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Original article

Evaluation of the Contents of Manganese and Lead and their Hazard Indices in some Coffee Brands

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Abstract
In this study Ten different coffee samples of different brands were collected from many Libyan Markets. The contents of Lead (Pb) and Manganese (Mn) were estimated in the selected samples by atomic absorption spectrometry (AAS). The concentrations of Manganese in the selected samples in this study fluctuated in the ranges of 0.100 and1.324 ppm. Whereas the concentrations of Lead ranged between 0.036 and 0.537 ppm. The higher concentration of Manganese was recorded in the Al Wasar Coffee sample, whereas the lower concentration of Mn was recorded in the Faysal coffee sample. On the other hand, the contents of Lead ranged between 0.036– 0.537 ppm. The higher concentration of Lead was recorded in the Al-Wasar Coffee sample, while the lower concentrations were recorded in the Dubai Coffee sample. The study concluded that the contents of the selected coffee samples were higher than the limits recorded by WHO. The values of Estimated Daily Intake (EDI) ranged between 0.009- 0.12 for manganese and from 0.003 to 0.048 for lead contents. On the side, the values (Estimated weekly Intake, EWI) for manganese ranged from 0.063 to 1.47 and from 0.021 to 0.336 for lead. On the other hand, the Target Hazard Quotient (THQ) values ranged from 0.0.0007 – 0.0095 for manganese and from 0.00031 – 0.0038 for lead. The results of these recorded high values of manganese contents are within the safety limits.
Keywords. Lead, Manganese, Coffee samples, imported, Hazard Indexes.

Introduction

The process of making coffee starts with the separation of the seeds from coffee cherries, which are the fruits of the coffee plant, to create unroasted green coffee beans. After being roasted, the "beans" are finely pulverized. The ground roasted beans used to make coffee are usually soaked in hot water and then filtered out. Although cold or iced coffee is frequently served, it is typically served hot. There are many ways to make and serve coffee, such as espresso, French press, coffee latte, or canned coffee that has already been made. To cover up the bitter taste or improve the flavor, sugar, sugar alternatives, milk, and cream are frequently added. Despite being a worldwide product, coffee has a long history of being strongly associated with Red Sea culinary customs. The oldest reliable accounts of coffee consumption date back to the middle of the 15th century, when Yemeni Sufis began using the plant [4][5]. Yemen supplied most of the world's coffee imports until the end of the 17th century. However, when coffee became increasingly popular, it began to be grown in Java in the 17th century and in the Americas starting in the 18th century [6]. C. arabica and C. robusta are the two varieties of coffee beans that are grown most frequently [7]. More than 70 countries grow coffee, mostly in the tropical regions of the Americas, Southeast Asia, the Indian subcontinent, and Africa. Unroasted, green coffee is traded as a product of agriculture [8]. Brazil produced 31% of the world's coffee beans in 2023, making it the top producer, followed by Vietnam. Coffee producers are disproportionately poor, even though coffee sales exceed billions of dollars globally each year. The coffee industry's detrimental effects on the environment, such as water use and land clearance for coffee cultivation, have been highlighted by its detractors. Estimate heavy metals have been conducted in many studies in Libya on different samples as water, soil, plants, and others [9-40]. Also, there are different chemical studies on different hazard compounds that may be found in food samples [41-89]. This study aims to estimate the contents of Lead and Manganese in different coffee samples collected from local markets in some Libyan cities.

Methods

Sampling

Ten different samples of commercial coffee brands were collected from different Libyan Markets. The samples were illustrated in (Table 1).

Samples preparation

0.5 gram of each sample was transferred to clean and dry conical flasks. Then, 5 ml of nitric acid and 25 ml of distilled water were added to the samples.

Digestion of the lead and Manganese metals

The samples were designed after adding nitric acid by used hot plate, where the samples were left for two hours and then allowed to cool. The sample, the samples were filtered, and completed the volume to 100

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mL, the digestion of the samples was carried out according to previous studies described on solid samples [10-15].

Table 1. The studied Coffee brand samples

Sample No	Sample Type
1	Al-Wasar
2	Mssafi
3	Faysal
4	Al Ameed
5	Dubai
6	Turkish
7	Alkalig
8	Dar Al Bon
9	AbuAuf
10	Sekeroglu

Determination of Manganese and Lead

The lead metal contents were measured by atomic absorption (Type Thermo) at the central laboratory of Omar Al-Mukhtar University.

Estimate the human health risk

The human health risk assessment of the intake of elements with coffee was based on the Estimated Daily Intake (EDI) (1) and the Target Hazard Quotient (THQ) (2, 3). For assessment of toxic element intake (Pb, Mn), the standard values proposed by EFSA were adopted: TWI (tolerable weekly intake) for. Due to the damage caused by Mn to human health, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) established a provisional tolerable monthly intake (PTMI) of 25 µg/kg BW and a BMDL value (benchmark dose lower confidence limit) for Pb, determined for adult consumers: BMDL01—1.5 µg/kg/bw per day.

Estimated Daily Intake (EDI)

The estimated Daily Intake was calculated from the following equation:

$$EDI = (MS \times C)/BW$$

Where MS is the daily coffee intake6.33 g/day [16] with 100 mL of water; C is the content of the element in the analyzed coffee (mg/kg); and BW is the reference body weight (70 kg).

Estimated Weekly Intake (EWI)

The weekly Intake values were estimated by the following equation:

$$EWI = EDI \times 7 \text{ [µg/kg bw/week]}$$

Target Hazard Quotient (THQ)

The total Target Hard quotient was calculated according to the following equation**:**

$$THQ = (EF \times ED \times MS \times C)/(RfD \times MS \times AT) \times 10^{-3}$$

$$THQ = (EF \times ED \times MS \times C)/(RfD \times MS \times AT) \times 10^{-3}$$

Where

EF: is the exposure frequency to trace elements (365 days/year); ED: is the exposure duration (70 years); MS: is the daily coffee intake 6.33 g/day [16]; C: is the concentration of trace elements in coffee (mg/kg); RfD: is the oral reference dose of trace element (mg/kg bw/day): Mn = 0.14; [28]; BW: is the reference body weight (70 kg); AT: is the averaged exposure time to non-carcinogenic trace elements (365 days × 70 years).

Results

The concentrations of Manganese in the selected samples in this study fluctuated in the ranges of 0.100 and1.324ppm. Whereas the concentrations of Lead ranged between0.036 and 0.537 ppm. The higher concentration of Manganese was recorded in the Al Wasar Coffee sample, whereas the lower concentration of Mn was recorded in the Faysal coffee sample. On the other hand, the contents of Lead ranged between 0.036– 0.537ppm. The higher concentration of Lead was recorded in the Al-Wasar Coffee sample, while the lower ones were recorded in the Dubai Coffee sample (Table 2) and (Figures 1&2).

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Table 2. The concentrations (ppm) of Mn and pb in the studied coffee samples

Sample No	Sample Type	Manganese Concentrations	Lead Concentration
1	Al-Wasar	1.324	0.537
2	Mssafi	0.704	0.149
3	Faysal	0.100	0.100
4	Al Ameed	0.864	0.184
5	Dubai	0.389	0.036
6	Turkish	0.899	0.130
7	Alkalig	0.516	0.099
8	Dar Al bon	0.232	0.044
9	AbuAuf	0.909	0.283
10	Sekeroglu	0.189	0.266
Average	-	0.612	0.182
±SD	-	0.330	0.330

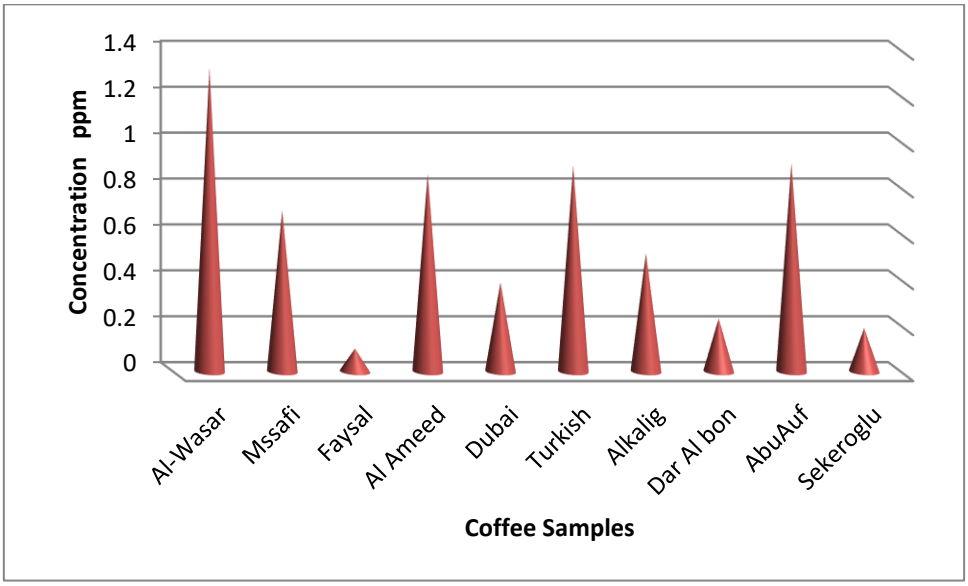

Figure 1. The concentrations of Manganese in the coffee samples

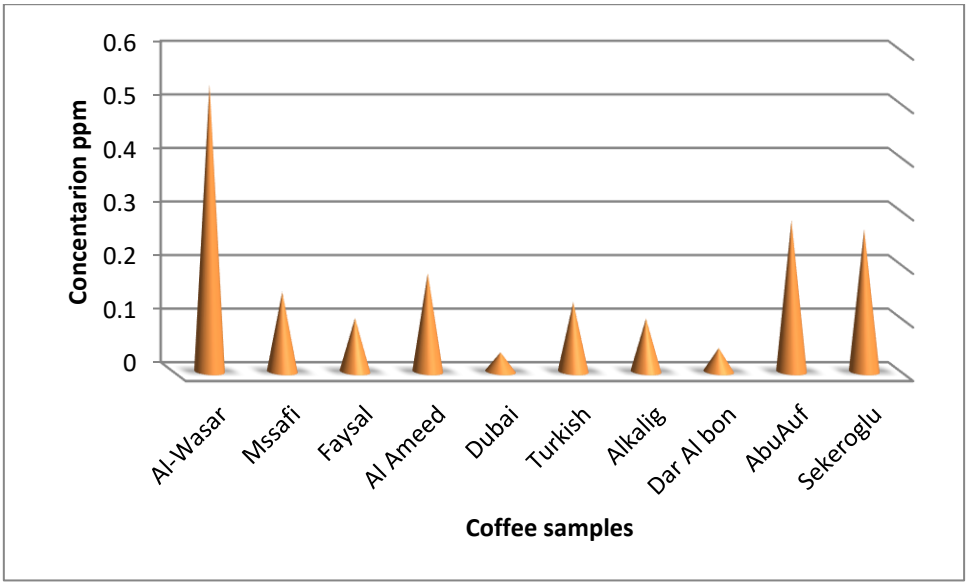

Figure 2. The concentrations of Lead in the Coffee samples

Estimated Daily Intake (EDI), Estimated Weekly Intake (EWI), and Target Hazard Quotient (THQ)
The values of were illustrated in (Table 3). The results of this study showed that the Daily Intake (EDI) of manganese ranged between (0.009 – 0.12), higher values were recorded for the sample (1), whereas the lower one was recorded in sample (3). The values of EDI of lead metal ranged between (0.003 – 0.048), the highest value was observed in sample No 1, and the lower one was recorded in sample No (8). For the EWI,

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the results of this study recorded that their values ranged between (0.063 – 1.47) and (0.021 – 0.336) for the manganese and lead content, respectively. The Target Hazard Index values showed that the higher values of manganese (0.336) were obtained in sample No.1, while the lower (0.021) value was recorded in sample No. (8). On the side, the higher value of Lead (0.0038) was recorded in sample No.1, whereas the lower one (0.00031) was observed in sample No.8 (Table 3).

Table 3. The values of EDI, EWI, and THQ of the studied samples

Sample	EDI Mn	EWI Mn	THQ Mn	EDI Pb	EWI Pb	THQ pb
1	0.12	1.47	0.0095	0.048	0.336	0.0038
2	0.06	0.42	0.0050	0.0054	0.0378	0.0010
3	0.009	0.063	0.0007	0.009	0.063	0.00071
4	0.078	0.546	0.0061	0.016	0.112	0.0013
5	0.035	0.245	0.0027	0.035	0.245	0.0017
6	0.081	0.567	0.0064	0.011	0.077	0.00054
7	0.0466	0.322	0.0036	0.008	0.056	0.00039
8	0.020	0.14	0.0016	0.003	0.021	0.00031
9	0.082	0.574	0.0064	0.007	0.049	0.0020
10	0.017	0.119	0.0013	0.024	0.168	0.0018

Discussion

The presence of trace elements, which make up 7% of coffee beans and can be crucial to the body's regular operation, has been linked to this impact. Iron, for instance, is involved in oxygen transfer, DNA synthesis, and electron transport. Coffee beverages may be a source of contaminants, including dangerous materials that are found in the environment because of either natural (volcanic eruptions, leaching from soil and rocks) or anthropogenic (industrial and agricultural operations, including ineffective waste management) sources [91]. The mineral content of coffee can vary and include dangerous elements like lead (Pb) and manganese (Mn), depending on the kind and variety of coffee, as well as the brewing procedure [92]. The purpose of this article was to determine the content of particular trace elements, including lead and manganese, in coffees sold in Libya and to compare the intake with the RDA (Recommended Dietary Allowance) of the elements studied in ground and instant coffee. It also determines the risk to consumers' health associated with drinking coffee and being around these ingredients. Because coffee is so widely consumed, it is crucial to understand its chemical makeup. Additionally, coffee can be used as a supplement for specific minerals, even though it is not usually advertised as a source of minerals. The average manganese concentration in the ground coffees under analysis was similar to what previous writers had found. However, earlier research found far lower manganese quantities in coffee, ranging from 24.6 to 49.5 µg/g, which is around three times greater than the current study's conclusion.

The average manganese concentration of the instant coffee under test in this investigation. On the other hand, other authors have reported a range of values, from 3.62 ppm to 38.85 ppm. The recommended daily intake of manganese is 2.3 mg for men and 1.8 mg for women. The THQ coefficient was 0.021 and 0.336 for manganese, and from 0.00031 to 0.0038 for lead; these values are lower than those found in earlier research. The average lead concentration in ground coffees was similar to findings from other authors, who discovered mean lead concentrations of 0.02 and 0.017 ppm, respectively. Instant coffee also had low amounts of lead, with an average of 0.002 ppm, 0.014 ±. The concentration of lead in instant coffee was significantly lower than that obtained by previous studies who found the mean value to range from 0.09 to 0.91 ppm [92].

Conclusion

This study showed the presence of Manganese and Lead in the studied samples (Coffeebrands) collected from local Markets at Al Bayda city, Libya.

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Conflict of interest. Nil

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