Alqalam Journal of Medical and Applied Sciences. 2025;8(3):1422-1431
https://doi.org/10.54361/ajmas.258324

Original article

Evaluating the Concentration of Heavy Metals in Commercial Coffee: A Comparative Study with Global Safety Levels

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Abstract
Given that coffee represents a widely popular beverage, and given the harm that this drink can cause as a result of the accumulation of some heavy metals in it. This study aimed to concentrations of the accumulation of heavy metals in coffee beans, in addition to evaluating the concentration of some heavy metals," such as iron (Fe), Lead (Pb), chromium (Cr), copper (Cu) and essential minerals (sodium (Na), potassium (K)" in different types of commercial coffee available in the Libyan market. Through a methodology based on analyzing the concentration of metals in 6 types of coffee widespread in the Libyan market and determining the concentration of metals in them, and comparing it to the internationally permissible percentage. The results indicated that most of the percentages are within the permissible limits, as Potassium concentrations were less than the permissible limits. Concentrations of (K) in the coffee samples reached between 0.01793 and 0.02193 parts per million, less than the permissible limit (0.07 ppm). As for Na concentration ranged between 0 and 0.00058 ppm, which is much less than the permissible limit (0.06 ppm). While the Cu concentration exceeded the permissible limit (0.02 ppm), which constitutes a threat to public health, as well as the Pb concentration ranged between 88.9015 and 132.983 ppm, exceeding the permissible limit (0.04 ppm). The concentration of Cr^3 ranged between 5.4687 and 5.5886 ppm, exceeding the recommended daily dose (0.03 ppm).
Keywords. Coffee, Heavy Metal Concentrations, Permissible Percentages, Harms, Benefits.

Introduction

Coffee is the most famous and most consumed beverage in the world, coming in second place after tea, with the equivalent of 2.5 billion cups of coffee consumed daily. Consumption rates vary according to different countries, regions, and environments. In Canada, it occupies first place in the world, and countries such as Bosnia, Brazil, Lebanon, and Poland occupy advanced positions, as the rates of coffee consumption are high [1]. The research problem relates to the possibility of coffee being contaminated with some heavy and toxic metal elements, such as lead (Pb), and chromium (Cr), in addition to basic metal elements such as sodium (Na), potassium (K), and copper (Cu). These elements may enter coffee through soil, water, manufacturing processes, or packaging and storage [2]. Given that it is one of the most common beverages and the safety of coffee is related to human health, which is the center of the planet, there was a necessary need for precise scientific studies through which the concentration of these metals could be measured in the different types of commercial coffee most traded in the markets, especially the Jordanian markets, and the potential health risks of consuming them can be assessed [3, 4]. This pollution raises questions about the safety of coffee consumption for public health, especially with increasing scientific reports linking the accumulation of these heavy metals in the body to the occurrence of negative health effects that include neurological damage, chronic diseases, and even cancer [5]. Hence, the need for a precise scientific study that measures the concentration of these elements in different types of commercial coffee traded in Libyan markets and assesses the potential health risks associated with their regular consumption [6].

Heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), and copper (Cu) are reported to accumulate in the body over a long period, leading to serious health abnormalities, including neurological dysfunctions, kidney impairments, and carcinogenic properties [7]. The World Health Organization (WHO) and regulatory agencies have established maximum allowable limits of such metals in foods and drinks [8]. Given the importance of this drink, this study aims to evaluate the concentration of some heavy metals "such as lead Pb, chromium Cr, copper Cu, iron Fe' and essential minerals (sodium Na, potassium K)" in different types of commercial coffee available in the different market at Al-Bayda City-Libyan and to compare them with the standards recommended by the "World Health Organization (WHO)".

Methods

Some tools were used, whether software tools or laboratory tools, and coffee sample analysis techniques were chosen to determine and analyze the concentration rates of heavy metals in different types of coffee.

Materials and Ingredients

Nitric acid (HNO3 65%), Hydrochloric acid (HCL, 37%), and distilled water were the main chemical solutions that were used in the experiment.

Received*: 08-05-2025 -* ***Accepted****: 06-07-2025 -* ***Published****: 19-07-2025*

Samples Collection and Preparation

Samples were collected in the period between September and October 2023, from commercial markets or shops selling coffee in the City of Al-Bayda. Six samples were taken for each type of coffee then placed the data for these samples as shown in Table 1.

Table1. Common name and code from different types of Coffee

Common name	Sample code
Turk	CT
Masafiy	CM
Bala	CB
Albriani	CA
Krista	CK
Kawa	CKAWA

Samples digestion

After samples were collected, wet digestion was carried out as follows: 0.5 g of dry sample was placed in a beaker, then 5 mL of concentrated HNO_3 was added. The beaker was heated until the brown oxides evaporated, then 5 ml of concentrated HCl was added after evaporating to half volume. Samples were diluted and filtered into a 100ml volumetric flask. The volume was completed up to the mark by adding distilled water. Instrumentation UV-Visible spectrophotometer (DU 800, BECKMAN Coulter) was used to determine the heavy metals, and a Flame photometer was used to determine the mineral metals in the coffee samples under study.

Standard preparation

The standard stock solution was prepared of (iron, copper, chrome, and lead) at 1000 ppm, then serial working solution was made at (2, 4, 6, 8, 10 ppm) and 1000 ppm for (Sodium, Potassium) at (4.6.8,10 ppm)'' concentration for the flame photometer.

Statistical analysis

A set of statistical tests was used, which is one of the most important tools to analyze the results. linear regression, the analysis of variance, and correlation are used to determine the degree of importance of P-VLUE, which has a marginal value of 5%, and the less the marginal value is less than 5%, the greater the importance of P-value.

Results and discussion

Although mineral elements and heavy metals should exist in nature and human and animal life within acceptable bounds, their concentrations shouldn't rise above these bounds because of the metals' distinctive bioaccumulation, as shown in Table 2.

Table 2. Permissible limits for minerals in Coffee, estimated in ppm according to WHO / FAO [8].

The studied metals	Permissible concentrations for metals in Coffee (ppm)
Sodium	0.06
Potassium	0.07
Iron	0.02
Copper	0.02
Lead	0.04
Chrome	0.03

According to the findings, the potassium content of the coffee under study varied from 0.01793 to 0.02193 parts per million. 0.02193 was the concentration value with the highest concentration, while 0.01793 was the concentration value with the lowest. All of the values were below the 0.07 parts per million allowable limits set by the Food and Agriculture Organization and the World Health Organization. The sodium concentration in the coffee under study ranged from 0 to 0.00058 parts per million, according to the data. In 0.00058, the concentration value was the highest, while in 0, the concentration value was the lowest. All of the results fell within the World Health Organization's and Food and Agriculture Organization's acceptable levels, which are 0.06 parts per million [1,8], as shown in Table 3.

The Next Table shows the percentages of sodium and potassium concentrations in the six samples that were chosen. Looking at the table, we find that the P-VALUE value for all samples is less than 5%, which is the borderline value for P-VALUE, which means that the data is of a great degree of importance, and the

Received: *08-05-2025* - ***Accepted***: *06-07-2025* - ***Published***: *19-07-2025*

coefficient of variation F is a large value, which means that the data has differences and statistical significance.

Table 3. The Concentration of mineral metals in coffee samples

Name of Samples	Concentration of K^+ g/ml	Concentration of Na^+ g/ml	F	P-Value
CT	0.01873	0.00038	5.3	0.005
CB	0.02173	0.00018	5.1	0.008
CA	0.02013	0.00018	5.2	0.008
CK	0.01793	0.00058	5.3	<0.001
CM	0.02133	0.00018	5.2	0.008
CKAWA	0.02193	0	5.2	0.012

Figure 1 illustrates the concentration of potassium (K^+) and sodium (Na+) in coffee in different samples of coffee (CT, CB, CA, CK, CM, CKAWA) compared to the WHO recommended limit. All coffee samples have relatively low and similar concentrations of potassium, ranging from 0.015–0.025 g/ml. For comparison, the WHO value is significantly higher at about 0.07 g/ml. This is to say that the amount of potassium in all the samples analyzed is way less than the WHO acceptable limit, which signifies no health risk.

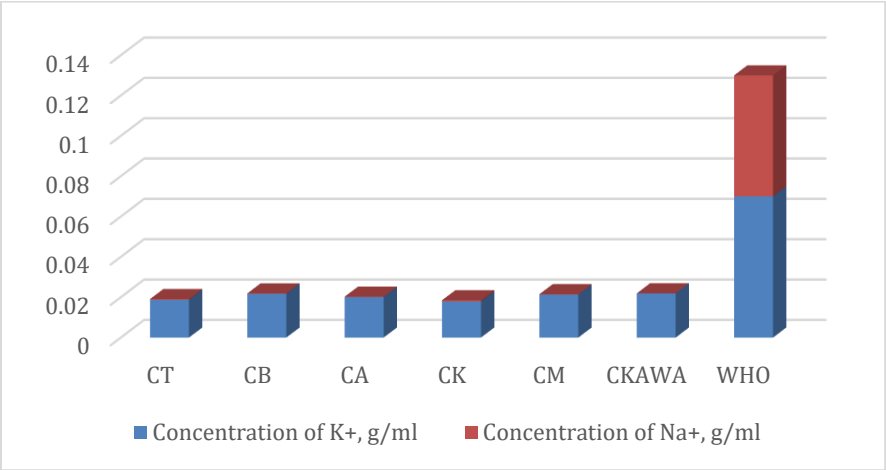

Figure 1. Concentration of potassium (K^+) and sodium (Na^+) in coffee samples

Figure 2 shows a linear relationship between the amount of potassium (K^+) in g/ml and intensity of emission. The equation for the line is y = 1.5x - 4, and R^2 is 1, indicating a complete linear relationship. With an increase in the amount of K^+, the emission also increases linearly. This suggests that the measurement method used is highly dependable and precise for the determination of potassium levels under the tested range.

Figure 3 shows the linear relationship between emission intensity and sodium ion (Na^+) concentration. The equation of the line is y = 1.05x - 1.1, and R^2 = 0.9692, indicating a high positive correlation. With increasing Na^+ concentration, the emission also increases linearly. The high R^2 value confirms that the linear model fits the data well and can be used to make predictions of unknown Na^+ concentrations from measurements of emission [9].

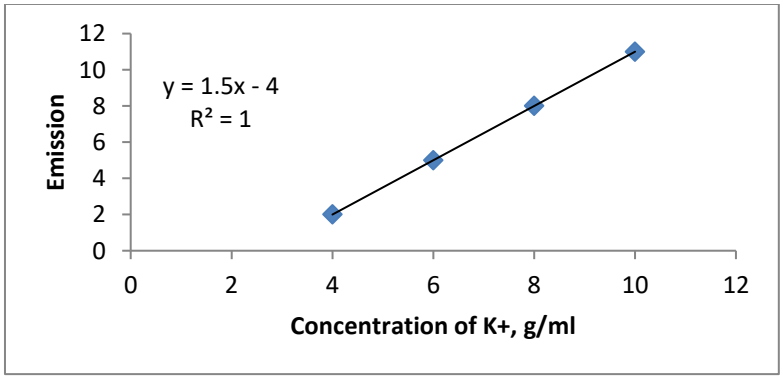

Figure 2. The standard Calibration curve of absorbance of K^+

***Received**: 08-05-2025 - **Accepted**: 06-07-2025 - **Published**: 19-07-2025*

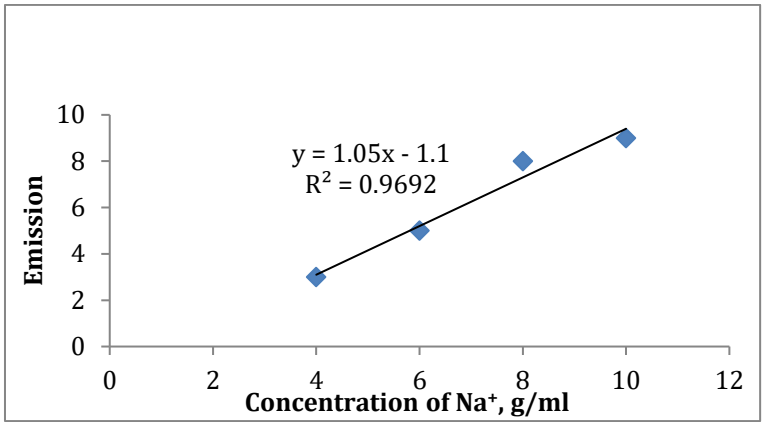

Figure 3. The standard Calibration curve of absorbance of Na+

One of the essential minerals for human health is iron. A lack of it in the blood can lead to anemia and other health problems, while an excess of it can cause iron poisoning, nausea, vomiting, and stomach discomfort. The iron content of the coffee under study in this paper is depicted in the image. According to the findings, the coffee under study had an iron content ranging from 47.8652 to 114.782 parts per million. The concentration values that were found to be the highest and lowest, respectively, were 114.782 and 47.8652. All the results were high over the permissible limits allowed by the World Health Organization / Food and Agriculture Organization, which is 0.02 parts per million. As shown in Table 4.

The wide distribution of iron in the soil and the metal's variable air pollution are probably the causes of the variation in iron content. According to the table, find that the P-VALUE value for all samples is less than 5%, which is the borderline value for P-VALUE, which means that the data is of a great degree of importance, and the coefficient of variation F is a large value, which means that the data has differences and statistical significances.

The study revealed that copper, iron, lead, and chromium levels in coffee samples exceeded WHO/FAO permissible limits. High copper intake can lead to anemia, hypertension, nervous disorders, cancer, liver damage, and behavioral issues in children. Iron concentrations ranged from 649.391 to 1702.56 ppm, far above the 0.02 ppm limit. Lead, highly toxic especially to children, ranged from 88.9015 to 132.983 ppm, exceeding the 0.04 ppm safe limit and posing serious health risks such as organ damage and mental retardation. Chromium, although essential in small amounts, showed concentrations between 5.4687 and 5.5886 ppm, also exceeding the recommended daily intake of 0.03 ppm. These findings suggest significant contamination in coffee samples (Table 4).

Table 4. The Concentration of heavy metals in coffee samples

Name of Samples	Concentration of Fe^{3+} (ppm)	Concentration of Cu^{2+} (ppm)	Concentration of Pb^{2+} (ppm)	Concentration of Cr^{3+} (ppm)	f	p-value
CT	111.07	649.391	88.9015	5.4687	5.8	0.001
CB	90.3664	1702.56	132.983	5.57222	5.2	0.001
CA	47.8652	691.583	95.6263	5.6372	5.9	0.015
CK	114.782	1085.71	90.8851	5.5576	5.2	0.022
CM	93.717	686.259	99.1471	5.568	5.2	0.021
CKAWA	63.7993	862.908	99.1058	5.5886	5.3	0.011
WHO	13	0.2	0.1	0.5	5.2	0.02

(Figure 4) represents a calibration curve for the determination of Fe^{+3} concentration using absorption spectroscopy. The x-axis is the concentration of Fe^{+3} in parts per million (ppm), and the y-axis is the corresponding absorption. There is a linear relationship between the concentration and absorption from the data points plotted, which are best described by the linear equation y = 0.1672x - 0.0117. The high coefficient of determination, R^2 = 0.9841, demonstrates that the concentration of Fe^{+3} has a high correlation with measured absorption, reflecting the applicability of this calibration curve for quantitative analysis [10]. Correlation with measured absorption, reflecting the applicability of this calibration curve for quantitative analysis [10].

The bar chart (5) represents the concentration of Fe^{+3} (iron (III)) in parts per million (ppm) in the different water samples labeled as CT, CB, CA, CK, CM, and CKAWA. Each bar's height indicates the concentration of Fe^{+3} in a given sample. Interestingly, water from all of the samples presents significantly greater amounts of iron in comparison to the World Health Organization (WHO) guideline value, marked by a nearly infinitesimal bar near zero. This suggests the iron contents within the aforementioned samples greatly exceed the WHO-specified limit.

Received: *08-05-2025* - ***Accepted***: *06-07-2025* - ***Published***: *19-07-2025*

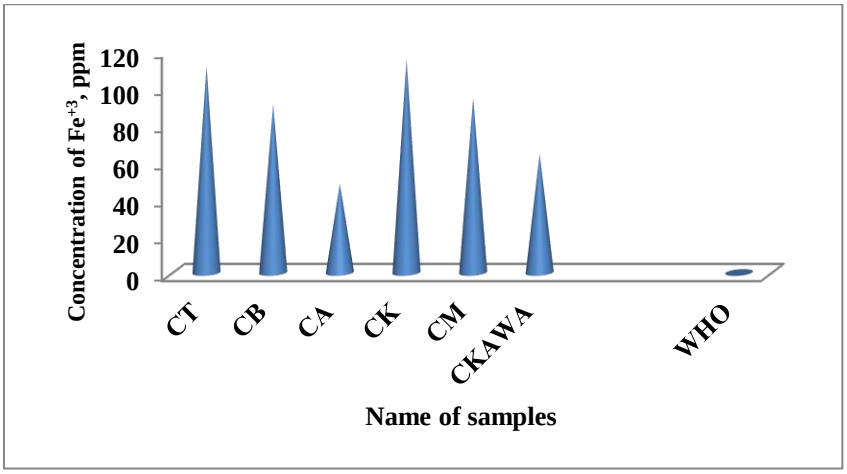

Figure 4. Concentration of Iron in coffee

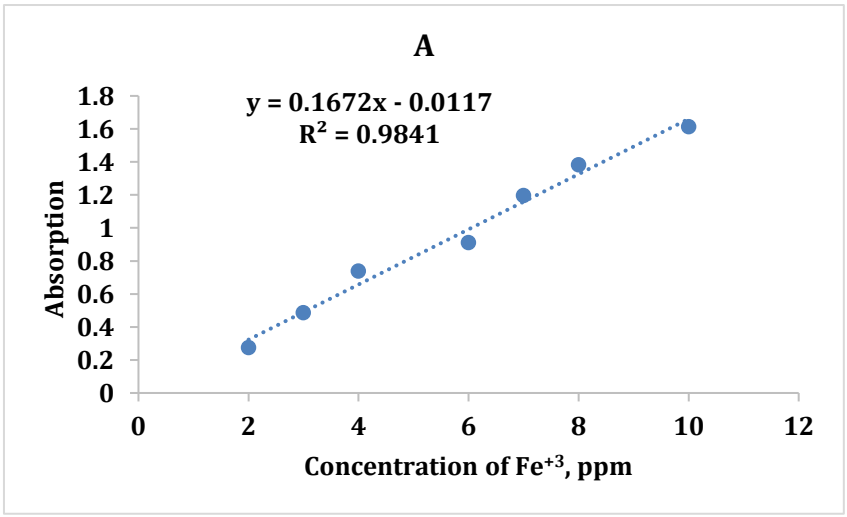

Figure 5. The standard Calibration curve of absorbance of Fe^{+}

The curve is a calibration curve for the determination of Cu^{+2} (copper (II)) concentration through absorption spectroscopy. The x-axis is the concentration of Cu^{+2} in parts per million (ppm), and the y-axis is the respective absorption reading. The data points are linear, and the relationship is provided by the equation y = 0.0007x + 0.0692. The R-squared value of 0.9951 is almost 1, indicating a perfect linear fit and a strong positive correlation between the copper concentration and the measured absorption. This suggests that this calibration curve can be employed with confidence to estimate the concentration of copper (II) in unknown samples from their absorption (Figure 6).

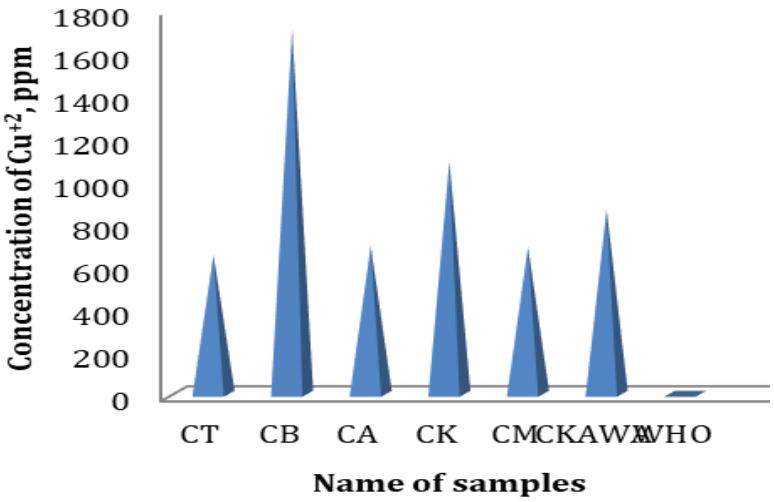

Figure 6. Concentration of copper in coffee

Received*: 08-05-2025 -* ***Accepted****: 06-07-2025 -* ***Published****: 19-07-2025*

Figure 7 illustrates the copper (II) (Cu^{2+}) concentration in parts per million (ppm) of various water samples labeled as CT, CB, CA, CK, CMCK, and CKAWA. The length of each bar corresponds to the measured copper concentration of the respective sample. One of the most interesting findings is that the copper concentration in all the samples in question is rather higher than the recommended guideline value according to the World Health Organization (WHO), as indicated by a very small bar to the left near zero. This broad gap suggests a high level of copper contamination in these water samples above the safety threshold recommended by WHO [11].

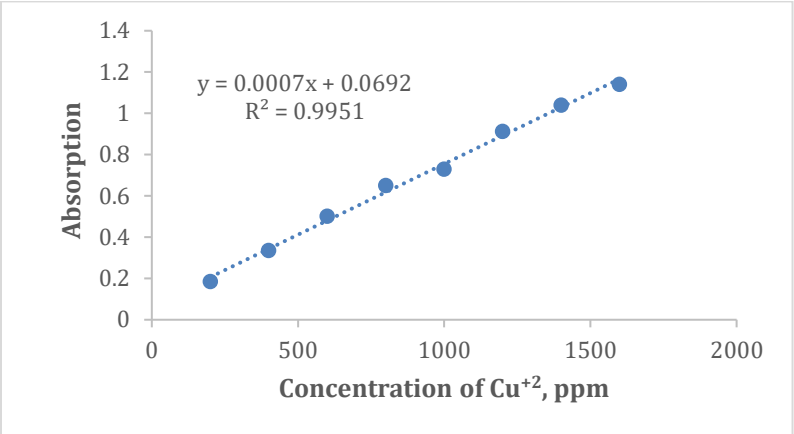

Figure 7. The standard Calibration curve of absorbance of Cu^{+2}

The bar chart shows the concentration of Pb^2 (lead (II)) in parts per million (ppm) of different water samples named CT, CB, CA, CK, CM, and CKAWA. The height of each bar shows the concentration of Pb^2 (lead (II)) found in the respective sample (Figure 8).

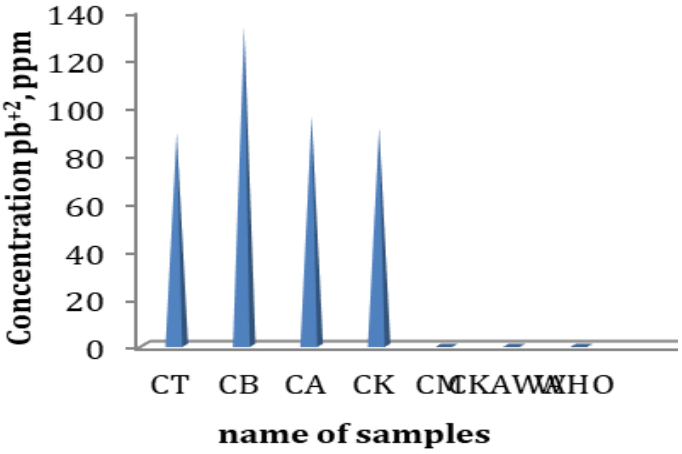

Figure 8: Concentration of lead in coffee

Figure 9 illustrates a calibration curve to measure Pb^2 (lead (II)) concentration by absorption spectroscopy. The y-axis is the respective absorption values, while the x-axis is the concentration of Pb^2 in parts per million (ppm). The plotted data points show a good linear relationship, given by y = 0.3846x + 0.1251. A large value of the coefficient of determination, R^2 = 0.9956, shows a nearly perfect linear association and a strong positive correlation between the lead concentration and measured absorption. The existence of such a strong association means this calibration curve shall be highly trustworthy to quantify the lead (II) concentrations of unknown samples as per their measured absorptions [12].

Received: *08-05-2025* - ***Accepted***: *06-07-2025* - ***Published***: *19-07-2025*

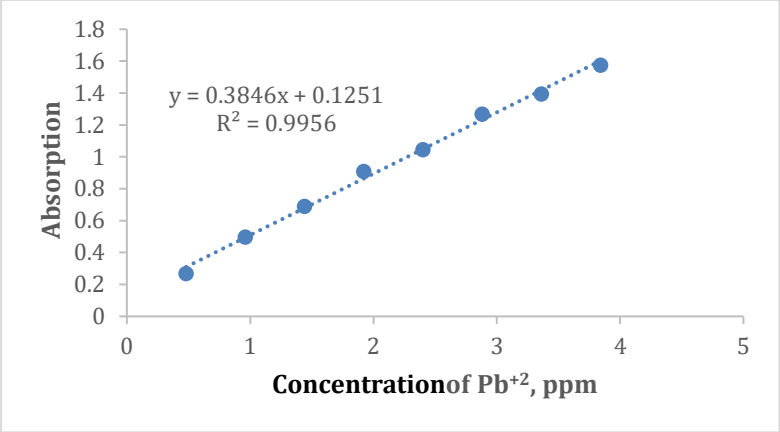

Figure 9: The standard Calibration curve of absorbance of Pb^{+2}

The bar chart shows the concentration of Cr^{+3} (chromium ions) in parts per million (ppm) of different water samples named CT, CB, CA, CK, CM, and CKAWA. The height of each bar shows the concentration of chromium found in the respective sample. It can be noted that the concentrations of chromium in all the tested samples are much higher than the World Health Organization (WHO) guideline recommended values (Figure 10). This indicates that the chromium level in these water samples is higher than the safe recommended value [13].

The graph displays a calibration curve for quantifying the concentration of Cr^{+3} ions. The x-axis represents the concentration of Cr^{+3} in parts per million (ppm), and the y-axis represents the absorption values for the concentrations (Figure 11). The points on the graph relate linearly according to the equation y = 1.1468x + 0.2187. The R2 value of 0.9991 indicates an excellent correlation between Cr^{+3} concentration and absorption and means that this calibration curve can be used for accurate quantitative analysis of Cr^{+3} in unknown samples [14].

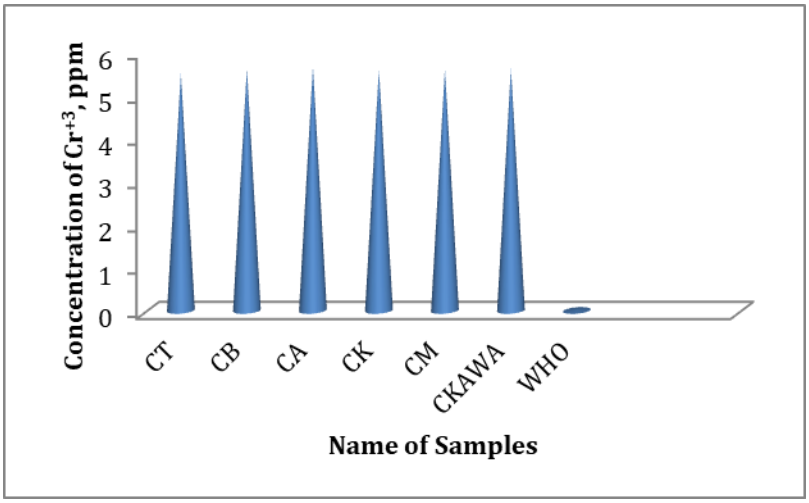

Figure 10: Concentration of Chrome in coffee

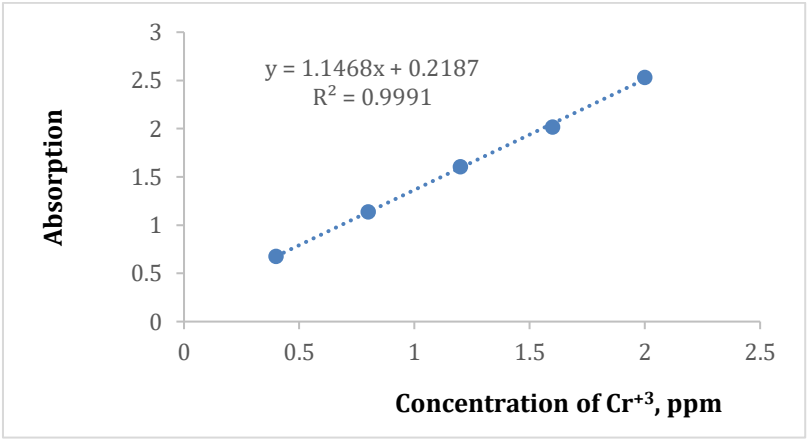

Figure 11: The standard Calibrat samples. Ion curve of absorbance of Cr^{+3}

Received: *08-05-2025* - ***Accepted***: *06-07-2025* - ***Published***: *19-07-2025*

(Figure 12). shows the line fit plot for lead, where the x-axis represents the expected Pb^{2+} concentration values and the actual Pb^{2+}, Y axis concentration values obtained from the analysis of six types of coffee. It is clear that there is a slight difference between the actual and real values, which means the success of the analysis of the samples. The legend in the plot also distinguishes between the actual and expected "Y" values, which makes it possible to visually evaluate the suitability of the linear model.

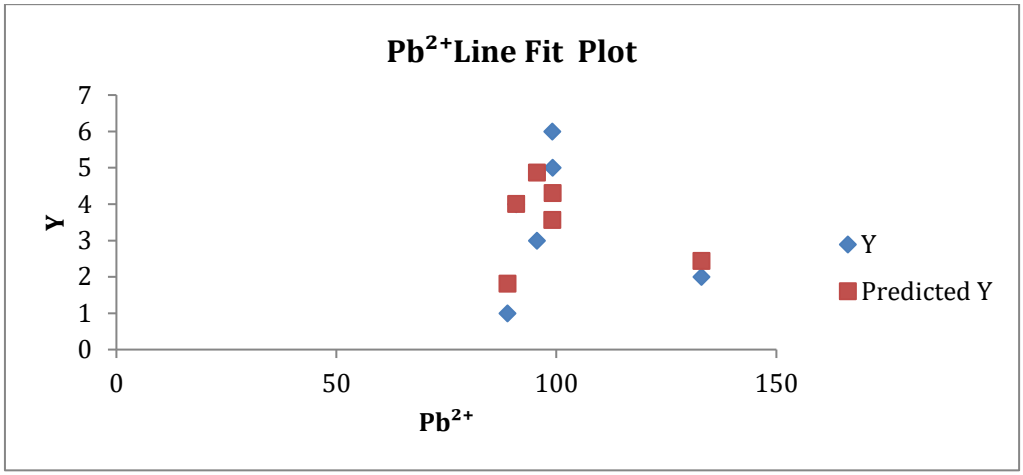

Figure 12: pb+2 fit lone plot

(Figure 13) shows the line fit plot for lead, where the x axis represents the expected Cu^{+2} concentration values and the actual Cu^{+2}, Y axis concentration values obtained from the analysis of six types of coffee. It is clear that there is a slight difference between the actual and real values, which means the success of the analysis of the samples. The legend in the plot also distinguishes between the actual and expected "Y" values, which makes it possible to visually evaluate the suitability of the linear model.

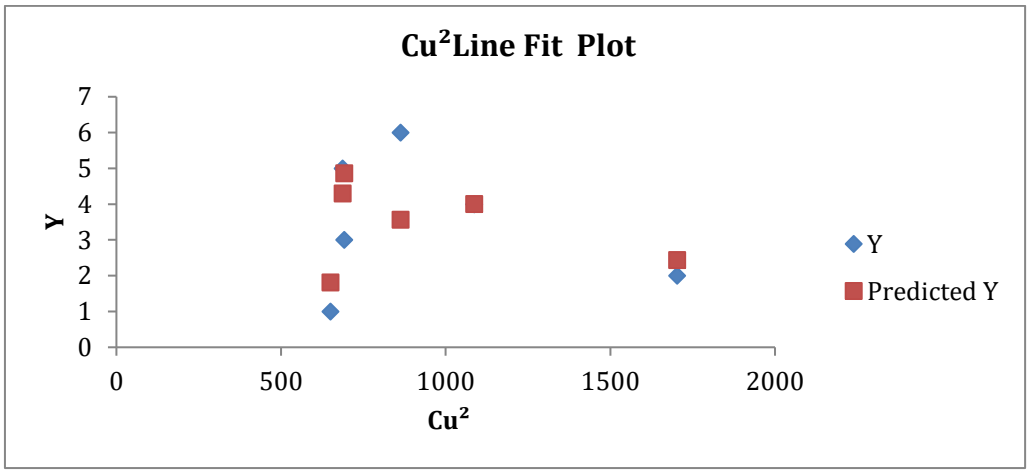

Figure 13. Cu+2 fit lone plot

Figure 14 shows the line fit plot for lead, where the x-axis represents the expected Fe^{+3} concentration values and the actual Fe^{+3}, Y axis concentration values obtained from the analysis of six types of coffee. It is clear that there is a slight difference in the actual and real values, which means the success of the analysis of the samples. The legend in the plot also distinguishes between the actual and expected "Y" values, which makes it possible to visually evaluate the suitability of the linear model.

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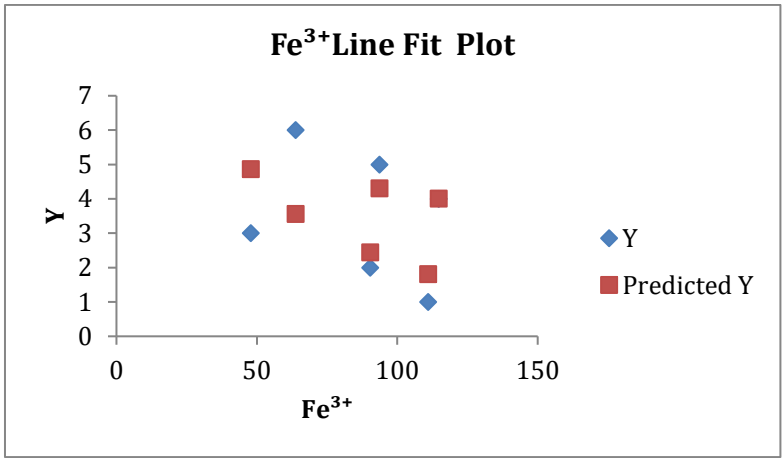

Figure 14. Fe+3 fit lone plot

Figure 15 shows the line fit plot for lead, where the x-axis represents the expected Cr+3 concentration values and the actual Cr^{+3}, Y axis concentration values obtained from the analysis of six types of coffee. It is clear that there is a slight difference between the actual and real values, which means the success of the analysis of the samples. The legend in the plot also distinguishes between the actual and expected "Y" values, which makes it possible to visually evaluate the suitability of the linear model.

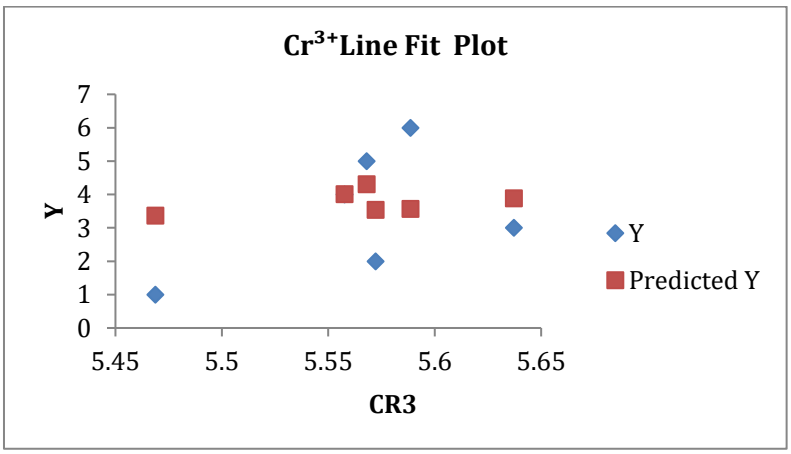

Figure 15. Cr+3 fit lone plot

Table 5 presents the correlation coefficients between the concentration of four metals (Fe^{3+}, Cu^{2+}, Pb^{2+}, and Cr^{3+}) and coffee extraction in six different samples (CT, CB, CA, CK, CM, and CKAWA). The data reveals significant variation in the strength of correlations for every metal across the samples. For instance, iron (Fe^{3+}) is found to have a relatively high correlation with coffee extraction in samples CT (21%) and CK (22%), while its influence is significantly lower in CKAWA (12%). Copper (Cu^{2+}) is found to have a very high correlation in sample CB (30%), suggesting that this metal may be a significant factor in coffee extraction in some conditions. Lead (Pb^{2+}) presents moderate correlations, ranging from 14% to 21%, which indicates its ongoing but lesser impact. Chromium (Cr^{3+}) presents minimal variability in most of the samples, with the values clustered around 16.6%, except in CT and CB, where one observes slightly greater or lesser percentages. Overall, the results suggest that the impact of these metals on coffee extraction varies by composition of the samples, with Fe^{3+} and Cu^{2+} being more varied and potentially significant than Pb^{2+} and Cr^{3+}. This suggests the necessity of considering sample-specific factors in exploring the relationship between metal concentration and coffee quality.

To sum up, the height of each bar shows the concentration of chromium found in the respective sample. It can be noted that the concentrations of chromium in all the tested samples are much higher than the World Health Organization (WHO) guideline recommended values. This indicates that the chromium level in these water samples is higher than the safe recommended value. The results showed that the concentration of sodium and potassium is below the allowable limit, and the concentration of lead, chromium, iron, and copper is above the permissible limit [15, 16]. The accumulation of heavy metals and essential minerals in various types of commercially available coffee in the Libyan market, focusing on their potential health risks and adherence to internationally permissible limits. Results indicate that potassium concentrations are below the permissible limit of 0.07 ppm. Sodium levels varied between 0 and 0.00058 g/ml, significantly lower than the allowable threshold of 0.06 ppm. However, concerning heavy metals, copper concentrations exceeded the permissible limit of 0.02 ppm, posing a potential public health risk.

Received: *08-05-2025* - ***Accepted***: *06-07-2025* - ***Published***: *19-07-2025*

Lead concentrations were far surpassing the acceptable limit of 0.04 ppm. Similarly, chromium levels exceeded the recommended daily dose of 0.03 ppm. Statistical analysis revealed significant differences among samples, with F-values ranging from 5.1 to 5.3 and p-values indicating statistical significance (<0.001 to 0.012). Correlation coefficients further highlighted the varying influence of metals on coffee extraction.

Table 5. Correlation coefficients of metal concentration with coffee extraction (sample)

Sample	Concentration of Fe^{3+} (ppm)	Concentration of Cu^{2+} (ppm)	Concentration of Pb^{2+} (ppm)	Concentration of Cr^{3+} (ppm)
CT (%)	21	11	14	16.30
CB (%)	17	30	21	16.60
CA (%)	9	12	15	16.80
CK (%)	22	19	16	0.166
CM (%)	17	12	16	0.166
CKAWA (%)	12	15	16	0.166

Conclusion

The study evaluated the concentration of a few components in six distinct coffee varieties that were gathered from various El-Beyda City stores. These findings underscore the need to consider sample-specific factors when assessing metal contamination in coffee, as Fe^{3+} and Cu^{2+} exhibit greater variability and potential impact on coffee quality compared to Pb^{2+} and Cr^{3+}. Collectively, this study emphasizes the importance of monitoring heavy metal concentrations in coffee to mitigate health risks while ensuring compliance with international safety standards.

Conflicts of Interest

The authors declared no conflict of interest.

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Received*: 08-05-2025 -* ***Accepted****: 06-07-2025 -* ***Published****: 19-07-2025*