

Evaluation of various digestion procedures for trace element contents of some food materials

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Abstract

The levels of trace elements in different types of food material consumed in Turkey were determined by flame and graphite furnace atomic absorption spectrometry. Food samples were digested with dry ashing, wet ashing and microwave digestion procedures in this study. The microwave digestion procedure was chosen for the digestion of all the food samples because it required shorter time and made higher recovery (specially for Se). Fe, Cu, Mn, Zn, Al and Se were determined by flame and graphite furnace atomic absorption spectrometry, respectively. Relative standard deviations (RSD) were found below 10%. The accuracy of the procedure was confirmed by certified reference materials. Moreover, this procedure was easier to use when compared with dry and wet digestions.

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1. Introduction

Advances in technology and an increase in population have led to notable improvement in production methods. However, serious environmental problems have occurred as a result of mass production and rapid developments in technology. Among these problems, environmental pollution has posed a growing, long-term threat to human health.

Human beings are encouraged to consume more food materials such as vegetables and fruits, which are good sources of vitamins and minerals beneficial to human health [1]. They, on the other hand, contain both essential and toxic metals over a wide range of concentration [2–8].

Trace amounts of some metals such as manganese, iron, copper, zinc, cobalt and selenium are essential micro-nutrients and have a variety of biochemical functions in all living organisms. While these elements are essential, they can be toxic when taken in excess. However, some elements like lead, cadmium and arsenic are non-essential metals as they are toxic, even in

traces [9]. Metals such as aluminum, cadmium and lead are found throughout the environment and are present virtually in all food at the extremely low levels [10].

It is well known that foods take up trace metals from soils, fertilizers, air, industrial process, transportation and package materials. Heavy metals are mobile and easily taken up by plants in the environment [11,12]. Since heavy metals are mobile and easily absorbed by plants in the environment, they are transmitted to the human body through nourishment.

The steady increase in food contamination necessitates the analysis and monitoring of toxic species that could become a serious potential hazard if not controlled. A lot of researches on the type, amount, source and precaution of the toxic metal in contaminated foods have been carried out at various countries in recent years.

Onianwa et al. [13] have been determined the concentrations of some trace metals in Nigeria foods. Concentrations of Hg, Pb and Cd in canned Tuna fish were investigated by Voegborlo et al. [14]. Doner and Akman [15] examined the sample preparation procedure for the determination of iron and zinc in bulgur (boiled pounded) wheat by graphite furnace atomic absorption spectrometry. Ranau et al. [16] investigated the content of aluminum in fish smeared with aluminum folio. Trace element determi-

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nations of the Spanish tea were proposed by Fernandez et al. [17]. Racz et al. [18] examined contents of trace metal in culture mushrooms. Tuzen [19] determined the concentrations of heavy metals in some fish samples.

Many analytical methods including atomic absorption spectrometry used for trace element determination in food materials require the decomposition of the sample [20]. The wet and dry ashing and microwave digestion methods have been used for the sample decomposition prior to the determination of trace elements by atomic absorption spectrometry [21–23].

The purpose of the present study was to determine the concentration levels of some elements at trace levels in different types of foods consumed in Turkey. The performances of digestion procedures, namely, dry ashing, wet ashing and microwave digestion were compared in this study. Various acid mixtures have been tested for digestion of food samples. The reliability of the method for estimation of trace elements in samples has been checked by analyzing certified reference material. Optimized method was applied to various food samples.

2. Materials and method

2.1. Apparatus

A Perkin-Elmer Analyst 700 model atomic absorption spectrometer equipped with a deuterium background corrector was used for determination of trace elements. Measurements of Fe, Cu, Mn and Zn were carried out in an air/acetylene flame. The concentrations of Se and Al were determined with graphite furnace atomic absorption spectrometer. Argon as inert gas was used in studies with graphite furnace. Certified reference materials were digested in a Mileston Ethos D model closed system microwave oven (maximum temperature 300 °C, maximum pressure 1450 psi). Teflon reaction vessels were used in all digestion procedures. The reaction vessels were cleaned by using 5 mL of concentrated nitric acid before each digestion.

2.2. Reagents

Analytical reagent-grade chemicals were employed in the preparation of all solutions. Doubly distilled deionised water (Milli-Q Millipore 18.2 M Ω /cm) was used in all experiments. HCl, HNO₃ and H₂O₂ were of suprapure quality (E. Merck). All the plastic and glassware were cleaned by soaking in dilute nitric acid (1+9) and were rinsed with distilled water prior to use. The standard solutions of analytes for calibration procedure were produced by diluting a stock solution of 1000 mg/L of the investigated element supplied by Sigma. Ten microliters of 0.015 mg Pd and 0.010 mg Mg(NO₃)₂ as matrix modifier was added to 20 μ L sample in the determination of Se. Twenty microliters sample and 5 μ L Mg(NO₃)₂ were used in the determination of Al.

2.3. Sample collection

Some food products (tomato sauce, rice, chickpea, bulgur, walnut, hazelnut, white seed, black seed, pumpkin seed, garlic,

pistachio, biscuit, mushroom, beef, chicken meat, milk, red wine and beer) purchased from the local markets in Tokat, Turkey were investigated in this study. Solid food samples were dried at a temperature of 105 °C for 24 h. The dried samples were homogenized using an agate homogenizer and stored in polyethylene bottles until analysis.

2.4. Digestion procedures

2.4.1. Dry ashing

The reliability of the method for the estimation of trace elements in samples was checked by analysing certified reference material (CRM). For digestion with dry ashing, 0.2 g from certified reference material was used. One gram from samples for digestion with dry ash of real samples was used. Samples were dry-ashed in furnace at a temperature of 450–500 °C for 16 h. The ashed sample was then treated with 1 mL of concentrated nitric acid to whiten the ash, and this mixture was ashed again for 6 h. Then, the residue was dissolved in 1–2 mL of concentrated HNO₃ and filtered through blue band filter paper. The sample was diluted to 10 mL with distilled water.

2.4.2. Wet ashing

0.2 g from certified reference material for digestion with wet ashing procedure was used. For digestion with wet ashing, 1 g from real samples was used. Wet digestion of samples was performed by using mixtures of different acids, namely, HNO₃–H₂O₂ (6:2), HNO₃–HCl (3:1), HNO₃–HCl (1:3), HNO₃–H₂SO₄ (6:2). Sixteen millilitres of each mixture was used for a 1.0 g sample. Each mixture was heated up to 130 °C for 4 h on the hot plate. Then, acid mixtures were added again. After cooling, 5 mL of distilled water was added to the sample and mixed. The residue was filtered through blue band filter paper. Then the sample was diluted to 10 mL with distilled water. The blank digestions were also carried out in the same way.

2.4.3. Microwave digestion

For microwave digestion, the certified reference materials and food samples were accurately weighed out 0.2 and 1 g, respectively. The samples were transferred to 100 mL Teflon vessels. Samples were digested by making use of HNO₃/H₂O₂ (6:2), HNO₃/HCl (3:1), HNO₃/HCl (1:3), HNO₃/H₂SO₄ (6:2) acid mixtures in a microwave digestion system and diluted to 10 mL with double deionized water (Milli-Q Millipore 18.2 M Ω cm⁻¹ conductivity). Blank digest was carried out in the same way. Digestion conditions for the microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min.

3. Results and discussion

Both the detection limit (based on three times the standard deviations of the reagent blank) and the characteristic masses (based on 0.0044 absorbance) were calculated for the investigated analyte ions. The detection limit values of the investigated elements for flame AAS were found to be 0.013 mg/L for Cu,

Table 1
Comparison of digestion conditions of Cu, Zn and Mn using NIST SRM 1515 Apple Leaves certified reference material, $N=4$

Elements	Certified value (mg/kg)	Methods	Solvent	Found value (mg/kg) ^a	Recovery (%)
Cu	5.64	Microwave	HNO ₃ /H ₂ O ₂ : 6:2	5.53 ± 0.32	98
			HNO ₃ /HCl: 6:2	5.49 ± 0.40	97
			HNO ₃ /HCl: 2:6	5.45 ± 0.30	97
			HNO ₃ /H ₂ SO ₄ : 6:2	5.20 ± 0.48	92
		Wet ashing	HNO ₃ /H ₂ O ₂ : 6:2	5.35 ± 0.50	95
			Dry ashing	5.30 ± 0.49	94
Zn	12.5	Microwave	HNO ₃ /H ₂ O ₂ : 6:2	12.7 ± 0.8	102
			HNO ₃ /HCl: 6:2	12.1 ± 0.9	97
			HNO ₃ /HCl: 2:6	11.9 ± 0.7	95
			HNO ₃ /H ₂ SO ₄ : 6:2	11.7 ± 0.9	94
		Wet ashing	HNO ₃ /H ₂ O ₂ : 6:2	11.9 ± 1.1	95
			Dry ashing	11.5 ± 0.9	92
Mn	54	Microwave	HNO ₃ /H ₂ O ₂ : 6:2	52.1 ± 3.2	96
			HNO ₃ /HCl: 6:2	52.9 ± 4.8	98
			HNO ₃ /HCl: 2:6	51.8 ± 4.4	96
			HNO ₃ /H ₂ SO ₄ : 6:2	51.9 ± 4.1	96
		Wet ashing	HNO ₃ /H ₂ O ₂ : 6:2	51.4 ± 4.9	95
			Dry ashing	50.6 ± 4.7	94

^a Mean ± standard deviation.

0.019 mg/L for Zn, 0.011 mg/L for Fe, and 0.010 mg/L for Mn. Se and Al were below detection limit of flame AAS. So, these elements were determined in graphite furnace AAS. The characteristic mass values were Al: 17 pg, and Se: 22 pg in graphite furnace AAS. In the precision test, the average RSD % for all analytes was in the range of 1–10%.

Performances of each digestion procedure (dry ashing, wet ashing and microwave digestion) prior to the determination with AAS of some trace elements in food samples were compared in this study. Different types of acid mixtures, namely, HNO₃/H₂O₂: 6:2, HNO₃/HCl: 6:2, HNO₃/HCl: 2:6, HNO₃/H₂SO₄: 6:2 were used for digestion of samples. The correctness of results was verified by analyzing of certified ref-

erence materials. The optimized method was applied to some food materials. The concentrations of Cu, Zn, Mn and Fe were determined by flame atomic absorption spectrometry, the concentrations of Se and Al were determined by graphite furnace atomic absorption spectrometry after the proper digestion procedure for some food samples was followed.

Both the analysis and the digestion of NIST SRM 1515 Apple Leaves certified reference material, USA were employed to check the correctness of digestion methods. The certified and observed values for the SRM were given in Tables 1 and 2. As can be seen in Tables 1 and 2, quantitative recoveries for Cu, Zn, Mn and Fe were obtained whichever of the three digestion methods was used. When the microwave digestion method was adopted,

Table 2
Comparison of digestion conditions of Fe, Se and Al using NIST SRM 1515 Apple Leaves certified reference material, $N=4$

Elements	Certified value (mg/kg)	Methods	Solvent	Found value (mg/kg) ^a	Recovery (%)
Fe	83	Microwave	HNO ₃ /H ₂ O ₂ : 6:2	81.5 ± 3.7	98
			HNO ₃ /HCl: 6:2	80.9 ± 6.3	97
			HNO ₃ /HCl: 2:6	79.5 ± 5.5	96
			HNO ₃ /H ₂ SO ₄ : 6:2	78.3 ± 7.1	94
		Wet ashing	HNO ₃ /H ₂ O ₂ : 6:2	78.9 ± 6.4	95
			Dry ashing	77.5 ± 6.8	93
Se	0.05	Microwave	HNO ₃ /H ₂ O ₂ : 6:2	0.048 ± 0.004	96
			HNO ₃ /HCl: 6:2	0.045 ± 0.003	90
			HNO ₃ /HCl: 2:6	0.046 ± 0.004	92
			HNO ₃ /H ₂ SO ₄ : 6:2	0.041 ± 0.004	82
		Wet ashing	HNO ₃ /H ₂ O ₂ : 6:2	0.030 ± 0.003	60
			Dry ashing	0.011 ± 0.001	22
Al	286	Microwave	HNO ₃ /H ₂ O ₂ : 6:2	280 ± 15	98
			HNO ₃ /HCl: 6:2	275 ± 20	96
			HNO ₃ /HCl: 2:6	270 ± 19	94
			HNO ₃ /H ₂ SO ₄ : 6:2	252 ± 24	88
		Wet ashing	HNO ₃ /H ₂ O ₂ : 6:2	265 ± 21	93
			Dry ashing	247 ± 25	86

^a Mean ± standard deviation.

Table 3
Comparison of digestion conditions for trace metals investigated using NIST SRM 1573a Tomato Leaves certified reference material, $N=4$

Elements	Certified value (mg/kg)	Methods	Found value (mg/kg) ^a	Recovery (%)
Cu	4.7	Microwave	4.65 ± 0.20	99
		Wet ashing	4.47 ± 0.42	95
		Dry ashing	4.23 ± 0.38	90
Zn	30.9	Microwave	29.9 ± 1.6	97
		Wet ashing	29.4 ± 2.5	95
		Dry ashing	29.7 ± 2.8	96
Mn	246	Microwave	238.6 ± 10.3	97
		Wet ashing	226.3 ± 17.5	92
		Dry ashing	223.9 ± 20.4	91
Fe	368	Microwave	360.6 ± 20.3	98
		Wet ashing	353.3 ± 15.2	96
		Dry ashing	349.6 ± 26.7	95
Se	0.054	Microwave	0.052 ± 0.003	96
		Wet ashing	0.038 ± 0.003	70
		Dry ashing	0.016 ± 0.002	30
Al	598	Microwave	574.1 ± 32.5	96
		Wet ashing	550.2 ± 43.9	92
		Dry ashing	532.2 ± 38.4	89

^a Mean ± standard deviation.

recovery values for Se were quantitative: for wet ashing, only 60% of the recovery, and for dry ashing, only 22% of the recovery was obtained. The underlying reason for getting these results might be that the element of Se is volatile. While the recovery value of Al was 86% when dry ashing procedure was employed, the recoveries of Al were quantitative when microwave digestion and wet ashing procedures were used.

The effects of different acid mixtures used for the digestion of food samples were investigated. For that purpose, HNO₃/H₂O₂: 6:2, HNO₃/HCl: 6:2, HNO₃/HCl: 2:6, HNO₃/H₂SO₄: 6:2 mixtures were used. As can be seen in Tables 1 and 2, Cu, Zn, Mn and Fe were quantitatively recovered whichever mixture was used. The quantitative recoveries for Al were obtained with first three acid mixtures. The recovery values of Se were found to be quantitative as a result of using HNO₃/H₂O₂ (6:2) and HNO₃/HCl (2:6) mixtures. Very good recovery values for investigated elements in this study were obtained with HNO₃/H₂O₂ (6:2) mixture. Therefore, HNO₃/H₂O₂ (6:2) mixture was used in microwave digestion and wet ashing procedure in all samples.

The accuracy of digestion procedures was confirmed by NIST SRM 1573a Tomato Leaves certified reference materials, USA. Comparison of found values with certified values pointed out that the recoveries obtained as a result of applying any of the three digestion procedures for Cu, Zn, Mn and Fe were quantitative (Table 3). As a consequence of using microwave and wet ashing procedures for Al, found value for Se under a microwave procedure was perfectly consistent with the certified values. These experimental results seemed to be in coherence with data in Tables 1 and 2.

The recoveries obtained by using microwave and wet ashing procedures in the digestion of NIST SRM 8418 Wheat Gluten, Canada and NIST SRM 1577b Bovine Liver certified reference

Table 4
Comparison of digestion conditions for trace metals using NIST SRM 8418 Wheat Gluten certified reference material, $N=4$

Elements	Certified value (mg/kg)	Methods	Found value (mg/kg) ^a	Recovery (%)
Cu	5.94	Microwave	5.88 ± 0.26	99
		Wet ashing	5.41 ± 0.44	91
Zn	53.8	Microwave	54.3 ± 0.31	101
		Wet ashing	51.1 ± 0.48	95
Mn	14.3	Microwave	13.9 ± 0.9	97
		Wet ashing	13.6 ± 1.1	95
Fe	54.3	Microwave	53.2 ± 4.2	98
		Wet ashing	50.5 ± 4.9	93
Se	2.58	Microwave	2.45 ± 0.20	95
		Wet ashing	1.68 ± 0.15	65
Al	10.8	Microwave	10.4 ± 0.9	96
		Wet ashing	10.1 ± 0.9	94

^a Mean ± standard deviation.

materials were given in Tables 4 and 5, respectively. The found recovery values were quantitative except for wet ashing procedure for Se. The result that Se was quantitative only under a microwave procedure was similar to data in Tables 1–3.

The relative standard deviations were less than 10% for all the investigated elements. If the analyzed concentration levels of the most common matrix constituents of certified reference materials and the accuracy of the presented methods are considered together, it can be concluded that the proposed method is free from interferences of various constituents.

Performances of dry ashing, wet ashing and microwave digestion procedures in food samples were compared. For that purpose, a tomato sauce sample was used. The results were given in Table 6. The slightly high trace metal levels were obtained when the microwave oven was used. The microwave digestion procedure was chosen for the digestion of all the food samples because it required shorter time and made higher recovery (spe-

Table 5
Comparison of digestion conditions of trace metals using NIST SRM 1577b Bovine Liver certified reference material, $N=4$

Elements	Certified value (mg/kg)	Methods	Found value (mg/kg) ^a	Recovery (%)
Cu	160	Microwave	158.4 ± 9.5	99
		Wet ashing	152.1 ± 13.4	95
Zn	127	Microwave	128.5 ± 10.4	102
		Wet ashing	121.9 ± 11.7	96
Mn	10.5	Microwave	10.2 ± 0.9	97
		Wet ashing	9.8 ± 0.8	93
Fe	184	Microwave	176.6 ± 12.6	96
		Wet ashing	169.3 ± 15.3	92
Se	0.73	Microwave	0.70 ± 0.06	96
		Wet ashing	0.55 ± 0.05	75
Al	3	Microwave	2.94 ± 0.15	98
		Wet ashing	2.85 ± 0.27	95

^a Mean ± standard deviation.

Table 6

Trace metal contents with dry ashing, wet ashing and microwave methods in tomato sauce sample (mean \pm standard deviation), $N=4$

Methods	Concentrations ($\mu\text{g/g}$)					
	Cu	Zn	Mn	Fe	Se	Al
Microwave	6.81 \pm 0.43	5.84 \pm 0.32	6.70 \pm 0.51	33.6 \pm 2.2	0.331 \pm 0.016	0.39 \pm 0.02
Wet ashing	6.66 \pm 0.50	5.62 \pm 0.47	6.42 \pm 0.59	31.9 \pm 2.8	0.237 \pm 0.020	0.34 \pm 0.03
Dry ashing	6.31 \pm 0.61	5.20 \pm 0.50	5.97 \pm 0.60	30.8 \pm 3.2	0.083 \pm 0.010	0.30 \pm 0.03

Table 7

Contents of trace metal of some solid food samples (mean \pm standard deviation), $N=3$

Samples	Concentrations ($\mu\text{g/g}$)					
	Cu	Zn	Mn	Fe	Se	Al
Tomato sauce 1	6.81 \pm 0.43	5.84 \pm 0.32	6.70 \pm 0.51	33.6 \pm 2.2	0.331 \pm 0.016	0.39 \pm 0.02
Tomato sauce 2	10.1 \pm 0.9	16.5 \pm 1.2	8.16 \pm 0.65	41.6 \pm 3.7	0.801 \pm 0.060	1.05 \pm 0.10
Rice	1.97 \pm 0.14	1.57 \pm 0.15	6.15 \pm 0.57	5.06 \pm 0.38	0.092 \pm 0.005	0.29 \pm 0.03
Chickpea	8.43 \pm 0.65	8.70 \pm 0.67	17.9 \pm 1.5	50.2 \pm 3.8	0.095 \pm 0.006	0.43 \pm 0.03
Bulgur	3.82 \pm 0.20	10.9 \pm 0.8	12.7 \pm 1.1	11.8 \pm 0.9	0.082 \pm 0.007	0.42 \pm 0.04
Walnut	7.97 \pm 0.63	10.9 \pm 0.9	27.1 \pm 2.5	32.7 \pm 1.9	0.028 \pm 0.002	0.41 \pm 0.03
Hazelnut	18.8 \pm 1.5	9.55 \pm 0.73	38.1 \pm 2.9	27.2 \pm 2.1	0.054 \pm 0.004	0.12 \pm 0.02
White seed	21.3 \pm 1.1	4.44 \pm 0.32	14.3 \pm 1.2	50.2 \pm 3.7	0.106 \pm 0.010	0.27 \pm 0.03
Black seed	21.1 \pm 1.7	10.7 \pm 0.8	13.4 \pm 1.2	45.9 \pm 3.5	0.132 \pm 0.010	0.08 \pm 0.005
Pumpkin seed	15.6 \pm 1.3	5.06 \pm 0.37	32.6 \pm 2.6	50.8 \pm 4.7	0.370 \pm 0.021	0.06 \pm 0.005
Garlic	4.05 \pm 0.35	13.8 \pm 1.2	6.15 \pm 0.52	12.7 \pm 1.1	0.151 \pm 0.012	0.34 \pm 0.03
Pistachio	11.2 \pm 1.1	5.40 \pm 0.36	9.07 \pm 0.54	27.6 \pm 2.3	0.103 \pm 0.010	0.08 \pm 0.006
Biscuit	1.05 \pm 0.10	1.62 \pm 0.14	3.59 \pm 0.28	7.62 \pm 0.56	0.072 \pm 0.005	1.54 \pm 0.12
Mushroom	27.8 \pm 2.5	5.06 \pm 0.43	9.43 \pm 0.75	310.1 \pm 17.8	0.241 \pm 0.018	1.30 \pm 0.10
Beef	1.74 \pm 0.14	35.9 \pm 2.8	BLD	46.7 \pm 3.9	0.381 \pm 0.025	1.19 \pm 0.10
Chicken meat	BLD	11.5 \pm 0.9	BLD	8.04 \pm 0.73	0.188 \pm 0.014	1.51 \pm 0.12

BLD: below the detection limit.

cially for Se). Moreover, this procedure was easier to use when compared with dry and wet digestions.

The contents of Fe, Cu, Mn, Zn, Se and Al in some food samples were determined by AAS after digested by closed microwave system. Concentrations of investigated trace metals in some solid food and liquid food samples were given in Tables 7 and 8, respectively. Samples were taken from the local markets in Tokat, Turkey.

The FAO/WHO has set a limit for heavy metal intake depending on body weight. For an average adult (60 kg body weight), the provisional tolerable daily intake (PTDI) for iron, copper and zinc are 48, 3 and 60 mg, respectively [24].

Copper is known to be vital and toxic for many biological systems. It may enter the food materials from soil through mineralization by crops, food processing or environmental contamination. For instance, in the application of agricultural

practices, copper-based pesticides are in common use in farms in some countries [25]. The lowest and highest contents of copper in solid food samples were found as 1.05 $\mu\text{g/g}$ for biscuit and 27.8 $\mu\text{g/g}$ for mushroom, respectively. The mean copper content of the biscuit samples in another of our studies was found as 1.9 $\mu\text{g/g}$ [20]. Minimum and maximum values of copper in mushroom samples in a study in Turkey were found as 13.4 and 50.6 $\mu\text{g/g}$ [26]. Copper values in vegetable samples were reported to be in the ranges: 2.5–16 $\mu\text{g/g}$ [3]. The copper content in rice flour was found as 1.42 $\mu\text{g/g}$ by Lemos et al. [27]. Copper values in mushroom samples were reported to be 10.0–14.0 and 21.1–42.6 $\mu\text{g/g}$, respectively, in the literature [28,29]. Copper contents found in this study were consistent with those reported in the literature. Copper values in liquid food samples were found below the detection limit of the flame AAS.

Table 8

Contents of trace metal of some liquid food samples (mean \pm standard deviation), $N=3$

Samples	Concentrations ($\mu\text{g/mL}$)					
	Cu	Zn	Mn	Fe	Se	Al
Milk 1	BLD	2.63 \pm 0.16	BLD	BLD	0.070 \pm 0.005	0.38 \pm 0.03
Milk 2	BLD	2.46 \pm 0.23	BLD	BLD	0.082 \pm 0.007	0.35 \pm 0.04
Red wine	BLD	10.1 \pm 0.9	0.86 \pm 0.07	5.49 \pm 0.44	0.030 \pm 0.002	0.42 \pm 0.03
Beer	BLD	2.50 \pm 0.15	BLD	BLD	0.026 \pm 0.002	0.23 \pm 0.02

BLD: below the detection limit.

Zinc is known to be involved in most metabolic pathways in humans. Zinc deficiency can lead to loss of appetite, growth retardation, skin changes and immunological abnormalities. The lowest and highest levels of zinc were found as 1.57 $\mu\text{g/g}$ for rice sample and 35.9 $\mu\text{g/g}$ for beef sample, respectively. The highest Zn level in liquid food samples was found as 10.1 $\mu\text{g/mL}$ for red wine. The values for Zn in milk samples were found as 2.46–2.63 $\mu\text{g/mL}$. Zinc values in milk samples have been reported to be in the ranges: 2.38–4.16 $\mu\text{g/mL}$ [30]. Our results were consistent with values in the related literature [30]. The lowest and highest levels of zinc in vegetable samples in one study in Tanzania were found as 14.8 $\mu\text{g/g}$ for lettuce sample and 49.3 $\mu\text{g/g}$ for cabbage sample, respectively [3]. The maximum tolerable daily intake of Zn is 0.3–1 mg/kg. Our values for Zn for all the samples were below WHO's values [31].

The concentration of manganese was found in the range of 3.59–38.1 $\mu\text{g/g}$. The mean concentration of Mn was 14.67 $\mu\text{g/g}$. Mn concentrations in walnut, hazelnut and pumpkin seed samples were higher than average manganese level. Mn was determined as 0.86 $\mu\text{g/mL}$ only in red wine among the investigated liquid food samples. The content of Mn was found to be in the range of 3.27–38.9 $\mu\text{g/g}$ in flour samples [32]. The Institute of Medicine recommends that intake of manganese from food, water and dietary supplements should not exceed the tolerable daily upper limit of 11 mg/day [33]. The intake of Mn in our investigated samples is well below the tolerable daily upper limit of 11 mg/day.

The iron level in solid food samples varied from 5.06 $\mu\text{g/g}$ in rice to 310.1 $\mu\text{g/g}$ in mushroom samples. Iron values in mushroom samples have been reported to be in the ranges: 31.3–1190 $\mu\text{g/g}$ [34]. The content of iron was found as 5.49 $\mu\text{g/mL}$ in the red wine sample. The iron content of the wine sample in a study in Nigeria was found as 5.53 ppm [13]. The iron content of wine sample found in our study was consistent with the one mentioned in the literature. It is well known that adequate iron in a diet is very important for decreasing the incidence of anemia. Iron deficiency occurs when the demand for iron is high, e.g., in growth, high menstrual loss, and pregnancy, and the intake is quantitatively inadequate or contains elements that render the iron absorption [35]. Poor bioavailability is considered to be an important factor leading to iron deficiency in many countries.

Selenium is recognized as an essential micronutrient in animal and humans. Moreover, it plays important biological roles as antioxidant, as a regulator of thyroid hormone metabolism or as anti-carcinogenic agent. However, it has been pointed out that the selenium concentrations in the range 2–8 mg/g in foods are harmful [36]. The lowest and highest levels of selenium were found to be 0.028 $\mu\text{g/g}$ for walnut and 0.801 $\mu\text{g/g}$ for tomato sauce 2 sample, respectively. The concentration of selenium in liquid samples was found in the range of 0.026–0.082 $\mu\text{g/mL}$. Selenium values in garlic samples in a study in Turkey have been reported to be in the ranges: 365–485 ng/g [37]. Se content of our garlic sample was determined as 151 ng/g. This value seemed to be lower than the value mentioned in the literature. Daily intake of selenium in Turkey has been reported as 30 $\mu\text{g/day}$ [38]. However, selenium requirement of adults

is calculated to be 70 and 55 $\mu\text{g/day}$ for males and females, respectively [39].

Aluminum is sufficiently widespread in nature, air, water, and plants; consequently in all the food chain [40]. The main sources of aluminum for the human organism are foods and drinking water. Aluminum is present in food naturally, or it is added as food additives, or Al is used in food preparation and storage [41]. A tolerable daily intake (TDI) for aluminum of 1 mg per kilogram of body weight per day has been established by an international committee of experts under the auspices of the World Health Organization (WHO) and the Food and Agricultural Organization of the United Nations [42]. Even at the highest level reported, intake of aluminum was well below the tolerable daily intake. The lowest aluminum level was found as 0.08 $\mu\text{g/g}$ for black seed and pistachio samples, whereas the highest Al level was 1.54 $\mu\text{g/g}$ in the biscuits. The mean concentration of Al in investigated liquid samples was 34.5 $\mu\text{g/mL}$.

4. Conclusion

The microwave digestion procedure was preferred to dry and wet digestion procedures because of three reasons: It yielded more accurate results, it required shorter time and it achieved better recovery in the samples. Moreover, the obtained analytical parameters make this method more suitable for the determination of Cu, Mn, Fe, Zn, Se and Al in various food samples. Microwave digestion method is necessary for digestion of volatile elements such as selenium. The results obtained for trace metals in analyzed food samples were acceptable to human consumption at nutritional and toxic levels.

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