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QUALITY ASSESSMENT OF EDIBLE VEGETABLE OILS FOR PRESENCE OF SOME TOXIC HEAVY METALS

(With 4 Tables)

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(Received at 3/10/2009)

تقييم جودة الزيوت النباتية عن تواجد بعض المعادن الثقيلة السامة

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يعتبر عنصرى الرصاص والكادميوم من أهم العناصر الثقيلة وأشدها ضررا بصحة الأنسان ويتم التعرض لتلك الملوثات من خلال الغذاء ولما كانت الزيوت تمثل جانبا أساسيا فى الوجبات الغذائية فقد أجريت هذه الدراسة لمعرفة مدى تواجد مستويات كلا من الرصاص والكادميوم فى الزيوت المختلفة ومقارنة هذه التركيزات بالحدود المسموح بها دوليا. تم تحليل ٤٥ عينة من مخلوط زيت فول الصويا وعباد الشمس ، زيت عباد الشمس ، زيت الذرة (١٥ عينة لكل صنف) قبل وبعد المعاملة الحرارية. وقد أسفرت الدراسة أن عنصر الرصاص فى عينات الزيت يتراوح من ٠,٠٢٥٤ -٠,٠٨٨٥ و٠,٠٣٢٦ -٠,٠٥٧٧ و٠,٠٤٦٣ -٠,٠٤٩١ مج/كجم على التوالى بينما عنصر الكادميوم فى الزيوت يتراوح بين غير مكتشف- ٠,٠٠١٦ و ٠,٠٠٠٧- ٠,٠٠١٤ و ٠,٠٠١٥- ٠,٠٠٢٩ مج/كجم على التوالى. ولقد وجد أن هناك انخفاض ملحوظ في تركيز الرصاص والكادميوم بعد المعاملة الحرارية. وقد أظهرت النتائج أن جميع عينات الزيت لاتتعدى الحد المسموح به دوليا. هذا وقد تم مناقشة المصادر المختلفة لتلوث الزيوت بالمعادن الثقيلة وكذلك خطورتها على الصحة العامة. لذا ينصح بإتباع نظم تحديد المخاطر في منع أو تقليل تلوث الزيوت بالمعادن الثقيلة.

SUMMARY

A total of 45 samples of vegetable oils including soybean and sunflower mixture, sunflower and corn oils (15 each) were examined for detection of the levels of lead (Pb) and cadmium (Cd) before and after frying. The oil samples were evaluated according to their safety for human consumption based on provisional tolerable weekly intake (PTWI). The obtained results revealed that the lead concentrations before frying were ranged from 0.0254 - 0.0885, 0.0326 - 0.0577 and 0.0463 - 0.0491 mg/kg for the examined samples, respectively. The cadmium levels before frying were ranged from below detectable limits (BDL) - 0.0016, 0.0007 - 0.0014 and 0.0015 - 0.0029 mg/kg for the examined samples, respectively. Moreover, the results pointed out that a significant decrease in the levels of metals in the examined oil samples after frying. The concentrations of lead and cadmium were within the maximum permissible limits (MPL). The results also illustrated that PTWI of the examined samples not exceeded the permissible limit fixed for lead and cadmium. The source of metals contamination and public health significance were also discussed.

Key words: *Vegetable oils, soybean, sunflower, heavy metals, lead, cadmium.*

INTRODUCTION

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. They also play an important role in metabolic reactions in the human body. They contain fatty acids, which are susceptible to attack by a number of agents e.g. light, oxygen and metals (Erol *et al.,* 2008).

Vegetable oils are beneficial and popular due to their cholesterol lowering effect. In contrast to animal fats, which are predominately saturated and hence do not react readily with other chemicals especially oxygen, unsaturated vegetable oils are more reactive (Matalgyto and Al-Khalifa, 1998). The quality of edible oils is directly related to the concentration of metals. Levels of trace metals like Fe, Cu, Ca, Mg, Co, Ni and Mn are known to increase the rate of oil oxidation, while other element such as Pb and Cd are very important on account of their toxicity and metabolic role (Anthemidis *et al.,* 2005).

The content of metals and their chemical forms in edible oils depends on several factors. The metals might originate from the soil and fertilizers and intimately incorporated in the oil. Many reports have described the deleterious effects that trace metal contamination have on the flavor and oxidative stability of oil, as they can act as autooxidation accelerators altering the flavor and quality of the product over the time (Hendrikse *et al.,* 1991; Eunok Choe and David Min, 2006).

Determination of heavy metals in vegetable oils is one of the criteria for the assessment of quality of oil in regard to freshness, keeping properties and storability. Determination of lead and cadmium in vegetable oils include potentiometry, spectrophotometry, atomic spectrometry and hydride generation-atomic absorption spectrometry, inductively coupled-plasma atomic emission spectroscopy, graphite furnace atomic absorption spectroscopy, neutron activation analysis and direct current plasma atomic emission spectroscopy (Zeiner et al., 2005; Cindric *et al.,* 2007; Mehtap *et al.,* 2008; Abbasi *et al.,* 2009 and Mendil *et al.,* 2009).

The widespread of contamination with heavy metals in the last decades has raised public and scientific interest due to their dangerous effects on human health. This has led researchers allover the world to study the pollution with heavy metals in air, water and food to avoid their harmful effects and to determine their permissibility for human consumption. Therefore, the present work was designed to study the following:

1. Determination of lead and cadmium levels in some commercial vegetable oils.
2. The effect of frying on the levels of lead and cadmium in the examined oil samples.
3. Calculation of the provisional tolerable weekly intake for both metals.

MATERIALS and METHODS

Sampling

In this study, 45 samples of vegetable oils include soybean and sunflower mixture, sunflower and corn oils (15 each) were collected from different markets in their plastic bottles (1 liter capacity) and transferred directly to the laboratory for analysis. Each sample was divided into two parts after being thoroughly mixed. The first part was analyzed for levels of lead and cadmium, while the other part was analyzed after frying for about (20-30 min.)

Digestion of samples (Leonardis *et al.,* 2000)

All steps in the sample preparation procedure were carried out in a laboratory equipped for trace element analysis to avoid contamination of the specimens. Weight 2.0-3.0 g of each oil sample after carefully thoroughly mixing directly into test tube and then add 1 ml of 10% diluted nitric acid. The oil-acid mixture was shaken for one min. using a test tube mixer until the layers were completely mixed. The capped-test tube was placed in shaking water bath at 50°C for 2 h. After centrifugation at 2800 rpm for 10 min, the lower acid aqueous layer was withdrawn with a pipette into a Macarteni tube and then completed to 25 ml by adding deionized water.

Preparation of blank solution

Ten ml of conc. HNO_3 in screw-capped digestion tube was heated at 50°C for 2 h., and then diluted with 25 ml deionized water. The reagent blanks were prepared and measured in the same way as samples.

Recovery experiment

To assure the accuracy of the data reported, recovery experiments were performed. A known amount of each metal (5 and10 µg) of lead and cadmium were added to a known weight of oil (3 g). The samples were digested and measured in the same way as samples. The recovery rates were calculated and the metal concentrations were determined on a wet weight as µg/kg.

Measurement of lead and cadmium levels

The extracted samples were analyzed for lead and cadmium levels using Thermometer electron corporation, S series Atomic Absorption Spectrometere-Type S4AA system (AAS), S-No. GE 711838) at a wave length of 405.8 nm and 326.1nm for lead and cadmium, respectively. The experiment were carried in Microanalytical Laboratory, Faculty of Agriculture. Suez Canal University.

Calculation of PTWI

The acceptable weekly intake of Pb and Cd was calculated on the basis that an adult person (60 kg b.w.) consuming 7 teaspoonful (35 g) oil according to USDA (1994). The results were compared with those recommended by WHO (1993).

Statistical analysis

Data were statistically analyzed by T-test as a pair using SPSS (version 10.0 for Windows; SPSS Inc., Chicago, IL. USA).

RESULTS

Table 1: Recovery rates for accuracy evaluation of the determination method.

Element	Amount of element added (µg)	Amount found (µg)	Recovery rate
Lead	5	4.8	97%
	10	9.7	
Cadmium	5	4.9	98%
	10	9.8	

Table 2: Lead concentrations (mg/kg) in the examined oil samples before and after frying

Type of sample	Min	Max	Mean ± SE
Soybean and sunflower oil mixture before frying	0.0254	0.0885	0.0499±0.004[ns]
Soybean and sunflower oil mixture After frying	0.0243	0.0721	0.0472±0.003[ns]
ns : non significant ($P > 0.05$)			
Sunflower oil before frying	0.0326	0.0577	0.0431±0.002[a]
Sunflower oil after frying	0.0318	0.0423	0.0392±0.001[b]
a and b:Highly significant ($P \leq 0.01$)			
Corn oil before frying	0.0463	0.0491	0.0479±0.0001[c]
Corn oil after frying	0.0457	0.0475	0.0464±0.0001[d]
c and d:Highly significant ($P \leq 0.01$)			

Table 3: Cadmium concentration (mg/kg) in the examined oil samples before and after frying

Type of sample	Min	Max	Mean ± SE
Soybean and sunflower oil mixture before frying	BDL	0.0016	0.0005±0.0001[a]
Soybean and sunflower oil mixture after frying	BDL	0.0007	0.0003±0.00005[b]
a and b: Significant ($P > 0.05$)			
Sunflower oil before frying	0.0007	0.0014	0.0011±0.00005[c]
Sunflower oil after frying	0.0001	0.0005	0.0003±0.00003[d]
c and d: Highly significant ($P \leq 0.01$)			
Corn oil before frying	0.0015	0.0029	0.0024±0.0001[e]
Corn oil after frying	0.0003	0.0006	0.0004±0.00002[f]
e and f: Highly significant ($P \leq 0.01$)			

BDL: below detectable limit

Table 4: The Maximum estimated Provisional tolerable weekly Intake value of lead and cadmium (mg/kg b.w./week) within the calculated intake from the examined edible oil samples

Type of oil	Calculated daily intake of Pb and Cd from consumption of oil (mg/kg body weight/week)	
	PTWI of Pb	PTWI of Cd
Soybean and sunflower oil mixture	0.0002	0.000002
Sunflower oil	0.0001	0.000004
Corn oil	0.0002	0.00001

[a]: according to USDA Recommendation

DISCUSSION

The presence of heavy metals in food has relieved considerable attention during the last few decades. Most human beings ingest heavy metals via food during daily diets, although their quantity varies from place to place depending on dietary habits and levels of environmental pollution. Vegetable oils are widely used in the cooking and food processing, cosmetics, pharmaceutical and chemical industries. Therefore, oils represent a significant source of heavy metals (Dugo *et al.*, 2004).

The accuracy of the method was evaluated by mean of trace element determination. The achieved results reported in Table (1) reveal that the recovery rates of Pb and Cd in oil were 97 % and 98 %., respectively.

The concentration levels of Pb in the analyzed oils are illustrated in Table (`2). Lead concentration in edible oils before frying were found between 0.0254 – 0.0885, 0.0326 – 0.0577 and 0.0463 – 0.0491 mg/kg for the examined oil samples, respectively. The obtained results of lead was found to be within the maximum permissible limit of Codex Standard (1999), and European Community (2001) and Egyptian Standard (2005), which fixed that the legal concentration for lead in vegetable oils must not exceed 0.1 mg/kg.

The recorded results were agreed with those obtained by Hendrikse *et al.* (1991), who found that the lead level in soybean oil was ranged from 0.018-0.090 mg/kg. Erol *et al.* (2008) and Mendil *et al.* (2009) detected lead in sunflower oil at arrange of 0.0013-0.0026 mg/kg and 0.01-0.03 μg/kg, respectively. Moreover, Agilent Technologies publication (2008) reported the level of lead in sunflower and corn oil at the levels of 0.11 and 0.55 μg/kg, respectively. On the other hand, Erol *et al.* (2008) couldn't detect lead in an of the examined soybean and corn oil samples

Lead is a very important heavy metal because it shows toxic effect on living systems. Human absorbs lead in small amounts from food, water and air. The lead ions inhibit a select group of enzymes, including thiol-dependent enzymes involved in heme synthesis and mitochondrial energetic. The toxicological effect of lead may result from the ability of it to uncouple oxidative phosphorylation and modify mitochondrial ion transport. Lead also decreases glucose-6-phosphate dehydrogenase activity in human, and thus decreases the glutathione level in red blood cells. When the blood lead concentrations are near to

80 mg/L or greater, basophilic stripping occurs in erythrocytes (Abbasi *et al.,* 2009). According to WHO, 15-18 million children in the developing countries have suffered permanent from brain damage as a result of lead poisoning (Tong *et al.*, 2000).

Cadmium concentration in edible oils before frying were found between BDL – 0.0016, 0.0007 – 0.0014 and 0.0015 – 0.0029 mg/kg for the examined oil samples, respectively (Table, 3). The cadmium levels are considered within the maximum permissible limits approved by WHO (1993) which fixed the allowable weekly intake of cadmium at 7 µg/kg of body weight.

Nearly similar results were recorded by Tahsin and Yankov (2007); Agilent Technologies publication (2008); Erol *et al.* (2008); Mehtap *et al.* (2008) and Mendil *et al.* (2009), who detected cadmium in sunflower oil samples at levels of 0.03 mg/kg; 0.6 µg/kg; 0.0008-0.0045 mg/kg; 0.55-1.53 µg/g and 0.09-4.57 µg/kg, respectively. Agilent Technologies publication (2008); Erol *et al.* (2008) and Mehtap *et al.* (2008) detected cadmium in corn oil samples in concentration of 0.6848 µg/kg; 0.0002-0.0013 mg/kg and 0.58-1.55 µg/g, respectively.

According to Tahsin and Yankov (2007) cadmium is a microelement and its presence in non-biological doses in living organisms bring to appearance of high toxic effect. Cadmium intoxication and its accumulation in the liver and kidney are connected with the formation of the low-molecular protein metalotionein that contains cistein which combines with Cadmium. While the time of accumulation continues, the quantities of metal in organs also increase. These properties of Cadmium make it especially dangerous.

The results reported in the same tables also revealed that soybean and sunflower mixture oil contained higher values of lead (0.0499±0.004), followed by corn oil (0.0479±0.0001) and sunflower oil (0.0431±0.002). While for Cd, the high levels was found in corn oil (0.0024±0.0001), followed by sunflower oil (0.0011±0.00005) and soybean and sunflower mixture oil (0.0005±0.0001). The variations in the metal concentrations reported may be attributed to many factors including both endogenous factor connected with the plant metabolism and hexogenous factors due to contamination from soil fertelizers, the agronomic techniques of production and collection of plants and seeds, irrigation water, during oil extraction and treatment process systems (as bleaching, hardening, refining and deodorization) which make the oils come in contact with metallic surface area often at high temperatures, materials of packaging and storage, as well as presence of industry or highways near plantation (Erol *et al.,* 2008; Mendil *et al.,* 2009).

Regarding effect of frying on the concentration values of lead and cadmium, the results presented in the same tables pointed out that a significant decrease in the levels of metals in the examined oil samples after frying, this results are run parallel to that obtained by (Atta *et al.,* 1997; Morgan, 1999; Gemma *et al.,* 2008), who mentioned that cooking of food reduced level of metal concentration as food can adsorb metals during cooking. These depend on several factors such as time, temperature and medium of cooking.

The result illustrated in Table (4) revealed that the calculated provisional tolerable weakly intake of lead for adult person (60 kg) consuming 35 gm of oil was 0.0002, 0.0001and 0.0002 mg/kg b.w./week for the examined oil samples, respectively. In case of cadmium, the PTWI was 0.000002, 0.000004 and 0.00001 mg/kg b.w./week, respectively. The PTWI of lead and cadmium is likely not exceeded the limit approved by WHO (1993) which were 0.025 and 0.007 mg/kg b.w./week, respectively. Considering the fact that heavy metals could reach human body from different sources as food, water or by inhalation and once the heavy metals fall in human body do not decompose but are accumulated in certain quantities and harm some organs especially liver, kidney, heart and immune systems. Also, lead has severe health effects even at relatively low levels in the body that it can cross the placenta and damage developing fetal nervous systems (Dugo *et al.,* 2004).

In conclusion, the present study revealed that commercial oil samples examined contain lead and cadmium at levels not exceed maximum permissible limits. Also, frying had a significant decrease in the levels of metals in the examined samples. It should be noticed that human could take metals from different sources and their effects becomes apparent only after years of exposure. Therefore, application of HAACP system on manufacturing process of oils beside the food chain of the oil seed plant should be applied to produce oils safe for human consumption.

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