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Investigation of the levels of some element in edible oil samples produced in Turkey by atomic absorption spectrometry

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ABSTRACT

The element contents (Fe, Mn, Zn, Cu, Pb, Co, Cd, Na, K, Ca and Mg) in edible oils (olive oil, hazelnut oil, sunflower oil, margarine, butter and corn oil) from Turkey were determined using atomic absorption spectrometry after microwave digestion. The concentrations of trace element in the samples were found to be 291.0–52.0, 1.64–0.04, 3.08–1.03, 0.71–0.05, 0.03–0.01, 1.30–0.50, 84.0–0.90, 50.1–1.30, 174.2–20.8 and 20.8–0.60 μ g/g for iron, manganese, zinc, copper, lead, cobalt, sodium, potassium, calcium, and magnesium, respectively. Cadmium was found to be 4.57–0.09 μ g/kg. The high heavy metal and minerals accumulation levels in the samples were found in olive oil for Cu, Pb, Co, margarine for Fe, K, corn oil for Zn, Mn, butter for Na, Mg, sunflower oil for Ca and hazelnut oil for Cd, respectively.

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1. Introduction

Edible oils are very important food for word. The human body uses oils and fats in the diet for three purposes, as an energy source, as a structural component and to make powerful biological regulators. Oils and fats also play an important role in metabolic reactions in the human body [1].

Vegetable oils are beneficial and popular due to their cholesterol-lowering effect. In contrast to animal fats, which are predominantly saturated and hence do not react readily with other chemicals, especially oxygen, unsaturated vegetable oils are more reactive [2,3]. Vegetable oils are essential in global nutrition depending on the regional conditions, a variety of oils are produced in different qualities [4].

The quality of edible oils is directly related to the concentration of trace metals [5]. Levels of trace metals like Fe, Cu, Ca, Mg, Co, Ni and Mn are known to increase the rate of oil oxidation while other elements such as Cr, Cd, and Pb are very important on account of their toxicity and metabolic role [6]. The presence of metals in edible oils may be due to different factors: the metals can be incorporated in to the oil from the soil or be introduced during the manufacturing of food stuff [7,8]. A possibility of metal entry into edible oils other than the technological one is the environmental exposure to a large variety of elements. They arrive in the plants via deposition as well as bioaccumulation from the soil due to natural metal sources and environmental pollution. Copper and nickel determinations are important in the industrial production of vegetable oils because of the use of these metals as hydrogenation catalysts. Copper and iron are potential contaminants of the oil deriving from processing equipment [9]. Lead and copper can be present in oils because of environmental contamination [9,10].

The significance of trace elements and toxicological effects of heavy metals on human health and nutrition have been increasingly studies in recent years. Some elements (such as Cu, Zn and Fe) can act as nutrients and are important for health, while others (such as Ni, Pb, Cd, As and Hg) may be harmful for humans if excessive amounts are consume [11]. Heavy metals are considered as serious inorganic pollutants because of their toxic effects for life [12]. The heavy metals enter the human body through inhalation and ingestion. The intake via ingestion depends upon food habits. It is well established that Pb and Cd are toxic and children are more sensitive to these metals than adults. The metals, namely Cu and Zn, are essential micro-nutrients and have a variety of biochemical functions in all living organisms. While Cu and Zn are essential they can be toxic when taken in excess; both toxicity and necessity vary from element-to-element [13].

In the presented study, the concentration of heavy metals and minerals in some edible oils samples produced in Turkey and collected from Turkish supermarkets were determined by flame and graphite furnace AAS after microwave digestion procedure.



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Table 1 Instrumental conditions for investigated elements.

Element	Acetylene (L/min)	Air (L/min)	Wavelength (nm)	Slit width (nm)	
Condition	s for FAAS				
Fe	2.0	17.0	248.3	0.2	
Mn	2.0	17.0	279.5	0.2	
Zn	2.0	17.0	213.9	0.7	
Cu	2.0	17.0	324.8	0.7	
Na	2.0	17.0	589.0	0.2	
K	2.0	17.0	766.5	0.7	
Ca	2.0	17.0	422.7	0.2	
Mg	2.0	17.0	285.2	0.2	
		Pb	Cd	Со	
Condition	s for GFAAS				
Argon fl	low (mL/min)	250	250	250	
Sample	volume (µL)	20	20	20	
Modifie	r (μL)	5	5		
Heating p	rogram temperature	(°C) (ramp tin	ne (s), hold time (s))	
Drying 1	100 (5, 20)		100 (5, 20)		
Drying 2	140 (15, 15)		140 (15, 15)	140 (15, 15)	
Ashing	Ashing 700 (10, 20)		850 (10, 20)	400 (10, 20)	
Atomizati	on 1800 (0, 5)		1650 (0, 5) 2500 (0, 5)		
Cleaning	2600 (1, 3)		2600 (1, 3)	2600(1,3)	

2. Materials and methods

2.1. Sampling

Total 60 samples and six varieties of edible oils produced various plants in Turkey (10 olive oil samples, 10 hazelnut oil samples, 10 sunflower oil samples, 10 margarine samples, 10 butter samples and 10 corn oil samples) were collected in Turkish supermarkets during 2007. The collected oil samples were packed in polyethylene bags and stored below -20 °C until analysis.

2.2. Reagents

All reagents were of analytical reagent grade unless otherwise stated. Double deionized water (Milli-Q Millipore 18.2 M Ω cm resistively) was used for all dilutions. HNO₃ and H₂O₂ were of suprapure quality (Merck, Darmstadt, Germany). All the plastic and glassware were cleaned by soaking with the contact overnight in a 10% nitric acid solution and then rinsed with double deionized water. The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg/L of given element, supplied by Sigma Chemical Co. (St. Louis, MO).

2.3. Apparatus

1

A PerkinElmer Analyst 700 atomic absorption spectrometer (FAAS) equipped with HGA graphite furnace and with deuterium background corrector was used in the experiments. For flame measurements, a 10 cm long slot-burner head, a lamp and an airacetylene flame were used. Fe, Mn, Zn, Cu, Na, K, Ca and Mg were

oil samples. N = 4.

Table 2

Trace element concentrations in certified reference material (NIST SRM 1577b bovine liver), N = 4.

Element	Certified value ($\mu g/g$)	Our value (µg/g)	Recovery (%)
Cu	160	155 ± 10	97
Cd	0.5	0.49 ± 0.04	98
Pb	0.129	0.125 ± 0.01	97
Mn	10.5	10.4 ± 0.8	99
Со	0.25	0.24 ± 0.01	96
Zn	127	125 ± 8	98
Fe	184	182 ± 15	99

determined in flame AAS. The other elements (Pb, Cd and Co) were determined in graphite furnace AAS. For graphite furnace measurements, argon was used as inert gas. The operating parameters both FAAS and GFAAS for the working elements were set as recommended by the manufacturer that were given in Table 1.

2.4. Microwave digestion

One gram samples were digested with 6 mL of HNO_3 (65%) (Suprapure, Merck, Darmstadt, Germany), 2 mL of H₂O₂ (30%) (Merck) in microwave digestion system and diluted to 10 mL with double deionized water. A blank digest was carried out in the same way (digestion conditions for 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, respectively).

3. Results and discussion

In this study, microwave digestion system was preferred because of it is higher accuracy with respect to both time and recovery values. The recovery values were nearly quantitative for microwave digestion method. The relative standard deviations were less than 10% for all investigated elements. t-Test was used in this study (p < 0.05). The accuracy of the method was evaluated by means of trace element determination in standard reference material (SRM). The achieved results were in good agreement with certified values. The results for this study are given in Table 2. All metal and mineral concentrations were determined on a wet weight as $\mu g/g$ except cadmium.

The concentration levels of the elements (Fe, Mn, Zn, Cu, Pb, Co, Cd, Na, K, Ca and Mg) in the analyzed six typical edible oils are given in Table 3. Metal concentrations in edible oils were found between as 291.0-52.0, 1.64-0.04, 3.08-1.03, 0.71-0.05, 0.03-0.01, 1.30-0.50, 84.0-0.90, 50.1-1.30, 174.2-20.8 and 20.8-0.60 µg/g for iron, manganese, zinc, copper, lead, cobalt, sodium, potassium, calcium, and magnesium, respectively. Cadmium was found to be 4.57-0.09 µg/kg.

Vegetable oils and fats contain trace levels of various metals depending upon many factors, such as species, soil used for the cultivation, irrigation water, variety, and stage of maturity. Main elements are Ca, Mg, P, and Fe followed by ultra trace level of Zn, Cr, Mn, Ni, and Cu [14].

Table 3	
The concentration levels of elements $(\mu g/g)$ in edibl	e

Sample	Fe	Mn	Zn	Cu	Pb	Со	Cd ^a	Na	К	Ca	Mg
Olive oil	139.0 ± 10.1	0.04 ± 0.004	1.03 ± 0.1	0.71 ± 0.06	$\textbf{0.03} \pm \textbf{0.003}$	1.30 ± 0.1	0.15 ± 0.02	8.7 ± 0.8	2.14 ± 0.2	76.0 ± 7.5	0.60 ± 0.05
Hazelnut oil	127.0 ± 11.4	0.13 ± 0.01	1.15 ± 0.1	0.05 ± 0.004	0.01 ± 0.01	0.54 ± 0.04	4.57 ± 0.4	0.9 ± 0.1	1.30 ± 0.1	20.8 ± 2.1	3.30 ± 0.3
Sunflower oil	105.3 ± 10.3	0.12 ± 0.01	1.10 ± 0.1	0.11 ± 0.01	0.01 ± 0.01	0.54 ± 0.05	3.76 ± 0.4	1.8 ± 0.1	2.45 ± 0.2	174.2 ± 17.0	7.04 ± 0.7
Margarine	291.0 ± 28.2	0.12 ± 0.01	2.71 ± 0.2	0.09 ± 0.01	$0.01{\pm}~0.01$	0.53 ± 0.05	3.66 ± 0.3	75.4 ± 6.9	50.1 ± 5.0	22.6 ± 2.0	18.3 ± 1.8
Butter	132.6 ± 12.5	0.05 ± 0.003	1.17 ± 0.1	0.41 ± 0.04	0.01 ± 0.01	1.03 ± 0.1	2.84 ± 0.3	84.0 ± 7.5	47.4 ± 4.3	71.0 ± 6.9	20.8 ± 2.1
Corn oil	52.0 ± 4.8	1.64 ± 0.1	3.08 ± 0.3	BDL	BDL	0.50 ± 0.05	0.09 ± 0.01	$\textbf{6.6.} \pm \textbf{0.6}$	2.18 ± 0.2	135.5 ± 13.5	0.79 ± 0.08

^a µg/kg; BDL: below detection limit.



Fig. 1. Distribution of iron in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.



Fig. 2. Distribution of zinc in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.

The lowest and highest metal concentrations were observed in cadmium and iron in all samples. The iron concentrations in the samples ranged from 291.0 μ g/g in margarine to 52.0 μ g/g in corn oil (Fig. 1).

Zinc is widespread among living organisms due to its biological significance. The recommended daily intakes of zinc and copper are 15 mg Zn for adult males and 12 mg Zn for adult females and 1.5–3.0 mg Cu [15]. Zinc is known to be involved in most metabolic pathways in humans and zinc deficiency can lead to loss of appetite, growth retardation, skin changes and immunological abnormali-



Fig. 3. Distribution of manganese in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.



Fig. 4. Distribution of copper in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.

ties. The highest content of zinc and manganese were $3.08 \,\mu g/g$ (Fig. 2) and $1.64 \,\mu g/g$ (Fig. 3) in corn oil, whereas the lowest manganese and zinc content were 0.04 and $1.03 \,\mu g/g$ in olive oil. Fe value has been reported lower than our values in the literatures [16,17]. Fe, Mn and Zn concentrations were reported as 15.31, 0.06 and $3.39 \,\mu g/g$ in the literature [9].

Copper is known to both vital and toxic for many biological systems and may enter the food materials from soil through mineralization by crops, food processing or environmental contamination, as in the application of agricultural inputs, such as copper-based pesticides which are in common use in farms in some countries [18,19]. Minimum and maximum values of copper were 0.05 and 0.71 μ g/g (Fig. 4). The highest and lowest levels of copper were found in olive oil and hazelnut oil. Copper contents of edible oil samples in the literature have been reported in the range of 12.71–50.5 µg/kg [17], 2.10–3.10 mg/100 g [20], respectively. Our copper values in the investigated oil samples are in agreement with reported in the literatures [9,16]. The FAO/WHO [21] has set a limit for heavy metal intake based on body weight. For an average adult (60 kg body weight), the provisional tolerable daily intake (PTDI) for lead, iron, copper and zinc are 214 µg, 48 mg, 3 mg and 60 mg, respectively [21].

Cobalt is an important element for human life due to its main importance of B-12 vitamin. The highest cobalt contents in samples were found to be $1.30 \,\mu$ g/g (Fig. 5). Cobalt content was reported as $0.92-5.45 \,\mu$ g/g in literature. Our cobalt values are lowest than literature values [9].



Fig. 5. Distribution of cobalt in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.



Fig. 6. Distribution of lead in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.



Fig. 7. Distribution of cadmium in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.

Fe, Ni, Cu, Pb, Cd and As are the most often determined elements in edible oils. According to national and international requirements, the approved contents of these metals in oils are: 1-1.5 mg/kg (Fe), 0.2 mg/kg (Ni), 0.1 mg/kg (Cu, Pb, As) and 0.05 mg/kg (Cd) [22]. In this study, lead and cadmium concentrations in samples were found to be lower than 0.03μ g/g. The lowest and highest lead and cadmium levels in the samples were in the range of $0.01-0.03 \mu$ g/g (Fig. 6) and $0.09-4.57 \mu$ g/kg(Fig. 7), respectively. The previous studies, lead levels in the samples have been reported as <50 μ g/kg [17]. The fact that toxic metals are present in high concentrations in food



Fig. 8. Distribution of sodium in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.



Fig. 9. Distribution of potassium in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.



Fig. 10. Distribution of calcium in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.

samples is of particular importance in relation to the FAO/WHO [23] standards for Pb and Cd as toxic metals. The maximum permissible doses for an adult are 3 mg Pb and 0.5 mg Cd per week, but the recommended doses are only one-fifth of those quantities [23]. Cadmium may accumulate in the human body and may induce kidney dysfunction, skeletal damage and reproductive deficiencies. Chromium is considered as an essential trace element. The amount of chromium in the diet is of great importance as Cr is involved in insulin function and lipid metabolism [24,25]. The recommended daily intake of chromium is 50–200 μ g [26].



Fig. 11. Distribution of magnesium in edible oil samples. (1) Olive oil; (2) hazelnut oil; (3) sunflower oil; (4) margarine; (5) butter; (6) corn oil.

Maximum sodium and potassium levels were found in butter $(84.0 \ \mu g/g)$ (Fig. 8) and margarine $(50.1 \ \mu g/g)$ (Fig. 9). These values are higher than reported earlier studies in the literature [9,16]. The calcium and magnesium levels in edible oil samples were found in the range of 174.2–20.8 $\ \mu g/g$ (Fig. 10) and 20.8–0.60 $\ \mu g/g$ (Fig. 11), respectively. The literature values for calcium and magnesium were reported as 90–12.8 mg/100 g and 175–58.3 mg/100 g [20].

4. Conclusion

Trace elements play important negative and positive roles in human life [27–30]. The results obtained for trace elements in analyzed edible oils produced in Turkey were acceptable to human consumption at nutritional and toxic levels. The levels of Fe, Mn, Zn, Cu, Pb, Co, Cd, Na, K, Ca and Mg in some oils were found the recommended legal limits for human consumption. The levels may be reduced by more careful handling practices and processing of raw materials.

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