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Physicochemical changes and weight loss during freezing, storage and thawing of food products - review of selected issues

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Abstract

The paper shows changes occurring during freezing, storage and thawing of food products. In particular, it refers to weight loss associated with moisture loss. The influence of the chosen freezing method and the type of packaging (or lack thereof) on the amount of water lost in the product is shown. Characteristics of the rate of moisture loss depending on the conditions of storage of products in cold storage chambers are described. The methods of preventing greater loss of moisture in stored products are indicated. The article also contains a short description of the product thawing methods and methods of preventing excessive moisture loss.

Keywords: weight loss, freezing, storage.

1 Introduction

The storage season is underway. The products have been frozen, are stored in cold stores, they will be thawed, and as a result hit our tables. In the above-mentioned subsequent processes, there is a systematic decrease in the quality loss of fresh product. Water is an important component of food with the largest mass share, and its loss causes a decrease in the quality of food products. It is worth recalling some facts about the refrigeration treatment of food products and related weight loss caused mainly by moisture loss.

Freezing food means lowering the product temperature below the cryoscopic temperature (freezing temperature), which depends on the chemical composition of the product and is often lower than the freezing point of water under normal conditions (0^oC). Specific freezing of food usually takes place at a temperature of -25^oC to -40^oC and storage at a temperature of -18^oC to -30 ^oC [15]. Lowering the product temperature leads to a decrease in the energy of the molecules and weakens the interactions between them. This slows down chemical and enzymatic processes, which effectively extends the shelf life of products. Lowering the temperature by 10K causes about two or three times slowing down of chemical processes occurring in the product, which allows to largely maintain the nutritional values available in the fresh product. Freezing also protects against chemical contamination and infection with pathogenic microorganisms. Changes that occur in the product during refrigeration treatment depend on the properties and chemical composition, method of pre-treatment, freezing technique and speed, type of packaging, method of storage and thawing of products [3]. We divide them into physical, chemical, biochemical and microbiological.

The cause of physical changes is the phase change of water into ice, which is the essence of freezing. As the physical state changes, the volume also changes. The average volume increase is around 8%. The beginning of the transformation occurs at a temperature (from -1^o C to -4^o C) and depends on the concentration of the substance. During the gradual freezing of water, the concentration of solutes increases, which reduces the freezing point of the remaining product. The size of the resulting ice crystals also depends on the speed of freezing the product. When the freezing speed is low, few crystallization centers are formed, which causes the formation of very large ice crystals. This phenomenon results in damage to the cell structure, and also affects large leakage during thawing food products. However, rapid freezing is characterized by the formation of small ice crystals in a very large number of places inside the cells, which slightly damages the structure of the product's tissues. During the thawing of the product, small water droplets are quickly resorbed by the tissues and causing much less water loss after thawing [3]. Physical changes are also associated with weight loss of products, i.e. Drying-. The freezing method has the greatest impact on the weight loss [5]. Drying depends also on the speed of freezing, as well as on the characteristics of frozen food and

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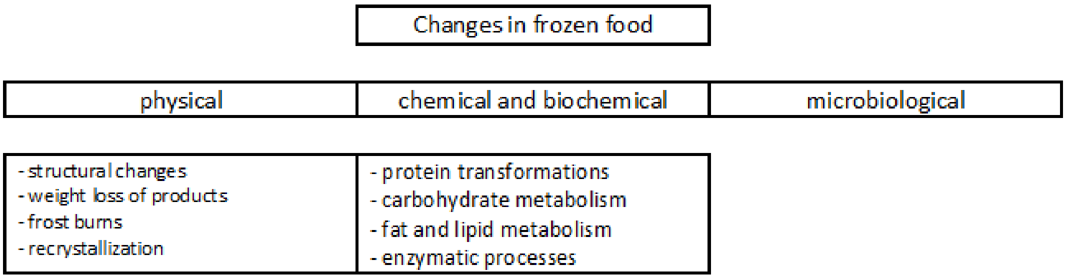

Figure 1. Changes in frozen food

can be from 0.2% to even 3% of the weight of the fresh product. Substantial drying of the product can lead to the formation of spots on the surface of products that are called frost burns.

Freezing food causes a change in the course of many chemical and biochemical processes. In frozen foods, chemical reactions such as fat oxidation and hydrolysis, oxidation of ascorbic acid and tocopherols may occur. Another phenomenon occurring in frozen food is freezing denaturation, which consists in a decrease in solubility of proteins, mainly myofibrillar, reduction of ATPase activity and the number of free -SH groups. An additional effect of denaturation may also be deterioration of water binding capacity, larger defrosting leakage, and general deterioration of product characteristics and consistency. Carbohydrates undergo significant changes during the freezing process only if the process is slow - in this case fermentation processes may occur in the products. After thawing in products rich in carbohydrates, unfavorable changes may occur, such as: mealiness, surface roughness, non-enzymatic browning reactions or aggregation of high molecular weight polysaccharides. Fat and lipid metabolism are very important for the quality of frozen products. Oxidation and enzymatic hydrolysis play an important role in these processes. Fat oxidation processes usually occur spontaneously, in the initial stages slowly, and with the passage of time processes begin to take place faster and faster. As a result of oxidation, unstable connections are formed (formed in secondary desmolysis or polymerization reactions), which lead to the destruction of particles or an increase in their size. In order to reduce oxidation processes, appropriate packaging is used, whose task is to limit the availability of oxygen or special compounds with antioxidant activity. Enzyme processes have the greatest impact during long-term storage of food, then significant changes can occur in the product that affect its quality. An example is the formation of an almond smell in cherries and plums [4].

Microbiological changes in frozen food result from the development of microbes in it. Freezing water in the product slows down the multiplication of microorganisms and inhibits their metabolism, however, it does not eliminate them completely. The resistance of microorganisms to low temperatures is much better than to high temperatures. The nature of the freezing process affects changes in microbial cells. Depending on the process, it can damage or completely destroy bacteria. The best way to stop microbiological processes is to freeze almost the total amount of water.

[2, 8]

2 Weight loss during the freezing process

The problem of weight loss during the implementation of the process of freezing and storage of food is a very important issue in refrigeration technology. The cushion has a very large impact on the quality of products, but the main reason that affects the attempts to reduce it is the economic aspect (large weight loss causes significant losses when storing wholesale quantities of goods).

The formation of mass losses during the freezing process is associated with the transfer of heat and moisture from the surface of frozen products. During the freezing of cold and dry air flowing through the products, it absorbs heat and moisture (mass) from their surface, absorbs it and transfers it to the surface of the radiator evaporators, where it releases the collected heat and precipitates moisture. The dried and chilled air returns to the products and the cycle repeats. When the freezing point is reached on the surface, the process is slowed down and the evaporation process sublimates.

Dryness (weight loss) during air freezing of products can be expressed in terms of dependence:

$$\Delta m \approx \frac{\Delta i_p * \overline{\Delta P} * \tau * A_p}{\alpha * \overline{\Delta T}} \, [kg] \tag{1}$$

where:

Δi_p - product enthalpy difference $\left[\frac{kJ}{KG}\right]$

$\overline{\Delta P} = \overline{P_p} - \overline{P_f}$ - average total difference of partial vapor pressures on the product surface and in the air [Pa],

τ - process time [s],

A_p - product surface [m^2],

α - heat transfer coefficient $\left[\frac{W}{m^2 \cdot K}\right]$

$\overline{\Delta T} = \overline{T_p} - \overline{T_f}$ - average total temperature difference of product surface and air [K].

As can be seen from formula (1), the weight loss during freezing of food is affected by the enthalpy of products Δi_p, less enthalpy difference results in less weight loss. The enthalpy difference depends on the product's initial temperature, the lower it is, the smaller the enthalpy difference. If you want to lower the initial temperature, you can subject the product to pre-cooling in the air [6, 16], however, this does not give the expected effect, on the contrary, it causes an increase in the total weight loss. Another parameter that affects the drying is the average total differential pressure of the water vapor $\overline{\Delta P}$. For a dry product surface, the vapor diffusion from its interior to the environment is inhibited due to the cell structure, which indicates that the vapor pressure on the surface is lower than the saturation pressure. Fig. 2 shows the relationship between the impact of the partial pressure difference and the average total temperature difference $\overline{\Delta T}$.

A drop in air temperature during the process affects the temperature drop on the product surface, which results in a decrease in the partial pressure P_p , wherein ΔT practically does not change. This effect leads to a reduction in dryness and is shown in Fig. 3.

The duration of the process in the formula τ and product surface A_p are interrelated. Increasing the active surface of the product, for example during fluidized freezing, increases evaporation and at the same time reduces the process time. It also affects the heat transfer coefficient α, which increases during the process, while the surface temperature of the product decreases, and this decreases ΔP. This effect also causes, as in the previous case, a reduction in the dry weight [10]. The heat transfer coefficient α has an impact on the intensification of heat exchange, the greater its intensification, the smaller the mass loss. The heat transfer coefficient is a function of many parameters, such as density, specific heat, dynamic viscosity, thermal conductivity coefficient and temperature and pressure difference value. Therefore, changing each of them will affect the value of α. The heat coefficient takes different values depending on the freezing method used, in Table 1, examples are given for various methods.

Table 1. List of heat transfer coefficients α in various freezing methods [4]

Freezing method	$\alpha \left[\frac{W}{m^2 * K}\right]$
The chamber is densely loaded, poor ventilation	3-4
The chamber is densely loaded, poor ventilation u=1-3 $\frac{m}{s}$	8-15
Wind deflectors with strong ventilation u=3-6 $\frac{m}{s}$ special wind deflector apparatus with directed air flow (automatic frame freezing, spiral apparatus)	20-40
Contact apparatus	130-180
Immersion freezing, solution movementL	500-1000
weak	300-400
stron	500-700
LIN apparatus (liquid nitrogen spray)	1000-2000

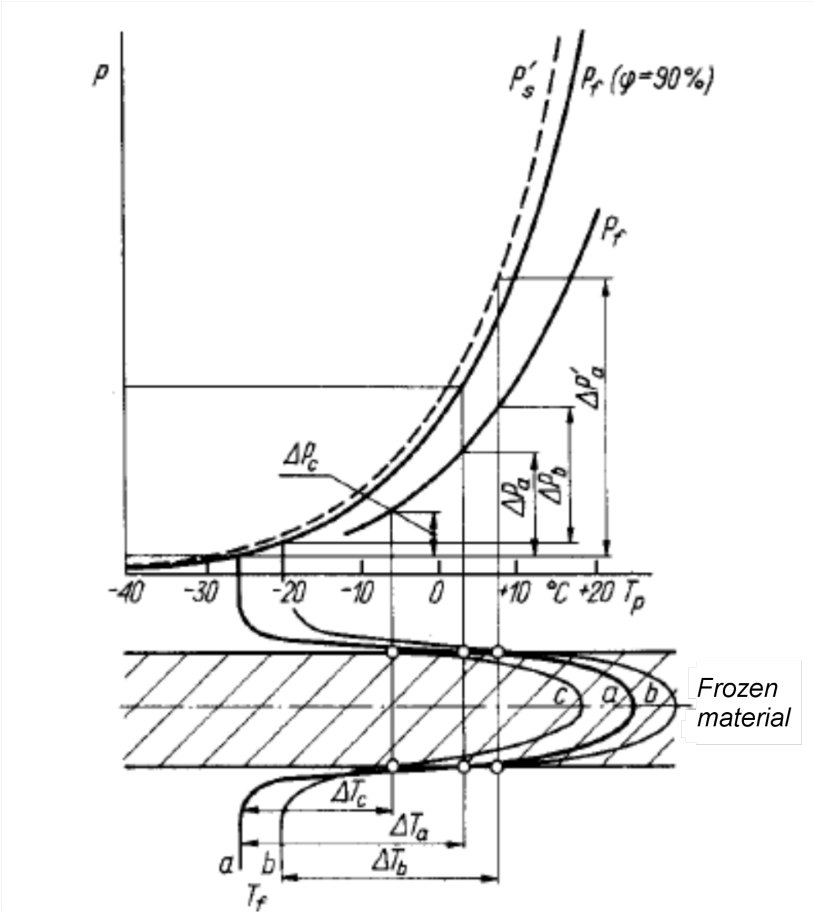

Figure 2. Active differential pressure $\overline{\Delta P}$ and temperature difference $\overline{\Delta T}$ between the product surface and air during the freezing process (according to Astrom ; Freezing equipment infulence on weight. SOS, Washington 1970 DC): a) and b) temperature curves in the product at T_f= od -25^{o}C do -20^{o}C c) product temperature curve at T_f = -25^{o}C and increased coefficient α. $\overline{P_f}$ - partial vapor pressure in the air (ϕ =90%), $P_s{}'$ – vapor pressure on the product surface (wet surface), P_s – dry surface ΔP_a, ΔP_b, ΔP_c, ΔT_a, ΔT_b,ΔT_c - differential pressure of steam and temperature difference in conditions a, b, c (dry product surface), $\Delta P_a{}'$ - difference in vapor pressure in wet conditions [4]

In the process of air freezing, three phenomena affecting moisture losses can be taken into account: mass exchange on the moving sublimation front, moisture from the front through the dehydrated layer towards the surface and discharging it to the environment. Depending on the product and the tunnel structure, weight losses during freezing freez up to 2 to 3%. Table 2 presents weight loss values for products frozen in bulk and in the packaging. Based on the data, it can be seen that the use of packaging during freezing of food significantly reduces the problem of drying out.

Table 2. Comparison of weight loss for a product in packaging and without packaging [4].

Product type frozen by air	**Loss of weight**
Carcasses of loose poultry	2.0-2.5%
Carcasses of poultry when using vapor-tight casings	0.1%
Fish in metal trays uncovered	1.0%
Fish in metal trays with cover	0.2-0.4%

Cryogenic freezing is a method in which the product particles are directed to a liquid with a very low boiling point. When the liquid comes into contact with the product, the liquid evaporates, which allows for intensive heat exchange.

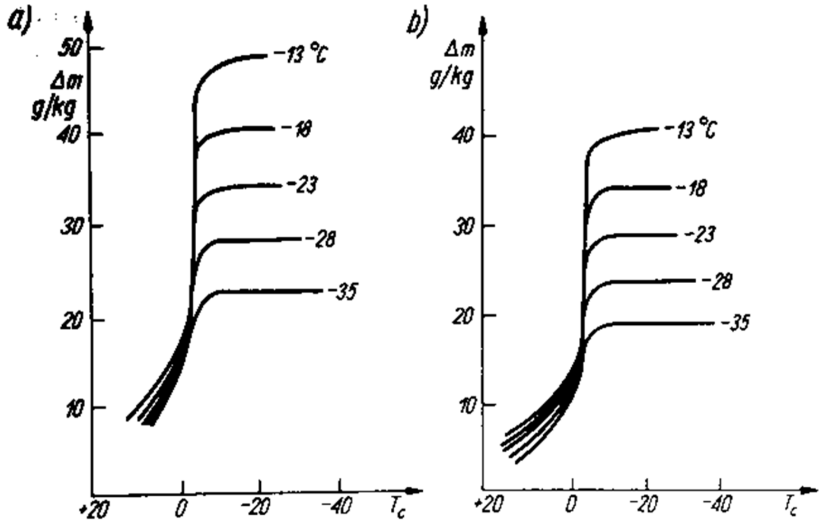

Figure 3. Drying of frozen products in the air stream at -13 to -35^{o}C (according to Astrom et al; In: Quality and stability of frozen food. Time-temperature tolerance and its significance New York, Wiley 1969): a) diced carrot, b) peas [4].

During cryogenic freezing, liquid nitrogen and carbon dioxide are used, which are harmless to food products, as well as cheaper than other factors. The high value of the heat transfer coefficient allows for a very short freezing time. Thanks to this, products frozen by the cryogenic method are of high quality and have a negligible moisture loss, which is why this method is perfect for freezing soft fruits and vegetables [4, 12].

During cryogenic freezing, the inert gas injected almost completely displaces the air, which affects the formation of weight losses. According to the assumption of liquid nitrogen consumption 1 kg per 1 kg of product, 0.8 m^3 of gas per 1 kg of product is produced in the apparatus. Assuming that the gas leaving the apparatus has a temperature of about -20^{o}C, it should not absorb more moisture than 0.5g from 1kg of product, i.e. the weight loss for this process would be 0.05% [4]. This assumption was unfortunately not reflected during experimental studies, as it was demonstrated in them that losses during freezing in boiling liquids are from 0.35% to 0.82% by mass.

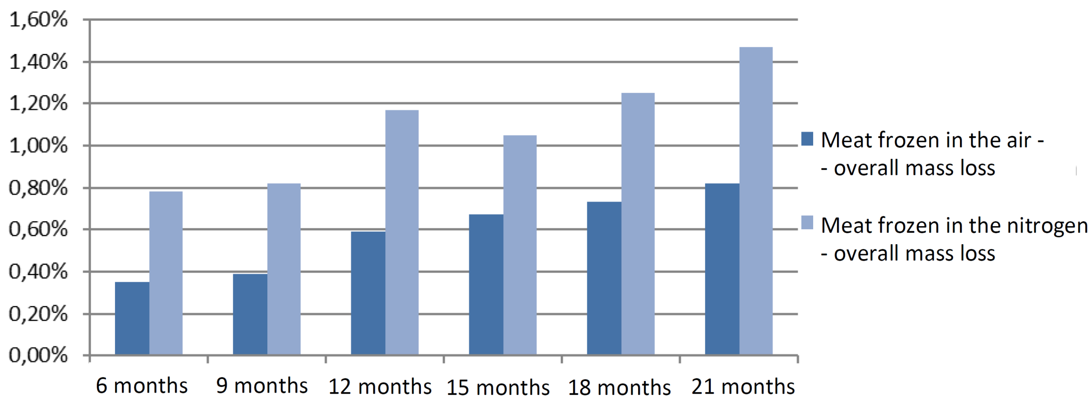

Figure 4. General drying of frozen pork meat [1]

Comparing both methods of freezing on an exemplary product, which was tomatoes, it was shown that weight loss during freezing by airflow method in the refrigeration chamber is significantly greater than weight loss when freezing the product in liquid nitrogen (Fig. 5).

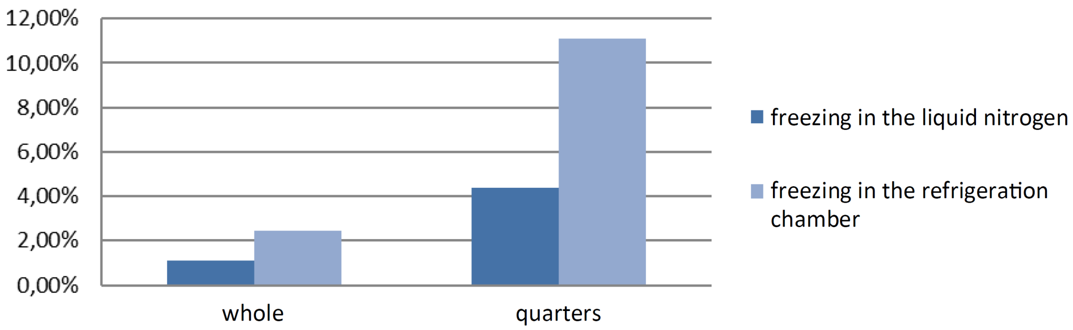

Figure 5. Weight loss of tomatoes depending on the freezing method [1]

3 Storage weight losses

Products that have been properly packaged show very little weight loss when freezing. A much more serious problem is the occurrence of the phenomenon of weight loss during storage of food. As can be seen in Fig. 4, weight loss does not only depend on the freezing method, but its value increases with storage time. Looking at the bar graph, it can be seen that the percentage weight loss after 21 months of storage was almost twice as large as the weight loss after 6 months [1, 9].

When storing products, the following factors are very important: the average total difference in partial pressure of water vapor on the product surface and in the air, the average total difference in the temperature of the product surface and the air, the speed of air flow in the immediate environment and the storage time of frozen food.

$$\Delta G = \beta' * A * (P - \phi P_0) \left[\frac{g}{h}\right] \tag{2}$$

where:

β' - diffusion coefficient, $\left[\frac{g}{h-m^2 mmHg}\right]$,

A - active sublimation surface, $\left[m^2\right]$,

P – saturation vapor pressure above the product surface, [Pa],

P_0 - partial pressure of steam in the room, [Pa],

ϕ - relative air humidity [4, 13]

Equation 2 proposed by Dalton is a classic formula that allows you to calculate weight loss, but it does not reflect the real processes occurring during food storage. It does not meet the conditions necessary for this theory, i.e. free surface of sublimation and isothermal course of the process.

The thermodynamic theory of hygrothermal processes in refrigeration chambers is correct for these conditions. According to it, the drying of products during storage (and during cooling and freezing of the air deflector) depends only on two parameters: the inflow of heat to the room and its temperature. An important role for this assumption is played by gravitational forces, which create a closed circulation stream. Any change in the factor affecting the intensity of sublimation causes the formation of a compensation process in the enclosed space of the chamber.

It is roughly assumed that weight loss during storage of frozen food is not proportional only to the supply of external heat to the chamber, but it largely depends on the system used to cool it. It was found that forced circulation of air in the chamber increases weight loss by about 60% compared to the gravitational cooling system. This is due to the work of fans, which increases the amount of heat input by 15-20%, as well as the increase in the value of diffusion coefficient by about 50% [10].

Due to the slight migration of water in frozen products (vegetables, fruits, meat), the surface nature of sublimation means that moisture losses are not compensated during the migration of water from inside the product. This creates a highly dehydrated outer layer (water content in the layer 25-35%) with a porous structure that promotes oxidation and odor absorption.

In the case of meat, another factor that affects storage weight loss is the half-carcass density. They also depend on the location of the goods in the freezer storage room. For the horizontal arrangement, the largest are from the outside of the chamber, medium by the internal walls, and the smallest in the middle of the stack. However, for the vertical arrangement, the largest are on the surface, medium ones in the bottom of the stack, and the smallest in the middle [4].

The weight loss of the cold store is also affected by the degree of loading of the cold store [10]. This particularly affects the storage of meat carcasses without packaging. Fig. 6 shows the relative and absolute weight loss during storage of frozen loose meat. The graph shows that the absolute weight losses (G in tonnes) are not dependent on the quantity of meat stored, while the relative weight losses (g in% per unit of weight) decrease with increasing chamber loading.

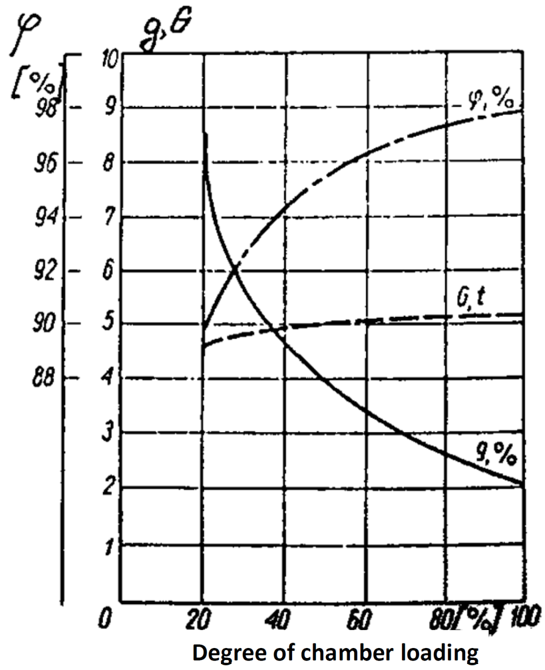

Figure 6. Relative (g in%) and absolute (G in tonnes) annual losses of frozen meat loose storage, depending on the degree of chamber loading [10]

In addition to the density of the refrigeration chamber loading, the weight loss also affects its structure. One-storey cold rooms are characterized by the fact that the defects in them are larger than in multi-storey ones, and in modern panel cold rooms they are smaller than in those with an outdated insulation system [10].

Weight losses also change throughout the year. In the summer, during an increased heat supply for the Polish climate zone, they are even 4-5 times larger than in the coldest month of the year. Both lowering the chamber operating temperature and improving their insulation have a positive effect on reducing weight loss. By lowering the temperature inside the chambers from -20^{o}C to -30^{o}C, you can reduce weight loss by up to 20%, while additional insulation improvement prevents increased heat input, which can reduce losses up to 50% in this case.

The average monthly weight loss for meat was determined based on experimental data depending on the storage temperature.

Nowadays, loose meat storage has been virtually eliminated, and packaging is a very important factor that determines the preservation of high quality frozen food. Particularly modern packaging has a significant impact on extending the shelf life of frozen food, as well as reducing weight loss. It is possible to eliminate practically completely the drought by using vapor-tight packaging that adheres tightly to the product's surface. However, if the packaging does not adhere exactly to the product, so-called internal cushion, which does not change the gross weight of the packaging. This is due to the effect of a continuous process of sublimation of water vapor from the product surface. Under the influence of temperature fluctuations, water evaporating from the surface of the product is deposited in the form of a characteristic frost on the colder internal wall of the package in the air spaces between it and the product. In some cases, the inner shell may turn out to be larger than the outer shell for the same products that are stored in

Table 3. Average monthly meat loss at various temperatures [4]

Temperature [^{o}C]	Weight loss [%]
-10	0.59
-15	0.38
-20	0.25
-25	0.16
-30	0.10

traditional packaging [11].

The method that reduces weight loss during storage of frozen fish is glazing. It consists in spraying chilled water on the surface of the fish with a small addition of antioxidants. However, it is not always possible to obtain a uniform layer on the entire surface of the product. Different glaze thickness means that the sublimation process is not uniform over the entire surface. That is why packaging with high vapor tightness is more often used nowadays. Protective coatings were also discontinued, mainly from alginates and acetoglycerides, and edible coatings derived from natural resources were experimentally applied to this place. These coatings can be carriers of spices, dyes, antibacterial or antioxidant substances, and can also protect against aroma loss.

As part of limiting weight loss, attempts were made to use additional technical measures, such as covering meat piles, humidifying air or shielding entire chambers by applying thin layers of ice to covers and screens. These actions limited the drying to some extent, while also leading to increased frosting of the radiator evaporator. Unfortunately, in most cases these treatments were too expensive and ineffective.

4 Weight loss during defrosting

Weight losses do not occur only during the freezing and storage process, a significant part of them also occurs during thawing of products. Many factors have a significant impact on this process, including:

- defrosting time (for meat the best defrosting results can be obtained when freezing and thawing times are equal),
- relative air humidity,
- thawing environment temperature.

In a collective work, Kopeć A., Dolik K., Lipiecka A. [7] presented the results of a study carried out on frozen herring, the purpose of which was to compare thawing methods: in moist standing air, in air saturated with steam, in air saturated with steam forced. Fig. 7 shows the weight loss depending on the freezing method used. Based on the results of mass loss measurement, it can be concluded that the largest weight loss occurred during thawing in humid standing air conditions (2.48%). The smallest weight loss was obtained during thawing in air saturated with water vapor (1.08%). The reason for the larger weight loss in the case of thawing in humid standing air was the long defrosting time (12.5 hours), and the lack of air saturation with steam, which could affect the formation of drying. Shorter defrosting time for saturated air (7.5h) and saturated with water vapor together with forced convection (4.17h) caused a reduction in evaporation from the surface of thawed herrings [7].

5 Frost burn

The frost burn is an extreme case of qualitative changes due to the strong dehydration of part of the surface of frozen products. This phenomenon can occur in both plant and animal tissues, as well as in fruit juices. Animal products such as carcasses of poultry, liver, fish, and vegetable products such as beans and peas are susceptible to frost burns. A characteristic feature of frost scalds are spots with clear contours and a distinctive color from the rest of the product. In the case of poultry, resulting from oxygen penetration, the spots take on a light color, while in the case of the liver, as a result of the concentration of cell components, the spots take on a dark color. Color changes disappear during defrosting, eliminating the unwanted optical effect. However, in the case of very strong tissue dehydration (associated with the loss of about 50-52% of water content), burns may have fat oxidation processes, protein denaturation and

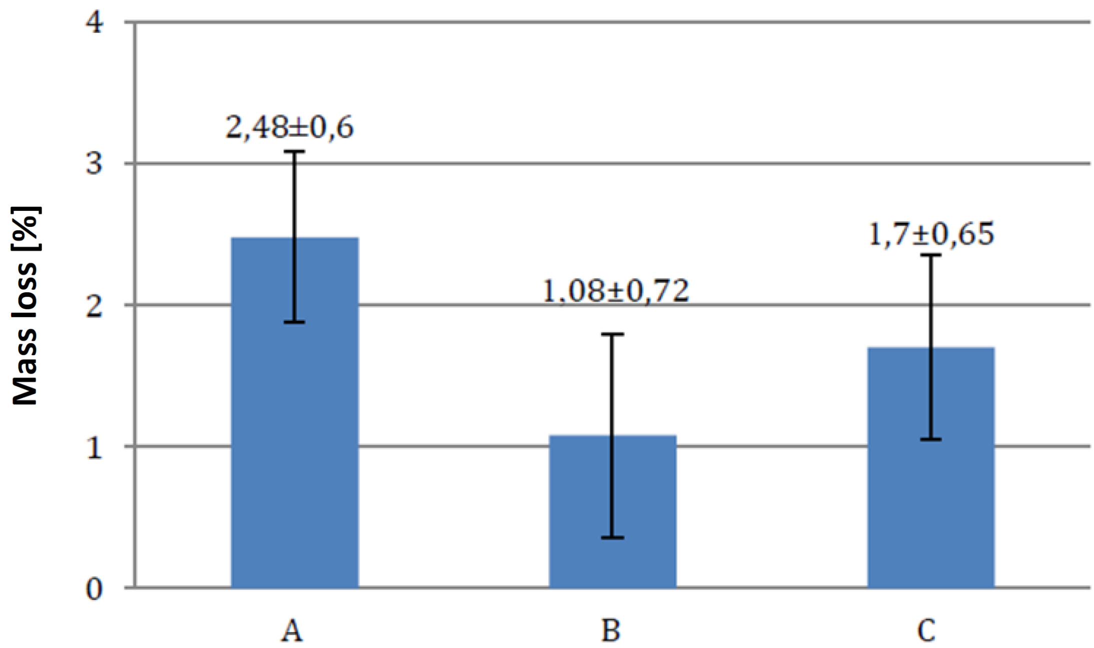

Figure 7. Results of mass loss measurement during defrosting: A - air, B - air saturated with water vapor, C - air saturated with water vapor with forced convection [7]

sensory changes. The conditions that prevail during storage and freezing of food have a significant impact on the formation of burns. The quick freezing process and thus smaller water losses may result in a higher probability of scalding. Storage temperature also plays an important role in the presence of burns. Losses that occur as a result of drying at -20^{o}C are definitely smaller than those that occur at -10^{o}C. Reduction of frost scald can be achieved by maintaining a low and constant temperature of food storage as well as by isolating products from the environment (including the use of vacuum packaging). [4, 10, 14]

6 Conclusions

As follows from the above considerations, the conditions of freezing, storage and thawing food have a huge impact on its quality. During freezing, the process method has a significant impact. During the tests, it was noticed that smaller mass losses can be obtained using various methods, for example freezing in liquid nitrogen is more advantageous in terms of mass loss than freezing in a refrigerating chamber. The impact of packaging techniques is also significant. The best solution to prevent the formation of drying is to use vapor tight packaging that adheres directly to the product. They mainly help reduce the process of sublimation of water from the product surface. As noted, the freezing and storage temperature also plays a very important role, the lower it is, the lower the weight loss. It was also found that weight loss may vary depending on the type of refrigeration chamber, its loading density and insulation. Weight losses also occur during the thawing process of food. Not only the process temperature affects the defects, but the defrosting time and relative humidity are also very important. You also can't forget about the economic aspect of the processes under consideration. Proper management and process management allows you to minimize losses that are an integral part of freezing, storage and thawing food. Large percentage weight losses translate into significant monetary losses. Therefore, producers are constantly making attempts to improve the economic result of their business.

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