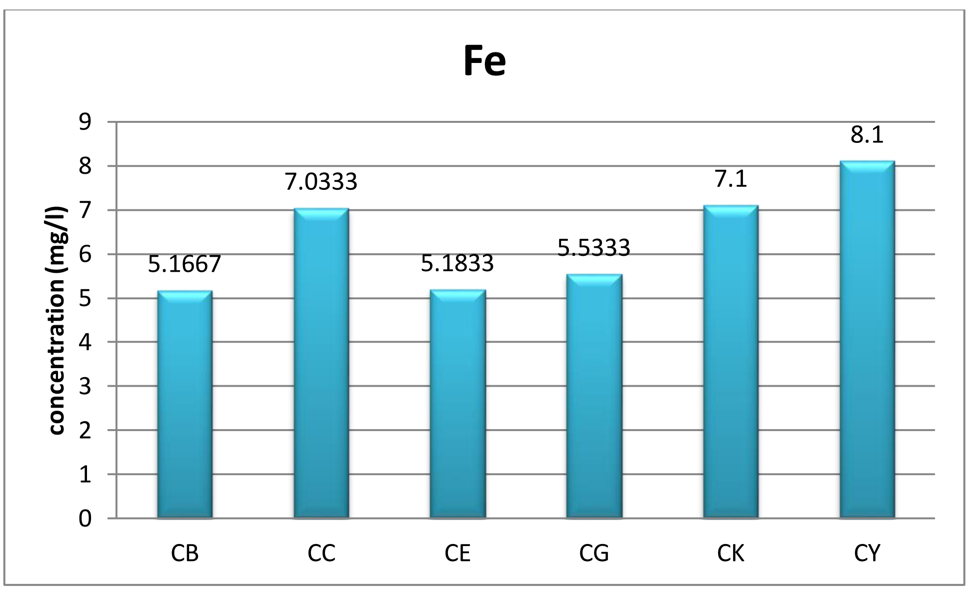

Figure 4.9. Iron levels in different coffee samples

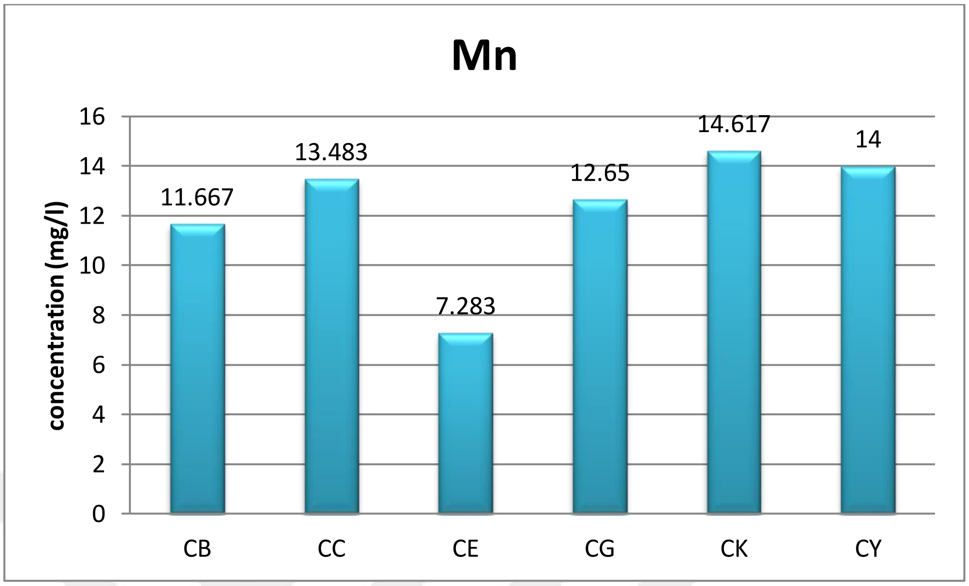

Figure 4.10. Manganese levels in different coffee samples

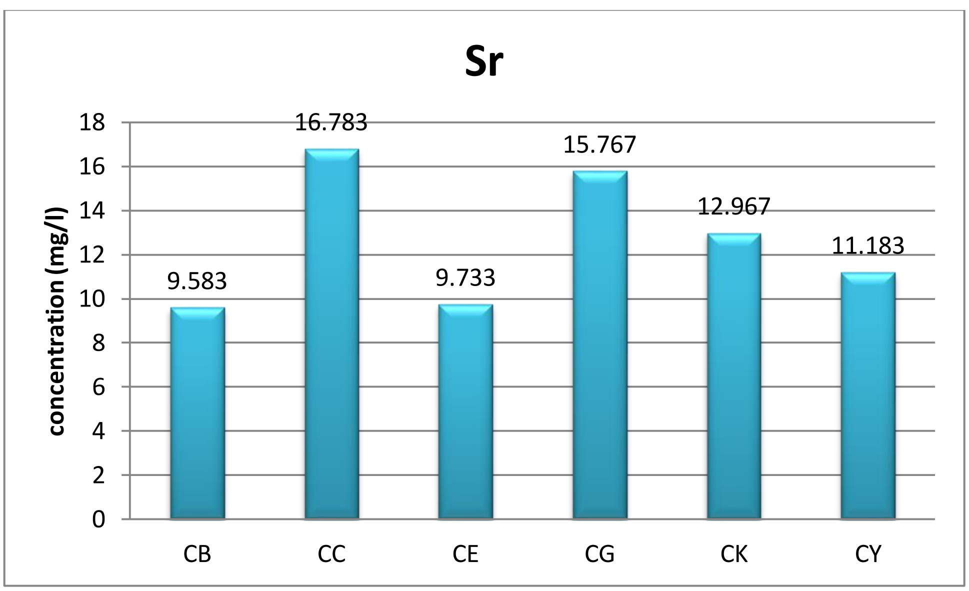

Figure 4.11. Strontium levels in different coffee samples

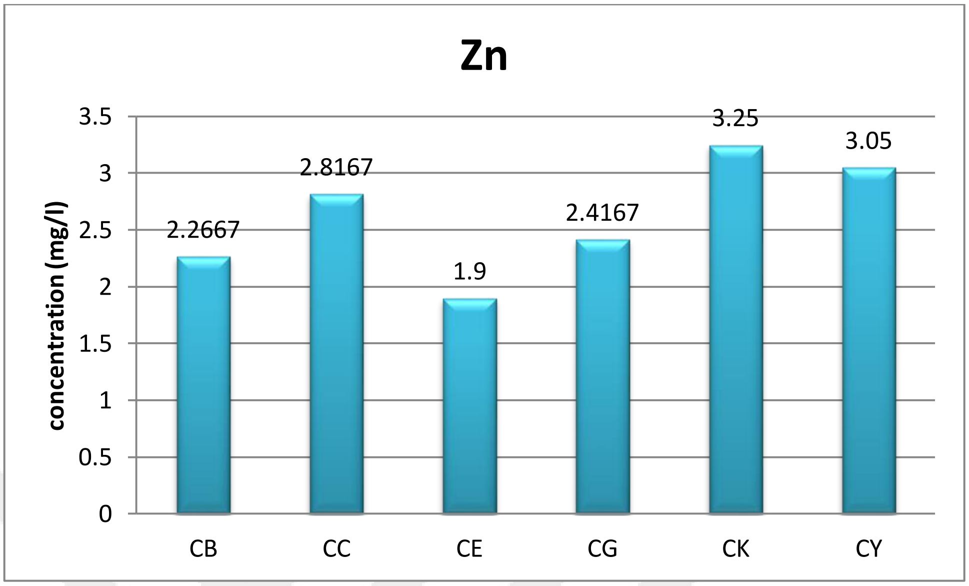

Figure 4.12. Zinc levels in different coffee samples

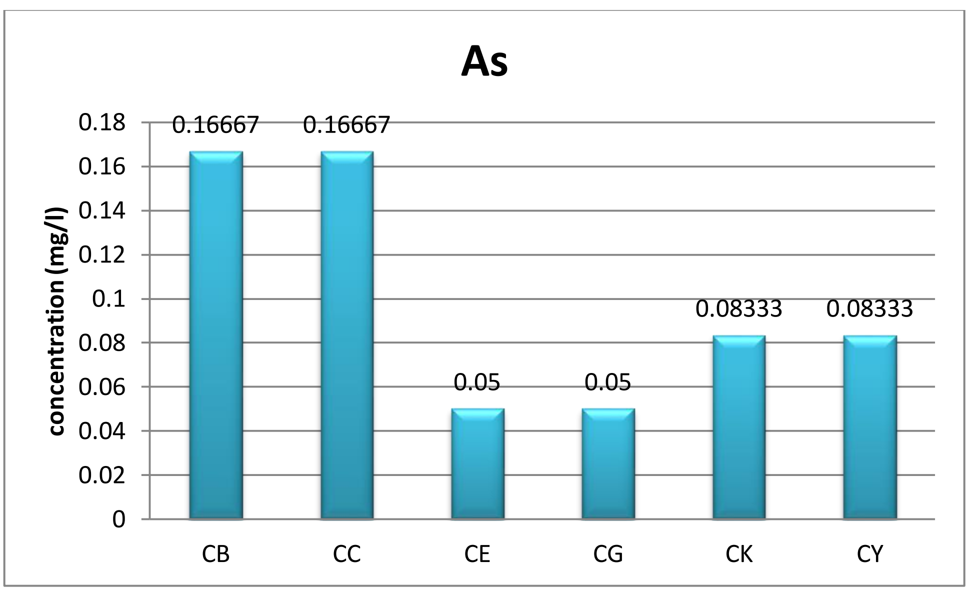

Figure 4.13. Arsenic levels in different coffee samples

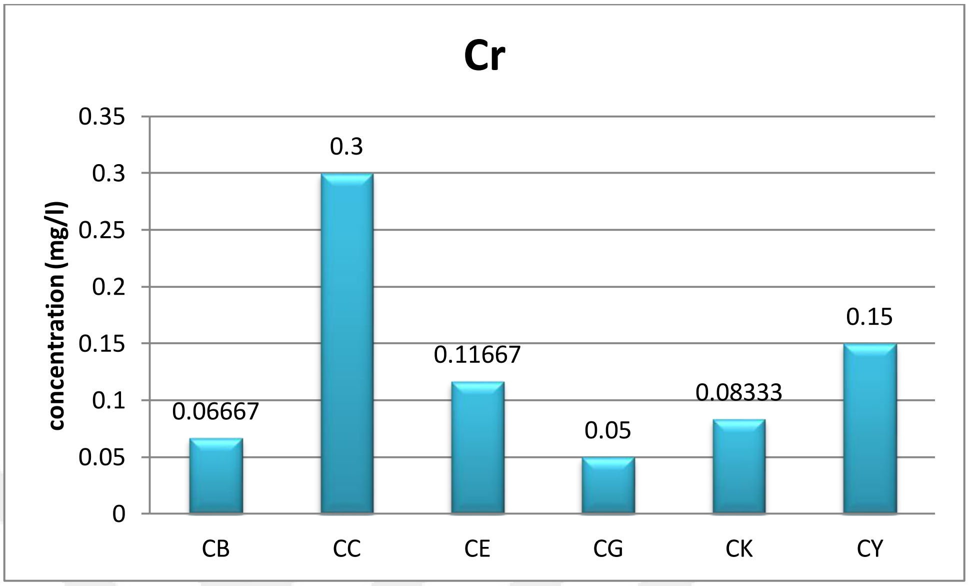

Figure 4.14. Chromium levels in different coffee samples

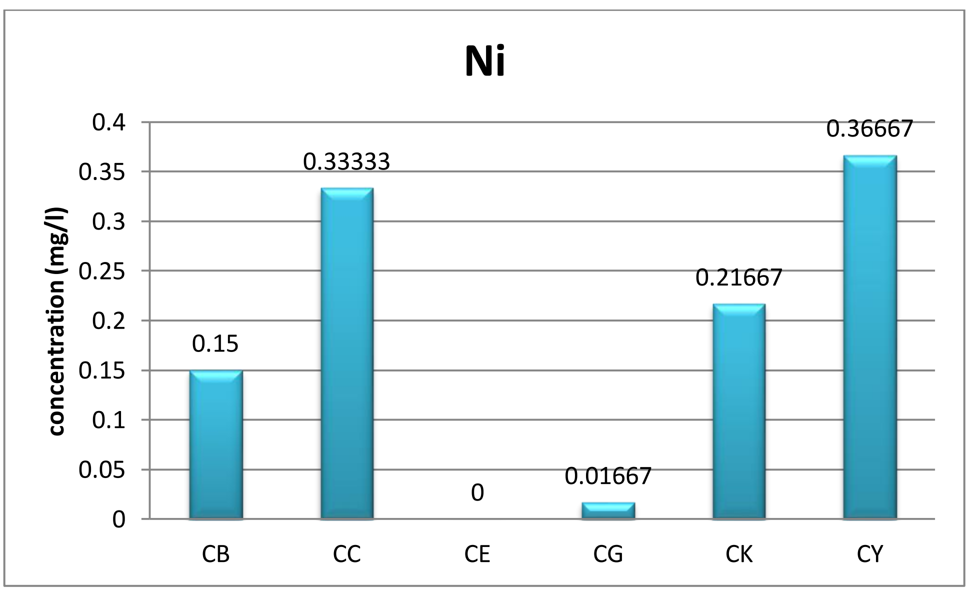

Figure 4.15. Nickel levels in different coffee samples

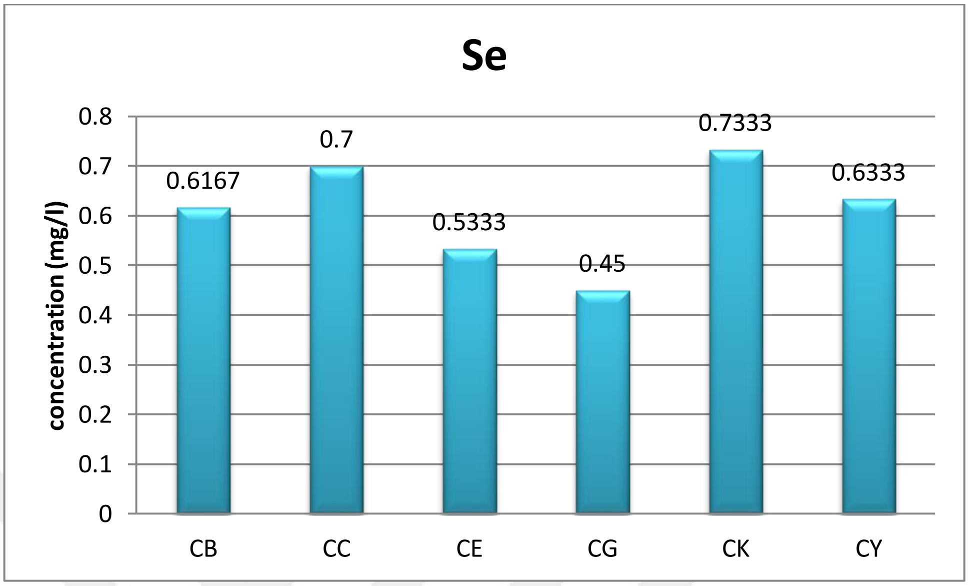

Figure 4.16. Selenium levels in different coffee samples

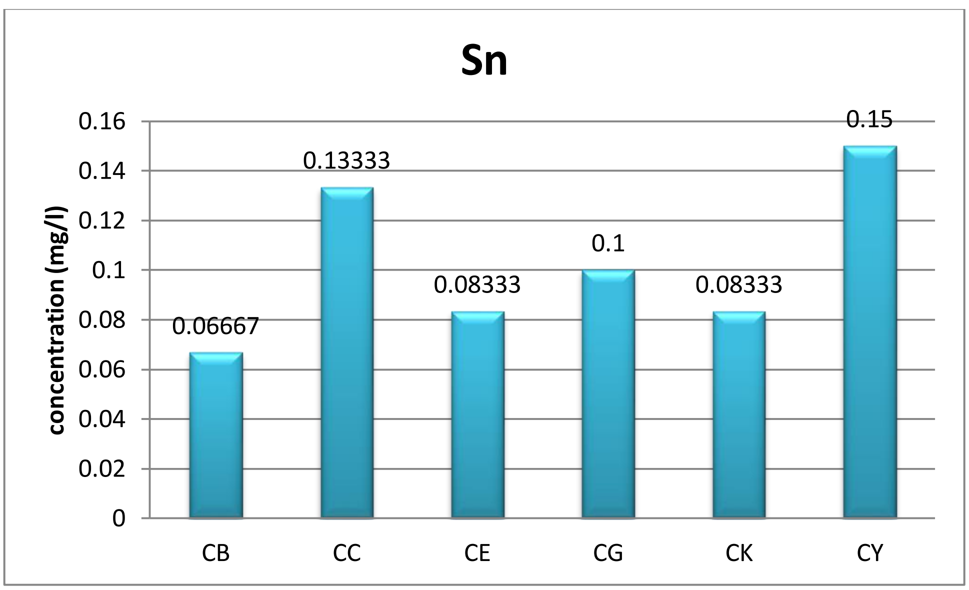

Figure 4.17. Tin levels in different coffee samples

4.3. Comparison of Elemental Content of Coffee Samples with Other Reported Values

Here we compared the results obtained in present study to previous studies have been done on coffee in the world; in general the results that obtained in this study showed good agreement with most of the reported values except for some of the macro elements in which the results obtained here is slightly lower than previous reported values. Table 4.2, Table 4.3, and Table 4.4 shows comparison between macro, micro and trace elements in this study with some other previous studies have been done on different coffee samples.

Concentrations of calcium, potassium, sodium, magnesium, iron, and nickel in coffee samples obtained in present study were lower than the reported values by Krivan et al. 1993 [70], Santos et al. 2008 [87], Martin et al. 1999 [88], and Sussela et al. 2001 [92]. Concentrations of sodium (Na) in present study were higher than the reported values by Tagliaferro et al. 2007 [91], and Anderson and Smith 2002 [73].

Amount of phosphorus (P), aluminum (Al), barium (Ba), copper (Cu), manganese (Mn), zinc (Zn), arsenic (As), chromium (Cr), and selenium (Se) found in coffee samples in present study as showed in Table 4.2, Table 4.3, and Table 4.4 were in good agreements with the values reported previously, while concentration of strontium (Sr) obtained in present study were slightly higher than values that reported by Santos et al. 2008 [87], martin et al. 1999 [88], and sussela et al. 2001 [92].

Table 4.2. Comparison of the concentration of macro elements (Ca, K, Na, P, Mg) in coffee samples in present study with previous studies on coffee samples

Elements	Concentration (mg/l)	Reference
Ca	**243.93---334.73**	**Present study**
	490---2200	[73], [86], [81], [87], [90], [80], [62], [91], [92], [58]
K	**9360---11635**	**Present study**
	11400---29100	[73], [87], [88], [89], [80], [62], [91], [92], [58]
Na	**240.73---353.38**	**Present study**
	606---1467	[73], [88], [89], [90], [62], [91], [58]
P	**251.07---342.38**	**Present study**
	190---4030	[73], [87], [88], [62]
Mg	**420.63---500.77**	**Present study**
	750---3100	[73], [81], [87], [88], [90], [80],[62], [92], [58]

Table 4.3. Comparison of the concentration of micro elements (Al, Ba, Cu, Fe, Mn, Sr and Zn) in coffee samples in present study with previous studies on coffee samples

Elements	Concentration (mg/l)	Reference
Al	**2.95---4.5833**	**Present study**
	3---200	[85], [73], [86], [81], [87]
Ba	**0.9333---6.9167**	**Present study**
	0.8---10.1	[86], [87], [88], [89]
Cu	**2.85---3.3333**	**Present study**
	0.4---30.1	[73], [81], [87], [88], [80], [62], [92], [58]
Fe	**5.1667---8.1**	**Present study**
	12---617	[73], [81], [87], [88], [89], [90], [80], [62], [91], [92], [58]
Mn	**7.283---14.617**	**Present study**
	6.6---320	[73], [81], [87], [88], [89], [90], [80], [62], [92], [58]
Sr	**9.583---16.783**	**Present study**
	1.1---11.9	[87], [88], [92]
Zn	**1.9---3.25**	**Present study**
	1.2---803	[73], [86], [81], [87], [88], [89], [80], [62], [91], [92], [58]

Table 4.4. Comparison of the concentration of trace elements (As, Cr, Ni, Se) in coffee samples in present study with previous studies on coffee samples

Elements	Concentration (mg/l)	Reference
As	**0.05---0.16667**	**Present study**
	<0.2	[86], [87]
Cr	**0.05---0.3**	**Present study**
	0.02---1.29	[81], [87], [89], [62], [92]
Ni	**0.01667---0.36667**	**Present study**
	0.5---4.3	[81], [62],[92]
Se	**0.45---0.7333**	**Present study**
	0.014---<5.8	[87], [89]

4.4. Statistical Analysis of the Results

4.4.1. One Way Variance Analysis (ANOVA)

The obtained results were analyzed by one way analysis of variance (ANOVA), and Duncan test to show the elements which have large variations and significant differences in their concentrations levels in different coffee samples. And the results showed that there are significant differences between the concentration of (Al, Ba, K, Na, Ni, Sr, and Zn) for coffee samples from different origins, while for elements like (As, Se, Sn, and Mg) no significant differences were observed for different coffee samples.

For other elements significant difference is observed between the concentrations of only one or two coffee sample with other samples. ANOVA results for macro, micro and trace elements are showed in Table 4.5, Table 4.6, and Table 4.7 respectively, different matching letters in each column of the tables means significant difference according to Duncan test.

Table 4.5. Concentration (mg/l) and standard deviation values of macro elements (Ca, K, Na, P and Mg) in coffee samples, different matching letters in a column mean significant differences according to Duncan test ($P < 0.05$)

Samples	Ca	K	Na	P	Mg
CB	$283.82^{cd} \pm 14.07$	$10357^{d} \pm 21$	$302.82^{c} \pm 3.87$	$295.27^{c} \pm 12.82$	$463.48^{ab} \pm 18.64$
CC	$306.87^{ab} \pm 17.25$	$10012^{e} \pm 161$	$293.45^{d} \pm 1.89$	$299.73^{c} \pm 10.38$	$455.35^{ab} \pm 25.14$
CE	$243.93^{e} \pm 9.93$	$10723^{bc} \pm 68$	$240.73^{e} \pm 4.58$	$325.98^{ab} \pm 14.84$	$420.63^{cd} \pm 21.24$
CG	$298.03^{bc} \pm 10.97$	$11635^{a} \pm 154$	$333.42^{b} \pm 2.60$	$251.07^{e} \pm 5.09$	$447.75^{bc} \pm 16.50$
CK	$310.88^{ab} \pm 14.54$	$9360^{f} \pm 83$	$294.57^{d} \pm 1.80$	$342.38^{a} \pm 11.98$	$500.77^{a} \pm 24.18$
CY	$334.73^{a} \pm 9.70$	$10964^{b} \pm 216$	$353.38^{a} \pm 0.65$	$283.67^{cd} \pm 6.23$	$493.60^{a} \pm 14.08$
f-calculated	16.60	103.70	541.13	26.49	6.44

Table 4.6. Concentration (mg/l) and standard deviation values of trace elements (As, Cr, Ni, Se and Sn) in coffee samples, Different matching letters in a column mean significant differences according to Duncan test ($P < 0.05$)

Samples	As	Cr	Ni	Se	Sn
CB	$0.166^{a} \pm 0.076$	$0.066^{cd} \pm 0.076$	$0.150^{bc} \pm 0.050$	$0.617^{bc} \pm 0.126$	$0.066^{cd} \pm 0.076$
CC	$0.116^{ab} \pm 0.125$	$0.300^{a} \pm 0.100$	$0.333^{a} \pm 0.076$	$0.700^{ab} \pm 0.229$	$0.133^{ab} \pm 0.763$
CE	$0.050^{abc} \pm 0.043$	$0.116^{bc} \pm 0.057$	<DL	$0.533^{cd} \pm 0.125$	$0.083^{bc} \pm 0.028$
CG	$0.050^{abc} \pm 0.000$	$0.050^{cd} \pm 0.025$	$0.016^{d} \pm 0.028$	$0.450^{cd} \pm 0.132$	$0.100^{bc} \pm 0.050$
CK	$0.083^{ab} \pm 0.028$	$0.083^{cd} \pm 0.028$	$0.216^{b} \pm 0.028$	$0.733^{ab} \pm 0.057$	$0.083^{bc} \pm 0.057$
CY	$0.083^{ab} \pm 0.057$	$0.150^{ab} \pm 0.050$	$0.366^{a} \pm 0.028$	$0.633^{bc} \pm 0.160$	$0.150^{ab} \pm 0.000$
f-calculated	1.28	6.54	32.31	1.52	1.03

Table 4.7. Concentration (mg/l) and standard deviation values of micro elements (Al, Ba, Cu, Fe, Mn, Sr and Zn) in coffee samples, Different matching letters in a column mean significant differences according to Duncan test ($P < 0.05$)

Samples	Al	Ba	Cu	Fe	Mn	Sr	Zn
CB	$3.633^{a} \pm 0.160$	$0.933^{f} \pm 0.028$	$2.850^{de} \pm 0.100$	$5.166^{cd} \pm 0.650$	$11.667^{cd} \pm 0.562$	$9.583^{ef} \pm 0.029$	$2.266^{de} \pm 0.175$
CC	$4.250^{a} \pm 0.050$	$6.916^{a} \pm 0.028$	$3.266^{ab} \pm 0.202$	$7.033^{ab} \pm 0.828$	$13.483^{ab} \pm 0.825$	$16.783^{a} \pm 0.252$	$2.816^{bc} \pm 0.175$
CE	$2.950^{c} \pm 0.100$	$3.200^{d} \pm 0.050$	$2.916^{cd} \pm 0.076$	$5.183^{cd} \pm 0.664$	$7.283^{e} \pm 0.404$	$9.733^{e} \pm 0.126$	$1.900^{ef} \pm 0.132$
CG	$2.950^{c} \pm 0.132$	$6.450^{b} \pm 0.050$	$2.966^{cd} \pm 0.104$	$5.533^{bc} \pm 0.505$	$12.650^{bc} \pm 0.541$	$15.767^{b} \pm 0.104$	$2.416^{d} \pm 0.104$
CK	$4.500^{a} \pm 0.450$	$3.983^{c} \pm 0.057$	$3.016^{bc} \pm 0.125$	$7.100^{ab} \pm 0.785$	$14.617^{a} \pm 0.709$	$12.967^{c} \pm 0.076$	$3.250^{a} \pm 0.180$
CY	$4.583^{a} \pm 0.104$	$1.300^{e} \pm 0.000$	$3.333^{a} \pm 0.076$	$8.100^{a} \pm 0.427$	$14.000^{ab} \pm 0.436$	$11.183^{d} \pm 0.208$	$3.050^{ab} \pm 0.132$
f-calculated	37.16	11375.08	7.78	10.39	59.30	1207.51	33.56

4.4.2. Correlation between Elements

To determine correlation between concentrations of elements in coffee samples, Pearson's correlation coefficient were assessed. Very high positive correlation ($r > 0.9$) is observed only for Cu-Fe, Ca-Mn, Ba-Sr and Zn-Mn pairs of elements, it means that these pairs of elements are strongly related to each other and by increasing or decreasing the concentration of one of the elements in each pair concentration of other element in that pair will also increase or decrease. Very high correlation exist between Cu-Fe with correlation coefficient of (0.901) which means by increasing or decreasing the concentration of Cu in coffee samples concentration of Fe will also increase or decrease and vice versa, concentration Mn in coffee samples is highly related to the concentration of both of Ca and Zn with a correlation coefficient of (0.923) and (0.911) respectively and by increasing or decreasing concentration of Mn concentrations of both Ca and Zn will also increase or decrease and vice versa. Amount of Ba and Sr in coffee samples are also highly related to each other with correlation coefficient of (0.918) and by increasing concentration of one of them in the coffee samples the other one will also increase or decrease.

high positive correlations ($0.7 < r > 0.9$) is observed for the following pairs of elements: Ca-Al, Ca-Cu, Cr-Cu, Al-Fe, Fe-Ca, Al-Mn, Fe-Mn, Ni-Al, Ni-Cu, Ni-Fe, Ni-Mn, Zn-Al, Al-Mg, Ca-Zn, Ca-Mg, Fe-Zn, Fe-Mg, Mn-Mg, Zn-Ni, Zn-Mg, Mn-Na and Ni-Ca. concentration of Al is highly related to the concentration of; Ca, Fe, Mn, Ni, Zn, and Mg with correlation coefficients of; 0.716, 0.790, 0.731, 0.867, 0.851, and 0.736 respectively that means by increasing or decreasing amount of Al in coffee samples, concentration of these elements will also either increase or decrease and vice versa. High correlation also observed between concentration of Ca with elements like (Cu, Fe, Na, Ni, Zn, Mg) with correlation coefficients of 0.739, 0.846, 0.787, 0.772, 0.874, and 0.832 for Ca-Cu, Ca-Fe, Ca-Na, Ca-Ni, Ca-Zn and Ca-Mg respectively, which means by increasing or decreasing concentration of one of these elements in coffee samples is either increase or decrease or vice versa.

Correlation coefficient of (0.811) is observed for relation between Cu and Ni which means that concentration of these two elements in coffee samples were highly related to each other and by increasing or decreasing concentration of one of them concentration of other elements will also either increase or decrease.

Iron (Fe) concentration is highly related to concentrations of Mn, Ni, Zn, and Mg with correlation coefficients of 0.724, 0.859, 0.883, and 0.801 for Fe-Mn, Fe-Ni, Fe-Zn, and Fe-Mg respectively and by increasing or decreasing amount of Fe in coffee samples amounts of Mn, Ni, Zn, and Mg either increase or decrease. Mn concentration in coffee samples are highly related to the amount of Na, Ni, and Mg with correlation coefficients of 0.716 for Mn-Na, 0.704 for Mn-Ni and 0.813 for Mn-Mg that means by increasing or decreasing concentration of Mn in coffee samples concentration of Na, Ni, and Mg either increase or decrease as well. Concentration of Ni in coffee samples are highly related to the concentration of Zn with correlation coefficient of 0.777 that means when the concentration of Ni increase or decrease in a coffee sample then the concentration of Zn may increase or decrease. High correlation coefficient of 0.874 is observed between Zn and Mg which it means by increasing or decreasing concentration of one of them concentration of other will also increase or decrease as well.

High negative correlations exist between P-K and Al-Ba and concentration of these two pairs of elements are inversely related to each other. high negative correlation between P and K with a correlation coefficient of (-0.767) is exist which means that by increasing the concentration of P in the coffee samples concentration of K will decrease and vice versa, and also high negative correlation exist between Al-Ba with correlation coefficient of (-0.716) that means when the amount of Al increased in the coffee samples then the amount of Ba will be decreased.

For other pairs of elements, either positive or negative correlation are established but they are moderate correlation with correlation coefficients of ±0.4 to ±0.7, low correlation with correlation coefficients of ±0.2 to ±0.4 or almost negligible correlation with correlation coefficients from 0 to ±0.2. Correlations between all measured elements in coffee samples are shown in Table 4.8.

Table 4.8. Correlations between the elements according to Pearson's correlation coefficient

	Al	As	Ba	Ca	Cr	Cu	Fe	K	Mn	Na	Ni	P	Se	Sn	Sr	Zn
As	0.227 0.365															
Ba	-0.716 0.489	-0.216 0.388														
Ca	0.716 0.001	0.073 0.772	0.028 0.911													
Cr	0.365 0.136	-0.044 0.862	0.332 0.179	0.259 0.299												
Cu	0.615 0.007	-0.117 0.643	0.141 0.577	0.739 0.000	0.733 0.001											
Fe	0.790 0.000	-0.013 0.960	-0.010 0.967	0.846 0.000	0.536 0.022	0.901 0.000										
K	-0.586 0.011	-0.216 0.390	0.040 0.875	-0.065 0.797	-0.225 0.370	0.004 0.988	-0.224 0.372									
Mn	0.731 0.001	0.129 0.610	0.165 0.512	0.923 0.000	0.209 0.406	0.562 0.015	0.724 0.001	-0.265 0.288								
Na	0.375 0.126	0.031 0.904	-0.079 0.756	0.787 0.000	-0.096 0.705	0.417 0.085	0.459 0.055	0.378 0.122	0.716 0.001							
Ni	0.867 0.000	0.185 0.461	-0.111 0.661	0.772 0.000	0.644 0.004	0.811 0.000	0.859 0.000	-0.385 0.114	0.704 0.001	0.437 0.070						
P	0.310 0.211	0.040 0.874	-0.199 0.428	-0.177 0.488	0.187 0.459	0.002 0.994	0.199 0.430	-0.767 0.000	-0.112 0.657	-0.665 0.003	0.128 0.613					
Se	0.499 0.035	-0.361 0.141	-0.071 0.778	0.271 0.271	0.362 0.140	0.283 0.256	0.358 0.144	-0.592 0.010	0.337 0.171	-0.014 0.957	0.514 0.029	0.363 0.139				
Sn	0.300 0.227	-0.016 0.949	0.106 0.677	0.402 0.098	0.393 0.106	0.526 0.025	0.456 0.057	0.146 0.564	0.267 0.285	0.278 0.264	0.411 0.090	-0.119 0.638	-0.071 0.781			
Sr	0.107 0.673	-0.100 0.964	0.918 0.000	0.380 0.119	0.396 0.104	0.361 0.141	0.246 0.325	0.028 0.912	0.504 0.033	0.271 0.277	0.196 0.435	-0.342 0.165	0.022 0.930	0.241 0.334		
Zn	0.851 0.000	0.044 0.861	0.084 0.740	0.874 0.000	0.318 0.198	0.667 0.003	0.883 0.000	-0.432 0.073	0.911 0.000	0.513 0.029	0.777 0.000	0.212 0.398	0.421 0.082	0.313 0.206	0.366 0.135	
Mg	0.736 0.001	0.131 0.605	-0.249 0.319	0.832 0.000	0.135 0.593	0.558 0.016	0.801 0.000	-0.330 0.182	0.813 0.000	0.505 0.033	0.669 0.002	0.270 0.278	0.340 0.168	0.218 0.384	0.028 0.912	0.874 0.000

4.5. Conclusion

Coffee plays a major social and economic role. It is one of the most widely consumed beverages throughout the world. In this study 17 inorganic elements were determined in six coffee samples from different origins. Concentration of elements were determined by using inductively coupled plasma optical emission spectroscopy (ICP-OES), sample preparation procedure based on the partial decomposition in aqua regia is simple, safe, reproducible, and reliable for the determination of total concentrations of As, Ba, Ca, Cr, Cu, Fe, K, Mn, Na, Ni, P, Se, Sn, Sr, Zn, and Mg. in addition , the use of aqua regia improves the sample solubilisation, reduces the reagents consumption and the time of analysis.

The results obtained in this study showed there are significant differences between different elemental content of different coffee samples due to their origin of growth, for most of the elements determined especially macro and micro elements coffee beans from Yemen (CY) and Kenya (CK) have higher concentration than other samples, except for the elements like Ba and Sr in which Colombian coffee beans (CC) contain highest amount and K and As in which coffee beans from Guatemala (CG) and Brazil (CB) contain higher amount of these two elements respectively.

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CURRICULUM VITAE (CV)

Personal Information

Full name: Sabah Hassan Mohammedazeez Al-Jaf

Place of birth: Sulaymaneah-Iraq

Date of Birth: 13 / September / 1987

Marital status: Single

Contact Information

Phone: 00964 (0) 770 508 81 97

Address: Kalar-Sulaymaneah-Iraq

Email: Sabah.hassan@garmian.edu.krd, sabah.chemistry@gmail.com,

Education

2007-2011 BSc. in chemistry at University of salahaddin, Iraq

2015-present MSc. student in Analytical chemistry at Firat University, Turkey