

## Substantiation of rational modes of semi-finished milk-plant stuffings freezing

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### Abstract

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**Introduction.** The rational regimes of freezing of semi-finished milk-plant stuffings based on buttermilk concentrate were substantiated and experimentally confirmed.

**Materials and methods.** Milk-carrot, milk-pumpkin, milk-zucchini stuffings, as well as cottage cheese control sample stuffing, were studied. The research was carried out on a high-resolution spectrometer Tesla BS 567A with a working frequency of 100 MHz on protons by the Kuntz method.

**Discussion of the results of study.** It was established that at the temperature of 20 °C in the nuclear magnetic resonance spectrum of the semi-finished milk-plant stuffing an intense water signal is recorded, which significantly decreases with intensity while sample cooling to a temperature of -25 °C. The presence of a nuclear magnetic resonance signal indicates that non-freezing water does not disappear completely when cooling the sample to a temperature of -25 °C, which implies the possibility of biochemical reactions proceeding in the stuffing. It is determined that developed semi-finished stuffings require a deeper overcooling than a control sample, since in designed samples of stuffings water binding with carbohydrates is processing.

It was investigated that at -25 °C the control sample contains 0,21 g of H<sub>2</sub>O per gram of dry matter, when the semi-finished milk-carrot stuffing contains 0,40 g of H<sub>2</sub>O per gram of dry matter, milk-pumpkin stuffing – 0,39 g of H<sub>2</sub>O per g of dry matter, milk-zucchini stuffing – 0,37 g of H<sub>2</sub>O per gram of dry matter at the same temperature. At -30 °C the control sample contains 0,20 g of H<sub>2</sub>O per gram of dry matter, when in the semi-finished milk-carrot stuffing the content of H<sub>2</sub>O reaches 0,32 g per gram of dry matter, in the milk-pumpkin stuffing – 0,25 g per gram of dry matter, milk-zucchini stuffing – 0,24 g per gram of dry matter at the same temperature. It is proved that the smallest amount of non-freezing water in the stuffings is kept at a temperature of -25 ... -30 °C and amounts 0,26 ... 0,40 g of H<sub>2</sub>O per 1 g of dry matter, which allows to recommend a given range of temperatures for their rapid freezing.

**Conclusions.** The temperature of milk-plant stuffings freezing is substantiated (-25...-30 °C). The possibility of frozen stuffings storage at a temperature of -18...-19 °C, which is the standard temperature of industrial freezing chambers, is proved.

## **Introduction**

A promising direction in creating qualitatively new foods is the combination of dairy and plant raw materials [1].

The technology of fundamentally new foods in the form of multifunctional semi-finished products on the basis of protein-carbohydrate dairy and plant raw materials is developed [2]. The new approach to the use of uninvolved natural properties of dairy and plant raw materials gives the possibility to maximize their functional properties, increasing the economic efficiency of technologies by reducing the use of nutritional additives, as well as increasing the nutritional and biological value of finished products [1].

Semi-finished milk-plant stuffings can be used for the production of a wide range of restaurant foods (sweet dishes, flour dishes, pastry, e.t.c.) [3].

It is advisable to store the developed semi-finished milk-plant dtuffings in frozen form [2]. The advantages of the use of frozen semi-finished milk-plant stuffings in the foods production at restaurant establishments are the possibility of using quick-frozen semi-finished products in the fast food system, reducing of labor and producing costs, the flexibility of the technological process, the long storage time of semi-finished milk-plant stuffings, significant expansion of the range of culinary products in restaurants and possibility to transport frozen semi-finished products at long distances [4, 22].

## **Literature review**

To extend the storage time of foods it is expedient to use a freezing process, in particular quick freezing [22]. Quick freezing is one of the methods of preservation, which guarantees long-term storage of raw material properties due to the action of low temperatures on the development of microflora [5]. The decrease in temperature is accompanied by a slowing down of reactions related with the activity of enzymes and microorganisms [5, 22].

The effect of low temperatures on food causes changes in their consistency and structure, affects the quality of products after defrosting [5–7]. The degree of these changes depends on the speed and temperature of freezing, the duration and conditions of storage, the method of defrosting and composition of products [6,7].

The study of the influence of the freezing-defrosting process on the structure of milk-protein foods could be found in the works of domestic and foreign scientists [8–18].

It is known [8] that a large number of small crystals is formed in the process of milk-protein products quick freezing. In general, the negative influence on the quality of the milk-protein product is made by the pressure of the formed crystals of ice on the protein complexes, which leads to their breaks, cuts and loss of the native structure [9]. Besides, an increase in the concentration of dissolved chemicals occuring during crystallization creates the conditions for the rearrangement of protein micelles, changes in the structure of the product, which leads to an intense moisture distribution [8]. At the same time, the difference in the quality of milk-protein semi-finished foods based on the cottage cheese, frozen in various ways, almost disappears after several months of storage at -20 °C due to the migratory recrystallization – the growth of large crystals after melting of small ones [9]. The mover of this process is considered to be the temperature difference in the middle of the product and on its surface, as well as the difference in pressure on the surface of large and small crystals [8].

The technology of cottage cheese, which envisages the enrichment by the microparticulates of serum proteins, is developed. The storage time of the developed product exceeds the storage time of cottage cheese by 30% [9].

A method to increase the storage time of cottage cheese using different fermentation, protein coagulation and serum removal techniques is known [10]. The method of improvement of the refrigeration reservation technology of cottage cheese is developed. The method justifies the choice of optimal parameters of cottage cheese microwave defrosting, but requires experimental confirmation [11].

In the work [12] the changes of organoleptic parameters of protein bars during storage were investigated. The bars were stored at the temperature 22 °C, 32 °C or 42 °C for 42 days. It was established that the bars made using milk-protein concentrate have a higher softness regardless of the storage temperature. It is determined that the change in the surface color of the bars based on the milk-protein concentrate is minimal when stored at 22 °C, but increased at 32 °C and 42 °C [12].

The rheological properties and solubility of milk-protein concentrate during storage are investigated [13,14]. It is established that the final complex module and the tension decrease exponentially with an increase in the storage time of the milk protein concentrate. The increase in the storage temperatures intensify this effect [13]. The solubility also decreases exponentially over time, and serum proteins remain soluble, unlike caseins that become lactosilated [14].

In the work [15] the effect of low temperatures on the structure of the milk-protein concentrate was investigated and it was determined that the quick freezing of the studied foods at -20...-30 °C with subsequent storage at that temperature is rational. It is determined that the rational storage period of milk-protein concentrate, taking into account the change of color-parametric characteristics in the storage process, is 30 days from the moment of manufacturing.

It is proved that the making of protein-plant mixtures before freezing contributes to the losses reducing beyond the regulatory of milk-protein base (cottage cheese) due to changes in the state of the free-bound moisture and its leakage after defrosting [16, 17]. It is confirmed that rice and wheat extruders in combination with cottage cheese have the ability to change the state of the free-bound moisture – to prevent active synergistic phenomena after defrosting [18].

In the technology of semi-finished milk-plant stuffings the use of carrot, pumpkin, and zucchini purees is proposed to provide compatibility with the milk protein base (buttermilk concentrate) at the organoleptic level, economic expediency (use of local raw materials of the regions) and perform the technological function of wet-binding, due to high content of pectin substances in vegetable purees [2,3].

In connection with the foregoing, the study of the effect of plant raw materials on the state of water during freezing-defrosting of semi-finished milk-plant stuffings and the definition of rational modes of their freezing is an urgent task.

The purpose of the work is to study the influence of plant raw materials on the state of water during freezing-defrosting of semi-finished milk-plant stuffings and the definition of rational regimes of their freezing.

To reach the goal, the following tasks were solved:

- to investigate the influence of plant raw materials on the processes of phase transition and the state of water during freezing-defrosting of semi-finished milk-plant stuffings;
- to substantiate the freezing temperature of milk-plant stuffings;
- to substantiate the temperature of further storage of frozen milk-plant stuffings.

## Materials and methods

### Researched materials

As materials were defined: semi-finished milk-plant stuffings (milk-carrot stuffing, milk-pumpkin stuffing, milk-zucchini stuffing) and a control sample (cottage cheese stuffing).

Cottage cheese stuffing was obtained by adding flour and melange prepared in advance to the wiped cottage cheese and by mixing them.

To obtain milk-plant stuffings, milk-protein concentrate based on buttermilk is wiped, mixed with prepared melange, wheat flour, sugar (salt), carrots, pumpkin or zucchini purees, then the mixture is stirred for 5-60 s, syringed in a cellophane shell and freezed until reaching the temperature of 3 °C in the center of the loaf.

The prescription components are taken in the following ratios, weight%:

1. For milk-carrot stuffing: milk-protein concentrate based on buttermilk – 68,0%, carrot puree – 16,0%, melange – 6,0%, wheat flour – 6,0%, sugar – 4,0%;

2. For milk-pumpkin stuffing: milk-protein concentrate based on buttermilk – 68,5%, pumpkin puree – 15,0%, melange – 6,0%, wheat flour – 6,5%, sugar – 4,0%;

3. For milk-zucchini stuffing: milk-protein concentrate based on buttermilk – 71,0%, zucchini puree – 15,0%, melange – 6,0%, wheat flour – 7,0%, salt – 1,0%.

### Description of methods

The research was carried out on a high-resolution spectrometer Tesla BS 567A with a working frequency of 100 MHz on protons by the Kuntz method [19].

### Results processing

For statistical probability, all experiments under laboratory conditions were performed in a fivefold repetition. The results of experimental studies were subjected to statistical processing by the least squares method to determine the error of the obtained data. In the series of each experiment, the average value of the indicator and the dispersion were calculated:

$$\bar{y} = \frac{\sum_{i=1}^n y_i}{n}, S_i^2 = \frac{\sum_{i=1}^n (y_i - \bar{y})^2}{n-1},$$

where  $\bar{y}$  – average value of the indicator;  $y_i$  – value of the indicator in each experiment session;  $n$  – number of parallel experiment sessions.

In order to calculate the reliability of the obtained results, the Student's criterion was used. To check the differences between the two meanings, the formula was used:

$$t = \frac{\bar{X}_a - \bar{X}_b}{\sqrt{x_a^2 + x_b^2}},$$

where  $t$  – Student's criterion;

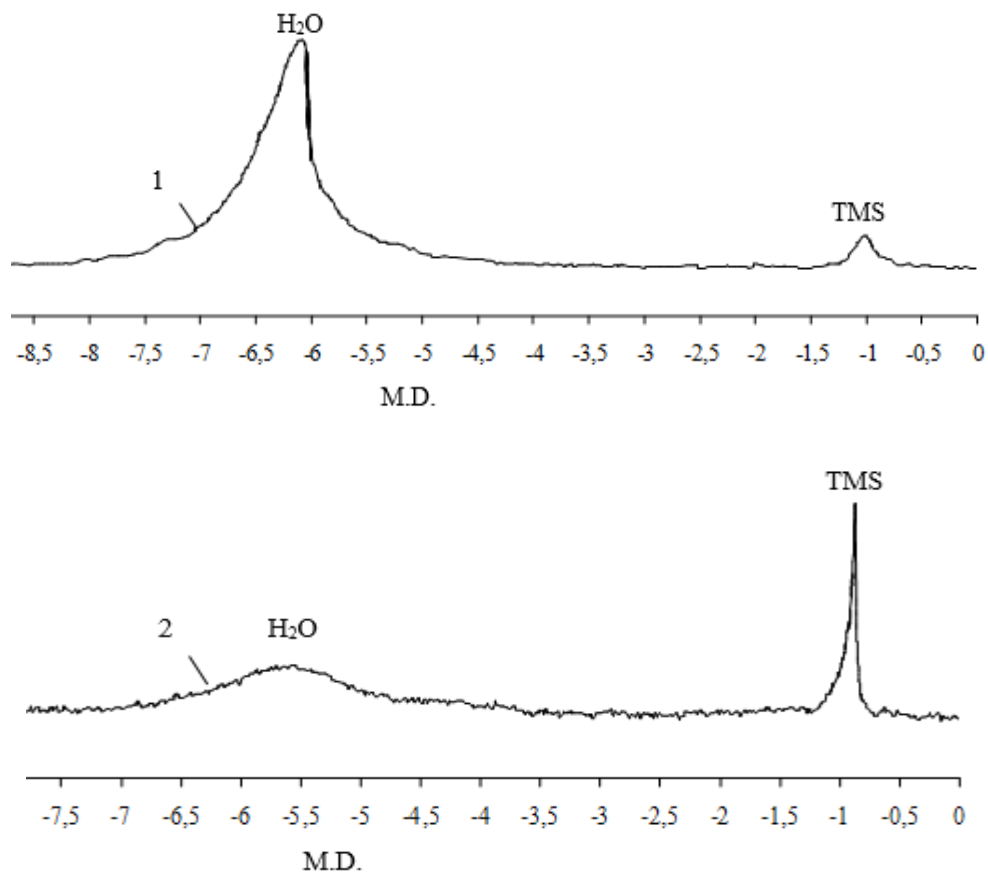
$\bar{X}_a, \bar{X}_b$  – the average of the A and B sample;

$x_a, x_b$  – the error of the arithmetic mean of A and B sample.

## Results and discussion

### Results of study of nuclear magnetic resonance spectrum of semi-finished milk-carrot stuffing

Typical spectrum of nuclear magnetic resonance of semi-finished milk-carrot stuffing at temperatures of + 20 °C and -25 °C are shown in Figure 1. The signals of the water and the standard – tetramethylsilane (TMS) – are recorded in the nuclear magnetic resonance spectrum.



**Figure 1. Spectrum of  $^1\text{H}$ - nuclear magnetic resonance of semi-finished milk-carrot stuffing based on buttermilk concentrate:  
1 - at the temperature of 20 °C, 2 - at the temperature of -25 °C**

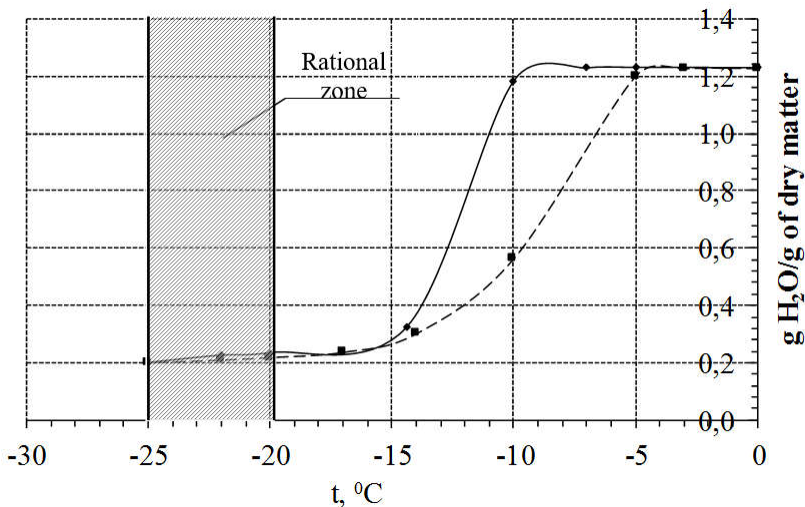
Analysis of data given at Figure 1 shows that at a temperature of 20 °C in the nuclear magnetic resonance spectrum of semi-finished milk-carrot stuffing (Figure 1) an intensive water signal is recorded, which decreases significantly with intensity while sample cooling to a temperature of -25 °C. The presence of a nuclear magnetic resonance signal indicates

that non-freezing water does not disappear completely when cooling the sample to a temperature of  $-25\text{ }^{\circ}\text{C}$ , which implies the possibility of biochemical reactions proceeding in the stuffing.

Taking into account that the intensity of the nuclear magnetic resonance signal, that is the area under the corresponding resonance line, is the measure of the substance amount, the effect of freezing temperature on the amount of non-freezing water in semi-finished milk-carrot stuffing was investigated in the next step.

### Study of the freezing temperature effect on the amount of non-freezing water in the control sample

The Figure 2 shows the results of the study of the freezing temperature effect on the amount of non-freezing water in the control sample.



**Figure 2.** The influence of freezing temperature on the amount of non-freezing water in the control sample (— cooling, - - - - heating)

In the temperature range from  $0\text{ }^{\circ}\text{C}$  to  $-9\text{ }^{\circ}\text{C}$  while cooling the intensity of the water signal in the spectrum of nuclear magnetic resonance does not change (Figure 2), that is, all water in the sample is recorded as non-freezing. Crystallization of ice in the control sample while its cooling is observed in the temperature range  $-9\text{ }^{\circ}\text{C}$  ...  $-15\text{ }^{\circ}\text{C}$ , which is recorded at a sharp drop in the intensity of the water nuclear magnetic resonance signal. The amount of non-freezing water in the control sample decreases from  $1,24\text{ g of H}_2\text{O per gram of dry matter}$  to  $0,28\text{ g of H}_2\text{O per gram of dry matter}$ .

A slight decrease in the amount of non-freezing water (up to  $0,20\text{ g of H}_2\text{O per gram of dry matter}$ ) is observed with a decrease in temperature to  $-17\text{ }^{\circ}\text{C}$  ...  $-18\text{ }^{\circ}\text{C}$ , with further decrease in temperature the amount of non-freezing water does not change. At  $-25\text{ }^{\circ}\text{C}$  the amount of non-freezing water in the control sample amounts  $0,20\text{ g of H}_2\text{O per gram of dry substance}$ .

The amount of non-freezing water in the experimental sample at a temperature below  $0\text{ }^{\circ}\text{C}$  does not coincide at the cooling and heating stages (Figure 2), which is explained by the overcooling of the liquid in the sample at a temperature decrease. Water systems are characterized by a very high propensity to overcooling [20, 21]. Conversely, while heating a

frozen water solution, the melting occurs at the «liquid – solid» equilibrium point. Therefore, in the cooling-heating cycle in water systems the fraction of non-freezing water is sensitive to the temperature hysteresis, which is proved by the data of Figure 2.

**Results of the study of the freezing temperature effect on the amount of non-freezing water in semi-finished milk-plant stuffings**

At the next stage, the effect of freezing temperature on the amount of non-freezing water in semi-finished milk-carrot (Figure 3), milk-pumpkin (Figure 4), milk-zucchini (Figure 5) stuffings was investigated.

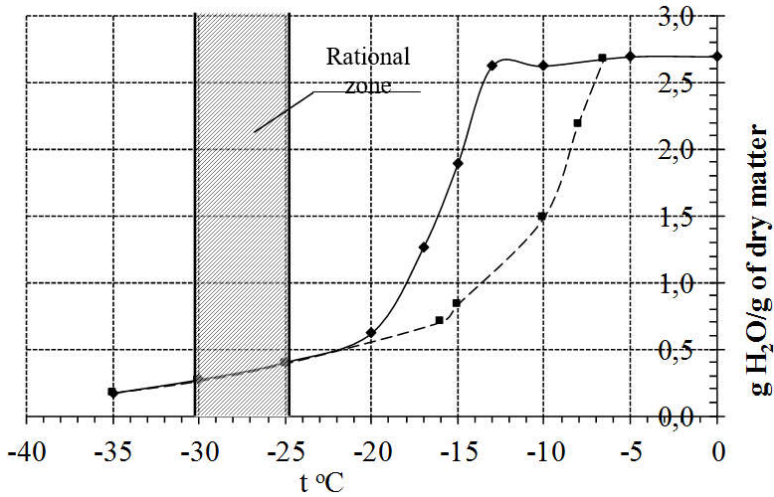


Figure 3. The influence of freezing temperature on the amount of non-freezing water in the semi-finished milk-carrot stuffing (——— cooling, - - - - - heating)

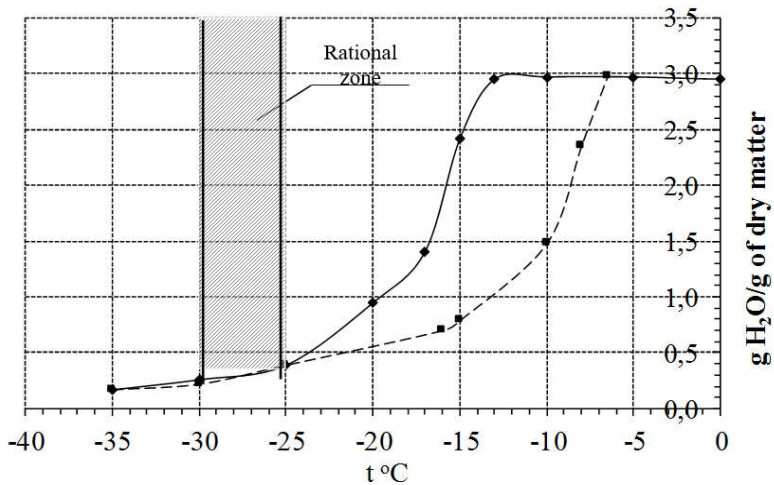
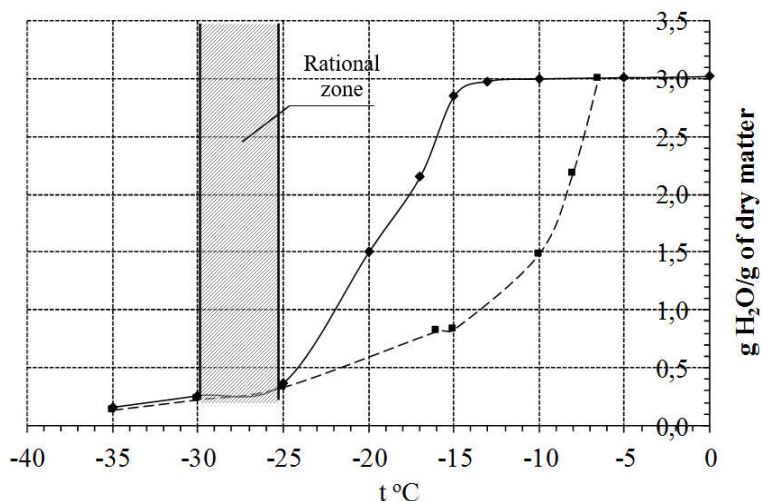


Figure 4. The influence of freezing temperature on the amount of non-freezing water in the semi-finished milk-pumpkin stuffing (——— cooling, - - - - - heating)



**Figure 5. The influence of freezing temperature on the amount of non-freezing water in the semi-finished milk-zucchini stuffing (— — cooling, - - - - - heating)**

Analysis of Figures 3–5 shows that the crystallization of ice with a decrease in temperature begins in the overcooled state of the samples.

#### **Substantiation of the freezing temperature of semi-finished milk-plant stuffings**

It is determined that the developed semi-finished milk-plant stuffings require a deeper overcooling than a control sample. This is related to the presence of vegetable purees in the stuffing, containing a large amount of carbohydrates, which bind water and stabilize its condition in the composition of stuffings. Such impact of vegetable purees creates more favorable conditions for the long-term quality storage of the frozen stuffings.

The comparison of the non-freezing water presence, registered by the method of nuclear magnetic resonance in protons at the temperature of -25 °C, indicates an increase in this water fraction amount in all investigated semi-finished milk-plant stuffings comparing with this amount in the control sample. For example, at -25 °C the control sample contains 0,21 g of H<sub>2</sub>O per gram of dry matter, when for the semi-finished milk-carrot stuffing the amount of H<sub>2</sub>O per gram of dry matter is 0,40 g, for milk-pumpkin stuffing – 0,39 g, for milk-zucchini stuffing – 0,37 g at the same temperature. At the temperature of -30 °C the control sample contains 0,20 g of H<sub>2</sub>O per gram of dry matter, and the semi-finished milk-carrot stuffing – 0,32 g of H<sub>2</sub>O per gram of dry matter, milk-pumpkin stuffing – 0,25 g of H<sub>2</sub>O per gram of dry matter, milk-zucchini stuffing – 0,24 g of H<sub>2</sub>O per gram of dry matter. This fact further confirms the conclusion that in the samples of semi-finished milk-plant stuffings the water is bound by carbohydrates (sugars).

The conducted studies (Figures 3-5) show that the smallest amount of non-freezing water in samples of semi-finished milk-plant stuffings is kept at a temperature of -25...-30 °C and amounts 0,26...0,40 g of H<sub>2</sub>O per 1 g dry matter or 8,1...11,1% of its amount in stuffing samples at a temperature of 0 °C. It is established that during further freezing, the content of non-freezing water is almost not reduced, which allows to recommend an indicated temperature range for the freezing of semi-finished stuffings.



## Substantiation of the further storage temperature of frozen milk-plant stuffings

It is determined that further storage of semi-finished milk-plant stuffings at a temperature of  $-18...-19$  °C (which is a normative temperature of the majority of industrial freezing chambers used in the food industry and recommended for storage of frozen foods and semi-finished products) contributes to a slight increase in the content of non-freezing water in them. If we take into account that at the temperature of  $-25...-30$  °C the amount of non-freezing water in semi-finished stuffings is the smallest and makes 8,1...11,1% of its amount at 0 °C, then at the temperature of  $-18...-19$  °C, which is recommended as the storage temperature of semi-finished stuffings, the non-freezing water will amount 22,2...23,8%. Since the increase in the amount of non-freezing water in semi-finished milk-plant stuffings is insignificant, the temperature of  $-18...-19$  °C can be recommended for the further storage of frozen stuffings.

## Conclusions

1. Presence of carbohydrates in carrot, pumpkin or zucchini purees increases the content of bound water in stuffings and creates more favorable conditions for the long-term storage of frozen semi-finished milk-plant stuffings.
2. The smallest amount of non-freezing water in semi-finished milk-plant stuffings is kept at a temperature of  $-25...-30$  °C and is equal to 0,26...0,40 g of H<sub>2</sub>O per 1 g of dry matter, which allows to recommend this temperature range for quick freezing of stuffings.
3. Frozen semi-finished milk-plant stuffings should be kept at a temperature of  $-18...-19$  °C during the storage.
4. To determine the rational storage terms of semi-finished milk-plant stuffings, changes in their microbiological parameters, organoleptic properties and acidity during storage should be investigated, which is the prospect of further research.

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