EFFECT OF SOME TECHNOLOGICAL TREATMENTS ON THE MINERAL BALANCE BETWEEN THE SOLUBLE AND COLLOIDAL PHASES OF CAMEL MILK

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ABSTRACT

In dairy technology, mineral equilibrium in milk is important for understanding milk properties and for optimizing milk processing. The objective of this study was to examine the effect of some technological treatments (acidification, cold storage and heat treatments) on the mineral balance between the soluble and colloidal phases of camel's milk by using ultracentrifugation technique. The results showed that, as the pH reduced, the calcium (Ca), phosphate (P), magnesium (Mg) and citrate (Cit) present in the colloidal phase of camel's skim milk (CSM) were gradually displaced into the soluble phase. When the pH of CSM decreased to 4.7, the almost colloidal Ca and P were solubilized (more than 92.2 and 93.5%), respectively. Moreover, the colloidal Mg and Cit were totally solubilized at pH 5.2 and remained constant until pH 4.7. Furthermore, at this pH value small amounts of Mg and Cit were bound to colloidal casein (1.5-3%), respectively. Also, at pH 4.7 the ratio of colloidal Ca/P decreased from 2.07 to 1.68. On the other hand, the results affirmed that the cold storage of CSM at 4 ℃ over a period of 7 days had marked influence on the concentration and distribution of Ca, P, Mg and Cit in camel milk. After 7 days of cold storage at 4℃ of CSM there were an increase in the soluble Ca, P, Mg and Cit contents by 11.9, 10.5, 5.3 and 9.0%, respectively. Furthermore, increasing heating temperature caused a significant decrease in the soluble Ca, P and Cit, but insignificant ($p<0.05$) effect on the Mg concentration was observed. Moreover, increasing heating temperature on CSM resulted in a significant decrease in the colloidal ratio of Ca/P from 2.07 to 1.64. Moreover, when CSM was boiled-treated, the soluble Ca, P, Mg and Cit concentration decreased by 6, 9.6, 5.6 and 8.5%, respectively. Pasteurization LTLT (Low-Temperature Long-Time) and HTST (High-Temperature Short-Time) led to a slight increase in the colloidal Ca, P, Mg and Cit concentration.

Key words: Camel milk, mineral balance, soluble and colloidal phase.

INTRODUCTION

Camel milk represents one of the basic ingredients available to human nutrition in many parts of the world, especially in the arid and semi-arid areas and support of the economy of desert farmers. There is a fast growing demand for camel milk around the world as a result of its health and nutritional benefits (Faye and Bonnet, 2012). The use of camel milk as a treatment for series diseases has been the subject of intense study and debate over the years. There have been several reviews on the use of camel milk therapeutically against jaundice, dropsy, a problem of the spleen, biles, tuberculosis, asthma (El-Agamy *et al.*, 2009), anti-cancer (Magjeed, 2005) and anti-diabetic (Agrawal *et al.*, 2011), respectively which make it more superior to cow milk.

The milk salts, particularly colloidal calcium phosphate (CCP) and ionic Ca play an important role in the stability of the proteins and in their nutritional and organoleptic characteristics. In addition, the mineral content has a pronounced effect on the technological properties of milk, as it affects its susceptibility to renneting, fouling of heat exchangers, micellar stability (Lucey and Fox, 1993 and De La Fuente *et al.*, 1999).

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Few investigations have focused on studying the chemical composition and nutritional quality of camel milk (Konuspayeva *et al.,* 2009; Al Kanhal, 2010; Ibrahim and Khalifa, 2015). Although the overall mineral composition of camel milk has been studied, there is very little information available on the distribution of salts between the soluble and colloidal phases of camel milk as compared to caprine, ovine, bovine and buffalo milk. Camel milk has high minerals content ranged between 0.60 to 0.90% (Main mineral salts are Ca, Na, P, Mg and Cit) (Elamin and Wilcox, 1992; Konuspayeva *et al.,* 2008 ; Ahmed *et al.,* 2014).

The technological processes to which the milk is subjected to obtain a more prolonged shelf life or to improve the final quality of milk products could cause alterations in the equilibrium state of the milk salts present in that milk (Zurera-Cosano *et al.,* 1994 ; Anema, 2009).

Acidification is the important factor for the processing of milk (*e.g.* manufacture of many types of cheese, fermented dairy products and caseins) and it has a pronounced effect on the final structure, texture and functionality of dairy products (Lucey and Fox, 1993; Lucey and Singh, 1998). When the pH of milk has been decreased, the solubility of CCP and the small amounts of Mg and Cit associated to casein micelles were increased and move out from the micelles into the serum phase. However, the CCP is completely present in the serum at pH 5.2. Indeed, at this pH value, all of the colloidal Cit, and a large part of Mg were solubilized (Anema, 2009; Mekmene *et al.,* 2010; Koutina *et al.,* 2014 ; Li and Corredig, 2014). On the other hand, Farah and Rüegg (1989) and Kherouatou *et al.* (2003) studied the state of casein micelles during acidification of camel milk and concluded that the maximum CCP micelle demineralization occurs at approximately pH 5.0 versus pH 5.5 for cow milk.

On the other hand, although the cold storage improves the bacteriological quality of milk, but modifies several of its properties include solubilization of the milk salts. These changes were affected on reduce gel strength and curd firmness during renneting. When milk is cooled, a part of casein dissociates from the micelles and remains in a soluble state (De La Fuente *et al.,* 1997 ; Raynal and Remeuf, 2000). May and Smith (1998) and Koutina *et al.* (2014) noticed that the soluble Ca increased slightly during cold storage of raw milk approximately 9% in 60 hours and these changes are reversible depend on re-warming. At the same time, the cold storage decreased amount of water associated to casein micelles and a release of β-casein from the micellar structure (Pouliot *et al.,* 1994 ; Holt, 1995).

On the other hand, the thermal treatment modifies the equilibrium state of the Ca, P, Mg and Cit present in that milk, depending on the severity of the treatment. Among these changes, transfers of the soluble salts of milk to the colloidal phase result in increasing the heating temperature (Pouliot *et al.,* 1989 a,b; Anema, 2009 ; De La Fuente *et al.,* 2002). Pouliot *et al.* (1989a) and May and Smith (1998) estimated that about (5–12%) of the soluble Ca and (10–18.0%) of the soluble P were transferred to the colloidal phase during the pasteurization of milk (lower than 90°C) and that this loss was recovered. In contrast, increasing the heating temperature up to 100°C caused irreversible changes in the salt partition.

This study was undertaken to determine the effects of some manufacturing processes involving acidification, cold storage and heat treatments on the distribution of camel milk salts between the soluble and colloidal phases to the knowledge of nutritional and technological characteristics and evaluate the impact of these factors on the processing quality of the camel milk.

MATERIALS AND METHODS

Milk Source

Fresh raw camel milk from healthy Magrabi camel's (*Camelus dromedarius*) in middle lactation was obtained from a local farm in Matrouh areas, Matrouh Governorate, North West Coast, Egypt. The samples were preserved with 0.03% (*W/W*) sodium azide NaN_3 (Sigma-Aldrich Co., St. Louis, MO) to inhibit bacteria growth. Camel milk samples was immediately transported to the laboratory in isothermal containers and stored at 4°C until it was processed in the laboratory.

Sample preparation

To avoid the complication due to the presence of fat globules in the milk, camel milk was skimmed by centrifugation at 4000g for 20 min. at room temperature about (25°C). Raw pooled camel's skim milk (CSM) was used in all experiments. For each experiment, untreated CSM was used as a control.

Experimental Procedure

Acidification of camel milk

CSM was prepared according to the method described by Koutina *et al.* (2014). To obtain a certain level of pH, CSM was warmed at 30°C in a water bath and held for 30 min., then acidified by adding predetermined amounts of crystalline glucono-δ-lactone (GDL) (Sigma Chemical Co., St Louis, MO, USA) and mixed for one minute. The initial pH of the camel milk was 6.7. After GDL hydrolyzed the pH gradually decreased and produced acidification rates such that pH 6.2, 5.7, 5.2 and 4.7. The pH of the samples was regularly measured with a pH-Meter and combined glass electrode (Hanna Instruments Deutschland GmbH, Karlsruhe, Germany). All acidified CSM treatments were performed in duplicate.

Cold storage of camel milk

CSM was prepared according to the method described by Raynal and Remeuf (2000). CSM samples (2500 ml) were divided into equal five portions each of 500 ml. The first one was kept as control and other portions were chilled at 4°C in cold chambers for (1, 2, 4 and 7 days). The milk temperature reached 4°C in 5 hours. Before ultracentrifugation this milk was stored for one night at 12±1°C, then the milk samples was held at room temperature at least 1 hr. All CSM treatments were performed in duplicate.

Heat treatments of camel milk

CSM was heat-treated according to the method described by Andrew and Law (1996). CSM samples (4 L) were divided into four equal portions, first portion was kept as a control (raw) and the second was LTLT (Low-Temperature Long Time) heat-treated at 65°C for 30 min. The third one was HTST (High-Temperature Short Time) heat-treated at 72°C for 15 sec. in a thermostatically controlled water bath. The last portion was boiled in oil bath for 2 min., then all treated samples were immediately cooled in an ice-water bath 4±0.5°C for 12 hours. After that, all milk samples were left at room temperature and held at that temperature for 90 min before ultracentrifugation. All heating treatments were performed in duplicate.

Analytical Methods

Minerals separation to the soluble and colloidal phases

Before analysis, all milk samples were thoroughly homogenized in a vortex. Minerals of raw and treated CSM samples were separated to the soluble and colloidal phases by ultracentrifugation according to the method described by López-Fandiño *et al.* (1998). An amount of 30 ml of CSM in polypropylene threaded bottles with a shoulder and screw cap sealing assembly was centrifuged 110.000g at 20°C for 1 hour using a Beckman L7-65 ultracentrifuge with Rotor type 70.1 Titanium (Serial No. 93U, 33 53 made in the USA). After ultracentrifugation, the supernatant (soluble phase) was carefully removed and vacuum filtered through Whatman No.40 paper.

Wet digestion procedures

After centrifugation, five milliliters of homogeneous raw or treated CSM samples ware placed in a 20 ml tube and mineralized by addition of 3 ml of concentrated sulphuric acid H_2SO_4 (95%), 2 ml of concentrated nitric acid HNO_3 (65%) and 5 ml of hydrogen peroxide H_2O_2 (30%) in a glass vessel that was subsequently heated on a hot plate at 180°C for 2.5 hours. After that, the digested materials were quantitatively transferred to a 20 ml volumetric flask and diluted with Milli-Q water (Moreno-Torres *et al.,* 2000).

Mineral Analyses

Determination of total and soluble Ca, Mg, P and Cit concentrations

Total and soluble concentrations of Ca and Mg were determined according to the method described by Murthy and Rhea, (1966) using atomic absorption spectrophotometer (Unicam Analytical System, Model 919, Cambridge, UK) using an air-acetylene flame and wavelength of 422.7 nm and 285.2 nm, respectively. Total and

soluble milk phosphates were determined colorimetrically by the molybdenum blue method in digested samples (De La Fuente and Juàrez, 1995). Briefly, aliquots (2 ml) of the diluted filtrates were mixed with 2.6 ml of the molybdate-ascorbic acid solution to form a blue colored complex. The absorbance at 820 nm was then measured within 15-30 minutes by UV spectroscopy (Jenway 6850 Jenway Instruments, Beacon Road, Staffordshire, ST15 OSA, UK).

Total and soluble milk citrate was determined by the modified method of White and Davies, (1963) as citric acid. An aliquot (1ml) of the samples was mixed with (1.5ml) Trichloroacetic acid 12%, (1.3 ml) of pyridine and (5.7 ml) of acetic anhydride to form a yellow colored complex. The sample was placed in a 32°C water bath for 30 min. and the absorbance was measured at 428 nm by a spectrophotometer (Jenway 6850 Jenway Instruments, Beacon Road, Staffordshire, ST15 OSA, UK). The Ca, Mg, P and Cit concentrations in the colloidal phase were calculated as the difference between the total value and the soluble one. Concentrations of the constituents were expressed in mg/100 g skimmed milk. Analyses were carried out in duplicate.

Statistical Analysis

One way ANOVA of the results was carried out by using the SPSS statistics package, (SPSS V. 18, 2012) for Windows. The results were considered significantly different at ($P<0.05$).

RESULTS AND DISCUSSION

The mean values $\pm$ SD of the Ca, P, Mg and Cit (mg/100 ml) in CSM and their distribution between the colloidal and soluble phases as a function of acidification are shown in Table 1. The results indicated that, at initial pH 6.7 of CSM the maximum mean values of total Ca, P, Mg and Cit were observed. There were 130.0 $\pm$ 4.2, 101.0 $\pm$ 2.1, 11.5 $\pm$ 0.1 and 155.7 $\pm$ 2.1 mg/ 100 ml, respectively. These results are in agreement with those reported by Farah and Rüegg (1989), Kherouatou et al. (2003) and Haddadin (2008) for raw camel milk.

On the other hand, a gradual solubilization of the Ca, P, Mg and Cit from colloidal to the serum phase of CSM was observed as a function of pH. Furthermore, at initial pH 6.7 of CSM,

the soluble Ca, P, Mg and Cit contents were approximately 30.9, 57.0, 61.6 and 68.0% of total were present in the serum phase, respectively. From these results, it seemed that the percentage of the soluble Ca, P and Mg was approximate with that found in the earlier report by Farah and Rüegg (1989) and Kherouatou et al. (2003) they studied the partition of mineral salts between the serum and micellar phases of camel's milk and noticed that the proportion of soluble forms of the minerals 33% for Ca, 69% for Mg, 52% for P and 60% for Cit of their total concentrations. This means that the amount of citrate in the serum phase was higher in the present study.

On the other hand, the evolution of the colloidal and soluble Ca and P during CSM acidification could be separated into two different stages: from initial pH 6.7 to 5.2 and from pH 5.2 to 4.7 values. In the first stage (from initial pH 6.7 to 5.2), solubilization of the CCP markedly increased with the pH decrease. At pH 5.2, the Ca and P were mainly soluble (more than 88.8 %) and a part of colloidal Ca and P remained in the colloidal phase. Indeed, at this pH value, the colloidal P was more solubilized than colloidal Ca. This solubilization of P was accompanied by a release of colloidal Ca and an increase in soluble Ca in the aqueous phase. These results are in agreement with those reported by Van Hooydonk (1986). They noticed that, during milk acidification the Ca and, P equilibrium between the colloidal and the soluble phase are modified due to solubilization of CCP, more Ca and P move out from casein micelles into the soluble phase of the milk.

In the second stage (pH 5.2 to 4.7), the almost totality of colloidal Ca and P were solubilized with the observation that P followed the same pattern as Ca. These results in agree with Attia et al. (2000) and Kherouatou et al. (2003). They reported that, during acidification of CSM, the changes in the solubilization of Ca, P and Mg showed similar trends to those observed in cow's milk and the demineralization of CSM occurred, at approximately pH 5.5 vs. pH 6.0 for cow's milk, but the totally solubilized of CSM occurred at below pH 5.0. Furthermore, Mekmene et al. (2010), Wolfschoon-Pombo and Andlinger (2013) and Koutina et al. (2014) concluded that, at pH values below 5.2, the Ca

Table1. The changes in the concentration of calcium, phosphate, magnesium and citrate and their distribution between the soluble and colloidal phases during acidification of camel skim milk (mg/100 ml)

pH value	Mineral distribution	Calcium	Phosphate	Magnesium	Citrate	Ratio of Ca/P
	Total	$130.0^b\pm4.2$	$101.0^c\pm2.1$	$11.5^a\pm0.1$	$155.7^b\pm2.1$	1.29
	Soluble	$40.2^e\pm1.6$	$57.6^d\pm1.2$	$7.1^d\pm0.2$	$105.8^d\pm1.4$	0.70
6.7	Colloidal	$89.9^a\pm2.6$	$43.5^a\pm0.9$	$4.4^a\pm0.2$	$49.8^a\pm0.7$	2.07
	Sol.(%) of total	30.9	57.0	61.6	68.0	
	Col. (%) of total	69.1	43.0	38.4	32.0	
	Total	$135.5^{ab}\pm0.7$	$104.4^{bc}\pm0.9$	$11.6^a\pm0.1$	$157.6^{ab}\pm0.6$	1.30
	Soluble	$49.2^d\pm1.9$	$61.5^d\pm1.3$	$7.6^c\pm0.2$	$111.8^c\pm1.5$	0.80
6.2	Colloidal	$86.4^a\pm1.2$	$42.9^a\pm0.4$	$3.9^b\pm0.2$	$45.8^a\pm2.0$	2.01
	Sol.(%) of total	36.3	58.9	66.1	71.0	
	Col. (%) of total	63.7	41.1	33.9	29.0	
	Total	$136.5^{ab}\pm0.7$	$106.5^{ab}\pm0.7$	$11.6^a\pm0.1$	$158.0^{ab}\pm1.3$	1.28
	Soluble	$62.6^c\pm2.3$	$67.1^c\pm1.4$	$8.4^b\pm0.1$	$118.8^b\pm1.6$	0.93
5.7	Colloidal	$73.9^b\pm3.0$	$39.4^a\pm0.7$	$3.1^c\pm0.1$	$39.2^b\pm2.8$	1.88
	Sol.(%) of total	45.9	63.0	73.0	75.2	
	Col. (%) of total	54.1	37.0	27.0	24.8	
	Total	$137.5^a\pm2.1$	$108.5^a\pm2.1$	$11.6^a\pm0.1$	$158.5^{ab}\pm0.7$	1.27
	Soluble	$121.0^b\pm4.0$	$96.3^b\pm2.1$	$11.3^a\pm0.1$	$151.7^a\pm2.0$	1.26
5.2	Colloidal	$16.5^c\pm6.1$	$12.3^b\pm4.2$	$0.3^d\pm0.1$	$6.8^c\pm1.3$	1.51
	Sol.(%) of total	88.0	88.8	97.5	95.7	
	Col. (%)of total	12.0	11.2	2.5	4.3	
	Total	$141.0^a\pm2.8$	$108.0^a\pm0.1$	$11.7^a\pm0.1$	$160.6^a\pm0.6$	1.31
	Soluble	$130.0^a\pm4.2$	$101.0^a\pm2.1$	$11.5^a\pm0.1$	$155.7^a\pm2.1$	1.29
4.7	Colloidal	$11.0^c\pm1.4$	$7.0^b\pm2.1$	$0.2^d\pm0.1$	$4.9^c\pm2.7$	1.68
	Sol.(%) of total	92.2	93.5	98.5	97.0	
	Col. (%) of total	7.8	6.5	1.5	3.0	

Means (±SD). [a,b,c] in the same column with different superscript letters are significantly differ (P<0.05).

Sol. (%) of total = Soluble (%) of total   Col. (%) of total = Colloidal(%) of total

and P is completely solubilized from casein micelles and CCP is completely dissolved below pH 4.9.

On the other hand, the colloidal and soluble Mg and Cit can be divided into two regions. In the first region from pH (6.7 to 6.2 -5.2), the solubilization of colloidal Mg and Cit increased slightly with the pH decrease. In the second stage (pH 5.2 to 4.7) the colloidal Mg and Cit were totally solubilized at pH 5.2 and remained constant until pH 4.7. Furthermore, at this pH value small amounts of Mg and Cit were bound to casein (1.5-3%). These results are in agreement with Le Graët and Brule′ (1993), Gaucheron et al. (1996) and Gaucheron (2005). They showed similar results, the totally solubilization of colloidal Mg and Cit occurred at about pH 5.2 in cow's milk.

These differences in the solubilization of the Ca, P, Mg and Cit during acidification between camel and cow milk may be due to the higher buffering capacity of CSM than cow milk. Al-Saleh and Hammad (1992), Ramet (2001) and El-Agamy (2006) reported that the CSM has a maximum buffering capacity at pH 4.95 versus at pH 5.65 for cow's skim milk.

Furthermore, the statistical analysis of the soluble Ca, P, Mg and Cit concentrations confirmed a significant increase (P<0.05) during milk acidification from pH 5.7 to 4.7 while from pH 6.7 to 5.7 there were a slight increase.

Moreover, at pH 4.7, the ratio of the total, soluble and colloidal Ca/P was 1.31, 1.29 and 1.68. These values are in the range of previous values obtained by Griffin et al. (1988); Dalgleish and Law, (1989) and Mekmene et al. (2010). They reported that the values of colloidal Ca/P ratio ranged between 1.5 -1.9 at pH.4.9. Furthermore, Holt et al. (1989), Anema (2009) and Koutina et al. (2014) found that the ratio of the soluble Ca/P was ranged between 1.2 -1.10. On the other hand, Holt et al. (1986) noticed that the highest values of the colloidal Ca/P ratio are likely to be related to the simultaneous release of calcium phosphate and of casein-bound Ca where calcium phosphate is dissolved by decreases pH.

The change in concentration and distribution of CSM minerals between the soluble and colloidal phases during the cold storage at 4°C for 7 days is presented in Table 2.

Results showed that, the mean values of total Ca, P, Mg and Cit of all samples increased slightly with increasing storage period for 7 days with no significant difference (P<0.05) recorded between treated samples. Similar results were reported by Malacarne et al. (2013). They noticed that, insignificant variations in total Ca, P and Mg contents were observed during cold storage of raw cow's milk at 4-6ºC.

Moreover, during the first day of cold storage at 4°C, there was a slight increase in the soluble Ca, P, Mg and Cit contents while after 2 days of cold storage, the changes were more appreciable and the soluble Ca, P, Mg and Cit contents increased by 7.0, 6.7, 3.9 and 5.8%, respectively. These results agree with Davies and White, (1960). They found that, after cold storage of cow's milk at 3°C for 2 days the concentrations of Ca and P in the soluble phase increased by 6 and 7%, respectively.

Furthermore, the highest significant (P<0.05) mean values of soluble Ca, P, Mg and Cit contents were observed up to 7 days of cold storage. It was 57.3±2.1, 70.0±1.5, 7.8 ±0.1 and 121.6±1.6 mg/100 ml, respectively.

Overall, this study shows that, prolonged storage of camel milk for 7 days at 4°C has markedly influence on the soluble Ca, Mg, P and Cit contents. After 7 days of cold storage at 4°C there was an increase in the soluble Ca, P, Mg and Cit contents by 11.9, 10.5, 5.3 and 9.0%, respectively. The levels of soluble Ca, Mg, P and Cit contents of CSM seem higher than reported by De La Fuente et al. (1997). They reported that, after cold storage of goat's milk at 3°C for 7 days, the soluble Ca, Mg, and P contents increased by 10.3, 3.1 and 9.4%, respectively. In addition, Ichilczyk-Leone et al. (1981), May and Smith (1998) and Lewis (2011) showed that, during cold storage of raw cow's milk the soluble Ca content was slightly increased by 10% and these changes were reversible after re-warming.

On the other hand, when the milk is cooled the CCP not only dissolved, but also induced β-casein diffusion towards the soluble phase and increasing the loss of colloidal Ca linked to

Table 2. The change in the concentration of calcium, phosphate, magnesium and citrate and their distribution between the soluble and colloidal phases in camel skim milk during the cold storage at 4°C for 7 days (mg/100 ml)

Storage period (day)	Mineral distribution	Calcium	Phosphate	Magnesium	Citrate	Ratio of Ca/P
Control Raw milk	Total	$130.0^a \pm 4.2$	$101.0^a \pm 2.1$	$11.6^a \pm 0.1$	$155.7^a \pm 2.1$	1.3
	Soluble	$40.2^b \pm 1.6$	$57.6^b \pm 1.2$	$7.1^b \pm 0.1$	$105.9^c \pm 1.3$	0.7
	Colloidal	$89.9^a \pm 2.6$	$43.5^a \pm 0.9$	$4.5^a \pm 0.2$	$49.8^a \pm 0.7$	2.1
	Sol.(%) of total	30.9	57.0	61.6	68.0	
	Col. (%) of total	69.1	43.0	38.4	32.0	
1	Total	$131.7^a \pm 0.4$	$102.9^a \pm 1.1$	$11.5^a \pm 0.1$	$156.5^a \pm 0.4$	1.3
	Soluble	$43.8^b \pm 1.6$	$59.8^b \pm 1.2$	$7.2^b \pm 0.1$	$107.8^c \pm 1.4$	0.7
	Colloidal	$88.0^a \pm 1.2$	$43.2^a \pm 2.3$	$4.4^{ab} \pm 0.2$	$48.7^a \pm 1.8$	2.0
	Sol.(%) of total	33.3	58.1	62.4	69.0	
	Col. (%) of total	66.7	41.9	37.6	31.0	
2	Total	$133.3^a \pm 0.3$	$103.3^a \pm 0.2$	$11.6^a \pm 0.1$	$156.5^a \pm 0.6$	1.3
	Soluble	$53.6^a \pm 2.0$	$66.9^a \pm 1.4$	$7.7^a \pm 0.2$	$117.1^b \pm 1.5$	0.8
	Colloidal	$79.7^b \pm 2.3$	$36.4^b \pm 1.2$	$3.9^{ab} \pm 0.1$	$39.5^b \pm 2.1$	2.2
	Sol.(%) of total	40.3	64.8	66.3	74.8	
	Col. (%) of total	59.7	35.2	33.7	25.2	
4	Total	$133.6^a \pm 0.3$	$103.6^a \pm 0.7$	$11.6^a \pm 0.1$	$157.8^a \pm 1.1$	1.3
	Soluble	$55.5^a \pm 2.1$	$68.7^a \pm 1.5$	$7.8^a \pm 0.2$	$120.1^{ab} \pm 1.6$	0.8
	Colloidal	$78.2^b \pm 2.3$	$35.0^b \pm 2.2$	$3.9^b \pm 0.4$	$37.8^b \pm 0.5$	2.2
	Sol.(%) of total	41.5	66.3	66.7	76.0	
	Col. (%) of total	58.5	33.7	33.3	24.0	
7	Total	$133.8^a \pm 0.4$	$103.7^a \pm 0.3$	$11.7^a \pm 0.1$	$157.8^a \pm 0.4$	1.3
	Soluble	$57.3^a \pm 2.1$	$70.0^a \pm 1.5$	$7.8^a \pm 0.1$	$121.6^a \pm 1.6$	0.8
	Colloidal	$76.5^b \pm 1.7$	$33.8^b \pm 1.8$	$3.9^b \pm 0.1$	$36.3^b \pm 1.2$	2.3
	Sol.(%) of total	42.8	67.4	67.0	77.0	
	Col. (%) of total	57.2	32.6	33.0	23.0	

Means (±SD). [a,b,c] in the same column with different superscript letters are significantly differ (P<0.05).

Sol. (%) of total = Soluble (%) of total   Col. (%) of total = Colloidal (%) of total

β-casein (Van Hooydonk, 1986; Raynal and Remeuf, 2000). In addition, Hassan *et al.* (2009) recorded a slight decrease in camel milk β-casein during cold storage (4°C/48 hr.).

However, the apparent loss of minerals from the colloidal to the soluble phase in CSM can be explained by the camel's milk had a higher content of β-casein compared to the cow's milk. Furthermore, the average proportion of camel's milk β-casein is higher than cow's milk and constitutes about 65% of total camel's milk casein (Kappeler *et al.,* 1998 ; Farah and Fischer 2004) versus 39% for cow's milk casein (Mehaia *et al.,* 1995; El-Agamy *et al.,* 2009) and this may explain why casein is solubilized to a greater extent in camel milk than in cow milk and other milk.

On the other hand, during the cold storage at 4°C for 7 days the ratios of total, soluble and colloidal Ca/P ware 1.3, 0.8 and 2.3, respectively. These results are in agreement with De La Fuente *et al.* (1997). They found the ratios of soluble Ca/P were 0.8 for stored milk at 4°C over a period of 7 days.

The effect of heat treatments on the Ca, P, Mg and Cit concentrations and their distribution between the soluble and colloidal phase of raw and heat-treated CSM is summarized in Table 3. The results demonstrated that, after heat-treatment the total Ca, P, Mg and Cit contents progressively increased, but insignificant differences (P<0.05) were observed between the raw and heat-treated skim camel milk. A similar tendency was found by Suliman *et al.* (2013) and Yoo *et al.* (2013). They affirmed that, the heat treatment did not influence on the total Ca, P, Mg and Cit contents in milk.

Moreover, the results appeared that the colloidal Ca, P, Mg and Cit contents increased with increasing the temperature. The boiled-treated CSM contained the highest significant (p<0.05) mean values of the colloidal Ca, P, Mg and Cit. It was 106.7±1.3, 60.3±0.9, 5.2±0.5 and 66.2±2.5 mg/100 ml, respectively. These results are in good agreement with the work done by De La Fuente *et al.* (2002) and Anema, (2009). They observed that, the solubility of the CCP is temperature dependent and increasing the temperature resulted in a rapid conversion of the soluble Ca and P to the colloidal phase. Also,

this effect could be a result of the reduction in pH during the heating process of milk (Fox and McSweeney, 1998).

On the other hand, when CSM was boiled-treated the soluble Ca, P, Mg and Cit concentration decreased by 6, 9.6, 5.6 and 8.5%, respectively. These values are in good agreement with Pouliot *et al.* (1989b); May and Smith, (1998) and Lewis, (2011). They observed a decrease in the soluble Ca, P contents by 5.7 and 10.0%, respectively in heat-treated of cow's milk, but that it recovered quickly during cold storage.

On the other hand, increasing temperature progressively increased the loss of soluble Ca, P, and Cit levels in CSM while small changes in soluble Mg were observed. Boiled-treated of CSM markedly increased the levels of colloidal Ca, P, Mg and Cit, while pressurization LTLT and HTST led a small increase in colloidal Ca, P, Mg and Cit concentration. These findings indicate that the Ca, P, Mg and Cit bound directly to casein remained largely unaffected by heating below 90°C. Kocak *et al.* (1984), Pouliot *et al.* (1989 a,b), Holt (1995) and De La Fuente (1998) maintained that, when milk is heated to (below 95°C/several minutes) and then cooled at 5°C the soluble Ca, P and Cit transfer to the colloidal phase and most of this decrease in soluble Ca and P occurs within the first minutes of heating. Furthermore, the diffusible Ca, P and Cit concentrations are restored to about their original level.

However, a significant decreased (P<0.05) in the soluble Ca, P and Cit concentrations was observed after heat-treated of CSM, while the soluble Mg owing to a slight decrease in the concentrations with no significant (P<0.05) recorded at any temperature studied. These results are in agreement with those reported by Rose and Tessier (1959). They indicated that there was little change in soluble Mg during heat-treated of cow milk at 95 °C for up to 80 min, and also suggests that little P will be precipitated as the Mg salt.

On the other hand, the results indicated that the ratios of colloidal Ca/P of heat-treated CSM ranged between1.64 to 2.07. Results in the present study are in good agreement with those reported by Konuspayeva *et al.* (2008). They

Table 3. The influence of the different heat treatments of calcium, phosphate, magnesium and citrate concentration and their distribution between soluble and colloidal of raw and heat-treated camel skim milk (mg/100 ml)

Heat treatment	Minerals distribution	Calcium	Phosphate	Magnesium	Citrate	Ratio of Ca/P
	Total	$130.0^b\pm4.2$	$101.0^b\pm2.1$	$11.6^a\pm0.1$	$155.7^b\pm2.1$	1.29
	Soluble	$40.2^a\pm1.6$	$57.6^a\pm1.2$	$7.1^a\pm0.1$	$105.9^a\pm1.3$	0.70
Raw skim milk	Colloidal	$89.9^c\pm2.6$	$43.5^b\pm0.9$	$4.5^a\pm0.2$	$49.8^c\pm0.7$	2.07
	Sol.(%) of total	30.9	57.0	61.6	68.0	
	Col. (%) of total	69.1	43.0	38.4	32.0	
	Total	$137.5^a\pm0.7$	$112.1^a\pm2.3$	$11.6^a\pm0.2$	$160.7^a\pm0.9$	1.28
Pressurization LTLT	Soluble	$39.0^{ab}\pm1.5$	$57.0^{ab}\pm1.2$	$7.0^a\pm0.2$	$100.6^b\pm1.3$	0.68
	Colloidal	$98.6^b\pm2.2$	$55.1^a\pm3.5$	$4.6^a\pm0.4$	$60.1^b\pm0.4$	1.98
	Sol.(%) of total	28.3	50.9	61.0	62.6	
	Col. (%) of total	71.7	49.1	39.0	37.4	
	Total	$140.5^a\pm2.1$	$113.7^a\pm1.0$	$11.7^a\pm0.1$	$163.0^a\pm1.3$	1.26
Pressurization HTST	Soluble	$38.6^{ab}\pm1.5$	$56.5^{ab}\pm1.2$	$6.8^a\pm0.2$	$99.5^b\pm1.3$	0.71
	Colloidal	$102.0^{ab}\pm3.6$	$57.3a\pm0.2$	$4.9^a\pm0.2$	$63.5^{ab}\pm2.5$	1.76
	Sol.(%) of total	27.5	49.6	58.0	61.0	
	Col. (%) of total	72.5	50.4	42.0	39.0	
	Total	$142.0^a\pm0.0$	$114.4^a\pm0.2$	$11.8^a\pm0.3$	$163.6^a\pm1.2$	1.28
	Soluble	$35.4^d\pm1.3$	$54.1^b\pm1.1$	$6.6^a\pm0.2$	$97.4^b\pm1.3$	0.77
Boiling	Colloidal	$106.7^a\pm1.3$	$60.3^a\pm0.9$	$5.2^a\pm0.5$	$66.2^a\pm2.5$	1.64
	Sol.(%) of total	24.9	47.4	56.0	59.5	
	Col. (%) of total	75.1	52.6	44.0	40.5	

Means (±SD). ^{a,b,c} in the same column with different superscript letters are significantly differ (P<0.05).

LTLT = Low Temperature Long Time   HTST = High Temperature Short Time

Sol.(%) of total = Soluble (%) of total   Col. (%) of total = Colloidal(%) of total

indicated that the ratio of the Ca/P ranged between 0.57 - 1.93 for the heat-treated camel's milk. In addition, Holt, (1982); Holt *et al.* (1986) and Griffin *et al.* (1988) found the ratio of the colloidal Ca/P ranged between 1.61- 2.08 for heat-treated cow's milk.

Conclusion

The balance of soluble and colloidal minerals play a fundamental role in the nutritional and the technological properties of dairy products. The present study was carried out to obtain further information about the effects of acidification, cold storage and heat treatments on the concentration and distribution of camel milk minerals between the soluble and colloidal phase. It was found that the concentration and distribution of Ca, P, Mg and Cit between the soluble and colloidal phases are markedly dependent on the acidification, cold storage and heat treatments of camel milk. During milk acidification by the addition of GDL the Ca, P, Mg and Cit equilibriums are modified due to solubilization of colloidal Ca, P, Mg and Cit and moves out from casein micelles into the soluble phase of the milk. At pH 4.7 the almost of colloidal Ca and P were solubilized (more than 92.2 and 93.5%) while the colloidal Mg and Cit were totally solubilized at pH 5.2 and remained constant until pH 4.7. On the other hand, refrigerated storage of CSM at 4°C markedly increases the soluble Ca, Mg, P and Cit contents. After the cold storage of CSM at 4°C for 7days, there were an increase in the soluble Ca, P, Mg and Cit contents by 11.9, 10.5, 5.3 and 9.0%, respectively. Furthermore, when CSM is boiled-treated the soluble Ca, P, Mg and Cit concentration decreased by 6, 9.6, 5.6 and 8.5%, respectively. Pressurization LTLT and HTST caused small increase in colloidal Ca, P, Mg and Cit concentrations. Overall, these data give good useful information as to the assessment of the mineral distribution of Ca, P, Mg and Cit in camel's milk under the effect of acidification, cold storage and heat treatments. Moreover, if camel's milk is used in cheese-making the most of the soluble elements are lost in the whey during manufacture; the knowledge of this element distribution would allow evaluating the influence of these technological treatments on the mineral content in cheese. Future studies should focus on the kinetics of the changes in the colloidal and the soluble phase distribution of Ca, P, Mg and Cit could help to increase the efficiency of manufacturing processes of camel's milk.

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تأثير بعض المعاملات التكنولوجية على التوازن المعدنى ما بين الحالة الذائبة والغروية للبن النوق

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إن للمعاملات التكنولوجية التي تجرى على لبن النوق بهدف الحفظ أو التصنيع تأثير على تركيز وتوزيع العناصر المعدنية بين الحالة الذائبة والغروية وإن معرفة ذلك التأثير يمكن أن يسهم في زيادة كفاءة عمليات التصنيع للبن النوق، الهدف من هذا البحث هو دراسة تأثير بعض المعاملات التكنولوجية مثل التحميض المباشر للبن، التخزين البارد وثلاث معاملات حرارية على التوازن المعدني بين الحالة الذائبة والغروية للبن النوق باستخدام تقنية الطرد المركزي فائق السرعة، أظهرت النتائج أنه بزيادة درجة حموضة لبن النوق فان محتوى اللبن من الكالسيوم، الفوسفات، الماغنسيوم والسترات الموجود في الحالة الغروية يحدث له تحول تدريجي من الحالة الغروية إلى الحالة القابلة للذوبان. فعند الوصول إلى الرقم الهيدروجيني ٤.٧ للبن يحدث معظم التحول للكالسيوم والفوسفات من الحالة الغروية إلى الحالة الذائبة (أكثر من٩٢.٢% و٩٣.٥%) على التوالى بينما يحدث معظم التحول للمغنسيوم والسترات الغروية عند الوصول إلى الرقم الهيدروجيني ٥.٢ بنسبة (أكثر من ٩٧.٥% و٩٥.٧%) على التوالى ويستمر التحول بنسبة قليلة في تركيز كل من المغنسيوم والسترات الغروية عند الوصول الى الرقم الهيدروجيني ٤.٧ حيث تبقى كميات صغيرة من الماغنسيوم والسترات مرتبطة مع الكازين الغروية حوالى (١.٥-٣.٠%) تقريباً، وأيضاً أوضحت النتائج انه عند أنه بزيادة درجة حموضة لبن النوق إلى الرقم الهيدروجيني ٤.٧ فانه يحدث انخفاض في نسبة الكالسيوم/ الفوسفات من ٢.٠٧ إلى ١.٦٨. وأظهرت النتائج أن التخزين البارد للبن النوق على٤ درجات مئوية على مدى ٧ أيام له تأثير واضح على تركيز وتوزيع الكالسيوم والفوسفات، المغنسيوم والسترات وتحولها من الحالة الغروية إلى الحالة الذائبة فبعد ٧ أيام من التخزين البارد كانت هناك زيادة في تركيز الكالسيوم والفوسفات، المغنسيوم والسترات الذائبة بنسبة ١١.٩، ١٠.٥، ٥.٣ و ٩.٠ % على التوالي، علاوة على ذلك فإنه لوحظ انه بزيادة درجة الحرارة التي يتعرض لها لبن النوق فانه يحدث تحويل سريع للكالسيوم، الفوسفات، المغنسيوم والسترات من الحالة الذائبة إلى الحالة الغروية وأظهرت النتائج تأثير معنوى كبير ($P<0.05$) لمعاملة لبن النوق بالغليان حيث حدث انخفاض فى تركيز الكالسيوم، الفوسفات، المغنسيوم والسترات الذائب بنسبة ٦، ٩.٦، ٥.٦ و ٨.٥% على التوالي، في حين أن معاملة اللبن بطريقة البسترة LTLT (درجات الحرارة المنخفضة وقت طويل) أو بطريقة HTST (درجة الحرارة مرتفعة وقت قصير) أدت إلى زيادة طفيفة في تركيز الكالسيوم والفوسفور والسترات الغروية بينما لم تظهر النتائج أي تأثير معنوى ($P<0.05$) للمعاملة بأي من طريقتي البسترة على محتوى اللبن من المغنسيوم وأيضاً لوحظ انه بزيادة درجة حرارة المعاملة الحرارية التى يتعرض لها لبن النوق فانه يحدث انخفاض في نسبة الكالسيوم/ الفوسفات من ٢.٠٧ إلى ١.٦٤.