Original Article

Determination of Heavy Metals in Apricot and Almond Oils

Issa Mohammadpourfard ***Nabi Shariatifar** Gholam Reza Jahed-Khaniki Eayob Ebadi-Fathabad

Department of Environmental Health, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

***nshariati@tums.ac.ir**

(Received: 6 Aug 2014; Revised: 23 Sep 2014; Accepted: 9 Feb 2015)

Abstract

Background and purpose: Determination of heavy metals in oils is necessary to establish quality standards on a country level. This study aimed to determine of heavy metal contents (Cr, Ni, As, Cd, Hg, Pb, Sb, Sn, Sr, Al) in 12 seed oil samples in Iran by inductively coupled plasma-optical emission spectrometry (ICP-OES).

Materials and Methods: The concentrations of heavy metal were determined by wet acid digestion methods with nitric acid (65%) and 4 ml peroxide hydrogenate on same samples using ICP-OES.

Results: Results showed that the average of most important toxic metals detected in apricot oil samples was as follows; 721.72 µg/kg for Al 15 µg/kg for Cd, 18 µg/kg for Pb, 14 µg/kg for As and <1 µg/kg for Hg. Furthermore, The average of heavy metals detected in almond oil samples were as follows; 1019.73 µg/kg for Al, 10 µg/kg for Cd, 21 µg/kg for Pb and 11 µg/kg for As and <1 µg/kg for Hg. Also in the studied samples, Al was the highest concentrations among all metals.

Conclusion: Most of the samples of oils were found to be contaminated with notable amounts of toxic metals which could be a threat to oil quality and human health.

[Mohammadpourfard I, *Shariatifar N, Jahed-Khaniki GhR, Ebadi-Fathabad E. **Determination of Heavy Metals in Apricot and Almond Oils**. IJHS 2015; 3(1): 18-24] http://jhs.mazums.ac.ir

***Key words*:** Heavy metals, Seed oil, Food safety, Inductively Coupled plasma-optical emission spectrometry

1. Introduction

Heavy metals are toxic elements which can enter into the food and affects the health of people who consume the contaminated foods. Levels of heavy metals in food and environmental samples are an important key to environmental pollution (1) and their attention worldwide due to its toxic effects even at very low concentrations is given (2). There are a number of factors that contribute to pollution of heavy metal in agricultural soils such as fertilizers, pesticides, atmospheric deposition from town and urban wastes, industrial emissions, and metal production (3) When agricultural soils contaminated with heavy metals, they may easily enter the food chain through plants. This is clearly documented that several factors may affect the behavior of heavy metals in soils, its availability to plants, and transfer from plants to humans (4,5). It is known that some organisms have the ability to accumulate certain elements in its structure, especially metals at high concentrations (6,7). Heavy metals can find in milk and milk products (9), fish (10), water (11), rice, bread (13), edible salts (14), vegetables (15), tea (16), and other food products. Vegetable oils are food products which are widely used in the cooking and food processing, cosmetics, pharmaceutical and chemical industries (7-17). The presence of trace metals is an important factor as far as the quality of edible oil is concerned. The presence of heavy metals in edible oils is due to both endogenous factors, connected with the plant metabolism, and exogenous factors due to contamination during the agronomic techniques of production and the collection of apricot and almond seeds during the oil extraction and treatment processes, as well as systems and materials of packaging and storage (18-20). There are no data about heavy metals in almond and apricot kernel oil in Iran, and it is important to know the safety of these food products. The aim of this study was the determination of toxic metals content in apricot and almond oil samples which produce in high volume in Azerbaijan province of Iran.

2. Materials and Methods

12 samples of apricotkenel (8 samples) from four cities (Marand, Maraghe, Osku and Bonab, Iran) and almond pits (4 samples) of two cities (Osku and Bonab, Iran) picked by hand during the crop season 2013 (July-September). The endocarps were removed from kernels by hand. All the samples were stored in the refrigerator at a temperature below 4°C until required for extraction of oil.

Oil samples were extracted from almond and apricot kernel by the Soxhlet method extraction using n-hexane (15 g seed powder with 250 ml n-hexane) with a temperature from 60°C for 8 h. Then, the solution was filtered, and the remaining solvent was evaporated using a rotary evaporator at 40°C. The pure oil was transferred into a small and dark glass vial, flushed with nitrogen and maintained at −18°C until determine the amount of heavy metals (21).

For the seed oil samples analysis, seed oil was digested in 100 ml pyrex glass beaker. For this take 1 g of seed oil adds 10 ml nitric acid (65%) and 4 ml peroxide hydrogenate. Then evaporated by a hot plate for 4 h and finally volume of the extract was made up to 25 ml using double distilled water (22).

A number of 12 samples of apricot and almond kernel oils were used for determinate heavy metal content. A calibration curve was obtained to see the linear relationship between absorbance and metal concentration in the concentration range being used (23). Metal ion concentrations of Al, As, Pb, Hg, Cd, Ni, Sr, Sn, Cr, and Sb were determined as three replicates by SPECTRO inductively coupled plasma - optical emission spectrometry (ICP-OES).

Results of the research were analyzed for statistical significance by analyses of variance.

Standard deviations were calculated for oils and are based on measurements in triplicate. Comparison among the means was carried out using least significant differences at the 95% confidence level. All data were analyzed by a statistical software package SPSS for Windows (version 19, SPSS Inc., Chicago, IL, USA).

3. Results

The amount of metal (µg/kg) recovered in two experiments with regards to the additional standards are given for the experimental section. Al (100.3%) highest concentration, while Pb (88.3%) is present in the smallest detectable concentration, therefore, the accuracy of the results, estimated in a percent average of the standard addition recoveries, was higher than 88% for all metal ions (Table 1). The World Health Organization has a limit to the use of toxic metals can be adjusted according to body weight For an average adult (60 kg body weight), the provisional tolerable daily intake for copper, nickel, and lead are 3 mg, 100-300 µg/g, and 214 µg/g, respectively (24).

In order that edible oil standards for heavy metal do not exist, the detection of Cr, Ni, As, Cd, Hg, Pb, Sb, Sn, Sr, Al metals in 12 seed oil samples have been determined by ICP-OES method. They were extracted nitric acid. Results for each oil and are based on measurements in triplicate in table 2. The average amount of most important toxic metals detected by ICP in 12 samples were selected from edible vegetable oil was as follows; 721.72 µg/kg (for Al), 15 µg/kg (for Cd), 18 µg/kg (for Pb), 14 µg/kg (for As) and < 1 µg/kg (for Hg). Furthermore, the average of heavy metals detected in almond oil samples was as follows; 1019.73 µg/kg (for Al), 10 µg/kg (for Cd), 21 µg/kg (for Pb), and 11 µg/kg (for As). And < 1 µg/kg (for Hg). In this study, Al had the highest levels, whereas Hg had the lowest concentration among other toxic metals in almond and apricot oils.

4. Discussion

Edible oil contains traces heavy metal such as Cu and Zn at concentration 0.1-0.7 mg/kg. They can originate from the seed oil itself and from storage tank and pipes. The trace metal in oils and fats are unpleasant because they play an important role in catalyzing the oxidation reaction (25). Heavy metals, both in chronic and acute exposure, interact with many different cellular components, there are interfering with the normal metabolic functions, causing cellular damages, and in extreme cases, death of organism (26). Heavy metal such as lead and cadmium cause both acute and chronic poisoning, adverse effects on the liver, heart, kidney, skin vascular, and immune systems (27).

Table 1. The average quantities of recovery percent for toxic metals (ppb) Recovery %used in the examination

Sample	Standards conc.	Read out conc.	Recovery %	Detection limit
Al 167.078 (ppb)	1000	1003.1 ± 14.0	100.3 ± 1.4	0.1
As 189.042 (ppb)	100	95.3 ± 2.5	95.3 ± 2.5	1.2
Cd 214.438 (ppb)	100	93.7 ± 0.7	93.7 ± 0.7	0.1
Cr 205.618 (ppb)	100	96.4 ± 1.7	96.4 ± 1.7	0.1
Hg 184.950 (ppb)	100	98.2 ± 1.2	98.2 ± 1.2	1.0
Ni 221.648 (ppb)	100	90.2 ± 1	90.2 ± 1	0.3
Pb 220.353 (ppb)	100	88.3 ± 2.1	88.3 ± 2.1	2.0
Sb 206.833 (ppb)	100	96 ± 0.6	96 ± 0.6	0.5
Sn 189.991 (ppb)	100	94.2 ± 0.3	94.2 ± 0.3	0.2
Sr 407.771 (ppb)	1000	981.6 ± 4.0	98.2 ± 0.4	0.1

Table 2. The average amount of toxic metals in apricot and almond kernel oil (ppb)

Oil	Cr	Ni	As	Cd	Hg	Pb	Sb	Sn	Sr	Al
Apricot oil										
Marand										
Sweet	28 ± 1.4	29.0 ± 1.0	12.0 ± 0.3	15 ± 0.6	< 1	18.0 ± 1.1	< 0.5	19.0 ± 1.0	11.0 ± 1.0	357.0 ± 9.1
Bitter	42.0 ± 2.3	26.0 ± 0.6	6.0 ± 0.1	3.0 ± 0.1	< 1	8.0 ± 0.3	< 0.5	21.0 ± 0.5	18.0 ± 1.6	1239.0 ± 23.7
Maraghe										
Sweet	51.0 ± 2.1	47.0 ± 2.5	10.0 ± 0.4	9.0 ± 0.1	< 1	18.0 ± 0.6	< 0.5	25.0 ± 2.0	16.0 ± 1.2	1927.0 ± 50.7
Bitter	31.0 ± 0.7	84.0 ± 3.9	5.0 ± 0.1	3.0 ± 0.1	1.0 ± 0.1	7.0 ± 0.5	< 0.5	27.0 ± 1.3	16.0 ± 1.7	1591.0 ± 19.5
Osku										
Sweet	30.0 ± 1.1	43.0 ± 1.4	14.0 ± 0.2	15.0 ± 0.7	1.0 ± 0.0	20.0 ± 1.8	< 0.5	12.0 ± 1.0	6.0 ± 0.1	1110.0 ± 40.3
Bitter	23.0 ± 0.9	76.0 ± 3.1	27.0 ± 1.9	28.0 ± 2.4	< 1	28.0 ± 1.4	< 0.5	47.0 ± 3.6	12.0 ± 0.1	781.0 ± 13.4
Bonab										
Sweet	28.0 ± 1.5	39.0 ± 0.8	20.0 ± 1.3	26.0 ± 0.7	< 1	27.0 ± 2.1	< 0.5	17.0 ± 1.5	13.0 ± 0.1	197.0 ± 22.4
Bitter	9.0 ± 0.4	46.0 ± 2.6	15.0 ± 0.9	18.0 ± 0.5	1.0 ± 0.2	20.0 ± 0.3	< 0.5	19.0 ± 0.4	26.0 ± 1.9	2459.0 ± 41.5
Average	30	49	14	15	< 1	18	<0.5	23	15	1208
SD	11.72	19.45	6.80	8.81	0	7.15	0	9.80	5.54	721.72
LSD (95%)	0.335	0.274	0.195	0.182	-	0.266	-	0.783	0.416	0.711
Almond oil										
Osku										
Sweet	29.0 ± 1.3	251.0 ± 9.1	11.0 ± 0.4	11.0 ± 0.5	< 1	25.0 ± 0.5	< 0.5	18. 0± 1.2	11.0 ± 0.5	673.0 ± 11.7
Bitter	32 ± 3.5	157 ± 5.6	12.0 ± 0.1	9.0 ± 1.5	< 1	18.0 ± 0.9	< 0.5	24.0 ± 1.8	9.0 ± 0.3	1234.0± 35.2
Bonab										
Sweet	41.0 ± 1.2	31.0 ± 1.2	10.0 ± 0.3	8.0 ± 1.1	< 1	17.0 ± 0.4	< 0.5	30.0 ± 2.3	51.0 ± 4.6	561.0 ± 19.4
Bitter	34.0 ± 1.9	37.0 ± 1.4	12.0 ± 0.4	13.0 ± 0.5	< 1	22.0 ± 0.1	< 0.5	24.0 ± 1.5	119.0 ± 6.5	3103.0 ± 80.1
Average	34	119	11	10	< 1	21	< 0.5	24	47	1393
SD	4.59	91.34	0.83	1.92	0	3.20	0	3.96	44.37	1019.73
LSD (0.95)	0.207	0.069	0.698	0.870	-	0.688	-	0.293	0.158	0.569
LOD	0.1	0.3	1.2	0.1	1.0	2.0	0.5	0.2	0.1	0.1

SD: Standard deviation, LSD: Least significant differences, LOD: Limit of detection

Some micronutrients such as Al and Zn are essential for plant growth and human nutrition at a low amount but may also be toxic for humans, animals and plants at a high amount. Cu and Zn are required in our diet because they exhibit a wide range of biological functions such as components of enzymatic and reduction and oxidation systems (27). ICP/OES is one of the most common techniques used for the determination of metals in oil samples. Because edible oil standards for inorganic species do not be, the detection of cobalt, chromium, lead, cadmium, and nickel metals have been determined by ICP/OES technique (28). Dugo et al. was determined the content of Cd(II) and Pb(II) in commercial peanuts, sunflower, soy, maize, rice, grape-seed, and hazelnut oils. Theirs results showed that the mean levels of cadmium were lower than 4.90 µg/kg and the average content of lead ranged from 8.60 to 55.61 µg/kg, were higher than observed in this study Cd (15 ppb), Pb (18 ppb), and Hg (< 1 ppb) in apricot oils and Cd (10 ppb), Pb (21 ppb), and Hg (< 1 ppb) for almond oils)which may be due to differences in heavy metal content in soil, water, climatic conditions, and agricultural sources such as fertilizers and fungicides (23).

Ansari et al. were determinate concentration of cadmium, lead, and zinc in 16 newly breaded varieties of sunflower seed oil. Their results showed that there was Cadmium, lead, and zinc present in different varieties of sunflower oil (29). Mendil et al. were determined concentration of metal ion (Fe, Mn, Zn, Cu, Pb, Co, Cd, Na, K, Ca, and Mg) in edible oils such as olive oil, hazelnut oil, sunflower oil, margarine, butter, and corn oil obtain from Turkey marketing using atomic absorption spectrometry after microwave digestion. Theirs showed that the concentrations of trace element in the oil samples to be 1.03-3.08 and 0.5-1.3 µg/g for zinc and lead, respectively. Similar results were observed in this study (30).

Foran et al. were determined the concentration of mercury in 5 brands of fish oil on marketing. Result showed that levels of mercury in the 5 different brands of fish oil ranged from non detectable (6 mg/L) to negligible (10-12 mg/L). The mercury content of fish oil was similar to the basal concentration normally found in human blood (31). La Pera et al. were determined the average amount of heavy metal on a large number of Italian olive oil samples in concentrations ranging from 0 to 2.1 µg/kg for Cd, 9.1-50 µg/kg for Cu, 15.4-70 µg/kg for Pb, and 68.0-576.0 µg/kg for Zn, although little data were found about the presence of these elements in seed oils (32,33). Golimowski et al. were determined the amount of toxic metal such as cadmium, lead, and copper in wine (34). Tuzen was determinate the amount of heavy metals (Fe, Cd, Cu, Mn, Pb, and Zn) in fish samples. He was found that the amount of heavy metals in the fish samples were below those of Public Health Regulation in Turkey (35).

Because edible vegetable oil standards for heavy metal do not exist, but heavy metal contents in the investigated oils are lower than other studies heavy based on our results we could suppose that almond and kernel of apricot with a high resistance to toxic metal contamination. These oils an excellent source of nutrients, trace elements and also bioactive compounds, and it plays the important role in the human nutrition.

According to information obtained from the present study comes to the conclusion that kernel of apricot and almond oils has level of heavy metal under safe limits. Due to all of the kernel were collected from the East Azerbaijan (west part of Iran), in a region with low industrial activity, the heavy metal contamination of the soil, plants, and kernel can be considered as low. Heavy metals, including lead can be hazardous to human health, especially that of a sensitive population, such as children and elderly (36). Thus, materials that provide considerable exposure, including food, should be closely monitored to ensure that concentrations of elements that might be risky should be very low. The results measured in this set of samples were very low and did not violate any of the current standards. The attendance of heavy metals emphasizes the need for regular inspection and a more stringent food safety regular and meticulous monitoring in order to control the heavy metals at the acceptable levels.

Acknowledgement

This study was part of a M.S thesis supported by Tehran University of Medical Sciences.

References

1. Rubaljot K, Mahajan BVC, Dhillon WS. Heavy metal contamination in vegetables, fruits, soil and water-a critical review. International Journal of Agriculture, Environment and Biotechnology 2014; 7(3): 603-12.
2. Khaniki G. Chemical contaminants in milk and public health concerns: a review. Int J Dairy Sci 2007; 2(2): 104-15.
3. Romic M, Romic D. Heavy metals distribution in agricultural topsoils in urban area. Env Geol 2003; 43(7): 795-805.
4. Agrawal A. Toxicity and fate of heavy metals with particular reference to developing foetus. Adv Life Sci 2012; 2(2): 29-38.
5. Liu J, Goyer RA, Waalkes MP. Toxic effects of metals. In: Klaassen CD, editors. Casarett and Doull's toxicology: the basic science of poisons. 7th ed. New York, NY: McGraw-Hill; 2008. p. 931-79.

6. Demirbaṣ A. Concentrations of 21 metals in 18 species of mushrooms growing in the East Black Sea region. Food Chemistry 2001; 75(4): 453-7.
7. DemirbaṣA. Heavy metal bioaccumulation by mushrooms from artificially fortified soils. Food Chemistry 2001; 74(3): 293-301.
8. Crosby NT. Determination of metals in foods. A review. Analyst 1977; 102(1213): 225-68.
9. Cruz GC, Din Z, Feri CD, Balaoing AM, Gonzales EM, Navidad HM, et al. Analysis of toxic heavy metals (arsenic, lead and mercury) in selected infant formula milk commercially available in the Philippines by AAS. E-International Scientific Research Journal 2009; 1(1): 40-51.
10. Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. Journal of Hazardous Materials 2003; 97(1-3): 219-43.
11. Cao H, Chen J, Zhang J, Zhang H, Qiao L, Men Y. Heavy metals in rice and garden vegetables and their potential health risks to inhabitants in the vicinity of an industrial zone in Jiangsu, China. J Environ Sci (China) 2010; 22(11): 1792-9.
12. Roy D, Greenlaw PN, Shane BS. Adsorption of heavy metals by green algae and ground rice hulls. Journal of Environmental Science and Health Part A 1993; 28(1): 37-50.
13. Ashraf W, Mian AA. Levels of selected heavy metals in black tea varieties consumed in Saudi Arabia. Bull Environ Contam Toxicol 2008; 81(1): 101-4.
14. Soomro MT, Zahir E, Mohiuddin S, Khan AN, Naqvi II. Quantitative assessment of metals in local brands of tea in Pakistan. Pak J Biol Sci 2008; 11(2): 285-9.
15. Narin I, Colak H, Turkoglu O, Soylak M, Dogan M. Heavy metals in black tea samples produced in Turkey. Bull Environ Contam Toxicol 2004; 72(4): 844-9.
16. Khaniki GRJ, Yunesian M, Mahvi AH, Nazmara S. Trace metal contaminants in Iranian flat breads. J Agric Soc Sci 2005; 1(4): 301-3.
17. Khaniki GRJ, Dehghani MH, Mahvi AH, Nazmara S. Determination of trace metal contaminants in edible salts in Tehran (Iran) by atomic absorption spectrophotometry. J Biol Sci 2007; 7(5): 811-4.
18. Pehlivan E, Arslan G, Gode F, Altun T, Ozcan M. Determination of some inorganic metals in edible vegetable oils by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Grasas y Aceites 2008; 59(3): 239-44.
19. Lo Coco F, Ceccon L, Ciraolo L, Novelli V. Determination of cadmium(II) and zinc(II) in olive oils by derivative potentiometric stripping analysis. Food Control 2003; 14(1): 55-9.
20. Farzin L, Moassesi ME. Determination of metal contents in edible vegetable oils produced in Iran using microwave-assisted acid digestion. Journal of Applied Chemical Research 2014; 8(3): 35-43.
21. Moayedi A, Rezaei K, Moini S, Keshavarz B. Chemical Compositions of Oils from Several Wild Almond Species. J Am Oil Chem Soc 2011; 88(4): 503-8.
22. Khemnani S, Aswani B, Arora A, Sindal RS. Detection of heavy metal contents in the seed oil of solanum malongena (egg plant) of arid zone. International Journal of Basic and Applied Chemical Science 2012; 2 (1); 59-65.
23. Dugo G, La Pera L, La Torre GL, Giuffrida D. Determination of Cd(II), Cu(II), Pb(II), and Zn(II) content in commercial vegetable oils using derivative potentiometric stripping analysis. Food Chemistry 2004; 87(4): 639-45.
24. World Health Organization. Quality directive of potable water. 2nd ed. Geneva, Switzwerland: WHO; 1994. p. 197.
25. Kale V, Katikaneni SPR, Cheryan M. Deacidifying rice bran oil by solvent extraction and membrane technology. J Amer Oil Chem Soc 1999; 76(6): 723-7.
26. Prasad MNV. Heavy metal stress in plants: from biomolecules to ecosystems. New York, NY: Springer; 2004.
27. Hayes RB. The carcinogenicity of metals in humans. Cancer Causes Control 1997; 8(3): 371-85.
28. Montaser A, Golightly D. Inductively coupled plasmas in analytical atomic spectrometry. New York, NY: Willey; 1987.
29. Ansari R, Kazi TG, Jamali MK, Arain MB, Wagan MD, Jalbani N, et al. Variation in accumulation of heavy metals in different verities of sunflower seed oil with the aid of multivariate technique. Food Chemistry 2009; 115(1): 318-23.

30. Mendil D, Uluozlu OD, Tuzen M, Soylak M. Investigation of the levels of some element in edible oil samples produced in Turkey by atomic absorption spectrometry. J Hazard Mater 2009; 165(1-3): 724-8.
31. Foran SE, Flood JG, Lewandrowski KB. Measurement of mercury levels in concentrated over-the-counter fish oil preparations: is fish oil healthier than fish? Arch Pathol Lab Med 2003; 127(12): 1603-5.
32. La Pera L, Lo Coco F, Mavrogeni E, Giuffrida D, Dugo G. Determination of copper (II), lead (II), cadmium (II) and zinc (II) in virgin olive oils produced in Sicily and Apulia by derivative potentiometric stripping analysis. Italian Journal of Food Science 2002; 14(4): 389-99.
33. La Pera L, Lo Curto S, Visco A, La TL, Dugo G. Derivative potentiometric stripping analysis (dPSA) used for the determination of cadmium, copper, lead, and zinc in Sicilian olive oils. J Agric Food Chem 2002; 50(11): 3090-3.
34. Golimowski J, Valenta P, Nurnberg H. Toxic trace metals in food. Z Lebensm Unters Forch 1979; 168(5): 353-9.
35. Tuzen M. Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. Food Chemistry 2003; 80(1): 119-23.
36. Muchuweti M, Birkett JW, Chinyanga E, Zvauya R, Scrimshaw MD, Lester JN. Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: Implications for human health. Agriculture, Ecosystems and Environment 2006; 112(1): 41-8.