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Determination of Lead and Cadmium in Different Types of Milk Samples Collected from Different Markets in Benghazi-Libya

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Abstract – Milk and its products are the most consumed food by humans, especially children, so it is important to investigate the extent of the toxic heavy metals and determine their concentrations in milk samples. In this study, seventy-eight random samples of milk powder, infant milk, evaporated milk, and sterilized milk were collected from different markets during 2015-2016 in Benghazi city, Libya. In all milk samples, cadmium and lead metals were determined using Graphite Furnace Atomic Absorption Spectrometer (GFAAS), after wet digestion process. The analyzed data revealed that the mean values in the examined milk powder, infant milk, evaporated milk, sterilized milk, samples were 0.006, 0.006, 0.001, 0.0001, 0.0002 and 0.0003 mg/kg of cadmium, respectively and 0.36, 0.39, 0.03, 0.01, 0.01 and 0.01 mg/kg of lead, respectively. The mean concentration of cadmium metal in milk samples was exceed the permissible limits set by WHO/FAO. While the mean concentration of lead in examined milk. In evaporated milk samples, the mean concentrations of lead were nearly similar to WHO/FAO permissible limits. While the sterilized milk samples have mean concentration of lead below the recommended permissible limits by the WHO/FAO.

Keywords - Toxic Metal, GF-AAS, Powder Milk, Infant Milk, Evaporated Milk, Sterilized Milk, Benghazi.

I. INTRODUCTION

Heavy metals are a group of metals and semimetals (metalloids) that have been associated with contamination and potential toxicity. At high concentrations, heavy metals are harmful due to their interference with normal metabolic process. The contamination chain of heavy metals always follows a cyclic order: industry, atmosphere, soil, water, foods, and human. Heavy metals may enter the dairy production system in a variety of ways. These ways include atmospheric deposition, land application of inorganic fertilizers, animal feed [1], bio solids, agrochemicals, and animal manures; however, sewage irrigation may pose certain environmental risks, most significantly the pollution of soil with heavy metals [2]. Post contamination during several steps of the manufacturing processes, reagents, accidental contamination during storage and marketing and leaching form containers may lead to increase the level of heavy metals in milk and milk products [3].

Concentrations of several toxic metals have been largely increased because of human activities. They can disturb important biochemical processes, constituting an important threat for the health of plant and animals [4].

Generally, heavy metals disrupt metabolic function in two basic ways: First, they accumulate and thereby disrupt function in vital organs and glands such as the heart, brain, kidneys, bone, liver, etc. Second, they displace vital nutritional minerals from where they should be in the body to provide biological function. Toxicity of metals is closely related to age, route of exposure, level of intake, solubility, metal oxidation state,

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retention percentage, duration of exposure, frequency of intake, absorption rate and mechanisms and efficiency of excretion [5, 6]. The mechanism of heavy metal toxicity is not specifically known but in general lead, mercury, cadmium and other heavy metals have a high affinity for sulfhydryl (-SH) groups, inactivating numerous enzymatic reactions, amino acids, and sulfur-containing antioxidants, with subsequent decreased oxidant defence and increased oxidative stress [7].

Cadmium and lead are well known toxic metals, even when taken in small quantities [8]. Children have been shown to be more sensitive to cadmium and lead than adults [9]. Cadmium is considered as one of the most harmful metal poisons. Since it is toxic at extremely low levels. Long term exposures to cadmium results in renal dysfunctions and high inhalations of contaminated dust and fumes can cause pulmonary problems such as obstructive lung disease. The symptoms of effects, depending of the seriousness of the expose, include nausea, vomiting, abdominal cramps, dyspnea and muscular weakness. A strong expose may cause pulmonary odema and death [10]. The best-known health problem due to cadmium has been the itai-itai disease where a long-term high-level cadmium exposure caused severe damages to the Japanese population. For this reason, the WHO recommended a tolerable weekly intake of cadmium of 7 µg/kg body weight [11]. Cadmium affects calcium metabolism and skeletal changes resulting from calcium loss and ends in a decrease bone mineral density and also causes softening of bones [12]. Cadmium may induce prostate cancer and functional and morphological changes in many body organs. Cadmium could induce anaemia and alteration of antioxidant and metabolic status of red blood cells and recently it alters membrane skeleton one of the structures responsible for erythrocyte deformability [13].

The regular absorption of small amounts of lead, may cause serious effects on the health of growing children, including mental retardation (e.g. reading and learning disabilities) [10, 14]. Lead also causes a wide range of toxicity effects; the most serious one is the teratogenic effect, inhibition of the haemoglobin synthesis, dysfunctions in the renal, muscle- skeleton, reproductive and cardiovascular systems. Lead, also causes a acute and chronic damage to the central and peripheral nervous systems [10]. The Joint Expert Committee on Food Additives (JECFA) established a provisional tolerable weekly intake (PTWI) for lead as 0.025 mg/kg body weight [15].

Regulations of Cadmium and Lead metals in Milk

Owing to cadmium and lead harmfulness to human health their levels in milk are prohibited or restricted by global international regulations and national regulations in different countries. Table (1) shows some international and national regulations of many countries on permissible limits of both cadmium and lead metals in milk [5, 16, 21].

Table 1. Permissible Standards Limits for both cadmium and lead metals in different types milk.

Daniel din Si	Maximum Permissible	D-f		
Regulation/Year	Cadmium	Lead	Reference	
FAO/WHO	0.01	0.02	[16]	
European Union	0.01	0.02	[17]	
China, 2014	-	0.02	[18]	



Egypt, 2013	0.105	0.05	[19]
Hungary, 2012	-	0.02	[20]
Malaysia, 2010	1	-	[21]
Turkey, 2009	0.01	0.05	[5]

Libyan standard Regulations also stipulates that the number of mineral pollutants in milk should not exceed the latest limits permitted by the World Health Organization [22].

Review of Literature

Contamination of milk and milk products with metallic pollutants is one of the major problems confronting public health. Ingested contaminated feeding stuffs have been considered as the main source of metal residues in milk. Moreover, contamination from soldered cans is one of post contamination of milk products. The highly advanced analytical methods, included Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma-Mass Spectrometry (ICPMS), are frequently used for determination of metals in milk and milk product samples. There are large number of published articles for detection of toxic metals in milk samples collected from different regions in Nigeria, Egypt, Saudi Arabia, Pakistan, Romania, Palestine, Brazil, Philippines, Iran, India [23], Canada [24]. The detections of toxic metals were applied in different types of milk, included evaporated milk [22-25], powder milk [19, 26-34], infant milk [29, 34-38], sterilized milk [28, 32, 33, 36, 39]. Stripping voltametric methods have used to determine the concentrations of some heavy metals in milk and milk products [34, 40]. Recently, an overview of the toxicity of different heavy metals on human health, their sources in milk and other dairy products by emphasizing on methods and regulatory limits for heavy metals in milk were represented by Parisa Z. [41].

However, few studies were published on the milk analysis in Libya; those studies included microbiological analysis and aflatoxin M1 detection in milk and other dairy products that's been vended in the markets of Libya, to make their safety [42, 43]. Also, the physicochemical parameters and trace element contents of different raw milk samples in Misurata-Libya, were detected [44].

However, no attempts have been done to investigate the presence of heavy metals in milk from Benghazi markets. Therefore, the purpose of this study is the determination of the pH values, ash contents and the levels of two toxic metals in some commercially available milk in markets of Benghazi. The milk samples will be analysed to determine the two toxic metals, including cadmium and lead using Graphite Atomic Absorption Spectrophotometer (FAAS). The obtained values of the analysed samples will be compared with the literature data and the maximum limits permitted by FAO/WHO [15, 16].

II. EXPERIMENTAL

A. Collection of the samples

A Total of seventy-eight random samples of powder milk, infant milk, evaporated milk, and sterilized milk were purchased from three different markets in Benghazi city. The same milk products were thoroughly mixed to get homogenous and representative samples. Each sample was labelled to identify the source, site, and date of sampling, and preserve in freezing till analysed. The samples were given different code number such as 1-a to 7-



a for seven samples of milk powder, 8-b to 13-b for six samples of infant milk, 14-c to 21-c for eight samples of evaporated milk and 22-d to 26-d for five samples of sterilized milk. An additional information about the collected milk samples, has shown in Table 2.

B. Chemicals and Reagents

All chemicals and reagents used in this study were of analytical grade. These chemicals included nitric acid (65%) was obtained from SEELZE-HANNOVER, hydrogen peroxide (30%) was obtained from EUROSTAR SCIENTIFIC LTD. Lead and cadmium standards solutions (1000mg/L) were purchased from BDH. These standards were used to prepare calibration solutions for each metal. All the solutions were prepared using deionized water (18 $M\Omega$ /cm).

C. Instruments

In this study, Digital pH meter (JENWAY mode 3150) was used to measure the pH of the solutions. Muffle furnace (CARBOLITE AAF 1100) was used to ashing the milk samples. The cadmium and lead concentrations were determined using GF-AAS (VARIAN, GTA 120) after wet digestion process [45].

D. Determination of Physicochemical Parameters of Milk Samples pH-Value

The pH of each sample was measured using a Digital pH-meter equipped with combined glass electrode. The pH values of the liquid milk samples were measured directly, while the solid milk samples were measured by dissolving 2g of sample in 4ml distilled water. The mixture was well mixed for 10 seconds. Then pH was measured by immersing glass electrode in the supernatant solution and pH values were recorded for each sample when the meter has Stabilized [46].

E. Determination of Ash Content

Three grams of each milk sample was weighted in well-dried silica crucible and kept into muffle furnace, maintained at 550 ± 20 °C, for four hours till grey ash formation. The crucible is transferred to desiccators and weighted when completely cooled [47]. Then, the ash percentage is calculated using equation (1).

Ash% =
$$([(W)]_2-W_1)/(\text{weigh of milk sample}) \times 100$$
 (1)

Where, W2 = weight of crucible with ash, W1 = weight of empty crucible.

Table 2. List of the collected milk samples, their codes and some information on the sample container's label.

Type of milk	Product Name	Sample Code*	Production Date	Expired Date	Production Country
	Nido Nestle	1-a	04-2012	04-2014	Egypt
	Dano, Daily	2-a	06-2012	06-2014	Denmark
	Al Sheraa	3-a	01-2012	01-2014	U.A.E
Powder Milk	Puck	4-a	01-2012	01-2014	Denmark
	Nido-Nestle	5-a	08-2012	08-2014	Holland
	Nido-Nestle	6-a	03-2013	06-2014	U.A.E
	ERIELAC	7-a	01-2012	01-2014	France



	Humana-1	8-b	02-2012	02-2014	Germany
Infant Milk	My Boy eldolzan 2	9-b	06-2012	06-2014	Holland
	My Boy eldolzan 1	10-b	04-2012	04-2014	Holland
	Hero Baby	11-b	04-2012	04-2014	Spain
	Guigoz 2	12-b	06-2012	06-2014	France
	Bebelac 2	13-b	02-2013	08-2014	France
	Coast	14-c	11-2012	5-2014	Holland
	Judi	15-с	07-2012	07-2014	Germany
	Rain Bow	16-с	09-2012	03-2014	Holland
Evaporated Milk	Mana	17-с	08-2012	08-2014	Germany
	Milcow	18-c	07-2012	07-2014	Germany
	Azahrat	19-с	09-2012	03-2014	Holland
	Corniche	20-с	06-2012	12-2013	Holland
	Нарру Day	21-с	12-2012	12-2014	Germany
	Judi	22-d	05-2013	11-2013	Libya
Sterilized Milk	Rayhan	23-d	11-2013	05-2014	Libya
	Juhayna	24-d	11-2013	05-2014	Egypt
	Nadec	25-d	11-2013	08-2014	Saudi Arabia
	Milcow	26-d	11-2013	11-2014	Germany

^{*}Each sample represented a homogeneous mixture of three same products from three different markets.

F. Preparation the Working Standard Solutions of Cadmium and Lead

Mono-element, cadmium and lead, calibration standards for GF-AAS were prepared by sequential diluting stocks solutions, containing 1000 mg/L of these elements in 0.5% (v/v) nitric acid, to obtain working standard solutions in the range $0.1\mu g/L$ - $0.5\mu g/L$ and 4-20 $\mu g/L$ for cadmium and lead, respectively. The instrument operating conditions and parameters, for measuring each element, were adjusted according to the standard guidelines of the manufacture, as shown in Table (3). The absorbance of the standards of each metal is plotted automatically against the corresponding concentration, to construct the calibration curve for each metal, (see Table 3).

G. Analysis of Cadmium and Lead in Milk samples

In the present work, accurately certain amount of each milk sample (0.5g milk powder or infant milk, 5g evaporated milk, 10g sterilized milk,), was measured into clean dry Pyrex digestion flask. 10 ml of 65% nitric acid was added, followed by the addition of 3 ml of 30% hydrogen peroxide. The digestion flask was heated gently until frothing subsided. The sample was then heated to dryness. The samples were cooled down to room



temperature. Then the residue is dissolved in deionized water and filtered with No. 42 Whatman filter paper in volumetric flasks 50 mL. The solution is diluted to final volume using deionized water [47-49]. The resulted solutions were analysed by GF-AAS for cadmium and lead. The calibration curve of each element was used to determine the metal concentrations in (μ g/L). The concentrations in (μ g/kg) of both cadmium and lead in the examined milk samples were calculated using equation (2).

$$Metal Conc (mg/kg) = \frac{Metal Conc (\mu g/L)}{Sample Weight (g)} \times Dilution Factor$$
(2)

Before the digestion process, all the glassware was soaked in water and soap and rinsed several times with tap water. Then, they were cleaned by soaking for 24 hours in the bath containing 10% nitric acid solution, then rinsed with ultrapure water, to ensure that any contamination has removed [39, 50].

Table 3. Instrumental working conditions for measuring Cadmium and Lead metals by GF-AAS.

Operation Parameter	Element			
	Cadmium	Lead		
Wave length(nm)	228.8	283.3		
Slit width (mm)	0.5	0.5		
Lamp current (m A)	8	10		
Sample volume(µl)	20	20		
Drying step (°C)	500	800		
Atomization step (°C)	2200	2400		
Cleaning step (°C)	2400	2500		
Background correction	D2	D2		
Limit of Detection	0.0002	0.007		
Linear Working Range (ppb)	0.1-0.5	4-20		
Calibration of Standard Solution				
$Slop \pm SD \ (\mu g/L)$	0.639 ± 0.00019	0.025 ± 0.00002		
Intercept ± SD	0.01 ± 0.0037	0.01 ± 0.00025		
Correlation Coefficient (r)	0.999	0.998		

H. Statistical Analysis

Basic variation statistical values (arithmetic mean, standard deviation, maximum and minimum values) were calculated using SPSS. The data was analysed using one-way analysis of variance (ANOVA) to examine statistical significance at 95% (P<0.05) confidence level. Least Significant Difference (LSD) was used to evaluate significance of difference.

III. RESULTS AND DISCUSSION

In this study, a total of seventy-eight samples of four different types of milk were randomly collected from different local markets in Benghazi / Libya. The pH values, ash contents and the lead and cadmium contents we-

.80 - 1.580

0.62 - 1.56



Range

-re determined in all milk samples using suitable methods of analysis.

A. Physicochemical Properties of Milk Samples

The pH values and the ash contents of all types of milk samples were illustrated in Table 4.

4.36 - 5.63

Type of milk/ Samples Code **Physiochemical Properties Evaporated Milk** Milk Powder **Infant Milk** Sterilized Milk Samples: 1a-7a Samples 8b-13b Samples: 9c-21c Samples: 22c-26c pН Mean ±SD 6.59 ± 0.17 6.78 ± 0.14 6.33 ± 0.14 6.72 ± 0.22 6.22 - 6.74 6.53 - 6.96 6.16 - 6.48 6.35 - 6.90 Range Ash Content % Mean ± SD 5.353 ± 0.45 3.19 ± 0.52 1.309 ± 0.34 0.856 ± 0.40

Table 4. The pH values and Ash contents in the milk samples.

The pH values of milk samples were recorded at 6.59 ± 0.17 , 6.78 ± 0.14 , 6.33 ± 0.14 , 6.72 ± 0.22 , for powder milk, infant milk, evaporated milk, and sterilized milk, respectively. In general, the pH of milk samples was in normal range of pH milk. In fact0, the milk usually has a pH range between 6.5 - 6.7 [5]. Values higher than 6.7 denoted mastitis milk and values below pH 6.5 denote the presence of Colostrum or bacterial deterioration.

2.60 - 3.99

In this study, the average pH value of sterilized milk samples was in agreement with the pH value that reported by Enb *et al.*, 2009 [51]. While the average of pH of milk powder samples was little bit lower than the values reported by Elkhier and Yagoub, 2009 [52]. The average pH of evaporated milk is higher than that reported by Adams and Happiness, 2010 [25].

No statistically significant difference was observed for pH values between the types of milk (p<0.05).

As shown in Table (4), the ash contents of the analysed milk samples were ranged between 4.36-5.63% in milk powder, 2.60-3.99% in infant milk, 0.80-1.580% in evaporated milk, 0.621.56% in sterilized milk. The ash contents in powder milk samples were higher than that in infant milk and other types of milk samples. The ash contents found in milk powder agreed with that was reported by Elkhier and Yagoub., 2009 [52]. The ash contents found in evaporated milk samples were lower than that reported by Adams and Happiness., 2010 [25]. The ash contents found in the analysed sterilized milk were higher than the ash contents reported by Enb *et al.*, 2009 [51].

No significant difference (P<0.05) was observed in terms of ash content between all types of milk. But it must be noted the highest ash contents values, were observed in powdered and infant milk samples, Table (4).

B. Analysis of Toxic Metals in Different types of Milk Samples

Two toxic metals (cadmium and lead) were determined in four different types of milk, using GFAAS method after wet digestion process [53]. Table 5 displayed the results of cadmium and lead concentrations in the analyz-



-ed milk samples.

Table 5. Concentration of cadmium and lead metals in milk samples.

Type of Milk	Code	Cadmium, Conc. ×10 ⁻³ (mg/kg)	Lead Conc. (mg/kg)
Milk Powder	1-a	9.50	0.346
	2-a	3.00	0.258
	3-a	15.90	0.863
	4-a	7.10	0.318
	5-a	4.90	0.309
	6-a	1.00	0.219
	7-a	2.70	0.202
	Mean ±SD	6.30 ± 5.11	0.359 ± 0.23
	Range	15.90 - 1.00	0.863 - 0.202
	8-b	4.50	0.192
	9-b	4.20	0.410
	10-b	4.80	0.362
T. C N. C. I	11-b	3.40	0.438
Infant Milk	12-b	8.60	0.327
	13-b	10.50	0.594
	Mean ± SD	6.0 ± 2.85	0.387 ± 0.13
	Range	10.50 - 3.40	0.594 - 0.192
	14-c	1.40	0.033
	15-c	0.20	0.006
	16-c	0.90	0.030
	17-c	0.50	0.005
E	18-c	0.20	0.011
Evaporated Milk	19-с	0.10	0.048
	20-с	0.20	0.062
	21-с	0.80	0.015
	Mean ± SD	0.538 ± 0.46	0.0262 ± 0.021
	Range	1.40 - 0.10	0.062 - 0.005
	22-d	0.01	0.007
Sterilized Milk	23-d	0.30	0.016
	24-d	0.04	0.016



Type of Milk	Code	Cadmium, Conc. ×10 ⁻³ (mg/kg)	Lead Conc. (mg/kg)
	25-d	0.10	0.018
	26-d	0.01	0.006
	Mean ±sd	0.092 ± 0.12	0.0126 ±0.006
	Range	0.10 - 0.01	0.18 - 0.06

C. Powder Milk

As shown in Table (5), it is evident that the cadmium concentrations in milk powder samples were ranged from 0.001 to 0.0159 mg/kg, with a mean value at 0.006 ± 0.005 mg/kg. The concentrations of cadmium in our milk powder samples were lower than that reported by Zamir and Hussein, 2001[29], Sami and Amer, 2005[29], Abdukhaliq *et al.*, 2012[33] and AbdElaal, 2012[27]. On another hand, these results of cadmium were higher than results reported by Birghila *et al.*, 2008 in powder milk [32].

The Concentrations of lead in powder milk, as shown in Table (5), were ranged from 0.202 to 0.863 mg/kg. The mean concentration of lead metal in milk powder samples (0.359 \pm 0.23 mg/kg) was higher than the maximum limit established by the FAO/WHO (0.02 mg/kg) [15, 16]. The concentrations of lead in milk powder samples were also higher than results recorded by Zamir and Hussein, 2001 [29], and lower than those values reported by Sami and Amer., 2005 [13], Abdu Khaliq *et al.*, 2 012 [33] and Abd-Elaal, 2012 [27] for lead in milk powder.

D. Infant Milk

As shown in Table 5, the range of cadmium amounts in infant milk samples varied between 0.0034- 0.0105 mg/kg, with an average corresponding to 0.006 ± 0.003 mg/kg. Our result of cadmium metal in infant milk were lower than cadmium concentrations reported for infant milk [27, 35, 36]. On another point of view, these levels of cadmium in infant were higher than that reported by Hafez and Kishk, 2008 [53].

The concentrations of lead in the collected infant milk samples, as shown in Table (5), were ranged from 0.192 to 0.594 mg/kg. However, the mean concentration of lead was, 0.387 ± 0.13 mg/kg. This value was higher than the maximum limit established by the FAO/WHO for lead in infant milk. In the same time, the mean value of lead was higher that the results reported by Zamir and Hussein., 2001 [29], Hafez and Kishk, 2008 [53] in the infant milk samples. However, our result of lead concentrations was similarly to those published by Jannat *et al.*, 2009 [34] for infant milk samples analysis.

E. Evaporated Milk

The results of both cadmium and lead metals in evaporated milk samples were shown in Table (5). The concentrations of cadmium in evaporated milk samples ranged between 0.0001-0.0014 mg/kg. Our results declared that cadmium detected in [25] evaporated milk samples that collected from Benghazi markets were lower than all data reported for cadmium analysis in evaporated milk in available literatures [25-28]. Whereas the concentrations of Lead in evaporated milk were ranged between 0.005 to 0.062 mg/kg, with a mean concentration corresponded to 0.0262 ± 0.021 mg/kg, as shown in Table (5). However, the levels of lead in the analysed evaporated samples were nearly like those reported by Khalil and Seliem, 2013[28]. On the other hand,



our results were lower than the results of lead concentration reported by Abd Elaal, 2012 [27] and Adams and Happiness, 2010 for evaporated milk.

F. Sterilized Milk

Both cadmium and lead metals were detected in all sterilized milk sample, expect sample 22d, (Table 5). The lead content in this sample was less than the detection limit.

The mean values of cadmium and lead concentrations in the sterilized milk samples were 0.0001 ± 0.0001 mg/kg and 0.013 ± 0.006 mg/kg, respectively. Our results were lower than the maximum limits for cadmium and lead that established by the FAO/WHO [16].

IV. CONCLUSION

The present study was conducted to determine the concentrations of toxic elements, included cadmium and lead, in seventy-eight samples of four types of milk, including milk powder, infant milk, evaporated milk, sterilized milk. The samples under investigation were collected from different markets in Benghazi city, Libya during 2015-2016. All samples were digested and analysed by GFAAS. Our results indicated that both toxic metals were detected in all milk samples. The mean concentrations of cadmium and lead in the analysed samples varied in the following order: milk powder > infant milk > evaporated milk > sterilized milk.

The concentrations of cadmium metal in our samples were lower that maximum limit that permitted by the FAO/WHO for cadmium in milk. In the present study, the maximum concentration of cadmium was recorded at $15.9 \,\mu\text{g/kg}$ and $10.5 \,\mu\text{g/kg}$ in powdered and infant milk samples, respectively.

The maximum concentrations of lead in the analysed milk samples were recorded at 0.863 mg/kg, 0.594 mg/kg and 0.062 mg/kg in powdered infant and evaporated milk samples, respectively. Some of these results were higher than the maximum allowed limit that permitted by FAO/ WHO for lead metal in milk.

The presence of these toxic metals in milk were mainly due to greater pollution of the environment which has resulted in an increased concentration of heavy metals in air, water, and soil subsequently; these metals are taken by plants and animals, then to take their way into milk. Also, heavy metals may be added to milk during production, processing, and storage as well as by contamination from containers. On the other hand, continual increase in the number of industries and agricultural processes producing these pollutants and their participation in increasing the incidence of some chronic diseases.

To minimize the hazardous effect of these toxic metals, further studies are necessary to evaluate the contents of toxic heavy metals on a greater number of milk samples from various Markets in Libya. Routine analysis of the imported milk samples, in national laboratories, to confirm the absence of possible toxicological risks of heavy metals, before reaching the consumer.

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