Вивчено вплив параметрів низькотемпературного заморожування та термінів зберігання на показники якості молочно-білкових концентратів (МБК) зі сколотин. Досліджено особливості низькотемпературних фазових переходів та склування МБК. Встановлено, що використання пюре калини та журавлини як коагулянтів сприяють збільшенню частки зв'язаної вологи та покращенню збереженості продуктів. Визначено зміни кольоропараметричних характеристик концентратів при зберіганні. Обґрунтовано режими та терміни зберігання МБК

Ключові слова: молочно-білковий концентрат, диференціальна скануюча калориметрія, кольропараметричні характеристики, термін зберігання

Изучено влияние параметров низкотемпературного замораживания и сроков хранения на показатели качества молочно-белковых концентратов (МБК) из пахты. Исследованы особенности низкотемпературных фазовых переходов и стеклования МБК. Установлено, что использование пюре калины и клюквы в качестве коагулянтов способствуют увеличению доли связанной влаги и улучшению сохранности продуктов. Определены изменения цветопараметрических характеристик концентратов при хранении. Обоснованы режимы и сроки хранения МБК

Ключевые слова: молочно-белковый концентрат, дифференциальная сканирующая калориметрия, цветопараметрические характеристики, срок хранения

UDC 664.67.067.1
DOI: 10.15587/1729-4061.2018.120749

SURVEY OF CHARACTERISTICS OF DAIRY-PROTEIN CONCENTRATES IN THE LOW-TEMPERATURE STORAGE PROCESS

V. Gnytsevych
Doctor of Technical Sciences, Professor*
E-mail: flamber1965@gmail.com

T. Yudina
Doctor of Technical Science, Associate Professor*
E-mail: olegdmu@rambler.ru

L. Deinychenko
Postgraduate student
Department of commodity science, management of safety and quality**
E-mail: deliugri@gmail.com

R. Nykyforov
PhD, Associate Professor***
E-mail: nikradion@yandex.ua

I. Nazarenko
PhD, Associate Professor***
E-mail: Nazarenko@donnuet.edu.ua

*Department of Technology and the organization of restaurant business**
**Kyiv National University of Trade and Economics
Kyoto, str., 19, Kyiv, Ukraine, 02156
***Department of technology in a restaurant economy that hotel and restaurant business
Donetsk National University of Economics and Trade named after Mykhailo Tugan-Baranovsky
Ostrovskoho str., 16, Kryvyi Rih, Ukraine, 50005

1. Introduction

Today there is no doubt that the leading role in nutrition belongs to natural products which can provide the body with essential nutrients and energy. The level of protein deficiency in the world is increasing [1], therefore special attention should be paid to the content of proteins in food products, especially of animal origin. After all, it is they that contain more amino acids that are essential to the human body, in comparison with their analogues of plant origin.

Among the proteins of animal origin, a special place is taken by milk proteins. These compounds determine the biological value and caloric content of dairy products, are well digested and assimilated by the human body. They contain a significant amount of mineral and biologically active substances, and also have expressed hypotensive, immunity-stimulating and antithrombotic properties [2].

A valuable source of milk proteins is protein-carbohydrate dairy raw materials, in particular, buttermilk [3], which is becoming increasingly used in innovative food technologies. One of the areas of buttermilk use is the production of milk-protein concentrates (MPC). The use of MPC will ensure more rational use of raw materials and increase the economic efficiency of production of protein concentrates. Products based on MPC will allow expanding the range of food products and increasing their biological value.

Today there are many methods of precipitation of protein substances from dairy raw materials. But MPC, obtained with the use of berry purees as coagulants, are new products whose properties have not been investigated. As in the case of most protein concentrates, the main purpose of these foods production is their further use in food technologies as semi-finished products.

In view of the increased interest in this topic, the study of the quality of the obtained MPC is of great scientific and practical value. Herewith, the storage factor, that has a direct impact on both organoleptic properties and the shelf life of any product, will be decisive.

But the effect of storage, particularly at low temperatures, on the quality and safety of MPC has not been investigated. Therefore, the research of changes in the structure and organoleptic characteristics of MPC in the process of low-temperature treatment is important for determining storage periods and conditions.

2. Literature review and problem statement

Today, changes in the quality of milk proteins in the storage process are the object of interest of many food industry specialists. A significant step in this direction was made by Japanese scientists, who have studied the change in the quality of caseinates of milk proteins when stored at low temperatures. It has been found that the lower the storage temperature, the longer milk proteins can be stored. However, the storage time cannot be extended for more than 4 months. The reason for this limitation is protein flocculation, which occurs even at –20 °C [4].

In work [5], a change in the quality of cottage cheese, enriched with the microparticulates of whey proteins, was investigated. According to the literature data, the shelf life of the obtained product exceeds that of the cottage cheese by 30 %.

It is also known about the development of the technology of cottage cheese with increased storage time [6]. The technology involves the use of various yeast starters, protein coagulation methods and whey removal techniques. In addition, scientists of the Institute of Dairy Industry presented a methodology for improving the technology of refrigeration storage of cottage cheese. The method justifies the choice of optimal parameters of microwave defrosting of cottage cheese, but requires experimental confirmation [7].

It is known [8] about the studies to analyze changes in the solubility of MPC obtained with the use of NaCl and KCl, during long-term storage. It has been determined that storage at 4 °C and 25 °C with the addition of chlorides reduces the harmful effect on the solubility of the samples, while storage at 55 °C negatively affects the solubility regardless of the salt content.

Scientists of the USA have studied changes in the organoleptic parameters of protein bars during storage. During the experiments, the bars were stored at 22 °C, 32 °C or 42 °C for 42 days. According to the results obtained, the bars produced using MPC had a higher softness regardless of the storage temperature. At the same time, the change in the color of the surface of the bars with MPC was minimal when stored at 22 °C, but increased at 32 °C and 42 °C [9].

In work [10], the effect of storage temperature and time on rheological properties and solubility of MPC with a protein content of 85 % was investigated. It is established that the conclusive complex module and tension decrease exponentially with the increase in the storage time of MPC. At the same time, when the storage temperature increases, this effect is intensified. The solubility also decreases exponentially over time, with whey proteins remaining soluble, unlike caseins that become lactosilated [11].

No solid research was conducted to determine the effect of freezing and storage conditions on the structure and organoleptic characteristics of MPC obtained with the use of berry purees. Therefore, this problem remains unresolved.

3. The aim and objectives of the study

The aim of this work is to determine the optimal conditions for MPC freezing and to study changes in the quality during the storage process.

To achieve this aim, the following objectives have been identified:

– to study the influence of low temperatures on the MPC structure and to determine the conditions of freezing and storage of these products;

– to determine the rational storage time of MPC, taking into account the change in the color-parametric characteristics during the storage process.

4. Materials and methods of study of low-temperature phase transitions and color-parametric characteristics of milk-protein concentrates

The material for the research were MPC of buttermilk obtained with the use of viburnum puree (MPCV) or cranberry puree (MPCC) as coagulants [12].

Changes in the physical properties of food products, depending on temperature, can be observed by means of devices and techniques for thermal analysis [13], including differential thermal analysis (DTA) and differential scanning calorimetry (DSC). DTA and DSC are based on the change of heat absorption that occurs during phase transitions when the temperature changes at a controlled rate.

More detailed materials and methods of study of low-temperature phase transitions and color-parametric characteristics of milk-protein concentrates are given in work [14].

5. Results of the study of structure and color of MPC in the process of freezing and storage

Thermophysical properties, according to contemporary researchers [15–17], are one of the most important parameters in the evaluation of stability of food products when stored in a frozen state. Therefore, a study of low-temperature phase transitions and glass transition of MPC using the DSC method was conducted. For the experiment, samples of concentrates weighing 1 g were placed in a thin-walled stainless steel glass. The glass was covered with a lid and cooled by immersion in liquid nitrogen. The low-fat cottage cheese was used as the control sample.

The average cooling rate of the process was 200 °C/min. The thermograms were recorded during heating at a rate of 0.5 °C/min. The temperature measurement error was ±0.2 °C. The obtained thermograms are shown in Fig. 1.

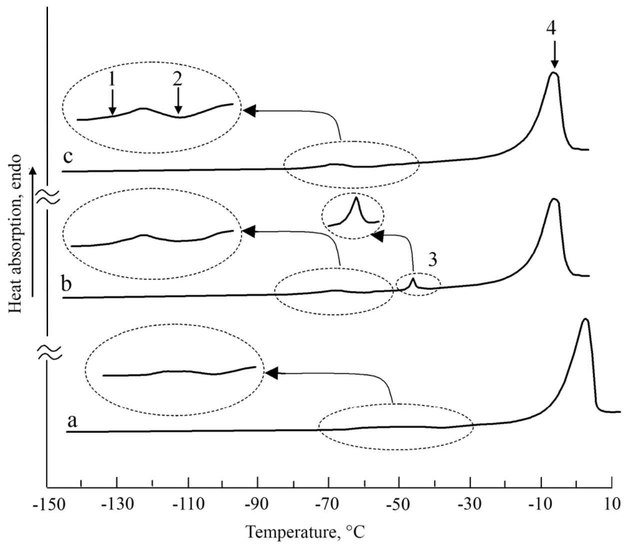

Fig. 1. DSC – thermograms: *a* – control sample; *b* – MPCC; *c* – MPCV

In Fig. 1, it can be seen that the heat absorption leap 1 at the glass transition temperature Tg (–40...–80 °C for the concentrates and –50...–60 °C for the control sample) corresponds to the glass retransition, namely, the transition of the substance from the glassy state into a supercooled liquid.

The term “glass transition temperature” refers to a range of temperatures at which the glassy material is softened and converted to a liquid state. The value of the glass transition temperature is determined by the point of inflection in the area of heat absorption leap 1.

Fuzzy exothermic effect 2 at the crystallization temperature (Tc) is associated with the completion of ice crystallization, which was interrupted by rapid cooling.

The endothermic peak 3, which corresponds to the temperature of melting of eutectic compositions (Tme), is also recorded on the MPCC thermogram. The intense endothermic peak 4 at the melting temperature (Tm) corresponds to the complete melting of ice in the samples of the concentrates.

In addition to the structure that determines the technological properties and the way of further use of MPC, other organoleptic characteristics are also important, as they essentially affect consumers’ interest in the product, creating demand for it. In the storage process, the change in most of the organoleptic characteristics, such as appearance, taste and smell, is quite noticeable, but it is more difficult to trace the change of others, in particular, color.

The color of any product depends on its ingredient composition, technology, parameters and method of processing for further use. For MPC, the color is due to the addition of berry purees at the stage of coagulation of the clot, as well as the temperature and time of protein precipitation. A color change can be revealed during the organoleptic evaluation of the product, but the data obtained will be subjective, not to mention the human eye cannot catch a slight change in shades. Therefore, it is expedient to estimate the change in color-parametric characteristics with the help of computer equipment and programs based on known methods for determining the color characteristics.

The CIEXYZ and CIELab methods were used to study the colorimetric characteristics of MPC. Studies were conducted immediately after making the MPC sample, as well as after 30, 60 and 90 days of storage in a frozen state.

The reflection spectra of MPC samples are shown in Fig. 2–5.

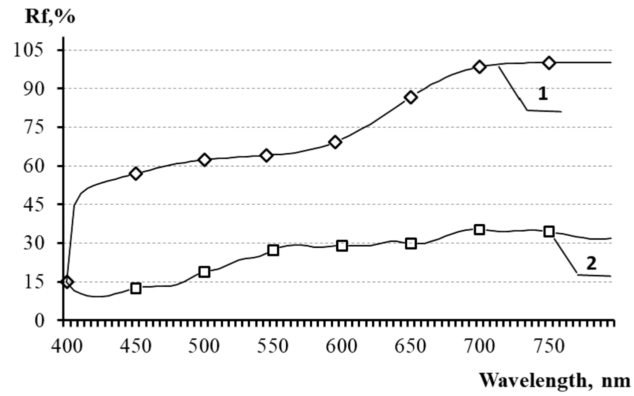

Fig. 2. Reflection spectra of MPCC (1) and MPCV (2) after making

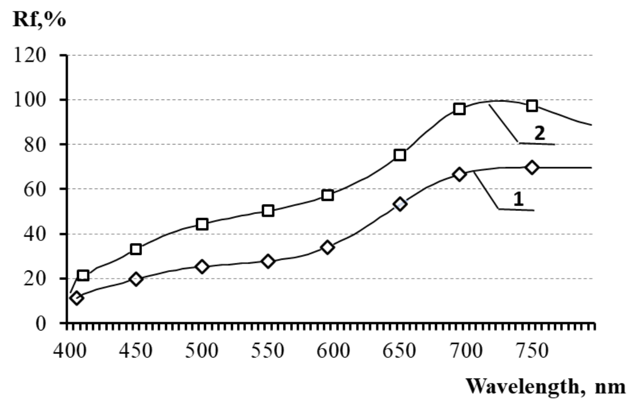

Fig. 3. Reflection spectra of MPCC (1) and MPCV (2) after 30 days of storage

Any curve of the spectral refractive index contains information that the sample color corresponds to the color tone of radiation of the spectrum part where the object reflects the light most. The intensity of light, in turn, corresponds to the curvature of the curve of the spectral refractive index, that is, the degree of reflection selectivity.

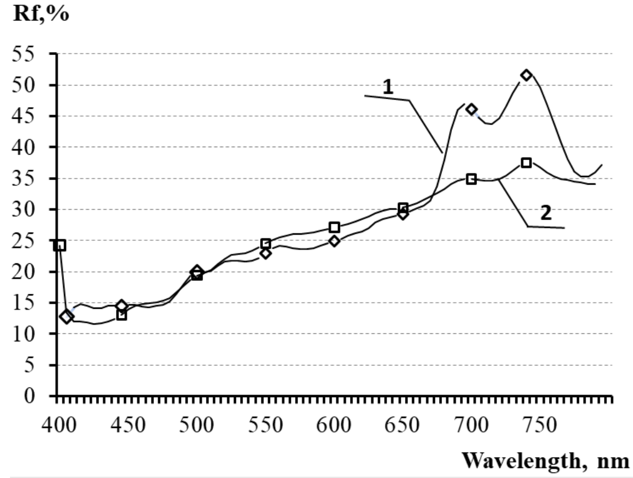

Fig. 4. Reflection spectra of MPCC (1) and MPCV (2) after 60 days of storage

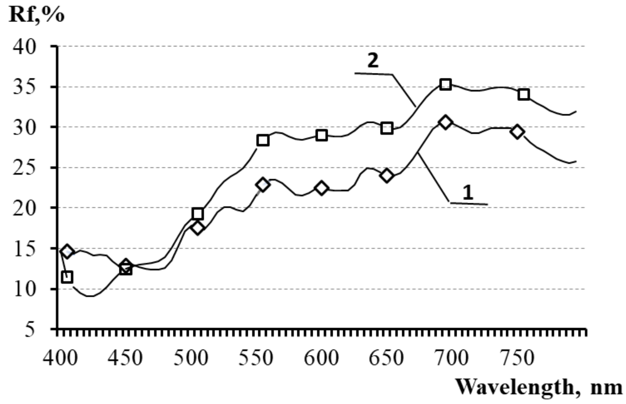

Fig. 5. Reflection spectra of MPCC (1) and MPCV (2) after 90 days of storage

The calculated color-parametric characteristics of MPCV are given in Table 1.

Table 1

Color characteristics of MPCV

Parameter	MPCV sample			
	After making	After 30 days of storage	After 60 days of storage	After 90 days of storage
CIEXYZ system				
x	0.3617	0.3639	0.3685	0.3801
y	0.3723	0.3711	0.3856	0.4048
λ, nm	578.9	579.9	576.9	575.5
T, %	37.2	37.1	38.6	40.5
P, %	33.62	33.68	40.79	50.75
Spectral color (dominant tone)	Yellow	Yellow	Yellow	Yellow
CIELab system				
L^*	84.94	77.31	56.47	57.93
a^*	3.22	4.25	0.60	–1.26
b^*	22.76	21.08	20.36	27.06
a^*/b^*	0.14	0.20	0.03	–0.05

Color-parametric characteristics of MPCC are presented in Table 2.

There is an interconnection between the two systems due to mathematical transformations, so the color indexes of the Hunter system (CIELab) were obtained using appropriate mathematical algorithms.

Table 2

Color characteristics of MPCC

Parameter	MPCC sample			
	After making	After 30 days of storage	After 60 days of storage	After 90 days of storage
CIEXYZ system				
x	0.3355	0.3737	0.3599	0.3569
y	0.3427	0.3628	0.3745	0.3777
λ, nm	585.1	585.4	577.7	575.8
T, %	34.3	36.3	37.5	37.8
P, %	12.58	32.49	34.12	34.73
Spectral color (dominant tone)	Yellow-orange	Yellow-orange	Yellow	Yellow
CIELab system				
L^*	85.18	61.82	50.68	52.87
a^*	4.35	9.17	1.17	–0.53
b^*	8.35	16.91	16.28	16.09
a^*/b^*	0.52	0.54	0.07	–0.03

6. Discussion of the results of the study of changes in the structure and color of MPC in the process of storage

The results of the study of the MPC structure show (Fig. 1) that the glass transition observed during the cooling of all the samples is explained by the existence of bound water in them. The latter does not have time to crystallize due to the high cooling rates used in the experiments.

The molecular movements in the glassy state are limited by vibrations and short-acting rotational motions. Thus, amorphous concentrates can be considered relatively stable in the solid state. The substance thus has the form of a mixture of ice crystals and solid amorphous inclusions. It should be noted that when the temperature or relative humidity increases, the materials pass from the glassy state to the supercooled viscous liquid. Since the structure of the studied products is amorphous, such transition will have a negative effect on consistency. From this, one can conclude that the concentrates must be kept below the temperature Tg, that is, below –80 °C, when the whole liquid remains in the solid state.

On the other hand, attention should be paid to the endothermic peak 3 on the MPCC curve (Fig. 1, *b*). It can be explained by the melting of the eutectic compositions that have passed to a solid crystalline state at the cooling stage. This can be an additional damaging factor in the low-temperature storage of this semi-finished product. In this case, the storage temperature of the concentrates is limited to the melting point of the eutectic compositions, which is –45 °C.

The complete melting of ice in the studied samples corresponds to the endothermic peak 4. The melting point for the concentrates is 7...10 °C. The formation of ice macrocrystals with the use of conventional freezing contributes to the destruction of the cell structure of the concentrates and, as a consequence, the deterioration of the organoleptic properties.

Given the above, rapid freezing of the studied products at –20…–30 °C with subsequent storage at this temperature is rational.

The intensity of heat absorption leaps is higher for the concentrates obtained with the use of berry purees than for the control sample. This indicates a larger amount of bound fluid in the products, which allows reducing the crystallization at the cooling stage and increasing the amount of glassy phase. Since the growth of ice crystals leads to physical deformation of cells and, consequently, to significant changes in the structure of foods, the reduction of crystallization in MPC indicates the improvement of preservation in the frozen state.

The results of the study of diffuse reflection spectra of the concentrates (Fig. 2) indicate the absence of maxima on them, which proves the non-selectivity of reflection virtually in the entire range of 400…750 nm. By this characteristic, the color of the samples is close to white, for which the reflection indexes in the range of visible light approach 100 %. However, the values of the reflection index of MPCC are gradually reduced in the range of 400…650 nm. This indicates the appearance of the purple-red shade, because the accumulation of the substances responsible for this shade is characterized by an increase in light absorption in the green-blue part of the spectrum. At the same time, the sample color is visually characterized as light pink.

The curve of reflection spectra of MPCV is characterized by lower Rf values, which do not exceed 40 %. In the mid- and long-wave areas of the spectrum (range of 500…750 nm), there is a slight increase in reflection intensity, indicating the increased contribution of yellow and red components of the color. Visually, the sample color is characterized as light yellow.

Curves of reflection spectra of the samples after 30 days of storage (Fig. 3) indicate a small difference between spectra of diffusion reflection with respect to the previous data. The spectral curve has no selective reflection; however, the reflection coefficients gradually increase. So, the increase is from 16 % to 75 % for MPCC and from 20 % to 100 % for MPCV.

The increase in reflection intensity for both samples falls in the range of the spectrum of 600…750 nm, which corresponds to orange-red shades. At the same time, the samples after the first month of storage almost do not visually differ from their directly produced analogues.

Spectral curves of diffuse reflection of MPCC and MPCV after 60 days of storage (Fig. 4) have a more complex shape. The values of reflection indexes for MPCV increase gradually, whereas for MPCC they are characterized by a sharp increase in the red area of the spectrum (650…750 nm). Simultaneously, the highest values of Rf for MPCV and MPCC do not exceed 40 % and 55 %, respectively, which indicates the darkening of the product.

After the 90-days storage of the samples, the curves of reflection spectra are characterized by an even larger decrease in reflection indexes (Fig. 5), which are a maximum of 36 % for MPCV and 32 % for MPCC. Taking into account the previous data, one can conclude that with the extension of the storage time for more than 30 days from the time of making, the color of MPC significantly darkens. The largest increase in reflection intensity for both MPC corresponds to 550…700 nm, that is, the yellow-red area of the spectrum. Visually, the samples darken and acquire a yellow-orange color with a white shade.

Comparing the data after making and during the storage of MPCV (Table 1), it should be noted that for all the samples the dominant spectral color is yellow. Although the brightness parameter in the CIEXYZ system grows with increased storage life (from 37.2 % to 40.5 %), the dominant wavelength is gradually shifted to the yellow region of the visible spectrum (from 578.9 nm to 575.5 nm). This is also indicated by the purity of the tone, which gradually changes from 33.62 % to 50.75 %, which indicates an increased contribution of the yellow component of the spectrum to the total sample color, that is, on the yellowing of MPCV during the storage process.

While analyzing Table 2, one can note, that the dominant spectral color of MPCC during the first 30 days of storage is orange. However, the next 30…60 days there is an intense yellowing of the product. The brightness parameter in the CIEXYZ system remains almost unchanged, moving from 34.3 % to 37.8 %, and the dominant wavelength (585.1…575.8 nm) indicates a slight shift in the product shade towards the yellow color. The purity of the tone, which varies from 12.58 % to 34.73 %, also indicates a significant yellowing of MPCC during the storage process.

The value of the parameter of light (L^*) by the CIELab system indicates a significant contribution of white color to the total color of both products, as for all the samples it amounts from 85 to 50 %. The calculated parameters a^* and b^* in most cases have a value >0, that is, the dominant colors of the products are red and yellow.

Therefore, one can conclude that storage of samples in the frozen state for 30 days from the time of making almost does not affect the organoleptic properties of the product. At the same time, further storage promotes rapid darkening of MPC.

7. Conclusions

1. The influence of low temperatures on the MPC structure was investigated and it was determined that rapid freezing of the studied products at –20…–30 °C with subsequent storage at this temperature is the most rational, which is connected with a lower content of free moisture and, consequently, lower crystallization and destruction.

2. It is determined that the rational storage time of MPC, taking into account the change in the color-parametric characteristics during storage, is 30 days from the time of making. Further storage leads to a deterioration of the color-parametric characteristics of the product and, accordingly, its organoleptic characteristics.

References

1. Seheda S. A. Otsinka spozhyvannya osnovnykh prodovol'chykh produktiv v Ukrayini [Estimation of consumption of basic food products in Ukraine] // Zbirnyk naukovykh prats' VNAU. 2012. Issue 3. P. 195–199.
2. Gnitsevich V. A., Yudina T. I. Analiz i perspektyvy vykorystannya bilkovo-vuhlevodnoyi molochnoyi syrovyny v Ukrayini [Analysis and prospects of using of protein-carbohydrate dairy raw materials in Ukraine] // Materials of the international scientific-practical conference «Globalization Challenges for the Development of National Economies». Kyiv: KNTEU, 2016.

3. Gnitsevich V. A., Deinychenko L. G. Innovaciyi u vyrobnycztvi molochno-bilkovyh koprecypitativ [Innovations in the production of milk-protein co-precipitates] // Tourist, hotel and restaurant business: innovations and trends. Abstracts of international science-practice conference. Kyiv: Kyiv. nats. torh.-ekon. un-t, 2016.
4. Timchuk A. V., Grek O. V. Vplyv zamorozhuvannya na pokaznyky albuminnoyi masy [The effect of freezing on the parameters of albumin mass] // Prospects for the development of meat, dairy and oilseed industries in the context of European integration: program and materials of the 4th international sci.-tech. conf. Kyiv: NUKhT, 2015. P. 110–111.
5. Issledovanie form svyazi vlagi v tvoroge s mikropartikulyatom syivorotochnyih belkov [Study of the forms of moisture binding in cottage cheese with microparticulate of whey proteins] / Korotkov E. G. Melnikova E. I., Kuznetsova I. V., Stanislavskaya E. B. // Molochnaya promyishlennost. 2016. Issue 8. P. 31–32.
6. Biotehnologicheskie i mikrobiologicheskie aspektyi proizvodstva tvoroga s uvelichennyim srokom godnosti [Biotechnological and microbiological aspects of production of cottage cheese with increased shelf life] / Zobkova Z. S., Zenina D. V., Fursova T. P., Gavrilova A. D., Shelaginova I. R. // Molochnaya promyishlennost. 2016. Issue 4. P. 49–50.
7. Fridenberg G. V., Lukashova T. A. Sovershenstvovanie tehnologii holodilnogo rezervirovaniya tvoroga [Improvement of technology of cottage cheese refrigerating redundancy] // Molochnaya promyishlennost. 2014. Issue 6. P. 59–62.
8. Short communication: Effect of storage temperature on the solubility of milk protein concentrate 80 (MPC80) treated with NaCl or KCl / Sikand V., Tong P. S., Walker J., Wang T., Rodriguez-Saona L. E. // Journal of Dairy Science. 2016. Vol. 99, Issue 3. P. 1791–1795. doi: 10.3168/jds.2015-10158
9. Banach J. C., Clark S., Lamsal B. P. Texture and other changes during storage in model high-protein nutrition bars formulated with modified milk protein concentrates // LWT – Food Science and Technology. 2014. Vol. 56, Issue 1. P. 77–86. doi: 10.1016/j.lwt.2013.11.008
10. Effect of storage time and temperature of milk protein concentrate (MPC85) on the renneting properties of skim milk fortified with MPC85 / Hunter R. J., Hemar Y., Pinder D. N., Anema S. G. // Food Chemistry. 2011. Vol. 125, Issue 3. P. 944–952. doi: 10.1016/j.foodchem.2010.09.086
11. Effects of storage temperature on the solubility of milk protein concentrate (MPC85) / Anema S. G., Pinder D. N., Hunter R. J., Hemar Y. // Food Hydrocolloids. 2006. Vol. 20, Issue 2-3. P. 386–393. doi: 10.1016/j.foodhyd.2005.03.015
12. Gnitsevich V. A., Yudina T. I., Deynichenko L. G. Tekhnolohiya ta biolohichna tsinnist' molochno-bilkovykh kopretsypitativ [Technology and biological value of milk-protein co-precipitates] // Tovaryi i ryinki. 2016. Issue 2. P. 148–158.
13. Roos Y. H., Drush S. Phase Transitions in Foods. 2nd ed. Cork: Academic Press, 2015. 380 p.
14. Definition of quality indicators of dairyprotein concentrates in the storage process / Gnitsevych V., Yudina T., Deinychenko L., Nykyforov R., Nazarenko I. // EUREKA: Life Sciences. 2018. Issue 1. P. 10–17. doi: 10.21303/2504-5695.2018.00526
15. Telis V. R. N., Sobral P. J. A. Glass transitions for freeze-dried and air-dried tomato // Food Research International. 2002. Vol. 35, Issue 5. P. 435–443. doi: 10.1016/s0963-9969(01)00138-7
16. Telis V. R. N., Sobral P. J. do A., Telis-Romero J. Sorption Isotherm, Glass Transitions and State Diagram for Freeze-dried Plum Skin and Pulp // Food Science and Technology International. 2006. Vol. 12, Issue 3. P. 181–187. doi: 10.1177/1082013206065953
17. State diagram of apple slices: glass transition and freezing curves / Bai Y., Rahman M. S., Perera C. O., Smith B., Melton L. D. // Food Research International. 2001. Vol. 34, Issue 2-3. P. 89–95. doi: 10.1016/s0963-9969(00)00128-9