

Original Article

Determination of Heavy Metals in Apricot and Almond Oils

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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.

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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 apricot kernel (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 ($\mu\text{g}/\text{kg}$) 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 $\mu\text{g}/\text{g}$, and 214 $\mu\text{g}/\text{g}$, 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 $\mu\text{g}/\text{kg}$ (for Al), 15 $\mu\text{g}/\text{kg}$ (for Cd), 18 $\mu\text{g}/\text{kg}$ (for Pb), 14 $\mu\text{g}/\text{kg}$ (for As) and $< 1 \mu\text{g}/\text{kg}$ (for Hg). Furthermore, the average of heavy metals detected in almond oil samples was as follows; 1019.73 $\mu\text{g}/\text{kg}$ (for Al), 10 $\mu\text{g}/\text{kg}$ (for Cd), 21 $\mu\text{g}/\text{kg}$ (for Pb), and 11 $\mu\text{g}/\text{kg}$ (for As). And $< 1 \mu\text{g}/\text{kg}$ (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 \pm 14.0	100.3 \pm 1.4	0.1
As 189.042 (ppb)	100	95.3 \pm 2.5	95.3 \pm 2.5	1.2
Cd 214.438 (ppb)	100	93.7 \pm 0.7	93.7 \pm 0.7	0.1
Cr 205.618 (ppb)	100	96.4 \pm 1.7	96.4 \pm 1.7	0.1
Hg 184.950 (ppb)	100	98.2 \pm 1.2	98.2 \pm 1.2	1.0
Ni 221.648 (ppb)	100	90.2 \pm 1	90.2 \pm 1	0.3
Pb 220.353 (ppb)	100	88.3 \pm 2.1	88.3 \pm 2.1	2.0
Sb 206.833 (ppb)	100	96 \pm 0.6	96 \pm 0.6	0.5
Sn 189.991 (ppb)	100	94.2 \pm 0.3	94.2 \pm 0.3	0.2
Sr 407.771 (ppb)	1000	981.6 \pm 4.0	98.2 \pm 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	0.335	0.274	0.195	0.182	-	0.266	-	0.783	0.416	0.711
(95%)										
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	0.207	0.069	0.698	0.870	-	0.688	-	0.293	0.158	0.569
(0.95)										
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.

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