






Evaluation of heavy metals in Roasted Coffee powder in Iran and Turkey

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ABSTRACT

Nowadays coffee is a popular beverage around the world used in many food industries such as chocolate, dairy industry and also confectionery. Therefore, its quality required special attention. On the other hand, heavy metals have been attracted the attention in food products due to their toxicity and health risks in the food chain. Since coffee is a desirable widely used drink in the world for different age groups, this study aims to measure the concentration of heavy metals and some other elements in several brands of coffee powder from Iran and Turkey markets. After sample collection and preparation, heavy metals were measured using ICP-MS according to the AOAC method. The results showed that fortunately lead, cadmium, cobalt, silver, chromium, and mercury were not detected in any coffee samples. Also, it was observed that Nickel was only found in 3 samples, which was less than the standard limits. The pH of all samples was measured and the range was 5.03 to 6.32 in Iranian and Turkish samples. However, there was a lack of evidence in heavy metals amounts in coffee, this study reveals successful practical information in this field in Iranian and Turkish market but also according to the importance of this issue, further comprehensive studies is needed all over the world.

Key words: Coffee; lead; cadmium; mercury; ICP-MS.

1 INTRODUCTION

Coffee belongs to the genus *Coffea*, Rubiaceae family. More than 100 species of coffee plant are known up to now (Ferreira, 2019; Jae-Hoon et al., 2014; Rosales-Villarreal, 2019). Among all, the two popular species are cultivated in many tropical countries; Arabica and Robusta (Anthony et al., 2010; Campuzano-Duque et al., 2021). The coffee plant grows wild and abundant in Brazil and eastern Africa (Dos Santos et al., 2021; Jeklin, 2016). Coffee was introduced from Africa to Arabia in pre-Islamic days as a luxurious good (Brice et al., 2002). There are two main sources of coffee beans of commercial importance, *Coffea Arabica* and *Coffea Robusta* (known also as “*Canephora*”), which differ in chemical components (Araujo et al., 2021). Coffee includes valuable chemicals including carbohydrates, lipids, nitrogenous compounds, vitamins, minerals, alkaloids, and phenolic compounds (Bicho et al., 2013; Massoud et al., 2019a). It has been reported that Arabica coffee contains more lipids, while Robusta contains more caffeine and polyphenols (Godos et al., 2014). Arabica makes up 80% and Robusta 20% of the world market (Konieczka et al., 2020; Liu et al., 2019). Usually a combination of *Coffea Arabica* and Robusta is used in the world. Roasted coffee beans used to make coffee in different degrees (very dark, dark, medium, and light). Roasting process affect the amount of chemical composition in coffee (Santos, 2015). Carbohydrates are the most important component and about 60% of the total weight

of raw coffee beans is made up by various carbohydrates (Araujo et al., 2021). The unique taste and color of coffee beans are also formed during the roasting process of raw coffee beans (Saud et al., 2021). Coffee is a complex food matrix with multiple phytochemical components that has antioxidant activity. It also acts as a pro-oxidant to chelate metal ions. It is also claimed to protect the gastrointestinal tract against oxidative stress (Cordoba et al., 2020; Liang; David, 2014). A lot of benefits and advantages of coffee such as a reduced risk of liver, kidney and, to some extent, premenopausal breast and colorectal cancers are mentioned in many scientific studies (Ferreira et al., 2019; Harpaz et al., 2017; Saab et al., 2014; Nkondjock, 2009). In addition coffee has some mental benefits over physical ones like improving energy levels, improving various aspects of brain function such as memory and mood (Brice et al., 2002; Philippa et al., 2021; Samoggia, 2019; Wilhelmus, 2017).

Heavy metals are an important issue caused many environmental and health problems (Munir et al., 2022). Recently they have attracted a lot of attention in food products due to their ability to be stored in the food chain and make so many health risks and cancers (Briffa et al., 2020). The coffee plant would adsorb the metals from the soil and environment and store in the leaves, roots and grains (Da Silva et al., 2017). There are 35 metals that are major concern of exposure for humans and 23 of them are heavy metals (Jaishankar et al., 2014). Some metals are biologically

essential in low concentrations for living organisms (Cu, Cr, Co, Mn, Ni, Zn) however, some others (toxic metals) exert harmful effects (As, Cd, Pb, Hg, Ti, U) (Da Silva et al., 2017). Lead (Pb), Cadmium (Cd), Zinc (Zn), Mercury (Hg), Arsenic (As), Silver (Ag), Chromium (Cr), Copper (Cu), Iron (Fe) are in heavy metals group (Length, 2007). The maximum levels of these metals has become a concern of the quality standard worldwide.

The toxicity of the metals depends on the absorbed dose, the duration and amount of exposure (Jaishankar et al., 2014; Massoud et al., 2020; Witkowska et al., 2021). Exposure to heavy metals can suppress the immune system and increase the production of toxic products in the body and cause serious health problems (Massoud et al., 2019b; Siddharth et al., 2017; Witkowska, 2021). Therefore, it's necessary to do some research on the presence of some heavy metals in coffee as it is the most popular and widely consumed beverage in daily life all over the world.

2 MATERIAL AND METHODS

2.1 Materials

25 packages of roasted coffee powder were collected from Iranian (14 samples) and Turkish (11csamples) markets; Arabica (100%, South America) (6 brands in total), Robusta (100%, Southwest Asia) (2 brand in total) and a mixture of Robusta (Southwest Asia) and Arabica (South America) (9 brands in total).

2.2 Methods

The coffee samples were prepared according to the AOAC method (AOAC 920.91-1920). 0.05 gr coffee powder is weighted. For pre-digestion, the deionized water was added then Nitric acid and hydrochloric acid were added to the solution and digested at a specific temperature (180 °C). After that the digested samples were cooled. The selected heavy metals and other elements (Hg, Ag, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn) were measured by ICP-MS (7800 Agilent, U.S.A) at certain wave length for each metal according to AOAC-Method-2015.01. The pH of the samples also was measured with pH meter (KNT/CH, Germany). All analyzes were performed in three replications.

2.3 Limits of detection (LOD) and quantification (LOQ)

LOD and LOQ of each element were determined using the roasted coffee powder in three times and 10 times. The signal to noise ratios was calculated by LCMS software, by using the S/N calculation tool. The limit of detection (LOD) and the limit of quantification (LOQ) for heavy metals in coffee was 0.1 µg kg⁻¹ and 0.3 µg kg⁻¹, respectively.

2.4 Statistical Analysis

The data were expressed as the mean ± SD (standard deviation). The data were statistically analyzed using the SPSS 24 on replicated test data. Analyses of variance were performed by SS Type 3. P-value of 0.05 or less was considered statistically significant.

3 RESULTS

Heavy metals are classified in terms of toxicity (Bhargava et al., 2017). The non-toxic elements in this study include Calcium, Iron, Magnesium, Manganese, Sodium, Potassium, Zinc and Copper. Zinc is an essential element in human and animal nutrition. Studies on this element in animals have shown that high levels in the diet can cause anemia and reduce the absorption of Copper and Iron and reduce the activity of several important enzymes in the body (Panel; Allergies, 2014). The studies showed that Cadmium, Chromium, Lead, Mercury, Nickel (Siddharth et al., 2017) and Cobalt are classified in the group with moderate to high toxicity (Bauer, 2013). Silver ion is a highly toxic substance in terms of function (as an enzymatic and metabolic inhibitor) and biochemically silver ions (Ag⁺) can act as a potent inhibitor of some enzyme (Pradana-lópez et al., 2021).

The levels of heavy metals are shown in Table 1. Fortunately Mercury, Cadmium, Chromium, Cobalt, Silver and Lead were not found in any samples. Nickel was only found in 3 samples (2 Iranian and 1 Turkish). Zinc levels were observed in almost all coffee samples except 2 Iranian samples. Among all, the highest amount of Zinc was observed in the Iranian sample (Arabica + Robusta) and it was 0.019± 0.1767 mg.kg⁻¹.

Table 1: Mean Amount of heavy metals in Roasted Coffee Powder Samples collected from Iranian and Turkish Markets (mg.kg⁻¹ ±SD).

Metals	Cd	Cr	Pb	Hg	Ni	Co	Zn	Ag
Markets	Mean Concentration ± SD							
Iran	<LOQ	<LOQ	<LOQ	<LOQ	0.003 ± 0.6151	<LOQ	0.009 ± 0.4398	<LOQ
Turkey	<LOQ	<LOQ	<LOQ	<LOQ	0.002 ± 0.0057	<LOQ	0.007 ± 0.3972	<LOQ

The levels of some other elements are shown in Table 2. The mean amount of Mg, Mn and K in both Iranian and Turkish samples were similar, while amount of Ca and Na in the collected Turkish samples were higher than Iranian samples. The amount of Fe and Cu in the Iranian roasted samples were higher than Turkish ones. The highest amount of Ca in all samples belonged to the Arabica samples. The lowest amount of Fe belonged to mixed coffee (Arabica+ Robusta) sample.

4 DISCUSSION

In this study, all the elements we put in two groups of trace elements (0-0.12 mg.kg⁻¹) and major elements (0-35 mg.kg⁻¹) in all coffee samples. Figures 1 and 2 represents the trace elements and figures 3 and 4 shows the major elements in coffee samples.

The highest and lowest amount of Manganese (respectively 1.812±0.1767 and 0.633±0.3472 mg.kg⁻¹) were found in the mixed (Arabica+ Robusta) samples. The results were same in the Iranian samples. The Lowest amount of Iron in the Iranian samples was found in the samples of Arabica coffee (0.006±0.0849 mg.kg⁻¹) and the highest amount was observed in the Arabica sample (0.076±0.0847 mg.kg⁻¹). The

results in the Turkish samples were quiet different in terms of Iron , the studies shows that the highest amount of Iron was found in the Arabica coffee sample while the lowest amount was in the mixed coffee sample group (Arabica + Robusta).

According to statistical observations and laboratory analyzes, 2 samples (Arabica + Robusta from Iran) did not contain Copper while in the case of Nickel, 2 Iranian samples (Robusta; Arabica + Robusta samples) and 1 Turkish (Arabica + Robusta) samples contained Nickel.

The highest amount elements in all samples belonged to Potassium followed by Magnesium, Calcium, and Sodium in both Iranian and Turkish collected coffee samples. The reported average was 10.003± 0.0648 mg. kg⁻¹ and the highest level of Potassium (13.908±0.2701 mg.kg⁻¹) was in Turkish (Arabica+ Robusta) sample.

Zinc was higher than 10 mg.kg⁻¹ in 6 samples which one belonged to Iranian Roasted sample (Arabica group) and the others were from Iranian and Turkish (Arabica+ Robusta) samples.

The concentration order of observed elements in the coffee samples in this study (both Iranian and Turkish samples) are as the following:

K > Ca > Mg > Na > Fe > Mn > Cu > Zn > Ni > Cd, Cr, Pb, Hg, Co, Ag

Table 2: Mean Amount of some elements in Roasted Coffee Powder Samples collected from Iranian and Turkish Markets (mg.kg⁻¹ ±SD).

Metals	Ca	Fe	Mg	Mn	Na	Cu	K
Markets	Mean Concentration ± SD						
Iran	1.481 ± 0.070	0.040 ± 0.236	1.312 ± 0.057	0.022 ± 0.201	0.772 ± 0.113	0.014 ± 0.529	8.973 ± 0.077
Turkey	1.511 ± 0.025	0.037 ± 0.034	1.342 ± 0.098	0.026 ± 0.191	0.940 ± 0.270	0.012 ± 0.423	8.422 ± 0.407

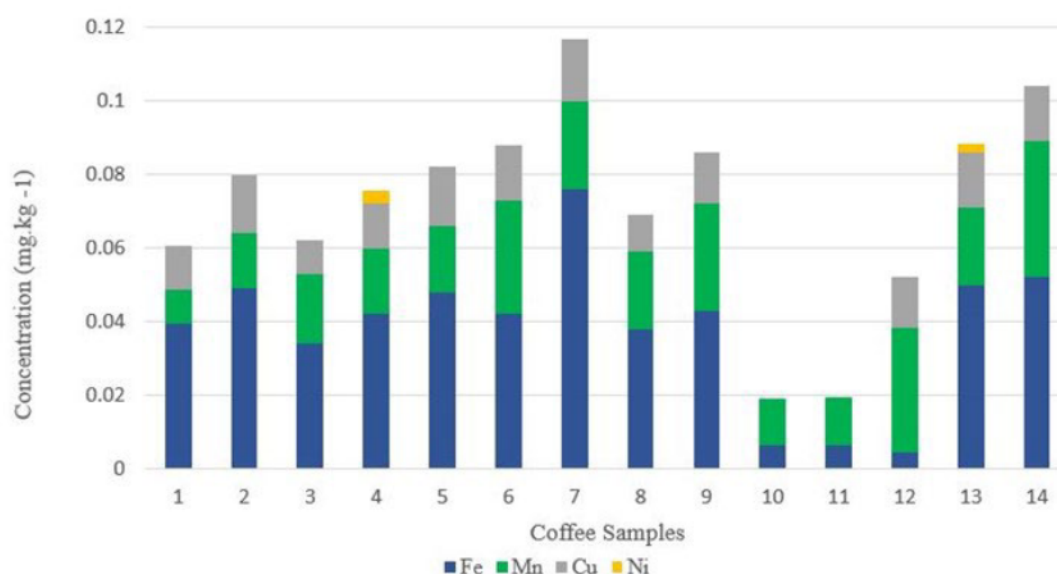


Figure 1: The amount of trace elements (Fe, Mn, Cu and Ni) in the Iranian samples (mg.kg⁻¹).

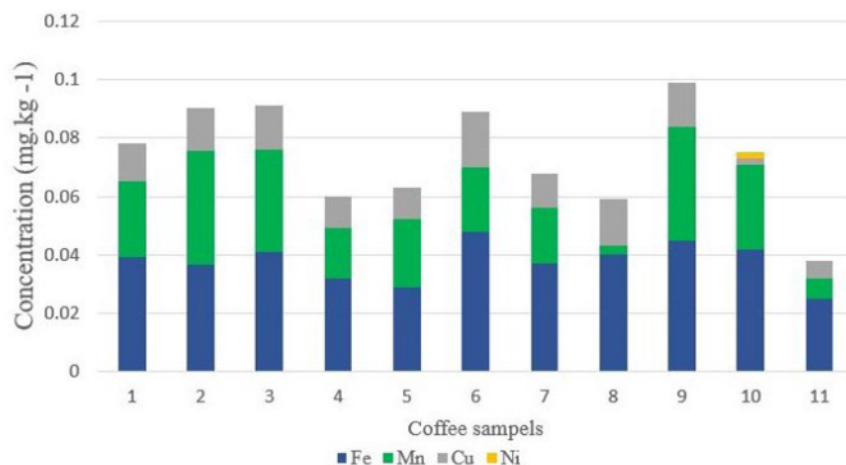


Figure 2: The amount of trace elements (Fe, Mn, Cu and Ni) in the Turkish samples (mg.kg⁻¹).

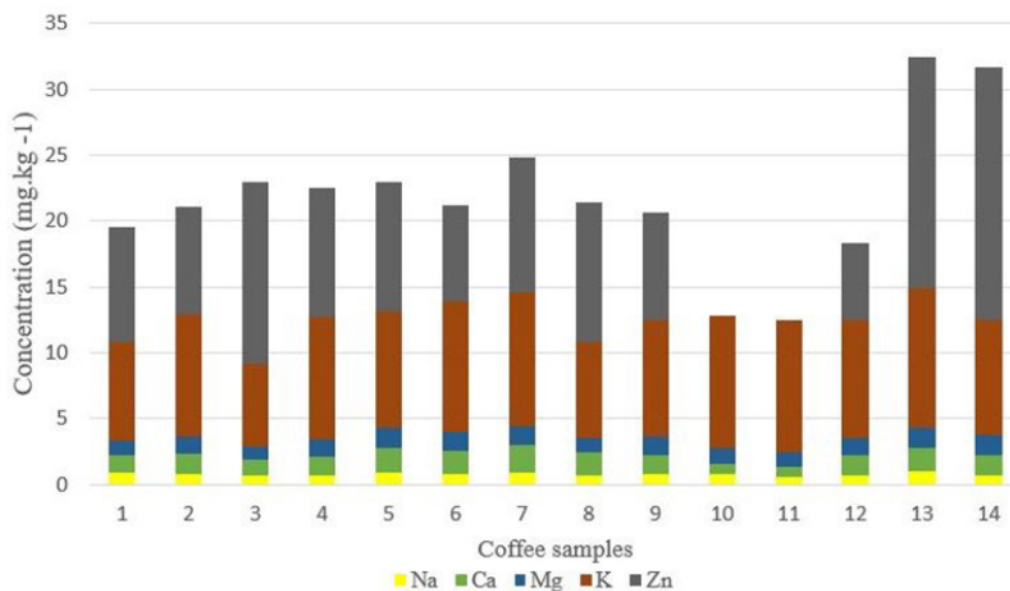


Figure 3: The amount of major elements (Na, Ca, Mg, K and Zn) in Iranian samples (mg.kg⁻¹).

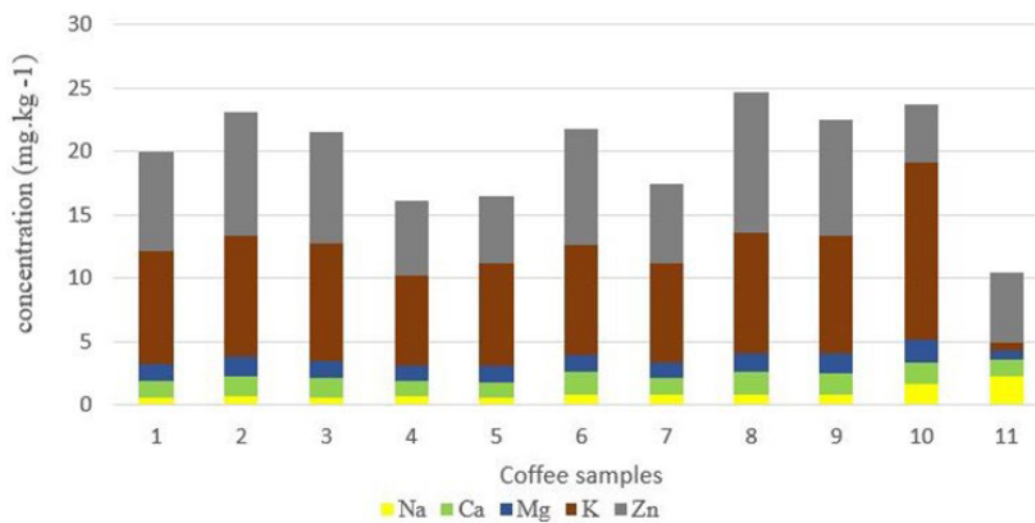


Figure 4: The amount of major elements (Na, Ca, Mg, K and Zn) in Iranian samples (mg.kg⁻¹).

In a study the concentration of some elements was compared among different types of coffee consumed in Jordan. The amount of metal element levels in coffee samples; Green and roasted coffee beans from Brazil, Ethiopia, Kenya, Colombia, and India were measured. In their study twenty-two elements include some toxic elements such as Potassium, Magnesium, Calcium, Iron, Aluminum, Manganese, and Copper. Barium, Strontium, Zinc, Chromium, Lead, Nickel, Vanadium, Cobalt, Gallium, Uranium, Cadmium, Silver, Lithium, Indium, Bismuth, Thorium, and Thallium were determined using ICP-MS. The result showed that the levels of elements were close to each other among all five types of coffee. Similar to our results Potassium and Zinc were high in the samples (Albals et al., 2021).

Also Cadmium, Chromium, Copper, Manganese, Nickel, Lead and Zinc were measured by atomic absorption spectrophotometer in roasted ground coffee beans in Brazil, in which lead was higher than standard limits in 70% of the samples (Da Silva et al., 2017).

Ashu and Bhagwan (2011), evaluated nine essential elements (Potassium, Magnesium, Calcium, Sodium, Manganese, Iron, Copper, Zinc, and Cobalt) and two heavy metals (lead, cadmium) in coffee. Three brands of Ethiopian roasted coffee were analyzed by (FAAS). They claimed that samples was nearly similar and no heavy metals were observed (Ashu; Bhagwan, 2011).

In another study, the amount of ash content and heavy metals in roasted coffee were determined. The heavy metals (Cadmium, Lead, Copper, Chromium, Nickel, and Zinc) was determined by atomic flame absorption spectrophotometry. The results showed that the content of all metals were in the range of standards limit set by the Brazilian safety organization (Pigozzi et al., 2018).

The quantity of heavy metals (Copper, Lead, Chrome, Cadmium, Nickel, Aluminum, and Mercury) in roasted coffee

beans from Colombia and Nicaragua was evaluated by ICP-MS (Várady et al., 2021). Nickel and cadmium in Colombian samples were higher than other samples but in the standard range. In the case of other metals, their content was relatively low. (Várady et al., 2021).

The relationship between stressful environment and chromium accumulation in Conilon coffee seedlings were carried out and the results showed chromium in different parts of seedlings and leaf. More chromium accumulation was observed in both the top and the roots of plants. These kinds of studies are the comprehensive cases that help researchers to have a deeper understanding of the plant mechanism (Berilli et al., 2016).

The measured pH values of Iranian and Turkish coffee samples is shown in Figure 5 in. *The importance of measuring pH is in coffee consumption.* The samples' pH was in the range of 5.03 to 6.32 in Turkish samples and 5.45 to 6.15 in Iranian samples. In all samples, the highest pH was observed in mixed one (Arabica+ Robusta) in Turkish sample.

As Figure 5 shows, the samples collected from the Turkish market had higher pH values than Iranian samples. The chemical components, types of coffee species, their origin, different growing seasons, and some other factors will affect the pH values.

According to the statistical analyzes performed in this study, it was observed that there was no statistically significant relationship between the type of coffee (Arabica or Robusta or their mixture) and their pH ($P \leq 0.05$).

According to research by Silva et al. (2014), pH changes can be helpful in choosing the best type of coffee for consumption. The most important issue is acceptance of the product by consumers as a tasty brown liquid without excessive bitterness or high acidity. According to this research, the preferable pH of desirable coffee in Brazil was 4.99-5.98 (Silva et al., 2014).

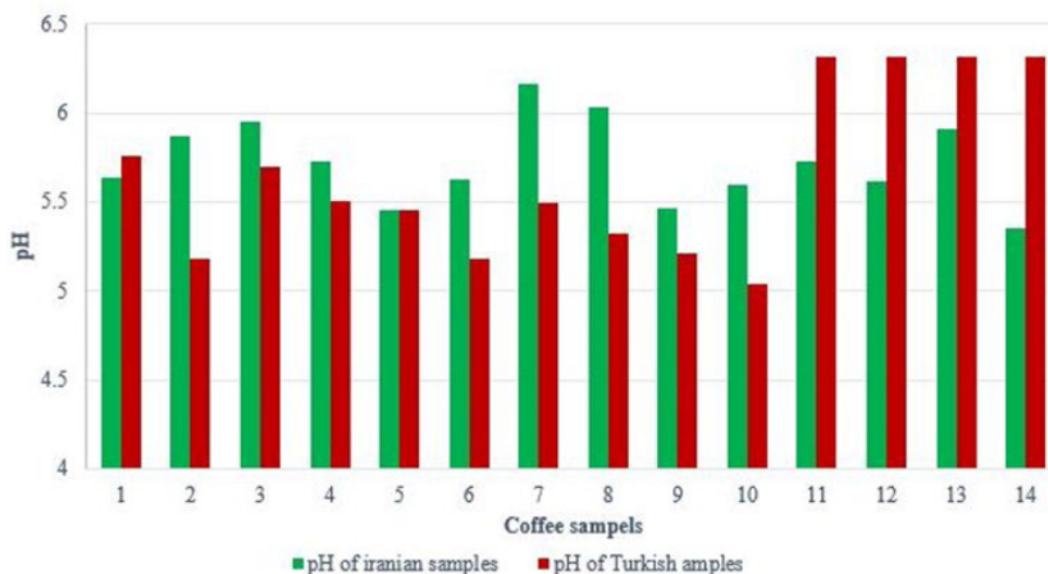


Figure 5: The pH value in Iranian and Turkish samples.

The pH of some in hot and cold brewed coffee samples was compared. The pH of the samples ranged from 4.18 to 5.2. Their results showed that hot brewed coffees have higher concentrations of total titrable acids as well as a higher antioxidant activity. They stated that the hot brew method tends to extract non-protonated acids more along with lower pH and higher antioxidant activity in hot coffee samples (Rao et al., 2018).

According to another study, the chemical parameters like pH, soluble solids and caffeine were measured in Arabica and Robusta green coffees. Their results showed that pH, soluble solids and caffeine in Robusta green coffee were higher than other samples but totally the above parameters in Arabica and Robusta green coffees were not significantly different (Bicho et al., 2013).

5 CONCLUSIONS

The coffee beans were imported in to both Iran and Turkey market and only roasting, and grinding operations were carried out in both countries. According to the test results, the results were similar and acceptable in standard level. In this study, some metals were measured using ICP-MS.

This study showed no certain relationship between the type of coffee and the presence of the measured metals in the roasted coffee powders, but maybe the type and method of coffee roasting would influence the final amount of metals in the coffee samples.

Much research has been done on the duration of roasting and its effects on coffee's heavy metal content. However, it is highly recommended to check the amount of heavy metals in coffee from the beginning of harvest until it is placed in the consumer's cups. The physiology of the coffee plant in terms of heavy metals besides the soil of the origin where it grows, is highly recommended. Studying on the effect of roasting method on the amount of heavy metals in the final product would be another future recommendation.

Studying the effect of machinery and equipment in coffee processing and packaging on the amount of heavy metals is recommended. The impact of packaging time and type on the amount of heavy metals is also recommended.

6 AUTHORS' CONTRIBUTION

FMM wrote the draft and performed the experiment, **RM** supervised the experiment and finalized the manuscript, **and NMM & AM** review and approved the final version of the work, **FMM & SFMM** conducted all statistical analyses.

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