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Heavy Metals Contents in Some Commercially available Coffee, Tea, and Cocoa Samples in Misurata City – Libya

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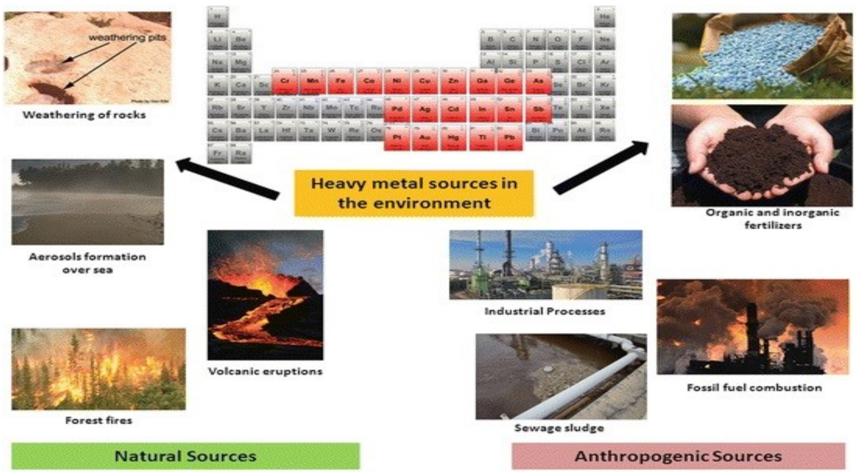
GRAPHICAL ABSTRACT



KEYWORDS

Heavy Metals
Coffee
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Microwave Plasma Atomic Emission Spectrometry

ABSTRACT

The purpose of the present study was to evaluate the concentrations of Mn, Cr, Fe, Cu, Zn, Pb, and Cd in 18 types of commercially available coffee, tea, and cocoa on Misurata city markets. The samples were dry digested and then measured by Microwave Plasma-Atomic Emission Spectrometry (MP-AES). The heavy elements levels were differed among the various types of analyzed samples. The concentrations of Mn were relatively higher than the other analyzed elements and varied between 1.0 – 673.3 mg/kg. The observed concentration ranges of the other elements, were as follows: Cr (0.1- 131.0 mg/kg), Fe (0.3 – 40.6 mg/kg), Cu (0.3 – 13.6 mg/kg), Zn (1.0 -20.9 mg/kg), Pb (1.8 – 4.4 mg/kg) and most Cd samples were below the instrument detection limits. The values determined for Mn, Cr, Fe, Cu, and Zn were lower than the maximum permissible limits. However, the concentrations of Pb were high according to the Brazilian law and Mercosul regulations, and the regulations of the European Union. Monitoring of heavy metal in food, like coffee, teas, and cocoa, provides useful information on safety features of food in regulatory procedures in terms of suitability of food for consumption, as well as its nutritional value.

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1. Introduction

Coffee beans are one of the most exceedingly traded products in the world. More than 100 different plant kinds of the Coffea genus are present in the world. Regardless of the great variety, only two kinds have considerable economic value in the world coffee market: Coffea arabica L. and Coffea canephora Pierre ex A. Formerly known as arabica coffee and robusta coffee or conilon, respectively [1]. Also, tea is one of the most consuming beverages in the world after water and it is made from the leaves of the bush Camellia sinensis. It is usually prepared by pouring boiled water on dried leaves of the tea plant and it is an aromatic beverage. Tea is additionally an infusion of the dried leaves of Camellia sinensis, a member of the Theacea family, in water [2]. Tea can commonly be partitioned into types based on the way it is processed. Some kinds involve Oolong (or wulang), green, black (called red tea in China), yellow, and post-fermented tea (or black tea for the Chinese). Green and black teas are the most common brands of tea. Green tea is made by drying and steaming the leaves, whereas black tea is obtained after a fermentation process [3]. Finally, cocoa products are favorably consumed nutrients worldwide. Cocoa beans are used as raw materials for production of cocoa powder, beverages, candies, and chocolate [4].

Numerous elements that are existed in food at major, minor and trace levels are considered to be important to human well-being; however, the uncontrolled intake of these elements can cause severe health complications. The ideal amount desired for this purpose widely varies relying on the kind of element and the sex and age of the consumers. The human body needs both non-metallic and metallic elements for healthy growth, development and adequate working. Thus, the determination of these elements in food, plant beverages, water, and soil is of most importance and is presently the subject of studies by numerous researchers [5-7]. The determination of trace elements in food is considerably vital due to these elements play important functions in the complex metabolic pathways in the human system, and their lack or excesses may result in diseases. Heavy metals may usually be introduced into the environment and accordingly, living organisms by means of water, air, soil, or even food. However, the degree of their levels relies on the sort of heavy metals and the activities that exist in a particular area [8].

At present, the utmost widespread analytical methods for evaluating heavy metals concentrations of food and other products are atomic absorption spectrometry (Flame-AAS and Graphite Furnace-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectroscopy (ICP-MS), atomic fluorescence spectrometry (AFS), or electrodes. Among these instrumental techniques, optical emission spectrometry based on plasma is the most exceedingly applied due to its high specificity, selectivity and sensitivity, low detection limits, and ease of operation. ICP-OES displays also various features, particularly for routine analysis [9-11]. This work is aimed to evaluate the concentration of some heavy metals: Fe, Cu, Zn, Ni, Mn, Cr, Pb and Cd from different types of coffee, tea, and cocoa commercially available in Misurata city in Libya.

2. Experimental

2.1. Reagents

All reagents were of analytical grade. Deionized water was used as the solvent to prepare the stock and standard solutions, and all glassware was washed, cleaned and dried. All sample containers and glassware were acid soaked in 10 % v/v nitric acid for at least 24 h and then rinsed several times with de-ionized water before use. The stock solutions of metals (1000 ppm) were prepared by dissolving an appropriate salts weight and then diluted before use. The dynamic range of metal concentrations and matrix effect required the dilution of the sample before the analysis.

2.2. Sample Collection and Preparation

Various frequently commercially available and consumed samples were randomly obtained from local supermarkets in Misurata city, Libya. A total of 18 samples of commercially available products (11 coffee samples, 4 tea samples, and 3 cocoa samples) were purchased from several supermarkets. The type and code for each product are summarized in Table 1.

2.3. Sample Preparation

For the evaluation of heavy metals using atomic emission spectrometry, the samples require to be in soluble and clear form. Therefore, the sample has to be digested using concentrated acids.

Table 1. The name and symbol of the analyzed products

Sample type	Origin	Code
Al-Fanous Coffee Beans	Columbia	1
Al-Fanous Coffee Ground		2
Indian Coffee Beans	India	3
Indian Coffee Ground		4
Brazilian Coffee Ground	Brazil	5
Syrian Coffee Beans	Syria	6
Syrian Coffee Ground		7
Columbian Coffee Beans	Columbia	8
Columbian Coffee Ground		9
Instant Coffee	Spain	10
Cappuccino	Indonesia	11
Black Tea-1	India	12
Black Tea-2	Egypt	13
Green Tea	China	14
Black Tea-3	China	15
Cocoa-1	United States	16
Cocoa-2	Italy	17
Cocoa-3	France	18

The sample preparation step primarily aims at reducing matrix effects originating from organic compounds and releasing elements in the form of their simple ions. Firstly, 2.00 g of sample was weighed, placed in a crucible, and transferred to a muffle furnace set at 600°C. After 4 h, the sample was removed from the furnace and cooled. Then the sample was dissolved in 5 M HNO_3. The solution was filtered through Whatman filter paper (No. 42) and Millipore filter paper (< 0.45 µm) and then quantitatively transferred to a 25 mL volumetric flask and completing the volume by adding deionized water [12].

2.4. Sample Analysis

A Microwave Plasma-Atomic Emission Spectrometer (MP-AES Agilent 4100) was used to evaluate the heavy metal contents. The calibration standard curves provided the basis to quantify the metal contents.

3. Results and Discussion

Monitoring of heavy metals like Mn, Cr, Pb and Cd in coffee, tea, and cocoa is essential due to their toxicity and can be transported into humans and animals via the food chain. Heavy metals such as Fe, Cu, and Zn are necessary to maintain adequate metabolic activity in living organisms, however, at elevated levels; they can cause toxicity to living organisms. The concentrations of Cu, Cr, Ni, Cd, Mn, Fe, and Pb in three types of beverage samples are shown in Tables 2, 3, and 4.

3.1. Manganese (Mn)

Manganese is the heavy metal found in elevated concentrations in all samples with a concentration range of: (2.9 – 72.8 mg/kg) for beans and ground coffee samples, (162.0 – 673.3 mg/kg) for tea samples, and (1.0 – 22.4 mg/kg) for cocoa samples. Morgano et al. [13] reported a mean manganese concentration of 31.77 mg/kg in all coffee samples and an average content of 30.33 mg/kg for the coffee samples from the Alto Paranaíba region in Brazil. The contents of Mn in black tea samples from China have been determined by Xie et al. as 607 ± 200 mg/kg [14]. Awudza et al. [4] reported an average of 72.64 mg/kg in a cocoa samples from Mampong in Ashanti Region in Ghana. Food is the utmost important source of Mn exposure in the common population. The consumption can be higher for vegetarians because higher levels of manganese exist in food of plant origin. The elevated tissue levels of manganese have been reported in the kidney, pancreas, liver, and adrenals. Accessible information clearly display that Mn can cause adverse impacts in humans, the most important target being the central nervous system. The syndrome recognized as manganism is characterized by muscle pain, anorexia, apathy, and slow clumsy movement of the limbs[15]. The levels of manganese in all samples are shown in Figure 1.

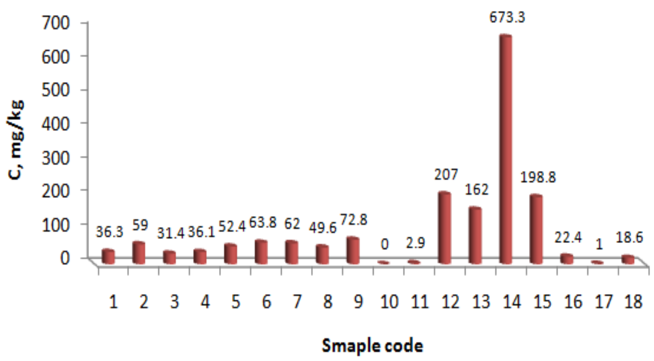

Fig. 1. Manganese contents in all samples

Table 2. Concentrations of heavy metals in Coffee samples

M.	Con. mg/kg	1	2	3	4	5	6	7	8	9	10	11
Mn	$\bar{X}$	36.3	59.0	31.4	36.1	52.4	63.8	62.0	49.6	72.8	ND	2.9
	% RSD	0.90	0.10	1.60	2.00	5.10	2.00	0.80	0.10	1.80	-	0.40
Cr	$\bar{X}$	0.5	0.8	0.3	0.4	ND	1.0	7.5	0.4	0.4	0.1	0.6
	% RSD	0.20	0.01	0.04	0.07	-	0.07	1.50	0.03	0.04	0.04	0.09
Fe	$\bar{X}$	21.9	21.5	23.6	27.5	18.3	27.9	23.5	13.9	18.6	0.3	2.0
	% RSD	0.18	1.03	0.66	0.11	0.21	0.62	0.76	1.14	1.76	0.06	0.09
Cu	$\bar{X}$	10.3	11.3	10.3	10.5	10.9	13.6	10.1	9.4	10.8	0.6	2.4
	% RSD	1.42	0.87	1.09	0.34	0.34	1.37	0.79	0.52	1.08	0.07	0.33
Zn	$\bar{X}$	1.9	1.9	1.4	2.0	1.8	1.9	1.8	2.0	2.0	0.1	2.8
	% RSD	0.08	0.09	0.06	0.09	0.06	0.20	0.40	0.40	0.40	0.03	0.10
Cd	$\bar{X}$	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.3
	% RSD	-	-	-	-	-	-	-	-	-	-	0.08
Pb	$\bar{X}$	2.1	2.1	2.3	2.5	0.9	2.6	2.4	2.1	2.4	ND	3.9
	% RSD	0.30	0.07	0.30	0.10	0.01	0.30	0.20	0.20	0.13	-	0.23

$\bar{X}$: Average of 3 readings

% RSD: Relative Standard Deviation

ND: Not Detected

Table 3. Concentrations of heavy metals in Tea samples

M.	Con. mg/kg	12	13	14	15
Mn	$\bar{X}$	207.0	162.0	673.3	198.9
	% RSD	0.35	1.35	0.44	0.30
Cr	$\bar{X}$	12.0	22.5	131.0	1.5
	% RSD	2.08	2.54	0.17	0.21
Fe	$\bar{X}$	3.6	5.5	40.6	16.6
	% RSD	0.30	0.90	4.47	1.08
Cu	$\bar{X}$	1.5	0.3	12.4	4.8
	% RSD	0.09	0.10	0.17	0.66
Zn	$\bar{X}$	1.0	1.5	4.6	4.6
	% RSD	0.03	0.20	0.52	0.29
Cd	$\bar{X}$	ND	ND	0.1	0.4
	% RSD	-	-	0.07	0.06
Pb	$\bar{X}$	2.0	2.3	4.4	2.3
	% RSD	0.60	0.12	0.20	0.40

Table 4. Concentrations of heavy metals in Cocoa samples

M.	Con. mg/kg	16	17	18
Mn	$\bar{X}$	22.4	1.0	18.6
	% RSD	1.09	0.07	2.30
Cr	$\bar{X}$	2.9	2.0	16.4
	% RSD	0.60	0.41	1.31
Fe	$\bar{X}$	9.0	1.0	32.0
	% RSD	1.70	0.06	0.81
Cu	$\bar{X}$	6.3	0.8	4.5
	% RSD	0.30	0.18	0.11
Zn	$\bar{X}$	9.1	0.4	20.9
	% RSD	0.80	0.02	0.20
Cd	$\bar{X}$	0.3	ND	ND
	% RSD	0.06	-	-
Pb	$\bar{X}$	2.1	1.8	ND
	% RSD	0.10	0.07	-

The evaluated safe dietary intake per year for adults is 730–1825 mg, founded by the U.S. National Research Council[15]. Thus, the outcome from our works is that Mn intake from coffee is negligible compared to the requirement. The amount of Mn intake from coffee during a year does not cover even a small percentage of the annual requirement from the element.

3.2. Chromium (Cr)

Cr was detected in all samples except in Brazilian coffee sample. Elevated chromium levels were found in tea samples with a range of (1.5 – 131.0 mg/kg). The chromium concentrations in coffee samples were over 0.1 mg/kg (except No. 5 and No. 10), the highest set by the Brazilian legislation [1], and the coffee sample containing the highest Cr concentration was the Syrian coffee. The content of Cr in Cocoa samples was in a range of 2.0 – 16.4 mg/kg. In National Regulation estimates of permissible levels of Cr for chocolate and chocolate products aren't specified [16]. Alagić [16] evaluated an average concentration of Cr in chocolate and commonly consumed cocoa products in Bosnia and Herzegovina of ND – 5.37 mg/kg. Chromium is everywhere, present in water, soil and biological systems. Determination is ordinarily limited to Cr III because this is an essential element in human nutrition. Chromium effects protein, lipid, and carbohydrate metabolism via an impact on insulin action. However, the mechanism is still not obvious and neither is the accurate structure of the biologically active form of chromium. Chromium-deficient diabetics have recognized beneficial effects from chromium intake, since adding the diet with chromium decreased lowered insulin levels, improved glucose tolerance, fasting blood glucose levels, and decreased total cholesterol and triglyceride levels. Presently, there is no formal Recommended Dietary Allowance (RDA) for chromium [17]. The levels of manganese in all samples are shown in Figure 2.

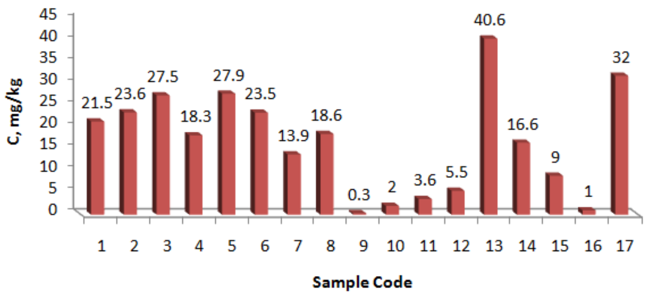

Fig. 2. Chromium contents in all samples

3.3. Iron (Fe)

Iron, important micro-bio-element necessary for oxygen transfer by red blood cells, fundamental in the production of hemoglobin and some enzymes, was evaluated in concentration range of (0.3 – 27.9 mg/kg) in coffee samples, and the coffee samples containing the highest Fe levels were Indian and Syrian coffee samples. The levels evaluated are relatively close the Nova Brasilia coffee range of 24 mg/kg reported by Gogoasa [18]. The concentration of Fe in Tea samples was in a range of 3.6 – 40.6 mg/kg. Fe level was the highest in Chinese Green Tea and the lowest in Indian Black Tea. The bioavailability of this element is affected by the polyphenols present in tea that can remarkable inhibit the absorption of iron [19]. These values were lower than those estimated by Soliman [20]. The comparison to which shows that all the analysis of tea samples is in consistency. In Cocoa samples, the least value was determined in Italian Cocoa sample while the highest value of 32.0 mg/kg was determined in French Cocoa sample. Comparing the levels detected with the recommended levels, it can be said that values determined are lower than the recommended dietary allowance (RDA) values [4]. Figure 3 shows the levels of Fe in all samples.

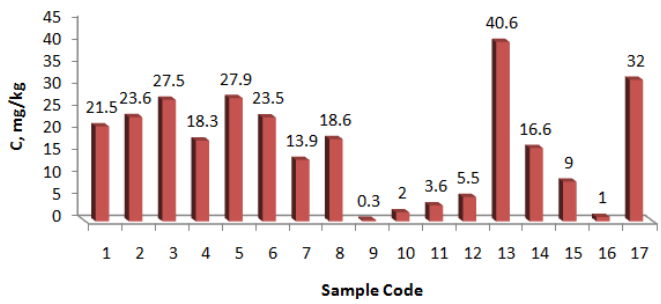

Fig. 3. Iron contents in all samples

3.4. Copper (Cu)

In coffee samples, the Cu contents ranged from 0.6 to 13.6 mg/kg. For all coffee samples analyzed, the Cu concentrations were lower than the maximum limit (30 mg/kg) established by Brazilian legislation [1]. Morgano et al. [13] reported mean Cu values higher than the results of our study (29.86 mg/kg). However, dos Santos et al. [21] reported mean Cu levels from 7.15 to 14.9 mg/kg in coffees produced in other region in Brazil. These results show that the mineral level is related to the origin of the coffee, species, pesticides, and agricultural treatment, among other factors.

The concentrations of Cu in our tea samples have been ranged from 0.3 to 12.4 mg/kg. Cu is an important trace metal for humans health, also, for example, it is a necessary component for some enzyme systems. The accessible data indicate that deficiency of Cu is greater hazard compared to the excess intake of this metal for human health. Cu contamination could ordinarily result from the rolling machine and fungicides. High levels of Cu are serious for human. Thus, the daily quantity of Cu in consumed food, water and other beverages such as tea must be monitored. The variation of Cu levels in the teas is affected by some factors such as different circumstances of the growth areas [22]. Xie et al and Ferrara et al [14, 23] determined the Cu levels in tea. Also, in a work by Han et al, high levels of Cu in some tea leaves were reported.

For cocoa samples, the least mean value of 0.8 mg/kg detected in Italian cocoa, while, the highest value of 6.3 mg/kg was detected in the cocoa sample from United State. The United States Food and Nutrition Board (US FNB) has specified the upper limit of copper at 10 mg/day whiles Linus Pauling Institute proposes 900.0 mg/day as the recommended dietary allowance (RDA) levels for adults. The values determined were far lower than the RDA and US Food and Nutrition Board [4] values. This shows that the level of copper in the samples cannot cause any health hazard to humans. Figure 4 shows the levels of Cu in all samples.

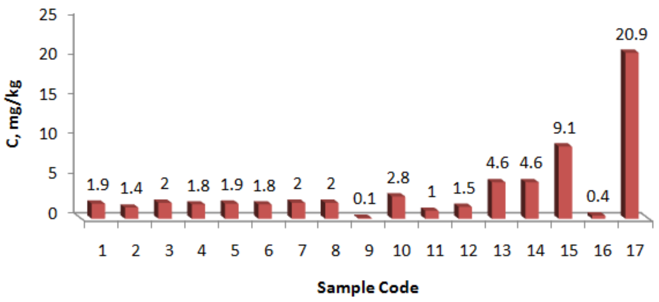

Fig. 4. Copper contents in all samples

3.5. Zinc (Zn)

Zinc concentrations for the coffee samples ranged from 0.1 to 2.8 mg/kg**.** Morgano et al. [13] announced an average level of zinc in two raw Brazilian coffees being about 8.33 mg/kg and 7.04 mg/kg. Grembecka et al. [24] also announced values around these with mean concentrations of zinc 9.5 mg/kg for the Arabica coffee samples. The maximum acceptable amounts of 50 mg/kg for zinc in general foods [1]. The concentration of Zn in tea samples were found to range from 1.0 mg/kg to 4.6 mg/kg. Indian tea showed the lowest level whilst Chinese's tea recorded the highest. The concentrations of Zn in all the tea samples were below the acceptable limit of 10 mg/kg [25]. Zinc is necessary in metabolic function and growth in human. However, dangerous effects of Zn usually begin at levels 10-15 times higher than the amount needed for good health. Intake of large doses, even for a short time, can cause nausea, stomach cramps, and vomiting. Taken longer, it can result in anaemia and minimize the levels of good cholesterol [15]. Zinc was determined with a range of 0.4 mg/kg observed in Italian cocoa and high value of 20.9 mg/kg was observed in French cocoa. The recommended dietary permitted for zinc has been set at 12 – 15 mg/day and the upper limit (UL) is set at 40 mg/day for all foods, water and supplements [4]. However, the concentrations determined once again were far lower than the RDA values set for the metal zinc indicating that there is no risk of contamination of the cocoa beans determined with respect to zinc. Figure 5 shows the levels of Zn in all samples.

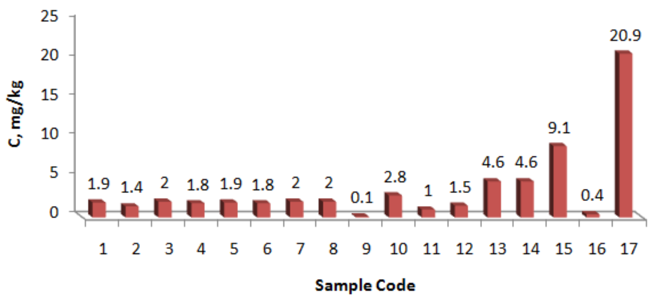

Fig. 5. Zinc contents in all samples

3.6. Cadmium (Cd)

Cd was not found in the analyzed samples, except No. 11 which was 0.3 mg/kg. dos Santos et al. [24] reported mean Cd levels between 0.70 and **0.75** mg/kg in coffee of two different samples in the Bahia state in Brazil. The maximum allowance limit for cadmium established by the regulations of Mercosul [1] and the European Union (European Commission Regulation, 2008) [26] is 0.1 mg/kg. The cadmium content in Indonesian cappuccino sample exceeded the limit drawn by the European Union and Mercosul regulations. Cd is a very toxic metal that human being can be exposed with it in the environment or at work situations. This metal can accumulate to a large extent in the human body throughout life. Cd is harmful to the kidney and bone; it can increase demineralization of bone. In the industry extreme exposures to Cd can lead the cancer of lung [27]. For tea samples, cadmium was detected in two samples with concentrations of 0.1 and 0.4 mg/kg. Seenivasan et al. [28] determined a lower mean Cd content in black tea samples from South India as 0.14±0.06 mg/kg. Elbagermi et al. [29] in their study of heavy metals in Herbal teas in Libya reported a concentration range from 0.035 to 0.38 mg/kg. Waqar and Mian, [30] and Narin et al. [3] monitored a higher mean Cd concentration as 1.1 ± 0.5 and 2.0 ± 0.8 mg/kg leaves from Saudi Arabia and Turkey, respectively. Shen and Chen [31], in their work of metal content in green and black tea in Taiwan reported a mean Cd concentration of 0.07 mg/kg in black tea, which is lower than our study[32-34].

For cocoa samples, cadmium was detected in only one sample with concentration of 0.3 mg/kg (United States sample). The values determined in some samples were higher or close to the maximum permissible levels of 0.100 mg/kg in fruits, cocoa butter and chocolate but were less than the limit set by Codex in cocoa mass and cocoa powder of 1.0 mg/kg [4, 35]. Concentrations of cadmium determined, however, compare positively with the level set for plant parts at 0.l00 mg/kg fresh weight. In 2006 the European Union on cocoa conference suggested for adoption, a level of 0.8 mg/kg. It is supposed that concentrations of cadmium in soils range from 0.010 mg/kg to 7.00 mg/kg [36]. This metal exists in phosphate fertilizers in trace quantities and might be absorbed by plants grown with the use of these fertilizers [4, 37-39]. The use of pesticides is an important source of the element. To fight disease causing pests in cocoa production, pesticide spraying is done throughout the year. This may cause accumulation of cadmium by the plant leading to toxicity. It is supposed; however, that accumulation occurs more in the leaves than seeds [40]. Figure 6 shows the levels of cadmium in all samples.

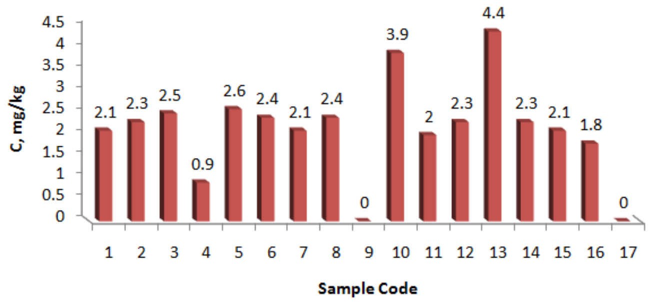

Fig. 6. Cadmium contents in all samples

3.7. Lead (Pb)

Lead as an element was absent only in one of the analyzed coffee samples (Instant coffee). Values ranging from 0.9 to 3.9 mg/kg were determined in the coffee samples. Actually, 10 of the 11 coffee samples analyzed contained lead concentrations higher than the maximum allowance under Brazilian law and Mercosul regulations [1] (0.5 mg/kg), some samples containing about 8 times this value. Also, 91 % of tested samples, the lead concentrations was above the permitted by the regulations of the European Union [26] (0.2 mg/kg). Lead gets accumulated in the body and is a very toxic and. The main harmful effects of lead on health are endocrinological, hematological, neurological, cardiovascular, gastrointestinal and hepatic systems also influences growth, reproduction and development, and contains a carcinogenic potential [26]. Thus, the high lead content samples should not be sold in the market to preserve consumer health.

The levels of lead (Pb) in tea samples were in range of 2.0 to 4.4 mg/kg. Detected values of the current study were near to those reported by Narin et al. [3] and Ashraf and Mian [30], and were higher than those reported by Matsuura et al [41]. In our work, Pb levels in all the black tea samples were less than the limit specified under the PFA Act 1954, India and the WHO (1998) limit of 10 mg/kg [25].

The concentrations of lead observed in the cocoa samples ranged from 1.8 mg/kg to 2.1 mg/kg. The highest level was measured in United States sample while the least value was detected in Italian sample. The concentrations determined in this work are, however, above the Codex Alimentaruis, Maximum level of 0.10 mg/kg in fruits and vegetables and 1.00 mg/kg maximum allowance levels for cocoa powder and cocoa mass [4]. Figure 7 shows the level of lead in all samples[42-44].

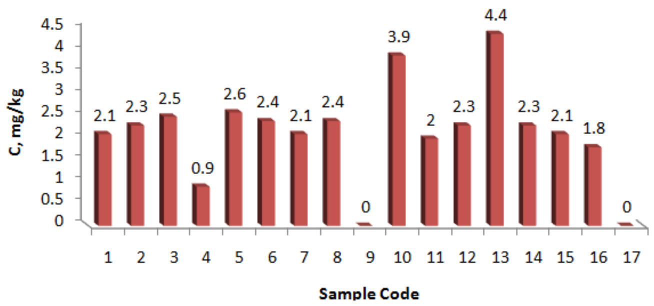

Fig. 7. Lead contents in all samples

4. Conclusion

Coffee, Tea, Cocoa are familiar beverages for people in Arabic and North African countries. The study displays that the contents of the manganese, chromium, iron, copper, and zinc determined are generally within safe limits and compare well with levels in similar samples from other areas of the world. However, the concentrations of the lead and cadmium (in some samples) were exceeded the maximum permitted under Brazilian law and Mercosul regulations, and the regulations of the European Union (European Commission Regulation, 2008). Routine examination and periodic analysis of foodstuff is desired to avoid the risk of exceeding the ingestion beyond the tolerance limits standards.

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