SALT COMPOSITION OF A PROTEIN–MINERAL CONCENTRATE OBTAINED BY ELECTROPHYSICAL PROCESSING OF WHEY

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Summary: The mineral composition of milk and whey is analyzed. The significance of the main macroelements (calcium, phosphor, magnesium) and microelements for vital functions of the organism is noted. The importance of the balanced proportion of calcium and phosphor ions in nutrition is emphasized; the ratio of these elements in the protein–mineral concentrate is noted. The conditions and possible mechanisms, which influence the formation of protein concentrates, are analyzed on the basis of the experimental data related to the pH variation, the quantity of the recovered protein, and Ca:P ratio for various current densities. The determination of mechanisms of protein–mineral concentrate formation is important for preparation of end products, including those with the specified mineral composition.

Keywords: mineral composition of whey, major macroelements (calcium, phosphorus, and magnesium), electrophysical treatment, calcium–to–phosphorus ratio.

Introduction

The problems of environmental protection, of elaboration of wasteless technologies as well as methods for their implementation are important, topical and pressing today in many fields of scientific, industrial and practical activities. In the past years, in the food production area, the environmental requirements concerning waste have been under serious re–examination. Production of dairy food is one of such areas, first of all, as refers to the dairy by–products. Development of wasteless technologies and processing of whey in a closed cycle is one of the major global challenges (Sinelinikov B., 2006) [1]. Still, in milk processing whey is formed that cannot be entirely used because of large quantities of it with a low level of solid shear, but it is very valuable and healthy. The level of using primary dairy products and its by–products is strongly dependent on both climatic and economic conditions of each country. As stated by the IDF, about 50% of whey goes in sewage water, which is neither economically good nor environmentally friendly (Introduction to Dairy Science and Technology: www.foodsci.uoguelph.ca) [2].

Mineral substances are vital to the human body because they are a necessary constituent of the human diet. They are divided into two large groups: macroelements, which make up 99% of the elemental composition of the body, and microelements. The mineral composition of whey is diversiform and primarily depends on the type of the resulting primary dairy product, the time of year, the processing conditions, and other factors. In terms of biology, it is optimally balanced and diverse (table) (de Wit, J.N., 1998) [3].

Table *Composition of whey derived in the production of different types of primary dairy products, g/L*

Content	Caseic whey	Acid whey	Gouda whey	Camembert whey
Solids	65.0	65.0	65.0	65.0
True proteins	6.0	6.0	6.2	6.2
Lactose	47.0	40.0	47.0	45.0
Lipids	0.3	0.3	0.5	0.5
Minerals (ash)	7.9	7.9	5.3	5.6
Calcium	1.6	1.6	0.6	0.6
Phosphorus	1.0	1.0	0.7	0.7
Lactic acid	0.2	0.6	0.2	0.3
pH	4.7	4.5	6.4	6.0

About 22% of the total amount of calcium in milk is tightly bound to casein (calcium structurant) with the remainder (78%) being composed of salts, such as phosphates, citrates, etc. (Smolyanskii, B.L., 2010.) [4]. The assimilability of calcium is a complex process that depends on many factors and the ratio of food ingredients, mostly fats, magnesium, and phosphorus; calcium ion transport is governed by the presence of vitamin D. The assimilability of calcium is worse if the food contains low amounts of the protein required for the formation of the framework of bones; however, an overconsumption of this protein (over 1–1.2 g/kg of the body weight per day) leads to an increase in the loss of calcium. A high amount of animal fats hinders the absorption of calcium (Buslaeva, G.N., 2009) [5]. The main natural sources of calcium are milk and dairy products (curd and hard cheese), fish, and eggs. The daily requirement for calcium is about 800 mg.

Phosphorus also falls into the group of macroelements; its role in human life support is very important. In common with calcium, phosphorus performs an important plastic function being involved in the formation of bones and teeth (they contain 85% of the phosphorus of the body). Phosphorus compounds are of great importance in almost all the processes of vital activity; it is particularly important in metabolism and in functions of the nervous and brain tissues, enzymes, and hormones (Evdokimov, I.A., 2006) [6].

Phosphorus is contained in milk in mineral and organic forms. Inorganic compounds are phosphates of calcium and other metals, and their content is 45– 100 mg % (63–66% of the total amount of phosphorus on the average) (Liflyandskii, V.G., 2011) [7]. Organic compounds comprise phosphorus as part of casein, phospholipids, phospho– ric esters of carbohydrates, some coenzymes, nucleic acids, etc. Calcium phosphates can be in the form of $Ca_3(PO_4)_2$, $CaHPO_4$, $Ca(H_2PO_4)_2$, and other more complex salts; calcium citrates are $Ca_3(C_6H_5O_7)_2$ and $Ca(C_6H_6O_7)$. The form in which calcium phosphates and citrates are contained in milk is still not clear; however, it is known that most of these salts are in a colloidal state and a small portion (about 30–40%) are in the form of a true solution. Equilibrium is estab– lished between them. The ratio of these forms plays an important role in maintaining a certain degree of dis– persion, the hydration of protein particles, their stabi– lization during heat treatment, and in the occurrence of rennet clotting. The content of calcium and phos– phorus in milk is well balanced, which provides their relatively high assimilability. The Ca : P ratio in dairy products is the highest compared to other food prod– ucts: it is 1 : 1 to 1.4 : 1 in milk (1 : 1.5 to 1 : 2 in curd and cheese), while it is 1 : 13 and 1 : 1 in meat and fish, respectively (Gorbatova, K.K., 1993) [8].

Calcium and phosphorus are the most important macroelements of milk, in which they are contained in an easily digestible form and well–balanced proportions. Their compounds are also of great significance for milk processing (Lodygin, A.D., 2010) [9]. Most of the calcium salts in milk (pH 6.47–6.67) are phosphates exhibiting low solubility and an insignificant degree of dissociation. Only a small portion of them is contained in the form of a true solution; the major portion is in the form of a colloidal solution. Colloidal calcium phosphate bonded to calcium caseinate is contained in milk in the form of the so–called calcium caseinate–calcium phosphate complex (CCCPC) (Bogatova, O.V. and Dogareva, R.G, 2004) [10].

Magnesium, potassium, sodium, and chlorine are also transferred into whey. These elements are present in the form of various soluble substances: NaCl, KCl, $K(H_2PO_4)$, $K_3(C_6H_5O_7)$, $MgHPO_4$, $Ca_3(PO_4)_2$,$CaCl_2$, Na_2CO_3, K_2CO_3, etc. The quantitative ratio of anions (5.831 g/L) and cations (3.323 g/L) is almost identical to that in milk. The content of microelements in whey is as fol– lows, μg/kg: iron, 674; zinc, 3108; copper, 7.6; cobalt, 6.08; they are contained in more than 20 compounds. Ultramicroelements are contained in about 16 com– pounds. Whey cations are composed of K, Na, Ca, Mg, and Fe; the anions are formed by radicals of phos– phoric and citric acids and by chlorine. Inorganic salts of lactic acid contain 67% phosphorus, 78% calcium, and 80% magnesium (Khramtsov, A.G. 1990) [11].

Results and discussion

Studies of the mineralization of protein concentrates during the electrophysical treatment of whey are of great interest because these studies make it possible to elucidate the mechanism of the protein isolation.

The electrophysical treatment of whey was conducted in a diaphragm cell in a cathode chamber; the current density was constant throughout the entire process. The variations in the voltage, temperature, and pH were recorded. The amount of whey proteins transferring into the PMC was determined by Wartburg’s spectrophotometric method. The relative content of calcium and phosphorus in the concentrates obtained at different pH values was found by X_ray spectrometry. The treatment was deliberately conducted at low current densities to provide a slow increase in the pH of the medium in order to trace in detail the relationship between the quantitative transfer of the protein into the PMC and the Ca: P ratio. The variation in the pH value preserves the pattern of an aqua– to hydrocomplex transition, which is attributed to the isolation of protein fractions and the formation of mineral complexes (Fig. 1). The isolation of whey proteins into mineral concentrates increases with increasing current density; the process occurs simultaneously with the isolation of calcium and phosphorus (Fig. 2).

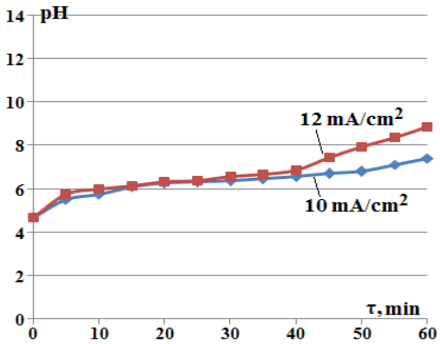

Fig. 1. pH variation under the electrophysical treatment of whey (at varying current density).

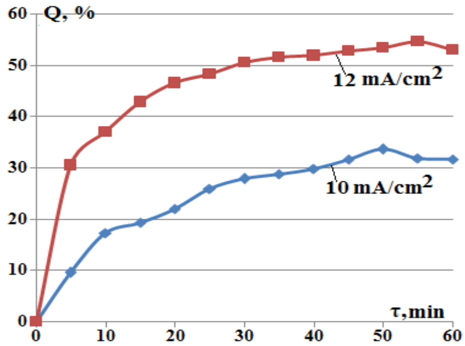

Fig. 2. Variation of the amount of isolated protein under the electrophysical treatment of whey (at varying current density).

According to different literature sources, the Ca: P ratio varies; an important role is possibly played by the research methods, the region, the time of year, the species of animals, the type of feeding, and other factors (Chervetsov, V.V. et al., 2007) [12]. The Ca: P ratio in whey is about 1.09 (Khramtsov, A.G. 1990) [11].

Simultaneously with the recording of the basic parameters of the electrophysical process and the determination of the level of isolation of the whey proteins in the PMC, we studied the variation of the content of calcium and phosphorus in the concentrate and the variation of their ratio during the treatment, which is the most important factor. This ratio is one of the key parameters in estimating the biological value of the resulting concentrates (Figs. 3, 4). The pattern of transfer of the Ca and P depends on a variety of factors: the type and condition of the membrane, the cell's geometry, the electrophysical parameters, and the temperature of the treated liquid, the anode liquor, and the treatment technology.

A slight increase in the current density (from 10 to 12 mA/cm^2) leads to an increase in the isolation of the protein fractions in the PMC (Fig. 2) and an increase in the Ca: P ratio in the resulting concentrates (Figs. 3, 4). The mechanism of transfer of the major ions into the PMC and the formation of protein complexes were studied by X–ray spectrometry; the nonuniform transfer of Ca and P into the concentrate was observed. Calcium is directly involved in the isolation of proteins by the proposed method. This is evident, on the one hand, from its decreasing amount in the residual whey throughout the process and, on the other hand, from its dominant amount in the mineral composition of the PMC.

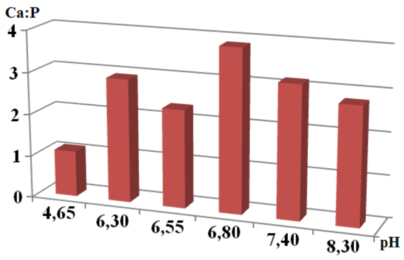

Fig. 3. Ca : P ratio at varying pH during the electrophysical treatment of whey at a current density of j = 10 mA/cm^2.

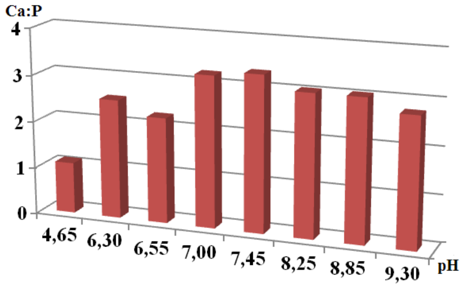

Fig. 4. Ca : P ratio at varying pH during the electrophysical treatment of whey at a current density of j = 12 mA/cm^2.

Phosphorus is the second largest ash constituent in the concentrate. Deproteinized whey exhibits the almost complete depletion of phosphate ions, while only a part of them transfers in the PMC (Bologa, M., et al. 2009) [13]. A significant portion of the ions migrate into the anode chamber. The gradual depletion of phosphorus in the treated whey caused by the migration of the di–and monohydrophosphates into the anode chamber is responsible for an increase in this ratio. The maximum transfer of the elements is observed in the case of the maximum isolation of the protein fractions.

Some mechanisms of formation of protein complexes are given in (Sprincean (Vrabie), E., *2010*) [14]. All the above mechanisms of formation of PMCs have an effect on the Ca : P ratio in them to a varying degree. The pattern of change in the Ca: P ratio is not identical during treatment and does not correspond to the absolute values of the calcium and phosphorus concentrations in the prepared samples. These values increase until the achievement of the maximum amount of isolated protein and decrease under a long term treatment because of the depletion of these elements in the residual whey partially owing to the conducted process. The mineral concentrates obtained at different pH values (different treatment durations) have different Ca: P ratios and, accordingly, different compositions of the whey proteins (Bologa M. K. et al. 2013) [15]. The electrophysical treatment of whey makes it possible to isolate concentrates with different predetermined compositions. These studies will provide the preparation of protein concentrates with different mineral and protein compositions for improving the quality of the end products.

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