PERSPECTIVE FOR THE USE OF CHITIN MINERAL FOOD ADDITIVES IN THE TECHNOLOGY OF HARD-SMOKED SAUSAGES

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Abstract

The problem of calcium deficiency in the diet of modern man is well known. Calcium deficiency can lead to osteoporosis and frequent bone fractures, rickets, skeletal muscle cramps, thrombosis, hypertension, allergies, and rectal cancer, etc. There is also a shortage of dietary fibre due to excessive refined products. This problem is proposed to be solved by the manufacture of a functional food product-dry-cured sausage, with the addition of biologically active chitin-mineral food supplement "Hizitel" based on dietary fibre. The food supplementwas obtained by processing the shell-containing raw materials in the electrolyser. The selected method does not provide for the use of aggressive substances, thereby preserving the native structure of the chitin-mineral complex of the shell. The effect of the concentration of chitin-mineral food supplement in dry-cured sausage on the acidity and solid content in the product has been studied. The optimal concentration of added hizitel has been determined to prolong the shelf life and enrich the product with minerals and vitamins.

Keywords: "Hizitel", nutritional and biological value, chitin-mineral substance, dietary supplement, calcium, shelf life

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1. Introduction

Meat and meat products are an integral part of the human diet, which is already traditional, but at the same time unique. The uniqueness of meat raw material is that it has high energy intensity and digestibility, a balanced amino acid composition of proteins, as well as the presence of biologically active substances. This ensures the full mental and physical development of man. One of the most dangerous and common disorders in the diet is inadequate calcium intake. On average, calcium intake is in the range of 200–500 mg/day at the recommended rate of 1250 mg/day, that is, 2.3–6.3 times less than the physiological need. Calcium is one of the main elements in the human body, not only in quantitative but also in functional terms. It is rather difficult to provide optimal calcium intake at the expense of ordinary food, so the question of its compensation in the body is particularly relevant. One of the ways to solve this problem is to create biologically active food additives and functional foods with high calcium content.

Growing consumer awareness of the effects of nutrition on human health is causing changes in consumer habits. As a result, there is an increasing demand for food products that improve the health of consumers [1]. Meat and meat products are important sources of essential amino acids, minerals, and vitamins that provide a balanced diet. The most commonly consumed meat is pork (15.6 kg per capita per year), followed by poultry (13.6 kg per capita per year) and beef (9.6 kg per capita per year) [2].

Sausages are a meat product with high popularity due to fine gustatory quality, readiness to eat, and a variety of products on the food market. Meat of animals grown without the use of antibiotics and with the consumption of natural food not containing genetically modified components, is considered natural and safe to use [3].

Over the past decade, a steady tendency has emerged for meat products with improved composition. The reduction of fat, cholesterol, salt, and nitrite, as well as the improvement in the fatty acid profile and the inclusion of bioactive compounds, are increasing worldwide [4]. The consumption of antioxidants protects cells from damage caused by free radicals, while omega-3 fatty acids reduce inflammation and increase the rate of protein synthesis [5]. A high-quality protein diet is important for optimal stimulation of muscle protein synthesis. The consumption of natural antioxidants and omega-3 fatty acids contributes to the preservation of muscle function [6]. This work is devoted to the study of the effect of the «Calcium-D3-Hezitel» dietary supplement [7] on dry-cured sausages.

2. Materials and Methods

A dry-cured sausage was selected as the object of study, the recipe of which included: beef of 1 grade (rump, hock) and pork belly (flank, belly bacon) in a ratio of 50:50; nitrite salt – in the amount of 2.2% to the weight of unsalted raw materials; dry marjoram; fresh garlic; black peppercorns; Armenian cognac for refinement of aroma and taste.

The technology of production of dry-cured sausageincludedthe following steps: freezing meat raw material for 3 h at $t=-18^{\circ}\text{C}$, then grinding it (6–8 mm) and cooking the minced meat with salt, spices, and brandy. Next, maturation occurs within 24–36 h, as well as filling of the shells with stuffing mass, followed by draft for 2–3 days (t=11–15°C, ϕ =80–85%) and drying for 5–7 days (t=11–15°C, ϕ =75–85%). This sausage was enriched with a biologically active food supplement with calcium enriching properties of Calcium-Hezitel based on the crustacean chitin–mineral complex.

Getting hizitel from the shell-containing raw material was performed by an electrochemical method according to the method described in the patent number 2182822 of the Russian Federation.

Infrared spectra were recorded on a Perkin Elmer 16 PC FT-IR spectrometer. Samples (2 mg) were dried for 12 h at 80°C under reduced pressure. Then, they were mechanically blended with 100 mg of KBr. The thickness of the KBr disk was 0.5 mm. It was dried for 24 h at 110°C under reduced pressure before measuring. The background of the spectra was subtracted based on the individual peaks or on the group of peaks using the PeakFit for Windows.

The solid content of the products was determined by the following procedure: A portion of the product weighing 5 g was dried in a preheated weighing bottle at a temperature of $103\pm2^{\circ}$ C to constant weight. Weighing was carried out on scales with an error of no more than ± 0.001 g. A mass fraction of water was calculated from the difference in the mass of the samples [8].

The acidity of the product sample was investigated by the pH of the aqueous extract according to the following procedure: A portion of the sample weighing 10.00±0.02 g was thoroughly crushed and placed in a beaker, and a water extract was prepared in a ratio of 1:10. Then it was extracted with distilled water for 30 min, stirring occasionally. The extract obtained is filtered and determined the pH using the potentiometer [8].

Microbiological indicators were determined in accordance with rules and regulations [9].

3. Results and Discussion

Dry-cured sausage, as well as raw smoked sausage, represents a class of traditional meat products that are produced without pasteurization, that is, they are not subjected to heat treatment. The process by which fermentation (ripening) and drying of sausages takes place is considered one of the oldest technological methods of canning meat. This type of sausage refers to meat products with a long shelf life, which allows for simplifying the transportation and sale of this product.

Calcium contained in natural sources is better absorbed since it is in the form of calcium hydroxyapatite, which is easily digestible in the body. When processing crustaceans for food purposes, about 50–80% of shell-containing waste (SCW) is formed, which allows for organizing industrial production of calcium-fortified preparations. In OJSC "Giprorybflot" (St. Petersburg), an electrochemical technology was developed for the processing of SCW, and a new product of a unique composition was obtained—hesitel, which is a chitin–mineral complex of the shell. The technology provides for the processing of the shell-containing raw materials in the electrolyser without the use of aggressive substances, which allows for preserving the native structure of the chitin–mineral complex of the shell as much as possible. "Hizitel" is an absolutely natural compositional product consisting of chitin polysaccharide (20–40%) and mineral substances (60–80%, depending on the type of raw material), which are part of the crustacean's shell.

It was observed the presence of all characteristic bands in the infrared (IR) spectrum of the chemical absorption characteristic of chitin. Namely, characteristic bands at 3440 - $3450~{\rm cm^{-1}}$ related to stretching vibrations of O-H groups, absorption bands of stretching vibrations NH– bonds in the amido group -symmetric and asymmetric, absorption bands of deformation vibrations of C – H groups at $2980–2990~{\rm cm^{-1}}$, Amid I stretching bands and Amid II deformation vibrations characteristic of acetamide bonds at 1650 and 1550 cm $^{-1}$, as well as stretching, a symmetric and symmetric vibrations C-O groups of the glucopyranose ring at $1070~{\rm and}~1030~{\rm cm^{-1}}$.

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However, in the infrared spectrum of the chitin–mineral complex of "Hizitel", an absorption band at 872 cm⁻¹ and a more intense absorption in the region of 1620–1450 cm⁻¹, due to the presence of mineral components in it, are noted (**Fig. 1**).

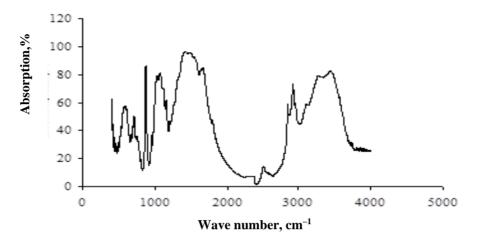


Figure 1. The infrared spectrum of chitin–mineral food supplement.

The mineral composition of hizitel is represented by the following most important biogenic elements: calcium, 22–28%; magnesium, 3–4%; phosphorus, 1.3–1.5%; sodium, 1.26%; potassium, 0.25%; iron, 0, 12%; and zinc, 0.09%, as well as copper, chromium, etc. As health care product, "Hizitel" normalizes the indicators of fat metabolism, due to which it has a lipotropic and anti-atherosclerotic effect. This was manifested in the processes of lowering total lipids, triglycerides, and low-density lipoproteins. When intoxicated with heavy metals, hizitel has a detoxifying effect and is able to bind toxic elements and reduce their levels in the blood and bones. "Hizitel" also normalizes intestinal microflora.

In the body, "Hizital" does not accumulate, does not cause an astringent sensation in the mouth, and does not dissolve in the gastrointestinal tract (GIT) (unlike chitosan), due to which it does not penetrate through the walls of the GIT, and it also normalizes increased acidity. "Hizitel" does not adversely affect the processes of digestion and assimilation of food [7]. It should also be noted that hizitel, which is a scaly powder with a low bulk density, is not soluble in water and, therefore, is not very convenient for direct consumption.

For the study, dry-cured sausage was enriched with a biologically active food supplement with calcium enriching properties of "Calcium-Hizitel" on the basis of hizitel. Eight samples of dry-cured sausage were made and tested. Samples differed from each other in the concentrations of this food additive. Sample Ne1 acted as control (without adding "Hizitel"); Ne2 - 0.5% of "Hizitel"; Ne3 - 1%; Ne4 - 1.5%; Ne5 - 2.0%; Ne6 - 2.5%; Ne7 - 5%; Ne8 - 10%; photographs are presented in Fig. 2.



Figure 2. Dry-cured sausages with "Hizitel" content from 0.5 to 10 mass%.

Fig. 3 and Fig. 4 show the results of the determination of pH values and dry substances in samples of sausages (No. 1–8).

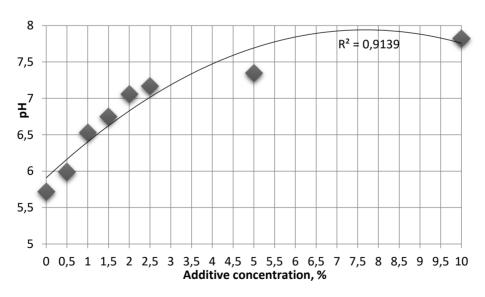


Figure 3. The dependence of the pH on the concentration of "Hizitel" additive in sausages.

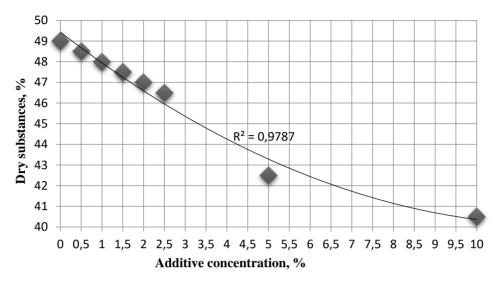


Figure 4. The dependence of the change in the amount of dry substances in sausages on the concentration of the additive "Hizitel"

From the data in Fig. 3, it follows that with increasing concentration of the additive, the pH value of the sausage increases from about 5.7 to 7.8. An increase in pH will adversely affect the storage time of the sausage. At the same time, with increasing concentration of the additive, the solid content decreases. The corresponding data is presented in Fig. 4. Comparison of the data presented in Fig. 3 and Fig. 4 shows that with increasing concentration of the additive an increase in pH and an increase in water content occur (Fig. 5).

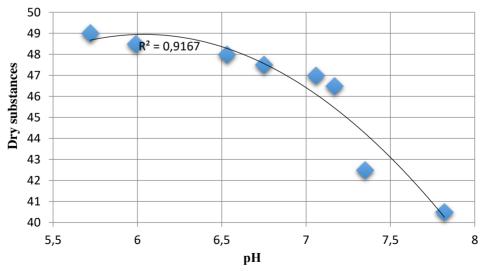


Figure 5. Dependence of the pH value on the solid content.

The pH shift to the alkaline side is probably associated with an increase in the calcium salt content when "Hizitel" is added, which creates an alkaline environment. The shift of pH in the alkaline region and the removal of proteins from the isoelectric point leads to an increase in the negative charge on the proteins and, consequently, to an increase in their hydration. Increasing the water content and shifting the pH to the alkaline side will lead to a decrease in storage stability and shortening of the shelf life of sausages due to the emergence of more favourable developmental conditions for microorganisms [10]. On the other hand, it is necessary to consider Hizitel's antimicrobial action, but it will also decrease as the pH shifts to an alkaline area. Therefore, in order to obtain sausages intended for long-term storage, it is necessary to make a chitin-mineral additive in a limited amount, which, on the basis of our research, is not more than 1%. In sausages with a short shelf life, "Hizitel" can be made in large quantities. The use of a vacuum shell will further increase the shelf life.

Table 1 presents the recommended daily consumption rates of macronutrients and their optimal ratio for calcium absorption (MR 2.3.1.2432-08 Norms of physiological needs for energy and nutrients for various groups of the population of the Russian Federation). At the same time, in the developed functional food product (FFP) it is necessary to reduce their concentration by approximately by 3 times.

| Macronutrients | Recommended daily intake of macronutrients for adults | The optimum ratio for calcium absorption between calcium and auxiliary micronutrients | Content in FFP according to optimal ratios between calcium and auxiliary micronutrients | | |
|-----------------|--|---|---|--|--|
| Calcium (mg) | 1250 | _ | 250-400 | | |
| Magnesium(mg) | 400 | 1.0:0.5 | 125-200 | | |
| Phosphorus (mg) | 800 | 1.0:1.0-1.8 | 250-720 | | |

Table 1. Recommended daily intake of macronutrients for adults

The content of vitamins and macronutrients in the developed FFP should not exceed 30% of the recommended daily intake rate, namely: B - 0.56 mg; B2 - 0.66 mg; PP -6.84 mg; Fe - 4.95mg; Mg - 133.6 mg; Ca - 412 mg; P - 264 mg; K - 912 mg; Na - 650 mg, respectively.

From the data of Table 1 and Table 2, it follows that the dry-cured sausage meets the requirements for vitamin and phosphorus content, but it does not have calcium and magnesium-enriching properties. "Hizitel", on the contrary, contains an insufficient content phosphorus satisfactory amount with a of magnesium.Introduction of 1.2% hizitel to the sausage recipe solved this problem and created a product balanced in vitamin and macronutrient composition.

Also, for 60 days of storage at temperatures ranging from -2°C to +6°C, microbiological studies of dry-cured sausage were carried out, the results of which are presented in Table 3 and Table 4.

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Table 2. The content of vitamins and macronutrients in dry-cured sausage enriched with "Hizitel" and the percentage of the daily norm of their consumption

| | Vitamins | | | Minerals | | | | |
|---|----------|------|------|----------|-------|------|--------|--------------------|
| Nutrients | B1 | B2 | PP | Fe | Mg | Ca | P | Ratio Ca: Mg: P |
| Content per 100 g of dry-cured sausage, mg | 0.51 | 0.33 | 7.3 | 2.1 | 28 | 36 | 225 | |
| Percentage of daily allowance (%) | | | | | 7.02 | 2.88 | 27.9 | |
| Content per 1g of hizitel, mg | | | | | 30 | 280 | 13.5 | |
| Content per 100g of dry- cured sausage with hizitel 1.21%, mg | 0.51 | 0.33 | 7.3 | 2.1 | 64.3 | 375 | 241.34 | 1:0,17:0,6 |
| Percentage of daily allowance (%) | 29.4 | 16.5 | 36.5 | 14 | 16.08 | 30 | 30.17 | |
| Content per 100 g of dry- cured sausage with hizitel 1.6%, mg | 0.51 | 0.33 | 7.3 | 2.1 | 77.71 | 500 | 247.37 | 1:0,16:0,5 |
| Percentage of daily allowance (%) | 29.4 | 16.5 | 36.5 | 14 | 19.43 | 40 | 30.92 | |
| Content per 100g of dry- cured sausage with hizitel 2.1%, mg | 0.51 | 0.33 | 7.3 | 2.1 | 91 | 625 | 253.4 | 1:0,15:0,42 |
| Percentage of daily allowance (%) | 29.4 | 16.5 | 36.5 | 14 | 22.75 | 50 | 31.67 | |

Table 3. Microbiological indicators of dry-cured sausage over 60 days of storage at temperatures from -2° C to $+6^{\circ}$ C

| Indica- | Sample | Sample | Sample | Sample | Sample | Sample | Sample | Sample N≥8 |
|---|----------|----------|-----------------|-----------------|-----------------|----------|----------|------------|
| tors | №1 | №2 | №3 | №4 | №5 | №6 | №7 | |
| Coliforms are not allowed in | Not | Not | Not | Not | Not | Not | Not | Not |
| | detected | detected | detected | detected | detected | detected | detected | detected |
| Sulfite-reducing clostridia are not allowed in 0.01 g | detected | detected | Not detected | Not detected | Not detected | detected | detected | detected |

Table 4. Microbiological indicators of dry-cured sausage, packed under vacuum, in a modified atmosphere for 60 days of storage at temperatures from -2° C to $+6^{\circ}$ C.

| Indicators | Sample №1 | Sample №2 | Sample №3 | Sample №4 | Sample №5 | Sample №6 | Sample №7 | Sample №8 |
|--|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Coliforms are not allowed in 0.1 g | Not detected |
| Sulfite- reducing clostridia are not allowed in 0.1 g | Detected | Detected | Not detected | Not detected | Not detected | Not detected | Not detected | Not detected |

4. Conclusions

Studies have shown that for long-term storage, sausages should be prepared with a content of the additive "Hizitel" not exceeding 1–1.2%. Higher concentrations of "Hizitel" should not be added to sausages intended for long-term storage. This is due to an increase in pH as the concentration of "Hizitel" increases. The increase in pH is due to the influence of calcium, which is an alkaline earth element that is part of "Hizitel".

Also, the use of special packaging for products with high pH content (vacuum or packaging in a modified gaseous medium) allows sausages with a high calcium content to be stored for a longer time.

It has been established that the introduction of 1.0–1.2% of "Hizitel" into the formulation of sausages ensures that FFP is balanced in vitamin and macronutrient composition, which makes it possible to recommend these products for the prevention of

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osteoporosis and other diseases associated with insufficient consumption of calcium and magnesium. Also, the introduction of this dietary supplement, belonging to the group of dietary fibre, is beneficial for improving the motility of the gastrointestinal tract.

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