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DETERRMINATION AND EVALUATION OF HEAVY METALS IN COLOSTRUM AND SOME DAIRY PRODUCTS

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ABSTRACT

A total of 47 random samples (colostrum of buffalo's and cows, ice cream, butter, balady yoghurt, baby foods, yoghurt and kishk) were collected from different outlets in Assiut Governorate. The collected samples were analyzed for the detection of lead, cadmium, iron, selenium, manganese and mercury by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The analyzed data showed that the mean values in the examined colostrum buffalo's and cows were (0.0155 and 0.0157) lead, (0.0008 and 0.0.0006) cadmium, (1.5528 and 0.5838) iron, (0.0055 and 0.00023) selenium, (0.0236 and 0.0379) manganese and (0.0094 and 0.0003) ppm mercury, respectively. Results revealed that the mean values in ice cream, baby foods, balady yoghurt, yoghurt, kishk and butter samples for lead, cadmium, iron, selenium, manganese and mercury were (0.0139, 0.0103, 0.0155, 0.0119, 0.0544 and 0.0179); (0.0014, 0.0006, 0.0003, 0.0000, 0.0008 and 0.000004); (0.3912, 2.9768, 7.6998, 0.3189, 4.0753 and 0.6160); (0.0027, 0.0035, 0.0041, 0.0000, 0.0012 and 0.0035); (0.0409, 0.1309, 0.0543, 0.0221, 1.6603 and 0.0173) and (0.0023, 0.0069, 0.0000, 0.0000, 0.0006 and 0.0000)) ppm, respectively. The results showed that there were a significant levels of positive correlation ($p<0.05$) between the Pb and Cd contents, and highly significant positive correlation ($p<0.01$) between the levels of Pb and Mn as well as between the values of Se and Hg, respectively.
Keywords: Heavy metals, Colostrum, Baby foods, Dairy products, ICP-OES.
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INTRODUCTION

Milk and its dairy products are important sources of major minerals, particularly calcium, phosphorus, magnesium, potassium and trace elements such as zinc. The mineral content of milk is influenced by several factors, including the stage of lactation, environmental conditions, genetics, lactation period, feed type, milk yield, amount of the trace element in each cow's feeding, postpasteurization handling of milk, storage conditions, and accuracy of analysis. For these reasons, there may be wide variation in the content of specific minerals in milk. Trace elements in dairy products also vary with the processing methods and technologies applied (Merdivan *et al.*, 2004 and Miller *et al.,* 2007).

Minerals of milk are divided into two main groups: macrominerals and trace elements. All contribute to the well-being of offspring and are important for growth of most organs, particularly, for mineralization of bone matrix (Anderson, 1992). Heavy metals are recognized as cumulative toxic substances due to its low elimination rates from the body. Moreover, the heavy metals could not be metabolized, thus they persist in the body and exert their toxic effects which result in serious health hazards to human, depending on their levels of contamination (Amer *et al.,* 2005).

Milk and milk products represent an important part of the human feeding, especially, children's diet. So, the contamination of milk and its products by heavy metals is one of the major threats confronting the public health (Jensen, 1995)

Although heavy metals have industrial uses, their potential toxicity for people and animals is the object of several studies. For some elements the effects are accumulative and it is necessary to control their level in consumed food. So, measurements of minor and trace elements contents, comprising Pb, Cd, Fe, Se, Mn and Hg are also very helpful in assessment of quality of milk during its production and manufacturing treatment (Li *et al.*, 2005 and Birghila *et al.,* 2008).

Heavy metals represent the chemical residues which have a major effect on animal and human health. Environmental pollution with heavy metal increased the interest metal contamination in milk, water and feed stuffs which play an important role in human and animal diet. Heavy metals are among the most dangerous forms of pollutants that have a tendency to accumulate in living tissues and organs (Antoniou et al., 1989).

Colostrum, the initial mammary secretion after parturition, contains more mineral salts and protein, less ash than later milk and its fat content higher than that of milk. The composition of colostrum differs more among individual animals than does the composition of milk. The most remarkable difference between colostrum and milk is the high concentration of immunoglobulins. (Jenness, 1988). The purpose of colostrum is to provide the calf with antibodies and nutrition that will aid in the fortification of the immune system. Bovine colostrum contains many beneficial substances. The most important of these substances are: immunoglobins, lactoferin, proline-rich polypeptide, cytokines and vitamins (Kelly, 2003).

The present study was done to (a) estimation the content of trace elements in the colostrum of both buffaloes and cows, as well as in some dairy products collected from Assiut Governorate by using inductively coupled plasma atomic emission spectrometry (ICP-OES) in ppm, and (b) compare the data obtained with the literature values.

MATERIALS AND METHODS

A total of 47 random samples including colostrum of buffaloes & cows, butter, ice cream, yoghurt, kishk and baby foods were collected from different local markets in Assiut governorate. All samples were collected in polyethylene bags and taken to the laboratory without delay. Each sample was labeled to identify the source of sampling. Delayed samples were stored in ice bag. Sampling procedure was performed according to Ayar *et al.* (2009).

The levels of Pb, Cd, Fe, Se, Mn and Hg in samples had been estimated (ppm) according to the method described by James (1995) in Analytical Chemistry of Foods. A weight of 5.0 g of samples was ashed in muffle furnace at 550˚C overnight. The obtained ash was dissolved in 5 ml HCl (36.6%) and the volume was completed to 50.0 ml by distilled water, then dilutions were applied to estimate the levels of investigated elements using inductively coupled plasma atomic emission spectrometry (ICP-OES) (ICAP6200) in the central laboratory, Faculty of Agriculture, Assiut University. The working conditions for ICP-OES are given in Table 1.

Table 1. Operating conditions for the instrument parameter

Parameter	Setting
Pump tubing	Tygon orange/white
Pumb speed	45rpm
Nebulizer	Standard concentric
Nebulizer argon flow	0.6 L/min
Spray champer	Standard cyclonic
Center tube	1.5mm
RF forward power	1150W
Purge gase	Argon
Coolant gase flow	12 L/min
Auxiliary gase flow	0.5 L/min

Results were evaluated statistically by using the software program; the SAS system for windows, release 8.02 TS level 02M0, SAS Institute Inc., Cary, NC, USA (SAS, 1999).

RESULTS AND DISCUSSION

The levels of elements in buffalo's and cow's colostrum are shown in Table 2. The mean contents of Pb, Cd, Fe, Se, Mn and Hg in both buffalo's and cow's colostrum were found to be 0.015 and 0.016, 0.0008 and 0.0006, 1.553 and 0.584, 0.0055 and 0.0023, 0.024 and 0.038 and 0.0094 and 0.0003 ppm, respectively. On the other hand, the concentrations of Cd, Fe, Se and Hg elements were found higher in buffalo's colostrum than that in cow's one. The levels of both Pb and Mn were higher in the collected samples of cows colostrum than that of buffalo's one. These results are in agreement with those obtained by Salih *et al.*, (1987), Amer *el al.*, (2005), and Enb *et al*., (2009). The obtained results of Fe contents in buffalo's colostrum were in agreement with those obtained by Lonnerdal *et al.* (1981), while in the case of cow's colostrum were lower than that reported in the literature (1-2 mg/L) by Anderson (1992) and Kincaid and Cronrath (1992).

Yanardğ and Orak (1999) reported that buffalo milk contained a mean value of selenium 32.89 ng/g ranged from 13.00 to 49.93 ng/g. Present value was higher than that of Hungarian (Sarudi *et al.,* 1994) and Indian (Giri *et al.,* 1988). The selenium contents in cow's milk were 70 ng/mL (Egypt), 40 ng/mL (Australia), 9 ng/mL (France), and 19 ng/mL (India). On the other hand, this element content in buffalo's milk of Hungry and India were 19.10 and 16.10 ng/mL, respectively (Yanardğ and Orak, 1999).

Table 2. Residues concentration of some heavy elements in buffalo's and cows colostrum (ppm).

Elements		Pb	Cd	Fe	Se	Mn	Hg
Buffalo's colostrum n*=7	Min	0.0086	0.0008	0.211	0.0000	0.01156	0.0000
	Max	0.0200	0.0009	5.597	0.0113	0.0396	0.0394
	Mean	**0.0155**	**0.0008**	**1.5528**	**0.0055**	**0.0236**	**0.0094**
	±S.E	±0.0021	±0.00003	±1.0211	±0.0023	±0.0051	±0.0076
Cow's colostrum n=7	Min	0.0100	0.0000	0.2029	0.0000	0.01425	0.0000
	Max	0.0197	0.0012	1.4180	0.0065	0.0871	0.0009
	Mean	**0.0157**	**0.0006**	**0.5838**	**0.0023**	**0.0379**	**0.0003**
	±S.E	±0.0014	±0.0002	±0.1608	±0.0010	±0.0088	±0.0001

*** N: Number of Samples**

The sources of contamination with lead are: lead piping and lead-lined tanks in domestic water supplies, canning and use of the pottery glaze for storing beverages (Ayar el al., 2009). It is clear from data presented in Table 3 that the mean levels of lead (Pb) were the highest in Kishk samples with an average of 0.0544 ppm, followed by butter with an average of 0.0179 ppm and the lowest value was found in samples of baby foods with an average of 0.0103 ppm. Ayar *el al.* (2009) showed that the contents of Pb were ranged from 0.10-0.15, 0.02-0.18 and 0.06-0.14 in butter, ice cream and yoghurt, respectively. The Pb contents of baby foods in present study were lower than that reported by Abd- El Aal (2012) and Abdou and Koarshy (2001) and also Saad *et al.* (2001). The levels of Pb contents in butter, Yoghurt and ice cream were lower than that of Abdou and Koarshy (2001).

Table 3.Residues concentration of elements (ppm) in some dairy products.

Elements		Pb	Cd	Fe	Se	Mn	Hg
Ice cream n*=5	Min	0.0129	0.0012	0.3148	0.0019	0.0341	0.0012
	Max	0.0148	0.0017	0.4676	0.0036	0.0479	0.0034
	Mean ±S.E	**0.0139** ±0.0005	**0.0014** ±0.0001	**0.3912** ±0.0441	**0.0027** ±0.0005	**0.0409** ±0.0039	**0.0023** ±0.0006
Baby foods n=4	Min	0.0007	0.00002	0.0053	0.0007	0.0019	0.0000
	Max	0.0151	0.0016	5.8100	0.0058	0.3629	0.0208
	Mean ±S.E	**0.0103** ±0.0049	**0.0006** ±0.0005	**2.9768** ±1.6771	**0.0035** ±0.0015	**0.1309** ±0.1162	**0.0069** ±0.0069
Balady yoghurt n=5	Min	0.0134	0.0000	0.3890	0.0000	0.0133	**ND**
	Max	0.0181	0.0006	22.1400	0.0070	0.1132	
	Mean ±S.E	**0.0155** ±0.0014	**0.0003** ±0.0002	**7.6998** ±7.2203	**0.0041** ±0.0021	**0.0543** ±0.0302	
Yoghurt n=4	Min	0.0119	**ND****	0.3188	**ND**	0.02206	**ND**
	Max	0.0119		0.319		0.02208	
	Mean ±S.E	**0.01197** ±0.00001		**0.3189** ±0.00001		**0.0221** ±0.00001	
Kishk n=11	Min	0.0161	0.0000	1.9360	0.0000	1.1520	0.0000
	Max	0.2591	0.002258	6.9730	0.0059	2.1490	0.0039
	Mean ±S.E	**0.0544** ±0.0210	**0.0008** ±0.0002	**4.0753** ±0.5495	**0.0012** ±0.0006	**1.6603** ±0.1178	**0.0006** ±0.0004
Butter n=4	Min	0.0151	0.00004	0.4026	0.0002	0.0111	**ND**
	Max	0.0223	0.00021	0.7813	0.0058	0.0267	
	Mean ±S.E	**0.0179** ±0.0021	**0.000004** ±0.000001	**0.6160** ±0.1119	**0.0035** ±0.0017	**0.0173** ±0.0048	

*** N: Number of Samples** ****ND: Not Detected**

Cd (cadmium) is found in low amounts in soil. It is transported via air and water from intensive industrial regions to the soil and sea. It is considered to be the most important contaminant in modern times (Ayar el al., 2009). The highest level recorded for cadmium (Cd) was in ice cream with an average of 0.0014 ppm, while the lowest value was found in butter (0.000004 ppm). On the other hand, the cadmium element was not detected in plant yoghurt. These results are similar to those of Ayar *et al.* (2009). The contents of Cd of baby foods, butter, yoghurt and ice cream in present study were lower than that reported by Saad *et al.* (2001), Abdou and Koarshy (2001) and Abd- El Aal (2012).

The (selenium) Se, as one of the important microelements, was recently reported to be a considerable antioxidant based on the latest knowledge of nutrition (Hejtmankova *et al.* 2002). Se was found in different concentrations in all examined dairy products except plant yoghurt. Data in Table 3 revealed that baby foods and butter contain the highest value of Se elements (0.0035 ppm) while, the lowest value was found in Kishk with an average of 0.0012 ppm. The Se contents in Italian products of yoghurt were 0.11 ppm as reported by Gambelli *et al.* (1999). The present results are in accordance with those of Ayar *et al.* (2009) for yoghurt. On the other hand, the selenium contents in butter found in this study were lower than that reported by Ayar *et al.* (2009).

The major nutritional importance of iron lies in it being a component of hem of hemoglobin, myoglobin and cytochromes that involved in human body, so the common consequence of incorrect nutrition was anemia (Ziemlamski, 1994). Data in Table 3 showed the content of iron in some dairy products. The balady yoghurt was characterized by higher contents of iron followed by kishk while, the lowest values of iron was found in plant yoghurt and ice cream. Moreover, these values in the balady yoghurt are higher than those reported in the previous literature. It was indeed found that the amount of iron in the plain yoghurt is 0.4 mg/kg (Pennington and Young, 1990), 0.47 mg/kg and 0. 5 mg/kg (Garcia Martinez *et al*., 1998).

Manganese is required for various metabolic processes, including metabolism, it can be found in dairy products in different concentration. Milk is a poor source of manganese as its mean value in cow's milk from different breeds ranged from 10-50 µg/L (Koops and Westerbeek, 1993). Although the amount of Mn in the human body has been estimated as 5.00 mg, the amount in milk is miniscule. The levels recorded for manganese (Mn) showed that the highest levels found in Kishk with an average of 1.660 ppm followed by baby foods with average of 0.1309 ppm, while the lowest value was found in butter. This result was lower than those obtained by Saad *et al.* (2001), Abdou and Koarshy (2001) and Amellal-Chibane and Benamara (2011).

Heavy metal such as mercury has no known vital or beneficial effect on the living organisms (WHO, 1976). All chemical forms of mercury can cross the placental barrier and also secreted in milk. Mercury has the ability to cross the blood brain barrier for example methyl-mercury. It causes the toxicity of central nervous system in animals and as well as in humans (Montesinos *et al.*, 1997). Hg was not detected in butter, plant yoghurt and balady yoghurt. From obtained data (Table 3) it has been found that the highest mean level of mercury (Hg) was found in baby foods with an average of 0.0069 ppm followed by ice cream with average of 0.0023 ppm.

Data in Table 4 show the correlations between the estimated trace elements in colostrum and some dairy products. It could revealed that there was a levels of significant positive correlation ($p<0.05$) between the Pb and Cd contents, and highly significant positive correlation ($p<0.01$) between the levels of Pb and Mn as well as between the values of Se and Hg, respectively.

Table 4. The correlations between heavy metals in colostrum and some dairy products.

Correlations						
Elements	**Pb**	**Cd**	**Fe**	**Se**	**Mn**	**Hg**
Pb	1	0.3733*	0.0689	-0.0509	0.4541**	0.0079
Cd		1	-0.0512	0.1008	0.3016	0.2087
Fe			1	-0.2797	0.2581	-0.0649
Se				1	-0.3131	0.5572**
Mn					1	-0.1241
Hg						1

*** Correlation is significant at the 0.05 level**
**** Correlation is significant at the 0.01 level**

CONCLUSIONS

It could be concluded that the heavy metal residues were found in different concentrations in both colostrum and some dairy products. Some heavy metals such as cadmium, selenium and mercury were not detected in some dairy products especially in plant yoghurt, balady yoghurt and butter.

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تقدير وتقييم المعادن الثقيلة في السرسوب وبعض منتجات الألبان

عادل على تمام [1] ، على محمد عبد الرحيم [1] و طارق حمدى محمد [2]
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أجري هذا البحث لتقدير بقايا المعادن الثقيلة في لبن السرسوب البقري والجاموسي ، الآيس كريم ، الزبد ، الزبادي البلدي ، زبادي المصانع ، الكشك واغذية الأطفال. حيث تم تجميع عدد ٤٧ عينة عشوائية من مناطق مختلفه في محافظة أسيوط من اللبن ومنتجاته موضع الدراسة و بعد ذلك تم تجهيزها و هضمها ثم قياسها باستخدام جهاز انبعاث الطيف بالبلازما (نظام الحث الكهربي الحراري المزدوج للبلازما).

وقد اظهرت النتائج ان متوسط القيم لكل من عينات السرسوب الجاموسي والبقري المختبرة هي (٠.٠١٥٥ ، ٠.٠١٥٧) رصاص ، (٠.٠٠٠٨، ٠.٠٠٠٦) كادميوم ، (١.٥٥٢٨، ٠.٥٨٣٨) حديد ، (٠.٠٠٥٥، ٠.٠٠٠٢٣) سيلينوم ، (٠.٠٢٣٦، ٠.٠٣٧٩) منجنيز و (٠.٠٠٩٤، ٠.٠٠٠٣) جزء في المليون زئبق علي التوالي.

كما اشارت الدراسة ان محتوي كل من الرصاص والكادميوم والحديد والسيلنيوم والمنجنيز والزئبق في عينات الآيس كريم واغذية الأطفال و الزبادي البلدي وزبادي المصانع والكشك والزبد المختبرة كانت (٠.٠١٣٩، ٠.٠١٠٣، ٠.٠١٥٥، ٠.٠١١٩، ٠.٠٥٤٤ ، ٠.٠١٧٩)، (٠.٠٠١٤، ٠.٠٠٠٦، ٠.٠٠٠٣، ٠.٠٠٠٠، ٠.٠٠٠٨، ٠.٠٠٠٠٤) ، (٠.٣٩١٢، ٢.٩٧٦٨، ٧.٦٩٩٨، ٠.٣١٨٩، ٤.٠٧٥٣، ٠.٦١٦٠) ، (٠.٠٠٢٧، ٠.٠٠٣٥، ٠.٠٠٤١، ٠.٠٠٠٠، ٠.٠٠١٢، ٠.٠٠٣٥) ، (٠.٠٤٠٩، ٠.١٣٠٩، ٠.٠٥٤٣، ٠.٠٢٢١، ١.٦٦٠٣، ٠.٠١٧٣) و (٠.٠٠٢٣، ٠.٠٠٦٩، ٠.٠٠٠٠، ٠.٠٠٠٠، ٠.٠٠٠٦، ٠.٠٠٠٠) جزء في المليون علي التوالي.

كما أكدت النتائج الي وجود تأثير موجب مع وجود اختلافات معنوية عند مستوي احتماليه ٠.٠٥ بين كل من محتوي الرصاص والكادميوم ، بينما هناك علاقة موجبة مع اختلافات معنوية كبيرة عند مستوي ٠.٠١ بين كل من الرصاص والمنجنيز وكذلك السيلينيوم والزئبق علي التوالي.

قام بتحكيم البحث

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