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Determination of Trace Elements in Some Dried Winter Foods

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The levels of trace elements in nine food of winter which are grown in Elazig, Turkey were determined. Flame atomic absorption spectrometry (F-AAS) and high performance liquid chromatography (HPLC) were used in this work. The levels of trace metals in food samples were found in the ranges, 60-250, 8.60-58.60, 13.20-44.8, 0.75-3.92, 0.18-0.42 μg g^{-1} (dry matter) for Fe, Zn, Cu, Ni and Co, respectively. The accuracy and precision of the analysis were checked against the standard reference materials SRM (NIST 1573 a-tomato leaves). The results obtained for Cu, Zn, Fe, Ni and Co were in an excellent agreement with the certified values.

Key Words: Heavy metal, Trace element, HPLC, winter food.

INTRODUCTION

Metal ions and metal complexes materials having an important role in vital functions of organisms. Because of this, various inorganic, organic, analytical and physical techniques are stated to be used for these substances synthesis, structures, formations, stabilities and analysis[1]. Zinc, Mn and Fe are important co-enzymes; Cu is bound to amino acids[2]. Iron and cobalt are cause substantial catalytic activity and have been shown to be essential elements for nitrogen fixation in addition to their usefulness for the formation of vitamin B_{12}[3]. Iron is an essential activator for enzymes catalyzing reactions involved in chlorophyll synthesis and for ferrodoxin nitrate reductase[4]. Generally, the main characteristics of essential elements depend on the regulatory mechanisms, which are able to keep the elements at the nutrition level. Macro- and microelements, measured in this work, are critical components of many antioxidant processes. Deficiency of any of these essential elements may impair the function of overall oxidant system[5].

Heavy metals composition of foods is of interest because of their essential or toxic nature. For example, iron, zinc, copper, chromium, cobalt and manganese are essential, while lead, cadmium, nickel and mercury are toxic at certain levels[6-8].

To assure that foods quality concerning trace metal contamination, food samples should be periodically analyzed. When vegetables and fruits were produced around industrial zone or when intensive use of fertilizers was employed to improve productivity the monitoring of trace metal contamination become important. Therefore, it is of importance to develop sensitive methods for determining trace metals in environmental and biological samples[9].

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There are a lot of analytical procedures to carry out the determination of trace elements in food such as neutron activation analysis (NAA)[10], inductively coupled plasma optic emission spectrometry (ICP-OES)[11], inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS)[12], differential pulse anodic stripping voltametry[13] and chromatography.

In this study, five trace elements (Fe, Zn, Cu, Ni, Co) in nine winter foods of Turkish origin were determined, using FAAS and HPLC.

EXPERIMENTAL

The standard metal solutions of, Zn(II), Fe(III), Ni(II), Co(III) and Cu(II) (1000 mg L^{-1}, grade of analytical, Merck) were diluted to the desired concentrations with 0.2 M HNO_3. Concentrated HNO_3 and $HClO_4$ for digestion samples were used ultra pure grade (Merck). Deionizers doubly distilled water. 4-(2-Pyridylazo)resorcinol (PAR) monosodium salt hydrate was obtained from Aldrich and solutions of the dye were freshly prepared in water-methanol before use. Other chemical reagents used in the analysis were analytical grade and obtained from Merck (Darmstadt, Germany).

Ati-Unicam 929 flame atomic absorption spectrometry (FAAS) equipped with Ati Unicam hollow cathode lamps was used for the determination of Cu, Fe and Zn. The chromatographic system was equipped with a Shimadzu LC-9A pump, SPD-M10AVP photodiode array detector. Luna reversed-phase column (4.6 mm × 200 mm 5 μm, phenomex, USA) was used for separation of Ni-PAR and Co-PAR. Microwave-assisted acid digestions have been made using a Premier microwave system.

Samples: Corn, pepper, sweet basil, bean, aubergine samples used in study were gathered from vegetable market in August 2007 taking into consideration to be grown in Elazig. Each of these three numbers corn, pepper, aubergine and a hundred each gram packed green bean and sweet basil samples were obtained from various sales. All the samples were washed rather nice with city system of water lines in the same day, they were torn to pieces and were dried under the sun for 20 d. Tarhana, Bulgur, Red lentil and chickpea were bought from cereal market in Elazig. Tarhana, a traditional fermented food made from a mixture of white wheat flour and yoghurt, is widely consumed in Turkey[14].

Preparation of sample solutions for FAAS: Winter's food was digested microwave system. 2.00 g portion of each sample dried at 80 °C was accurately and 0.50 g directly weighted into PTFE bombs. For the samples decomposition concentrated 4 mL HNO_3 and 1 mL $HClO_4$ acid were added. In a tightly closed system, the following six-step microwave digestion program was applied according to literature[15]. PTFE bomb was kept for 1 h to cool and was carefully opened. Colourless solution was transferred into beaker and evaporating to dryness with hot plate. Afterwards final volume was diluted 20 mL with 0.1M HNO_3. 10 mL solution was used for analysis of Co and Ni with HPLC, 10 mL solution was used for analysis of Fe, Cu and Zn with FAAS.

Sample solutions were analyzed with method of direct calibration curve by flame atomic absorption spectrometry for every element. Device setting is controlled every five readings. In addition, diluting reagents which are used are read by device as blank. Readings were done in duplicate. The optimum conditions for FAAS are given Table-1.

TABLE-1
OPERATING PARAMETERS FOR FAAS WHICH ARE USED IN ANALYSIS OF TRACE ELEMENTS

Parameters	Fe	Cu	Zn
Wavelength (nm)	248.3	324.8	213.9
HCl current (mA)	15.0	3.0	7.5
Acetylene flow rate (L/min)	0.6	0.5	0.6
Air flow rate (L/min)	4.0	4.0	4.0
Slit (nm)	0.2	0.5	0.5

Preparation of sample solutions for determinations of Co and Ni: The plants samples were treated as follows: 2 mL of 1×10^{-3} mol L^{-1}acetate solution, 2 mL of 1×10^{-3} mol L^{-1} PAR solution, 2 mL of 1×10^{-3} mol L^{-1} EDTA solution 25 mL volumetric flask and then 10 mL the digested samples solution was added. The pH was adjusted to 6.3 with dilute acetic acid solution and 2 mol L^{-1} sodium hydroxide. Afterwards, final volume was diluted 25 mL with water. Then sample solution was filtered through a 0.45 μm filter before a 50 μL aliquot was injected into the HPLC. For quantitative analysis, the analyte concentrations were determined by comparison peak area of standard solution[16,17].

The standard solutions were prepared as follows: 2 mL of 1×10^{-3} mol L^{-1} acetate solution, 2 mL of PAR 1×10^{-3} mol L^{-1} solution, 2 mL of 1×10^{-3} mol L^{-1} EDTA solution was added to a 25 mL volumetric flask and then a standard solution of cobalt(III) and nickel(II) were added, the pH was adjusted to 6.3 with dilute acetic acid solution. EDTA was found to be a useful ligand to mask metal ion contaminants from the chromatographic system and for buffer solution. Afterwards, final volume was diluted 25 mL with water. Then inject an aliquot of the solution into the chromatograph with a 50 μL loop injector. The optimum condition for flow rate is 0.6 mL min^{-1}.

RESULTS AND DISCUSSION

Trace metal levels in the analyzed samples are listed in Table-2. Trace element concentrations were determined on dry weight as μg g^{-1} and the relative standard deviations were less than 10 % for all elements.

The contents of iron, zinc, copper, nickel and cobalt in foods were found to be 60-250, 8.60-58.60, 13.20-44.8, 0.75-3.92, 0.18-0.42 μg g^{-1} (dry matter), respectively. The accuracy and analytical quality assurance for the present method was verified by reference material tomato Leaves-NIST 1573 (Table-3). Good agreement was noticed between measured and certified values.

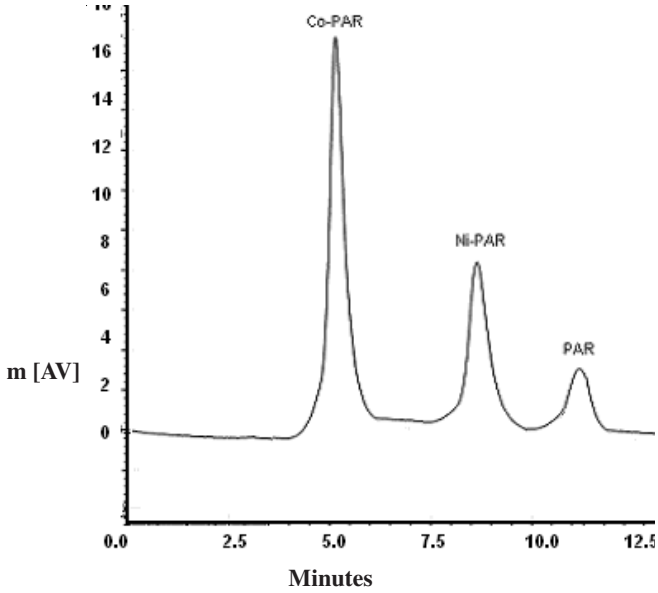

Fig. 1. Chromatography of standard chelates PAR of Co(III) and Ni(II) ions (50 µL injection, 0.25 mg L^{-1})

TABLE-2
AMOUNT OF TRACE ELEMENTS PRESENT IN VEGETABLES (µg g^{-1})

Food	Cu	Zn	Fe	Ni	Co
Corn	13.2±2.1	25.7±3.8	155±12	2.19±0.18	ND
Pepper	21.5±2.8	21.4±4.1	120±8	0.75±0.06	ND
Sweet basil	30.2±4.5	58.6±6.4	250±16	2.82±0.24	0.32±0.02
Bean	28.7±5.8	29.1±2.4	165±14	3.92±0.35	0.42±0.05
Aubergine	38.7±4.7	8.6±1.4	60±4	0.87±0.05	ND
Bulgur	24.5±1.5	14.4±1.6	74±6	1.45±0.09	0.18±0.01
Tarhana	16.4±1.4	21.1±1.8	96±8	3.24±0.28	0.35±0.03
Red lentil	44.8±5.2	64.3±5.3	162±18	2.56±0.21	0.28±0.04
Chickpea	18.2±2.1	24.8±3.2	136±9	2.88±0.32	ND

Data presented are in means ± standard deviation (n = 4); ND = Not detected.

TABLE-3
RESULTS FOR CERTIFIED REFERENCE MATERIAL
(NIST 1573 A-TOMATO LEAVES)

Element	Found[a]	Certified	Recovery (%)
Cu	4.65±0.20	4.70±0.14	98.9
Ni	1.56±0.12	1.59±0.07	98.1
Co	0.59±0.06	0.57±0.02	103.0
Fe	389±8.00	368±7.00	105.0
Zn	29.6±1.10	30.9±0.70	95.7

[a]Mean and Standard deviation from four determinations.

Minimum and maximum values of copper were 13.2 and 44.8 μg g^{-1}. The highest and lowest levels of copper were found in red lentil and corn (Fig. 2).

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].

The mean Zn concentrations in the corn, pepper, sweet basil, bean, aubergine, bulgur, tarhana, red lentil and chickpea were *ca.* 25.7, 21.4, 58.6, 29.1, 8.6, 14.4, 21.1, 64.3 and 24.8 μg g^{-1}, respectively (Fig. 3).

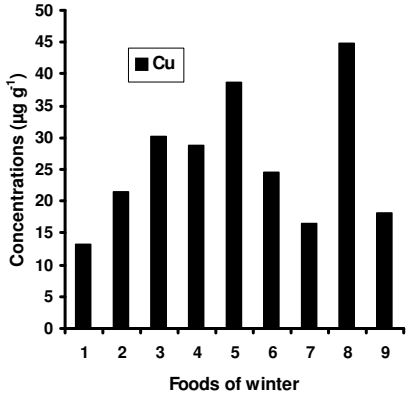

Fig. 2. Distribution of copper in foods: 1, Corn; 2, Pepper; 3, Sweet basil; 4, Bean; 5, Aubergine; 6, Bulgur; 7, Tarhana; 8, Red lentil; 9, Chickpea

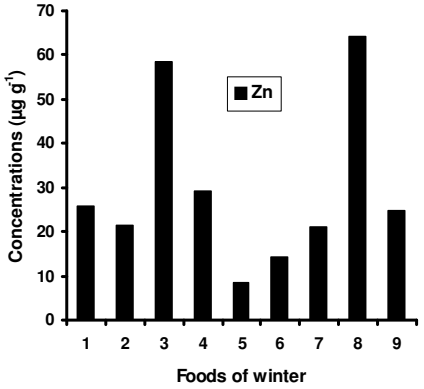

Fig. 3. Distribution of zinc in foods: 1, Corn; 2, Pepper; 3, Sweet basil; 4, Bean; 5, Aubergine; 6, Bulgur; 7, Tarhana; 8, Red lentil; 9, Chickpea

Several biological roles for Zn have been reported and over 200 proteins and enzymes contain Zn. Some of these enzymes may be of particular importance in function of reproductive tissues, but little is known about how Zn deficiency influences manifestations of Zn-dependent functions. A role in reproduction may involve Zn as an essential component or activator of enzymes involved in steroidogenesis[19,20].

The lower iron content was found 60 μg g^{-1} in aubergine. The higher iron content was found 250 μg g^{-1} in sweet basil (Fig. 4). The most cobalt amounts were determined in bean as 0.42 μg g^{-1}. The amount of cobalt in nine kind of plants have the order Bean > Tarhana > Sweet basil > Red lentil > Bulgur. The cobalt is not determined in corn, pepper, aubergine and chickpea (Fig. 5). Cobalt in the form of vitamin B_{12} (hydroxocyanocobalamin) is essential for humans. Vitamin B_{12} supports important synthetic reactions in metabolic processes and is essential for the production of red blood cells and several enzymes[21].

The contents of nickel in samples were found in the ranges 0.75-3.92 μg g^{-1}. The higher nickel content was found in bean and tarhana. The lower nickel content found was in aubergine and pepper (Fig. 6). Nickel was thought be essential to plants

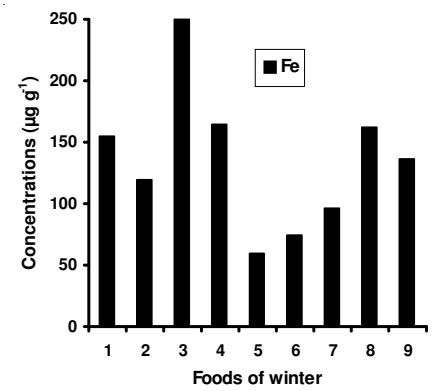

Fig. 4. Distribution of iron in foods: 1, Corn; 2, Pepper; 3, Sweet basil; 4, Bean; 5, Aubergine; 6, Bulgur; 7, Tarhana; 8, Red lentil; 9, Chickpea

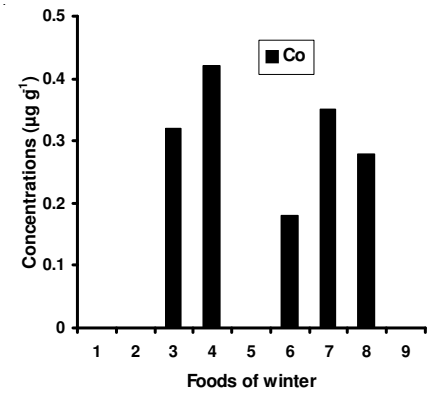

Fig. 5. Distribution of cobalt in foods: 1, Corn; 2, Pepper; 3, Sweet basil; 4, Bean; 5, Aubergine; 6, Bulgur; 7, Tarhana; 8, Red lentil; 9, Chickpea

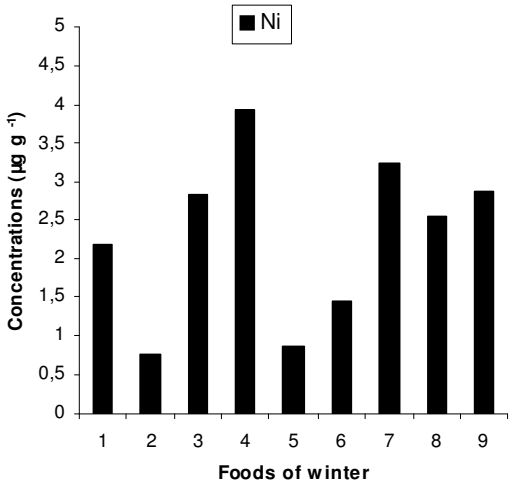

Fig. 6. Distribution of nickel in foods: 1, Corn; 2, Pepper; 3, Sweet basil; 4, Bean; 5, Aubergine; 6, Bulgur; 7, Tarhana; 8, Red lentil; 9, Chickpea

and some domestic animals[22] but not considered to be a metal of biological importance until 1975, when Zerner discovered that urease is a nickel enzyme[23].

Nickel is essential constituent in plant urease. Urease-rich legumes such as jack beans and soybeans generally contain high nickel concentrations[24]. Compared with other transition metals, nickel is a moderately toxic element. Nickel can cause a skin disorder known as nickel-eczema[25]. Therefore, it is necessary and important to develop sensitive methods for determining nickel in environmental, biological and food samples[26].

The reported trace metal values in the literature for plants were 4.47-14.08, 8.4-54.5 and 47-546 µg g^{-1} (dry matter) for Cu, Zn and Fe respectively[27].

The other reported study has been founded level of trace element, 41.0, 4.0, 20.0, 0.07 and 0.40 μg g^{-1} in pepper; 67.0, 6.0, 24.0, 1.83 and 0.07 μg g^{-1} in bean, 31, 5, 15, 0.02, 0.03 μg g^{-1} in aubergine for Fe, Cu, Zn, Co and Ni, respectively[28]. Literature studies showed that iron, copper and nickel contents of foods were lower than present results. The levels of zinc in foods are in agreement with those reported in the literature, but cobalt contents were very low.

REFERENCES

1. P. Wang and H.K. Lee, *J. Chromatogr. A*, **789**, 437 (1997).
2. J.Y. Shi, Y.X. Chen, Y.Y. Huang and W. He, *Micron*, **35**, 557 (2004).
3. E.W. Russell, Soil Conditions and Plant Growth, London, The English Language Book Society, pp. 849-855 (1973).
4. D.J.F. Bowling, Uptake of Ions by Plant Roots, London, Champan Hall, pp. 212-218 (1976).
5. E. Lemberkovics, E. Czinner, K. Szentmihalyi, A. Balazs and E. Szoke, *Food Chem.*, **78**, 119 (2002).
6. H.A. Schroeder, The Trace Elements and Nutrition, London, Faber and Faber, pp. 37-49 (1973).
7. E. Somer, *J. Food Sci.*, **39**, 215 (1974).
8. E.J. Underwood, Trace Element in Human and Animal Nutrition, New York, Academic Press, pp. 196-242 (1971).
9. M.G. Pereira and M.A.Z. Arruda, *Microchim. Acta*, **146**, 215 (2004).
10. F.Y. Iskander, T.L. Bauer and D.E. Klein, *Analyst*, **111**, 107 (1986).
11. A. Bakoglu, E. Bagci and H. Ciftci, *J. Food Agric. Environ.*, **7**, 343 (2009).
12. H. Ciftci and A. Olcucu, *Int. J. Sci. Technol.*, **2**, 29 (2007).
13. N. Venkata, V. Gyothi, P.M. Chandra, S. Reddy and J. Reddy, *J. Trace Elem. Med. Biol.*, **17**, 79 (2003).
14. A. Koca, F. Yazici and M. Anil, *Eur. Food Res. Tech.*, **215**, 293 (2002).
15. H. Ciftci and A. Olcucu, *Int. J. Sci. Tech.*, **2**, 105 (2007).
16. H. Ciftci, *Asian J. Chem.*, **20**, 3025 (2008).
17. H. Ciftci, A. Olcucu, A. Ozkaya and T. Ciftci, *Asian J. Chem.*, **21**, 2643 (2009).
18. P.C. Onianwa, A.O. Adeyemo, O.E. Idowu and E.E. Ogabiela, *Food Chem.*, **72**, 89 (2001).
19. J. Apagar, *Ann. Rev. Nutr.*, **5**, 43 (1985).
20. J.K. Chesters, *World Rev. Nutr. Diet.*, **32**, 135 (1978).
21. E. Merian and V.C.H. Weinheim, Metals and Their Compounds in The Environment, Occurrence, Analysis and Biological Relevance, pp. 257-286 (1991).
22. K. Wang, Nickel Trace Elements in Life Science, Chinese Measurement Press, Peking, China, pp. 278-280 (1991).
23. B. Zerner, *Bioorg. Chem.*, **19**, 116 (1991).
24. E. Merian, M. Anke, M. Ihnat and M. Stoeppler, Elements and Their Compounds in the Environment, Wiley/VCH, Weinheim, Vol. 2, edn. 2, pp. 1251-1258 (2004).
25. J. Kristiansen, J.M. Christensen, T. Henriksen, N.H. Nielsen and T. Menne, *Anal. Chim. Acta*, **403**, 265 (2000).
26. S. Baytak and A.R. Turker, *J. Hazard. Mater.*, **129**, 130 (2006).
27. R. Slavica, O. Antonije, D. Svetlana, S. Latinka and P. Aleksandar, *Talanta*, **67**, 233 (2005).
28. P. Ekholm, H. Reinivuo, P. Mattila, H. Pakkala, J. Koponen, A. Happonen, J. Hellström and M.L. Ovaskainen, *J. Food Comp. Anal*., **20**, 487 (2007).

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