New data on cryoscopic temperatures of commercial fish species

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Abstract. The results of experimental studies to determine the values of cryoscopic temperatures of the following (commercial) fish species are presented: blue shark (prionace glauca), stellate stingray (amblyraja radiata), Pacific herring (clupea pallasii), Atlantic salmon (salmo salar), pink salmon (oncorhynchus) gorbusha), West African mackerel (scomberomorus tritor), red salmon (oncorhynchus nerka), mullet (mugil cephalus), Far Eastern navaga (eleginus gracilis), muksun (coregonus muksun), sea pollock (theragra chalcogramma), white-bellied flounder (lepidopsetta bilineata), bluebore halibut (reinhardtius hippoglossoides), black sea red mullet (nullus barbatus ponticus), pike-perch (sander lucioperca), Pacific cod (gadus macrocephalus), scrub hake (hake) (merluccius bilinearis), sea bass (sebastes alutus), icefish (champsocephalus gunnari), laced yellowtail (seriola quinqueradiata), sardine (sardinops) (sardinops ocellatus), haddock (melanogrammus aeglefinus), pike (esox lucius), crucian carp (carassius gibelio). A wide range of values of cryoscopic temperatures of the studied objects confirms the need for their accumulation, systematization and classification. It is proposed to use the value of cryoscopic temperature as a classification factor necessary to unify and simplify the substantiation of the modes of their refrigerated storage.

1. Introduction
The use of cold is one of the most common ways to ensure safety, preserve the quality and increase the shelf life of fish food products. According to FAO data, the share of chilled and frozen fish food products in different years accounts for more than 80% of the total amount of fish food products.

Chilled fish has a number of advantages over frozen fish (nutritional and biological value, organoleptic properties) and is in preferential demand among consumers, who believe that chilled fish food products are fresher and more convenient to prepare [1]. However, a significant limitation in expanding the volume of its production is the limited shelf life.

Frozen fish food products have a longer shelf life, but they do not provide complete reversibility of the process. In this regard, the improvement of methods of refrigeration processing, ensuring the production of a product close in its properties to fresh unfrozen fish, is of great importance.

In the 20th century, in some cases of fish harvesting, the method of freezing became widespread. In frozen fish, posthumous changes proceed similarly to chilled fish and retain their general orientation, but the rate of their flow is lower, as a result of which its shelf life increases by 1.5-4 times. A feature of the freezing method is the storage of the product at low temperatures with partial freezing of moisture (from 5 to 50%) [2]. The feasibility of using this method is scientifically substantiated by Russian,
English and Portuguese scientists [3]. The use of freezing can help reduce the use of freeze-thaw cycles, reduce labor costs, energy costs and product weight loss [4].

The main parameter that determines the quality of frozen fish products is the percentage of water transfer to ice. According to Russian scientists, the initial state of muscle tissue when freezing moisture up to 40% can be completely restored and in terms of its indicators is comparable to chilled fish. The data of works by foreign authors [5] allow up to 30% ice in the product, while noting a slight decrease in the water-retaining properties of muscle tissue by 15 days of storage [3, 5, 6]. This discrepancy in the data requires further experimental research to determine the permissible percentage of ice, which ensures the preservation of the quality indicators of the product, comparable to chilled products.

An important characteristic of raw materials in research on the development and scientific substantiation of refrigerated storage regimes in a frozen state of fish is its cryoscopic temperature (Tcr), the values of which for most food products are in the range from minus 0.5 to minus 2.8 °C. In the articles of Russian and foreign authors, there is a fairly large number of scattered and partially contradictory data on the values of cryoscopic temperatures [6, 7, 8, 9, 10, 11].

Meanwhile, the choice of storage temperatures and the amount of frozen water in the product and, as a consequence, the quality of the product and the duration of its storage depend on the value of the cryoscopic temperature. In accordance with the current Technical Regulations of the Eurasian Economic Union (TR EEU) 040/2016 "On the safety of fish and fish products": frozen fish food products - fish, aquatic invertebrates, aquatic mammals and other aquatic animals, as well as algae and other aquatic plants, freezing to 1.0 °C or 2.0 °C below the freezing point of the tissue juice inside them.

The Regulation "On the safety of fish and fish products" does not establish fixed (absolute) temperature limits for the storage of frozen fish food products, but indicates relative temperatures that depend on the freezing point of the tissue juice of a particular product. Proceeding from this, in order to establish the limits of the temperature range of freezing regimes for fish food products, it is necessary to determine the freezing temperatures of tissue juice.

Thus, the cryoscopic temperature of raw materials is an extremely important characteristic in the development and scientific substantiation of freezing and refrigerated storage modes; therefore, the purpose of this work was to determine the values of the cryoscopic temperature of certain fish species.

2. Objects and methods of research

The objects of the study were the following (commercial) fish species: blue shark (prionace glauca), stellate stingray (amblyraja radiata), Pacific herring (clupea pallasii), Atlantic salmon (salmon) (salmo salar), pink salmon (oncorhynchus gorbuscicanha), West African scomberomorus (tritom), red salmon (oncorhynchus nerka), mullet (mugil cephalus), Far Eastern navaga (eleginus gracilis), muksun (coregonus muksun), walleye pollock (theragra chalcogramma), whitefish (hypomesus jaspine), blue-headed halibut (reinhardtius hippoglossoides), pike perch (sander lucioperca), Pacific cod (gadus macrocephalus), northern grenadier (macrourus berglax), Atlantic mackerel (scomber scomber) bilinearis), sea bass (sebastes alutus), ice fish (champsocephalus gunnari), lacedra yellowtail (seriola quinqueradiata), sardine (sardinops) (sardinops ocellatus), haddock (melanogrammus aeglefinus), pike (esox lucius), crucian carp (carassius gibelio).

For experimental work, the samples were purchased chilled from food chains or from suppliers of the HoReCa segment (except: Pacific herring, pink salmon, northern grenadier and pollock - these samples were purchased frozen and thawed). Next, the fish was cut into skinless fillets. The prepared samples were cooled to a temperature of 1±0.5 °C and placed in flasks with thermocouple clamps. The samples were frozen in a freezer at a temperature of minus 22.0±1.0 °C. The minimum number of measurements to be carried out is 5 (for 5 copies of each type).

2.1. Determination of cryoscopic temperature

The cryoscopic temperature was determined by the thermographic method described in the method of James et al., 2011 by the formation of the same temperature on the temperature change curve of the sample using a precision temperature meter (electronic temperature meter LTA/2-N-N, Russia) [7].
2.2. Calculation of the amount of frozen water
To determine the amount of frozen water in frozen fish food products, D. Ryutov’s dependence (formula) was used as the most correct calculation method. Data on the substantiation and confirmation of the correctness of this method are presented in the work of M.A. Dibirasulaev [11].

\[
\omega = \left[ 1 - b \left( \frac{1}{w} - \frac{1}{t_{cr}} \right) \right] \left( 1 - \frac{t_{cr}}{t} \right)
\]

where: \( \omega \) - the proportion of frozen water in the product; \( w \) is the total water content in products (g per 1 g of product); \( b \) is the content of bound water in the product (g per 1 g of dry matter); \( t_{cr} \) - cryoscopic temperature of the product, °C. The share of frozen water in the product, determined by the formula, depends not only on the cryoscopic temperature of the product (\( t_{cr} \)), but also on the mass fraction of moisture in the product \( w \) (table 3) and the amount of bound \( b \) [12].

2.3. Determination of the mass fraction of water
The mass fraction of water (Ww) in the samples was determined by the drying method. To calculate the amount of bound water, free water was determined by pressing according to G. Grau and R. Hamm. These methods are described in a previously published article [9].

3. Results and their discussion
In the studied samples, the cryoscopic temperature and mass fraction of moisture were determined, the data obtained are presented in table 1.

| Objects under investigation | \( T_{cr} \) ±S | Ww, % ±S |
|-----------------------------|----------------|---------|
| Blue shark (Prionace glauca) | -2.35 ±0.05 | 74.7 ±0.2 |
| Star ray (Amblyraja radiata) | -2.35 ±0.05 | 78.4 ±0.2 |
| Pacific herring (Clupea pallasii) | -2.20 ±0.05 | 69.0 ±0.2 |
| Atlantic salmon (Salmo Salar) | -1.30 ±0.08 | 66.4 ±0.2 |
| Pink salmon (Oncorhynchus gorbuscha) | -1.30 ±0.10 | 68.8 ±0.2 |
| West African mackerel (scomberomorus tritor) | -1.20 ±0.05 | 64.2 ±0.2 |
| Sockeye salmon (Oncorhynchus nerka) | -1.20 ±0.08 | 65.3 ±0.2 |
| Mullet (Mugil cephalus) | -1.15 ±0.05 | 74.6 ±0.2 |
| Far Eastern Navaga (Eleginus gracilis) | -1.05 ±0.05 | 81.1 ±0.2 |
| Mukun (Coregonus muksun) | -1.00 ±0.05 | 74.3 ±0.2 |
| Pollock (Gadus chalcogrammus) | -0.95 ±0.05 | 82.4 ±0.3 |
| Smelt (Hypomesus japonicus) | -0.95 ±0.05 | 73.9 ±0.2 |
| White-bellied flounder (Lepidopsetta bilineata) | -0.95 ±0.05 | 79.5 ±0.2 |
| Blue-bark halibut (Reinhardtius hippoglossoides) | -0.95 ±0.05 | 81.4 ±0.2 |
| Black sea mutton (Mullus barbatus ponticus) | -0.95 ±0.05 | 74.7 ±0.2 |
| Sudak (Sander lucioperca) | -0.93 ±0.06 | 78.4 ±0.2 |
| Atlantic cod (Gadus morhua) | -0.91 ±0.04 | 82.7 ±0.3 |
| Northern grenadier (Macrourus berglax) | -0.90 ±0.10 | 79.8 ±0.2 |
| Atlantic mackerel (Scomber scombrus) | -0.90 ±0.05 | 65.9 ±0.2 |
| Hake (hake) (Merluccius bilinearis) | -0.85 ±0.05 | 77.5 ±0.3 |
| Perch (Sebastes alutus) | -0.80 ±0.03 | 77.4 ±0.2 |
| Ice fish (Champscocephalus gunnari) | -0.80 ±0.03 | 79.8 ±0.2 |
| Japanese lakeda (Seriola quinqueradiata) | -0.75 ±0.05 | 75.3 ±0.3 |
| Sardine (sardinops) (Sardinops ocellatus) | -0.61 ±0.03 | 76.8 ±0.3 |
| Haddock (Melanogrammus aeglefinus) | -0.60 ±0.03 | 80.5 ±0.2 |
| Sample Type                  | Cryoscopic Temperature (°C) | ± Standard Deviation | % Water | ± Standard Deviation |
|-----------------------------|-----------------------------|----------------------|---------|----------------------|
| Pike (Esox lucius)          | -0.60                       | ±0.03                | 72.3    | ±0.2                |
| Crucian carp (Carassius gibelio) | -0.41                       | ±0.04                | 78.0    | ±0.2                |

Analysis of these values of cryoscopic temperatures of the studied samples showed that the maximum value (tcr = -0.41 °C) falls on the samples of crucian carp, and the minimum (tcr = -2.35 °C) falls on the samples of the blue shark and stellate stingray, that is, the values of the cryoscopic temperatures of the samples differs by 5.73 times.

Thus, in accordance with the requirements of TR EEU 040/2016 "On the safety of fish and fish products", silver carp can be cooled to a temperature (-0.41 °C), and blue shark and star stingray can be cooled to a lower temperature (-2.35 °C). Such a wide range of cryoscopic temperatures of the samples under study makes it possible to make an assumption about the need to determine, systematize and take into account their values in order to further develop a scientifically grounded approach and recommendations for the development of temperature regimes for storing aquatic biological resources in a frozen and chilled form.

The amount of frozen water formed when the temperature drops affects the quality, safety and storage capacity of frozen fish food products, which is reflected in the studies of M.A. Dibirasulayev on beef, V.V. Gushchina on poultry meat, E.N. Kharenko on fish [10,11,13].

To substantiate the importance of determining the values of cryoscopic temperatures, the calculation of the amount of frozen moisture in the objects of study with the minimum, maximum and average value of Tcr was performed. The calculation was carried out under the condition of using freezing with the assumption of 40% frozen water. It should be noted that according to the EAEU CU TR 040/2016 "On the safety of fish and fish products", the temperature below the cryoscopic temperature is allowed to drop by 1-2 °C, and the admission of 40% of frozen moisture is included in the range permitted by the regulations.

The results of calculating the proportion of frozen water by the calculation method taking into account experimental data on determining the cryoscopic temperature and mass fraction of moisture are shown in figure 1.

![Figure 1. Dependence of the amount of frozen water in fish on temperature.](image-url)
Analysis of the obtained data (figure 1) shows that the amount of frozen moisture in fish of different species has a significant difference at the same temperature storage conditions. For silver carp fillet samples, the proportion of frozen moisture of 40% occurs at a temperature of minus 0.7 °C, and for blue shark - at minus 4.2 °C, which differs by 6 times.

Thus, experimental and calculated data have been obtained, the analysis of which reflects the need to determine the cryoscopic temperature for each type of aquatic biological resources and take it into account when developing and justifying individual storage regimes.

This confirms the importance of differentiating raw materials according to the values of cryoscopic temperatures. At the same time, given the large number of commercial fish and aquatic invertebrates, it seems irrational to develop individual temperature regimes specifically for each type of raw material. In this regard, it is relevant to develop a classification and identify groups that are close in values of cryoscopic temperatures for unification and simplification of the selection of temperature regimes for freezing.

In the proposed classification of aquatic biological resources, the value of the cryoscopic temperature (Tcr) is taken as the classification factor, which is determined when the object is frozen, as the initial temperature of crystal formation.

According to the proposed classification of commercial fish, three groups are distinguished:

- raw materials that form ice crystals at temperatures above minus 1.0 °C (Tcr > -1.0);
- raw materials that form ice crystals at temperatures from minus 2.0 to minus 1.0 °C (-2.0 ≤ Tcr ≤ -1.0);
- raw materials that form ice crystals at temperatures below minus 2.0 °C (Tcr < -2.0).

The ability of commercial fish to form ice crystals when the temperature drops is an important parameter of raw materials in the development and substantiation of temperature regimes for freezing and storage. The rationale for the selection of three groups of raw materials was the amount of frozen water, which is formed as a result of a decrease in temperature, the content of which is directly influenced by the value of the cryoscopic temperature of a particular fish species.

4. Conclusion

Experimental studies have been carried out to determine the cryoscopic temperature of more than 25 species of commercial fish. It was revealed that the values of cryoscopic temperatures of the studied samples have a wide range of values from minus 0.41 °C to minus 2.35 °C.

The calculation of the amount of frozen water was carried out taking into account the experimentally obtained cryoscopic temperatures of the objects under study. It was revealed that the proportion of frozen-out moisture of 40% occurs for specimens of silver carp fillets at a temperature of minus 0.7 °C, and for a blue shark at minus 4.2 °C, which differs by 6 times.

The necessity of forming a classification of commercial fish based on the values of their cryoscopic temperature, as a particularly important technological indicator necessary for the development of modes of their refrigerated storage, has been scientifically substantiated.

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