



Development of innovative technology for processing secondary raw materials in the meat industry

Desarrollo de tecnología innovadora para el procesamiento de materias primas secundarias en la industria cárnica

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ABSTRACT

The slaughtered animals' blood is a valuable secondary raw material in the meat industry. In this investigation, we propose a separation freezing technology for the blood, blood plasma and hemoglobin solution concentration. The processes of secondary meat raw materials separation freezing were studied for which the experiments for freezing in a capacitive crystallizer were conducted. The dependence of the freezing duration on the heat exchange surface temperature is determined and the cryoconcentration efficiency criterion is calculated. It is proved that the greatest freezing efficiency is observed at the heat exchange surface temperature of minus 2°C. At this temperature, the lowest dry matter loss was observed. The experiment in the separation freeze drying of a hemoglobin solution with the use of re-cryoconcentration was conducted. It is established that this technology can significantly reduce the dry matter loss. The pig blood plasma analysis before and after crystallization was conducted. It was found that crystallization has almost no effect on the amount and ratio of amino acids in the product.

Keywords: low-temperature concentration; secondary raw material; pig blood.

RESUMEN

La sangre de los animales sacrificados es una valiosa materia prima secundaria en la industria cárnica. En esta investigación, proponemos una tecnología de congelación de separación para la concentración de sangre, plasma sanguíneo y solución de hemoglobina. Se estudiaron los procesos de congelación de separación de materias primas cárnicas secundarias para lo cual se realizaron los experimentos de congelación en un cristizador capacitivo. Se determina la dependencia de la duración de la congelación con la temperatura de la superficie de intercambio de calor y se calcula el criterio de eficiencia de la criocentración. Se demuestra que la mayor eficiencia de congelación se observa a la temperatura de la superficie de intercambio de calor de menos 2°C. A esta temperatura se observó la menor pérdida de materia seca. Se realizó el experimento de separación por liofilización de una solución de hemoglobina con el uso de recrioconcentración. Se establece que esta tecnología puede reducir significativamente la pérdida de materia seca. Se realizó el análisis de plasma de sangre de cerdo antes y después de la cristalización. Se encontró que la cristalización casi no tiene efecto sobre la cantidad y proporción de aminoácidos en el producto.

Palabras claves: concentración a baja temperatura; materia prima secundaria; sangre de cerdo.

1. INTRODUCTION

Food is one of the most important factors affecting human health (Ameratunga et al., 2016; Yilmaz et al., 2018; Tomás-Barberán, Espín, 2019). Recent decades presented not only a significant increase in scientific and technological progress, but also a marked deterioration of the environmental situation, which in turn has led to a decrease in the average life expectancy of the population (Butenko, Ligaj, 2013; Hong et al., 2018; Tian et al., 2016). This is a consequence not only of man-made impact, but also of increased psycho-emotional stress, deterioration in the quality of food and a strenuous life rhythm.

If we consider the nutrition aspect, it should be noted that the negative impact on health is also due to the fact that in agriculture, the intensity of use of various growth stimulants, pesticides, herbicides, etc. has recently increased.

It is possible to redound to diseases prevention caused by the above factors by means of proper, full-fledged nutrition and functional products consumption. Meat industry secondary raw materials, in particular the slaughtered animals' blood and its derivatives, are a valuable source of biologically active substances, such as proteins, fats, minerals, amino acids, etc. (Zhang et al., 2016; Lynch et al., 2017). The approximate chemical composition of pig blood and its components is shown in table 1 (Pozharskaya et al., 1971). It is worth noting that the blood composition of animals may differ within certain limits depending on the season, breed of animal, conditions of keeping and feeding, etc. It should be noted that the animals blood composition may differ within certain limits depending on the season, animal breed, conditions of keeping and feeding, etc.

Hemoglobin, which is part of the red blood cell mass, can be successfully used in the production of functional products and biologically active additives as a natural source of heme iron. Blood plasma can be used in the food industry as a foaming agent and a protein source in the protein therapeutic and preventive food production (Kriger, 2014; Parés et al., 2014). As for whole blood it is used not only for the production of Hematogen but also for additives in various kinds of blood sausages, canned meat, potions, etc.

Table 1. Various substances content in pig blood and its components, %

Value	Whole blood	Blood plasm	Concentrated red cells
Water	79,056	91,761	62,561
Total dry matter:	20,944	8,239	37,438
including:		6,741	51,872
protein	18,481		
blood sugar	0,0686	0,1212	-
cholesterin	0,0444	0,0409	0,0489
lecithin	0,2309	0,1426	0,3456
fat	0,1095	0,1956	-
fatty acids	0,0475	0,0794	0,0062
phosphorus in the form of a nuclein	0,0578	0,00128	0,01045
ferric oxide	0,0696	-	0,1599
natrium	0,2406	0,4251	-
kalium	0,2309	0,027	0,4957
calcium	0,0068	0,0122	-
magnesium	0,00889	0,00412	0,015
chlorine	0,269	0,3627	0,1475
total phosphorus	0,1007	0,01972	0,2058
including inorganic phosphorus	0,074	0,00524	0,1653

In order to extend the shelf life and obtain ready-made canned products, or to separate certain components from them, such a technological operation as concentration is often used in the food industry (Ermolaev, 2014; Korotky et al., 2020; Balde, Aider, 2019). It can also be used for thickening secondary meat raw materials: blood, plasma, serum and red blood cell mass, for example, if this is required by the product recipe composition. In addition, concentration can slow down undesirable biochemical and microbiological processes, as well as decrease the volume of storage liquid, which reduces the economic costs of transporting and storing raw materials.

One of the most promising concentration methods is separation freezing. This method essence is that in the course of successive liquid solution crystallization, first of all, pure moisture is frozen, and dry substances are pushed into the unfrozen part by the formed crystal phase. The advantage of this concentration method is the absence of a negative effect of temperature on the thermolabile components of the product.

Thus, this work purpose was to develop a technology for separating freezing of meat industry secondary raw materials

2. MATERIALS AND METHODS

The research objects were:

- whole stabilized pig blood;
- pig blood plasma;
- a pig blood hemoglobin solution.

Pig's blood was collected in accordance with Russian Federation Sanitary Regulations and Norms 2.3.2.1078-01. There were Siberian Northern pigs, 1 year old, raised in the Kemerovo region.

The blood stabilization was performed by adding 8.5% sodium tripolyphosphate solution (the ratio of stabilizer to pig blood is 0.025:1).

The blood plasma was obtained from stabilized blood using a centrifuge with a separation factor of 2000. In order to obtain a hemoglobin solution cleared from foreign components, newly collected pig blood was defibrinated for 12 minutes in a defibriner, the resulting clots were removed by filtering through sterile gauze. Then the defibrinated blood was sent to a centrifuge for its separation into serum and red blood cell mass with a separation factor of 2000. The red blood cell mass was washed twice with saline solution, then it was diluted with distilled water in a ratio of 1:9, which provided 100% hemolysis of the formed elements. The resulting hemolysate was cleared from the red blood cells vacant shells by centrifugation for 20 minutes.

The separation freezing was performed on a laboratory capacitive cryoconcentrator, the scheme of which is shown in figure 1.

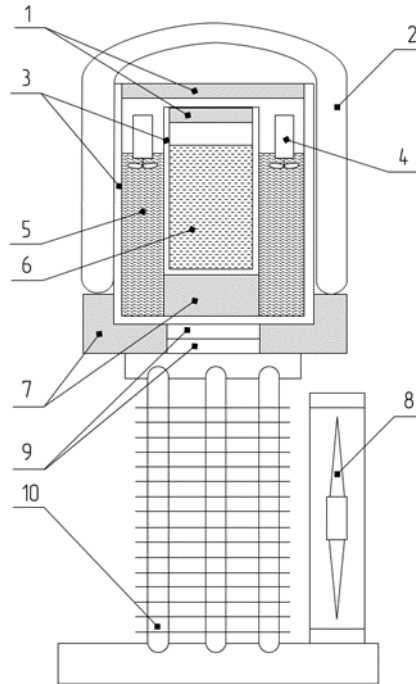


Figure 1. Laboratory cryoconcentrator diagram: 1-adiabatic cover; 2-Dewar vessel; 3-aluminum container; 4-agitator; 5-coolant; 6-concentrated product; 7-heat-insulation; 8-fan; 9-Peltier elements; 10-radiator

The product is placed in a working container 3 (internal), which is immersed in a coolant filled in a larger container 3 (external). Heat is removed from the coolant using two Peltier elements 9 connected in series. In the coolant the temperature distribution uniformity is provided by the agitators 4 operation. The heat from the Peltier elements is removed via the radiator 10. In order to reduce heat leakage from the environment, heat insulation 7 and a Dewar vessel 2 are provided. Also in order to ensure that the heat is diverted from the working container mainly from the side cylindrical surface, it is installed on a thermal insulation stand 7.

The dry substances content was carried out in accordance with ISO 1442:1997 "Meat and meat products – Determination of moisture content (Reference method)".

The protein mass fraction was determined with the help of the "Rapid N Cube" protein nitrogen analyzer (ELEMENTAR Analysensysteme GmbH, Germany) using the Dumas method.

The amino acid content was determined using an Aracus amino acid analyzer manufactured by PMA GmbH (Germany).

The experiments were carried out in triplicate, the final value was taken as the arithmetic mean result from all three measurements.

3. RESULTS AND DISCUSSION

The research subject had the following values of the moisture mass fraction:

- blood stabilized - 81.3%;
- blood plasma-91.6%;

- a solution of hemoglobin of 95.8%.

At first, we studied the secondary raw materials separation freezing processes in a capacitive crystallizer depending on the concentration duration. The heat exchange surface temperature was minus 2°C. The experiment was carried out until the degree of freezing reached 90%. The dependence of the frozen product amount on the cryoconcentration duration is shown in Figure 2.

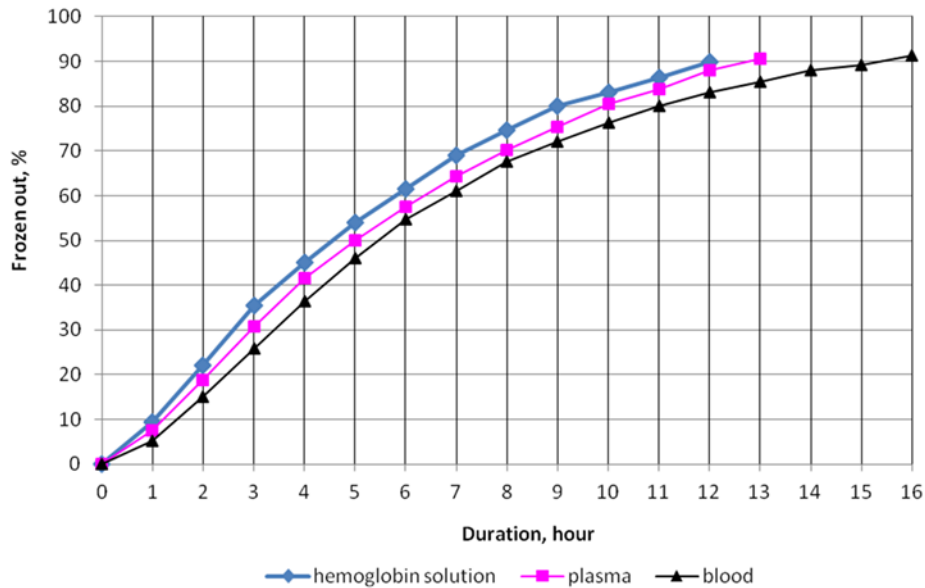


Figure 2. Dependence of the frozen product amount on the cryoconcentration duration at the heat exchange surface temperature the minus 2°C

According to the experimental data results the highest ice formation rate is observed in the time interval of 1...3 hours (Figure 1) and is 10-13%/hour. During the hemoglobin solution cryoconcentrating 90% of the product froze after 12 hours, plasma after 13 hours and blood after 15.5 hours. This difference is caused by the difference in the dry matter content and the different cryoscopic temperature, which decreases as the moisture freezes in the product unfrozen part.

Further experiments were conducted in order to study the effect of the crystallizer heat exchange surface temperature on the freezing duration. This parameter was changed at the limit from minus 2 to minus 6°C. The results are presented in table 2.

Table 2. The dependence of the secondary meat raw materials freezing duration on the crystallizer surface temperature

Crystallizer surface temperature, °C	Freezing duration, hour.		
	Hemoglobin solution	Blood plasma	Stabilized blood
minus 2	12	13	15,5
minus 4	6,5	7	8,5
minus 6	4	4,5	5,5

There is a nonlinear change in the freezing duration with a decrease of the crystallizer surface temperature. The shortest cryoconcentration duration was observed at a temperature of minus 6°C and ranged from 4 to 5.5 hours. The lower the temperature, the more linear the dependence diagram of freezing on the cryoconcentration duration and the freezing out rate is higher (Figure 3).

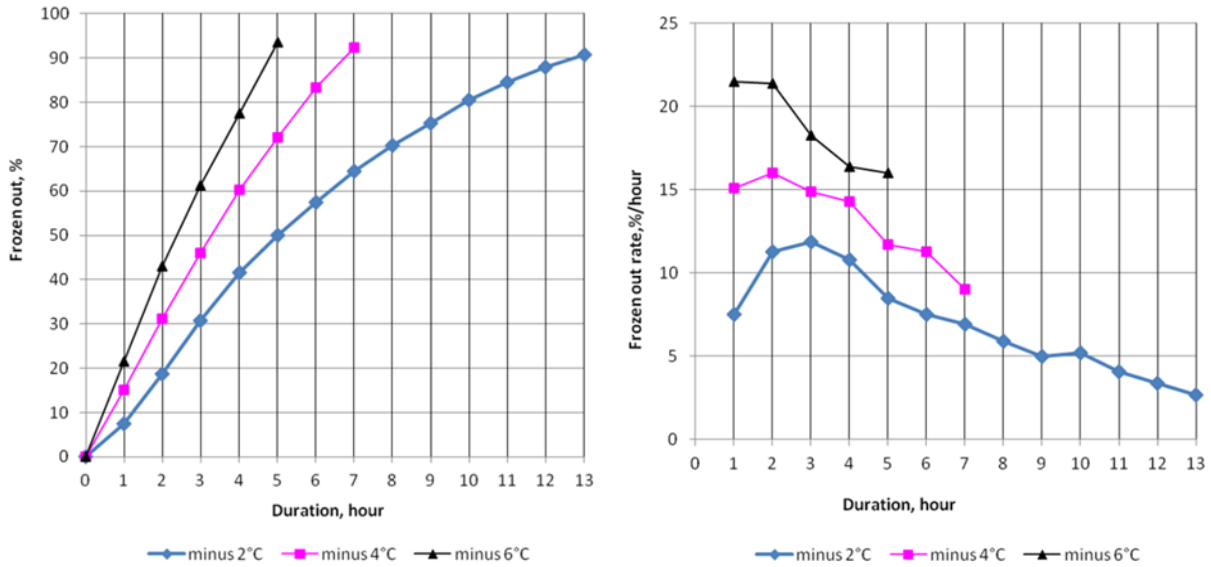


Figure 3. The dependence of the frozen product (a) amount and the freezing rate (b) on the blood plasma cryoconcentration duration

Then we studied the separation freezing parameters effect on the cryoconcentration efficiency. In order to do this, the amount of dry substances in the solution unfrozen part was determined during freezing. As an example, figure 4 shows the corresponding data for a hemoglobin solution.

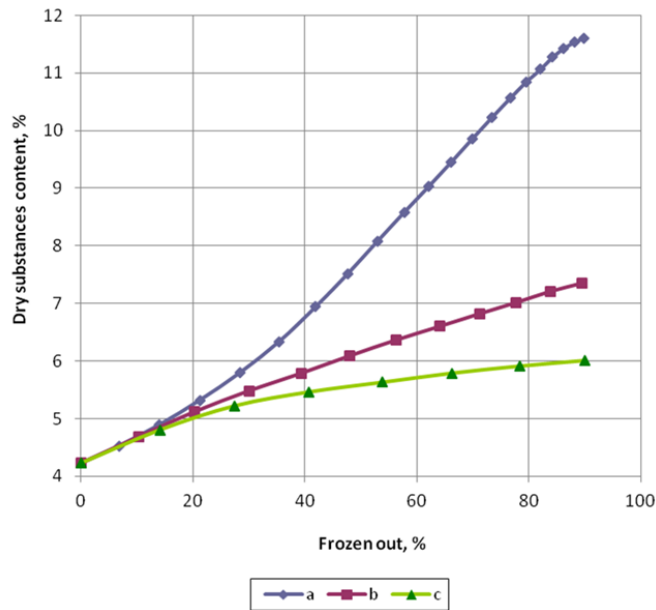


Figure 4. Dependence diagrams of the hemoglobin solution unfrozen part dry substances content on the degree of freezing at the heat exchange surface temperature of minus 2 ° C (a), minus 4 ° C (b) and minus 6 ° C (c)

At the heat exchange surface temperature of minus 2°C the highest rate of increase in the dry substances concentration is observed in the time interval of 2...4 hours. At heat exchange surface lower temperatures, the highest rate of increase in the dry substances concentration was observed during the first 30-60 minutes.

It is worth paying attention to the fact that several factors influence on the increase degree in the dry substances' concentration in the solution unfrozen part. It is known that at a low freezing rate, correctly ordered hexagonal crystal structures are formed in the product. At higher freezing rates, structures such as irregular dendrites and spherulites are formed, which causes a more intense dry matter molecules capture by the resulting crystal front (Shulga, 2009). As moisture freezes, the ice formation rate decreases. At the same time due to a decrease in the ice formation rate the cryoconcentration efficiency should increase. However, it is necessary to take into account the fact that the freezing out rate on the contrary increases relative to the solution unfrozen volume. In addition during separation freezing out the dry substances concentration increases in the unfrozen part of the solution, which reduces the cryoscopic temperature. In turn this leads to changes in the ice formation rate and the degree of dissolved solids capture by the crystal front.

Due to the difference in the ice formation rate during the first 2 hours at a heat exchange surface higher temperature the dry substances concentration in the unfrozen part is slightly lower. However, during further freezing at a higher temperature the concentration efficiency was higher and the unfrozen solution contained more dry substances by the end of the process.

The table 3 shows data on the dependence of the increase degree in the dry substances concentration in the unfrozen solution on the freezing degree for all three research subjects.

Table 3. Increase degree in the dry substances concentration

Research subjects	Frozen out, %		
	30	60	90
The heat exchange surface temperature is minus 2°C			
Hemoglobin solution	1,42	2,04	2,76
Stabilized blood	1,21	1,68	1,95
Blood plasma	1,33	1,91	2,50
The heat exchange surface temperature is minus 4°C			
Hemoglobin solution	1,31	1,54	1,75
Stabilized blood	1,18	1,29	1,39
Blood plasma	1,22	1,36	1,55
The heat exchange surface temperature is minus 6°C			
Hemoglobin solution	1,24	1,36	1,43
Stabilized blood	1,16	1,21	1,27
Blood plasma	1,20	1,29	1,34

From the submitted data it follows that the higher the initial dry substances concentration and the lower the heat exchange surface temperature in the product, the less effective cryoconcentration is performed. The highest concentration degree during freezing of 90% of the product was observed in the hemoglobin solution (1.43-2.76), the lowest is in the blood (1.27-1.95).

In order to determine the overall efficiency of the freezing separation that takes into account the degree of solids concentration, the formed concentrate amount and dry substances gross losses in formed ice, the effectiveness criterion ϵ , which represents the ratio of the amount of concentrate obtained in the real process with account of the dry substances loss to the theoretically possible (at which the formed ice does not contain solids) with the same degree of concentration, was used and calculated as follows (Komyakov, 1996):

$$\varepsilon = \frac{C_{\kappa}}{C_H} \cdot \frac{C_H - C_w}{C_{\kappa} - C_w} \quad (1)$$

where C_{κ} – dry substances concentration in an unfrozen solution, %; C_H – dry substances concentration in the initial solution, %; C_w – dry substances concentration in the crystallized phase, %;

Figure 5 shows the dependence diagrams of the criterion for the blood cryoconcentration efficiency on the increase degree in the dry substances concentration at different heat exchange surface temperatures.

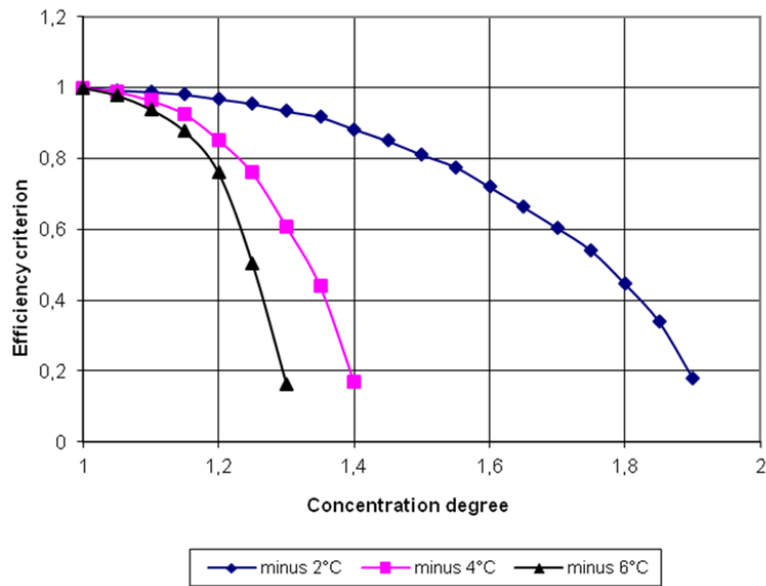


Figure 5. the dependence diagram of the criterion for the blood separation freezing effectiveness on the increase degree in the dry substances concentration

It is determined that when the concentration level increases, a nonlinear change takes place in the efficiency criterion. At the heat exchange surface temperature of minus 2°C the efficiency criterion decreased by less than 0.8 at the concentration level above 1.5 while at the heat exchange surface temperature of minus 6°C the efficiency criterion became less than 0.8 at the concentration level of 1.2.

Based on the above the recommended crystallizer heat exchange surface temperature amounts to minus 2°C during secondary raw materials freezing.

In order to reduce the dry matter loss, the ice can be melted and sent for repeated cryoconcentration after separation freezing. As an example, the Figure 6 shows the hemoglobin solution separating freezing scheme. the corresponding experiments was carried out for scheme drawing up.

The initial hemoglobin solution is frozen out for 12 hours at the heat exchange surface temperature of minus 2°C. In this case a hemoglobin concentrate with a dry substances content of 11.6% and ice with a dry substances content of 3.4% are formed. The ice melts and is sent for repeated freezing out at the same temperature for 1.5 hours. The resulting concentrate has the same dry substances content as the initial solution and can be sent back to the "head" of the process, while the crystallized material with a dry substances content of 0.3% is melted and removed from the system (Bastías-Montes et al., 2019; Orellana-

Palma et al., 2019; Korotkiy et al., 2019; Zielinski et al., 2019; Gushchin et al., 2017). Thus, due to the existence of the melted ice re-freezing out stage after the first stage, it is possible to reduce the dry substances loss significantly, it reduces from 72% to 4.6%, while maintaining a relatively high degree of single-stage freezing out by 2.8 times.

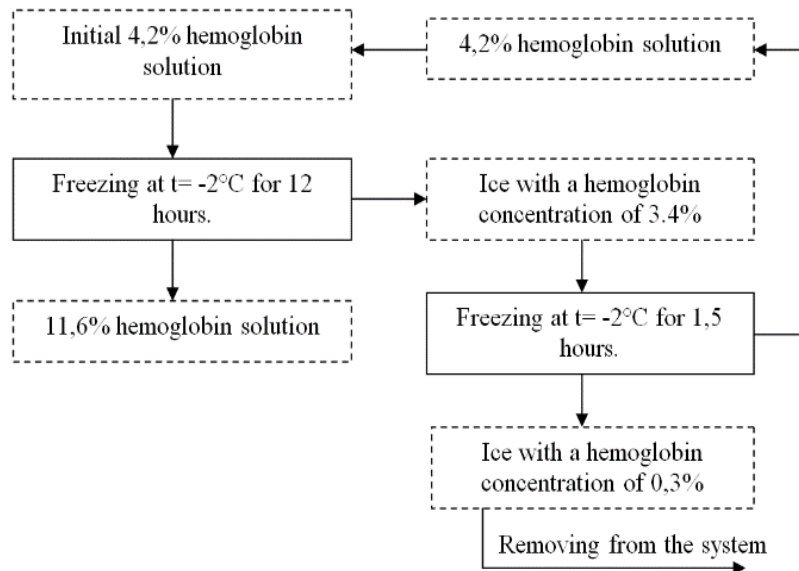


Figure 6. Hemoglobin solution cryoconcentration technological scheme

The disadvantage of the presented technology may be a change in the product components after crystallization. In order to study this factor, a blood plasma amino acid composition analysis was carried out the before freezing and after (in the formed ice). Freezing was also carried out until the crystallization degree of 90% was reached at the heat exchange surface temperature of minus 2°C. The results are shown in the table 4.

Table 4. Blood plasma amino acid composition before and after crystallization

Amino acid name	Before crystallization	After crystallization
Alanine	0,42	1,02
Arginine	0,59	1,50
Amino isovaleric acid	0,62	1,54
Histidin	0,25	0,60
Glycocine	0,28	0,69
Amino glutaric acid	0,67	1,67
Isoleucine	0,26	0,61
Leucine	0,70	1,69
Lysin	0,83	2,05
Methionine	0,05	0,11
Proline	0,51	1,23
Serine	0,47	1,07
Tyrosine	0,38	0,95
Threonine	0,46	1,10
Phenylalanine	0,35	0,82
Cystine	0,04	0,11

The initial blood plasma was characterized by a protein content of 6.9%. After freezing this indicator increased to 16.7%. The results indicate that crystallization does not have a noticeable effect on the plasma proteins amino acid composition. The increase in the amino acids content is determined by an increase in the dry substances content. The ratio of individual amino acids does not change after crystallization practically.

The presented results have theoretical and practical value for researchers and employees of the meat processing industry.

The separation freezing can also be used as a preliminary step before drying. In this case it is possible to reduce significantly the energy cost of removing moisture from the product: after all, the specific energy consumption for cryoconcentration is about 100 W/kg of removed moisture (at an ambient temperature of 25°C) (Korotkiy et al., 2016) while vacuum drying is about 2.0-2.5 kW/kg of moisture (Semenov et al., 2011), and freeze-drying is 2.5-4.0 kW/kg of moisture (Semenov et al., 2017). The dehydrated secondary raw materials are also widely used in various areas of the food industry (Fernandez-Moure et al., 2018; Hou et al., 2019).

4. CONCLUSION

As a result of this work, the processes of secondary meat raw materials cryoconcentration were studied. It was found that it is advisable to freeze blood plasma, hemoglobin solution and whole blood at the heat exchange surface temperature of minus 2°C. A technological scheme is proposed for using re-freezing in order to reduce the dry substances loss while maintaining relatively a high concentration degree.

A possible direction for further research is a more detailed study of the secondary meat raw materials separation freezing laws in order to improve the cryoconcentration technology such as reducing the dry substances loss, the duration of freezing and energy consumption to a minimum.

In conclusion, it should be noted that the separation freezing technology can be used to concentrate most food products and it has undeniable advantages over other methods such as low energy consumption, high product quality and the ability to allocate certain components.

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