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ICP-MS Analysis of Commercial Coffees Available in the US Market

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As coffee constitutes a global cultural phenomenon consumed at 9 million tons annually across 167 countries, its scientific studies attract widespread attention. Accordingly, the present study investigates trace elements in coffee samples available in the US market, spanning sensory, health, environmental, and toxicological dimensions. Specifically, the study employs Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the analysis of 14 elements in 12 diverse coffee brands. Geographical variations, sustainability implications, and a leaching experiment further enrich our understanding. The findings contribute insights for consumers, producers, and regulators, shaping the evolving landscape of the coffee industry.

Keywords: ICP-MS; coffee samples; lead; cadmium; leachate

Introduction

Coffee is a widely consumed food commodity worldwide, with a significant annual consumption of 9.0 million tons and exports to 167 countries [1, 2]. Studying trace elements in coffee is important for several reasons. Firstly, these elements contribute to the sensory experience of coffee, affecting its flavor, aroma, and overall quality [3-5]. By understanding the presence and concentrations of trace elements, researchers can identify key compounds responsible for desirable or undesirable characteristics in coffee [6].

Secondly, trace elements in coffee can have significant health implications. Some elements, such as antioxidants, have potential health benefits, while others, like heavy metals, can pose health risks if present in excessive amounts [7-9]. There are several methods for analyzing trace metals, among them, inductively coupled plasma mass spectrometry (ICP-MS) has been the method of choice for the determination of toxic metals and metalloids of plants and soils, with low detection limits down to 0.1 ppb, simple sample preparation, high throughput and the ability to measure many elements simultaneously [10-14].

Thirdly, trace elements can act as indicators of coffee origin and quality. Different regions and growing conditions yield coffee beans with distinct elemental compositions [15]. Analyzing trace elements can provide valuable information for authentication, traceability, and quality control in the coffee industry, helping to prevent fraud and ensure product integrity.

Furthermore, studying trace elements in coffee can contribute to environmental sustainability. Coffee cultivation practices, soil composition, and processing methods can influence the elemental content in coffee beans. By investigating these factors, researchers can identify sustainable farming practices that minimize environmental impacts and optimize trace element profiles in coffee [16, 17].

Lastly, studying trace elements in coffee advances our scientific understanding of this beloved beverage. It deepens our knowledge of the complex chemical composition of coffee and fosters innovation in brewing techniques, product development, and sensory analysis. Overall, this study contributes to the continuous improvement and appreciation of coffee as a cultural and culinary experience.

Experimental part

Materials and methods

All chemical reagents (70% w/w HNO_3 and 37% w/w HCl) used were ordered from Millipore Sigma and were purified by redistillation, ≥99.999% trace metals basis. A 2 mg/L stock solution was prepared by adding 2.00 mL from 1000 mg/L ICP stock standards with each element and followed by diluting to 1 L from HNO_3/HCl solution (3% v/v HCl and 1% v/v HNO_3). Then, 0.4 – 2000 µg/L calibration standards were prepared from the 2 mg/L stock solution followed by diluting with 3% HCl and a 1% HNO_3 solution.

Determination of trace elements

Digestion was performed by placing 100 mg of each coffee sample in a Teflon beaker followed by adding 10 mL of concentrated 3:1 (35% w/w HCl and 69% w/w HNO_3) HCl: HNO_3 mixture. To facilitate the digestion process, the resulting mixture was heated to 150°C for 30 minutes. The digests were then allowed

to cool to room temperature and were individually filtered with a Whatman grade 1 cellulose filter paper (10-20 µm pore size). The solutions were then transferred to 50 mL volumetric flasks and diluted up to the mark with Milli-Q water (2.1 *µ*S/cm)

For quality control, a reagent blank and a 0.10 g aliquot of NIST SRM 1570A was used to monitor the percent recovery for the available elements. Three aliquots of each sample and reference material were digested to test the reproducibility. The mass fractions of each element were calculated as follows:

$$C\ (mg/kg) = (I_{sample} - I_{blank}) \cdot S \cdot V / M,$$

where, I is the intensity of the sample solution, S (µg/L) is the slope of the calibration series, V (L) is the final volume of the sample solution and M (g) is the mass of the sample.

Calculations were based on using reagent blanks, additionally instrumental errors were avoided by subtracting ICP intensities with intercepts obtained from multipoint (more than 8 data points) calibration series.

Leaching experiments

0.10 g of each sample was weighed in a 50 mL polypropylene tube, and 25 mL of de-ionized water was added to each tube and shaken at 200 rpm on an orbital shaker for 6 hrs. The filtrates were filtered through Whatman grade 1 filter papers. Three aliquots of each sample were prepared and analyzed to test the reproducibility among the samples. Leaching percentages of each element were calculated as follows:

$$\text{Leaching percentage } (\%) = ((C \times V/m)/Q) \times 100\%,$$

where C (µg/L), V (L), and m (g) are the final concentration and volume in the solutions and sample weight, respectively, where Q (*µ*g/g) is the mass fraction of trace elements present in the sample.

Instrument parameters

ICP-MS operational parameters are shown in Table 1.

Table 1. ICP-MS operational parameters

RF Power	1100 W
Lens Voltage	6 V
Nebulizer Gas Flow	0.95 L/min
Cool Gas Flow	15 L/min
Auxillary Gas Flow	1.2 L/min
Scanning Mode	Peak hopping
Resolution	0.7 amu
Dwell Time	50 ms/amu
Sweeps per Reading	3
Readings per Replicate	3
Number of Replicates	3
Sample Flow Rate	2.4 mL/min
Isotope Monitored	^{7}Li, ^{23}Na, ^{24}Mg, ^{31}P, ^{39}K, ^{52}Cr, ^{59}Co, ^{63}Cu, ^{66}Zn, ^{90}Zr, ^{118}Sn, ^{138}Ba, ^{208}Pb, ^{238}U

Results and discussion

In this study, a set of 12 coffee brands were selected, as these coffee samples are among the most consumed for espresso and Turkish types of coffee. The analytical core of this study lies in the examination of metal contents within the various coffee powders, achieved through Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The outcomes of this analysis, graphically depicted in Figure 1, serve as a visual testament to the diversity and complexity of metal compositions across the selected brands. Importantly, the presentation of observed metal contents offers a portrayal, providing insight into both average concentrations and the variability within each set. This statistical depth is further enriched by including standard deviations, derived from two separate analytical runs for each brand, thereby enhancing the robustness and reliability of the findings.

Essential minerals, including certain metals and metalloids, play crucial roles in bone and tooth formation, heart health, nerve function, muscle contraction, immunity, and metabolism. Minerals account for approximately 4% of our body weight [18]. They are categorized as either macrominerals (required in amounts exceeding 100 mg/day) or microminerals (required in amounts less than 100 mg/day) [18]. This study focused on the macrominerals potassium (K), magnesium (Mg), phosphorus (P), and sodium (Na), as well as the microminerals copper (Cu) and zinc (Zn).

The elements in this study necessary for human metabolism can be broken down into two main categories; macrominerals (K, Mg, P, and Na) and microminerals (or trace) minerals (Cu and Zn). Macrominerals are elements required at amounts higher than 100 mg/day while microminerals are required at less than 100 mg/day [19, 20].

A list of coffee samples used in this study is shown in Table 2, including both espresso capsules and Turkish-style coffee. Each coffee type is listed with its purchase date. This table is important for the study as it shows the variety of coffee samples analyzed and helps the interpretation of the next table which looks into the different elements found in these coffees. This table is also helpful for understanding the range of coffee types being studied.

Table 3 shows the range of metal concentrations for different elements analyzed in this study. It provides an overview, highlighting the variety in elemental composition of the elements analyzed in this study.

In comparison to mineral concentrations identified in by Albals *et al.*, the sequencing of tested elements available for comparison between the two groups differed, particularly for Zn, Ba, Cr, Li, Co, and U [21]. Our findings presented the sequence as Zn > Ba > Cr > U > Co > Li > Sn, whereas Albals *et al.* indicated the sequence to be Ba > Zn > Cr > Co > U > Li, with the elements aligning within a magnitude order of agreement or less [21]. The disparities in the order of

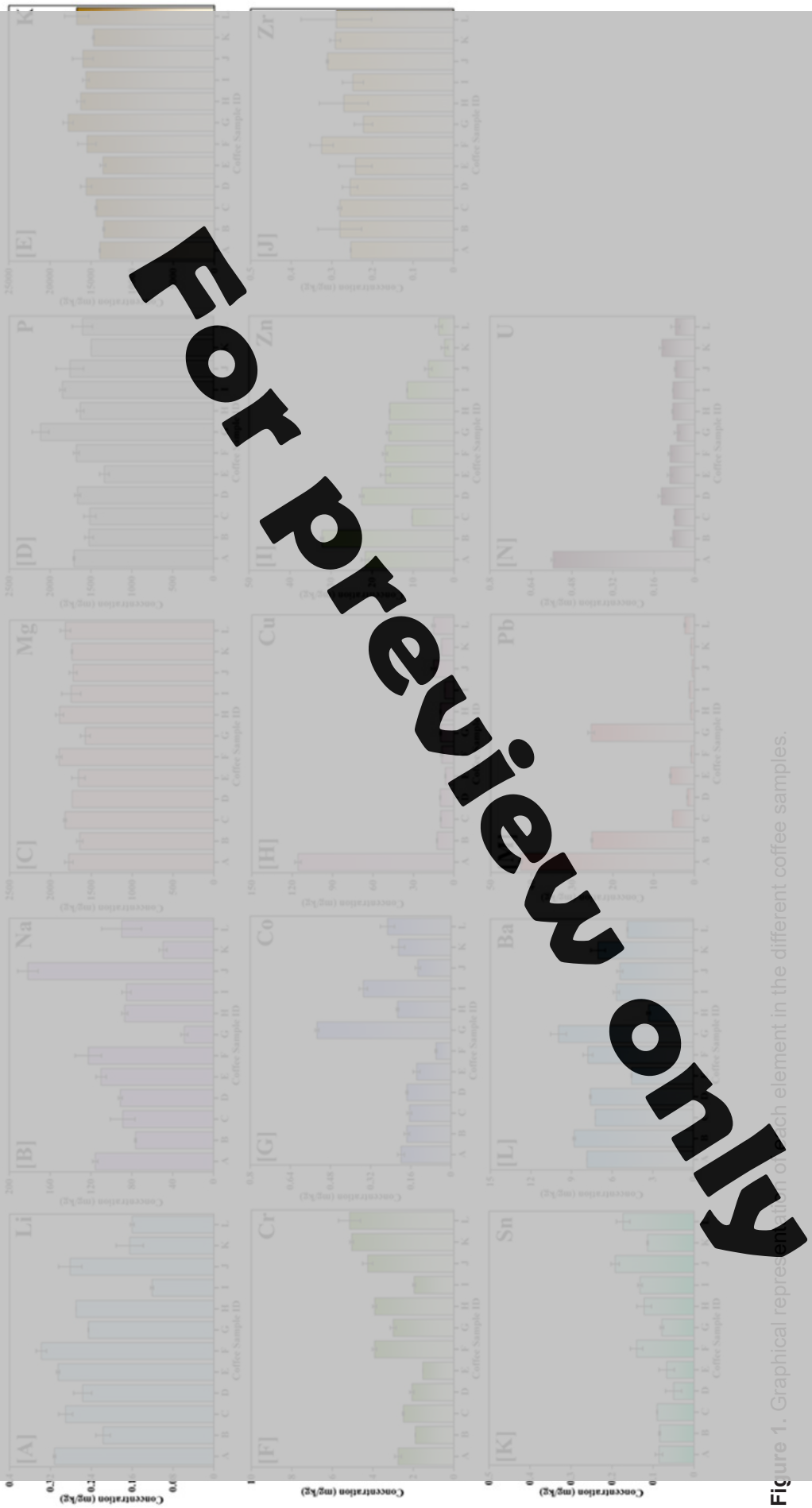

Figure 1. Graphical representation of each element in the different coffee samples.

Table 2. Types of coffee samples analyzed with the purchase date.

Coffee Sample ID	Type (Espresso, Greek Etc.)	Purchase date
1	Espresso capsule	01/20/2022
2	Espresso capsule	01/20/2022
3	Espresso capsule	01/20/2022
4	Espresso capsule	01/20/2022
5	Espresso capsule	01/20/2022
6	Espresso capsule	01/20/2022
7	Turkish-type coffee	01/20/2022
8	Turkish-type coffee	01/20/2022
9	Turkish-type coffee	01/20/2022
10	Turkish-type coffee	01/20/2022
11	Turkish-type coffee	01/20/2022
12	Turkish-type coffee	01/20/2022

Table 3. Concentration ranges of elements in this study.

Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
Li	0.12-0.4	Cu	6.3-115.7
Na	28.6-122.6	Zn	2.3-32.2
Mg	1574-1895	Zr	0.22-0.32
P	1336-2113	Sn	0.05-0.19
K	13451-17791	Ba	3.3-10.0
Cr	1.5-5.1	Pb	0.6-42.7
Co	0.06-0.53	U	0.07-0.55

Zn, Ba, Cr, Li, Co, and U may be attributed to various factors, such as geographical variations, sample characteristics, and analytical techniques employed.

It is noteworthy that our results, with the sequence Zn > Ba > Cr > U > Co > Li > Sn, present a unique perspective on the elemental hierarchy. This distinctive ordering could be influenced by specific environmental conditions or variations in the sources of the samples under consideration.

The comparison with Albals *et al.*, demonstrates that Ba > Zn > Cr > Co > U > Li is within a close range of agreement, suggesting a degree of consistency in elemental patterns. This marginal variation could be indicative of subtle environmental differences or methodological distinctions that contribute to the nuanced results [10, 21].

Table 4 shows the lowest Li values were observed in samples I, L, and K, following the order I < L < K. In contrast, the highest concentrations were found in samples E, A, and F, corresponding to the order E < A < F. The lowest Na values were identified in samples G, K, and B, adhering to the order G < K < B. In contrast, the highest Na concentrations were observed in samples A, F, and J, following the order A < F < J. The lowest Mg concentrations were found in samples G, B, and E, adhering to the order G < B < E, while the highest concentrations were observed in samples L, H, and F, aligning with the order L < H < F. The lowest P values followed the order E < K < C, with the highest concentrations identified in samples J, I, and G (J < I < G). The lowest K values followed the order E < K < A, whereas the highest concentrations were observed in samples H, L, and G (H < L < G). The lowest Cr values followed the order E < B < I, while the highest concentrations were identified in samples J, K, and L (J < K < L). The lowest Co values followed the order F < J < E, while the highest concentrations were observed in samples L, I, and G (L < I < G). The lowest Cu values followed the order E < I < F, while the highest concentrations were identified in samples L, J, and A (L < J < A). The lowest Zn values followed the order K < L < J, while the highest concentrations were observed in samples A, D, and B (A < D < B). The lowest Zr values followed the order G < E < I, while the highest concentrations were identified in samples K, J, and F (K < J < F). The lowest Sn values followed the order D < E < G, while the highest concentrations were observed in samples F, L, and J (F < L < J). The lowest Ba values followed the order G < D < K, while the highest concentrations were identified in samples E, A, and F (E < A < F). The lowest Pb values followed the order J < F < K, while the highest concentrations were observed in samples B, G, and A (B < G < A). The lowest U values followed the order G < J < L, while the highest concentrations were identified in samples K, D, and A (K < D < A).

Table 4. Comparison of elemental concentrations among the different samples.

Element	Lowest	Highest
Li	I<L<K	E<A<F
Na	G<K<B	A<F<J
Mg	G<B<E	L<H<F
P	E<K<C	J<I<G
K	B<E<A	H<L<G
Cr	F<B<I	J<K<L
Co	F<B<E	L<I<G
Cu	B<I<F	L<J<A
Zn	K<L<J	A<D<B
Zr	G<E<C	K<J<F
Sn	D<E<G	F<L<J
Ba	G<D<K	E<A<F
Pb	J<F<K	B<G<A
U	G<J<L	K<D<A

These variations suggest potential associations with soil characteristics, climatic conditions, or processing techniques. The findings contribute insights into the nuanced interrelationships between elemental content and environmental factors, providing a foundation for further exploration into the role of the aforementioned elements in shaping the distinct qualities of each coffee sample.

The multi-element NIST SRM 1570A standard reference material (SRM) serves as a valuable benchmark for the elemental analysis of plants and plant-derived products, such as coffee beans. Derived from freeze-dried and processed spinach leaves, this SRM encompasses a spectrum of elements crucial for plant nutrition and health, including Na, Mg, P, K, Co, Cu, Zn, and U. Ranging from a high concentration of 22.562 mg/kg for potassium to a low of 0.392 mg/kg for cobalt, the SRM provides a comprehensive span of elemental concentrations representative of real-world plant materials. Percent recoveries of NIST SRM 1570A are provided in Table 5.

Leaching Experiment

To understand coffee's elemental composition and its potential impact on consumers, we conducted a leaching experiment, detailed in Figure 2. We focused on key elements in coffee beans, excluding potassium, magnesium, phosphorus, sodium, and lithium. The order of elements in coffee beans was found to be K > Mg > P > Na > Cu > Zn > Ba > Cr > Zr > Li > Co > U > Sn. However, the leached coffee displayed a different elemental sequence, with elements like copper and zinc showing notable shifts in concentration. This change prompted an investigation into the reasons behind these alterations, revealing discrepancies in elemental concentrations between the beans and the brewed coffee. The study highlights the importance of considering the full spectrum of elements when evaluating coffee's impact on consumers, acknowledging the influence of brewing on its elemental makeup.

Table 5. Percent recoveries of NIST SRM 1570A of the various elements.

Element	Reference Value	% or mg/kg	Concentration (mg/kg) from digestion	Recovery %
Li	N/A	-	1.9±0.2	-
Na	1.821	%	15097±408	82.9±2.2
Mg	0.9	%	7168±330	79.6±3.7
P	0.5187	%	4567±92	88.0±1.8
K	2.9	%	22562±272	77.8±0.9
Cr	N/A	-	3.3±0.1	-
Co	0.393	mg/kg	0.392±0.01	99.8±3.4
Cu	12.22	mg/kg	7.6±0.1	62.3±0.7
Zn	82.3	mg/kg	115.8±1.4	140.7±1.7
Zr	N/A	-	0.49±0.07	-
Sn	N/A	-	0.11±0.02	-
Ba	N/A	-	7.6±0.2	-
Pb	N/A	-	139.1±3.2	-
U	0.155	mg/kg	0.20±0.02	126.1±11.3

Figure 2. Graphical representation of each element in the coffee leaching experiment.

Conclusion

In conclusion, this study utilized Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to analyze trace elements in a variety of coffee samples from the U.S. market. Key findings include a diverse range of metal compositions in these coffees, influenced by factors such as geographical origin and cultivation practices. This research enhances the understanding of trace element profiles in coffee, providing valuable insights for consumers, producers, and regulators. It highlights the need for further studies on the nutritional and toxicological implications of these elements, as well as their impact on coffee quality and sustainability. The study contributes significantly to the evolving landscape of the coffee industry, combining scientific analysis with practical considerations for coffee consumption and production.

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