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ANALYSIS OF MILK SOME PHYSICAL-CHEMICAL PROPERTIES AFTER INTRODUCTION OF NEW REQUIREMENTS TO ITS ACIDITY

Some consequences of recent change of the demands to cow fluid milk acidity are discussed.

The average results of freezing point, titratable and active acidities, conductivity, water activity, density, moisture, nonfat milk solids of milk were analyzed. The samples of market pasteurized milk, ultra-high-pasteurized milk, sterilized milk and baked milk were investigated.

The factors that affect the normalized titratable and active acidities value were described. The relationship between the study of physical and chemical properties is shown. The dynamics of their changes in drinking milk in recent years is traced.

Losses of the freezing point, pH and titratable acidity of dairy products following the introduction of new requirements to its acidity were demonstrated.

The amount of ions and nonfat milk solids in pasteurized milk were increased.

The water activity and nonfat milk solids in ultra-high-pasteurized milk were not changed.

The stabilization of moisture in sterilized milk and increase the conductivity of baked milk is shown.

The technological modes produces of drinking milk led to increase the pH value range.

Key words: freezing point, titratable acidity, active acidity, conductivity, water activity, density, moisture, milk.

Introduction. According to the change in the standard [1], which entered into force on 01.07.2012, the acidity of the liquid milk as the finished product must not exceed 19.0°T, which is 2.0°T lower than the previous norm.

The fresh milk corresponds to the acidity of 16.0 to 18.5°T. Milk, with a very low protein content, is observed to decrease in titratable acidity to 15.0°T [2].

Since the fresh raw milk does not contain lactic acid, the acidity is caused by proteins, which account for 4–5°T, acid salts – about 11°T, carbon dioxide and other titratable chemicals – about 1–2°T [3].

The definition of this indicator in the dairy industry is needed to identify the sour milk. Production of many dairy products is based on the relationship between the titratable acidity of raw milk and the properties [2].

Indicators of raw milk and of milk changes during the heat treatment are described in detail in literature.

In the article we have analyzed general dynamics of changes in temperature of freezing heat-treated milk in 2010–2013, described for three types of finished products from different local producers, as well as the observed lowering the freezing point of milk products after introduction of more stringent requirements for raw acidity [4].

Data on the effect of tightening the regulatory requirements for heat-treated milk drinking acidity to other physical-chemical parameters, as well as their long-term dynamics, is not enough.

Main part. Pasteurized, ultra-pasteurized, sterilized and baked milk are the objects of our study.

All dairy products were produced by Belarusian enterprises. Samples of finished products were bought in the consumer packaging in the retail trade network in Minsk.

The temperature of freezing of dairy products was determined by the freezing point depression method with thermoelectric milliosmometer-cryoscope MT 5-01 (Russia). Other physical parameters, such as electrical conductivity, were measured with desktop HI 2300 conductivity meter (HANNA Instruments, Germany) with automatic temperature compensation (25°C). Analysis of free water fraction was run by the dew point chilled mirror by measuring the "water activity" (A_w) with a device Roremeter RM-10 of NAGY Messsysteme GmbH company. The active acidity of dairy products was determined with a pH meter HI 221 (HANNA Instruments) or pH meter-millivoltmeter pH-150M (Belarus), while titratable acidity was determined by the method [5]. The measurements of pH were performed with these devices under automatic temperature compensation (25°C). The density of milk was determined by the method [6].

The measurements of moisture and dry matter content of samples were carried out with the accelerated method by Radwag hygrometer (Poland) using dried filter paper. Drying profile was selected with the standard drying temperature of 125°C and automatic shut-off, when the mass loss of less than 1 mg to 120 s.

The weight proportion of skimmed substance of dry non-fat milk solids (calculated SNF) C_0 (%) was calculated according to the following formula:

$$C_0 = C - a,$$

where C stands for the mass fraction of solids, %; and a stands for the mass fraction of fat as it was indicated at the product consumer packaging, %.

Table 1

Changes in average values of some physical and chemical parameters of pasteurized and ultra-pasteurized milk with the requirements of the standard to its acidity

Index	Type of heat treatment of milk			
	Pasteurization		Ultra-pasteurization	
	Before 01.07.2012	After 01.07.2012	Before 01.07.2012	After 01.07.2012
Freezing Point, °C	–0.484 ± 0.009	–0.513 ± 0.009	–0.489 ± 0.008	–0,520 ± 0,009
Titratable Acidity, °T	19.3 ± 0.6	17.2 ± 0.6	19.0 ± 0.5	17,0 ± 0,6
Specific Conductivity, mS/cm	4.45 ± 0.05	4.46 ± 0.08	4.48 ± 0.05	4,43 ± 0,08
pH	6.92 ± 0.07	6.62 ± 0.07	6.82 ± 0.07	6,68 ± 0,07
Water Activity, A_w	0.990 ± 0.020	0.986 ± 0.020	0.986 ± 0.022	0,990 ± 0,020
Density*, kg/m^3	1,028.0 ± 0.6		1,026.2 ± 0.8	
Humidity*, %	87.92 ± 0.16		87.35 ± 0.43	
Calculated SNF*, %	8.31 ± 0.13		7.96 ± 0.06	

* Index measurements were carried out after 01.07.2012.

Table 2

Changes in average values of some physical and chemical parameters of sterilized and baked milk with the requirements of the standard to its acidity

Index	Type of heat treatment of milk			
	Sterilization		Baking	
	Before 01.07.2012	After 01.07.2012	Before 01.07.2012	After 01.07.2012
Freezing Point, °C	–0.498 ± 0.009	–0.517 ± 0.008	–0.496 ± 0.009	–0.516 ± 0.009
Titratable Acidity, °T	19.8 ± 0.6	17.8 ± 0.5	21.0 ± 0.5	18.1 ± 0.6
Specific Conductivity, mS/cm	4.45 ± 0.10	4.69 ± 0.06	5.01 ± 0.05	4.62 ± 0.07
pH	6.86 ± 0.07	6.59 ± 0.07	6.66 ± 0.07	6.50 ± .08
Water Activity, A_w	1.000 ± 0.025	0.988 ± 0.020	0.983 ± 0.024	0.988 ± 0.020
Density*, kg/m3	1,028.0 ± 0.6		1,027.4 ± 0.6	
Humidity*, %	88.34 ± 0.22		88.10 ± 0.18	
Calculated SNF*, %	8.45 ± 0.15		8.24 ± 0.09	

* Index measurements were carried out after 01.07.2012.

The research results and the spread of the obtained values of physical and chemical parameters of drinking milk are presented in Tables 1 and 2.

Table 1 shows titratable acidity of pasteurized milk to reduce of 2°T that resulted in a strong decrease in freezing temperature and pH. On the other hand, the values of conductivity and "water activity" index didn't change. Similar results were obtained for other samples, except the values of conductivity of sterilized and baked milk.

There are numerous reasons of these changes: chemical composition of the resulting raw milk; collecting milk of a certain composition and, consequently, quality of the processing plant producing a specific product; working out of technological modes of production; equipping plant with modern efficient equipment; age, breed of the animal, feeding ration, maintenance, lactation, health, and etc.

In our opinion, modification of physical and chemical properties of milk (denaturation of protein; partial decomposition of lactose, that is followed by sterilization with increasing acidity of milk at 2–3°T; deposition of mineral sediment due to transition of soluble salts of calcium and phosphorus into insoluble state; removal of gases and volatile substances) by heat treatment make the maximum contribution to all occurring phenomena [3].

The values of specific conductivity depend on the presence and concentration of ions' of dissociated salts concentration. With the decrease of titratable acidity (decrease in the number of ions), values are obvious to increase the conductivity of sterilized milk due to production technology and chemical composition of the applied raw material. As a rule, the best grades of raw milk are used for preparation of sterilized milk. Moreover, sterilization of milk causes the breakdown of lactose with the formation of carbon dioxide and acids [3].

High temperature and the duration of milk exposure are likely to increase ions concentration, which are stronger than their decline with a decrease of titratable acidity.

Feature of baked milk production is sure to influence greatly on the analyzed indexes: many hours of exposure at temperatures of 85–99°C to

impart a characteristic color, odor and taste, namely, the evaporation of moisture and thus increase of concentration of conductive ions.

The obtained results show that the decline of titratable acidity of at least 2.0°T resulted in a significant decrease in the freezing point, which may indicate the improvement of quality of initial and processed milk.

Such conclusion can be made by the submitted data (Tables 3 and 4, figure) on the change in the analyzed indexes of thermally processed milk in 2009–2015.

Table 3

The average values of certain physical and chemical parameters of the heat-treated milk in 2009–2015

Indexes	Type of heat treatment of milk			
	Pasteurization	Ultra-pasteurization	Sterilization	Baking
Freezing Point, °C	–0.499 ± 0.009	–0.516 ± 0.009	–0.513 ± 0.008	–0.513 ± 0.009
Titratable Acidity, °T	17.5 ± 0.6	17.2 ± 0.6	18 ± 0.5	18.2 ± 0.6
Specific Conductivity, mS/cm	4.46 ± 0.07	4.44 ± 0.07	4.67 ± 0.06	4.64 ± 0.07
pH	6.65 ± 0.07	6.70 ± 0.07	6.62 ± 0.07	6.51 ± 0.08
Water Activity, A_w	0.988 ± 0.020	0.990 ± 0.020	0.987 ± 0.020	0.987 ± 0.020
Density*, kg/m^3	1,028.0 ± 0.6	1,026.2 ± 0.8	1,028.0 ± 0.6	1,027.4 ± 0.6
Humidity*, %	87.92 ± 0.16	87.35 ± 0.43	88.34 ± 0.22	88.10 ± 0.18
Calculated SNF*, %	8.31 ± 0.13	7.96 ± 0.06	8.45 ± 0.15	8.24 ± 0.09

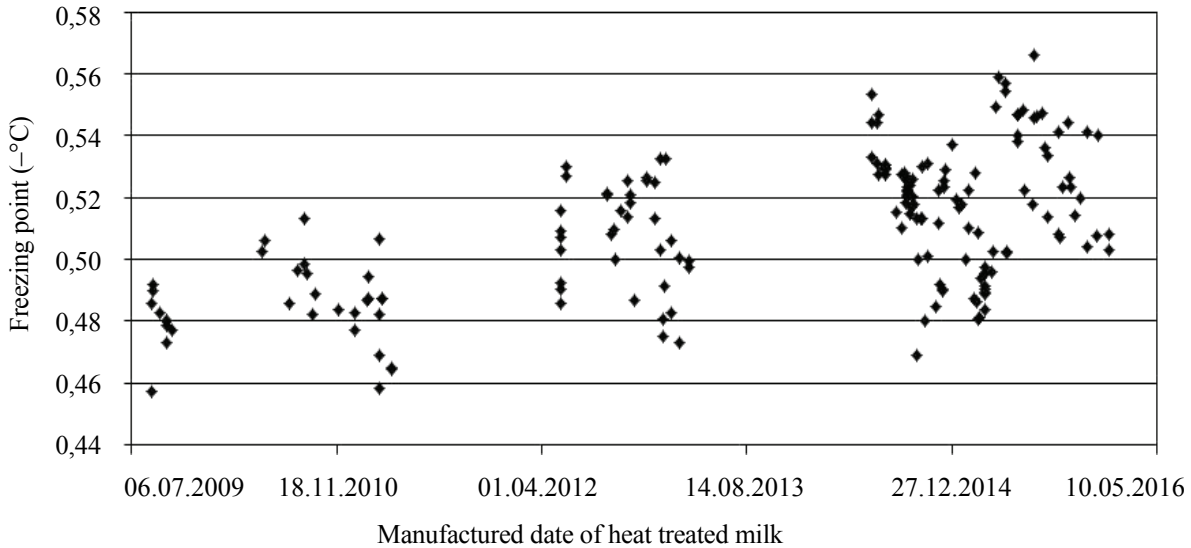
* Index measurements were carried out after 01.07.2012.

Table 4

The range of average values of certain physical and chemical parameters heat-treated milk in 2009–2015.

Indexes	Type of heat treatment of milk			
	Pasteurization	Ultra-pasteurization	Sterilization	Baking
Freezing Point, °C	–0.552...–0.430	–0.563...–0.467	–0.558...–0.474	–0.567...–0.479
Titratable Acidity, °T	16.0...20.0	15.0...19.5	16.5...21.0	16.5...21.0
Specific Conductivity, mS/cm	3.84...5.41	3.78...5.02	3.82...5.18	4.04...5.04
pH	6.26...6.95	6.44...6.86	6.30...6.88	6.14...6.79
Water Activity, A_w	0.956...1.000	0.957...1.000	0.950...1.000	0.937...1.000
Density*, kg/m^3	1,026.5...1,029.4	1,022.7...1,029.4	1,024.8...1,030.6	1,026.3...1,028.8
Humidity*, %	87.10...89.34	85.68...90.95	85.69...90.90	87.38...90.04
Calculated SNF*, %	6.96...9.21	7.45...8.41	7.18...11.54	7.46...8.82

* Index measurements were carried out after 01.07.2012.



Correlation freezing point of heat treated milk with manufactured date

During this period, the freezing point of all the samples of drinking milk has decreased. Freezing point of all drinking milk samples has decreased much more than proposed definition (by some authors) of raw milk freezing point over 17.5°T at each degree of acidity in Turner [7, 8].

After the introduction of the changes [1], titratable acidity reduced to the maximum permissible level and its gradual depression was observed over time.

In the study of pasteurized milk, minimum fixed acidity value was 18.5°T until 01.07.2012, and that date it constituted 15.0°T for ultra-pasteurized milk.

The acidity of most products did not exceed 18°T and ranged mainly from 16 to 18°T. The value of the electrical conductivity of dairy products ranged from 4.50 to 4.80 mS/cm. During the analyzed period, values of acidity, free moisture proportion, density, humidity, and drinking milk SNF have not changed.

However, values of certain indicators have changed for certain products of one type of thermal treatment. The water content of pasteurized drinking milk decreased with simultaneous proportional increase in the calculated SNF.

Since September 2014, products humidity is in the range of 87–88%, while the conductivity increased steadily and by the end of 2015 it was less than 4.80 mS/cm. Freezing point, titratable acidity, conductivity, density, and moisture content of ultra-pasteurized milk have decreased in varying degrees, while moisture proportion and calculated SNF stood unchangeable.

According to the results of experimental measurements of the freezing temperature data, titratable acidity and pH of sterilized milk there was a decrease of the mean values of the studied parameters. The values of density and calculated SNF of products rose slightly, conductivity, index of "water activity", the humidity remained unchanged. The range of average values of moisture content in drinking sterilized milk decreased significantly and amounted to 88–89%.

In addition to the general downward trend of freezing temperature, pH and titratable acidity of baked milk the opposite situation were observed in the measurement of conductivity. The rest of the product figures did not change significantly during the analyzed period.

The obtained results of measurements of physical and chemical parameters in the products of various manufacturers differ, sometimes significantly.

It should be noted that pH decrease in all the investigated products was observed under increasing the spread of the values of this parameter.

Typically, the pH of raw milk is in the range 6.6–6.8, and the pH value below 6.5 indicates the beginning of milk souring [2]. However, our measurements of the pH of drinking milk have been received until 6.15 when the titratable acidity of not more than 19°T. Obviously, this is due to changes in chemical composition that were occurred in the heated to 100°C milk. It is assumed the decrease in the solubility of calcium phosphate and colloidal form of calcium phosphate, whereby the hydrogen ions are bound, which results in lowering of pH. In such heating mode, the volatilization of CO_2 leads to a certain increase in pH [2]. Perhaps, the degree of influence of outgassing is much smaller than the formation of colloidal calcium phosphate.

Correlation between the analyzed physical and chemical parameters observed neither for the products of one heat treatment type, not for the all drinking milk samples.

Conclusion. Changes in the level of milk acidity had a positive impact on the values of certain physical and chemical parameters of drinking milk. Thus, the titratable acidity values of the products on the average dropped 2.0–3.5°T, which even exceeds the difference between the normalized values of the acidity.

In general, the toughening of requirements to the level of the finished product acidity in not equally (for the production of the same heat treatment) resulted in:

– decrease the freezing temperature, titratable acidity pH and of the liquid milk;

– increase conductivity and SNF pasteurized milk;

– decrease the analyzed parameters, except for the "water activity" and SNF in UHT milk;

– stabilize the humidity of sterilized milk;

– increase conductivity of melted milk.

A larger variation of pH values are obviously linked to the creation of technological modes of production at various manufacturing plants.

The results can be used by enterprises of the dairy industry in the development of measures to improve the quality of products.

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