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Trace Metal Content of Snacks and Appetizers Consumed in Turkey

M. Soylak,[1] H. Colak,[1] O. Turkoglu,[1] M. Dogan[2]

[1] Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039 Kayseri, Turkey
[2] Hacettepe University, Faculty of Science, Department of Chemistry, 06532, Beytepe, Ankara, Turkey

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Heavy metals are widely distributed in the environment (Awadallah *et al.,* 1986, Soylak and Kirnap 2001, Polkowska *et al.,* 2004, Fan 2005) and are significant in nutrition, either for their essential nature or toxicity. Traces metals like iron, copper, zinc, cobalt and manganese are essential metals since they play important roles in biological systems (Mashi *et al.,* 2004, Garcia *et al.,* 2005). Metals such as lead and cadmium are toxic and harmful to human health. The essential metals can also produce toxic effects when the metal intake is excessively elevated. Trace heavy metals have recently received considerable attention from analytical chemists, because of their physical and environmental importance (Soylak *et al.,* 1995, Kenduzler and Turker 2003, Ghaedi *et al.,* 2005, Kramarova *et al.,* 2005). Food is also primary intake source of metal ions like iron, cobalt, copper and zinc, which are essential for human body, and must be taken at certain doses in daily diet. The consumption of contaminated foods causes diseases and deaths therefore contamination of traces heavy metals is considered as important issues by World Health Organization (WHO) (Naqvi *et al.,* 2004, Sarkozi *et al.,* 2005). Snack and appetizers can be valuable nutritional source of minerals specially Zn and Cu. The health benefit of them can be enjoyable in food and food products such as additives (Azar *et al.,* 2004). The snack and appetizers analyzed are widely consumed in Turkey like other countries in Asia and Middle East. For example sunflower (Helianthus annuus) kernels salted roasted after are popular as snacks. Legumes go through several primary processes (e.g., dehulling, boiling, roasting, splitting, and grinding, etc.) before they are used in different food preparations. The roasted chickpea product (leblebi) is widely consumed as a traditional snack food in Turkey. The contents of trace heavy metals in snack and appetizers samples have been performed by the various researchers around the world (Reeves and Vanderpool 1997, Garcia *et al.,* 2003, Coskuner and Karababa 2004).

In the present work, some metal levels of some snack and appetizers produced in Turkey have been determined by flame atomic absorption spectrometry.

MATERIALS AND METHODS

All the chemicals used in the present work acquired from E. Merck, Darmstadt were of analytical grade and were used as such from freshly opened bottles. No

Correspondence to: M. Soylak

attempt was made to purify them further. Freshly prepared doubled distilled water, from quartz still, was used in all experiments. Standard stock solutions containing 1000 mg/l analyte ions were prepared from nitrate salts of analytes at analytical grade in 1% of HNO_3 into 1 liter calibrated flasks. Diluted standard and model solutions were daily prepared from the stock standard solutions.

A Perkin Elmer Model 3110 atomic absorption spectrometer without deuterium background corrector was used. A 10 cm long slot-burner head, a lamp and an air-acetylene flame were used. The atomic absorption signal was measured as a peak height mode against an analytical curve. The calibration curves for analytes were drawn after setting various parameters of flame atomic absorption spectrometry including wavelength, slit width, lamp current at an optimum level (Table 1).

Table 1. Operating conditions for each analyte.

Element	Wavelength (nm)	Slith width (nm)	Lamp Current (mA)	Flow rates of flame gases Air (L/min)	Acetylene (L/min)
Cu	324.8	1.3	7.5	9.5	2.3
Fe	248.3	0.2	15.0	9.5	2.3
Ni	232.0	0.2	15.0	9.5	2.2
Zn	213.9	0.7	10	9.0	2.0

The optimum concentration ranges and regression equations for analytes were given in Table 2. The statistical calculations are based on the average of triplicate readings for a standard solution the analytes. The precision of the method was investigated by using the model solutions containing the spiked elements on the optimal conditions of the method.

Table 2. Calibration curves of the analytes.

Analyte	Correlation coefficient	Linear range (mg/L)	Regression Equation
Manganese	0.9990	0.1-3.0	A= 0.08 C + 0.003
Nickel	0.9992	0.5-5.0	A= 0.032 C + 0.001
Iron	0.9989	0.5-5.0	A= 0.037 C + 0.001
Zinc	0.9996	0.05-1.0	A= 0.28 C + 0.004
Copper	0.9999	0.5-5.0	A= 0.054 C +0.001

A: absorbance, C: concentration of analyte

Twelve snack and appetizers produced in Turkey were purchased from local markets. The samples were dried at 105 °C for 3 h andwere homogenized using an agate pestle and ground to pass through 200 mesh sieve. The samples were stored in pre-cleaned polyethylene bottles until analysis. Accordingly, 1.00 g of exactly weighed samples were placed into a 250 ml beaker then digested for 3 h at 90 °C with concentrated $HCl:HNO_3$ (3:1) (8 ml). The residue was filtered and the filtrate was combined with the leachate and diluted to 25 ml with water. A blank digest was carried out in the same way. The amount of analytes was determined in triplicate experiments by flame AAS.

RESULTS AND DISCUSSION

The concentration of manganese, nickel, iron, zinc and copper in the some snack samples marketed in Kayseri-Turkey have been analyzed by flame atomic absorption spectrometry (FAAS) after digestion with aqua regia. Relative standard deviations (RSD) were calculated from pooled data for method. In the precision test, the average RSD % of snack samples for all metals are in the range of 1-9 % (n=18) for method.

A recovery test of analytical procedure was carried out for some of the metals in selected samples by spiking analyzed samples with aliquots of metal standards and then reanalyzing the samples. Acceptable recoveries (> 95%) were obtained for the analyte ions. Detection limit is defined as the concentration corresponding to three times the standard deviation of ten blanks. Detection limit values for FAAS were found to be as 0.09 mg/l for Mn, 0.08 mg/l for Fe, 0.11 mg/l for Cr, 0.10 mg/l for Pb, 0.11 mg/l for Ni, 0.05 mg/l for Cd, 0.06 mg/l for Cu, 0.11 mg/l for Co and 0.03 mg/l for Zn.

The results, which were repeated in triplicate, were given in Table 3. The values are given as mean ± SD (standard deviation). The trace heavy metal contents in the samples studied depend on the analyzed species. Levels of the essential metals in the appetizers samples were found to be higher than those of the non-essential metals. Lead, chromium, cobalt and cadmium levels were found the below the detection limits of flame atomic absorption spectrometry. Iron is the highest level, while the concentration of zinc is the lowest.

Manganese activates numerous essential enzymes in our body. Foods contain relatively small amounts of manganese. The lowest and highest contents of manganese were found as 22.3 ± 1.1 μg/g for pistachio nut and 138.4 ± 10.8 μg/g for hazelnut, respectively. The average manganese level in hazelnut sample was given as 36.5 μg/g by Kargosha and Noroozifar (2003).

Trace amounts nickel may be beneficial as activate of some enzyme systems, but its toxicity at higher levels is more prominent. However, nickel toxicity in humans is not a very common occurrence because the absorption of nickel is very low from environmental sources. Ni levels in the samples varied from 12.0 μg/g in hazelnut to 25.8 μg/g in walnut. Nickel level of snack samples from Spain by Cabrera *et al.* (2003) has been reported as 0.31 μg/g for almond, 0.25 μg/g for peanut, 0.36 μg/g for pistachio and 0.25 μg/g for peanut. The levels of nickel in the present study were higher than in samples from Spain (Cabrera *et al.*, 2003).

Iron is required by plants in the largest amount of all the micronutrients. The lowest level of iron was found in pistachio nut sample as 44.6 μg/g, while the highest in salted and toasted pumpkin seeds as 113.4 μg/g. The contents of iron in almond, hazelnut, peanut, pistachio, roasted corn, walnuts and sunflower seed samples from Spain (Cabrera *et al.*, 2003) has been reported as 45.0 μg/g, 17.3 μg/g, 22.8 μg/g, 73.5 μg/g, 50.3 μg/g, 22.5 μg/g, and 40.9 μg/g, respectively.

Table 3. Metals in some snacks and appetizers produced marketed in Turkey.

	Concentration (µg/g)*				
Sample	Mn	Ni	Fe	Zn	Cu
Pistachio Nut	22.3 ± 1.1	13.8 ± 1.2	44.6 ± 1.3	7.1 ± 0.2	24.9 ± 0.3
Peanut	37.9 ± 1.4	13.8 ± 1.1	59.8 ± 4.2	9.2 ± 0.7	17.3 ± 1.2
Hazelnut	138.4 ± 10.8	12.0 ± 0.3	69.3 ± 6.1	6.8 ± 0.3	31.5 ± 1.8
Roasted peas	31.3 ± 2.4	13.7 ± 0.9	79.9 ± 0.8	11.9 ± 0.8	19.6 ± 2.0
Dried mulberries	30.5 ± 3.3	15.6 ± 0.3	81.0 ± 2.6	6.7 ± 0.4	10.5 ± 1.0
Salted and toasted pumpkin seeds	77.8 ± 3.6	16.2 ± 1.1	113.4 ± 10.8	20.4 ± 1.2	24.9 ± 1.3
Sunflower kernels	62.3 ± 2.0	19.8 ± 2.1	84.5 ± 3.8	16.3 ± 0.3	44.3 ± 2.9
Walnut	48.0 ± 1.8	25.8 ± 1.7	56.4 ± 4.9	10.1 ± 0.3	27.2 ± 2.8
Nondehulled Roasted Chickpeas	48.6 ± 4.4	19.1 ± 1.1	47.3 ± 1.0	8.9 ± 0.5	17.2 ± 1.5
Dehulled Roasted Chickpeas	37.7 ± 2.9	15.0 ± 1.0	94.2 ± 9.2	8.8 ± 0.3	30.5 ± 1.7
Almond	43.5 ± 3.7	17.4 ± 0.6	53.8 ± 5.3	10.1 ± 0.4	23.8 ± 2.3
Roasted corn zea mays	22.6 ± 1.1	17.4 ± 0.3	79.6 ± 2.8	7.0 ± 0.4	11.8 ± 1.1

* Mean ± standard deviation

Zinc is essential traces metal for organisms. It is one of an important metal for normal growth and development of human. Deficiency of zinc is of growing concern in the developing world. The lowest and highest levels of zinc were found as 6.7 µg/g for dried mulberries and 20.4 µg/g for salted-toasted pumpkin seeds, respectively. The concentration of zinc in samples was generally in the lower range of other studies.

Copper is also one of the essential micronutrients, its adequate supply for growing plants should be ensured through artificial or organic fertilizers. The levels of copper in the analysed snacks were in the range of 11.8-44.3 µg/g. The highest and lowest levels of copper were found in sunflower kernels and roasted zea mays, respectively. Legumes and nuts are rich for copper. Copper level of almond, hazelnut, peanut, pistachio, roasted corn, walnuts and sunflower seed samples from Spain (Cabrera *et al.,* 2003) has been reported as 11.1 µg/g, 16.6 µg/g, 6.9 µg/g, 9.2 µg/g, 6.6 µg/g, 22.0 µg/g, and 13.6 µg/g, respectively. The levels for copper for snack samples were comparable with the values reported by Cabrera *et al.* (2003). The concentration of copper in hazelnut from our country has been reported as 11.8 µg/g (Dalman *et al.,*2002). The level of copper in the present study for hazelnut was 31.5 µg/g.

In the light of our findings, the contents of the analyte ions were at acceptable levels given by WHO/FAO. The results of trace metal ions for snack and appetizers samples from our country are agreed with the literature values for the same kind of samples around the world.

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