Assessment of Toxic Heavy Metals in Some Dairy Products and the Effect of Storage on its Distribution

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Abstract: A total of 120 dairy product samples (30 each of condensed milk, infant formula, milk powder and sterilized milk) were collected from Zagazig city, Sharkia Governorate, Egypt and classified into three groups: each group include 10 cans of each product. All samples stored at room temperature (17.5-31.5 ◦C) for 210 days (from August 2011 to March 2012). All groups were analyzed by Atomic Absorption Spectrophotometer (the first group at zero day, the second at 60 days and the third at 210 days) to determine the level of toxic heavy metals (Pb, Cd, Al and Sn) to study the effect of storage on the distribution of these metals in the examined dairy products.

The statistical analysis of the data indicated that 100% of the examined samples contained (lead, cadmium, aluminium and tin). The analyzed data revealed that the mean values of Pb, Cd, Al and Sn in condensed milk samples during storage period (0-60-210 days) were (0.548, 0.115, 0.600, 1.400); (0.660, 0.250, 1.650, 1.400) and (0.770, 0.245, 2.300, 1.520) ppm, respectively. While, in case of infant formula samples were (0.410, 0.210, 1.350, 1.550); (0.561, 0.280, 1.350, 1.760) and (0.815, 0.285, 1.850, 1.660) ppm, respectively and in milk powder samples were (0.488, 0.225, 1.150, 1.580); (0.572, 0.330, 1.650, 1.500) and (0.800, 0.345, 2.500, 1.760) ppm, respectively. Otherwise, in sterilized milk samples were (0.497, 0.150, 1.150, 1.170); (0.636, 0.220, 1.300, 1.640) and (0.765, 0.380, 1.850, 1.680) ppm, respectively.

When comparing the obtained results there were significant change ($p<0.05$) in the level of Pb, Cd, Al and Sn in all examined dairy product samples from 0, 60 and 210 days**.** The public health hazards of these metals were discussed.

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1. Introduction

Milk and dairy products have been recognized all over the world for their beneficial influence on human health because they are quantitatively important in the diet and their regular consumption is recommended especially for young children where they provide a great sense of eating pleasure due to their flavor and characteristic smooth taste as well as they are good sources of protein, calcium, riboflavin, phosphorus, potassium, vitamin A and vitamin D **(Yuzbas_ı *et al.*, 2009).**

Milk and dairy products may contain varying amounts of different toxic contaminants **(Ataro *et al.*, 2008).** The level of toxic metals are an important component of safety and quality of milk and dairy products. Metals are widely released in the environment and have two major origins**:** human activities and geological background **(Loska *et al.*, 2004)** where they are present in soil through fertilizers or following atmospheric deposition and from natural weathering of the bedrock.

Ruminants take up a small fraction by ingestion of vegetation during grazing and soil from surface layers which generally contains the highest MTE concentrations **(Laurent *et al.*, 2005)**. The different routes of excretion from the animal are urine, faeces and milk **(Sola-Larranaga and Navarro-Blasco, 2009)**. Also, trace metals may enter our foods from other sources as: (i) water used in food processing or cooking, (ii) equipment, containers and utensils used for food processing and (iii) packaging, storage and cooking. Intestinal absorption is dependent on the metal considered and is carried out by passive diffusion or active transport **(US EPA, 2003).** MTEs are then distributed by the blood via metalloproteins to the different tissues **(Bourrelier *et al.*, 1998)** and show significant variations depending on various factors (e.g., species, age of the individual, speciation of the MTE, physiological status).

The risk associated with the exposure to trace metals in food products had aroused widespread concern in human health. Acute and chronic symptoms, dizziness, nausea, vomiting, diarrhea, sleeping disorders, loss of appetite and reduced conception rate are the symptoms of heavy metal toxicity. Also, it connected to Alzeihemer's, Parkinson's, autism, lupus, amyotrophic lateral sclerosis, cardiovascular disease, depressed growth, impaired fertility, nervous and immune system disorders, increased spontaneous abortions, and elevated death rate among infants **(Yuzbas _ı *et al.*, 2003** and **Jack, 2005).** The mineral composition of milk and milk products has been investigated **(Lante *et al.*, 2006)** and the microbiological quality, such as microorganism occurrence and load has also been examined **(Han *et al.*, 2007).** But, the influence of technological treatments such as storage needs more experimentally examination.

So, the present work was performed to determine the level of contamination of dairy products with some toxic heavy metals (lead, cadmium, aluminium and tin) as well as to study the effect of storage on the distribution of these metals in the examined dairy products (condensed milk, infant formula, milk powder and sterilized milk) during 210 days storage.

2. Material and Methods

1- Collection of samples:

A total of 120 random dairy product samples (30 each of condensed milk, infant formula, milk powder and sterilized milk) were collected in their original package from different markets in Zagazig city, Sharkia Governorate, Egypt. Collected samples were taken to the laboratory without delay. Each sample was labeled to identify the source, site and date of sampling. Collected samples were classified into three groups: each group include 10 cans of each product. All samples stored at room temperature (17.5-31.5 ◦C) according to **Ortega and Garcia (1992)** for 210 days (from August 2011 to March 2012). Prior to storage, each can was examined for damage and notations and examinations were made periodically about once a week.

All groups were analyzed by Atomic Absorption Spectrophotometer (the first group at zero day, the second at 60 days and the third at 210 days) to determine the level of toxic heavy metals (Pb, Cd, Al and Sn) and to study the effect of storage on the distribution of these metals in examined dairy products.

2-Preparation of samples:

A measured weight (1g.) of condensed milk and (0.3 g.) of milk powder and infant formula and a measured volume (2cc) of thoroughly homogenized sterilized milk was transferred in clean and acid washed screw capped digestion tubes. Prepare two tubes from each sample and all digestion tubes were identified for examination.

3- Analysis of the prepared samples:

For determination of Pb, Cd and Sn, the first tube of each prepared sample was digested according to **Tsoumbaris and Papadop (1994)**. While, for determination of aluminium the procedure was carried out on the second tube according to **Dabeka and Mckenzie (1992).** All filtered samples were analyzed for their metal contents according to methods of **Medina *et al.* (1986)** by using "perkia-Elmer Atomic Absorption Spectrophotometer model d 2380, USA, 1998" at the microanalytical laboratory, Department of chemistry, Faculty of science, El-Mansoura university, Egypt. Instrumental analysis of Pb and Cd, were conducted by air lacetylene Flame Atomic Absorption Spectrophotometer (FAAS). For determination of Sn Flameless Atomic Absorption Spectrophotometer (FLAAS). While for determination of Al use Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS). The analytical detection limits of Pb, Cd, Al and Sn for the used instrumentation were 0.02, 0.0006, 0.02 and 0.01 ppm, respectively. The analysis determined by using Atomic Absorption spectrophotometer due to it become the most important technique in the quantitative determination of trace metals in food stuffs. It has a gained favour with analysis because it both specific and sensitive.

4- Statistical analysis:

All the data analyzed using SPSS/PCT **(Foster, 2001).** One way ANOVA were performed to evaluate differences.

3. Results

Table (1): Heavy metals concentration in examined condensed milk samples during 210 days storage period.

Metals	Mean ±S.E. At 0 day (N=10)	Mean ±S.E. At 60 days (N=10)	Mean ±S.E. At 210 days (N=10)
Lead	0.548^{c} ±0.013	0.660^{b} ±0.000	0.770^{a} ±0.039
Cadmium	0.115^{b} ±0.008	0.250^{a} ±0.000	0.245^{a} ±0.014
Aluminium	0.600^{c} ±0.163	1.650^{b} ±0.198	2.300^{a} ±0.082
Tin	1.400^{b} ±0.000	1.400^{b} ±0.000	1.520^{a} ±0.055

*Means with different superscript (a, b and c) in each raw are significantly differed at level (P<0.05).

Table (2): Heavy metals concentration in examined infant formula samples during 210 days storage period.

Metals	Mean ±S.E. At 0 day (N=10)	Mean ±S.E. At 60 days (N=10)	Mean ±S.E. At 210 days (N=10)
Lead	0.410^{c} ±0.000	0.561^{b} ±0.035	0.815^{a} ±0.019
Cadmium	0.210^{b} ±0.016	0.280^{a} ±0.008	0.285^{a} ±0.019
Aluminium	1.350^{b} ±0.076	1.350^{b} ±0.076	1.850^{a} ±0.076
Tin	1.550^{c} ±0.043	1.760^{a} ±0.016	1.660^{b} ±0.016

*Means with different superscript (a, b and c) in each raw are significantly differed at level (P<0.05).

Table (3): Heavy metals concentration in examined milk powder samples during 210 days storage period.

Metals	Mean ±S.E. At 0 day (N=10)	Mean ±S.E. At 60 days (N=10)	Mean ±S.E. At 210 days (N=10)
Lead	0.488^{c} ±0.024	0.572^{b} ±0.022	0.800^{a} ±0.000
Cadmium	0.225^{b} ±0.021	0.330^{a} ±0.008	0.345^{a} ±0.014
Aluminium	1.150^{c} ±0.076	1.650^{b} ±0.076	2.500^{a} ±0.000
Tin	1.580^{b} ±0.042	1.500^{c} ±0.000	1.760^{a} ±0.016

*Means with different superscript (a, b and c) in each raw are significantly differed at level (*P*<0.05).

Table (4): Heavy metals concentration in examined sterilized milk samples during 210 days storage period (N=10)

Metals	Mean ±S.E. At 0 day (N=10)	Mean ±S.E. At 60 days (N=10)	Mean ±S.E. At 210 days (N=10)
Lead	0.497^{c} ±0.022	0.636^{b} ±0.012	0.765^{a} ±0.042
Cadmium	0.150^{c} ±0.000	0.220^{b} ±0.008	0.380^{a} ±0.015
Aluminium	1.150^{b} ±0.076	1.300^{b} ±0.082	1.850^{a} ±0.076
Tin	1.170^{b} ±0.015	1.640^{a} ±0.016	1.680^{a} ±0.033

*Means with different superscript (a, b and c) in each raw are significantly differed at level (*P*<0.05).

Figure (1) Heavy metals concentration in examined condensed milk samples during 210 days storage period.

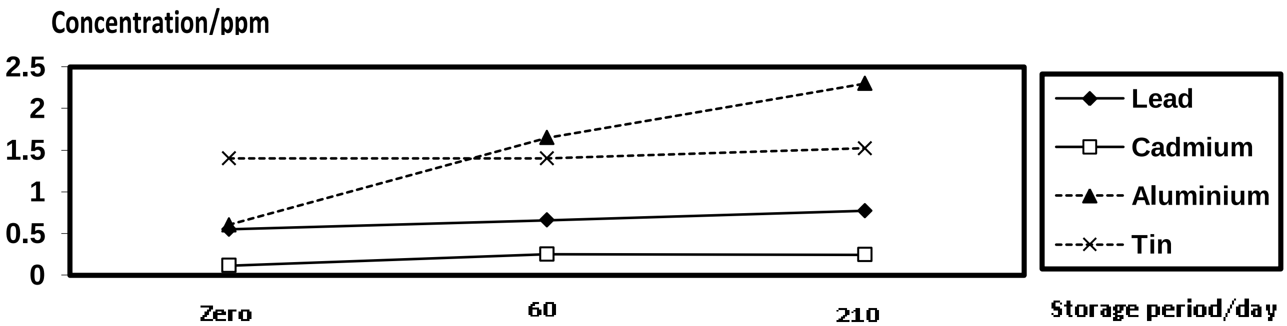


Figure (2) Heavy metals concentration in examined infant formula samples during 210 days storage period.

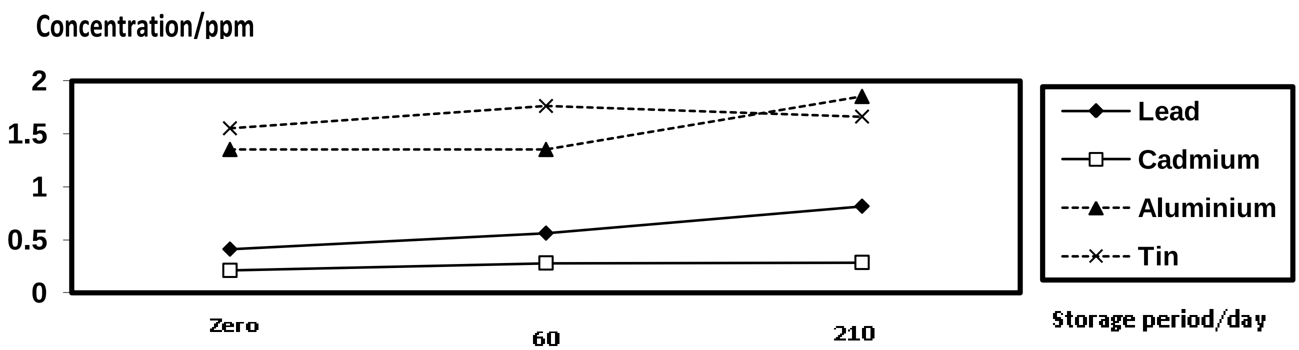


Figure (3) Heavy metals concentration in examined milk powder samples during 210 days storage period.

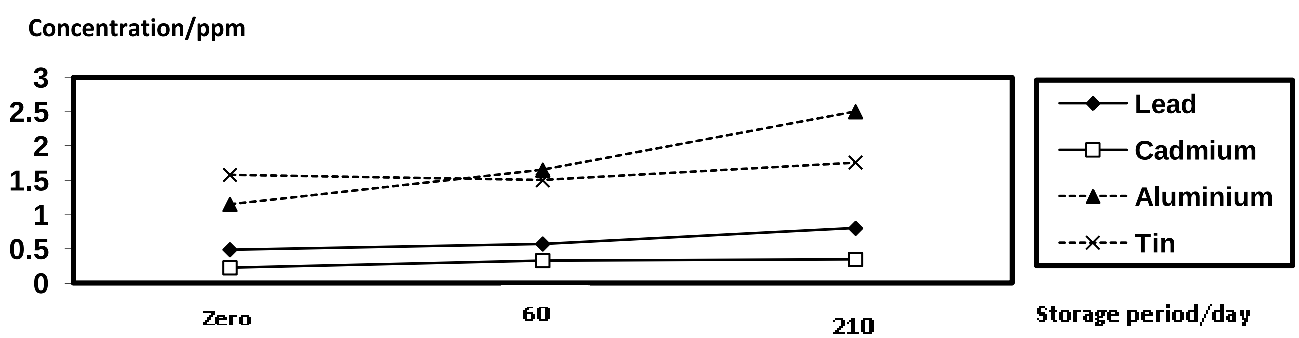
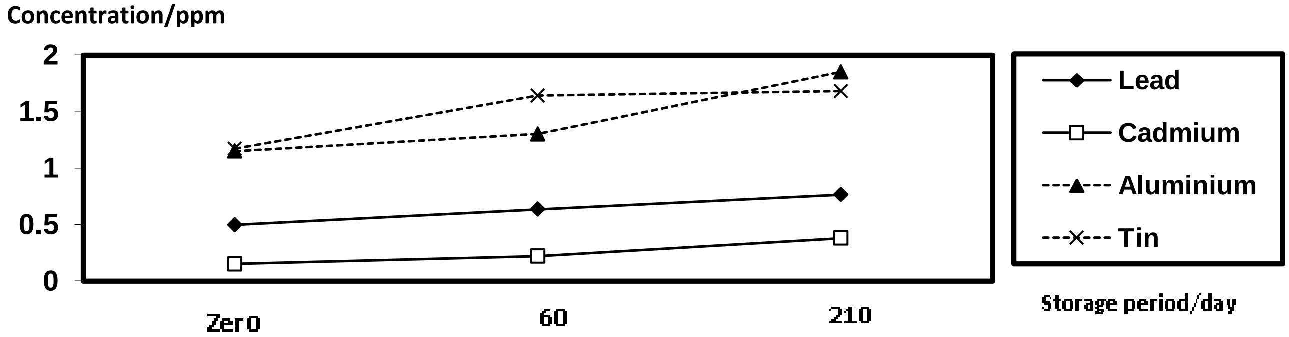


Figure (4) Heavy metals concentration in examined sterilized milk samples during 210 days storage period.



4. Discussion

The statistical analysis indicated that all examined dairy product samples contained lead, cadmium, aluminium and tin and there were considerable changes in the levels of all elements but the change occurred may be significant or non significant.

Considering the heavy metals concentration in examined condensed milk samples, Table (1) revealed that the mean values of Pb, Cd, Al and Sn during storage period (0-60-210 days) were (0.548, 0.115, 0.600, 1.400); (0.660, 0.250, 1.650, 1.400) and (0.770, 0.245, 2.300, 1.520) ppm, respectively. From the previous results there was significant increase in the level of Pb and Al from 0 to 60 to 210 days and there was also significant change ($p<0.05$) in the level of Cd from 0 to 60 days and no change after that. In case of Sn the increase in the level starts after 60 days storage to the end (Figure, 1).

Results summarized in Table (2) declared that the average levels of Pb, Cd, Al and Sn in case of examined infant formula samples were (0.410, 0.210, 1.350, 1.550); (0.561, 0.280, 1.350, 1.760) and (0.815, 0.285, 1.850, 1.660) ppm during storage period (0-60-210 days), respectively. The analyzed data indicated that there was significant change in the level of Pb and Sn from 0 to 60 to 210 days. Although, Cd level was changed from 0 to 60 days and not changed after that, Al level was not changed from 0 to 60 days and changed after that (Figure, 2).

Recorded results in Table (3) showed that the average concentrations of heavy metals (Pb, Cd, Al and Sn) in analyzed milk powder samples during storage period (0-60-210 days) were (0.488, 0.225, 1.150, 1.580); (0.572, 0.330, 1.650, 1.500) and (0.800, 0.345, 2.500, 1.760) ppm, respectively. Regarding the effect of storage on heavy metals concentration we found that there were significant differences in the level of Pb, Al and Sn from 0 to 60 to 210 days but Cd level changed from 0 to 60 days only (Figure, 3).

Concerning the heavy metals concentration in examined sterilized milk samples Table (4) revealed that the mean values were (0.497, 0.150, 1.150, 1.170); (0.636, 0.220, 1.300, 1.640) and (0.765, 0.380, 1.850, 1.680) ppm of Pb, Cd, Al and Sn during storage period (0-60-210 days), respectively. Also, tabulated results declared that there was significant change in the level of Pb and Cd from 0 to 60 to 210 days. While, Al level were not changed from 0 to 60 days and changed after that. Otherwise, Sn level was changed from 0 to 60 and not changed from 60 to 210 days (Figure, 4).

From the previously mentioned results, it is evident that the trace metal contents of dairy products are variable because of factors such as characteristics of the manufacturing procedures and possible contamination from the equipment during processing, packaging, and storage. So, it is necessary to control the manufacturing process at each step, in order to determine the source and levels of contamination and to ensure the desired product quality **(Ayar *et al.*, 2009).**

Other observation that the migration of tin and cadmium from the cans to the products during storage period were highest in sterilized milk in comparison with other dairy products. On the other hand, migration of aluminium was highest in condensed milk. While the migration of lead was highest in infant formula.

These results are nearly similar to findings obtained by **Sami, 2005.** The obtained results can be attributed to the fact that the migration of tin from the surface of the can to the products is caused not only by the length of storage but also, by the consistency of milk product, in this products (as in sterilized milk) the concentration of these metals increased more rapidly than in condensed milk, due to it‘s consistency which is usually thick.

These results are inagreement with that mentioned by **Tchekulayeva *et al.*, (1981)** who explain that as it affects on the deeper layers of tinned plate and certain changes of the cover occur so, the transition of tin into canned products is accelerated. Probably due to this reason for more intensive transfer of tin and lead into canned milk products in the first months of storage is observed **(Ramonaityte, 2001)** and for the same reason, the level of lead has been decreased significantly depending on the gradual replacement of packaging types and welding, which may release lead during the storage **(Okada *et al.*, 1997).**

Also, it may be due to the nature of tinned can manufacture (which consists of in 98.8%, small amount of lead beside soldering of seams with lead-containing paste, copper, cadmium, aluminium from the Al-foil cover and some other metals) capable of participating in electrochemical transformation **(Arvanitoyannis and Bosnea, 2004).**

The complex manufacturing process of infant formula and milk powder plays an important role in the degree of aluminium contamination where it comes from the chemicals used, machinery and dust particles **(Navarro-Blasco and Alvarez-Galindo, 2003).**

The selection of a suitable packaging material has an important role in dairy products storage because a toxicological effect of component migration from packages into foods is crucial problem. Food packaging can interact with the packaged foodstuff by diffusion controlled processes and dissolution of metals (notably tin and lead) may occur, resulting in unavoidable changes in concentrations of trace elements in the product, on which product quality and safety for consumption depend.

This interaction mainly depend on chemical properties of the food contact material, and the foodstuff, temperatures at packaging, during heat treatment and storage, exposure to UV light, water activity, quantity of salts and acids in the product, its PH value and storage time of the product **(Muncke, 2009).**

Regarding the public health hazards of the detected metals, accumulation of lead produces damaging effects in the hematopoetical, hematic, renal, gastrointestinal systems **(Svancara *et al.*, 2010).** On the other hand, cadmium is considered to be one of the most toxic metals where it is implicated in high blood pressure, prostate cancer, mutations and foetal (embryonic) death **(Economou, 2005** and **Arduini *et al.*, 2007)**.

While, the risk of aluminium accumulating may be raised especially in infants with renal immaturity linked to a low aluminium clearance due to decreased urine excretion **(Sedman *et al.*, 1984).** Also, it has adverse effects on bone mineralization by interactions with both calcium and phosphorus **(Bougle *et al.*, 1997)** and massive amounts of aluminium have been associated with pulmonary disease but trace amounts induced a progressive encephalopathy in animals. Some investigations have found that aluminium was present in higher concentrations in the neocortex of human brains affected by Alzheimer's disease therefore; it was assumed that aluminium may be involved in the pathogenesis of Alzheimer's disease **(Jack, 2005)**.

Otherwise, Metallic tin of low toxicity because it's poor absorption and could cause gastrointestinal disturbance resembling food poisoning but organo-tin compounds were more toxic because these compound absorbed through the gastrointestinal tract and skin resulting in irritation of the mucous membrane of eyes and skin, and others cause cerebral oedema, chronic renal failure and hepatic necrosis **(Harbison, 1997)**.

Conclusion

From the conducted study, it may be concluded that the chemical composition of dairy products, depends not only on the concentration of raw milk components and on its treatment, but also on the mode of packing and quality of the packing materials and on the conditions and time of storage.

Also, it is preferable that consumption of milk products should be as early as possible from the date of manufacture to reduce the migration of heavy metals from the containers to the products during storage period.

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