Detection of lead and cadmium in some colored dried food products and quick-prepared

Nibras Mohammed A. Alsaffar
Assistant Professor, Market Research & Consumer Protection Center, University of Baghdad, Iraq,
Mahmud Abdullah Jasim Alkhafaji
PhD, Assistant Professor, Market Research & Consumer Protection Center, University of Baghdad, Iraq,

Abstract
In the present study, the concentrations of two heavy metals lead and cadmium (Pb, and Cd) in 26 different of dried fruits samples (Orange, Mango, Pear, green Apple, read apple, Banana, Normal melon, Pineapple melon, Coconut, Lemon), chips and pasta samples were determined by Flame Atomic Absorption Spectroscopy after wet digestion. Samples were collected from different stores in Baghdad market, Iraq. The average of Cd mg/kg concentration in the selected analyzed samples was 0.0220-0.2261 for pasta, 0.0467-0.2797 for chips, 0.0385-0.2261 for dried fruit. For Pb mg/kg average was 0.0090-0.0167 for pasta, not detected-0.0626 for chips, 0.0031-0.088 for dried fruits. The highest concentrations of Cd were found in chips, and the highest of Pb were found in dried fruit. The concentrations of the highly toxic metals (Pb and Cd) in all analyzed samples were below or equivalent to the permissible limits set by different health organizations, including Iraqi Standards. The contamination of these products could be a significant source of consumer exposure to heavy metals when these products are a part of life.
Key word: Fruits , vegetables , toxic metals.

Introduction

Fruits and vegetables are an important component of the human diet as they are major sources of nutrients such as vitamins, fibers, sugars, carbohydrates, and essential minerals that are useful for human health [1]. Several studies have shown that fruits and vegetables consumption are significantly reduce the risk of several chronic ailments such as cancer, heart disease, and stroke [2]. Dried fruits are fruits where a large proportion of their water content is removed either through sun drying, shade drying, solar drying, or the use of an artificial dryer [3]. Dried fruits such as raisins, dates, plums, figs, apricots, peaches, apples, pears, or berries are one of the most important component of the human diet that is widely consumed around the world due to their availability all the seasons, easy to store, and being a healthy alternative to high sugar foods [4]. They are important raw materials in the confectionery industry like candies, jams, and cookies [5]. Dried fruits are concentrated sources of various compounds such as phenol antioxidants, essential minerals, sugars, vitamins, and dietary fibers. Therefore, they have several beneficial effects on human health such as antioxidants, anticancerogens, antimutagens, and antibacterial compounds [6]. Although dried fruits are of great importance in human diet, the health benefits of them can be significantly reduced because of the presence of heavy metals contamination. However, the consumption of dried fruits contaminated with toxic heavy metals may result in a serious risk to human health [7]. In recent years, there is an increasing concern about human exposure to toxic heavy metals as a serious health and environmental problem overall the world [8]. Human exposure to heavy metals has largely increased as a result of rapid urban and industrial

developments [9]. Heavy metals are commonly classified into two types; essential heavy metals and toxic heavy metals. The first type contains heavy metals that are essential and necessary for human biochemical processes such as (Fe, Cu,V, Zn, Se, Co, Mn, Cr2+, Mg and Mo) [10,11]. However, excessive levels of these metals in foodstuffs can be toxic and have adverse effects on the human health [12]. The second type contains the highly toxic heavy metals even at low concentrations like (Hg, Cd, Pb, Cr6+ , Sn, Ni and As)[13]. In general, deficiency or excessive levels of both these two types of metals in foodstuffs may have adverse effects on the human health [14]. Toxic heavy metals are hazardous environmental contaminants since they are not biodegradable, thermostable, and have long biological half-lives [15]. Therefore, they have the ability to accumulate in human body, soil, vegetables, fruits, seawater, and sediments leading to serious health problems [16]. Fruits and vegetables can be contaminated by toxic heavy metals through the absorption of them from the contaminated soil, irrigation with contaminated water, adsorption of vehicular and industrial emissions on the fruits or vegetables surfaces, or by using of large quantities of chemical-based fertilizers and pesticides [17]. Additionally, heavy metals contamination might occur during transportation, packaging, marketing, processing, and storage [18]. In the last years, there is growing interest in monitoring of contamination levels of toxic and essential heavy metals in a wide variety of dried fruits [19].

The objectives of study

the main objectives of this study were (i) to determine the concentrations of toxic (Cd, and Pb) heavy metals in imported dried fruits of different brands sold in the local markets in Baghdad and (ii) to compare the results obtained in this study with similar studies performed in neighboring countries and other countries worldwide.

Food quality and safety

Food quality and safety are perhaps the most important public health issues. Food available on the markets should be free of all chemical contaminants which pose a risk to consumer health, and its safety is not only the responsibility of food producers, but also state governments and agencies that systematically monitor and control food quality [20,21]. A significant risk to the health of potential consumers is food contaminated with heavy metals, such as cadmium (Cd) and lead (Pb), exceeding the maximum permissible limits for food products [22,23]. Heavy metals can be the cause of many chronic diseases whose symptoms are different depending on the level of toxicity of an element, as well as the duration and level of exposure [24,25]. Kidneys and liver are the main organs especially sensitive to Cd toxicity [20]. In the human body, Cd most often causes damage to both of these organs, as well as the testicles, lungs and bones. In addition, it causes a carcinogenic effect, initiating cancers of the prostate, kidneys, pancreas and testicles [27]. This element negatively affects the function of the skeletal system by disturbing the metabolism of calcium, magnesium, zinc, copper and iron. In turn, Pb is a neurotoxic element in general, and specially in children, elevated levels of Pb in the blood may cause changes in the brain, manifested by: lowering of the Iraqin level, a problem with proper perception and concentration and a hyperactivity [28]. Chronic exposure to Pb can be associated with an increased risk of developing neurodegenerative diseases [29]. Moreover, it has been demonstrated that Pb could have a role in the pathogenesis of deep vein thrombosis of lower limbs [30].

Environmental and heavy metals contamination

In the case of vegetables and fruits, the source of their contamination with heavy metals may be the environmental conditions in which the cultivation was carried out [31]. The food product contamination with heavy metals may have also resulted from the migration of these elements from the packaging material. Contamination may have occurred during the technological processes that prepare the products for consumption, for example as the result of using metal kitchen tools [32,33]. In the case of foodstuffs stored in metal cans, the packaging coating may corrode, especially when stored foods have an acidic pH. Corroded metal packaging can become a source of migration of heavy metals, such as tin (Sn), Cd and Pb to the stored product, that increase their content in food [34,35,36]. Human risk assessment can identify methods to minimize exposure to heavy metals, for example by reducing the weekly consumption of contaminated food products [37]. According to the recommendations of the Food and Agriculture Organization of the United Nations, operating at the World Health Organization (FAO/WHO), the daily intake of fruits and vegetables for an adult should be at least 400 g (5 times × 80 g per day) [38]. Due to the seasonality of agricultural production, in countries located in the temperate climate zone there is a need to process food, freeze or dry it, especially those species of vegetables and fruits that are not available for sale all year. This procedure also applies to perishable food, such as soft fruits like strawberries or raspberries. Eating processed, frozen or dried fruits or vegetables can complement a daily diet, especially in periods, when the availability of fresh products is limited. However, not many scientific research concerns the quality of this type of food and its safety for the consumer are studied.

MATERIALS & METHODS

Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade. A multi- element standard solution of 1000 mg/L of each tested element including Cd, and Pb (analytical grade) was obtained from Merck KGaA, Darmstadt, Germany. Nitric acid (HNO_3, 69% v:v, extra pure-trace analysis grade) was obtained from Carlo ERBA reagents, France. Hydrogen peroxide (H_2O_2, 35% w:w, extra pure) was obtained from Scharlau Chemie, Barcelona, Spain. Ultrapure deionized water was used to prepare standard and sample solutions. The working solutions of each examined metal were freshly prepared by diluting an appropriate aliquot of the stock solutions using 0.1% (v:v) HNO_3 and all working done in laboratory of Market Research and Consumer Protection Center in University of Bagdad, Iraq.

Sample collection and pretreatment

With the aim to reduce the risk of contamination and ensure accurate results, all required precautions were taken during sample collection, preparation, and analysis. First, the dried fruit samples were collected in dried polyethylene bags and prepared in a laboratory. A trace element grade nitric acid HNO_3 (extra pure grade) was used for digestion and solution preparation. All glassware apparatus were effectively cleaned and previously soaked in 20% (v:v) HNO_3 for 24 hours and then thoroughly rinsed several times with ultrapure deionized water prior to use. Each sample was analyzed in triplicate. A total of samples consisting of 26 different of dried fruit(Orange, Mango, Pear, green apple, read apple, Banana, Normal melon, Pineapple melon, Coconut, Lemon), chips and pasta samples of different brands Each sample item was purchased by systematic random sampling from four different stores. Samples were carefully washed in de-ionized water to remove dust particles. They were then dried at 105 °C for 24 hours to a constant

weight. The dried samples were then ground and homogenized using blender with stainless steel cutters and stored in clean dry air-tight polyethylene bags until analysis.

Sample preparation

In this study, sample solutions were prepared with some minor modifications. A 2.0 g of homogenized dried fruit sample was placed in 100 mL Erlenmeyer flask, 20 mL concentrated HNO_3 (69%, v:v) was added. The sample was then heated at 145-160 °C until the solubility of the sample was completed and a clear solution was obtained. After that, 3 mL H_2O_2 (35%, w:w) was added to the solution and left to cool down to room temperature. Finally, the solution was filtered and the volume was made up to 25 mL with ultrapure deionized water and then placed in 100 mL polyethylene bottles [39]. Each extract solution of collected samples was analyzed by flame atomic absorption spectrophotometry. All samples were prepared in triplicates. The same procedures were applied for preparation of blank solutions. Samples of tests were taken from local markets and symbolized as in tables (1,2,3) and format as in shown figure(1,2,3,4,5).

Table (1) representing the symbols and types of pasta samples

Symbol	Sample
C1	Non
C2	Read
C3	Green

Table (2) representing the symbols and colors in Chips samples

Symbol	Sample
D1	Green
D2	light pink
D3	Deep pink
D4	Caramel
D5	Orange
D6	Yellow
D7	Blue
D8	Non
D9	Yellow
D10	Read
D11	Orange

Table (3) representing the symbols and colors in dried fruit samples

Symbol	Sample
F1	Orange
F2	Mango
F3	Pear
F4	green apple
F5	read apple
F6	Pear
F7	Banana

F8	Normal melon
F9	Pineapple melon
F10	Coconut
F11	Lemon
F12	Non

Figure (1) colors of pasta samples

Figure (2) colors of Chips samples

Figure (3) colors of finger chips samples

Figure (4) colors in dried fruit samples

Figure (5) colors in dried fruit samples

RESULTS & DISCUSSION

The Iraqi standard no. 1183, 2015 first update for Pasta products macaroni, vermicelli and spaghetti explain the maximum concentration for some heavy element as in illustrated in table (4), in the point 3-1-1-6 indicated that the final product did not contain industrial colors, in this study we did not tested that [40]. The results obtained of the concentration of Pb and Cd in pasta products macaroni, vermicelli and spaghetti showed in table 5, determined in ppm.

Table (4) Iraqi standard no. 1183, 2015 for the maximum metal contaminants in pasta products macaroni, vermicelli and spaghetti in ppm

Metal contaminants	mg/kg max.
Pb	0.2
Cd	0.1

Table (5) concentrations of lead and cadmium in pasta samples in ppm

Sample	Pb ppm	Cd ppm
C1	0.0090	0.0220
C2	0.0099	0.2261
C3	0.0167	0.1148

The Iraqi standard no. 3782, 2001 of the maximum allowable of minerals in fluorinated starchy food semi manufactured (chips), indicated that the quantity of the lead element not exceeding 1 ppm and the rest of the elements are calculated as lead not exceeding 2 ppm as in table (6) [41]. The results obtained of the concentration of Pb and Cd in chips showed in table 7, determined in ppm.

Table (6) Iraqi Standard no. 3782 of 2001 fluorinated starchy food semi manufactured (Maximum Level (ML) of Cd mg/kg) in ppm

Maximum level	Mineral
1	Pb
2	Heavy metal calculated as lead

Table (7) Concentrations of lead and cadmium in chips samples in ppm

Sample	Pb ppm	Cd ppm
D1	0.0626	0.1395
D2	0.0592	0.1808
D3	0.0490	0.0591
D4	0.0116	0.0921
D5	0.0031	0.2797
D6	0.0116	0.2076
D7	0.0575	0.1210
D8	Nil	0.2096
D9	0.0507	0.0467
D10	0.0456	0.2282
D11	0.0371	0.0880

The Iraqi standard no. 2270/9, 2006 first update for microbiological limits in food/part 9, microbiological limits of dried fruits and vegetables and it explain the microbiological limits in food, Technical requirement for vegetables and dried fruits that have no Iraqi standard specifications, technical requirement or any international or Arabic reference, and it adopted at the Accreditation Commission Meeting No. 367 in 18/10/2011 under the title of Technical Requirement No. 70 of 2011 and were pollutants as in Table (8).

Table (8) Technical Requirement No. 70 of 2011 for pollutants limits of dried fruits and vegetables

Metal pollutants	max. limits
Pb	According to codex specifications No. 193
Cd	

Table (9) Codex 193: limits of Cd in fruits

Commodity/Product Name	Maximum Level (ML) of Cd mg/kg	Maximum Level (ML) of Pb mg/kg
Brassica vegetables	0.05	0.1
Bulb vegetables	0.05	0.1
Fruiting vegetables	0.05	0.05

Leafy vegetables	0.2	0.3
Legume vegetables	0.1	0.1
Fruits	-	0.1

The results obtained of the concentration of Pb and Cd in dried fruits and vegetables showed in table (10), determined in ppm.

Table (10) lead and cadmium in Dried fruit samples

Sample	Pb ppm	Cd ppm
F1	0.0881	0.2158
F2	0.0830	0.2261
F3	0.0014	0.0612
F4	0.0371	0.1230
F5	0.0201	0.2199
F6	0.0167	0.1478
F7	0.0422	0.2199
F8	0.0048	0.0818
F9	0.0405	0.0426
F10	0.0031	0.0385
F11	0.0405	0.1271
F12	0.0167	0.0405

Study samples were evaluated for determining the concentrations of two heavy metals including Cd, and Pb, using flame atomic absorption spectrometry. The concentrations of each studied metal in samples are listed in tables 5, 7, and 9. All metals concentrations were determined on a dry weight basis. Metal concentrations of Cd ppm in dried fruit samples were found to be in the range of 0.0220-0.2261 for pasta, 0.0467-0.2797 for chips, and 0.0385-0.2261. for (Pb) 0.0090-0.0167 for pasta, nil - 0.0626 for chips, 0.0031-0.088 for dried fruit and all of this in ppm. The high contamination found in fruit might be closely related to the pollutants in irrigation water, farm soil, fertilizers and also industrial and low pollution household emissions. Differences in levels of contamination between fruits and vegetables may result from the specificity of the geographical area from which they are collected, their diverse capacity to accumulate heavy metals, as well as the way they are processed. It should be pointed out that in polluted environments (soil, water, and air). the presence of toxic metals in elevated concentrations is not uncommon. Due to the structure of consumption of various groups of food products both in Poland and other countries, a significant risk of exposure to heavy metals is associated with the consumption of fruits and vegetables, which are one of the main elements of the diet. Unfortunately, complete elimination of elements such as Cd or Pb from these products is impossible, and the technological processes used in food production can only remove a small part of the impurities from selected products or even contribute to their increased contamination. Thus, there is a need for regular monitoring of heavy metals on every kind of foodstuff, not only in fresh products, in order to estimate the health risk from heavy metals in the human food chain.

Toxic metals

Cadmium is toxic heavy metal and its accumulation in the human body leads to serious health problems such as kidney disfunction, bone diseases, skeletal damage, and reproductive deficiencies [25,28]. According to the Turkish Food Codex and European communities, the maximum Cd concentration permitted in dried fruits is 0.05 μg/g [48,49]. In addition, the Official Gazette of the Republic of Serbia No. 5/92, 11/92, 32/2002, 25/2010 and 28/2011 established the maximum allowable Cd concentration permitted in dried fruits as 0.30 μg/g [17,50]. In this study, results show that the highest Cd concentration was found in dried apricots with a mean of 0.05 ppm, while the lowest Cd concentration was found in dried cranberries with a mean of 0.01 ppm. These results indicate that the average concentrations obtained for Cd in the analyzed dried fruits in this study were found to be within the acceptable range or below the permissible limits set by different health organizations. This implies that the dried fruits investigated in this study are safe for human consumption.

Conclusion

In conclusion, detecting lead and cadmium in some colored dry food products, particularly quick-prepared ones, is essential for ensuring public health and safety. The presence of these toxic heavy metals in food products can lead to serious health risks, including developmental issues in children, organ damage, and various other long-term health problems. The levels of lead and cadmium can be accurately determined through proper testing and monitoring, including the use of advanced techniques like atomic absorption spectrometry (AAS 7000) and inductively coupled plasma mass spectrometry (ICP-MS). Regulatory standards should be enforced to limit the acceptable concentrations of these contaminants in food products to prevent any harmful exposure.

Additionally, public awareness, alongside stringent food safety regulations, is crucial in mitigating the risks associated with contaminated food products. By ensuring the safety of quick-prepared and colored dry foods, we can protect consumers from potential health hazards.

Results obtained in this study showed that the concentrations of toxic heavy metals (Pb and Cd) in the analyzed sample were found to be below or in good agreement with the permissible limits set by different health organizations. Therefore, it can be concluded that the consumption of imported dried fruits sold was safe according to these health organizations.

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