Performance of skim goat milk mineral content submitted to the block freeze concentration process

ABSTRACT

The goat milk possess good nutritional and health-promoting properties, and besides it is considered an exceptionally important food because is rich in mineral content, being also able to influence in the dairy technology. The aim of this study was to evaluate the goat milk mineral performance submitted to block freeze concentration process. Therefore, at the end of this study it was possible to note that with the freeze concentration stages increase, calcium, magnesium, sodium, potassium, and zinc contents increased in both concentrated and ice fractions. However, the phosphate content showed no difference between concentrated and the initial skim goat milk. All mineral content showed high efficiency of process and concentration factor. Finally, it was observed an increase in the minerals contents evaluated with the increasing of freeze concentration stages of skim goat milk. This behavior was highlighted for the results obtained to the efficiency of mineral concentration determined in the first stage of the freeze concentration process.

Keywords: Goat milk concentrated, concentration process, main mineral elements, efficiency of process, concentration factor.

1. INTRODUCTION

Goat milk and its products are important in human nutrition and have become a part of the current trend of healthy eating around the world [1, 2]. The goat milk has high added value because it is a source of nutritional compositional of excellent quality, including the quantity of minerals [3, 4]. The goat milk present some major and minority minerals in larger amounts than cow milk [5-7]. Minerals are fundamental for human health, as they are required for many physiological functions such as tissue growth, regulation of enzyme activities, blood clotting, and to facility of membrane transport of essential nutrients [8, 9]. Besides their effects on health, minerals influence milk technological traits, casein micelle structure and aggregation, rennet coagulation time, curd structure, and cheese yield [8, 10-11].

It is known that most people consume foods that have less than two-thirds of one or more essential minerals [12]. In addition, because of that the production of mineral-supplemented foods is a growing as an important strategy to prevent mineral deficiencies. Milk and milk based products are good candidates for mineral fortification due to their worldwide consumption by all groups at risk of deficiency, and also because of their high nutritional value, of the buffering effect on digestion and absorption processes, and of the positive effects on growth [9]. The concentration of milk may be an alternative to supplementation of these products. New methods are developed to increase goat milk and its derivate quality. Also, the development of new added value products has led to increased interest in specific studies focused on the suitable ways of improve goat milk nutrition, quality, and consumption.

The block freeze concentration technology makes it possible to produce food concentrateds with high quality by recovering a food solute based on the separation of pure ice crystals from a freeze-concentrated aqueous phase. When compared with traditional concentration processes, such as evaporation, freeze concentration not only shows some

significant potential advantages for the production of a concentrated where no vapor/liquid interface exists but also can protect thermally fragile food compounds [13]. According to Sánchez et al. [14], the freeze concentration reduces around three times the total cost off the process (including capital, cleaning and energy), when compared to the evaporation or reverse osmosis processes.

The freeze concentration has highly promising applications, especially, in the production of foods and ingredients that have high nutritive value [15]. In this technology, a food liquid solution is completely frozen and then, the whole frozen solution is thawed, with separation of concentrated fraction from ice fraction by gravitational thawing. Sometimes the separation may be carried out assisted by other techniques to enhance separation efficiency [16, 17]. The concentration of solutes retained in the ice formed determines the efficiency of this process [15]. This technique has been used in concentration of different foods, such as cheese whey [14, 18], milk [19], skim milk [20], wine [17], fruit juices [13, 21, 22], coffee extract [23], and tofu whey [24].

Studies are conducted on the properties of concentrated skim goat milk prepared by ultrafiltration [11]. However, in the light of our knowledge, there are no reports in the literature on how mineral performance of skim goat milk are affected by the block freeze concentration technology. A better understanding of this behavior is necessary to further understand the use of freeze concentrated milk in production and processing of new dairy products. Therefore, the aim of the present study was to concentrated skim goat milk by block freeze concentration process and to evaluate the impact of the process on mineral performance of the concentrated and the ice fractions.

2. MATERIAL AND METHODS

2.1 Material

Commercial skim UHT goat milk (Caprilat®, CCA Laticínios, Rio de Janeiro, Brazil) was used as the start material. The skim goat milk composition was 8.46 ± 0.01 g total solids 100 g⁻¹, 2.91 ± 0.05 g total protein 100 g⁻¹, 3.93 ± 0.05 g lactose 100 g⁻¹ and 0.89 ± 0.03 g ash 100 g⁻¹. All reagents were of analytical grade.

2.2. Protocol of the skim goat milk freeze concentration procedure

The freeze concentration procedure used to concentrated the skim goat milk was carried out by applying the block freeze concentration technique, according to the process proposed by [25]. An initial volume of 20 L of skim goat milk was separated into twenty batches of 1 L. Each 1L of skim goat milk was fractionated in plastic containers and were frozen at - 20 ± 2 °C in a freezer unit (Consul, Biplex CRD41D, São Bernardo do Campo, Brazil). After the skim goat milk has been completely frozen, 50 % of the initial volume was defrosted at room temperature (20 ± 2 °C), obtaining two fractions, the concentrated goat milk (CG1) and the ice (I1). The defrosted liquid (CG1) was frozen at - 20 ± 2 °C and used as feed solution in the second stage. This procedure was repeated until the third stage (Figure 1). After each stage, a portion of concentrated (CG1, CG2, and CG3), and ice fractions (I1, I2 and I3) was collected and stored at - 20 ± 2 °C until the analysis.

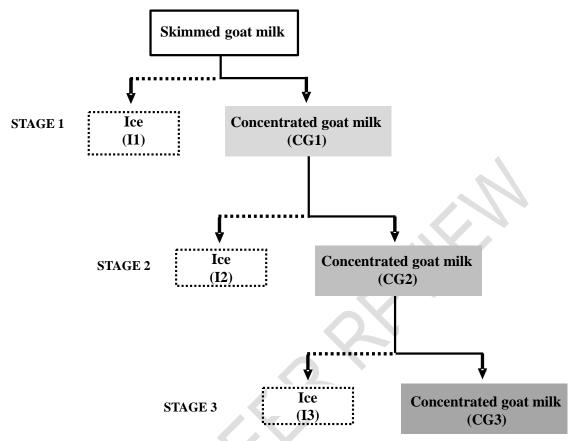


Fig. 1. Diagram of the skim goat milk block freeze concentration process.

2.3 Mineral fractions analysis

2.3.1 Calcium, magnesium, and zinc content

The determination of mineral elements Ca, Mg, and Zn content (mg kg⁻¹) were realized by flame atomic absorption spectrometry (F-AAS) according to Navarro-Alarcón et al. [26], with modifications. The spectrometer used was the AAnalyst 200 model (PerkinElmer, Inc., Waltham, MA, EUA) equipped with the background corrector, and the deuterium arc illumination, using the Echelle resolution system. Acetylene (purity 99.7%) was employed as fuel gas to heat the atomization system and as compressed gas was used the compressed air. Before the measurement, all samples were calcined at 520 °C, and the ash obtained were treated with hydrochloric acid 8 mol L⁻¹. The analytical and instrumental parameters were adjusted to obtain the best sensitivity for each element (Table 1). For this, the samples were diluted with Milli-Q water for interpolation in the linear range of each mineral element. Cathode lamps (PerkinElmer, Inc., Waltham, MA, USA) were employed to determinate minerals elements. All analyses were carried out in triplicate, and blanks were prepared with bidistilled deionized water.

Minerals	Wavelengths (nm)	Linear range (mg kg ⁻¹)
Ca	422.67	1.00 - 5.00
Mg	285.21	0.10 - 0.30
Zn	213.86	0.10 - 1.50

2.3.2 Phosphorus content

Phosphorus content (mg kg⁻¹) was measured by molecular spectrometry at 420 nm in a spectrophotometer UV-Vis, with deuterium lamp (Thermo Fisher Scientific Inc., Waltham, MA, USA). The samples were initially calcined (520 °C), and complexed with molybdenum phosphoric acid. Samples results were interpolated in calibration curves constructed with diacid phosphate of potassium, in the range of 1 to 20 mg L⁻¹. All analyses were carried out in triplicate, and blanks were prepared with bidistilled deionized water.

2.3.3 Sodium and potassium content

The sodium and potassium content (mg kg⁻¹) were determined through the technique of atomic emission spectrometry (F-AES), with a flame photometer 910M (Analyser Comércio e Indústria Ltda., São Paulo, Brazil) at 589.0 e 710 nm, respectively. For the evaluation of these minerals, the samples were calcined at 520 °C, and treated with nitric acid 4 mol L⁻¹. Sample results were interpolated in calibration curves constructed in the range of 1 to 10 mg L⁻¹. All analyses were carried out in triplicate, and blanks were prepared with bidistilled deionized water.

2.4 Freeze concentration parameters

2.4.1 Concentration factor

The concentration factor (CF) was calculated in agreement with the method proposed by Aider and Ounis [27]. The CF of each freeze concentration stage was determinate as a function of the increase of mineral content, using the following Equation 1:

$$CF(\%) = \frac{MC_{in}}{MC_{in}} \times 100 \tag{1}$$

 where MC_n is the mineral (mg kg⁻¹) content of the concentrated goat milk from each freeze concentration stage and MC_0 is the mineral (mg kg⁻¹) content of the initial skim goat milk.

2.4.2 Process efficiency

The process efficiency (eff) was calculated based on the increase of mineral content (mg kg $^{-1}$) in the concentrated goat milk (MC $_{n}$) in relation to the mineral content (mg kg $^{-1}$) remaining in the ice (MC $_{i}$) from each freeze concentration stage (n), as described in the Equation 2:

$$eff(\%) = \frac{MC_n - MC_t}{MC_n} \times 100 \tag{2}$$

2.5 Statistical analysis

 Data were expressed as means and standard deviations. Statistical analysis of data was performed using the software STATISTICA 13.3 software (TIBCO Software Inc., Palo Alto, CA). One-way analyses of variance (ANOVA) and Tukey's studentized range (5 % significance) were carried out to test significant differences between the results.

3. RESULTS AND DISCUSSION

The goat milk is considered an exceptionally important food because is rich in mineral content. The mineral fractions of skim goat milk, concentrated (CG1, CG2, and CG3), and ice fractions (I1, I2, I3) are shown in Table 2. Overall, by increasing of freeze concentration stages, the mineral content in the concentrated and ice fraction increased. When verified the concentration of major elements such as Ca, Mg, Na, K and P, it was possible to note that the values of Ca, Mg, Na, K were higher (P < 0.05) in all concentrated fractions (CG1, CG2, and CG3), when compared with the initial skim goat milk. Besides that, these minerals contents in CG1, CG2, and CG3 increased (P < 0.05) with the increase of the freeze concentration stages. This performance over the freeze concentration stages was expected, because similar behavior was reported in block freeze concentration process of the skim cow milk [20]. The concentration of Ca and Mg were higher than those founded by Moreno-Montoro et al. [11] during the ultrafiltration of skimmed goat milk. Ca and Mg contents are related to casein structure, which is primarily involved in the coagulation process and curd formation, and a higher concentration of Ca to milk decreases rennet clotting time and increases curd firmess [10, 28-30]. The P content showed no difference (P > 0.05) between the initial skim goat milk and concentrated fraction (CG1, CG2, and CG3). It was noted a slight progressive increase in relation to Ca, Mg, Na, K, and P contents for the ice fractions of freeze concentration stages. However, I1 and I2 fractions showed lower values (P < 0.05) of these minerals when compared with the initial skim goat milk.

Table 2. Mineral contents performance of skim goat milk, concentrated (CG1, CG2, and CG3), and ice (I1, I2, and I3) fractions during block freeze concentration stages.

Samples	Ca	Mg	Na	K	Р	Zn
	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)	(mg kg ⁻¹)
Skim goat milk	987.48 ± 3.38 ^{dB}	82.52 ± 1.21 ^{dB}	676.59 ± 0.32dB	1429.89 ± 108.48 ^{dB}	476.74 ± 35.62 ^{aB}	6.97 ± 0.03 ^{dA}
CG1	1720.38 ± 3.31°	147.36 ± 0.01°	1004.86 ± 1.19°	1842.38 ± 239.03°	508.25 ± 4.55 ^a	10.71 ± 0.01 ^b
	122.30 ± 0.01°	7.11 ± 0.12°	316.00 ± 6.00°	316.02 ± 6.50°	242.52 ± 5.96 ^D	0.93 ± 0.01 ^D
CG2	2307.57 ± 6.66 ^b	235.97 ± 1.20 ^b	1258.26 ± 0.56 ^b	2831.08 ± 1.26 ^b	503.99 ± 0.22a	7.94 ± 0.03°
I2	707.34 ± 6.52 ^c	13.97 ± 0.01 ^c	608.27 ± 0.52 ^c	1216.55 ± 1.05 ^c	420.83 ± 0.11°	2.55 ± 0.01°
CG3	10388.28 ± 213.62 ^a	458.99 ± 9.44 ^a	1652.70 ± 33.99 ^a	3305.39 ± 67.97 ^a	522.40 ± 10.74 ^a	17.36 ± 0.36 ^a
	1494,75 ± 6.67 ^A	136.45 ± 1.20 ^A	880.67 ± 1.28 ^A	1907.97 ± 204.80 ^A	529.81 ± 0.17 ^A	5.26 ± 0.01 ^B

a.b.c Within a column, means ± standard deviations with different superscript lowercase letters denote significant differences (P < 0.05) between the skim goat milk and the concentrated fraction of each freeze concentration stage.

A.B.C Within a column, means ± standard deviations with different superscript uppercase letters denote significant differences (P < 0.05) between the skim goat milk and the ice fraction of each freeze concentration stage. CG1: concentrated fraction of first freeze concentration stage. I1: ice fraction of first freeze concentration stage. CG2: concentrated fraction of second freeze concentration stage. I2: ice fraction of second freeze concentration stage. I3: ice fraction of third freeze concentration stage.

The Zn content decreased (P < 0.05) for the CG2 in comparison with the CG1, and with the skim goat milk. At the third stage, the Zn content increased (P < 0.05), showing higher values for the CG3. The initial skim goat milk showed higher (P < 0.05) Zn content than all ice fractions. According to Gao et al. [31], and Aider and Ounis [27], freezing of salt solution above its eutectic temperature causes rejection of salt (poorly soluble in ice) to the surrounding medium, creating water with very high salt content brine.

Minerals content of Ca, P, K, Na and Mg were higher than those founded by Balde and Aider [20] during the block freeze concentration of skim cow milk. This performance could be

related to the fact the goat milk present some mineral contents, such as Ca, P, K ans Mg, in larger amounts than cow milk [5-7].

Regarding mineral efficiency concentration (Fig. 2), overall notable values were achieved. However, the best value was obtained at concentration of Mg with an efficiency of approximately 95 % in the first stage and around 70% at the third stage. The lowest efficiency was to P concentration with an efficiency of 52%, 16%, and 17% at the first, second, and third stages, respectively. In general, the highest process efficiencies were recorded at the end of the first freeze concentration stages. These results indicate that more minerals were entrapped in the ice fraction at the final stages of freeze concentration process (I2 and I3). This performance was also stated by Aider, de Halleux, and Melnikova [32] for the freeze concentration of skim acidic milk.

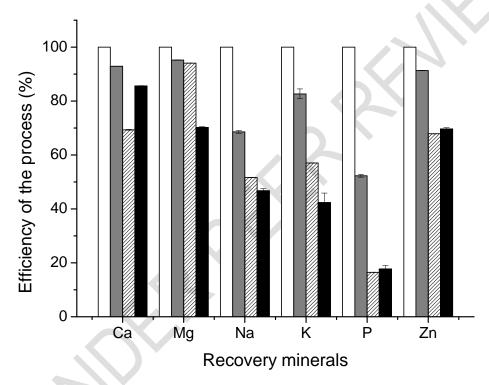


Fig.2. Performance of freeze concentration process on the efficiency (eff) of goat milk minerals concentration as a function of freeze concentration stages (\square initial skim goat milk, \square stage 1, \square stage 2, and \blacksquare stage 3).

In the present study, for all mineral content evaluated, the concentrated factor (CF) (Fig. 3) showed an opposite performance than those observed by the mineral efficiency concentration. An increase (P < 0.05) of the concentrated factor was observed over the freeze concentration stages, reaching a CF of 10000% for the Ca content in the third freeze concentration stage.

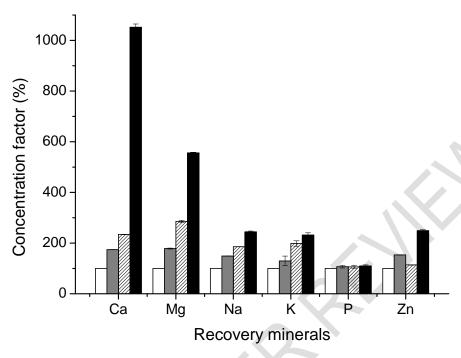


Fig.3. Performance of freeze concentration process on the concentration factor (CF) of goat milk minerals concentration as a function of freeze concentration stages (\square initial skim goat milk, \square stage 1, \square stage 2, and \square stage 3).

As observed by Ceballos et al. [5], Yadav, Singh, and Yadav [7], and Campos et al. [33] in the present work it is possible to highlight that contents main elements contents of skim goat milk are noted higher than cow milk. Finally, in a near future, the generate results from the block freeze concentration process of skim goat milk mineral content performance can be usually used by dairy industries, in order to produce nutritive products with high mineral contents without mineral supplementation, which positively affects the economic and the nutritive value of milk products.

4. CONCLUSION

The mineral content of skim goat milk was successfully freeze concentrated by applying the block freeze concentration. As the freeze concentration stages increase, Ca, Mg, Na, K, and Zn contents increased in both concentrated and ice fractions. It was possible to concentrated Ca and Mg after three stages, around 10 and 6 times more than the initial skim goat milk, respectively. Indeed, the K, Na and Zn were concentrated after three stages, almost 3 times more than initial skim goat milk, respectively. However, the phosphate showed no difference of concentrated fraction in the three stages compared with the initial skim goat milk. All mineral content showed high efficiency and concentration factor during the freeze concentration process. At least of results obtained on the freeze concentration performance of mineral content, we concluded that the concentrated from the first stage was the best. This is because in this stage was reached higher efficiencies results.

COMPETING INTERESTS

248249

250 Authors have declared that no competing interests exist.

251 252

REFERENCES

253

- 1. Hassan FAM, Abbas HM, Abd El-Gawad MAM, Enab AK. (2014). Goats Dairy Products as a Potentially Functional Food. Life Sci. J. 11;648–657.
- 2. Sosnowski M, Rola JG, Osek J. (2016). Alkaline phosphatase activity and microbiological quality of heat-treated goat milk and cheeses. Small Rumin. Res. 136:132–136.
- 258 3. Olalla M, Ruiz-López M, Navarro M, Artacho R, Cabrera C, Giménez R, et al. (2009).
- 259 Nitrogen fractions of Andalusian goat milk compared to similar types of commercial milk.
- 260 Food Chem. 113;835-838.
- 4. Yangilar F. (2013). As a Potentially Functional Food: Goats' Milk and Products. J. Food
- 262 Nutr. Res. 1;68-81.
- 5. Ceballos LS, Morales ER, de la Torre Adarve G, Castro JD, Martínez LP, Sampelayo,
- MRS, (2009). Composition of goat and cow milk produced under similar conditions and
- analyzed by identical methodology. J. Food Compos. Anal. 22;322–329.
- 6. Raynal-Ljutovac K, Lagriffoul G, Paccard P, Guillet, I, Chilliard Y. (2008). Composition of
- goat and sheep milk products: An update. Small Rumin. Res. 79;57–72.
- 268 7. Yadav AK, Singh J, Yadav SK. (2016). Composition, nutritional and therapeutic values of
- goat milk: A review. Asian J. Dairy Food Res. 35;96–102.
- 270 8. Stocco G, Cipolat-Gotet C, Bittante G, Cecchinato A. (2016). Variation of major mineral
- 271 contents in Mediterranean buffalo milk and application of Fourier Transform Infrared
- spectroscopy for their indirect prediction. J Dairy Sci. 99(11);8680-8686.
- 9. Lombardi J, Pellegrino J M, Soazo M, Corrêa A P F, Brandelli A, Risso P. et al. (2018).
- 274 Mineral fortification modifies physical and microstructural characteristics of milk gels
- coagulated by a bacterial enzymatic pool. Colloids Surf., B. 161;296-301.
- 276 10. Franzoi M, Niero G, Penasa M, Cassandro M, De Marchi M. (2018). Development and
- 277 validation of a new method for the quantification of soluble and micellar calcium,
- 278 magnesium, and potassium in milk. J Dairy Sci. 101(3):1883-1888.
- 279 11. Moreno-Montoro M, Olalla M, Giménez-Martínez R, Bergillos-Meca T, Ruiz-López MD,
- 280 Cabrera-Vique C. et al. (2015). Ultrafiltration of skimmed goat milk increases its nutritional
- 281 value by concentrating nonfat solids such as proteins, Ca, P, Mg, and Zn. J. Dairy Sci.
- 282 98;7628–7634.
- 283 12. Achanta K, Aryana KJ, Boeneke CA. (2007). Fat free plain set yogurts fortified with
- various minerals. LWT-Food Sci Technol. 40(3);424-429.
- 285 13. Petzold G., Moreno, J., Lastra P., Rojas K., Orellana P. (2015). Block freeze
- 286 concentration assisted by centrifugation applied to blueberry and pineapple juices. Innov.
- 287 Food Sci. Emerg. Technol. 30;192–197.

- 288 14. Sánchez J., Hernández E., Auleda J.M., Raventós M., 2011. Freeze concentration of
- whey in a falling-film based pilot plant: Process and characterization. J. Food Eng. 103:147-
- 290 155.
- 291 15. Aider M, de Halleux D. (2009). Cryoconcentration technology in the bio-food industry:
- 292 Principles and applications. LWT Food Sci. Technol. 42;679–685.
- 293 16. Orellana-Palma P, Petzold G, Pierre L, Pensaben JM. (2017). Protection of polyphenols
- 294 in blueberry juice by vacuum-assisted block freeze concentration. Food Chem. Toxicol.
- 295 109;1093-1102.
- 296 17. Petzold G, Orellana P, Moreno J, Cerda E, Parra P. (2016). Vacuum-assisted block
- freeze concentration applied to wine. Innov. Food Sci. Emerg. Technol. 36;330–335.
- 298 18. Canella, MHM, Muñoz IB, Pinto SS, De Liz GR, Müller CMO, Amboni RDMC. et al.
- 299 (2018). Use of Concentrated Whey by Freeze Concentration Process to Obtain a Symbiotic
- 300 Fermented Lactic Beverage. Adv. J. Food Sci. Technol. 14;56–68.
- 301 19. Muñoz IB, Canella, MHM, Verruck S, Müller CMO, De Liz GR, Amboni RDMC. et al.
- 302 (2017). Potential of Milk Freeze Concentration for the Production of Functional Fresh
- 303 Cheeses. Adv. J. Food Sci. Technol. 13:196–209.
- 304 20. Balde A, Aider M. (2016). Impact of cryoconcentration on casein micelle size distribution,
- 305 micelles inter-distance, and flow behavior of skim milk during refrigerated storage. Innov.
- 306 Food Sci. Emerg. Technol. 34;68–76.
- 307 21. Hernández E, Raventós M, Auleda JM, Ibarz A. (2009). Concentration of apple and pear
- 308 juices in a multi-plate freeze concentrator. Innov. Food Sci. Emerg. Technol. 10;348–355.
- 309 22. Miyawaki O, Omote C, Gunathilake M, Ishisaki K, Miwa S, Tagami A. et al. (2016).
- 310 Integrated system of progressive freeze-concentration combined with partial ice-melting for
- 311 yield improvement. J. Food Eng. 184;38–43.
- 312 23. Moreno FL, Quintanilla-Carvajal MX, Sotelo LI, Osorio C, Raventós M, Hernández E. et
- 313 al. (2015). Volatile compounds, sensory quality and ice morphology in falling-film and block
- freeze concentration of coffee extract. J. Food Eng. 166;64–71.
- 315 24. Belén F, Benedetti S, Sánchez J, Hernández E, Auleda JM, Prudêncio ES. et al. (2013).
- 316 Behavior of functional compounds during freeze concentration of tofu whey. J. Food Eng.
- 317 116;681–688.
- 318 25. Aider M, de Halleux D, Akbache A. (2007). Whey cryoconcentration and impact on its
- 319 composition. J. Food Eng. 82;92–102.
- 320 26. Navarro-Alarcón M, Cabrera-Vique C, Ruiz-López MD, Olalla M, Artacho R, Giménez, R.
- 321 (2011). Levels of Se, Zn, Mg and Ca in commercial goat and cow milk fermented products:
- 322 Relationship with their chemical composition and probiotic starter culture. Food Chem.
- 323 129;1126–1131.
- 324 27. Aider M, Ounis WB. (2012). Skim milk cryoconcentration as affected by the thawing
- 325 mode: Gravitational vs. microwave-assisted. Int. J. Food Sci. Technol. 47;195–202.

- 326 28. Landfeld A, Novotná P, Houška M. (2002). Influence of the Amount of Rennet, Calcium
- 327 Chloride Addition, Temperature, and High-Pressure Treatment on the Course of Milk
- 328 Coagulation. Czech J. Food Sci. 20(6);237–244.
- 329 29. MalacarneM, Franceschi P, Formaggioni P, Sandri S, Mariani P, Summer A. (2014).
- 330 Influence of micellar calcium and phosphorus on rennet coagulation properties of cows milk.
- 331 J. Dairy Res. 81;129-136.
- 332 30. Visentin G, Penasa M, Gottardo P, Cassandro M, De Marchi M. (2016). Predictive
- ability of mid-infrared spectroscopy for major mineral composition and coagulation traits of
- 334 bovine milk by using the uninformative variable selection algorithm. J. Dairy
- 335 Sci. 99(10);8137-8145.
- 336 31. Gao W, Smith DW, Sego DC. (2004). Treatment of pulp mill and oil sands industrial
- 337 wastewaters by the partial spray freezing process. Water Res. 38;579–584.
- 338 32. Aider M, de Halleux D, Melnikova I. (2009). Skim acidic milk whey cryoconcentration and
- assessment of its functional properties: Impact of processing conditions. Innov. Food Sci.
- 340 Emerg. Technol. 10;334-341.
- 33. Campos MS, López-Aliaga I, Alférez MJM, Nestares T, Barrionuevo M. (2003). Effects of
- 342 goats' or cows' milks on nutritive utilization of calcium and phosphorus in rats with intestinal
- 343 resection. Br. J. Nutr. 90;61-67.