RESIDUES BEHAVIOR OF SOME HEAVY METALS DURING MANUFACTURING OF SOME MILK PRODUCTS

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ABSTRACT

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This investigation was run to study the residue behavior of some heavy metals during manufacturing of some milk products. Samples of buffalo's milk as well as some milk products manufactured from it were analyzed for evaluation their contents of some metals that represents in 5 elements: manganese (Mn), copper (Cu), nickel (Ni), magnesium (Mg) and iron (Fe). The buffalo's milk was obtained from a dairy shop located in Assiut city, Egypt, while the manufactured milk products were represented in cream, butter, ghee and Kareish cheese. Before manufacturing of milk products, milk was divided into 2 portions; the first as control for estimation and the second was added by standards of the investigated metals in a concentration of 1 ppm. All samples were digested and analyzed using ZEEnit 700P Atomic Absorption Spectrophotometer. The obtained results showed that the milk contents of Mn, Cu, Ni, Mg and Fe were at concentrations of 2.3, 0.7, 0.07, 0.01 and 2.14 mg/kg, respectively. With viewing to the recorded limits of International Dairy Federation (IDF), Mn, Cu and Fe were found to exceed these limits. Mn was found to disappear from fat concentrated milk products (cream, butter and ghee), while concentrated in their by-products. Cu concentrated in cream and butter. Ni disappeared in ghee but concentrated in Kareish cheese. No obvious concentration of Mg in milk products while Fe concentrated in by-products skim milk, butter milk and whey. Although milk products contained more total metals content like in cream (3.502 mg/kg), butter (3.64 mg/kg) and ghee (4.7712 mg/kg) more than in the initial milk (5.23 mg/kg), the total metals content was more concentrated in by-products like in skim milk (7.89 mg/kg), butter milk (7.6171 mg/kg) and whey (5.206 mg/kg). But in case of Kareish cheese, it (3.493 mg/kg) contained total metals content lower than in initial milk. The public health significance of the examined metals, as well as, the recommended hygienic measures for human safety were discussed.

Key words: Milk, Milk products, Heavy metals, Manganese, Copper, Nickel; Magnesium, Iron.

سلوك بقايا بعض المعادن الثقيلة أثناء تصنيع بعض منتجات الألبان

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تم إجراء هذا البحث لدراسة سلوك بقايا بعض المعادن الثقيلة أثناء تصنيع بعض منتجات الألبان. وقد تم تحليل عينات من اللبن الجاموسي وبعض منتجات الألبان المصنعة منه لتقييم محتواها من بعض العناصر التي تمثلت في عدد ٥ عناصر هي المنجنيز والنحاس والنيكل والمغنسيوم والحديد. وتم احضار اللبن الجاموسي من أحد محلات الألبان في مدينة أسيوط، مصر، بينما تمثلت منتجات الألبان المصنعة في القشطة والزبد والسمن والجبن القريش. وقبل تصنيع منتجات الألبان، فقد تم تقسيم اللبن إلى جزئين، الأول كنترول للقياس والثاني قد أضيف له نفس العناصر المفحوصة بصورة مرجعية بتركيز جزء في المليون. وقد تم هضم كل العينات وتحليلها باستخدام جهاز الامتصاص الذري الطيفي ZEEnit 700P. وأظهرت النتائج أن محتوى اللبن من عناصر المنجنيز والنحاس والنيكل والمغنسيوم والحديد كان بتركيزات 2.3، 0.7، 0.07، 0.01، 2.14 مج/كجم، على الترتيب. وبالنظر إلى الحدود المسجلة لإتحاد الألبان الدولي (IDF) فإن المنجنيز والنحاس والحديد قد تخطى النسب المسموح بها. وقد وجد المنجنيز مختفيا من منتجات الألبان المركزة بالدسم (القشطة والزبد والسمن) بينما تركز في منتجاتهم الثانوية. وقد تركز النحاس في القشطة والزبد بينما اختفى النيكل من السمن ولكن تركز في الجبن القريش، ولم يكن هناك تركيز واضح للمغنسيوم في منتجات الألبان بينما تركز الحديد في منتجات الألبان الثانوية اللبن الفرز ولبن الزبد والشرش. وبالرغم من أن منتجات الألبان تحتوي على محتوى معادن كلي مثل ما في القشطة (3.502 مج/كجم) والزبد (3.64 مج/كجم) والسمن (4.7712 مج/كجم) زيادة عن اللبن الأصلي (5.23 مج/كجم) فإن محتوي المعادن الكلي قد تركز أكثر في منتجات الألبان الثانوية مثل اللبن الفرز (7.89مج/كجم) ولبن الزبد (7.6171 مج/كجم) والشرش (5.206 مج/كجم). ولكن في حالة الجبن القريش فإنها تحتوي محتوى معادن كلي (3.493 مج/كجم) إقل من اللبن الأصلي. وقد تمت مناقشة الأهمية الصحية للمعادن المفحوصة، وذلك بالإضافة إلى الطرق الصحية الواجب اتباعها لسلامة الإنسان.

الكلمات الكاشفة: *اللبن، منتجات الألبان، المعادن الثقيلة، المنجنيز، النحاس، النيكل، المغنسيوم، الحديد.*

INTRODUCTION

Increase in industrial and agricultural processes have resulted in increased concentration of metals in the air, water and soil. These metals are taken in by plants and consequently accumulate in their tissues. Animals that graze on such contaminated plants and drink from polluted waters also accumulate such metals in their tissues and milk if lactating (Yahaya *et al*., 2010). A large amount of these metals taken in by plants and animals subsequently find their way into the food chain. This ever increasing pollution has given rise to concern on the intake of harmful metals in humans. Metals enter the human body through inhalation, ingestion or absorption through the skin (Ahmed, 2002; Ogabiela *et al*., 2010). The intake through ingestion depends on food habit.

Although metals are essential nutrients and have a variety of biochemical functions in all living organisms and important industrial uses, their potential toxicity to humans and animals is a source of concern. They can be toxic when taken in excess; both toxicity and necessity vary from element to element and from species to species (Tripathi *et al*., 1997). It is therefore necessary to monitor and control their levels in consumed food. The measurement of metal levels is helpful not only in ascertaining risk to human health but also in the assessment of environmental quality (Farid *et al*., 2004; Birghila *et al*., 2008). Many reports indicated heavy metals in milk and attributed the presence of these heavy metals in milk and dairy products to exposure of lactating cows to environmental pollution, consumption of contaminated feed stuffs and water as well as the production process. Some of these metals, such as Cu, Ni, Mn, Cr and Fe, for example are essential in very low concentration for the survival of all forms of life (Watson, 2001). Higher levels of Cr, Ni and Co are toxic which released to the environment. They originated from dumping industrial wastes in the rivers, as well as the application of phosphate fertilizers (Venugopal and Luckey, 1978).

Abnormal accumulation of Cu in the tissues and blood is a point of similarity with genetic disease of man called Wilson's disease (Jones and Hunt, 1983; Lee and Garvey, 1998). Most absorbed Cu is stored in liver and bone marrow where it is bound to metallothionein (Sarkar *et al.*, 1983), the acute exposure to Cu result in nausea, vomiting, bloody diarrhea, hypertension, uremia and cardiovascular collapse (Gossel and Bricker, 1990).

Toxicity of metal is closely related to age, sex, route and duration of exposure, level and frequency of intake, solubility, metal oxidation state, retention percentage, absorption rate and mechanisms/efficiency of excretion (Venugopal and Luckey, 1978; Mertz, 1986).

Milk and milk products are the most diversified of the natural foodstuffs in terms of composition, contains more than 20 different trace elements. Most of them are essential and very important such as Cu, Zn, Mn and Fe (Schroeder, 1973; WHO, 1973; Somer, 1974). These metals are co-factors in many enzymes and play an important role in many physiological functions of man and animals. Lack of these metals causes disturbances and pathological conditions (Koh and Judson, 1986; Schuhmacher *et al.*, 1991). The amount of metals in uncontaminated milk is admittedly minute, but their contents may be significantly altered through manufacturing and packaging process as well as metals that may be contaminate different cattle's feed and environment such as Pb, Cd, Cr, Ni and Co could be excreted into milk at various levels (Abou-Arab *et al.*, 1994; Abou-Arab, 1997) and causing serious problems.

Milk is known as an excellent source of Ca, and it can supply moderate amounts of Mg, smaller quantity of Zn and very small contents of Fe and Cu (Pennigton *et al.*, 1995). On the other hand, due to the growing environmental pollution it is also necessary to determine and monitor the levels of toxic metals in milk, because they can significantly influence the human health (Steijns, 2001; Licata *et al.*, 2004).

The presence of heavy metals in dairy products may be attributed to contamination of the original cow's milk, which may be due to exposure of lactating cow to environmental pollution or consumption of feeding stuffs and water (Carl, 1991; Okada *et al.*, 1997). Moreover, raw milk may be exposed to contamination during its manufacture (Ukhun *et al.*, 1990; El-Batanouni and Abo El- Ata, 1996).

The aim of this investigation was to follow up the residues behavior of metals in different milk products during their manufacturing process originated from buffalo's milk on the concentration levels of Mn, Cu, Ni, Mg and Fe.

MATERIALS and METHODS

I. Samples:

I.1. Bulk milk: A total amount of 14 kg of market buffalo's milk was collected in a clean stockpot from a dairy shop in Assiut city, and then transferred to the laboratory with a minimum of delay. In the laboratory and after thoroughly mixing of the bulk milk, 4 kg was taken in another clean stockpot for control milk and milk products samples, and the rest 10 kg was taken for standard milk and milk products samples.

I.2. Control milk sample: After thoroughly mixing of the 4 kg milk, 1 ml was taken as a control milk sample and the rest was subjected to the manufacture of some milk products.

I.3. Control milk products and by-products samples: The rest of 4 kg milk was thoroughly mixed and subjected to a separator; cream (product) and skim milk (by-product) were obtained. The obtained cream was subjected to churner; butter (product) and butter milk (by-product) were obtained. Ghee (product) and morta (by-product) were obtained after subjection the obtained butter to a boiler. The obtained skim milk was subjected to rennet; Kareish cheese (product) and whey (by-product) were obtained. From each obtained milk product and by-product, 1 g and/or ml was taken as a control milk product sample or control milk by-product sample.

I.4. Standard milk sample: After thoroughly mixing of the previously separated 10 kg milk in its stockpot, 10 ml (1000 mg/L) of each of standard stock solutions of heavy metals (Merck, K GaA, 64271 Darmstadt, Germany) of manganese (Mn), copper (Cu), nickel (Ni), magnesium (Mg) and iron (Fe) was added. That is means; 1 mg/kg of each metal was added to the milk (1 ppm). After thoroughly mixing of the milk with standards, 1 ml was taken as a standard milk sample and the rest was subjected to the manufacture of some milk products.

I.5. Standard milk products and by-products samples: The rest of 10 kg milk was subjected for obtaining milk products and by-products in the same way described before. From each obtained milk product and by-product, 1 g and/or ml was taken as a standard milk product sample or standard milk by-product sample.

II. Manufacturing of milk products:

II.1. Cream manufacture: It was manufactured through separation process using electrical separator (Alva-Laval, Germany). Before separation, milk was warmed and then separated to obtain cream and skim milk.

II.2. Butter manufacture: It was manufactured through churning process using electrical mixer (Moulinex). The aforementioned manufactured cream was churned to obtain butter and butter milk according to the method of Eckles *et al.* (1951).

II.3. Ghee manufacture: It was manufactured through boiling process. The aforementioned manufactured butter was boiled till conversation of butter into ghee and curd (morta) according to the method described by El-Sadek *et al.* (1972).

II.4. Kareish cheese manufacture: It was manufactured through addition of rennet to the aforementioned obtained skim milk. No salt was added to avoid any metals can be added from it.

III. Preparation of the samples:

All glassware were washed, before use with distilled water, soaked in nitric acid (30%), then rinsed in redistilled water and air dried. The glassware was kept in clean place to avoid contamination. After that, each sample following weighing was transferred into a clean digestion flask, previously acid–washed then de-ionized water and dried. All digestion flasks were identified for examination.

IV. Digestion procedures of the samples:

Each prepared sample was treated with 5 ml nitric: perchloric acid mixture (HNO_3:$HCLO_3$ = 4:1 v/v) as per Kolmer *et al.* (1951). The samples were left to be stand for the cold digestion overnight, then the samples were heated on the hot plate 1030 (Ru Mo 100 El Basaten St. Cairo) at 70°C till dryness of the samples. Further addition of 5 ml nitric : perchloric acid mixture (HNO_3:$HCLO_3$ = 4:1 v/v) to each sample was undertaken followed by heating again on the hot plate but at 50°C till the brown fumes of NO_3 disappeared and the sample become clear. After cooling, each digest was diluted to 25 ml with de-ionized water and filtered through ashless filter paper (Whatman). The clear filtrate of each sample was kept in refrigerator to avoid evaporation. A blank (without sample) was prepared in the same way.

V. Metal analysis using Atomic Absorption Spectrophotometer:

The metal analysis of the samples was carried out in the Central Laboratory of the Faculty of Veterinary Medicine; Assiut University, Egypt. All samples (controls and standards) in addition to the blank were analyzed for detection and/or measurement of Mn, Cu, Ni and Mg by using of ZEEnit 700P Atomic Absorption Spectrophotometer with Graphite Furnace Unite (AASG) (Perkin-Elmer Atomic Absorption Spectrophotometry model 2380, USA). While the measurement of Fe was done using flame Atomic Absorption Spectrophotometer.

VI. Quantitative determination of the studied heavy metals:

The concentration of Mn, Cu, Ni, Mg and Fe in the examined samples was calculated according to the following equation:

$$C = R \times D/W$$

Where:
C = Concentration of heavy metal (mg/kg) wet weight (ppm)
R = Reading of metal concentration on digital scale of Atomic Absorption Spectrophotometer
D = Final volume of prepared sample in ml
W = Weight of the wet sample

The contents of heavy metals were expressed as mg/kg of the sample based on wet weight. The concentration of absorbance values of heavy metals in the blank samples were also calculated and subtracted from each analyzed sample to exclude any traces of metals that might be present in the used acids for digestion.

RESULTS

Table 1: Some recorded metals content (mg/kg) in milk.

Metal	IDF (1979)	Abou-Arab (1991)	El-Prince and Sharkawy (1999)		Florea *et al.* (2006)	Birghila *et al.* (2008)	Enb *et al.* (2009)		Ogabiela *et al.* (2011)		The present study
			Cow's	Buffalo's	Cow's	Cow's	Cow's	Buffalo's	Cow's (Kano region)	Cow's (Zaria region)	Control buffalo's
Mn	0.025	0.06	-	-	0.051	0.08	0.047	0.072	0.179	0.219	2.30
Cu	0.1	0.22	0.592	0.825	0.14	0.17	0.131	0.201	0.252	0.214	0.71
Fe	0.37	0.95	0.428	0.322	0.97	0.72	0.572	0.880	5.99	3.24	2.14

Table 2: The metals concentration (mg/kg) in the control samples.

Metal	Milk	Cream	Skim milk	Butter	Butter milk	Ghee	Morta	Kareish cheese	Whey	Rennet
Mn	2.3	0	3.9	0	3.01	0	0.17	0.71	1.86	5.7
Cu	0.71	0.986	0.64	1.04	0.59	0.86	2.06	0.99	0.92	22.9
Ni	0.07	0.03	0.07	0.05	0.05	0	0	0.13	0.06	0.4
Mg	0.01	0.016	0.03	0.01	0.0171	0.0012	0.004	0.033	0.016	1.6
Fe	2.14	2.47	3.25	2.54	3.95	3.91	3.25	1.63	2.35	7.68
Total	5.23	3.502	7.89	3.64	7.6171	4.7712	5.484	3.493	5.206	38.28

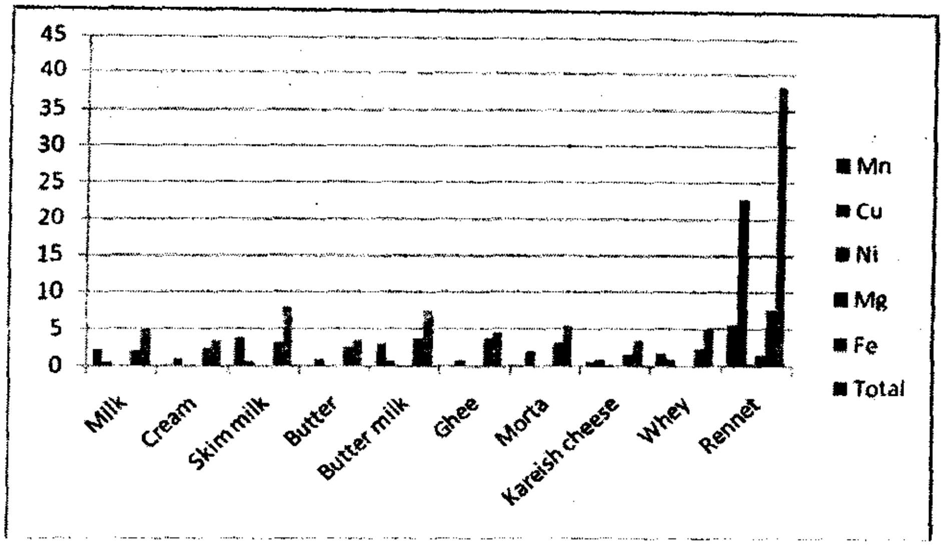

Figure 1: The metals concentration (mg/kg) in the control samples.

Table 3: The metals concentration (mg/kg) in the standards samples.

Metal	Milk	Cream	Skim milk	Butter	Butter milk	Ghee	Morta	Kareish cheese	Whey	Rennet
Mn	3.26	0	4.50	0.497	6.78	0	0.37	7.03	2.59	5.7
Cu	1.80	1.96	1.92	1.18	2.7	0.94	4.5	7.14	1.28	22.9
Ni	0.15	0.08	0.20	0.07	0.22	0	0.01	0.24	0.143	0.4
Mg	0.02	0.026	0.15	0.02	0.028	0.008	0.03	0.16	0.03	1.6
Fe	2.70	4.60	4.15	4.1	4.24	4.12	4.96	3.34	4.25	7.68
Total	7.93	6.666	10.92	5.867	13.968	5.068	9.87	17.91	8.293	38.28

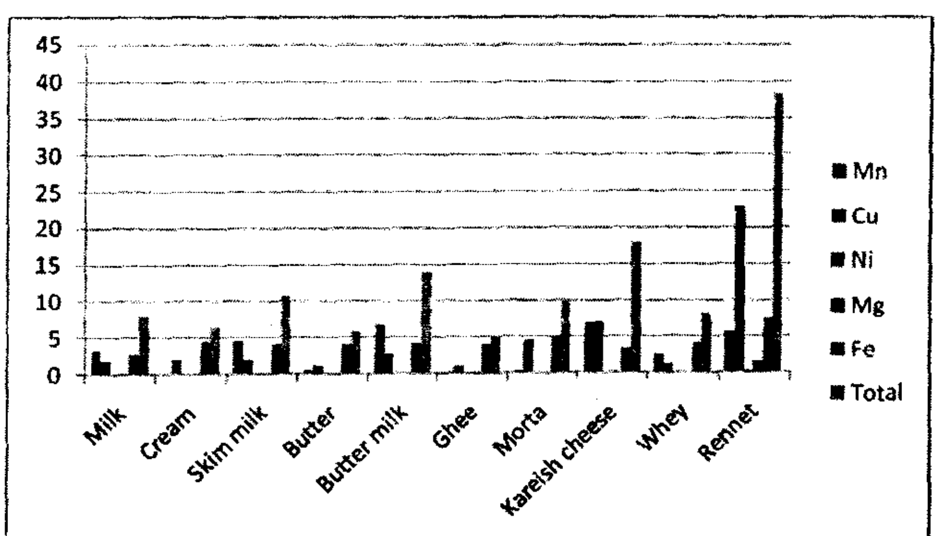

Figure 2: The metals concentration (mg/kg) in the standards samples.

Table 4: Percentage (%*) of increasing of metals in standards than their corresponding control samples.

Metal	Milk	Cream	Skim milk	Butter	Butter milk	Ghee	Morta	Kareish cheese	Whey	Rennet
Mn	29.45	0.00	13.33	100.00	55.60	0.00	54.05	89.90	28.19	0.00
Cu	60.56	49.69	66.67	11.86	78.15	8.51	54.22	86.13	28.13	0.00
Ni	53.33	62.50	65.00	28.57	77.27	0.00	100.00	45.83	58.04	0.00
Mg	50.00	38.46	80.00	50.00	38.93	85.00	86.67	79.38	46.67	0.00
Fe	20.74	46.30	21.69	38.05	6.84	5.09	34.48	51.19	44.71	0.00
Total	34.05	47.46	27.75	37.96	45.47	5.86	44.44	80.49	37.22	0.00

%* = 100 - (Cont. / Stand. × 100)
Cont. = The metals concentration (mg/kg) in the control samples
Stand. = The metals concentration (mg/kg) in the standards samples

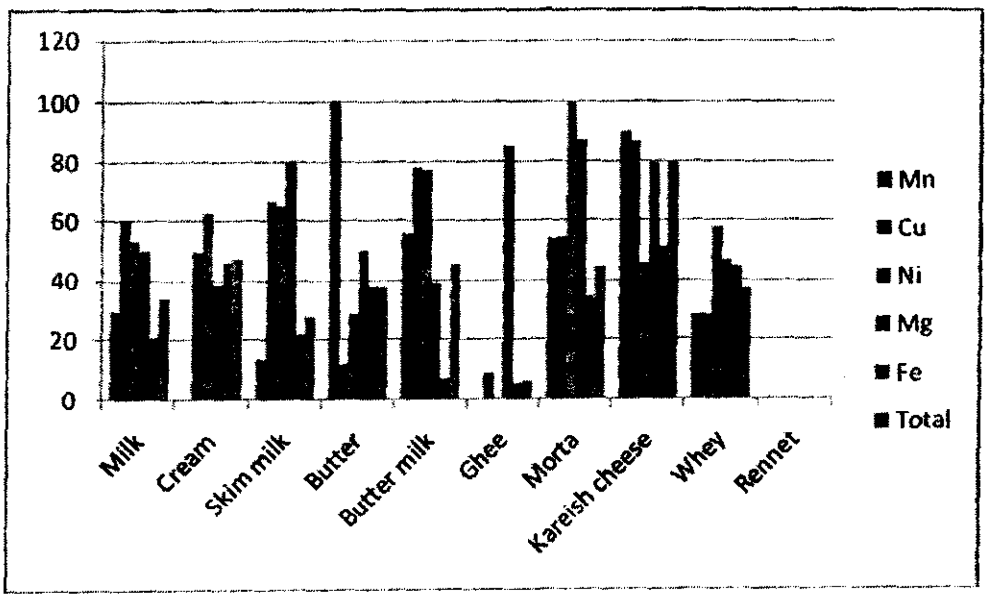

Figure 3: Increasing metals % in standards than their corresponding control samples.

DISCUSSION

Before throwing the lights towards the residue behavior of the examined metals in the manufactured milk products, there is a question: Are the studied metals in the initial milk (control milk sample) came in the acceptable limits? Unfortunately, the values of Mn, Cu and Fe were found to exceed the recorded limits of IDF (International Dairy Federation), and also higher than the recorded results of Abou-Arab (1991), Florea *et al.* (2006), Birghila *et al.* (2008) and Enb *et al.* (2009) as mentioned in Table 1. While, El-Prince and Sharkawy (1999) found higher level of Cu in buffalo's milk than our obtained result. Higher levels of Fe and Ni than our obtained results were recorded by

Ogabiela *et al.* (2011) as they found Fe (5.99 and 3.24 mg/L) and Ni (3.013 and 2.097 mg/L) in 2 regions of Nigeria (Kano and Zaria), respectively. Ogabiela *et al.* (2011) mentioned that their results of Fe were within the recommended daily allowance (15 mg by Durdana *et al.*, 2007).

High levels of heavy metals in this study may be attributed to the high contamination of animal feed and water by such pollutants and could be excreted into milk at various levels (Abou-Arab *et al.*, 1994; Abou-Arab, 1997) and also may be reached to milk through handling procedures.

The distribution patterns of the studied metals in the examined buffalo's milk and derived milk products (control samples) were recorded in Table 2 and Figure 1, and the distribution patterns for the standard samples were recorded in Table 3 and Figure 2. A question arises: why standard samples were used in this investigation? The answer is to add a more metals content to the control samples to give a clearer view about the residues behavior of the studied metals. Thus, the interpretation may be more obvious if a known amount of metals is added to the control samples. Furthermore, the percentages of increase of metals content in the standards samples more than their corresponding control samples can be calculated as shown in Table 4 and Figure 3.

With attention to the residue behavior of manganese (Mn), It was found that Mn disappeared from the fat concentrated milk products starting from cream to butter and finally by ghee, while it concentrated in their by-products skim milk (3.9 mg/kg), butter milk (3.01 mg/kg) than the initial control milk sample (2.3 mg/kg). Although butter was manufactured from cream and cream had no detectable contents of Mn, Mn was concentrated in butter milk than the initial control milk sample. When manufacturing Kareish cheese; Mn was concentrated in whey more than in Kareish cheese (Table 2 and Figure 1). The results of the standard samples were in accordance with the control ones except for butter and Kareish cheese. Although 1 mg/kg of Mn was added to the standard milk sample over its original content of 2.3 mg/kg, standard cream and standard ghee had no detectable amount of Mn; and it concentrated in standard skim milk (4.5 mg/kg) and standard butter milk (6.78 mg/kg) (Table 3 and Figure 2). This obtained results of residue behavior of Mn in standard cream and ghee confirmed those of the control ones. Therefore, percentage of increasing of Mn in the standard samples than their corresponding control ones (Table 4 and Figure 3), showed 0.00% increase in cream and ghee. Thus, it can be concluded that, Mn residues were not concentrated in the fat concentrated milk products.

With regards to copper (Cu) content, it was concentrated in cream and butter. For nickel (Ni), it disappeared in ghee but concentrated in Kareish cheese (Table 2 and Figure 1); and the standard samples confirmed this result (Table 3 and Figure 2), in addition, it concentrated in skim milk and butter milk.

When through the light towards magnesium (Mg) residue behavior, standard skim milk and standard Kareish cheese showed obvious concentration than corresponding control ones (Table 3 and Figure 2), therefore, Table 4 and Figure 3 showed 80.00 and 79.38% increasing of Mg in standard skim milk and standard Kareish cheese, respectively, than control ones. For iron (Fe), it was concentrated in skim milk, butter milk, whey, i.e. by-products. Also total metals content was more concentrated in by-products skim milk, butter milk and whey, although the milk products cream, butter and ghee contained more total metals content than the initial milk sample (Table 2 and Figure 1). In butter, the total metals levels were concentrated by 0.69 fold as compared to initial milk, and 1.04 fold as compared to cream. In the study of Enb *et al.* (2009), higher levels of metals concentration were recorded than the present study as they found metals levels in buffalo's butter were concentrated by 5.6-7.7 folds as compared to initial milk, and 1.4-1.6 folds as compared to cream. Abou-Arab (1991) obtained similar results of Enb *et al.* (2009) who reported that, metals concentrated in cream.

In the examined study, ghee contained total metals content more than butter and cream; and consequently more than initial milk. The concentrated factors of the total metals in ghee were 0.91 fold than that in initial milk, and 1.36 fold than that in cream, and 1.31 fold than that in butter. Enb *et al.* (2009) found higher levels of metals concentration in ghee in comparison to the present study as they found buffalo's samna (ghee) contained concentrated metals 6.7-9.2 folds than that in initial milk, and 1.6-1.8 folds than that in cream; while 1.1-1.2 folds than that in butter was lower in comparison to the present investigation.

Concerning the examined manufactured Kareish cheese, results in Table 2 indicated that all the examined metals were detected but the total metals content (3.493 mg/kg) was lower than in initial milk (5.23 mg/kg) as the reduction level in Kareish cheese was 1.49 fold than in initial milk.

In conclusion, Mn was found to disappear from fat concentrated milk products (cream, butter and ghee), while concentrated in their by-products. Cu concentrated in cream and butter. Ni disappeared in ghee but concentrated in Kareish cheese. No obvious concentration of Mg in milk products while Fe concentrated in by-products skim milk, butter milk and whey. Although milk products contained more total metals content like in cream, butter and ghee more than in the initial milk, the total metals content was more concentrated in by-products like in skim milk, butter milk and whey. But in case of Kareish cheese, it contained total metals content lower than in initial milk.

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