Quality assessment of the canned fish made of capelin of the prolonged storage period produced by the soft conditions of fish smoking

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Abstract. The study focuses on the manufacturing techniques of canned food «Smoked Capelin in oil» from the little-used fish raw materials of the Arctic region – Barents Sea capelin (Mallotus villosus) of the prolonged storage period. The special feature of the offered technology is the application of the soft conditions of the preliminary heat treatment (PHT) of fish – smoking at the lowered temperatures. This technology prevents the risk of nitrosamines formation and entering of such cancerogenic substances as polycyclic aromatic hydrocarbons into the final product. The study also provides data on the influence of raw materials properties and temperature parameters on the duration of dehydration process while preparation of a smoked semi-finished product from a capelin. The results of organoleptic assessment made it possible to find the optimal PHT temperature and time parameters of smoked capelin semi-finished products and ready canned food. It was established that the usage of the soft PHT cold smoking modes increases the amount of a semi-finished product due to the decrease in losses of moisture. The aim of this research was to study the possibility of canned food production from frozen raw materials of the prolonged period of storage. The results are based on the analysis of how the quality of both frozen fish and the produced canned food changed over the time (on microbiological, chemical and organoleptic indicators). The industrial sterility of canned food was confirmed by microbiological researches, thus there is some evidence, that the developed mode of sterilization of canned food «Smoked Capelin in oil» can be regarded as effective. The study indicates the parameters of the chemical, amino-acid and fatty-acid composition of the canned food made on the developed technology, and assesses its safety and biological value. Research conducted on the qualitative characteristics of a new product in the process of storage made it possible to develop and approve specifications and the technological instruction for production of canned food «Smoked Capelin in oil». It was confirmed that the storage period of canned food «Smoked Capelin in oil» produced of frozen capelin does not exceed six months at a temperature not above minus of eighteen degrees Celsius.

1. Introduction
Due to their biological properties fish and seafood are often referred to as the unique food, including a number of the major nutrients, such as full-fledged proteins, fats, including PUFAs, vitamins, micro and macrocells. According to The Food and Agriculture Organization of the United Nations fish
products are a source of animal protein for 3.1 billion people, which makes up to 20% of the general consumption [1].

Several researches confirm that our health and the life expectancy are closely connected to the fish and seafood consumption [2]. Seafood is recognized as an integral part of a healthy diet, especially due to the content of polyunsaturated fatty acids. For example, at average daily consumption of canned food from sardines in oil among the EU consumers comprises 130.3% of the recommended consumption of EPA+DHA [3].

According to FAO the Russian Federation takes the fifth place around the world on production of aquatic foods (more than 4.7 million tons in 2016) [4]. According to the Federal State Statistics service in 2017 the level of consumption of fish and seafood among the resident of Russia averaged 21.5 kg a year that corresponds to an indicator of 2016 [5]. It is insignificantly below the indicator recommended by the Russian Ministry of Health – 22 kg.

According to forecasts, by 2030 an average consumption will increase up to 27 kg [6]. Due to the growing consumption of seafood, fishing companies refocus on the production of remunerative objects of trade. This is proved be the fact that, according to the official information by Federal Agency for Fishery, despite the reduction of catch of traditional objects of trade, there has been a gradual increase in volumes of catch for the last five years.

Canned fish is traditionally in demand with the population. Its average annual production in Russia is about 520 million standard cans, though in recent years the production tends to go down [7].

The share of canned food in the Russian fish market is on an equal basis with ungutted and gutted fish, preserves, semi-finished products and finished goods (20% each of the listed groups), the remained 15% refer to fillet and 5% to other fish products [8].

One of the perspective objects of trade is the capelin, quotas for which accustom insufficiently effectively because of low demand. According to researches stocks of Barents Sea capelin will increase [9]. Based on the example of the market analysis for the Murmansk region it is possible to draw a conclusion that the capelin is generally sold in frozen and cooled forms. It is important for the regional innovative and technological development to enhance the production of a Barents Sea capelin [10]. Thus, development of cutting-edge technologies of deep extent capelin processing and diversification of the range of fish products can be seen as a relevant task. One of the perspective directions of capelin processing is its use for canned food production, including the «Smoked Capelin in oil». Taking into consideration the traditional demand for canned food of this type (especially smoked seafood) in the consumer market of the Russian Federation, «Smoked Capelin in oil» can become popular.

To resolve the problem of low demand for capelin it is needed to develop a new technology of canned food processing («Smoked Capelin in oil») and to establish a period of storage of the frozen raw materials, which can be used for the production of this type of canned food.

To a large extent the quality of canned food depends on the quality of the raw materials directed to their production. State Standard Specification 32366-2013 «Frozen fish. Specifications.» states the storage period of frozen capelin either at a temperature not higher than minus 18 °C (no more than four months) or at a temperature not higher than minus 25 °C (no more than six months). Raw materials can be used for production of canned food when the period of storage does not exceed ⅔ of the allowed storage period (which makes four months). The assumption that a period of storage of this type of products can be prolonged is justified by the wide usage of modern technologies of freezing, the latest equipment and quality control systems.

The conventional problem of the smoked food production is the risk that polycyclic aromatic hydrocarbons (PAH), can get into the final product together with smoke. It refers generally to such toxic (cancerogenic) substances as benzo(a)pyrene and nitrosamines, which are formed at high temperatures of heat treatment. The International Association of Studying of Cancer (IASC), the Agency on toxic substances and the register of diseases (ATS-DR), the Environmental Protection Agency and the EU mentioned PAH in the list of major pollutants because of their cancerogenic and mutagen properties [11].
Taking into account the aforesaid, the purpose of the research was to achieve a considerable reduction in the amount of cancerogenic substances in the final product due to the use of the proposed preliminary heat treatment of raw materials (the soft conditions of smoking). It was also decided to focus on the study of a possible extension of storage periods of the frozen capelin used for production of the sterilized canned food.

2. Materials and methods

The object of the researches was the capelin (Mallotus villosus) caught by the trade company JSC Murmansk Trawler Fleet around the Barents Sea in March, 2011. The fish was frozen and brought to the Murmansk port. During the experiments the capelin was subjected to refrigerator storage within 12 months at a temperature from minus 18 °C to minus 20 °C that, according to the normative documents existing in Russia, three times exceeds storage life. Development of the proposed technology and production of canned food from a semi-finished product of cold smoking were carried out in the laboratories and the educational development workshop of the Murmansk State Technical University (MSTU). The smoker of chamber type developed in MSTU was used for carrying out experimental works by preparation of a semi-finished product from a capelin with the usage of the cold smoking technology.

The organoleptic assessment of prototypes of canned food was carried out by a specially formed council in accordance with State Standard Specification 26664-85 «Canned and preserved fish and sea products. Methods for determination of organoleptic characteristics, net mass and components fraction of total mass».

Organoleptic assessment of the produced canned food was conducted on the basis of a specially developed 20-mark scale (Table 1) including importance coefficients from which the highest ones refer to the most basic organoleptic indicators: appearance, taste and consistence [12, 13].

| Characteristic      | Point | Coefficient of the indicator of Importance | Assessment (with the degree of importance) |
|--------------------|-------|---------------------------------------------|--------------------------------------------|
| Visual appearance  | -5    | 0,8                                         | 0,8–4,0                                    |
| Consistence        | -5    | 0,8                                         | 0,8–4,0                                    |
| Flavour            | -5    | 1,0                                         | 1,0–5,0                                    |
| Smell              | -5    | 0,7                                         | 0,7–3,5                                    |
| Colour             | -5    | 0,7                                         | 0,7–3,5                                    |
| Total score        |       |                                             | 4,0–20,0                                   |

The research has been conducted with the usage of the chemical, biochemical and microbiological methods accepted in modern science. The mass fraction of water, lipids, protein, amine nitrogen, volatile basic nitrogen, acid value, mineral substances in the raw materials and canned food was determined by the standardized techniques. Content of the general nitrogen was determined by the Kjeldahl method with the usage of the equipment consisting of two elements: BLOCK–DIGEST–12 for a mineralization of samples and the automatic PRO-NITRO A distillation installation (J.P. Selecta, Spain). Content of fat was determined by the Soxhlet method by means of an extractor Selecta DET/GRAS (Spain).

The amino-acid structure of canned food was determined by hydrolysis of a sample by hydrochloric acid or alkali in the process of heating [14], subsequent modification of the received amino acids phenylisothiocyanate, division phenylthiocarbamyl of derivative amino acids with the subsequent registration by the spectrophotometric detector SPD-20AV on the liquid LC-20 Prominence chromatograph of Shimadzu (Japan).

Amino-acid score (AAS) [15, 16] was calculated by means of a formula:

$$AAS = \frac{m_1}{m_2} \cdot 100, \%$$  \hspace{1cm} (1)

where $m_1$ is the content of essential amino acid in 1 g of protein, protein mg/g; $m_2$ is the content of essential amino acid in 1 g of reference protein, mg/g of reference protein.
Coefficient of rationality of $R_c$ was calculated by means of a formula
\[ R_c = \frac{\sum_1^n A_i K_i}{\sum_1^n A_i} \]  
(2)
where $A_i$ is the maintenance of irreplaceable $i$-amino acid, protein mg/g; $K_i$ – coefficient of utility of $i$-amino acid;

Coefficient of utility of $i$-amino acid was calculated by means of a formula
\[ K_i = \frac{A_{AS_{min}}}{A_{AS_i}} \]  
(3)
where $A_{AS_{min}}$ – minimum amino-acid score; $A_{AS_i}$ - amino-acid score $i$-amino acids.

Determination of the fatty acids content was carried out by the method of a highly effective liquid chromatography on the chromatograph liquid «Agilent 1100» with the diode and matrix detector, the column Hypersil ODS. The method is based on the induction of the previously prepared sample into the solvent current (a mobile phase) and passing of its components through the chromatographic column filled with a motionless phase (adsorbent).

Chemically clean reactants were used to carry out chemical analyses. The standards of amino acids and fatty acids for a chromatography and standard samples for atomic and absorbing spectroscopy were acquired from the Sigma Aldrich Company (Germany).

Statistical processing of results of experiments was carried out by the method of nonlinear regression and creation of mathematical dependences was carried out with the use of the computer Datafit 9.1 programs (Oakdale Engineering) and Microsoft Office of Excel-2007.

Preparation of samples for microbiological indication was carried out in accordance with the State Standard Specification 8756.0 [17].

The industrial sterility of canned food was defined in accordance with the State Standard Specification 30425 [18].

The study was partially executed on the basis of the research laboratory of Chamber of Commerce and Industry department. Microbiological researches were conducted in the microbiological laboratory of «The center of researches of raw materials and products» of Chamber of Commerce and Industry department. The smoker of chamber type was developed in MSTU in order to carry out experimental works on preparation of a semi-finished product from capelin with the usage of the cold smoking technology. Production of canned food from a semi-finished product of cold smoking was carried out with the help of the equipment on the basis of the industrial canning site (H33) in the Educational and Experimental Workshop of MSTU.

3. Results of researches and their discussion
The chemical composition of muscular tissue of the Barents Sea capelin depends on a catch season: the smallest water content and the largest content of fat are noted at the end of feeding. The greatest amount of moisture and the smallest amount of fat are registered during the spawning and post-spawning periods. Therefore when developing products of a new type it is important to find out how the chemical composition affects technological properties of raw materials. Results of the study of the chemical composition of the capelin are presented in Table 2.

**Table 2.** Average chemical composition of frozen capelin

|            | Water, % | Lipids, % | Protein (N•6,25), % | Ashes, % |
|------------|----------|-----------|---------------------|----------|
|            | 69,5±0,5 | 2,5±0,4   | 16,5±0,6            | 1,5±0,4  |

The research defined the moisture content of capelin in the process of preliminary heat treatment (PHT). Cold smoking was applied for preliminary heat treatment. For the purpose of preservation of the biologically valuable highly unsaturated fatty acids, essential amino acids, albumens and minimization of content of cancerogenic 3.4- benzo(a)pyrene, nitrosamines it was decided to use the following temperature condition of PHT (temperature of smoking from 26 to 28 °C). These conditions are softer than of the traditional production technology of canned food of this group (temperature from 80 to 110 °C). Lower temperatures allow to receive a product of a higher quality, by means of increase in moisture losses at PHT and also to increase an amount of the produced semi-finished.
product of cold smoking. In order to define the storage mode for raw materials before processing, there were chosen the key influencing factors, such as the carcass size, the chemical composition and the temperature of heat treatment. As a result of the carried-out research it was possible to study the influence of the raw materials properties and mode parameters on duration of dehydration in the process of preparation of smoked semi-finished product from capelin.

The choice of the PHT mode was made proceeding from the results of organoleptic assessment of both smoked semi-finished product, and ready canned food. On the basis of the generalized indicator of quality of canned food it was revealed [19] that for canned food «Smoked Capelin in oil» the loss of weight in the course of PHT should not be less than 25 % [20]. The results of the conducted researches were used in the process of the PHT mode development.

One of the most important development stages in the technology of the canned food production is the scientific justification of the sterilization mode, for it is developed not only for the safety of a product, but also for the purpose of maintaining its nutrition value. Proceeding from the received results [20], [21] mode of sterilization of canned food «Smoked Capelin in oil» were evidence-based and approved in accordance with the established procedure: (5-15-45-20)/120 °C – 0.2 MPa; F = 8.0 min.

On the basis of the developed mode the pilot batch of canned food was produced.

Microbiological researches confirmed the industrial sterility of the canned food. As a result of the carried-out analysis on the toxic substances it was defined that the content 3.4-benzo(a)pyrene in the canned food «Smoked Capelin in oil» was <0.0001 mg/kg, nitrosamines were absent. Thus it was proved the product was in compliance with safety requirements imposed on canned food from smoked fish.

Organoleptic and physical-chemical indicators of products also conformed to requirements imposed on this type of canned food. The products were approved by the tasting council of MSTU.

The conducted researches allowed to develop and approve specifications and the technological instruction for production of canned food «Smoked Capelin in oil» (Technical Conditions 9271-011-00471633-12, Technological Instructions 011-2012) [19].

So as to assess the nutrition value of the canned food it was needed to define the general chemical, amino-acid, fat and acid structure of the product. The chemical composition and food value of the canned food is presented in Table 2.

The results of researches of the amino-acid structure and calculation of biological value of canned food which was carried out in accordance with the recommendations of World Health Organization [16] are presented in table 3.

| Amino acid       | A<sub>i</sub>, mg in 1g protein | Reference value, mg in 1 g protein | AAS, % | K<sub>i</sub> |
|------------------|---------------------------------|-----------------------------------|--------|--------------|
| Tryptophan*      | 12,1                            | 6                                 | 200    | 0,66         |
| Lysine*          | 93,2                            | 45                                | 207    | 0,63         |
| Histidine*       | 22,6                            | 15                                | 151    | 0,87         |
| Threonine*       | 42,4                            | 23                                | 184    | 0,71         |
| Cysteine*        | 21,2                            | Methionine+Cysteine               | 173    | 0,76         |
| Methionine*      | 27,6                            | 22                                | 131    | 1,00         |
| Valine*          | 51,2                            | 39                                | 154    | 0,85         |
| Isoleucine*      | 46,3                            | 30                                | 146    | 0,90         |
| Leucine*         | 86,1                            | 59                                | 187    | 0,70         |
| Tyrosine*        | 33,7                            | 38                                |        |              |
| Phenylalanine*   | 37,4                            |                                   |        |              |
| Arginine         | 95,1                            |                                   |        |              |
| Aspartic acid    | 65,4                            |                                   |        |              |
Serine 43,9
Glutamic acid 144,8
Proline 52
Glycine 56,2
Alanine 74,7
Sum of essential acids * 473,8

For the assessment of essential amino acids balance in comparison to the reference protein it was necessary to find out the coefficient of rationality of Rc. The provided data confirmed that the product contained all the proteinaceous amino acids. The total amount of essential amino acids is 473.8 mg/g of protein; the limiting amino acids are absent. The study noted the content of a considerable amount of the glutamine acid, arginine, lysine and leucine (144, 95, 93, 86 mg/g of protein respectively). The minimal registered score has valine (131%). The coefficient of rationality Rc equals 0.79 that confirms both the amino-acid balance and a high biological value of a product.

The range of the higher fatty acids is presented from dodecanoic (lauric) C12:0 to docosahexaenic acid C22: 6. The bulk of saturated fatty acids consists of myristinic (C14: 0), stearin (C18: 0) and palmitic ones (C16: 0). Their content in fat equals 2,07, 3,56 and 7.34 % respectively. The Fatty acid composition of lipids of the studied canned food (Table 4) has definite unsaturated character: the sum of unsaturated fatty acids – 86.1%, including the monoenoic fatty acids (MUFA) – 43.42% and polyenic fatty acids (PUFA) – 42.65%.

Table 4. The fatty acid composition of the canned fish «Smoked Capelin in oil»

| Acids   | % of content in fat | In 100 g of product, g |
|---------|---------------------|------------------------|
| SFAs    | 14,0                | 4,2                    |
| MUFAs   | 43,4                | 13,0                   |
| PUFAs   | 42,6                | 12,8                   |
| Omega-6 | 41,3                | 12,4                   |
| Omega-3 | 1,3                 | 0,4                    |

The high content of polyunsaturated fatty acids allows to relate the product to biologically valuable.

Thus, it can be concluded that the studied samples of canned food are safe and biologically complete. They also have good consumer properties and high nutrition value.

To justify the possibility of the storage period extension of frozen raw materials, it was important to conduct researches on how the quality of frozen fish changes in the course of storage and, respectively, to study the impact of these changes on the quality of canned food. According to the methodical instructions 4.2.1847-04 «Sanitary and epidemiologic assessment of expire dates prolongation and storage conditions of food» it was needed to develop the schedule of tests on frozen capelin in process of storage. The purpose of these tests was to define microbiological indicators (figure 1), the nitrogen of the flying bases (NFB), organoleptic and rheological indicators [22].
Opportunistic microorganisms in the studied raw materials were not defined.

The analysis of the chemical composition of raw materials showed that as a result of storage within twelve months content of water, fat and the general nitrogen practically in frozen fish did not change. In the course of 12-month storage of capelin the content of volatile basic nitrogen, water-retaining capacity, acid value of lipids, was checked periodically (1 time in 3 months). Research data is provided on figures 2 – 4.

It was established that lipid hydrolysis took place in frozen capelin in the course of refrigerator storage. That was confirmed by accumulation of free fatty acids. So, Acid value of lipids in capelin in the course of 9 months storage increased by reached 39 mg KOH /g. Hydrolysis of fabric lipids is the factor influencing a denaturation of muscle proteins during refrigerating storage of fish. In 6 months storage period the contents of Volatile basic nitrogen increased from 13 to 26 mg %, in 12 months of storage its contents reached 65 mg of %. It was noted an insignificant reduction of water-retaining ability (WRC) of fish. By the end of the 9 months storage period it made up 67.5%. Despite it, raw materials on indicators of quality conformed to requirements of State Standard Specification 32366-2013 «Frozen fish. Specifications». So as to justify the prolongation possibility of storage period of the frozen capelin directed to production of canned food it was necessary to establish the compliance of quality of finished goods (canned food) during the whole period up to the expire date of canned
food established in standard documentation. According to the developed technology we produced the pilot batch of canned food «Smoked Capelin in oil» made of raw materials with various period of storage (0.5; 6; 9 and 12 months). Canned food was stored at a temperature not above 20 °C and relative humidity no more than 75%. The analysis of quality of canned fish was carried out at the initial period of storage (0.5 months from the moment of production) and further on after 6, 9 and 12 months of storage. On the basis of State Standard Specifications 4.31-82 «The Quality Indicator System (QIS). Canned food and preserved food made of fish and seafood. Product indicators (Change N 1)» the list of the quality indicators was chosen in order to estimate the canned fish quality in the course of its storage period.

The pilot batch of canned fish processed with the help of the developed technology was made of raw materials of the various periods of storage (0.5, 6, 9 and 12 months). It was stored at a temperature of not above 20 °C and relative humidity of no more than 75%.

In figure 5 there is a chart of tasting assessment of canned fish, carried out directly after its production from raw materials with the different periods of storage. Figure 6 provides the results of researches of the same prototypes from the point of their quality. The canned capelin with a period of storage 0.5 months had high level of quality (from 100% to 95%) within 12 months of storage. The canned food made of a frozen capelin with the 6 months period of storage showed the quality of 93.2%. The samples of canned fish made of raw materials with a period of storage within nine months showed high quality of taste; however there was also hardly noticeable taste of bitterness in separate samples and a slightly weakened consistence. At the canned food made of frozen capelin with the period of storage up to twelve months, the level of quality was 83% (figure 6), the taste of bitterness was more noticeable. Therefore the canned fish made of raw materials with a long period of storage (twelve months) was removed from storage. The change of product quality indicators was studied in the course of the canned fish storage.

![Figure 5. Organoleptic evaluation of the product](image)
Figures 7-11 – present the results of researches of prototypes on the content of the volatile basic nitrogen (VBN), the amino nitrogen (AmN), moisture retention capacity (MRC), the acid number (AN) of lipids and oil.

**Figure 7.** Change of volatile basic nitrogen in canned fish during storage, mg %

**Figure 8.** Change of amino nitrogen in canned fish during storage, % increase in content of nitrogen of the flying bases and aminy nitrogen in the process of canned fish storage reflects the intensitz of proteolysis and acceleration of protein hydrolysis (Figures 7, 8).
As a result of researches it was established that the quality of the canned food conformed to the requirements established for this type of sterilized products within the 12 month storage period. It refers both to the canned fish produced from fresh capelin and the raw materials stored up to 9 months.
Thus, it was experimentally established that for the production of canned fish «Smoked Capelin in oil» can be used frozen raw materials with a storage temperature not higher than minus 18 °C. Taking into account a safety factor, the storage period must not exceed 6 months.

4. Conclusion
The conducted researches made it possible to develop the production technology of canned fish «Smoked Capelin in oil» with application of the soft conditions of smoking. Experiments demonstrated that the produced canned smoked capelin conformed to safety requirements, had excellent consumer properties and was characterized by high nutrition value.

Besides it was experimentally established that for the production of canned fish «Smoked Capelin in oil» can be used frozen raw materials with a storage temperature not higher than minus 18 °C and the storage period up to six month.

The received results can be used at revision of expire dates of frozen capelin directed to the production of canned food.

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