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STUDY OF THE DIETARY SUPPLEMENTS TRACE ELEMENTS PENETRATION INTO CRUCIAN CARP TISSUES IN DIFFERENT WAYS OF SALTING

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Abstract. The article substantiates the expediency of improving of technological methods of processing unprofitable small fish and expanding of the food products range from them. It proposes enriching of the flesh of freshwater fish with trace elements by adding chelate complexes based dietary supplements to salt or brine during the salting of raw materials. The kinetics of penetration of the chelate complexes micronutrients based dietary supplement into the muscle tissue of crucian carp was researched using the method of electronic paramagnetic resonance (EPR). The salting was performed using three methods. In the first, dry method of salting the fish was mixed with sodium chloride NaCl with the addition of a chelate complex based dietary supplement in the amount of 20–25% and 0.1% of the weight of raw material, respectively. In the second, brine method the fish was salted in brine, which was a solution of sodium chloride NaCl in the amount of 2 kg of salt per 1 kg of raw material. The amount of the chelate complex based dietary supplement was 0.1% of the weight of raw material. In the third method, the salting was performed in brine with the same concentrations of sodium chloride and dietary supplement, but the fish raw material was previously treated with ultrasound. The salting of fish lasted for 6 days. The distribution of Mn ions in the plane (i, j) was researched. The kinetics of penetration of the trace element into the volume of crucian carp muscle tissue was researched using the EPR method. The kinetics of Mn^{2+} ions distribution in the researched muscle tissue samples and the tomograms of these surfaces were determined. The values of the area under the EPR spectrum were normalized to the values of the area under the maximum EPR signal. In the dry salting method the signal from the liquid in which the raw material was during the salting was selected as the maximum EPR signal; and in the brine method the signal from the brine sample was selected as the maximum EPR signal. It is noted that the kinetics of penetration of the trace element is determined by the area of contact of the raw material with the diffusing substances and the method of intensification of the internal transfer of these substances inside the raw material. It was found that in the brine method and in the brine method with pre-sonication, the amount of trace element in the depth of the crucian carp muscle tissue varied within the error margin. This indicates the homogeneity of distribution of the trace element of the chelate complex based dietary supplement in these methods of salting.

Key words: small freshwater fish, an additive based on a chelate complex, brine salting, dry salting.

Introduction. Problem statement

Functional food products that have increased biological value and are balanced by main macro- and micronutrients play an important role in nutrition of the population of modern Ukraine. Food processing is the industry that uses nutritionally valuable raw material [1]. Improving of technologies of fish raw material processing may provide for new fish products

with increased nutrient value by enriching of muscle tissue with mineral substances, essential fatty acids and other vital substances [2].

Analysis of recent research and publications

Ukraine has a substantially big number of water bodies that are used in the integrated multi-industrial way [3]. Fishery management is a very important field of exploitation of biological resources that are generated under the influence ofnature, climate and anthropogenic factors. It should be pointed out that due to the change in the species composition of the raw material base of the fishery basin, the fish from the "other freshwater" category present considerable interest for the industrial processing [4].

There are various known methods of the industrial processing of freshwater fish. This raw material is used to make fermented fish farce [5], preserves [6], canned fish [7], etc. A group of so called small freshwater fish like rudd, goldfish, and white bream should be pointed out. The small freshwater fish belong to the unprofitable group; processing of such fish with traditional technologies is ineffective due to its morphological and size-mass specifics: big number of small bones in the flesh tissue and little yield of edible portion [8]. Based on this research, improvement of technological methods of processing of unprofitable small fish and expansion of assortment of food products made of it remain the issues of present interest.

One of the ways to increase consumption attractiveness of small freshwater fish and to increase assortment of food products made from it is the production of dried fish [9]. Dried fish is a popular snack, which is used with various beverages and as a separate meal [10]. Naturally, the nutrition and consumption value of dried freshwater fish is significantly lower than that of salt-water fish [11]. However, there is a way of enriching of freshwater fish flesh with trace elements by adding them during the preliminary preparation of the raw material for drying. Introduction of trace elements is done by adding chelate complex based dietary supplements to salt or brine during the salting process [12,13].

Purpose of the research – to achieve uniformity of distribution of trace elements of chelate complex based dietary supplement throughout the volume of the raw material (small freshwater fish) by identifying of the rational method of salting prior to drying.

The following **tasks** were set to achieve the goal:

– to research the kinetics of penetration of the trace elements of chelate complex based dietary supplement into the muscle tissue of crucian carp in dry salting

– to research the kinetics of penetration of the trace elements of chelate complex based dietary supplement into the muscle tissue of crucian carp in brine salting

to research the kinetics of penetration of the trace elements of chelate complex based dietary supplement into the muscle tissue of crucian carp in brine salting with pre-sonication.

Research materials and methods

The subject of the research was the muscle tissue of crucian carp. The specimens of the muscle tissue were prepared as follows. We selected the fish with the weight 0.8 to 0.9 kg and 3 to 4 years of age. The fish was washed and moved to salting.

The research used the dietary supplement based on Mn chelate. The raw for making of the chelate complex based dietary supplement are the chelates produced by TOV "Nanomaterials and Nanotechnologies" (Kyiv). The chelate complex based dietary supplement is a powder mix, without taste or scent that uses NaCMC as a matrix carrier of chelate compounds; the powder is mixed with the chelate solution in 1:30 ratio. The mix is allowed to stand for 60…90 minutes. 96% ethyl alcohol is used for the sedimentation of the derived NaCMC-chelate complex. After the sedimentation the complex is dried in the drying cabinet followed by crushing. It ensures obtention of dietary supplement rich in critical elements, which can be used in technology of broad spectrum of food products of everyday use.

The salting was performed by three methods. In the first, dry method the fish was mixed with the sodium chloride NaCl with addition of the chelate complex based dietary supplement in the amounts, respectively 20…25% and 0.1% of the mass of the raw material. In the second, brine method the fish was held in the brine composed of solution of sodium chloride NaCl with the density of 1 kg of salt to 1 kg of the raw material. The amount of added chelate complex based dietary supplement was 0.1% of the raw material mass. In the third method, the salting was performed in brine with the same concentrations of sodium chloride and dietary supplements, but the fish raw material was first treated with ultrasound. The salting of fish lasted for 6 days.

To treat the fish raw material we used the laboratory installation – sonicator UZDN-2T manufactured by NVP "Ukrrosprylad" (Sumy, Ukraine) adapted to the experiment conditions (Fig. 1) [14].

The concept of operation of the sonicator is as follows [14] – when the ultrasound generator is turned on, the transformer coil powers up. Accordingly, in the magnetostrictional transformer the electrical energy is transformed into the energy of mechanical vibrations of the transformer amplified by the concentrator. The magnetostrictional transformer is made from ferromagnetic alloys and composed of U- or O-shaped plates. The use of transformers of such type allows more rational use of power. The excitation winding is positioned on the bars thus creating closed magnetic current. The radiator transmits elastic vibrations into the brine by the wide wavefront. Upon occurrence of cavitation, pressure and exhaustion zones appear which

creates the ultrasonic microcurrents that intensify the processes of mass exchange and mass transfer. The ultrasound treatment of the fish raw material was performed in a cylindrical metal chamber (11) filled with brine with appropriate characteristics.

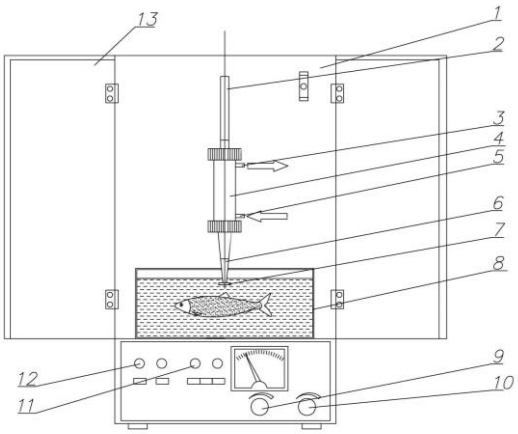

Fig. 1. Layout of the experimental installation: 1 – body; 2 – mount; 3,5 – inlet and outlet water nozzles; 4 – water-cooled transformer; 6 – concentrator; 7 – radiator; 8 – frequency regulator; 9 – power regulator; 10 – sound-insulating valves; 11 – working chamber; 12 – frequency switch; 13 – impulse switch

After that, specimens of the muscle tissue were cut from the fish salted by the above methods, in the parallelepiped shape with the dimensions of 21x21x21 mm (Fig. 2). Parallelepiped shape specimens of the muscle tissue were conventionally divided into cubic volume elements with the characteristic dimension of b≈7 mm. A probe was taken from the inside of each volume element a_{ijk} (where i=0, 1, 2; j=0, 1, 2; k=0, 1, 2) for examination by the method of electronic paramagnetic resonance (EPR).

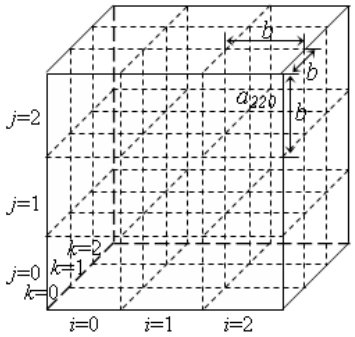

Fig.2. Conventional division of the specimens of the muscle tissue of crucian carp for examination by the EPR-method

Registration of the EPR spectrums was done by the RE 1301 radio spectrometer (made in Ukraine) that works on the fixed wave length λ=3,2 cm [15]. The spectrums were registered in the form of the first-order derivative of the absorption of the UHF energy E by the examined paramagnetic during the scan of the magnetic field H [16].

Assessment of distribution of trace elements of the supplement in the volume of the food system is possible due to the fact that the supplement contains Mn^{+2} ion. The ion of the transition metal Mn^{+2} in this research is used as a spin label for the method of EPR spin labels [17].

The signal of the examined specimens of the crucian carp muscle tissue is comprised of two: wide single line without hyperfine structure and the divided spectrum of six peaks of equal intensity (Fig. 3)

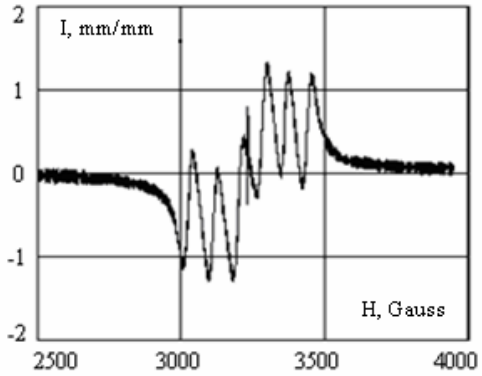

Fig.3. EPR-spectrum of the examined specimens of the crucian carp muscle tissue

Concurrently, the area under the spectrum, i.e. under the wide line and under the six-peak spectrum is proportionate to the number of resonating spins of Mn^{+2} ions and, consequently, to the number of trace elements contained in the examined volume.

Results of the research and their discussion

Since the salting of fish was performed throughout six days, the kinetics of penetration of the trace elements of the dietary supplement in the volume of the food raw material at the end stage of the process presents more interest. By the kinetics of penetration of the trace elements of the dietary supplement in the volume of the food raw material we mean the change of distribution of Mn^{2+} trace element with time. Distribution was determined on the 4th, 5th, and 5th day.

At the first stage the distribution of Mn^{2+} ions in the plane (i, j) was researched. It should be noted that the salting of the specimen occurred along the k-coordinate (Fig.2). The gradient of concentration of the diffusing substance was created specifically along this axis. In other words, the specimen of the muscle tissue was cut in such a manner that the area of the parallelepiped with coordinate k=0 was closest to the external surface of the body of the fish. The research has established that the areas under the EPR spectrums that are proportionate to the number of Mn^{2+} ions differ in the area with one k number in no more than 1–2%. Therefore, an assumption has been made that it would be expedient to examine distribution of trace elements specifically along coordinate k, i.e. to examine the depth of penetration of the dietary supplement trace

elements into the volume of the food raw material. It should be noted that the test probe was taken from inside of the volume elements with coordinates along the 0k axis and were equal to 3.5 mm, 10.5 mm, 17.5 mm.

Further on, using the EPR method we researched the kinetics of penetration of the trace element in the volume of the crucian carp muscle tissue. Figures 4, 5, and 6 show surfaces (letter a) that illustrate kinetics of Mn^{2+} ions distribution in the examined specimens of the muscle tissue and the tomograms of these surfaces (letter b). It should be noted that the values of the area under the EPR spectrums have been normalized to the values of the area under the maximum EPR signal. In the dry salting the signal from the liquid in which the raw material was during salting was selected as the maximum EPR signal; and in the brine method the signal from the brine sample was selected as the maximum EPR signal.

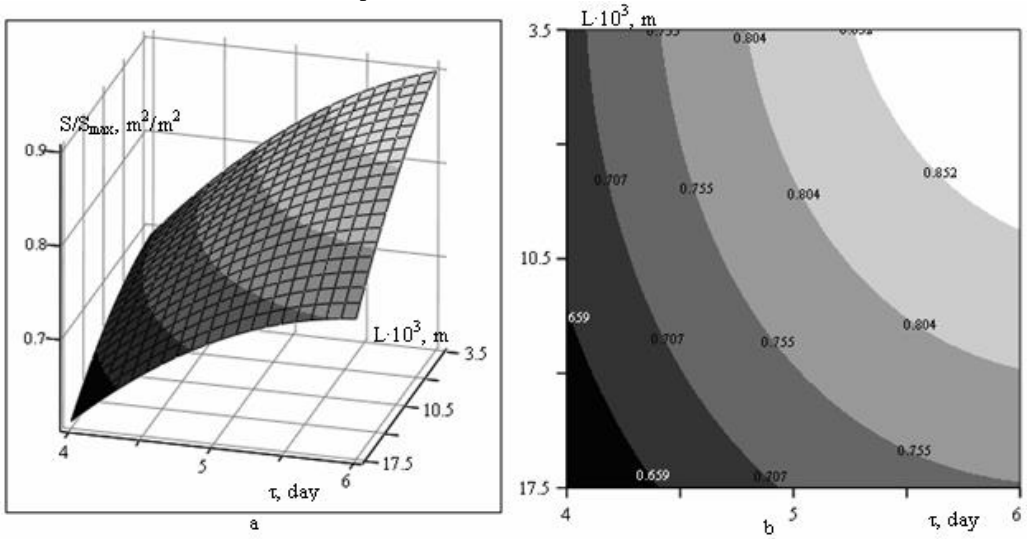

Fig.4. Kinetics of penetration of Mn^{2+} in the volume of the dry salted crucian carp muscle tissue: a – change of area under the EPR spectrum with time in the depth of the examined specimen; b – the tomogram of the surface

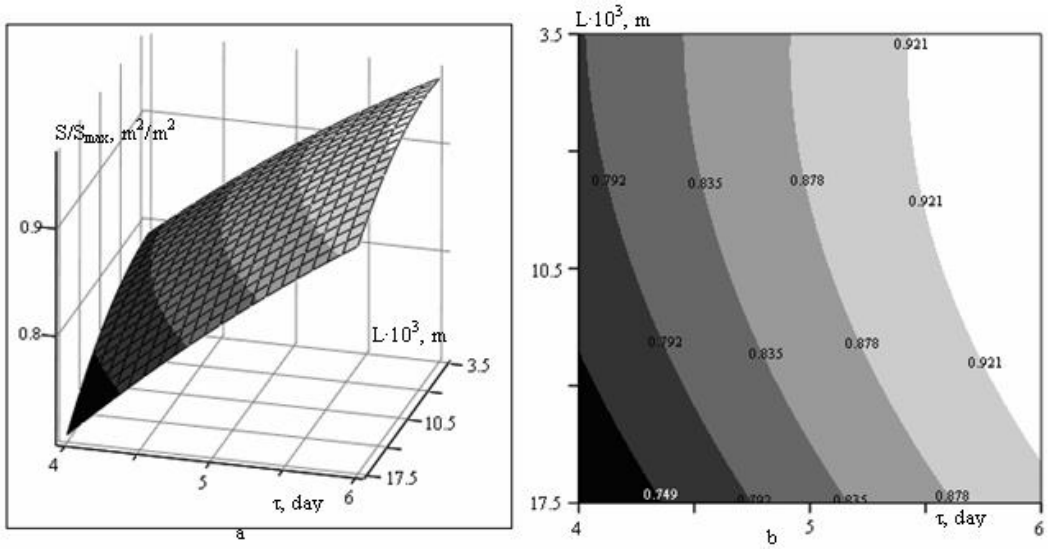

Fig.5. Kinetics of penetration of Mn^{2+} in the volume of the brine salted crucian carp muscle tissue: a – change of area under the EPR spectrum with time in the depth of the examined specimen; b – the tomogram of the surface

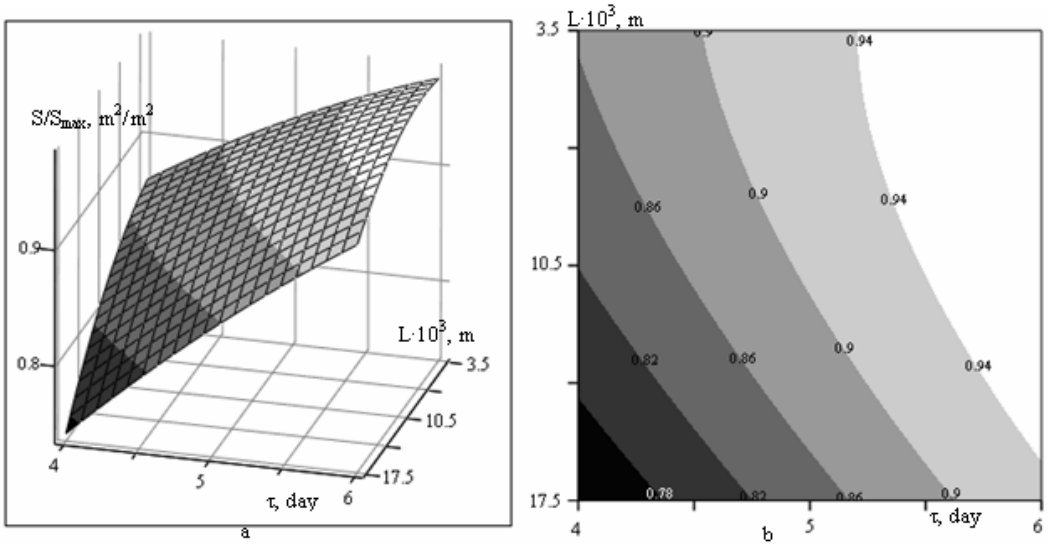

Fig.6. Kinetics of penetration of Mn^{2+} in the volume of the brine salted crucian carp muscle tissue with pre-sonication: a – change of area under the EPR spectrum with time in the depth of the examined specimen; b – the tomogram of the surface

The illustrated results show that the number of Mn ions that penetrated into the crucian carp muscle tissue increases with the increase of the salting process duration in various salting methods, which is obvious. However, the kinetics of penetration of the trace element by the depth is different. Specifically, in dry salting 76% of Mn ions penetrated to the depth of 17.5 mm in 4 days, and 26% in the following 2 days. In brine salting 82% of ions penetrated to the depth of 17.5 mm in 4 days; and in the brine method with pre-sonication – 88% of the total amount of Mn ions. The probes with other depths (3.5 mm and 10.5 mm) demonstrate the same tendency. The obtained result is explained by the fact that the dry salting is the lengthiest of all researched methods. Since in the dry salting process the fish mixed with sodium chloride and the powder of the dietary supplement start loosing moisture for dissolving of NaCl and the supplement, the extra time is required. In the brine salting process the raw material is placed into the solution of NaCl and the supplement right away. This method results in increase of the diffusion process due to the increase area of contact of the raw material with the diffusing substances. Additionally, the ultrasonic treatment contributes to the intensification of the internal transfer as the convective microcurrents appear in the capillaries of the raw material, which furthers the increase of effective coefficient of diffusion [14].

In all the examined specimens the surface that characterizes the change of area under the EPR spectrum with time in depth of the examined specimen, has a bend from the area that shows the duration of salting and from the coordinate of the examined volume element. The same is proven by the shape of isocurve on the tomograms of these surfaces. The bend of the surface points to the non-linear nature of the salting process and to the inhomogeneity of the trace element distribution by the depth. The kinetics of the salting process does not require analysis since it obviously has an exponential character. As for the distribution of the trace element by the depth of examined specimens of the muscle tissue, the section of the surfaces as of the sixth day, which is the recommended duration of salting, are shown on Fig. 7.

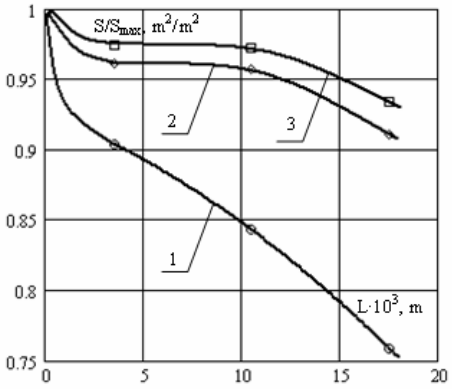

Fig.7. Distribution of Mn^{2+} ion by the depth of specimen of the crucian carp muscle tissue in various salting methods:
1 – dry salting; 2 – brine salting; 3 – brine salting with pre-sonication

Fig. 7 demonstrates that the distribution for all specimens is non-linear. With the increase of the depth of the probe the area under the EPR spectrum and, respectively, the number of Mn ions in the specimens of the crucian carp muscle tissue decreases. However, this difference is the most visible in the specimen obtained in dry salting. Specifically, the number of the trace element in the depth of 17.5 mm of the dry salting is 25% less compared to the liquid where this raw material was salted. In other words, there is a significant inhomogeneity in the distribution of trace elements by the volume of the researched food raw material.

For the specimens obtained in brine salting with and without pre-sonication the number of ions of the trace element differs not more than 7–9% compared to the number of ions in the brine. The obtained results give reasons to suggest that these methods of salting of the crucian carp with the weight 0.8 to 0.9 kg and 3 to 4 years of age allow homogeneity of distribution of the trace element of chelate based dietary supplement.

It should be noted that the results of the muscle tissue specimens obtained by the brine salting and the brine salting with pre-sonication differ by not more than 2…3%. With that in mind, from the perspective of energy efficiency the brine salting without pre-sonication is a more efficient method of enrichment of the examined raw material with the chelate complex based dietary supplement since the raw material in this method does not require additional treatment and therefore, additional equipment and related energy costs.

Approbation of the research results

The results of the research can be used in technologies of enrichment of food products and can be implemented in the freshwater fish processing facilities. The outcome of such implementation will be a new technology of freshwater fish salting and expanding of the assortment of food products enriched with trace elements.

Conclusions

The research of kinetics of penetration of trace elements of the chelate complex based dietary supplement into the muscle tissue of crucian carp in dry salting, brine salting, and brine salting with pre-sonication:

1. Established that the number of Mn ions that have penetrated inside the muscle tissue of crucian carp increases with the increase of duration of salting in various methods of salting. With that, kinetics of penetration of the trace element within the first 4 days to the depth of 17.5 mm is as follows: for dry salting method – 76% of the total number of Mn ions; for brine salting – 82%; for brine salting with pre-sonication – 88%. It is noted that such kinetics of salting is determined by the area of contact of the raw material with the diffusing substances and the manner of internal transfer of these substances inside the raw material.

2. Established that the distribution of the trace element in the depth of the muscle tissue of crucian carp in the researched methods of salting on the sixth day (which is recommended) is non-linear. It was established that with the increase of the depth of the muscle tissue the number of ions of the trace element decreases. It was noted that the most significant inhomogeneity in the distribution by the number of trace elements in the volume of the researched food raw material was established for the dry salting method – 25%. It was further noted that for the brine salting with and without pre-sonication the number of ions of the trace element differs not more than 7–9%. The established findings suggest that these methods of salting of the crucian carp with the weight 0.8 to 0.9 kg and 3 to 4 years of age allow homogeneity of distribution of the trace element of chelate based dietary supplement.

3. Established that from the perspective of energy efficiency the brine salting without pre-sonication is a more efficient method of enrichment of freshwater fish with trace elements with the chelate complex based dietary supplement.

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ДОСЛІДЖЕННЯ ПРОНИКНЕННЯ МІКРОЕЛЕМЕНТІВ ДІЄТИЧНОЇ ДОБАВКИ В М'ЯСО КАРАСЯ ЗА РІЗНИХ СПОСОБІВ ПОСОЛУ

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Анотація. Обґрунтовано доцільність удосконалення технологічних прийомів переробки малорентабельних дрібних риб і розширення асортименту харчової продукції з них. Запропоновано збагачувати м'ясо прісноводної риби на мікроелементи шляхом додавання до солі або тузлуку дієтичних добавок на основі хелатних комплексів. Методом електронного парамагнітного резонансу (ЕПР) досліджено кінетику проникнення мікроелементів дієтичної добавки на основі хелатного комплексу в м'язову тканину карася. Посол проводили трьома способами. За першим сухим способом соління рибу змішували з хлоридом натрію NaCl з додаванням дієтичної добавки у кількості, відповідно, 20–25% та 0,1% від маси сировини. За другим тузлучним способом соління рибу витримували в тузлуку, який являв собою розчин хлориду натрію NaCl у кількості 2 кг солі на 1 кг сировини. Кількість внесеної дієтичної добавки складала 0,1% від маси сировини. За третім способом посол проводили в тузлуку з тими ж концентраціями хлориду натрію та дієтичної добавки, однак попередньо рибну сировину обробляли ультразвуком. Соління риби проводилось впродовж 6 діб. Досліджено розподілення іонів Mn в площині (i, j). ЕПР-методом було досліджено кінетику проникнення мікроелементу в об'єм м'язової тканини карася. Визначено кінетику розподілення іонів Mn^{2+} в досліджуваних зразках м'язової тканини та томограми даних поверхонь. Значення площі під ЕПР-спектрами пронормовані на значення площі під максимальним ЕПР-сигналом. За максимальний ЕПР-сигнал для сухого соління обрано сигнал від рідини, в якій знаходилась сировина під час посолу, а під час тузлучного – сигнал від зразка тузлуку. Відмічено, кінетика проникнення мікроелементу визначається площею контакту сировини з дифундуючими речовинами та способом інтенсифікації внутрішнього переносу даних речовин всередині сировини. Встановлено, для тузлучного посолу та тузлучного посолу з попередньою обробкою ультразвуком кількість мікроелементу по глибині м'язової тканини карася відрізняється у межах похибки. Це свідчить про однорідність розподілення мікроелементу дієтичної добавки на основі хелатного комплексу за таких способів посолу.

Ключові слова: дрібна прісноводна риба, добавка на основі хелатного комплексу, тузлучний посол, сухий посол.

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