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Evaluation of heavy metal concentration in black tea and coffee marketed in Erbil, Iraq: a consumer health risk assessment

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ABSTRACT

Black tea and coffee are popular and widely consumed beverages worldwide. However, the potential accumulation of heavy metals in food products raises concerns regarding their toxicity. In this study, we investigated the concentrations of arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), zinc (Zn), and iron (Fe) in 102 samples of black tea and coffee purchased from Erbil city market in Iraq. Additionally, we determined the Hazard Quotient (HQ) and Hazard Index (HI) levels of heavy metal intake to evaluate the non-carcinogenic health risks for adult consumers. The mean concentrations of As, Cd, Cu, Cr, Pb, Mn, Zn, and Fe in black tea and coffee were found to be 0.023, 0.11, 10.29, 0.60, 1.69, 294.99, 25.59, and 39.80 mg/kg, respectively. In the case of black tea, the highest mean concentration observed was 607.28 mg/kg for Mn, while the lowest was 0.035 mg/kg for Cd in coffee. Arsenic was below the detection limit in coffee. Our results revealed that, except for Cd content in some tea samples, the concentrations of the studied metals were within the standard levels. The HQ and HI values for all elements were found to be less than one, indicating no adverse health effects associated with consuming these beverages. However, continuous monitoring is essential to ensure the ongoing safety of black tea and coffee.

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Black tea; coffee; heavy metal; risk assessment

1. Introduction

Tea and coffee are two of the most widely consumed and significant beverages all over the world [1]. Tea, derived from the leaves of Camellia sinensis, has experienced a steady growth rate of more than 1.8% per year over the past decades [2]. In Iraq, the average per capita consumption of black tea stands at approximately 11.4 kg per year, with the country relying entirely on imports [3]. Among the various tea categories, black tea is the most commonly consumed variety in the Middle East. The leading tea-producing countries are China, India, Kenya, and Sri Lanka, respectively [4]. Numerous studies have highlighted the positive effects of tea consumption on human health [5–7]. Black tea contains a range of bioactive components, including dietary flavonoids, polyphenols, amino acids, tannic acid, minerals, and trace

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elements. Moreover, its consumption has been associated with a reduced risk of cardiovascular diseases, cancer, immune disorders, high blood pressure, stroke, blood cholesterol, and blood glucose levels [8]. Additionally, black tea represents a significant source of potassium, chromium, manganese, bromine, selenium, strontium, zinc, and copper [9].

Coffee, another globally popular beverage, is estimated to be consumed in 500 billion cups annually [10]. Coffee has held a significant place in social life for hundreds of years. Many individuals consume coffee for its energy-boosting properties and to enhance work performance. Previous studies have also suggested potential health benefits, such as contributing to the prevention of inflammatory and oxidative stress-related diseases, type 2 diabetes, and a reduced risk of certain types of cancer [11,12]. Coffee comprises a complex mixture of chemicals, including carbohydrates, lipids, nitrogenous compounds, vitamins, minerals, isoflavonoids, and other trace ingredients. The composition of these components can vary based on the variety, origin, and processing methods of the coffee beans [13]. Caffeine, a primary component of coffee, has been shown to alleviate the burden of Alzheimer's and Parkinson's diseases [14].

However, the potential benefits of consuming black tea and coffee may be compromised by the presence of toxic substances, such as heavy metals. These substances can accumulate in the plants used to produce black tea and coffee through contaminated soil or during storage and processing [15].

Therefore, the metal content in a cup of tea or coffee is directly related to the level of contaminants in the raw materials and the steps involved in processing them. Cadmium (Cd), lead (Pb), arsenic (As), and chromium (Cr) are among the most toxic elements and major public health concerns [16]. In Iraq, Alwan [3] reported the contamination of tea powders and infusions with Cd and Pb. Guadalupe et al. [17] also quantitatively determined the content of As, Cd, Hg, and Pb in Peruvian coffee and found that the metals are within acceptable levels. Most heavy metal exposure occurs through the food chain, and the absorption and bioaccumulation of these toxic metals in the body can lead to a wide range of health issues. Lead toxicity, for instance, can cause damage to various systems in the human body, particularly the nervous, haematopoietic, cardiovascular, and reproductive systems, with long-term effects including kidney and brain damage [18]. Arsenic has been linked to adverse effects on metabolic, cardiovascular, and immune functions, as well as an increased risk of skin, lung, and urinary bladder cancers [19]. Cadmium, another widespread toxic metal in the environment, can induce renal disturbances, lung insufficiency, bone lesions, cancer, and hypertension depending on the route, dose, and duration of exposure [20]. Chromium is a crucial trace element involved in glucose, protein, and fat metabolism, but excessive absorption can lead to kidney stones, asthma, lung cancer, skin diseases, liver problems, and heart issues [21]. In addition, the excess intake of other metals including copper (Cu), manganese (Mn), zinc (Zn), and iron (Fe) can be harmful for human.

Considering the popularity of coffee and tea in Iraq and the importance of ensuring consumer health and safety, it is necessary to evaluate the levels of heavy metals in these products and assess the associated health risks. Therefore, the aim of this study was to investigate the concentrations of As, Cd, Cu, Cr, Pb, Hg, Mn, Zn, and Fe in a total of 102 black tea and coffee samples obtained from retail markets in Erbil, Iraq, using atomic absorption spectrometry. Additionally, the Hazard Quotient (HQ) and Hazard Index (HI) was calculated to assess the potential health risks posed by these metals.

2. Materials and methods

2.1. Sampling

The present cross-sectional study was conducted on a total of 102 samples, including 60 black tea and 42 coffee from various brands available in local markets of Erbil, Iraq in 2023. The collected samples represent the major brands on the market. The samples were coded and preserved at room temperature until further analysis.

2.2. Preparation

Before initiating the test, the samples were heated in an 80°C oven for 60 minutes until a constant weight was reached. A digital scale with an accuracy of 0.0001 was used to weigh 0.5 grams of each dried powder sample. The weighed sample was then added to a Teflon digestion vessel (Mettler Toledo s.p.a., Novate Milanese, Milan, Italy) along with 8 mL of concentrated nitric acid (HNO_3) and 2 mL of hydrogen peroxide (H_2O_2). To ensure no leakage or loss of volatile components during the digestion process, the vessel was tightly sealed. The digestion vessels containing the tea and coffee samples were shaken and placed in a microwave oven (Ethos-One; Milestone s.r.l. Sorisole, Bergamo, Italy). The digestion programme was initiated by increasing the temperature to 200°C over 10 minutes and maintaining it at 200°C for 20 minutes. The maximum power was set at 1000 W. Once the digestion process was completed, the vessels were allowed to cool down to a safe temperature, and the pressure was released. The resulting solutions were transferred to 50 mL volumetric flasks and diluted with deionised water to the marked volume. Finally, the samples were stored at 4°C until analysis. The concentration of As, Cd, Cu, Cr, Pb, Hg, Mn, Zn, and Fe in the prepared samples was measured using inductively coupled plasma-optical emission spectrometry (ICP-OES) device. The cleaning of vessels was performed by adding 8 mL of concentrated HNO_3 to the vessels and placing them in the microwave oven set to 1000 W for 10 minutes. Afterwards, the vessels were allowed to cool for 20 minutes without any power.

2.3. Chemicals and reagents

All standard solutions for were purchased from Merck (Darmstadt, Germany). Nitric acid (HNO_3, 65%) and hydrogen peroxide (H_2O_2, 30%) obtained from Merck (Darmstadt, Germany) were used for sample digestion. Deionised water was used throughout the study.

3. Inductively coupled plasma optical emission spectrometry (ICP-OES)

The quantitative analysis of heavy metals in each sample was conducted using ICP-OES with a flared end EOP Torch (2.5 mm). The optimal operating parameters were as follows: an RF generator power of 1400 W, high purity argon gas for plasma and nebuliser, and a flow rate of 14.50 L/min for plasma, 0.90 L/min for auxiliary gas, and 0.85 L/min for nebuliser gas. The initial stabilisation time, rinse time, and sample uptake time were 45 seconds each. There was no delay time or time between replicate analyses. The experiment was performed in triplicate, and the RF generator operated at a constant frequency of 27.12 MHz. The solid state was cyclonic, the detector was a Charge Coupled Device (CCD), and the spray chamber was a modified Lichte. Sample delivery was facilitated by a computer-controlled precision peristaltic pump with four channels, ensuring accurate sample flows. The prewash pump operated at a speed of 60 rpm for 15 seconds, while the sample injection pump operated at a speed of 30 rpm for 45 seconds.

4. Validation of the analytical method

The limits of detection (LOD) and limits of quantification (LOQ) of the ICP-OES method for all elements were calculated. Stock standard solutions for calibration were prepared at three different concentrations (100, 500, and 1000 ppm). The matrix effects were evaluated by adding the standard stock solutions to 10 mL of blank samples. After preparation, the solution was mixed for one minute and then analysed using the ICP-OES technique to eliminate the matrix effects. Furthermore, correlation coefficients and calibration equations were determined. The relative standard deviations (%), LODs, and LOQs (mg/kg) determined by ICP-OES analysis are presented in Table 1. The recoveries for all studied elements ranged between 96.2% and 101.9%. All measurements were performed in triplicate.

4.1. Risk assessment

In the current study, we assessed the risk of exposure to As, Cd, Cu, Cr, Pb, Hg, Mn, Zn, and Fe through the consumption of black tea and coffee. To estimate the risk, we utilised the estimated daily intake (EDI), HQ, and HI. The EDI was calculated using the following equation [22]:

$$\mathrm{EDI} = C \times IR/BW \times 1000$$

Where C represents the concentration of each metal (mg/kg), and IR is the ingestion rate (g/person/day). Based on a previous study, the ingestion rate of black tea and coffee was assumed to be 11.4 g/person/day and 5 g/person/day for adults, respectively. Additionally, BW represents the average weight of consumers, which was taken as 70 kg. The risk of non-carcinogenic effects associated with heavy metal ingestion in the collected samples was calculated using the HQ as follows [23,24].

$$HQ = \mathrm{EDI}/RfD$$

Table 1. Method validation parameters obtained by ICP-OES analysis in tea and coffee samples.

Element	Wavelength (nm)	LOD (mg/kg)	LOQ (mg/kg)	R^2
As	189.042	0.00358	0.01074	0.99
Cd	228.802	0.00098	0.00294	0.99
Cu	324.754	0.00612	0.01836	0.99
Cr	267.716	0.00920	0.0276	0.99
Pb	283.305	0.04332	0.12996	0.99
Mn	257.611	0.00132	0.00396	0.99
Zn	206.198	0.00540	0.0162	0.99
Fe	259.941	0.00320	0.0096	0.99

In the above equation, RfD is the acceptable daily reference dose (mg/kg/day). The RfD values for As, Cd, Cu, Cr, Pb, Mn, Zn, and Fe are 0.0003, 0.001, 0.04, 0.003, 0.0035, 0.14, 0.3, and 0.7 mg/kg/day, respectively [25,26]. When the Hazard Quotient is ≤ 1, the non-carcinogenic human health risks are not considered significant. However, if the HQ is > 1, it indicates a significant non-carcinogenic health risk. Additionally, the Hazard Index, which assesses the potential non-carcinogenic effects of multiple elements on human health, is evaluated using the following equation [27]:

$$HI = HQ_1 + HQ_2 + HQ_3 + \ldots + HQ_n$$

If the HI value is ≤ 1, the health risk is considered unlikely. However, if the HI exceeds 1, it indicates that the exposed consumers are at considerable health risk.

5. Data analysis

The analysis of data was performed using SPSS software, version 20 (SPSS Inc., Chicago, IL, USA). In this analysis, *p* value <0.05 were considered statistically significant. The data were reported as mean ± standard deviation.

6. Results and discussion

6.1. The concentration of PTEs

The mean concentration and standard deviation of the heavy metals, including As, Cd, Cu, Cr, Pb, Hg, Mn, Zn, and Fe, in black tea and coffee brands collected from different markets in the Erbil city, are shown in Tables 2. The concentration of As, Cd, Cu, Cr, Pb, Mn, Zn, and Fe in black tea samples was found to range from not detected (ND) to 0.11, ND to 0.4, 3.46 to 15.82, ND to 3.65, 0.3 to 4.04, 129.52 to 607.28, 10.42 to 58.92, and 9.14 to 72.26 mg/kg, respectively. The concentration range of Cd, Cu, Cr, Pb, Mn, Zn, and Fe detected in coffee samples was ND to 0.08, 0.1 to 13.2, ND to 1.92, 0.02 to 1.62, 0.74 to 16.88, ND to 8.18, and 1.5 to 36.88 mg/kg, respectively. However, the concentration of As in coffee was below the detection limits.

Heavy metals are commonly present in the environment, and their concentration can be influenced by human activities. These elements may enter the soil from various sources and accumulate in plants. Previous studies have indicated that high levels of heavy metals in black tea and coffee, as well as their absorption into the human body, can lead to poisoning and pose various health problems. To determine the safety of analysed samples, the results were compared to the recommended standards and other conducted studies in plants.

Evaluating black tea and coffee samples is crucial for ensuring human safety due to their extensive global consumption. For instance, some metals such as Fe, Cu, and Zn are essential for the body in certain levels, while toxic metals such as As, Cd, Pb, and Cr can be harmful. As is a toxic element, and its chronic ingestion can cause many adverse health effects [28]. Among the 102 analysed samples of tea and coffee, the presence of As was found only in some tea samples, with concentrations ranging from N.D to 0.11 ± 0.02 mg/kg, which was lower than the maximum permissible level (0.5 mg/kg) [29]. Similarly, Naghipour et al. [30] examined the concentration of trace elements in various kinds of tea available in the North of Iran. They reported that the concentration of As in black tea

Table 2. Mean and standard deviation of heavy metals in black tea and coffee samples.

Beverages	Statistic	As	Cd	Cu	Cr	Pb	Mn	Zn	Fe
Black tea	Mean	0.023 ± 0.005	0.11 ± 0.004	10.29 ± 0.08	0.60 ± 0.02	1.69 ± 0.13	294.99 ± 8.61	25.59 ± 2.06	39.80 ± 3.20
	Min	ND*	ND*	3.46	ND*	0.3	129.52	10.42	9.14
	Max	0.11	0.4	15.82	3.65	4.04	607.28	58.92	72.26
coffee	Mean	ND*	0.035 ± 0.002	6.22 ± 0.14	0.61 ± 0.06	0.51 ± 0.03	9.90 ± 0.11	4.37 ± 0.04	19.43 ± 1.122
	Min	ND*	0.00	0.1	ND*	0.02	0.74	ND*	1.5
	Max	ND*	0.08	13.2	1.92	1.62	16.88	8.18	36.88

ND; not detected.

was in the range of 0.03 to 0.1 mg/kg. Contrary to our findings, Voica et al. [31] reported a mean concentration of 0.05 mg/kg in collected coffee samples.

Among the 60 analysed samples of black tea, 8 samples (13%) had cadmium levels slightly exceeding the permitted limit set by the World Health Organization (WHO) at 0.3 mg/kg [29]. The maximum level of Cd in the current study was higher than the measured values in black tea in Pakistan and Saudi Arabia [32,33]. On the other hand, the range of Cd in all the coffee samples was within the allowable levels. In accordance with our findings, a study by Adler et al. [34] showed that the content of Cd varied from 0.011 mg/kg to 0.022 mg/kg in roasted coffee. Another study by Grembecka et al. [35], reported that the cadmium content in coffee samples originated from Africa, America, and Asia was below the level of detection.

Pb is considered a toxic environmental pollutant, and its toxicity in humans has been associated with mental impairment, behavioural abnormalities, seizures, and other health problems. This metal can accumulate in tea leaves and coffee, raising concerns for consumers [36]. The analytical data revealed that all samples contained a low level of Pb, ranging from 0.02 to 4.04 mg/kg. These values were below the WHO permitted limit of 10 mg/kg [29]. Our Pb results were in line with the study by Kowalska [15], who evaluated the amount of some heavy metals in tea and coffee samples in the Polish market. They found that the concentrations of Pb in analysed samples ranged from 0.010 mg/kg to 0.791 mg/kg. These results were lower than those published by Nogaim et al. [37], and Zazouli et al. [38]. Lower levels were reported by Vezzulli et al. [39] (<LOQ to 0.4 mg/kg) for coffee, and Pourramezani et al. [40] (0.21 mg/kg) for Indian tea.

Cu and Zn are important non-protein trace elements that play significant roles in biological systems and living organisms [41]. However, excessive intake of these elements can lead to various problems such as kidney and liver damage, inflammation, and oxidative stress [42]. The measured levels of Cu in the black tea samples ranged from 3.46 to 15.82 mg/kg, while the range for coffee samples was 0.1 to 13.2 mg/kg. The mean concentration of Zn in the analysed samples of black tea and coffee was 25.59 ± 2.06 and 4.37 ± 0.04 mg/kg, respectively. The highest levels of Cu and Zn were found in black tea. A study on Chinese and Indian black tea brands also reported higher Cu and Zn levels (10.15 ± 3.13 mg/kg for Cu and 27.90 ± 5.60 mg/kg for Zn) compared to the our findings [43].

Cr is another essential mineral necessary for the growth and metabolism of lipids and glucose. However, exposure to high levels of Cr can have adverse effects on human health [44]. In the black tea and coffee samples, Cr was detected in 45% and 50% of the tested samples, with maximum contents of 3.65 ± 0.2 and 1.92 ± 0.08, respectively. Similarly, a conducted survey by Zhong et al. [45] on Chinese tea in 2015 illustrated that the amount of Cr was below the maximum residue limit (5 mg/kg). While the content of Cr was not detected in coffee from different countries [46,47].

Mn and Fe were found to be the most abundant metals in black tea and coffee, respectively. Mn is involved in the activation of many enzymes and is required for glucose and lipid metabolism, while Fe is essential for various metabolic reactions in the body [48,49]. Despite mentioned benefits, high doses of Mn and Fe can lead to side effects in humans [50,51]. The concentrations of Mn and Fe in black tea samples varied from 129.52 to 607.28 mg/kg and 9.14 to 72.26 mg/kg, respectively. These results were lower than the values reported in a study by Dambiec et al. [52], which noted relatively high concentrations of Mn and Fe in dry tea material. In coffee samples, Mn and Fe concentrations ranged from 0.74 to 16.88 mg/kg and 1.5 to 36.88 mg/kg, respectively. The Mn and Fe levels found in this study were lower than those reported in coffee analysed in Algeria [53], and Brazil [54], while other studies reported lower values of these metals in various types of coffee [35].

The differences in findings are due to the difference in plant origin, soil properties, processing, and other environmental conditions [55]. In addition, the use of fertilisers and pesticides during cultivation may be significant contributors to the content of heavy metals in plants [56]. The use of the fermentation process to produce black tea seems to be effective in increasing its trace metal content [57]. It has been previously demonstrated that the type of coffee (raw or roasted), species, brewing methods, and other processing conditions affect the levels of metals in the resulting coffee [58].

The EDI of all investigated metals through the consumption of black tea and coffee is summarised in Tables 3 and 4. The highest EDI value was shown by Mn in both tea and coffee. According to the results, the EDI values for all elements were below the oral reference dose (RfD) in the collected samples, and therefore, do not seem to pose a health risk. The HQ level of elements in black tea showed the following order: Mn > Pb > Cu > Cr > Cd > As > Zn > Fe, while in coffee, it was ranked as follows: Cr > Cu > Pb > Mn > Cd > Fe > Zn. All beverages had HQ values less than one, which indicates no potential health effects for Iraqi consumers (Tables 3 and 4). Additionally, we found that the HQ of all metals in black tea was higher compared to coffee. The HI, which expresses the combined non-carcinogenic effects of the investigated heavy metals in black tea and coffee, was calculated as 0.52 and 0.04, respectively. Furthermore, HI values of less than one indicate that there are no significant health risks related to our samples. Similar results were also obtained in

Table 3. Calculation of ADI and HQ for heavy metals in black tea samples.

Heavy metal	ADI (mg $kg^{-1}day^{-1}$)	HQ
As	3.74×10^{-6}	1.2×10^{-2}
Cd	1.79×10^{-5}	1.7×10^{-2}
Cu	1.6×10^{-3}	4×10^{-2}
Cr	9.7×10^{-5}	3×10^{-2}
Pb	2.75×10^{-4}	7×10^{-2}
Mn	4.8×10^{-2}	34×10^{-2}
Zn	4.1×10^{-3}	1×10^{-2}
Fe	6.3×10^{-3}	1×10^{-3}

Table 4. Calculation of ADI and HQ for heavy metals in coffee samples.

Heavy metal	ADI (mg $kg^{-1}day^{-1}$)	HQ
As		
Cd	2.5×10^{-6}	2.5×10^{-3}
Cu	4.4×10^{-4}	1.1×10^{-2}
Cr	4.3×10^{-5}	1.4×10^{-2}
Pb	3.6×10^{-5}	1×10^{-2}
Mn	7.07×10^{-4}	5×10^{-3}
Zn	3.12×10^{-4}	1×10^{-3}
Fe	1.3×10^{-3}	1.8×10^{-3}

a previous study [59], which reported an HQ value < 1 for Cd, Pb, As, Cu and HI less than one in imported black tea for Iranian consumers. In another study by Taghizadeh et al. [60] on coffee and tea, the amounts of HQ and HI for As, Cd, Cr, Cu, Fe, Hg, Ni, and Pb were below the value of 1.0, which is consistent with the present study.

7. Conclusion

The findings of the current study illustrated that the concentration of most heavy metals in black tea and coffee samples from the Erbil markets was within allowable levels. Only in 8 black tea samples, Cd was slightly higher than the standard. Calculations of HQ and HI values for the studied metals showed that consuming these beverages poses no significant non-carcinogenic health risks. However, due to the increasing sources of toxic contaminants, continuous monitoring of such toxic elements and the development of domestic guidelines to ensure consumer safety are recommended.

Disclosure statement

No potential conflict of interest was reported by the author.

References

[1] M. Jeszka-Skowron, A. Zgoła-Grześkowiak and T. Grześkowiak, (Springer, Cham, Switzerland, 2021), pp. 193–225.

[2] L. Karimzadeh, G.A. Bagheri, A. Pour Ali, M. Gholipour, Z. Mohammadi, and B. Moshrefi, M.H. Esfahanizadeh, and E. Salehifar, Maz. Univ. Med. Sci. **23**, 2–10 (2013).

[3] S.W. Alwan and Casp, J. Environ. Sci. **20**, 629–635 (2022). doi:10.22124/CJES.2022.5707.

[4] X. Yong-Mei, Q. Fang-Bin and H. Ji-Kun, J. Integr. Agric. **21**, 552–565 (2022). doi:10.1016/S2095-3119(21)63850-9.

[5] A. Greyling, R.T. Ras, P.L. Zock, M. Lorenz, M.T. Hopman, D.H. Thijssen and R. Draijer, PLOS ONE **9**, e103247 (2014). doi:10.1371/journal.pone.0103247.

[6] J. Yang, Q.-X. Mao, H.-X. Xu, X. Ma and C.-Y. Zeng, BMJ open **4**, e005632 (2014). doi:10.1136/bmjopen-2014-005632.

[7] Y. Zhao, S. Asimi, K. Wu, J. Zheng and D. Li, Clin. Nutr. **34**, 612–619 (2015). doi:10.1016/j.clnu.2014.06.003.

[8] Z. Rasheed, Int. J. Health Sci. **13**, 1–3 (2019). doi:10.33545/26649187.2019.v1.i1a.11.

[9] R. Mentaverri, M. Brazier, S. Kamel and P. Fardellone, Curr. Mol. Pharmacol. **5**, 189–194 (2012). doi:10.2174/1874467211205020189.

[10] H. Dieng, S.B. Ellias, T. Satho, A.H. Ahmad, F. Abang, I.A. Ghani, S. Noor, H. Ahmad, W. F. Zuharah, R.E. Morales Vargas, N.P. Morales, C.N. Hipolito, S. Attrapadung and G.T. Noweg, Environ. Sci. Pollut. Res. **24**, 14782–14794 (2017). doi:10.1007/s11356-017-8711-4.

[11] R. Poole, O.J. Kennedy, P. Roderick, J.A. Fallowfield, P.C. Hayes and J. Parkes, bmj. **359**, (2017). doi:10.1136/bmj.j5024.

[12] P.V. Dludla, I. Cirilli, F. Marcheggiani, S. Silvestri, P. Orlando, N. Muvhulawa, M.T. Moetlediwa, B. B. Nkambule, S.E. Mazibuko-Mbeje, N. Hlengwa, S. Hanser, D. Ndwandwe, J.L. Marnewick, A. K. Basson and L. Tiano, Mol. **28**, 6440 (2023). doi:10.3390/molecules28186440.

[13] M.A. Spiller, editor, Caffeine (CRC, Boca Raton, FL, 2019), pp. 97–161.

[14] J.-H. Bae, J.-H. Park, S.-S. Im and D.-K. Song, Integr. Med. Res. **3**, 189–191 (2014). doi:10.1016/j.imr.2014.08.002.

[15] G. Kowalska, Int. J. Environ. Res. **18**, 5779 (2021). doi:10.3390/ijerph18115779.

[16] A. RoyChowdhury, R. Datta and D. Sarkar, Elsevier. 2018, 359–373. doi:10.1016/B978-0-12-809270-5.00015-7.

[17] G.A. Guadalupe, S.G. Chavez, E. Arellanos and E. Doménech, Food **12**, 3254 (2023). doi:10.3390/foods12173254.

[18] A. Mohajer, P. Safaei, H. Sleman Ali, H. Sarwar Karim, P. Sadighara, E. Molaee-Aghaee and K. Ghanati, Int. J. Environ. Health. Res. **34**, 839–850 (2024). doi:10.1080/09603123.2023.2175798.

[19] A. Mohajer, A.N. Baghani, P. Sadighara, K. Ghanati and S. Nazmara, J. Food Compos. Anal. **86**, 103384 (2020). doi:10.1016/j.jfca.2019.103384.

[20] A.E. Charkiewicz, W.J. Omeljaniuk, K. Nowak, M. Garley and J. Nikliński, Mol. **28**, 6620 (2023). doi:10.3390/molecules28186620.

[21] D.Y. Shin, S.M. Lee, Y. Jang, J. Lee, C.M. Lee, E.-M. Cho and Y.R. Seo, Int. J. Mol. Sci. **24**, 3410 (2023). doi:10.3390/ijms24043410.

[22] H. Cao, L. Qiao, H. Zhang and J. Chen, Sci. Total Environ. **408**, 2777–2784 (2010). doi:10.1016/j.scitotenv.2010.03.019.

[23] H. Cao, J. Chen, J. Zhang, H. Zhang, L. Qiao and Y. Men, J. Environ. Sci. **22**, 1792–1799 (2010). doi:10.1016/S1001-0742(09)60321-1.

[24] G.R. Mostafaii, A. Moravveji, B. Hajirostamloo, M. Hesami Arani, M. Dehghani, Z. Heidarinejad, Y. Fakhri and A.M. Khaneghah, J. Environ. Anal. Chem. **102**, 1192–1204 (2022). doi:10.1080/03067319.2020.1734195.

[25] USEPA, in *U.S. Environmental Protection Agency*, edited by U.S.E.P. Agency (2019). https://www.epa.gov/iris

[26] H.R. Ghaffari, Z. Kamari, V. Ranaei, Z. Pilevar, M. Akbari, M. Moridi, K.M. Khedher, V.N. Thai, Y. Fakhri and A. Mousavi Khaneghah, Environ. Res. **201**, 111567 (2021). doi:10.1016/j.envres.2021.111567.

[27] M. Idrees, F.A. Jan, A. Ara, Z.M. Begum, M. Mahmood and H. Gulab, Carpath. J. Earth Environ. **12**, 641–648 (2017).

[28] M.S. Rahaman, M.M. Rahman, N. Mise, M.T. Sikder, G. Ichihara M.K. Uddin, Kurasaki M, Ichihara S., Environ. Pollut. **289**, 117940 (2021). doi:10.1016/j.envpol.2021.117940.

[29] WHO (World Health Organisation), *WHO Guidelines for Assessing Quality of Herbal Medicines with Reference to Contaminants and Residues* (WHO, Geneva, Switzerland, 2007).

[30] D. Naghipour, A. Amouei, M. Dadashi and M.A. Zazouli, J. Maz. Univ. Med Sci. **26**, 211–223 (2016).

[31] C. Voica, I. Feher, A. Iordache, G. Cristea, A. Dehelean, D. Magdas and V. Mirel, Anal. Lett. **49**, 2627–2643 (2016). doi:10.1080/00032719.2015.1116003.

[32] M. Idrees, F.A. Jan, S. Hussain and A. Salam, Biol. Trace Elem. Res. **198**, 344–349 (2020). doi:10.1007/s12011-020-02059-1.

[33] A.A. Shaltout and O.H. Abd-Elkader, Biol. Trace Elem. Res. **174**, 477–483 (2016). doi:10.1007/s12011-016-0728-x.

[34] G. Adler, A. Nędzarek and A. Tórz, Slovenian. J. Pub. Health. **58**, 187–193 (2019). doi:10.2478/sjph-2019-0024.

[35] M. Grembecka, E. Malinowska and P. Szefer, Sci. Total Environ. **383**, 59–69 (2007). doi:10.1016/j.scitotenv.2007.04.031.

[36] U. Zulfiqar, M. Farooq, S. Hussain, M. Maqsood, M. Hussain, M. Ishfaq, M. Ahmad and M. Z. Anjum, J. Environ. Manage. **250**, 109557 (2019). doi:10.1016/j.jenvman.2019.109557.

[37] Q. Nogaim, S. Al-Dalali, A. Al-Badany and M. Farh, J. Appl. Chem. **2**, 13–18 (2014).

[38] M.A. Zazouli, A.M. Bandpei, A. Maleki, M. Saberian and H. Izanloo, Asian J. Chem. **22**, 1387 (2010).

[39] F. Vezzulli, M.C. Fontanella, M. Lambri and G.M. Beone, J. Sci. Food Agric. **103**, 4303–4316 (2023). doi:10.1002/jsfa.12490.

[40] F. Pourramezani, F.A. Mohajeri, M.H. Salmani, A.D. Tafti and E. Khalili Sadrabad, Food Sci. Nutr. **7**, 4021–4026 (2019). doi:10.1002/fsn3.1267.

[41] K. Jomova, M. Makova, S.Y. Alomar, S.H. Alwasel, E. Nepovimova K. Kuca, Rhodes CJ, Valko M., Chem. Biol. Interact. **367**, 110173 (2022). doi:10.1016/j.cbi.2022.110173.

[42] K. Asgari and W.M. Cornelis, Environ. Monit. Assess. **187**, 1–13 (2015). doi:10.1007/s10661-015-4565-8.

[43] G. Barone, R. Giacominelli-Stuffler and M.M. Storelli, Food Chem. Toxicol. **87**, 113–119 (2016). doi:10.1016/j.fct.2015.12.008.

[44] K.L. Mandiwana, N. Panichev and S. Panicheva, Food Chem. **129**, 1839–1843 (2011). doi:10.1016/j.foodchem.2011.05.124.

[45] W.-S. Zhong, T. Ren and L.-J. Zhao, J. Food Drug Anal. **24**, 46–55 (2016). doi:10.1016/j.jfda.2015.04.010.

[46] Y.S. Berego, S.S. Sota, M. Ulsido and E.M. Beyene, Peer J. **11**, 14789 (2023). doi:10.7717/peerj.14789.

[47] T. Getachew and N. Worku, Int. J. Res. **1**, 2348–6848 (2014).

[48] L. Li and X. Yang, Oxid. Med. Cell. Longev. **2018**, 7580707 (2018). doi:10.1155/2018/7580707.

[49] M. Han, L. Guan, Y. Ren, Y. Zhao, D. Liu, D. Zhang, L. Liu, F. Liu, X. Chen, C. Cheng, Q. Li, C. Guo, Q. Zhou, G. Tian, R. Qie, S. Huang, X. Wu, Y. Liu, H. Li, X. Sun, M. Zhang, D. Hu and J. Lu, Asia Pac. J. Clin. Nutr. **29**, 309–321 (2020). doi:10.6133/apjcn.202007_29(2).0014.

[50] Y. Huang, D. Cao, Z. Chen, B. Chen, J. Li, R. Wang, J. Guo, Q. Dong, C. Liu, Q. Wei and L. Liu, Crit. Rev. Food Sci. Nutr. **63**, 2910–2927 (2023). doi:10.1080/10408398.2021.1982861.

[51] A. Santamaria, Indian J. Med. Res. **128** (4), 484–500 (2008).

[52] M. Dambiec, L. Polechońska and A. Klink, J. Food Compos. Anal. **31**, 62–66 (2013). doi:10.1016/j.jfca.2013.03.006.

[53] Z. Anissa, B. Sofiane, A. Adda and J. Marlie-Landy, Biol. Trace Elem. Res. **201**, 5455–5467 (2023). doi:10.1007/s12011-023-03582-7.

[54] D. Albals, I.F. Al-Momani, R. Issa and A. Yehya, Sci. Prog. **2**, 1–17 (2021). doi:10.1177/00368504211026162.

[55] Y.H. Senkondo, F. Tack and E. Semu, Commun. Soil Sci. Plant Anal. **45**, 2032–2045 (2014). doi:10.1080/00103624.2014.919312.

[56] S.L. Ferreira, V.A. Lemos, L.O. Silva, A.F. Queiroz, A.S. Souza, E.G. da Silva, W.N.L. dos Santos and C.F. Das Virgens, Microchem. J. **121**, 227–236 (2015). doi:10.1016/j.microc.2015.02.012.

[57] T. Karak and R. Bhagat, Int. Food Res. **43**, 2234–2252 (2010). doi:10.1016/j.foodres.2010.08.010.

[58] M. Árvay J, M.H. Šnirc, J. Bilčíková, A. Bobková, L. Demková, L. Demková, M. Hudáček, M. Hrstková, T. Lošák, M. Král, A. Kováčik and J. Štefániková, Biol. Trace Elem. Res. **190**, 226–233 (2019). doi:10.1007/s12011-018-1519-3.

[59] E. Abbasi, M.H. Yousefi, S. Hashemi, S. Hosseinzadeh, A.H. Ghadimi, M. Safapour and A. Azari, J. Food Compos. Anal. **106**, 04277 (2022). doi:10.1016/j.jfca.2021.104277.

[60] S.F. Taghizadeh, M. Azizi, G. Hassanpourfard, R. Rezaee and G. Karimi, Biol. Trace Elem. Res. **201**, 1520–1537 (2023). doi:10.1007/s12011-022-03239-x.