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ORIGINAL ARTICLE

Determination of potentially toxic elements and health risk assessment of dried fruits

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Abstract This study aims to measure the concentrations of As, Cd, Pb, Cr, and Ni in dried fruits and examine the health effects of these trace metals in relation to people's daily dietary intake. 29 samples of dried fruits purchased at bazaar place were analyzed in terms of toxic elements, which have been reported as cancerous by the World Health Organization (WHO). Dried fruits were digested in a microwave oven with HNO_3 and H_2O_2. Metal concentrations (As, Cd, Cr, Ni, and Pb) in these samples were measured using inductively coupled plasma mass spectrometry (ICP-MS). Linearity, limit of detection (LOD), limit of quantification (LOQ), specificity/selectivity, and recovery (%) were all evaluated. The correlation coefficients of elements in this method were good ($R^2 > 0.9997$). The amount of consumption in the area was used to calculate a health risk assessment. The results showed that the samples of dried fruit, which are widely consumed in the identified area, had variable levels. All dried fruits had element concentrations that were lower than the WHO/FAO safe limit.

Keywords Dried fruit · Health risk assessment · Inductively coupled plasma mass spectrometry · Trace element determination

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Introduction

Fruit are the most commonly used to maintain health and cure ailments. These are considered a component of herb/fruits because they have beneficial impacts on human health. Fruits consumption has recently increased as a result of its favorable effects on human health. To ensure durability, fruits can be dried using air or solar heat (Jeszka-Skowron et al. 2017). It has been popular in the diet due to the components (Martín-Domingo et al. 2017).

Dried fruits have both healthy nutrients and toxic metals. Some investigations have found chemical contaminants such as hazardous metals, pesticides, and mycotoxins in these fruits throughout the production process. These contaminations are having adverse impacts on the health of humans (Aung and Jenner 2004; Fang et al. 2010). According to studies, the number of health-related problems caused by this contamination is increasing (Carne et al. 2021).

Trace elements can be harmful depending on their concentration. They have a lengthy half-life and can build up in biological networks. Because Cd, Cr, Ni, and Pb are prevalent in sediments, soil, water, and the atmosphere, they accumulate in food chains and enter the human body. In this situation, it accumulates in food chains and spreads to the human body. Cd has negative consequences such as oxidative stress and increased cancer risk (Jaishankar et al. 2014). Cr has the ability to irritate epithelial cells (Emadi et al. 2021). Ni, for example, can cause heart issues and respiratory cancer (Genchi et al. 2020). As well as causing neurological system disorders and cancer (Prakash and Verma 2021). Pb has extremely negative neurological effects (Zanjani et al. 2017). The International Agency for Research on Cancer has designated this chemical as a carcinogen (IARC 2006).

Metal intake studies that are both beneficial and hazardous to human health are required. As a result, the amount of hazardous metal content in dried fruit consumed must be used to assess risk levels in terms of food safety. As a result, the study sought to ascertain the concentrations of As, Cd, Cr, Ni, and Pb in dried fruits, as well as to assess the hazards to human health associated with consumption by determining dietary exposure levels. The tolerable daily intake (TDI), the target hazard quotient (THQ), and the hazard index (HI) were used to compare the results. Furthermore, statistical analysis was performed and the outcomes were evaluated.

Materials and methods

Chemicals and apparatus

All elements calibration standard solutions were made from 10 µg mL^{-1} of a Perkin Elmer multi element standard solution. The standards came with the necessary purity certification. Merck supplied the HNO_3 (Suprapure® grade, 65%) and H_2O_2 (30%). Ultrapure water was obtained using a Millipore®ultrapure water purification system (Bedford) at a pressure of 18.2 MΩ cm. For the examination of the trueness, the standard reference materials (1573a tomato leaves and LGC7162 strawberry leaves) were employed.

Analysis of sample preparation using microwave digestion

Each of the 29 dried fruit samples (rosehip, mulberry, date, fig, apricot, blueberry, İzmir grape, apple, plum, Damson plum, and black grape) was purchased in 500 g increments from open bazaar locations (Fig. 1). To begin, all dried fruit samples were washed in distilled water to eliminate dust and particulates (Rehan 2003). Each fruit was chopped into smaller pieces using a teflon knife and dried for 4 h in a 70 °C oven. The samples were then crushed. Matrix was created using three different dried fruit samples. Recovery trials were conducted using the produced matrix. A sample of approximately 0.5 g was transferred to the digestion vessel of a Milestone microwave digestion system. Closed-vessel microwave digestion with 6 mL HNO_3 and 2 mL H_2O_2 was used for trace element determination. The microwave oven was set to heat at 75 °C for 5 min, 220 °C for 20 min, and 70 °C for 5 min. Ultrapure water was used to dilute the samples to a final amount of 20 mL. CRM (1573a tomato leaves and LGC7162 strawberry leaves) were digested and studied in the same method (Kilic 2020).

Instrumentation

Firstly, Performance tests and tune parameters of the ICP-MS device were performed. It was aspirated with 2% HNO_3 while the ICP-MS device was operating. Before the sample analysis, the calibration tests were tested using their own solutions in the software of the device. It was determined that the obtained data were within the working ranges of all calibration parameters and performance tests. A Perkin-Elmer ELAN DRC-e model ICP-MS system equipped with a Scott Spray Chamber was used for simultaneous multi-element detection of ^{75}As, ^{111}Cd, ^{52}Cr, ^{60}Ni, and ^{208}Pb. The ICP-MS operational conditions were shown in Table 1.

Method validation

The linearity, limit of detection (LOD), limit of quantification (LOQ), and recovery of the analytical method were all assessed (Kilic et al. 2015). The regression line was used to determine the linearity of the investigated elements. The

Fig. 1 Sample bazaarplace

Table 1 ICP-MS operating conditions

Instrument	Elan DRC-e (Perkin Elmer SCIEX, Norwalk, CT, USA)
Sample introduction	Scott Spray Chamber
RF power (W)	1000
Skimmer/sampler cone	Nickel
Gas flow rates (L min^{-1})	Nebulizer gas flow: 0.89, auxiliary gas flow:1.20, plasma gas flow:19
Nebulizer	Meinhard TQ plus quartz 0.5 ml
Scanning mode	Peak hopping
Analytical masses (amu)	Standard mode ^{75}As, ^{111}Cd, ^{52} Cr, ^{60}Ni, ^{208}Pb
Number of sweeps/readings	20
Number of readings/replicates	1
Number of replicates	3
Auto sampler	CETAX ASX-520
Dwell time per AMU (ms)	50
Sample flush	Time (50), speed (±rpm)-48
Read delay	Time (15), speed (±rpm)-20

MDL was determined as three times the standard deviation based on ten analyses of the lowest calibration level standard (Kilic and Soylak 2020).

$$LOD = (3 \times \sigma)/\mathrm{S} \text{ and } LOQ = (10 \times \sigma)/\mathrm{S}$$

LOD, limit of detection; LOQ, limit of quantification (Both measured in μg L^{-1}); σ, standard deviation and S, slope (μg L^{-1}).

For method validation investigations, certified reference materials (1573a tomato leaves and LGC7162 strawberry leaves) were used. Eurachem criteria were followed for method validation (Kilic et al. 2018).

Health risk assessment

Because toxic metal contamination in fruit causes substantial health problems, there are several national and international regulations/standards in place to reduce it. In this context, the Food and Agriculture Organization (FAO)/World Health Organization (WHO) determined the tolerated weekly intake amounts of heavy metals (Joint FAO/WHO 1993). Tolerable Daily Intake (TDI) of toxic metals is calculated according to the following formula:

$$EDI = (C \times W)/BW \quad (1)$$

C, metal amount; W, daily average consumption amount (kg/day); BW, total body weight (kg) BW: 72.8 (Tuik 2018). In the calculation of health risk analysis; Health risks from consumption were evaluated according to the target hazard quotient (THQ).

$$\mathrm{ADD} = \frac{(\mathrm{C} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED})}{(\mathrm{BW} \times \mathrm{AT})} \times 10 - 3 \quad (2)$$

ADD Average daily dose (mg/kg-day), EF exposure frequency (365 day/year), ED, lifetime (70 years) exposure time, FI, average intake rate (301 g/person / day), MC is the metal concentration in the dried fruit (μg g^{-1}) and the AT average lifespan (70 years × 365 days/year), THQ target hazard quotient;

$$THQ = \frac{ADD}{RfD} \quad (3)$$

Oral RfD for As, Cd, Pb, Cr and Ni is suggested by the USEPA (2011) as 3×10^{-4} mg/kg day, 1×10^{-3} mg/kg day, 4×10^{-3} mg/kg day, 3×10^{-3} mg/kg day and 2×10^{-2} mg/kg day, respectively. THQ ≥ 1 average non-carcinogenic effects can be composed. THQ < 1 averages non-carcinogenic effects cannot be composed (Mohammadpour et al. 2022).

Statistical analysis

The Pearson's correlation between results was also calculated. The SPSS 23 statistics program was used to do statistical analysis on the data acquired from samples (SPSS Inc., Chicago, IL, USA).

Results and discussion

Method validation results

The standards were prepared from the stock standard solution at concentrations of 2, 5, 10, 25, 50, 100, and 200 μg L^{-1}. The correlation coefficient of the calibration lines for each of the observed isotopes was 0.999. This demonstrates strong linear linkages.

The calibration curves were created using the standard addition method. Three samples were combined, and the resulting mixture served as the calibration matrix for standard addition. Each element's 7-point calibration curve was used to measure the element concentrations. Standard solutions generated at concentrations of 2, 5, 10, 25, 50, 100, and 200 µg L^{-1} from 10 mg L^{-1} stock standard solution were added during calibration. The correlation coefficient of the calibration lines for all the isotopes under observation was 0.9997. Good linear relationships can be seen here. From seven replicate analyses of the lowest calibration level standard, the LOD was assessed at three times the standard deviation. The LOD ranged from 0.13 to 0.25 (µg L^{-1}). The result is displayed in Table 2. In the literature, validation studies using food samples were discovered to be comparable to this investigation (Ismail and Afify 2022).

Calculations were made to determine the specificity/selectivity of the method, accuracy, and recoveries of the spiked standards within the specified calibration range. The SRMs and the calibration standards of the three fortification levels for metals were used to perform the spiking. For accurate computations, the spiking was done on the sample matrix at the three fortification levels that correspond to the first (4 µg L^{-1}), middle (20 µg L^{-1}), and last (40 µg L^{-1}) parts of the linear range. From 97.95 to 104.69% of the losses were recovered. Tables 3 and 4 contain the mean recovery data. Similar recovery outcomes were discovered in other investigations (Kilic et al. 2015).

Table 2 Method performance parameters

Elements	LOD (µg L^{-1}) (N = 10)	LOQ (µg L^{-1}) (N = 10)	Regression equation	Correlation coefficient (R^2)
As	0.25	0.82	y = 941.9x + 255.6	0.9998
Cd	0.16	0.53	y = 1483x + 182.8	0.9999
Cr	0.18	0.60	y = 5494x + 8558	0.9997
Ni	0.13	0.42	y = 1602x + 3617	0.9997
Pb	0.17	0.56	y = 12,417x + 10,024	0.9999

Table 3 Recovery results of elements (as matrix spike)

Elements	4 (µg L^{-1}) Spiked conc./measured (µg L^{-1}) (N = 10)	Recovery ± std. deviation (N = 10)	20 (µg L^{-1}) Spiked conc./ measured (µg L^{-1}) (N = 10)	Recovery ± std. deviation (N = 10)	40 (µg L^{-1}) Spiked conc./ measured (µg L^{-1}) (N = 10)	Recovery ± std. deviation (N = 10)	∑ RSD%
As	3.93 ± 0.08	97.95 ± 0.08	20.03 ± 0.32	100.17 ± 0.32	39.21 ± 0.41	98.01 ± 1.02	0.27
Cd	4.19 ± 0.05	104.69 ± 1.32	19.76 ± 0.39	98,78 ± 0,39	40.01 ± 0.38	100.03 ± 0.95	0.27
Cr	3.92 ± 0.06	98.05 ± 1.51	19.97 ± 0.11	99,87 ± 0,56	39.83 ± 0.24	99.58 ± 0.61	0.90
Ni	3.94 ± 0.04	98.55 ± 1.05	19.62 ± 0.38	98,12 ± 0,38	39.79 ± 0.50	99.47 ± 1.26	0.31
Pb	4.04 ± 0.06	101.02 ± 1.41	20.26 ± 0.27	101,28 ± 0,80	40.68 ± 0.17	101.69 ± 0.42	0.49

Table 4 Percent recoveries of elements in SRMs

Elements	Certified (mg kg^{-1})	Measured (mg kg^{-1})	Recovery (%)
LGC7162 strawbery leaves			
As	0.28	0.28 ± 0.07	100.61 ± 0.36
Pb	1.80	1.81 ± 0.40	100.59 ± 0.92
Cd	0.17	0.17 ± 0.04	100.38 ± 0.97
Ni	2.60	2.59 ± 0.70	99.87 ± 0.11
Cr	2.15	2.14 ± 0.34	99.89 ± 0.09
1573a SRM tomato leaves			
As	0.1126	0.1112 ± 0.0024	98.83 ± 1.43
Cd	1.517	1.516 ± 0.027	99.96 ± 0.49
Ni	1.582	1.578 ± 0.041	99.81 ± 0.16
Cr	1.989	1.989 ± 0.034	100.05 ± 0.19

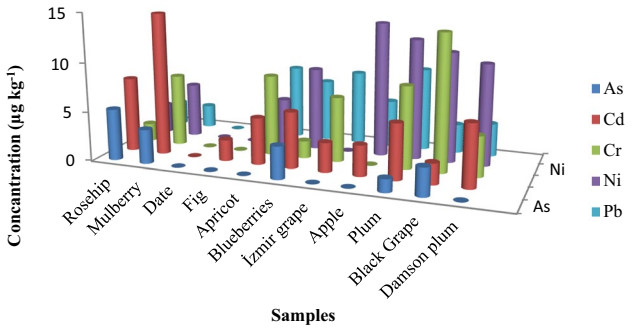

Fig. 2 Mean element concentration in samples

Elemental analysis of samples

Figure 2 summarizes the metal content of dried fruits ingested. According to the results, As, Cd, Cr, Ni, and Pb were found in the samples following microwave digestion using ICP-MS. Concentrations of As, Cd, Cr, Ni, and Pb ranged from < LOD to 5.22 µg kg^{-1}, < LOD—14.46 µg kg^{-1}, < LOD—8.39 µg kg^{-1}, < LOD—13.59 µg kg^{-1} and < LOD—8.42 µg kg^{-1}, respectively in all samples. The average metal concentrations was found to be decreased in the following order for dried rosehip: Cd > As > Ni > Pb > Cr; dried mulberry: Pb > As > Ni > Cr > Cd; dried apricot: Cr > Pb > Ni > Cd > As; dried blueberries: Cr > As > Cd > Pb > Ni; dried İzmir grapes: Pb > Cr > Cd > As = Ni; dried plums: As > Cd > Cr > Pb > Ni; dried black grape: Cd > As > Pb > Ni > Cr; dried damson plum: As > Pb > Cr > Cd > Ni. While no elements were detected in dried dates, only cadmium was detected in dried figs. The presence of Pb and Cd elements in this study can be attributed to the urban atmosphere's influence on the location where we collected our samples. After converting the log-normal distribution to the normal distribution, the log of the data is obtained and the Pearson correlation is applied to the data in order to control the data quality. When measuring from nominal continuous data, Pearson correlation is the most appropriate (Kiernan 2014). Strong correlation coefficients between several elements (Pb and Cd, Pb and Ni) were observed ($p < 0.05$). Anthropogenic substances, like As, have correlation coefficient values higher than 0.5. These high r values are typically anticipated when the analysis's findings are accurate.

The literature has reported Cr values in dried fruit samples ranging from 4.76 to 28.90 µg kg^{-1} (Saracoglu et al. 2009). Various dried fruits have been found to contain Ni values ranging from 0.6 to 9.4 µg g^{-1} (Duran et al. 2008). Dried fruit has been found to contain Cd amounts ranging from 0.722 to 6.61 µg g^{-1}. According to reports, the Pb contents in dried fruits range from 1.001 to 10.002 µg g^{-1} (Manzoor et al. 2013).

Turkish Food Codex and European communities agree that 0.05 µg g^{-1} of Cd is the maximum concentration allowed in dried fruits (Commission of the European Communities 2001; Anonymous 2002). The World Health Organization (1996) states that the maximum amount of Pb that is permitted in food is 10 µg g^{-1}. Additionally, the Official Gazette of the Republic of Serbia Nos. 5/92, 11/92, 32/2002, 25/2010, and 28/201 set a 3.0 µg g^{-1} maximum Pb content allowed in dried fruits (The Official Gazette of the Republic of Serbia 2011). Cr would concur with the 0.12 µg g^{-1} dosage that the US Food and Drug Administration (FDA) has suggested (Pereira et al. 2014). In our investigation, all dried fruits had element amounts below the WHO/FAO permissible range.

Health risk assessment results

The results showed that the samples of dried fruit, which are widely consumed in the identified area, had variable levels. The elements concentrations discovered and the rates of dried fruit consumption were used to determine the risk to the population's health. The THQ results revealed that all of the tested samples had values less than one. This shows that they did not endanger the local community's health.

Conclusion

The levels of trace metals (As, Cr, Ni, Cd, and Pb) in imported dried fruits (apple, plum, Damson plum, black grape, rosehip, mulberry, date, fig, apricot, blueberry, and İzmir grape) sold in the Antalya local bazaar were measured using ICP-MS. According to the findings, dried fruit samples, which are popular in the research area, have variable levels of various elements. The THQ results, on the other hand, revealed that because the levels were less than one, the local population was not at risk. The amounts of dangerous elements (Pb, Cd, and Cr) in the dried fruits tested were found to be below the allowable limits set by many health organizations. The metal concentrations obtained in this analysis were found to be consistent with those reported in comparable investigations. Additional research in this subject is also recommended from the aspect of public health in order to analyze the concentrations of the elements in fruits, cereals, processed foods, and other food products.

Authors contributions SK: Corresponding Author, methodology, investigation, validation, visualization, supervision, writing-original draft, writing-review and editing.

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Data availability All data generated during this study are included in the article.

Declarations

Conflict of interest The author declares that she has no conflict of interest.

Consent for publication Author has given their full consent to publication.

Ethical approval Ethics approval is not required for this research that not use any human or animal.

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