Research Article

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Inductively coupled plasma mass spectrometry assessment of essential and toxic trace elements in traditional spices consumed by the population of the Middle Eastern region in their recipes

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Abstract: Inductively coupled plasma and microwave digestion are used in this article to analyze various food matrices. Different natural herbs are used in the recipes for the food items that the people of the Middle Eastern part of the world eat; they use these herbs as spices in different proportions. The study examines the potential effects on human health associated with consuming trace and toxic elements, such as Ni, Mn, Pb, Cd, Fe, Zn, Ca, Mg, K, and Na. The targeted spices include sumac, za'atar, black lemon, cumin seed, and kabsa powder; these were used in a variety of recipes for the food items the people of Saudi Arabia eat but not limited to fattier, kabsa, tabbouleh, humus, haysa Al tumreya, and other traditional foods. The herbs were collected from the Saudi Arabian market. For microwave digestion, Merck's ultrapure nitric acid and 30% hydrogen peroxide were used. For elemental analysis, a highly sophisticated technique of inductively coupled plasma mass spectrometry was applied. The average potassium values in black lemon (Loomi), kabsa powder, cumin seed, za'atar, and sumac were 1,283, 1,248, 1,739, 500, and 500 mg/100 g, respectively. These spices help fulfill the human body's daily requirements of elemental content.

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1 Introduction

There is a continuing need to investigate the dietary intake of several trace and toxic elements by the people of Saudi Arabia through the consumption of various spices in different traditional or non-traditional foods. The consumption of these trace and toxic elements is essential to accurately assess the nutritional status of a population and determine the potential public health risk associated with the dietary intake of these elements [1,2]. Owing to environmental pollution or intentional adulteration, e food consumed by the people of Saudi Arabia may contain trace and toxic elements [3]. The human body has a reasonable tolerance level for each element; however, exceeding this tolerance level may adversely affect the biochemical system. Therefore, the determination of metal ions in food and biological materials is essential to monitor the safety of diet and health [4]. The daily intake of major and minor amounts of trace elements through various food items, especially targeted spices, is of particular concern because of human health and diseases [5]. *Black Lemon*: Black Lemon, also called Loomi, is a traditional Saudi spice that is regularly used. It belongs to the citrus fruit family and is rich in K. These elements play a role in heart muscle function and hence regulate the pumping of blood; it does have a role in the digestive system to excrete harmful bacteria and accumulate toxins to expel out of the body and hence considered a colon cleanser. Traditionally in the Middle Eastern part of the world, Loomi is known to be helpful for women in post-delivery because of its minerals and vitamins and hence improve the immune system. A study showed that 45% of the study's population used lemon as a supplement as well, especially during the Covid Pandemic time during the years 2020–2021 in Saudi

Arabia [6]. *Za'atar* is a culinary herb (*Origanum syriacum*) native to the middle east. It is a 2.5 ft-tall short shrub. However, as a commercial product, it is also available in the market as a traditional mixture of various spices called the Za'atar, including roasted sesame seeds and dried Sumac, and is used to evaluate essential and trace elements in various food matrices [7–9]. *Cumin seed*: belongs to the family: Apiaceae, Genus: Cuminum, and Species: *C. cyminum*, commonly used in various Saudi recipes [10]; it has a pleasant flavor that enhances the flavor of food with its unique aroma [11]. Cumin seed is known to be of medicinal importance for a long time, especially for heartburn, diarrhea, and flatulence. The modern home creates remedies [12,13]. The cumin seed comprises macronutrients and heavy metals, such as Mg, Na, Ca, K and Zn, Cu, Fe, and heavy metals Cd, Co, Pb, and Ni [14]. The literature showed that cumin contains K as the most abundant macronutrient in Cumin seed compared to other elements, followed by Ca and P, Mg, and heavy metals [15]. *Sumac:* Sumac is a tree shrub belonging to the Genus Rhus (*Rhus coriaria* L.) with various spices. The name Sumac is derived from Sumaga, which in Syria signifies RED [16]. It does contain flavonoids, organic acids, nitrates, and nitrites [17]. It has nine fragrances, a citrus flavor, and a color that is rich in spices. It is served as a sprinkle on traditional salads and other foods like humus, mutable, etc. The Syrian Sumac contains K and Ca in sufficient quantity, whereas Na, Fe, Mg, and P are in appreciable quantities [18]. The spicy *Sumac* is commonly used in Saudi Arabia as a topping on salad and a traditional dish, which enhances the outlook of the dish with attractive color and zesty flavor; it has a lot of K, Ca, Mg, and P in its fruit [19]. *Kabsa powder*: An Arab cuisine very popular in Arabian Peninsula, Kabsa cuisine, is a significantly century-old tradition that comprises various herbs and a mixed spice that is frequently used in traditional food recipes consumed by the people of Saudi Arabia and has a significant impact on the body's absorption of minerals through this spice.

2 Materials and methods

2.1 Sample collection and preparation for inductive coupled plasma mass spectrometry (ICP-MS)

Saudi Arabian spices were collected from various regions of the country, including grocery stores and other open markets, where people buy the ingredients for their recipes. The samples were then prepared using microwave-purified oxidizing acid and hydrogen peroxide, and after that, preconcentrated standards of various groups of elements were used for calibration, allowing the quantification of trace and toxic elements. The result of this project may provide a clear picture for the population who knowingly or unknowingly consume some elements in their everyday food items, eventually helping the people of the Kingdom of Saudi Arabia establish a healthy diet in terms of dietary intake of trace and toxic elements.

2.2 Reagents and chemicals

The analysis reagents used were 65% Suprapur Nitric acid (Merck, Germany) and hydrogen peroxide 30%. Milli Q water from the Millipore integral system was used for sample preparation. Preconcentrated standard solutions from inorganic Ventures IV–LMPS-71A were used to obtain the curve of elements analyzed, including Cr, Ni, Zn, Cu, Fe, Mn, Ca, Mg, K, and Na, to obtain the results with high precision and accuracy.

2.3 Instrumentation

ICP-MS from Perkin Elmer was used for the sample analysis throughout the research. Since the samples were prepared using microwave digestion, Anton Par microwave 3000 was used to accurately prepare the sample, and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) techniques were employed to identify various organic components of the samples analyzed. The advantage of ATR attachment is that it provides uncountable possibilities for those samples that cannot be analyzed directly by transmission.

2.3.1 Calibration and sample analysis by ICP-MS

Microwave digestion was used to accurately prepare the samples, followed by the proper dilution and ICP-MS analysis. The calibration curve was obtained from a suitable range of standard solutions using the ICP-MS; the data were obtained using the validated software Elan DRC. For this study, an autosampler was used to run the sample for quantitative analysis of metal ions, such as sodium, magnesium, potassium, calcium, phosphorous, iron, nickel, lead, copper, manganese, chromium, and zinc. Prior to analysis, the ICP-MS was tuned, cleaned with a cleaning

solution, and optimized using tuning solution smart Tune Elan DRC/plus/II solutions. For optimal performance, resolution at low mass is indicated by magnesium isotopes 23.94, 24.98, and 25.98, and resolution at high mass is indicated by lead isotopes 205.974, 206.975, and 207.976, and calibration was adjusted to 0.05 amu. Stock standard solutions were used as the calibration standards, and working standard solutions between 50 and 500 ppb were prepared. The results were calculated using the linear regression values that were obtained after samples were adequately diluted to find the appropriate response in the range of standard intensities. To obtain precise and accurate data, an autosampler was used. The precision and accuracy of the analysis were demonstrated by the %RSD of replicate analysis, which was observed to be <2.0% in all samples analyzed by ICP_MS. The isotopes for the determined elements have been discussed. The limit of quantification of elements was mentioned as follows:

Na = 0:002; Mg = 0:004; P = 0:011; K = 0:001; Mn = 0:001; Fe = 0:03; Ni = 0:006; Cu = 0:001; Zn = 0:004; Pb = 0:003.

2.3.2 FTIR-ATR

FTIR-ATR (BRUKER ALPHA II Germany) scanning was carried out on the samples of Saudi spices including Loomi, Za'atar, kabsa powder, cumin seed, and sumac. The ground samples were subject to scanning the wavenumber range of 400–4,000 cm^{-1} on ATR. The functional groups of all samples were analyzed individually as those samples which cannot be analyzed by direct transmission. The ground solid powders were placed on the crystal of ATR-FTIR.

3 Results and discussion

Using ICP-MS, the elemental analysis of Saudi spices was effectively carried out. Elements play a significant role in health care, diseases, and the therapeutic efficacy of these spices. All results are given as ranges and averages and are expressed in mg/100 g. It was found that the analyzed spices demonstrated the safety of their use in regional food recipes. The analysis of metal ions is distributed into two groups. Group "A" (Mn, Ni, Cu, Zn, Cd, and Pb) and Group "B" (Na, K, Mg, and Ca). As elements play a pivotal role in medicinal values in health and disease, they help them energize the human need. Data were collected following the procedure and analyzed using ICP-MS software. It is observed from Table 1 that Fe was found in high content among all seven elements in the spices; the lowest Fe content was found in Za'atar at 14.80 mg/100 g, and the highest Fe content was found in Black Lemon at 30.83 mg/100 g. Zn concentration ranges from 5.51 mg/100 g in Za'atar to 15.60 mg/100 g in Kabsa powder. Mn was also observed to be highest in Kabsa powder at 14.69 mg/100 g, whereas it was lowest to be in black dried lemon; the other heavy metals are reported in Table 1 including Ni, Cd, and Pb, which were observed to be less than 1.0 mg/100 g, whereas Cu was found to be between 1.0 and 2.0 mg/100 g in all five spices (Black Lemon, Sumac, Za'atar, Kabsa powder, and cumin seed). It is observed from Table 2 that Na contents are higher in Sumac and Za'atar. Sumac is an essential part of Saudi salad, and Za'atar is used in the recipe of some special food composed of bread. These two spices need to be used carefully, especially for people suffering from cardiovascular problems, to avoid any unforeseen situations because of their use. Na in kabsa and black lemon is observed at 84 mg/100 g, which, in fact, also helps make their use well with cardiovascular patients, as K, Ca, and Mg are found in high concentrations in them, as discussed below, and beneficial to human health.

Table 1: ICP-MS analysis of Saudi spices

mg/100 g Averages of a group of each spice							
	Mn	**Fe**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
Black lemon	0.86	30.83	0.76	1.48	10.09	0.01	0.19
Kabsa	14.69	27.79	0.30	1.99	15.60	0.01	0.43
Sumac	4.90	16.22	0.50	1.39	8.37	0.01	0.16
Za'atar	4.59	14.80	0.10	2.01	5.51	0.01	0.07
Cumin seed	3.31	47.02	0.30	1.63	6.24	0.01	0.13

The K content of group B was found to be highest in cumin seed (1,739 mg/100 g), followed by black dried lemon (1283.54 mg/100 g), and Kabsa powder (1,247 mg/100 g), which really plays a vital role in heart muscle strength and controlling blood pumping. Table 2 shows that the concentration of Ca was highest in Black lemon, followed by kabsa powder, za'atar, and sumac. Hence, the role of Saudi spices discussed in this study is very helpful in regulating epithelial functions [20]. Mg is also one of the major elements that help

Table 2: ICP-MS analysis of Saudi spices

mg/100 g Averages of a group of each spice				
Saudi spices	**Na**	**Mg**	**K**	**Ca**
Black lemon	84	112.44	1283.54	306.89
Kabsa	84.93	214.09	1247.92	229.01
Sumac	2953.45	172.6	501.9	77.59
Za'atar	1164.75	172.03	449.2	117.26

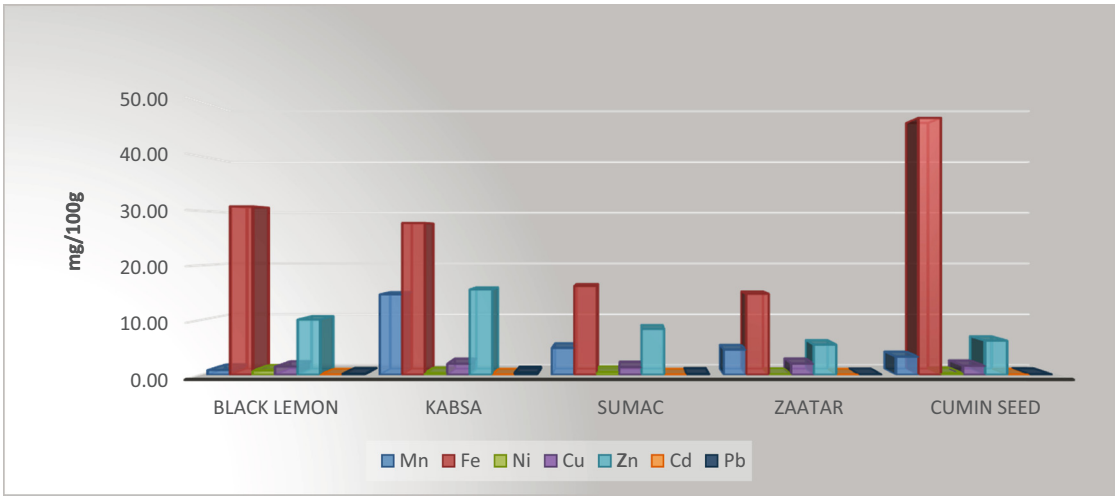

Figure 1: Elemental analysis of Saudi spices.

in cardiac muscle strength and blood pumping. Mg, a mineral the body needs for normal muscles, nerves, and bones, plays a pivotal role in regulating the heart muscles through diet. It also helps keep a steady heart rhythm, a healthy immune system, normal blood sugar levels, and blood pressure, and it is also involved in making energy and protein for the body. For adult women, the recommended dietary allowance (RDA) is about 300 mg and for adult men, 400 mg. These spices can be used in everyday meals to provide adequate assistance.

According to WHO/FAO, the acceptable limit for Zn is 27.4, Cu 3.00, Cr 0.02, and Mn 2 ppm. From the assumed results, it is settled that the levels of these elements are within normal limits.

Zn and Cu are the metals that help in body activities. Zn not only plays a role in immune functions but also in a number of cellular and humoral immunity-related processes and serves as an antioxidant. According to the NIH's Office of Dietary Supplements, the average daily requirement of Zn in adults is about 11 mg. Acute Zn poisoning may occur after ingestion of 4–8 g of zinc. The symptoms include nausea, vomiting, and dullness. Cu, as a co-factor linked with proteins, results in copper peptides, which help in the field of dermatology by keeping the skin firm and smoother, preventing the elasticity in the skin, and aiding in wound healing; if consumed in excess of the RDA 900 mcg, it may cause toxicity, but our studies indicated that the values are nearby RDA, which sounds healthy.

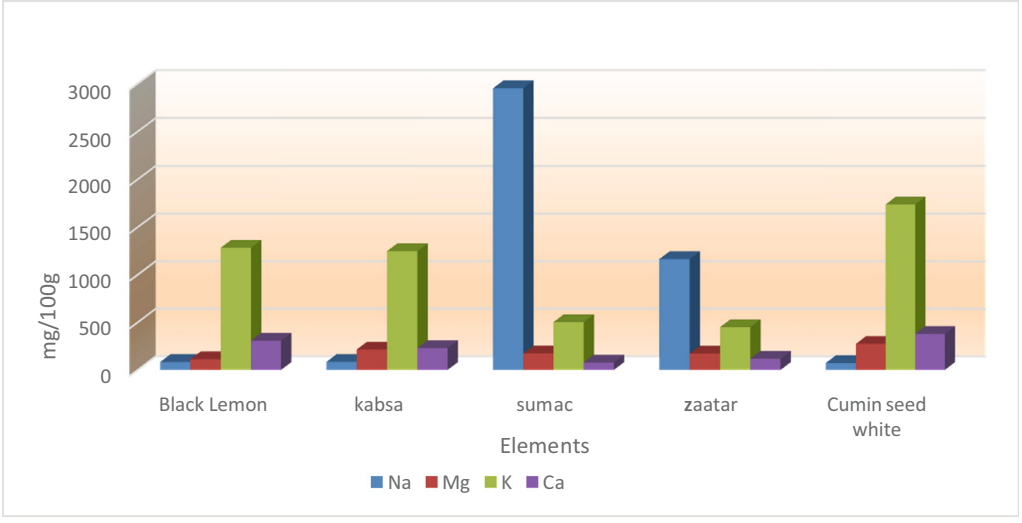

Figure 2: Elemental analysis of Saudi spices.

Ni is a micronutrient found in the human body; nucleic acids, specially referred to as ribonucleic acid (RNA), play a role in the construction or function of RNA. Its presence in spices improves healthy life. According to the NIH, RDA is 900 mcg; in tested spices, Mn is a micronutrient that is quite safe given that humans require 11 mg of Mg at high concentrations, which can result in tremors, muscle spasms, tinnitus, and hearing loss [21–23].

Considering the matrix effects between the argon and the contents of the sample, which was most commonly seen, pretreatment was carried out using nitric acid and hydrogen peroxide oxidizing solid agents. Under conditions of higher temperature and acidic vapors, the plasma generated a non-reactive argon gas, which then established the ideal environment for the production of 40ArO16+, 40ArN14+, 40Ar12C+, 40Ar35Cl+. These ions interferes with the detection of iron, manganese, chromium, and arsenic. 40Ar23Na+ interferes with the detection of 63Cu. With high levels of chloride and Ca, spectral overlaps from 40Ca35Cl+ and 40Ar35Cl+ interfere with low-level determinations of 75As+. With the proper instrumental settings for aerosol flow rate, radiofrequency, and dynamic reaction cell assistance, large levels of interference were removed in the matrix while using a Perkin Elmer ICP_MS DSR II. The ratio of isotopes could be determined using ICP-MS, which has various applications like geological dating. The test was

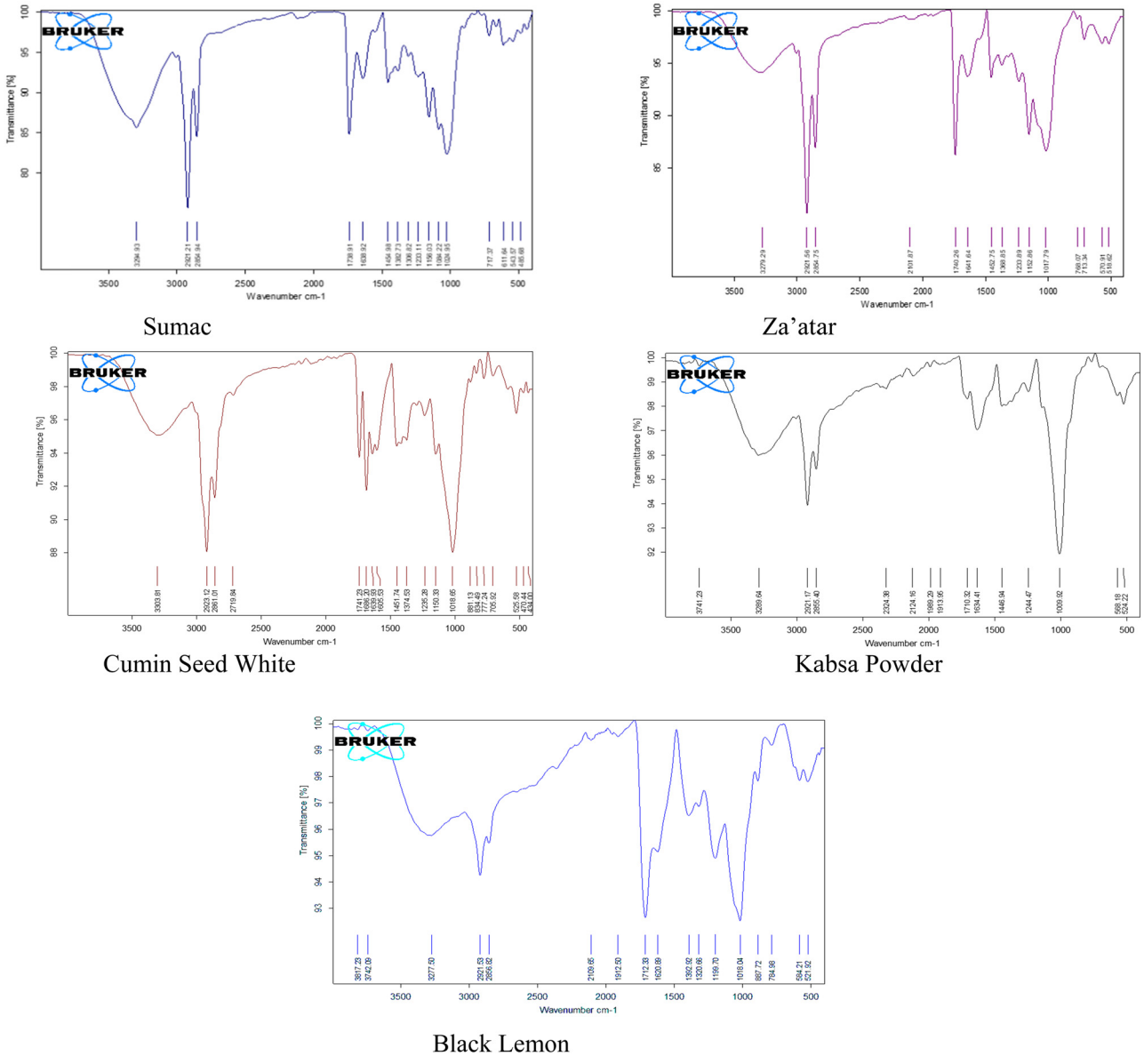

Figure 3: FTIR Spectra of *Sumac*, *Za'atar*, Cumin seed white, Kabsa powder, *Black lemon.*

performed to observe how the chemicals present in various spices interacted chemically together. *Sumac*: The FTIR data verifying the presence of carbonyl groups 1,738 cm^{-1} and a broad band of the OH group at 3,294 cm^{-1} in the sample collected for analysis may indicate the presence of maleic acid (Figure 1). *Za'atar*: The organic contents in Za'atar include maleic acid, citric acid, carvacrol, cymene, and other volatile oils. The typical OH bend at about 3,283 cm^{-1} and the C═O peak at 1,741 cm^{-1} indicate the presence of acidic compounds in Za'atar (Figure 2). Cumin seeds do have organic contents such as terpineo and cumin aldehyde and other carbonyl groups containing chemical components, attenuated total reflection spectrum supported by their characteristics peak at 3,280 cm^{-1} and C═O 1,741 cm^{-1}. *Kabsa powder*: It is a combination of mixed spices including cardamom, black pepper, bay leaves, cloves, and black pepper. The FTIR spectrum reveals typical −OH peaks at 3,287 cm^{-1}. The presence of nitrates in Linalool, a compound found in Bay leaves, is indicated by the peak at 1,241 cm^{-1} O–N–O bending the presence of nitrates. *Black lemon* has an acidic substance called citric acid and carboxylic acid contained in the chemical composition of lemon. The presence of acid compounds of utmost benefit to human health is indicated by peaks at 3,277 cm^{-1} for the –OH group and 1,712 cm^{-1} for the carbonyl group [24]. The FTIR-ATR spectra suggested that the availability of different health-concern compounds in all spices analyzed in this study benefits human health (Figure 3).

4 Conclusions

The outcome of research to assess the contents in term of metal ions in spices and their role in human health and organic compounds and their importance in spices related to health. We conclude as K and Mg are high (~1,300 mg/100 g) in Kabsa powder, Black lemon, and Cumin seed (1,739 mg/100 g) with low contents of Na ~84 mg/100 g in all Kabsa powder, Black Lemon, cumin seed. These results help in average blood pressure by maintaining a steady heartbeat, hence maintaining the heart health and health of nerves. Na initiates the triggering contractions of cardiac muscle fiber, Za'atar and Sumac, which are used in various Saudi recipes, like salad and fata'ir, have high Na contents and low K and Ca. As a result, Za'atar and Sumac should be consumed by a human with care by those who suffer from cardiovascular problems. These studies might pave the way for more extensive investigation into the local human population.

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Conflict of interest: Authors declare no conflict of interest.

Ethical approval: The conducted research is not related to either human or animal use.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

References

[1] Freiberg L, Norberg GF. Handbook on the toxicity of the metals. Amsterdam: Elsevier/North Holland Bio-Med; 1985.
[2] Venogopal B, Lucky TD. Metal toxicity in mammals. Vol 1 & 2. London, New York: Plenum Press; 1978.
[3] Crosby NT. Determination of metals in food. Analyst. 1977;102–225.
[4] Nurnberg HW. Pollutant and their ecotoxicological significance. New York: John-Wiley and sons; 1985.
[5] Igwegbe AO, Hassan TM. Trace metal elements (Pb, Cd and As), 15N nitrogen and phosphorus isotopes accumulation in three varieties of tomato from conventional and agro-ecological farming systems in Burkina Faso. J Food Saf. 1992;13:7–8.
[6] Al Najrany SM, Asiri Y, Sales I, AlRuthia Y. The commonly utilized natural products during the COVID-19 pandemic in Saudi Arabia: A cross-sectional online survey. Int J Environ Res Public Health. 2021;18(9):4688. Published online. doi: 10.3390/ijerph18094688.
[7] Djingova R, Ivanova J, Kuleff I. Comparative evaluation of the possibilities of INAA, ED-XRF, ICP-AES, and AAS in the analysis of plants. J Radioanal Nucl Chem. 1998;237(1–2):25–34.
[8] García Alonso JI, Marchante-Gayón JM. New developments in food analysis by ICP- MS. 2015. doi: 10.1002/9781118654316.ch12.
[9] Baxter, MJ, Crews HM, Robb P, Strutt PR. Quality control in the multi- element analysis of foods using ICP-MS. R Soc Chem. 1997;202:95–108.
[10] "Cumin Seed" Food Data Central, United States Department of Agriculture. 2017; Retrieved 24 February 2018.

[11] Merah O, Sayed-Ahmad B, Talou T, Saad Z, Cerny M, Grivot S, et al. Biochemical composition of cumin seeds, and biorefining study. Biomolecules. 2020;10(7):1054. doi: 10.3390/biom10071054.
[12] Moawad S, El-Ghorab A, Hassan M, Nour-Eldin H, El-Gharabli M. Chemical and microbiological characterization of Egyptian cultivars for some spices and herbs commonly exported abroad. Food Nutr Sci. 2015;6:643–59. doi: 10.4236/fns.2015.67068.
[13] Peter KV. Handbook of herbs and spices. Vol. 1. Abington Abington Hall, Cambridge, England: Wood Head Publishing Limited; 2001. p. 1–332.
[14] Sekeroglu N, Meraler SA, Ozkutlu F, Kulak M. Variation of mineral composition in different parts of Mahaleb. Asian J Chem. 2012;24(12):5824–8.
[15] Özkutlu F, Kara SM, Şekeroğlu N. Determination of mineral and trace elements in some spices cultivated in Turkey. Acta Hortic. 2007;756:321–8.
[16] Wetherilt, H, Pala, M. Herbs and spices indigenous to Turkey. In: Charalambous G, Editor. In Spices, herbs and edible fungi. Developments in food science. Vol. 34. Elsevier: Amsterdam, The Netherlands; 1994. p. 285–307.
[17] Shabbir A. Rhus coriaria Linn, a plant of medicinal, nutritional and industrial importance: A review. J Anim Plant Sci. 2012;22:505–12.
[18] Kossah R, Nsabimana C, Zhao J, Chen H, Tian F, Zhang H, et al. Comparative study on the chemical composition of Syrian Sumac (*Rhus coriaria* L.) and Chinese Sumac (*Rhus typhina* L.) Fruits. Pak J Nutr. 2009;8(10):1570–4.
[19] Ozcan M. Mineral contents of same plants used as condiments in Turkey. Food Chem Nat Compd. 2004;84(3):437–40. doi: 10.1016/s0308-8146(03)00263-2.
[20] Syed SA, Al-Qahtani A, Aldughaim MS, Bari A, Kazi M. Comparative analysis of metal ions and texture of ajwa seed powder using inductively coupled plasma–Mass spectrometry. Food Anal Methods. 2021;14:1011–20. doi: 10.1007/s12161-020-01945-7.
[21] National Institute of Health Sciences, Office of Dietary Supplements. DC: National Academy Press; 2001.
[22] Ullah R, Alqahtani AS. GC-MS analysis, heavy metals, biological, and toxicological evaluation of Reseda muricata and Marrubium vulgare methanol extracts. Evid-Based Complementary Altern Med. 2022;2022:1–9.
[23] Haseeb A, Fozia, Ahmad I, Ullah H, Iqbal A, Ullah R, et al. Ecotoxicological assessment of heavy metal and its biochemical effect in fishes. BioMed Res Int. 2022;2022.
[24] Saidani M, Dhifi W, Marzouk B. Lipid evaluation of some Tunisian Citrus seeds. J Food Lipids. 2004;11(3):242–50.