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FAAS DETERMINATION OF CADMIUM AND LEAD CONTENT IN FOODSTUFFS FROM NORTH-EASTERN ROMANIAN MARKET

Constantin CIOBANU*, Bogdan Gabriel ȘLENCU, Rodica CUCIUREANU
Department of Environmental and Food Chemistry, Faculty of Pharmacy
University of Medicine and Pharmacy "Gr. T. Popa" Iași, Romania

ABSTRACT. Toxic metals may enter foods from various sources: soil, chemicals used for agricultural land, water used in food processing or cooking, equipment, containers and utensils used for food processing etc. The presence of cadmium and lead in the environment and foodstuffs represents an important problem in most of the countries. Exposure to toxic metals through consumption of contaminated food products is associated with various health risks and has aroused widespread concern in human health. Toxic metals are connected to cardiovascular disease, impaired fertility, nervous and immune system disorders, increased spontaneous abortions etc. Concerns about lead exposure as an important public health problem increased, as witnessed by the adverse health effects at lower levels. Moreover, this problem is complicated by the fact that these two metals show no biological function in humans. The aim of this study was to determine the levels of cadmium and lead in various foodstuffs from northeastern Romanian market.

Keywords: cadmium, lead, foodstuffs, F-AAS, food

INTRODUCTION

Lead and cadmium are natural constituents of earth's crust, their omnipresence resulting largely from anthropogenic activities: mining and siderurgical activities, burning fossil fuels, paint industry, waste storage and incineration etc. (EFSA, 2009, 2010; Nordberg et al., 2007). Air is considered to be a pollution source with lead and cadmium, as metal particles emitted from factories, cars etc. are carried by air currents and are deposited on soil and plant surface. Metals can change their chemical form but cannot be degraded or destroyed, which means that they are persistent in the environment and can bioaccumulate in the animal or plant body. Cadmium and lead toxicity and their ability to bioaccumulate in the tissues of living organisms required the adoption of an European legislation that establishes the maximum levels of certain metals, including cadmium and lead in foods (EC, 2001, 2005).

Plants are important components of the ecosystem because they transfer essential elements from the abiotic environment into the biotic one. The main sources of elements for plants are: air, water, soil. Water used for the irrigation of cereals, vegetables, fruits may be contaminated with these toxic metals as a result of wastewater treatment activities, discharge of domestic waste in the surface water etc. (Skerfving et al., 2007; Nordberg et al., 2007). When due to repeated irrigation with sewage waters the soil capacity to retain these toxic metals is reduced, cadmium and lead can pass into ground waters (Chary et al., 2008).

Diet is the main route of exposure to heavy metals in the case of non-smoking population (ATSDR, 2007; Jarup et al., 2009), representing more than 90% compared with other routes of exposure (inhalation, skin contact). Exposure to these toxic metals has been associated with a broad range of biochemical, physiologic and behavioural dysfunctions (Courtois et al., 2003; ATSDR, 2008). Therefore, the accumulation of these two metals in the environment represents a stringent problem, due to the food safety issues and potential risks to human health (Zheng et al., 2007; Castro-Gonzaleza et al., 2008; Mingli et al., 2008). Although the quantities of cadmium and lead in food are relatively low and absorption in the gastrointestinal tract is reduced, daily exposure for a long period of time and the long half-lives in the body leads to a significant accumulation of the metals.

Grains, fruits and vegetables grown on soils contaminated with these metals retain large enough quantities to constitute a major source of exposure to these toxics (Chaudri et al., 2007). Another problem represents the use of chemicals: fertilizers, insecticides, fungicides and herbicides. These products may contain metals and their addition can increase the concentration of toxic metals in soil (Frost et al., 2000). However, the chemical and physical form of the metals found in the soil can influence their uptake by plants (Barnard et al, 1997).

Another important source of food pollution with lead and cadmium is represented by the foodstuff's contact with the processing machineries, preserving foodstuffs in metal packaging and of course, the influence of processing factors (temperature and the processing type) (Ersoy et al., 2006). The lead and cadmium content in food products varies depending on numerous factors: the nature of the food product, geographic area, time of the year in which it was cultivated or produced (Caggiano et al., 2005; Yuzbasi et al., 2003). Various methods used for processing and packaging food products can influence the chemical parameters and implicitly the metals content. As a result, lead and cadmium content varies on a broad range and that is why the permanent monitoring of these toxic metals is necessary.

**Correspondence:* Ciobanu Constantin, University of Medicine and Pharmacy "Gr. T. Popa" Iași, Faculty of Pharmacy, Department of Environmental and Food Chemistry, 16th Universitatii Street ,700115, Iași, Romania, email: costy_pharm@yahoo.com
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Lead and cadmium are known not only for their toxicity but also because they interfere with the metabolism of some essential metals. Nutritional deficiencies amplify the risk of exposure to lead and cadmium from food consumption by increasing the absorption and toxicity of the two metals. Essential metals which are influenced by the concentrations of lead and cadmium are calcium, iron and zinc (Goyer, 1995). After ingestion of lead and/or cadmium, their gastrointestinal absorption is influenced by various physiological factors (e.g. age, fasting, pregnancy, etc.) and the physicochemical characteristics of the ingested material (particle size, solubility, etc). Cadmium absorption in the gastrointestinal tract is less than 5%, but if the body's reserves of iron, calcium and zinc are low, then cadmium's absorbtion may increase (ATSDR, 2008). In lead's case, its gastrointestinal absorption is about 3-10% in adults and up to 50% in children (ATSDR, 2007). The International Agency for Research on Cancer (IARC) has classified cadmium as a human carcinogen (group 1) and lead as being carcinogen for animals and possible carcinogen for humans (group 2A) on the basis of "limited evidence" in humans and "sufficient evidence" in animals (WHO, 2010).

All these factors have led to the spread of toxic metals in the environment and consequently affecting the health of the population which consumes the food contaminated with these harmful elements. Therefore, risk assessment resulting from exposure to toxic metals is a major concern for public health protection.

The aim of this study was to determine the levels of cadmium and lead in various foodstuffs from north-eastern Romanian market in order to establish the consumer's risk of exposure to these toxic metals.

MATERIALS AND METHODS

Sampling

Cadmium and lead concentrations were determined from a total of 183 food samples purchased from different markets across north-eastern Romania in 2010 and 2011. For each food type there were taken between 3 and 10 samples from different locations and for each sample there were collected 3 subsamples, which were subsequently homogenized prior the analysis. The parts of the samples that were mechanically damaged or rotten were removed and only the edible parts of the samples were used for analisys. To mimic the human intake conditions, the samples were cut into smaller pieces.

Reagents

All the reagents used for the digestion of the samples were of analytical grade. Purified water was used for all dilutions. All the glassware was cleaned by soaking in a 10 % nitric acid solution and rinsing them with purified water prior to use to prevent contamination. The element stock solutions (1000 μg/ml) were provided by Inorganic Ventures (Madrid, Spain).

Apparatus

The concentrations of cadmium and lead were determined in an air-acetylene flame by HR-CS AAS (High Resolution Continuum Source Atomic Absorbtion Spectrometry) (ContrAA 300, Analytic Jena, Germany). Instrumental parameters were optimized in accordance with manufacturer's recommendations. AAS working conditions are given in Table 1.

Sample preparation

Approximately 20 to 30 grams of homogenized samples were left overnight at a temperature of 105 º C and after that the samples were dry-ashed at a temperature of 450 º C using a muffle furnace (Nabertherm, Germany) until a white or grey ash residue was obtained. The residue was treated with 5 ml HNO3 65% and maintained on a sand bath at a temperature of approximately 150 º C in order to dissolve the remaining ash. The solution was filtered and brought up to a volume of 25 ml with purified water. A blank digest was carried out in the same way.

Statistical analysis

The results were statistically analyzed using Microsoft Excel 2007. Values were expressed as mean ± standard deviation.

Table 1

Operating conditions of flame atomic absorption spectrometry

Analised metal	Cd	Pb
Wavelenght (nm)	228.8018	217.0005
Flame Length Burner (mm)	100	100
Flame	Air-Acetylene	Air-Acetylene
Gas mixture flow (L/h)	50	65

RESULTS AND DISCUSSIONS

The average concentrations (mg/kg) ± standard deviation, the minimum and maximum values of lead and cadmium in some foodstuffs from the northeastern Romanian markets are presented in Table 2.

Lead and cadmium were found to vary widely among studied foodstuffs. Cadmium levels were observed to be the lowest (except the cow kidney) while the levels of lead were the highest (fig. 3). These toxic metals affect the nutritional principles of the fruits and vegetables and also have negative effects on human and animal organism. International regulations on food quality set the maximum permissible levels of toxic metals in human food; therefore monitoring the concentrations of toxic metals in foodstuffs is an important aspect (Radwan et al., 2006).

Lead was found in 90% of the analyzed samples. The distribution of lead in the positive samples was: 54.88% in samples of plant origin foodstuffs, 31.1% in meat product samples and 14.02% in sweets samples (fig. 1). Regarding cadmium levels, 88% of the analyzed samples were found to be positive: 58.64% in plant origin foodstuff samples, 32.1% in meat product samples and 9.26% in sweets samples (fig. 2). The medium lead content in food products varied between concentrations which were lower than the detection limit in the case of milk and eggs and high concentrations of 0.132 mg/kg and 0.122 mg/kg in dried parsley, respectively dill leafs, 0.137 mg/kg lead in fresh spinach leafs, 0.222 mg/kg lead in cow kidney. These values are below the maximum permissible limits established by the European authorities.

High lead content was determined in shelled sunflower seeds, with a mean concentration of 0.393 mg/kg and a maximum value of 1.264 mg/kg. Murillo et al. (1999) showed that sunflower (Helianthus annum) can retain high quantities of cadmium and lead if the soils on which these plants are cultivated have a high content of these toxic metals. Although the degree in which these toxic metals are accumulated in seeds is 18 times lower than that observed in the case of leafs (Murillo et al., 1999), consumer health can be at risk because lead and cadmium have a cumulative effect, with a half-life which exceeds 10 years (Rabinowitz, 1991; Jarup et al., 1998; ATSDR, 2007; ATSDR, 2008).

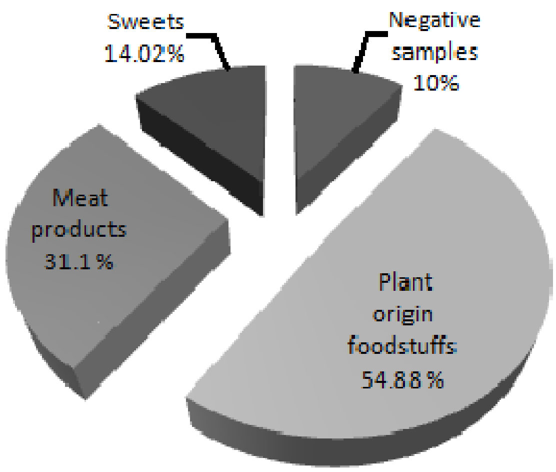

Fig. 1 Lead distribution in analyzed samples

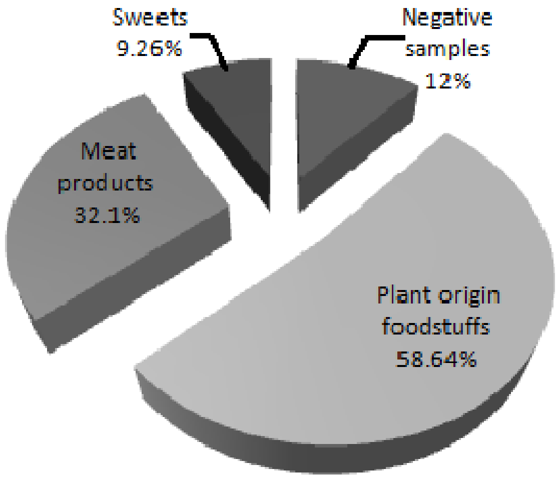

Fig. 2 Cadmium distribution in analyzed samples

Plant pollution with toxic metals represents a problem for consumers, especially in the case of vegetables, fruits, cereals cultivated near areas with intense traffic (highways, roads, etc.). These pollutants, which are deposited on the surface of the plants, can influence considerably the toxic metals content in plants. The level of metals depends largely on the morphological characteristics of the plants (Naszradi et al., 2004). A study carried out in Turkey showed that cadmium and lead levels in apples, grapes, belly pepper and parsley cultivated near areas with intense traffic can be very high: 0.098 mg/kg in tomatoes, 0.061 mg/kg in parsley (fresh product) for cadmium and 0.18 mg/kg in apples, 0.231 mg/kg in grapes, 0.175 mg/kg in tomatoes, 0.139 mg/kg in belly pepper and 0.585 mg/kg in parsley (fresh product) for lead (Bakirdere et al., 2008). Compared with this study, cadmium and lead levels obtained in our study are much lower for these fruits and vegetables. Thus, it is not likely that these fruits and vegetables were cultivated in an area exposed to excessive pollution with these metals. The obtained cadmium and lead levels were 0.02 mg/kg in tomatoes, 0.05 mg/kg in parsley (dried product) for cadmium and 0.092 mg/kg in tomatoes and 0.132 mg/kg in parsley (dried product) for lead.

The medium cadmium content in food products varied between concentrations which were lower than the detection limit in the case of milk and eggs and high concentrations of 0.057 mg/kg in celery roots, 0.229 mg/kg in sunflower kernels and 0.420 mg/kg in cow kidney. Cadmium is accumulated mainly at renal and hepatic level, this is why these two organs contain considerable amounts of cadmium (Satarug et al., 2000). The level of cadmium which was determined in this study is higher than that which was obtained by Galal-Gorchev (1993) (0.32 mg/kg in viscera). Numerous studies showed that the cadmium levels in food products based on cow kidney can exceed the maximum acceptable limit. Still, the daily cadmium intake through consumption of these food products is low because the viscera are relatively rarely used in the diet (Lopez Alonso et al., 2002). The population which exceeds the cadmium intake limit through food consumption established by WHO is that of Greenland, because seal liver represents the main source for cadmium intake (Johansen et al., 2000).

Table 2

Cadmium and lead concentrations in some foodstuffs from the Romanian market

		Cadmium (mg/Kg)			Lead (mg/Kg)		
N°	Foodstuffs	N°. of analised samples / n°. of positive samples	Minimum/ maximum value	Mean value ± Standard deviation	N°. of analised samples / n°. of positive samples	Minimum/ maximum value	Mean value ± Standard deviation
1	Corrots	6 / 6	0.006 / 0.046	0.021 ± 0.014	6 / 5	0.044 / 0.115	0.092 ± 0.028
2	Tomatoes	9 / 8	0.007 / 0.080	0.020 ± 0.024	9 / 8	0.020 / 0.072	0.046 ± 0.019
3	Hot peppers	4 / 4	0.012 / 0.074	0.030 ± 0.029	4 / 4	0.035 / 0.102	0.081 ± 0.031
4	Potatoes	7 / 7	0.006 / 0.041	0.025 ± 0.015	7 / 6	0.053 / 0.154	0.092 ± 0.040
5	Fried peanuts	8 / 8	0.011 / 0.085	0.041 ± 0.027	8 / 8	0.050 / 0.185	0.087 ± 0.043
6	Brown bread	6 / 6	0.012 / 0.076	0.039 ± 0.027	6 / 6	0.019 / 0.113	0.069 ± 0.034
7	Dried parsley leaves	5 / 5	0.020 / 0.062	0.050 ± 0.017	5 / 4	0.060 / 0.207	0.132 ± 0.078
8	Dried dill leaves	3 / 3	0.015 / 0.071	0.042 ± 0.028	3 / 3	0.085 / 0.143	0.122 ± 0.031
9	Black olives	3 / 3	0.004 / 0.076	0.029 ± 0.041	3 / 2	0.081 / 0.099	0.090 ± 0.012
10	Celery – root	5 / 5	0.042 / 0.070	0.057 ± 0.011	5 / 3	0.087 / 0.141	0.106 ± 0.030
11	Bananas	6 / 4	0.002 / 0.028	0.011 ± 0.011	6 / 6	0.017 / 0.107	0.056 ± 0.039
12	Oranges	3 / 3	0.006 / 0.033	0.015 ± 0.014	3 / 3	0.022 / 0.080	0.056 ± 0.030
13	Soya - dried	3 / 3	0.003 / 0.066	0.027 ± 0.034	3 / 2	0.050 / 0.101	0.076 ± 0.025
14	Spinach leaves	6 / 4	0.014 / 0.047	0.030 ± 0.017	6 / 5	0.022 / 0.255	0.137 ± 0.102
15	Canned sardines**	4 / 4	0.011 / 0.036	0.029 ± 0.011	4 / 4	0.081 / 0.106	0.093 ± 0.012
16	Canned sardines***	8 / 8	0.008 / 0.046	0.026 ± 0.015	8 / 8	0.023 / 0.182	0.090 ± 0.052
17	Fish roe	7 / 5	0.004 / 0.029	0.014 ± 0.009	7 / 6	0.035 / 0.081	0.059 ± 0.018
18	Coffe	8 / 6	0.005 / 0.016	0.011 ± 0.003	8 / 6	0.018 / 0.109	0.078 ± 0.031
19	Baloney	10 / 10	0.010 / 0.080	0.037 ± 0.027	10 / 9	0.050 / 0.143	0.090 ± 0.031
20	Frankfurters	5 / 5	0.010 / 0.076	0.034 ± 0.030	5 / 5	0.030 / 0.099	0.059 ± 0.030
21	Salami	9 / 9	0.007 / 0.070	0.019 ± 0.019	9 / 9	0.027 / 0.105	0.061 ± 0.022
22	Hen eggs	2 / 0	< LOD*	< LOD*	2 / 0	< LOD*	< LOD*
23	Cow milk	2 / 0	< LOD*	< LOD*	2 / 0	< LOD*	< LOD*
24	Corn flour	4 / 4	0.004 / 0.020	0.012 ± 0.007	4 / 3	0.036 / 0.062	0.047 ± 0.013
25	Wheat flour	8 / 8	0.005 / 0.031	0.020 ± 0.008	8 / 8	0.032 / 0.082	0.058 ± 0.015
26	Cow kidney	6 / 6	0.229 / 0.736	0.420 ± 0.239	6 / 6	0.140 / 0.267	0.222 ± 0.060
27	Vegetal pâté	4 / 4	0.004 / 0.015	0.007 ± 0.005	4 / 4	0.034 / 0.114	0.071 ± 0.037
28	Chocolate with nuts	6 / 5	0.004 / 0.027	0.017 ± 0.009	6 / 6	0.045 / 0.082	0.062 ± 0.015
29	Chocolate****	8 / 4	0.016 / 0.046	0.034 ± 0.016	8 / 8	0.038 / 0.077	0.058 ± 0.014
30	Candies – berries	3 / 2	0.008 / 0.012	0.010 ± 0.002	3 / 3	0.022 / 0.061	0.043 ± 0.019
31	Sunflower kernels	4 / 4	0.003 / 0.407	0.293 ± 0.193	4 / 4	0.077 / 1.264	0.393 ± 0.581
32	Fruit jelly	6 / 4	0.013 / 0.016	0.014 ± 0.001	6 / 6	0.041 / 0.083	0.064 ± 0.016
33	Poultry	5 / 5	0.005 / 0.021	0.013 ± 0.007	5 / 4	0.023 / 0.103	0.068 ± 0.035

** Limit of detection; ** in tomato sauce; *** in vegetable oil; ****Home-made chocolate*

Cadmium content of the fruits and vegetables studied ranged between 0.011 mg/kg in bananas and 0.057 mg/kg in celery root. These concentrations were below the maximum limits. The maximum cadmium level set by the Eeuropean Commission for leafy vegetables, root vegetables and mushrooms is 0.2 mg/kg and 0.05 mg/kg for fruits (EC, 2001; EC, 2005; EC, 2006). Cadmium concentrations found in our study meet the safe limits set by the authorities.

Regarding the medium cadmium and lead levels in canned fish, the levels were situated between 0.09 mg/kg and 0.093 mg/kg for lead and 0.026 mg/kg and 0.029 mg/kg for cadmium; in the case of poultry the medium levels for lead and cadmium were 0.068 mg/kg, respectively 0.013 mg/kg. Yilmaz et al. (2007) reported that cadmium concentrations in various fish species were 0.01 – 0.08 mg/kg and 0.07 – 0.92 mg/kg for lead. According to the recommendations of the European Commission, the lead and cadmium concentrations in fish meat must not exceed 0.3 mg/kg and respectively 0.1 mg/kg and in the case of poultry 0.1 mg/kg and respectively 0.05 mg/kg respectively (EC, 2006).

The values for the two toxic metals which were obtained in this study are below the recommended limit established by the European authorities, both in the case of poultry and in the case of fish, although in the case of lead, the value is near the imposed upper limit. A lead concentration from fish meat usually reflects the metal levels from the environment in which the fish live (sediments, water, food) (Alquezar et al., 2006).

The food products which were analyzed have lead and cadmium concentrations which are lower than the maximum acceptable limits established by the European authorities, so the consumption of moderate quantities of these food products doesn't represent a risk for the consumer's health.

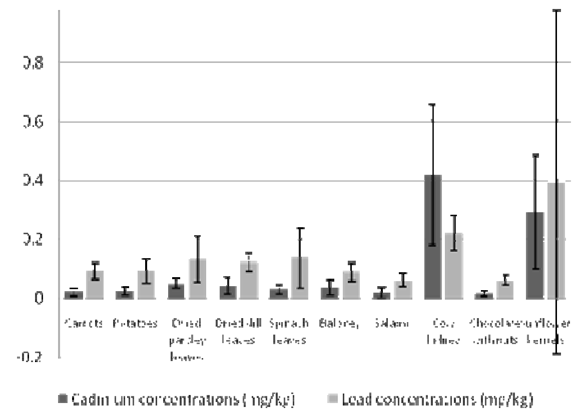

Fig. 3 Comparative levels of cadmium and lead in some food products

CONCLUSIONS

The flame atomic absorption spectrometry method used for determining the concentrations of the two metals in food products is rapid, precise and implies minimum costs. Also, this study provides data regarding the lead and cadmium concentrations in some food products found on the north-eastern Romanian markets and it also can help to evaluate the consumer's risk of exposure to the levels of toxic metals which were presented. As a result, periodic surveys regarding the content of heavy metals in food products should be conducted, in order to evaluate if there are certain risks for public health.

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