Multi-element determination of essential and toxic metals in green and roasted coffee beans: A comparative study among different origins using ICP-MS

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Abstract
The aim of this study is to compare the elemental composition among different coffee varieties consumed in Jordan. Levels of different metallic elements in coffee samples; green and roasted coffee beans from five origins; Brazil, Ethiopia, Kenya, Columbia, and India, collected from the Jordanian market were investigated. Twenty-two elements, including essential and toxic elements such as potassium (K), magnesium (Mg), calcium (Ca), iron (Fe), aluminum (Al), manganese (Mn), copper (Cu), barium (Ba), strontium (Sr), zinc (Zn), chromium (Cr), lead (Pb), nickel (Ni), vanadium (V), cobalt (Co), gallium (Ga), uranium (U), cadmium (Cd), silver (Ag), lithium (Li), indium (In), bismuth (Bi), thorium (Th), and thallium (Tl), were determined using inductively coupled plasma-mass spectrometry (ICP-MS). The detected heavy metals and their intake per 1 cup of coffee did not largely contribute to the recommended daily intake (RDI) and tolerable upper limit of daily intake (TULD) in an adult with an average body weight of 80 kg. The ICP-MS versus flame atomic absorption spectrometry (FAAS) results were linearly fitted, and the correlation coefficients \(R^2 > 0.95\) were better than 0.95 for the three checked elements. No significant difference between the results of the two techniques was observed \((p > 0.05)\). The ANOVA results

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indicated the presence of a significant difference between the levels of Cr, Co, and Zn in green and roasted coffee beans. The results of this study indicated that the coffee consumed in Jordan did not contain toxic levels of heavy elements and is safe for consumption according to health organizations.

**Keywords**
Roasted coffee, green coffee, Jordan, ICP-MS, heavy metals, toxicity

**Introduction**

Essential elements such as K, Ca, Mg, and Fe play an important role in bone and tooth formation and normal nerve function.\(^1\) The recommended amounts of these elements may vary according to age, sex and health condition.\(^2\) Moreover, some of them, such as copper or zinc, are vital for human metabolism and serve as activators for many enzymes.\(^3\) Metal toxicity results in the elevation of essential or toxic metals in the body when excess amounts are ingested in supplements, food and water.\(^4\) As environmental pollutants, toxic metals upon exposure can be responsible for damage to vital organ systems, in addition to having adverse effects on cognitive abilities and the reproductive system.\(^5,6\) Chronic exposure can lead to a gradual increase in neurodegenerative processes, which is related to diseases such as multiple sclerosis and Alzheimer's disease.\(^7–9\) Patients with chronic kidney disease and liver diseases can be more vulnerable than others.\(^10,11\) According to the international agency for research on cancer (IARC), toxic metals such as arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), and mercury (Hg) are classified as category (1) carcinogens, as they increase cancer risk in humans even with mild to moderate exposure.\(^5,12\) Therefore, the World Health Organization (WHO)\(^7\) has set guideline standards including permissible limits (PLs) for essential and toxic heavy metal contents in both food (vegetables, grains, fruit, fish\(\text{shellfish, meat}\)) and beverages including milk, water, tea, and coffee as well. Humans may be exposed to these elements through different routes; mainly through consumption of contaminated drinking water and food.\(^13\) This is may be due to performing some farming practices through application of organic fertilizers, minerals and pesticides to the agricultural soil that contribute to serious levels of these elements in the final agricultural/animal products.\(^13\) However, the source of exposure to these elements through food is different from element to other.\(^13\) For example, Cd is found at low levels in whole grain, cereals, fruit, and root vegetables, whereas high levels can be found in mussels and fish. Also, Cu and Co are mainly found at high levels in most green vegetables such as Spanish, herbs, and grains when grown in contaminated soil.\(^14\) In various part of the world, different levels of heavy and trace elements in many kinds of food stuff were observed. Voica et al.\(^15\) determined seven trace elements in cocoa, cheese, pepper, milk, bread, and carrot using ICP-MS. The study showed that concentrations of As, Pb, and Sn were below the permissible limits for all studied samples whereas Cd and Cu and Hg concentration were above the limits in bread, coffee, carrots samples, respectively. A review by Nkwunonwo et al.\(^16\) indicated that heavy metal contamination affects Nigeria’s
According to this study, the amounts of these toxic substances found in beverages, food condiments, and some aquatic animals were found within safe levels. Also, Akbari et al. determined the contents of some heavy and trace elements in 10 different honey brands from Iranian markets. The result of the study showed that the contents of Hg, Al and As were above the permissible limits in the tested honey samples. In 2019, Altweiq et al. determined the concentrations of Pb, Ni, Cd, Cu, and As in cereals, breads, rice, canned tuna, soft drinks and processed meat available in the Jordanian market. The study showed that most of the elements were within acceptable levels except some Seri lank and Chinese rice samples which contained high As concentration than the acceptable levels. A study by Makedonski et al. was performed on different Bulgarian fish species (shad, sprat, horse mackerel, Atlantic bonito) showed that the highest concentrations of Cu, Zn, and Pb were measured in muscle tissues of shad and sprat whereas the highest value for Hg was in the edible part of horse mackerel. Atlantic bonito species predominantly accumulates As in their tissue. Despite of that, the results obtained for the elements in analyzed samples were within acceptable limits for human consumption. In 2017, Massadeh et al. investigated Pb, Zn, Cr, Ni, Cu, As, and Cd in different brands of canned vegetables and fruits; canned tomato sauce (ketchup), canned green beans, canned whole carrots, and canned juice (pineapple) imported to Jordanian market. The results obtained showed that Pb and As have the highest concentrations in the most of samples analyzed, whereas, the lowest concentrations obtained were mainly in Cd. The study concluded that consumption of canned vegetable and canned fruit food samples sold in Jordan were not safe according to the WHO.

Coffee beverages may be consumed not only for their stimulating effect but also for their good taste, pleasant aroma and beneficial effect. Coffee consumption accounts for approximately 75% of adult intake of caffeine-containing drinks in the United States. Studies have revealed that daily intake of coffee is associated with a lower risk of depression in women and prostate cancer in men. High intake (3–6 cups a day) stimulates the release of the antidiabetic hormone adiponectin and lowers the risk of diabetes. Recent evidence suggests that coffee may protect against brain changes associated with Alzheimer’s and Parkinson’s disease. A review by investigating the evidence of health benefits associated with coffee consumption showed that coffee consumption was associated with a lower risk of some diseases, such as diabetes, obesity, and cardiovascular diseases. Nevertheless, high levels of heavy metal contamination in soil and the use of chemical fertilizers and pesticides could affect coffee quality.

Currently, the coffee production industry is modernized and uses new processing techniques where roasting of coffee beans is the primary processing method used to develop distinguishing flavor characteristics. The preparation method, grinding and degree of roasting affect not only the final biochemical composition of coffee but also its heavy metal content. Therefore, it is of great importance to estimate the daily intake of heavy metals in order to evaluate any possible health risks associated with coffee consumption.
The aim of this study was to determine the levels of 22 metallic elements in green and roasted coffee beans from five origins, Brazil, Ethiopia, Kenya, Columbia, and India, collected from the Jordanian market. The results of this study were compared with those obtained in other countries and the maximum allowed levels established by national and international authorities. In addition, the content of each heavy metal per cup of coffee was determined and compared to the recommended daily intake (RDI) and tolerable upper limit of daily intake (TULD) of metals determined by the WHO.32

**Materials and methods**

**Coffee bean samples**

In this study, 56 random coffee beans samples were purchased from commercially available varieties on the Jordanian market. Samples from different origins, including Brazil, Kenya, Ethiopia, Colombia, and India, were included. In addition, for each coffee variety, samples prepared via different treatment methods, namely, roasted, half-roasted, and green coffee beans, were used (samples were imported in 2019). The distribution of the studied coffee samples according to origin and treatment method are showed in Table 1. Half-roasted coffee beans are usually made using a temperature of 400°C for 10 min, while roasted coffee beans are treated at 400°C for 20 min.

**Chemicals and reagents**

Deionized water (18.2 MΩ·cm) obtained from a Milli-Q system (Millipore, USA) was used to prepare all solutions and to wash all tools and glassware throughout. Nitric acid (HNO₃ 65%, w:w, suprapure) was obtained from Carlo ERBA reagents, France. Hydrogen peroxide (H₂O₂ 35%, w:w) was obtained from Scharlau Chemie, Barcelona, Spain. Standard solutions containing 100 mg/L⁻¹ of

| Table 1. Distribution of the studied coffee samples according to origin and treatment method category. |
|---------------------------------------------------------------|
| Origin                          | Total number of the samples | Roasted coffee beans | Half-roasted coffee beans | Green coffee beans |
| Brazil                          | 15                           | 6                    | 7                        | 2                  |
| Kenya                           | 11                           | 4                    | 5                        | 2                  |
| Ethiopia                        | 6                            | 1                    | 2                        | 3                  |
| Colombia                        | 17                           | 6                    | 8                        | 3                  |
| India                           | 7                            | 2                    | 3                        | 2                  |
| Total                           | 56                           | 19                   | 25                       | 12                 |
the elements under study were obtained from Merck (Merck Millipore, Darmstadt, Germany). Multielement standard solutions for the construction of calibration curves by ICP-MS were prepared by proper dilution.

**Digestion procedure**

A microwave oven (Anton Paar, Multiwave Eco.) equipped with 16 digestion vessels made of Teflon was used in this study. Before each digestion, the PTFE digestion vessels were rinsed with 5 ml of concentrated nitric acid and thoroughly washed with doubly distilled water. A total of 0.3–0.4 g of a homogenized sample was accurately weighed and transferred into the specified vessel. To each vessel, 6.0 mL of 60% suprapure nitric acid and 2.0 mL of ultrapure 30% hydrogen peroxide were added. Details of the procedure were adapted from Gebretsadik et al.40 with a slight modification. All samples were allowed to stand for at least 5 min under a fume hood and then tightly sealed. The digestion procedure was carried out in three steps using the microwave program shown in Table 2. After digestion, the vessels were allowed to cool to room temperature. The contents were filtered if necessary (using a Whatman No. 40 filter), transferred into a 25 mL volumetric flask and diluted to volume with distilled deionized water. All samples were stored in polyethylene bottles until the time of analysis.

**ICP-MS analysis**

The 22 investigated heavy metals were determined using a Thermo Fisher Scientific inductively coupled plasma-mass spectrometry (ICP-MS) supported by Qtera Intelligent Scientific Data Solution (ISDS) software (iCAP Q series, 2013, USA). The samples were analyzed at the faculty of engineering/Jordan University of Science and Technology (JUST)/Jordan. The analysis was carried out following the manufacturer’s recommended procedure. The generator was operated at a forward power of 1150 W; the plasma, auxiliary, and nebulizer gases were argon with flow rates of 12.0, 0.5, and 0.5 L/min, respectively. The pump flow rate was 1.5 mL/min. The carrier gas flow rate was optimized to obtain maximum signal-to-background ratios.

The validation of ICP-MS measurements was performed using working calibration solutions of all the investigated metal ions. These solutions were

| Step | Power (W) | Ramp (min) | Hold (min) | Fan |
|------|-----------|------------|------------|-----|
| 1    | 600       | 10         | 15         | 1   |
| 2    | 850       | 10         | 10         | 3   |
| 3    | 0         | 10         | 10         | 3   |

Temp. = 200°C.
prepared using appropriate stepwise dilutions of certified standard stock solutions (100 mg/L\(^{-1}\)). The ICP-MS instrument was adjusted to measure the samples, and the correlation coefficient and the RSD were greater than 0.9998 and less than 2%, respectively. The limits of detection (LoD) were calculated as 3SE/slope. SE; standard error of the ordinate intercept the regression of fitting (Table 3).

During the analysis, it was found that the K content in all coffee samples was above the detection limit established with the ICP-MS method. Therefore, randomly chosen coffee samples were prepared with serial dilutions to adjust the readings to fall within the detection range of ICP-MS. The estimated range and average value of K content were then determined in coffee samples regardless of their origin or the treatment method used.

**Quality control and quality assurance of measurements**

To estimate the actual concentrations of elements, at least one laboratory reagent blank was prepared every 10 samples. Laboratory reagent blanks were treated exactly as the samples, including exposure to all steps. After analysis, the average blank value was calculated for each element and subtracted from the measured sample concentration. The sample-to-blank ratios for the measured elements were >10, indicating that blank subtraction did not have a significant contribution to the measured concentrations.

The accuracy and precision were checked by periodic analysis of quality control samples containing known concentrations. These were analyzed within every 15 samples. The coefficients of variation for the concentrations found were within ±5%. The excellent agreement between replicates ensured excellent overall precision. The accuracy of the results is reflected by the closeness of the found concentrations to the expected concentrations. Excellent matching was found for all measured elements.

Moreover, the measurement of Fe, Mn, and Cu were double-checked with an FAAS in 10 randomly selected samples (Varian Spectra AA 55B, Australia). Calibration curves for FAAS were constructed using single-element commercial standards. Excellent agreement between the results of both techniques was observed. The ICP-MS versus FAAS results were linearly fitted, and the correlation coefficients \((R^2 > 0.95)\) were better than 0.95 for the three checked elements. No significant difference between the results of the two techniques was observed \((p > 0.05)\). These findings reveal that the standards used to calibrate the ICP-MS instrument are consistent which supports the accuracy of the final results.

**Results**

**Profile of heavy metals in different coffee bean varieties**

Based on the coffee bean origin, all treatment types were blended in equal ratios and analyzed. A total of 22 (10 macro- and micro essential elements, 12 toxic elements) were identified, and their concentrations were determined. These elements
Table 3. Average concentrations (µg/g) and the limit of detection (ppb) of selected essential and toxic metals in all coffee varieties (based on their origin) available on the Jordanian market.

| Element | LoD* (ppb) | Concentration in ppm (µg/g) | Avg ± SD | Brazil | Colombia | Ethiopia | India | Kenya | Average (all samples) | Range (Min-Max) |
|---------|------------|-----------------------------|---------|--------|----------|----------|-------|-------|----------------------|-----------------|
| **Major** |            |                             |         |        |          |          |       |       |                      |                 |
| 39K     | 3.3119     |                             |         |        |          |          |       |       | 40654.8 ± 5.0         | 33550–45751     |
| 24Mg    | 6.4863     | 4705.8 ± 565.9              | 4347.7 ± 753.5 | 4721.2 ± 537.2 | 4423.0 ± 402.9 | 4640.8 ± 437.7 | 4588.5 ± 600.2 | 4347.7–4721.1 |
| 40Ca    | 6.7032     | 1354.5 ± 904.7              | 1073.4 ± 408.8 | 1047.4 ± 257.2 | 1061.1 ± 272.0 | 1640.1 ± 1390.7 | 1249.5 ± 813.7 | 1047.4–1640.1 |
| 57Fe    | 1.2957     | 161.9 ± 47.5                | 163.7 ± 66.7 | 132.2 ± 109.1 | 196.0 ± 30.1 | 173.5 ± 72.0 | 160.7 ± 65.7 | 132.2–196.0 |
| 27Al    | 6.9479     | 181.8 ± 190.6               | 70.9 ± 48.3 | 158.2 ± 164.3 | 87.0 ± 97.1 | 153.3 ± 160.1 | 136.5 ± 151.7 | 70.9–181.8 |
| 55Mn    | 0.0299     | 71.7 ± 12.4                 | 78.2 ± 23.1 | 45.1 ± 10.3 | 67.0 ± 8.9 | 86.2 ± 39.1 | 71.9 ± 25.6 | 45.1–86.2  |
| **Minor** |            |                             |         |        |          |          |       |       |                      |                 |
| 63Cu    | 0.0252     | 29.67 ± 9.54                | 30.81 ± 8.39 | 24.85 ± 2.62 | 30.32 ± 6.23 | 27.42 ± 3.67 | 27.59 ± 9.58 | 24.85–30.81 |
| 137Ba   | 0.0223     | 7.50 ± 4.24                 | 18.24 ± 8.03 | 14.74 ± 2.47 | 11.68 ± 3.34 | 18.92 ± 10.39 | 14.12 ± 8.21 | 7.50–18.92 |
| 88Sr    | 0.1143     | 5.84 ± 1.08                 | 13.76 ± 6.48 | 8.13 ± 1.85 | 8.34 ± 2.24 | 11.97 ± 3.47 | 10.10 ± 5.05 | 5.84–13.76 |
| 66Zn    | 0.3517     | 6.99 ± 8.80                 | 5.99 ± 6.93 | 7.46 ± 4.89 | 8.57 ± 9.48 | 10.57 ± 10.30 | 7.41 ± 8.05 | 5.99–10.57 |
| 52Cr    | 0.0216     | 2.12 ± 0.64                 | 2.51 ± 1.89 | 2.03 ± 0.54 | 4.06 ± 1.94 | 2.72 ± 1.42 | 2.45 ± 1.43 | 2.03–4.06 |
| 208Pb   | 0.0329     | 1.93 ± 1.80                 | 1.04 ± 0.55 | 2.55 ± 1.40 | 1.44 ± 1.79 | 1.38 ± 0.97 | 1.52 ± 1.32 | 1.04–1.93 |
| 60Ni    | 0.0089     | 0.75 ± 0.29                 | 1.16 ± 0.42 | 0.86 ± 0.31 | 2.67 ± 1.10 | 1.18 ± 0.59 | 1.34 ± 1.22 | 0.75–2.67 |
| 51V     | 0.0121     | 1.03 ± 1.06                 | 0.98 ± 0.76 | 0.72 ± 1.09 | 1.62 ± 1.39 | 0.86 ± 0.62 | 1.00 ± 0.92 | 0.72–1.62 |
| 59Co    | 0.0015     | 0.58 ± 0.14                 | 0.89 ± 0.31 | 0.27 ± 0.08 | 0.97 ± 0.40 | 0.46 ± 0.22 | 0.76 ± 0.57 | 0.27–0.97 |
| 69Ga    | 0.0052     | 0.35 ± 0.14                 | 0.95 ± 0.58 | 0.67 ± 0.10 | 0.53 ± 0.14 | 0.92 ± 0.43 | 0.70 ± 0.45 | 0.35–0.95 |
| 23Ba    | 0.0012     | 0.23 ± 0.51                 | 0.20 ± 0.82 | 0.54 ± 0.66 | 0.00 ± 0.00 | 0.13 ± 0.43 | 0.20 ± 0.59 | 0.13–0.54 |
| 111Cd   | 0.0004     | 0.26 ± 0.44                 | 0.15 ± 0.18 | 0.29 ± 0.23 | 0.10 ± 0.12 | 0.14 ± 0.09 | 0.18 ± 0.26 | 0.10–0.29 |
| 107Ag   | 0.0023     | 0.15 ± 0.18                 | 0.16 ± 0.16 | 0.22 ± 0.17 | 0.50 ± 0.92 | 0.14 ± 0.18 | 0.18 ± 0.28 | 0.14–0.50 |
| 7Li     | 0.0042     | 0.05 ± 0.05                 | 0.06 ± 0.08 | 0.20 ± 0.36 | 0.10 ± 0.12 | 0.07 ± 0.05 | 0.10 ± 0.14 | 0.05–0.20 |
| 11In    | 0.0040     | 0.12 ± 0.29                 | 0.04 ± 0.12 | 0.13 ± 0.14 | 0.03 ± 0.05 | 0.04 ± 0.05 | 0.07 ± 0.17 | 0.03–0.13 |
| 209Bi   | 0.0005     | 0.04 ± 0.04                 | 0.07 ± 0.10 | 0.02 ± 0.02 | 0.06 ± 0.04 | 0.07 ± 0.07 | 0.05 ± 0.07 | 0.02–0.07 |

* Limit of Detection (ppb).
** The concentration of potassium (K) was calculated using different coffee samples chosen randomly, regardless of their origin or treatment method used, and prepared with serial dilutions to adjust the reading to fall within the detection range of the ICP-MS method.
were then classified based on their prevalence (average concentration) in each variety into two groups: major and minor metals (Table 3).

Overall, it was found that the concentrations of major (K, Mg, Ca, and Fe) and minor elements (V, Co, Ga, U, Cd, Ag, Li, In, and Bi) among the five varieties of coffee were close to each other. Th and Ti were not detected in the majority of the coffee bean samples; therefore, their values are not shown.

Of the major metals, potassium (K) was found to be the predominant element, followed by Mg, Ca, and Fe. Al and Mn were found at the lowest concentrations among the major elements analyzed. Al was found to be the highest in Brazilian, Ethiopian, and Kenyan varieties and the lowest in Colombian and Indian varieties. Mn showed the lowest concentration in Ethiopian coffee in comparison with other varieties.

Of the minor elements, Cu was found to be predominant, followed by Sr and Ba. All varieties showed similar concentrations of minor elements except for Ba and Sr, which exhibited the lowest concentrations in Brazilian coffee.

The significance of variations in the concentrations of measured elements was statistically evaluated by means of one-way analysis of variance (ANOVA). The level of significance was set to 0.05. Except for Co ($p < 0.05$), the ANOVA results show that there is no significant difference between the concentrations of measured elements in coffee beans from different countries.

**Profile of heavy metals in coffee beans with different treatment types**

The quantitative content of 22 metallic elements in green, roasted, and half-roasted coffee beans from different origins available on the Jordanian market were determined (Table 4).

In general, the concentrations of the major and minor metals detected in all treatment types were found to be approximately within the same range. Considering minor elements, roasted coffee beans were found to contain the highest concentrations of Ba and Sr. The Zn concentration was found to be the highest in half-roasted beans. ANOVA results showed the existence of a significant difference in mean concentrations of Cr, Co, and Zn ($p < 0.05$) in green and roasted coffee beans.

**Discussion**

**Estimated daily intake of heavy metals through coffee consumption in Jordan**

Table 5 shows that for all the detected heavy metals, their intake per 1 cup of coffee prepared by boiling 2 g of ground coffee beans in 50 ml of tap water does not largely contribute to the RDI or to the TULD in an adult with an average body weight of 80 kg who consumes only 1 cup of coffee daily, according to the values in the published report of a joint FAO/WHO expert panel on the risks and benefits of coffee consumption$^{33,34}$ FAO and WHO joint meeting 2011.
Of the heavy metals that were defined as major elements, K and Ca contributed to less than 1% of the RDA, whereas Mg, Fe, Cu, Pb, and Mn contributed to less than 10% of the RDI. Cr contributed to 14% and 4.08% of the RDI and TULD limits, respectively. While the RDAs for Al and Cd have not yet been determined, they contributed to 2.39% and 3.015% of the weekly TULD, respectively.

Regarding the other minor elements, their contributions to the RDI or TULD values were negligible if intake was limited to the consumption of a moderate amount of coffee as a beverage. To the best of our knowledge, neither RDA nor TULD limits for Ba, Sr, Ga, U, Ag, Li, In, Bi, Th, and Ti have been reported yet.

Whether coffee should be considered as an appreciable source of minerals may vary.\textsuperscript{35} Coffee ranks among the top five daily sources for K among the U.S. population.\textsuperscript{36} A cup of coffee contains 116 mg of potassium, and six cups would provide

### Table 4. Average concentrations (µg/g) of selected essential and toxic metals in all coffee types (based on treatment method) available on the Jordanian market.

| Element | Concentration (µg/g) |
|---------|---------------------|
|         | Avg ± SD            |
| **Major** |                   |
| 39K     | 4287.47 ± 568.19    |
| 24Mg    | 963.46 ± 264.48     |
| 48Ca    | 162.42 ± 60.92      |
| 57Fe    | 68.75 ± 62.78       |
| 355Mn   | 65.36 ± 22.47       |
| **Minor** |                  |
| 63Cu    | 25.54 ± 14.28       |
| 137Ba   | 14.93 ± 9.28        |
| 88Sr    | 11.52 ± 6.16        |
| 66Zn    | 2.27 ± 2.24         |
| 52Cr    | 1.72 ± 0.53         |
| 208Pb   | 0.75 ± 0.56         |
| 60Ni    | 1.33 ± 1.65         |
| 51V     | 0.86 ± 0.62         |
| 59Co    | 0.97 ± 0.83         |
| 69Ga    | 0.82 ± 0.59         |
| 238U    | 0.00 ± 0.00         |
| 111Cd   | 0.06 ± 0.05         |
| 107Ag   | 0.12 ± 0.11         |
| 7Li     | 0.10 ± 0.13         |
| 113In   | 0.00 ± 0.01         |
| 209Bi   | 0.03 ± 0.02         |

\* The concentration of potassium (K) was calculated using different coffee samples chosen randomly, regardless of their origin or treatment method used, and prepared with serial dilutions to adjust the reading to fall within the detection range of the ICP-MS method.
| Elements | Avg $\pm$ SD* ($\mu$g/g) | Range (max-min) ($\mu$g/g) | Daily intake (µg/2 g) | RDI | % RDI | TULD | % TULD |
|----------|--------------------------|-----------------------------|----------------------|-----|-------|------|-------|
| $^{39}$K | 406.53 ± 5.00            | 33.550–45.751              | 39,162.020           | 4700 mg | 0.83 | ND   | –     |
| $^{24}$Mg| 4588.45 ± 600.23         | 4347.70–4721.1             | 9176.900             | 320–420 mg | 2.18 | 750 mg/day | 1.22 |
| $^{48}$Ca| 1249.50 ± 813.66         | 1047.40–1640.1             | 2499.000             | 1000–1200 mg | 0.21 | 2500 mg/day | 0.10 |
| $^{57}$Fe| 160.67 ± 65.74           | 132.18–195.99              | 321.340              | 10–15 mg | 2.14 | 45 mg/day | 0.71 |
| $^{27}$Al| 136.45 ± 151.65          | 70.94–181.84               | 272.900              | ND   | –     | 1 mg/kg bw/week | 2.39 |
| $^{55}$Mn| 71.88 ± 25.6             | 45.07–86.18                | 143.760              | 1.8–2.3 mg | 6.25 | 11 mg/day | 1.31 |
| $^{63}$Cu| 27.59 ± 9.58             | 24.85–30.81                | 55.180               | 0.9–2 mg | 2.76 | 10 mg/day | 0.00 |
| $^{66}$Zn| 7.41 ± 8.05              | 5.99–10.57                 | 14.820               | 10–15 mg | 0.10 | 40 mg/day | 0.04 |
| $^{52}$Cr| 2.45 ± 1.43              | 2.03–4.06                  | 4.900                | 25–35 µg | 14.00 | 120 µg/day | 4.08 |
| $^{208}$Pb| 1.52 ± 1.32              | 1.04–1.93                  | 3.040                | 0.02–3 µg/kg bw | 1.27 | 25 µg/kg bw/day | 0.15 |
| $^{60}$Ni| 1.34 ± 1.22              | 0.75–2.67                  | 2.680                | 70–170 µg/kg | 0.02 | 1 mg/day | 0.27 |
| $^{51}$V | 1.00 ± 0.92              | 0.72–1.62                  | 2.000                | –     | –     | 1.8 mg/day | 0.11 |
| $^{59}$Co| 0.76 ± 0.57              | 0.27–0.97                  | 1.520                | 700–900 µg/day | 0.17 | 5000–10,000 µg/day | 0.00 |
| $^{111}$Cd| 0.18 ± 0.26              | 0.10–0.29                  | 0.360                | ND   | –     | 7 µg/kg bw/week | 3.15 |

bw: body weight; ND: not determined.

*Average values calculated for all coffee samples varieties regardless of method of treatment.
between 690 and 780 mg of potassium in a day, which represents approx. 22.0% of the recommended dietary intake for potassium (4700 mg/day). Whereas the daily requirement of magnesium for adults is 420 mg, only 7 mg can be found in a cup of coffee (8 oz.).

Among all the determined metals in this study, only the permissible levels of Zn, Pb, and Cu are listed in Jordanian legislation (Table 6) (JS 314:1997-Green coffee beans and JS315:2004-Roasted coffee, crushed roasted, and ground coffee). Therefore, a comparison was made only for those items presented in Table 6.

Regarding the roasted coffee beans, Zn (2.27 ± 2.24 µg/g) and Cu (25.54 ± 14.28 µg/g) were found to occur at lower contents than the allowed maximum limits determined by Jordanian legislation, 50 mg/kg for both elements. The Pb concentration was found to exceed the limit, with measured and limit values of 0.75 ± 0.56 µg/g and 0.50 mg/kg, respectively. This observation is similar to what was reported by Alomary et al. regarding Pb levels in medicinal herbs from Jordan.

For green coffee beans, the determined contents of Zn (6.57 ± 4.72 µg/g), Pb (2.09 ± 1.71 µg/g), and Cu (28.58 ± 6.65 µg/g) were lower than the maximum allowed limits determined by Jordanian legislation.

Previously, many papers have been published around the world regarding the determination of essential and toxic heavy metals in different pharmaceuticals, foods and beverages, including coffee. Coffee is not cultivated in Jordan; it is imported from other countries, mainly Brazil and Ethiopia. The values of essential and toxic metals detected in coffee samples included in this study were slightly different from those reported by da Silva et al. and Gebretsadik et al. in roasted and green beans collected from Brazil and Ethiopia, respectively. Both previous studies were performed using atomic absorption spectroscopy (AAS), whereas in

### Table 6. Comparison of heavy metal average concentrations measured in roasted and green coffee with the maximum allowed limits according to Jordanian legislation.

| Element | Roasted coffee beans | Green coffee beans |
|---------|----------------------|--------------------|
|         | Jordanian legislation (µg/g) | Present study (µg/g) | Jordanian legislation (µg/g) | Present study (µg/g) |
| Zn      | 50                   | 2.27 ± 2.24        | 50                   | 6.57 ± 4.72        |
| Pb      | 0.50                 | 0.75 ± 0.56        | 5                    | 2.09 ± 1.71        |
| Cu      | 50                   | 25.54 ± 14.28      | 50                   | 28.58 ± 6.65       |

*JS 314:1997-Green coffee beans, JS315:2004-Roasted coffee, crushed roasted, and ground coffee.*
this study, we used inductively coupled plasma mass spectrometry (ICP-MS), which has many advantages over AAS: less time is needed for analysis, and the cost is lower if the determination of more than 10 elements/sample is required.

The findings of this study, utilizing data for both roasted and green coffee beans (no published data were found for the half-roasted treatment), were compared with those published in the literature from Brazil and Ethiopia only because of the lack of published data on Colombian, Indian, and Kenyan beans.

Regarding the roasted coffee samples, the data obtained by ICP-MS revealed that the metal contents in roasted coffee samples were different from previously reported values obtained using the AAS method (Table 7). However, in comparison to the reported results for Ethiopian and Brazilian varieties, higher concentrations of Mg, Mn, Cu, and Cr were observed in the present study. In contrast, Zn was found to occur at lower concentrations. For the other elements, Fe, Al, Ba, Sr, V, Co, Ga, U, Ag, Li, In, and Bi, there were no reported values for these two coffee varieties in the literature. Published data regarding the heavy metal content in green coffee beans were available for the Ethiopian variety only and were obtained using the AAS method. Table 7 shows that higher concentrations of Mg, Fe, Mn, Cu, Cr, Pb, Co, and Cd and a lower concentration of Zn were found in the present study than in the previous studies on Ethiopian beans. For the other elements, Al, Ba, Sr, V, Ga, U, Ag, Li, In, and Bi, there were no published data on their occurrence in the Ethiopian variety.

To the best of our knowledge, this is the first study conducted in Jordan to determine the essential and toxic metal contents in five coffee varieties using the ICP method. These findings may help to modify the current local legislation in Jordan with respect to heavy metal content. Similarly, coffee infusions analyzed using ICP-MS by41 revealed that Pb consumption in heavy drinkers of coffee may contribute to the disease burden.

Conclusion

The concordance of heavy elements’ levels to the international standards affirms that the imported coffee beans to Jordan are subjected to the assigned standards imposed by the government and the Jordan Food and Drug Administration (JFDA). As expected, the results indicated that no significant differences in the levels of the measured elements in coffee beans that are subjected to different levels of roasting (treatment). This is can be justified as the treatment temperature is below the required temperature for evaporation of these elements. Regardless of the origin of coffee beans, the majority of heavy metals did not show significant differences among the tested samples. Therefore, coffee beans available in the Jordanian market did not contain toxic levels of the measured elements.
Table 7. Comparison of the average concentrations (µg/g) of 22 essential and toxic metals in roasted and green coffee beans available on the Jordanian market, including Brazilian and Ethiopian varieties, as reported by Alomary et al.38; Da Silva et al.39 and Massadeh et al.20

| Element | Concentration (µg/g) | Present study* | Da Silva et al.38, ** | Gebretsadik et al.40, ** | Gure et al.28, ** |
|---------|---------------------|----------------|-----------------------|--------------------------|-----------------|
|         | Avg ± SD            | Roasted Brazilian coffee | Green Ethiopian coffee | Roasted Brazilian coffee | Roasted Ethiopian coffee | Green Ethiopian coffee |
| Major   |                     |                             |                       |                          |                          |                       |
| 39K     |                     | ND                          | ND                    | NR                       | 19610 ± 343         | 17000 ± 1020          |
| 24Mg    | 4899.07 ± 459.29    | 4424.247 ± 353.843         | 5246.940              | NR                       | 2030 ± 98           | 1690 ± 40             |
| 48Ca    | 1484.33 ± 987.04    | 936.531 ± 242.458          | 1210.420              | NR                       | 1009 ± 18           | 1250 ± 70             |
| 57Fe    | 186.117 ± 39.046    | 95.508 ± 75.603            | 319.970               | NR                       | NR                 | 44.0 ± 40             |
| 27Al    | 115.07 ± 82.89      | 186.572 ± 204.257          | 111.057               | NR                       | NR                 | NR                    |
| 55Mn    | 79.457 ± 8.874      | 45.449 ± 13.262            | 43.847                | 19.44 ± 4.32             | 23 ± 0.5            | 19.0 ± 1.0            |
| Minor   |                     |                             |                       |                          |                          |                       |
| 63Cu    | 27.064 ± 7.394      | 24.143 ± 2.809             | 27.781                | 10.38 ± 2.52             | 13 ± 0.2            | 22.9 ± 2.2            |
| 137Ba   | 6.954 ± 1.674       | 14.039 ± 3.261             | 15.913                | NR                       | NR                 | NR                    |
| 88Sr    | 6.188 ± 1.151       | 7.471 ± 1.950              | 9.002                 | NR                       | NR                 | NR                    |
| 66Zn    | 7.061 ± 10.423      | 6.300 ± 5.751              | 11.225                | 6.62 ± 2.26              | 18 ± 0.3            | 21.1 ± 0.1            |
| 52Cr    | 2.024 ± 0.745       | 2.256 ± 0.541              | 1.540                 | 0.34 ± 0.30              | NR                 | 0.28 ± 0.01           |
| 208Pb   | 1.188 ± 0.846       | 2.453 ± 1.786              | 3.009                 | 0.75 ± 0.33              | ND                 | 0.06 ± 0.005          |
| 60Ni    | 0.723 ± 0.186       | 0.831 ± 0.390              | 0.891                 | 0.70 ± 0.38              | NR                 | 2.5 ± 0.02            |
| 51V     | 0.883 ± 0.934       | 0.352 ± 0.290              | 2.884                 | NR                       | NR                 | NR                    |
| 59Co    | 0.667 ± 0.112       | 0.271 ± 0.104              | 0.319                 | NR                       | NR                 | 8.4 ± 0.20            |
| 69Ga    | 0.331 ± 0.046       | 0.661 ± 0.134              | 0.686                 | NR                       | NR                 | NR                    |
| 238U    | 0.00 ± 0.00         | 0.193 ± 0.386              | 1.596                 | NR                       | NR                 | NR                    |
| 111Cd   | 0.103 ± 0.075       | 0.246 ± 0.280              | 0.450                 | 0.01 ± 0.01              | ND                 | < 0.01                |

(continued)
| Element | Concentration (µg/g) |
|---------|---------------------|
|         | Avg ± SD            |
| Present study* |                     |
| Roasted Brazilian coffee | Green Ethiopian coffee | Roasted Ethiopian coffee | Roasted Brazilian coffee | Roasted Ethiopian coffee | Green Ethiopian coffee |
| 107Ag   | 0.080 ± 0.086       | 0.145 ± 0.162       | 0.390                   | NR                      | NR                      | NR                      |
| 7Li     | 0.030 ± 0.043       | 0.261 ± 0.454       | 0.061                   | NR                      | NR                      | NR                      |
| 113In   | 0.019 ± 0.035       | 0.114 ± 0.170       | 0.222                   | NR                      | NR                      | NR                      |
| 209Bi   | 0.017 ± 0.018       | 0.026 ± 0.014       | 0.005                   | NR                      | NR                      | NR                      |
| 232Th   | 0.007 ± 0.005       | 0.002 ± 0.002       | 0.005                   | NR                      | NR                      | NR                      |
| 205Ti   | 0.002 ± 0.001       | 0.00 ± 0.00         | 0.001                   | NR                      | NR                      | NR                      |

NR: not reported; ND: not determined.

*Method used is ICP-MS.

**Method used is AAS.

The concentration of potassium (K) was calculated using different coffee samples chosen randomly, regardless of their origin or treatment method used, and prepared with serial dilutions to adjust the reading to fall within the detection range of the ICP-MS method.
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